

# PREDICTING $^{13}\text{C}$ NMR MEASUREMENTS OF CHEMICAL STRUCTURE OF COAL BASED ON ELEMENTAL COMPOSITION AND VOLATILE MATTER CONTENT

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## INTRODUCTION

Devolatilization models based on quantitative measurements of chemical structure, such as available through  $^{13}\text{C}$  NMR analysis, have been successful in predicting tar volatiles yields as a function of heating rate, temperature, pressure, and coal type.<sup>1</sup> However, due to limited resources,  $^{13}\text{C}$  NMR structural parameters have only been obtained for about 35 coals at the present time. Industrial interest in coal devolatilization has led to several attempts to correlate structural parameters affecting devolatilization as a function of the ultimate analysis of coals. Serio, et al.<sup>2</sup> used a triangular (i.e., linear) interpolation technique to estimate the input parameters for the FG-DVC devolatilization model.<sup>3</sup> Niksa and Kerstein<sup>4</sup> also developed a procedure that estimates the coal structural parameters based on simple linear correlations of ultimate analysis.<sup>5,6</sup>

An extensive statistical analysis to determine the validity of linear correlations of  $^{13}\text{C}$  NMR structural parameters based on ultimate analysis; preliminary results of this analysis were presented by Genetti and coworkers.<sup>7</sup> A database including elemental composition, the ASTM volatile matter content, and  $^{13}\text{C}$  NMR structural parameters for 30 coals of widely varying rank and composition was used in the analysis. The database was closely examined using the SPSS<sup>®</sup> statistical computer package. Using SPSS<sup>®</sup>, a correlation matrix was calculated between all of the chemical structural parameters obtained from the NMR analysis. From the correlation matrix, the strength of relationships between the individual elements and the derived parameters were easily determined. The parameters were also examined for relationships among themselves. Multi-variate linear regression was then performed to derive equations that predict each of the parameters as a function of the elemental composition and volatile matter content. The  $r^2$  value was then determined for each correlation.

The  $r^2$  value is the coefficient of determination which determines the relative strength of correlation ( $r^2=1$  is a perfect correlation). In this analysis the  $r^2$  values ranged from 0.17 for  $\sigma+1$  to 0.59 for  $M_8$  ( $r^2=0.49$  for  $P_0$  and  $r^2=0.38$  for  $MW_{cl}$ ). The low  $r^2$  values indicate a only weak linear correlation between the  $^{13}\text{C}$  NMR structural parameters and the ultimate analysis. However, even when  $r^2$  is zero, a strong non-linear correlation is possible. As a result of this study, it was determined that correlations based on linear regressions of ultimate analysis are unsuitable for predicting  $^{13}\text{C}$  NMR structural parameters with reasonable accuracy. The purpose of this investigation is to develop non-linear correlations that predict the chemical structure parameters generally measured by  $^{13}\text{C}$  NMR and required for the CPD devolatilization model:<sup>1</sup> (i) the average molecular weight per side chain ( $M_8$ ); (ii) the average molecular weight per aromatic cluster ( $MW_{cl}$ ); (iii) the ratio of bridges to total attachments ( $P_0$ ); and (iv) the total attachments per cluster ( $\sigma+1$ ).

## CORRELATION OF $M_8$ , $MW_{cl}$ , $P_0$ , AND $\sigma+1$

The database collected for 30 coals of varying rank used by Genetti, et al.<sup>7</sup> is shown in Table 1. The database includes the elemental composition, the volatile matter content, and the measured values of the four chemical structural parameters derived from  $^{13}\text{C}$  NMR analysis that are required in the CPD model.

Coals 1-7 are Argonne premium coals, 8-16 are coals used at Sandia National Laboratories, data for 17-18 came directly from Advanced Fuel Research, and coals 19-30 are coals from the Penn State coal sample bank. The volatile matter content data for the Penn State coals were taken directly from the Penn State coal sample database. Ultimate analysis on the Penn State coals was performed independently by Western Analytical and Huffman Laboratories and the average values are listed in Table 1. It is apparent that a diverse range of coals were used in this investigation.

Each  $^{13}\text{C}$  NMR parameter was plotted against the different elemental constituents and the volatile matter content in order to determine relative dependence on each variables. This made it possible to see visually and quantitatively any possible correlation patterns. A non-linear (e.g., polynomial) correlation was then made for each of these plots, and the  $r^2$  value was calculated to determine the strength of correlation. For example, it was determined that the value of  $M_8$  depends significantly on the relative contents of carbon, hydrogen, oxygen, and volatile matter. Once it was determined that  $M_8$  was dependent on carbon, hydrogen, oxygen, and volatile matter content, the best fit equations from the four plots were added together. Once the form of the equation was determined, coefficients were determined by minimization of the sum square error between the measured value and the predicted value of  $M_8$ . Any obvious outlying points were removed. Only the DECS-13 coal was a consistent outlier for the  $M_8$  correlation. The following is the equation resulting from the final optimization ( $r^2=0.87$ ).

$$M_8 = c_1 + c_2 x_C + c_3 10^{4.2H} + c_4 x_O + c_5 x_O^2 + c_7 VM + c_8 VM^2 \quad (1)$$

where C, H, O, and VM represent the mass percent carbon, hydrogen, oxygen, and ASTM volatile content on a daf basis, and the  $c_i$  are empirical coefficients. This procedure was repeated for  $\sigma+1$ ,  $P_0$ , and  $MW_{cl}$ . A modified cubic correlation was also determined ( $r^2 = 0.88$ ), but this correlation gave unrealistic values of  $MW_{cl}$  and  $\sigma+1$  for low rank coals ( $\%O > 25\%$ ) and high rank coals (VM

< 10%). For example, values of  $MW_{cl}$  for low rank coals were less than 100 daltons; the lowest NMR measurement for any coal was ~200 daltons. These unrealistic values seemed to be the result of extrapolations of the cubic curve fit beyond the original data set. Quadratic-type correlations did not give such poor extrapolations, and hence are shown here. Correlations for  $MW_{cl}$ ,  $P_0$ , and  $\sigma+1$  were made with the following form:

$$y = c_1 + c_2C + c_3C^2 + c_4H + c_5H^2 + c_6O + c_7O^2 + c_8N + c_9N^2 + c_{10}S + c_{11}S^2 + c_{12}VM + c_{13}VM^2 \quad (2)$$

Coefficients for the quadratic fits are shown in Table 2. Coals with dry ash free carbon contents exceeding 95% (i.e., anthracites) were removed from the correlation. Thus, this model is only useful for coals with up to 95% C (daf). Additional  $^{13}C$  NMR data are needed for coals with high carbon contents before a reliable correlation can be made for these coals.

It is anticipated that elemental composition may correlate with the coal structure parameters for many coals. However, it is recognized that often it is the exception to the rule that causes problems, and hence the need for additional  $^{13}C$  NMR data, especially for "problem" coals. Therefore, these types of correlations should be used as a representation of the average of a database of coals and will fail occasionally for unique coals. Also, note that no cross correlations were used in Eqs. 1 or 2; this may be a subject of future work.

To determine the accuracy of the models, the measured values were plotted against the predicted values for each of the four structural parameters and the  $r^2$  values were determined. The following  $r^2$  values were determined: for  $M_5$ ,  $r^2=0.87$ ; for  $MW_{cl}$ ,  $r^2=0.53$ ; for  $P_0$ ,  $r^2=0.71$ ; for  $\sigma+1$ ,  $r^2=0.73$  (see Table 2). The outlier coals for each correlation are listed and were omitted from the  $r^2$  calculation.

### CORRELATION FOR $C_0$

The CPD model requires an estimation for the number of stable bridges existing in the parent coal or that are formed early in the pyrolysis process for low rank coals. This parameter has generally been used for low volatile bituminous coals to represent bi-aryl linkages and for lignites to represent early crosslinking. In the past, this has been a tuning parameter for these types of coals, and had to be changed as a function of heating rate, since crosslinking occurs at different rates as a function of heating rate. Based on the research performed below, a rough correlation for  $C_0$  was developed for high heating rate applications. For low rank coals, oxygen content in the parent coal was used, since this correlates well with early crosslinking. For high rank coals, carbon content was used, since this may correlate well with the bi-aryl linkages. The correlation for  $C_0$  becomes:

$$C_0 = \max\{(0.0177 \%C - 1.4542), 0.0\} + \max\{(0.0143 \%O - 0.1136), 0.0\} \quad (3)$$

Equation 5 was used below for all CPD model predictions that used the correlated chemical structure parameters. It is hoped that additional research on bi-aryl linkages and the chemistry behind early crosslinking in low rank coals will eliminate the need for such empiricism.

### CPD MODEL PREDICTIONS

Five coals for which  $^{13}C$  NMR and devolatilization data are available were tested in the CPD model. Volatiles yields were taken from the FFB experiments reported by Fleicher and Hardesty.<sup>8</sup> Ultimate analysis and volatile matter data were used in the correlations to estimate the  $^{13}C$  NMR parameters required as input for the CPD model. The CPD model was then used to predict tar and total mass release. The CPD model predictions made using the correlation were then compared against the measured experimental yields as well as versus yields predicted using the actual  $^{13}C$  NMR measurements (from Table 1). Figure 1 compares the measured values and the predicted values of mass release for the five coals tested. It can be seen that the use of the structural parameters from the correlation gives predictions of total mass release that are as good or better than the use of the actual NMR data. This may be due to the fact that the correlation tends to smooth the NMR data.

Seventeen coals reported by Xu and Tomita<sup>9</sup> were also used to test the reliability of this correlation. Table 3 lists these coals with their ultimate analysis and the four  $^{13}C$  NMR parameters estimated by the correlation. It appears by looking at the estimated  $^{13}C$  NMR values that the correlation works quite well overall; all estimated values are within expected ranges. Table 4 lists the predicted and measured values of mass and tar release for the 17 coals. Figure 2 shows the predicted and measured mass release vs. %C in the parent coal for the data from Xu and Tomita.<sup>9</sup> The predicted mass release compares relatively well to the measured mass release for most of the coals tested. The correlation coefficient between the predicted and measured total volatiles yield was 0.89. The predictions of tar yield are lower than measured experimentally, especially for the low rank coals. The exact cause for this discrepancy is not known. In the Xu and Tomita experiment; the mass of char and the concentrations of major light gases are measured, and the tar yield is obtained by difference. This may lead to errors if light gases are present that are not measured, or if some fragmentation occurs. The tar yields reported by Xu and Tomita for low rank coals seem to be much higher than reported elsewhere in the literature.

The CPD model currently subtracts 7 daltons from the value of  $M_5$  in order to account for some methyl (-CH<sub>3</sub>) groups attached permanently to the aromatic cluster. However, since  $M_5$  for the Hongay coal was 6 daltons, a minimum corrected value of 1 dalton was used in all CPD calculations. It may be necessary to develop a separate correlation for coals with carbon contents greater than 90% daf.

## CONCLUSIONS

The non-linear correlation of  $^{13}\text{C}$  NMR measurements with ultimate analysis and volatile matter content is a promising approach to obtain data to model devolatilization behavior where  $^{13}\text{C}$  NMR data are not available. The correlation, combined with the CPD model, works very well in predicting total volatiles yield for low to high rank coals. Coals of very high rank (>95 %C) were not included in this correlation due to drastically different structure and lack of sufficient data. Flat flame burner devolatilization tests are planned on a number of these coals to obtain provide additional volatile yield data.

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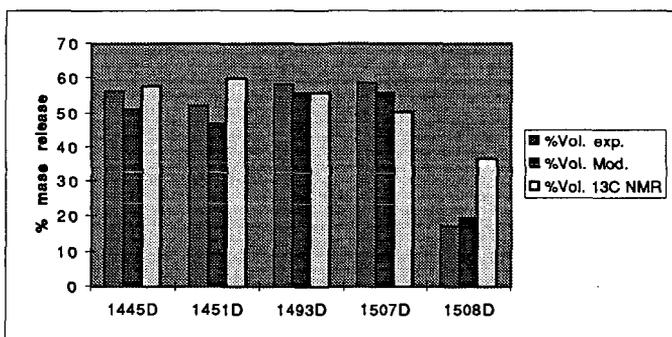


Figure 1. Comparison of total mass release with measured total volatile yields in a flat flame burner (Fletcher and Hardesty<sup>8</sup>).

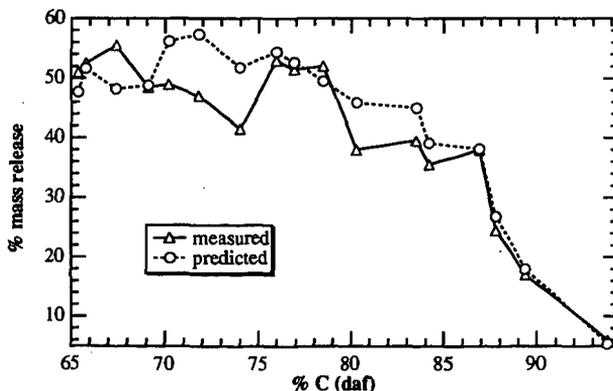


Figure 2. Predicted and measured mass release vs. %C in the parent coal for the data from Xu and Tomita.<sup>9</sup>

**Table 1**  
Coal Data Set Used for Development of Empirical Correlations

#	COAL SAMPLE	C	H	O	N	S	VM	$\sigma+1$	$P_o$	MW <sub>cl</sub>	M <sub>s</sub>
1	NORTH DAKOTA	72.94	4.83	20.34	1.15	0.70	49.78	4.10	0.64	269	40
2	WYODAK	75.01	5.35	18.02	1.12	0.47	49.03	5.60	0.55	408	42
3	BLIND CANYON	80.69	5.76	11.58	1.57	0.37	48.11	5.10	0.49	366	36
4	ILLINOIS #6	77.67	5.00	13.51	1.37	2.38	47.39	5.00	0.63	322	27
5	PITTSBURGH #8	83.20	5.32	8.83	1.64	0.89	41.67	4.70	0.64	330	28
6	STOCKTON	82.58	5.25	9.83	1.56	0.65	37.64	4.80	0.69	272	20
7	UPPER FREEPORT	85.50	4.70	7.51	1.55	0.74	31.62	5.30	0.67	312	17
8	POCAHONTAS	91.05	4.44	2.47	1.33	0.50	19.53	4.40	0.74	307	13
9	PSOC 1443	72.34	5.21	20.11	1.35	0.94	78.67	4.80	0.59	297	36
10	PSOC 1488	76.00	5.23	17.27	0.94	0.53	44.22	4.70	0.54	310	37
11	PSOC 1468	95.36	1.38	1.86	0.84	0.53	3.92	4.70	0.89	656	12
12	PSOC 1445D	75.60	5.26	17.33	1.32	0.49	48.17	5.00	0.48	384	45
13	PSOC 1451D	84.23	5.54	7.56	1.65	1.01	38.69	4.80	0.48	329	33
14	PSOC 1493D	74.12	4.96	13.18	1.45	6.29	43.37	5.50	0.52	402	39
15	PSOC 1507D	66.56	4.26	25.16	1.12	2.89	49.59	4.40	0.59	392	58
16	PSOC 1508D	88.83	4.37	5.14	1.06	0.60	17.18	4.20	0.70	285	18
17	GOUDEY A	87.90	3.77	4.65	1.31	2.37	36.94	4.80	0.64	284	21
18	GOUDEY B	88.49	4.94	1.40	3.42	1.75	19.27	5.00	0.65	295	19
19	DECS-1	71.62	7.11	18.84	1.33	1.10	56.52	5.80	0.42	505	55
20	DECS-7	73.67	6.04	18.22	1.08	1.00	48.11	5.10	0.55	381	43
21	DECS-11	67.81	6.85	23.66	0.91	0.76	62.01	4.60	0.68	329	42
22	DECS-13	87.03	5.19	5.48	1.65	0.65	26.08	4.50	0.72	483	72
23	DECS-18	80.15	6.04	7.44	1.62	4.75	46.93	5.30	0.48	370	35
24	DECS-20	85.16	5.81	6.49	1.52	1.01	39.70	4.70	0.64	247	21
25	DECS-21	93.61	2.77	2.90	0.17	0.56	5.08	3.80	1.00	216	13
26	DECS-27	76.73	6.14	15.03	1.32	0.79	41.50	5.20	0.55	361	34
27	PSOC-1515	89.23	4.13	4.95	0.90	0.78	11.92	6.00	1.00	231	4
28	PSOC-1516	87.34	4.92	4.12	1.37	2.24	20.83	4.50	0.35	354	21
29	PSOC-1520	69.55	6.45	21.70	0.91	1.39	62.47	3.70	0.64	282	46
30	PSOC-1521	89.96	4.67	2.79	1.70	0.88	22.11	4.40	0.69	225	14

$\sigma+1$ : Attachments per cluster

MW: Average molecular weight per cluster

$P_o$ : Intact bridges

M<sub>s</sub>: Average molecular weight per side chain

VM: ASTM volatile matter (daf)

**Table 2**  
Coefficients for Quadratic Correlation of <sup>13</sup>C NMR data

	M <sub>s</sub>	MW	$P_o$	$\sigma+1$
C <sub>1</sub>	161	-587.73	-0.39	-2.2
C <sub>2</sub>	-1.76	22.32	-4.0E-03	0.32
C <sub>3</sub>	5.28E7	-0.17	2.0E-04	-2.6E-03
C <sub>4</sub>	-2.37	90.31	-5.4E-02	-2.1
C <sub>5</sub>	-1.27	-8.40	5.3E-03	0.19
C <sub>6</sub>	3.42E-2	-0.52	5.9E-03	0.10
C <sub>7</sub>	8.76E-1	0.04	6.3E-04	-4.5E-03
C <sub>8</sub>	-9.04E-3	1.28	5.5E-03	1.321
C <sub>9</sub>		-0.01	2.5E-04	-0.20
C <sub>10</sub>		-5.67	0	0
C <sub>11</sub>		2.49	0	0
C <sub>12</sub>		0.37	-1.8E-05	-1.2E-02
C <sub>13</sub>		-0.02	1.1E-06	3.9E-05
r <sup>2</sup>	0.87	0.535	0.71	0.73
Outliers	DECS-13	PSOC-1468	PSOC 1516	PSOC-1515
	PSOC-1468		DECS 1	PSOC-1468
			PSOC-1515	

**Table 3**  
17 Coals Tested by Xu and Tomita<sup>9</sup>.

	<b>Cdaf</b>	<b>Hdaf</b>	<b>Odaf</b>	<b>Ndaf</b>	<b>Sdaf</b>	<b>VMdaf</b>	<b>σ+1</b>	<b>P<sub>o</sub></b>	<b>MW</b>	<b>M<sub>6</sub></b>
Yallourn	65.40	4.90	28.80	0.6	0.3	53.93	3.33	0.75	362	59.3
Rhein Braun	65.80	5.50	27.60	0.8	0.3	56.46	3.67	0.71	358	57.5
Morwell	67.40	5.00	26.80	0.5	0.3	52.54	3.52	0.71	362	54.7
Velva	69.10	4.80	23.90	1.4	0.6	52.34	4.77	0.64	356	50.3
Soyakoishi	70.20	5.20	22.40	1.8	0.2	46.42	5.18	0.62	366	48.0
South Baulah	71.80	4.70	19.20	1.4	2.9	44.70	5.25	0.55	364	44.6
Colowyo	74.00	5.00	18.60	1.9	0.4	38.75	5.56	0.59	363	40.0
Taiheiyō	76.00	6.50	16.00	1.2	0.3	56.02	5.19	0.57	318	37.1
Millmerran	76.90	6.60	15.40	0.5	0.6	54.80	4.54	0.58	313	35.8
Wandoan	78.50	5.80	14.40	0.9	0.4	49.76	4.69	0.59	327	33.5
Hunter Valley	80.30	5.00	12.20	2	0.4	37.18	5.55	0.59	337	30.0
Liddell	83.50	5.40	8.40	2.1	0.6	37.58	5.30	0.60	318	26.6
Newvale	84.20	5.00	8.90	1.4	0.5	34.18	4.87	0.63	316	24.3
Yubari Shinko	86.90	5.60	5.20	1.9	0.3	40.51	4.73	0.66	293	23.7
Vicary Creek	87.80	4.70	4.90	2.1	0.4	24.74	4.97	0.68	298	17.8
Keystone	89.40	4.40	3.10	2.2	0.8	16.83	4.91	0.71	284	12.8
Hongay	93.70	3.30	1.30	1.2	0.8	7.66	4.66	0.85	207	5.3

**Table 4**  
Predicted and Measured Mass Release and Predicted Tar Yield  
(data from Xu and Tomita<sup>9</sup>)

<b>COAL</b>	<b>% mass release (daf)</b>		<b>% tar release (daf)</b>	
	<b>pred.</b>	<b>meas.</b>	<b>pred.</b>	<b>meas.</b>
Yallourn	48	51	14	20
Rhein Braun	52	53	14	22
Morwell	48	56	15	26
Velva	49	49	17	18
Soyakoishi	56	49	9	21
South Baulah	57	47	14	17
Colowyo	52	42	10	19
Taiheiyō	54	53	16	30
Millmerran	53	52	22	30
Wandoan	50	52	21	28
Hunter Valley	46	38	15	22
Liddell	45	40	19	22
Newvale	39	36	19	19
Yubari Shinko	38	38	17	22
Vicary Creek	27	25	12	12
Keystone	18	17	10	8
Hongay	5	6	4	3