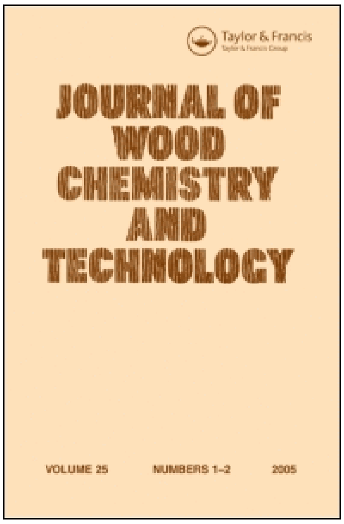

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Attempted Removal of Metal Ions and Subsequent Vacuum Pyrolysis of Barks from Five Species of Softwoods

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ATTEMPTED REMOVAL OF METAL IONS AND SUBSEQUENT VACUUM PYROLYSIS OF BARKS FROM FIVE SPECIES OF SOFTWOODS

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ABSTRACT

Samples of whole bark were collected from sub-alpine fir, Engelmann spruce, Douglas fir, western larch and lodgepole pine. Attempts to remove metal ions from the barks by ion exchange with dilute acid at room temperature showed that up to one third of these ions (especially calcium) are inaccessable to aqueous acid and hence not removed. The barks were subjected to vacuum pyrolysis before and after acid washing and the tars analyzed by gas chromatography as trimethylsilyl ethers. The incomplete removal of metal ions resulted in significant increase in pyrolytic production of the major products derived from polysaccharides (viz. levoglucosan and anhydroarabinose).

INTRODUCTION

In an earlier paper[1] we examined some of the major products from vacuum pyrolysis of inner and outer bark from Ponderosa pine (Pinus ponderosa) (PIPO). Nine major peaks were identified in the gas chromatogram of the trimethylsilyl ethers of the barks, all of which (except pinitol) probably originated predominantly from pyrolysis of the polysaccharide components of the bark. The yield

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of these compounds was considerably improved by acid washing of the bark (especially the phloem) to remove metal ions, so that after the most rigorous acid washing process the phloem yielded a tar from vacuum pyrolysis at 350°C, of which the above nine products comprised 53% (i.e. 16% yield of these products based on the washed bark).

These studies made it evident that a much cleaner pyrolysis resulted from bark after the removal of metal ions, but that this removal was incomplete even after washing the bark with molar hydrochloric acid or with EDTA. In contrast, we have found[2] that virtually all metal ions can be removed from sapwood with 0.05 M hydrochloric acid at room temperature and this complete deionization is believed to be very desirable in any attempt at pyrolytic utilization of lignocellulosics. We have therefore now examined the ease and extent of deionization and the pyrolytic behavior of barks from five other species of commercial trees in order to show whether the problems observed with bark from Ponderosa pine are typical.

EXPERIMENTAL

Materials

All barks were collected and processed as described earlier for Ponderosa pine[1], except that phloem was not separated from outer bark. The yields of bark for four species are indicated in Table 1. Lodgepole pine (_Pinus_ _contorta_) (PICO) whole bark was stripped from mature, apparently healthy trees, without record of age or size and dried and ground in the same way. All bark samples were collected in late summer (August, September).

General Procedures

Acid washing with 0.05 M hydrochloric acid at room temperature followed by very rigorous water washing with conductivity water, pyrolysis, and analyses of materials and pyrolysis products, were all carried out as described earlier[1].

TABLE 1

Yields of Bark

Species	Age (yrs)	Bole Used		Phloem Thickness		Yield of Whole Bark (g. air dry)
		diam. (cm)	length (cm)	mm	(%)[a]	
Sub-alpine Fir (*Abies lasiocarpa*) (ABLA)	42	14	200	3-5	(75-80)	1340
Engelmann Spruce (*Picea engelmannii*) (PIEN)	45	21	175	5	(70-80)	2760
Douglas Fir (*Pseudotsuga menziesii*) (PSME)	46	15	200	2-5	(20-40)	2590
Western Larch (*Larix occidentalis*) (LAOC)	65	15	200	5	(35-70)	2200

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[a] Approximate thickness of phloem as % of total bark.

RESULTS AND DISCUSSION

The yields of bark from four softwood species are shown in Table 1. Obviously, these results are of very limited statistical significance, but it is at least evident that considerably less bark would result from ABLA than from a comparable harvest of the other species. It is estimated that the yield of bark from PICO was approximately comparable with ABLA.

The polysaccharide contents of the barks are indicated by Table 2. These values represent absolute contents of anhydroglycose units, corrected for acid degradation. The phloem contains a greater proportion of polysaccharides than outer bark[1], but there is no doubt that both layers contain significant carbohydrate. However, the PSME and PICO barks contain much less total carbohydrate than the other three species in Table 2, or than PIPO[1]. This effect is not associated with an unusually low proportion of phloem, since ABLA has a higher ratio of phloem to outer bark than PIPO. The effect may be partly due to lower starch content in PSME and PICO barks, in accordance with their lower glucose contents. All five species of bark in Table 2 contain abundant pectic acid as indicated by their high uronic acid and arabinose contents, but the greatest amount of uronic acid is present in ABLA and PIEN barks and these two species have the highest ratio of phloem to total bark. In accordance with their high uronic acid contents they also have the highest ash contents (see below). It is interesting that the high arabinogalactan content of LAOC wood (5 - 35%)[3] is not reflected in the bark of this species, which has relatively low arabinose and galactose content, but relatively high mannose content.

The attempt to remove metal ions by washing the barks with dilute acid and then with water at room temperature resulted in considerable weight loss (up to 40%, Table 2). This is in sharp contrast with the same treatment of wood. Thus PIPO sapwood loses approximately 7% of its weight in the above treatment[4], while cottonwood (<u>Populus tremuloides</u>) loses 5%. Only a small proportion of the weight loss in the barks is due to removal of metal ions (see

TABLE 2

Glycan Content of Barks (% Dry Weight)

Bark	% Wt. loss in acid wash[a]	Arabinose	Xylose	Mannose	Galactose	Glucose	Uronic Acids	Total Carbohydrate
Untreated								
Sub-alpine Fir		3.4	1.4	1.5	1.9	24.4	11.2	43.8
Engelmann Spruce		2.9	1.4	1.7	2.1	25.3	11.3	44.7
Western Larch		1.9	1.8	4.1	2.2	22.0	7.9	40.8[b]
Douglas Fir		3.5	1.6	2.4	2.1	16.0	7.9	33.5
Lodgepole Pine		3.6	2.3	1.8	2.2	15.2	8.7	33.8
Acid Washed								
Sub-alpine Fir	25.3	5.2	2.1	2.8	2.7	16.2	12.8	41.8
Engelmann Spruce	40.4	6.9	3.5	2.6	2.2	22.6	18.2	56.0
Western Larch	23.5	4.6	3.8	4.4	2.4	22.9	9.7	47.8
Douglas Fir	20.1	4.1	1.5	1.7	1.0	14.6	9.4	32.3
Lodgepole Pine	11.9	5.8	4.0	1.7	1.9	15.5	9.4	38.3

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[a] Dry basis.

[b] Includes 0.9% rhamnose.

Table 3) and the major effect is the loss of water-solubles. For example, with PIPO phloem, room temperature water alone removes 35% of the weight, while the sequential acid and water wash remove 37%[1]. The cold water soluble constituents of barks are most abundant in the phloem and include significant sucrose, glucose, fructose, and glycosides. However, Table 2 shows a general increase in carbohydrate content and hence the water-solubles must be predominantly non-carbohydrate, except for PSME and ABLA barks where the carbohydrate content remained approximately constant despite considerable weight loss. About half of the glucose in ABLA bark is lost in the acid/water wash and this effect would merit further study. The uronic acid, xylose and arabinose contents before and after acid wash indicate that neither the pectins nor the xylan hemicelluloses are extracted and that there is no significant hydrolysis of arabinofuranoside units by the acid treatment. The increases in arabinose content resulting from acid washing are in fact greater than could be accounted for if the material removed by the acid and water were entirely free from arabinose. Thus, e.g., with Engelmann spruce, the loss of 40.4% of the bark without any loss of arabinose, should increase the arabinose content from 2.9% to only 4.9%, where as the "washed" value is 6.9%. This situation is difficult to explain, and since the same trend occurs in four of the five barks, it seems unlikely that it is due to experimental error. We are forced to the tentative conclusion therefore that the arabinose contents in the original barks may represent lower values than the truth. A possible explanation is that the precipitation of insoluble products during the acid hydrolysis in the glycan analysis (e.g. by acid catalyzed oxidative condensation of polymeric proanthocyanidins in the bark), "traps" some of the galactose constituents (and perhaps other glycoses) in the insoluble products and thus prevents their inclusion in the glycose analysis.

The metal ion content of the barks and the extent of removal of these ions by the acid wash are shown in Table 3. The total metal ion content of the barks varies considerably from 2.1 to 0.9%.

TABLE 3

Cation Content of Barks (ppm)

Bark	Al	Ca	Co	Cu	Fe	Mg	Mn	P	K	Si	Na	Zn	Ti	Total M%	Ca/K
Untreated															
Sub-alpine Fir	95	14257	<1	9	63	666	845	965	4160	101	32	49	3	2.12	3.4
Engelmann Spruce	33	10248	<1	19	32	570	334	492	3437	64	9	123	1	1.54	3.0
Western Larch	161	5916	<1	10	130	804	279	1737	3034	227	24	17	10	1.23	1.9
Douglas Fir	243	7031	<1	13	113	297	278	372	1503	195	31	84	8	1.02	4.7
Lodgepole Pine	224	6664	<1	15	147	446	109	150	777	190	63	41	9	0.88	8.6
Acid Washed															
Sub-alpine Fir	48	4606	<1	10	41	26	76	812	627	49	31	5	2	0.63	7.3
Engelmann Spruce	28	3622	<1	9	30	18	22	381	241	44	44	14	2	0.45	15.0
Western Larch	100	2675	<1	5	106	204	22	738	180	161	22	2	8	0.42	14.9
Douglas Fir	88	1297	<1	16	78	26	11	236	22	120	9	3	6	0.19	58.9
Lodgepole Pine	93	1227	<1	9	80	17	4	83	33	116	17	5	6	0.17	37.2

In all cases (as for most plant materials), calcium and potassium predominate and their ratio ranges from 8.6 to 1.9. Apart from these two elements the most notable features are the unusually high manganese content of ABLA bark and the high magnesium and phosphorous content of barks from LAOC and ABLA. The major conclusion regarding the attempted removal of metal ions by acid washing, is that it is very incomplete, especially considering that the similar treatment of wood results in almost complete removal of these ions[2]. Evidently then, these five barks, like PIPO[1], have domains containing metal ions which are not accessible to the aqueous acid. The potassium ions are more extensively removed than calcium and this situation may represent a combination of two effects, viz. a higher concentration of the latter ions in the inaccessible domains, and the stronger binding of the divalent cation by the ion exchange groups in the barks. We have previously noted that potassium ions are preferably (compared with calcium) extracted from wood by hot water[2] and have concluded that they may be predominantly associated with cell contents rather than cell wall materials. The magnesium and manganese may have a similar source in bark and are both also relatively readily removed by the acid/water wash. The phosphorus is surprisingly resistent to removal, and we conclude that it is extensively contained in inaccessible domains, presumably as phosphates.

Table 4 shows the gross yields from vacuum pyrolysis of the barks at 350°C. Rather surprisingly, the original barks gave slightly lower yields of tar and similar or higher yields of char than the acid washed barks. In general, it has been observed that the presence of mineral additives in lignocellulosics has the effect of increasing char and decreasing tar[5]. The tars were converted to trimethylsilyl (TMS) ethers, after addition of glucitol as internal standard, and analyzed by gas chromotography (GC). The results for tars from untreated barks are shown in Table 5, where all of the major GC peaks are shown. These only account for a minor proportion of the tar (up to 18%), but they indicate that the bark with the

TABLE 4

Vacuum Pyrolysis of Barks, 350°C, 30 min.

Bark	% Tar	%Distillate	% Char	% Total Recovery
Untreated				
Sub-alpine Fir	30	25	35	90
Engelmann Spruce	16	21	47	84
Western Larch	14	19	47	80
Douglas Fir	12	18	50	80
Lodgepole Pine	19	17	46	82
Acid Washed				
Sub-alpine Fir	32	16	33	80
Engelmann Spruce	26	17	38	81
Western Larch	20	16	44	80
Douglas Fir	17	14	51	82
Lodgepole Pine	23	14	46	83

TABLE 5

Major Peaks from G.C. of TMS Ethers of Tars from Untreated Barks as % of Dry Bark.*
Pyrolysis Conditions, 350°/30 min.

Bark	Sub-alpine Fir	Engelmann Spruce	Western Larch	Douglas Fir	Lodgepole Pine
Tar yield	30	16	14	12	19
1,5-Anhydroarabinose	0.3 (0.8)	0.2 (1.1)	0.2 (1.7)	0.3 (2.6)	0.8 (4.3)
Levoglucosan pyranose	0.1 (0.3)	1.5 (9.1)	1.3 (9.2)	0.6 (4.6)	1.6 (8.6)
Levoglucosan furanose	N.D.	N.D.	N.D.	N.D.	0.1 (0.4)
Pinitol	0.3 (0.9)	0.1 (0.8)	0.1 (0.3)	0.1 (0.7)	<0.1 (0.1)
1,2-Dihydroxybenzene[a]	0.2 (0.7)	0.1 (4.9)	0.6 (4.3)	0.4 (3.2)	0.4 (2.1)
1,4-Dihydroxybenzene	<0.1 (0.1)	0.8 (0.7)	0.1 (0.8)	0.1 (1.0)	0.1 (0.5)
1,2,3-Trihydroxybenzene	0.1 (0.5)	0.1 (0.7)	0.1 (0.8)	0.1 (0.5)	0.1 (0.6)
1,2,4-Trihydroxybenzene	0.1 (0.2)	0.1 (0.7)	0.1 (0.8)	0.1 (0.4)	0.1 (0.3)
Total "recovery" of tar (%)	4	18	18	13	17

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*Figures in Parenthesis are % content in tar.

[a] Includes 5-(hydroxymethyl)-2-furaldehyde.

N.D. not detected.

Table 6

Major Peaks from G.C. of TMS Ethers of Tars from Acid Washed Barks as % of Dry Bark[*]
Pyrolysis Condition, 350°C/30 min

Bark	Sub-alpine Fir	Engelmann Spruce	Western Larch	Douglas Fir	Lodgepole Pine
Tar Yield	32	26	20	17	23
1,5-Anhydroarabinose	1.0 (3.1)	1.2 (4.6)	0.6 (3.2)	0.9 (5.3)	0.7 (3.1)
Levoglucosan pyranose	1.9 (5.9)	2.7 (10.4)	4.0 (20.2)	2.7 (15.7)	3.1 (13.4)
Levoglucosan furanose	<0.1 (0.1)	0.1 (0.5)	0.2 (0.9)	0.1 (0.7)	0.2 (0.7)
Pinitol	N.D.	N.D.	N.D.	N.D.	N.D.
1,2-Dihydroxybenzene[a]	N.D.	0.2 (0.9)	0.2 (0.9)	0.2 (1.2)	0.3 (1.3)
1,4-Dihydroxybenzene	N.D.	0.1 (0.3)	0.1 (0.2)	0.1 (0.5)	0.1 (0.4)
1,2,3-Trihydroxybenzene	0.1 (0.2)	0.1 (0.2)	0.1 (0.3)	<0.1 (0.2)	0.1 (0.3)
1,2,4-Trihydroxybenzene	<0.1 (0.1)	0.1 (0.2)	0.1 (0.3)	<0.1 (0.2)	<0.1 (0.1)
Total "recovery" of tar (%)	9	17	26	24	19

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[*] Figures in parenthesis are % content in tar.

[a] Include 5-(hydroxymethyl)-2-furaldehydes.

N.D. not detected.

highest ash content (ABLA) give the lowest yield of levoglucosan, despite the fact that it gave the highest yield of tar. It is particularly evident in this case therefore that some major pyrolysis products remain to be identified. After partial removal of ions by acid washing, the pyrolysis of the barks gave tars with the TMS ether, GC analyses, shown in Table 6. Despite the residual metal ions, these results show significant increase in yield of the predominant pyrolysis products derived from the polysaccharides (viz. levoglucosan and anhydroarabinose), but the di- and trihydroxybenzenes which result from pyrolysis of cellulose in presence of salts[6] were still present. The proportion of total tar accounted for by this method was also increased (up to 26%). However, the hoped-for improvement in yield of major pyrolysis products was still relatively small due to the residual metal ions.

It is evident that any attempt to improve thermochemical processing of barks by removal of metal ions before pyrolysis will not succeed because of the resistance of the ions to ion-exchange under mild aqueous conditions, although the process has considerable potential for wood. These results also emphasize the limitations of the currently available methods for tar analysis by GC of TMS ethers. We believe that direct GC and mass spectrometric methods on underivatised tars also have major deficiencies which result in failure to determine a true perspective of tar components and we are pursuing solutions to such problems.

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