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COMPOSITIONAL ANALYSIS OF AN H-COAL LIQUID BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY-COMPUTER TECHNIQUE*

JOHN L. WONG* and C. M. GLADSTONE

Department of Chemistry, University of Louisville, Louisville, KY 40292 (U.S.A.)

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SUMMARY

The H-Coal atmospheric still overhead (ASO) liquid was subjected to preparative high-performance liquid chromatography on Porasil followed by gas chromatographic and gas chromatographic-mass spectrometric analysis of the collected fractions, except for the forerun and column residue. Among the intermediate 5 fractions, there were 29 single compounds and 12 compound types identified. This analysis involved interpretation of 60 mass spectra aided by the PBM and STIRS computer search of the Cornell mass spectral data base. The identified compounds represent about half of the H-Coal liquid.

INTRODUCTION

The commercial feasibility of the H-Coal process (developed by Hydrocarbon Research, Inc.) to liquefy coal to produce refinery feedstock has been tested in a large scale demonstration plant¹. A thorough knowledge of the composition of the liquid distillates will facilitate the assessment of process efficiency and quality assurance. The gas chromatography-mass spectrometry (GC-MS) method is particularly applicable to the volatile components as has been shown in many analyses of coal-derived samples²⁻⁴. Such an analysis generates a high volume of ion detection data, the interpretation of which is suited to a computer search technique using the "Probability Based Matching" (PBM) system and the interpretive algorithm "Self-Training Interpretive and Retrieval System" (STIRS) developed by McLafferty and co-workers^{5,6}. In our continuing studies of the physicochemical properties of H-Coal liquids, we have determined the distributions of molecular weights by gel permeation chromatography^{7,8} and of aliphatic and aromatic carbons by carbon-13 Fourier transform nuclear magnetic resonance spectroscopy (FT-NMR)^{9,10}. We wish to report herein a compositional analysis of the H-Coal atmospheric still overhead (ASO). This is achieved by fractionating the ASO liquid by normal-phase high-performance liquid chromatography (HPLC) and subjecting the intermediate fractions, except for the forerun (fraction 1, baseline material according to an UV-absorbance detector) and

* Part of a series of reports on the physicochemical properties of H-Coal liquids.

the polar residue (fraction 7, methanol backflush from the column), to GC-MS-computer analysis. By virtue of this combined separation and analytical technique, we have made assignments by compound structure or compound type for ≈ 50 wt. % of the ASO liquid.

EXPERIMENTAL

Materials

The liquified coal sample under investigation was received from the University of Kentucky Institute for Mining and Minerals Research (IMMR). The liquefaction was performed by Hydrocarbon Research Inc., Trenton, NJ, U.S.A., by the H-Coal process in the "Syncrude" mode with reactor temperature at 454°C, exit reactor partial pressure of hydrogen at 2245 p.s.i.g. The sample designated atmospheric still overhead (ASO) has a nominal boiling range of C₄-200°C.

TABLE I
GAS CHROMATOGRAPHY ANALYSIS OF FRACTION 2

Temperature ramp 50°C (1 min) and 5°/min increase to 290°C. Retention times are relative to tetralin.

Sample			Standards	
Peak No.	% of peak areas	RRT	Compound	RRT
1	1.8	0.21		
2	0.9	0.24		
3	7.5	0.28	<i>n</i> -Propylcyclohexane	0.28
4	4.5	0.36		
5	1.0	0.40	Camphane	0.39
6	6.5	0.44	Hexahydroindane	0.44
7	3.5	0.47		
8	3.8	0.53		
9	17.6	0.57	<i>trans</i> -Decalin	0.58
10	5.7	0.68	Adamantane	0.68
11	5.9	0.72		
12	6.9	0.81		
13	1.0	0.89		
14	2.8	0.94		
15	1.3	0.98		
16	3.4	1.03		
17	2.0	1.07		
18	7.9	1.15	Bicyclohexyl	1.15
19	1.1	1.19	Cyclododecane	1.20
20	3.5	1.25		
21	3.4	1.29		
22	2.8	1.32		
23	3.0	1.39		
24	1.1	1.42		
25	1.1	1.55		

High-performance liquid chromatography

The instrument for chromatography consisted of a U6K injector, M6000A pump and Model 440 absorbance detector operating at 254 nm, purchased from Waters Assoc. (Milford, MA, U.S.A.). The packing material, Porasil A, also obtained from Waters, was dry packed into two 610 × 7.8 mm stainless-steel columns, each containing 14.1 g. The two columns were connected in series and eluted with *n*-hexane at 4.0 ml/min. In preparative runs, injections of 100 μl of the coal liquid sample (143 mg/ml) were made. Collected fractions were distilled to remove hexane, the residues weighed and submitted to GC-MS analysis as methanolic solutions. Fraction 7, the polar material, was collected by backflush of the column with methanol.

GC-MS analysis

GC separation of a fraction collected above was carried out on a 6 ft. × 2 mm glass column packed with 3% OV-17 (methyl phenyl silicones, 50% each of methyl and phenyl) on Supelcoport (100-120 mesh), with helium carrier at 30 ml/min, using a Hewlett-Packard 5830A gas chromatograph equipped with a flame ionization detector. The temperature ramps were as specified below: fractions 2-4, 50-290°C, 5°/min; fractions 5 and 6, 100-290°C, 6°/min. For GC-MS analysis, the Finnigan Model 3300 gas chromatograph-mass spectrometer was used. The spectrometer was operated in the electron impact mode at 70 eV. The PBM/STIRS analysis^{5,6} of each mass spectrum was executed on the IBM VM 370/165 computer of Cornell University via terminal, through the TYMNET time sharing system.

RESULTS AND DISCUSSION

The ASO fraction was subjected to preparative HPLC on Porasil A eluted with *n*-hexane. The separation is expected to be by chemical class, yielding in the order of alkanes, benzenes, naphthalenes and polyaromatics as that observed on μPorasil by Dark *et al.*¹¹. The forerun, fraction 1, contained UV-inactive aliphatics (12%, w/w), and the methanol backflush, fraction 7, the polar aromatic residue (11%, w/w). The five intermediate fractions 2-6 accounted for 14, 17, 20, 15 and 11% (w/w) respectively, of the coal liquid. The HPLC was followed by a temperature-programmed GC analysis of the latter five fractions. The relative retention times (RRTs) of the GC peaks as well as those of reference compounds, chromatographed under the same conditions, are shown for fractions 2-6 in Tables I-V, respectively. The standard compound is listed by the unknown peak only when comparison of the relative retention times is within 0.01 deviation. For fraction 2, 7 of the 25 peaks, accounting for 47% of total peak area, correlate with cycloalkane standards. For fraction 3, 14 of 26 peaks, representing 65% of total peak area, correlate with standards of the alkyl-benzenes. For fraction 4, 92% of the twelve peak areas is contributed by eight peaks which find correlation with standard naphthalenes, whereas four of the nine peaks in the fraction 5 chromatogram, with 24% of the peak area, are correlatable with biphenyl types. Only 18% of the fifteen peak area for fraction 6 is identifiable with four tri- and tetraaromatic compounds.

Mass spectral analysis of these GC peaks was undertaken. From a total of 87 peaks in these five fractions, there were 60 mass spectra obtained from the Finnigan

TABLE II
 GAS CHROMATOGRAPHY ANALYSIS OF FRACTION 3
 Temperature ramp 50°C (1 min) and 5°/min increase to 290°C.

Sample			Standards	
Peak No.	% of peak areas	RRT	Compound	RRT
1	0.3	0.45	<i>n</i> -Propylbenzene	0.45
2	2.8	0.47	1,3,5-Trimethylbenzene	0.48
3	0.2	0.52	<i>tert.</i> -Butylbenzene	0.53
4	1.5	0.54	1,2,4-Trimethylbenzene	0.54
5	8.1	0.68	1-Phenylbutane	0.67
			Indane	0.69
6	6.1	0.78	2-Phenylpentane	0.77
7	0.4	0.86		
8	5.9	0.92	1-Phenylpentane	0.91
9	2.8	0.96		
10	15.0	1.00	Tetralin	1.00
11	2.4	1.05	1,2,3-Trimethylbenzene	1.06
12	6.9	1.10		
13	3.6	1.14	1-Phenylhexane	1.13
14	12.4	1.23		
15	2.5	1.25		
16	7.2	1.33	Phenylcyclohexane	1.33
17	1.8	1.35	1-Phenylheptane	1.36
18	1.0	1.40		
19	2.8	1.44		
20	0.8	1.49		
21	5.2	1.51	Tetrahydroacenaphthene	1.50
22	1.7	1.55		
23	4.4	1.61	Hexamethylbenzene	1.61
24	5.2	1.72		
25	0.6	1.78		
26	2.8	1.84		

GC-MS system. In Tables VI-X are tabulated the mass spectra and computer analysis. For Each GC peak, the mass spectrum, if obtained, is described in terms of five major mass ions, the total number of significant peaks and the molecular ion. Assignment of a tentative structure to each mass spectrum was made by comparison with the EIHC (Electron Impact on Hydrocarbons) file of coal-related organic compounds maintained at the mass spectral library of IMMR and the GC correlations shown above. As confirmation and further elaboration of the structural assignments, the MS data were matched by a computer search method using the Cornell University Mass Spectral Identification Systems^{5,6}. This involves the retrieval system known as Probability Based Matching (PBM) which employs weighting of mass and abundance data and reverse searching, a system which has been shown to be superior for un-

TABLE III

GAS CHROMATOGRAPHY ANALYSIS OF FRACTION 4

Temperature ramp 50°C (1 min) and 5°/min increase to 290°C. Retention times are relative to tetralin.

Sample			Standards	
Peak No.	% of peak areas	RRT	Compound	RRT
1	30.2	1.11	Naphthalene	1.12
2	3.1	1.23		
3	9.4	1.31		
4	14.9	1.36	2-Methylnaphthalene	1.36
5	4.2	1.41	1-Methylnaphthalene	1.41
6	16.5	1.50	Tetrahydroacenaphthene	1.50
7	4.9	1.59	2,6-Dimethylnaphthalene	1.58
8	2.9	1.64	1,3-Dimethylnaphthalene	1.63
9	5.9	1.82	Acenaphthene	1.81
10	3.2	1.94		
11	2.4	2.01		
12	2.4	2.17	9,10-Dihydrophenanthrene	2.17

known spectra of mixtures. For further interpretation of the spectra, the MS data were treated to the only generally available interpretive algorithm "Self-Training Imperative and Retrieval System" (STIRS) which is applicable to most classes of organic compounds. The matching of the unknown data against the library files led to the identification of substructures or compound types. The structural candidates

TABLE IV

GAS CHROMATOGRAPHY ANALYSIS OF FRACTION 5

Temperature ramp 100°C (1 min) and 6°/min increase to 290°C. Retention times are relative to tetralin.

Sample			Standards	
Peak No.	% of peak areas	RRT	Compound	RRT
1	54.9	2.16		
2	1.7	2.41	Diphenylmethane	2.42
3	2.2	2.50		
4	13.6	2.66	4-Methylbiphenyl	2.65
5	5.1	shoulder		
6	12.1	2.88		
7	0.8	3.08	3,3'-Dimethylbiphenyl	3.09
8	8.0	3.29	9-Methylfluorene	3.29
9	1.6	3.78		

TABLE V
GAS CHROMATOGRAPHY ANALYSIS OF FRACTION 6

Temperature ramp 100°C (1 min) and 6°/min increase to 290°C.

Sample			Standards	
Peak No.	% of peak areas	RRT	Compound	RRT
1	0.7	2.45		
2	0.9	2.68		
3	2.5	2.72		
4	1.2	2.92		
5	2.1	3.16		
6	49.2	3.25		
7	4.9	3.80	9-Methylfluorene	3.29
8	22.1	3.81		
9	10.8	4.28	Phenanthrene	4.27
10	0.8	4.73		
11	0.6	4.88		
12	0.9	4.99		
13	0.6	5.51	Fluoranthene	5.50
14	0.9	5.75		
15	1.8	6.33	1-Methylpyrene	6.33

thus obtained are entered under the respective headings of PBM and STIRS in Tables VI-X.

Regarding fraction 2, 20 mass spectra out of 25 GC peaks were generated. From the EIHC file, peaks 3, 6, 9 are assigned single structures, 5, 7, 20 structure types and the remainder, except two, with molecular formula information. The PBM search is not particularly useful for this fraction because of high background level. Nevertheless, it has allowed assignment of structures to 6 and 10, and the assignment of structural types to 2 and 5. The STIRS has confirmed structures for 6 and 10, assigned a structure to 23 and showed the substituents for 2 and 5. These results are shown in Table VI.

From fraction 3 there were obtained 25 mass spectra out of 26 GC peaks. Of these, the EIHC file has produced tentative assignments of specific structures for thirteen peaks (1, 2, 4, 5, 10, 12, 13, 14, 15, 18, 19, 21, 25), structural types for four (6, 11, 15, 26), molecular formulas for three, but no information on five (7, 9, 22, 23, 24). The computer search for this and subsequent fractions was quite fruitful. PBM has supplied fourteen specific structures, six structural types and one molecular formula, while STIRS substantiated nine structures and nine structural types. Only two (5, 20) of the tentative assignments were not further identified, and peaks 7, 23 and 24 remain unknowns. These results are shown in Table VII.

Of the twelve GC peaks in fraction 4, mass spectra are available for eight, all of which have received tentative assignments. They are analyzed by PBM/STIRS to yield identifications of six specific compounds and two compound types. These results are shown in Table VIII.

TABLE VI
IDENTIFICATION OF COMPONENTS IN FRACTION 2 BY MS-COMPUTER ANALYSIS

Italicized values denote base peaks as 100% intensity.

GC peak no.	MS data		Tentative assignment		Computer search	
	Major m/e	No. of significant peaks	M ⁺ obs.	Compound or type	PBM	STIRS
1	40, 41, 53, 54, 97	20	126	Cyclo C ₉ H ₁₈	An alkylcyclohexane	Me
2	41, 53, 54, 96, 97	12	126	C ₉ H ₁₈		
3	53, 54, 81, 82, 83	20	126	Propylcyclohexane	An alkylcyclohexane	Me, Et, Pr
4	40, 53, 54, 96, 97	40	140	C ₁₀ H ₂₀		
5	40, 41, 54, 55, 97	13		an alkylcyclohexane	cis-Hexahydroindane	cis-Hexahydroindane
6	66, 67, 81, 82, 97	23	124	Hexahydroindane		
7	53, 54, 81, 82, 83	17	140	A butylcyclohexane	Bicyclo C ₁₀ + cyclo C ₁₁	
8	66, 67, 80, 81, 96	21	138, 154	Bicyclo C ₁₀ + cyclo C ₁₁		
9	66, 67, 68, 81, 95	20	138	Decalin	2-Methyl-trans-decalin	2-Methyl-trans-decalin
10	66, 67, 81, 95, 152	65	152	Bicyclo C ₁₁		
12	40, 41, 54, 55, 56	26		Bicyclo C ₁₂	Bicyclo C ₁₂	
14	41, 53, 54, 82, 83	64	166			
15	53, 54, 62, 81, 82	35	166	C ₁₂ H ₂₀	C ₁₂ H ₂₀ C ₁₂ H ₂₂	
16	40, 41, 54, 55, 56	68	164			
18	53, 54, 66, 67, 82	24	166	C ₁₂ H ₂₀	An ethylbicyclodecane	
19	41, 53, 54, 67, 97	29	164			
20	53, 54, 67, 82, 83	59	166			
23	66, 67, 81, 95, 137	55	152	A methylbicyclodecane	A methylbicyclodecane	2-n-Butyl-decalin
24	54, 67, 81, 96, 97	30	164	C ₁₂ H ₂₀		
25	66, 67, 81, 135, 192	64	150, 164	C ₁₁ H ₁₈ + C ₁₂ H ₂₀		

TABLE VII
IDENTIFICATION OF COMPONENTS IN FRACTION 3 BY MS-COMPUTER ANALYSIS
Italicized values denote base peaks as 100% intensity.

GC peak no.	MS data		Tentative assignment		Computer search		STIRS
	Major m/e	No. of significant peaks	M ⁺ obs.	Compound or type	PBM		
1	64, 65, 90, 91, 120	16	120	<i>n</i> -Propylbenzene	A substituted benzene		Phenyl
2	77, 79, 91, 105, 120	28	120	1,3,5-Trimethylbenzene	1,3,5-Trimethylbenzene		A C ₃ H ₇ -benzene
3	77, 79, 91, 105, 120	14	120	C ₉ H ₁₂			
4	77, 91, 103, 105, 120	24	120	1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene		
5	91, 115, 117, 118, 119	37	118	1-Phenylbutane + indane			
6	91, 115, 117, 132, 133	39	132	A methylindane	1-Methylindane		1-Methylindane
7	77, 91, 119, 120, 131	30					
8	77, 91, 105, 106, 148	30	148	C ₁₁ H ₁₆	A substituted benzene		<i>p</i> -Isobutyltoluene or a dimethylethylbenzene
9	91, 115, 117, 118, 132	36	132		Monomethylindanes		Monomethylindanes
10	78, 91, 104, 115, 132	39	132	Tetralin	Tetralin		
11	91, 115, 117, 131, 132	22	146	A methyltetralin	5-Methyltetralin		1- or 2-methyltetralin
12	91, 104, 115, 131, 146	26	146	2-Methyltetralin	2-Methyltetralin		2-Methyltetralin
13	91, 115, 117, 131, 132	38	146	5-Methyltetralin	5-Methyltetralin		5-Methyltetralin
14	117, 118, 131, 132, 146	48	146	6-Methyltetralin	6-Methyltetralin		6-Methyltetralin
15	91, 115, 117, 118, 131	70	160	A propylindane	A substituted indane		An alkylindane
16	91, 104, 117, 118, 160	67	146, 160	Phenylcyclohexane and a 2, <i>x</i> -dimethyltetralin	Phenylcyclopentane and 2,7-dimethyltetralin		Phenylcyclopentane and 2,7-dimethyltetralin
18	115, 117, 118, 129, 145	48	146, 160	A dimethyltetralin	1,1-Dimethyltetralin		1,1-, 1,5-, 2,6-, 2,7-dimethyltetralin
19	91, 115, 117, 131, 132	57	148	5-Ethyltetralin	An ethyltetralin		An ethyltetralin
20	91, 92, 105, 129, 148	20	148	C ₁₁ H ₁₆			
21	115, 128, 129, 130, 131	46	158	Tetrahydroacenaphthene	2a,3,4,5-Tetrahydroacenaphthene		2a,3,4,5-Tetrahydroacenaphthene
22	91, 117, 118, 131, 132	37			C ₁₀ H ₁₂		C ₁₀ H ₁₂
23	115, 129, 130, 131, 145	27					
24	91, 117, 129, 159, 160	40					
25	91, 104, 105, 131, 132	22	188	2-Butyltetralin	A tetralin		2- <i>tert</i> -Butyltetralin
26	115, 117, 131, 145, 146	30	188	5- or 6-butyltetralin	6-Butyltetralin		5- or 6-butyltetralin

TABLE VIII
IDENTIFICATION OF COMPONENTS IN FRACTION 4 BY MS-COMPUTER ANALYSIS
Italicized values denote base peaks as 100% intensity.

GC peak no.	MS data		Tentative assignment		Computer search	
	Major m/e	No. of significant peaks	M ⁺ obs.	Compound or type	PBM	STIRS
1	51, 63, 102, 127, 128	32	128	Naphthalene	Naphthalene	
3	73, 117, 118, 131, 148	39	146	A methyltetralin	5- or 6-methyltetralin	
4	63, 115, 139, 141, 142	53	142	2-Methylnaphthalene	2-Methylnaphthalene	
5	63, 115, 139, 141, 142	40	142	1-Methylnaphthalene	1-Methylnaphthalene	
6	115, 128, 129, 150, 145	52	158	Tetrahydroace-naphthene	Tetrahydroace-naphthene	
7	115, 128, 129, 141, 156	38	156	An ethylnaphthalene	A naphthalene	2-Ethylnaphthalene
9	129, 144, 152, 153, 154	22	154	Acenaphthene	A naphthalene	Acenaphthene
11	115, 128, 129, 141, 142	27		A naphthalene	A naphthalene	A naphthalene

TABLE IX
IDENTIFICATION OF COMPONENTS IN FRACTION 5 BY MS-COMPUTER ANALYSIS
Italicized values denote base peaks as 100% intensity.

GC peak	MS data		Tentative assignment		Computer search	
	Major m/e	No. of significant peaks	M ⁺ obs.	Compound or type	PBM	STIRS
1	51, 76, 152, 153, 154	60	154	Biphenyl	Biphenyl	Biphenyl
4	51, 63, 115, 152, 168	30	168	A methylbiphenyl		4-Methyl-biphenyl
6	52, 53, 64, 139, 168	27	168	Dibenzofuran	Dibenzofuran	
8	45, 82, 83, 152, 153	45		9-Methylfluorene		A diaromatic

TABLE X
IDENTIFICATION OF COMPONENTS IN FRACTION 6 BY MASS SPECTRA-COMPUTER ANALYSIS
Italicized values denote base peaks as 100% intensity.

GC peak	MS data		Tentative assignment		Computer search	
	Major m/e	No. of significant peaks	M ⁺ obs.	Compound or type	PBM	STIRS
6	63, 82, 139, <i>165</i> , 166	31	166	Fluorene	Fluorene	Fluorene
8	40, 74, 75, 76, 89	25	180	1-Methyl-fluorene	1-Methyl-fluorene	1-Methyl-fluorene
9	63, 75, 76, 89, 178	17	178	Phenanthrene	Phenanthrene	Phenanthrene

TABLE XI

COMPOSITION SUMMARY OF FRACTIONS 2-6 OF H-COAL ASO LIQUID

Fraction 1 (12%) contains UV-inactive aliphatic hydrocarbons and fraction 7 (11%) the polar or polynuclear aromatics.

Fraction	Components identified (% of GC trace)	% of fraction by GC peak area	% of ASO*	Av. mol. wt.	Av. molecular formula
2	Alkylcyclohexanes (5.4), hexahydroindane (6.5), methyldecalin (5.7)	17.6	2.4	129	C ₉ H ₁₇
3	Trimethylbenzenes (4.3), methylindanes (8.9), tetralin (15.0), alkyl- tetralins (32.3), tetra- hydroacenaphthene (5.2)	65.7	11.4	143	C ₁₁ H ₁₄
4	Tetrahydroacenaphthene (16.5), methyltetralins (9.4), naphthalene (30.2), alkylnaphthalenes (24.0)	80.1	16.1	141	C ₁₁ H ₁₁
5	Biphenyl (54.9), dibenzofuran (12.1)	67.0	10.1	157	C ₁₂ H ₁₀
6	Fluorene (49.2), methyl- fluorene (22.1), phenanthrene (10.8)	82.1	8.9	172	C ₁₃ H ₁₁

* Calculated from % of fraction × % (w/w) of fraction.

There are nine GC peaks for fraction 5, of which four, representing 89% of the total peak area, have yielded mass spectra. The same analysis routines have led to determination of three compounds and one tentative assignment. These results are shown in Table IX.

Although only three mass spectra were derived from fifteen of the GC peaks of fraction 6, the spectra are indicative of 83% of the material as represented by GC peak area. Three single compounds were unanimously picked by the three MS analysis routines as shown in Table X.

CONCLUSIONS

The HPLC fractions 2-6 have yielded 60 mass spectra from 87 GC peaks. Interpretation of the MS data by making use of the EIHC file of coal-related compounds and the huge Cornell mass spectra library have generated structures for 29 single compounds and 12 compound types. It appears that the HPLC fractionation of the H-Coal ASO liquid on Porasil A is by chemical class. Fraction 1 is comprised of UV-inactive aliphatic hydrocarbons. Fraction 2 contains cycloalkanes from al-

kylcyclohexanes to alkyldecalins. Fraction 3 is made up of monoaromatics from a trimethylbenzene to an alkyltetralin. The fraction 4 materials are naphthalenes, fraction 5 the biphenyl types and fraction 6 the fluorenes and phenanthrenes. The larger polynuclear aromatics are probably contained in the polar fraction 7. In Table XI are summarized the above compositional analyses. The components identified as single compounds or compound types, their distributions in each HPLC fraction and in the whole liquid are shown. The average molecular weights and molecular formulas are calculated for each fraction on the basis of the components identified. It is noted that $\approx 49\%$ by weight of ASO is accounted for by components containing about eleven carbons.

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