Color and Surface Chemistry Changes of Pine Wood Flour after Extraction and Delignification

Yao Chen,[a] Mandla A. Tshabalala,[b] Jianmin Gao,[a,]* Nicole M. Stark,[b] and Yongming Fan[a]

A detailed study was undertaken to examine the color and chemistry changes of pine wood flour when its extractives are removed and when it is delignified. The solvent systems employed were toluene/ethanol (TE), acetone/water (AW), and hot-water (HW), while sodium chlorite/acetic acid were used for delignification (*i.e.,* lignin removal (LR)). Samples were analyzed by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, Fourier transform Raman (FT-Raman) spectroscopy, and colorimetry. The study demonstrated that color parameters (*i.e.,* CIE *L a b*) were only slightly affected by the removal of extractives, but changed noticeably when extractions were followed by delignification. TE extraction was more effective at removing the yellow colored substances, whereas AW mostly removed red colored substances that contained C=O groups. Inclusion of a HW extraction step after extraction with AW (AW-HW) removed components that contained conjugated C=O structures. Inclusion of a delignification step after extraction with AW followed by HW extraction (AW-HW-LR) was effective at removing yellow substances that contained non-conjugated C=O groups.

***Keywords:* Woodflour; Extractives; Lignin; Surface chemistry; Color; Extractives; Delignification**

***Contact information:* a: MOE Key Laboratory of Wooden Material Science and Application, College of Material Science and Technology, Beijing Forestry University, Beijing 100083, China; b: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, United States; * Corresponding author: jmgao@bjfu.edu.cn**

INTRODUCTION

The use of wood flour as a reinforcement in wood–plastic composites (WPCs) has recently gained significant interest. However, one of the main problems of WPCs is the weak interfacial adhesion between hydrophilic wood and hydrophobic plastic. The other problem is when these WPCs are used in exterior environments such as decking, railings, window frames, and doors, as they undergo discoloration. In an effort to resolve this problem, Stark and Gardner (2008) added pigments and photo-stabilizers to the mixture of wood flour and plastic. This approach was ineffective at mitigating the color change of WPCs during weathering. Stark and Matuana (2003) showed that WPC color change caused by weathering is primarily related to discoloration of the wood component of the composite.

The wood cell wall is composed of polymeric components: cellulose, hemicellulose, and lignin, in addition to relatively small quantities of extractives. Extractives can be divided into three major classes: (1) aliphatic compounds (*e.g.,*fatty acids, fatty alcohols, waxes, fats, gums, and glycosides), (2) terpenes and terpenoids (*e.g.*, pinene, cadinene, and abietic acid), and (3) phenolic structures (*e.g.,* phenolic acids, tannins, flavonoids, lignans, and stilbenes). Although extractives comprise a relatively small fraction of the whole wood, they have a significant influence on its properties, such as color, durability, moisture resistance, dimensional stability, and weathering characteristics. The influence of extractives on the surface chemistry of wood fibers plays an important role in diverse industrial applications of wood, such as coatings, pulping, and wood-based composites.

The color of wood is determined by both extractives and lignin. Pew and Connors (1971) attributed the color of southern pine sapwood to chromophoric groups in lignin, and Hon and Minemura (2001) identified these chromophores as phenyl-substituted benzoquinone structures. The presence of phenolic substances including flavonoids, stilbenes, lignans, tannins, and quinones contribute to the color of wood (Hon and Minemura 2001). Most extractives can be removed with a single solvent or a combination of solvents, such as ethanol, water, benzene, acetone, chloroform, or a solvent mixture of ethanol/benzene or toluene/ethanol. Removal of the extractives with solvents does not damage the wood structure. Lignin can be removed by the treatment of ground wood with either chlorine gas, acidified solution of sodium chlorite, or peracetic acid solution (Easty and Thompson 1991).

There is conflicting evidence about the effects of removing extractives on wood surface color. Pandey (2005) observed an increase in the lightness of wood surface color after extraction with ethanol. Nzokou and Kamdem (2006) observed insignificant changes in wood surface lightness after extraction with organic solvents alone, but observed significant decreases in lightness when the wood was extracted with organic solvents followed by hot water. Fan *et al.* (2010) observed that extraction with polar solvents increased the optical reflection and lightness, which resulted in a higher total color difference than extraction with less polar or non-polar solvents. Chang *et al.* (2010a, b) conducted a series of experiments where *Acacia confusa* and *Cryptomeria japonica* wood was extracted with a mixture of ethanol and toluene. The UV-Vis absorption bands of the extracted wood in the spectral region of 300 to 800 nm showed a decrease in intensity that could be attributed to the removal of biphenyls, aromatic conjugated C=C, and C=O structures, and/or quinoids. X-ray photoelectron spectroscopy analysis of the surface chemistry of *A. confusa* wood showed an increase in the O/C ratio that was attributed to the removal of carbon-rich extractives, such as fatty acids, terpenes, and phenolics (Chang *et al.* 2010b).

In the current study, we investigated the effect of exhaustive removal of different classes of extractives on the surface chemistry and color of pine wood flour (WF). The effect of delignification on the surface chemistry and the wood flour color was also investigated. The chemistry and color of the WF were investigated by ATR-FTIR, FT-Raman spectroscopy, and colorimetry. The color of the WF was measured according to the CIE L a b system. The CIE L a b color system is a three-dimensional color space measuring the lightness (L^*) of the sample and color coordinates (a^* and b^*). L^* represents reflectance of a sample that ranges between 0 and 100 (black and white, respectively). An L^* of 0 means the sample does not reflect light, whereas an L^* of 100 means the sample reflects all the incident light. An increase in L^* means the color has faded or has become lighter (+ΔL^*= lightening), while a decrease in L^* means the color has darkened (–ΔL^*= darkening). The color coordinates a^* and b^* do not have a specific range. a^* is defined as the red/green coordinate(+Δa^* signifies a color shift toward red, –Δa^* toward green). b^* is defined as the yellow/blue coordinate (+Δb^* signifies a color shift toward yellow, –Δb^*

toward blue) (Papadakis *et al.* 2000; Segnini *et al.* 1999; Yam and Papadakis 2004). Chroma C^* is derived from a^* and b^*:

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

It corresponds to color saturation and varies from dull (low value) to vivid (high value).

We expect that the results from this study will provide a better understanding of the role of lignin and extractives on the chemistry and color of wood fibers. Such knowledge could be used to improve the appearance and performance of WPCs reinforced with pine wood flour.

EXPERIMENTAL

Materials

Pine WF was selected because it is the most common WF used in commercial WPC decking. The pine WF supplied by American Wood Fibers (AWF 4020; Schofield, Wisconsin) was derived from mixed pines, primarily ponderosa pine (*Pinus ponderosa*). WF was sieved through a 40-mesh screen (0.425 mm) to remove the larger particles and through a 60-mesh screen (0.250 mm) to remove the fine particles. The WF was stored in a sealed polyethylene (PE) bag until required for further experimentation.

Methods

Wood extraction

Three different solvent systems, toluene/ethanol (TE), acetone/water (AW), and hot-water (HW), were used to remove extractives from the WF, depending on the different polarity of these solvent systems. No single organic solvent is capable of removing all these substances, and different solvents remove different combinations of components (Browning 1967). TE co-solvent was prepared based on a 2:1 volume ratio of toluene-to-ethanol. AW co-solvent was prepared based on a 9:1 volume ratio of acetone-to-distilled water. Lignin was removed by sodium chlorite acidified with acetic acid (denoted as LR). In addition to extraction with single solvent system, TE, AW, HW or LR, samples of WF were also subjected to one or more extraction steps designated as TE-AW, TE-HW, TE-LR, TE-AW-HW, TE-AW-LR, TE-HW-LR, TE-AW-HW-LR, AW-HW, AW-LR, AW-HW-LR, and HW-LR. For example the designation TE-AW means the sample was subjected to two successive extraction steps: TE followed by AW; and TE-AW-HW-LR means that the sample was subjected to four successive extraction steps: TE followed by AW, HW, and LR in that order. Each extraction step was performed for 24 h in a Soxhlet apparatus to ensure exhaustive removal of extractives. The delignification step (LR) was performed according to the method developed by Wise *et al.* (1946) with slight modifications. All samples of WF, including non-extracted control, were vacuum-dried before further experimentation.

Characterization of WF

The surface chemistry of the wood fibers was characterized by ATR-FTIR and FT-Raman spectroscopy. ATR-FTIR was conducted on a Nicolet iZ10 module (Thermo Scientific, Verona, Wisconsin) using a Smart iTR Basic accessory. A single bounce, diamond crystal with 45° incident angle was used, and the spectra were detected using a room temperature deuterated triglycine sulphate (DTGS) detector. Spectra were recorded in absorbance units as an average of 64 scans in the range of 4000 to 600 cm^{-1} at 4 cm^{-1} resolution. The peaks were analyzed without smoothing the data. The peaks were baseline corrected and normalized on the peak at 1030 cm^{-1} as the internal standard. The peak at 1030 cm^{-1} is attributed to C-O in cellulose, which is stable to solvent extraction or to delignification.

FT-Raman spectroscopy was conducted on a Bruker MultiRam spectrometer (Bruker Instruments, Inc., Billerica, Massachusetts). This Raman system was equipped with a 1,064-nm 1,000-mW continuous wave (CW) diode-pumped Nd:YAG laser. The laser power used for sample excitation was 300 mW, and 512 scans were accumulated. Bruker's OPUS software program was used to find peak positions and carry out baseline corrections. The peaks were normalized on the peak at 1096 cm^{-1} as the internal standard. The Raman bands of the wood flour in the range from 1050 to 1150 cm^{-1} are due primarily to stretching vibrations of C-C and C-O bonds in cellulose and hemicellulose (Agarwal and Ralph 1997), which are stable with respect to solvent extraction or to delignification.

Color Measurement

For color measurements, the WF samples were pressed into pellets with a 30-mm-diameter die using a hydraulic press. Color was measured at three locations on each sample. A Minolta CR-400 Chroma Meter (Minolta Corp., Ramsey, New Jersey) was used to measure optical properties with a C standard illuminant according to the CIE L^*a^*b color system. In this study, ΔL^*, Δa^*, and Δb^* were calculated according to Eqs. (2-4).

$$\Delta L^* = L^*_{\text{treated}} - L^*_{\text{control}} \tag{2}$$

$$\Delta a^* = a^*_{\text{treated}} - a^*_{\text{control}} \tag{3}$$

$$\Delta b^* = b^*_{\text{treated}} - b^*_{\text{control}} \tag{4}$$

A positive value indicates an increase, while a negative value signifies a decrease. Their corresponding total color difference (ΔE^*) was calculated according to Eq. 5.

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{5}$$

RESULTS AND DISCUSSION

Change in Color Parameters of WF After Extraction or Delignification

The color parameters, a^*, b^*, and C^*, of the WF are plotted in the color diagram (Fig. 1). The iso-C^* (chroma) lines were drawn based on Eq. 1. There was a shift towards blue (decrease in yellow-blue coordinates b^*) with the exception of sample extracted with HW alone. The chroma values, C^* followed the same trend as the b^* values. This indicates that the yellow color of the extracted WF faded and became less saturated or less vivid. It is interesting to note that WF extracted with TE had the lowest b^* and C^* values when compared with the non-extracted control and the other extracted samples. This indicates that the removal of TE-soluble extractives was more effective in decreasing the yellow color and making the WF dull when compared with the other solvent systems, whereas AW mainly removed the red color substances. It should also be noted that the color of the WF shifted toward green, with the exception of those extracted with HW alone or when HW was included as the last step (*i.e.*, TE-HW, TE-AW-HW, or AW-HW). Apparently, when substances that cause color change are water-soluble, they migrate to the surface, where they accumulate and oxidize as a result of exposure to air. Based on the polarity and compatibility, extractives with higher polarity such as flavone-glycosides, quinone-glycosides, and tannins can be dissolved in water. It is hypothesized that accumulation of these oxidation products results in a vivid yellow-red color (*i.e.*, increase in *a**, *b**, and *C**) on the wood fiber surface. This color change presumably is due to oxidative coupling of compounds related to tannins. Hydrolysis and oxidative transformation of polyphenols to an insoluble dark color polymer can also be considered as another possible contributor to the color change of the WF. Quinones, the oxidation products of phenolic substances, have been identified as the potential reason for discoloration (Bekhta and Niemz 2003).

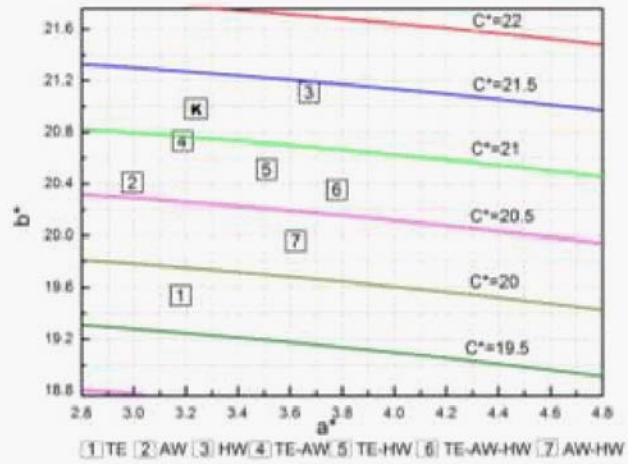

Fig. 1. Chromaticity coordinates *a**, *b**, and *C** of extracted and non-extracted WF

Compared with the non-extracted control ("K" in Fig. 1), chromaticity coordinates *a**, *b**, and *C** decreased considerably after delignification (Fig. 2).

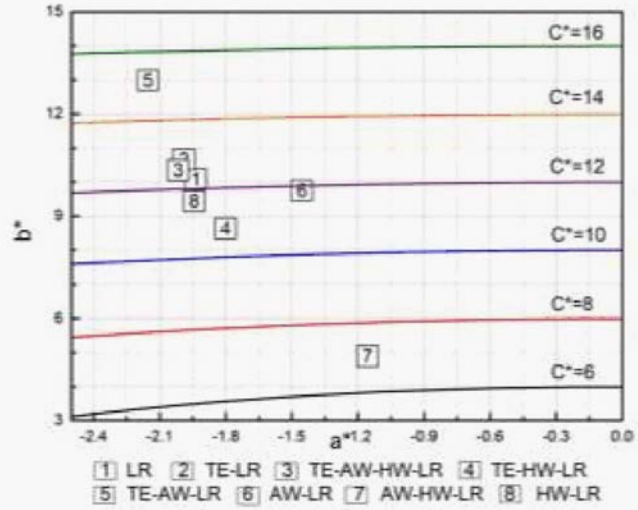

Fig. 2. Chromaticity coordinates *a**, *b**, and *C** of WF after delignification or after treatment with a combination of extraction and delignification

The a^* values decreased to negative values. The WF after extraction with TE-based solvent system followed by delignification resulted in lower a^* values when compared with AW-based solvent systems. It is interesting to note that compared to other samples that included a delignification step, the sample that was subjected to the extraction sequence, AW-HW-LR, had the lowest b^* and C^* value, but the highest a^* value. On the other hand, higher b^* and C^* values were observed for the TE-AW-LR extraction sequence, which had the lowest a^* value. A plausible explanation for this behavior could be that the extraction sequence, AW-HW-LR was most effective in removing the yellow substances, and making the WF dull compared with the other solvent systems; on the other hand, the red substances were readily removed by the TE-AW-LR extraction sequence.

There was a significantly greater change in the L^* values after delignification, regardless of the extraction treatments applied or their combinations (Table 1). Extraction with TE-HW resulted in slightly greater AL* value. However, AW-HW and HW extraction resulted in decrease in lightness (negative values of ΔL^*). Large positive changes of AL* values were observed when WF was subjected to the extraction steps TE-HW-LR or TE-AW-LR. Thus, it is reasonable to conclude that these two extraction sequences resulted in increased lightness of the WF.

Removal of extractives had little effect on the total color change (ΔE^*) (Table 1), with the exception of AW-HW extraction, which yielded a slightly greater AE* value. By contrast, delignification (LR) alone or solvent extractions followed by delignification, resulted in significant color change (large AE* values). However, it should be noted that there was no significant difference in AE* among samples of WF that were treated with TE-LR, AW-LR, or HW-LR. It can be seen that the greatest color change was obtained after the AW-HW-LR treatment.

Table 1. Changes in Lightness (ΔL^*) and Color Difference (ΔE^*) of WF after Extraction or Delignification, or after Combined Extraction Followed by Delignification

Treatment	Alone		+HW		+LR		+(HW-LR)	
	ΔL^*	ΔE^*	ΔL^*	ΔE^*	ΔL^*	ΔE^*	ΔL^*	ΔE^*
TE	0.3 (± 0.1)[a]	1.5 (± 0.1)	1.2 (± 0.0)	1.3 (± 0.1)	10.7 (± 0.0)	15.8 (± 0.1)	11.2 (± 0.0)	16.3 (± 0.1)
AW	0.7 (± 0.3)	0.9 (± 0.1)	-1.7 (± 0.0)	2.1 (± 0.0)	10.3 (± 0.1)	16.0 (± 0.0)	10.0 (± 0.1)	19.5 (± 0.0)
TE-AW	0.3 (± 0.1)	0.4 (± 0.2)	0.2 (± 0.0)	0.9 (± 0.0)	11.0 (± 0.1)	17.3 (± 0.1)	10.0 (± 0.1)	13.9 (± 0.2)
HW	-0.4 (± 0.0)	0.6 (± 0.0)	ND [b]	ND	9.5 (± 0.1)	15.8 (± 0.2)	ND	ND
LR	10.6 (± 0.0)	16.0 (± 0.0)	ND	ND	ND	ND	ND	ND

[a] Numbers in parentheses represent the standard deviation of five replicates.
[b] ND, Not determined

Surface Chemistry of WF After Solvent Extraction or Delignification

For those cases where the WF was extracted with single solvents TE, AW, or HW, or was treated with LR (Fig. 3), the absorption peak at 1733 cm^{-1}, which was assigned to non-conjugated C=O stretching vibration, increased and shifted slightly to a higher wavenumber (1737 cm^{-1}); the only exception to this was the AW extraction. One explanation for the shift is the possible enrichment of esters or acids that absorb at or near 1737 cm^{-1}. Extraction with AW resulted in the removal of extractives containing non-conjugated C=O groups. The decrease in carbonyl structures is consistent with the larger decrease in the *a** value for the WF obtained after extraction with AW versus TE or HW. This indicates that the red color of the WF can largely be attributed to the non-conjugated C=O functional groups of wood components. A possible explanation for the large values of AL* and AE* for the delignified samples is the formation of muconic acid type structures upon lignin oxidation during the acid chlorite delignification process. The peak at 1643 cm^{-1}, which was assigned to conjugated C=O stretching vibration, coniferyl alcohol and aromatic ketones (Faix 1988; Yamauchi *et al.* 2005), decreased significantly after extraction or delignification. This indicates that aromatic conjugated ketones were partly removed by extraction or delignification. The decrease was lower in the case of TE extraction when compared with other solvent extractions. This is consistent with the lowest *b** and *C** obtained after TE extraction compared with AW or HW extraction. It should be noted that HW extraction was less effective in removing the components containing C=O groups when compared with TE or AW, probably because of the relatively higher polarity of HW or because of its lower affinity for high-molecular weight carbonyl compounds. The intensity of aromatic vibrations at 1595 cm^{-1}, which were also assigned to C=C unsaturated linkages, decreased slightly after extraction. Delignification resulted in a practically complete disappearance of the peak at 1595 cm^{-1}. This is consistent with the decrease in *b** and chroma *C** after delignification, and also with the significant decrease in the red coordinate *a**.

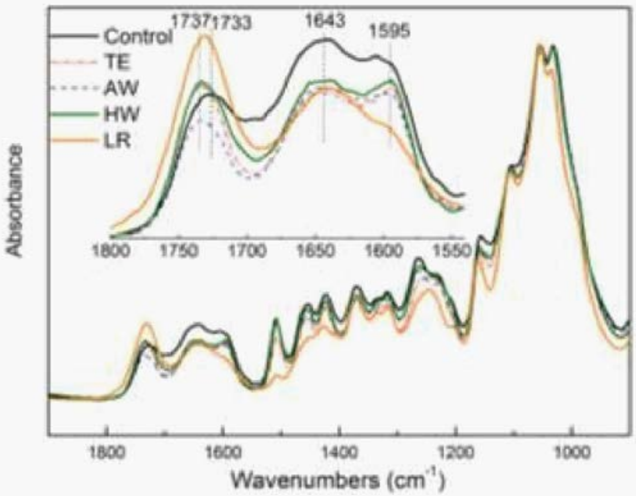

Fig. 3. ATR-FTIR spectra of TE, AW, HW, and LR treated WF

The effect of multiple treatments of AW-based or HW-based solvents system on the intensity of the peaks at 1733 cm^{-1}, 1643 cm^{-1}, and 1595 cm^{-1} are illustrated in Fig. **4.** The absorption at 1733 cm^{-1} decreased after extraction with AW-HW or treatment with AW-HW-LR, whereas a substantial increase was observed after treatment with HW-LR or AW-LR. The absorptions at 1643 cm^{-1} and 1595 cm^{-1} decreased after solvent extraction or extraction combined with delignification. Treatment with AW-based solvent systems (AW-LR) led to lower absorption at 1643 cm^{-1} compared with HW-based solvent system (HW-LR). The lowest absorption intensity was observed after treatment with AW-HW-LR. This is consistent with the lowest *b** and *C** values of the AW-HW-LR treatment of WF. It suggested that the yellow color of wood was largely attributed to the conjugated C=O functional groups on the wood fiber surface.

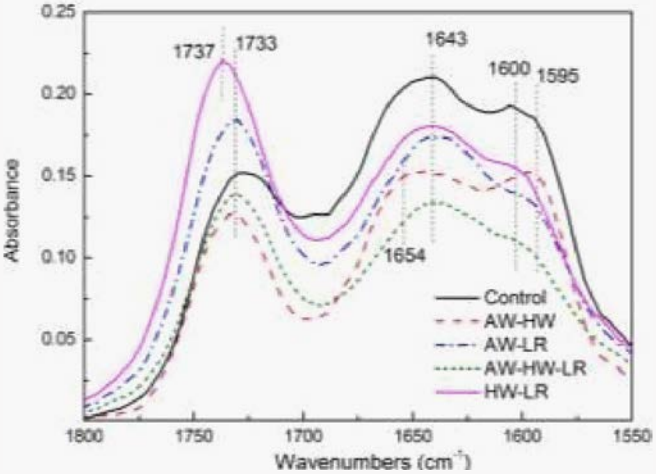

Fig. 4. ATR-FTIR spectra of WF after treatment with AW-based solvent systems

For WF treated with TE-based solvent systems (Fig. 5), the absorption at 1737 cm^{-1} was decreased with the removal of TE-HW, TE-AW, and TE-AW-HW-soluble substances. Comparing the spectra of holocellulose and lignin (Owen and Thomas 1989) reveals that the absorption located at 1737 cm^{-1} is caused by the C=O stretch in non-conjugated ketones, carbonyls and in ester groups. This indicates that C=O and the phenolic substances that contribute to the formation of quinone structures were removed. However, the removal of lignin resulted in an increase in the absorption intensity at 1737 cm^{-1}. The highest absorption was observed for WF treated with the TE-AW-HW-LR process; this treatment process also had higher *b** and *C** values. One explanation for the increase is the possible enrichment of esters or acids that absorb at or near 1737 cm^{-1}. Extraction with any of these solvent systems decreased the surface concentration of conjugated C=O groups at 1643 cm^{-1}.

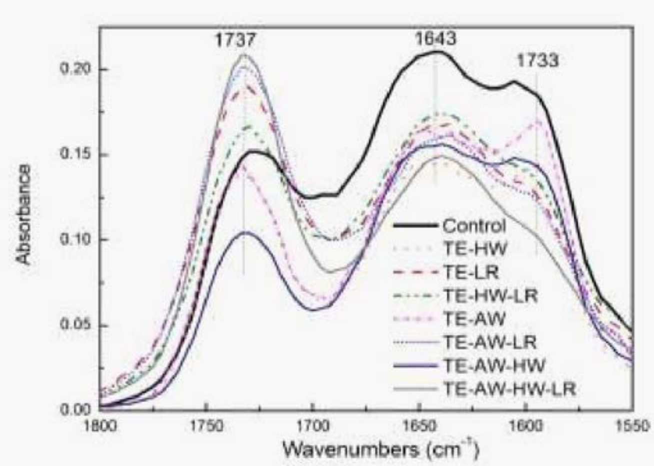

Fig. 5. ATR-FTIR spectra of WF after treatment with TE-based solvent systems

The FT-Raman spectra of WF samples that were either delignified or extracted with TE, AW, or HW was analyzed in the region of 1775 cm^{-1} to 1550 cm^{-1} (Fig. 6). The peak at 1600 cm^{-1}, which is assigned to the ethylenic C=C bond in coniferyl alcohol units, decreased considerably, and the peak at 1660 cm^{-1}, which is attributed to *a*- and *γ*-C=O groups in coniferaldehyde units in lignin (Yamauchi *et al.* 2005), could not be detected after delignification. Also, on the basis of earlier work, it is known that the Raman spectrum of spruce wood contains a strong band at 1600 cm^{-1} as a result of phenyl groups in lignin (Atalla and Agarwal 1985). This happens to be the most intense Raman band of lignin in the spectrum of spruce. The presence of this band, albeit with much lower intensity, in the spectrum of delignified wood sample indicated that some phenyl groups (or lignin) survived the acid-chlorite treatment. However, the scattering intensity of these peaks decreased slightly after solvent extraction. Among the solvents used in this study, AW extraction was more effective at removing these groups when compared with TE and HW extraction. HW extraction had the least effect on the removal of C=C and C=O structures. The results are consistent with what was observed in FTIR spectra and color measurements.

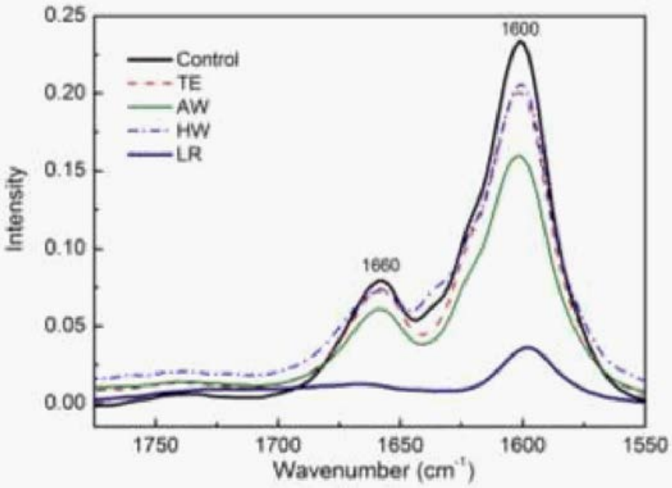

Fig. 6. Raman spectra of WF after delignification or extraction with various solvents

It should be noted from the Raman scattering spectra (Fig. 7) of the samples extracted with AW or HW followed by one or more of the other solvent systems that the peaks at 1660 cm^{-1} and 1600 cm^{-1} decreased slightly after AW-HW extraction, but decreased considerably after AW-LR, HW-LR, or AW-HW-LR treatment. Contribution from coniferaldehyde units is expected at 1660 cm^{-1}.

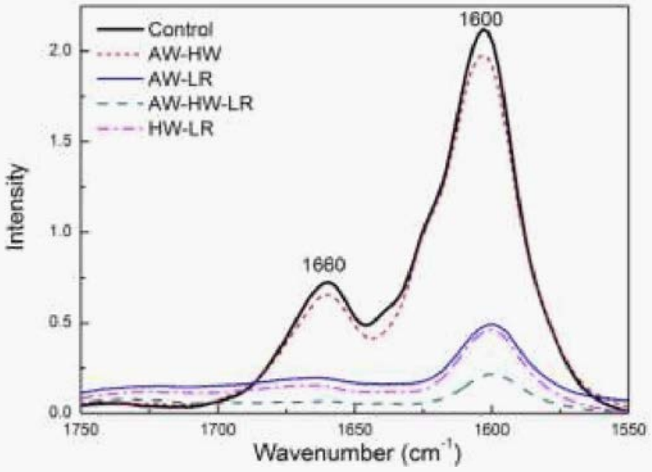

Fig. 7. Raman spectra of WF after treatment with AW-based solvent systems

The peak at 1600 cm^{-1} is attributed to ring-conjugated C=C stretching vibration of coniferylalcohol and C=O stretching vibration of conifer aldehyde (Agarwal *et al.* 2011). There was no significant difference between the AW-LR and HW-LR treatments on the intensity of these peaks. However, successive extraction with AW and HW followed by delignification (AW-HW-LR) substantially decreased the intensity. It was observed that lignin's most intense Raman band (1600 cm^{-1}) significantly declined upon chlorite treatment. In addition, it is reasonable to assume that, in addition to the lignin, the scattering at 1600 cm^{-1} was also partially due to AW-HW soluble extractives.

When WF was subjected to extraction with TE followed by one or more of the other solvent systems, the intensity of the Raman peaks at 1660 cm^{-1} and 1600 cm^{-1} (Fig. 8) decreased slightly with the TE-HW or TE-AW extraction, and decreased significantly with TE-AW-HW extraction. This is attributed to a slight decrease in the concentration of components containing C=C and C=O groups. It can be inferred that HW extraction removed different types of components containing C=C and C=O groups compared to the AW extraction. The decrease in these groups appears to be in good agreement with the result obtained from chromaticity analysis, where TE-AW-HW extraction resulted in lower *b** and *C** values when compared to TE-HW or TE-AW extraction. The lowest intensity at 1600 cm^{-1} was obtained for WF treated with TE-AW-HW-LR, which had the lowest a* values.

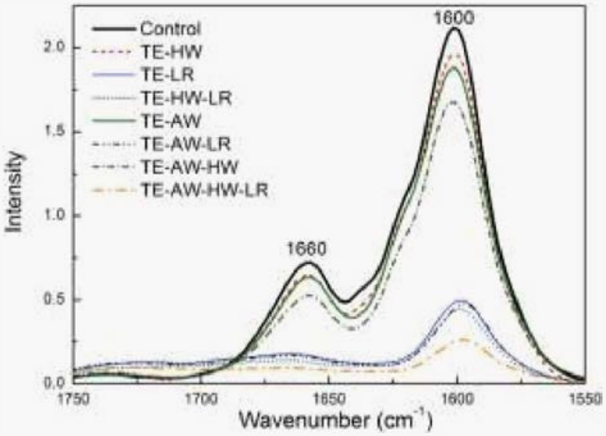

Fig. 8. Raman spectra of WF after treatment with TE-based solvent systems

CONCLUSIONS

1. This study investigated the surface chemistry and color of pine WF before and after extraction with TE, AW, or HW-based solvent systems either alone or in combination with acid chlorite delignification. The results demonstrated that color parameters were only slightly affected by the removal of extractives. However, noticeable changes were observed in these parameters when extractions were followed by delignification.
2. The lowest *b** and *C** values were obtained when the WF was treated with AW-HW-LR, which effectively removed substances containing conjugated C=O groups. The yellow color of wood was largely attributed to the conjugated C=O functional groups on the wood fiber surface. Extraction with AW-HW removed more of the non-

conjugated C=O structures. AW-based solvent systems were the most effective at removing C=O groups.

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