Infrared and colorimetric characterization of discolored kiln-dried hard maple lumber

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Abstract

Discoloration of hard maple lumber commonly occurs during kiln-drying. In this study, discolored and nondiscolored kiln-dried hard maple lumber boards were characterized using a colorimetric method and Attenuated Total Reflectance-Fourier Trans. form Infrared Spectroscopy (ATR-FTIR). Colorimetric measurements (L*, a*, b*) were found to be in good agreement with visual grading. Brightness or lightness (L*) of hard maple lumber decreased with discoloration while redness (a*) and yellowness (b*) increased with discoloration. The pH and metal ion content of lumber appeared to play no role inthe discolorationprocess. ATR-FTIR spectra of lumber revealed that althoughall lumber boards exhibited similar features inthe fingerprint and other regions, there were differences in intensities of some absorption bands One significant difference between accepted and rejected lumber boards was in the 1600-1717 cm^{-1} region. ATR-FTIR alone was not sensitive enough to adequately describe changes in chemistry of discolored and discolored hard maple lumber boards.

Hard maple (*Acer saccharum* Marsh.) lumber is susceptible to discoloration during kiln-drying. The color of kiln-dried hard maple varies from the bright white color highly preferred by furniture plants, to the light reddish-brown or yellowish-brown color least desired by the industry. Wood products manufactured from bright white hard maple are expensive. Consequently, discoloration results in a great loss of market value.

Three major types of chemical stain are usually associated with kiln-dried hard maple lumber: 1) a reddish-brown discoloration, which manifests itself as yellowish-brown and occurs throughout the board; 2) greying, which is usually confined to the board surface or occurs in radial or irregular patterns in the interior of lumber; and 3) sticker stain, which is located above or underneath stickers placed between lumber boards. This study focused on the first type of discoloration. Overall, discolorations in wood during kiln-drying have been ascribed to many phenomena. Earlier studies by McMillen (1975) attributed chemical discoloration to the oxidation of chemical precursors present in wood. Chemical precursors in wood may initially be compartmentalized in various cells and organelles in intact trees (Hillis 1987). During conversion of logs, these cells are disrupted by sawing or cutting actions releasing their contents into the wood sap. Oxidizing enzymes such as polyphenoloxidases, which may also be initially compartmentalized, are similarly released and made available for the oxidation of the chemical precursors. Chemical precursors and enzymes move and concentrate on the lumber surface as a result of the moisture gradient between the surface and interior regions of the wood. On the wood surface, they undergo enzyme-catalyzed oxidation or autoxidation to produce high molecular weight compounds that may not be extractable by organic solvents.

Catalyzed oxidation of chemical precursors in wood may also occur through microbial activity (Koltzenburg 1975). A case in point is the oxidation of leucoanthocyanidins (flavan-3,4-diols) to

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produce brown and reddish discoloration in sycamore maple (*Acer pseudoplatanus*) (Rowe and Conner 1979). pH may also play a role in wood discoloration. Ilomba (*Pycnanthus angolensis* Exell.), a West African hardwood, changes color from bright yellow at weakly acidic pH of 5.5 to dark brown at an alkaline pH of 8.7 (Yazaki et al. 1985). In red oak (*Quercus* Sec. robur) heartwood, Bauch et al. (1991) attributed discoloration during kiln-drying to several processes, including dark pigmentation of fungal hyphae; biochemical reactions involving enzymes such as phenoloxidases and chemical precursors (polyphenols); and chemical reactions that are driven by physical factors such as temperature, moisture, oxygen, pH, and metal ions. In radiata pine (*Pinus radiata*) sapwood, brown discoloration observed during kiln-drying may be caused by an Amadori-Maillard reaction between sugars and nitrogen concentrated on the wood surface (Kreber et al. 1998).

Wood discoloration during kiln-drying is a poorly understood complex process. In contrast to previous wet-chemistry approaches, *in-situ* characterization of chemical changes in the wood during kiln-drying may shed new light on the underlying mechanism and facilitate the development of consistent and efficacious control methods.

Changes in wood color that traditionally have been monitored by visual methods can be measured by colorimetric methods that use Chroma meters. Color changes in wood are directly related to their chemical components, notably extractives, lignin, and polyoses (cellulose and hemicellulose). Wood discoloration, if it emanates from changes in the chemistry of the wood and functional groups present, may be detected by infrared red spectroscopy. Anderson et al. (1991) employed this technique to monitor functional group changes in the surface of weathered redcedar and southern pine. Infrared spectroscopy, notably, Diffuse Reflectance Spectroscopy (DRIFT), has been extensively used to study weathering in wood (Feist and Hon 1984, Tolvaj and Faix 1995, Faix and Nemeth 1988) and characterize pulp (Nimz 1973, Schultz and Glasser 1986). Chemical changes in western redcedar during mechanical pulping have also been characterized by DRIFT (Johansson et al. 2000). However, DRIFT is sensitive to the nature of wood surface, exhibiting distortion of the intensities of very strong absorption peaks (Anderson et al. 1991). A surface infrared semi-destructive technique that is devoid of these limitations is Attenuated Total Reflectance -Fourier Infrared Spectroscopy (ATR-FTIR).

The primary objective of this study was to characterize colorimetric parameters and chemical functional group changes in the surface of discolored and nondiscolored hard maple using ATR-FTIR. Metal ion content and wood surface pH were also determined.

Materials and methods

Lumber samples

Four kiln-dried hard maple samples were selected from a kiln-dried lumber charge at a local kiln-plant. Boards 1 and 4 were visually graded as bright/acceptable and discolored/non-acceptable, respectively Boards2 and 3 displayed various levels of yellowish streaks.

Brightness of lumber

Brightness or lightness (L*) of each piece of lumber at 30 randomly selected spots was measured using a Minolta Chroma Meter Model CR-300, which consisted of the CR-300 measuring head and Data Processor DP-301. In the CIE 1976L* a* b* color system employed in this study, color is considered to consist of three major dimensions: hue, chroma, and lightness. L* is the lightness or brightness variable, a* and b* represent the chromaticity (hue and chroma) coordinates. This system mimics human sensitivity to color (Minolta 1991). Total color difference (DE*ab) was computed using the equation $DE^*ab = (DL^{*2} + Da^{*2} + Db^{*2})^{1/2}$ (Maruyama et al. 2001).

ATR-FTIR of lumber

Samples for the infrared spectra were thin wood wafers taken with a chisel from the lumber surface. Each wafer measured approximately 12.5 by 25 mm. The infrared spectra of wafer samples were obtained on a Mattson FTIR spectrophotometer (Model Genesis II) at a resolution of 4 cm^{-1}. One hundred scans were co-added for each spectrum. Infrared absorbance spectra were measured over the range of 4000-500 cm^{-1} and horizontal attenuated total reflectance (HATR) (Gemini, Spectra-Tech) was used for transfer of infrared radiation. No baseline correction was used during spectra analysis and peak assignments were performed using the WinFIRST software.

pH of lumber

Surface pH measurements at 10 randomly chosen spots on each lumber board were made using a Sentron SurFET pH IntelliProbe. The IntelliProbe consists of an ISFET pH sensor, a reference system, and a temperature sensor in a single probe (Sentron Inc. 1999). This system is capable of processing ISFET and temperature signals to accurately correspond to glass pH electrode signals at the same temperature. The SurFET IntelliProbe, which permits direct surface measurements of material, has been used in the pulp and paper and paints and coating industries.

Metal ions content

Using a power drill fitted with a 5-cm-diameter cutterhead, wood shavings per each lumber board were taken at five random spots up to a depth of 6.25 mm Wood samples were ground in a Wiley Mill to pass a No. 40 sieve and ashed as per ASTM Standard D 1102-84 (ASTM 1993). The resulting ash was pressed onto the surface of a Chemplex wafer under a 15-ton total load and analyzed by x-ray diffraction analysis using a Phillips PW 1800 diffraction unit employing CuK_a, single crystal monochromated radiation (Solliday et al. 1999).

Statistical analysis

All color and pH measurements were analyzed by one-way analysis of variance (ANOVA), between-groups design, using SAS software (SAS 1997). In case of significant effect oftreatment, means were compared using Tikey's Studentized Range test.

Results and discussion

Results of colorimetric measurements of kiln-dried hard maple lumber based on the CIE L*a*b* system are presented in Table 1. Board 1, visually graded as acceptable, was the brightest (L* = 78.38) while the rejected board 4 was the least bright (L* = 70.04). One-way ANOVA indicated a significant effect for brightness of boards ($F[3, 111] = 57.45$, $p < 0.0001$). Tikey's HSD test showed that brightness for all boards was significantly different from each other, except between boards 2 and 3. The highest difference in brightness (DL*) between boards was recorded for boards 1 and 4. One-way ANOVA also

Table 1. — pH and optical characterization of boards. [a]

Board no.	pH	L*	a*	b*	DL*	Da*	Db*	DEa*b*
1	5.47 ± 0.15	78.38 ± 0.74	1.15 ± 0.26	21.70 ± 0.70	--	--	--	--
2	5.33 ± 0.17	75.08 ± 1.35	2.62 ± 0.57	23.09 ± 0.44	3.20 ± 0.25	-1.46 ± 0.08	-1.34 ± 0.15	3.97 ± 0.24
3	5.22 ± 0.29	76.26 ± 1.92	2.04 ± 1.24	25.10 ± 1.12	2.00 ± 0.43	-0.88 ± 0.24	-3.36 ± 0.31	4.61 ± 0.40
4	5.10 ± 0.16	70.04 ± 4.21	3.78 ± 0.94	25.72 ± 0.70	8.22 ± 0.76	-2.61 ± 0.17	-3.97 ± 0.24	9.68 ± 0.74

[a] $DL^* = L^*_1 - L^*_i$ where $i = 2$ or 3 or 4; $Da^* = a^*_1 - a^*_i$ where $i = 2$ or 3 or 4; $Db^* = b^*_1 - b^*_i$ where $i = 2$ or 3 or 4; total color difference, $DE^*ab = (DL^{*2} + Da^{*2} + Db^{*2})^{1/2}$.

Table 2. — Percent elemental composition of lumber boards based upon total metal ion concentration. [a]

Board no.	MnO	K_2O	SiO_2	Al_2O_3	SO_2	Fe_2O_3	Na_2O	MgO	TiO_2	P_2O_5	CaO
1	3.00	31.38	3.51	1.14	2.74	< 0.001	2.25	8.51	< 0.001	2.65	44.99
2	1.54	25.56	6.82	1.83	1.81	< 0.001	6.78	5.94	< 0.001	2.02	45.97
3	1.64	28.21	4.23	2.01	2.87	< 0.001	*5.02*	7.07	< 0.001	3.24	45.71
4	1.37	33.64	3.95	1.43	2.81	< 0.001	2.56	7.17	< 0.001	3.04	44.08

[a] Elements are expressed as oxides.

revealed a significant effect for redness ($F[3, 111] = 33.58, p < 0.0001$) and yellowness ($F[3, 11] = 142.78, p < 0.0001$) in the boards. Tukey's HSD test indicated that redness (a*) and yellowness in boards significantly increased ($p < 0.05$) from acceptable lumber (board 1, a* = 1.15, b* = 21.70) to rejected lumber (board 4, a* = 3.78, b* = 25.72). As observed earlier for brightness, the highest differential in redness and yellowness for the kiln-dried hard maple lumber occurred between accepted and rejected boards (Da* = -2.61, Db* = -3.97). Total color difference (DE*ab) between accepted and rejected boards followed a similar trend. The highest total color difference (9.68) occurred between accepted and rejected lumber boards.

This study clearly demonstrates that changes in brightness and color (discoloration) that sometimes occur in lumber during kiln-drying may be monitored accurately by colorimetric methods. Earlier studies by Charrier and Haluk (1992) support these results. Using a Chromameter based onthe CIE L*a*b* standard system, they monitored discoloration in European red oak heartwood during kiln-drying. Discoloration of lumber was attended by a decrease in brightness (L*) and an increase in redness and yellowness (a*, b*).

pH changes during wood processing can contribute to color changes in wood. Maruyama et al. (2001) suggested that color changes observed in sugi (*Cryptomeria japonica* D. Don) black heartwood following thermal treatment is caused by a decrease in heartwood pH. Normal heartwood of sugi, which is red in color, is weakly acidic while the black heartwood is weakly alkaline. In contrast, pH of kiln-dried lumber in this study showed very little variation (Table 1). One-way ANOVA failed to show a significant effect for pH ($F[3, 36] = 6.23$, $p = 0.0016$). The differences in lumber pH were not significant ($p > 0.0016$).

Color changes observed in wood have sometimes been ascribed to metal ion content. Elevated levels of alkali metal ions notably potassium were reported to be present in the ash of sugi black heartwood (Abe and Oka 1994, Kubo and Ataka 1998). The majormetal ions present in all boards were calcium and potassium at about the same concentration (Table 2). Manganese was higher in board 1. Results of this study show no direct relationship between metal ions present and their concentrations with the colorimetric parameters measured for kiln-dried maple lumber.

ATR-FTIR spectra of lumber boards are presented in Figure 1. The assignments of the ATR-FTIR spectra for the four boards are given in Table 3. The infrared spectra of all boards exhibited similar features in the fingerprint region and the 2000-4000 cm^{-1} region (not shown). However, distinct changes in intensities of certain absorption bands were discernible. All boards showed a broad -OH stretch band between 3258 cm^{-1} and 3303 cm^{-1} (Feinsten 1995, Tolvaj and Faix 1995, Smith 1999). There were two bands in the 2842- 3000 cm^{-1} region and they were assigned to -CH stretch in methyl and methylene groups (Feinsten 1995, Tolvaj and Faix 1995, Smith 1999). These were most intense for board 3, medium for boards 2 and 4, and considerably reduced and weak for board 1.

The most characteristic peaks appeared in the 1600-1700 cm^{-1} region. Boards 2 and 3 showed sharp absorption bands at 1741 cm^{-1} and 1744 cm^{-1}, respectively. These may be assigned to -C = 0 stretch for an ester. These assignments are supported by the presence of -C-C-O stretch at 1239 cm^{-1} and 1240 cm^{-1}, respectively. While board 1 exhibited a prominent peak at 1718 cm^{-1}, board 4 showed a weak absorption band at 1717 cm^{-1}. Absorption bands at 1717 cm^{-1} and 171 8 cm^{-1} can be assigned to -C = O stretch in carboxylic acid. The major difference in the spectra of boards l and4 occurredinthe 1717-1600 cm^{-1} region.

The chemistry of extractives of various wood species may play an important role in color changes that accompany various wood processes. A direct relationship between the extractives in *Eucalyptus pilularis* veneers and their redness values (a*) was reported by Yazaki et al. (1985). Yellowness (b*) in wood, notably in pulp, has been primarily ascribed to changes in lignin structure (Nimz 1973) although the role of extractives cannot be ruled out. Tolvaj and Faix (1995) attributed the yellow-reddish color in locust to its extractives. Yoshimoto (1989) described specific extractives that are associated with color changes in wood after exposure to UV irradiation. While gallic acid and catechin are present in clear (bright) hard maple, they are absent in discolored wood. Scopoletin (7-hydroxy-6-metho-

Table 3. — Infrared frequencies and band assignments for kiln-dried hard maple lumber boards.

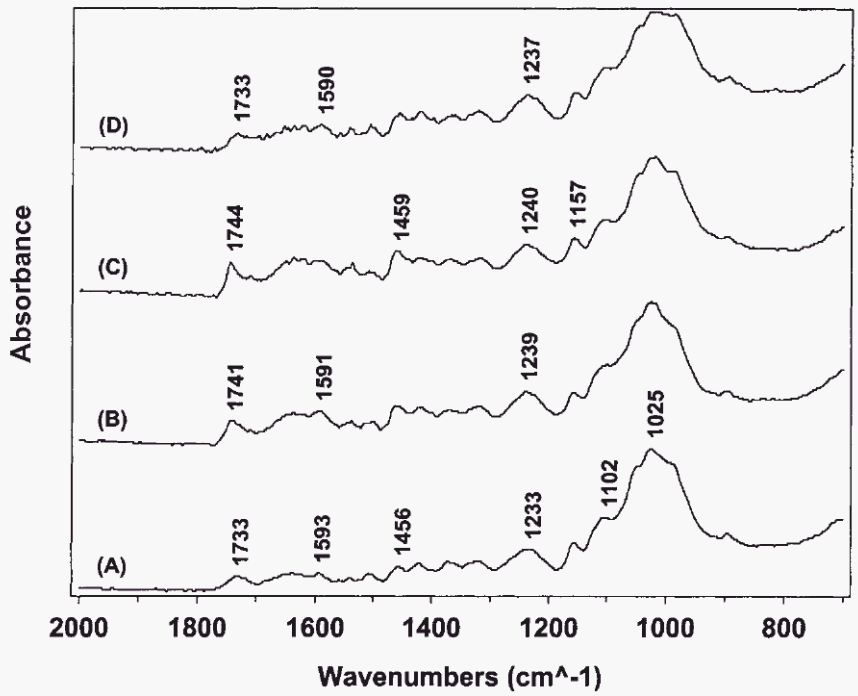
		Band assignment for kiln-dried sugar maple lumber board				
Ord. no.	Wave no. (cm^{-1})	Board 1	Board2	Board3	Board4	Comments
1	1717				-C = O, weak carboxylic	(Feinstein 1995, Smith 1999)
	1718	-C = O, intense, broad carboxylic				
	1741		-C= O, intense, sharp, ester			
	1744			-C= O, intense, sharp, ester		
2	1502	Sharp	Sharp	Weak	Sharp	Aromatic skeletal vibrations (Machado et al. 1996)
	1537	Weak	Sharp	Sharp	Sharp	
	1648	Broad intense, conjugate -C= O	Weak, broad conjugate -C= O	Weak, broad conjugate -C = O	Probably absent, conjugate -C = O	
3	1421	Intense, -CH deformations	Intense, -CH deformations	Weak, deformations-CH	Intense, -CH deformations	Aromatic vibrations combined with -CH in-plane deformations (Machado et al. 1996)
	1457	Relatively weak, -CH deformations			Intense, -CH deformations	
	1459			Intense, -CH deformations		
	1461		Intense, deformations-CH			
4	1321					Syringyl ring breathing with CO stretching (Machado et al. 1996)
5	1233					C_{aryl} -O stretching (Tolvaj and Faix 1995)
	1238					
	1239					
	1240					
6	1158					C-O-C stretching asymmetric (Smith 1999)
7	1026					Probably ester O-C-C stretch (Smith 1999)

xycoumarin) has been isolated from discolored hard maple. Infrared spectra, although it can indicate the presence and absence of various functional groups, "does not lend itself for trace analysis" (Tolvaj and Faix 1995). Consequently, chemical compounds responsible for the discoloration of kiln-dried hard maple, if present in trace amounts, may not be detected by the ATR-FTIR method. To overcome these limitations, planned future work will include other surface analytical tools, e.g., static secondary ion mass spectrometry (SSIMS) or dynamic secondary ion mass spectrometry (DSIMS) or laser microprobe mass analyzer (LAMMA). These techniques have demonstrated their complementary utility for the study of polymer surface contamination and also characterization of modified polymer surfaces (Chan 1994).

Conclusion

This study demonstrated that discoloration in kiln-dried hard maple is attended by a decrease in brightness (L*) and an increase in both redness (a*) and yellowness (b*). Measured colorimetric parameters were in good agreement with the visual grading results. Colorimetric analysis by Chroma meters using the CIE L*a*b* system is a good technique for monitoring discoloration in kiln-dried hard maple. pH and metal ion concentration in hard maple showed no relationship to discoloration. Although distinct differences in ATR-FTIR spectra of accepted and rejected lumber could be discerned, it could not be used to adequately explain the chemical basis of the observed discoloration.

The results presented here are preliminary and represent our initial efforts to understand the mechanism underlying



A = board 1; B = board 2; C = board 3; D = board 4.

Figure 1. — ATR-FTIR spectra of kiln-dried hard maple lumber boards.

the discoloration of hard maple during kiln-drying by the application of *in-situ* semi-nondestructive surface analytical techniques. Future studies will expand the size of the study and include other surface analytical tools to enhance the effectiveness of the ATR-FTIR technique.

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