

## ORGANIC STRUCTURAL STUDIES OF LIGNITE COAL TARS

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### INTRODUCTION

The Grand Forks Energy Technology Center is operating a 900 kg/hr slagging fixed-bed gasification pilot plant. The pilot plant was installed in 1958 and was first operated until 1965 (1). The renewed interest in producing synthetic natural gas and the environmental concerns associated with commercial-scale gasification facilities led to resumption of operations of the Grand Forks gasification pilot plant in 1976. A major objective of the renewed gasification program was to utilize the gasifier to acquire environmental assessment data for a variety of low-rank coals (2). Of particular interest was the identification and characterization of effluents. It has been shown that tar composition can be correlated with the chemical properties of the lignite gasified (3). A detailed understanding of the chemical composition and structure of effluents, such as coal tar, is of two-fold importance. First, such understanding, when coupled with information about reaction conditions such as temperature and partial pressure of hydrogen, provides clues for deducing structural relationships in the lignites. Second, knowledge of the tar composition also provides guidance for designing down-stream effluent treatment or by-product recovery unit operations.

A previous publication (4) presents data on the low-voltage mass spectrometric analysis of nine tar samples, obtained from the gasification of four low-rank coals at a variety of gasification conditions. Extensive statistical analysis of the data, similar to that presented here, showed that the major factors affecting on tar composition are the partial pressure of hydrogen and the residence time of the coal in the gasifier. These results agree with conclusions developed in other laboratories (5). The success obtained in deriving these relationships from the mass spectrometric analyses and the agreement with known behavior of other systems led to the present study in which attention was focused on two tar samples obtained from the gasification of similar lignites under identical conditions. The results reported here are compared with data from other laboratories to suggest relationships between tar composition and possible structural features in the parent lignites.

### EXPERIMENTAL

#### Sample Preparation

Samples of as-received gasifier tar were distilled at reduced pressure to remove water and volatile light oils. Saturate determinations were performed by column chromatographic elution with hexane from neutral alumina. Fractions for high resolution mass spectroscopic analysis were prepared by a method previously described (6).

#### Mass Spectrometry (HRMS and LVMS)

The instrument used was an AEI MS-30\* single-beam high-resolution mass spectrometer interfaced with a DS-50 data system. Approximately 1 mg of gross sample or of column chromatography fractions was introduced into the mass spectrometer using an all-glass heated inlet system operating at 300°C. Source temperature was 300°C, the ion source pressure was  $2.0\text{-}2.7 \times 10^{-4}$  Pa and the ionizing

voltage was 70 eV. A medium resolution spectrum (8000-9000 resolving power) was obtained for each fraction and for the gross sample for molecular formula assignment.

Quantitative data was obtained by lowering the ionization potential to 10 eV (7) and decreasing the resolution to 1500. A minimum of six scans are averaged and calibration with known hydrocarbons, oxygen compounds and nitrogen compounds was used to calculate concentrations from the low-voltage intensity data.

Gas Chromatography - Mass Spectrometry (GC-MS)

Materials were analyzed by GC-MS using a Varian 2740 gas chromatograph coupled with a DuPont 21-491B mass spectrometer. A 1.2 m x 2 mm i.d. glass column packed with 3% OV-17 on 80/100 Supelcoport was used for compound separation. The helium carrier gas flow rate was 30 ml/min and the column temperature was programmed from 70-300°C at 6°C/min. GC peak areas were determined using a Spectra Physics System I computing integrator and response factors were measured with appropriate pure standards. The ion source was at 250°C and ionizing voltage was 70 eV.

\* Reference to specific brand names or models is done to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy.

RESULTS AND CONCLUSIONS

The mass spectrometric analysis of tars from the gasification of two North Dakota lignites, Indian Head (IH) and Baukol-Noonan (BN), provide the basis for this study. The as-received proximate analyses of these coals are nearly identical as shown in Table 1. The ultimate analyses, also shown in Table 1, indicate that Indian Head lignite has a much lower carbon/hydrogen atomic ratio than does Baukol-Noonan lignite, 1.2 and 2.3 respectively. However, the maf oxygen and nitrogen content of these coals are nearly identical. The operating conditions for gasification of the two lignites were nearly identical: 2.1 MPa operating pressure, 170 m<sup>3</sup>/hr oxygen feed rate, 1.0 oxygen/steam molar ratio, and 41 minutes average coal residence time. The two tests from which these samples were obtained are RA-52 (IH) and RA-66 (BN) in the current gasification program. Details of these tests have been published elsewhere (8).

Table 2 gives the low-voltage mass spectrometric carbon number data for the aromatic portion of Indian Head (35%) and Baukol-Noonan (37%) tars. Comparison of the tar analyses indicate several trends. Baukol-Noonan

TABLE 1. - Analyses of coals gasified

	<u>Indian Head</u> <u>lignite</u> Mercer Co Central, ND	<u>Baukol-Noonan</u> <u>lignite</u> Burke Co Northwest, ND
Proximate analyses, % as rec'd		
Moisture	29.1	32.6
Volatile matter	28.0	26.5
Fixed carbon	34.7	34.6
Ash	8.2	6.3

Ultimate analyses, % maf		
H	4.8	2.7
C	70.8	73.7
N	0.9	0.9
S	1.8	0.7
O (by difference)	21.7	22.1

1/ These values do not represent as-mined moisture because of partial drying during storage and handling.

tar contains generally larger amounts of compounds with no substitution and larger amounts of two-, three-, and four-ring compounds. Indian Head tar generally tends to have more one-ring compounds. Table 3 shows some of the comparisons.

Indian Head and Baukol-Noonan tar analyses were compared with data obtained by Hayatsu and co-workers (9). They reported the results of gas chromatographic analysis of the hydrocarbon-rich fraction of 3:1 benzene/methanol extraction of Decker lignite. Their chromatograms identified approximately 25 compounds isolated from the lignite extract. The mass spectrometric analysis of the gasifier tar contains 17 of the same compound types, based on Z number and molecular weight matches. The major difference between the lignite extract and the gasifier tar is that the latter lacks the highly substituted compounds, such as C<sub>10</sub> benzenes or C<sub>5</sub> tetralins. This difference is expected when conditions under which the samples were produced are taken into account since it is generally considered that aliphatic side chains are vulnerable to thermal cleavage during coal tar formation (10).

Ranking compounds in gasifier tar by quantity found provides a correlation with published data for the thermal stability of various polynuclear aromatic hydrocarbons. Sharkey and co-workers (11) determined the thermal stability of 20 compounds from the product ratio of the liquid-phase pyrolysis of polynuclear aromatic hydrocarbons. Table 4 shows the comparison between the published thermal stability ranking and quantities observed in Indian Head gasifier tar.

In general, only those compound types that could be identified unambiguously are included in the table. For example, compounds with a Z number of -16 may be fluorenes or acenaphthalenes; and therefore are not included in the table. An exception is 2,6-dimethylnaphthalene (Z= -12, MW=156); although an unambiguous assignment was not made, the 2,6-isomer is reported to be more stable than some other dimethylnaphthalenes (12) and is one of only two isomers reported in low temperature carbonization tar in an extensive compilation (13). The similarity of tar from the GFETC gasifier to that of other low-temperature carbonization processes has been shown previously (14).

Since unequivocal identifications were not made as a part of the study reported here, no attempt was made to correlate these compounds with other data. The Spearman rank correlation (15) found for this ranking was 0.725; a value of this magnitude could occur by chance with less than 0.01 probability.

The tar samples used in this study were chosen from tests at identical gasification conditions to eliminate the effects of operating conditions on tar composition which have been reported previously (16). The major difference between the two lignites, carbon/hydrogen ratio, indicates that Baukol-Noonan has a more aromatic nature than does Indian Head lignite. Thermal cracking of these coals during gasification results in distinctly different tars. Baukol-Noonan lignite produces a more aromatic tar, presumably as a result of the initial loss of smaller aliphatic units during carbonization. An indication of this reaction may be the greater amounts of methane produced during the gasification of Baukol-Noonan lignite as compared to Indian Head lignite (Table 5). It has been shown previously

TABLE 2. - Low Voltage Mass Spectrometric Analysis of the Aromatic Portion of Indian Head and Baukol-Noonan Tars

Probable Structural Type	Z#	Carbon Number																	Total
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21		
Benzenes	-6	0.04	0.17	0.22	0.40	0.00													0.83
		0.02	0.16	0.18	0.33	0.00													
Indanes/Tetralins	-8	0.07	0.71	1.27	1.05	0.69	0.40												4.19
		0.14	0.65	0.94	1.00	0.78	0.48												
Indenes	-10	0.00	0.32	0.00															0.32
		0.05	0.24	0.00															
Naphthalenes	-12	3.00	2.16	1.34	0.98	0.87	0.66	0.46	0.31	0.24									10.03
		0.58	1.23	1.18	1.10	1.17	0.98	0.65	0.45	0.31									
Acenaphthene/Biphenyl	-14	0.83	0.62	0.48	0.37	0.24	0.16	0.11											2.81
		0.92	0.74	0.67	0.49	0.32	0.23	0.15											
Fluorene/Acenaphthalenes	-16	2.01	2.86	0.69	0.43	0.39	0.25	0.21	0.18										7.02
		1.76	3.03	0.92	0.61	0.51	0.36	0.26	0.22										
Phenanthrene/Anthracenes	-18																		4.78
Pyrenes/Fluoranthenes	-22																		2.88
Chrysenes	-24																		0.96
Benzopyrenes	-28																		1.19

Indian Head  
Baukol-Noonan

TABLE 3. - Comparison of Indian Head and Baukol-Noonan tars

	<u>Z#</u>	<u>Mass</u>	<u>IH (%)</u>	<u>BN (%)</u>
1 Ring	-6	92	0.2	0.2
		106	0.2	0.2
		120	0.4	0.3
	-8	132	0.7	0.6
		146	1.3	0.9
		160	1.1	1.0
	-10	130	0.3	0.2
2 Ring	-12	128	3.0	0.6
		142	2.2	1.2
		156	1.3	1.2
	-14	154	0.8	0.9
		168	0.6	0.7
		182	0.5	0.6
	-16	152	2.0	1.7
		166	2.8	3.0
		180	0.7	0.9
	3 Ring	-18	178	2.3
192			0.9	1.2
206			0.6	0.9
4 Ring		-22	202	1.8
	216		0.6	0.8
	-24	228	0.6	0.7
		242	0.2	0.3

TABLE 4. - Comparison of thermal stability with  
observed quantity in Indian Head tar

<u>Compound</u>	<u>Thermal stability ranking</u>	<u>Quantity observed in Indian Head tar</u>	<u>Rank</u>
Naphthalene	1	3.00	1
Pyrene	2	1.81	3
Chrysene	3	0.59	8
2 - Methylphenanthrene	4	0.91	5
Acenaphthene	5	0.83	6
1 - Phenyl-naphthalene	6	0.47	10
2,6 - Dimethylnaphthalene	7	1.34	4
$\alpha$ - Methyl-naphthalene	8	2.16	2
1,2 - Diphenylethane	9	0.48	9
Dihydroanthracene	10	0.69	7
1 - (o-tolyl) - Naphthalene	11	0.31	11
Indene	12	0.00	13
Indane	13	0.07	12

TABLE 5. - Analyses of hydrocarbons in product gas

<u>Component (%)</u>	<u>IH</u>	<u>BN</u>
CH <sub>4</sub>	5.1	6.0
C <sub>2</sub> H <sub>4</sub>	0.2	0.2
C <sub>2</sub> H <sub>6</sub>	0.3	0.3
C <sub>3</sub> H <sub>6</sub>	0.1	0.1
C <sub>3</sub> H <sub>8</sub>	0.0	0.0
C <sub>4</sub> H <sub>10</sub>	0.0	0.0
Total HC's	5.7	6.6

(17) by two-sided comparison of the means that the difference is statistically significant at the 95% confidence level. Conversely, Indian Head lignite, a more aliphatic coal, produces a tar consisting of primarily small and highly substituted aromatic compounds. This is possibly due to cleavage of hydro aromatic units in the coal at methylene bridges and reactions with available hydrogen.

The good correlation between the quantities of compounds in Indian Head tar and the thermal stabilities of those compounds indicates that the organic units found in the tar are the survivors of thermal degradation processes in the gasifier. At the same time, however, the relationships between the compound types in the tar and those obtained from mild solvent extraction conditions suggest that the molecular structures in the tar are determined not only by thermal processes but also by structural relationships in the parent lignite.

Since tar structures very likely reflect coal structures, differences in the tar analyses can be related to structural differences in the coals. The development of an understanding of the effect of the molecular frameworks in coal and the likely mechanisms of tar formation will assist in assessing and predicting the chemical nature of such effluents.

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