

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.

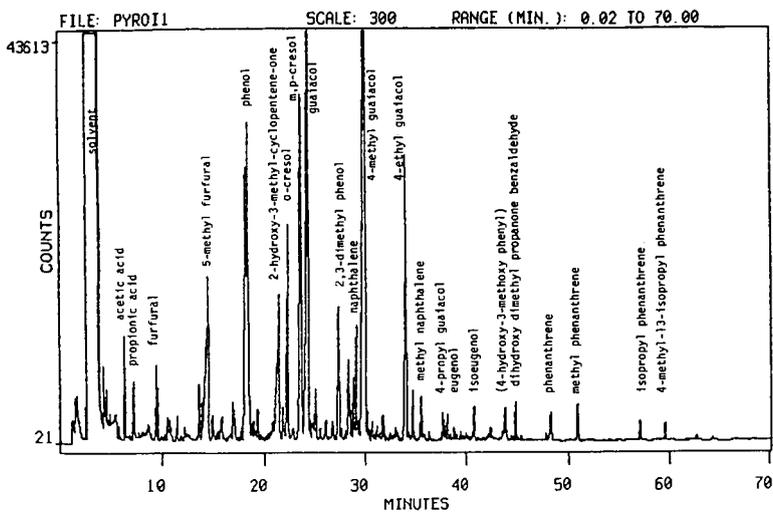


FIGURE 1. Volatiles of Tech-Air Pine Waste Pyrolysis Oil

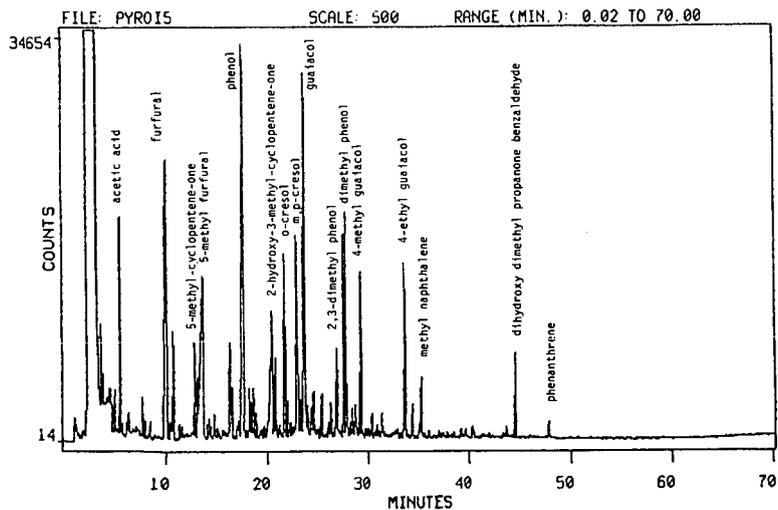


FIGURE 2. Volatiles of Corn Cob Gasification Tar

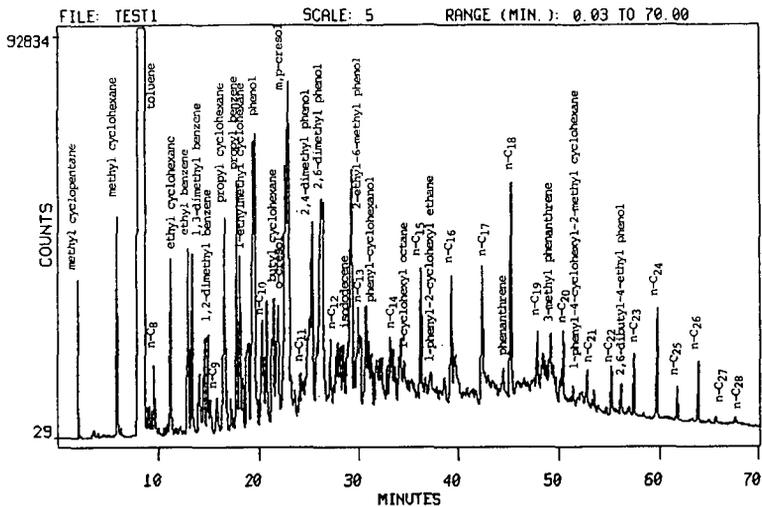


FIGURE 4. Volatiles of Hydroprocessed Tech-Air Pyrolysis Oil

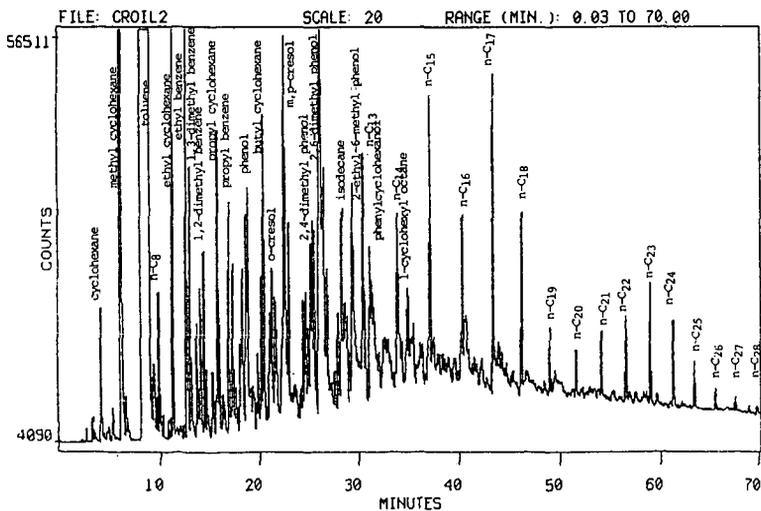


FIGURE 5. Volatiles of Hydroprocessed Corn Cob Gasification Tar

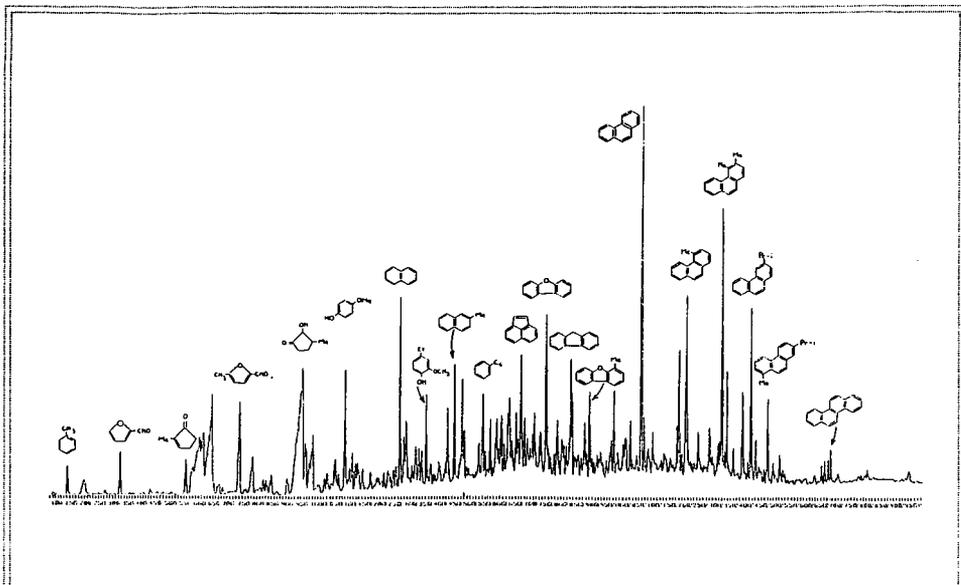


FIGURE 8. Aromatic Fraction (#4), Tech-Air Pyrolysis Oil

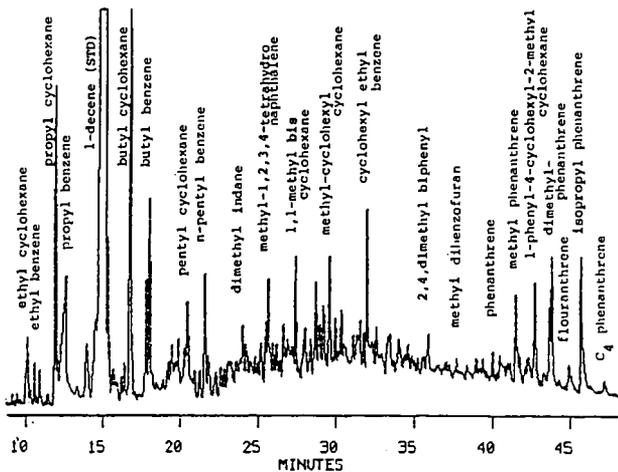


FIGURE 9. Aromatic Fraction (#4), Hydroprocessed Tech-Air Oil