#### I. INTRODUCTION

Ever increasing energy consumption in Southeast Asia has brought to the forefront the need to produce energy in this region of the world more efficiently, more cleanly, and more economically. Resources such as coal provide a cost-effective way to produce energy, especially for coal sources that are located near the power plant. In order to identify the best approach for clean and efficient use of coal, the fundamental principles driving the coal reactions should first be understood. This work gives insight into the way in which nitrogen is released from coal during rapid pyrolysis. Additionally, a nitrogen model has been formulated which greatly improves the time-temperature resolution of the rate of nitrogen release during coal devolatilization. This tool will allow better optimization of the balance between minimization of  $NO_x$  formation and maximization of efficiency during coal combustion or liquefaction.

# **II. OBJECTIVES AND APPROACH**

The objective of this project is to better understand and model the chemical structural changes occurring during coal devolatilization, especially those involving the release of nitrogen from the coal.

The approach taken was two-fold. First rapid pyrolysis experiments were performed using eight coals of a wide range of rank and origin, and the products of those experiments characterized to show the detailed chemical structural changes taking place during devolatilization. Second the data from these experiments were used to help develop a nitrogen model which describes the chemical structural changes responsible for the release of nitrogen from coal/char during devolatilization.

# **III. PYROLYSIS TESTS**

Thirty-two high heating rate coal pyrolysis tests were conducted, most of which were performed in the drop tube reactor at BYU, with some tests also performed in the flat flame reactor (FFR) at BYU.

### **Experimental Procedure**

Eight parent coals were ground, sieved, and split for use in drop tube and flat flame reactor experiments and for coal characterization. Pyrolysis products in each experiment were carefully collected, stored, and split for sample characterization.

#### Sample Preparation

Eight parent coals were ground and sieved in an inert atmosphere to obtain the 45-75 micron ( $\mu$ m) size fraction for distribution to each of the project collaborators. All coal and char samples were stored in glass bottles with tight fitting lids, topped with argon, and kept at -10 °C until used in order to prevent oxidation or other reaction of the samples. When coal or char samples were split into representative sub-samples, whether for characterization, for distribution to other collaborators, or for use in experimental tests, proven techniques were used which preserve the characteristics of the sample in terms of particle size distribution, density, and composition.<sup>1</sup>

### Drop Tube Reactor

The drop tube reactor is an electrically heated laminar flow drop tube which was operated at about one atmosphere absolute pressure, although capable of operation at pressures as high as 25 atmospheres.<sup>2, 3</sup> Maximum particle heating rates were on the order of  $10^4$  K/s. A water-cooled injection probe entrained the coal particles in a small (primary) nitrogen flow and prevented the particles from being heated until they left the probe. The particles were injected at a slow rate (~1g/hr) in order to approximate single particle behavior.

Gas temperatures along this center axis were carefully measured with the injection and collection systems in place (except the cyclone) using a type S thermocouple inserted from beneath the virtual impactor. Pyrolysis products in the drop tube were immediately quenched in cold nitrogen gas upon entering a water-cooled collection probe. Char was separated from most of the tar by a virtual impactor in series with a one-inch cyclone. About 20% of the tar condensed on the sides of the collection system. These tar losses were estimated after each run by scraping and wiping the inside of the collection system and weighing the scrapings.

#### Flat-Flame Reactor

The flat-flame pyrolyzer used in this study is the same as that used by Ma et al.<sup>4</sup> Maximum particle heating rates in the flat flame reactor were on the order of  $10^5$  K/s. Coal particles were injected

up the center axis of a 5.1 cm by 5.1 cm cross section quartz tower and entrained within a laminar flow of combustion products from a fuel-rich high temperature methane-air flat flame. The coal particles were entrained in a small stream of nitrogen at a rate of about 1 gram/hour to obtain single particle behavior as the stream of particles was pyrolyzed. Centerline gas temperatures were measured in the flat flame reactor (FFR) with a type B thermocouple.

### *Experimental test matrix*

Thirty-two different pyrolysis experiments were performed, including twenty-six drop tube tests and eight flat flame reactor tests as outlined in Figure 1. In Figure 1, each box represents an experiment performed at the corresponding condition using the corresponding sieved coal. For each pyrolysis test, tar and char yields were carefully measured. Char yields were also calculated by mass balance on titanium and aluminum as has been described elsewhere<sup>5</sup>, using either Inductively Coupled Plasma (ICP) analysis for titanium (Ti) and aluminum (Al) determination or Atomic Adsorption Spectroscopy (AAS) for Al determination only. Mass release for each test was assumed to be the value obtained using the Al tracer technique, except when Ti data was available, in which case the Al and Ti results were averaged. The mass release for tests in which Yallourn coal was used was calculated by overall mass balance, since the Ti and Al tracer methods gave unreasonably high values of mass release.

Table 1 further describes each condition at which experiments were performed. The 950 and 975 K conditions were used in place of the 900 K condition for Pittsburgh and Taiheiyo coals, respectively. Because of a net radiative heat transfer to the particles from the hot walls of the drop tube, maximum particle temperatures in this apparatus were slightly higher than maximum gas temperatures.

Condition	Max. Gas Temp. (K)	Max. Particle Temp. (K)	Residence Time (ms)
900 K	895	960	384
950 K	960	1015	376
975 K	1000	1055	351
1000 K	1000	1035	337
1100 K	1085	1125	322
1250 K	1245	1270	380
1650 K	1640 (FFR)	1560	18

Table 1. Summary of conditions at which pyrolysis experiments were performed in the drop tube and the flat flame reactor (FFR).

### Sample Characterization

The elemental composition of each char and tar (or soot) sample was also carefully analyzed. Chars from sixteen of the pyrolysis tests were analyzed by <sup>13</sup>C NMR at the University of Utah, as indicated in Figure 1. In addition, nine tars from the aforementioned sixteen tests were analyzed by <sup>13</sup>C NMR to complete the structural characterization of nine matching char/tar sets.

## Results

A summary of the proximate and ultimate analyses as determined for the eight parent coals used in this study is presented in Table 2. A summary of the proximate and ultimate analyses and total mass release for the chars generated in this project are shown in Table 3, with the corresponding parent coal data also shown for comparison. Except for tests using Yallourn coal, mass release values were calculated using Al and/or Ti tracer, as described in the previous section. Mass release values, as calculated by overall mass balance were within 1% of the value obtained using the tracers for about half of the tests. For all other tests the overall mass balance values were 2-6% (absolute) higher than those obtained using tracers. A summary of the ultimate analyses and yields for the corresponding tars generated in these pyrolysis experiments is shown in Table 4, with the corresponding parent coal data again shown for comparison.



**Figure 1.** Matrix of experimental pyrolysis tests performed in the drop tube and flat flame reactor (FFR). Samples for which <sup>13</sup>C NMR analyses were performed are also indicated.

Coal	Rank	%C (daf)	%H (daf)	%N (daf)	%S (daf)	%O (daf) (by diff.)	% ash (dry)	% moist.	VM <sup>†</sup> (daf)
Yallourn	brown	65.31	4.76	0.52	0.18	29.22	1.58	8.98	58.5
South Banko	brown	70.57	5.46	1.19	0.44	22.34	2.65	7.53	56.0
Taiheiyo	sub	76.41	6.58	1.16	0.25	15.59	11.12	2.64	57.4
Miike	hvb	79.91	6.13	1.18	4.48	8.30	18.79	0.88	53.9
Hunter Valley	hvb	81.25	5.45	2.12	0.47	10.70	9.25	1.39	38.2
Pittsburgh	hvb	82.77	5.48	1.64	3.38	6.73	8.83	0.72	41.7
Upper Freeport	mvb	84.15	5.13	1.55	4.56	4.60	15.75	0.31	31.6
Pocahontas	lvb	91.57	4.57	1.36	0.76	1.74	5.06	0.22	19.5

Table 2. Proximate/Ultimate analyses of the coals used in this study.

† ASTM volatile matter

Table 3.	Summary of ultimation	te analyses.	, dry ash,	and mass	release	(%MR) f	or chars
produce	d in the drop tube a	nd flat flam	e reactor	(FFR) pyr	olysis ex	perimen	ts.

Coal	Condition	% C (daf)	% H (daf)	% N (daf)	% S (daf)	% O (daf) (by diff.)	% ash (dry)	$\% MR^{\dagger} \\ (daf)$
Yallourn	coal	65.31	4.76	0.52	0.18	29.22	1.58	-
	900 K	75.32	3.33	0.68	0.18	20.49	3.27	$46.0^{\dagger}$
	1000 K	84.09	2.95	0.73	0.14	12.09	2.95	$55.0^{\dagger}$
	1100 K	87.65	2.57	0.70	0.13	8.94	3.50	57.8 <sup>†</sup>
	1650 K	91.84	1.27	0.58	0.14	6.18	4.46	69.0 <sup>†</sup>
South Banko	coal	70.57	5.46	1.19	0.44	22.34	2.65	-
	900 K	78.25	3.77	1.52	0.46	16.00	4.18	41.6
	1000 K	81.61	3.16	1.59	0.30	13.35	4.57	51.1
	1100 K	84.18	2.91	1.58	0.24	11.09	4.79	54.4
	1250 K	91.33	1.74	1.42	0.35	5.16	5.17	58.3
	1650 K	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	64.1
Taiheiyo	coal	76.41	6.58	1.16	0.25	15.59	11.12	-
	975 K	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	53.3
	1000 K	84.25	3.34	1.49	0.18	10.74	22.28	58.3
	1100 K	85.16	3.04	1.49	0.18	10.13	23.23	60.4
	1650 K	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	64.4
Miike	coal	79.91	6.13	1.18	4.48	8.30	18.79	-
	900 K	N.M.	N.M.	N.M.	N.M.	N.M.	40.82	66.8
	1000 K	N.M.	N.M.	N.M.	N.M.	N.M.	36.94	63.9
	1100 K	89.97	3.00	1.40	4.49	1.13	38.50	64.7
	1650 K	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	68.9

Coal	Condition	% C (daf)	% H (daf)	% N (daf)	% S (daf)	% O (daf) (by diff.)	% ash (dry)	$\% MR^{\dagger} \\ (daf)$
Hunter Valley	coal	81.25	5.45	2.12	0.47	10.70	9.25	-
	900 K	87.18	4.08	2.35	0.46	5.92	13.87	38.6
	1000 K	88.05	3.42	2.47	0.31	5.74	15.47	43.8
	1100 K	89.94	2.84	2.48	0.34	4.41	16.14	47.9
	1650 K	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	52.4
Pittsburgh	coal	82.77	5.48	1.64	3.38	6.73	8.83	-
	900 K	82.99	4.22	1.82	3.87	7.10	14.76	45.1
	950 K	86.57	4.17	1.94	4.04	3.28	15.25	47.2
(replicate exp.)	950 K	84.16	4.00	1.89	4.45	5.50	14.81	46.4
	1000 K	87.49	3.37	1.92	3.82	3.41	15.72	50.7
	1100 K	87.99	3.08	1.78	3.72	3.43	16.87	54.4
	1250 K	92.18	1.72	1.76	3.68	0.66	18.76	59.8
	1650 K	88.56	2.64	1.73	4.48	2.59	19.27	59.1
Upper Freeport	coal	84.15	5.13	1.55	4.56	4.60	15.75	-
	900 K	85.47	3.09	1.61	4.82	5.01	24.68	42.9
	1000 K	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	49.0
	1100 K	89.35	2.77	1.78	4.87	1.22	25.56	45.2
	1650 K	92.17	2.05	1.64	3.24	0.90	24.82	43.6
Pocahontas	coal	91.57	4.57	1.36	0.76	1.74	5.06	-
	900 K	91.54	4.32	1.35	0.73	2.05	5.79	13.4
	1000 K	93.31	3.45	1.43	0.67	1.14	6.24	21.7
	1100 K	92.45	2.96	1.42	0.61	2.56	6.34	25.8
	1650 K	95.41	2.14	1.33	0.61	0.51	6.33	24.7

† Mass release for Yallourn chars determined by overall mass balance, not tracer mass balance.

Table 4.	Summary	of ultimate	analyses an	d yields (	of tars/soots	produced in	the drop
tube and	flat flame	reactor (FF	R) pyrolysis	experin	nents.	-	-

Coal	Condition	% C (daf)	% H (daf)	% N (daf)	% S (daf)	% O (daf) (by diff.)	% tar yield (daf)
Yallourn	coal	65.31	4.76	0.52	0.18	29.22	-
	900 K	73.25	5.79	0.54	0.12	20.30	10.5
	1000 K	79.19	4.64	0.78	0.17	15.22	6.6
	1100 K	86.37	4.58	0.91	0.23	7.90	3.9
(FFR)	1650 K	96.18	2.19	0.18	0.08	1.36	5.1
South Banko	coal	70.57	5.46	1.19	0.44	22.34	-
	900 K	78.82	6.69	1.18	0.41	12.90	15.0
	1000 K	81.48	4.82	1.69	0.54	11.46	9.0

Coal	Condition	% C (daf)	% H (daf)	% N (daf)	% S (daf)	% O (daf) (by diff.)	% tar yield (daf)
	1100 K	84.66	4.65	1.77	0.58	8.35	7.4
	1250 K	93.76	4.06	1.37	0.60	0.22	6.8
(FFR)	1650 K	98.09	2.05	0.29	0.13	-0.56	6.9
Taiheiyo	coal	76.41	6.58	1.16	0.25	15.59	-
	975 K	N.M.	N.M.	N.M.	N.M.	N.M.	22.5
	1000 K	N.M.	N.M.	N.M.	N.M.	N.M.	17.1
	1100 K	N.M.	N.M.	N.M.	N.M.	N.M.	12.9
(FFR)	1650 K	96.68	2.32	0.47	0.11	0.42	15.1
Miike	coal	79.91	6.13	1.18	4.48	8.30	-
	900 K	N.M.	N.M.	N.M.	N.M.	N.M.	24.7
	1000 K	N.M.	N.M.	N.M.	N.M.	N.M.	31.2
	1100 K	89.89	4.36	1.65	2.40	1.69	25.4
(FFR)	1650 K	96.67	1.74	0.54	0.63	0.42	19.5
Hunter Valley	coal	81.25	5.45	2.12	0.47	10.70	_
	900 K	N.M.	N.M.	N.M.	N.M.	N.M.	22.3
	1000 K	N.M.	N.M.	N.M.	N.M.	N.M.	21.8
	1100 K	91.12	4.44	2.54	0.48	1.42	19.5
(FFR)	1650 K	96.61	1.78	0.83	0.17	0.61	14.8
Pittsburgh	coal	82.77	5.48	1.64	3.38	6.73	_
	900 K	84.12	5.87	1.71	0.97	7.33	31.8
	950 K	85.50	5.65	1.76	1.02	6.08	28.5
(replicate exp.)	950 K	86.55	5.66	1.81	1.03	4.94	-
	1000 K	86.50	4.85	1.91	1.38	5.36	28.7
	1100 K	88.92	4.43	1.99	1.47	3.20	25.1
	1250 K	93.31	2.87	1.51	1.24	1.06	26.6
(FFR)	1650 K	95.02	1.75	0.81	0.40	2.01	21.0
Upper Freeport	coal	84.15	5.13	1.55	4.56	4.60	-
	900 K	87.95	5.53	1.60	0.97	3.94	18.4
	1000 K	89.51	4.73	1.79	1.15	2.82	27.7
	1100 K	92.25	4.24	1.93	1.31	0.27	27.5
(FFR)	1650 K	94.96	1.32	0.74	0.33	2.65	17.7
Pocahontas	coal	91.57	4.57	1.36	0.76	1.74	-
	900 K	90.80	5.26	1.34	0.69	1.91	7.5
	1000 K	92.32	4.78	1.41	0.69	0.81	15.1
	1100 K	92.64	4.50	1.45	0.67	0.74	14.2
(FFR)	1650 K	98.25	1.31	0.63	0.21	-0.40	10.7

Coal	Condition	$f_a$	$f_a^{C}$	$f_{a^{\prime}}$	$f_a^{H}$	$f_a^{N}$	f <sub>a</sub> <sup>P</sup>	$f_a^{\ S}$	f <sub>a</sub> <sup>B</sup>	$f_{al}$	$f_{al}^{\ H}$	${\rm f_{al}}^{*}$	$f_{al}^{O}$
Yallourn	coal	67	10	57	16	41	16	9	16	33	23	10	9
	2-D coal <sup>b</sup>	67	10	57	16	41	19	22	0	33	23	10	9
	1100 K	96	5	91	37	54	6	21	27	4	3	1	3
South Banko	coal	62	8	54	17	37	9	13	15	38	28	10	5
	Sv. coal <sup>c</sup>	61	8	53	16	37	9	13	15	39	30	9	5
	900 K	86	6	80	24	56	10	18	28	14	8	6	2
	1000 K	95	5	90	32	58	8	20	30	5	3	2	2
	1100 K	95	4	91	34	57	7	20	30	5	4	1	2
	1250 K	93	10	83	17	66	7	19	40	7	5	2	5
Taiheiyo	coal	56	5	51	16	35	6	14	15	44	32	12	4
	1100 K	97	3	94	33	61	5	19	37	3	2	1	2
Miike	coal	66	2	64	22	42	6	17	19	34	24	10	3
	1100 K	96	8	88	30	58	9	25	24	4	3	1	2
Hunter Valley	coal	74	3	71	25	46	8	19	19	26	17	9	4
	1100 K	95	4	91	34	57	5	20	32	5	4	1	3
Pittsburgh	coal	71	1	70	27	43	6	15	22	29	21	8	4
	950 K	92	2	90	32	58	6	19	33	8	4	3	1
	1000 K	93	2	91	34	57	5	19	33	7	4	3	2
	1100 K	95	3	92	40	52	5	21	26	5	4	1	2
	1250 K	92	11	81	20	61	7	17	37	8	6	2	5
(FFR)	1650 K	95	10	85	29	56	8	22	26	5	4	1	3
Upper Freeport	coal	81	0	81	28	53	4	20	29	19	11	8	2
	1100 K	97	4	93	33	60	5	21	34	3	2	1	2
Pocahontas	coal	86	0	86	33	53	2	17	34	14	9	5	1
	1100 K	97	2	95	36	59	3	19	37	3	2	1	2

Table 5. Parameters measured via 13C NMR at the University of Utah for chars produced in the drop tube and flat flame reactor (FFR) pyrolysis experiments.<sup>a</sup>

<sup>a</sup> Percentage carbon (error):  $f_a = \text{total sp}^2$ -hybridized carbon (±3);  $f_a' = \text{aromatic carbon (±4)}$ ;  $f_a^C = \text{carbonyl, } d > 165 \text{ ppm (±2)}$ ;  $f_a^H = \text{aromatic with proton attachment (±3)}$ ;  $f_a^N = \text{nonprotonated aromatic (±3)}$ ;  $f_a^P = \text{phenolic or phenolic ether, } d = 150\text{-}165 \text{ ppm (±2)}$ ;  $f_a^S = \text{alkylated aromatic } d = 135\text{-}150 \text{ ppm (±3)}$ ;  $f_a^R = \text{aromatic bridgehead (±4)}$ ;  $f_{al} = \text{aliphatic carbon (±2)}$ ;  $f_{al}^H = \text{CH or CH}_2$  (±2);  $f_{al}^* = \text{CH}_3$  or nonprotonated (±2);  $f_{al}^{O} = \text{bonded to oxygen, } d = 50\text{-}90 \text{ ppm (±2)}$ . <sup>b</sup> As analyzed by 2-D <sup>13</sup>C NMR <sup>c</sup> Sieved coal (45-75 µm fraction)

Examination of the trend with rank of tar yields shows that, except for high rank coals such as Upper Freeport and Pocahontas, tar release is essentially complete at the lowest (900 K) condition.

A summary of data from the <sup>13</sup>C NMR analyses performed at the University of Utah on selected char and tar samples is given in Tables 5 and 6 for chars and tars, respectively. The corresponding derived structural parameters for these samples are found in Tables 7 and 8. The team at the University of Utah is the first ever to perform detailed <sup>13</sup>C NMR analysis of solid tar samples. The tar data reported here represent the first time a set of tars collected over increasingly severe pyrolysis conditions has ever been analyzed by solid-state <sup>13</sup>C NMR. This compilation of solid-state <sup>13</sup>C NMR tar data is practically the only such data in existence. The values of  $M_{cl}$  and M reported here differ slightly from the values originally reported by the team at the University of Utah, because the elemental composition reported for each of the samples is slightly different due to improvements in the elemental analysis technique and reanalysis of some of the samples.

## Discussion

Mass release values were confirmed independently of the overall mass balance (for all coals except Yallourn) by the use of Ti and Al as tracers. For the chars produced at 1100 K, for which <sup>13</sup>C NMR structural data are available, mass release values can also be estimated as the sum of tar yields and the estimated total light gas yields. The percent of parent coal forming light gas is estimated as the percent decay in  $M_{cl}$  (the molecular weight per cluster) in the char relative to the parent coal. This can be calculated as:

Estimated light gas yield = % 
$$M_{cl} decay = 1 - \frac{M_{cl,char}}{M_{cl,coal}} = \frac{M_{site,coal}}{M_{site,char}} = 100\%$$
 (1)

where  $M_{site}$  is the molecular weight of aromatic portion of an average cluster. In equation (1) the molecular weight decay is adjusted to eliminate variations in  $M_{site}$ , which is assumed to remain constant at the parent coal value throughout primary pyrolysis.

This method of mass release estimation assumes that the chars and tars at 1100 K have approximately the same percentage of mass which is aromatic. The chemical structural data show this assumption to be valid for both the South Banko and Pittsburgh 1100 K pyrolysis products. The light gas yield estimate is then added to the measured tar yield to obtain an estimate of the percent daf mass release. As can be seen in Figure 2, the resulting estimated values of the mass release are very close to the measured values for all eight parent coals pyrolyzed at 1100 K. Thus the <sup>13</sup>C NMR analyses, together with the tar yield measurements, independently validate the experimental mass release values. Conversely, the mass release measurements (via Ti and Al tracer) validate the tar yield and <sup>13</sup>C NMR aromaticity measurements. Note that according to Figure 2, the measured Miike 1100 K mass release value may be as much as 4 % (absolute) too high.

Coal	Condition	f <sub>a</sub>	f <sub>a</sub> <sup>C</sup>	$f_{a^{\prime}}$	$f_a^{H}$	$f_a^{N}$	f <sub>a</sub> <sup>P</sup>	f <sub>a</sub> <sup>S</sup>	$f_a^{B}$	f <sub>al</sub>	$f_{al}^{\ H}$	$f_{al}^{*}$	$f_{al}^{\ O}$
South Banko	coal	62	8	54	17	37	9	13	15	38	28	10	5
	900 K	69	6	63	23	40	9	15	16	31	21	10	3
	1000 K	88	4	84	40	44	9	17	18	12	6	6	2
	1100 K	90	2	88	44	44	7	18	19	10	6	4	3
	1250 K	95	1	94	49	45	3	18	24	5	4	1	2
Pittsburgh	coal	71	1	70	27	43	6	15	22	29	21	8	4
	950 K	78	2	76	33	43	6	17	20	22	13	9	3
	1000 K	87	1	86	40	46	6	18	22	13	7	6	2
	1100 K	90	1	89	43	46	4	17	25	10	6	4	3
	1250 K	93	5	88	36	52	5	17	30	7	6	1	4
(FFR)	1650 K	91	7	84	29	55	5	14	36	9	7	2	5

Table 6. Parameters measured via <sup>13</sup>C NMR at the University of Utah for tars produced in the drop tube and flat flame reactor (FFR) pyrolysis experiments.<sup>a</sup>

<sup>a</sup> see footer to Table 5.

Table 7.	Structural Parameters Derived from 13C NMR for chars produced in t	the drop
tube and	flat flame reactor (FFR) pyrolysis experiments. <sup>a</sup>	-

Coal	Condition	b	C <sub>cl</sub>	+1	P <sub>0</sub>	B.L.	S.C.	M <sub>cl</sub>	М
Yallourn	coal	0.281	14	6.1	.6	3.7	2.4	452	46
	$2\text{-}\text{D} \operatorname{coal}^{\dagger}$	0.000	6	4.3	0.76	3.3	1.0	189	27
	1100 K	0.297	14	4.2	0.96	4.0	0.2	211	9
South Banko	coal	0.278	13	5.3	0.55	2.9	2.4	410	47
	Sv. coal <sup>‡</sup>	0.283	14	5.8	0.59	3.4	2.4	450	48
	900 K	0.350	17	6.0	0.79	4.7	1.3	326	20
	1000 K	0.333	16.5	5.1	0.93	4.7	0.4	270	13
	1100 K	0.330	16	4.7	0.96	4.5	0.2	251	11
	1250 K	0.482	24	7.4	0.92	6.8	0.6	380	12
Taiheiyo	coal	0.294	14	5.5	0.40	2.2	3.3	432	47
	1100 K	0.394	19	4.9	0.96	4.7	0.2	285	10
Miike	coal	0.297	14	5.0	0.57	2.9	2.1	329	31
	1100 K	0.273	13	5.0	0.97	4.9	0.1	197	7
Hunter Valley	coal	0.268	13	4.9	0.67	3.3	1.6	271	22
	1100 K	0.352	17.5	4.8	0.96	4.6	0.2	257	8
Pittsburgh	coal	0.314	15	4.5	0.62	2.9	1.6	311	28
	950 K	0.367	18	5.0	0.88	4.4	0.6	277	11

Coal	Condition	b	C <sub>cl</sub>	+1	P <sub>0</sub>	B.L.	S.C.	M <sub>cl</sub>	М
	1000 K	0.363	18	4.7	0.88	4.1	0.6	272	10
	1100 K	0.283	14	3.9	0.96	3.7	0.2	208	8
	1250 K	0.457	22	6.5	0.92	6.0	0.5	354	13
(FFR)	1650 K	0.306	15	5.3	0.97	5.1	0.2	239	10
Upper Freeport	coal	0.358	18	5.3	0.67	3.6	1.7	317	18
	1100 K	0.366	18	5.0	0.96	4.8	0.2	260	7
Pocahontas	coal	0.395	20	4.4	0.74	3.3	1.1	305	13
	1100 K	0.389	19	4.4	0.95	4.2	0.2	260	6

<sup>a</sup>  $_{b}$  = fraction of bridgehead carbons, C<sub>Cl</sub> = aromatic carbons per cluster, +1 = total attachments per cluster, P<sub>0</sub> = fraction of attachments that are bridges, B.L. = bridges and loops per cluster, S.C. = side chains per cluster, MW<sub>cl</sub> = the average molecular weight of an aromatic cluster, MW = the average molecular weight of the cluster attachments.

Table 8. Structural Parameters Derived from 13C NMR for tars produced in the drop tube and flat flame reactor (FFR) pyrolysis experiments.<sup>a</sup>

Coal	Condition	b	C <sub>cl</sub>	+1	P <sub>0</sub>	B.L.	S.C.	M <sub>cl</sub>	М
South Banko	coal	0.278	13	5.3	0.55	2.9	2.4	410	47
	900 K	0.254	12	4.5	0.58	2.6	1.9	290	31
	1000 K	0.214	10.5	3.3	0.77	2.5	0.8	184	16
	1100 K	0.216	11	3.0	0.84	2.5	0.5	177	13
	1250 K	0.255	12	2.7	0.95	2.6	0.1	164	5
Pittsburgh	coal	0.314	15	4.5	0.62	2.9	1.6	311	28
	950 K	0.263	13	4.0	0.61	2.4	1.6	240	20
	1000 K	0.256	12	3.3	0.75	2.5	0.8	194	13
	1100 K	0.281	13.5	3.2	0.81	2.6	0.6	205	11
	1250 K	0.341	17	4.2	0.95	4.0	0.2	249	9
(FFR)	1650 K	0.429	21	4.8	0.89	4.3	0.5	316	12

<sup>a</sup> see footer to Table 7.

Data from <sup>13</sup>C NMR analysis of matched tar and char sets for the South Banko and Pittsburgh coals allowed comparison of the chemical structure of these pyrolysis products at various stages of devolatilization. For example, the number of bridges and loops (B.L., Figure 3) in the early char is higher than in the parent coal, meaning the char clusters are more interconnected after tar release. This early increase in the number of char bridges and loops was also seen in all 3 chars produced by Watt at 900 K<sup>6</sup> and all 5 chars produced by Hambly at a more severe pyrolysis condition (1080 K).<sup>2</sup> On the other hand, primary tar clusters (900 K) appear to have slightly less bridges and loops and side chain material than are found in the parent coal (also shown in Figure 3). Similarly, the number of bridges

and loops in 5 of 5 tars produced by Hambly at 1080 K were significantly lower than the initial parent coal value.<sup>2</sup>



**Figure 2.** Validation of % daf mass release calculated from tracer measurements at 1100 K condition using tar yield and <sup>13</sup>C NMR data.



**Figure 3.** Trend with temperature of bridges and loops per cluster (B.L.) for South Banko and Pittsburgh drop tube and flat flame reactor (FFR) chars and tars.

Char and tar average cluster sizes can also be compared throughout devolatilization. At temperatures below 1250 K, chars and tars appear to have almost the same number of aromatic carbons per cluster as their parent coals, an important assumption of most major devolatilization models. A closer look reveals that the number of aromatic carbons per cluster (Figure 4) in the early chars may be somewhat higher than the coal value, consistent with the findings of Watt.<sup>6</sup> Tar, on the other hand

appears to initially have less aromatic carbons per cluster than the parent coal, a phenomenon also seen in 3 of 5 tars produced in a recent study by Hambly.<sup>2</sup>



**Figure 4.** Trend with temperature of aromatic carbons per cluster for South Banko and Pittsburgh drop tube and flat flame reactor (FFR) chars and tars.

It appears that there are three types of changes generally occurring in the South Banko and Pittsburgh tars and chars over the course of pyrolysis. First, tar is released, and the primary tar and char lose aliphatic material as pyrolysis severity increases. This is evidenced in both the chars and the tars by the decrease in number (S.C., Figure 5) and mass (M) of side chains, while the number of bridges and loops remains nearly constant (Figure 3).

If the particle temperature exceeds about 1200 K, a second change occurs in most of the chars and tars as ring opening reactions cause the formation of what appears to be carbonyl carbon  $(f_a^{\ C})$  at the expense of aromatic carbon (see hypothetical reaction in Figure 6). This is evidenced by a dramatic rise in carbonyl carbon (Figure 7) with increasing pyrolysis severity at temperatures above 1100 K, accompanied by nearly equal and opposite changes in the fraction of aromatic carbon (Figure 8). A similar phenomenon was also seen in chars produced using in a flat flame reactor at Sandia with 1600 K maximum gas temperature and 43 ms residence time.<sup>5</sup> Due to line broadening in samples from severe pyrolysis experiments, it is not clear just what types of carbon are included in  $f_a^{\ C}$  for such samples. Based on the amount of oxygen present in the parent coals and less severely pyrolyzed chars, it is probable that much of what appears to be carbonyl carbon is really something else, although it is unclear what this might be. Thus after high temperature (<1200 K) rapid coal pyrolysis, evidence of ring opening reactions is usually seen in both the tar and the char.

A third change, cluster coalescence, is sometimes also seen at particle temperatures above 1200 K. Cluster coalescence is evidenced by a significant increase in the number of aliphatic and aromatic (see Figure 4) carbons per cluster and the number of bridges and loops per cluster (see Figure 3). In

other words, the tar and char clusters become both larger and more interconnected. This cluster coalescence is minimal in the Pittsburgh flat flame reactor char, consistent with the flat flame reactor chars produced by Fletcher and Hardesty.<sup>5</sup> This may be due to the shorter residence times or the higher heating rates used in flat flame reactor experiments compared to the 1250 K drop tube experiments. It also means that under certain conditions ring opening reactions can occur without causing cluster coalescence. On the other hand, every tar and char sample showing evidence of cluster coalescence also appeared to have undergone ring opening reactions, suggesting that ring opening reactions may be prerequisite to cluster coalescence.

It is significant that no evidence for either ring opening or cluster coalescence reactions is seen in the South Banko tar produced at 1250 K. This may be related to the low tar yield from South Banko coal (1/3 the yield of tar from the Pittsburgh coal). This means that under identical pyrolysis conditions, interactions between (gaseous) South Banko tar molecules would occur less than 1/3 as often as they would occur between Pittsburgh tar molecules. The absence of these reactions in the South Banko tar could also be due to the slightly smaller cluster size (12.5 carbons per cluster at 1100 K) as compared to the Pittsburgh tar (15.2 carbons per cluster at 1100 K).

These data represent the first time matched sets of chars and tars from both lignite and bituminous coals pyrolyzed at increasingly severe conditions have been analyzed by solid-state <sup>13</sup>C NMR. The data confirm much of what has been reported by previous investigators about the structural progression of coal chars during pyrolysis. Evidence of three types of structural changes were seen in both chars and tars during rapid pyrolysis, two of which have never been noted before: ring opening and cluster coalescence. Understanding of such changes may contribute to the development of better soot formation models or improve modeling of char devolatilization at extreme pyrolysis conditions.



**Figure 5.** Trend with temperature of side chains per cluster (S.C.) for South Banko and Pittsburgh drop tube and flat flame reactor (FFR) chars and tars.







**Figure 7.** Trend with temperature of fraction of carbon which is carbonyl for South Banko and Pittsburgh drop tube and flat flame reactor (FFR) chars and tars.



**Figure 8.** Trend with temperature of the fraction of carbon which is aromatic  $(f_{a})$  for South Banko and Pittsburgh drop tube and flat flame reactor (FFR) chars and tars.

#### **IV. NITROGEN RELEASE MODEL**

Previously published network devolatilization nitrogen release models have described nitrogen release via (a) tar release and (b) light gas nitrogen release. Light gas nitrogen release is often modeled as a first order char nitrogen decay with empirically derived rank dependent rate constant parameters and a wide distribution of activation energies.<sup>7, 8</sup> None of the existing models attempt to explain why pyrolytic light gas nitrogen begins to be released from coal at 900-1000 K,<sup>9, 10</sup> while thermal decomposition of pyrrole does not become significant until about 1200 K<sup>11</sup>, and pyridine until about 1300 K.<sup>12</sup> In fact, the average activation energy used in FLASHCHAIN for light gas nitrogen release is about 50 kcal/mol,<sup>8</sup> while the C-N bond energy in pyrrole is about 90 kcal/mol, and the activation energy for pyrrole thermal decomposition is about 70 kcal/mol.<sup>11</sup>

A preliminary nitrogen model was formulated for this study by Genetti to better match the rate of nitrogen release as measured using chemical structural char data.<sup>13</sup> This model treated (a) nitrogen release with the tar, and (b) nitrogen release from the char using a first-order distributed activation energy model based on the mass fraction of nitrogen per aromatic mass in the char. In doing so, it was necessary to include a stable nitrogen fraction not released from the char during pyrolysis Predictions from the preliminary nitrogen model match data from a variety of pyrolysis tests including parent coals of a wide range of rank and temperatures between 880 and 1650 K (see Figures 9-11).



Residence Time (ms)

**Figure 9.** Comparison of predicted and measured  $N_{site}$  and daf % N in char ( $N_{char}$ ) values of a Blue #1 high volatile bituminous coal. Blue #1 was pyrolyzed in a drop tube reactor with a peak temperature of 1250 K and a residence time of 240 ms.<sup>5</sup> Predictions made using the preliminary (stable nitrogen fraction) model.<sup>13</sup>



**Figure 10.** Comparison of predicted and measured char daf % N values of five coals pyrolyzed by Hambly in a drop tube reactor at Brigham Young University with peak temperatures of 820, 1080, and 1220 K.<sup>2</sup> Predictions made using the preliminary (stable nitrogen fraction) model.<sup>13</sup>



**Figure 11.** Comparison of predicted and measured mass and nitrogen release data of five coals pyrolyzed by Hambly in a drop tube reactor at Brigham Young University with peak temperature of 1220 K.<sup>2</sup> Predictions made using the preliminary (stable nitrogen fraction) model.<sup>13</sup>



**Figure 12.** Comparison of predicted nitrogen release values with measured and predicted nitrogen release values reported by Genetti<sup>13</sup> for flat flame reactor pyrolysis experiments at 1650 K and 78 ms residence time. Also shown are predicted and measured mass release values reported by Genetti.<sup>13</sup>

Measured mass and nitrogen release data reported by Genetti for flat flame reactor tests at 1650 K and 78 ms residence time were also used to evaluate the preliminary nitrogen model (see Figure 12).<sup>13</sup> The preliminary nitrogen model did not accurately describe nitrogen release for high heating rate pyrolysis at long residence times. Furthermore, the preliminary model did not explain the reason some coal nitrogen was released at low temperatures while some nitrogen was "stabilized" in the char. Therefore, a more rigorous model for prediction of light gas nitrogen release was developed which better describes the rank dependence of char chemical structural evolution during devolatilization. This model couples the light gas nitrogen release with total light gas release, thus "stabilizing" the fraction of nitrogen remaining in the char once all the light gas has been released. Because this model assumes that light gas nitrogen release is initiated by unstable free radicals in the coal, the activation energy barrier is much lower. This would explain why coal nitrogen is released at much lower temperatures than are required for thermal decomposition of model compounds such as pyrrole or pyridine. Predictions using this model (the radical mechanism model) are compared to predictions made using the preliminary model for high heating rate, long residence time pyrolysis tests. This radical mechanism model is developed and evaluated in the remainder of the report, using both published data and the pyrolysis data presented earlier.

### **Model Development**

A simplified nitrogen release model was developed which includes three pathways for nitrogen release from coal char during rapid pyrolysis:

- A) TAR: Nitrogen-containing tar clusters transport nitrogen away from the char during tar release.
- B) FAST LIGHT GAS: Reaction of ring nitrogen in both the tar and char occurs quickly and at temperatures as low as 1000 K as a result of char stabilization reactions during light gas release.
- C) SLOW LIGHT GAS: Ring nitrogen is slowly broken out of the char clusters at very high temperatures in a process analogous to thermal decomposition of nitrogen containing rings. This has a moderate activation energy.

Tar clusters are assumed to have the same average structural properties as the char clusters from which they were released, including the average molecular weight per cluster, average aromatic mass per cluster, and the mass of nitrogen per aromatic mass. Although this is not strictly true, as shown earlier in this report, the assumption is close enough to be practically useful. Any devolatilization model that can model these properties may be used with this nitrogen model. In this study, the Chemical Percolation Devolatilization model<sup>14</sup> was used to track changes in average char and tar structural properties throughout devolatilization.

Models which describe the kinetics of chemical reactions (such as fast light gas nitrogen release) are usually valid for a wide range of conditions only if based on a reasonable mechanism of elementary steps. Complex mechanisms with hundreds of elementary steps can often be described by much simpler global mechanisms with fewer steps (which are not elementary). In this model, fast light gas nitrogen release (pathway B) was assumed to occur via a three-step global mechanism as follows:

- 1) Cluster  $-R R^{\prime}$  k<sub>1</sub> Cluster  $-R^{\prime} + R^{\prime}(gas)$  (r<sub>1</sub>)
- 2) Cluster  $-R^{\cdot} + RingN^{k_2}$  Cluster + LightgasNspecies (r<sub>2</sub>)
- 3) Cluster -R' + R''  $k_3$  Cluster -R R''  $(r_3)$

where Cluster-R-R' and Cluster-R-R" are char (or coal) clusters with various aliphatic attachments, Cluster-R' is a free radical formed within the char matrix, 'R' is a light gas precursor which is also a free radical, ring N is nitrogen contained within the aromatic portion of the char, and R" is any material in the char which competes with ring N for char free radicals.

Although some initial fraction of char free radicals (Cluster-R') may build up which are stabilized by resonance throughout the char network, once the cluster is saturated any new radicals formed via step (1) will be reactive (unstable). At that point steps 2 and 3 compete for the unstable char free radicals thus formed. Step 3 is a general solid-phase free radical stabilization step which occurs very quickly and probably includes thousands of specific reactions including hydrogenation, char bridge formation, crosslinking, etc. A rate equation can be developed from this global mechanism as outlined below. The rate of disappearance of ring nitrogen is the rate of step 2 ( $r_2$ ).

$$-\frac{d[ring N]}{dt} = r_2 = k_2 [Cluster - R'][ring N]$$
(2)

where the square brackets denote concentration (grams/gram of aromatic material). Assuming no accumulation of *unstable* cluster free radicals (steady state approximation) gives:

$$\frac{d[Cluster - R^{\bullet}]}{dt} = 0 = r_1 - k_2 [Cluster - R^{\bullet}][ring N] - k_3 [Cluster - R^{\bullet}][R^{"}]$$
(3)

Solving Equation (3) for [Cluster-R'] yields:

$$\left[Cluster - R^{\bullet}\right] = \frac{r_1}{k_2 [ring \ N] + k_3 [R^{"}]}$$
(4)

Since experimentally we observe that light gas nitrogen species molecules released make up only a very small fraction of the total light gas species released, it can be assumed that  $r_2 << r_3$ , and thus  $k_2$ [ring N]  $<< k_3$ [R"]. Accordingly Equation (4) becomes:

$$\begin{bmatrix} Cluster - R^{\bullet} \end{bmatrix} \quad \frac{r_1}{k_3 [R^{\bullet}]} \tag{5}$$

which can be substituted into Equation (1) to give:

$$\frac{-d[ring N]}{dt} = k_2 \frac{r_1}{k_3[R]} [ring N] = \frac{k_2}{k_3} \frac{r_1}{[R]} [ring N]$$
(6)

where  $k_{2}$  and  $k_{3}$  are the Arrhenius rate constants for steps 2 and 3 respectively.

This rate equation predicts that once unstable char radicals begin to form, the rate of ring nitrogen decay should be proportional to the concentration of ring nitrogen and to the overall rate of light gas release  $(r_1)$ . The rate of light gas formation  $(r_1)$  is defined as the negative fractional change in the molecular weight per cluster as follows:

$$r_1 = -\frac{1}{M_{cl}} \frac{d(M_{cl})}{dt}$$
(7a)

Ring N concentration ([ring N]) is defined on a per aromatic mass basis because aromatic mass per cluster in the char is fairly stable during primary pyrolysis, remaining essentially unchanged during both tar release and light gas release. A ring nitrogen concentration so defined will be referred to as  $N_{site}$ , which can be calculated as:

$$N_{site} = \% \, daf \, N \quad \frac{M_{cl}}{M_{site}} \tag{7b}$$

where daf % N is the mass percent nitrogen in the char on a dry ash free basis,  $M_{site}$  is the measured average aromatic mass per cluster, and  $M_{cl}$  is the measured average total mass per cluster. It is also assumed that [R"] is proportional to the average total mass per cluster ( $M_{cl}$ ). Since [R"] competes with  $N_{site}$  for free radicals, it must be expressed on the same basis as  $N_{site}$ , that is, per average aromatic mass per cluster as follows:

$$[R"] = \frac{M_{cl}}{M_{site}} \tag{7c}$$

Substituting the above definitions and assumptions into Equation (6) yields:

$$-\frac{d(N_{site})}{dt} = \frac{k_2}{k_3} \quad \frac{-\frac{1}{M_{cl}}}{\frac{M_{cl}}{M_{site}}} \quad N_{site} = -\frac{k_2}{k_3} \quad \frac{M_{site}}{(M_{cl})^2} \quad \frac{d(M_{cl})}{dt} \quad N_{site}$$
(8)

If the rate constants in Equation (8) are expanded and combined as:

$$\frac{k_2}{k_3} = \frac{A_2}{A_3} \exp \frac{-(E_2 - E_3)}{R T_p} = A_N \exp \frac{-E_N}{R T_p}$$
(9)

where R is the universal gas constant and  $T_p$  is the particle temperature.  $A_2$ ,  $A_3$ , and  $A_N$  are the preexponential factors and  $E_2$ ,  $E_3$  and  $E_N$  are activation energies for steps 2, 3 and the overall global rate expression respectively. Substituting Equation 9 into Equation 8 gives the final rate equation:

$$\frac{d(N_{site})}{dt} = A_N \exp \frac{-E_N}{R T_p} \frac{M_{site}}{(M_{cl})^2} \frac{d(M_{cl})}{dt} N_{site}$$
(10)

Changes in the average total mass per cluster during devolatilization is already predicted by the Chemical Percolation Devolatilization (CPD) model, and can also be calculated if <sup>13</sup>C NMR data are available for samples obtained at different stages of pyrolysis.

Slow light gas nitrogen release (pathway C) is assumed to be first order in  $N_{\mbox{\tiny site}}$  as follows:

$$-\frac{d(N_{site})}{dt} = A_4 \quad \exp \frac{-E_4}{R T_p} \quad N_{site} \tag{11}$$

where  $A_4$  is the pre-exponential factor,  $E_4$  is the activation energy, R is the universal gas constant, and  $T_p$  is the particle temperature. Although slow light gas nitrogen release is probably more realistically modeled using a distributed activation energy, the activation energy in this model was not distributed due to a lack of long residence time high temperature pyrolysis data.

While developing this model, a large number of options were explored in an attempt to model nitrogen release. Initially, a simple first order rate expression (with no coal-dependent parameters) for the disappearance of  $N_{site}$  in the char was tried, but this failed to describe the way in which nitrogen release quickly levels off as mass release levels off. Next, a distributed activation energy was added, but this failed to capture the trend with rank of light gas nitrogen release. Once it became clear that light gas nitrogen release was coupled with light gas release, several mechanisms were developed which did not correctly describe the changes in the nitrogen as a function of the char chemical structure. These included reaction of char ring nitrogen with gas phase free radicals (light gas pre-cursors) and the reaction of ring nitrogen with char free radicals formed from both tar and light gas release. Three other mechanisms were tried which did not correctly describe the decay of  $N_{site}$  during pyrolysis: (a) omitting the reaction which competes for char free radicals, (b) adding a second-order free radical destruction step which competes for char radicals, and (c) assuming that [R"] is proportional to the aliphatic char material only. In contrast, the final radical mechanism model properly describes both the manner in which  $N_{site}$  changes during pyrolysis and the rank dependence of light gas nitrogen release.

### Validation of the use of N<sub>site</sub>

In using  $N_{site}$  (Equation 7b) to describe the release of nitrogen to the light gas, it was assumed that aromatic mass was conserved in the pyrolysis products throughout devolatilization. Data from this study have been used to check this assumption for an analogous parameter, aromatic carbon (see Figure 13). It can be seen that the aromatic carbon balance ranges from 16% to 6% high for the South Banko drop tube tests between 900 and 1100 K. This may mean that measured char yields are 5-15% too high for these tests, a possibility which is not inconsistent with the ultimate yield observed in the flat flame reactor. For each of the Pittsburgh tests below 1250 K, the aromatic carbon balance is within the error of the data.

If it is assumed that aromatic mass is conserved in the pyrolysis products and that both tar and char undergo the same fractional decay of  $N_{site}$ , then the light gas nitrogen released (as a fraction of the coal nitrogen) can be estimated as the fractional decay of  $N_{site}$  in the char (equation 7b, see Perry for a full derivation<sup>15</sup>). Because NMR data used to calculate  $N_{site}$  are not available for most of the tars produced in this study, it is assumed that tar  $N_{site}$  decay is similar to char  $N_{site}$  decay. Based on the South Banko and Pittsburgh chemical structural data for the 1100 K condition, these assumptions are fairly good, except that tar  $N_{site}$  decay is about 10% (absolute) less than char  $N_{site}$  decay. Figure 14

shows that, in fact, fairly good agreement exists between the fractional char  $N_{site}$  decay and the estimated fractional light gas yield at the 1100 K condition. The bias of the data toward the upper left quadrant in Figure 14 is consistent with the observation that char  $N_{site}$  decay is somewhat larger than the tar  $N_{site}$  decay, whereas in Figure 14 they are assumed to be equal.



**Figure 13.** Balance on aromatic carbon for pyrolysis experiments using South Banko and Pittsburgh parent coals.



Figure 14. Comparison of estimated fractional light gas nitrogen yields with decay of nitrogen mass per aromatic mass  $(N_{site})$  in the chars for drop tube experiments at the 1100 K condition. The dashed line represents perfect agreement.

Even though for tests performed at 1250 K and above aromatic carbon is not conserved (as described in the Pyrolysis Tests section of this report), the extrapolated use of  $N_{site}$  beyond particle temperatures of 1200 K may still be appropriate for prediction of light gas nitrogen release from char. Once aliphatic release from the char is nearly complete (i.e. at or above the 1000 K condition of this study),  $N_{site}$  decay can be approximated by the decay of the nitrogen to carbon ratio (N/C), since almost all the carbon in the char is aromatic. Since aromatic mass is directly proportional to the carbon aromaticity, increases in aromaticity with increasing pyrolysis severity will cause slightly less N/C ratio decay than  $N_{site}$  decay. As can be seen by the solid lines in Figure 15, the N/C ratio of the Pittsburgh and South Banko *chars* changes nearly linearly with changes in char mass (or yield) between 1000 and 1650 K. Thus the rate of nitrogen release from the char is probably not significantly altered by the ring opening and cluster coalescence reactions which occur above 1200 K (due to the low concentrations of N and O). On the other hand, *tar* N/C ratios (dashed lines in Figure 15) change drastically above 1200 K, with little change in the tar mass (yield). Note that the South Banko char N/C ratios may be affected by large changes in oxygen concentration as pyrolysis severity increases.



Figure 15. Comparison of N/C ratios for South Banko and Pittsburgh chars and tars.

# Nitrogen Model Rate Constant Regression

The full nitrogen model has been added to the Chemical Percolation Devolatilization (CPD) model to predict how coal nitrogen is distributed among char, tar, and light gas products during devolatilization. In so doing, the slow nitrogen release step (eq. 11) was modeled with a rate constant of  $800 \exp(-11,400/T_p) \sec^{-1}$ . These rate constant parameters were regressed using the long residence time flat flame reactor data of Genetti (shon earlier in Figure 12)<sup>13</sup> and the high temperature fast flow furnace

data of Pohl and Sarofim (see Figure 16).<sup>16</sup> For these values of the rate constant parameters, slow light gas nitrogen release does not release significant amounts of nitrogen from the char at the devolatilization conditions used in this study (i.e. the conditions shown in Table 1). Due to a lack of long residence time data, a distributed activation energy regression was not possible.

For the fast nitrogen release portion of the nitrogen model, decay of  $M_{cl}$  and  $N_{site}$  was also predicted in order to regress appropriate values for the pre-exponential factor ( $A_N$ ) and activation energy ( $E_N$ ) using experimental data. This regression was performed using data published by Fletcher and Hardesty<sup>5</sup> for which measured particle temperatures and <sup>13</sup>C NMR chemical structural data were available for experiments performed at 1050 K, 1250 K, and 1600 K. Chemical structural data from experiments performed at the 1100 K condition in the present study were also used to help determine appropriate values for  $A_N$  and  $E_N$ . It was found that  $A_N=18.0$  (unitless) and  $E_N=6$  kcal/mol fit the data fairly well (see Figures 17 and 18). It should be noted that activation energy values as low as 3.5 kcal/mol also could be made to fit the data fairly well.



**Figure 16.** Comparisons of predicted and measured nitrogen retained in char as a fraction of parent coal nitrogen for a lignite and a bituminous coal pyrolyzed in a drop tube or fast flow furnace. Measured data reported by Pohl and Sarofim.<sup>16</sup> Chemical structure approximated to be those of Beulah Zap lignite and Pittsburgh #8 for the lignite and bituminous coals respectively (structural data from Fletcher and Hardesty)<sup>5</sup>. Particle temperature profiles are only rough approximations corresponding to the reported maximum gas temperatures.

Because the CPD model assumes that the molecular weight per aromatic site remains constant throughout primary devolatilization, measured values of char molecular weight per cluster ( $M_{cl}$ ) were corrected to have the same molecular weight per site ( $M_{site}$ ) as the parent coal. In this way CPD predictions of  $M_{cl}$  (expressed as a fraction of the coal  $M_{cl}$ ) could be compared with an adjusted molecular weight per cluster defined as:

$$\frac{M_{cl,char}}{M_{cl,coal}}_{adjusted} = \frac{M_{cl,char}}{M_{cl,coal}} - \frac{M_{site,coal}}{M_{site,char}}$$
(12)

It was assumed that the radicals formed during the initial 6% of light gas release were stable. This means that  $N_{site}$  was assumed to remain at the value in the parent coal until the molecular weight per cluster had decayed to 94% of the coal value. It is not clear whether this empiricism is really necessary, although it seems to fit data for very high rank coals somewhat better.

#### **Devolatilization Modeling Procedure**

Measured centerline gas temperature profiles and calculated gas velocity profiles for each condition were used with the Chemical Percolation Devolatilization (CPD) model to predict time resolved particle temperature profiles. Approximate centerline gas velocity profiles were calculated by performing a simple average gas velocity calculation at each centerline temperature along the reactor length for the proper cross sectional area and total mass flow rate. An average particle size of 55  $\mu$ m was assumed for all tests. Although most of the model predictions use actual <sup>13</sup>C NMR structural data for the coal dependent CPD model input parameters, predictions were also made at the 1100 K and 1650 K conditions using a correlation reported by Genetti et al.<sup>17</sup> to estimate the chemical structural parameters needed by the CPD model from the parent coal proximate and ultimate analyses. The correlation developed by Genetti<sup>13</sup> for the initial fraction of char bridges in the coal (c<sub>0</sub>) was used except for predictions for the tests using Pocahontas coal, for which it was assumed that c<sub>0</sub>=0, which gave better tar and total mass release predictions.

### **Modeling Results**

The nitrogen model was used with the CPD model to make predictions of  $M_{cl}$ ,  $N_{site}$ , tar yield, tar nitrogen, total mass release, and total nitrogen release for all the pyrolysis tests performed in this study. Similar predictions were made for published pyrolysis data from various sources.

# $N_{site}$ Predictions

In Figure 17 comparisons of predicted and measured  $M_{cl}$  and  $N_{site}$  are made for chars produced in a drop tube with a maximum gas temperature of 1250 K quenched at various points along the pyrolysis path. Char values for  $M_{cl}$  and  $N_{site}$  are normalized to the parent coal values for ease of comparison. For the data shown in Figure 17, it appears that the higher the coal rank, the more steep the slope of  $N_{site}$ decay, a trend which is correctly imitated by the nitrogen model predictions. Although the final change in  $M_{cl}$  is not always perfectly predicted by the CPD model, the model parameters were adjusted to give the correct  $N_{site}$  trajectory for a given coal rather than only matching the endpoint  $N_{site}$  value. For example, although the endpoint  $M_{cl}$  value is under-predicted by the CPD for the Illinois #6 coal at this condition (and thus the endpoint  $N_{site}$  is also under-predicted), the trajectory follows the experimental data fairly well.



**Figure 17.** Predicted decay (lines) of  $N_{site}$  compared to values calculated from measured chemical structural data (symbols) published by Fletcher and Hardesty<sup>5</sup> for drop tube pyrolysis of five coals at 1250 K maximum gas temperature and 250-300 ms residence time. Char  $M_{cl}$  values are adjusted for changes in the mass of aromatics (see eq. 12)



**Figure 18.** Predicted decay of  $N_{site}$  compared to values calculated from <sup>13</sup>C NMR data for chars generated at 1100 K condition in this study. Char  $M_{cl}$  values are adjusted for changes in the mass of aromatics (see eq. 12)

Chars produced in this study at 1100 K showed the same trend with rank for  $N_{site}$  decay (see Figure 18). Again, the nitrogen model captures this trend with rank quite well, although the devolatilization model under-predicts the amount of  $M_{cl}$  decay in every case.

#### Nitrogen Distribution Predictions

The nitrogen release model was used to predict the partitioning of nitrogen between char, tar, and light gas for each of the tests performed in this study. One measure of the performance of a nitrogen release model is the ability to predict char nitrogen content during devolatilization. For the coals and conditions of this study, generally good agreement was observed between measured and predicted daf nitrogen contents (see Figure 19). Note that the nitrogen model correctly describes the trend with temperature of the nitrogen content, generally predicting nitrogen contents within experimental error (about  $\pm$  5% relative) for every coal.



**Figure 19.** Comparison of measured (points) and predicted (lines) nitrogen content for chars from drop tube and flat flame reactor pyrolysis tests.

CPD predictions of tar, tar nitrogen, mass release, and nitrogen release (as a percentage of daf coal values) are compared to measured values in Figure 20. Trends with rank are well predicted for both tar release and total mass release. Because primary tars undergo secondary reactions in our drop tube,

measured tar yields are somewhat lower than the primary tar actually released. Measured tar yields are at a maximum at the 1000 K condition for most coals. At 1000 K, tar release is predicted fairly well from the Yallourn and South Banko coals, but is over-predicted from the Taiheiyo coal and greatly under-predicted from the bituminous coals. Similarly, total mass release is greatly under-predicted at every condition for every coal except Taiheiyo and Pocahontas (for which  $c_0$  was arbitrarily set to zero). This result was surprising since the CPD model agrees with data from many other experiments.<sup>13, 14, 18</sup> The discrepancy between the predicted and measured nitrogen release is about the same as the discrepancy between the predicted and measured nitrogen release.

One possible cause for this disagreement is error in the calculation of the particle temperature profiles. In these calculations it was assumed that the particles traveled down the center of the drop tube. However, if the particles traveled away from the centerline, they may have experienced temperatures as much as 100 °C higher than those used for the CPD predictions. This would give under-prediction of both the tar and ultimate volatiles yields. Also, the 1250 K drop tube and 1650 K flat flame reactor tests were performed at pyrolysis conditions more severe than any used to generate data to which the CPD model parameters were originally fit. Another possible cause for this disagreement is that the activation energies for bridge breaking and side chain release may be coal dependent. Currently, the CPD model assumes that the rate coefficients are independent of coal type; future research will use these data to explore activation energies that are functions of the bridge mass.

In spite of the lack of quantitative agreement between predicted and measured mass and nitrogen release, predictions from the nitrogen release model correctly match the shape of the nitrogen release curve as a function of mass release. Measured values of nitrogen release are plotted versus mass release in Figure 21. Predicted values of nitrogen release are plotted versus predictions of mass release in Figure 22. Both Figures 21 and 22 show large horizontal and vertical spreads in the data at each of the drop tube temperatures, converging to a much tighter line with a nearly 1:1 correspondence between nitrogen and mass release at the temperature of the flat flame reactor (1650 K).

Predictions were also made using a correlation developed by Genetti et al. for predicting the <sup>13</sup>C NMR chemical structural parameters used as input to the CPD model based only upon the elemental composition and ASTM volatile matter content of the parent coal.<sup>17</sup> In Figure 23, these predictions are compared to measured values for the tests performed at the 1100 K condition. The trend with rank is again very nicely predicted by the CPD model. Except for over-prediction of the tar yields of the low rank coals, the predictions made using the correlation actually agree better with the data than the predictions made using the actual NMR values. This may be due to the fact that the fraction of intact bridges in the parent coal ( $p_0$ ) is significantly higher in these coals than in coals of comparable rank used in the development of the CPD model. This possibility was suggested by Genetti, who left coals with unusually high  $p_0$  out of his <sup>13</sup>C NMR parameter correlation so that the correlation would not predict unusually high  $p_0$  values which would give abnormally low CPD volatiles predictions.<sup>13</sup>



**Figure 20.** Comparison of predicted and measured tar and tar nitrogen yields and predicted and measured total mass and nitrogen release for drop tube and flat flame reactor pyrolysis experiments. Predictions made using measured <sup>13</sup>C NMR structural parameters and assuming  $c_0=0$  for tests using Pocahontas coal.



Figure 21. Measured nitrogen release compared to measured mass release for all coals and conditions used in this study.



**Figure 22.** Predicted nitrogen release compared to predicted mass release for all coals and conditions used in this study.



**Figure 23.** Comparison of predicted and measured tar and tar nitrogen yields and predicted and measured total mass and nitrogen release for 1100 K drop tube and 1650 K flat flame reactor pyrolysis experiments. Predictions made **using correlation of Genetti et al.**<sup>17</sup> to estimate parent coal structural parameters and assuming c<sub>0</sub>=0.36 for tests using Pocahontas coal.

#### **V. CONCLUSIONS**

A new solid-state <sup>13</sup>C NMR technique was used to produce the very first detailed chemical structural analyses of matched tar and char sets which allow comparison of the structural evolution of chars and tars during devolatilization. The data confirm much of what has been reported by previous investigators about the structural progression of coal chars during pyrolysis. Evidence of three types of structural changes were seen in both chars and tars during rapid pyrolysis, two of which have never been noted before: ring opening and cluster coalescence. Ring opening and cluster coalescence appear to occur only at particle temperatures above 1200 K. Cluster coalescence was minimal for char from a flat flame reactor (high heating rate, short residence time) experiment, and was seen in most chars and tars from drop tube experiments at the 1250 K condition. Surprisingly, neither ring opening reactions nor cluster coalescence occurred in the South Banko tar produced at the 1250 K condition.

A nitrogen model based on a three-step free radical global mechanism was also developed. The mechanism assumes that nitrogen in the char competes with other mass in the char for reaction with char free radicals formed during light gas release. This radical mechanism model provides realistic explanations for the low apparent activation energy of light gas nitrogen release and for the relative stability of char nitrogen once mass release has ceased. Furthermore, this is the first time that solid-state NMR data has been used to develop a nitrogen release mechanism and rate equation and to fit the rate constants for light gas nitrogen release. When used with the CPD devolatilization model and coal-specific chemical structural input data, this nitrogen model adequately predicts nitrogen content, tar and light gas nitrogen yields, and char chemical structure for pyrolysis of coals of a wide range of rank produced under a variety of pyrolysis conditions.

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