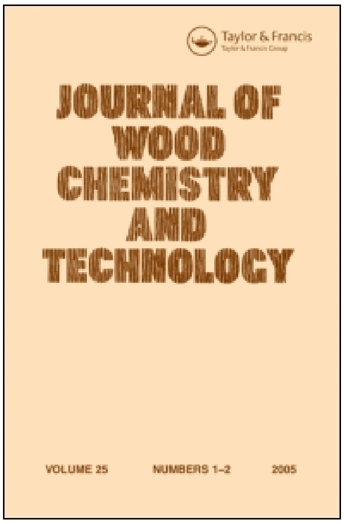

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Inverse Gas Chromatography for Determining the Surface Free Energy and Acid-Base Chemical Characteristics of a Water Extracted Hardwood (*Acer rubrum*)

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Abstract: Hardwood hemicellulose extracts can be used as a feed stock for ethanol plants or for renewable polymer applications. Extraction of *Acer rubrum* wood strands with water at 160°C and for 90 minutes removed approximately 16% of the wood weight. The extract was composed primarily of acetylated glucuronoxylans (63.9%) and lignin (17.6%). The dispersive surface energy and acid-base surface characteristics for a multi-component freeze dried mixture of hot water extracted *Acer rubrum* components was determined by inverse gas chromatography (IGC). The dispersive surface energy of the extract was found to be non-sensitive to thermal variations and has a magnitude of 34.6 ± 0.2 mJ/m^2 with a K_a of 0.13 and K_b of 0.46. The maple wood had a regressed surface energy of 42.7 mJ/m^2 at 20°C following extraction, and the surface energy before extraction was 40.4 mJ/m^2 at 20°C. Also, before extraction the K_a and K_b of the red maple were 0.19, 0.92, respectively, and after extraction the K_a and K_b were 0.15 and 1.17. Infrared spectroscopy (IR) was used to characterize the wood surfaces and the IR data correlated to the surface energy values. These findings indicate that the hemicellulose-extract components influence the overall average surface energy of maple wood by lowering the surface energy relative to other surface components.

Keywords: *Acer rubrum*, composites, extraction, inverse gas chromatography, surface energy

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INTRODUCTION

Background

Hemicellulose extracts have been studied as a possible source of biopolymers and chemicals. However, most of the previous work has focused on the purification of the different fractions in the extracts based on their molecular size and/or chemical characteristics.[1–7] A different approach is to use hemicelluloses extracts directly where their very particular chemical characteristics are a match for specific applications. Hemicellulose extracts from wood have both hydrophobic and hydrophilic regions and may be utilized in composites or converted to renewable polymers and fuels. This article introduces basic properties of hemicellulose extracts obtained from a hardwood (*Acer rubrum*) by hot water extraction to be considered for further applications. Also, the surface of wood is analyzed before and after the hot water extraction.

The purpose of doing this work is to expand the understanding of the physical surface characteristics of wood before and after extraction as well as the extract itself. The use of the inverse gas chromatography (IGC) technique creates acid–base characteristics and surface energy values for the materials that may be helpful in determining applications for the extract and extracted wood.

IGC Background for Determining Acid–Base Interactions

The Lewis acid base theory is critical to IGC analysis of fiber/matrix acid base interactions. IGC uses probe liquids to determine the acid base character of the solid packed in the column. The retention time of both the carrier gas and the probe gas is recorded. These retention times are related to thermodynamic quantities that can be used to ascertain the acid–base character of the solid phase. The retention time of a probe is measured and then used in the following relationship:

$$V_g = \frac{273.15}{T_c} * \frac{1}{w} * Q(T_r - T_i) \tag{1}$$

The retention time measured by IGC is the net retention volume (the volume of carrier gas required to elute a zone of solute vapor), per gram of adsorbent, and is determined by Eq. (1), where T_c is the column temperature, w is the mass in grams of adsorbent packed into the column, Q is the corrected flow rate of the helium gas, and T_r and T_i are the retention time of probe and inert gas. From the retention volume, the Gibbs free energy of the system can be determined.[8] Schultz and Lavielle[9,10] developed a method for relating the

Gibbs free energy to the dispersive surface energy of the gas phase probes and the solid particles in the IGC column and Donnet et al.,[11]expanded on this work with what is known as the polarization method. Both the Schultz and Lavielle and polarization methods of IGC analysis have been utilized in the literature and compared.[12,13]

By running IGC experiments at different temperatures, the acid–base Gibbs free energy of absorption is measured, and the parameter is related to the acid–base enthalpy of adsorption by the following expression:

$$\Delta G_{AB} = \Delta H_{AB} - T\Delta S_{AB} \tag{2}$$

From this equation the acid–base enthalpy of adsorption can be determined by plotting ΔG_{AB} versus T, producing a straight line where the intercept is ΔH_{AB}.

Gutmann's approach of using electron donors and acceptors for the enthalpy of acid–base interactions can now be applied.

$$-\Delta H_{A}^{AB} = K_a DN + K_b AN \tag{3}$$

The *AN* and *DN* are the acceptor and donor numbers related to chemical references. The donor number, *DN*, was defined as the negative of the enthalpy of formation for the chemical made by the acid–base reaction with antimony pentachloride. The corresponding electrophilicity of a chemical species was determined from the ^{31}P NMR shifts induced by triethylphosphine oxide, a basic probe. The K_a and the K_b are constants that show how the solid differs from the references used with the standards.[14]

MATERIALS AND METHODS

Wood Material Preparation

Red Maple (*Acer rubrum*) trees were harvested and debarked. Then, bolts were cut for stranding. The stranding was done at a thickness of 0.025″.

Approximately 5 kilograms of the strands were air dried at room temperature and moisture content was determined in oven at 105°C based on oven dry weight. The dried wood material was stored in double plastic bags for later extraction experiments.

Extraction Procedure

The extractions were done using a modified ASE-100 extractor operating at pressures of 100–150 atm. Approximately 30 grams of dry wood were used for the extraction. Pure water was used as extraction liquid. The extraction was done at 160°C for 90 min.

Glass fiber filters were placed at the inlet and outlet of the extraction cell. At the end of the extraction process, the liquid in the extraction cell was displaced into a collection bottle using fresh water at a volume of 1.5 times that of the extraction cell (150 ml). The wood remaining after the displacement process was removed from the extraction cell.

The liquid and solid phases were treated separately. The weight and pH of the liquid phase are recorded. Two samples of approximately 25 ml are taken, centrifuged to remove fine particles, and then freeze dried for solids content determination. Both the freeze dried solids and the remaining liquid phase are stored in a refrigerator for future analysis. The remaining wood material in the extraction cell was oven dried overnight at 105°C (±5) and its weight determined.

The gravimetric extraction yield was calculated by comparing the amount of oven dry extracted wood before and after extraction.

Chemical Analysis Procedure

The mono-sugar composition of the liquid phase (hemicellulose extract) was determined by a two-step hydrolysis (as described here for total lignin content determination) and high performance anion exchange chromatography (HPAEC) and pulsed amperometric detection (PAD). Chromatography of the samples was performed using a Dionex LC system coupled to an AS 50 autosampler. The high-performance liquid chromatography (HPLC) system was equipped with a CarboPac PA1 column (4 × 250) in combination with a CarboPac guard column and run at 20°C. Separation was performed at a flow rate of 0.7 ml/min in the column and 1 ml/min in the post column using a combined gradient of three eluents prepared from degassed distilled HPLC grade water: eluent A, distilled water; eluent B, 0.3 M NaOH prepared from a 50% solution NaOH to minimize the carbonate content in the final eluent; eluent C, 0.17 sodium acetate (NaAc) in 0.2M NaOH prepared accordingly. The eluents were degassed by flushing helium and pressurized continuously with the eluent degas module of Dionex. Gradients of NaOH and NaAc were used simultaneously to elute the monosaccharides by mixing the three eluents. This resulted in the following gradient of NaOH: 0–5 min, 40%; NaAc: 0–5 min, 60%; water: 6–36.6 min. Samples (20 uL) were injected at 15.5 min. The effluent was monitored using a pulsed-electrochemical detector in the pulse-amperometric mode with a gold working electrode and a Ag/AgCl reference electrode to which potentials of E1 0.1 V, E2 –2 V, E3 0.6 V, and E4 –0.1 V were applied for duration times T1 0.4 s, T2 0.02 s, T3 0.01 s, and T4 0.07 s. Quantification of the samples was performed using the response factors calculated from the peak areas of the mixed standard solutions for five sugars (glucose, mannose, galactose, arabinose, and xylose). Fucose was used as internal standard.

The total lignin content is referred to the sum of the precipitate after a two-step hydrolysis and the lignin remaining in the liquid phase. For the two-step hydrolysis 100 mg of freeze dried hemicellulose extract sample was placed in a vial and put in contact with 1.5 mL of 72% sulfuric acid at 30°C in a water bath for one hour. Then the sample was transferred to a 125 mL flask and the solution was diluted to 4% sulfuric acid by adding HPLC grade water. The flask was autoclaved at 120°C for one hour. The precipitate was measured gravimetrically and it includes the Klason lignin[15] and aromatic compounds that were extracted during the hot water extraction. The total aromatic compounds were determined as the sum of the precipitate plus the acid soluble lignin in the liquid phase measured spectrophotometrically at 205 nm using Nicolet Evolution 100 model (Thermo, Electron Corporation). Total acetyl groups were determined by the acetic acid content in the hydrolyzed sample after the two-step hydrolysis for total lignin determination. The analysis was performed using a Shimadzu HPLC CTO-10A and refractive index detector (RID-10A). Protein content was determined as a function of the nitrogen content in the extract. Glucuronic acids were determined by methanolysis and gas chromatography.[16]

IGC Measurements

IGC columns were packed with the maple before extraction, after extraction, and the extracted mixture then was conditioned at 103°C in the GC oven with 10 standard cubic centimeters (sccm) of helium until the flame ionizing detector recorded a background signal of <5 pA at 30°C.

Experiments were conducted on a fully automated Surface Measurements Systems SMS IGC with head space temperature control. The IGC columns into which the particles are packed were supplied by Surface Measurement Systems and are custom silane-treated glass tubes. The hemicellulose extracted materials were analyzed using the SMS IGC at 30°C, 35°C, and 40°C. Vapors of HPLC grade polar and non-polar probes were sampled by micro syringe and an infinite dilute concentration of probe was injected into the packed column and the retention time measured by a flame ionization detector. An infinitely dilute sample of methane was also injected to determine the "dead time" in the column. The probe retention time and the methane retention time were entered into Eq. (1) with the mass of the packed material in the column. Values of retention time were used for calculating the γ_S^d, K_a, and K_b for the red maple wood. Calculations were done using an Excel spread sheet and packaged software from SMS. To calculate K_a and K_b Eq. (3) is written in y = mx + b form and AN^* (in energy/mole) is used instead of AN, which is a unitless value:

$$\frac{-\Delta H_A^{AB}}{4.184AN^*} = \frac{DN}{AN^*}K_a + K_b \tag{4}$$

Table 1. Physical constants for probes used in IGC experiments, (13)

Probe	Polarizability Index $\alpha_o(h\nu)^{0.5} \times 10^{49} C^{3/2} m^2 V^{-1/2}$	DN Kcal/Mole	AN* Kcal/Mole	Specific Characteristic
n-Hexane	9.2	—	—	Non-polar
n-Heptane	10.3	—	—	Non-polar
n-Octane	11.4	—	—	Non-polar
n-Nonane	12.5	—	—	Non-polar
n-Decane**	13.6	—	—	Non-polar
n-Undecane**	14.7	—	—	Non-polar
Acetone	5.8	17	2.5	Amphoteric
Chloroform	7.8	—	4.8	Acidic
Tetrahydrofuran	6.8	20	0.5	Basic
Ethyl acetate	7.9	17.1	1.5	Amphoteric

**Indicates the values were calculated by extrapolation as Donnet et al. did for n-Nonane in their original work.[11]

Values of *DN* and *AN* were found from the literature and reported in Table 1 for the probes used in IGC.

Temperatures of 30°C, 35°C, and 40°C were used for determining γ_S^d and K_a and K_b determined for the hemicellulose extracted material.

Diffuse Reflectance IR Analysis

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) was performed on freeze dried hemicellulose extract samples and ground wood samples. Wood before extraction and extracted wood were ground to under 1 millimeter using a laboratory mill Wiley Mill-Model 4 and screened to 60 mesh maximum particle size. The powdered extract and wood samples were mixed with KCl to form a 3% extract in KCl mixture and infrared spectra were obtained after purging the water out of the infrared chamber by pumping the chamber down with nitrogen at 5 ml/min for 2 hours.

RESULTS AND DISCUSSION

Chemical Analysis

The calculated extraction yield was about 16% based on the original wood. The final pH of the extract was 3.5. Table 2 shows the chemical composition for the freeze dried hemicellulose extract.

Table 2. Chemical analysis of freeze dried hemicellulose extract (all values in g/100 g of dried extract)

Component	Weight percentage g/100 g
Cellulose	3.94
Acetylated glucuronoxylan	63.92
Mannan	2.89
Galactan	4.55
Proteins	1.54
Total lignin	17.59
Ash	1.97
Total	**96.40**

IGC Measurements

In Table 3 the dispersive surface energy is shown at 30, 35, and 40°C. Typically the dispersive surface energies calculated by IGC tend to decrease with increasing temperature due to an increase in the entropic contribution to the Gibbs free energy. However, with hemicellulose extract the dispersive surface energy seems to be unresponsive to temperature change. This may be due to the amorphous nature of the hemicellulose extract being non-sensitive to thermal changes and in a lowest energetic state. The maple after extraction had the highest surface energy with 42.7 mJ/m^2 at 20°C and the maple before extraction was at 40.4 mJ/m^2 at 20°C. These results are consistent with the findings of Walinder and Gardner[17] where extracted heartwood samples had higher dispersive surface energies then wood samples before extraction.

In Figure 1, the n-alkanes exhibit a linear relationship representing the apolar characteristic of the hemicellulose extracted material, and the Schultz and Lavielle method uses this relationship to determine γ_S^d.

From the slope and intercept of the data in Figure 2, K_a and K_b are determined. The K_a, K_b, and γ_S^d of the hemicellulose material, the maple

Table 3. Dispersive surface energy at 20°C, 30°C, 35°C, and 40°C

	γ_s^d (mJ/m^2)				
T (°C)	40	35	30	20 (regressed)	Rsq
Extract	34.7	34.4	34.7	34.6	0.00
Maple before extaction	36.3	36.9	38.5	40.4	0.93
Maple after extraction	38.3	39.1	40.6	42.7	0.97

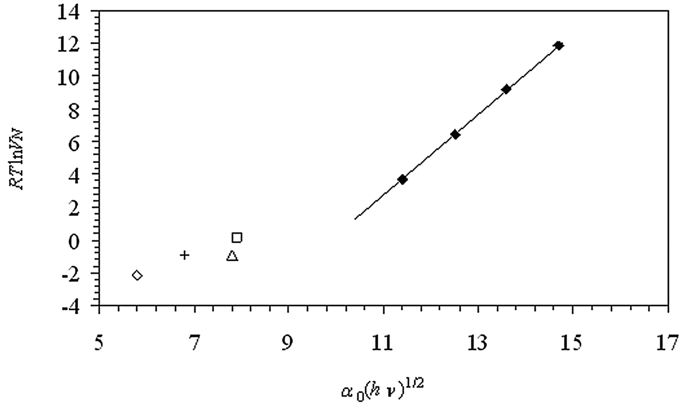

Figure 1. Example polarization plot at 30°C to determine acid base characteristics of the hemicellulose extracted material with n-alkanes ♦, ethyl acetate □, tetrahydrofuran +, chloroform △, acetone ◇.

before extraction, and after extraction are reported in Table 4. To the authors' knowledge, no other papers have reported K_a and K_b values for hemicellulose.

The surface energy trend of increase in surface energy as extract is removed corresponds well with literature results found by Gardner et al.,[18] where results indicate that low molecular weight compounds lower the surface energy of wood materials. Conversely, the result that the surface energy increases as

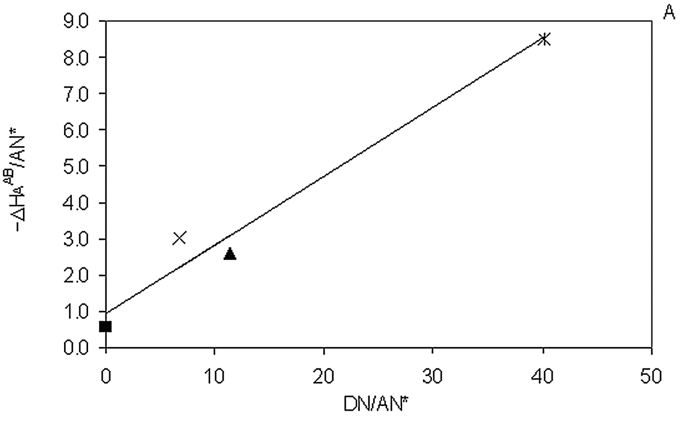

Figure 2. Example relationship for determining K_a and K_b using data from the polarization method at 30°C, 35°C, and 40°C for the maple wood before extraction with chloroform ■, ethyl acetate ▲, acetone ×, and tetrahydrofuran ∗.

Table 4. γ_d, K_b, and K_a for the wood materials

	γ_d(mJ/m^2)	K_b	K_a
Extract	34.6	0.46	0.13
Red maple	40.4	0.92	0.19
Extracted red maple	42.7	1.17	0.15

these low molecular weight compounds are removed from the surface is to be expected.

Also, the surface energy trend found that for the increase in surface energy as extract is removed is well correlated with the increase in the K_b of the wood material, as shown in Figure 3.

The difference in the electron acceptor surface character is not deemed to be significant. A further analysis of the surface properties may give more insight into the nature of the wood and extract surface.

Diffuse Reflectance IR Analysis

IGC gives a dispersive energy value and acid–base values for a surface, but does not give any information on the specific functional groups on the surface. Infrared spectroscopy is a technique that detects different functional groups on a surface and this information complements the IGC analysis. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) was performed on freeze

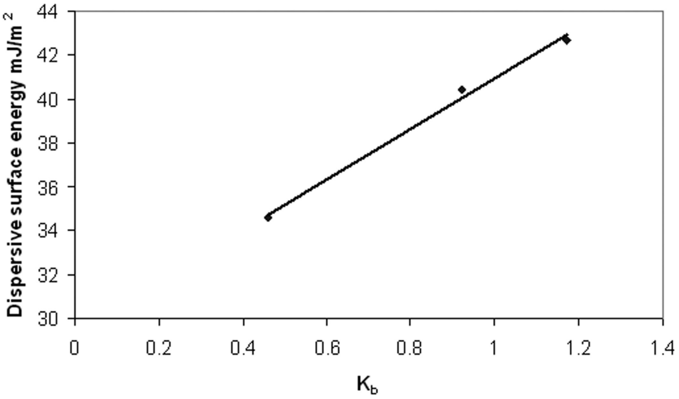

Figure 3. Dispersive surface energy as a function K_b of the extract, maple wood, and extracted maple wood $R^2 = 0.99$.

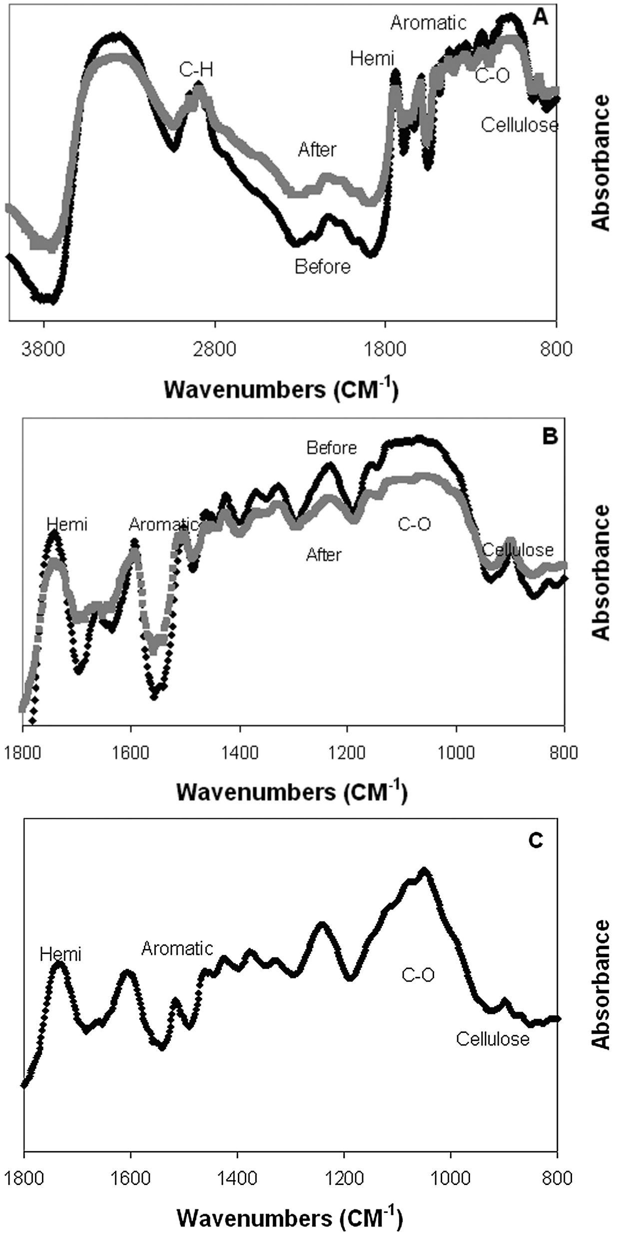

Figure 4. Drift spectra for (A) maple before and after extraction 800 to 4000 cm^{-1}, (B) wood before extraction and after extraction 800 to 1800 cm^{-1}, (C) hemicellulose extract from 800 to 1800 cm^{-1}. All spectra are labeled "after" for after extraction, "before" for before extraction spectra, "Hemi" for hemicellulose, "C-H" for aliphatic C-H stretching, "Cellulose" for cellulose, "Aromatic" for lignin aromatic compounds in the wavenumber ranges corresponding to peaks due to those functional groups and compounds.

dried hemicellulose extract samples. The powdered extract was mixed with KCL and infrared spectra were obtained after purging the water out of the infrared chamber for 2 hours.

Grandmaison et al.[19] used DRIFT spectroscopy with extracts of *Populus tremuloides* and very similar spectra were obtained. The following spectra analysis is based on Gradmaison's et al.[19] work. In Figure 4A, a band at 2900 cm^{-1} is seen and is attributed to aliphatic C-H stretching; Figure 4A is an example of the overall spectrum seen for all wood specimens. The rest of the analysis is focused on Figures 4B and 4C. From Table 2, the composition of the extract contains hemicellulose, lignin, and cellulose and these components should be seen in the DRIFT scans. The spectral region of 1450–1595 cm^{-1} has peaks that are attributed to the aromatic lignin. The large peak at 1505 cm^{-1} is due to the lignin aromatic ring vibration. The peak attributed to cellulose is at 895 cm^{-1} and for this peak the relative peak area in Figure 4B is larger for the maple after extraction than before extraction, indicating that the surface concentration of cellulose for the maple increases with the removal of the extract. The peak attributed to hemicellulose is found at 1740 cm^{-1} and is seen before and after extraction and in the extract. The 1740 cm^{-1} peak is the second largest peak after the peak at 1035 cm^{-1} attributed to the C-O bonds in all the polysaccharides, lignin alcohols, and lignin ethers showing that hemicellulose is a macromolecule found in the extract and on the surface of the wood.

CONCLUSIONS

The extraction yield using hot water at 160°C and 90 minutes was approximately 16%. The major two components in the extract were acetylated glucuronoxylans (63.9%) and lignin (17.6%). The IGC technique determined a thermally stable dispersive surface energy of 34.6 ± 0.2 mJ/m^2 with a K_a of 0.13 and K_b of 0.46 for the hemicellulose-extract material. The red maple exhibited a surface energy of 42.7 mJ/m^2 at 20°C for the wood after extraction and at 40.4 mJ/m^2 for the maple before extraction at 20°C. Also, for the maple before extraction the K_a and K_b are 0.19, 0.92 and after extraction the K_a and K_b are 0.15, 1.17. The increase in surface energy for the wood after extraction may be of value when trying to create composite materials or through improved adhesion to substrates. Knowing the surface energy and acid–base values for the extract may elucidate an application or end use for the extract "as is" in composite materials. The DRIFT scans of the extract wood before and after extraction closely resembled DRIFT scans of other wood samples found in the literature. The DRIFT scans before and after extraction reveal that there is a higher concentration of cellulose on the wood surface after extraction.

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