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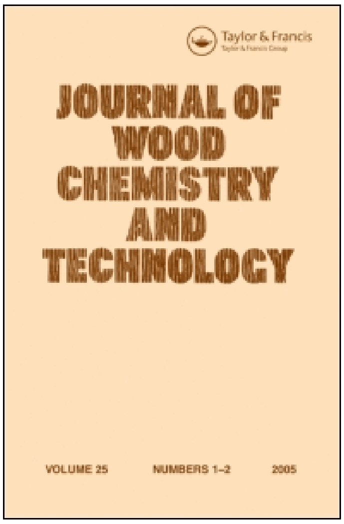

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Analytical Pyrolysis of Hardwood and Softwood Lignins and Its use in Lignin-Type Determination of Hardwood Vessel Elements

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ANALYTICAL PYROLYSIS OF HARDWOOD AND SOFTWOOD LIGNINS AND ITS USE IN LIGNIN-TYPE DETERMINATION OF HARDWOOD VESSEL ELEMENTS

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ABSTRACT

Pyrolysis-gas chromatography-mass spectrometry was performed on milled wood lignins (MWLs) and wood samples. Among the major pyrolysis products identified from loblolly pine lignin were guaiacol, 4-methylguaiacol, 4-vinylguaiacol, vanillin, coniferaldehyde, and coniferyl alcohol. White oak lignin pyrolysis products also included guaiacol, 4-methylguaiacol, and vanillin and additionally 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, syringaldehyde, and sinapaldehyde. By identification of these pyrolysis products from either wood or MWL it is possible to classify lignins as either guaiacyl-type or syringyl/guaiacyl-type. Pyrolysis of isolated vessel elements from white oak, white birch, and American elm indicated that vessel lignin is of the syringyl/guaiacyl-type.

INTRODUCTION

Determination of hardwood lignin type and distribution is of both scientific and technological interest. Although lignin structure influences the chemical and physical behavior of wood during pulping and the use of the resulting fibers, no widely accepted description of the lignin in hardwoods has been presented.

The conflicting argument whether hardwood lignin is composed of a syringyl/guaiacyl copolymer or of discrete syringyl and

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guaiacyl polymers has been briefly reviewed.[2] The major evidence for the existence of discrete syringyl and guaiacyl lignins in various morphological regions in hardwoods was the result of the ultraviolet microscopy report of Musha and Goring.[3] Among other findings, these authors determined that the normalized ultraviolet absorbance of lignin contained in vessel elements from hardwoods, such as eastern cottonwood, American elm, red alder, black cottonwood, trembling aspen, yellow birch, and white birch, was as high as that of typical softwood lignin from any morphological region of Douglas-fir and black spruce. Because softwoods have essentially no syringyl character, these results[3] have been interpreted[4,5] as indicative of the presence of pure guaiacyl lignin in hardwoods.

Direct chemical analysis of vessel lignin should provide a meaningful test of the conclusions based upon ultraviolet microscopy because the UV experiments indicated that both the middle lamella and the vessel wall contained only guaiacyl-type lignin. However, large amounts of vessel elements are not easily obtained and preparation of milled wood vessel lignin has not been feasible. Vessel lignin monomer composition has been investigated by nitrobenzene oxidation,[6,7] and by methoxyl determination[2] on isolated vessel cells, and all results indicate that vessel lignin had at least some syringyl character.

Analytical pyrolysis was considered potentially useful for vessel lignin characterization because large sample sizes are not required. Pyrolysis of lignin yields phenols from cleavage of ether and carbon-carbon linkages, and analysis of these phenolic products should allow description of the polymer. However, analytical pyrolysis of lignin and wood has received little attention. Most of the current interest in lignin pyrolysis is in batch pyrolysis with the goal of producing valuable chemical products from pulping waste and biomass. Kratzl, Czepel, and Gratzl[8] indicated that pyrolysis-gas chromatography (py-gc) could be used in lignin analysis. Stahl et al.[9] classified guaiacyl-type and syringyl/guaiacyl-type lignins by thermofractography (pyrolysis followed by thin layer chromatography). Pyrolysis-gas chromatography-mass

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spectrometry (py-gc-ms) of milled wood lignins (MWLs) has been recently shown to be a rapid method for determination of lignin type.[10]

Presented here are the initial findings, notably on hardwood vessel lignin, from a study of the analytical pyrolysis of lignins of loblolly pine, white oak, white birch, and American elm.

EXPERIMENTAL

MWLs were prepared from loblolly pine (Pinus taeda L.) wood and the fiber fraction from a high-yield, white oak (Quercus alba L.), NSSC pulp.[2] Hardwood and softwood crill (a fraction enriched in middle lamella) were prepared from kraft pulps.[2] Because the proportion of middle lamella lignin of the total pulp lignin is not known, the exact enrichment of middle lamella lignin in the crill is not known. However, it is estimated that the crill contains three times, or more, middle lamella lignin than wood. The Klason lignin content of the loblolly pine crill was 42%, that of American elm (Ulmus americana L.) was 35%. White oak vessels were isolated as previously.[2] White birch (Betula papyrifera Marsh.) and American elm vessels were isolated from high-yield kraft pulps. The thoroughly washed pulps were slurried in water and the vessels were removed with a capillary pipette under a microscope.

The samples were pyrolyzed using a Chemical Data Systems Pyroprobe 120. A coil probe was used with a quartz tube containing approximately 0.7 mg of wood or MWL. The rate of temperature rise was about 900° C/s (ramp off) to a final temperature of 800° C which was held for 10 s. Sample tubes were cooled and weighed.

Gas chromatography was with a 0.315 mm x 60 m, DB-5 0.25-μ film thickness fused-silica capillary column (J & W Scientific, Inc., Rancho Cordova, Calif.), temperature programmed from 80° C, 0.2 min, at 4° C/min to 220° C. The helium linear velocity was 30 cm/s.

Electron impact mass spectra were obtained on a Finnigan 4510 (Finnigan MAT Corp., San Jose, Calif.) at 70 electron volts.

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Masses 50 to 400 were scanned with a scan time of 1 s. Because of the small sample size for white birch (75 ng) and American elm (240 ng) vessels, only selected masses were scanned. The Multiple Ion Detection (MID) parameters were:

Interval	Begin mass	End mass	Time (s)
1	104.5	112.5	0.105
2	133.5	140.5	.092
3	146.5	155.5	.118
4	162.5	168.5	.158
5	175.5	183.5	.105
6	191.5	197.5	.158
7	206.5	211.5	.131

Pyrolysis products were identified by comparison of relative retention times to those of authentic compounds and upon the basis of their mass spectra. A mass spectral library of the anticipated pyrolysis products was created, and pyrogram mass spectra were matched to library spectra by an algorithm in the INCOS system (Finnigan MAT Corp.). However, assignments were made only after careful inspection of mass lists.

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RESULTS AND DISCUSSION

The pyrolysis products identified from loblolly pine MWL were those anticipated based upon knowledge of lignin structure and included guaiacol, 4-methylguaiacol, 4-vinylguaiacol, vanillin, coniferaldehyde, and coniferyl alcohol (Table 1; refer to table at end of text). The pyrolysis products from white oak fiber MWL included 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, syringaldehyde, acetosyringone, and sinapaldehyde as well as guaiacyl-type products (Table 2; refer to table at end of text). Thus, it was verified that py-gc-ms can quickly and clearly distinguish between guaiacyl and syringyl/guaiacyl lignins.

Structures of all of the major pyrolysis products from oak and pine MWLs could be assigned on the basis of their mass spectra and relative retentions. No syringyl-type pyrolysis products were identified from loblolly pine MWL.

It is interesting to note that it was reported that pyrolysis of beech MWL gave 3,5-dimethoxyphenol[10] whereas pyrolysis of <u>Eucalyptus</u> <u>regnans</u> MWL reportedly gave 3,4-dimethoxyphenol.[11] Neither of these dimethoxyphenols could be identified in the pyrogram of white oak MWL or wood. Hardwood MWLs are expected to yield 2,6-dimethoxyphenol as a major product[12] and were found here to do so. The other isomeric dimethoxyphenols must be considered unusual and unexpected products because there are no obvious parent structures in lignin which could give rise to them by pyrolysis. In the first instance,[10] after inspection of the nomenclature used, it is suspected that the product identified as 3,5-dimethoxyphenol was misnamed and actually is 2,6-dimethoxyphenol. In the latter case,[11] pyrolysis products were identified on the basis of computer matching to National Bureau of Standards (NBS) library spectra. At this time, the NBS library does not contain the spectrum of 2,6-dimethoxyphenol. The best match with authentic 2,6-dimethoxyphenol then is 3,4-dimethoxyphenol. Other unusual hardwood and softwood lignin pyrolysis products were also reported[11] and assignments similarly may be uncertain. In neither study were mass spectral data presented and it is not possible to ascertain the assignments.

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<u>Pyrolysis of Wood and MWL</u>

Pyrolysis of isolated lignins has been done, but analytical pyrolysis of wood to determine lignin structure has not been described. Pyrograms of loblolly pine and white oak woods, as well as pyrograms of their corresponding MWLs, are shown in Figures 1 and 2. Although the pyrogram of the wood and its MWL differed in each case, a sufficient number of products was identified to allow classification of the lignin in the wood as either guaiacyl-type or syringyl/guaiacyl-type.

Pyrolysis of the loblolly pine MWL gave a significantly greater amount of vanillin, relative to guaiacol, than did pyrol-

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TABLE 1

Relative Retention and Mass Spectral Data from the Pyrolysis-Gas Chromatography of Loblolly Pine Milled Wood Lignin

Scan No.	Relative retention	Relative retention of authentic compounds	Assignment	Reconstructed ion count	Mass list
					m/z (%)
490	0.72	0.73	Phenol	1,180	95(9) 94(100) 66(24) 65(16) 63(3) 55(5) 53(2) 51(2) 50(2)
607	0.89	0.89	o-Cresol[1]	1,466	109(4) 109(100) 107(80) 90(13) 89(6) 80(5) 79(24) 78(4) 77(25)
640	0.94	0.94	p-Cresol[1]	2,396	109(3) 108(88) 107(100) 91(1) 90(4) 80(4) 79(15) 78(2) 77(22)
681	1.0	1.0	Guaiacol	9,200	125(4) 124(84) 110(4) 109(100) 81(63) 65(4) 63(4) 53(19) 52(10) 51(8)
779	1.14	1.15	Dimethylphenol[2]	2,014	123(4) 122(100) 121(47) 108(3) 107(99) 91(11) 79(8) 78(5) 77(21) 65(5)
812	1.19	1.20	4-Ethylphenol[1]	179	122(22) 107(100) 79(9)
873	1.28	1.26	Catechol	9,904	111(5) 110(100) 92(9) 82(4) 81(11) 64(35) 63(17) 55(7) 54(4) 53(10)
878	1.29	1.28	4-Methylguaiacol	20,960	139(7) 138(100) 124(6) 123(93) 107(2) 106(2) 95(30) 77(17) 67(19) 55(17)
1,054	1.55	1.53	4-Ethylguaiacol	2,563	153(2) 152(38) 138(4) 137(100) 122(5) 109(2) 94(3) 91(4)
1,128	1.66	1.62	4-Vinylguaiacol	5,488	151(6) 150(100) 136(3) 135(77) 108(1) 107(28) 91(2) 89(3) 79(7) 78(4)

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1,190	1.75	1.77	Eugenol	461	164(100) 149(24) 137(9) 133(7) 131(16) 104(7) 103(16) 91(15)
1,194	1.75	1.78	4-Hydroxybenzaldehyde	2,320	123(3) 122(87) 121(100) 94(2) 93(33) 66(3) 65(32) 64(1) 63(5) 62(2)
1,237	1.82	1.81	4-Propylguaiacol[1]	427	166(14) 137(100)
1,259	1.85	1.83	4-Ethylcatechol	1,148	138(30) 124(4) 123(100) 91(3) 77(6) 65(2) 59(2) 55(3) 53(2) 51(5)
1,291	1.90	1.89	Vanillin	32,032	153(7) 152(94) 151(100) 137(4) 123(14) 109(16) 108(6) 95(1) 93(1) 81(24)
1,295	1.90	1.91	cis-Isoeugenol[1]	45	164(100) 149(73)
1,390	2.04	2.04	trans-Isoeugenol	7,080	165(8) 164(100) 149(31) 137(3) 133(10) 131(17) 121(10) 104(9) 103(19) 91(18)
1,414	2.08		Homovanillin[3]	4,504	167(1) 166(25) 138(6) 137(100) 123(1) 122(15) 94(8) 77(4) 66(3) 65(3)
1,472	2.16	2.18	Acetoguaiacone	4,464	167(2) 166(46) 152(5) 151(100) 136(1) 123(7) 108(5) 77(4) 73(4) 60(19)
1,638	2.40	2.40	Vanillic acid	4,084	169(5) 168(100) 154(2) 153(69) 151(12) 125(13) 123(3) 108(2) 97(22) 79(4)
1,953	2.87	2.88	Coniferaldehyde	25,760	179(10) 178(100) 162(3) 161(15) 147(31) 146(7) 135(36) 118(12) 107(27)
1,956	2.87	2.90	Coniferyl alcohol	10,000	181(4) 180(68) 152(3) 151(5) 138(7) 137(100) 138(8) 124(61) 119(22) 103(13)

---

[1] Pyrolysis of a larger sample gave a higher ion count and allowed identification on the basis of mass spectrometry.

[2] Substitution pattern is uncertain; best match is for 3,4-dimethylphenol.

[3] This structure was suggested by C. Saiz-Jimenez (private communication). Its mass spectrum was the best match for authentic homovanillin.

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TABLE 2

Relative Retention and Mass Spectral Data from the Pyrolysis-Gas Chromatography of White Oak Fiber Milled Wood Lignin

Scan No.	Relative retention	Relative retention of authentic compounds	Assignment	Reconstructed ion count	Mass list
					m/z (%)
491	0.72	0.73	Phenol	94	94(100)
607	0.89	0.89	o-Cresol[1]	88	108(100) 107(70)
641	0.94	0.94	p-Cresol[1]		108(100) 107(99)
681	1.0	1.0	Guaiacol	2,412	125(3) 124(83) 110(3) 109(100) 81(62) 65(4) 62(2) 53(17) 52(7) 51(6)
778	1.14	1.15	Dimethylphenol[1,2]	128	123(4) 122(100) 121(38) 107(95) 91(9) 79(6) 77(28) 65(6)
872	1.28	1.26	Catechol	1,376	111(3) 110(100) 92(5) 82(2) 81(7) 64(29) 63(12) 55(6) 54(2) 53(7)
877	1.29	1.28	4-Methylguaiacol	3,072	139(4) 138(100) 124(3) 123(94) 95(26) 77(13) 67(16) 55(14)
1,054	1.55	1.53	4-Ethylguaiacol[1]	238	152(37) 137(100)
1,127	1.65	1.62	4-Vinylguaiacol	548	150(100) 135(73) 107(20) 77(22) 51(7)
1,203	1.77	1.76	2,6-Dimethoxyphenol	6,088	155(5) 154(100) 140(2) 139(44) 125(1) 111(20) 96(19) 93(17) 81(4) 79(4)
1,237	1.82	1.81	4-Propylguaiacol[1]	108	166(6) 137(100)
1,259	1.85	1.83	4-Ethylcatechol[1]	63	138(38) 123(100)
1,278	1.88	1.89	Vanillin	13,968	153(7) 152(94) 151(100) 137(3) 123(13) 109(16) 108(15) 95(1) 93(1) 81(23)
1,295	1.90	1.91	*cis*-Isoeugenol[1]	45	164(100) 149(70)
1,384	2.03	2.04	*trans*-Isoeugenol	1,011	165(6) 164(100) 149(20) 137(5) 133(7) 131(12) 121(8) 104(6) 103(12) 91(13)

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1,397	2.05	2.06	4-Methyl-2,6-dimethoxyphenol	7,568	169(7) 168(100) 154(2) 153(43) 125(22) 110(5) 109(2) 107(7)
1,407	2.07		Homovanillin[3]	3,216	167(1) 166(24) 138(5) 137(100) 123(1) 122(14) 94(7) 77(4) 66(3) 65(3)
1,465	2.15	2.18	Acetoguaiacone	952	166(47) 152(4) 151(100) 123(13) 108(3) 77(3)
1,555	2.28	2.27	4-Ethyl-2,6-dimethoxyphenol	723	183(520) 168(4) 167(100) 107(1) 79(3) 77(4)
1,627	2.39	2.40	Vanillic acid	1,358	169(4) 168(100) 153(63) 151(11) 125(10) 97(19) 79(6)
1,703	2.50	2.48	4-Allyl-2,6-dimethoxyphenol	2,888	195(7) 194(100) 193(1) 179(7) 177(1) 167(7) 163(4) 151(6) 147(7) 133(5) 131(9) 119(13)
1,817	2.67	2.64	Syringaldehyde	29,088	183(9) 182(100) 181(58) 167(12) 153(3) 135(7) 136(2)
1,882	2.76	2.74	<u>trans</u>-1-(2,6-Dimethoxy phenyl)-propene	5,376	195(9) 194(100) 193(2) 179(14) 177(1) 167(1) 163(2) 151(7) 147(4) 133(4) 131(8) 119(110)
1,894	2.78		Homosyringaldehyde[4]	8,976	197(2) 196(29) 168(10) 167(100) 153(1) 151(1) 137(1) 124(1) 123(7) 122(4) 106(3)
1,947	2.86	2.84	Acetosyringone	8,016	197(3) 196(50) 182(7) 181(100) 153(7) 138(2) 123(2) 110(2) 108(3) 95(1) 93(2)
2,091	3.07	3.08	Syringic acid	548	199(5) 198(100) 183(23) 181(3) 155(2) 153(2) 137(2) 127(11) 109(7) 93(3)
2,394	3.51	3.48	Sinapaldehyde	11,440	209(9) 208(100) 193(3) 180(24) 177(18) 165(39) 154(4) 147(2) 137(26) 122(6)

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[1] Pyrolysis of a larger sample gave a higher ion count and allowed identification on the basis of mass spectrometry.

[2] Substitution pattern is uncertain; best match is for 3,4-dimethylphenol.

[3] This structure was suggested by C. Saiz-Jimenez (private communication). Its mass spectrum was the best match for homovanillin.

[4] This structure is tentatively assigned. Authentic homosyringaldehyde was not available for comparison.

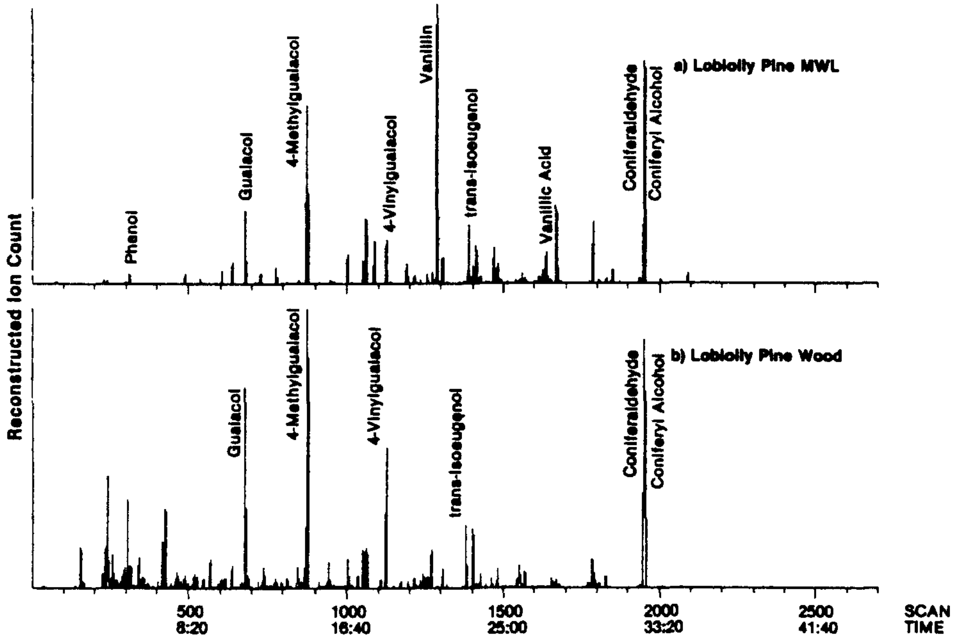

FIGURE 1.--Pyrograms of loblolly pine milled wood lignin (a) and wood (b).

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ysis of pine wood (Fig. 1). The increase in the amount of syringaldehyde relative to 2,6-dimethoxyphenol upon pyrolysis of white oak fiber MWL compared to oak wood was analogous. These results suggest several possibilities. Among them is that, in the pyrolysis of wood, reactive lignin products condense with carbohydrates and/or their degradation products. Another possibility is that vibratory ball milling may degrade the lignin, increasing the precursors that yield vanillin upon pyrolysis. However, the pyrograms of loblolly pine wood meal and vibratory ball milled wood each indicated relatively low yields of vanillin (Table 3). Thus, the increased yields of vanillin and syringaldehyde from pyrolysis of MWLs compared to wood are not solely a consequence of vibratory milling. The difference in the relative yields of pyrolysis products from MWLs and the woods from which they originate is of

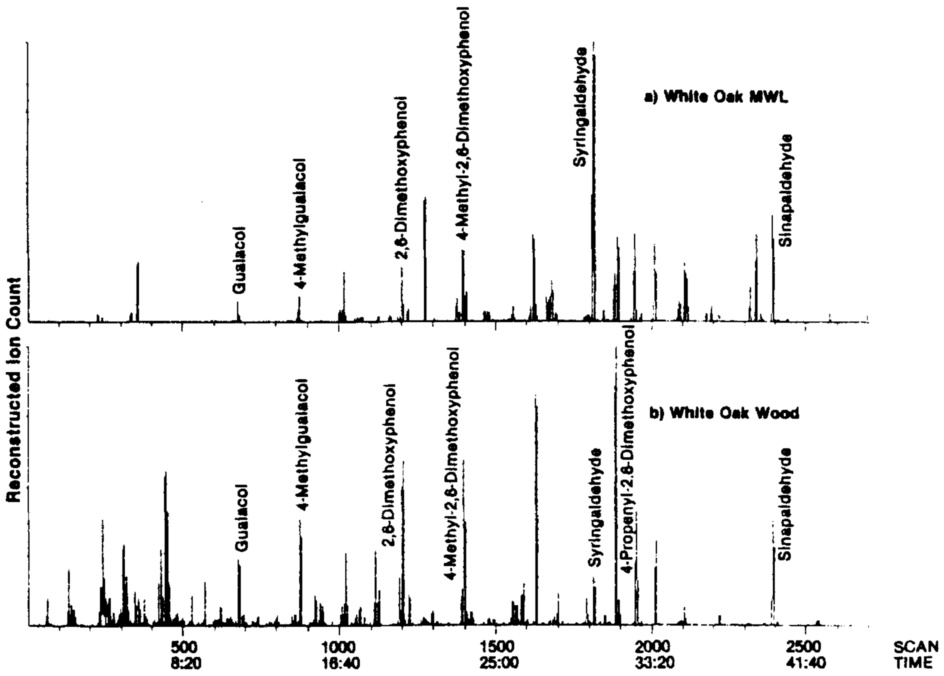

FIGURE 2.--Pyrograms of white oak fiber MWL (a) and wood (b).

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importance in structural investigations. Additional studies are in progress.

Quantitative Analysis

There are a number of conditions that must be satisfied to obtain quantitative results. For example, pyrolysis should be extensive. Measurement of sample weight loss after pyrolysis indicated that an appreciable amount of lignin remained as residue (Fig. 3). Pyrolysis parameters were chosen for this study on the basis of weight loss and upon the yield and composition of pyrolysis products obtained. Higher temperatures did not result in a higher yield of identifiable phenolics. Another important factor

TABLE 3

Comparison of Selected Pyrolysis Products as a Percentage of Total Peak Height, Measured as Total Ions, from Loblolly Pine.

Pyrolysis product	Percent of total peak heights: Wood meal 1 (60 mesh)	Wood meal 2 (60 mesh)	Vibratory ball-milled wood	Crill
Phenol	0.5	0.7	0.6	1.3
p-Cresol	1.1	1.3	1.2	2.4
Guaiacol	10.7	10.6	11.3	7.1
4-Ethylphenol	0.3	0.4	0.4	0.5
4-Methylguaiacol	18.4	17.8	19.8	19.2
4-Propylphenol	0.0	trace[1]	trace	trace
4-Ethylguaiacol	4.7	4.6	5.5	4.0
4-Vinylguaiacol	19.5	20.7	20.0	20.9
4-Hydroxybenzaldehyde	trace	trace	trace	0.0
Eugenol	8.1	8.2	8.4	7.9
4-Propylguaiacol	2.4	1.8	2.6	2.1
Vanillin + cis-Isoeugenol	5.3	5.3	4.4	7.1
trans-Isoeugenol	24.1	23.6	23.1	25.8
Coniferaldehyde	2.7	2.9	2.5	0.8
Coniferyl alcohol	2.0	2.2	0.3	0.8
Total	99.8	100.1	100.1	99.9

[1] Trace = <0.1%

is that not all of the sample volatilized is necessarily detected. Some pyrolysis products may be volatile at 800° C, but condense in the injector; some products may not chromatograph.

Another consideration arises when a mass spectrometer is used as a detector. The ion count for a compound depends not only upon the amount present but also upon the fragmentation pathway and the stability of the ions formed. Because equimolar amounts of two different compounds do not necessarily give the same ion counts, response factors are necessary to perform quantitative analysis.

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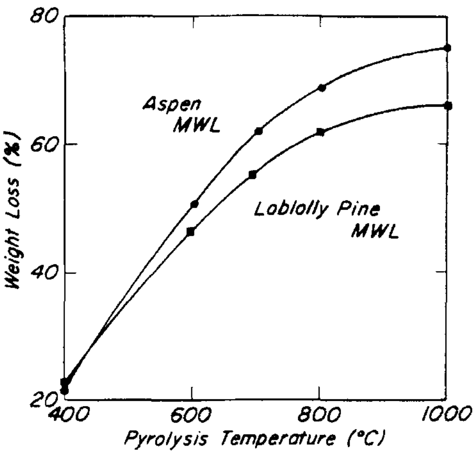

FIGURE 3.--Weight loss from milled wood lignins after pyrolysis at various temperatures (time at temperature = 10 s, in a helium atmosphere).

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To illustrate this, mass spectrometer relative response factors, on a molar basis, for guaiacol, phenol, 4-methylguaiacol, eugenol, 4-propylguaiacol, and vanillin were determined to be 1.0, 0.76, 0.85, 0.81, 0.81, and 0.44, respectively.

Although not all of the conditions for quantitative pyrolysis have been tested, pyrograms may be put on a relative numerical basis for comparison. Pyrolysis of loblolly pine wood meal (60 mesh) yields more than 50 products. Sixteen of the identified major products were chosen as representative of the pyrogram of the lignin in wood, and the amount of each as total ion count was calculated as a percentage of the total 16 (Table 3). When a second wood meal sample was pyrolyzed, the data so calculated was useful to show the reproducibility of pyrolysis (Table 3). A third sample of loblolly pine wood was pyrolyzed after it first had been vibratory ball milled. With the exception of the decreased amount of coniferyl alcohol, only slight differences from the wood meal pyrolysis were observed (Table 3).

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Structural Investigations

Lignin structural investigations have long been conducted in attempts to explain the pulping behavior of wood. The reactivity of lignin will influence pulping rates, and characterization of lignin from various morphological regions may help elucidate delignification kinetics. Loblolly pine crill was pyrolyzed and the results compared to wood pyrolysis (Table 3). Whereas the pyrograms of loblolly pine wood and crill were similar, there were some differences. For example, the yields of phenol and cresol were higher from the crill, but the relative amount of guaiacol and coniferaldehyde were lower (Table 3).

Recently, a method was proposed to determine the phenolic hydroxyl content of lignins by py-gc.[13] A major assumption in that study was that the amount of phenol and guaiacol formed upon pyrolysis are quantitatively representative of lignin structure. This assumption is unlikely because p-hydroxyphenyl and p-guaiacyl structures in lignin do not yield phenol and guaiacol exclusively; many other pyrolysis products are also formed. Guaiacol formed by pyrolysis of loblolly pine wood represented only about 10% of the total of 16 selected pyrolysis products compared in Table 3. The amount of phenol was less than 1% of the total 16 products (Table 3). Of course, the relative amounts of these two phenolics is even less of the total of all the pyrolysis products. The relative yields of phenol and cresol from the pyrolysis of loblolly pine crill were double those from wood. If only these two products are considered, the results here would be in agreement with the earlier study,[13] which concluded that the middle lamella contained over 40% p-hydroxyphenyl units. However, of the pyrolysis products compared in Table 3, those that must have originated from guaiacyl-type structures totaled 95.7% from the crill and 97.6% from the wood.

No significant increase in the amounts of 4-ethylphenol, 4-propylphenol, or 4-hydroxybenzaldehyde was observed from the crill pyrolysis. Other compounds, also anticipated to be formed upon pyrolysis of p-hydroxyphenyl units, such as 4-hydroxystyrene, 4-hydroxyphenylpropene, p-hydroxyacetophenone, and 4-propylphenol, were not detected in the pyrogram of either the wood or crill. It seems apparent, therefore, that the monomer composition of lignin cannot be quantitatively described by determining only two of the myriad of pyrolysis products obtained.

It was also reported[13] that softwood MWL did not yield phenol upon pyrolysis. This disagrees not only with this study (Table 1) but also with other lignin analytical pyrolysis studies.[10,11]

Pyrolysis of Vessel Elements

The pyrogram of isolated white oak vessels is shown in Figure 4. Pyrolysis products originating from syringyl/guaiacyl-type lignin were identified in agreement with previous studies showing the syringyl/guaiacyl nature of vessel lignin.[2,6,7] Quantitative evaluation of this pyrogram has not been achieved and is the subject of continuing research.

White oak vessel elements have been used in hardwood lignin studies because they are relatively easy to isolate.[2] However, because white oak was not included in the ultraviolet microscopic study by Musha and Goring,[3] it was desirable to perform py-gc-ms on vessels from hardwood species that Musha and Goring did include. White birch and American elm vessel lignins were shown to have a normalized ultraviolet absorbance equivalent to those of spruce and fir lignins.[3] This may be interpreted[4,5] as meaning that the vessel lignin is of the guaiacyl-type in these hardwoods. Because only small amounts of the birch and elm vessels were isolated, the mass spectral acquisition was modified to detect only pertinent masses of certain anticipated pyrolysis products. The resulting MID pyrograms for white birch and American elm vessels are shown in Figure 5. Within the constraints set for the MID experiment, guaiacol, vanillin, 2,6-dimethoxyphenol, syringaldehyde, and sinapaldehyde were identified from each.

Although quantitative determination by pyrolysis of the ratio of monomeric units in hardwood lignin has not yet been made, relative comparisons of the amounts of certain pyrolysis products may

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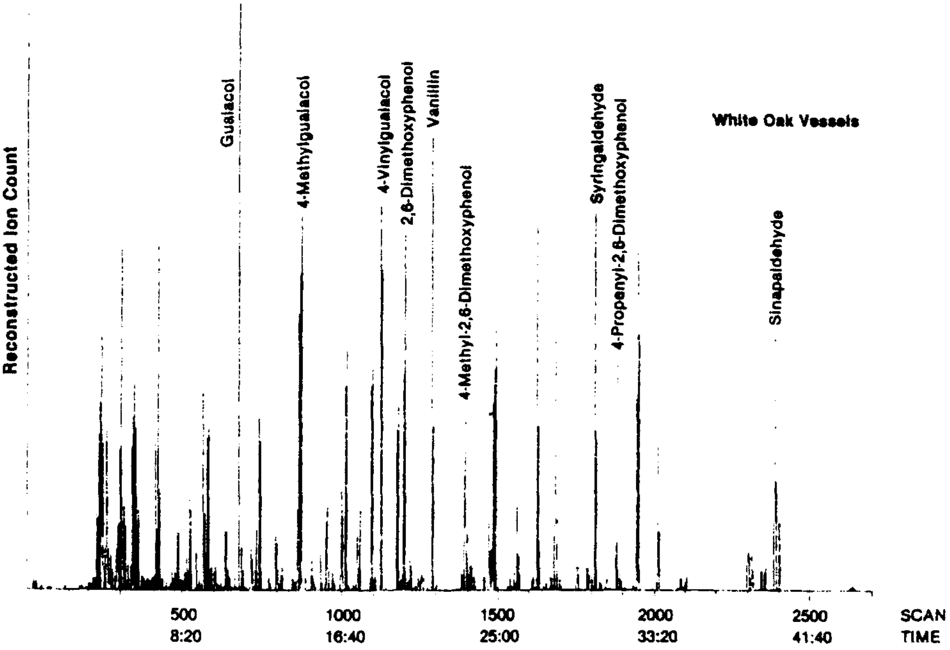

FIGURE 4.--Pyrogram of white oak vessels.

have some value. In an attempt to determine whether the syringyl pyrolysis products from vessel element lignin were present in trace or significant amounts, the relative peak heights, as total ions, of guaiacol, 2,6-dimethoxyphenol, vanillin, and syringaldehyde were compared for American elm wood meal, and for fibers and vessels from a high-yield kraft pulp (Table 4). The wood meal MID pyrogram showed the highest 2,6-dimethoxyphenol/guaiacol and syringaldehyde/vanillin ratios. Fibers were also pyrolyzed because they had received the same pulping treatment as the vessels and a vessel/fiber comparison may be more meaningful than a vessel/wood meal comparison. The pyrogram of the fibers indicated a lower ratio of syringyl to guaiacol pyrolysis products compared to the pyrogram of wood meal (Table 4). The 2,6-dimethoxyphenol/guaiacol pyrolysis ratio was lowest for the vessels, but the syringaldehyde/vanillin ratio was the same as that of the fibers. Although ratios among

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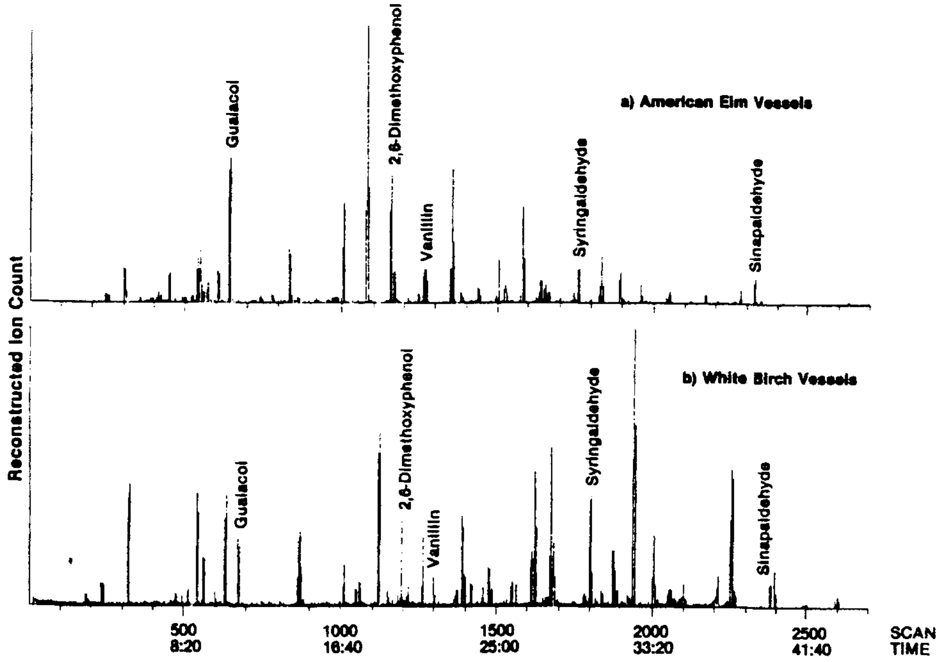

FIGURE 5.--Pyrogram of American elm (a) and white birch (b) vessels.

TABLE 4

Relative Amounts of Selected Syringyl and Guaiacyl Pyrolysis Products from American Elm (multiple ion detection acquisitions), Determined from Total Ion Peak Heights

	Peak height ratios			
	2,6-Dimethoxyphenol / Guaiacol	Syringaldehyde / Vanillin	Syringaldehyde / 2,6-Dimethoxyphenol	Vanillin / Guaiacol
Wood meal 1 (60 mesh)	5.6	1.9	0.4	1.1
Wood meal 2 (60 mesh)	4.6	1.7	0.5	1.2
Fibers 1	2.4	1.0	0.7	1.7
Fibers 2	2.5	0.9	0.9	1.6
Vessel elements	0.9	1.0	0.3	0.2

four pyrolysis products of hardwood lignins cannot quantitatively describe lignin structure, these values do suggest that the vessel lignin in American elm does have significant syringyl character.

As an indicator of the lignin pyrolysis reactions the ratios of syringaldehyde to 2,6-dimethoxyphenol and vanillin to guaiacol were calculated (Table 4). If the lignin in each sample was the same and the variables of pyrolysis were constant, then these ratios should be the same. However, the yields of syringaldehyde and vanillin relative to their respective methoxyphenols from pyrolysis of the fibers increased compared to that from wood meal. In contrast the yields of aldehydes relative to 2,6-dimethoxyphenol and guaiacol were very low from pyrolysis of the vessels. The reasons for these variations are presently unknown but are important for both absolute and relative quantitative analyses of lignin pyrograms.

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Pyrolysis of Hardwood Fiber and Crill MWLs

Milled wood lignins prepared from hardwood fiber and crill fractions have been compared previously.[2,14] Therefore analytical pyrolysis was performed in an additional attempt to compare hardwood fiber and crill MWLs. These comparisons were made by ratioing the sum of the peak heights of the major pyrolysis products of syringyl origin (2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, syringaldehyde, 4-propenyl-2,6-dimethoxyphenol, 4-propyl-2,6-dimethoxyphenol, sinapaldehyde, and sinapyl alcohol) to the sum of the peak heights of major products of guaiacyl origin (guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, vanillin, 4-propylguaiacol, and coniferyl alcohol) (Table 5). Because larger sample sizes were used, normal mass spectral acquisitions were possible and a greater number of pyrolysis products were used for comparisons than for the MID pyrograms (Table 4).

It was anticipated that determination of a pyrolysis syringyl/guaiacyl ratio would allow for a meaningful comparison among MWLs from various sources. It has been assumed that methoxyl content is a reliable indicator of the contribution of syringyl units to lignin composition. However, when the pyrolysis syringyl/guaiacyl

TABLE 5

Pyrolysis Syringyl/Guaiacyl Ratio[1] and Methoxyl Content of Hardwood Milled Wood Lignins

Milled wood lignin	Pyrolysis syringyl/guaiacyl	Methoxyl
		(%)
White oak fiber	2.8	21.5
White birch fiber	4.2	21.6
Crill	1.6	21.1
American elm fiber	1.0	19.8
Crill	0.9	19.3
Red oak fiber	1.1	21.3
Crill	0.8	21.2

[1] Syringyl derived products were 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, syringaldehyde, 4-propenyl-2,6-dimethoxyphenol, 4-propyl-2,6-dimethoxyphenol, sinapaldehyde, and sinapyl alcohol. Guaiacyl derived products were guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, vanillin, 4-propylguaiacol, and coniferyl alcohol.

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ratios were compared to the methoxyl values determined for these MWLs, no good correlation could be made (Table 5). Milled wood lignins with similar methoxyl contents gave significantly different pyrolysis syringyl/guaiacyl ratios. Thus, under the conditions employed in this study, py-gc-ms does not enable meaningful syringyl/guaiacyl comparisons among hardwood MWLs.

CONCLUSIONS

Pyrolysis of lignin, either from isolated MWLs or from wood, produces phenolic products that may be separated by capillary gas chromatography and subsequently identified by mass spectrometry. In this way, lignin may be classified as either guaiacyl-type or syringyl/guaiacyl-type. Although all of the conditions for quantitative analysis have not been achieved, pyrolysis-gas chromatography-mass spectrometry of hardwood vessel elements indicated that vessel lignin is of the syringyl/guaiacyl-type. This finding requires a reappraisal of the method of determining lignin type by ultraviolet microscopy. Pyrolysis syringyl/guaiacyl ratios were determined for hardwood MWLs from fiber and middle lamella enriched fractions but they did not correlate to the methoxyl values of the MWLs. With careful attention to obtaining quantitative results, pyrolysis-gas chromatography-mass spectrometry may have potential to become a valuable tool for characterization of lignin in wood and pulp as well as of isolated lignins.

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