

ANALYSIS OF PARTIALLY CONVERTED LIGNOCELLULOSIC MATERIALS

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ABSTRACT

The systematic analysis of the solid residues of the supercritical methanol extraction of Populus tremuloides was performed for samples prepared at temperatures varying from 250 to 350°C and pressures from 3.4 to 17.2 MPa, using such analytical techniques as wet chemistry, chromatography, thermogravimetric analysis, diffuse reflectance FTIR spectroscopy and photoelectron spectroscopy. The results allow to monitor the continuous changes in chemical composition of the samples from partly extracted wood samples to highly recondensed polyaromatic structures.

INTRODUCTION

In the recent studies of thermal and thermochemical processes of wood liquefaction, considerable progress has been reported in the analysis of gaseous and liquid products⁽¹⁾. Some attention has been given to the composition of the solid products by wet chemistry analysis^(2,3).

For the last twenty years much work has been done in the study of the thermal stability of lignocellulosic materials by thermal analytical methods. Since these materials are complex mixtures of organic polymers, thermogravimetric (TG) analysis causes a variety of chemical and physical changes depending on the nature of the sample and its treatment prior to analysis. These problems have been reviewed recently⁽⁴⁾.

Lignocellulosic material can also be analyzed by IR spectrometry. This analytical method was used, for characterization of modified lignin and cellulose in various ways⁽⁵⁻¹³⁾. Quantification by infrared spectrometry, has been reported, for example in analysis of the three basic constituents in sweetgum and white oak chips pretreated at temperatures ranging from 140 to 280°C⁽⁵⁾ using the diffuse reflectance FTIR spectrometry (DRIFT). The technique is simple and applicable to powdered solids and dark samples⁽¹⁴⁾ and can be used for the characterization of the chemical bonds and their modifications by thermal processes.

In this paper we report our efforts to characterize the solid residues produced in a series of experiments for the semicontinuous extraction of Populus tremuloides in supercritical methanol⁽¹⁵⁾, at temperatures ranging from 250 to 350°C (Supercritical Extraction residues or SCE residues), by using wet chemistry and chromatographic⁽¹⁶⁾, thermogravimetric and spectral methods such as DRIFT⁽¹⁷⁾ and ESCA⁽¹⁸⁾.

EXPERIMENTAL PROCEDURE

The solid residues analyzed here were produced by supercritical extraction with methanol of Populus tremuloides in a tubular reactor⁽¹⁵⁾. The analytical procedures used for these residues were described previously as elemental analysis, Klason lignin test, thioglycolic acid lignin test, recondensed material and carbohydrates⁽¹⁶⁾, thermogravimetric (TG/DTG) and FTIR⁽¹⁷⁾ and ESCA⁽¹⁸⁾. Table 1 reports results obtained using these procedures as well as conditions of extraction for each SCE residues.

RESULTS AND DISCUSSION

Wet Chemistry and Chromatography

For the analysis of wood, the Klason lignin test, performed in concentrated sulfuric acid, is the accepted method for the determination of lignin content. We performed similar tests using also trifluoroacetic acid (TFA), the results of which are almost identical to those of the Klason tests. TFA has the advantage to allow further analysis of the saccharides in the acid soluble fraction as it can easily be evaporated from the solution.

The acid insoluble fraction, usually designated as "Klason lignin", is referred to in this work as Klason residue. Figure 1 shows that in the most severe extraction conditions the whole SCE residue is almost entirely constituted of Klason residue. The fact that this Klason residue cannot be considered as lignin has been established through elemental analysis and IR spectroscopy in KBr pellets⁽¹⁶⁾.

In order to determine if the solid residues still contain lignin the old method of forming a soluble lignin derivative with thioglycolic acid was used. This reagent reacts by displacement of α -hydroxyl and α -alkoxy groups in lignin and the derivative so produced can be solubilized by alkali and recovered. Results are reported in Table 1 and Figure 1 showing that thioglycolic acid lignin (TGAL) decreases from 15.6% in wood to 3.3-5.9% in the samples prepared at 350°C. It was shown by IR spectrometry that the TGAL keeps the characteristic features of lignin even for SCE temperatures of 350°C⁽¹⁶⁾.

This confirms our belief that the thioglycolic acid test is a suitable method for the determination of uncondensed lignin in SCE residues. In spite of the fact that 1) the Klason test induces some condensation reactions, 2) the thioglycolic acid test may only extract those lignin fragments containing benzyl alcohol groups or aryl ether groups⁽¹⁹⁾, we would like to suggest that 1) the thioglycolic acid lignin represents a good estimate of unconverted lignin, 2) the Klason residue represents the summation of unconverted lignin and of condensation products formed by pyrolysis reactions during the SCE process.

As a consequence we suggest that the difference between the Klason residue and the thioglycolic acid lignin is representative of recondensed material (RM) in SCE residues. The calculated values for recondensed material in these residues are reported in Table 1. Figure 2 gives the values for the percent recondensed material expressed on a dry wood basis.

Figure 3 shows the percentage of recondensed material, expressed on dry wood basis, plotted as a function of lignin conversion. This graph suggests different condensation reactions at 250°C and at 300-350°C. At 250°C in particular, the condensation seems to be a secondary reaction of lignin conversion. As also shown on the figure, for several experiments the percents of recondensed material are higher than the value which would be calculated assuming that all converted lignin is transformed to recondensed material (line A). It is believed that this indicates that the condensation reaction involves not only products of degradation of lignin but also some of carbohydrates.

The glucose and xylose contents were determined in the soluble TFA acid hydrolysis fraction by liquid chromatography using a cation exchange resin (Ca⁺⁺ form) column. The results are reported in Table 1. Most of the samples prepared at 300-350°C show only minor amounts of hydrolyzed material except for samples MP-16, MP-13 and MP-14 prepared at low pressure or low flow rate. The percents of glucose and xylose for these samples as well as those for the samples prepared at 250°C, expressed on dry wood basis, are plotted on Figure 4. The rather well defined curve indicates that cellulose and hemicellulose are simultaneously degraded at or below 250°C.

Thermogravimetric Analysis

Thermogravimetric analysis (TG and DTG) under nitrogen atmosphere was performed for aspen wood and the 16 partially converted wood residues. The TG and DTG curves are reproduced in Figure 5 for untreated wood and for 4 selected representative SCE residues.

The examination of TG and DTG curves, shows that:

- a) aspen wood loses weight starting near 230°C (pyrolysis of hemicellulose ⁽²¹⁾), and between 350 and 420°C with a maximum rate of weight loss at 385°C (cellulose and lignin pyrolysis ⁽²¹⁾); the weight lost at 700°C is 89.4%.
- b) the SCE residues can be classified according to their temperature of extraction.

For the residues of type I prepared at 250°C (like sample MP-6), the weight loss takes place between 350 and 420°C, with a maximum rate at 375-390°C. The weight lost at 700°C is between 82.5 and 94.6%.

For the type II residues produced at 300°C (like sample MP-12), a continuous weight loss is observed from 300 to 600-700°C, with a maximum rate at temperatures ranging from 380°C to 510°C. The total weight loss at 700°C is less important than for samples of the previous type, ranging from 27.2 to 57%.

For samples of type III prepared at 350°C (like samples MP-11 and MP-8), the weight loss is slower than for those of type II but happens roughly on the same temperature range (300 to 600-700°C) and with maximum rates occurring at higher temperatures, from 380 to 620°C. The weight loss at 700°C is significantly smaller ranging from 8.2 to 34.2%.

A closer analysis of these curves shows that there is a continuous change in the shape of the thermogram of the residues as the SCE pressure is increased for experiments at the same SCE temperature. As shown in Figure 6 the temperature T_{max} corresponding to a maximum on the DTG curve shows a continuous evolution with the parameters of extraction. Two maxima are observed at the lower SCE pressure of 3.4 MPa showing that when the extraction is performed less efficiently, some of the unconverted lignin and cellulose is still present at relatively high content in the residue prepared at 350°C.

The smooth evolution in the temperature of the high temperature DTG peak reflects a change in the nature of the volatile fraction of the recondensed material.

A very good correlation was found between weight lost between 200 and 420°C and the weight of trifluoroacetic acid soluble plus unconverted lignin previously determined by wet chemistry (correlation coefficient is 0.994 if one excepts sample MP-16). These data suggest that the material still not volatilized at 420°C would be identical with what we defined as the recondensed material. It was indeed verified that the correlation between recondensed material and weight % of the solid not volatilized at 420°C is also excellent (correlation coefficient 0.984 when point MP-16 is excepted). From thermogravimetric data the recondensed material in a given SCE residue can thus be further characterized by the weight fraction of RM volatilized between 420 and 700°C.

Diffuse Reflectance Infrared Spectrometry

DRIFT spectra were obtained for the 17 afore mentioned samples and the spectra of the five representative samples used to present the TG/DTG data, are reported in Figure 7.

The spectrum of aspen wood (Figure 7.A) shows the presence of the three fundamental wood constituents. The bands for cellulose are at 898 cm^{-1} β -anomer in pyranose ring ⁽²²⁾, at 1043-1171 cm^{-1} (C-O bonds in primary and secondary alcohols). The

band at 1745 cm^{-1} is due to uronic acid and acetyl groups in hemicellulose⁽²²⁾. The bands from 1246 to 1607 cm^{-1} , specially the one at 1505 - 1515 cm^{-1} , are typical for lignin⁽¹⁹⁾.

As shown by the other spectra in Figure 7, these bands are significantly modified by the SCE treatment.

Spectral region 2850-3050 cm^{-1} . A band at 3050 cm^{-1} (aromatic and/or alkene C-H stretching) becomes evident at 300°C (MP-12, Figure 7-C) and dominates this region at 350°C (MP-8, Figure 7-E). The band in the 2900 cm^{-1} region (aliphatic C-H stretching) which is broad in the initial wood sample, is progressively resolved in three separate bands (2850 , 2900 and 2950 cm^{-1}) as the SCE temperature is increased (MP-12, MP-11 and MP-8, Figures 7C, D and E). The overall pattern in Figure 7E corresponding to the most carbonized sample is similar to the ones reported for higher rank bituminous coal⁽²³⁾ and for vitrinite⁽²⁴⁾, with the 3050 cm^{-1} even more intense in our MP-8 sample. As it was shown earlier that this sample contains 89.2% of recondensed material it may be concluded that this material has a coal-like polyaromatic nature. This is supported by the changes in the next spectral region.

Spectral Region 800-950 cm^{-1} . The band at 898 cm^{-1} is discernible in wood and MP-6 (SCE temperature 250°C) but disappears from spectra of samples treated at higher temperatures where saccharides analysis has also shown the absence of cellulose. As carbonization proceeds, the out-of-plane bending of one isolated (868 - 874 cm^{-1}) and two adjacent (815 - 816 cm^{-1}) aromatic H increase.

The band at 950 cm^{-1} , which is visible in MP-8, is probably due to elimination reaction giving t-alkenes⁽¹⁹⁾.

Spectral Region 1440-1600 cm^{-1} . The characteristic aromatic ring vibration at 1505 - 1515 cm^{-1} , clearly visible in the spectrum of wood, is gradually hidden with an increase in the SCE temperature. This corresponds to the progressive decrease in lignin content of the residue. Inversely, two bands at 1443 - 1461 and 1600 cm^{-1} become very intense and dominate in the spectra of residues produced at 300 and 350°C (Figures 7-C, D and E). These changes parallel the modifications in the 2850 - 3050 cm^{-1} region. The band at 1443 - 1461 cm^{-1} can be attributed to methyl and methylene bonding and also to aromatic ring modes^(24,19). The band at 1600 cm^{-1} is also assigned to aromatic ring stretching. Its high intensity in spectra 7-C, D and E, could possibly be given the three following explanations⁽²⁴⁾:

1) aromatic ring stretching in combination with a chelated conjugated carbonyl structure, 2) aromatic ring stretching mode, with possible intensity enhancement due to phenolic groups, 3) aromatic ring stretching of aromatic entities linked by methylene and possibly ether linkages.

Spectral Regions 1035-1378 and 1700-1745 cm^{-1} . The bands from 1035 to 1171 cm^{-1} (primary and secondary alcohols), present in wood and samples obtained at 250°C , drop in the spectra of SCE residues produced at and above 300°C . The aromatic ethers bands (up to 1378 cm^{-1}) which include phenolic stretching near 1250 cm^{-1} , decrease also.

The hemicellulose band, at 1745 cm^{-1} , present on untreated wood almost disappears in residues prepared at 250°C . The unconjugated carbonyl and/or carboxyl and/or ester of conjugated acids at 1720 - 1735 cm^{-1} from original lignin is still visible at 250°C when hemicellulose is partly removed but at higher SCE temperatures it is hidden by the highly intense 1700 cm^{-1} band. This last band can be attributed to a conjugated carbonyl or carboxyl structure but it would be surprising that carboxyl could resist at severe SCE conditions. Further study is necessary for definite assignment of this band.

Quantification. Schultz et al⁽⁵⁾ reported recently correlations of FTIR absorbance ratios with such variables as the percents in glucose, xylose and Klason lignin for

wood chips pretreated by the RASH process at temperature ranging from 140 to 280°C. These correlations do not fit correctly our data so that we developed our own equations by non-linear least squares regression. For quantitative evaluation of absorbances, baseline was defined as shown on spectrum 7E.

These equations are as follows.

$$\% \text{ Klason Lignin} = 174.6 - \left(101 \times \frac{A_{2950}}{A_{1376}}\right) + \left(150.4 \times \frac{A_{2950}}{A_{1376}}\right) - \left(196.7 \times \frac{A_{1220}}{A_{1376}}\right) + \left(223.4 \times \frac{A_{1700}}{A_{1376}}\right) - \left(190.1 \times \frac{A_{1245}}{A_{1376}}\right) \quad (1)$$

$$\% \text{ Unconverted Lignin} = -17.13 + \left(17.53 \times \frac{A_{2900}}{A_{1429}}\right) + \left(70.77 \times \frac{A_{1605}}{A_{1429}}\right) - \left(90.18 \times \frac{A_{1090}}{A_{1429}}\right) + \left(122.2 \times \frac{A_{1043}}{A_{1429}}\right) + \left(46.72 \times \frac{A_{895}}{A_{1429}}\right) \quad (2)$$

$$\% \text{ Reccondensed mat.} = 242.2 + \left(263.8 \times \frac{A_{1330}}{A_{1090}}\right) - \left(240.7 \times \frac{A_{1245}}{A_{1090}}\right) - \left(873.4 \times \frac{A_{1043}}{A_{1090}}\right) - \left(327.6 \times \frac{A_{895}}{A_{1090}}\right) - \left(45.62 \times \frac{A_{866}}{A_{1090}}\right) \quad (3)$$

$$\% \text{ Glucose} = -33.07 + \left(74.06 \times \frac{A_{1506}}{A_{1461}}\right) - \left(46.28 \times \frac{A_{1376}}{A_{1461}}\right) - \left(84.12 \times \frac{A_{1330}}{A_{1461}}\right) + \left(74.39 \times \frac{A_{1245}}{A_{1461}}\right) + \left(65.39 \times \frac{A_{1130}}{A_{1461}}\right) \quad (4)$$

$$\% \text{ Xylose} = -51.54 - \left(17.74 \times \frac{A_{1700}}{A_{1429}}\right) + \left(38.53 \times \frac{A_{1600}}{A_{1429}}\right) + \left(18.17 \times \frac{A_{1245}}{A_{1429}}\right) - \left(13.44 \times \frac{A_{1171}}{A_{1429}}\right) + \left(40.60 \times \frac{A_{1130}}{A_{1429}}\right) \quad (5)$$

Calculated results for the 16 samples of SCE residues showed standard deviations from experimental values of 5.12, 1.28, 4.96, 3.62 and 1.62% and correlation coefficients of 0.99, 0.97, 0.99, 0.98 and 0.98 for equations (1) to (5) respectively.

ESCA

ESCA is a surface sensitive technique, based on the measurement of kinetic energies of photoelectrons ejected from a given atomic energy level under the action of a monoenergetic X-ray beam. It provides quantitative information on the elemental composition as well as on the chemical environment of each atom (bonding and oxidation state).

The kinetic energy of photoelectrons (E_k), as measured with respect to the vacuum level, is expressed as:

$$E_k = E_x - (E_B + \phi + E_c) \quad (6)$$

where E_x is the energy of the incident photon, E_B is the binding energy of the electron on its original level, ϕ is the work function of the spectrometer and E_c is the energy lost in counteracting the potential associated with the steady charging of the surface. ϕ and E_c are essentially corrections. ϕ is depending on the spectrometer and not liable to be modified between experiments. E_c is high on low conductivity samples and can be made lower by the use of a flood gun.

ESCA spectra corresponding to carbon 1s peaks of *Populus tremuloides*, 3 samples isolated at three different SCE temperatures and 2 reference compounds are illustrated in Figure 8. There is a general agreement in the literature on the assignment of components C_1 , C_2 and C_3 in wood derived materials: C_1 corresponds to carbon linked to H or C, C_2 has one link to oxygen, whereas C_3 has two. In the solid phase, C_1 is referenced at 285.0 eV and C_2 and C_3 are usually close to 287.0 and 289.5 eV (25).

In all SCE residues, a fourth C_{1s} component is found on the low binding energy side of the spectrum, shifted from the C_1 component by 1.4 ± 0.5 eV. This is thereafter

designated as the C₀ component. As the temperature of extraction is increased from 250 to 300°C, the C₀ component increases continuously whereas the general trend of C₁, C₂ and C₃ components in a continuous decrease.

It is interesting to note that the uncorrected experimental C_{1s} binding energy for dibenz (a,h) anthracene is very close to the binding energy for this C₀ peak. As polyaromatic are electrical conductors, the charging is expected to be low and E_c close to 0. On this basis, C₀ component is assigned to carbon in polyaromatics. Usually, aromatic compounds show a shake up satellite located 5-7 eV above their C_{1s} peak (26). It can be seen however from Figure 8 that the intensity of this satellite in dibenz (a,h) anthracene is considerably lower than in o-biphenol. Thus the satellite from C₀ peak in SCE solid residues should only make a minor contribution to the overall C_{1s} band.

The ratio C_{RM}/C_{SR} (where C_{SR} is the carbon content of the whole solid residue as determined by elemental analysis, whereas C_{RM} is the calculated mass of carbon in the recondensed material contained in a given sample) was calculated for 5 samples (the elemental analysis for MP-13 was not available). Figure 9 shows not only that this ratio is correlated to the C₀ fraction of the C_{1s} peak, but that both values are almost equal for all samples.

Therefore it may be concluded that the ESCA technique provides a simple mean for the determination of the extent of recondensation reactions by a mere determination of the proportion of the C₀ component in the C_{1s} band of the solid residue.

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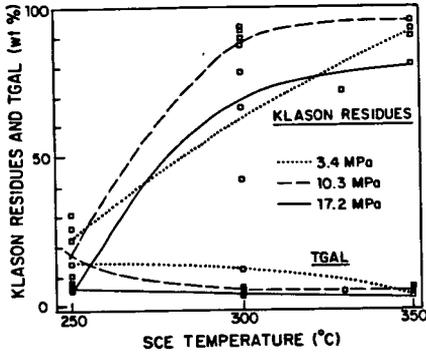


Figure 1. Klason residues and Thiolglycolic acid lignin in SCE solid residues.

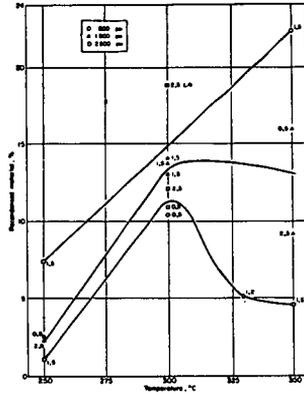


Figure 2. Effect of SCE conditions on recondensed material (expressed on dry wood basis).

Sample	SCE Temperature °C	SCE Pressure MPa	SCE Flowrate l/h	Residue yield wt%	Klason residue wt%	TGAL residue wt%	Recond. material wt%	Klason material soluble wt%	Glw wt%	Xyl wt%	% C	% H	% O
Wood	-	-	-	100.0	17.6	15.6	-	78.5	47.6	27.2	46.1	6.50	47.4
MP-22	250	3.4	1.5	74.8	26.1	14.3	11.8	70.8	45.7	18.0	50.0	5.84	44.2
MP-6	250	10.3	0.5	55.4	30.5	22.2	8.3	64.1	38.1	12.8	53.5	5.29	41.2
MP-17	250	10.3	2.5	69.7	10.6	6.5	4.1	89.9	38.0	19.2	45.0	6.49	48.6
MP-15	250	17.2	1.5	68.4	7.6	5.4	2.0	90.6	26.9	12.3	44.1	6.97	48.9
MP-16	300	3.4	0.5	40.5	42.2	12.1	30.1	46.4	25.9	7.9	64.9	5.82	29.2
MP-20	300	3.4	2.5	31.0	78.1	12.3	65.8	-	0.0	0.0	75.9	5.12	19.0
MP-9	300	10.3	1.5	16.4	92.1	4.3	87.8	5.0	0.0	0.0	78.2	4.96	16.8
MP-12	300	10.3	1.5	15.9	92.5	3.8	88.7	1.6	0.6	0.0	88.4	4.62	15.0
MP-21	300	10.3	1.5	15.7	89.2	4.5	84.7	2.4	0.0	0.0	79.8	5.35	14.8
MP-13	300	17.2	0.5	18.4	65.8	6.8	59.8	27.2	10.3	3.3	64.8	5.47	29.7
MP-18	300	17.2	2.5	15.8	86.7	5.3	81.3	4.0	0.7	0.0	73.3	5.17	21.6
MP-27	330	17.2	1.2	8.4	71.4	4.8	66.7	19.8	7.1	0.0	74.1	6.08	19.8
MP-14	350	3.4	1.5	26.9	98.0	5.2	85.1	11.1	4.8	1.5	74.8	4.34	20.8
MP-11	350	10.3	0.5	18.2	92.3	3.8	88.5	8.8	0.0	0.0	83.5	4.89	11.6
MP-8	350	10.3	2.5	10.2	95.1	5.9	89.2	1.2	0.0	0.0	92.8	3.84	3.33
MP-24	350	17.2	1.5	6.1	80.3	3.3	77.0	3.1	0.0	0.0	76.3	5.90	18.8

Table I. SCE residues, extraction conditions and analyses

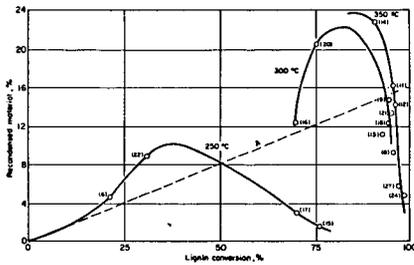


Figure 3. Recondensed material (expressed on dry wood basis) as a function of lignin conversion

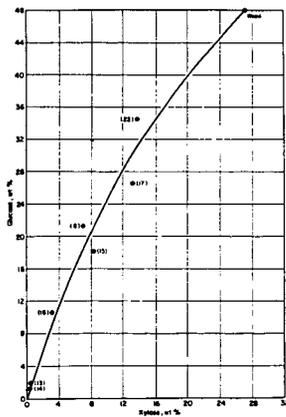


Figure 4. Residual hydrolyzed glucose as a function of residual hydrolyzed xylose (both expressed on dry wood basis).

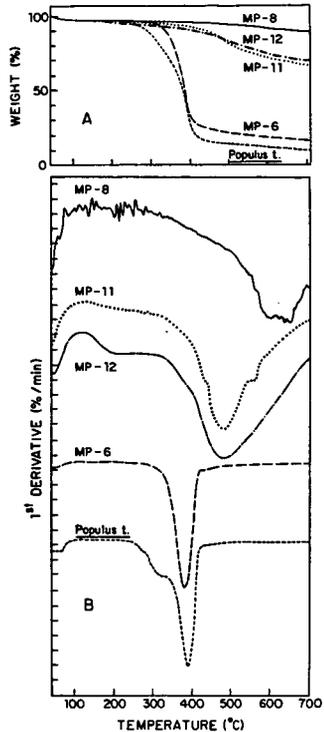


Figure 5. Thermogravimetric analysis of *Populus tremuloides* and of four SCE residues: TG (A) and DTG (B) in flowing nitrogen.

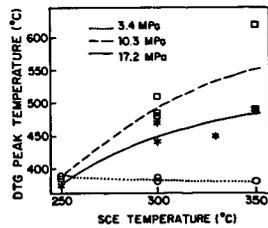


Figure 6. DTG peak temperature as a function of SCE temperature and pressure.

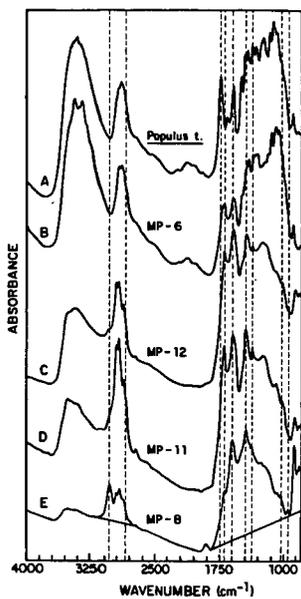


Figure 7. IRFT spectra of the same samples as in Figure 5.

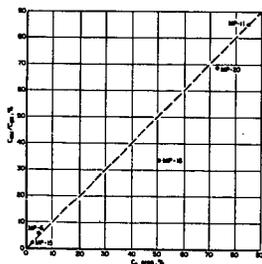


Figure 8. Relation between carbon in recomended material and polyaromatic carbon from ESCA C_a peaks

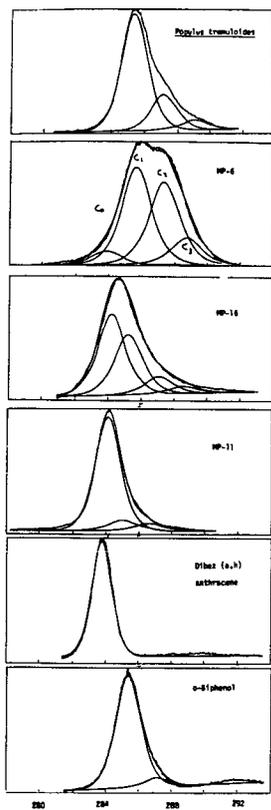


Figure 9. ESCA spectra (C_{1s} peaks) of *Populus tremuloides*, of 3 (three) SCE residues and of the standards compounds

**Some Aspects of Pyrolysis Oils Characterization
by High Performance Size Exclusion Chromatography (HPSEC)**

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ABSTRACT

The utilization of biomass pyrolysis oils or isolated fractions of these feedstocks requires a fast overall characterization technique. Gas chromatographic techniques typically analyze only the volatile fraction (5%-50%) of underivatized oils. With proper choice of solvent and detector systems, the HPSEC on polystyrene-divinylbenzene copolymer gels of the whole oils can provide valuable information on the apparent molecular weight distributions and changes that occur upon aging or chemical fractionation. Several pyrolysis oils have been analyzed as well as fractions isolated by solvent elution chromatography. In order to understand better the observed low-molecular-weight region, a number of model substances of the main classes of compounds found in pyrolysis oils have been investigated. While hydrogen bonding between the phenolic groups and tetrahydrofuran occurs, solute-solute interactions can be kept very small by operating at very low concentrations of solute; solute-gel interactions do occur when polycyclic aromatic compounds predominate. HPSEC provides very good information on shelf life, reactivity of pyrolysis oils, and comparison of oils as a function of process conditions.

INTRODUCTION

Many biomass pyrolysis processes produce 55%-65% conversion of the dry biomass to a very inexpensive pyrolysis oil (1-3). Costs of the oils will range from \$0.02-\$0.08/lb of oil, depending on the biomass feedstock cost (\$10-\$40/dry ton biomass). Therefore, these inexpensive oils, rich in phenolic fractions, acids, and furan-derivatives can be feedstocks for further upgrading or could be used because of their reactivity, in applications such as thermosetting resins and other wood-bonding methods. One of the important considerations for this use or further processing is the stability of the oil. Fast techniques to determine such properties become necessary. We present a method of characterization of pyrolysis oils and chemically isolated fractions using high-performance size exclusion chromatography (4-5), a technique commonly employed in the determination of the molecular weight distribution of polymers. We discuss the potential of the method and its limitations. Classes of model compounds commonly found in these oils have been investigated in the low-molecular-weight range to shed light on interactions between solute and solvent, solute and gel material (polystyrene-divinylbenzene), and solute-solute which can be kept to a minimum by operating at very dilute conditions.

EXPERIMENTAL

High performance size exclusion chromatography was performed on Hewlett-Packard 1084 and 1090 liquid chromatographs using HP1040A diode array and HP-1037A refractive index detectors. Data were stored on a HP 85 microcomputer. The columns (300 x 7 mm) used in this study were purchased from Polymer Laboratories Inc. and were a PL 100 A (10 μ particles) and a PL 50 A (5 μ particles). The solvent employed was tetrahydrofuran (Burdick and Jackson, chromatographic grade) used as received.

Details on the preparation of pyrolysis oils at SERI in the entrained-flow, fast ablative pyrolysis reactor can be found in a report by Diebold and Scahill (2).

The lignin model compounds were prepared by J. A. Hyatt (6); all the other model compounds were purchased from the Aldrich Chemical Co.

RESULTS AND DISCUSSION

Comparison of Pyrolysis Oils Obtained from Various Sources. The HPSEC of four wood pyrolysis oils obtained from the entrained flow, fast ablative pyrolysis reactor at SERI are shown in Figure 1. The oils were obtained from two separate runs and collected from two different scrubbers. The apparent molecular weight distributions of the four oils are very similar, indicating little selectivity on the basis of molecular weight distribution. Figure 2, however, shows the HPSEC chromatograms of a number of other pyrolysis oils obtained under a variety of conditions from many different sources. Clearly, some of the oils contain components of high apparent molecular weight even to the extent that some are excluded from the pores of the column polymer, indicated by the peaks at about 4.5 minutes in the chromatograms. The oils also have varying amounts of more sharply resolved components at lower apparent molecular weight. Thus, HPSEC may be used to characterize pyrolysis oils obtained from different sources, and comparisons may be drawn regarding their relative apparent molecular weight distributions as long as the analyses were carried out under the same chromatographic conditions.

The wood oil obtained from the packed scrubber in Run 41 at SERI was also subjected to fractionation by sequential elution by solvents chromatography (SESC) according to the method of Davis et al. (7). The fractions obtained were also analyzed by HPSEC and the chromatograms are shown in Figure 3. The HPSEC shows a general trend to higher apparent molecular weight as the polarity of the eluting solvent was increased up to methanol. A number of the fractions appear to contain relatively large amounts of distinct components (the sharp peaks) of lower apparent molecular weight. The sixth fraction was produced by going back to a less polar solvent. A seventh fraction was produced using a more polar eluant of 10% acetic acid in methanol which could not be analyzed by HPSEC because it was insoluble in tetrahydrofuran. About three-quarters of the oil was found in Fractions 3, 4, and 5, the last being the major fraction. If the chromatograms in Figure 3 were combined taking into account the yields of the various fractions then, as expected, a close comparison could be made with the chromatogram in Figure 1 of the unfractionated oil.

Doubts have been expressed that these pyrolysis oils could have molecular weights as high as indicated by these chromatograms as they are obtained by condensation of the primary vapors from pyrolysis. Analysis by techniques requiring revaporization of the oils consistently does not detect high-molecular-weight components, possibly because they are difficult to vaporize and also because they may be thermally degraded to either higher or lower molecular weight components (8) or both. It has been suggested that the high apparent molecular weights observed by HPSEC are the result of solute-solute or solute-solvent associations producing high-molecular-weight complexes. To verify the results obtained by HPSEC, the three major fractions and the original unfractionated oil were subjected to proton NMR analysis. The spectra of Fraction 5 and the original oil contain broad peaks characteristic of irregular polymers such as lignin, while the spectrum of Fraction 3 contains sharp peaks indicative of a mixture of simpler, low-molecular-weight compounds; Fraction 4 is intermediate between 3 and 5. Thus, the HPSEC and proton NMR spectra appear to be in general agreement in that this pyrolysis oil

contains mixtures of possibly higher molecular weight polymeric components and simpler low-molecular-weight compounds.

Many of the chromatograms shown here are of samples whose history of handling and age are not known in detail. It has been suggested that because of the very reactive and acidic nature of these oils that the high molecular weights observed are produced as the oils get older and are exposed to ambient conditions. Consequently, a study has been started to examine the effects of aging and the conditions under which pyrolysis oils are stored. A pyrolysis oil was produced in the SERI entrained-flow, fast ablative pyrolysis reactor. In this reactor, the primary vapors are scrubbed out with water such that about 90% are dissolved out. One sample of this aqueous solution of pyrolysis oil was stored at 4°C and the other was analyzed by HPSEC. The sample to be analyzed was made up by dissolving a small amount of the aqueous solution in tetrahydrofuran. Storage was under ambient conditions. The THF solution was analyzed several times over the period of a week to look for changes in its HPSEC chromatogram as shown in Figure 4. At the end of this period, the sample kept at 4°C was also analyzed to determine the effect of aging on the oil. Actually, a physical change took place on the aqueous sample stored at 4°C in that a small amount of tar separated out on the bottom of the vial. Consequently, two samples were made up in THF from the cooled sample, one from the aqueous part and one from the tar. Figure 5 compares the HPSEC of the sample kept at ambient conditions to those of the cooled samples. The HPSEC of the tar sample shows it consists of relatively much larger amounts of material higher in apparent molecular weight. The aqueous fraction of the cooled sample appears very similar to the sample stored at 25°C, although the latter does appear to contain a slightly larger relative amount of apparently higher molecular weight material. The degree to which storage at lower temperature has prevented any increase in molecular weight of the pyrolysis oil with time is difficult to ascertain because of the fractionation of the refrigerated sample. The sample kept at ambient conditions did not have the opportunity to fractionate because of the solvent it was dissolved in.

The HPSEC of the unrefrigerated sample (Figure 4) did indicate that the pyrolysis oil "aged" over the period of a week with increasing amounts of apparently higher molecular weight components being produced with time. Most of the samples obtained from outside of SERI are much older than one week. Pyrolysis oils are generally very reactive so that unless they are effectively stabilized in some way, increasing molecular weight should be expected as they get older.

What are the Limitations of HPSEC as a Technique When Applied to Pyrolysis Oil Characterization. One of the major advantages of HPSEC as a technique is that with the proper choice of solvent to dissolve the sample, the whole of the sample may be analyzed under very mild conditions. Because HPSEC is an isocratic technique, differential refractometers may be used as detectors so that, again, all of the sample may be detected. This is not a great concern when applied to pyrolysis oils, as they tend to absorb quite strongly in the ultraviolet. With a modern UV-visible diode array detector, a number of wavelengths can be monitored to ensure all the components of the oil are monitored. However, the eluting solvent must be chosen such that all the sample is dissolved, and as pyrolysis oils are fairly polar and often contain water, the solvent will also need to be fairly polar. The combination of polar solutes and polar solvents means that solute-solvent interactions through hydrogen bonding must be a concern. Tetrahydrofuran, probably the most popular solvent for HPSEC, can form hydrogen bonds with certain species such as phenols producing a complex molecule exhibiting greater molecular size and lower retention volume than would be expected (9). When nonpolar solvents are used such as toluene or chloroform, the molecular size should be relatively unaffected, but oil solubility then becomes very limited. The use of solvents of greater solvating

power, such as dimethyl formamide, also generates problems (10) due to solute-solute association, interaction between polystyrene standards and the column gel and column gel-solvent interactions.

The other major limitation of HPSEC as a technique comes from the desire to correlate solute elution time with molecular weight. As stated in its name, this is a method of separation based on molecular size. HPSEC columns contain a polymer gel of polystyrene-divinylbenzene produced with a controlled pore size distribution. Solutes of different size are separated by the different degrees of their penetration into the pores of the gel. The parameter that can be obtained from HPSEC is effective molecular length; e.g., material excluded from a column containing gel with 100 Å pores should have an effective molecular length of 100 Å or greater. To correlate retention times to molecular weight, it is necessary to use calibration standards similar in structure to the solute whose molecular weight is being determined. The most common calibration materials used are polystyrenes of low polydispersity. Others used include straight chain alkanes, polyethylene glycols, and the related materials IGEPALS™ that are 4-nonylphenyl terminated. If a column were calibrated with straight chain alkanes, it is unlikely to be much good for obtaining molecular weights of aromatic solutes, as a benzene ring is only about as long as propane, and anthracene is only about as long as hexane. When dealing with much larger molecules, it is difficult to estimate what their size might be in three dimensions in solution. Although pyrolysis oils have a high level of aromatic components, especially phenolics, they are a very complex mixture of components, and so it is unlikely that any one set of calibration standards would do a very good job. Despite these limitations, HPSEC can give an idea of the molecular weight distribution of an oil and certainly can be used in comparing oils. Establishing molecular weights for low-molecular-weight components is probably the most difficult task. Figures 6 and 7 compare the actual molecular weights of a variety of different types of compounds with their apparent molecular weights calculated from their retention times on 50 Å 5 μ HPSEC column calibrated with polystyrenes and IGEPALS. If the calibration was good for all compounds, then they should all fall on the straight lines. The aromatic hydrocarbons follow the calibration, but the aromatic acids and naphthalenes deviate greatly and in opposite directions. The aromatic acids contain both carboxylic and phenolic groups and so probably have higher apparent molecular weights than their actual molecular weights because of hydrogen bonding with the solvent tetrahydrofuran. The naphthalenes have lower apparent molecular weights than actual not only because their condensed structure makes them relatively small for their molecular weight, but also because of interactions between these solutes and the column gel. Philip and Anthony (9) observed retention volumes that were longer than expected for anthracene, benzopyrene, and coronene, considering their molecular size. They attributed this behavior to interaction of these highly aromatic solutes with the phenyl groups of the polymer chains of the gels.

The phenols and lignin model compounds follow the calibration quite closely, tending to show slightly higher apparent molecular weights than they actually have, probably because of association with the solvent. This is encouraging for the HPSEC of pyrolysis oils as these types of compounds are more likely to be present. Heavily cracked oils, however, can be rich in polynuclear aromatics.

Solute-solute association has not been observed for any of these molecules or for others when using tetrahydrofuran as solvent. Retention time changes of less than 0.01 minutes were observed in changing sample concentrations in the mg/mL range (~4 mg/mL) to the ng/mL range (~3 μg/mL) when injecting 5 μl of these solutions. HPSEC of pyrolysis oil samples made up in this concentration range should also be free of

solute-solute association which would artificially increase the apparent molecular weight of the oils.

CONCLUSIONS

HPSEC has been shown to be a useful method of characterizing pyrolysis oils because it examines the whole of the oil. Using polystyrene-divinyl benzene polymer gel columns, tetrahydrofuran as solvent and polystyrenes and IGPALS as calibration standards a good indication of molecular weight distribution can be obtained for oils from a variety of sources. The high apparent molecular weights observed appear to be real, and some corroboration is seen in proton NMR spectra. Although some solute-solvent association can be expected, use of phenolic model compounds has shown that HPSEC can give a good indication of molecular weight. However, if the oils contained large amounts of either much more polar compounds or condensed aromatic compounds, then interpretation of HPSEC on the basis of molecular weight would be much more difficult. Pyrolysis oils are reactive materials and an awareness of the length of time and conditions under which they are kept must be maintained and is important for further processing.

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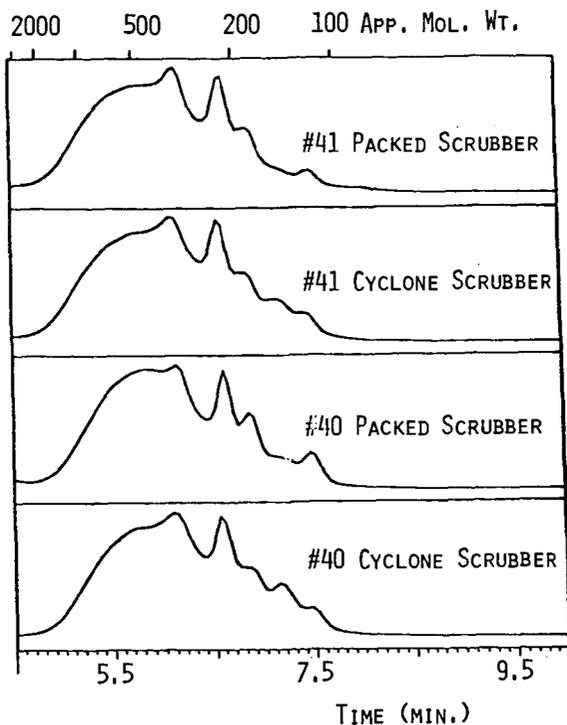


FIGURE 1. HPSEC OF WOOD PYROLYSIS OILS FROM THE SERI ENTRAINED-FLOW, FAST ABLATIVE PYROLYSIS REACTOR. ANALYSIS ON PL GEL 100Å, 10 μ GPC COLUMN USING THF AT 1 mL MIN⁻¹ WITH DETECTION AT 330 NM (BANDWIDTH 140 NM).

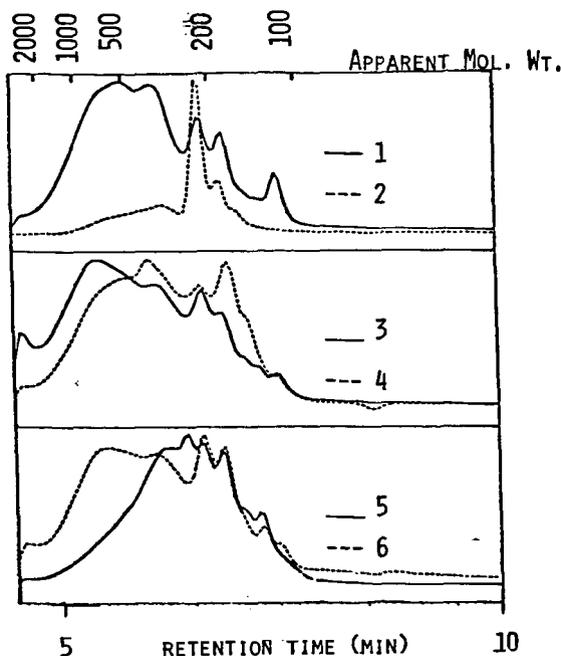


FIGURE 2. HPSEC OF WOOD PYROLYSIS OILS FROM A VARIETY OF SOURCES. ANALYSIS CONDITIONS AS PER FIGURE 1.

- 1 = OIL FROM D. S. SCOTT, U. OF WATERLOO, FLASH PYROLYSIS OF HYBRID POPLAR-ASPEN.
- 2 = OIL FROM C. ROY, U. DE SHERBROOKE, VACUUM PYROLYSIS OF AVICEL @ 306°C.
- 3 = OIL FROM C. ROY, U. DE SHERBROOKE, VACUUM PYROLYSIS OF ASPEN POPLAR @ 534°C, 2.2 MM OF HG.
- 4 = OIL FROM J. HOWARD, B. C. RESEARCH, SUPERCRITICAL ACETONE EXTRACTION OF ASPEN.
- 5 = OIL FROM S. KALIAQUINE, U. OF LAVAL, SUPERCRITICAL METHANOL EXTRACTION OF ASPEN @ 350°C, 1500 PSI.
- 6 = OIL FROM C. ROY, U. DE SHERBROOKE, VACUUM PYROLYSIS OF ASPEN @ 315°C, 0.7 MM OF HG.

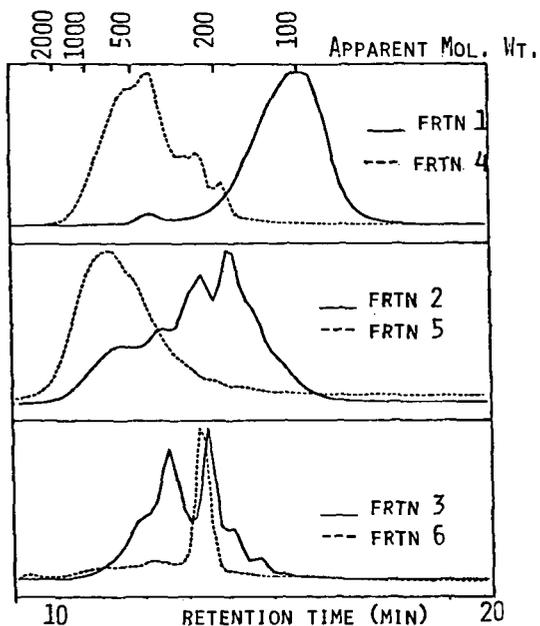


FIGURE 3. HPSEC OF SESC FRACTIONS FROM WOOD PYROLYSIS OIL RUN #41 PACKED SCRUBBER. ANALYSIS ON PL GEL 100 Å 10 μ GPC COLUMN USING THF AT 0.5 ML MIN⁻¹ WITH DETECTION AT 330 NM (BANDWIDTH 140 NM).

FRACTION 1 ELUTED WITH 15% TOLUENE IN HEXANE, YIELD 0.4%.

FRACTION 2 ELUTED WITH CHLOROFORM, YIELD 1.5%.

FRACTION 3 ELUTED WITH 7.5% ETHER IN CHLOROFORM, YIELD 15.6%.

FRACTION 4 ELUTED WITH 5% ETHANOL IN ETHER, YIELD 19.5%.

FRACTION 5 ELUTED WITH METHANOL, YIELD 38.1%.

FRACTION 6 ELUTED WITH 4% ETHANOL IN THF, YIELD 3.1%.

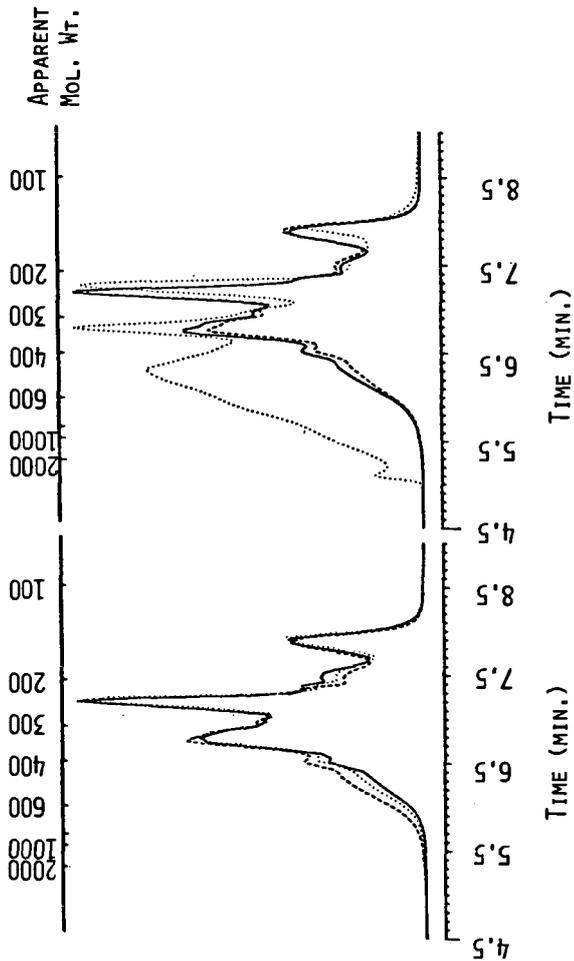


FIGURE 4. HPSEC OF PYROLYSIS OIL KEPT UNDER AMBIENT CONDITIONS AFTER 5 HRS (—), 3 DAYS (...), AND 7 DAYS (---). ANALYZED ON A PL GEL 50 Å, 5 μ GPC COLUMN USING THF AT 1 ML MIN⁻¹ WITH DETECTION AT 270 NM (BANDWIDTH 10 NM).

FIGURE 5. HPSEC OF PYROLYSIS OIL AFTER 7 DAYS KEPT UNDER AMBIENT CONDITIONS (—), TAR FRACTION OF REFRIGERATED SAMPLE (...) AND AQUEOUS FRACTION OF REFRIGERATED SAMPLE (---). ANALYSIS CONDITIONS AS PER FIGURE 4.

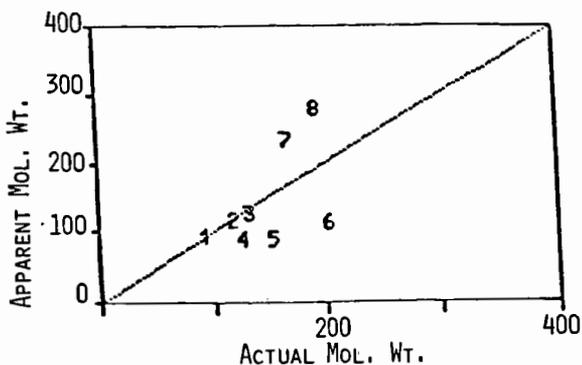


FIGURE 6. APPLICABILITY OF CALIBRATION FOR AROMATIC HYDROCARBONS, ACIDS, AND NAPHTHALENES. 1 = TOLUENE; 2 = PROPYL BENZENE; 3 = S-BUTYL BENZENE; 4 = NAPHTHALENE; 5 = 1,4-DIMETHYL NAPHTHALENE; 6 = 1-PHENYL NAPHTHALENE; 7 = VANILLIC ACID; 8 = 4-HYDROXY-3-METHOXY CINNAMIC ACID.

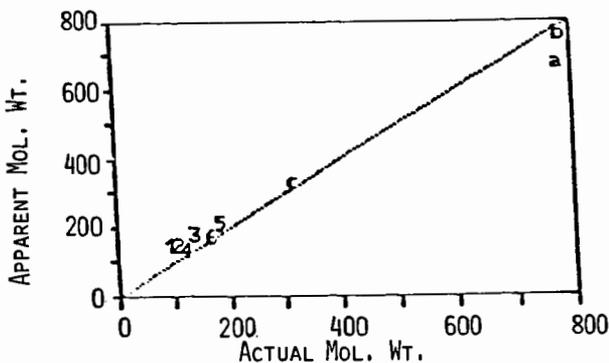


FIGURE 7. APPLICABILITY OF CALIBRATION FOR PHENOLS AND LIGNIN MODEL COMPOUNDS.

1 = PHENOL; 2 = P-CRESOL; 3 = 2-PROPYL PHENOL; 4 = GUAIACOL; 5 = SYRINGYL ALCOHOL;

6 = ACETOVANILLONE. LIGNIN MODELS: SEE REF. 6 FOR DETAILED DESCRIPTION.

A = 5,5'-BIPHENYL TETRAMER HEXAOL, $C_{42}H_{54}O_{14}$

B = β -O-4 TETRAMER HEPTAOL, $C_{41}H_{52}O_{15}$

C = β -O-4 DIMER TRIOL, $C_{17}H_{20}O_6$.

CHROMATOGRAPHY OF NON-DERIVATIZED PYROLYSIS OILS AND UPGRADED PRODUCTS

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ABSTRACT

Over a period of several years [1], the Department of Forest Science at Texas A&M University has been conducting studies in the hydroprocessing (catalyzed high pressure hydrocracking plus hydrotreating or hydrodeoxygenation) of pyrolytic tars produced in biomass pyrolysis and gasification. Processing details are given elsewhere in this volume [2]. This paper discusses various chromatography techniques used to study composition of the volatile components of raw tars produced for these studies, the composition of products produced from these tars in the upgrading studies as well as a gel permeation / gas chromatography technique used to separate functionalities in raw and upgraded tars for kinetic studies of tar hydroprocessing. In all cases, no derivatization was required prior to chromatography.

METHODOLOGY

Capillary Gas Chromatography. We found suitable, for both the volatiles of tars and their upgraded products, the use of a 30-meter DB-5 bonded phase fused silica capillary column (J&W Scientific). The column was used in a Tracor 560 gas chromatograph (Tracor Inc., Austin TX) in the split injection mode (ca. 100:1). Temperature programming for the tars was held for 5 minutes at 30°C, then to 280°C at 3°C per minute. For the hydroprocessed tars, temperature was held at 30°C for five minutes, then programmed to 280°C at 4°C per minute. Signals were detected by a flame ionization detector and stored in raw form on diskettes for later reconstruction with the CAPS program of an IBM Instruments 9000 Computer.

Capillary GC-Mass Spec. The same columns were used in capillary GC-MS runs to determine composition of the separated components. Analysis was performed in subcontracts to Radian Corporation (Austin TX) using a Hewlett-Packard 5985A instrument. Conditions generally were on-column injection, hydrogen gas flow at 1 ml per minute, temperature programming was typically split 30°C to 100°C at 3°C per minute then to 280°C at 6°C per minute. Identification of peak contents was by comparison of spectra obtained with those reported in the literature, and the EPA/NIH Mass Spectral Data Base [4]. Computer-assisted component identification was not used.

Gel Permeation Chromatography. Although gas chromatography is suitable for the separation of volatile components, it cannot be used for the larger non-volatile molecules found in biomass tars. For these, gel permeation chromatography can be used. In earlier experimentation when evaluating various columns for this purpose, we determined that GPC columns can separate tar components not only by molecular size, but also somewhat surprisingly by functionality [2,5]. GPC separations were performed on a Model ALC/GPC 202 liquid chromatograph (Waters Associates) equipped with a refractometer (model R401). Four Styragel columns (30 cm x 7.8 mm i.d.) were used in series. THF, refluxed and distilled with sodium wire under a nitrogen atmosphere, was used to reduce tar viscosity, and tar/THF solutions (typically 25% tar in THF) were filtered through micropore filters (Millipore, 0.5 pore size) before injection. Maximum injection volume was 250 microliters.

Fractions separated were collected and subjected to GC analysis on the DB-5 column. Another 12-foot SP-2100 packed glass column (Supelco) was used to analyze the volatiles which were defined as the total amount of components detected by GC relative to a 1-decene internal standard.

More recent work shows satisfactory performance in the use of a single 5-micron PLgel column (60 cm x 7.7 mm I.D.; Polymer Laboratories) used with a Varian 5560 ternary liquid chromatograph equipped with ultraviolet (Varian UV-200) and refractive index

(Varian RI-3) detectors. Signals, as per the capillary gas chromatography, are stored in raw form on diskettes for later reconstruction with the CAPS2 program of an IBM Instruments 9000 Computer.

RESULTS AND DISCUSSION

GC of Raw Tars. Tars produced via the thermochemical conversion of biomass materials are very complex in chemical composition, with very few components in excess of 1% concentration [6]. Further, standard chemical separation techniques used to separate fractions of similar functionality are complicated by the wide range of molecular weights and difficult solubility of the various components. For example, one tar produced by the Tech-Air Corporation at their demonstration plant in Cordele, Georgia exhibited the gross composition shown in Table I [7]. Approximately 45% of the tar was water-soluble.

Despite the fact that the tars are produced by condensation of volatile matter, much of the tars appear to be of low volatility, typically 50 to 60%, when simple distillations are attempted. It appears that pot temperature above 200°C cause condensation reactions resulting in intractable pot solids.

Knowing that the volatiles content of raw pyrolytic oils is very low, and that higher temperatures such as might be experienced in the injection port of a gas chromatograph could cause condensation/ polymerization reactions, it was understandably with much hesitation that we initially attempted direct injection of tars into capillary columns for gas chromatography. After several hundred injections, we can now claim few problems in the use of capillary columns in split or splitless modes. Maintenance of column performance consists of occasional cleaning of the injection system, frequent baking of the column at 300°C to remove any volatile fragments resulting from thermal cracking of non-volatiles at oven temperature, and occasionally breaking off the first two or three cms of column containing the non-volatile matter. The bonded phase columns in particular appear to suffer little in performance with continued use.

Figures 1 and 2 show the gas chromatograms for the volatiles of Tech-Air pyrolysis oil and corn cob gasification tar, respectively. Note the similarity in chemical composition. Lignin appears to leave a strong signature in the volatile components, with the alkyl guaiacols predominating. Small concentrations of organic acids are found (see Table II), and these are responsible for the corrosivity of pyrolysis oils, as determined by corrosion tests using ASTM G31-72 [1,8]. Figure 3 gives the GC-MS chromatogram of the same oil and the same column as in Figure 1, except that on-column injection was used. Note that on-column injection results in less fractionation of the oil as seen in the higher concentrations of less volatile components.

GC of Hydroprocessed Tars. Tar, once hydroprocessed, is much easier to analyze for chemical composition than raw tar since it is nearly completely volatile, and thus easily subjected to gas chromatography and gas chromatography-mass spectrometry examination. Chromatograms of the hydroprocessed Tech-Air pine pyrolysis oil and the hydroprocessed corn cob gasification tar are shown in Figures 4 and 5 [9]. Alkyl cyclohexanes and their corresponding aromatic counterparts are predominant chemical species, derived from lignin phenolics (alkyl guaiacols) via hydrocracking and hydrotreating reactions. Some phenolics are still present due to incomplete hydrotreating. If desired, higher yields of phenolics are possible through less complete hydrogen consumption at milder reaction conditions. Alternately, the phenolics can be eliminated completely by saturation of chemical entities with hydrogen under more drastic conditions [10].

Some surprises in chemical composition of both the hydroprocessed pine waste tar and corn cob tars were contents of straight-chain hydrocarbons, similar and identical to the hydrocarbons found in conventional gasoline and diesel fuels. Straight-chain saturated hydrocarbons in the paraffinic series from C5 to C30 have been identified. The mechanisms by which these are produced are under investigation.

The two hydroprocessed tars examined were from different feed materials, and produced in two different processes in differing yields. Yet the volatiles chemical compositions of the tars, both before and after hydroprocessing are remarkably similar. This suggests that thermal conversion of biomass, followed by hydroprocessing of the tars

produced, might be a somewhat universal method for producing similar products from dissimilar biomass feedstocks.

GPC/GC of Raw and Hydroprocessed Tars. Figures 6 and 7 display gel permeation chromatograms for the Tech-Air pyrolysis oil and its hydroprocessed product. Fraction 1 at lower retention volumes is high molecular weight polymeric material; Fraction 2, larger molecules (size of C₁₄ to C₄₄ hydrocarbons); Fraction 3, phenolics; Fraction 4, aromatics; and Fraction 5, solvent used in hydroprocessing plus some smaller molecules. Note that this analysis results in separation of chemical functionality, and this fact was used in subsequent kinetic studies of the hydroprocessing reaction [2]. Figures 8 and 9 are gas chromatograms of the aromatic fraction 4 for the raw and hydroprocessed oil, respectively.

Other Chromatography. Other chromatography, especially that showing similarities in the compositions of oils and hydroprocessed oils from nine different biomass feedstocks will be discussed in the oral version of this communication.

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TABLE I. GROSS FUNCTIONAL COMPOSITION OF TECH-AIR PINE PYROLYSIS OIL

	<i>Water Soluble %</i>	<i>Water Insoluble %</i>	<i>Total %</i>
Neutrals			
volatile	5.6	0.0	5.6
non-volatile	1.2	28.2	29.4
total	6.8	28.2	35.0
Phenols			
volatile	2.2	0.3	2.4
non-volatile	18.1	13.2	31.3
total	20.3	13.4	33.7
Acids			
volatile	5.2	0.0	5.2
Unextractables	13.1	2.0	15.1
Water	9.7	-	-
Losses	1.3	-	-
Total	56.4	43.6	100.0

TABLE II. RELATIVE ABUNDANCE AND PERCENTAGE COMPOSITION OF VOLATILE ACIDS IN PINE PYROLYSIS OIL

	<i>Formic Acid</i>	<i>Acetic Acid</i>	<i>Propionic Acid</i>	<i>Peak no.3</i>	<i>Butyric Acid</i>	<i>Peak no.5</i>	<i>Isovaleric Acid</i>
Relative Abundance	17.9	100.0	13.47	0.50	3.66	1.00	1.00
% Composition	0.32	1.70	0.24	0.01	0.06	0.02	0.02

Peaks no. 3 and 5 were not identified in gas chromatography, but exhibited acidic properties similar to the other components.

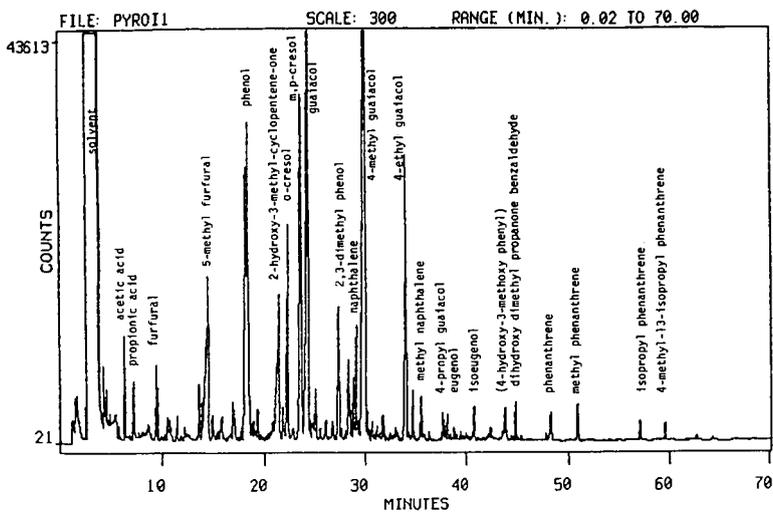


FIGURE 1. Volatiles of Tech-Air Pine Waste Pyrolysis Oil

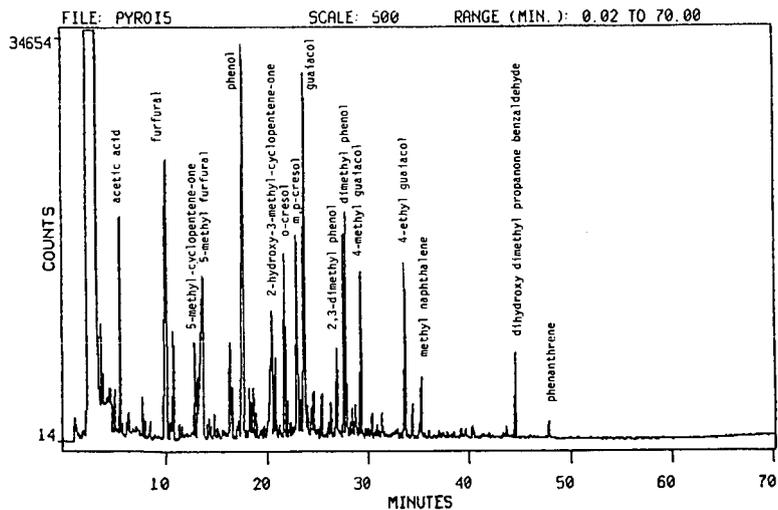


FIGURE 2. Volatiles of Corn Cob Gasification Tar

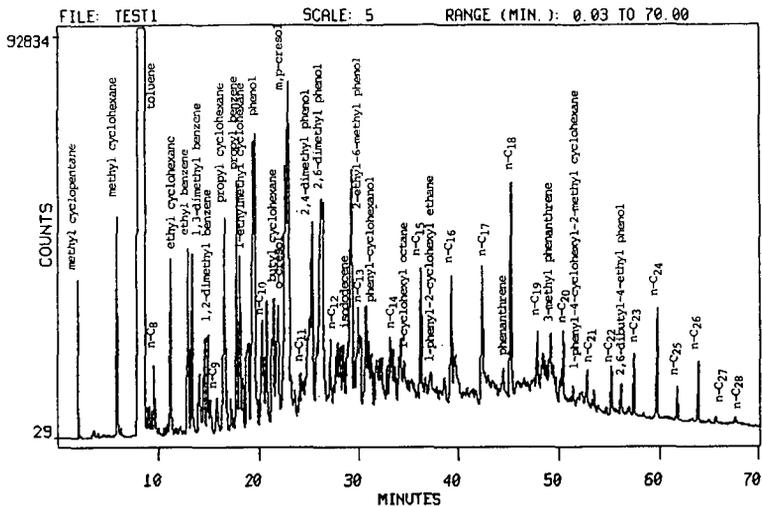


FIGURE 4. Volatiles of Hydroprocessed Tech-Air Pyrolysis Oil

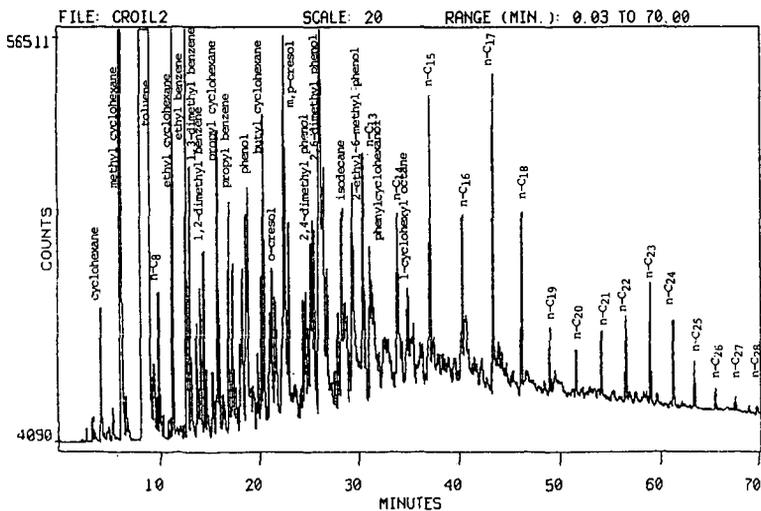


FIGURE 5. Volatiles of Hydroprocessed Corn Cob Gasification Tar

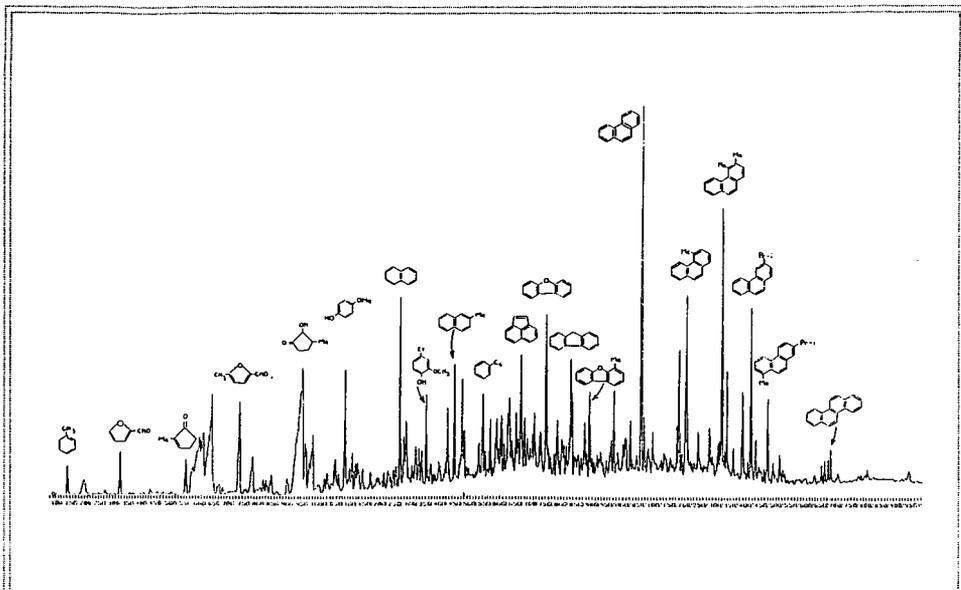


FIGURE 8. Aromatic Fraction (#4), Tech-Air Pyrolysis Oil

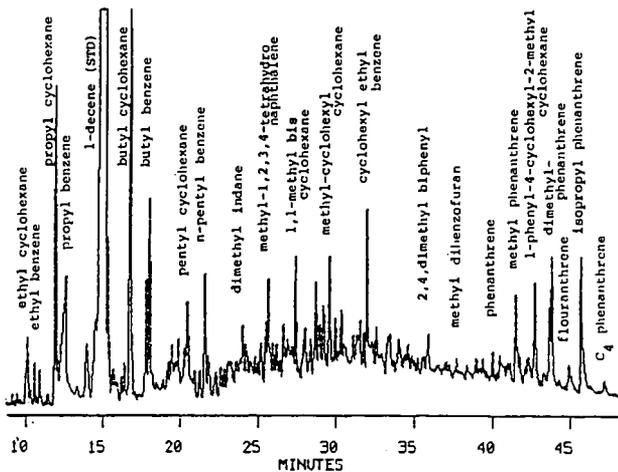


FIGURE 9. Aromatic Fraction (#4), Hydroprocessed Tech-Air Oil

PRODUCT ANALYSIS FROM DIRECT LIQUEFACTION OF SEVERAL HIGH-MOISTURE BIOMASS FEEDSTOCKS

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PROCESS RESEARCH IN DIRECT LIQUEFACTION OF BIOMASS

Significant progress has been made over the past fifteen years toward the development of processes for direct production of liquid fuels from biomass. Process research has generally progressed along two lines -- flash pyrolysis and high-pressure processing. Extensive analysis of the liquid products from these two types of processes has demonstrated the significant process-related differences in product composition. However, the effect of feedstock has received a lesser degree of attention.

Liquefaction Processes

Two generalized categories of direct liquefaction processes can be identified.(1) The first, flash pyrolysis, is characterized by a short residence time in the reactor (~1 second) at relatively high temperature (450-500°C) in order to obtain maximum yield of liquid product. The second, high-pressure processing, is usually performed at lower temperature (300-400°C) and longer residence time (0.2-1.0 hr). A typical operating pressure is 200 atm and often reducing gas and/or a catalyst is included in the process. The differences in processing conditions result in significant differences in product yield and product composition.

Product Analyses

Product analysis in support of the process development research in biomass direct liquefaction began at rudimentary level of determining solvent-soluble portions of the product. Analysis was soon extended to elemental analyses and proximate analyses, such as ash and moisture. Later, spectrometric analyses were performed followed by detailed chemical analyses used in conjunction with chromatographic separation techniques.

At all stages of development, the significant differences in composition between the products of flash pyrolysis and high-pressure processing have been evident. While polar solvents are most effective for both products, less polar solvents such as methylene chloride and even benzene and toluene have been used as extractants for high-pressure product oils. Comparative analysis has demonstrated the higher oxygen content and higher dissolved water content in the flash pyrolysis oils. Detailed analyses with spectrometric and chromatographic methods have added supporting evidence to these findings.

Variations in Product Due to Feedstock

While process-related differences in product composition have been evident, extensive study of the effect of feedstock on product composition has never been undertaken. Some limited comparative tests can be gleaned from the literature; however, most process research in direct liquefaction of biomass has been performed with woods of various species. Table 1 provides some of the results available in the literature for non-woody feedstocks. Significant differences in heteroatom content are evident, but only limited chemical analysis is available in most cases.

* Operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830

TABLE 1. Product Analyses from Liquefaction Tests with Various Biomasses

Feedstock	Temp. °C	Pressure psig	C	H	N	O	S	H/C
			percent					
<u>High-Pressure Processes</u>								
(2) newsprint	250	2,000	71.7	7.3	<0.3	~20.6	<0.1	1.21
(2) pine needles & twigs	250	2,000	72.2	8.7	1.05	18.0	0.10	1.43
(2) sewage sludge	250	2,000	77.0	10.7	2.80	8.8	0.64	1.65
(3) cellulose	250	2,000	72.4	7.0	.004	20.4	0.2	1.15
(3) sucrose	350	4,000	75.2	9.1	--	15.7	--	1.44
(4) municipal refuse	380	5,000	79.8	10.4	3.0	6.8	0.05	1.55
(4) manure	380	4,500 [∞]	80.4	9.4	3.0	6.9	0.26	1.39
(5) microalgae	400	4,000 [∞]	*81.2	8.6	5.4	3.5	--	1.26
<u>Flash Pyrolysis</u>								
(6) aspen	450	0	53.8	6.7	--	39.3	--	1.48
(7) sewage sludge	450	0	69.4	10.2	5.8	14.5	--	1.75
(8) poplar	500	0	49.8	7.3	0.0	42.8	0.0	1.74
(8) peat	520	0	67.1	9.0	3.4	20.3	0.1	1.59

[∞] estimate

* the microalgae analysis was calculated from the analysis of product fractions (oil and asphaltene) and the product distribution

The researchers at the Pittsburgh Energy Research Center (2,3,4) steadfastly maintained in their pioneering work that their oil products obtained from cellulosic wastes were paraffinic and cycloparaffinic in nature. They reported the presence of carbonyl and carboxyl functional groups but maintained that there was essentially no aromatic material produced except at higher temperature (then only in very small amounts). These conclusions were based on infrared and mass spectral analysis.(2) Later analysis of the sucrose-derived oil (3) included proton nuclear magnetic resonance spectral evaluation but resulted in the same conclusion. Most of the hydrogen was in methylene or methyl groups and about 4 percent was unsaturated but probably olefinic and not aromatic. Some ether linkages were also reported present in the sucrose-derived oil. Mass spectral analysis of the municipal refuse-derived oil (4) identified only two long chain fatty acids with certainty; however, not more than traces of aromatics were determined to be present. The manure-derived oil was found to be largely alicyclic hydrocarbon but contained heterocyclic nitrogen and alkyl phenolics.(4) These claims of the saturated hydrocarbon nature of the oil products are at odds with the reported elemental analyses (see Table 1). The low hydrogen to carbon ratios dictate that the oil products must contain a large fraction of aromatic or, at least, highly unsaturated compounds.

An algae-derived oil was reported to be principally n-paraffins and olefins with oxygen- and nitrogen-containing straight-chain hydrocarbons.(5) Polar compounds were reported to comprise 50-60 percent of the oil. Unfortunately, there is no indication of the type of analysis performed or detailed results of any kind; therefore, it is difficult to evaluate the veracity of these reported results.

The comparison of the peat and wood flash pyrolysis products is a good example of the effect of feedstock on product oil composition.(8) The poplar oil typically was composed of phenolic, ketone and furan compounds with a substantial fraction of low molecular weight organic acids. The main components of the peat oil were hydrocarbons, mostly straight chain olefins. Minor quantities of ketones were

noted but no acids, aldehydes or furans were identified by mass spectrometry. Phenols were also present in significant quantities.

A significant effort in comparing feedstock effects on product oil composition was reported by Russell et al.(9) Unfortunately, this effort did not include ultimate analysis of the oils for comparison. The report contains qualitative analysis by gas chromatography/mass spectrometry of five product oils derived from cellulose, hops field residue, softwood tree branches, peat, and sewage sludge. Phenols were a major component group for all feedstocks. Ketones and furans were also common. Hydrocarbons, aromatic and otherwise, were also identified primarily in the cellulose and softwood products. Nitrogen-containing products were absent from the cellulose and softwood products but could be found in the peat and sewage sludge-derived oils.

All of the above accounts can be contrasted with the large amount of analytical work on the chemical composition of wood-derived direct liquefaction products which has been reported over the past several years.(8,10-16) In all cases the majority of the product oils have been identified as phenolic with only minor amounts of pure hydrocarbon reported.

LIQUEFACTION EXPERIMENTS WITH MOIST BIOMASS

At Pacific Northwest Laboratory we have been testing the use of high-moisture biomass (marine and fresh-water biomass, post-harvest field residues and food processing wastes) in a thermochemical conversion system to produce useful fuels. Although the main focus of the work (17) has been gasification (catalytic production of methane) we have also performed a limited number of tests under high-pressure liquefaction conditions.

Feedstock Description

Five high-moisture biomass feedstocks were tested in these liquefaction experiments. They are characterized as follows:

Kelp - The sample used was a freshly harvested macrocystis kelp from Pacific Ocean seabeds off the southern California coast (El Capitan Beach, Santa Barbara Channel). It was packed in ice and flown to our laboratory where it was frozen in a polyethylene bag until used.

Water Hyacinth - Uprooted samples of hyacinths were recovered from the primary treatment lagoon at the Reedy Creek experimental sewage treatment facility near Orlando, Florida. The sample was packed in ice and flown to our laboratory where it was frozen in a polyethylene bag until used.

Spent Grain - The grain sample used was the residue following malting barley and water extraction of the sugars prior to fermentation. The sample was obtained from the Blitz-Weinhard Brewery in Portland, Oregon and was transported to our laboratory where it was frozen until used.

Napier Grass - Napier grass was collected after harvest by University of Florida researchers. The sample was bagged and shipped in a refrigerated container to our laboratory where it was stored in a freezer until used.

Sorghum - Grain sorghum was collected after the harvest of the grain by the University of Florida. The sample containing stems, stalks, and leaves was bagged and shipped in a refrigerated container to our laboratory where it was stored in a freezer until used.

Ultimate analysis, moisture contents and energy contents for the five feedstocks are provided in Table 2.

TABLE 2. Analysis of Moist-Biomass Feedstocks

	C	H	N	O	Ash	Moisture percent	HHV* BTU/lb
	percent, dried basis						
Kelp	26.9	4.0	1.2	30.2	38.4	88.9	7150
Water Hyacinth	43.0	5.8	5.6	29.5	15.3	94.9	7730
Spent Grain	48.6	6.8	3.4	35.3	3.4	80.5	9160
Napier Grass	44.5	5.9	<0.1	41.9	5.7	84.4	7870
Sorghum	44.7	5.8	0.2	37.5	7.9	77.0	8046

*HHV = higher heating value of dried biomass

Reactor Conditions

The experiments were performed batchwise in a one-liter, stirred autoclave. Approximately 300 g of moist-biomass was charged to the autoclave in a stainless steel liner. Sodium carbonate was added to the feedstock (approximately 0.1 g/g dry biomass) except in the case of kelp which already contains a high level of alkali as part of its chemical makeup.

The autoclave was then sealed, purged with nitrogen and then pressurized with carbon monoxide (approximately 50 atm). The reactor was heated to 350°C (approximately 30 minutes from 200° to 350°C) and held at that temperature for 30 minutes. The pressure within the autoclave at temperature typically increased from 270 atm to 340 atm over the period of the experiment. At the end of the allotted time cooling water was flushed through our internal cooling coil which brought the reactor temperature down to 200°C within 5 minutes.

Product Recovery and Analysis

After the autoclave had cooled completely, the gas product was vented. The typical gas composition included nearly equal parts of hydrogen and carbon dioxide with a 10-15 percent residual amount of carbon monoxide and minor amounts of hydrocarbons. [These results suggest a strong water-gas shift reaction as catalyzed by the sodium carbonate base.(18)] The autoclave was then opened and the two-phase liquid product was collected. The autoclave was rinsed with acetone and the resulting wash solution filtered. The liquid product was acidified to pH 2 with dilute HCl and then extracted with methylene chloride.

The soluble and insoluble products were analyzed for elemental content of carbon, hydrogen, nitrogen and oxygen with Perkin-Elmer 240 series instruments. The methylene chloride soluble oil product was also analyzed as a methylene chloride solution on a gas chromatograph equipped with a mass selective detector for qualitative analysis and a similar gas chromatograph equipped with a flame ionization detector for quantitative analysis. Identification of compounds was made by comparison of mass spectra with library listings of known compounds in conjunction with a comparison of chromatograph column residence time with similar known compounds. Quantitative analysis was based on a known amount of internal standard (trans-decahydronaphthalene) with detector response factors determined for various functional group types. Quantitation is estimated at within ± 20 percent. DB-5 capillary columns are used in both chromatographs.

LIQUEFACTION RESULTS AND PRODUCT DESCRIPTION

Liquefaction Experimental Results

Results from the liquefaction experiments with the five moist-biomass feedstocks are given in Table 3. The oil yield is based on the combined mass of acetone- and methylene-chloride soluble oils as a percent of the mass of dried feedstock calculated to an ash-free basis. The product oil elemental analysis is the calculated composite analysis for the combined acetone- and methylene chloride-soluble oils.

TABLE 3. Experimental Results for Liquefaction Experiments

	Oil Yield percent	C H N O H/C combined oil analyses				
Kelp	19.2	76.7	8.9	3.5	9.9	1.38
Water Hyacinth	26.0	76.3	9.9	3.3	10.5	1.54
Spent Grain	34.7	75.2	10.2	3.8	10.8	1.61
Napier Grass	34.4	74.5	8.5	0.4	16.7	1.36
Sorghum	26.6	75.9	8.7	1.7	13.7	1.36

The test results in Table 3 demonstrate oil product yields for liquefaction of the moist-biomass feedstocks at levels comparable to wood liquefaction. Reported yields for wood liquefaction in aqueous slurries, such as the LBL process, (19) have typically been in the 25 to 30 weight percent range. The quality of the moist-biomass liquefaction products fall in a general range which is also similar to reports for wood liquefaction products. However, certain examples of moist-biomass product oils appear to have elemental compositions suggesting higher quality products. Especially interesting are the high hydrogen to carbon ratios for the spent grain and water hyacinth products and the relatively low oxygen contents of the spent grain, water hyacinth and kelp products. A significant difference from wood-derived oils is the high nitrogen content in the oils from spent grain and aquatic biomasses.

Product Analysis Details

The detailed chemical analysis of the five moist-biomass derived oils by gas chromatography and mass spectrometry helps to better define the differences in oil composition. Over 190 different compounds and isomers were identified in the five oils. In order to better understand this large amount of information the components have been grouped by chemical functionality and these groups are listed in Table 4.

The compound groups consist of the following types of compounds:

esters/aldehydes/alcohols - four to six carbon oxygenates
cyclic ketones - five and six carbon rings, many unsaturated, most alkylated
furans - dihydrofuranones, hydroxymethyltetrahydrofuran
phenols - phenol and alkylated (up to five carbons) phenols
methoxyphenols - mono- and dimethoxyphenols and alkylated forms
benzenediols - dihydroxybenzenes and alkylated (up to five carbons) forms
naphthols - naphthols and methylated naphthols
aromatic oxygenates - bismethylguaiacol(?), phenylphenols, benzodioxin(?)
cyclic hydrocarbons-alkylcyclopentenes, alkylbenzenes(?), alkylindans, phenanthrene
long-chain hydrocarbons - C₁₄ to C₂₇ n-alkanes and olefins
fatty acids - C₁₂ to C₂₀ saturated and unsaturated acids
nitrogen cyclics-alkylpyrrolidinones, alkylaziridines(?), alkylpyrroles,
alkylindoles
amines/amides - C₈ to C₂₂ amines/amides(?)

TABLE 4. Chemical Functional Groups in Moist-Biomass Oil Products*

Compound Group	Kelp	Water Hyacinth	Spent Grain	Napier Grass	Sorghum
esters/aldehydes/alcohols	0 (1)	0 (0)	0 (1)	3 (4)	0 (0)
cyclic ketones	8 (13)	3 (9)	7 (10)	20 (25)	6 (12)
furans	0 (0)	1 (1)	4 (3)	2 (3)	2 (3)
phenols	11 (9)	22 (18)	26 (15)	35 (24)	21 (14)
methoxy phenols	3 (3)	3 (2)	3 (1)	5 (5)	10 (5)
benzenediols	11 (2)	6 (4)	0 (0)	6 (6)	25 (11)
naphthols	9 (5)	2 (3)	0 (0)	5 (9)	9 (6)
aromatic oxygenates	1 (2)	3 (3)	6 (2)	4 (5)	2 (2)
cyclic hydrocarbons	21 (15)	12 (18)	7 (9)	16 (24)	16 (19)
long-chain hydrocarbons	6 (3)	16 (15)	5 (4)	3 (9)	4 (4)
fatty acids	11 (3)	8 (7)	8 (4)	1 (2)	5 (4)
nitrogen cyclics	17 (11)	17 (11)	19 (7)	0 (0)	0 (0)
<u>amines/amides</u>	<u>3 (1)</u>	<u>6 (3)</u>	<u>15 (7)</u>	<u>0 (0)</u>	<u>0 (0)</u>
percent identified	10.3	17.8	14.2	20.4	17.8

* tabular listing is the mass percent of identified oil components in each compound group; the number in parentheses is the number of individual compounds and isomers in each compound group

Comparison to Earlier Results

These results verify that the carbohydrate structures found in biomass can be converted thermochemically to a mixture of primarily phenolic compounds. Hydrocarbons are not predominant yet they may survive the processing in a significant yield given an appropriate feedstock. Cyclic ketones are the other major component group which can be identified by GC/MS. Low molecular weight oxygenates and furans are minimized by the addition of base to the reaction medium as has been demonstrated by other researchers.(20)

The product compositions of the napier grass and sorghum-derived product oils shown many similarities to wood-derived oils. In comparing with high-pressure processed oil from Douglas fir the same groups of cyclic ketones, phenols, naphthols, and dihydroxybenzenes dominate. The traces of hydrocarbon in the sorghum and napier grass oils are significantly different from the Douglas fir and are apparently feedstock related. Nitrogen-containing compounds were not found in either the Douglas fir oils or the sorghum or napier grass oils reported here.

The large fraction of nitrogen-containing cyclic compounds is the distinguishing factor between the hyacinth, kelp and grain oils when compared to earlier wood oil analyses. Similar compounds were found earlier in peat and sewage sludge oils.(9) Our results now extend this trend to high protein feedstocks and green,

aquatic plants. It is obvious that a strong correlation exists between nitrogen content of the feedstock and the amount of nitrogen incorporated into the product oil. High-pressure liquefaction even with a reducing gas environment and alkaline catalysis cannot effect a preferential denitrogenation reaction. Substantial amounts of nitrogen are condensed into cyclic systems which remain in the oil product.

Utilization of Oil Products from Moist Biomass

The oil products from these high-moisture biomasses have properties similar to the more widely studied wood-derived oils. The numerous applications of wood-derived oil have been discussed by others (10a, 20). The moist-biomass oils should be amenable to the same types of applications. In addition, the nitrogen-containing compounds may be useful as chemical commodities. Indoles in particular may be recoverable for use as fragrances or flavors. The hydrocarbon component in the oils may facilitate the direct use of these oils as fuels.

The nitrogen-containing components in some of the moist-biomass oils is a source of concern when considering their use as fuels. Direct utilization of these oils would certainly lead to higher levels of emission of NO_x . The nitrogen-containing components have also been indicated as a source of fuel instability during storage and as cancer-causing agents in various chemical forms. Hydrotreating of these oil products to remove the nitrogen is a possible means of upgrading the products. However, hydrodenitrogenation of the heterocyclic compounds is a difficult and costly procedure compared to hydrodeoxygenation of the phenolics, which would also be accomplished in a hydrotreating type of oil upgrading.

Implications for Future Research

The high-moisture biomass feedstocks can be a source of useful liquid fuel products. The use of the high-moisture biomasses in high-pressure processing will allow their utilization in a thermochemical process without prior drying. Other research on the use of these feedstocks in high-pressure gasification has suggested the feasibility of feeding these materials as a slurry following maceration.(17) This same type of feeding should allow direct utilization of high-moisture biomass in high-pressure liquefaction processing. Experimental verification of this type of continuous processing needs to be undertaken.

The use of the nitrogen-containing feedstocks will lead to production of a nitrogen-containing oil product. Direct utilization of this oil product as a fuel will likely require development of appropriate emission control techniques in order to maintain air quality. Alternately, nitrogen-containing components can be removed from the oil product for use as specialty chemicals or by hydrotreating. Further development of hydrotreating technology specific to these oils may be necessary in order to process the heterocyclic nitrogen-containing compounds which require extensive processing in order to effect nitrogen removal.

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An Integrated Spectroscopic Approach to the Chemical
Characterization of Pyrolysis Oils

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ABSTRACT

The hydrocarbon ("oil") fraction of a coal pyrolysis tar prepared by open column liquid chromatography (LC) was separated into 16 subfractions by a second LC run. The first 13 of these fractions were chosen for integrated spectroscopic analysis. Low voltage mass spectrometry (MS), infrared spectroscopy (IR), and proton (PMR) as well as carbon-13 nuclear magnetic resonance spectrometry (CMR) were performed on the 13 fractions. Computerized multivariate analysis procedures such as factor or discriminant analysis followed by canonical correlation techniques were used to extract the overlapping information from the analytical data. Subsequent evaluation of the integrated analytical data revealed chemical information which could not have been obtained readily from the individual spectroscopic techniques. The approach described is generally applicable to multisource analytical data on pyrolysis oils and other complex mixtures.

INTRODUCTION

Due to the extremely complex nature of pyrolysis tars obtained from recent or fossil biomass samples structural and compositional analysis of such tars poses a formidable challenge to analytical chemists. Even when armed with an arsenal of sophisticated analytical techniques a detailed qualitative analysis requires careful, laborious combination and integration of voluminous chromatographic and spectroscopic data. True quantitative analysis is generally not within reach of current analytical methodologies, especially if the tar contains nonvolatile and/or highly polar or reactive components. Although in recent years impressive advances have been made with the physical coupling of two or more chromatographic and/or spectroscopic techniques into so-called "hyphenated" methods, e.g., GC/MS, LC/MS, GC/FTIR, MS/MS, etc., true integration of the analytical data by means of multivariate analysis methods such as canonical correlation analysis is rarely ever attempted. Yet, intuitively the potential advantages and benefits of data integration methods are easily understood. With these considerations in mind the authors carried out the present feasibility study of a coal-derived pyrolytic tar using a combination of chromatographic (LC), spectroscopic (MS, IR, PMR, CMR) and chemometrics (factor, discriminant and canonical variate analysis) techniques. In order to reduce the complexity of the analytical problem to more manageable proportions, a completely distillable coal tar was selected. Moreover, polar and/or highly reactive components were removed by open column LC. Preliminary results of this integrated analytical approach will be presented here.

EXPERIMENTAL

A pyrolysis tar from a high volatile B bituminous Hiawatha seam coal (Wasatch Plateau field, Utah) was obtained from the fixed bed Wellman Galusha gasifier operated by Black, Sivalls and Bryson in Minneapolis. Open column liquid chromatography (LC) on silica gel using four solvents and solvent mixtures of increasing polarity; i.e. hexane; hexane/benzene 8/1; benzene/ether 4/1; and benzene/methanol 1/1, was used to separate the whole tar into broad compound classes as described by McClennen *et al.* (1). The hexane and hexane/benzene eluted fractions constituted

complex mixtures, principally composed of hydrocarbons. These fractions were combined and further separated by a second IC run. Fractions were eluted from the column with a nonlinear gradient beginning with 100% n-hexane and stabilizing at 10% benzene/90% hexane over a period of 30 min. Sixteen fractions were collected and weighed over a total of 40 minutes. Approximately 1 ml was taken from each sample for low voltage MS analysis. The remaining subfractions were then rotary evaporated and weights of residue were recorded. The calculated elution volumes are shown in Figure 1.

Low voltage mass spectra were run on an Extranuclear 5000-1 quadrupole mass spectrometer with Curie-point heating inlet. Low voltage mass spectra of subfractions 1-15 were obtained using 1/4 ul glass capillary probe tips as described by McClennen et al. [2]. Electron energy was set at 12 eV. Samples were scanned from m/z 20 to m/z 300. The inlet was heated to 200°C. Mass spectra were stored on an IBM 9000 computer and printed out in the form of bar plots. Examples of low voltage mass spectra are shown in Figure 2.

FTIR spectra were obtained using neat samples on NaCl (salt) disks. The instrument was a Nicolet 7000 series spectrometer, resolution 4 cm^{-1} , 200 scans, operated in the absorbance mode. Samples were scanned from 4000-600 cm^{-1} . Absorbance intensities were recorded for 20-30 peaks in each spectrum. In this way 33 wavenumber variables were obtained. Examples of FTIR spectra are shown in Figure 3.

Proton NMR spectra of the hydrocarbon subfractions dissolved in CD_2Cl_2 (with TMS) were taken using a Varian 300 superconducting instrument over the 1-10 ppm region. Integrated peak intensities for eight regions of the spectrum were tabulated for each subfraction, in addition to a table containing an overall view of the number of aliphatic, aromatic and olefinic protons present.

Carbon 13 NMR spectra of subfractions were also run in CD_2Cl_2 on the Varian SC 300 from 0-180 ppm. Peak intensities were measured using integration curves. Twenty three variables were chosen. Table 1 shows overall data from FMR and CMR.

Computerized multivariate analysis was carried out using the interactive SIGMA program package developed at the University of Utah Biomaterials Profiling Center which affords scaling, as well as factor, discriminant and canonical correlation analysis (3). Chemical components were numerically extracted using the Variance Diagram technique described by Windig et al. (4).

RESULTS AND DISCUSSION

The emphasis of this paper is on the general method of multisource data integration using Factor Analysis and Canonical Correlation Analysis. Figure 4 shows the variances calculated for the factors in each data set. For mass spectral and IR data, only eigenvalues greater than 1.0 are shown, whereas all factors were used for the FMR and CMR data. The dashed line shows eigenvalues <1.0, e.g. in the FMR, only Factor 1 had an eigenvalue > 1.0. Six factors from each data set were used for the canonical correlation analyses. Figure 3b shows the percent variance from the original factors that was represented in the subspace spanned by the canonical variate functions. Between 40% (MS) and 80% (FMR) of the original variance is represented by Canonical Variate functions 1 + 2.

Our discussion of the factor analyses presented in Figure 5 will first identify components characteristic of early eluting samples and then move on to later eluting samples. Investigation of the correlated mass peaks loading on factors 1 and 2 (Figure 5a) by means of the variance diagram method revealed 8 components. In Figure 5a component (a) (130°) represents the ion series $\text{C}_n\text{H}_{2n-1}^+$, whereas component (b) (160°) shows $\text{C}_n\text{H}_{2n}^+$ ions from monocyclics or alkenes. A large component (c) ($190-240^\circ$) contains $\text{C}_n\text{H}_{2n-1}^+$ ions (190°), $\text{C}_n\text{H}_{2n-2}^+$ ion (220°) as well as fragment ions at m/z 149, 163, 177, and 191 characteristic of terpenoid resins or other $\text{C}_n\text{H}_{2n-4}$ compounds (240°).

Aromatic compounds, such as short (C_n , $n = 1, 2, 3$) alkyl substituted benzenes occur at component (d) (280°), with longer chain (C_n , $n = 5, 6, 7$) benzenes + tetralins at 320° ; component (e). Component (f) at 0° is thought to represent $\text{C}_n\text{H}_{2n-10}^+$ series. Naphthalenes are found at component (g) (30°) and acenaphthene/biphenyl ions are present at component (h) (50° , Figure 5a). Note that

the scores in this factor space roughly describe a circle, with the exception of fraction 13, which is found near sample 10. Factor 3 (not shown) distinguishes sample 13 from the others with a component axis containing anthracene/phenanthrene moieties as well as an ion series at m/z 180, 194, 208.

Factor analysis was performed on the IR spectra of subfractions 1 to 13 using all 33 wavenumber variables. Figure 5b shows the factor score plot of the IR data on subfraction 1 to 13 in the F1 vs. F2 factor space. Samples 1-7 are very close together, implying that infrared spectroscopy does not detect much difference between these dominantly aliphatic mixtures. Analysis of the underlying correlation between variables by means of the variance diagram method showed component (a) 350° represents methyl and methylene absorptions such as 2870, 2850, 2920, 1460 and 720cm^{-1} . Component axes (b) 120° with peak 1516cm^{-1} and (c) 160° with 3050, 3015 and 1600 represented aromatic absorptions. A component axis (d) 240° , which points to subfractions 12 and 13, represents peaks 750, 2940, 1030 and 1180cm^{-1} .

Initially, we tentatively assigned 1030 and 1180cm^{-1} as C-O stretches, but further examination of infrared spectra of aromatic standards showed that these are probably CH in plane bends, e.g., 1030cm^{-1} (benzene). An interesting feature of the IR data is the peak at 2868cm^{-1} which correlates with the F1 aromatic axis, although it is believed to represent a combination of methyl and methylene stretches. Painter et al., (4) also found this behavior in IR spectra of coal macerals. The data strongly suggest a reinterpretation of this peak assignment.

Several peaks in the F1+ direction of Figure 5b can be assigned as olefin CH out-of-plane bends. These turned out to be important in the combined (canonical variate) space and will be discussed later.

The factor score plot F1 vs. F2 (91% variance) of the PMR data in Figure 5c shows a general distribution of samples forming a circle. The variance diagram of F1 vs. F2 from the proton NMR data shows that the positive F1 axis contains methyl and methylene groups attached to aliphatic (sp^3 hybridized) carbon groups, and olefinic protons. The F1 axis contains aromatic protons, split into two groups. The component axis at 200° represents methyl substituted benzenes ($\text{CH}_3 + 1$ ring aromatic), oriented toward fractions 9 and 10. The 170° rotation contains 2-ring and 3-ring aromatics and longer chain aromatic substituents (CH_2) oriented toward fractions 11-13.

Factor analysis of the CMR data gave 6 factors with eigenvalues >1.0 . The score plot of F1 vs. F2 (56% of the variance) (Figure 5d) shows that samples 1-7 appear to be similar in this dimension oriented along the negative side of F1. Components in this direction include aliphatic peaks such as at 23, 30, 32 and 38 ppm and (with weaker loadings), at 97 and 114 ppm, probably olefinic carbons. Fraction 8 is somewhat removed from fractions 1-7 but still on F1-, and therefore predominantly aliphatic in character. Fractions 9-13 are widely spread on factor F1+. A component axis at 350° represents peaks at 20, 122, 126, 131 and 135 ppm. Fractions 10 and 11 have an associated component which includes the peaks at 40 and 134 ppm. Fractions 12 and 13 have an associated component axis with the peaks at 127, 129, 132 and 142 ppm. All peaks on F1+ (except at 20 and 40 ppm) are likely aromatic carbons. The 20 and 40 ppm peaks are sp^3 hybridized carbon substituents on aromatic rings.

Canonical correlation of the factor analysis results from the MS, IR, PMR and CMR data using 6 factors from each data set gave four canonical variate functions with correlation coefficient greater than 0.90. The variance associated with the four CV functions is shown in Figure 4. Figure 6 is a score plot of CV1 vs. CV2 for the four data sets. The scores from each fraction analyzed by the four methods are connected by lines. A small polyhedron implies that the methods see the sample in a similar way. The later eluting samples (9-13) appear to group into clusters that are widely separated from one another (e.g., 9 and 10, 11 and 12, 13) whereas early eluting samples (1-7) are close together in this space. Figure 7 shows a consensus picture of the component directions from each method found in this CV space. Correlated variables consistent with an interpretation of aliphatic compounds are clustered around CV1-, near fractions 1-4. Fraction 7 appears also in this direction. A component axis of alkyl benzenes (m/z 92, 106...) from the MS data loads weakly in this CV space. From the original factor analyses it can be seen

that the mass spectral and PMR data clearly differentiated fraction 7 from the other fractions, but that other data sets grouped 7 with fractions 1-6. The PMR data showed no unique component associated with fraction 7. This says that the mass spectral picture of fraction 7 is in a sense unique, and does not appear in the CV space. A component axis corresponding to olefinic variables (IR, PMR, CMR) appears at 150°, in the direction of fractions 5 and 6. The mass spectral data shows ion series with 2 and 3 units of unsaturation, one or more of these apparently being a double bond. The positive half of CVI reveals three components, each one consistent with an assignment of aromaticity. The PMR and IR (CH in-plane bend modes) show increasing fused ring aromaticity in the ccw direction (300° to 50°). The mass spectral data identified the component at 300° with indane/tetralin, the 0° component as >C₃ alkyl substituted naphthalenes and the 50° component as acenaphthene/biphenyls. A component axis at 80° (mass spectral data only) showed peaks characteristic of alkyl anthracene/phenanthrenes. The CMR data has not been interpreted in as great a detail, but groups of aromatic peaks found in these three directions are not inconsistent with interpretations from the other data sets. A point of interest is provided by the two CMR aliphatic peaks, 20 and 40 ppm (0°), which correlate with aromatic carbons and are from alkyl substituents.

CONCLUSIONS

Valuable information was gained by correlating the four analytical techniques. For example, mass spectral peaks of samples containing 2 and 3 units of unsaturation, as determined by PMR, were shown to contain double bonds, whereas mass spectral peaks corresponding to molecules containing one unit of unsaturation were found to be cyclic. Since all the techniques showed the predominantly aromatic fractions to be very different from each other when moving to higher fused ring systems, a better understanding of spectral interpretation of aromatic hydrocarbons mixture data appears possible.

A major limitation of the present study is that only that portion of the analytical data common to all four analytical techniques was interpreted. Future studies will have to address the highly important portions of the analytical data unique for each analytical method in order to reap the full benefits of the integrated spectroscopic approach.

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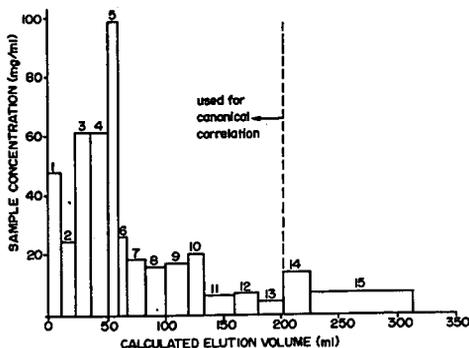


Figure 1. Reconstructed liquid "chromatogram".

TABLE I
INTEGRATED INTEGRITIES OF ALIPHATIC OLEFINIC AND AROMATIC
REGIONS OF THE NMR SPECTRUM FOR SUBFRACTIONS OF THE
HYDROCARBON FRACTION OF BIAXONA TAR

SUBTRACT.	(Proton NMR Data)				(Carbon 13 NMR Data)			
	ALIPHATIC (1-5 ppm)	OLEFINIC (4-6 ppm)	AROMATIC (6-9 ppm)	ALIPHATIC H- AROMATIC H	ALIPHATIC	OLEFINIC	AROMATIC	ALIPHATIC C- AROMATIC C
1	1.0				1	1.0		
2	1.0				2	1.0		
3	0.959	0.041			3	0.98	.02	
4	0.948	0.052			4	0.922	.078	
5	0.952	0.038			5	0.922	.078	
6	0.931	0.049			6	0.885	.063	
7	0.905	0.043	0.052	17.40	7	0.759	.121	.052
8	0.909	0.091	0.091	9.99	8	0.596		.404
9	0.827	0.173	0.173	4.78	9	0.513		.467
10	0.822	0.178	0.178	4.62	10	0.337		.643
11	0.789	0.211	0.211	3.74	11	0.333		.667
12	0.786	0.214	0.214	3.87	12	0.261		.739
13	0.849	0.151	0.151	5.62	13	0.211		.789

* integration from 50-150 ppm, olefinic and aromatic arbitrarily made equal.

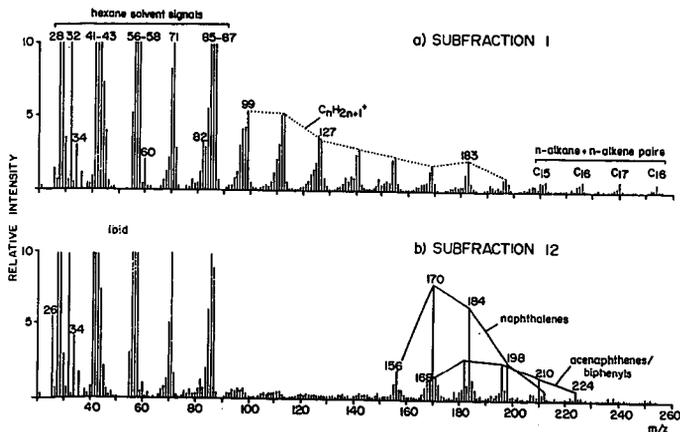


Figure 2. Low voltage mass spectra of (a) subfraction 1 and (b) subfraction 12.

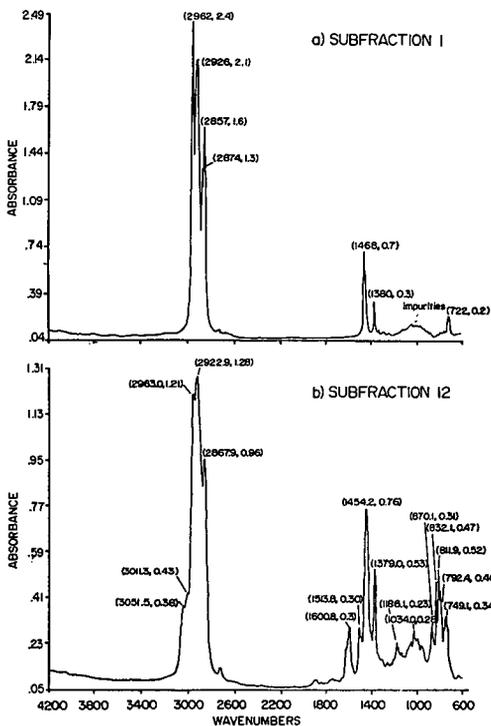


Figure 3. FTIR spectra of (a) subfraction 1 and (b) subfraction 12.

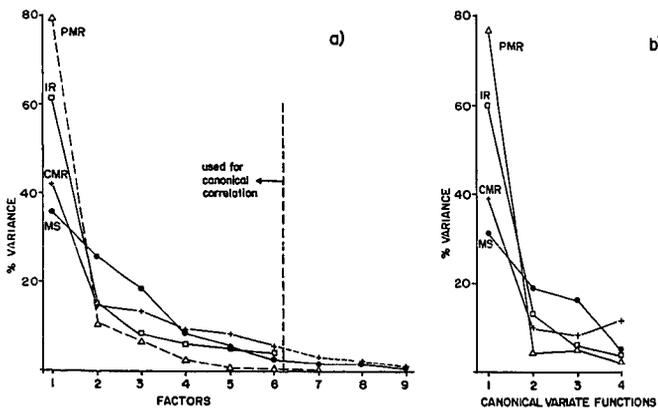


Figure 4. Percent total variance explained by (a) factors and (b) canonical variate functions.

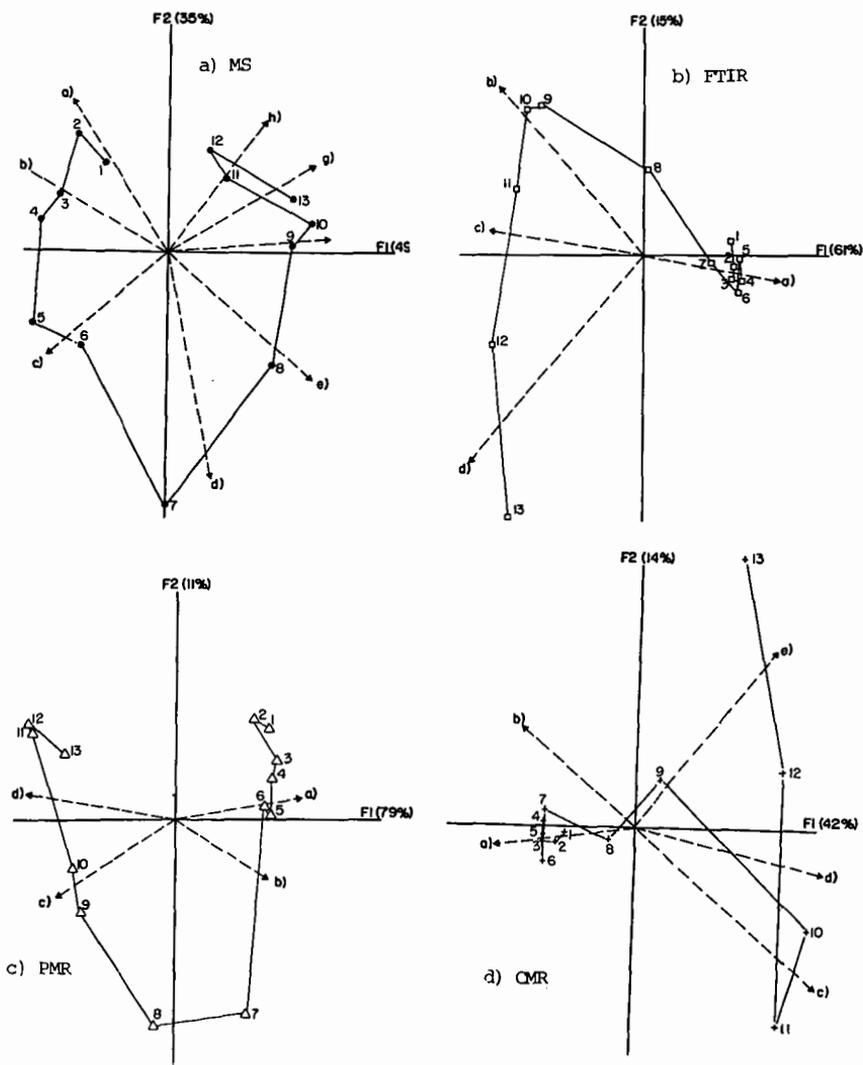


Figure 5. Factor score plots in FI/FII spaces of all four individual data sets.

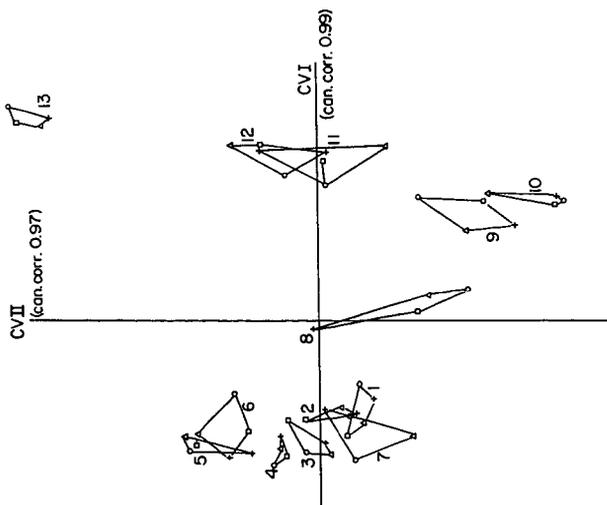


Figure 6. Combined score plots of integrated spectroscopic data in "common" CV1/CV2 space.

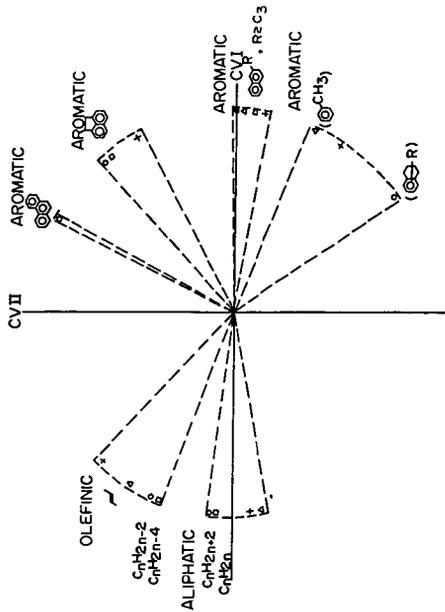


Figure 7. Combined loading plot of integrated spectroscopic data in CV1/CV2 space showing common chemical components.