

# CHEMICAL STRUCTURE OF COAL TAR DURING DEVOLATILIZATION USING SOLID-STATE $^{13}\text{C}$ NMR

E. M. Hambly<sup>1</sup>, T. H. Fletcher<sup>1</sup>, M. S. Solum<sup>2</sup>, and R. J. Pugmire<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering Brigham Young University, Provo, Utah 84602  
<sup>2</sup>Departments of Chemistry<sup>2</sup> and Chemical and Fuels Engineering<sup>3</sup>, University of Utah, Salt Lake City, Utah 84112

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## Introduction

Recent advancements in chemical analysis techniques have allowed quantitative investigations of the chemical structure of both coal and its pyrolysis products.<sup>1-2</sup> Solid-state  $^{13}\text{C}$  NMR spectroscopy has proven particularly useful in obtaining average values of chemical structure features of coal and char, while liquid phase  $^1\text{H}$  NMR spectroscopy has been used to determine some of the chemical features of coal tar.<sup>3-6</sup>

Watt et al.<sup>7</sup> performed pyrolysis experiments on 3 coals at 930 K, and reported solid-state  $^{13}\text{C}$  NMR analyses of the coals and chars and liquid  $^{13}\text{C}$  NMR analyses of the corresponding tars. Tars were dissolved in deuterated methylene chloride ( $\text{CD}_2\text{Cl}_2$ ) prior to analysis. The non-soluble tar portion was analyzed with standard solid-state  $^{13}\text{C}$  NMR techniques.<sup>7</sup> The soluble tar portion was analyzed using a high resolution  $^{13}\text{C}$  NMR technique developed for liquid phases.<sup>7</sup> The liquid  $^{13}\text{C}$  NMR data, as well as the composite tar data, indicated that the chemical structure of the tar was significantly different from the original coal. The number of bridges and loops per cluster in the tar was found to be much lower than that of either the coal or the char. Additionally, the number of aromatic carbons per cluster in the tar was found to be significantly lower than that of the coal or char. These data were in major disagreement with key assumptions in current network devolatilization models. Watt's data were subject to question based on (a) the use of a solvent prior to analysis of the tar, and (b) collection of tar at such low temperatures where devolatilization was not complete (e.g., ~38% mass release for an Illinois #6 coal). The experiments reported here were performed at a higher temperature (and hence higher degree of pyrolysis). The resulting tars were analyzed as received with standard solid-state  $^{13}\text{C}$  NMR techniques.

## Experimental Apparatus

Samples of tar and char were produced at atmospheric pressure in a laminar flow drop tube reactor similar to that used by Watt.<sup>7-8</sup> The tars and aerosols are collected on polycarbonate filters so that tar samples can be scraped from the filters rather than removed using a solvent. Coals were pyrolyzed at atmospheric pressure in 100% nitrogen at a gas temperature of 1080 K with a residence time of 282 ms. This temperature has been chosen since it provides a high degree of pyrolysis while minimizing secondary reactions of the resulting tar. Five coals of different rank were examined, with properties listed in Table 1. The 63-75  $\mu\text{m}$  size fraction was used in all of these experiments, resulting in heating rates of approximately  $10^4$  K/s. The "D" on the Penn State coal identification number signifies coals from a suite selected by the DOE Pittsburgh Energy Technology Center's Direct Utilization/AR&TD program. These coals have been well characterized and studied by many other researchers.<sup>4,7-12</sup>

## Results and Discussion

A summary of the pyrolysis yield data and elemental composition of the tar is provided in Table 2. As expected, the volatiles yields are high; the coals are nearly completely devolatilized. In addition, the shape of the total volatiles and tar yield curves versus rank are as expected, with relatively constant values from lignite through the high volatile bituminous coal, then dropping for the low volatile bituminous coal.<sup>3-5,11-12,13-16</sup> Elemental analyses of the corresponding chars are currently under way.<sup>17</sup>

Solid state  $^{13}\text{C}$  NMR techniques (CP/MAS and dipolar dephasing) were used to determine the chemical structural features of coals and coal tars.<sup>3,18</sup> The solid-state  $^{13}\text{C}$  NMR data for the tars are presented in Tables 3 and 4, along the corresponding analyses of the coals. The composite tar data from Watt<sup>7-8</sup> are also presented for comparison. Comparing the NMR data for the tar and the coal provides insight into the nature of the structural changes that occur during pyrolysis. The carbon aromaticity ( $f_a$ ) of the tar is 14 to 53 percent higher than in the parent coal (on a relative basis). In general, the aromaticity of the tars seems to increase slightly with coal rank.

The values of the average number of aromatic carbons per cluster ( $C_{Cl}$ ) in the tar range from 9 to 16 (see Figure 1). With the exception of the lignite, the value of  $C_{Cl}$  in the tar is similar to that of the corresponding parent coal. The data reported by Watt et al.<sup>7</sup> are also shown here, with  $C_{Cl}$  values of the composite tar ranging from 8 to 11. The solid-state tar data reported here

are thought to be less prone to error than the data from the liquid-phase analysis. Based on these new data, it appears that errors may be generated in using a solvent. These new data on tar help to confirm the assumption that the values of  $C_{Cl}$  in the tar are equal to those in the parent coals, an assumption that is used extensively in the network coal pyrolysis models.<sup>19</sup>

The number of side chains per cluster (S.C.) in the tar is much lower than in the corresponding coals (see Table 4). In the parent coals, the values of S.C. decrease with rank, while this trend is not seen in the resulting tars. The values of S.C. from the liquid-phase analysis were slightly higher than the values from the solid-state analysis, but still much lower than in the parent coal. The fact that the number of aromatic carbons per cluster are similar for both coal and tar and that the number of side chains per cluster is greatly lower in the tar is consistent with the increased aromaticity in the tars.

The number of attachments per cluster ( $\sigma+1$ ) in the tar is less than in the parent coal, as shown in Table 4. The liquid-phase analysis yielded values of  $\sigma+1$  that were slightly lower than observed from the solid-state analysis. Interestingly, while  $\sigma+1$  varies with coal type for the parent coals,  $\sigma+1$  is nearly constant with coal type for the tars. The number of bridges and loops per cluster (B.L.) in the tar is higher than in the corresponding coal, as shown in Table 4, although the increase is slight for the Illinois #6 coal. In contrast, the liquid phase analysis reported values of B.L. that were much lower than in the parent coal. For all coals, the average cluster molecular weight ( $MW_{Cl}$ ) in the tars is lower than in the parent coals (see Figure 2). This was also seen in the liquid-phase analysis. The values of  $MW_{Cl}$  in the coals decrease with increasing rank; this trend is not seen in the tars. Except for the Beulah Zap lignite, the  $MW_{Cl}$  in the tars is relatively constant with rank. Several sets of data indicate that tar molecular weight distributions peak in the range of 250 to 400 daltons.<sup>11,20-21</sup> The tars in this study have molecular weights per cluster in the range of 170 to 240 daltons. This discrepancy seems to indicate the presence of species in some of the reported tar data that contain more than one cluster (i.e., dimers and trimers rather than monomers); whereas the data reported in this work is based on the average molecular weight of monomer units. The slight increase in the number of bridges and loops per cluster (B.L.) in the tar may indicate that some form of polymerization may have occurred in the tars. This result would be consistent with the presence of dimers in the tar and would rationalize the differences in the mass of the monomer units defined by the NMR data and that reported by other investigators using different analytical techniques that do not define the basic monomer unit.

As seen in Figure 3, the average molecular weight of side chains ( $MW_s$ ) in the tar is much lower than that found in the parent coals. This result is different than that reported with the liquid-state analysis. While  $MW_s$  decreases steadily with rank, in the coals,  $MW_s$  in the tars is relatively constant with rank, within the experimental error of the data.

The main difference between the solid-state analysis and the liquid phase analysis seems to be in the number of side chains per cluster, which influences the aromaticity as well as the number of attachments per cluster. The fact that the liquid-phase analyses of tars dissolved in solvent produced NMR results that were quite different from the solid-state analyses seems to indicate that the use of solvents (such as  $CH_2Cl_2$ ) prior to other types of tar analysis may give misleading results.

The chemical structure of these tars, as determined from solid-state <sup>13</sup>C NMR spectroscopy, do not vary greatly with coal rank. The greatest differences seem to be in the tars from the lignite. However, large differences in tar yield are seen as a function of coal rank, as expected. The similarity in chemical structure of the coal tars is somewhat surprising since large differences are seen in the elemental composition of these tars. Additional experiments are underway to determine the chemical structural features of tars obtained at different temperatures and to compare the results with the corresponding chars.<sup>21</sup>

## Conclusions

Standard solid-state <sup>13</sup>C NMR techniques were used to analyze coal tar from five coals of different rank. This is the first set of solid-state data for coal tar. Tar was produced at atmospheric pressure in a drop tube reactor at a temperature of 1080 K and a residence time of 282 ms. The parent coals were also analyzed for comparison using solid-state <sup>13</sup>C NMR.

The tars analyzed in this study represent a nearly completely devolatilized coal. Previous data from liquid-phase <sup>13</sup>C NMR analyses of tars of partially devolatilized coals were compared with new solid-state analyses. These new tar data indicate that there may be significant errors associated with using solvents to study tar structure. Since tars from the two experiments were not obtained at the same temperature, it is recommended that low temperature pyrolysis experiments be performed and the tars analyzed with solid-state <sup>13</sup>C NMR techniques.

These new <sup>13</sup>C NMR data on coal tars indicate that the average chemical structure of tar does not vary greatly with coal type under the conditions used in this study, with the largest differences found in lignites, even though the variation in the chemical structures of the parent coals is much more significant.

**Table 1**  
**Coal Properties**

Coal	PSOC ID	Rank	%C (daf)	%H (daf)	%N (daf)	%S (daf)	%O (daf) (by diff.)	%Ash (dry)
Beulah Zap	1507D	ligA	64.16	4.78	0.94	1.81	28.32	13.92
Blue #1	1445D	subA	74.23	5.48	1.30	0.65	18.35	3.29
Illinois #6	1493D	hvCb	74.81	5.33	1.48	4.85	13.54	9.65
Pittsburgh #8	1451D	hvAb	82.77	5.61	1.74	0.98	8.90	4.29
Pocahontas #3	1508D	lvb	90.92	4.51	1.34	0.82	2.41	11.92

**Table 2**  
**Pyrolysis Yields and Tar Elemental Composition**

Coal	Vol. (% of daf coal)	Tar (% of daf coal)	%C	%H	%N
Beulah Zap	54.36	1.51	78.71	4.90	1.30
Blue #1	57.67	10.92	83.61	4.85	1.68
Illinois #6	59.91	12.47	85.23	4.89	1.80
Pittsburgh #8	46.24	19.92	87.68	4.94	1.96
Pocahontas #3	24.89	7.33	92.13	4.87	1.34

**Table 3**  
**<sup>13</sup>C NMR Analysis of Coals and Tars\***

Coal	Sample	f <sub>a</sub>	f <sub>a</sub> <sup>C</sup>	f <sub>a</sub> <sup>H</sup>	f <sub>a</sub> <sup>N</sup>	f <sub>a</sub> <sup>P</sup>	f <sub>a</sub> <sup>S</sup>	f <sub>a</sub> <sup>B</sup>	f <sub>al</sub>	f <sub>al</sub> <sup>H</sup>	f <sub>al</sub> <sup>*</sup>	f <sub>al</sub> <sup>O</sup>	
Beulah Zap	coal	65	8	57	19	38	7	14	17	35	24	11	11
Beulah Zap	tar	88	7	81	36	45	11	22	12	12	7	5	2
Blue #1	coal	60	5	55	19	36	8	13	15	40	29	11	7
Blue #1	tar	88	4	84	35	49	8	18	23	12	6	6	1
Watt Blue #1	tar*	64	7	57	27	31	8	16	7	36	27	10	na
Illinois #6	coal	66	3	63	21	42	7	16	19	34	24	1	8
Illinois #6	tar	88	2	86	36	50	7	19	24	12	6	6	1
Watt Illinois #6	tar*	74	3	71	35	36	6	16	14	26	17	9	na
Pittsburgh #8	coal	65	3	62	23	39	5	16	18	35	24	11	7
Pittsburgh #8	tar	86	2	84	36	48	5	18	25	14	7	7	2
Watt Pitt #8	tar*	73	2	70	37	33	6	16	12	28	18	10	na
Pocahontas #3	coal	78	1	77	32	45	2	15	28	22	15	7	7
Pocahontas #3	tar	89	1	88	38	50	3	18	29	11	7	4	2

\*Percentage carbon (error): f<sub>a</sub> = total sp<sup>2</sup>-hybridized carbon (±3); f<sub>a</sub><sup>C</sup> = aromatic carbon (±4); f<sub>a</sub><sup>H</sup> = carbonyl, δ > 165 ppm (±2); f<sub>a</sub><sup>H</sup> = aromatic with proton attachment (±3); f<sub>a</sub><sup>N</sup> = nonprotonated aromatic (±3); f<sub>a</sub><sup>P</sup> = phenolic or phenolic ether, δ = 150-165 ppm (±2); f<sub>a</sub><sup>S</sup> = alkylated aromatic δ = 135-150 ppm(±3); f<sub>a</sub><sup>B</sup> = aromatic bridgehead (±4); f<sub>al</sub> = aliphatic carbon (±2); f<sub>al</sub><sup>H</sup> = CH or CH<sub>2</sub> (±2); f<sub>al</sub><sup>\*</sup> = CH<sub>3</sub> or nonprotonated (±2); f<sub>al</sub><sup>O</sup> = bonded to oxygen, δ = 50-90 ppm (±2). \*Composite values reported by Watt et al.

**Table 4**  
**Derived Properties of Coal and Tar<sup>b</sup>**

Coal	Sample	$\chi_b$	$C_{Cl}$	$\sigma+1$	$P_0$	B.L.	S.C.	$MW_{Cl}$	$MW_\delta$
Beulah Zap	coal	0.246	14	5.2	0.48	2.4	2.8	440	52
Beulah Zap	tar	0.148	9	3.7	0.85	3.2	0.5	170	16
Blue #1	coal	0.270	13	5.0	0.48	2.4	2.6	371	42
Blue #1	tar	0.274	13	4.0	0.77	3.1	0.9	222	15
Watt Blue #1	tar*	0.112	8	3.2	0.58	1.8	1.4	205	35
Illinois #6	coal	0.300	15	5.5	0.52	2.9	2.6	368	35
Illinois #6	tar	0.279	13	3.9	0.77	3.0	0.9	213	13
Watt Illinois #6	tar*	0.197	11	3.4	0.56	2.0	1.3	228	30
Pittsburgh #8	coal	0.290	14	4.8	0.48	2.3	2.5	323	32
Pittsburgh #8	tar	0.298	14	3.8	0.70	2.7	1.1	228	14
Watt Pitt #8	tar*	0.163	9	2.8	0.52	1.5	1.3	178	25
Pocahontas #3	coal	0.364	18	4.0	0.59	2.3	1.7	316	23
Pocahontas #3	tar	0.330	16	3.8	0.81	3.1	0.7	237	10

<sup>b</sup>  $\chi_b$  = fraction of bridgehead carbons,  $C_{Cl}$  = aromatic carbons per cluster,  $\sigma+1$  = total attachments per cluster,  $P_0$  = fraction of attachments that are bridges, B.L. = bridges and loops per cluster, S.C. = side chains per cluster,  $MW_{Cl}$  = the average molecular weight of an aromatic cluster,  $MW_\delta$  = the average molecular weight of the cluster attachments. \*Composite values reported by Watt et al.<sup>7</sup>

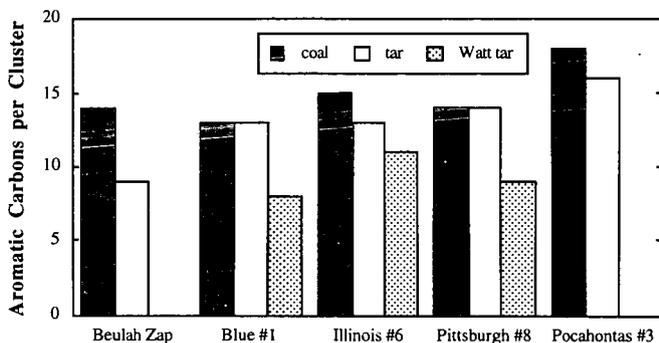


Figure 1. Aromatic carbons per cluster ( $C_{Cl}$ ) in coal and tar. Previously reported data from Watt et al.<sup>7</sup> are shown for comparative purposes.

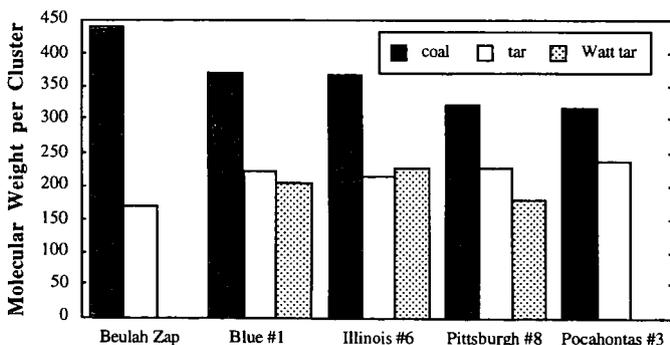


Figure 2. Molecular weight per cluster ( $MW_{Cl}$ ) in coal and tar. Previously reported data from Watt et al.<sup>7</sup> are shown for comparative purposes.

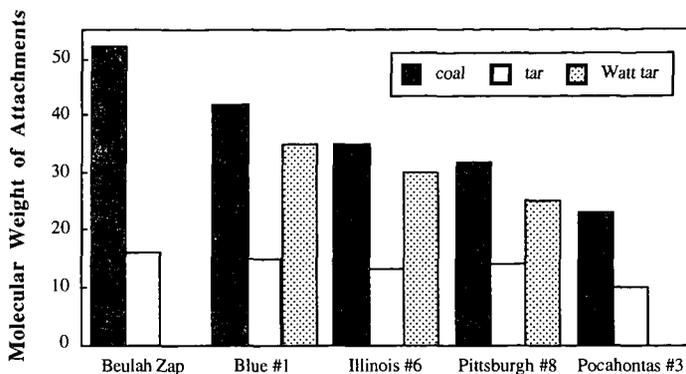


Figure 3. Molecular weight of cluster attachments (MW<sub>a</sub>) in coal and tar. Previously reported data from Watt et al.<sup>7</sup> are shown for comparative purposes.

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