

Examination of the Thermal Decomposition of Kraft Pine Lignin by Fourier Transform Infrared Evolved Gas Analysis

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The thermal decomposition of Kraft pine lignin has been examined by Fourier transform infrared evolved gas analysis (FT-IR-EGA), a technique designed for on-the-fly, simultaneous monitoring of multiple vapor phase species. Initial degradation occurs between ≈ 120 and ≈ 300 °C from bond fragmentation in the phenyl propane side chains evidenced by the formation of formic acid, formaldehyde, carbon dioxide, water, and sulfur dioxide. The presence of sulfur dioxide is supporting evidence that sulfur from the Kraft pulping process may be incorporated into the lignin structure in the form of sulfoxide and/or sulfone linkages. Major decomposition initiates at ≈ 300 °C and extends to 480 °C at which point 50% of the initial weight has been lost. Methanol, 2-methoxyphenol (guaiacol), and a 2-methoxy-4-alkyl-substituted phenol are the most apparent species evolving in this region and indicate fragmentation of the major chain linkages between the monomeric phenol units in the lignin structure.

A large volume of information has been published on the characterization of condensed phase products isolated from the chemical and thermal degradation of wood lignins. Many contributions have been made in areas ranging from the possible structures of lignins to pathways for their formation in nature. These works and resultant concepts have been well detailed in various reviews (Pearl, 1964; Marton, 1971; Adler, 1977). The vapor-phase products which evolve during the thermal degradation of lignins have not been examined exhaustively. This may be a result of the low concentrations observed in the vapor phase for those compounds such as phenolics which are useful in characterizing lignin degradation and which may provide structural information.

Work that has been reported in the area of lignin pyrolysis has focused primarily upon maximizing the yields of single ring phenolics which could have economic import. The successful commercializations of processes for the conversion of lignins to sulfur compounds and vanillin has provided an impetus for continued research in this area. Goheen et al. (1976) investigated the indirect pyrolysis of Kraft black liquors and reported guaiacol (2-methoxyphenol) as a major volatile component. More recently, researchers utilized a captive sample reactor to pyrolytically degrade a precipitated Kraft lignin (Iatridis and Gavalas, 1979). Their results indicated that a temperature of 200 °C was sufficient to transfer single ring phenolics into the vapor phase. Many reports along similar lines have also appeared in the literature of the USSR (Domburgs and Sergeeva, 1970; Domburgs et al., 1970, 1971, 1973, 1974).

It was the purpose of this investigation to examine the volatile phase evolving during the pyrolytic degradation of Kraft pine lignin. Fourier transform infrared evolved gas analysis (FT-IR-EGA), a technique capable of monitoring on-the-fly and, simultaneously, multiple gases was used to identify the products formed and to generate profiles of their evolution as a function of temperature (Liebman et al., 1976; Lephardt and Fenner, 1980). In addition to identification of the products formed, this technique also affords the ability to determine the number of thermal events leading to a single product.

EXPERIMENTAL SECTION

Apparatus. A detailed description of the FT-IR-EGA system hardware and data processing routines has been presented in a prior publication (Lephardt and Fenner,

1980). An abridged description will follow to provide continuity within the framework of this discussion. The system is comprised of a Digilab FTS-14 Fourier transform infrared spectrophotometer (fitted with a Digilab GC/IR accessory) connected with a computer-controlled pyrolysis furnace (20 by 1.5 in i.d. gold film oven, Trans Temp. Co., Chelsea, MA) by a heated transfer line (Figure 1). The oven temperature is controlled by a Xerox Sigma 9 computer routine which is addressable from a laboratory terminal. Isothermal running, temperature ramping, or a combination of these formats may be specified through program options. Provision also exists for the use of a single carrier gas or blended mixture of carrier gases to sweep the effluent gases from the sample into the spectrophotometer.

Procedure. The Kraft pine lignin was obtained from Westvaco Corp., Charleston, SC, and was examined in powdered form by using a 1-g sample for analysis. Evolved gas analysis was carried out at a heating rate of ≈ 6 °C/min from ambient to 850 °C with a nitrogen carrier gas flow rate of 60 mL/min. A total of 320 infrared spectra at 4-cm⁻¹ resolution were collected over the specified temperature range. Evolution profiles for specific gases as a function of temperature were generated as described previously (Lephardt and Fenner, 1980).

RESULTS AND DISCUSSION

Several structural schemes have been proposed for Kraft softwood lignins (Ball, 1965; Marton, 1971). One of these statistical schemes is shown in Figure 2. It should be noted that this structure is not exact but represents the type and number of functionalities determined to be present by certain analyses. Figures 3 and 4 show a TGA/DTGA curve for the Kraft pine lignin and a graphic representation of the evolved gases detected over the same temperature range by the FT-IR-EGA technique. The DTGA curve can be segmented into two weight loss regions: ≈ 120 to ≈ 300 °C and ≈ 300 to ≈ 480 °C. Subsequent discussion will focus upon each of these regions and the relationship between the vapor phase products and the statistical structure for the Kraft pine lignin.

Initial Decomposition: 120-300 °C. The first thermal decomposition (after surface and bound water loss at ≤ 100 °C) occurs between ≈ 120 and ≈ 300 °C and is evidenced by a small plateau in the DTGA profile. Formic acid, formaldehyde, sulfur dioxide, carbon dioxide, and water evolve from decomposition in this temperature region (Figure 4). These low-temperature products can be accounted for primarily by single bond fragmentation in the

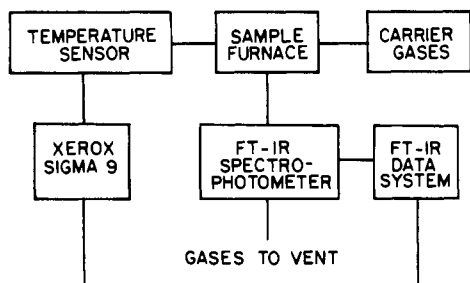


Figure 1. Schematic diagram of the FT-IR-EGA system.

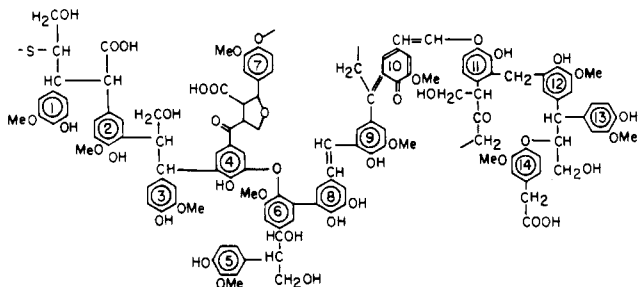


Figure 2. Statistical model of Kraft pine lignin [reprinted with permission from Marton (1971); copyright 1971 Wiley-Interscience].

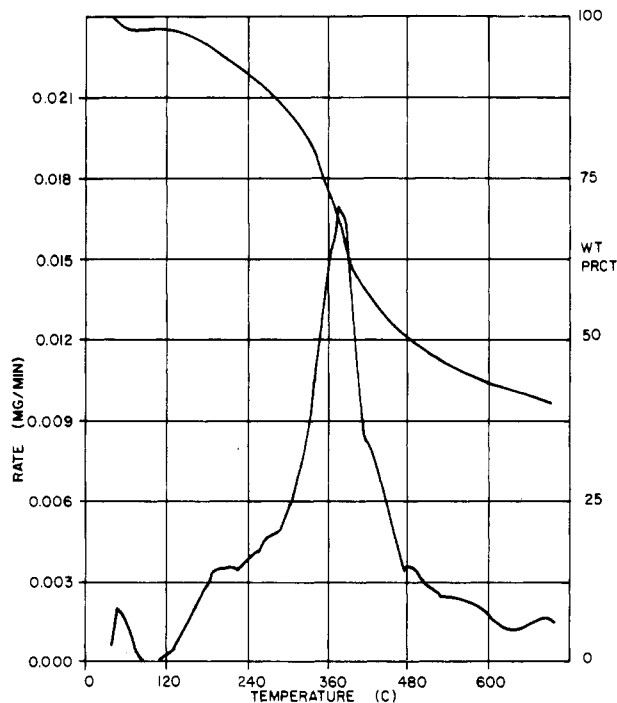


Figure 3. TG and DTG curve for Kraft pine lignin. Heating rate 5 °C/min; nitrogen atmosphere.

phenyl propane side chains.

The formation of formaldehyde (Figure 5) may be accounted for by fragmentation of the terminal hydroxymethylene groups ($-\text{CH}_2\text{OH}$) present in the phenyl propane side chains. Formaldehyde was identified as a decomposition product by spectral subtraction, a capability available with the FT-IR-EGA technique. Shown in Figure 6 is a portion of one sample spectrum before and after subtraction of water vapor interferences. A carbonyl stretching band arising from formaldehyde becomes readily apparent after the removal of these interfering bands.

The Kraft pulping process uses a $\text{NaOH}-\text{Na}_2\text{S}$ mixture (white liquor) to dissolve lignin from wood carbohydrates. A significant feature of this process appears to be the incorporation of sulfur into the lignin structure during

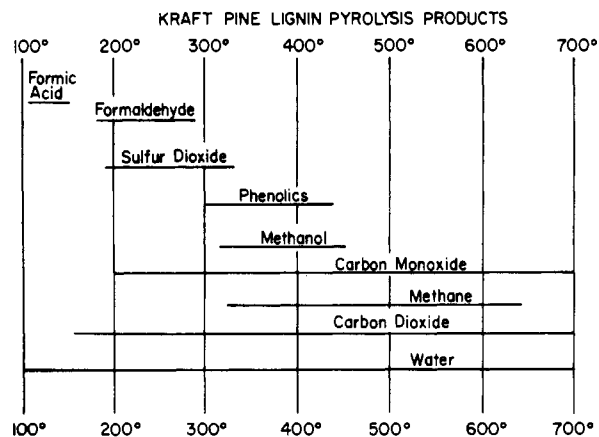


Figure 4. Gaseous evolution products from the pyrolysis of Kraft pine lignin in a nitrogen atmosphere.

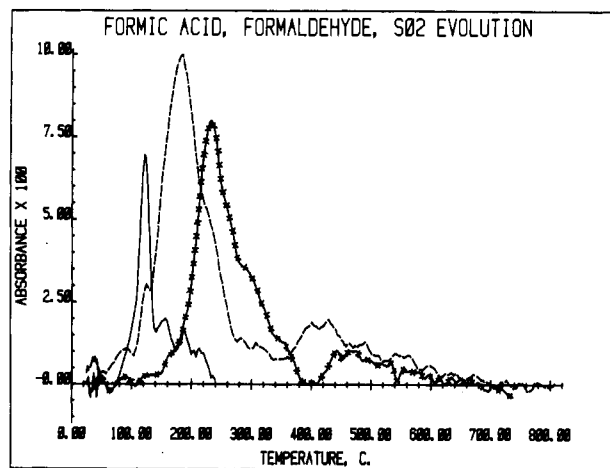


Figure 5. Evolution profiles of formic acid [(—) 3× expansion], formaldehyde [(---) 2× expansion], and sulfur dioxide (×) vs. temperature for Kraft pine lignin. Heating rate ≈ 6 °C/min; carrier N_2 , 60 mL/min. Data treated by the application of a Savitsky and Golay (1964) smoothing filter.

dissolution. Functionally, this sulfur incorporation is seen to facilitate fragmentation of the polymeric lignin while reducing undesirable condensation reactions. Sulfur is generally shown bonded at the β position in the phenyl propane side chains (Figure 2); however, the form of sulfur present in "isolated" Kraft lignins appears to vary. Evidence for sulfoxide and sulfone linkages has been reported for Kraft pine lignin (Marton, 1971). However, in more recent studies of Kraft Douglas fir lignin, products such as H_2S and mercaptans indicative of thiol and polysulfide functionalities were isolated (Iatradis and Gavalas, 1979). The presence of sulfur dioxide as a pyrolytic vapor-phase product in this study (Figure 5) lends credence to the sulfoxide- and/or sulfone-type linkage.

One apparent anomaly in the low temperature decomposition region is the evolution of formic acid (Figure 5). The small absorbance (low concentration), low temperature, and narrow temperature range observed are suggestive of free formic acid. Although terminal aliphatic carboxyl groups are known to exist in isolated Kraft lignins (Figure 2), these groups would be expected to decompose via decarboxylation, forming carbon dioxide. Sample spoilage or other contamination could account for the presence of the free acid, but the data are insufficient to permit anything other than speculation.

The evolution profile for water (Figure 7) shows a major convoluted band in the region where formaldehyde and sulfur dioxide are observed. Carbon dioxide evolution

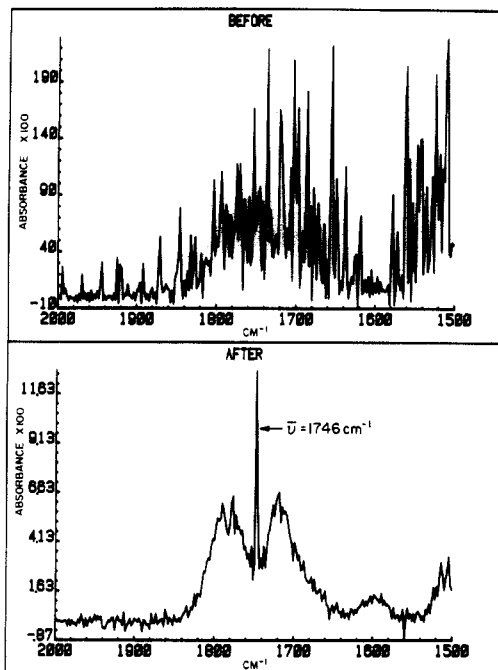


Figure 6. Infrared absorbance spectrum between 2000 and 1500 cm^{-1} of the formaldehyde carbonyl stretching band before and after subtraction of water interferences.

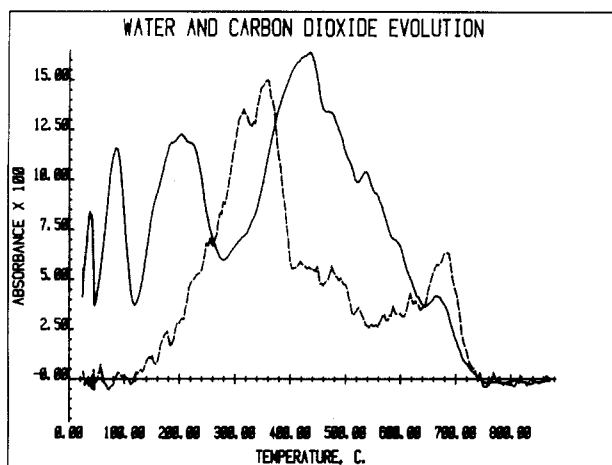


Figure 7. Evolution profiles of water (—) and carbon dioxide [---] 4 \times expansion vs. temperature for Kraft pine lignin. Heating rate ≈ 6 $^{\circ}\text{C}/\text{min}$; carrier N_2 , 60 mL/min. Data treated by the application of a Savitsky and Golay (1964) smoothing filter.

(Figure 7), possibly from decarboxylation and secondary degradation of initial products, is just beginning in this low-temperature region.

Major Decomposition: 300–480 $^{\circ}\text{C}$. The major weight loss region for the Kraft pine lignin occurs between 300 and 480 $^{\circ}\text{C}$, maximizing at ≈ 385 $^{\circ}\text{C}$. Methanol, carbon dioxide, carbon monoxide, water, methane, and two phenolic species tentatively identified as guaiacol and a 2-methoxy-4-alkyl-substituted phenol evolve in this region. Two carbonyl compounds, possibly acetone and acetic acid, also appear to be present. Pyrolytic degradation in this region can be characterized as fragmentation of major chain linkages releasing monomeric phenol units into the vapor phase, followed by secondary degradation at the higher temperatures.

The symmetrical shape and single maximum of the methanol evolution profile (Figure 8) suggest that a single mechanism or precursor is likely involved. The phenolic units in the lignin structure contain methoxyl substituents which are the most probable contributors to the formation

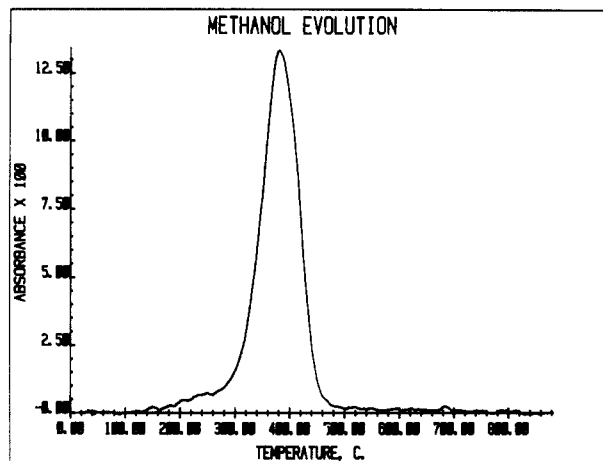


Figure 8. Evolution profile of methanol vs. temperature for Kraft pine lignin. Heating rate ≈ 6 $^{\circ}\text{C}/\text{min}$; carrier N_2 , 60 mL/min. Data treated by the application of a Savitsky and Golay (1964) smoothing filter.

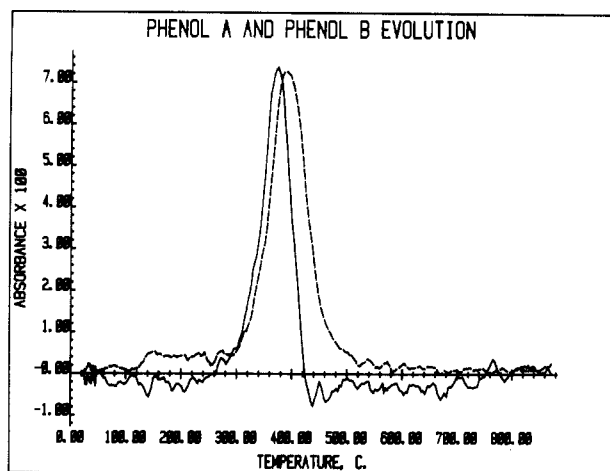


Figure 9. Evolution profiles of phenol A [(—) 2 \times expansion] and phenol B [---] vs. temperature for Kraft pine lignin. Heating rate ≈ 6 $^{\circ}\text{C}/\text{min}$; carrier N_2 , 60 mL/min. Data treated by the application of a Savitsky and Golay (1964) smoothing filter.

of methanol. As such, pyrolysis may be usable as a means of estimating the methoxyl content of lignins.

The evolution profiles for the phenolic compounds (Figure 9) contain two significant features: narrow thermal bandwidths of evolution and noncoincidence of the evolution maxima. Based upon the separation of the two maxima, spectral subtraction has been used to isolate the infrared spectrum of each compound independent of the other (Figure 10). Tentative identification of the fingerprint regions is based upon comparison with reference spectra of known compounds. The spectrum of phenol A is characteristic of 2-methoxy-4-alkyl-substituted phenols with a methyl or ethyl group as the most probable alkyl substituent. Phenol B gives a very close match with a reference spectrum of guaiacol (2-methoxyphenol). These data suggest that the yield of vapor-phase phenolics can be maximized by use of pyrolysis temperatures of 300 $^{\circ}\text{C}$ or slightly higher. This should result in maximum yields while minimizing time requirements and secondary degradation processes which become significant as one approaches 400 $^{\circ}\text{C}$.

Two carbonyl compounds are also present in minor quantities in the 300–480 $^{\circ}\text{C}$ temperature region. On the basis of only the carbonyl frequencies ($\nu_{\text{C=O}} \approx 1735$ and 1800 cm^{-1}), acetone and acetic acid are possibilities; however, coincident absorptions due to more concentrated

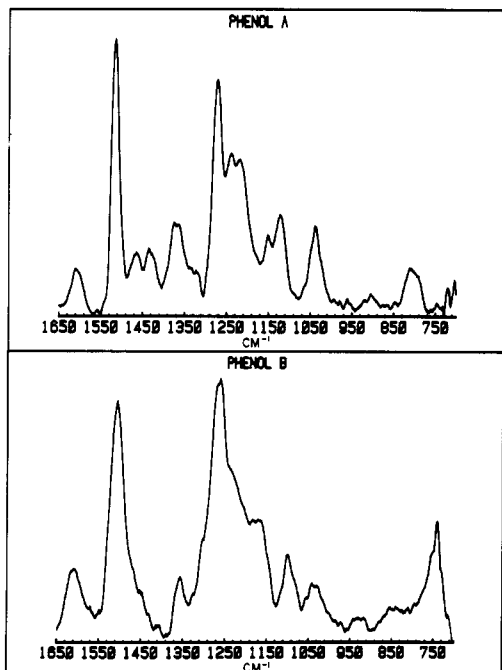


Figure 10. Infrared absorbance spectra between 1650 and 700 cm^{-1} for phenol A and phenol B. Data treated by an application of a Savitsky and Golay (1964) smoothing filter.

species prevent verification of other bands characteristic of these compounds.

The evolution of water and carbon dioxide (Figure 7) and methane and carbon monoxide (Figure 11) suggests that major fragmentation occurs in this temperature region. Although secondary degradation probably causes the evolution of these gases beyond 480 $^{\circ}\text{C}$, the major decomposition processes accounting for a weight loss of $\sim 50\%$ are essentially complete.

CONCLUSION

The results of this investigation indicate that the pyrolytic decomposition of Kraft pine lignin is describable as a two-stage process. Initial decomposition occurs between ≈ 120 and 300°C as a result of fragmentation in the phenyl propane side chains, particularly at the terminal positions, yielding formic acid, formaldehyde, water, carbon dioxide, and sulfur dioxide. The detection of sulfur dioxide supports evidence that sulfur from the Kraft pulping process may be incorporated into the lignin structure in the form of a sulfoxide and/or a sulfone. No evidence could be found indicative of the thiol or polysulfide type of linkage. Major decomposition initiates at $\approx 300^{\circ}\text{C}$ and extends to 480°C at which point 50% of the initial weight has been lost. Degradation in this region can be characterized by cleavage and fragmentation of principal linkages releasing monomeric phenols into the vapor phase, followed by the onset of secondary degradation at the higher temperatures. The vapor-phase products observed include methanol, water, carbon monoxide, carbon dioxide, methane, and two phenols tentatively identified as guaiacol and a 2-methoxyl-4-alkyl-substituted phenol. Minor amounts of two carbonyl compounds, possibly acetone and acetic acid, are also present.

From an applications viewpoint, two observations obtained may be potentially useful. First, the indication of

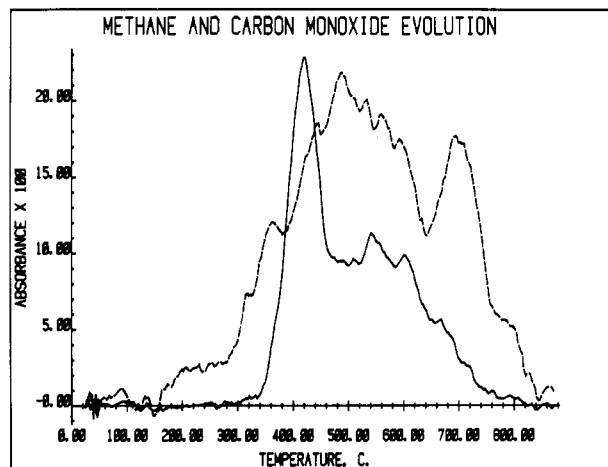


Figure 11. Evolution profiles of methane (—) and carbon monoxide [---] $4\times$ expansion vs. temperature for Kraft pine lignin. Heating rate $\approx 6^{\circ}\text{C}/\text{min}$; carrier N_2 , 60 mL/min. Data treated by an application of a Savitsky and Golay (1964) smoothing filter.

a single precursor for methanol suggests that pyrolysis may be usable as a means of estimating the methoxyl content of the Kraft lignins. Second, the FT-IR evolved gas analysis technique could be a useful tool for selecting operating criteria for the thermal conversion of lignins to specific chemical products, since it reflects the relative energies for releasing of the various products under certain conditions.

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