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GC/MS CHARACTERIZATION OF CONDENSABLE TARS IN
THE OUTPUT STREAM OF A STIRRED FIXED-BED GASIFIER

By
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December 1981

United States Department of Energy
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ABSTRACT

The output stream of the stirred fixed-bed gasifier at the Morgantown Energy Technology Center was sampled for total entrained material. A major portion of the entrained material, in addition to particles, is condensable tar that is subsequently removed from the process gas by wet scrubbing. Characterization of the entrained materials, specifically the tar, is important to establish contaminant levels and to evaluate performance of downstream cleanup units.

Samples of tars were collected from the process unit in a combined ice, dry ice, and liquid nitrogen sampler and stored in a refrigerator. The tar samples were then separated into asphaltene, neutral oil, tar acid, and base fractions by solvent extraction using toluene, pentane, sulfuric acid, and potassium hydroxide extraction. Characterization of the fractions obtained from these tars include IR, UV, GC, and GC/MS analysis. The mass spectrometer analysis of the various isolates shows that many individual peaks in the gas chromatograph are in fact mixtures that can be readily identified by the mass spectrometer. It was found that many of the species identified in these fractions were members of aromatic homologous series consisting of parent, mono, di, and tri substituted compounds. Compound identification was made by comparison of the data system library and standard reference spectra.

This paper will discuss the instrumental approach and limitation of the GC/MS and the results of the characterization studies of entrained hydrocarbons collected from the gasifier stream.

INTRODUCTION

It has become increasingly evident that a detailed knowledge of the organic chemical species present in the various phases of the gasification process system is necessary both to aid design of efficient cleanup systems, and to develop the methods to monitor their performance. The identification and characterization of the products formed during the gasification process are

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needed to select efficient cleanup systems. To help realize this objective, the fixed stirred-bed gasifier at the Morgantown Energy Technology Center was sampled for total entrained materials from the effluent process stream. A major portion of the entrained material, in addition to particles, was tars containing polynuclear aromatic hydrocarbons. The tars were collected from the process gas stream by a staged cooled sampling train. Characterization of the collected materials, specifically the PNA's of the tar becomes important to establish contaminant levels and to evaluate the performance of specific individual cleanup units.

EXPERIMENTAL

Sample Collection and Preparation

Samples of entrained materials were collected from the output stream of the METC 42-inch stirred fixed-bed gasifier operating with a Pittsburgh No. 8 feed coal. The sampling point was located on the main process stream after the cyclone, as shown in Figure 1. The sampler unit itself consisted of a series of three glass traps containing glass beads placed in dewar flasks filled with dry ice and liquid nitrogen. After collection, the traps were washed with toluene and pentane to recover the collected material. The samples were then placed into a refrigerator until separation of the samples was carried out using chemical techniques.

Separation of the samples included initially freezing out the water in the mixture and filtering the remaining solution through a millipore filter with a .22 μ m pore opening. The pentane was removed by evaporation and the toluene solution containing the tars and oils was fractionated into final samples of asphaltenes, acids, bases, and neutrals. Table 1 lists the relative percent of the fractions from Trap 1. The material collected in the trap represents 68 percent of the total collected. The sample from the first trap was chosen because the material from the last three traps contained small amounts of plasticizers leached from the sample unit connecting tubing. Comparison of the gross composition of the various traps showed that the material in each trap was similar with the exception of the known contaminant.

Fraction	Relative % Recovered
Tar Acids	10
Tar Bases	3
Neutral Oil	65
Pentane and Toluene Insolubles	22

Table 1. Relative Percent Recovery of the Fractions from Trap 1.

Gas Chromatographic and Mass Spectrometric Analyses

The initial analyses were performed using a Perkin-Elmer 910 Gas Chromatograph equipped with a flame ionization detector. The separation was made on a column 12 feet long and 1/8-inch in diameter packed with 6 percent Dexsil 300 on Chromosorb WHP. The temperature was programmed at 7.5°C/min starting at 150°C and reaching a final temperature of 350°C. The use of standard reference compounds produced identification and quantitative data for approximately 90 percent of all constituents in these fractions. The remaining unknowns were identified by GC/MS analysis using a Varian 2700 GC equipped with a flame ionization detector. Separation was accomplished on a column 12 feet long and 1/8-inch in diameter packed with 6 percent Dexsil 300 on Chromosorb WHP. Temperature was programmed from 150°C to 350°C at 8°C/min. The GC was interfaced to a DuPont 491B mass spectrometer with a Hewlett-Packard 2100A data acquisition system for mass spectrometric data reduction and storage. The typical mass spectrometer parameters were: ionization energy at 70Ev, resolution at 600, and the scanning rate at 2 sec/decade of mass. The calibration of the mass spectrometer was made with perfluorokerosene-H.

Results and Discussion

Figure 2 shows the chromatogram of the acid fraction isolated from the collected sample and Table 2 lists the compounds. The compounds from Table 2 that are most readily identified appear in Figure 1. It can be seen from the chromatogram that

Figure 2. Gas Chromatogram of the Acid Fraction Isolated from the Collected Sample.

many of the components remain unresolved and overlapping is extensive because of the separation inadequacy of the GC column. Approximately 230 mass spectral scans of data revealed that most peaks in the GC ionization curve were composed of several components that were substituted families of the parent component. Although the mass spectral data indicated the substance type, it was necessary to run standard reference compounds for insertion into the library of the data acquisition system. These reference compounds were used to verify specific substituted groups.

Peak Number	Molecular Weight	Compound Type	Formula
1	92	Toluene	C ₇ H ₈
2	94	Phenol	C ₆ H ₆ O
3	108	o-Cresol	C ₇ H ₈ O
4	108	m-Cresol	C ₇ H ₈ O
5	122	2,6-Dimethylphenol	C ₈ H ₁₀ O
6	122	2,5-Dimethylphenol	C ₈ H ₁₀ O
7			
8	122	2,3-Dimethylphenol	C ₈ H ₁₀ O
9	136	2,4,6-Trimethylphenol	C ₉ H ₁₂ O
10	136	3-Ethyl-5-methylphenol	C ₉ H ₁₂ O
11	124	3-Methylcatechol	C ₇ H ₈ O ₂
12	124	4-Methylcatechol	C ₇ H ₈ O ₂
13			
14			
15			
16			
17	154	Biphenyl	C ₁₂ H ₁₀
18	156	Ethyl naphthalene	C ₁₂ H ₁₂
19	156	2,6-Dimethylnaphthalene	C ₁₂ H ₁₂
20	156	1,6-Dimethylnaphthalene	C ₁₂ H ₁₂
21	144	2-Naphthol	C ₁₀ H ₈ O
22	170		
23	154	Acenaphthene	C ₁₂ H ₁₀
24	168	Dibenzofuran	C ₁₂ H ₁₀ O
25			
26			
27	182	3-Methylbenzofuran	C ₁₃ H ₁₀ O
28	182	2-Methylbenzofuran	C ₁₃ H ₁₀ O
29			
30	170		
31	180	2-Methylfluorene	C ₁₂ H ₁₀
32	196	Dimethyldibenzofuran	C ₁₄ H ₁₂ O
33			
34	167	Carbazole	C ₁₂ H ₉ N
35	192	3-Methylphenanthrene	C ₁₅ H ₁₂
36	192	2-Methylphenanthrene	C ₁₅ H ₁₂
37	192	9-Methylanthracene	C ₁₅ H ₁₂

Table 2. Components in the Acid Fraction Identified in Figure 2.

Figure 3 shows the chromatographic separation of the base fraction isolated from the collected sample, and Table 3 is the list of identified components in the chromatogram. The compounds from Table 3 that are most readily identified appear in Figure 3.

Figure 3. Gas Chromatogram of the Base Fraction Isolated from the Collected Sample.

Peak Number	Molecular Weight	Compound Type	Formula
1	129	Quinoline	C ₉ H ₇ N
2	142	1-Methylnaphthalene	C ₁₁ H ₁₀
3	143	9-Methylquinoline	C ₁₀ H ₉ N
4			
5			
6	157	2,4-Dimethylquinoline	C ₁₁ H ₁₁ N
7			
8			
9	171	2,3,4-Trimethylquinoline	C ₁₂ H ₁₃ N
10			
11			
12	185	2,4,7,8-Tetramethylquinoline	C ₁₃ H ₁₅ N
13			
14	180	2-Methylfluorene	C ₁₄ H ₁₂
15			
16	196	Dimethylbenzofuran	C ₁₄ H ₁₂ O
17			
18	178	Phenanthrene & Anthracene	C ₁₄ H ₁₀
19	167	Carbazole	C ₁₂ H ₉ N
20			
21	194	3-Methyl & 2-Methylphenanthrene	C ₁₅ H ₁₂
22	194	9-Methyl & 1-Methylphenanthrene & 2-Methylantracene	C ₁₅ H ₁₂
23			
24	194	9-Methylantracene	C ₁₅ H ₁₂
25			
26			
27			
28			
29			
30	202	Fluoranthene	C ₁₆ H ₁₀
31			
32	208 & 206	Pyrene & 9,10-Dimethylantracene	C ₁₆ H ₁₆ , C ₁₆ H ₁₄
33	216	1,2-Benzofluorene	C ₁₇ H ₁₂
34	216	2,3-Benzofluorene & 3,4-Benzofluorene	C ₁₇ H ₁₂
35			
36			
37			
38	228	Benzo(c)phenanthrene	C ₁₈ H ₁₂
39	252	Benzo(m,n,o)fluoranthene	C ₂₀ H ₁₂
40	228	Chrysene & Benz(a)anthracene	C ₁₈ H ₁₂

Table 3. Components in the Base Fraction Identified in Figure 3.

Although many hydrocarbon identifications can be assigned quite easily, it is sometimes very difficult to assign a structure to substituted species of these hydrocarbons because of their isomeric forms and their ring substitution. The mass spectra of these substituted hydrocarbon species are similar at 70 EV energy. In some cases, in order to distinguish them it is necessary to change ionization potentials. However, the limitation on the particular GC/MS configuration used in this study was the data system. It functioned only when the ionization potential was set at 70 EV. The only method that could be used to carry out the exact structure substitution identification was to read out spectra on an oscillograph and do an ionization study on each and every peak eluted from the GC. Obviously, this technique is tedious and quite long. Every peak has overlapping constituents and isolation of each constituent can only be done by manipulation of the data system.

Figure 4. Gas Chromatogram of the Neutral Fraction Isolated from the Collected Sample.

Peak Number	Molecular Weight	Compound Type	Formula
1	132	Tetralin	C ₁₀ H ₁₂
2	128	Naphthalene	C ₁₀ H ₈
3	146	Methyltetralin	C ₁₁ H ₁₄
4	142	2-Methylnaphthalene	C ₁₁ H ₁₀
5	142	1-Methylnaphthalene	C ₁₁ H ₁₀
6	154	Biphenyl	C ₁₂ H ₁₀
7			
8	156	Ethyl naphthalene	C ₁₂ H ₁₂
9	156	2,6-Dimethylnaphthalene	C ₁₂ H ₁₂
10	156	1,6-Dimethylnaphthalene	C ₁₂ H ₁₂
11	168	3-Methylbiphenyl	C ₁₃ H ₁₂
12	154	Acenaphthene	C ₁₂ H ₁₀
13	168	Dibenzofuran	C ₁₂ H ₁₀ O
14			
15	182	3,3'-Dimethylbiphenyl	C ₁₄ H ₁₄
16	166 & 182	Fluorene & 4,4'-Dimethylbiphenyl	C ₁₃ H ₁₀ & C ₁₄ H ₁₄
17	182	3-Methyl & 2-Methyldibenzofuran	C ₁₃ H ₁₀ O
18			
19			
20			
21	180	2-Methylfluorene	C ₁₄ H ₁₂
22			
23	196	3,4-Dimethyldibenzofuran	C ₁₄ H ₁₂ O
24	196	2,4-Dimethyldibenzofuran	C ₁₄ H ₁₂ O
25	178	Anthracene & Phenanthrene	C ₁₄ H ₁₀
26	167	Carbazole	C ₁₂ H ₉ N
27			
28			
29	192	3-Methylphenanthrene & 2-Methylphenanthrene	C ₁₅ H ₁₂
30	192	9-Methylphenanthrene & 1-Methylphenanthrene 2-Methylanthracene	C ₁₅ H ₁₂ C ₁₅ H ₁₂
31			
32	192	9-Methylanthracene	C ₁₅ H ₁₂
33			
34			
35	202	Fluoranthene	C ₁₆ H ₁₀
36	202 & 206	Pyrene & 9,10 Dimethylanthracene	C ₁₅ H ₁₂
37			
38			
39	216	2,3-Benzofluorene & 3,4-Benzofluorene	C ₁₇ H ₁₂
40	216	4-Methylpyrene	C ₁₇ H ₁₂
41			
42			
43	228	Benz(c)phenanthrene	C ₁₈ H ₁₂
44	252	Benz(m,n,o)fluoranthene	C ₂₀ H ₁₂
45	228	Chrysene & Benz(a)anthracene	C ₁₈ H ₁₂
46			

Table 4. Components in the Neutral Fraction Identified in Figure 4.

The ionization studies provided identification for only a small portion of the substituted hydrocarbons. Additional information was collected utilizing the data system mass spectral information. First, a correlation between the data scan number and the specific portion of the chromatogram was calculated. This was necessary to compensate for the interface between the GC and the source of the mass spectrometer that created a mixing of the eluted effluent. This correlation was essential in order to know the specific scan of the ionization curve to be analyzed. By manipulating the mass spectral data of the constituents of the mixture, the subtraction of spectral scans of two closely related compounds showed the specific substitution of the species, but not the exact position of the substitution. An example of this technique is shown in Figure 5.

Figure 5. Mass Spectrum of 1-Methylindan
Top - Mass Spectrum of the Mixture of Components in Scan 26.
Center - Mass Spectrum of Scan 25.
Bottom - Mass Spectrum of 1-Methylindan Resulting from Subtraction
of Scan 25 from Scan 26.

Figure 6 shows the gas chromatogram and the ionization curve for the neutral fraction. They were obtained simultaneously.

Figure 6. A Gas Chromatogram and a Total Ion Plot for the Neutral Fraction Obtained Simultaneously.

Top - Gas Chromatogram

Bottom - Total Ion Plot

It can be seen that the separation of peaks in the gas chromatogram is much more resolved than the ion curve. This was also observed for the acid and base fractions.

Results of this combined GC/MS study indicate that the properties of hydrocarbons from fluids collected from the effluent stream of the fixed-bed gasifier are similar to those reported from GC/MS studies performed on other fluids derived from coal by other investigators (1,2,3,4,5,6,7).

The limitations of the instrumentation used in our study gave an indication of needed refinement of the technique and the GC/MS system before the actual position of the substituted hydrocarbons can be ascertained. In addition, studies still need to be conducted on improved separation methods to reduce carry-over within the various fractions. This is currently being investigated by Morgantown Energy Technology Center and will be used in future characterization studies.

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