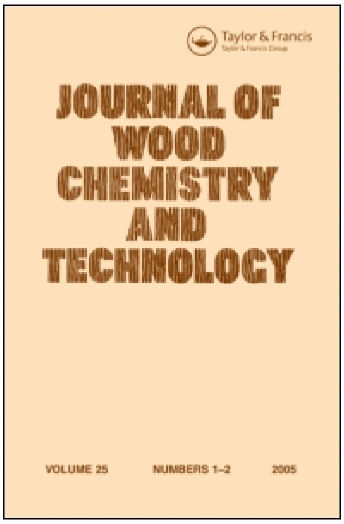

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THE PYROLYTIC BEHAVIOR OF SELECTED LIGNIN PREPARATIONS

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ABSTRACT

A pyrolytic study of a variety of lignins prepared from hardwood and softwood species, and of selected commercial lignins, was performed using isothermal and dynamic thermogravimetric analysis and pyrolysis-gas chromatography. The lignins were evaluated according to weight loss, rate of weight loss, and products formed during the pyrolysis in an inert atmosphere. These data were then compared to nitrobenzene oxidation data. Infrared spectroscopy was used to determine structural changes of lignin during initial weight loss in the temperature range of 250° to 320°C. Structural changes appear to occur without any appreciable weight loss. Lignin's thermal behavior during pyrolysis depends upon the degree of condensation present in the initial lignin. Thermogravimetric analysis is shown to be a simple and accurate method to determine the extent of lignin condensation. The yield of monomeric phenols is also dependent on the degree of lignin condensation.

INTRODUCTION

Over the past 30 years, the pyrolysis of lignin has been studied utilizing such methods as thermogravimetric analysis (TGA),[1,2] differential thermal analysis (DTA),[3] differential scanning calorimetry (DSC),[4] and pyrolysis-gas chromatography (PGC).[5] Studies on the pyrolysis of lignin include examining the effect of inorganic constituents in relation to both flame

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retardant capacity[2] and spent pulping liquor lignins.[6] In addition, different lignin preparations have been thermally characterized by TGA[1] and by PGC.[5] A review of lignin pyrolytic studies can be found in texts by Allan and Mattila[7] and Soltes and Elder.[8]

The pyrolysis of lignin model compounds has also been studied.[9,10] For the most part, model compound pyrolysis studies have concentrated on the thermal behavior of specific interunit linkages found in lignin molecules. Dynamic pyrolysis conducted using dimeric model compounds at a heating rate of 12°C/min showed that β-aryl ether compounds had a weight loss of 50% at 280°C for units with free phenolic hydroxyl groups, and at 310°C for compounds with etherified phenolic groups.[9] A conversion of 31% at 320°C was reported for β-aryl ether linked compounds by Kaymia.[11] It was shown by Klein and Virk[10] that ether linkages were the predominant linkages first broken in lignin model compounds during pyrolysis.

Results of these pyrolysis studies have led to information on reaction kinetics of thermal decomposition, product formation during lignin pyrolysis, and the production of chemicals from lignin by pyrolysis. However, since the mid 1970's, there have been a number of new lignin preparations introduced from various biomass pretreatment studies; i.e., steam-exploded lignin,[12] autohydrolyzed lignin,[13] and wet-oxidized lignin.[14] No information exists on the pyrolytic properties of these lignins. It is the purpose of this study to investigate the pyrolysis of these new lignin preparations as well as standard laboratory lignin preparations and commercial lignins.

METHODS AND MATERIALS

Lignin Preparations: Milled red oak, southern yellow pine (SYP), and mixed southern hardwoods were first extracted with ethanol/benzene. Hydrochloric (HCl) acid lignins were prepared according to the method of Schultz, et al.,[15] and Klason lignins were prepared according to the method of Browning.[16]

The mixed southern hardwood chips were obtained from a commercial wood yard, with analysis showing that approximately 82% consisted of wood chips, and the remainder of bark, twigs, and other material. Wet-oxidized lignins were prepared using oxygen at 1.65 MPa (240 psi) at 150°C for 30 minutes. Enzymatically liberated lignin from yellow poplar was obtained from Dr. C.-L. Chen at North Carolina State University. Steam-exploded lignin from mixed southern hardwood species and steam-exploded process sludge containing material from both southern hardwoods and pines were obtained from the Masonite® Corporation. The steam explosion pretreatment was carried out at 233°C for one minute.[17] The steam-exploded process sludge is part of the effluent from a commercial steam explosion process (Masonite®), and contains lignin, cellulose, hemicelluloses, waxes, and other trace chemicals. Both the wet-oxidation lignins and the steam-exploded lignins were extracted from the pretreated wood by 2% sodium hydroxide (NaOH) extraction followed by acid precipitation and neutralization. Kraft lignin (Indulin AT, Lot 02261) and sodium lignin sulfonate (Orzan S, Lot 80415) were obtained from Westvaco and Crown Zellerbach, respectively. Autohydrolyzed lignin from aspen was obtained from Dr. Morris Wayman at the University of Toronto.

The fifteen lignins were dried to a moisture content of 2% to 5% in a vacuum desiccator at 40°C. The lignins were analyzed for carbohydrate content after hydrolysis by gas chromatographic analysis,[18] and for ash content after ignition at 700°C.

Nitrobenzene Oxidation: Nitrobenzene oxidation was carried out at 160°C for 3 hours in a fluidized bed reactor. Ninety mg of lignin were added to 12 ml of 2N NaOH and 0.8 ml of nitrobenzene. Thirty mg of syringaldehyde and 20 mg of vanillin were used as controls. Continuous chloroform extraction of the reaction mixture was carried out for 3 hours and the chloroform discarded. The solution was then acidified and extracted for 20 hours with chloroform. The internal standard benzophenone was added to the chloroform, and the chloroform concentrated and acetylated with 6 ml of acetic anhydride and 1/2 ml of pyridine. Analysis was performed by GC using an OV-17 column.[19]

Thermogravimetric Analysis: The fifteen lignin preparations were analyzed by dynamic thermogravimetry (TG) and differential thermogravimetry (DTG) from 50° to 550°C at heating rates of 10°C/min with a Perkin-Elmer TGS-4 thermal analysis system. Cellulose and filter paper were used as controls. A nitrogen flow rate of 60 ml/min was used for the experiment.

Ten lignins were chosen for isothermal TGA studies at 293°C, with the other instrumental parameters remaining the same as in the dynamic runs. The temperature 293°C was chosen for the isothermal analysis because the lignins analyzed dynamically exhibited an increasing rate of weight loss at this temperature. To avoid unnecessary decomposition during the preheat period, the TGS-4 was programmed to reach 293°C at 50°C/min.

Infrared (IR) Spectroscopy Analysis: To determine what chemical changes are occurring in lignin during initial pyrolytic weight loss, HCl lignin (oak) was pyrolyzed at 250°C, 275°C, 300°C and 320°C, and subjected to IR Spectroscopy using a Perkin-Elmer 257 IR Spectrophotometer. Both acetylated and unacetylated pyrolyzates were examined. An unpyrolyzed sample was included as a control.

Pyroprobe Analysis: The 15 lignins were analyzed by pyrolysis-gas chromatography (PGC) with a Chemical Data System CDS 100 coil probe, with quartz tubes used to hold the sample. The pyrolysis temperature was 600°C, as determined by a thermocouple inserted into a quartz tube in the coil probe. The sample size for the probe quartz tubes was approximately 1 mg. The analyses were run in triplicate.

The pyrolysis products were analyzed with a Perkin-Elmer 3920 gas chromatograph interfaced with a Hewlett Packard 3990 recorder-integrator. After screening several columns, a 1.83-m (6-ft) OV-17 column was chosen for separation of pyrolysis products. While a capillary column would have given a better separation, a packed column was chosen since it could easily be repacked, or replaced at a low cost. Thus, any buildup of compounds on the column would be avoided. Instrument parameters for the gas chromatograph were as follows: injector temperature 200°C, detector temperature 275°C, and column temperature programmed from 105° to 260°C at 8°C/min. The carrier gas was nitrogen with a flow rate of 30 ml/min.

The standards for the lignin pyrolysis studies consisted of guaiacol, methyl guaiacol, syringol and syringaldehyde in a methanol solution. These compounds were chosen as standards because they were shown to be produced in sufficient quantity by lignin pyrolysis as shown by Martin, et al.,[20] and Schultz, et al.[15] Although vanillin, methyl syringol and isoeugenol are also produced by lignin pyrolysis, they were not used in the standard solution because they could not be separated from each other on the OV-17 column. Demethylated compounds (i.e., catechol, etc.) should also be formed during lignin pyrolysis, as shown by Klein and Virk[10] and Schultz, et al.[15] The authors were unable to analyze underivatized catechol using a 0.61-m (2-ft) SE-30 column. Thus, even though catechol derivatives may constitute a large proportion of the lignin pyrolysis products formed, the authors could not analyze for these types of products.

RESULTS AND DISCUSSION

The results of the carbohydrate analysis and ash content analysis of the various lignins are found in Table 1.

TABLE 1

Ash and Carbohydrate Content of Selected Lignins

Lignin type (species source)	Carbohydrates (wt. %)	Ash (700°C) (wt. %)
HCl lignin (red oak)	0.7	0.1
HCl lignin (mixed hardwoods)	5.7	1.0
HCl lignin (southern yellow pine)	4.8	0.1
Klason lignin (red oak)	0.0	2.3
Klason lignin (mixed hardwoods)	0.0	2.3
Klason lignin (southern yellow pine)	0.2	1.0
Wet-oxidized lignin (red oak)	5.1	4.8
Wet-oxidized lignin (mixed hardwoods)	4.4	1.8
Cellulase lignin (yellow poplar)	4.6	0.0
Steam-exploded lignin (mixed hardwoods)	0.7	0.6
Steam-exploded process sludge	38.4	6.4
2% NaOH extracted steam-exploded process sludge	6.1	0.5
Kraft lignin	0.4	2.5
Sodium lignin sulfonate	1.3	29.6
Autohydrolyzed lignin (aspen)	1.6	31.6

Steam-exploded process sludge contained 38.4 weight % carbohydrate material. The other lignins contained from 0 to 5.7 weight % carbohydrate material. Ash content for the lignins varied from 0% for the enzymatically liberated (cellulase) lignin to 31.6% for the autohydrolyzed lignin. Sodium lignin sulfonate contained 29.6% ash. Ash content of the other lignins varied from 0.1% to 6.4% ash.

The yield of products from the nitrobenzene oxidation of the lignins is found in Table 2. Nitrobenzene oxidation of lignin has long been used to measure the degree of condensation, i.e., the proportion of ether linkages to carbon-carbon interunit linkages.[21] Klason lignin, which is known to be a highly condensed lignin, gives a low yield of products from nitrobenzene oxidation. Lignin preparation techniques, such as cellulase lignin, which minimize chemical changes in the lignin structure, yielded greater product formation from nitrobenzene oxidation than Klason lignin.

The results of the dynamic TGA analysis are summarized in Table 3. TGA curves for a few lignins are found in Figure 1 and DTG curves for selected lignins are found in Figure 2. The thermal behavior of lignin has been shown to vary according to the technique used to separate the wood material.[1] We found this to be true, but also found that the thermal behavior is also species-dependent for the same preparation; i.e., Klason, hydrochloric acid and wet-oxidized lignins.

The residue at 550°C varied from 26.5% for the steam-exploded process sludge to 63.5% for the sodium lignin sulfonate. The low residue of the sludge is due to the presence of carbohydrate material. Sodium lignin sulfonate showed a high residue percentage due to both its condensation and high ash content.

Several analyses were performed to determine if any correlations existed between nitrobenzene oxidation yield and TGA data. It was reported by Nimz[22] that 65% of the linkages in

TABLE 2

Yield of Products From Nitrobenzene Oxidation of Selected Lignins

Lignin type (species source)	Product yields[a]		
	Vanillin	Syringaldehyde	Total
	---(weight %)---		
HCl lignin (oak)	6.0	18.3	24.3
HCl lignin (mix hardwoods)	5.4	14.3	19.7
HCl lignin (southern yellow pine)	9.5	0.2	9.7
Klason lignin (oak)	0.1	0.5	0.6
Klason lignin (mixed hardwoods)	0.1	0.3	0.4
Klason lignin (southern yellow pine)	0.2	0.1	0.3
Wet-oxdidized lignin (oak)	6.5	20.6	27.1
Wet-oxdidized lignin (mix hardwoods)	6.1	17.7	23.8
Cellulase lignin (yellow poplar)	8.7	29.7	38.4
Steam-exploded lignin (mix hardwoods)	4.5	13.6	18.1
Masonite sludge	2.4	8.1	10.5
2% NaOH extracted Masonite sludge	3.0	4.6	7.6
Kraft lignin	10.6	0.6	11.2
Sodium lignin sulfonate	7.1	0	7.1
Autohydrolyzed lignin (aspen)	2.4	6.3	8.7

[a] The analysis was run in duplicate.

TABLE 3

Thermal Behavior of Selected Lignins and Cellulose During Dynamic Thermogravimetric Analysis.

Lignin and cellulose type (species source)	Temp. at maximum rate of wt. loss (°C)	Maximum rate of wt. loss[a]	Decomposition temperature at 10% --weight loss-- (°C)	50% (°C)	Non-volatile residue at 550°C (wt.%)
HCl lignin (oak)	335	7.1[a]	295	445	39.2
HCl lignin (mixed hardwoods)	330	6.7	295	460	39.7
HCl lignin (southern yellow pine)	400	3.3	300	527	45.1
Klason lignin (oak)	375	3.5	335	---	51.7
Klason lignin (mixed hardwoods)	375	3.1	330	---	50.2
Klason lignin (southern yellow pine)	400	3.3	370	---	50.4
Wet-oxidized lignin (oak)	315	7.0	265	515	44.6
Wet-oxidized lignin (mixed hardwoods)	370	6.3	235	435	37.8
Cellulase lignin	365	8.9	290	395	29.5
Steam-exploded lignin (mixed hardwoods)	370	6.4	300	475	43.9
Steam-exploded process sludge	375	---	290	370	26.5
2% NaOH extracted steam-exploded process sludge	370	3.4	265	515	46.7
Autohydrolyzed lignin (aspen)	370	3.4	300	---	57.8
Kraft lignin	380	4.7	285	545	49.7
Sodium lignin sulfonate	320	2.8	270	---	63.5
Alpha cellulose	360	---	325	360	5.7
Filter paper	385	---	345	380	12.0

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[a] Maximum rate of weight loss was determined by measuring the maximum DTG peak height (mm) for each lignin and dividing it by the sample weight (mg).

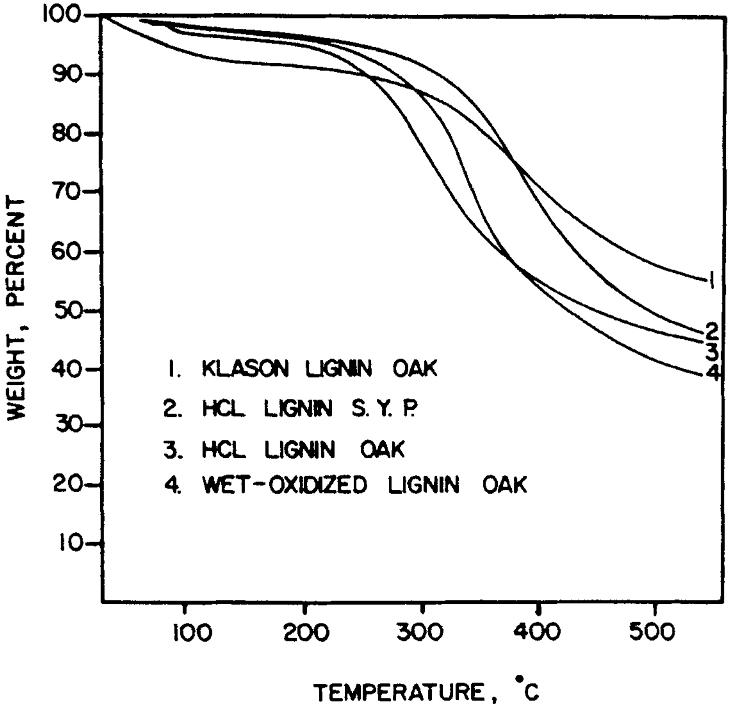


FIGURE 1. TGA curves for selected lignins.

native beech lignin are composed of α- and β-aryl ether linkages. As lignin becomes more condensed, the number of ether linkages will decrease while carbon-carbon interunit bonds increase. Since carbon-carbon bonds are more resistant to pyrolytic bond breakage than ether bonds,[10] the degree of condensation should influence the weight loss, rate of weight loss, and the amount of non-volatile residue. Accordingly, nitrobenzene oxidation product yield should be correlated with these pyrolytic properties of lignin.

It was shown by Domburgs[9] that β-aryl ether bonds in lignin model compounds are cleaved in the temperature range of around 310°C for compounds with etherified phenolic groups. In addition,

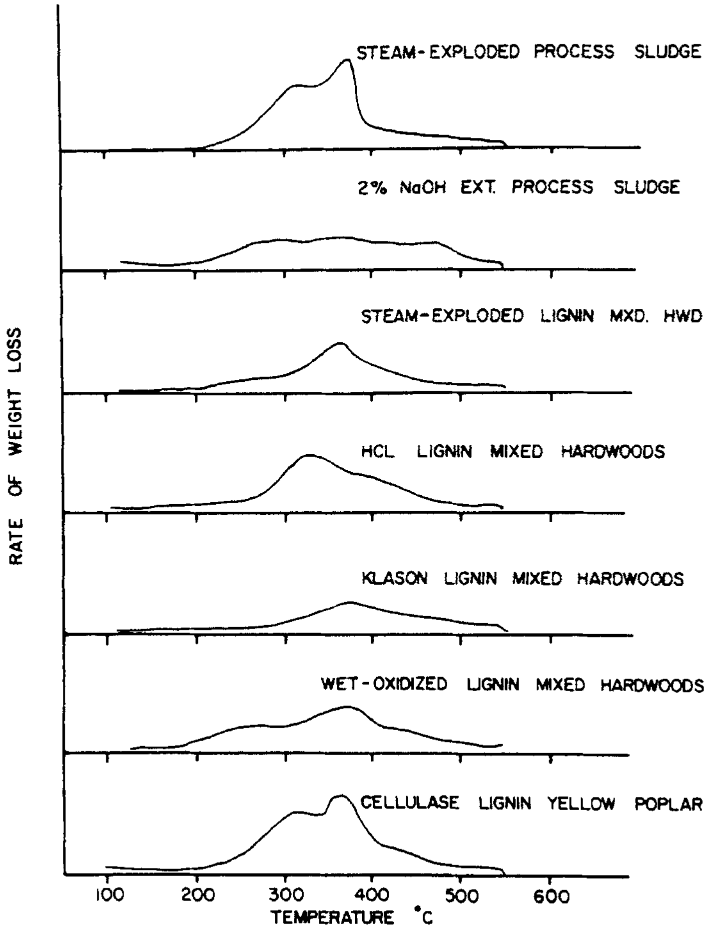


FIGURE 2. DTG curves for selected lignins.

it was shown by Klein and Virk[10] that ether bond cleavage yields volatile monomeric phenolic compounds. These results appear to correspond with both the TGA data and nitrobenzene oxidation data for enzymatically liberated lignin, which showed a DTG peak maximum at 320°C (Figure 2) and a high aldehyde yield from nitrobenzene oxidation (Table 2). To determine if this relationship existed for all lignins, correlation analyses were performed between weight loss and rate of weight loss at 320°C, and nitrobenzene oxidation yield. The correlations had r values of 0.85 and 0.71, respectively, the former being significant at the 99.9% level, and the latter at the 99% level.

Although the preceding correlations do exist for the lignins, a greater variety of interunit bond types were known to be present in the lignins examined. Highly uncondensed lignins, i.e. milled-wood lignin, have most of their interunit bonds consisting of only five different bond types,[23] while condensed lignins have a greater number of interunit bond types. Thus, instead of large weight losses occurring over a few specific temperatures, smaller weight losses should be seen over a range of temperatures. Also, chemical changes can occur during lignin pyrolysis without a large loss of weight.

Since the lignins examined varied greatly in degree of condensation and rate of thermal decomposition, it was theorized that a correlation should exist between nitrobenzene oxidation yield and the maximum rate of weight loss, determined by measuring the maximum DTG peak height for each lignin and dividing it by the sample weight. The correlation was highly significant, with r values of 0.96 for the hardwoods, and 0.95 for all species (Figure 3). It is believed the correlation for the maximum rate of weight loss was higher than the correlation of the peak height at 320°C because the lignins examined varied in interunit bond composition. An additional analysis showed a correlation between nitrobenzene oxidation yield and the non-volatile residue at 550°C with an r value of 0.78. The steam-exploded process sludge was intentionally left out of the analyses because of its high carbohydrate content.

The correlations between nitrobenzene oxidation data and TGA data indicate that TGA could be a useful technique for determining the condensation of lignin. TGA has definite advantages over the nitrobenzene oxidation technique. It is faster; requires less

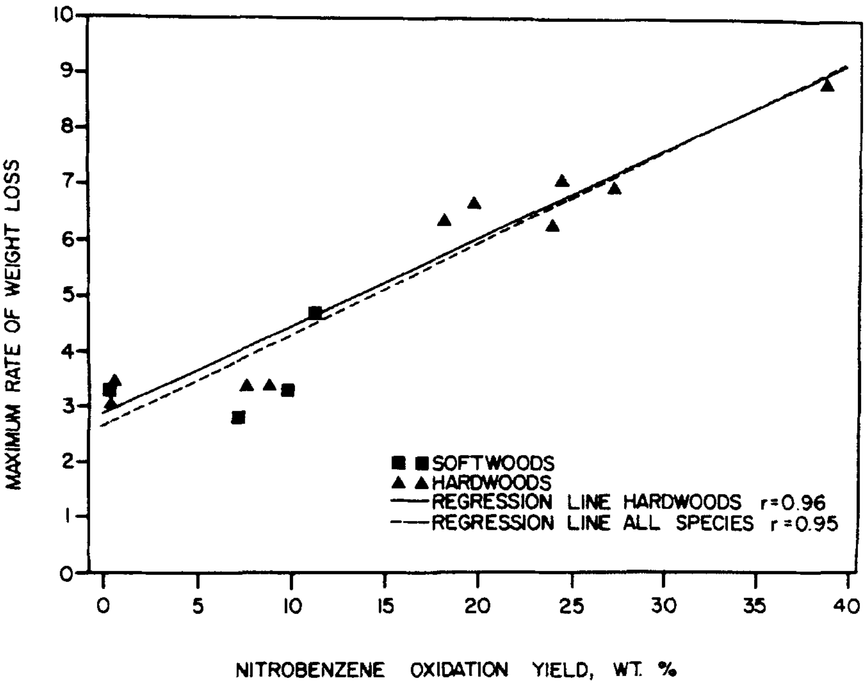


FIGURE 3. Relationship between maximum rate of weight loss against nitrobenzene oxidation yield.

exacting lab techniques (i.e., does not require the sample's moisture content or weight to be known); the equipment is entirely controlled by microprocessor; requires less sample (2 mg); and apparently can be used with both softwoods or hardwoods.

The chemical changes occurring in lignin during initial pyrolytic weight loss were examined using IR spectroscopy. Results are shown in Table 4 and Figure 4. The absorbance values of individual peak maxima were determined by the base line method.[24]

IR peaks of interest for the unacetylated pyrolyzates were hydroxyl (3400 cm^{-1}), aromatic ether (1235 cm^{-1}), methoxy/C_9 (1470 cm^{-1}), and uncondensed guaiacol (1035 cm^{-1}) bands; for the acetylated pyrolyzates they were aromatic acetyl (1760 cm^{-1}) and

TABLE 4

Relative Absorptivities of Selected IR Maxima for Pyrolyzed HCl Red Oak Lignin

Pyrolysis temperature of HCl lignin (oak)	Non-volatile residue (wt. %)	Unacetylated lignin cm^{-1}				Acetylated lignin cm^{-1}
		$\frac{3400}{1510}$	$\frac{1235}{1510}$	$\frac{1470}{1510}$	$\frac{1035}{1510}$	$\frac{1740}{1510}$
		---------------(relative ratios)---------------				
Unpyrolyzed	--	1.9	0.7	0.8	0.5	4.4
250°C	95	1.1	0.6	0.7	0.4	2.3
275°C	93	1.4	0.7	0.7	0.4	2.4
300°C	91	1.0	0.6	0.7	0.3	1.9
320°C	84	0.6	0.4	0.7	0.2	1.7

[a] Ratios of absorption peaks determined by the absorption ratio method.[24,25]

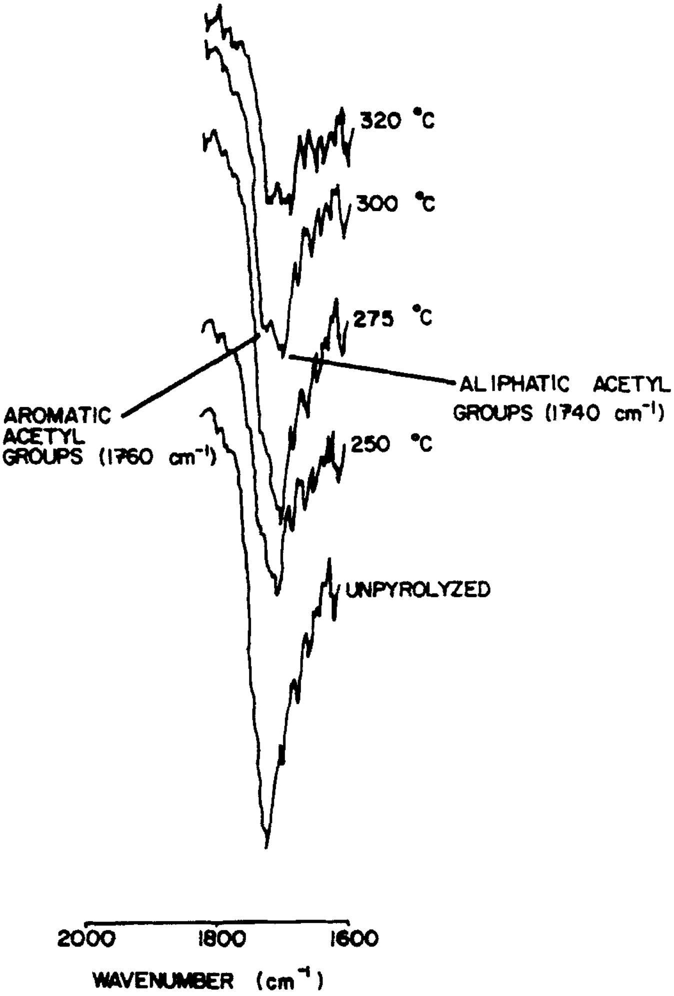


FIGURE 4. Infrared spectra of acetylated red oak lignin from 1600 cm^{-1} to 2000 cm^{-1} showing the effect of pyrolysis from 250° to 320°C.

aliphatic acetyl (1740 cm^{-1}) bands. Ratios of the absorption peaks of interest to the absorption peak at 1510 cm^{-1} were calculated. The absorption ratio method has been used by several investigators.[24,25]

As shown by the IR data in Table 4, distinct chemical changes occurred in the lignin structure over the ranges of temperatures examined. The results indicate that alkyl-aryl ether bonds are indeed broken over the temperature range of 300° to 320°C, since the ratio of aromatic ether linkages decreases, condensation of guaiacol increases and the aliphatic hydroxyl groups decrease. Also, a peak appears at 1760 cm^{-1} in the IR spectra of acetylated lignin at 300°C (Figure 4), which corresponds to the acetylated aromatic hydroxyl group for lignin. In contrast, the aromatic acetyl absorption for nonpyrolyzed HCl lignin suggests only a trace of phenolic hydroxyl groups. It was shown by Goldstein[26] that acetylated HCl lignin from sweetgum had little aromatic hydroxyl groups as determined by IR spectroscopy, and diazomethane methylation also indicated very little phenolic character, an observation in agreement with the results of acetylated HCl lignin from red oak. This suggests that some alkyl-aryl ether bonds are being broken at about 300°C.

Although methoxy (MeO) groups on the aromatic nucleus of lignin are connected by ether bonds, the ratio of MeO/C_9 units did not decrease over the temperature range examined. This phenomenon is supported by model compound studies in which Domburgs[27] showed that demethylation of methoxy groups occurred at 370° to 420°C, and Klein and Virk[10] showed that demethylation of guaiacol and substituted guaiacols are a secondary reaction which forms catechols at higher temperatures. The IR results should be viewed with caution since it is difficult to quantify IR data and the absorption of different bonds can overlap each other.

The results of the pyrolysis-gas chromatography of the various lignins are shown in Table 5. A sample chromatogram is

TABLE 5

Selected Pyrolysis Products from Selected Lignins[a]

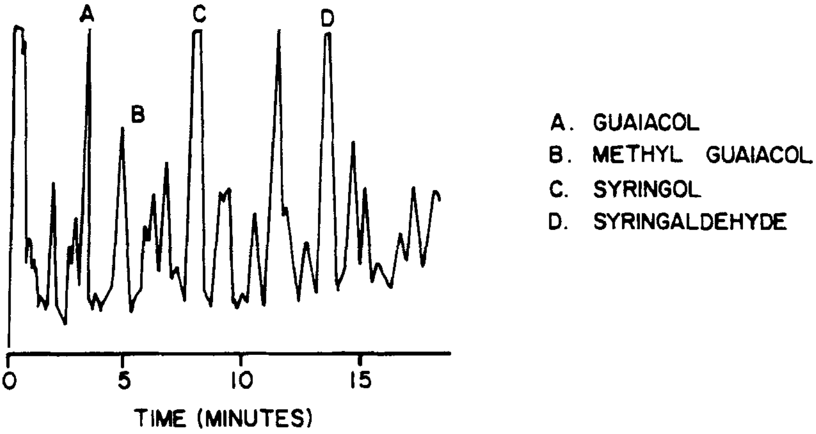
Lignin type (species source)	Pyrolysis products				
	Guaiacol	Methyl guaiacol	Syringol	Syringal-dehyde	Total
	----------------(weight %)----------------				
HCl lignin (oak)	0.23	0.30	0.85	0.52	1.9
HCl lignin (mixed hardwoods)	0.21	0.20	0.77	0.48	1.7
HCl lignin (southern yellow pine)	0.27	0.61	0.18	0.03	1.1
Klason lignin (oak)	0.08	0.03	0.18	0.02	0.3
Klason lignin (mixed hardwoods)	0.09	0.03	0.17	0.02	0.3
Klason lignin (southern yellow pine)	0.42	0.21	0.13	0.00	0.8
Wet-oxidized lignin (oak)	0.48	0.23	1.30	0.97	3.0
Wet-oxdidized lignin (mixed hardwoods)	0.24	0.34	0.85	0.75	2.2
Cellulase lignin (yellow poplar)	0.16	0.27	0.88	1.09	2.4
Steam-exploded lignin (mixed hardwoods)	0.21	0.31	0.88	0.48	1.9
Steam-exploded lignin process sludge	0.11	0.15	0.18	0.08	0.5
2% NaOH extracted process sludge	0.25	0.18	0.42	0.22	1.1
Kraft lignin	0.53	0.60	0.32	0.30	1.7
Sodium lignin sulfonate	0.16	0.04	0.03	0.04	0.3
Autohydrolyzed lignin (aspen)	0.16	0.19	0.45	0.14	0.9

[a] Demethylated products such as catechol may constitute a large amount of products formed. However, the authors were unable to find a column suitable for the analysis of underivatized catechols.

shown in Figure 5. The results indicate that there is a relationship between the lignin's condensation, as determined by nitrobenzene oxidation product yield, and the product yield from PGC (Figure 6). As discussed earlier, ether bonds will readily cleave under pyrolytic conditions. Thus, uncondensed lignins which have large proportions of ether linkages should result in a greater product yield during pyrolysis. An earlier study by Watanabe and Kitao[28] showed a mole ratio of syringol to guaiacol-related products from PGC to be related to the mole ratio of syringaldehyde to vanillin from nitrobenzene oxidation. We analyzed our results in the same manner using the ratio of syringol to guaiacol and ran a correlation of the data without the commercial lignins included. Our results showed no significant correlation. Obst[29] was not able to quantitatively analyze the syringyl/guaiacyl ratios of lignin using PGC.

The effect of inorganic constituents on the pyrolysis of lignin has been indicated by both TGA[2] and PGC methods.[30] Since the effect of inorganic salts on sulfuric acid lignin was already reported by Tang[2], it was decided to investigate the effect of NaCl, $ZnCl_2$, Na_2CO_3 and SiO_2 on HCl and Kraft lignin by both TGA and PGC.

Results for the thermal behavior of lignin during pyrolysis with and without the addition of inorganic salts are shown in Table 6. HCl lignin showed decreased residue at 550°C for NaCl, Na_2CO_3 and SiO_2, and an increased residue for $ZnCl_2$. Kraft lignin showed increased residue for all salts added. Zinc chloride had the largest effect, in terms of suppressing pyrolysis, for both HCl lignin and Kraft lignin, as indicated by the TGA results and the total pyroprobe products. Ash already present in the lignin would not appear to have a significant effect on either the TGA results or the PGC results, as shown by the correlation values for nitrobenzene oxidation data discussed previously.



NOTE: MULTIPLE PEAK AT 12 MIN. CONTAINS VANILLIN, ISOEUGENOL, AND METHYL SYRINGOL.

FIGURE 5. Chromatogram of wet-oxidized lignin (red oak) pyrolysis. Note: Multiple peak at 12 minutes contains vanillin, isoeugenol and methyl syringol.

All inorganic salts had a marked effect on the PGC product yield. This result should be interpreted with care since we were only looking at four specific pyrolysis products. The apparent effect of inorganic salts on the PGC product yield could be due to different mechanisms of thermal decomposition resulting in formation of different products. However, future studies may determine the effect of inorganic salts on the mechanism of lignin pyrolysis.

The data resulting from the isothermal TGA runs were evaluated in a fashion similar to two postulated reaction schemes.[1,2] The first scheme or model assumes that lignin follows a psuedo first-order reaction during pyrolysis;[2] the second model assumes that lignin follows a two-step degradation, a zero-order reaction followed by a first-order reaction.[1] The data for both

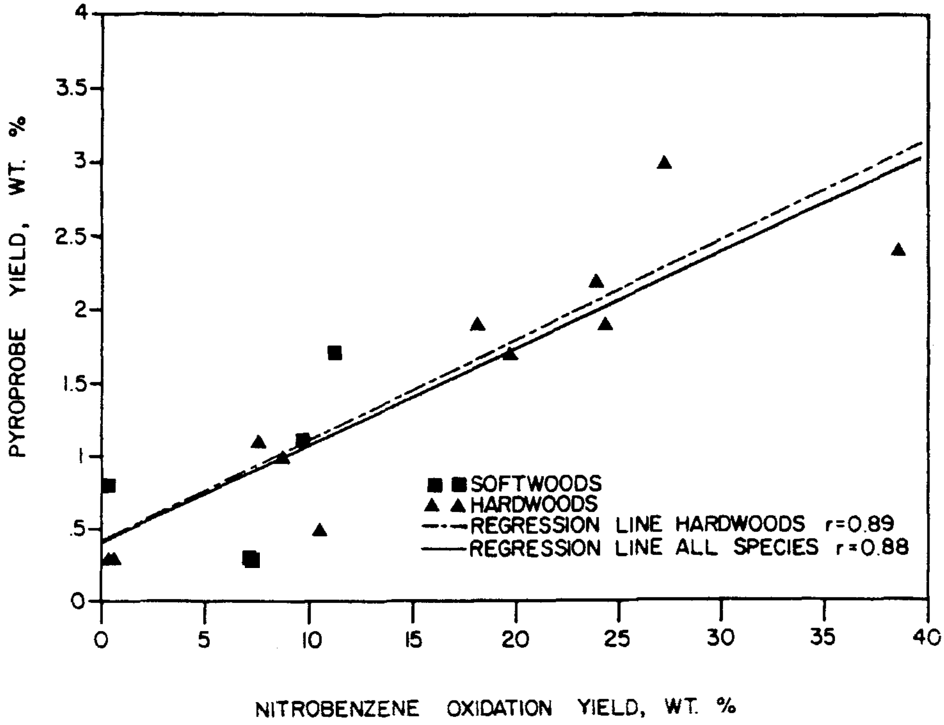


FIGURE 6. Relationship between pyrolysis-gas chromatography product yield and nitrobenzene oxidation product yield.

models were subjected to regression analysis. The correlation values are shown in Table 7.

As shown in Table 7, none of the lignins examined apparently followed pseudo first-order reaction kinetics during pyrolysis, as determined by measuring the correlation values which ranged from 0.6 to 0.91. Alpha cellulose, which is known to follow a first-order decomposition reaction,[31] had a correlation value of 0.99. The second model suggested by Beall[1] gave a better fit for the isothermal pyrolysis data of lignin.

Although isothermal techniques have been used before for studying wood component reaction kinetics, the data were

TABLE 6

The Effect of Inorganic Salts on the Thermal Behavior of HCl (oak) and Kraft Lignin

Lignin type	Salt	Temp. at maximum rate of wt. loss (°C)	Decomp. temp. at 10% --wt. loss-- (°C)	Decomp. temp. at 50% --wt. loss-- (°C)	Non-volatile residue at 550°C (wt. %)	Total selected PGC products (wt. %)
HCl lignin	(control)	335	295	445	39.2	1.9
HCl lignin	$ZnCl_2$	380	275	515	40.7	1.0
HCl lignin	NaCl	330	305	425	38.5	1.6
HCl lignin	SiO_2	340	300	460	38.1	1.6
HCl lignin	Na_2CO_3	330	305	470	37.1	1.9
Kraft lignin	(control)	380	285	545	49.7	1.7
Kraft lignin	$ZnCl_2$	400	305	---	53.8	1.3
Kraft lignin	NaCl	375	285	---	53.0	1.4
Kraft lignin	SiO_2	390	295	---	51.0	1.5
Kraft lignin	Na_2CO_3	390	310	---	51.0	1.5

TABLE 7

Correlation Coefficients from Both First-order and Zero-first Order Regression Analysis of Isothermal TGA Analyses for Selected Lignins and Alpha Cellulose

Lignin and cellulose type (species source)	Regression analysis Model I Psuedo first-order	 Model II Zero-order	 First-order
	--------------(correlation	values)--------	----
HCl lignin (mixed hardwoods)	0.88	0.97	0.98
HCl lignin (southern yellow pine)	0.91	0.99	0.98
Klason lignin (mixed hardwoods)	0.60	0.90	0.98
Wet-oxidized lignin (oak)	0.74	0.95	0.97
Cellulase lignin (yellow poplar)	0.86	0.96	0.98
Steam-exploded lignin (mixed hardwoods)	0.89	0.96	0.98
Steam-exploded process sludge	0.81	0.95	0.98
Kraft lignin	0.82	0.94	0.97
Sodium lignin sulfonate	0.86	0.96	0.99
Alpha cellulose	0.99	----	----

considered unsatisfactory because of excessive weight loss (35%) in the preheat period.[3] In our experiment, the preheat weight loss was 5% to 12%.

The results indicate that lignin does not necessarily follow a pseudo first-order reaction. However, the results are not conclusive enough to say that lignin follows a zero-order reaction followed by first-order reaction. It was reported by Stamm[32] that the thermal degradation of wood is a complex and variable process that involves many different reactions that take place simultaneously at different rates. The results indicate that this also holds true for lignin thermal decomposition.

Many TGA studies involving the pyrolysis of lignin have attempted to determine the activation energies of lignin thermal decomposition based upon empirical relationships using DTG data.[1,2,6] In these studies, as mentioned earlier, the order of the lignin pyrolysis reactions was assumed to be zero or one, and the kinetic parameters for the reactions were determined according to these assumptions. Most theoretical studies involving the use of TGA have been shown to be inadequate to use for determining reaction orders and activation energies of complex reactions.[33,34] Although assumptions concerning reaction order may hold true for the decomposition reactions of relatively simple compounds,[35] these results suggest that the use of TGA data for calculating activation energies of lignin should be used with caution.

CONCLUSIONS

The pyrolytic behavior of lignin is dependent on the amount of its condensation. Thermogravimetric analysis is an accurate method for determining the amount of condensation in lignin. The yield of monomeric phenols from lignin during pyrolysis also depends on its amount of condensation. Structural changes appear to occur in lignin during initial pyrolysis before there is any appreciable weight loss.

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