Spectroscopic characterization of extractives isolated with MTBE from straws

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ABSTRACT: The lipophilic extractives isolated with methyl tert-butyl ether from rye and rice straws were examined by FTIR spectroscopy, both ^{1}H and ^{13}C NMR spectroscopy, and thermogravimetry. Free fatty acids, sterols, waxes, and fats (mainly as triglycerides) were identified as the major five classes of lipids in the two straw extractives. The C=C cis stretching band at 1640 cm^{-1} in the rye straw extract was much stronger than that in the rice straw extract. This finding suggests that the rye extractives contain more unsaturated lipophilic compounds than the rice straw extractives contain. On the other hand, a rather weak band at 1030 cm^{-1} indicated that the two extracts were relatively free of polysaccharides. Thermal analysis showed that the melting temperatures of the extractives occurred between 44.3°C and 50.0°C for the rye straw extract and between 52.8°C and 68.7°C for the rice straw extract.

Application: Mills can use this rapid separation procedure to control pitch problems by removing wood or straw extractives before pulping.

Lipophilic extractives from wood and nonwood, commonly called "resin" or "pitch," are composed mainly of fatty acids, resin acids, fatty acid esters such as fats and waxes, and neutral compounds such as fatty alcohols and sterols (*1, 2*). The chemical composition is dependent on factors such as wood or nonwood species, growing age, and environmental conditions (*3, 4*). Although extractives are a minor component, often constituting less than 2% of the total dry matter, they make a major contribution to the characteristics of wood or straw.

In general, these extractives are low-molecular-weight compounds, and the different classes of extractives have different chemical behaviors during pulping and subsequent bleaching. Considerable amounts of the wood extractives can be dispersed or dissolved during mechanical fibrillation and mechanical pulp bleaching operations (*5*). However, these dispersed extractives are difficult to remove and can cause pitch problems.

In neutral and acidic processes, the lipophilic extractives are difficult to remove. During alkaline processes, such as kraft pulping, fats and certain waxes are completely saponified, and the fatty and resin acids dissolve as soluble soaps. However, sterols and some waxes do not form soluble soap under alkaline conditions and therefore have a tendency to deposit and cause pitch problems (6). In papermaking, the accumulation of these extractives can cause significant technical and economic problems for pulp and paper manufacturers (7).

It is therefore of considerable interest to characterize extractives that may lead to solutions to pitch problems and optimize techniques for removing the extractives prior to pulping. In an earlier paper published elsewhere (*8*), we reported gas chromotography (GC) studies of the chemical composition of the extractives isolated with methyl *tert*-butyl ether (MTBE) from rye and rice straws. In the study reported here, we characterize these two extractive fractions by the nondestructive techniques of Fourier transform infrared (FTIR), ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, and thermogravimetric analysis.

METHODS FOR ANALYZING EXTRACTIVES

Classical methods for quantitatively analyzing extractives require many steps, including solvent extraction, saponification, separation of the acid and neutral fractions, and analysis of the derivatized acids by gas chromatography. Through this multistep method, technicians can separate a mixture of extracted compounds into resin acids, free and combined fatty acids, and nonsaponifiables (*1, 4, 9*). A number of other techniques such as thin layer chromatography (TLC) (*2*), high-performance liquid chromatography (HPLC) (*10*), and high-performance size exclusion chromatography (HPSEC) (*11*) have been developed for analyzing extractives in wood samples. However, most methods are too laborious for analyzing a large number of samples.

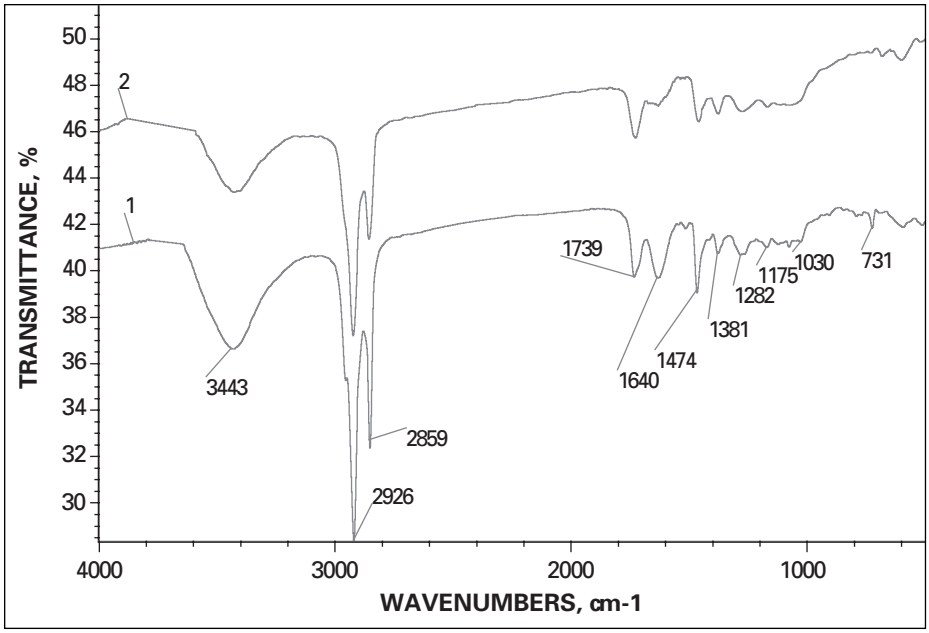
In recent years, FTIR spectroscopy has been the focus of considerable attention in both the qualitative and quantitative analysis of wood resin, contaminants in pulp, and pitch deposit extractives. FTIR has a major advantage over the conventional grating instruments in that the laser source offers more energy throughput, excellent reproducibility, and greater accuracy (*12*). Furthermore, FTIR is nondestructive and often permits a sample to be analysed *in situ*. The region between wavenumbers 800 cm^{-1} and 2500 cm^{-1} has been shown to have potential applications in the pulp and paper industry. As a result, FTIR has been used in determining wood resin directly on groundwood pulp (*1*).

In addition, ^{1}H or ^{13}C NMR spectroscopy is also a useful tool in the study of various problems related to lipid technology (*13*). Complementary information about the lipid class composition can be derived simultaneously from the same ^{13}C NMR spectrum (*13*). This technique enables quantification of the extractives in terms of total fatty acids, resin acids, fatty acid glycerides, and other fatty acid esters. The method was found to be as accurate as conventional methods for the analysis of extractives, with the advantages of being a nondestructive and fast analysis (*2*).

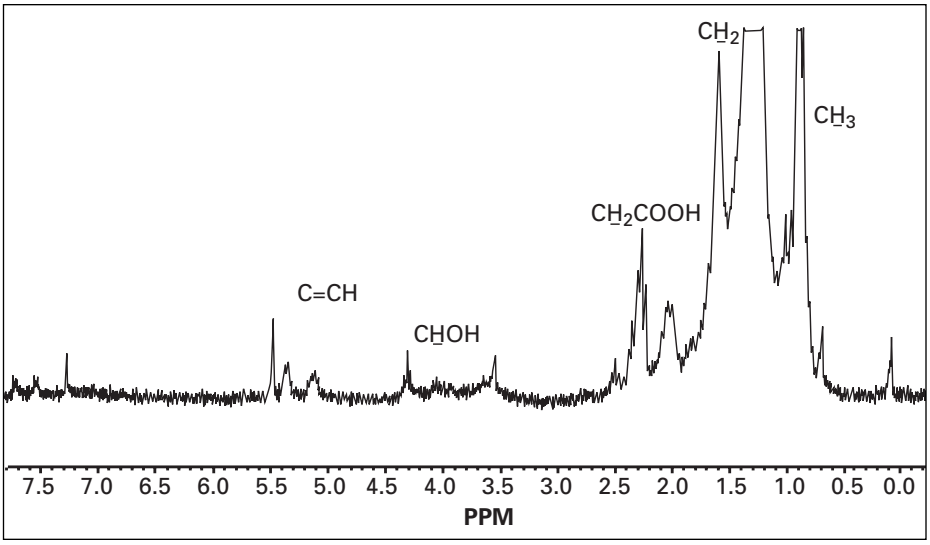
MATERIALS AND METHODS

Materials

Rye and rice straws were kindly supplied by the experimental farm of The North-Western University of Agricultural and Forest Sciences and Technology (Yangling, P. R. China). These raw materials were dried in sunlight and were then cut into small pieces. The cut straws were ground to pass



1. FTIR spectra of extractive fractions F1 and F2, obtained by extraction with MTBE from rye straw (Spectrum 1) and rice straw (Spectrum 2) for 12 h in a Soxhlet apparatus.



2. ^{1}H NMR spectrum of the rye straw extract (F1).

a 1.2 mm screen. The ground straws were further dried in a cabinet oven with air circulation for 16 h at 60°C and stored at 5°C before analysis.

For the determination of ash in the straws, the dried sample was transferred to a crucible, carbonized gently in a muffle furnace at 550±10°C for 6 h, and weighed as ash content.

Extraction

Dried rye and rice straw samples (about 50 g) were both extracted with 1800 mL of MTBE for 12 h in a Soxhlet apparatus. After solvent removal with a rotary vacuum evaporator at 35°C, the residues were dried in nitrogen steam and were weighed to determine the yield of extractives. The extract obtained from rye straw was referred to as "Fraction 1", or F1, and that obtained from rice straw was labeled "Fraction 2", or F2. The yield of extractives was measured on an oven-dried basis.

FTIR and ^{1}H and ^{13}C NMR spectroscopies

FTIR spectra were obtained on a Nicolet 510 spectrophotometer using a KBr disc containing 1% finely ground samples. The solution-state ^{1}H and ^{13}C NMR spectra were obtained on a Bruker MSL-300 spectrometer at 300 MHz and 74.5 MHz, respectively, in deuterochloroform. The ^{1}H NMR spectrum was recorded at 25°C from 15 mg of sample dissolved in 1.0 mL deuterochloroform, for a total of 32 scans with a pulse of 8 µs (about 90°C) and a delay time of 4 s between scans. The solution ^{13}C NMR spectrum was recorded at 25°C from 80 mg of sample dissolved in 1.0 mL chloroform-D after 3000 scans. We used a pulse flipping angle of 70°, a pulse width of 10 µs, and a delay time of 15 s between scans.

Thermal analysis

Thermal analysis of lipophilic extractives was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (NETZSCH STA-409). The apparatus was continually flushed with nitrogen. The sample weighed between 8 mg and 12 mg. Each sample was heated from room temperature to 600°C at a rate of 10C° per minute.

RESULTS AND DISCUSSION

FTIR analysis

Figure 1 presents the FTIR spectra of rye straw and rice straw extracts. These two spectra appeared to be rather similar in the wave number region that is characteristic of lipophilic substances, indicating that F1 and F2 are similar in composition. The prominent peak at 3443 cm^{-1} is assigned to the OH^{-} stretching vibration in sterols, mono- and diglycerides, co-extracted polysaccharides, or water in samples (*12*). Two strong bands at 2926 cm^{-1} and 2859 cm^{-1} originate from methylene and methyl stretching frequencies, respectively.

A band at 1739 cm^{-1} arises from the absorption by carbonyl bonds in esters (fats and waxes). The carbonyl bonds in free fatty and resin acids exhibit a stretching peak at 1712 cm^{-1} as a shoulder and are strongly overlapped with the previous one (*14*). The C=C *cis* stretching (in unsaturated fatty acids and their esters or in sterols and steryl esters) produces a strong absorption band at 1640 cm^{-1} in F1, while it appears as a broad band in F2.

Two sharp bands at 1474 cm^{-1} and 1381 cm^{-1} correspond to the methylene bending vibration and methyl symmetrical bending vibration, respectively (*14*).

The carbon single-bonded oxygen (C–O) stretching vibration or bonded hydroxyl (C–OH) bending in carboxylic

acids gives a broad band at 1282 cm^{-1} (*14*). The small band at 1175 cm^{-1} is characterized by the C–O stretching in the aliphatic esters. A rather weak absorption band at 1030 cm^{-1} represents the symmetrical stretching of an ether bond (C–O–C) in co-extracted polysaccharides (*15*). This rather weak band for polysaccharides indicates that the two extracts F1 and F2 contained only minor amounts of carbohydrates or were relatively free of them.

The band at 731 cm^{-1} is attributable to the aliphatic methylene (CH_2) rocking vibration (*16*).

^{1}H and ^{13}C NMR analyses

Figure 2 presents the ^{1}H NMR spectrum of F1. The most intense signal, occurring at 1.34 ppm, is attributed to the methylene aliphatic protons, while that centered at 0.88 ppm is assigned to methyl protons. Both methine and naphthenic peaks are hidden in the methylene peak (*4*).

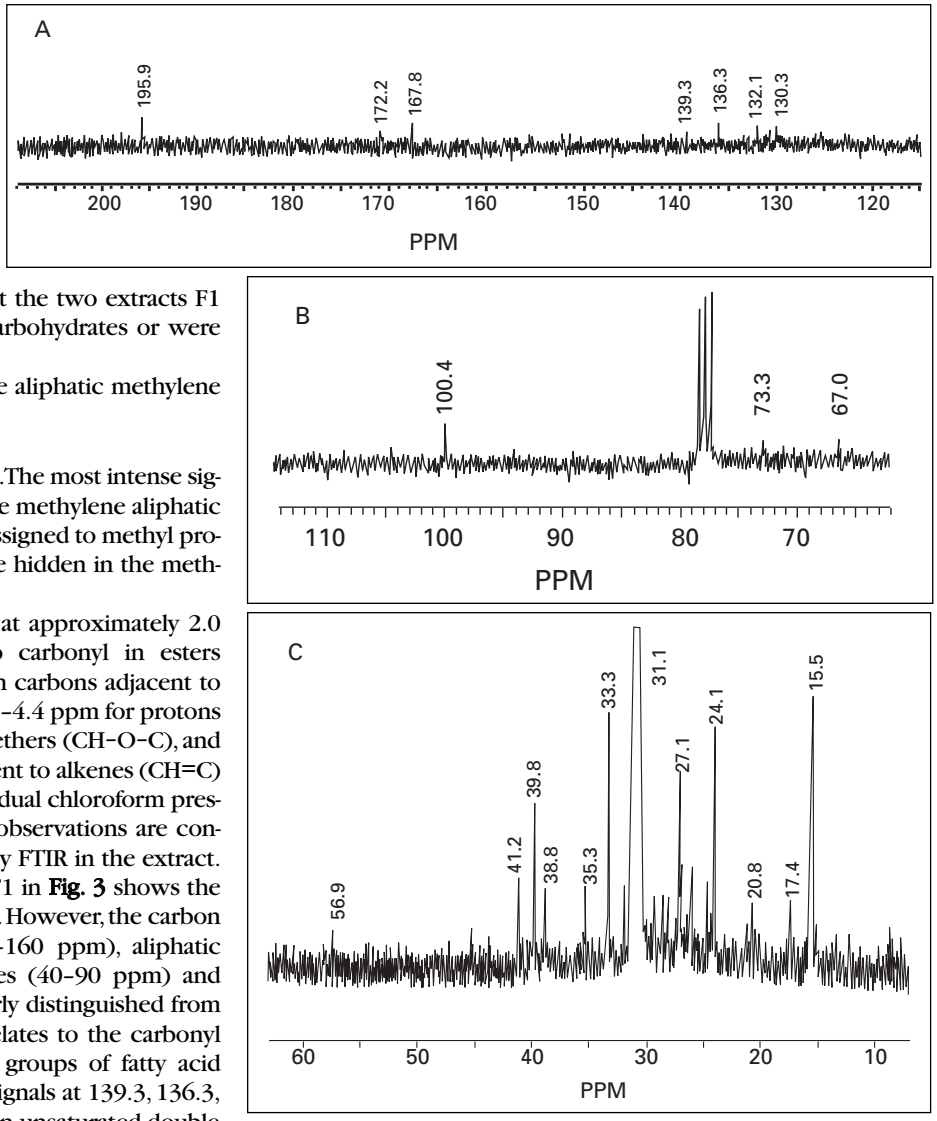
The spectrum also exhibits minor peaks at approximately 2.0 ppm for protons on carbons adjacent to carbonyl in esters (CH_2–C=O), at about 2.3 ppm for protons on carbons adjacent to an carboxylic acid group (CH_2–COOH), at 3.5–4.4 ppm for protons on carbons adjacent to alcohols (CHOH) or ethers (CH–O–C), and at 5.1–5.5 ppm for protons on carbons adjacent to alkenes (CH=C) (*17*). The signal at 7.28 ppm is due to the residual chloroform present in $CDCl_3$ and should be ignored. These observations are consistent with the functional groups revealed by FTIR in the extract.

The solution-state ^{13}C NMR spectrum of F1 in **Fig. 3** shows the great complexity of the lipophilic extractives. However, the carbon atoms from unsaturated compounds (110–160 ppm), aliphatic (0–34 ppm), and C–O substituted structures (40–90 ppm) and functional groups (170–200 ppm) were clearly distinguished from each other (*18*). The signal at 195.9 ppm relates to the carbonyl groups in lipophilic extracts. The carbonyl groups of fatty acid esters give a weak signal at 172.2 ppm. The signals at 139.3, 136.3, 132.1, and 100.4 ppm arise from the carbon in unsaturated double bonds (>C=) of resin acids or sterols and steryl esters, whereas the signal at 130.3 ppm is attributed to the carbon in unsaturated double bonds (–CH=CH–) of fatty acids or fatty acid esters.

Two weak signals at 73.3 and 67.0 ppm are assigned to the glycerol carbons (–C–O or >C–O) of triglycerides (*2*), corresponding to the results obtained by GC analysis (5.7% triglycerides). The carbon-bonded oxygen group (>C–O) in sterol or steryl esters exhibits signals at 56.9 ppm and 41.2 ppm. The signal at 15.5 ppm is characterized by the methyl end of the chain, whereas the methylene units in a long straight chain give signals at 17.4, 20.8, 27.1, 31.1, and 33.3 ppm (*17*). The methine group in resin acids and sterols or steryl esters produces signals at 39.8 ppm and 38.8 ppm.

TGA and DSC analysis

Figure 4 presents the TGA and DSC curves of F1. As shown, its decomposition temperature started at 150°C, and the maximum rate of weight loss occurred between 250°C and 450°C. The decomposition temperature at 10% weight loss occurred at 252°C. When the temperature was raised to 400°C, the weight loss increased to over 60%. The nonvolatile residue at 600°C was noticeable, at 16.8% of the total extractives. By comparison, approximately 25% of the nonvolatile material was found correspondingly in F2. This nonvolatile material was undoubtedly attributable to the contaminated ash or salts in the extractives.



3. ^{13}C NMR spectrum of the rye straw extract.

The results obtained were parallel to the content of ash in rye straw (3.0%) and rice straw (13.3%) and were in a good agreement with the purities of rye straw extract (85%) and rice straw extract (73%) analyzed by GC (*13*). Obviously, the nonlipid substances in the two extracts were composed mainly of ash or salts coming from the straws. In addition, the DSC was also performed to determine the melting temperatures and enthalpies of the extract in Fig. 4.

Interestingly, the melting temperatures of F1 occurred between 44.3°C and 50.0°C. Similar melting temperatures (52.8–68.9°C) were observed for F2. Furthermore, the DSC thermogram of the extractives gave one big broad exothermic peak with a maximum at 315°C. Such an observation has been previously reported from wood resins by Severtson *et al.* (*19*). **TJ**

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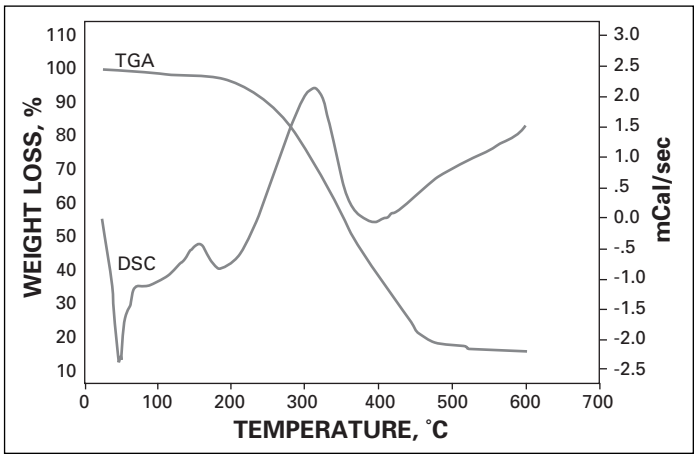

4. TGA and SCD analysis of the rye straw extract.

LITERATURE CITED

1. Sithol, B. B., *APPITA* 45: 260(1992).
2. Suckling, I. D., and Ede, R. M., *APPITA* 43(1): 77(1990).
3. Chen, T., Breuil, C., Carriere, S., and Hatton, J. V., *TAPPI J.* 77 (3): 235(1994).
4. Wallis, A. F. A., and Wearne, R. H., *APPITA* 50(5): 409(1997).
5. Ekman, R., and Holmbom, B., *Nordic Pulp Paper Res. J.* 1: 16(1989).
6. Gutierrez, A., del Ril, J. C., Gonzalez-Vila, F. J., and Martin, F., *Holzforschung* 53(5): 481(1999).
7. Gutierrez, A., del Ril, J. C., Gonzalez-Vila, F. J., and Martin, F., *J. Chromatogr.* 823: 449(1998).
8. Sun, X. F., and Sun, R. C., *Wood Fiber Sci.* 33(3): 386(2000).
9. Orsa, F., and Holmbom, B., *J. Pulp Paper Sci.* 20(12): J361(1994).
10. Richardson, D. E., Bremner, J. B., and Grady, O., *J. Chromatogr.* 595: 155(1992).
11. Sjostrom, J., and Holmbom, B., *J. Chromatogr.* 411: 363(1987).
12. Man, Y. B., Moh, M. H., and van de Voort, F. R. *JAOCS* 76(4): 485(1999).
13. Medina, I., Sacchi, R., and Aubourg, S., *JAOCS* 71(5): 479(1994).
14. Ajuong, E. M. A., and Breese, M. C., *Holz als Roh-und Werkstoff* 56: 139(1998).
15. Sun, R. C., Tomkinson, J., Geng, Z. C., and Wang, N. J., *Holzforschung* 54: 492(2000).
16. Man, Y. B., and Setiowaty, G., *Food Chemistry* 66: 109(1999).
17. Musser, B. J., and Kilpatrick, P. K., *Energy & Fuels* 12: 715(1998).
18. Gonzalez-Vila, F. J., Gutierrez, A., Martin, F., and Verdejo, T., *J. Anal. Appl. Pyrolysis* 40–41: 501(1997).
19. Severtson, S. J., Coffey, M. J., and Nowak, M. J., *TAPPI J.* 82(12): 67(1999).

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INSIGHTS FROM THE AUTHORS

Our earlier research work in this area was a study of the chemical composition of the lipophilic extractives. These extractives are hydrophobic low-molecular-weight compounds that can cause problems in pulp and paper mills by forming pitch deposits. In this part of the research work, we have continued the previous work and are supporting it with spectroscopic and thermogravimetric characterizations of the isolated extractives.

Traditional methods for separating and quantitatively analyzing extractives are tedious. Many steps are required, including solvent extraction, saponification, separation of the acid and neutral fractions, and analysis of the derivatized acids by gas chromatography. The step for the derivatization of free fatty acids, resin acids, and sterols is particularly time-consuming.

However, with the use of modern gas chromatographs with short-length, high-temperature capillary columns, it is now possible to separate free fatty acids, resin acids, sterols, waxes, steryl esters, and triglycerides in a single run of the gas chromatograph. Nevertheless, the method cannot identify the individual components of the sterols, waxes, steryl esters, and triglycerides.

In our study, we describe a convenient one-step method for separating lipophilic extractives. The method includes organic solvent extraction and subsequent chromatographic separation with gas chromatography with a medium-length, high-temperature capillary column without derivatization. Researchers in mills can use this rapid and simple separation procedure to remove and monitor wood or straw extractives prior to pulping in order to predict and control pitch problems.

As to the next step, we are currently studying extractives from sugar cane bagasse.

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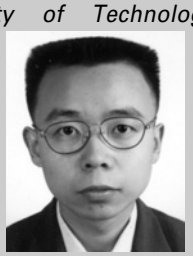

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