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Ayla Calimli[a]; Aral Olcay[a]
[a] Department of Industrial and Applied Chemistry, Faculty of Sciences, Ankara University, Ankara, Turkey

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Supercritical Dioxane Extraction of Spruce Wood and of Dioxane-Lignin and Comparison of the Extracts with the Pyrolysis Products

AYLA CALIMLI and ARAL OLCAY

DEPARTMENT OF INDUSTRIAL AND APPLIED CHEMISTRY
FACULTY OF SCIENCES
ANKARA UNIVERSITY
ANKARA, TURKEY

ABSTRACT

Samples of spruce wood and of dioxane-lignin prepared from spruce wood were subjected to supercritical dioxane extraction at 330°C. To compare the yield and the nature of the compounds present in distillate obtained upon pyrolysis to those of supercritical gas extract, the same samples were pyrolysed at 340°C.

The extracts and distillates were separated into three fractions by solvent fractionation using hexane and benzene successively. The simpler compounds were identified by GC/MS and the yields of phenols were compared. More complex compounds insoluble both in hexane and benzene have been characterized by ^1H NMR spectrometry. It was found that the supercritical extracts and the pyrolysis distillates contained similar compounds; however, demethoxylation during pyrolysis was extensive compared to supercritical gas extraction which occurred under rather mild conditions.

INTRODUCTION

Most investigators concerned with the utilization of wood for the production of chemical products have worked on the pyrolysis of wood and of lignin (1,2,3).

Lately, it has been shown that extraction with supercritical gases can be used successfully to volatilize high boiling materials from the nonvolatile materials (4) at a temperature below that at which pyrolysis occurs. It has therefore been claimed that the compounds obtained in supercritical gas extraction were not significantly degraded in contrast to those obtained by pyrolysis.

Previous work has established that significant yields of soluble material can be obtained by the supercritical gas extraction of wood (5). In fact, supercritical dioxane extraction of spruce wood gives the largest yield of liquid products.

The aim of this work was to compare the compounds and their yields obtained from pyrolysis with those obtained by supercritical dioxane extraction both of spruce wood and of dioxane-lignin* prepared from spruce wood.

In the past a variety of techniques has been used to identify the products present in "distillates" obtained from pyrolysis of wood. We have used a gas chromatograph-mass spectrometer system to analyse the low molecular weight components of the distillate and supercritical gas extract. For characterization of distillate and extract fractions containing higher molecular weight compounds their ^{1}H NMR spectra have been determined.

EXPERIMENTAL

Preparation of the Sample

30 mesh spruce wood powder was preextracted with benzene/ethyl alcohol (2/1) in a Soxhlet apparatus for 12 hours to remove extraneous components of wood. The residue was first dried in air and then in a dessicator over P_2O_5 under vacuum. The methoxyl content of the preextracted wood was 5.58% determined according to the Zeisel method (6). The Klason lignin content was 26.3% (7).

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*Dioxane-lignin is lignin extracted from wood by acidolysis in a dioxane-water solvent. See, e.g., Reference 6.

Dioxane-lignin was prepared according to the literature (8) with a yield of 10.5% (Klason lignin). The methoxyl content was 14.49%.

Pyrolysis of the Samples

For the pyrolysis experiments, 10 g of spruce wood or pre-extracted spruce wood or 5 g of dioxane-lignin were used. The air in the oven was replaced by a stream of dry nitrogen which was passed through the apparatus for 10 minutes. The temperature of the oven was then gradually increased and the final temperature was maintained for 30 minutes. The time required to reach the final temperature was about 60 minutes and various final temperatures in the range 300-400°C were examined in different experiments. No attempt was made to collect the gaseous products and the yield of gas was calculated by difference.

The distillate consisted of an oil. A very small amount of an aqueous fraction was observed. No attempt was made to separate water which might have been present in oil fractions.

Supercritical Gas Extraction of the Samples

The supercritical gas extractions of wood and of lignin were carried out as described previously (5).

Fractionation of the Distillate and of the Extract

a. The distillate or extract was first extracted with n-hexane and the insoluble compounds were further extracted with benzene. The hexane solubles (HS) were separated by adsorption chromatography on silica gel. Fractions were eluted successively with n-hexane, benzene, and methanol (7).

n-Hexane insoluble-benzene solubles (HIBS) were also subjected to adsorption chromatography on silica gel using benzene and methanol as eluants.

b. To separate phenolic compounds the distillate or extract was dissolved in chloroform and phenolic compounds were extracted by 10% sodium hydroxide. After subsequent acidification with 25% HCl the phenolic compounds were extracted with chloroform.

Identification of the Compounds

Each fraction was analysed by gas chromatography-mass spectrometry and individual compounds have been identified from their mass spectrum cracking pattern found in the literature (9,10,11) or obtained in our laboratory using model compounds.

Gas chromatography-mass spectrometry was carried out using a Packard 427 gas chromatograph fitted with a 1.8 m x 3 mm glass column with 3% SE-30 on Gas Chrom Q (100/120 mesh) and with a 1.8 m x 3 mm glass column packed with 5% DEGS on Chromosorb W (60/80 mesh) and coupled through a capillary glass jet separator to a Finnigan 3000E quadrupole mass spectrometer. Ionisation was carried out at 70 eV and 1.06 mPa pressure.

60 MHz ^{1}H NMR spectra of solutions of n-hexane insoluble-benzene soluble (HIBS) and n-hexane insoluble-benzene insoluble (HIBI) fractions in deuterated chloroform were recorded on a Varian T 60. Tetramethylsilane (TMS) was used as the internal standard. Solutions of fractions were shaken with D_2O to replace phenolic hydrogen by deuterium atoms.

RESULTS AND DISCUSSION

Earlier results obtained from thermogravimetric and differential thermal analyses of spruce wood and of dioxane lignin indicated that decomposition was complete at 400°C for both wood and lignin (12,13). Accordingly the maximum temperature used for pyrolysis was generally 400°C. However, to investigate the influence of temperature on the yields of distillate and coke and also on the composition of the distillate, wood was pyrolysed to final temperatures of 300, 340, and 400°C. Table 1 shows the yields of

TABLE 1

Yields of Distillates from Pyrolysis of Wood and of Lignin

Samples	Pyrolysis Temperature (°C)	Distillate (%)[a]	Coke (%)[a]	Aqueous Fraction (%)[a]	Gases and Loss (%)[a]
Preextracted Wood	300	19.7	38.1	1.6	40.6
Preextracted Wood	340	22.4	32.7	1.8	43.1
Preextracted Wood	400	31.2	28.7	1.8	38.3
Wood	400	31.8	28.2	2.0	38.0
Dioxane-lignin	400	27.8[b]	42.4[b]	0.4[b]	29.4[b]

[a] Yields are on the basis of dry, preextracted wood.

[b] Yields are on the basis of dry, dioxane-lignin.

distillate and of coke obtained from preextracted wood at three different temperatures; the yield of distillate and coke obtained at 400°C from wood which was not subjected to a previous extraction to remove extraneous substances and from dioxane-lignin are also shown in Table 1. As can be seen from the table the yield of distillate increases with increasing temperature of destructive distillation while the yield of coke decreases.

Table 2 indicates the yield of the supercritical dioxane extract of preextracted spruce wood and of dioxane-lignin. As can be seen in Table 2 the yield of products obtained from supercritical dioxane extraction of wood and from pyrolysis of wood at 340°C were similar. The yield of extract obtained from lignin was about 60% higher than the distillate of lignin obtained at 400°C.

The yields of HS and of HIBS and HIBI obtained from distillate and from supercritical extract are shown in Table 3. As can be seen from the table, as the temperature of pyrolysis increases from 340°C

TABLE 2

Yields of Extracts from Supercritical Dioxane Extraction of Wood and Lignin

Samples	Extraction Temperature[a] °C	Extraction Pressure[b] atm	Yields Extract (%)	Residue (%)	Gas and Loss (%)
Preextracted Wood	330	90	23.6[c]	27.9[c]	48.5[c]
Dioxane-lignin	330	100	45.7[d]	53.3[d]	1.0[d]

[a] Critical temperature of dioxane, 314°C.
[b] Critical pressure of dioxane, 51.4 atm.
[c] Yields are on the basis of dry, preextracted wood.
[d] Yields are on the basis of dry, dioxane-lignin.

TABLE 3

Yields of the Various Fractions of the Pyrolysis Distillate and the Supercritical Extract

Samples	n-Hexane Solubles (%)	HIBS[a] (%)[c]	HIBI[b] (%)[c]
Distillate of wood (at 400°C)	1.2	17.1	13.5
Distillate of preextracted wood (at 340°C)	0.2	13.9	8.3
Dioxane extract of preextracted wood (at 330°C)	2.7	17.4	3.5
Distillate of lignin (at 400°C)	2.1[d]	18.8[d]	6.8[d]
Dioxane extract of lignin (at 330°C)	5.6[d]	28.6[d]	11.5[d]

[a] n-Hexane Insoluble Benzene Solubles.
[b] n-Hexane Insoluble Benzene Insolubles.
[c] Yields are on the basis of dry, preextracted wood.
[d] Yields are on the basis of dry, dioxane-lignin.

to 400°C, the increase of the HIBI fraction of wood distillate was much higher than the increase of HIBS yield. While the extract and distillate yields of wood were similar at 330-340°C for both processes, the extract contained higher proportions of HS and HIBS fractions and lower proportions of the HIBI fraction, indicating that formation of higher molecular weight compounds occurred during pyrolysis.

The HS-hexane eluate of the extract and distillate of wood consisted of normal paraffins.

The HS-hexane eluate was not obtained either from lignin or from wood which had been subjected to a preliminary extraction to remove extraneous components of wood. The HS fractions of wood and lignin distillate did not give any significant benzene eluate. However, the benzene eluates of the HS fraction of wood and lignin extracts contain methylated derivatives of benzene and phenolic compounds.

The mass spectra of the methanol eluates of the HS fraction of distillate and extract indicated the presence of low molecular weight, simple phenolic compounds (some with carbonyl and carboxyl groups on the side chains) and small amounts of dimeric compounds containing guaiacyl nuclei.

The compounds present in HIBS fractions shown in Table 4 are similar to those present in benzene and methanol eluates of HS fractions but are present in larger amounts. Since all compounds present in the HIBS fraction could not be analysed by GC due to the presence of high molecular weight compounds, the ^{1}H NMR spectra of benzene and methanol eluates were determined for their further characterization.

The ratios of ArH/OCH_3 estimated from the relative proton distributions in ^{1}H NMR spectra of benzene and methanol eluates of the HIBS fraction from wood extract were 2.87 and 2.40 respectively. While this result might indicate the presence of some dimeric compounds in benzene eluates, in methanol eluates it suggests the presence of higher molecular weight compounds.

TABLE 4

HIBS Fractions of Extract of Wood and of Lignin

Compounds	Benzene Eluate	Methanol Eluate
Toluene	+	-
o-Xylene	+	-
p-Xylene	+	-
Isopropylbenzene	+	-
1,2,4,-Trimethylbenzene	+	-
1,2,5,-Trimethylbenzene	+	-
1-Methyl-4-n-propylbenzene	+	-
Phenol	-	+
o-Cresol	+	+
p-Cresol	+	+
Guaiacol	+	+
3,4-Dimethylphenol	+	+
Naphthalene	+	-
o-Ethylphenol	-	+
4,5-Dimethylphenol	-	+
p-Ethylphenol	-	+
6-Methylguaiacol	+	+
4-Methylguaiacol	+	+
p-Isopropylphenol	-	+
4-Ethylguaiacol	+	+
4-Methyl-6-isopropylphenol	-	+
Eugenol	-	+
4-n-Propylguaiacol	+	+
6-Isopropenylguaiacol	-	+
Vanillin	-	+
Isoeugenol	-	+
5-Propenyl(β,γ)-7-methoxy-benzofuran	-	+
Coniferyl alcohol	-	+
Guaiacylacetone	-	+
Coniferyl aldehyde	-	+
Propioguaiacone	-	+
4-Hydroxy-3-methoxyphenylpropionic acid	-	+
Ferulic acid	-	+
4-Hydroxy-3-methoxypropiophenone	-	+
4-Hydroxy-3-methoxyphenylpyruvic acid	-	+
1-(4-Hydroxy-3-methoxy-5-ethylphenyl)-propane-1,3-diol	-	+
1-(4-Hydroxy-3-methoxy-5-propylphenyl)-propane-1,3-diol	-	+
4-Hydroxy-3-methoxystyryl 2'-methoxyphenyl ether	-	+
4-Hydroxy-3-methoxy-phenethyl 2'-methoxyphenyl ether	-	+

TABLE 4
(con't.)

Compounds	Benzene Eluate	Methanol Eluate
4-Hydroxy-3-methoxybenzyl 2'-methoxyphenyl ether	-	+
1,2-bis(4-Hydroxy-3-methoxyphenyl)ethane	-	+
1-(4-Hydroxy-3-methoxyphenyl)-2-(6'-hydroxy-3-methoxyphenyl)ethane	-	+
1-(4-Hydroxy-3-methoxyphenyl)-2-(6'-hydroxy-5'-methoxy-3'-methylphenyl)-ethane	-	+
2-(3-Methoxy-4-hydroxyphenyl)-5-vinyl -7-methoxybenzodihydrofuran	-	+
2-(3-Methoxy-4-hydroxyphenyl)-5-propenyl-(β,γ)-7-methoxybenzodihydrofuran	-	+
Dihydrodiisoeugenol	-	+

The HIBI fractions were only characterized by their ^1H NMR spectra. The ^1H NMR spectra of HIBI fractions obtained from the distillate and from the extract of wood indicate different proton distributions. While in distillates ArH/OCH_3 ratios were 2.65-2.80, in extracts the same ratios were 2.35-2.38 indicating the presence of higher molecular weight compounds in the HIBI fraction of the extract.

The ^1H NMR spectrum of HIBI from wood extract was similar to that from lignin extract. However, relatively lower amounts of carbonyl and aliphatic protons were observed in the wood extract.

Table 5 compares the yields of phenolic compounds present in distillates of wood and of lignin. The amount of distillate obtained from preextracted wood increased steadily as the temperature of pyrolysis was increased from 300°C to 400°C (Table 1); consequently, the yield of phenolic compounds also increased though, in fact, the percentage of phenols present in distillates decreased as the temperature of pyrolysis was increased from 340°C-400°C. This

TABLE 5

Phenolic Compounds Present in Distillates and Extracts of Wood and Lignin

Samples	Amount of Product Phenolic Compounds on the Basis of the Product Distillate or Extract (%)	Amount of Product Phenolic Compounds on the Basis of Starting Material (%)
Distillate of Preextracted wood (at 300°C)	21.05	4.14
Distillate of preextracted wood (at 340°C)	26.27	5.89
Distillate of preextracted wood (at 400°C)	23.84	7.45
Dioxane extract of wood (at 330°C)	51.88	12.23
Distillate of dioxane lignin (at 400°C)	52.50	14.60
Dioxane extract of lignin (at 330°C)	28.68	13.11

result might indicate that at 400°C the formation of compounds other than phenols occurs more than at 340°C.

As can be seen from Table 5 similar amounts of phenolic compounds were obtained from the lignin distillate and from the supercritical gas extract of lignin.

It was remarkable that the highest yield of phenolic material was obtained from supercritical gas extracts of wood. That the amount of phenolic compounds from the wood extract was higher than that from wood distillate suggests that some of the phenols in the distillate cracked or polymerized during pyrolysis. It is known that polyhydric phenols, for example, are prone to do this. Comparison of the yield of phenolic compounds from wood extract and distillate with those obtained from lignin extract and distillate suggests that some phenolic compounds were lost by oxidative polymerization during the separation of the dioxane-lignin.

Further details of the phenols present in distillates of wood are given in Table 6. The figures in Table 6 are normalized molar ratios relative to the amount of phenol produced at 300°C. The figures, therefore, roughly parallel yields on a preextracted wood basis.

It will be seen from Table 6 that, whereas the yields of many phenols increase steadily with pyrolysis temperature, the yields of others increase and then decrease again: o-isopropylphenol, isoeugenol and coniferyl alcohol.

TABLE 6

Relative Amounts[a] of Phenolic Compounds Present in Distillate Obtained from the Pyrolysis of Spruce Wood at 300°C, 340°C, 400°C

Compounds	300°C	340°C	400°C
Phenol	1.00	2.12	3.20
o-Cresol	2.35	3.11	3.52
p-Cresol	1.38	2.03	2.76
Guaiacol	6.58	6.44	11.12
3,4-Dimethylphenol	1.31	1.38	1.46
p-Ethylphenol	0.86	1.57	1.46
4-Methylguaiacol	6.34	10.22	13.26
o-Isopropylphenol	0.23	0.44	0.29
p-Isopropylphenol	0.15	0.29	0.29
4-Ethylguaiacol	2.77	3.67	5.42
3-Methyl-6-isopropylphenol	0.14	1.26	0.43
Eugenol	1.05	1.34	1.75
4-n-Propylguaiacol	0.35	0.70	0.71
6-Isopropenylguaiacol	0.35	0.58	0.73
Vanillin	0.42	1.22	1.24
Isoeugenol	1.12	5.04	4.11
Acetovanillone	0.40	0.72	0.96
Coniferyl alcohol	0.09	0.22	0.18
Guaiacylacetone	0.44	0.89	1.43

[a] *Normalized molar ratios, on the basis of phenol in distillate* (at 300°C).

Table 7 shows a detailed comparison of the effects of supercritical gas extraction (using dioxane at 330°C) and of pyrolysis (at 340°C) on the yields of phenols. The process of isolation and identification of the phenols was the same in both methods of forming phenols. (In all treatments the phenols were isolated and identified in the same way.)

TABLE 7

Comparison of Relative Amounts[a] of Phenolic Compounds Present in Distillate and Extract of Wood

Compounds	Distillate (at 340°C)	Extract (at 330°C)
Phenol	2.12	1.60
o-Cresol	3.11	1.30
m-Cresol	-	0.10
p-Cresol	2.03	1.88
Guaiacol	6.44	18.45
3,4-Dimethylphenol	1.38	0.44
o-Ethylphenol	-	0.36
m-Ethylphenol	-	0.18
4,5-Dimethylphenol	-	3.08
p-Ethylphenol	1.57	1.15
6-Methylguaiacol	-	0.78
4-Methylguaiacol	10.22	21.19
o-Isopropylphenol	0.44	0.40
p-Isopropylphenol	0.29	0.63
3-n-Propylphenol	-	1.42
4-Ethylguaiacol	3.67	12.80
2-Isopropenyl-4-methylphenol	1.26	0.42
2-Isopropylphenol	-	0.45
Eugenol	1.34	1.96
4-n-Propylguaiacol	0.70	12.37
6-Isopropenylguaiacol	0.58	0.23
Vanillin	1.22	1.27
Isoeugenol	5.04	1.51
Acetovanillone	0.72	1.19
Coniferyl alcohol	0.22	0.78
Guaiacylacetone	0.89	0.12

[a] Normalized molar ratios, on the basis of phenol in distillate (at 300°C)

It should be emphasised that the duration of pyrolysis and supercritical gas extraction was of the same order of magnitude though the "heat up" period was longer for pyrolysis. The major difference between the two processes was that in supercritical gas extraction the phenols were formed in the presence of a large amount of diluent (dioxane). The supercritical dioxane extract contained more compounds that the distillates. Whilst m-cresol, 4,5-dimethylphenol, o-ethylphenol, m-ethylphenol, 6-methylguaiacol, 3-n-propylphenol and 2-isopropylphenol were present in supercritical dioxane extract of wood, they were not detected in the distillate.

The total yield of phenolic compounds in the extract of wood was about twice as high as the yield from wood distillate (Table 5) and it might naively be expected that the yields of each individual phenol would be in the same ratio. In fact the yields of 4-n-propylguaiacol, coniferyl alcohol, 4-ethylguaiacol and guaiacol were very much higher in the supercritical dioxane extract than in the wood distillate. The same guaiacyl compounds (except guaiacol) are also found in higher proportions in the supercritical extract of lignin than in the distillate from lignin (Table 8). (The figures in Table 8 are normalized molar ratios relative to the amount of phenol produced at 400°C. Therefore, the figures roughly parallel yields given on a dioxane-lignin basis.) Though the predominance is not so marked as in the comparison of the yields from wood, the results suggest that the guaiacyl compounds noted in this paragraph are primary products of the decomposition of wood and lignin and decompose further during pyrolysis when they are not protected by dilution.

A similar phenomenon is observed when one compares the yields of simple phenolic compounds. The presence of higher amounts of phenol, o-cresol, p-cresol, 3,4-dimethylphenol, p-ethylphenol in distillates indicates that the demethoxylation of guaiacyl compounds occurs more extensively during pyrolysis than during extraction. The high total yield of 4-n-propylguaiacal derivatives

TABLE 8

Comparison of Relative Amounts[a] of Phenolic Compounds Present in Distillate and Extract of Lignin

Compounds	Distillate (at 400°C)	Extract (at 330°C)
Phenol	1.00	0.47
o-Cresol	0.70	0.38
p-Cresol	1.00	0.80
Guaiacol	3.60	3.64
3,4-Dimethylphenol	0.50	0.09
o-Ethylphenol	-	0.09
4,5-Dimethylphenol	-	0.65
p-Ethylphenol	0.46	0.37
6-Methylguaiacol	-	0.30
4-Methylguaiacol	9.33	5.67
o-Isopropylphenol	0.10	0.11
p-Isopropylphenol	0.03	0.14
3-n-Propylphenol	-	0.28
4-Ethylguaiacol	2.60	2.81
4-Methyl-6-isopropylphenol	0.19	0.07
2-Isopropylphenol	-	0.09
Eugenol	0.57	0.18
4-n-Propylguaiacol	0.40	3.41
6-Isopropenylguaiacol	0.06	0.07
Vanillin	0.62	0.05
Isoeugenol	0.80	0.11
Acetovanillone	0.28	0.21
Coniferyl alcohol	0.14	0.23
Guaiacylacetone	0.23	0.16

[a] Normalized molar ratios, on the basis of phenol in distillate (at 400°C).

in the supercritical extract of lignin suggests that the cleavage of propyl side chains occurs more often during pyrolysis.

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