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ANALYSIS OF MEDIUM-BTU GASIFICATION CONDENSATES JUNE 1985 - JUNE 1986

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DISCLAIMER

SUMMARY

This report provides the final results of chemical and physical analysis of condensates from biomass gasification systems which are part of the U.S. Department of Energy (DOE) Biomass Thermochemical Conversion Program.

The work described in detail in this report involves extensive analysis of condensates from four medium-BTU gasifiers. The analyses include elemental analysis, ash, moisture, heating value, density, specific chemical analysis (gas chromatography/mass spectrometry, infrared spectrophotometry, Carbon-13 nuclear magnetic resonance spectrometry) and Ames Assay. This work was an extension of a broader study earlier completed of the condensates of all the gasifiers and pyrolyzers in the Biomass Thermochemical Conversion Program. (1) The analytical data demonstrates the wide range of chemical composition of the organics recovered in the condensates and suggests a direct relationship between operating temperature and chemical composition of the condensates. A continuous pathway of thermal degradation of the tar components as a function of temperature is proposed. Variations in the chemical composition of the organic components in the tars are reflected in the physical properties of tars and phase stability in relation to water in the condensate. The biological activity appears to be limited to the tars produced at high temperatures as a result of formation of polycyclic aromatic hydrocarbons in high concentrations. Future studies of the time/temperature relationship to tar composition and the effect of processing atmosphere should be undertaken. Further processing of the condensates either as wastewater treatment or upgrading of the organics to useful products is also recommended. The analyses were performed on condensate samples provided by the reactor operators and are considered representative of the operating conditions given but they are not necessarily representative of optimum operating conditions.

CONTRIBUTORS

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INTRODUCTION

This report describes the results from a project titled "Comparative Analysis of Gasifier Tars" which was funded through the Biomass Thermochemical Conversion Program Office at Pacific Northwest Laboratory by the Biofuels and Municipal Waste Technology Division (BMWTD) of the U.S. Department of Energy. This project was conducted as a follow on to an earlier effort to characterize liquid effluents from pyrolysis and gasification systems which has already been described in a Final Report.(1) Much of the background description included in the earlier report also pertains to this research, but will not be repeated, only referenced.

The purpose of the earlier project was to analyze the condensate byproducts from the eleven process research units (PRUs) which were being funded by BMWTD. The analytical results were to be used in three ways:

1. provide useful descriptive data on the composition and properties of the condensate for use by the researchers to evaluate and develop their processes
2. identify the relationship of biomass tar properties and gasifier operating conditions in order to develop a global theory which could describe the effects of gasifier environments on tar properties
3. suggest areas requiring additional study including a projection of the utility of such research.

The purpose of this project was to build on the results of the earlier research by additional studies of condensates from long-term tests performed in four of the medium-BTU gasifiers.

This analytical project could not be possible without the cooperation of the individual researchers who have responsibility for the gasification PRUs in the BMWTD program. The samples and processing information were provided by the following people:

Mr. Herman F. Feldmann Mr. Mark A. Paisley	Battelle Columbus Laboratories (BCL) Columbus, Ohio
Dr. Suresh Babu Mr. Michael Onischak	Institute of Gas Technology (IGT) Chicago, Illinois
Dr. Virgil J. Flanigan	University of Missouri - Rolla Rolla, Missouri

Dr. Tom Milne	Solar Energy Research Institute (SERI) Golden, Colorado
Dr. Michael S. Graboski Mr. Gregory A. Graham	SynGas, Inc. (SGI) Golden, Colorado

The samples analyzed in this project were the best available samples at the time of the study. In some cases, certain analytical procedures had to be omitted due to the small sample size available. In other cases the samples may not have been representative of optimum operating conditions for the particular processes. These complications are typical of an analytical program operating from the outside of the particular process research and development project. However, this project does provide a useful collection of analyses of condensates representing biomass gasification processing modes under development today. In addition, useful conclusions can be made about the effect of reactor environment on condensate composition when comparing these results as a single group which could not be made based on the analysis of condensates from any one process alone.

BACKGROUND

The production of condensable organic tars during the thermochemical conversion of biomass is well known. Given that a tar product from thermochemical conversion of biomass is unavoidable, an understanding of its chemical and physical properties becomes a necessary part of process development. Whether the tar is the major product as in low-temperature, fast pyrolysis or only a troublesome byproduct as in gasification, the properties of the tar must be known in order to devise engineering solutions for dealing with the tar. Analysis of the tar is necessary in order to determine the means of utilizing or disposing of the tar through any of a wide variety of means involving either fractionation, or chemical and biological transformations. With sufficient understanding of tar properties, such fractionations or transformations might be designed into a conversion process or added afterward as product or byproduct treatment.

A review of the current understanding of biomass tar formation and composition was prepared for our earlier report.(1) That review indicated that the majority of the knowledge of biomass tars is derived from the study of tar formation during charcoal production. This type of low temperature tar, produced at temperatures up to 500°C, bears little resemblance to the tars produced in biomass gasifiers operating at 700° to 1000°C. This realization has only recently been articulated in the field of biomass conversion although it is well known in the field of coal processing. The differences between low-temperature coal tar and high-temperature coal tar have been studied for decades. Only the most recent results in supporting analytical chemistry for biomass gasifier process development have demonstrated similar chemistry is involved in biomass conversion, when performed at higher temperatures (>600°C).

The conclusions of our earlier project, as stated in the Final Report(1) were as follows:

1. Variations in the chemical composition of the organic components in the tars are reflected in the physical properties of tars and phase stability in relation to the ever present water;
2. The chemical composition of the tar is a reflection of the reactor environment and major changes between low temperature (around 500°C) and

high temperature tar (around 800°C) were noted as were the similarities between coal tar and wood tar reactions;

3. The development of a series of chemical mechanisms to explain the changes in tar composition as a function of processing conditions is needed in order to better understand the chemistry of biomass gasification; with such an understanding in hand the potential exists to use the tar analysis as a diagnostic tool to determine gasifier bed conditions;
4. The effect of gasifier/pyrolyzer atmosphere such as steam, nitrogen, air, oxygen, carbon dioxide or methane, on the tar composition is not clear at this time and requires further study;
5. Further processing of condensates from biomass gasification/pyrolysis has received only limited attention; waste water treatment and tar utilization will require the development of a range of techniques in order to deal with the range of condensate materials produced in the various conversion processes under study; and
6. The biological activity (as measured by Ames Assay for mutagenicity and mouse skin tumor initiation/promotion tests appears to be limited to the tars produced at high temperatures as a result of the formation of polycyclic aromatic hydrocarbons in high concentrations;

ANALYTICAL PROCEDURES

The analytical procedures described in this report are derived from a number of sources. For the most part these procedures have been developed over the period of the last eight years at Pacific Northwest Laboratory (2) in support of the DOE-funded biomass liquefaction research effort. These procedures are in turn a combination of modern instrumental chemical analytical techniques, American Society of Testing and Materials (ASTM) standard methods for petroleum products and procedures specifically adapted for biomass-derived liquids. The specific analyses were chosen to provide a chemical and physical characterization of the product so that comparisons could be made and correlations between properties and operating conditions could be identified. The analyses were performed on the tars and aqueous samples "as received."

ELEMENTAL ANALYSIS

For analysis of carbon, hydrogen, nitrogen and oxygen, the Perkin-Elmer 240 and 240B analyzers were used. Sulfur analysis could not be performed with these instruments due to the low level of concentration. The concentration of nitrogen was also at or below the limit of detectability with the P-E 240. The P-E 240 determines carbon, hydrogen and nitrogen by detecting and measuring their combustion products (CO_2, H_2O and N_2) (3). Combustion occurs in pure oxygen under static conditions and the products are analyzed by thermal conductivity. Helium is used to carry the combustion products from the combustion furnace through a reduction tube (which reduces any NO_x) and through the series of detectors and traps. For oxygen analysis, a separate sample must be pyrolyzed in helium over platinized carbon so that oxygen is converted to carbon monoxide. The carbon monoxide is scrubbed free of acid gases and then oxidized and measured as carbon dioxide. In all cases, the instrumental readout is in millivolts, from which the composition is calculated based on reference compounds.

ASH

Ash was determined by combustion in a muffle furnace similar to ASTM method, D-482-80 (4). This method covers determination of ash from distillate and residual fuels, crudes oils and other petroleum products. Porcelain crucibles with lids were used throughout.

pH

An approximation of the pH of the aqueous condensates was made using a series of quantitative pH papers. No attempt was made to degas the samples prior to the measurement.

HEAT OF COMBUSTION

Heats of combustion were obtained by combustion of the products in a Parr oxygen bomb calorimeter. An adiabatic system is maintained through the use of a controlled temperature water bath. Combustion of the samples in the bomb is a straight forward procedure; however, some difficulty with ignition of the samples was noted due to the large percentage of water in the tars. In these cases a fine cotton thread was used as a wick as suggested by the manufacturer (5). Heats of combustion could not be performed on the condensates which were primarily water.

AMES ASSAY

Agar plate mutagenicity assays using *S. typhimurium* TA98 and TA100 were carried out as described by Ames *et al* (6). DMSO was used as solvent for all of the chemical fractions. Benzo(a)pyrene and 2-aminoanthracene were used as positive controls. Revertant colonies were counted using a Biotran II automated colony counter (New Brunswick Scientific Co., Inc., Edison, N.J.).

Mutagenic activity in revertant colonies, expressed as revertant colonies of S. typhimarium/μg test material was estimated by linear regression analysis of dose-response data. A positive test was defined as having a maximum mutagenic response two-fold or greater above background, and a correlation coefficient 0.8 or above for the regression line with a positive slope.

The gasifier condensates in this study were assayed over three fixed concentration ranges of 10, 20, 40, 50, 100, 250 μg per petri plate, 20, 40, 80, 100, 200, 500 μg per petri plate, and 40, 80, 160, 200, 400, 1000 μg per petri plate. Each concentration was assayed in duplicate. Stock solutions of 10,000 μg/ml DMSO were prepared for use throughout these experiments and stored at -80°C when not in use.

To prepare liver homogenates Aroclor 1254 (Monsanto Chemical Corp.), at a concentration 250 g/kg body weight, was injected intraperitoneally into male Wistar rats. The rats were sacrified on the fourth day after injection. After sacrifice, the livers were perfused with ice-cold 0.154 M KCl and removed for preparation of S9 homogenates, following standard procedures.

The Ames Assay is a widely used test for a preliminary measurement which suggests chemical activity for promoting primary DNA damage. In our analysis we have used the two most sensitive tester strains. However, it is possible that mutagens were present that were not detected, although based on available data this is unlikely. Without more exhaustive tests it is not possible to draw firm conclusions as to the potential for promoting DNA damage.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

Solutions of the various gasification tar products were prepared at a concentration of 10 mg/ml in methylene chloride and analyzed qualitatively by GC/MS. The column was a 60 x 0.25 ID mm DB-5 WCOT silica capillary purchases from J & W Scientific, Inc. The column was contained in Hewlett-Packard (HP) 5890 gas chromatograph directly coupled with HP5970 mass selective detector. The HP splitless injection system was used with an injector temperature of $300^{\circ}C$ and an injection port pressure of 5 psig with helium carrier gas. The column temperature was programmed to $300^{\circ}C$ at $10^{\circ}C$/min with a starting temperature of $40^{\circ}C$. The portion of the column passing through the transfer zone between the GC and the MS was maintained at $300^{\circ}C$. The 70 ev electron impact spectra were recorded from 20 to 300 m/e at a scan rate of 250 amu/sec. One-microliter injections were used for these analyses.

Library searches are performed automatically using the Hewlett-Packard Probability Based Search (PBS) software. The search algorithm evaluates the significance of a match between the unknown spectrum and a library spectrum in terms of the probability that the match might occur by change. The probability is rounded off so that it can be expressed as one chance in 10 to the K power. Thus, ions which are very common will have a low value of K and will also have little diagnostic value. Uncommon ions will have large K's and be highly significant in assigning identities to unknown substances. The sum of the K values obtained by comparing the unknown to a library spectrum is taken as a measure of the quality of the fit. Using the PBS search technique has been found to give very reliable library searches given that the sample spectrum is relatively free of contaminants and the search parameters are judiciously chosen.

Whenever possible, identifications made on the basis of mass spectra were confirmed by comparison of the retention times and mass spectra of an authentic sample of the compound analyzed under identical conditions. The components which are unidentified are for the most part chemicals in very small concentrations which are not resolvable chromatographically. Based on routine study of the ion spectra from these compounds it can be stated that these compounds usually belong to the same chemical families as those identified.

The concentrations of each component in the tar products were estimated by GC (HP5880) with a flame ionization detector (FID) using the same conditions as for the GC/MS analyses. The MS data showed that resolution was adequate to obtain integration of single component peaks with the FID, and the FID was expected to give relative areas more accurately reflecting the mass concentration of each component than could be obtained from total ion or single ion peak area in the absence of a complete set of standards. However, the response of the FID is known to vary from compound to compound and is particularly affected changes in functional groups. In order to quantify the components without standardizing each one, the chemicals were separated into classes of compounds. The response of the FID was measured for representative members of each of the classes of compounds present. For example, the range of response factor values is 0.57 to 0.75 for oxygenated compounds, with the response of decalin defined as 1.00. Thus, error based on the assumption of an average response factor for an entire class of compounds should not exceed 15% when areas are adjusted using the mean of the response factor founds for oxygenated compounds (7). A response factor of 0.97 was used for the PAH components in the tars, based on the average response factor of naphthalene and anthracene. An internal standard, decalin, was used to allow measurement of loss of product in the chromatograph through decomposition or low volatility. For the study of the highly polar and thermally unstable tars in this program, loss of material within the chromatograph was a significant effect. Comparison of the actual amount of tar which could pass through the chromatograph can be used as a qualitative measure of the tar.

In the case of samples consisting primarily of water the concentration of the organic constituents was too dilute for GC/MS analysis. In these cases a methylene chloride extract was analyzed on the GC/MS to provide qualitative information only. This method provided a cusory view of the types of organic contaminants but the chromatography was designed primarily for the higher molecular weight components. As a result, the highly polar low-molecular-weight acids, alcohols and carbonyls were slighted by this analysis due to limitations of the extraction step as well as the chromatography.

INFRARED SPECTROPHOTOMETRY (IR)

IR spectrophotometry was performed with a Perkin-Elmer 283. The model 283 is a double-beam, optical null instrument with a grating monochromator and operating range from 4000 to 200 wave numbers. Samples of the biomass gasification tar products, as received, were compressed to a thin film between two barium fluoride discs. The discs were then placed in the sample beam for analysis. Typical scan time from 4000 to 200 wave numbers was twelve minutes in a percent transmittance mode (8). No attempt was made at quantification of spectra. IR analysis of aqueous samples was not attempted.

The IR analysis is a useful study of the chemical functional groups in the whole tar. Analysis is not limited to volatile components as in the GC/MS. IR provides a check on the GC/MS analysis by verifying the functional groups found in the volatile chemicals identified by GC/MS and also can confirm the components or the nonvolatile components.

NUCLEAR MAGNETIC RESONANCE SPECTROMETRY (NMR)

NMR studies of carbon-13 nuclei were performed with a Varian FT-80A system. Deuterated chloroform was used as the internal standard for carbon-13 spectra. The tars were dissolved in a solvent ($CDCl_3$) and filtered before analysis. NMR analysis was not performed on the aqueous samples.

The NMR provides additional confirmation of the chemical functional groups in the tar. The only limitation is that the tar components be soluble and the above-mentioned solvents were chosen for maximum solubility of the tar.

MEDIUM-BTU GASIFICATION SYSTEMS

A detailed description of the four reactor systems which were sampled for this study is given below. Table 1 summarizes the reactor operating conditions for each of the samples analyzed in this report. The operating conditions given in this report are those reported to be existing when the condensate sample was produced; however, they may not represent the optimum operating conditions for the particular reactor system. In addition, the samples analyzed were those provided by the reactor system operator and the

TABLE 1. Reactor Operating Conditions

	BCl[a]				IGT[b]	UMO	SGI[c]	SGI[c]
Test Ident.	4.19A	5	6	7	3D	9/13	air	oxygen
Steam, #/hr	0	368	355	365	474	204	0	0
Other gas, #/hr	89.8	79.6	86.0	87.8	169	0	71	19
Wood, #/hr	380	429	336	391	748	200	950	1910
Temp, °C	926	1004	1011	1014	850	723	927	927
Wood feed moisture, %	5	7.7	8.0	5.9	10.8	8.7	23.0	10.0
Pressure, psig	10	7.6	6.7	6.3	309	atm	atm	atm
Type wood	pine	pine	pine	pine	mixed hardwood	oak	pine	pine

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[a] All BCL tests included nitrogen as the other gas.
[b] The IGT test was oxygen-blown.
[c] The other gas in the SGI tests is indicated by the test identifier.

detailed development of the collection procedures was outside the scope of this analytical program. Determination of the amount of tar produced by each gasifier configuration was outside the scope of this project.

BCL MULTI-SOLIDS FLUIDIZED BED GASIFICATION (9)

A schematic of BCL's gasification PRU is shown in Figure 1. The process employs a hot sand phase as a conveying and heat transfer medium. Wood is fed into the gasifier with no pretreatment except partial drying to utilize sensible heat present in the flue gas from the combustor. The biomass is gasified to produce the fuel gas and a quantity of char typically equal to 20 percent of the dry wood fed. The char and sand are deentrained and transferred to the combustor where the char is burned. The condensate samples were collected at the bottom of the spray tower in which the product gas is cleaned prior to combustion.

The combustion of the char reheats the sand which is returned to the gasifier to provide the heat for gasification. By this method medium BTU gas is produced without the need for oxygen. The 12 ton/day PRU consists of a 10 inch ID gasifier coupled to a 40 inch ID combustor. The gasifier was constructed without refractory lining to reduce start-up and cool-down time as well as the time required to reach steady-state conditions. The gasifier was designed to operate at up to 870°C and 5 psig. The nominal gas velocity is 20 ft/sec, which gives a gas residence time of about one second in the 20 ft, long reactor. The combustor operates at temperatures around 1040°C.

IGT PRESSURIZED BIOMASS GASIFICATION (10)

In the IGT PRU system, as shown in Figure 2, the feed hopper and the associated solids handling equipment are designed for continuous feeding to the fluidized-bed gasifier. At the top of the continuously pressurized feed hopper is a two foot ID by six foot high lockhopper, equipped with quick-opening and closing gate valves and the provision for cyclic pressurization and depressurization with nitrogen. The feed hopper is 4 feet in diameter, 9 feet high, and equipped with a multiple-screw, live bottom, which meters and discharges the biomass material into the gasifier injector screw feeder. The lockhopper, valves, and feed hopper are designed for an operating pressure up to 500 psig and are capable of continuously feeding pulpwood-chip-size biomass up to 1500 lb/h.

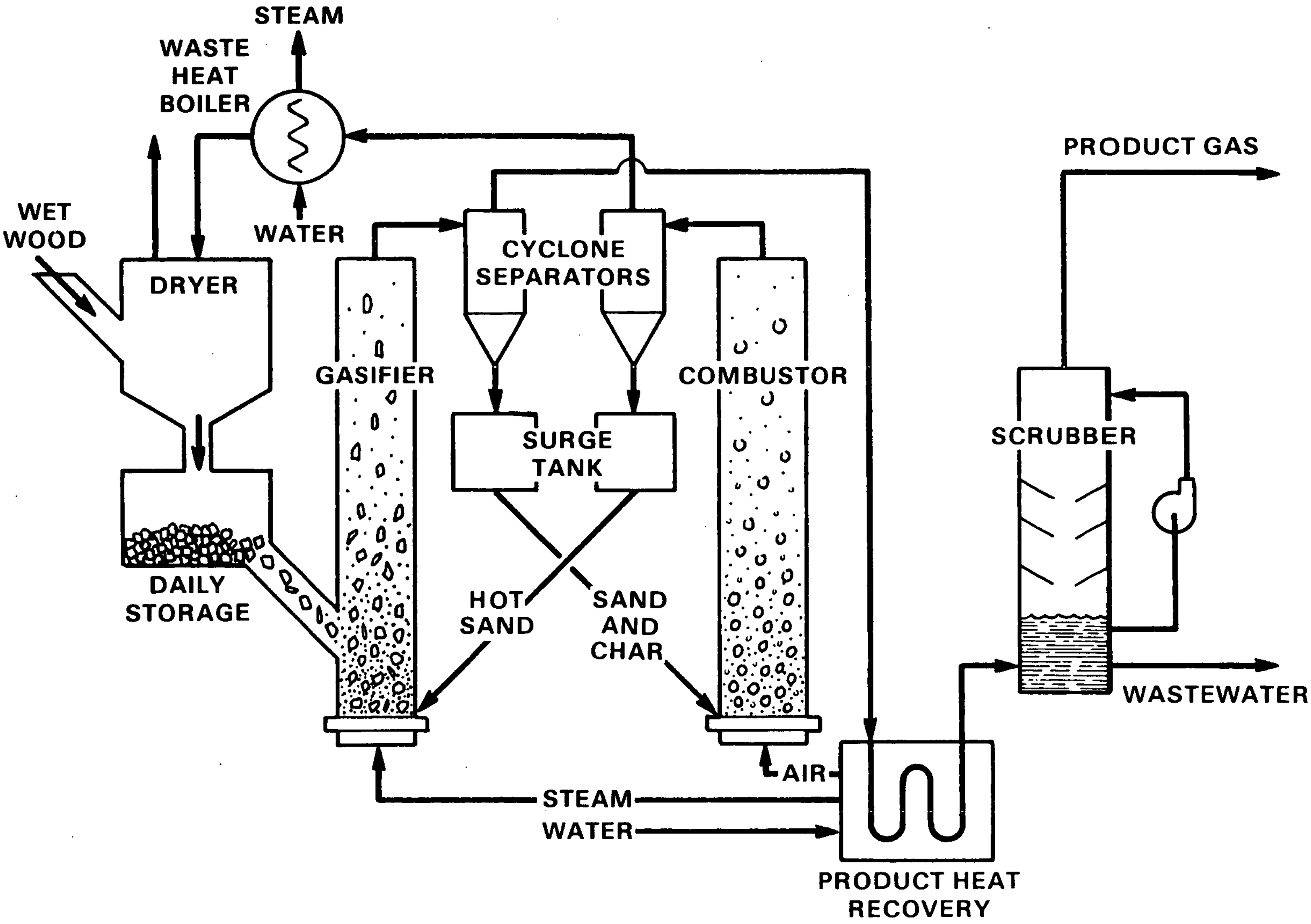

Figure 1. Battelle's Biomass Gasification Unit

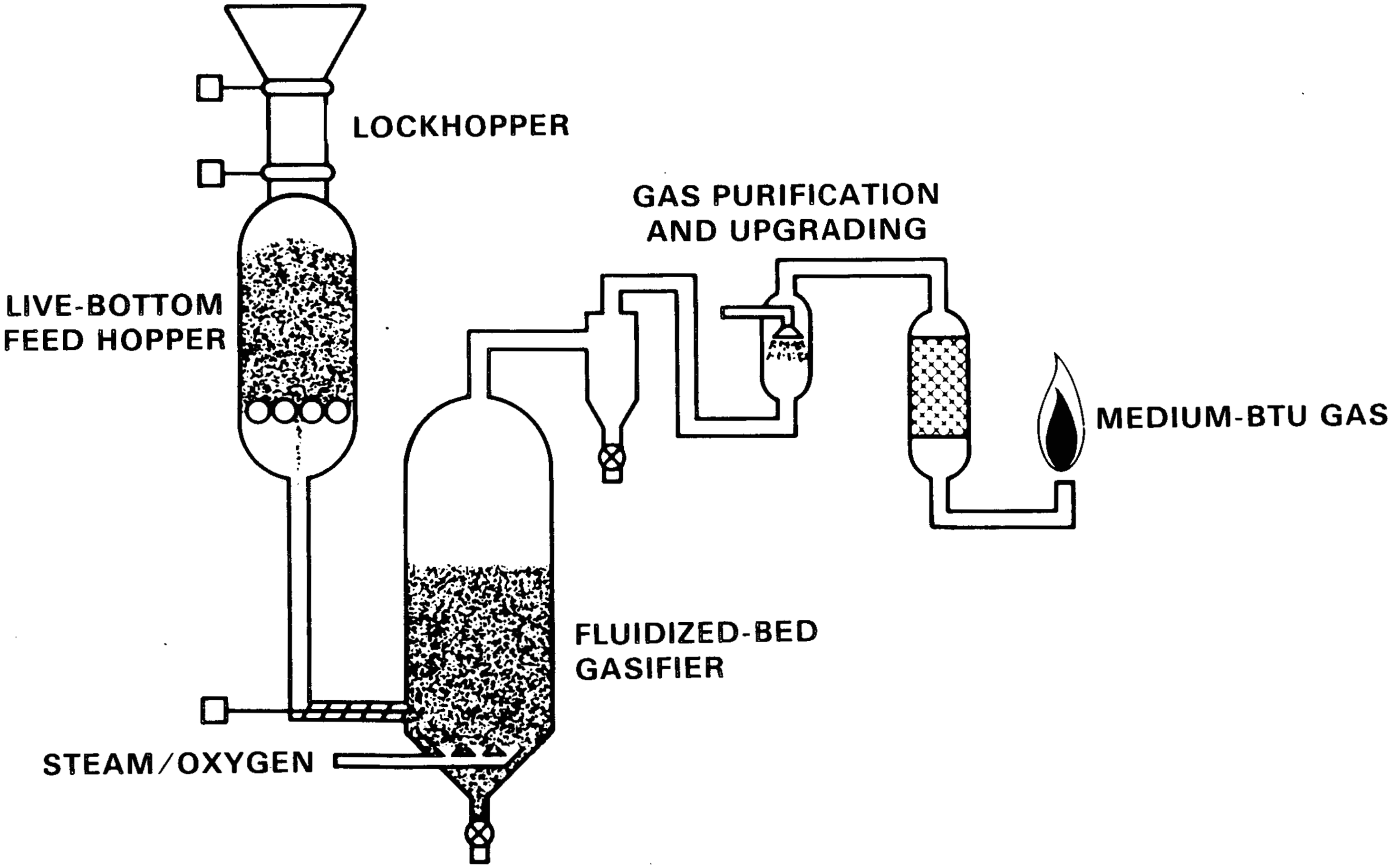

Figure 2. IGT Process Research Gasifier

The single-stage, fluidized-bed gasifier is a three foot OD, 22 foot high pressure vessel enclosing a 11.5 inch ID Incoloy 800H sleeve. It is well insulated for adiabatic operation at temperatures and pressures up to 980°C and 500 psig. The gasification zone is confined within a 11.5 inch ID, Incoloy 800H, balanced-pressure reactor liner, which is surrounded by one foot of low-thermal-conductivity fiber insulation. The enclosing three foot OD carbon steel pressure vessel with two horizontal six inch pipe nozzle positions about two feet apart for introducing the feed biomass materials. The total internal height of the gasifier is about 21 feet, with ten feet for the reaction zone at the bottom and eleven feet for an enlarged 1.5 foot diameter solids disengaging zone. The gasifier bottom closure flange has provisions for introducing the fluidization and gasification medium (steam and oxygen), a support lance for thermocouples and fluidized-bed differential pressure probes and a solids drain. Two fluidizing gas distributors are provided. One distributor is exclusively for steam and is positioned under the other to maintain fluidization around the steam-oxygen distributor. This eliminates the formation of a zone of stationary solids near the steam-oxygen distributor, reducing the exposure of the solids to possible sintering conditions.

The solids receiver vessel is a three foot ID, six foot high, carbon-steel pressure vessel. It is refractory lined to withstand hot raw gases. It functions as a hot, pressurized filter and contains three removable trays filled with a filter medium of pebbles or layers of stainless steel wool to trap the particles entrained with the raw gas stream. The filter media and baskets are weighed before and after each run to estimate solids carryover and the collected solids samples are analyzed chemically.

The piping between the gasifier and the solids receiver and between the solids receiver and the water spray quench line is also refractory-lined carbon-steel pipe. Partial quenching with water is done in the solids receiver and the quench tower just to cool the gases, avoiding liquid condensation, so that carbon steel pipe can be used to pipe the product gases to a flare for disposal.

The PRU is equipped with an on-line isokinetic sampling system at the gasifier exit to obtain large raw-gas samples for measuring the solids carry-over and condensable liquids production. The sampling system is operated for one-hour periods during the steady-state operation and withdraws a raw gas sample at a rate of approximately 1% of the total flow from the gasifier. The solids are first trapped in a hot sintered metal filter, then the steam is cooled and the liquids are condensed in a water-cooled condenser followed by an ice-water bath. The condensate-free raw gas is metered and vented.

UNIVERSITY OF MISSOURI-ROLLA FIRE TUBE GASIFICATION (11)

The gasifier system is shown in Figure 3. The steam is supplied by a 45 horsepower low pressure boiler. The output steam is superheated up to 650°C using a 178-Kw electrical preheater. The wood is stored in a large bin which supplies a weigh barrel. The weighed feed is dumped into the feed hopper which augers the dry wood into the bed of the reactor. The resulting gas passes through the cyclone for char removal and is piped to the flare.

The reactor is a 20 inch I.D. and 17 feet high stainless steel cylinder with several access ports. The feed ports were constructed to provide tangential feed entry. A special design was required at the top of the reactor to permit fastening of the wires used for supporting the fire tubes.

The fire tube heat exchanger was formed from 30 u-tubes using 0.824 inch I.D. x 1.05 inch O.D. rolled alloy tubes (RA 330). All the tubes were made to pass through the distributor plate and were circumferentially welded on the tube sheet. The assembled bundle was slipped into the opening of the tee section of a Van Packer combination chamber, a large section of prefabricated chimney, and set on a compressible gasket. The two propane burners were mounted on the ends of the tee section and the burners are capable of producing 2 million Btu/hr (586 Kw) at maximum firing. The burner control senses the bed temperature and the over temperature control senses the combustion chamber temperature.

The gasifier condensate was removed in a gas scrubber system. One liter of water contained in a filter flask was used as the scrubbing solution. During a twenty minute period 120 liters of product gas were passed through the solution to yield 1190 ml of condensate solution. The additional volume of solution is due to water vapor and tar condensation. The tar was present as a separate phase well-dispersed in the solution and adhering to the walls of the flask as tiny droplets.

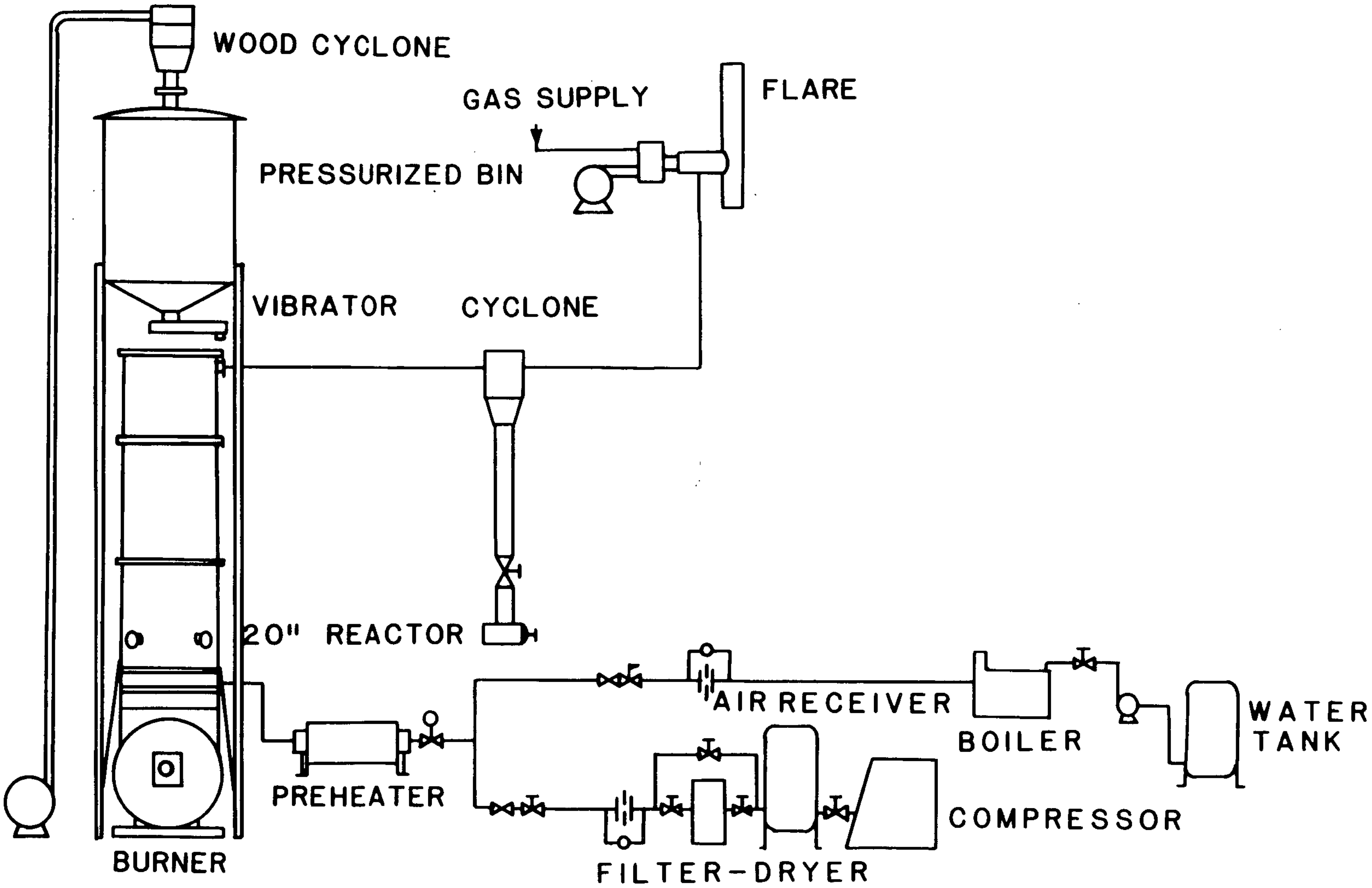

FIGURE 3. University of Missouri-Rolla Biomass Gasification Unit

SGI STRATIFIED DOWNDRAFT GASIFICATION (12)

A 20 ton/day moving-bed downdraft gasifier, built by SynGas Incorporated was the source of the samples analyzed in the second phase of our project. The unit is based on the stratified downdraft gasification concept as used in the SERI quartz reactor which was sampled in our earlier project. As shown in Figure 4, green wood chips are fed with air or oxygen into the top of the reactor. The bed height is maintained at 6 1/2 to 7 feet with a diameter of 30 inches. The reactor is fabricated of mild steel and is refractory-lined. Typical operating data for the air-blown case are 950 lb/hr wood and 325 SCFM air while in the oxygen-blown case representative operating data include 1910 lb/hr wood with 97 SCFM of oxygen. Maximum temperatures in the gasifier bed range up to 927°C in both cases. Product gases are withdrawn from the bottom of the reactor at a temperature of 732°C in the air-blown case and 650°C in the oxygen-blown case.

The gasifier condensates were collected by two different methods for these two tests. In the air-blown test we received the total condensate from a condenser on a slip stream of the product gas. Analytical results for both the aqueous phase and the insoluble tar phase are presented in this report. In the oxygen-blown case the product gas slipstream was passed through a wet-scrubber and only the insoluble tar collected from the bottom of the scrubber was analyzed.

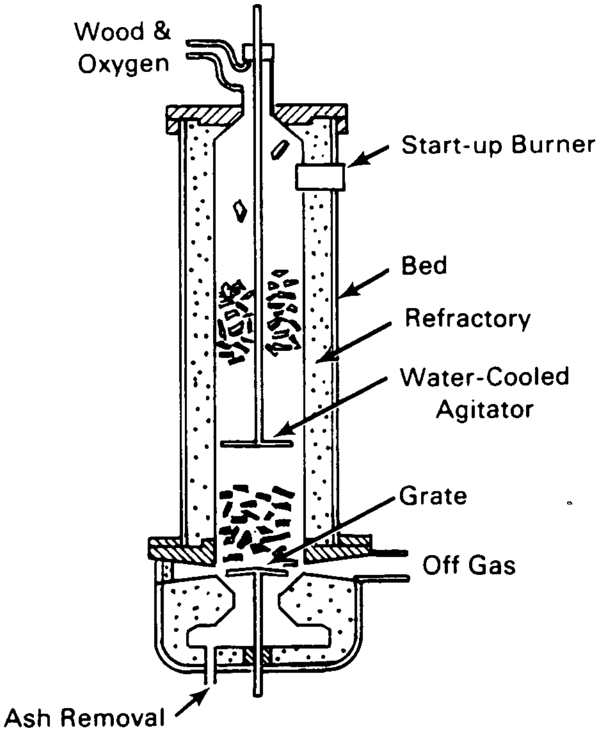

FIGURE 4. Diagram of the SGI Stratified Downdraft Gasifier

ANALYTICAL RESULTS

A number of samples from the different gasifier systems were analyzed in varying degrees of detail. The primary focus of this project has been the comparative use of the analytical data. Based on the analyses in this report the analyses presented in the earlier Final Report (1), some overall conclusions can be drawn. These conclusions are presented in the last section of this topical report.

Comparative analysis was performed for condensates from the four systems discussed earlier. Both aqueous and tar phases are present in the condensates analyzed in this phase of our project. The tar phases are considered first, followed by the aqueous phases. The results of biological tests (Ames Assay) are presented last.

The condensate samples from all the reactor systems in this project are subject to the effect of laboratory scale operation which can have large effects on the relative concentrations of tar and aqueous condensates due to the conditions of recovery. When comparing these samples, due consideration must be given to the means of collection of the samples.

Tar Phase Analysis

The samples include one each from the IGT, University of Missouri and SGI downdraft system in the air-blown and oxygen-blown mode and several from the BCL reactor representing operations over a range of temperatures. The results of the analyses of these tars are presented in Table 2. The results are for crude tars as produced and therefore contain varying amounts of water either by solution or emulsion. The small amounts of tar recovered for analysis in all but the BCL system make extensive analysis for moisture or ash content all but impossible. The IGT condensate had already passed through a hot filtration system to remove char (and, presumably, the ash) and its low oxygen content suggests that is contains very little water. The BCL tars, being entrained-flow tars, contain a noticeably higher ash content. Although these tars have passed through a hot cyclone for char separation, char carryover is suggested by both the high ash content and high level of insoluble (by acetone/xylene wash) material. The composition of these insoluble materials with be discussed more fully later.

TABLE 2. Analytical Data for Tars

	BCL				IGT	UMO	SGI	SGI
	4.19A	5	6	8	3D	9/13	air	O_2
carbon, %	51.3	84.9	78.4	83.7	93.5	74.5	60.0	66.0
hydrogen, %	7.6	4.5	5.2	4.3	6.0	5.4	7.1	7.6
oxygen, %	38.0	8.6	14.	8.2	0.5	17.2	31.4	25.0
ash, %	3.1	2.0	2.1	3.7	--	--	0.9	0.0
moisture, %	38	8	--	--	--	--	--	--
HHV, BTU/lb	--	14600	13500	14700	16860	--	8680	--
density, g/ml	>1	>1	>1	>1	--	--	--	>1
insolubles, %	14.2	37.0	49.5	39.6	--	--	--	--

More detailed chemical analysis was also undertaken for several of these tar samples. Both IR and NMR (carbon-13) were used and a GC/MS analysis was also done on the IGT, BCL 5, and SGI tars; the UMO sample was of such a limited amount that only the qualitative GC/MS analysis was practical. The IR spectra are collected in Appendix A; the NMR spectra are collected in Appendix B. Detailed listings of chemical components from the GC/MS analyses are included on Appendix C.

These analyses correlate well with the compositional analyses. The high temperature tars (BCL and IGT) are primarily aromatic hydrocarbons. The UMO and SGI tars, which have high oxygen levels, contain substantial amounts of phenolic and oxygenated hydrocarbon components. The presence of these oxygenated components correlates well with the low-temperature operation in the UMO gasifier but suggests a significant amount of channeling to bypass the hot zone in the SGI gasifier. The presence of such components as the guaiacyl components, which are typical of low temperature pyrolyzates, suggests that some of the tar product results from limited thermal treatment. The presence of the larger PAH suggests that other tar components were subjected to much more severe thermal treatment.

Aqueous Phase Analysis

The aqueous phase composition is a direct result of the tar composition. In the higher temperature gasifiers (IGT and BCL) which produce an aromatic hydrocarbon tar, the aqueous phase carries only a small amount of carbon due to the insoluble nature of the tar. The BCL 6 aqueous was measured at 0.02% carbon (200 ppm) and the IGT 3D aqueous was at 0.2% carbon (2000 ppm). The pH of both streams was at about 6.5. The SGI condensate aqueous phase from the air-blown case was highly contaminated (6.5% carbon, 3.2 pH). This analysis is in stark contrast to previous reports of downdraft gasifiers operating as tar-free gas generators. In fact, the sample bears no resemblance to the sample received from the SERI bench-scale stratified downdraft gasifier.(1) The low level of contamination in the UMO aqueous condensate (0.25% carbon, 6.0 pH) points up an important consideration. The UMO condensate was recovered by passing product gas through an aqueous bath to scrub out the tars. Based on the dilution factor of the scrubbing solution the calculated concentration of the actual condensate would be 1.6% carbon. It is highly doubtful that the UMO gas scrubber system is representative of large-scale operation.

Biological Activity Test Results

Limited biological testing was done on these samples. The BCL 5, IGT 3D, and SGI air tars were tested in the Ames Assay. With the TA100 strain the BCL was strongly active only with the S9 promotor. The IGT was slightly less active also only with the S9. With the TA98 strain both the IGT and BCL tars were active with and without the S9 promotor. The interference due to culture mortality was noted at concentrations of 200 µg/plate and above. The SGI air tar was inactive under all conditions and the culture mortality was not a factor. Detailed results are in Appendix D.

DISCUSSION OF RESULTS

The discussion of results in the Final Report(1) for the first phase of this project provides some useful insights which appear to be further substantiated by the analyses presented in this topical report. To summarize the Final Report discussion, the most significant fact which has been clearly demonstrated by this research is the wide variability of gasification "tars." The tar composition is dependent on operating conditions and appears to closely correlate with temperature, at least in short-residence-time fluidized-or entrained-bed reactors. The tar compositions are a continuum which change with processing temperature. There is no typical tar composition for all biomass gasifiers nor is it reasonable to classify the organic condensates as "primary oils" and "secondary tars" as has been attempted by some(7) since both categories merge into each other at intermediate processing conditions. The chemistry which transforms the biomass tar components over the operating range of 500° to 1000°C appears to be similar to that described earlier for coal tar pyrolysis. The chemistry which differentiates coal from biomass is essentially relegated to lower temperature conditions.

A general pathway of tar chemical functional degradation is suggested below. This hypothetical pathway is meant to represent the nature of the tar composition as a function of thermal processing with the full realization that specific mechanisms can bypass steps in the pathway or alternatively result in gas or char formation. The initial signs of breakdown of high molecular weight biomass polymers into low molecular weight oxygenates is outside the scope of this study.

mixed oxygenates → phenolic ethers → alkyl phenolics → heterocyclic ethers → PAH → larger PAH

PROCESSING CONDITION EFFECTS ON TAR COMPOSITION

In comparing the condensates from the four medium-BTU gasifiers in the BMWTD biomass gasification program (see Table 2) one is impressed with the large amount of variability in the tar compositions. While much of this variability results from the basic chemical mechanisms occurring within the gasifiers, another significant factor is the difference in condensate collection within each of the systems. The BCL system includes a char cyclone which appears to allow substantial entrainment of dust as shown by the high ash and insoluble char levels in the tar products. Also the quench system appears to be ineffective in recovery of the light aromatic hydrocarbons (BTX and naphthalene) which must be carried in the gas product stream. In contrast, the IGT system includes a hot filter unit which more cleanly separates the solids from the volatile material. In addition, the condenser in the isokinetic probe is more effective in collecting the light hydrocarbons as shown by their high concentrations in the condensate (see GC/MS data table, pg. C.1).

The lower operating temperature in the UMO gasifier results in a condensate tar of substantially different chemical content compared to the higher temperature IGT and BCL units. This tar should be more susceptible to biological degradation than the PAH-containing tars produced at higher temperature. While this type of tar is essentially inactive as a mutagen, it is likely to be significantly more toxic than the PAH-containing tars. The chemical composition of the SGI tars suggests that they too are low temperature products. This implies that some portion of the tar components were not exposed to the hot zones in the gasifier which are measured at temperatures in excess of 900°C. Apparently, there is a significant amount of channeling in the bed to bypass the hot zones.

In order to more clearly distinguish the effect of reactor operating temperature as opposed to system idiosyncracies, it was necessary to examine several products from the same gasifier. We were able to analyze several different tar products from the BCL gasifier as shown in Table 3. These products represent a range of operating temperatures but essentially the same gas residence time in the gasifier. Although there is some inconsistency in the data, several trends are evident. The following correlate with increasing operating temperatures:

- increasing aromatic composition, although the aromatic content is already very high even at the lowest temperature shown here,
- decreasing amount of methyl substitution on the aromatic structure,
- decreasing hydrogen to carbon atomic ratio and a decreasing amount of oxygen in the tar components,
- increasing amount of toluene insoluble material, indicating higher molecular weight tar components.

TABLE 3. BCL Multi-Solids Fluidized-Bed Gasifier Tar

Gasifier Temperature	Aromatic Composition 13C NMR(a)	Methyl Aromatic Composition 13C NMR(a)	DAF Tar Composition H/C:0%	DAF Toluene-Insoluble Solids	DAF Toluene Insoluble Solids Composition H/C:0%
880°C	95.2%	2.6%	0.81:8.8	19.0%	0.27:3.9
900°C	94.0%	3.1%	0.66:4.0	27.2%	0.27:6.0
930°C	98.3%	0.3%	0.79:7.1	24.1%	0.33:5.1
1000°C	98.8%	0.2%	0.50:1.7	41.2%	0.25:1.5

(a) NMR spectra are in Appendix B.

The elemental composition of the toluene insoluble material appears to not change over the temperature range given; only the amount of this highly condensed, aromatic material in the tar changes.

These correlations support the hypothesis of a changing chemical composition as a function of operating temperature at a short residence time. The high temperature reactions suggested by these results are cyclization and condensation to form aromatic structure, demethylation and dehydroxylation of the aromatic ring structure and also the formation oxygen-containing heterocyclic aromatic structures as suggested by the significant oxygen content left in the insoluble solids which are so hydrogen-deficient.

Additional tar analysis studies have also been undertaken recently at IGT(4) which support our own observations. They also found, in their reactor, that "higher operating temperatures, in addition to reducing the oil yield, also cause a sharp decline in the relative concentrations of hetero-cyclic and alkyl-substituted hydrocarbons in favor of unsubstituted aromatic hydrocarbons." Similar to our report of decreasing phenolic production [Figure 12 in our earlier report (1)] IGT found that phenols decline by 97-99% with an increase in gasifier temperature from 754° to 821°C.

The IGT researchers concluded that increased operating pressure and steam to wood feed ratios would also reduce tar formation in the gasifier. Increasing

[Figure 12 in our earlier report(1)] IGT found that phenols decline by 97-99% with an increase in gasifier temperature from 754° to 821°C.

The IGT researchers concluded that increased operating pressure and steam to wood feed ratios would also reduce tar formation in the gasifier. Increasing operating pressure from 102 to 300 psig decreased tar formation while steam to wood ratios of less than 0.7 lb/lb resulted in higher tar yields. Finally, the IGT researchers reported some correlation in tar yield as a function of feedstock type with the suggestion that non-woody biomass components (foliage and bark) resulted in higher tar formation.

CHANGES IN BIOLOGICAL ACTIVITY AS A RESULT OF VARIATION IN TAR COMPOSITION

Our results show activity only in high-temperature processed tars. Specifically the Ames assay shows activity only in the tars generated at temperatures above 800°C. An earlier mouse skin tumor initiation and promotion study(1) also suggested limited activity in tars generated at temperatures down to 750°C and in the updraft tar, which is likely a composite of tars produced over a broad range of temperature up to 1400°C. Tars produced at temperatures in the range of 500°C and dilute aqueous samples produced over the whole range of study show no activity in the Ames assay and, for the limited number of cases studied, no activity for mouse skin tumor initiation.

Table 4. has been included as a summary of the Ames Assay results for the three tars tested in this study and also similar tars from our earlier work (1). By the data in Table 4. one finds that the only biological activity is exhibited by the high temperature tars from the fluidized- or entrained-bed gasifiers (IGT and BCL). Neither of the samples from the downdraft gasifiers (SGI and Rocky Creek) showed any activity nor did the tar from the updraft gasifier (Rome, GA). The GA Tech tar is included to show that an entrained-bed pyrolyzer operated at lower temperatures will produce a tar without biological activity.

It is apparent that the activity correlates strongly with the concentration of high molecular weight PAH in the sample. This result is not surprising. Duncan (13) refers to a Japanese paper in which the carcinogenicity of skin creams derived from biomass tars could be correlated with the content of PAH. Other studies at PNL (14) with fractionated coal liquids have demonstrated that the mutagenic activity is concentrated in the organic base fraction in a hydrocarbon mixture; again suggesting that the higher molecular weight PAH are more active mutagens.(15)

Based on the above information, a potential processing dilemma has now been identified. Higher temperatures are generally perceived to improve the efficiency and rate of gasification. In addition, our data also suggests that less contamination will remain in the aqueous byproduct stream when the gasification is performed at higher temperature. On the other hand, the tar components that do remain following higher temperature processing are more highly condensed PAH which result in a higher level of mutagenic activity. Another consideration is the effluent treatment required for these contaminated aqueous streams. The transformation from phenolic to PAH is strongly a function of temperature in the range of 700° to 950°C. It is highly unlikely that the different waste water contaminants would all be treated by the same technique. Therefore waste water treatment requirements for the aqueous condensate stream will vary for different gasifier systems with operating temperature being the major independent variable.

Table 4. Ames Assay Results for Several Biomass Gasification Tars

µg/plate	BCL #5	IGT 3D	SGI air	BCL* pine	BCL* oak/maple	GA Tech*	Rocky Creek*	Rome GA*
TA98 w/o S9								
10-250	+	+	-	NT	NT	NT	NT	NT
20-500	+	+	-	++	+	-	-	-
TA98 w/S9 (20µl)								
2-50	NT	NT	NT	++	+	-	-	-
10-250	++	+	-	NT	NT	NT	NT	NT
20-500	++	+	-	+	+	-	-	-
TA100 w/o S9								
20-500	-	-	-	-	-	-	-	-
40-1000	-	-	-	NT	NT	NT	NT	NT
TA100 w/S9 (20µl)								
2-50	NT	NT	NT	++	++	-	-	-
20-500	++	+	-	NT	K	-	-	-
40-1000	++	K	-	NT	NT	NT	NT	NT

*samples from reference (1)
BCL Pine = softwood feed to BCL gasifier at 880°C
BCL oak/maple = hardwood feed to BCL gasifier at 900°C
GA Tech = primary pyrolyzate tar produced at 450°C
Rocky Creek = small downdraft gasifier
Rome GA = updraft gasifier

++ = strong activity + = probable activity - = activity not detectable

K = culture mortality interference

NT = sample not tested at specified concentration range

CONCLUSIONS

Based on the results of these analyses the conclusions from our earlier study(1) are reaffirmed. The conclusions are restated below.

1. Variations in the chemical composition of the organic components in the gasifier tars are reflected to some extent in the physical properties of tars and phase stability in relation to the ever present water;
2. The chemical composition of the gasifier tar is a reflection of the reactor environment and major changes between low temperature (around 750°C) and high temperature tar (around 1000°C) were noted as were the similarities between coal tar and wood tar reactions;
3. The development of a series of chemical mechanisms to explain the changes in tar composition as a function of processing conditions is needed in order to better understand the chemistry of biomass gasification; with such an understanding in hand the potential exists to use the tar analysis as a diagnostic tool to determine gasifier bed conditions;
4. The effect of gasifier/pyrolyzer atmosphere such as steam, nitrogen, air, oxygen, carbon dioxide or methane, on the tar composition is not clear at this time and requires further study;
5. Further processing of condensates from biomass gasification/pyrolysis has received only limited attention, waste water treatment and tar utilization will require the development of a range of techniques in order to deal with the range of condensate materials produced in the various conversion processes under study; and
6. The biological activity (as measured by Ames Assay for mutagenicity) appears to be limited to the tars produced at high temperatures as a result of the formation of polycyclic aromatic hydrocarbons in high concentrations.

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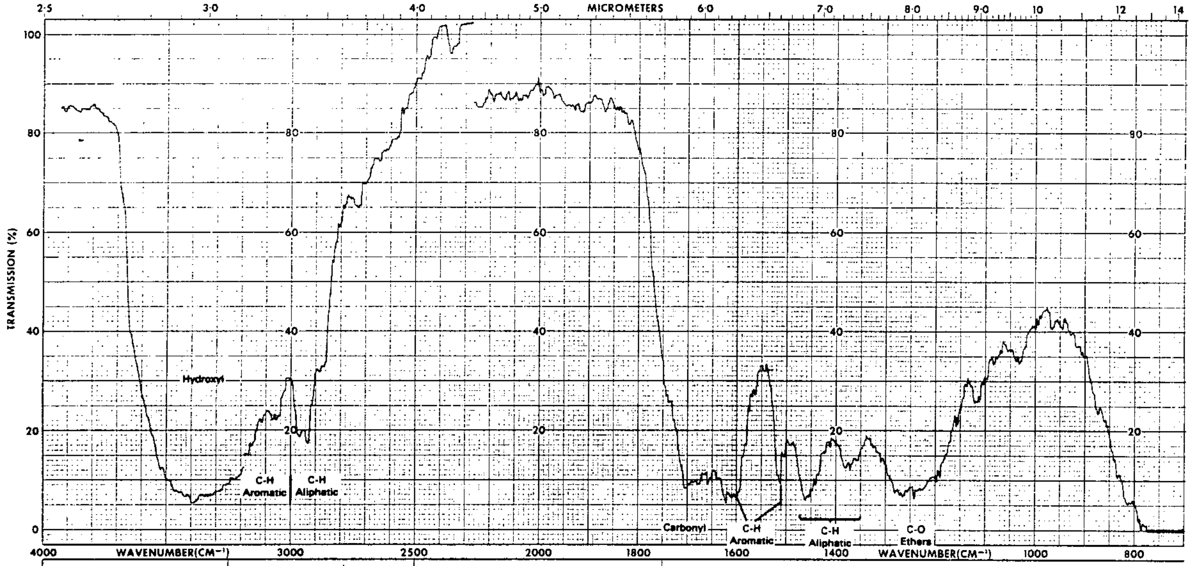
APPENDIX A

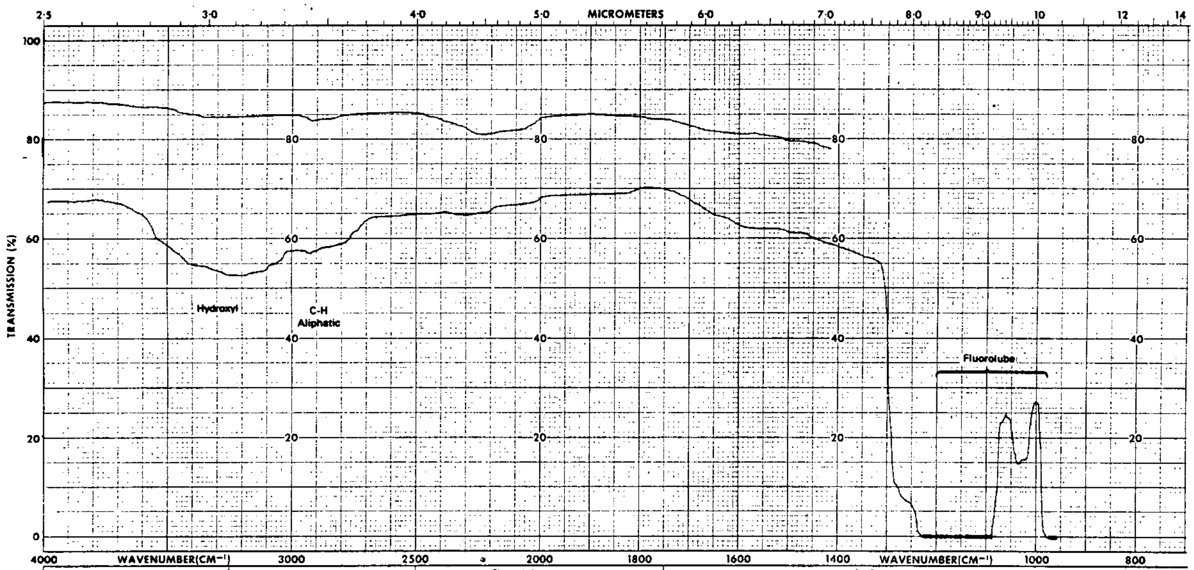
INFRARED SPECTRA OF BIOMASS GASIFICATION TARS

INFRARED SPECTRA OF BIOMASS GASIFICATION TARS

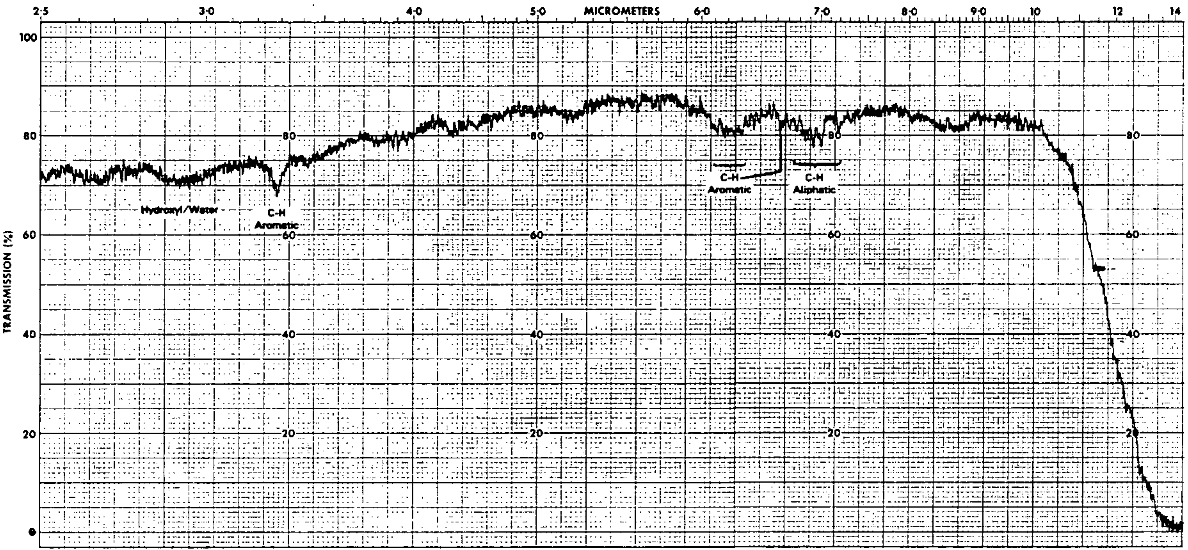
This appendix is a collection of four infrared spectra. The tar sample represented by each spectrum is identified on the spectrum. Scan times and sample presentation parameters are also identified on the individual spectra. Representative functional groups identified for the important adsorption bands have been identified on the spectra.



SAMPLE SGI-O_2 ORIGIN	REMARKS Normal Parameters 6 min. Scan w/Supp	SOLVENT Neat CONCENTRATION CELL PATH BaF_2 Plates REFERENCE Air



SAMPLE SGI-air ORIGIN	REMARKS Normal Parameters 6 min. Scan w/Supp	SOLVENT Fluorolube CONCENTRATION CELL PATH BaF_2 Plates REFERENCE Air



SAMPLE BCL #5

ORIGIN

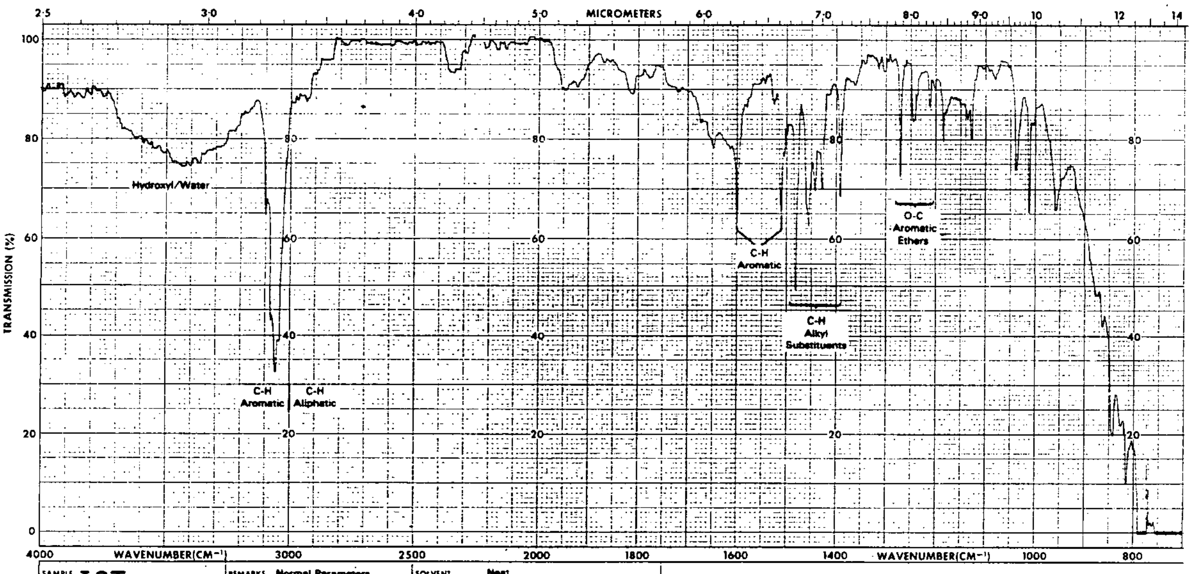
REMARKS Wide Slit Program 24-min. Scan

SOLVENT Neat

CONCENTRATION

CELL PATH BaF₂ Plates

REFERENCE Air



SAMPLE IGT

ORIGIN

REMARKS Normal Parameters 6 min. Scan w/Supp

SOLVENT Neat

CONCENTRATION

CELL PATH BaF₂ Plates

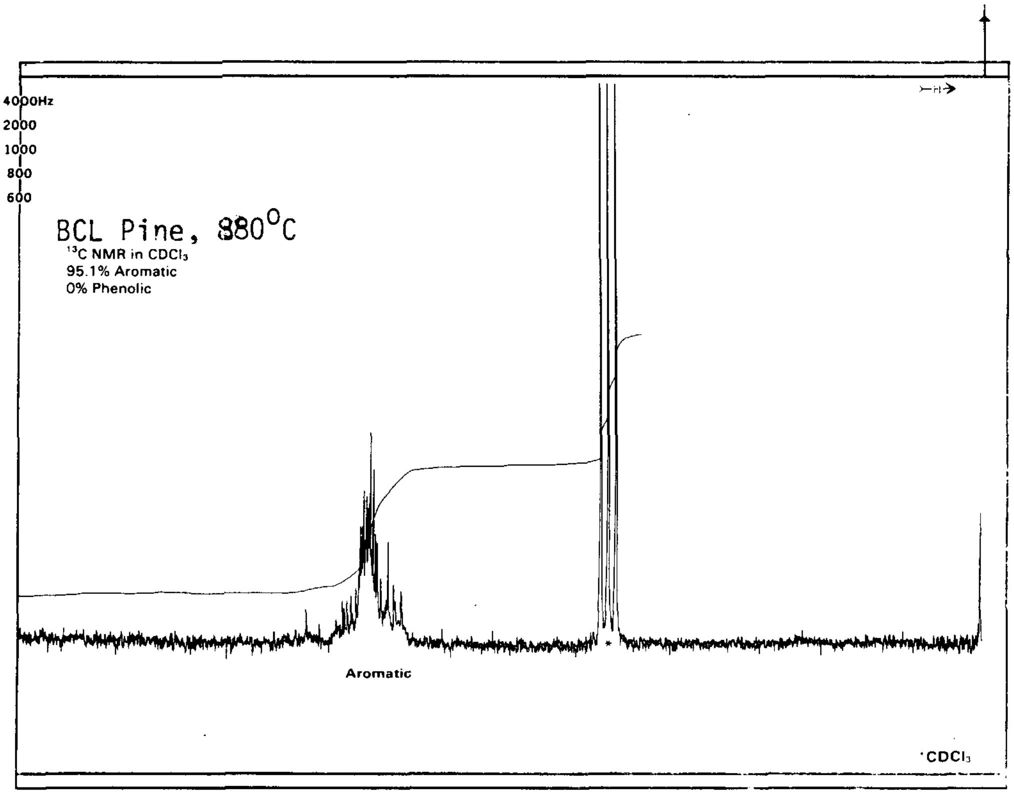
REFERENCE Air

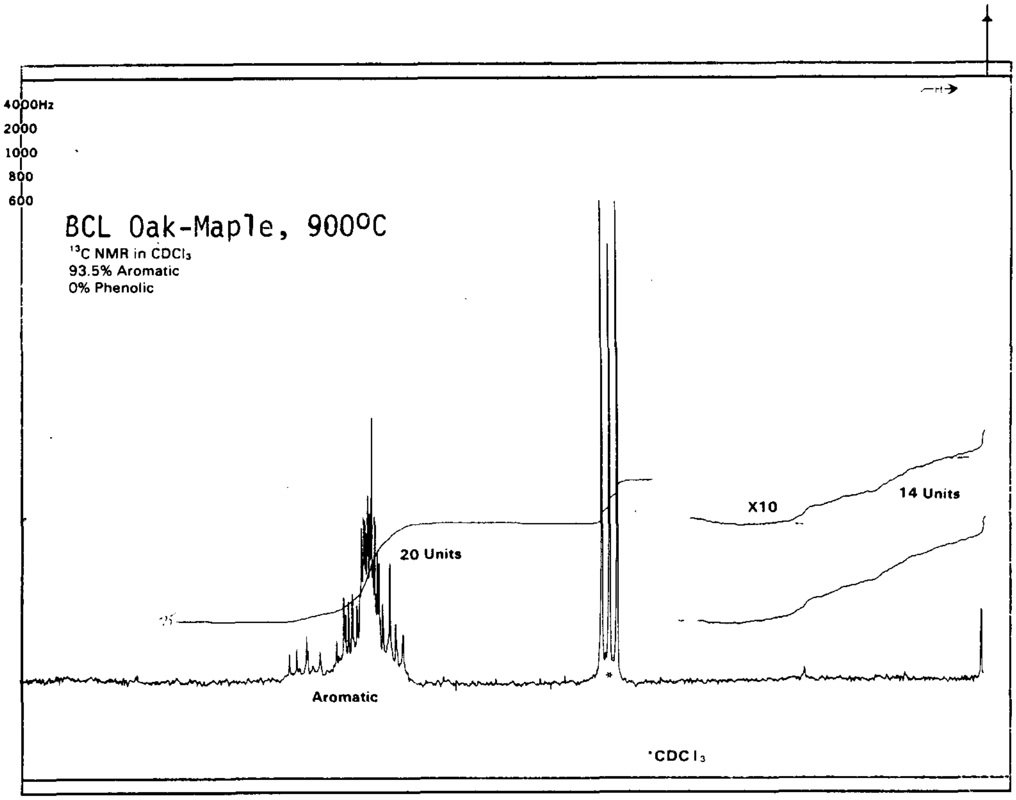
APPENDIX B

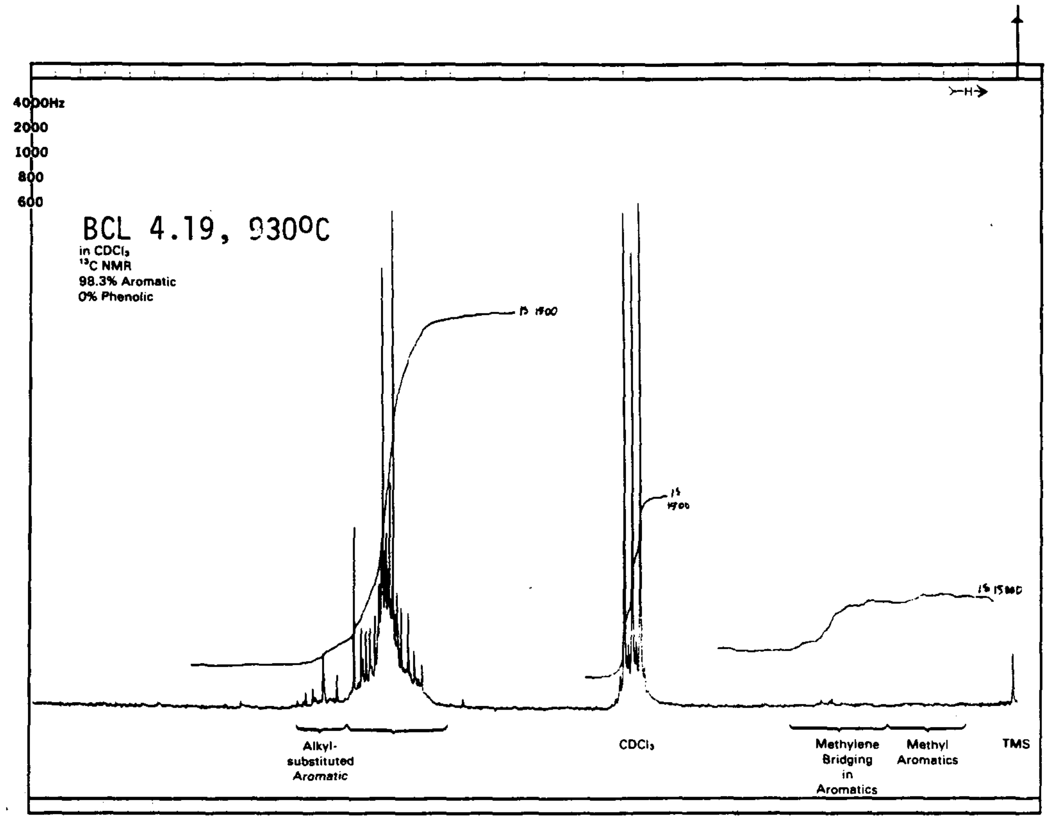
CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF BIOMASS GASIFICATION TARS

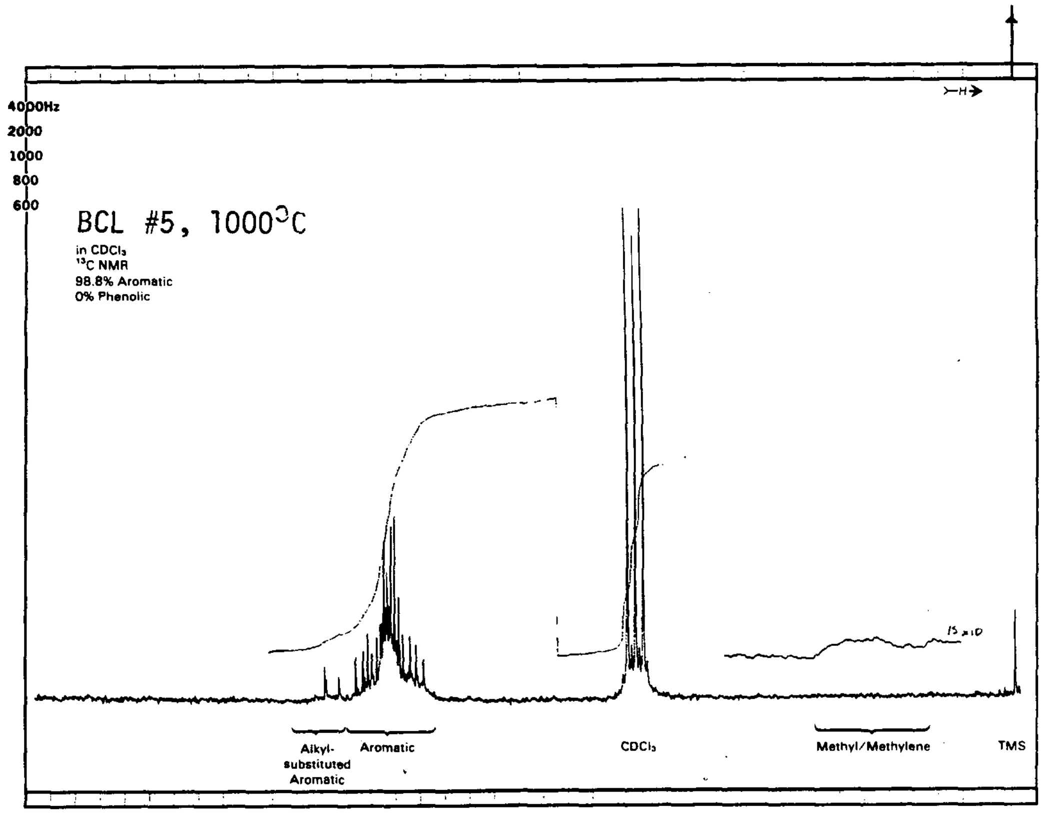
CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF BIOMASS GASIFICATION TARS

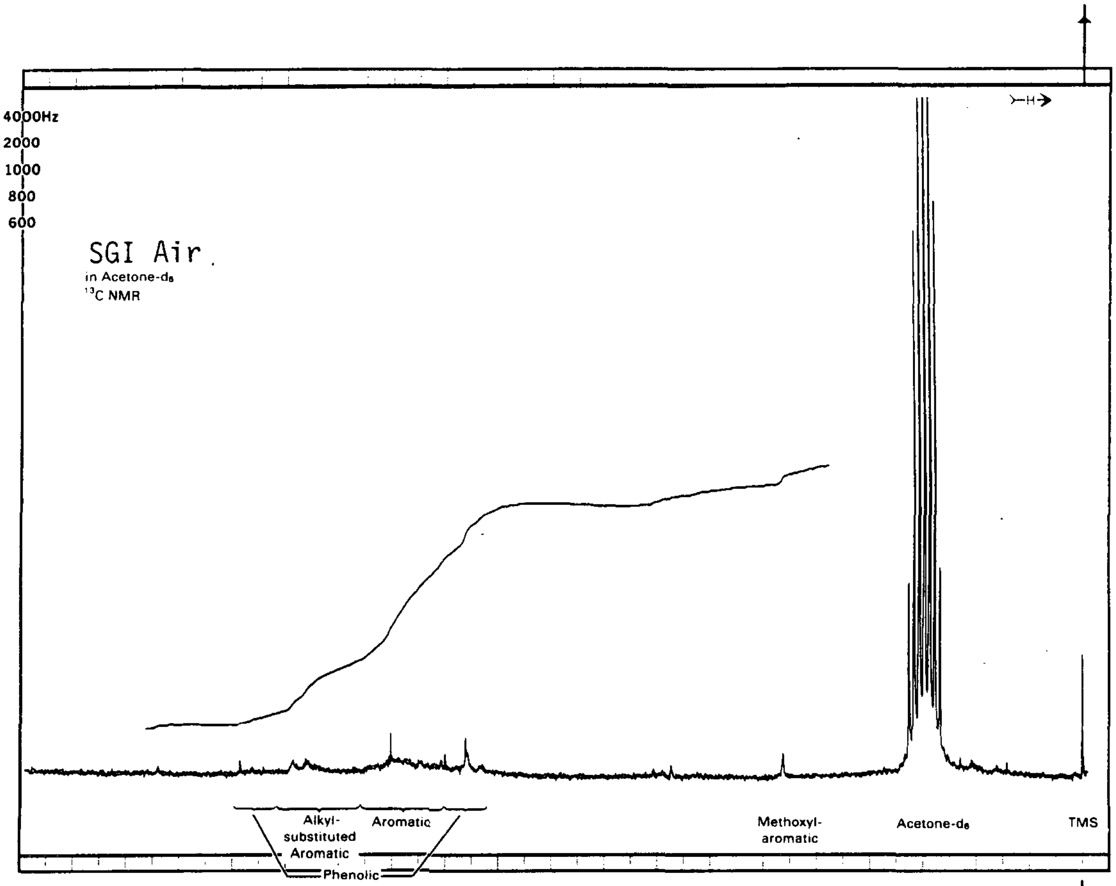
This appendix is a collection of six NMR spectra. The tar sample represented by each spectrum is identified on the spectrum. The sample solvents are also identified on the individual spectra. Representative functional groups identified for the important resonance bands have been indicated on the spectra.

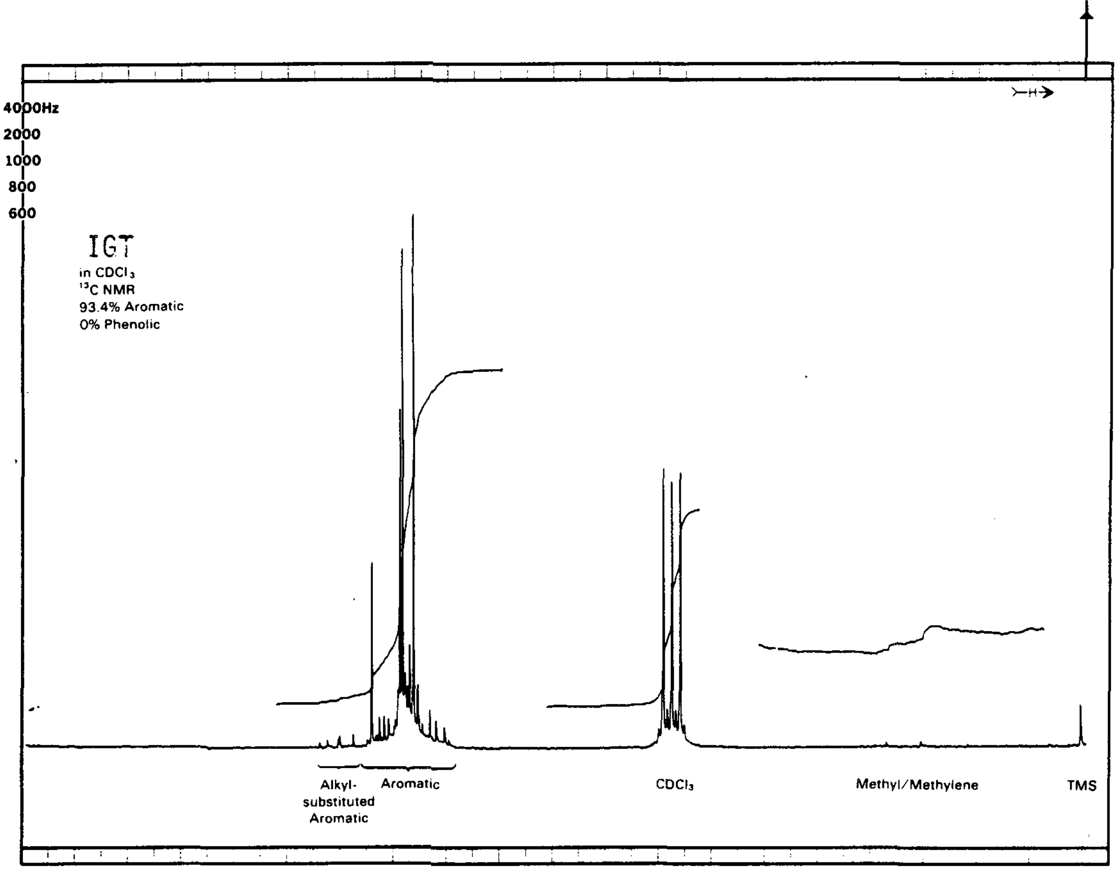

4000Hz
2000
1000
800
600
BCL Pine, 880°C
13C NMR in CDCl3
95.1% Aromatic
0% Phenolic
Aromatic
*
*CDCl3


4000Hz
2000
1000
800
600
BCL Oak-Maple, 900°C
13C NMR in CDCl3
93.5% Aromatic
0% Phenolic
20 Units
X10
14 Units
Aromatic
*
*CDCl3


4000Hz
2000
1000
800
600
BCL 4.19, 930°C
in CDCl₃
¹³C NMR
98.3% Aromatic
0% Phenolic
15 1900
15 1900
Alkyl-substituted Aromatic
CDCl₃
Methylene Bridging in Aromatics
Methyl Aromatics
TMS


4000Hz
2000
1000
800
600
BCL #5, 1000°C
in CDCl₃
¹³C NMR
98.8% Aromatic
0% Phenolic
Alkyl-substituted Aromatic
Aromatic
CDCl₃
Methyl/Methylene
TMS


4000Hz
2000
1000
800
600
SGI Air
in Acetone-d₆
¹³C NMR
Alkyl-substituted Aromatic
Aromatic
Phenolic
Methoxyl-aromatic
Acetone-d₆
TMS


4000Hz
2000
1000
800
600
IGT
in CDCl₃
¹³C NMR
93.4% Aromatic
0% Phenolic
Alkyl-substituted Aromatic
Aromatic
CDCl₃
Methyl/Methylene
TMS

APPENDIX C

CHEMICAL COMPONENTS IN BIOMASS GASIFICATION TARS IDENTIFIED AND QUANTIFIED USING GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

Table C.1 Detailed Listing of Components in Tars From Several Gasification Systems

Compound	RT	UMO		IGT 3D		BCL 5		SGI Air		SGI O_2	
		Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.
benzene	2.68	20.63	0.11	10990	7.07	74.67	0.26	189.75	1.18	80.04	0.19
toluene	4.21	—	—	844.51	0.55	—	—	—	—	38.68	0.09
furfural	5.12	—	—	—	—	—	—	128.27	0.96	224.05	0.63
methyl cyclopentenone	6.38	—	—	—	—	—	—	—	—	103.80	0.29
furanyl ethanone	6.44	—	—	—	—	—	—	33.32	0.25	—	—
benzaldehyde	7.34	—	—	—	—	—	—	69.43	0.52	115.08	0.32
methyl furfural	7.37	—	—	—	—	—	—	68.59	0.51	201.53	0.56
phenol	7.62	76.96	0.57	—	—	—	—	1900.85	16.62	1399.96	4.58
benzofuran	8.0	—	—	3.83	0.003	—	—	—	—	70.36	0.30
methyl styrene	8.85	—	—	—	—	—	—	—	—	137.93	0.45
o-cresol	8.93	125.78	0.92	—	—	—	—	474.83	4.15	1031.33	3.37
indene	8.93	—	—	1713.76	1.10	59.71	0.20	—	—	—	—
m,p-cresol	9.29	207.23	1.52	—	—	—	—	981.88	8.58	1670.5	5.46
trimethyl cyclopentenone	9.60	—	—	—	—	—	—	361.13	2.71	57.53	0.16
o-ethyl phenol	10.34	23.44	0.17	—	—	—	—	44.31	0.39	56.81	0.19
dimethyl phenol	10.52	164.52	1.20	—	—	—	—	264.34	2.31	733.09	2.40
methyl indene	10.7	—	—	—	—	—	—	—	—	143.62	0.40
m,p-ethyl phenol	10.81	181.03	1.32	—	—	—	—	265.41	2.32	930.40	3.04
dimethyl phenol	11.03	36.13	0.26	—	—	—	—	—	—	138.38	0.45
naphthalene	11.28	51.78	0.29	95933.2	61.69	3569.41	11.96	1056.26	6.60	1742.97	4.07
catechol	11.31	—	—	—	—	—	—	—	—	427.77	4.20
dihydrobenzofuran	11.49	—	—	—	—	—	—	—	—	192.91	0.76
methyl ethyl phenol	11.81	45.15	0.33	—	—	—	—	—	—	173.41	0.79
methyl ethyl phenol	11.98	85.54	0.62	—	—	—	—	111.43	0.97	283.83	0.93
methyl ethyl phenol	12.06	33.18	0.24	—	—	—	—	—	—	93.83	0.43
bifuran	12.07	—	—	—	—	—	—	—	—	113.09	0.44
methyl ethyl phenol	12.30	58.66	0.43	—	—	—	—	—	—	78.24	0.36
methyl catechol	12.34	—	—	—	—	—	—	64.18	1.20	167.74	1.65
ethyl guaiacol	12.67	—	—	—	—	—	—	233.95	2.34	225.99	1.18
propenyl phenol	12.74	137.90	1.01	—	—	—	—	—	—	—	—
methyl catechol	12.77	—	—	—	—	—	—	—	—	271.41	2.66
1-indanone	12.81	318.96	1.98	—	—	—	—	—	—	—	—
C_{12} alkane	12.84	—	—	—	—	—		261.08	1.62	—	—

Table C.1 (cont'd)

Compound	RT	UMO		IGT 3D		BCL 5		SGI Air		SGI O_2	
		Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.
propenyl phenol	12.96	172.00	1.26	—	—	—	—	—	—	—	—
methyl naphthalene	13.03	201.69	1.14	730.24	0.47	84.84	0.28	162.65	1.02	695.06	2.27
propenyl phenol	13.06	—	—	—	—	—	—	—	—	205.59	0.94
dimethyl ethyl phenol	13.12	70.59	0.52	—	—	—	—	—	—	—	—
methyl-1-indanone	13.20	23.11	0.14	—	—	—	—	—	—	—	—
methyl naphthalene	13.30	212.64	1.20	442.7	0.28	68.77	0.24	100.36	0.63	515.90	1.69
vinylbenzaldehyde	13.48	169.28	1.05	—	—	—	—	—	—	486.21	1.91
C_2 benzaldehyde	13.59	61.11	0.38	—	—	—	—	—	—	151.44	0.59
vinylbenzaldehyde	13.66	88.25	0.55	—	—	—	—	—	—	157.61	0.62
vinylbenzaldehyde	13.81	217.66	1.35	—	—	—	—	—	—	478.66	1.88
propenyl guaiacol	13.89	—	—	—	—	—	—	259.32	2.59	—	—
ethyl catechol	14.16	—	—	—	—	—	—	130.75	2.45	119.22	1.17
biphenyl	14.27	115.63	0.65	1431.24	0.92	345.71	1.15	—	—	367.05	1.20
C_{14} alkane	14.33	—	—	—	—	—	—	147.84	0.92	—	—
1-ethyl naphthalene	14.49	142.47	0.80	—	—	—	—	—	—	329.36	1.08
hydroxymethylbenzaldehyde	14.52	—	—	—	—	—	—	263.76	2.64	—	—
2-ethyl naphthalene	14.55	104.22	0.59	—	—	—	—	—	—	226.03	0.74
dimethyl naphthalene	14.66	218.33	1.23	—	—	—	—	—	—	223.58	0.73
dimethyl naphthalene	14.88	193.10	1.09	—	—	—	—	—	—	176.00	0.58
dimethyl naphthalene	14.93	180.98	1.02	—	—	—	—	34.94	0.22	186.66	0.61
acenaphthene	15.01	323.15	1.82	—	—	169.62	0.58	31.55	0.20	411.87	1.35
dimethyl naphthalene?	15.16	88.09	0.50	—	—	—	—	—	—	—	—
propenyl guaiacol	15.20	—	—	—	—	—	—	174.25	1.74	315.00	1.65
dimethyl naphthalene?	15.23	180.60	1.02	—	—	—	—	—	—	—	—
acenaphthylene	15.36	771.74	4.35	4096.12	2.64	4597.47	15.42	178.40	1.11	1715.43	5.61
C_{15} alkane	15.70	—	—	—	—	—	—	81.17	0.51	—	—
diphenylmethane	15.75	135.58	0.76	—	—	—	—	—	—	145.18	0.48
guaiacyl ethanone	—	—	—	—	—	—	—	246.16	2.46	—	—
acenaphthene?	15.83	278.17	1.57	1916.76	1.23	80.25	0.28	—	—	—	—
propyl naphthalene	16.03	101.62	0.57	—	—	—	—	—	—	—	—
naphthol	16.04	—	—	—	—	—	—	—	—	290.01	1.33
naphthol	16.16	—	—	—	—	—	—	—	—	277.29	1.27
phenyl phenol ? + ?	16.17	124.22	0.91	—	—	—	—	—	—	—	—

Table C.1 (cont'd)

Compound	RT	UMO		IGT 3D		BCL 5		SGI Air		SGI O_2	
		Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.
dibenzofuran	16.25	157.37	0.98	227.42	0.16	351.61	1.29	—	—	404.40	1.85
guaiacylpropanone	16.35	—	—	—	—	—	—	197.56	1.97	—	—
naphthofuran	16.54	224.41	1.39	—	—	—	—	—	—	151.62	0.69
naphthofuran	16.64	166.39	1.03	—	—	—	—	—	—	—	—
methylbiphenyl ?	16.78	40.47	0.23	—	—	—	—	—	—	171.64	0.56
methylacenaphthylene	16.90	322.91	1.82	53.92	0.04	—	—	—	—	190.62	0.62
? + naphthol ?	16.98	104.65	0.76	—	—	—	—	—	—	—	—
C_{16} alkane	17.00	—	—	—	—	—		54.78	0.34	—	—
methylacenaphthylene	17.08	269.69	1.52	—	—	—	—	—	—	199.89	0.65
fluorene	17.16	516.73	2.91	2940.18	1.89	828.32	2.78	—	—	582.79	1.91
methylacenaphthylene	17.20	225.67	1.66	—	—	—	—	—	—	92.11	0.30
methylfluorene	17.41	—	—	—	—	—	—	—	—	233.32	0.76
methylnaphthol	17.50	—	—	—	—	—	—	—	—	324.34	1.48
dimethylbiphenyl	17.61	—	—	—	—	—		93.49	0.58	234.34	0.77
methylacenaphthylene	17.70	461.82	2.61	76.70	0.05	—	—	—	—	240.69	0.79
phenylbenzaldehyde	17.78	204.72	1.27	—	—	—	—	—	—	166.56	0.71
guaiacylacetic acid	17.85	—	—	—	—	—	—	188.45	2.35	—	—
hydroxyfluorene ?	18.06	109.43	0.80	—	—	—	—	—	—	—	—
methylfluorene ?	18.51	202.08	1.14	—	—	—	—	—	—	—	—
methylfluorene	18.59	634.53	3.58	—	—	47.22	0.16	—	—	264.52	1.04
methylfluorene	18.68	319.30	1.80	—	—	—	—	—	—	—	—
methylfluorene	18.83	171.66	0.97	—	—	—	—	—	—	—	—
methylfluorene	19.10	445.20	2.51	—	—	—	—	—	—	146.33	0.53
methyl[(methylphenyl)methyl]benzene	19.22	—	—	—	—	—	—	—	—	85.22	0.31
dibenzodioxin	19.32	—	—	—	—	—	—	—	—	118.74	0.44
phenanthrene	19.62	648.93	3.66	7207.95	4.64	5535.9	18.55	220.40	1.79	926.19	2.81
anthracene	19.74	325.68	1.83	739.16	0.49	1030.4	3.45	—	—	276.48	0.84
methylphenanthrene	20.91	126.56	0.72	31.69	0.02	28.66	0.10	—	—	94.04	0.29
methylphenanthrene	21.08	240.42	1.35	42.93	0.03	—	—	—	—	184.90	0.56
methylenephenanthrene	21.16	—	—	—	—	—	—	—	—	383.00	1.25
methylphenanthrene	21.21	274.93	1.55	434.92	0.28	487.51	1.63	—	—	—	—
phenylnaphthalene	21.7	189.55	1.07	229.95	0.15	191.24	0.63	—	—	158.47	0.52

Table C.1 (cont'd)

Compound	RT	UMO		IGT 3D		BCL 5		SGI Air		SGI O2	
		Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.	Area	Amt.
fluoranthene	22.8	—	—	4111.15	2.64	2372.9	7.96	59.02	0.48	383.48	1.25
acephenanthrylene	23.0			231.19	0.15	466.14	1.57	—	—	158.28	0.52
pyrene	23.4	144.01	0.81	3982.16	2.56	2301.02	7.72	126.46	1.03	459.42	1.50
C_4 phenanthrene	24.2	—	—	—	—	—	—	38.02	0.31	109.14	0.36
218 PAH?	24.3	189.55	1.07	179.09	0.12	67.65	0.34	—	—	—	—
226 MW	26.0	—	—	47.15	0.03	162.43	0.81	—	—	—	—
226 benzfluoranthene	26.5	—	—			557.51	2.80	—	—	—	—
benzanthracene	26.6	18.34	0.11	353.69	0.22	139.37	0.69	—	—	134.10	0.44
chrysene	26.7	38.9	0.22	784.74	0.51	258.86	1.31	—	—	—	—
naphthacene	27.0	—	—	428.52	0.27	35.86	0.18	—	—	—	—
gualacyl pyranone	28.2	—	—	—	—	—	—	84.91	0.85	—	—
binaphthyl?	28.3	—	—	106.33	0.07	23.71	0.12	—	—	—	—
benzpyrene?	29.6	—	—	1343.63 579.75	0.86 0.37	109.43 153.66	0.73 1.03	—	—	—	—
252 PAH	29.9	—	—	146.25	0.10	35.84	0.24	—	—	—	—
252	30.5	—	—	1392.7	0.90	108.27	0.73	—	—	—	—
MW	30.7	—	—	1972.6	1.27	183.06	1.23	—	—	—	—
PAH	30.95	—	—	711.12	0.46	—	—	—	—	—	—
276	35.4	—	—	2213.42	1.42	87.06	0.57	—	—	—	—
MW	36.7	—	—	2169.68	1.39	99.38	0.67	—	—	—	—
PAH	37.3	—	—	902.87	0.59	44.17	0.30	—	—	—	—
functional groups as percent of identified compounds		-OH 14.2 carbonyl 9.5 furan 3.7 PAH 72.7 70.8% ident.		furan 0.2 PAH 99.8 97.6% ident.		furan 0.6 PAH 99.4 88.1% ident.		-OH 34.3 carbonyl/ furan 23.2 PAH 32.4 gualacyl 10.2 65.4% ident.		-OH 40.0 carbonyl/ furan 13.3 PAH 43.1 gualacyl 3.0 91.8% ident.	

RT = retention time

Area = integrated peak area from flame ionization detector

Amt. = amount of component as percent of whole tar

APPENDIX D

NUMERICAL RESULTS OF AMES ASSAYS

NUMERICAL RESULTS OF AMES ASSAYS

The data on the following pages are presented in units of revertant colonies per microgram of tar for each of the three tars tested (BCL #5, IGT #3D and SGI-air). The left-most column of numbers on each page lists the concentration of tar in units of micrograms per petri plate. Below each concentration range data group is a summary of the statistical evaluation of the data. A positive test is defined as having a maximum mutagenic response two-fold or greater above background, and a correlation coefficient 0.8 or above for the regression line with a positive slope.

TA98 w/S9 (20 µl)

µg/plate	BCL 5	IGT 3D	SGI* air
10	179 ± 12	127 ± 4	43 ± 4
20	241 ± 20	143 ± 7	49 ± 7
40	291 ± 15	157 ± 16	32 ± 5
50	325 ± 1	162 ± 7	43 ± 4
100	386 ± 10	156 ± 14	49 ± 2
250	392 ± 10	104 ± 12	46 ± 3
correlation coefficient	0.78 @ 100 µg	0.69 @ 50 µg	0.06 @ 500 µg
slope	2.97	1.94	0.01
Y intercept	135.4	79.8	42.4
background	43 ± 2		
20	282 ± 14	150 ± 19	47 ± 4
40	366 ± 3	171 ± 5	48 ± 2
80	448 ± 21	184 ± 15	49 ± 9
100	449 ± 21	175 ± 19	51 ± 5
200	521 ± 18	134 ± 1	44 ± 4
500	424 ± 32	50 ± 11	40 ± 4
correlation coefficient	0.79 @ 100 µg	0.58 @ 100 µg	0.86 @ 200 µg
slope	3.6	1.07	0.03
Y intercept	144.6	93.3	44.4
background	43 ± 2		

* for the SGI air tar concentration of tar in µg/plate is 2X that listed in left hand column.

TA98 w/o S9

µg/plate	BCL 5	IGT 3D	SGI* air
10	43 ± 0	42 ± 2	32 ± 1
20	50 ± 1	33 ± 4	26 ± 6
40	47 ± 17	46 ± 6	33 ± 2
50	62 ± 5	45 ± 4	24 ± 1
100	80 ± 15	43 ± 7	28 ± 2
250	73 ± 2	24 ± 5	29 ± 5
correlation coefficient	0.85 @ 100 µg	0.61 @ 50 µg	0.05 @ 500 µg
slope	0.51	0.41	0.01
Y intercept	31.6	27.4	26.7
background	20 ± 0		
20	54 ± 0	43 ± 14	26 ± 4
40	45 ± 6	36 ± 5	28 ± 1
80	70 ± 5	56 ± 5	30 ± 1
100	74 ± 5	48 ± 1	29 ± 8
200	88 ± 11	42 ± 6	36 ± 5
500	66 ± 2	21 ± 3	41 ± 2
correlation coefficient	0.82 @ 100 µg	0.66 @ 100 µg	0.85 @ 400 µg
slope	0.47	0.27	0.03
Y intercept	29.9	27.8	23.3
background	20 ± 0		

* for the SGI air tar, the concentration of tar in µg/plate is 2X that listed in the left hand column.

TA 100 w/S9 (20 µl)

µg/plate	BCL 5	IGT 3D	SGI air
20	550 ± 17	467 ± 8	248 ± 16
40	575 ± 5	462 ± 10	224 ± 11
80	645 ± 14	464 ± 20	252 ± 10
100	731 ± 7	545 ± 9	248 ± 13
200	878 ± 16	464 ± 13	244 ± 15
500	711 ± 7	166 ± 25	270 ± 6
correlation coefficient	0.77 @ 200 µg	0.60 @ 100 µg	0.54 @ 500 µg
slope	2.72	2.36	0.08
Y intercept	399.8	316.7	231.8
background	212 ± 12		
40	674 ± 69	468 ± 2	250 ± 2
80	731 ± 33	445 ± 1	235 ± 4
160	881 ± 40	303 ± 6	248 ± 10
200	814 ± 4	306 ± 23	233 ± 1
400	819 ± 37	203 ± 14	251 ± 7
1000	396 ± 60	95 ± 14	229 ± 2
correlation coefficient	0.66 @ 200 µg	0.00 @ 200 µg	0.30 @ 400 µg
slope	2.59	-0.09	0.06
Y intercept	413.9	355.4	229.9
background	212 ± 12		

TA 100 w/o S9

µg/plate	BCL 5	IGT 3D	SG1 air
20	226 ± 4	212 ± 17	221 ± 19
40	223 ± 1	228 ± 27	202 ± 16
80	232 ± 14	223 ± 10	200 ± 2
100	212 ± 16	193 ± 3	182 ± 19
200	212 ± 23	178 ± 15	203 ± 8
500	183 ± 2	118 ± 2	193 ± 3
correlation coefficient	0.18 @ 100 µg	0.00 @ 100 µg	0.07 @ 500 µg
slope	0.16	0.02	-0.02
Y intercept	209.7	208.8	201.6
background	193 ± 17		
40	230 ± 18	235 ± 12	210 ± 9
80	220 ± 17	225 ± 5	188 ± 13
160	270 ± 12	207 ± 8	196 ± 4
200	238 ± 6	173 ± 7	178 ± 2
400	220 ± 5	137 ± 10	189 ± 6
1000	168 ± 9	126 ± 18	220 ± 21
correlation coefficient	0.59 @ 200 µg	0.24 @ 200 µg	0.18 @ 400 µg
slope	0.26	-0.15	-0.03
Y intercept	205.4	220.7	196.9
background	193 [illegible] 17		

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