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Elemental analysis, chemical composition, cellulose crystallinity, and FT-IR spectra of *Toona sinensis* wood

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Abstract *Toona sinensis* wood was analyzed for main chemical composition, trace element content, and wood cellulose crystallinity by FT-IR spectroscopy and X-ray diffraction of its native and extracted forms. The results showed that the ash and the extractives content of *Toona sinensis* wood were higher than for other leafy trees. The holo-cellulose, cellulose, and lignin content of the wood were 722.2, 458.3, and 213.1 mg g^{-1}, respectively. Trace element content was: Ca 3.05 × 10^3, Mg 3.34 × 10^2, Fe 1.38 × 10^2, K 1.30 × 10^2, Na 58.0, Al 25.7, Zn 5.91, Cu 4.06, Mn 3.21, and Pb 0.534 μg g^{-1}. Extraction of *Toona sinensis* wood resulted in no significant chemical changes but the band at 1,736 cm^{-1} of C=O in lignin and hemicelluloses disappeared and a band at 1,245 cm^{-1} of CO–OR in hemicelluloses and C–O in lignin shifted to 1,234 cm^{-1} and weakened only in the spectrum of the sample extracted with 1 % (*w*/*w*) aqueous sodium hydroxide. The FT-IR crystallinity index of the sample extracted with 1 % (*w*/*w*) aqueous sodium hydroxide was less than that of the original wood. The X-ray diffraction crystallinity indices of nitric acid–ethanol cellulose in *T. sinensis* wood was 0.786. These results indicate that *T. sinensis* wood probably has good flexibility and strength, and has the potential for use as a biomaterial and/or a bioenergy feedstock.

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Introduction

Toona sinensis (A. Juss) Roem, a species of *Toona*, is a perennial hardwood native to China, where it is widely distributed and called "Xiangchun" in Chinese or "Chinese mahogany" in English. It has a long history of cultivation in China where its buds are used as a vegetable and its wood is used in construction. Many studies have been conducted on the cultivation, reproduction, and biological activity of *T. sinensis* [1–8] and on the physical characteristics of its wood [9–12]. However, there are few reports on the chemical composition of *T. sinensis* wood [13]. The main chemical composition of wood is an important property of the biomaterial because it affects the mechanical characteristics and natural durability of the wood, and its color and its behavior during processing and utilization.

Wood is a natural growth polymer and is mainly composed of cellulose, hemicelluloses, and lignin that are strongly intermeshed and bonded by both non-covalent forces and covalent cross-linkages. Conventional analysis [14] of wood includes ash, cold and hot water extracts, 1 % (*w*/*w*) aqueous sodium hydroxide solution extracts, alcohol–benzene solution extracts, lignin (Klason lignin and 72 % (*w*/*w*) sulfuric acid-soluble lignin), holocellulose (sum of cellulose and hemicelluloses), pentosan, and other contents.

Cellulose is a homopolysaccharide composed of β-D-glucopyranose units which are linked together by (1 → 4)-glycosidic bonds. Cellulose molecules are linear and have a

strong tendency to form intra and intermolecular hydrogen bonds. Bundles of cellulose molecules are aggregated together in the form of micro fibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions.

Hemicelluloses are a heterogenic group of polysaccharides and their derivatives which are formed through biosynthetic routes different from that of cellulose. Like cellulose, most hemicelluloses function as supporting material in the cell walls. Hemicelluloses are relatively easily hydrolyzed by acids to their monomeric compositions consisting of D-glucose, D-mannose, D-xylose, L-arabinose, and small amounts of L-rhamnose, in addition to D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, and D-galacturonic acid. Most hemicelluloses have a degree of polymerization of only 200, in contrast with celluloses with a degree of polymerization of the order of five times higher.

Lignin is a three-dimensional phenylpropanoid polymer in which benzene–propane units are linked to each other by ether bonds. Lignin is a natural polymer, and its amount is slightly lower than that of cellulose, with which it is always associated. Whereas cellulose has been used by humans for thousands of years, lignin has not been as widely used. The chemical composition of lignin directly affects the shape, quality, and mechanical characteristics of lignin products. The phenol hydroxyl groups in the lignin structure, which are important in determining the physical and chemical properties of the material, can be relatively easily removed by alkaline cooking in the paper-making process, which thereby has a great affect on pulp brightness and stability [15].

The trace element content of wood directly affects its properties, and its performance in pulping or papermaking and in biofuel processing technology [16, 17]. However, data on the trace element content of *T. sinensis* wood are scarce [18]. Atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP–AES), or inductively coupled plasma-mass spectrometry (ICP–MS) are the most frequent techniques used for trace elements determination. ICP–MS is the method with the highest potential in respect of detection limits, sensitivity, precision, multi-element determination, and speed [19]. ICP–AES is attractive for trace elements analysis, because of its satisfactory sensitivity, coupled with the advantage of simultaneous determination of several elements at several spectral lines. However, the great disadvantage both methods is that they require significant sample preparation; i.e., digestion by wet-acid or dry ashing by heating in a microwave oven or a furnace [20].

Fourier transform infrared (FT-IR) spectroscopy is a useful technique for studying wood chemistry, because minimal sample preparation is required and very small quantities of wood (a few milligrams) can be analyzed to provide detailed structural information about the wood [21–23], including determination of the lignin content of pulp, paper, and wood [24]. It has also been used to analyze the chemical changes that occur during wood weathering, decay, chemical treatment [25], and/or natural ageing [26].

Crystallinity is an important property of wood, having an effect on its physical, mechanical, and chemical properties. X-ray diffraction (XRD) has been used for decades as a rapid, non-destructive method to study wood crystallinity, determined by the diffraction peaks from cellulose crystals. Both X-ray diffraction analysis and methods based on the absorption of polarized infrared radiation have been used to study the crystalline structure of cellulose [27, 28].

The general objective of this study was to analyze for the trace element content, main chemical composition (cold water and hot water soluble extractives content, 1 % sodium hydroxide soluble materials content, alcohol–benzene solution soluble materials content, lignin content, cellulose and holocellulose content, and ash content) of the wood, and to assess the effects of extraction of *T. sinensis* wood on its functional groups and crystallinity index.

Results and discussion

Results from analysis of the main chemical composition of Toona sinensis wood

The results from analysis of the main chemical composition of *T. sinensis* wood are listed in Table 1. The phenolic hydroxyl content of organic solvents-soluble lignin [29] was 0.17 mmol g^{-1}. The amount of ash from *Toona sinensis* wood was 9.1 mg g^{-1}, higher than that from most wood (3–5 mg g^{-1}) [31]. As can be seen from Table 1, the contents of cold and hot water extracts, ethanol–benzene extracts, and 1 % (*w*/*w*) aqueous sodium hydroxide extracts of *T. sinensis* wood were higher than those for other leafy trees [31]. The total lignin content was low (213.1 mg g^{-1}) but higher than that of poplar wood (171.0 mg g^{-1}) [31]. The holocellulose content was approximately 722.2 mg g^{-1}, and the pentosan content was 224.8 mg g^{-1}. The nitric acid–ethanol cellulose content was 458.3 mg g^{-1}, which was lower than that of *Pinus massoniana* Lamb, *Larix gmelinii* Rupr., and *Pinus koraiensis* Sieb. et Zucc. wood, but higher than that of *Picea asperata* Mast spruce, *Cupressus funebris* Endl., and *Populus tremula* wood [31]. Cellulose, the main structural component of cell walls, which acts as the skeleton material, is a major source of cell wall strength. Hemicellulose (glucomannan, xylan) is attached to cellulose micro fibrils and lignin, most of xylan is connected to glucomannan and lignin, and glucomannan and cellulose micro fibrils are

linked closely together. The force between xylan and glucomannan is lower than that which occurs between the cellulose micro fibrils and glucomannan. Xylan in the cell wall acts as coupling agent connecting cellulose with lignin and its presence is important in maintaining the integrity of the cell wall mechanics. Lignin is attached to xylan, but this connection, which is very easy to damage, increases the mechanical properties of the cell wall to a limited extent only. So, it can be inferred from the results from analysis of its main chemical composition that *T. sinensis* wood probably has good flexibility and strength, and may be used as a biomaterial and/or a bioenergy feedstock.

Table 1 Results from analysis of the main chemical composition of *Toona sinensis* wood

Chemical composition	Content/mg g^{-1}
Ash	9.1 ± 0.1
Cold water extractives	47.2 ± 0.1
Hot water extractives	81.4 ± 0.1
1 % (*w*/*w*) aqueous sodium hydroxide extractives	249.2 ± 0.2
Alcohol–benzene extractives	35.8 ± 0.1
Klason lignin	159.8 ± 0.2
72 % (*w*/*w*) sulfuric acid-soluble lignin	53.3 ± 0.1
Total lignin	213.1 ± 0.2
Holo-cellulose	722.2 ± 0.4
Pentosan	224.8 ± 0.2
Nitric acid–alcohol cellulose	458.3 ± 0.3
Organic solvent-soluble lignin	242.0 ± 0.2

Results from analysis of the trace element content of Toona sinensis wood

Table 2 shows the working curves and detection limits for the trace elements; the results from analysis of the trace element content of *T. sinensis* wood were: Ca 3.05×10^3, Mg 3.34×10^2, Fe 1.38×10^2, K 1.30×10^2, Na 58.0, Al 25.7, Zn 5.91, Cu 4.06, Mn 3.21, and Pb 0.534 μg g^{-1}. Cd and Ni were not detected. These trace elements affect the combustion process by forming gaseous emissions, solid emissions, and by significantly affecting the melting behavior of the ash, and by fouling the furnace and the boiler [33]. The effects of these trace elements in *T. sinensis* wood on processing characteristics and in biomass energy applications remain to be further studied.

FT-IR spectra of Toona sinensis wood, lignin, and cellulose

FT-IR spectra of the wood

Figure 1 shows the FT-IR spectra of *T. sinensis* wood (d) and residues of the wood extracted by use of different solvents (a–c). Assignment of the absorption bands is presented in Table 3. Comparison of the spectra showed that the extraction treatment did not cause any significant changes in the FT-IR spectrum of the extracted wood samples. However, the band at 1,736 cm^{-1} of the C=O stretching vibration in non-conjugated ketones and the free aldehyde present in lignin and hemicelluloses [37, 39–42] disappeared and the band at 1,245 cm^{-1} of the acyl-oxygen CO–OR stretching vibration in hemicelluloses and C–O of the guaiacyl unit stretching vibration in lignin [40, 43]

Table 2 Linearity of working curves and concentration detection limits of concentration

Element	Analytical wavelength/nm	Linearity of working curve[a]	Correlation coefficient	Concentration range/mg dm^{-3}	Concentration detection limit/μg cm^{-3} [b]
Fe	238.2	$I = 24{,}600\rho + 4{,}385.6$	0.9999	0.000–100.000	0.08329
Mn	257.6	$I = 159{,}100\rho + 6{,}577.7$	0.9998	0.000–10.000	0.0112
Cu	327.4	$I = 78{,}960\rho + 263.5$	0.9999	0.000–2.000	0.009
Zn	206.2	$I = 17{,}310\rho - 3{,}834.5$	0.9985	0.000–10.000	0.006
Ca	317.9	$I = 21{,}040\rho - 2{,}242.8$	0.9999	0.000–100.000	0.00336
Mg	285.2	$I = 434{,}300\rho - 6{,}971.9$	0.9998	0.000–100.000	0.03278
Na	589.6	$I = 49{,}670\rho - 6{,}258.4$	0.9952	0.000–10.000	0.0114
K	404.7	$I = 3{,}331\rho - 758.4$	0.9988	0.000–100.000	0.00624
Al	396.2	$I = 17{,}520\rho + 36.3$	0.9999	0.000–10.000	0.04907
Pb	220.4	$I = 2{,}922\rho + 25.1$	0.9997	0.000–10.000	0.0672
Cd	228.8	$I = 18{,}140\rho - 1{,}705.8$	0.9941	0.000–2.000	0.0243
Ni	221.6	$I = 6{,}651\rho + 196.3$	0.9999	0.000–7.140	0.0037

[a] I is spectral intensity associated with the concentration of the detected inorganic element, and ρ is concentration of the detected inorganic element

[b] The concentration detection limit of for each element was defined as three times the relative standard deviation of the results obtained from replicate (tenfold) analysis of the blank solution [32]

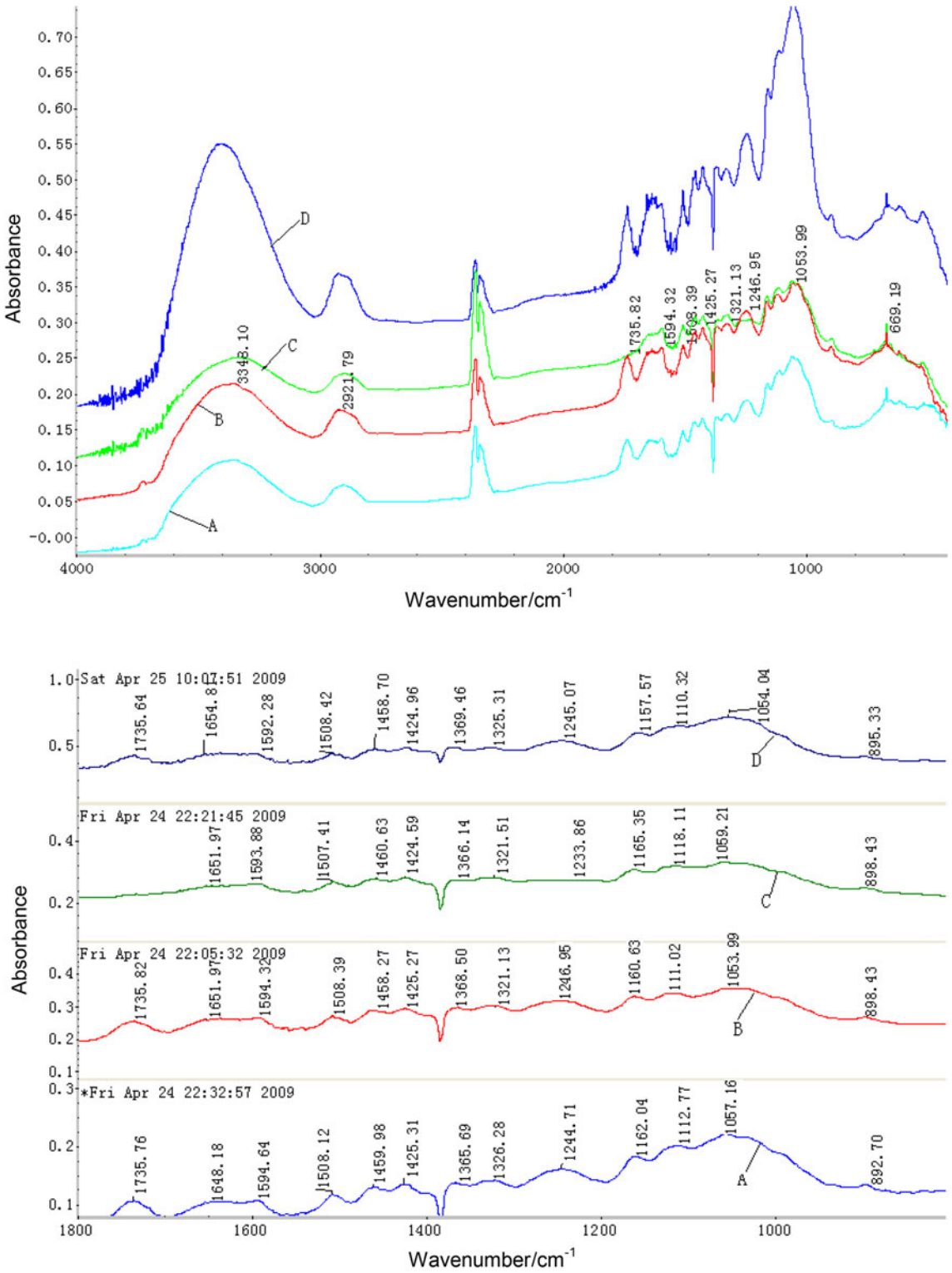

Fig. 1 FT-IR spectra of *T. sinensis* wood and residues extracted by use of different solvents: cold water (*a*), hot water (*b*), and 1 % (*w*/*w*) aqueous sodium hydroxide (*c*). *d* is the spectrum of the original wood

shifted to 1,234 cm^{-1} and weakened only in spectrum of the sample extracted by use of 1 % (*w*/*w*) aqueous sodium hydroxide (c). The band at 1,736 cm^{-1} disappeared, maybe because C=O in non-conjugated ketones turned into olefinic alcohol, then olefinic alcohol reacted with NaOH. Hemicellulose units with free aldehyde groups shed these

Table 3 FT-IR absorption bands in spectra obtained from *T. sinensis* wood samples, and their assignments

Wavenumber/cm^{-1}				Band assignment
a	b	c	d	
3,348	3,348	3,344	3,406	O–H stretching (hydrogen-bonded) [37, 38]
2,900	2,922	2,902	2,922	C–H stretching vibration in methyl and methylene groups [37, 38]
1,736	1,736	–	1,736	C=O stretching vibration in non-conjugated ketones and free aldehyde present in lignin and hemicellulose [37, 39–42]
1,648	1,652	1,652	1,655	C=O stretching in conjugated ρ-substituent aromatic ketenes [29, 40, 43]
1,595	1,594	1,594	1,592	C=C unsaturated linkages, aromatic rings present in lignin [22, 44]
1,508	1,508	1,507	1,508	C=C stretching vibration in aromatic structure of lignin [40, 45, 46]
1,460	1,458	1,461	1,459	C–H deformations, asymmetric bending vibration of $–CH_3$ and $–CH_2–$ groups from lignin [22, 42, 43, 46]
1,425	1,425	1,425	1,425	CH_2 stretching vibrations related to the structure of cellulose, aromatic skeletal bending vibrations [22, 40, 43]
1,366	1,369	1,366	1,369	C–H bending vibrations related to the structure of cellulose and hemicelluloses [37, 38]
1,326	1,321	1,322	1,325	C–H deformation vibration, O–H bending vibrations in phenols (lignin) [40, 43]
1,245	1,247	1,234	1,245	Acyl-oxygen CO–OR stretching vibration in hemicelluloses, C–O of guaiacyl unit stretching vibration in lignin [40, 43]
1,162	1,161	1,165	1,158	Asymmetric bridge stretching vibration of C–O–C group in the structure of cellulose and hemicellulose [22, 40, 43]
1,113	1,111	1,118	1,110	Hydroxy-association absorption band [50]
1,057	1,054	1,059	1,054	Aromatic C–H in-plane deformation, symmetrical C–O stretching [43]
893	898	898	895	Glucose ring stretching, C1–H deformation, C–H stretching out of plane of aromatic ring [22, 40, 46]

T. sinensis wood residues were obtained by extraction with different solvents: cold water (a), hot water (b), and 1 % (*w*/*w*) aqueous sodium hydroxide (c). (d) is the original wood. "–" do not form the absorbance peak

Table 4 FT-IR crystallinity index of *T. sinensis* wood samples and nitric acid–ethanol cellulose

Wood sample	Band intensity (absorbance) at wavenumber/cm^{-1}				$NO'KI_1$ $I_{1,372}/I_{2,900}$	$O'KI_2$ $I_{1,425}/I_{895}$
	1,372	2,900	1,425	895		
a	0.135 (1,366)	0.095 (2,900)	0.133 (1,425)	0.131 (893)	1.42	1.02
b	0.293 (1,369)	0.176 (2,922)	0.292 (1,425)	0.264 (898)	1.66	1.11
c	0.272 (1,366)	0.196 (2,902)	0.277 (1,425)	0.246 (898)	1.39	1.13
d	0.486 (1,369)	0.333 (2,922)	0.486 (1,425)	0.418 (895)	1.46	1.16
e	0.192 (1,371)	0.135 (2,919)	0.178 (1,430)	0.146 (895)	1.42	1.22

T. sinensis wood residues were obtained by extraction with different solvents: cold water (a), hot water (b), and 1 % (*w*/*w*) aqueous sodium hydroxide (c). (d) is the spectrum of the original wood. (e) is the nitric acid–ethanol cellulose

one by one until all the free aldehyde in hemicelluloses turned into carboxyl. The reaction then stopped and the hemicellulose units turned into the corresponding sodium carboxylates. The band at 1,245 cm^{-1} shifted to 1,234 cm^{-1} and weakened, possibly because of alkaline hydrolysis of hemicelluloses, which resulted in reduced acyl-oxygen CO–OR content, and loss of $–OCH_3$ in guaiacyl units, which were shed and formed the phenoxy anion, which resulted in less C–O of guaiacyl units in lignin.

The FT-IR crystallinity index [34, 35], calculated by use of Eq. (2), is shown in Table 4. The band at 1,372 cm^{-1} is typical of crystalline cellulose. The band at 1,425 cm^{-1} is characteristic of cellulose I. Bands at 2,900, 1,425, 1,372, and 895 cm^{-1} are especially sensitive to crystalline and amorphous regions. $NO'KI_1$ is the total crystallinity index (TCI, $I_{1,372}/I_{2,900}$) and $O'KI_2$ is the lateral order index (LOI, $I_{1,425}/I_{895}$). The first gives results for cellulose I and II and the second for cellulose I only.

FT-IR spectra of lignin

FT-IR spectra of lignin from *T. sinensis* wood are shown in Fig. 2. The corresponding band assignments are given in Table 5. Lignin samples presented a broad band attributed

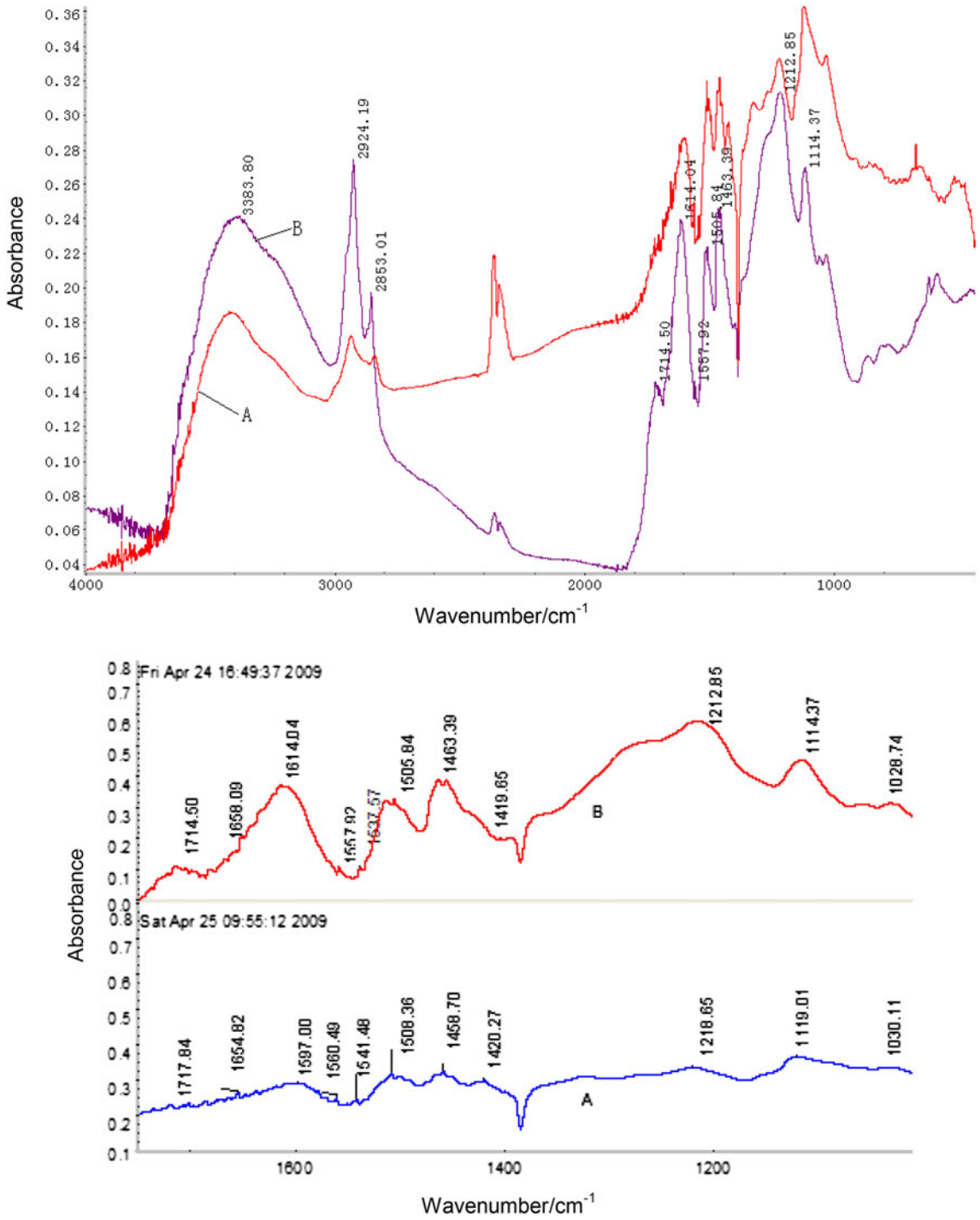

Fig. 2 FT-IR spectra of lignin from *T. sinensis* wood

to OH stretching (3,384–3,421 cm^{-1}) and peaks corresponding to C–H stretching of methyl and methylene groups (2,853–2,935 cm^{-1}) [37, 38, 47]. The spectra of lignin samples revealed the presence of two peaks at approximately 1,718 (1,715) and 1,655 (1,658) cm^{-1} assigned to unconjugated and conjugated C=O stretching, respectively, albeit with different intensities [31, 47–49]. The most characteristic vibrations of lignin correspond to those of aromatic rings and were identified at approximately 1,597 (1,614), 1,560 (1,558), 1,541 (1,538), 1,508 (1,506), 1,459 (1,463), and 1,420 cm^{-1} [31, 47–51]. A Klason lignin sample presented bands assigned to the three types of basic lignin unit. Bands at 1,219 (1,213) cm^{-1} (syringyl ring breathing), 1,119 (1,114) cm^{-1} (aromatic C−H in-plane deformation typical of syringyl units), 1,030 (1,029) cm^{-1} (aromatic in-plane C−H bending

Table 5 FT-IR absorption bands in spectra obtained from *T. sinensis* wood lignin samples, and their assignments

Wavenumber/cm^{-1}		Band assignment
a	b	
3,421	3,384	O–H stretching (hydrogen-bonded) [37, 38, 47]
2,935	2,924	C–H stretching vibration, methyl and methylene groups [37, 38, 47]
2,839	2,853	C–H stretching vibration in methoxy [37, 38]
1,718	1,715	C=O stretching in non-conjugated ketones, carbonyls in ester groups [31, 47, 48]
1,655	1,658	C=O stretching in conjugated ρ-substituent carbonyl and carboxyl [31, 47–49]
1,597	1,614	C=O stretching and C=C aromatic skeleton vibration [31, 47–51]
1,560	1,558	C=O stretching and C=C aromatic skeleton vibration [31, 48]
1,541	1,538	Aromatic C–C ring skeleton vibration [31, 47, 48]
1,508	1,506	Aromatic C–C ring skeleton vibration [31, 47, 48, 51]
1,459	1,463	C–H bend vibration, CH_3 and CH_2 asymmetrical bend vibration [31, 47–51]
1,420	1,420	Aromatic skeleton vibrations, C–H in-plane bend vibration [31, 47–50]
1,219	1,213	C–C and C–O of guaiacyl unit in lignin stretching, C=O stretching [31, 47–50]
1,119	1,114	Aromatic in-plane C–H bend vibrations, character of syringyl ring [31, 47–50]
1,030	1,029	Aromatic in-plane C–H bend vibrations, character of guaiacyl ring, C–O stretching from C–O ether vibrations, methoxy and β–O–4 in lignin [31, 47–52]

Klason lignin (a), organic solvent-soluble lignin (b)

vibrations, character of guaiacyl ring, C–O stretching from C–O ether vibrations, methoxy and β–O–4) were identified in the spectra of the lignin samples [31, 47–52].

There were a few differences between the FT-IR spectra of the two lignin samples. Most notably the band intensity at wavenumber 1,718 cm^{-1} of C=O stretching in non-conjugated ketones and carbonyls in ester groups [31, 47, 48] was weaker in Klason lignin, that may be because C=O in non-conjugated ketones was turned into olefinic alcohol, then esterification occurred between olefinic alcohol and sulfuric acid. The band intensity at wavenumber 1,420 cm^{-1} of aromatic skeleton vibrations and C–H in-plane bend vibration [31, 47–50] was weaker in the organic solvent-soluble lignin; this may be because the polymerization degree of the organic solvent-soluble lignin is less than that of Klason lignin.

FT-IR spectrum of nitric acid–ethanol cellulose

The FT-IR spectrum of nitric acid–ethanol cellulose from *T. sinensis* wood is shown in Fig. 3. The absorption band assignments are presented in Table 6. The bands at 1,371, 2,919, 1,430, and 895 cm^{-1} were selected to calculate FT-IR crystallinity index [34, 35, 48] by use of Eq. (2), yielding the results: $NO'KI_1 = 0.192/0.135 = 1.42$, $O'KI_2 = 0.178/0.146 = 1.22$, as shown in Table 4.

X-ray diffraction crystallinity of nitric acid–ethanol cellulose

X-ray diffraction intensity of nitric acid–ethanol cellulose from *T. sinensis* wood is shown in Fig. 4. There were the major crystal planes (101), (10-1), (002), and (040) at approximately 15.9° (756), 16.4° (705), 22.3° (1,786), and 34.4° (382), respectively [31]. The X-ray diffraction crystallinity indices (CrI) were used to indicate the relative, rather than absolute, amount of crystalline cellulose in the whole wood material or cellulose [27, 36]. The CrI of nitric acid–ethanol cellulose in *T. sinensis* wood calculated by use of Eq. (3) was 0.786 [(1,786–382)/1,786 = 0.786], which was less than 0.814 for *P. massoniana* Lamb wood flour delignified with nitric acid–ethanol [48].

Conclusions

The chemical composition of *T. sinensis* wood was investigated and twelve trace elements were determined. Cellulose crystallinity and FT-IR spectra of *T. sinensis* wood and its main chemical composition were analyzed. The results were:

1. The ash and extractives contents of *T. sinensis* wood were higher than for other leafy trees. The holocellulose, cellulose, and lignin contents were 722.2, 458.3, and 213.1 mg g^{-1}. The total lignin content was low, and the cellulose content was lower than that of *P. massoniana* Lamb, *L. gmelinii* Rupr., and *P. koraiensis* Sieb. et Zucc. wood, but was higher than that of *P. asperata* Mast spruce, *Cupressus funebris* Endl. and *Populus tremula* wood.
2. Comparison of FT-IR spectra obtained from extracted wood and original wood revealed that the extraction treatment did not cause any significant changes in the FT-IR spectrum of the extracted

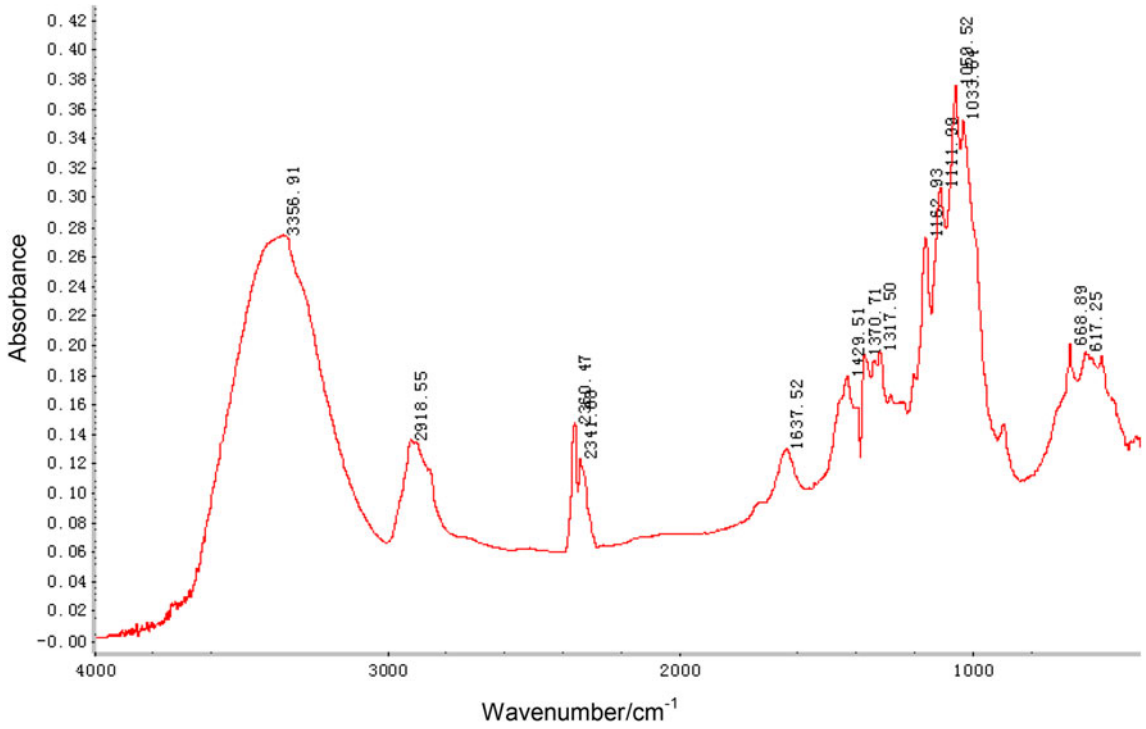

Fig. 3 FT-IR spectrum of nitric acid–ethanol cellulose from *T. sinensis* wood

Table 6 FT-IR absorption bands obtained from *T. sinensis* wood nitric acid–ethanol cellulose, and their assignment

Wavenumber/cm^{-1}	Band assignment
3,357	O–H stretching (hydrogen-bonded) [37, 38]
2,919	C–H stretching vibration in methyl and methylene groups [37, 38, 47, 48]
1,638	OH bending of absorbed water
1,430	CH_2 stretching vibrations related to the structure of cellulose [22, 40, 43, 49]
1,371	Symmetric C–H bending vibrations from methoxy group [37, 38, 49]
1,318	O–H bending vibration, in-plane
1,163	Asymmetric bridge stretching vibration of C–O–C group in the structure of cellulose [22, 40, 43, 48, 49]
1,112	OH associative absorption band [49]
1,060	C–O stretching vibrations: acetyl alkoxy bond stretching vibration [43, 48]
1,034	C–O stretching from C–O ether vibrations, methoxy [47–51]
895	Glucose ring stretching, C_1–H deformation; C–H stretching out of plane of ring due to β-linkage [22, 40, 46, 47, 49]

wood samples. The band at 1,736 cm^{-1} of the C=O stretching vibration in lignin and hemicelluloses disappeared and the band at 1,245 cm^{-1} of CO–OR in hemicelluloses and C–O of in lignin shifted to 1,234 cm^{-1} and weakened only in the spectrum of the sample extracted with 1 % (*w*/*w*) aqueous sodium hydroxide. The FT-IR crystallinity index of the sample extracted with 1 % (*w*/*w*) aqueous sodium hydroxide was less than that of the original wood. Specifically, the FT-IR crystallinity indexes of nitric acid–ethanol cellulose from *T. sinensis* wood was $NO'KI_1 = 1.42$ and $O'KI_2 = 1.22$. The X-ray diffraction crystallinity indexes of nitric acid–ethanol cellulose in *T. sinensis* wood were 0.786.

3. The trace element content of *T. sinensis* wood was: Ca 3.05×10^3, Mg 3.34×10^2, Fe 1.38×10^2, K 1.30×10^2, Na 58.0, Al 25.7, Zn 5.91, Cu 4.06, Mn 3.21, and Pb 0.534 μg g^{-1}, Cd and Ni were not detected. The effect of these trace elements in *T. sinensis* wood on the processing characteristics and on biomass energy applications remains to be further studied.

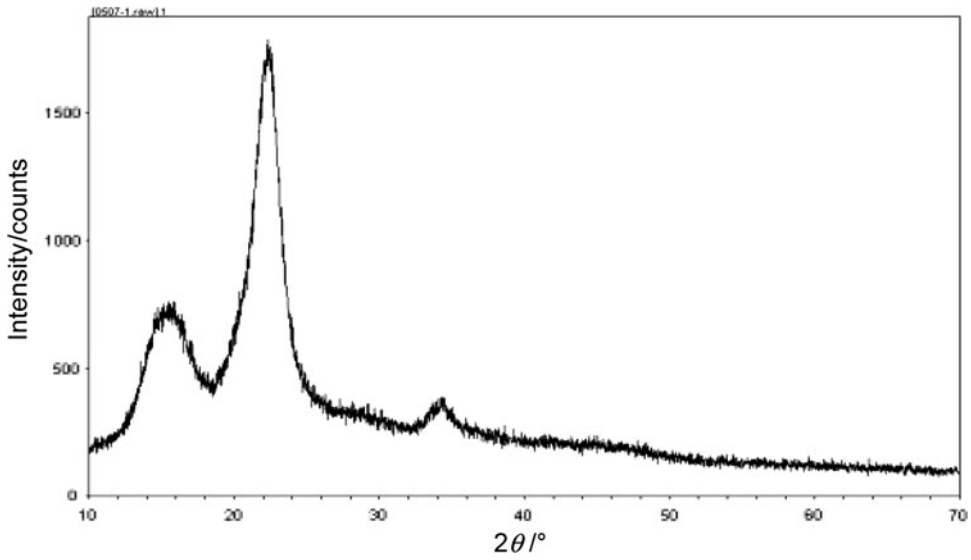

Fig. 4 X-ray diffraction intensity of nitric acid–ethanol cellulose from *T. sinensis* wood

Materials and methods

Wood materials and chemicals

Wood was collected in November 2008 on the campus of Guangxi University from trees identified as *T. sinensis* (age four years) by Professor Jianju Luo of the Forestry College of Guangxi University. Samples from the trees were collected and prepared according to methods in reference GB/T 2677.1-1,993 [14]. Three trees were selected as test trees. Cross-sectional disks five centimeters thick were taken from the trunks of the test trees at three different heights: 1.0 m above the ground (bottom), approximately one-third of full tree height (middle), and the tree top (top). The discs were air-dried for approximately 1 month, split into small pieces with an ax, dried, and milled with an FZ102 type micro-jet plant pulverizer. Powder of 0.25–0.38 mm size was selected from the wood powder sample by sieving, and stored in a closed glass container before being prepared for analysis. KBr was of spectroscopic grade. Standard solutions of Fe, Mn, Cu, Zn, Ca, Mg, Na, K, Al, Pb, Cd, and Ni, and all other solvents and chemicals were of analytical grade and obtained from local suppliers.

Methods for analysis of the main chemical composition

The main chemical composition of samples was determined by standard methods of the People's Republic of China, as identified in Table 7. So-called Klason lignin was obtained after removing polysaccharides from extracted (resin-free) wood by hydrolysis with 72 % sulfuric acid by GB/T2677·8-1994 (China).

Table 7 National standard methods of the People's Republic of China for analysis of the main chemical composition of plant fiber raw materials

Test items	Reference standard
Determination of moisture	GB/T2677·2-1993
Determination of ash content	GB/T2677·3-1993
Determination of water extractives content	GB/T2677·4-1993
Determination of 1 % (*w*/*w*) aqueous sodium hydroxide extractives content	GB/T2677·5-1993
Determination of alcohol–benzene extractives content	GB/T2677·6-1994
Determination of holocellulose content	GB/T2677·10-1995
Determination of Klason lignin content	GB/T2677·8-1994
Determination of 72 % (*w*/*w*) sulfuric acid-soluble lignin content	GB/T10337-1989
Determination of pentosan content	GB/T2677·9-1994

Determination of cellulose content by the nitric acid–ethanol method [14]

This method was based on use of a nitric acid and ethanol mixture (20:80 *v*/*v*) to treat the dried wood sample powder, so that lignin was converted into nitrated lignin, which dissolved in the ethanol. After the extraction, the residue was recovered by filtration, washed with water and ethanol, and dried to constant weight at 105 ± 2 °C. The nitric acid–ethanol cellulose content was calculated by use of Eq. (1):

$$X = \frac{(m_1 - m_2)}{m_0(100 - w)} \times 1,000 \quad (1)$$

where X is the amount of nitric acid–ethanol cellulose (mg g^{-1}), m_2 the weight of the dried glass containers (g), m_1 the weight of the dried glass containers and the residue

(*g*), m_0 the weight of the air-dried sample (*g*), and *w* the moisture content of the sample (%) determined by methods specified in GB/T2677·2-1993.

Determination of organic solvent-soluble lignin content

This method involved extracting the wood powder with ethanol–acetone–water 30:50:20 (*v*/*v*), catalyzed by sulfuric acid [29]. The phenolic hydroxyl content of organic solvent-soluble lignin was determined by the Folin–Ciocalteu method using phenol reagent for phenolic hydroxyl [30].

Determination of trace elements

Wood powder samples (5.00000 g) were prepared for elemental analysis by dry ashing at 550 °C in a furnace for 3 h. Ash was solubilized by addition of 10.00 cm^3 2.0 mol dm^{-3} HNO_3, 3 drops of 30 % (*w*/*w*) hydrogen peroxide aqueous solution, gentle boiling for 10 min, cooling, and filtration. Finally, the filtrate was transferred into a 50.00-cm^3 volumetric flask and filled to volume with 2 % nitric acid. The elements Fe, Mn, Cu, Zn, Ca, Mg, Na, K, Al, Pb, Cd, and Ni in *T. sinensis* wood were simultaneously determined by inductively coupled plasma-atomic emission spectrometry (ICP–AES Optima 5300DV; PerkinElmer, USA), employing a blank solution prepared by the same method.

Fourier transform infrared (FT-IR) spectra

FT-IR spectra were obtained by use of a Nicolet (America) FT-IR spectrometer model NEXUS470. Data analysis employed OMNIC 6.0 software. Pellets of 2 mg of dried wood powder samples were prepared by mixing with 200 mg spectroscopic grade KBr. The spectra were recorded in the absorption band mode in the range 4,000–400 cm^{-1}. The contribution of KBr was eliminated by measuring the background spectrum before every sample by use of a pure KBr pellet without any wood or its components.

The infrared spectra crystallinity index as defined by Nelson and O′Connor et al. [34, 35] was calculated by use of Eq. (2):

$$NO'KI_1 = \frac{\alpha_1}{\alpha_1'} \text{ or } O'KI_2 = \frac{\alpha_2}{\alpha_2'} \quad (2)$$

where α_1 and α_1' are the band intensities at 1,372 cm^{-1} and 2,900 cm^{-1}, and α_2 and α_2' are the band intensities at 1,425 and 895 cm^{-1}.

X-ray diffraction (XRD)

The relative crystallinity of the nitric acid–ethanol cellulose sample was analyzed with a Rigaku (Japan) X-ray diffractometer, model D/max-B, using Cu Kα radiation ($\lambda = 0.15418$ nm), generated at a voltage of 40 kV, with a current of 50 mA and a scan speed of 5°/min from 10° to 70°. Data analysis employed MDI Jade 5.0 software. Plots were normalized to unit area. Peaks were assigned according to the monoclinic cellulose I unit cell described by Sugiyama et al. [35]. The crystallinity indices (CrI) were calculated by use of the Segal method [36] from Eq. (3):

$$CrI_3 = \frac{(I_3 - I_3')}{I_3} \quad (3)$$

where I_3 is the intensity of the diffraction from the (002) plane, typically located in the range $2\theta = 21°$–$23°$, representing both crystalline and amorphous material, I_3' is the intensity of the background scatter measured at $2\theta = 18°$, representing only amorphous material.

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