The Chemical Structure of Coal Tar and Char During Devolatilization

A Thesis

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> Mathew Watt August 1996

This thesis by Mathew Watt is accepted in its present form by the Department of Chemical Engineering of Brigham Young University as satisfying the thesis requirement for the degree of Master of Science.

Thomas H. Fletcher, Advisor

John N. Harb, Advisory Committee

Ronald J. Pugmire, Advisory Committee

Paul O. Hedman, Advisory Committee

William G. Pitt, Graduate Coordinator

Date

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Nomenclature

Symbol	Definition
A	Area
anth	Anthracite coal
В	Blowing parameter
B.L.	Bridges and loops per aromatic cluster
C _{cl}	Aromatic carbons per aromatic cluster
C_p	Specific heat capacity
daf	Dry, ash free analysis
D_p	Diameter of particle
f_a	Total percent of sp ² -hybridized carbons
$f_a{}^B$	Percent of aromatic bridgehead carbons
f_a^C	Percent of carbonyl carbons
f _{a'}	Percent of aromatic carbons
f_a^{H}	Percent of aromatic carbons with proton attachments
f _{al}	Percent of aliphatic carbons
f_{al}^{H}	Percent of CH or CH ₂ aliphatic carbons
f_{al}^{*}	Percent of CH ₃ or nonprotonated carbons
$f_{al}O$	Percent of carbons bonded to oxygen
f_a^N	Percent of nonprotonated aromatic carbons
f_a^P	Percent of phenolic or phenolic ether
f_a^{S}	Percent of alkylated aromatic carbons
F_{g}	Force of gravity on a particle
F_k	Drag force of a particle
f_{Ti}^{coal}	Mass fraction of titanium in the dry coal
f_{Ti}^{char}	Mass fraction of titanium in the dry char
f_{Ti}^{ash}	Mass fraction of titanium in the ash
g	Acceleration due to gravity
h	Convective heat transfer coefficient
hvAb	High volatile A bituminous coal

hvBb	High volatile B bituminous coal
hvCb	High volatile C bituminous coal
k	Thermal conductivity
ligA	Lignite A coal
lvb	Low volatile bituminous coal
m _{coal}	Mass of the coal
<i>m</i> _{char}	Mass of the char
m _{ash}	Mass of the ash
m_{char}^{N}	Mass of nitrogen remaining in the char
M_{cl}^N	Mass of nitrogen per aromatic cluster
m_{coal}^{N}	Mass of nitrogen in the coal
m_{HCN}^{N}	Mass of nitrogen released as HCN
m_i	Mass fraction of coal
m_{tar}^{N}	Mass of nitrogen in the tar
mvb	Medium volatile bituminous coal
MW _{att}	Average molecular weight of cluster attachments
MW _C	Molecular weight of carbon
MW _{cl}	Average molecular weight per aromatic cluster
MW _{mer}	Molecular weight of a polymer of clusters
n	Number of clusters per tar polymer
N _{cl}	Nitrogens per aromatic cluster
n _{cl}	Number of moles of clusters per kilogram of parent coal
n _{cl}	Number of moles of clusters in char per kilogram of coal
coal n _{cl}	Number of moles of clusters per kilogram of coal
tar n _{cl}	Number of moles of clusters in tar per kilogram of coal
Nu	Nusselt number
Po	Fraction of attachments that are bridges
Re	Reynolds number
S.C.	Side chains per aromatic cluster
subB	Subbituminous B coal
subC	Subbituminous C coal
t	Time
Т	Temperature

T_b	Temperature of the thermocouple bead
T_{g}	Correct gas temperatures
T_s	Temperature of the walls
V	Velocity
V _g	Gas velocity
\mathcal{V}_p	Particle velocity
ν	Slip velocity
Xb	Fraction of bridgehead carbons
x_C	Weight percent of carbon in the coal(daf)
x _N	Weight percent of coal(daf)
Н	Change in enthalpy
δm_{tar}^N	Differential mass of nitrogen released with the tar
δm_{tar}	Differential mass of tar
ε	Emissivity
ρ	Density
$ ho_g$	Gas density
ρ_p	Density of particle
σ	Stefan-Boltzmann constant
	Standard deviation
+1	Total attachments per aromatic cluster
\mathbf{v}_{g}	Gas kinematic viscosity
μ_{g}	Gas viscosity

1. Introduction

Much progress has been achieved in coal devolatilization research in the last couple of decades. An understanding of how coal devolatilization, also known as pyrolysis, changes the coal structure and releases pyrolysis products is beginning to emerge. Devolatilization models have also changed dramatically. Models have progressed from simple empirical single-step expressions that predict total volatile release to more dynamic models that try to describe the actual physical and chemical processes that occur during devolatilization.

Coal is thought to consist of a large aromatic matrix structure, called the coal macromolecule. The coal macromolecule consists of carbon aromatic clusters joined together by non-aromatic bonds, known as bridges. The bridges are generally thought to be mostly aliphatic in nature. Attachments to the aromatic clusters that do not form bridges are called side chains. Side chains are thought to mainly consist of aliphatic and carbonyl groups.

Coal pyrolysis is thought to break the bonds of the bridges, that bind the aromatic clusters together, and the side chains of aliphatic and carbonyl groups. As these bridges and side chains are cleaved, small fragments are generated. If the fragments are small enough they will vaporize and form light gases and tars. The larger, higher molecular weight structures remain in the coal structure and will finally recombine to the coal macromolecule.

Understanding exactly how this entire process occurs is critical in order to properly model the rates, yields and products of devolatilization. To accomplish the goal of predicting coal devolatilization from measurements of the parent coal it is necessary to obtain good quantitative experimental data that relate to the reaction processes occurring on

a molecular scale. Current interest in coal devolatilization modeling is the ability to predict possible pollutant emissions, such as nitrogen evolution.

The power generation industry in the United States is being driven by regulations to reduce pollution formation, specifically NO_X emissions. It has been found that the most economical method is by changing near-burner aerodynamics with the use of low NO_X burners. Low NO_X burners influence the devolatilization process which has a significant effect on the rest of combustion and nitrogen oxide formation.¹⁻³ A better understanding of this phenomena, and how it affects nitrogen release is currently important to industry as a way to further improve burner designs.

Analysis techniques such as ¹³C NMR spectroscopy have proven particularly useful in obtaining average chemical structural features of coal and char, while ¹H NMR has been used to analyze the liquid phase pyrolysis products(i.e., coal tar). Pyridine extraction methods combined with NMR methods have also been useful in collecting information on coal devolatilization. Gas chromatography, X-ray photoelectron spectroscopy(XPS) analysis and other methods have also given valuable information.

Most of these methods allow for in-depth study of the carbon and hydrogen structure in the coal. Very few analysis techniques are available to specifically study the nitrogen forms in the coal and pyrolysis products. By combining techniques together this study has helped to improve the understanding of the nitrogen structure in the coal and the pyrolysis products.

This study also confirms and adds to the information already available on the coal pyrolysis process. Pyrolysis experiments were performed using a drop tube furnace and a methane-air flat flame burner. Chemical analysis of the coal, char and tar samples was performed at several outside laboratories. The work described here is the first reported analysis of matching coal, char and tar samples using ¹³C NMR. This was also the first time that high resolution X-ray photoelectron spectroscopy (XPS) was used to analyze

chars produced at high heating rates and temperatures. The significance of the results of these analysis methods is discussed with regards to current devolatilization models. Emphasis is given to the nitrogen structure in the coal, and possible methods are discussed to model nitrogen evolution during devolatilization. In all, the results presented here increase the understanding of the coal pyrolysis process and how to predict devolatilization behavior.

2. Literature Review

The literature review will cover what is currently known about the carbon and nitrogen structure of the coal. The pyrolysis process will be also be discussed, along with the carbon structure of the pyrolysis products. The nitrogen aspects for each of these areas will be discussed seperately, due to the emphasis on nitrogen in the literature and the importance that nitrogen has in this thesis. Devolatilization models are reviewed along with possible methods to model nitrogen release during devolatilization. A summary that concentrates on the weaknesses in the literature is presented.

Coal

Coal is thought to exist as a polymeric structure that forms a large macromolecule network.⁴ The macromolecular network consists of aromatic clusters that are linked and cross linked to other aromatic structures by bridges. The bridges between the clusters consist of a diverse set of structures. Most bridges are thought to be aliphatic in nature, but may also include other atoms such as oxygen and sulfur.^{5, 6}

Bridge structures have a large distribution of bond strengths.⁷ Bridges that contain oxygen as ethers are felt to be relatively weak in nature;⁸ other bridging bonds may be made up of only aliphatic carbons. Some bridges consist of a single bond between aromatic cluster groups(bi-aryl linkage). Figure 2.1 shows the structure of a hypothetical coal macromolecule.

A mobile phase interspersed with the coal macromolecule is theorized to also exist. The mobile phase would consists of smaller molecular groups that are not strongly bonded

to the macromolecule.^{9, 10} This mobile phase is considered to be either trapped in the molecular structure of the coal or weakly bonded with hydrogen or van der Waals type bonds. It is felt that this mobile phase is the material that can be chemically extracted with the use of weak solvents.



Figure 2.1. A hypothetical coal macromolecule structure with important structural characteristics labeled. Modified from Solomon et al.¹¹

13C NMR Analysis of Coal

Solid state ¹³C NMR is one of the few methods available to study the complete coal without breaking the structure apart. For this reason the ¹³C NMR analysis technique is probably the most reliable when related directly to the coal structure. Other methods, such

as solvent extraction and pyrolysis mass spectroscopy break the coal structure apart by the use of solvents or heat; and the liquid products are analyzed. The analysis of the liquid products is then used to extrapolate back to the coal structure. Extrapolation to the coal structure from extracts or pyrolysis products must be performed with care since the complete coal structure is not analyzed; in many cases the gas or liquid products analyzed represent only a small mass fraction of the coal.

With the use of solid state ¹³C NMR a number of investigators have been able to describe the average features of the coal macromolecule in great detail.¹²⁻¹⁴ A number of coals have been examined with these NMR techniques, spanning the range of rank from lignite to anthracites. Table 2.1 lists direct structural parameters obtained by ¹³C NMR for a number of coals and Table 2.2 shows the derived ¹³C NMR structural parameters for the same coals. The tables list the coals in order of rank from low to high so that trends in the data can be more easily seen.

The parameters obtained directly from ¹³C NMR analysis are able to give a general concept of the chemical structure of the coal. The value of f_a is the total fraction of aromatic, carboxyl and carbonyl carbons. This value is subdivided into f_a^C , which measures the fraction of carbonyl and carboxyl carbons, and f_a' , which measures the sp² hybridized carbons present in aromatic rings. The value of f_a' is subdivided into protonated f_a^H and f_a^N non-protonated aromatic carbons, and the non-protonated aromatic carbons are further split into f_a^P , f_a^S , and f_a^B , which are the fraction of aliphatic carbons is also measured and labeled as f_{al} . The aliphatic carbons are divided into (a) the fraction of CH and CH₂ groups, f_{al}^H , and (b) the CH₃ groups which are represented as f_{al}^* . The aliphatic carbons that are bonded to oxygen, f_{al}^O , are also shown.

Structural Farameters of the HOLIKO Could Determined from Could Read													
Coal	Rank	fa	f_a^C	fa	f_a^{H}	$f_a{}^N$	f_a^{P}	$f_a^{\ S}$	$f_a{}^B$	f _{al}	f_{al}^{H}	f_{al}^{*}	f _{al} O
Beulah Zap	ligA	65	10	55	22	33	9	15	9	35	26	9	11
Lower Wilcox	ligA	63	7	56	17	39	10	17	12	37	26	11	8
Wyodak	subC	63	8	55	17	38	8	14	16	37	27	10	10
Dietz	subB	64	8	56	19	37	9	15	13	36	25	11	5
Illinois #6	hvCb	72	0	72	26	46	6	18	22	28	19	9	5
Blind Canyon	hvBb	63	2	61	22	39	7	14	19	38	27	11	5
Pittsburgh #8	hvAb	71	1	70	27	43	6	15	22	29	21	8	4
Upper Freeport	mvb	81	0	81	28	53	4	20	29	19	11	8	2
L. Stockton	mvb	75	0	75	27	48	5	21	22	25	17	8	4
Pocahontas #3	lvb	86	0	86	33	53	2	17	34	14	9	5	1
Buck Mountain	anth	95	1	94	24	70	1	8	61	5	4	1	3

Table 2.1Structural Parameters of the ACERC Coals Determined from ¹³C NMR^{a12, 15}

^aPercentage carbon (error): $f_a = total sp^2$ -hybridized carbon (±3); $f_{a'} = aromatic carbon$ (±4); $f_a^C = carbonyl, > 165 ppm (\pm 2)$; $f_a^H = aromatic with proton attachment (\pm 3)$; $f_a^N = nonprotonated aromatic (\pm 3)$; $f_a^P = phenolic or phenolic ether, = 150-165 ppm (\pm 2)$; $f_a^S = alkylated aromatic = 135-150 ppm(\pm 3)$; $f_a^B = aromatic bridgehead (\pm 4)$; $f_{al} = aliphatic carbon (\pm 2)$; $f_{al}^H = CH$ or $CH_2 (\pm 2)$; $f_{al}^* = CH_3$ or nonprotonated (± 2); $f_{al}^O = bonded$ to oxygen, = 50-90 ppm (± 2).

Deriveu Stri		C INFR IOI THE ACERC COals"						
Coal	Rank	Xb	C _{cl}	+1	Po	B.L.	MW _{att}	MW _{cl}
Beulah Zap	ligA	0.16	9	3.9	0.63	2.5	40	269
Lower Wilcox	ligA	0.21	10	4.8	0.59	2.8	36	297
Wyodak	subC	0.29	14	5.6	0.55	3.1	42	408
Dietz	subB	0.23	11	4.7	0.54	2.5	37	310
Illinois #6	hvCb	0.31	15	5.0	0.63	3.2	27	321
Blind Canyon	hvBb	0.31	15	5.1	0.49	2.5	36	368
Pittsburgh #8	hvAb	0.32	16	4.5	0.62	2.9	28	310
Upper Freeport	mvb	0.36	18	5.3	0.67	3.6	17	310
L. Stockton	mvb	0.29	14	4.8	0.69	3.3	20	270
Pocahontas #3	lvb	0.4	20	4.4	0.74	3.3	13	307
Buck Mountain	anth	0.65	49	4.7	0.89	4.2	12	656

Table 2.2Derived Structural Parameters from ¹³C NMR for the ACERC Coals^{b12}

 ${}^{b}X_{b}$ = fraction of bridgehead carbons, C_{cl} = aromatic carbons per cluster, +1 = total attachments per cluster, P_{o} = 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_{att} = the average molecular weight of the cluster attachments.

The derived structural parameters give some of the most useful information. These parameters are calculated from the ¹³C NMR data with the use of assumptions and readily available information, such as the elemental composition.¹² To calculate the number of aromatic carbons per cluster (C_{cl}) a mathematical model was developed as a function of X_b from a study of polycondensed aromatic hydrocarbons. The value of C_{cl} is then used to determine most of the other derived structural parameters.

The derived ¹³C NMR parameters are important in being able to describe the average molecular structure of the coal. Some important parameters are the average number of aromatic carbons per cluster, C_{cl} , and the value of +1, which is the average number of attachments per aromatic cluster. The labeled aromatic cluster in Fig. 2.1 has 18 aromatic carbons and five attachments. The fraction of intact bridges, P_o , is the fraction of attachments that are bridges to a neighboring aromatic cluster. The number of bridges and loops per cluster, B.L., is the average value of bridges between clusters. This technique cannot distinguish between aliphatic loops that attach to two different carbons on the same aromatic cluster and bridges. Two other important values are MW_{cl} and MW_{att} which are the average molecular weight per cluster and the average molecular weight of side chains attached to aromatic clusters, respectively.

It is noted that coals increase in aromatic structure with increasing rank. This can be seen in the upward trends in aromaticity, aromatic carbons per cluster, and the fraction of bridgehead carbons. It is also noted that the aliphatic structures in the coal (f_{al} , f_{al}^{H} , f_{al}^{O}) decrease with increasing rank along with the molecular weight of attachments(MW_{att}). All of these finding are in agreement with the coalification process. It should be noted that these parameters are average values only. Coals contain a large distribution of structures that are only averaged in these parameters. Fletcher et al.¹³ studied eight other coals of varying rank with the use of ¹³C NMR, and found similar trends as a function of coal rank.

Nitrogen in Coal

Due to pollution effects, nitrogen is a very important species in the coal. Understanding the forms of nitrogen in coal is important in order to predict the evolution of nitrogen species during devolatilization.

The amount of nitrogen in coal is a slight function of rank, with the maximum amount of nitrogen occurring in coals with approximately 85% carbon, with the peak nitrogen contents of 1.8 to 2 wt.%.^{16, 17} Coal nitrogen is not expected to be found in significant quantities in side chains or aliphatic links, but is generally incorporated into the coal matrix as heterocyclic type structures, such as pyridine and pyrrole.^{18, 19} Figure 2.1 shows what a pyridinic and pyrrolic nitrogen structure might be like.

A number of studies have confirmed that the major species of nitrogen found in the coal are contained in forms similar to pyridine and pyrrole.¹⁷⁻²¹ The use of X-ray photoelectron spectroscopy (XPS)¹⁹ and X-ray absorption near edge spectroscopy (XANES)¹⁸ has provided new insights regarding nitrogen coal structure. The relative amounts of these compounds have been shown to vary slightly with the amount of carbon in the coal. As shown in Fig. 2.2, pyridinic nitrogen increases slightly with coal rank (where percent carbon is used to indicate rank), and that the pyrrolic nitrogen decreases slightly with rank.^{21, 22} These conclusions, however, are not confirmed by all investigators, and there are still some questions as to the accuracy of the XPS and XANES technique.^{17, 23}

One problem with both XANES and XPS is that they are both surface techniques and may not be completely representative of the overall coal macromolecule. Since both methods are surface techniques, great care needs to be taken to limit contamination and chemical surface reactions that may take place during sample preparation. Some inconsistencies in findings have been attributed to these problems.^{21, 22}



Figure 2.2. Nitrogen functional groups in coals as found by XANES(open symbols) and XPS(closed symbols) (taken from Solomon and Fletcher¹).

Recently, with more sensitive XPS equipment, quaternary nitrogen groups have also been confirmed.^{21, 22} Evidence is available that suggest that these quaternary nitrogen structures are protonated nitrogen in pyridinic form, and are chemically associated with oxygen functionalities.²² The quaternary nitrogen groups are most predominant in the low rank coals, with very little to no quaternary forms found in anthracites.²²

Although it has been suggested that amine structures are part of the coal macromolecule,²⁴ XPS has not yet been able to confirm the existence of such forms. It has been suggested, though, that amines may indeed exist at low levels (5 to 10 percent of the total nitrogen); at these levels XPS would be insensitive to the amine structures.²² Amines have been reported by XANES.¹⁸ XANES confirms that the amines level for the Argonne Premium coals were at or below 10 percent of the total nitrogen.

Another limitation to both the XPS and the XANES techniques is that the methods allow only a representative view of the chemical structure. Only general structure forms can be determined, such as pyridinic and pyrrolic forms.^{18, 21, 22} Neither method provides detailed nitrogen chemical structure.

Due to limitations of the XPS and XANES techniques, not much detail is known about nitrogen chemistry in the coal beyond the basic pyridinic and pyrrolic forms. Other methods to obtain information on the nitrogen chemistry in coal are only recently being perfected. These include quantitative solvent extraction methods and ¹⁵N NMR.

Pyrolysis

Pyrolysis is the first step in coal combustion. Peak temperature, heating rate, pressure, particle size, coal type and other factors are known to affect pyrolysis behavior.²⁵⁻²⁷ Major progress towards understanding the pyrolysis process has been made in the last 5-10 years, but quantitative description of the chemical reactions are still not feasible.

Pyrolysis is the break-down and reorganization of the coal macromolecule in the presence of heat but in the absence of oxygen. Pyrolysis is generally studied by heating the coal in an inert environment. As particle temperature increases, the bonds between the aromatic clusters in the coal macromolecule break, creating fragments that are completely detached from the macromolecule. The larger broken fragments in the coal are often referred to as metaplast. The metaplast fragments will either escape from the coal or be reincorporated into the coal macromolecule. Since vapor pressure is related to molecular weight, the metaplast that is vaporized as tar usually consists of the lower molecular weight fragments. Tar is defined as the gaseous pyrolysis products that are condensable at room temperature. The remaining metaplast eventually reincorporates into the coal by a reaction known as cross linking. Small side chains on the aromatic clusters are released from the coal as light gases, generally in the form of oxides or light hydrocarbons. The remaining solid material, including the crosslinked metaplast is referred to as char. Figure 2.3 shows

a schematic of how this pyrolysis process may occur for the hypothetical coal macromolecule in Fig. 2.1.



Figure 2.3. Hypothetical coal pyrolysis reaction. Modified from Solomon, et al.¹¹

Many high volatile bituminous coals exhibit thermoplastic behavior at heating rates of 10^4 K/s and temperatures around 700 K. These coals are referred to as softening or plastic coals. The coal melts into a non-Newtonian liquid causing the natural pores in the coal to close. The trapped tar and light gases form bubbles that cause swelling of the coal

particle. Tar and light gases are transported to the particle surface and escape via bubble formation and convection.

It is noted that coals of different rank exhibit very different devolatilization behavior. Low rank coals, such as lignites and subbituminous coals, are known to produce relatively high levels of light gases and very little tar products. Coals in the bituminous range produce significantly more tar than the low rank coals and moderate amounts of light gases. The higher rank coals tend to produce relatively low levels of both the light gases and tars. This trend can be seen in Fig. 2.4, where percent carbon is used as an indicator of rank. Some data scatter is present, but the overall trends are recognizable.



Figure 2.4. Tar and total volatile yields from devolatilization as a function of the carbon content of the parent coal (adapted from Fletcher, et al.²⁸). Solid lines are quadratic curve fits to the data, and are shown only for illustrative purposes.

Pyrolysis behavior is also affected by changes in coal particle temperatures and heating rate. Formation, vaporization and cross-linking of the tar and light gases are all very dependent on the temperature as well as the heating rate. This is due to the distribution of chemical bonds in the coal with differing activation energies.

Different pyrolysis steps have been suggested by a couple of investigators.^{26, 29} Suuberg et al.²⁶ pyrolyzed a lignite at a heating rate of 1000 K/s and indicated that at temperatures of just over 370 K the coal residual moisture evolves. The evolution of light gases begins at temperatures of 470 K to 770 K; these early gases consist mainly of oxides (CO and CO₂) and light hydrocarbons. Saxena et al.²⁹ studied coal pyrolysis at low heating rates (~ 1 K/s) and suggested that light gases, such as hydrogen, and nitrogens begin to evolve at temperatures of 670 K and above. Tar formation was seen in low heating rate experiments to begin at around 600 K and increases to temperatures above 800 K.³⁰ Cross-linking reactions are thought to occur at different temperatures, depending on the coal and heating rates. Pyrolysis experiments conducted with a number of coals at a heating rate of 30 K/min indicated that early cross-linking begins in the range of 670 to 770 K, later cross-linking continues as temperatures increase.^{31, 32} The exact temperatures at which many of these processes occur are dependent on numerous factors such as the coal and heating rate, however, the general processes of pyrolysis as described are relatively accurate.

Oxygen atoms are known to have a profound effect on the pyrolysis of coal. The oxygen in coal is often found in the bridges between aromatic clusters. These bridge sites are weak bond structures, creating breakage points for the depolymerization of the coal macromolecule.⁸ Recent work has suggested that oxygen found as heteroatoms in the aromatic coal clusters may contribute to depolymerization reactions.^{33, 34}

In the low rank coals the high levels of oxygen in the parent coal are correlated with early cross-linking of the metaplast. Cross-linking is known to occur in two steps, and at

distinct temperatures. In an experiment that pyrolyzed coals at 30 K/min, early crosslinking began at temperatures around 500 K in low-rank coals, prior to major bridgebreaking reactions. Later cross-linking started near 700 K and was most prominent in bituminous coals.^{35, 36} Cross-linking plays a large role in the low level of tar released during the pyrolysis of low rank coals. Sulfur and nitrogen may also be active in affecting pyrolysis. However, the exact mechanisms are not well known. Overall, pyrolysis is a complicated process, and a great deal of chemical and mechanistic information is required to properly model this process. Additional information on the changing physical and chemical structures of coals is critical to further improve our understanding of the mechanisms that control devolatilization. With improved understanding it is hoped that more accurate and detailed devolatilization models can be created.

Pyrolysis of Nitrogen

Low NO_x burner technology, now being implemented in industrial coal burner facilities, modify the aerodynamics of the near burner region in order to reduce NO_x formation from the volatile nitrogen in the coal. The ultimate effectiveness of these burners may be determined by the total amount and form of volatile nitrogen that is released during the devolatilization process. It is for this reason that the nitrogen distribution between the volatiles and char profoundly affects the final combustion NO_x levels.^{3, 24, 37} This influence can be seen in a study that devolatilized and combusted a lignite and a bituminous coal in a furnace at 1500 K and at a heating rate of approximately 2 x 10⁴ K/s. It was found that the volatile nitrogen contributed approximately 60 to 80 percent of the total NO_x levels.²⁴ Other studies which used coal-fired burners found that as much as 50% of fuel nitrogen may be converted to NO_x, and that approximately 75% of exhaust NO_x comes from the fuel nitrogen in the coal.^{3, 37} Determining how the volatile and char nitrogen effect NO_x levels has been as area of interest for the past couple of decades. The amount of nitrogen devolatilized from the coal is known to be a function of temperature. Blair, et al.² placed pulverized coal particles on a preheated graphite ribbon in an argon atmosphere. It was shown that as the pyrolysis temperature increases, volatile nitrogen increases proportionately and at a much faster rate than overall volatile release. The data can be seen in Fig. 2.5. Solomon and Colket³⁸ devolatilized coal with the use of a heated grid at temperatures of 570 to 1270 K and a heating rate of 600 K/s. They concluded that initial nitrogen evolution was found to be proportional to the evolved tar. Recent experiments that heated particles to 1000 K indicated that tar is the primary mechanism for nitrogen evolution during pyrolysis, even though it is not the only mechanism.^{39, 40} Since most coals exhibit light gas release either earlier or concurrent with tar release, nitrogen evolution lags total mass release during devolatilization.



Figure 2.5. Mass and nitrogen release during coal pyrolysis as a function of temperature. Particles placed on preheated graphite ribbon with an hold time of 2 min. (from Blair, et al.²)

Baxter, et al.⁴¹ assembled elemental mass release data from coal pyrolysis and char oxidation experiments in entrained flow reactors at high temperatures. The data indicate that coals ranging from lignite to bituminous rank release nitrogen at a lower rate than carbon during the devolatilization stage. Coals of higher rank, such as low-volatile bituminous, showed that nitrogen evolved at equal or higher rates than carbon, indicating that the rate of nitrogen release relative to carbon increased with increasing coal rank.

Total volatile nitrogen release is a function of coal rank. As indicated in Fig. 2.6, relative volatile nitrogen release at high heating rates ($\sim 10^5$ K/s) is relatively constant for low rank to high volatile bituminous coal (64 - 82% carbon), and then drops dramatically with increasing rank.⁴² It is also apparent that large differences in volatile nitrogen release occur with coals of the same general rank; note the differences between Illinois #6 and the Blue #1 coal (both approximately 75% C).



Figure 2.6. Nitrogen volatiles release versus rank. Coal pyrolyzed in 6 mole% O_2 with flat flame methane burner, 47 ms, 5×10^4 K/s (taken from Solomon and Fletcher¹).

Freihaut, et al.^{43, 44} pyrolyzed coal in heated grid experiments at moderate heating rates of 500 K/s. It was found that how nitrogen distributes between the volatiles and the char is a function of coal rank. The data, shown in Fig. 2.7, indicate that at moderate heating rates, low rank coals preferentially release more nitrogen as HCN, while the bituminous coals release more nitrogen in the tar. In agreement with data by Mitchell et al.⁴², Freihaut and coworkers showed that at high rank (low-volatile bituminous and higher) that a larger portion of the nitrogen remains in the char.



Figure 2.7. Distribution of nitrogen volatile release versus rank on an additive basis. Heated grid experiments 500 K/s to 1243 K, 4 s hold (taken from Freihaut, et al.⁴⁴).

The release of HCN comes from (a) ring opening reaction in the char and (b) ring opening reactions in the tar.^{45, 46} These two processes generally occur simultaneously, but after the tar is released. Therefore the presence of HCN is generally considered to be an

indicator of secondary pyrolysis in systems where hot gases surround the coal particle (such as entrained flow reactors). Secondary pyrolysis is the further break-down and reorganization of pyrolysis tars, at high temperatures and in the presence of an inert atmosphere, into lighter molecular structures and soot. Freihaut, et al.⁴⁵ used a heated grid apparatus and an entrained flow reactor to pyrolyze coal. In the experiments HCN was produced after tar release occurred and at temperatures in excess of 1100 K. It was hypothesized that at this temperature the ring structure of the tar and char started to break-down, creating HCN and indicating the start of secondary pyrolysis reactions.

Char Structure

Analysis of the chemical structure of the char is difficult because most analytical techniques need a liquid or gaseous sample at relatively low temperatures. These analysis forms include gas chromatography, mass spectroscopy and other methods. One method that has been successful in analyzing solid samples, including coal and char, is solid-state ¹³C NMR.⁴⁷ FTIR has also been used, but limited quantitative information has been obtained.³⁵

Fletcher et al.⁴⁷ studied five coals of different rank with NMR. The five coals were devolatilized and collected as a function of residence time. Pyrolysis conditions consisted of 100% nitrogen gas at temperatures of 1250 K and particle heating rates of $2x10^4$ K/s. The char samples were analyzed with the use of solid-state ¹³C NMR. It was shown that a number of the ¹³C NMR chemical structural parameters change dramatically during devolatilization.

One prominent trend observed in the NMR data for char was that the number of bridges and loops per cluster increased during pyrolysis, but that the total number of attachments per cluster remained relatively constant. This increase in bridges and loops was particularly prominent for the low rank Beulah Zap. The dramatic increase in the

lignite chars shows the very early cross-linking that is known to occur for lignites.³⁵ The other chars also showed an increase in the number of bridges and loops in comparison to the coal, indicating the extent of cross-linking that occurs in char during pyrolysis.

One of the most interesting findings was that the level of carbon aromaticity, cluster molecular weight, and aromatic carbons per cluster for the fully pyrolyzed coal chars appeared to be very similar. Even though these parameters were widely scattered for the parent coals of different rank, the char values converged to similar levels. The similarity in chemical structure for the char seems to indicate that similar chemical reactions are taking place for all the coals, and also that the chemical structure of the char may be less important during combustion than the physical structure (i.e. surface area, porosity, etc.).⁴⁷

It was also shown from the study that the carbon aromaticity increased for all the coals as a function of pyrolysis.⁴⁷ Cluster molecular weight was observed to decrease for the five coals as residence time increased (due to the release of side chains as light gas). The study also indicated that the aromatic carbons per cluster in the chars are similar to that in the parent coal. The total number of attachments per cluster (+1) either remained relatively constant or decreased slightly during devolatilization for the five coals in the study. This information together shows that the side chains are released from the aromatic clusters during pyrolysis and that reattachments by cross-linking occurs at existing side chain sites, and no growth in the aromatic cluster size occurs at devolatilization temperatures.

Another study that tried to obtain chemical structure information on coal chars used FTIR analysis.³⁵ A Beulah Zap lignite coal was pyrolyzed at heating rates of 0.5K/s, 3 K/s, and isothermal pyrolysis. Temperatures ranged from around 470 K to over 1000 K. It was shown that the chars did not change dramatically until temperatures of over 600 K were reached. The most dramatic changes occurred with the side chain and bridge structure of the coal. Significant decreases in the aliphatic nature of the coal was shown. Increases

in the aromaticity of the char structure in comparison to the coal was also apparent. These findings are in agreement with the 13 C NMR studies.^{47, 48}

Nitrogen in the Char

A limited number of chars have also been analyzed with the use of XPS in order to determine the nitrogen groups in char.^{21, 22} A number of investigators have shown that during slow pyrolysis and hydropyrolysis the quaternary form of nitrogen is almost completely lost from the coal. A quaternary nitrogens has four bonds attached to it creating a positively charged nitrogen structure. With the loss of quaternary nitrogen, a commensurate increase occurs in the pyridinic nitrogen forms.^{21, 22} This indicates that the nitrogen may be converted from the quaternary form in coal to the more stable pyridinic form in the char.

The study of the nitrogen chemical structure in char is very limited. Few good methods to specifically study the nitrogen chemical structure are available. XPS and XANES analysis are two methods that can be used, but they have only been used in a limited way and under few pyrolysis conditions. Much more research is needed to understand the chemical structure of nitrogen in the char.

Coal Tar and Volatiles Structure

Coal tar has traditionally been analyzed with the use of mass spectroscopy, gas chromatography, FTIR and ¹H NMR.⁴⁸⁻⁵¹ These methods are able to analyze the liquid tar products of pyrolysis. It is hoped that with an understanding of the chemical structure of the coal tar a more detailed concept of pyrolysis can be determined.

It has been shown with the use of mass spectroscopy and gas chromatography that molecular weights of the tar are generally found in the range of 300 to 450 amu.^{35, 43, 52} These techniques do have some weaknesses which limit the accuracy of the measurements.
It is generally agreed, however, that tar molecular weights are approximately in this range. Some investigators have shown some rank dependence on tar weight.⁴³ It is uncertain, however, if this rank dependence is an accurate phenomena or simply caused by variations in experimental methods.

Mass spectroscopy has been used to show that the tar molecular structure is dependent on the rank of the coal. Huai, et al.⁵³ showed that lower rank lignite coal tars contained high levels of phenols and other oxygen-containing molecular structures. Higher ranked coals exhibit more prominent levels of aromatic tar structures. Other studies performed by different techniques have also shown tar structural dependence as a function of coal rank.^{43, 49, 50}

A study of coal tars obtained from a number of different coals devolatilized in an entrained flow reactor showed how the tar chemical structure changes with pyrolysis temperature.^{48, 54} The coals were pyrolyzed at two different temperatures of 1050 and 1250 K, and samples collected at different pyrolysis levels. The tar analysis was done with the use of ¹H NMR.

Pugmire et al.^{48, 54} showed that the pyrolysis temperature has a profound effect on the structure of coal tars. The hydrogen aromaticity of the coal tars increases dramatically as the pyrolysis temperature increases. Carbon aromaticity was deduced from the hydrogen aromaticity. With the increase in pyrolysis temperature decreases in , and hydrogens indicate that substantial bond rupture occurs in the bridge structures of the tar. These bond ruptures in the tar are indicative of secondary tar reactions occurring at moderate temperatures (1250 K).

In summary, only a limited amount of information is available on the chemical structure of coal tars. The mass spectroscopy studies provide extreme detail on speciation, but do not give good quantitative detail with respect to particle mass. The ¹H NMR data are limited in nature to the proton structure. Elemental composition and FTIR analysis are

not very detailed with regard to quantitative analysis of chemical structure. Increased information is needed to further determine how pyrolysis releases tar structures and how the tar effects combustion processes and products.

Forms of Nitrogen in the Tar and Volatiles

When nitrogens are released in the light gases they are generally considered to be in the form of HCN and NH₃. The HCN is the most abundant nitrogen form in the light gases during pyrolysis and, depending on the experimental reactor, is both a primary and secondary nitrogen volatile product.^{39, 44-46} Secondary pyrolysis of volatile nitrogen products at high temperatures (> 1000 K) and long residence times (> 50 ms) eventually forms HCN with some NH₃.⁴⁵

Devolatilization experiments indicate that the forms of nitrogen in the volatiles is affected by heating rate and the type of reactor. Bassilakis and co-workers⁴⁶ measured high levels of NH₃, in comparison to HCN, in low heating rate TG-FTIR experiments. Others have also indicated the presence of NH₃ in experiments that used fluidized bed systems.^{23, 55} This is generally attributed to the extended contact of volatiles with char. In such a case, the volatile nitrogen may be converted to NH₃ on the char surface.^{23, 46, 50}. In comparison, NH₃ is generally not detected in entrained flow and drop tube reactors, where the volatiles from the coal are not able to maintain extended contact with the char.⁴⁶

It has been postulated that the pyrolyzed tar species of nitrogen are similar in structure to the nitrogen in the coal.³⁸ A study of coal tar, produced at low heating rates (0.5 K/s) and at a temperature of 673 K, was performed using XPS analysis techniques. The study showed that nitrogen is located in aromatic ring structures of pyrrolic and pyridinic forms.^{19, 22}

Nitrogen-specific gas chromatography (GC) has shown promise in revealing more detailed nitrogen chemistry. Nelson, et al.⁵⁰ studied three different coals and pyrolyzed

them at a high heating rate of 10⁴ K/s. The tars were studied with the use of nitrogen specific gas chromatography. It was shown that nitrogen in tar is similar in structure to the functional nitrogen groups in coal.⁵⁰ The GC method is also able to differentiate between different types of pyridinic and pyrrolic nitrogen forms. Indications from GC are that picoline, benzonitrile, quinoline, and indole types of structures are also present in the tar.⁵⁰ This makes GC useful in determining a more comprehensive concept of pyrolysis product chemistry. These GC experiments were able to help in the understanding of secondary tar reaction chemistry, but since detailed analysis of the parent coal was not available, nitrogen devolatilization chemistry was not studied.

Modeling Devolatilization

Devolatilization models have progressed, in the last couple of decades, from simple kinetic expressions that used only a couple of rate expressions to predict total volatiles release^{25, 56} to the much more complicated descriptions that take into account the macromolecular chemical structure of coal.^{28, 32, 57, 58} The three most advanced models are the CPD, the FG-DVC, and the FLASHCHAIN models.^{28, 32, 58} These three devolatilization models use a statistical network approach to describe the parent coal structure and subsequent devolatilization behavior.^{28, 32, 58} Coal is modeled as an array of aromatic clusters connected by bridges, known as labile bridges. Kinetic expressions are postulated for the rate of bridge scission, and statistical representations are used to determine the number of clusters liberated from the coal matrix as a function of the number of bridges cleaved. The vapor pressure of liberated clusters are calculated and used to determine yields of tar versus metaplast. Cross-linking reactions eventually connect the remaining metaplast to the char matrix.

Such models require knowledge of the average size of the aromatic clusters in the coal, the number of attachments (bridges and side chains) per cluster, the ratio of bridges to

side chains, and the average size of the bridges or side chains. Several reviews of these models have been published.^{1, 59} All three of these models use solid-state ¹³C NMR data to some extent to guide selection of coal-dependent input parameters to describe the coal matrix. The CPD model has demonstrated success in using solid-state ¹³C NMR data directly as the only coal-dependent structural input parameters.²⁸ One of the common assumptions in these models is that the aromatic clusters are not broken during the pyrolysis process, and hence the bridge-breaking rate largely controls the devolatilization rate. Therefore, the average number of aromatic carbons per cluster in the coal is equal to that in the char and in the tar.

These models are beginning to progress to where the volatile species are being modeled, not just the overall amount of volatiles. Nitrogen is one species that is of particular interest due to the possible pollutant problems with nitrogen oxides. In a recent paper, Niksa⁶⁰ postulated that nitrogen evolution during pyrolysis could be modeled assuming that the mass of nitrogen per aromatic cluster in the coal tar was equal to that in the parent coal and then using a coal-dependent HCN release rate from the char. The validity of this assumption is a topic for consideration in the current work.

Literature Summary

A great deal has already been learned about the coal structure and how pyrolysis occurs. The qualitative processes that occur during pyrolysis are well known; quantitative yields of char, tar and light gases have been measured for a number of conditions. Based on this body of experimental data, a number of relatively accurate models have been produced. These models use some knowledge of the chemical structure of the coal, along with information on how the coal structure breaks apart, to model pyrolysis. Even though these models have advanced a great deal in the last few years it is hoped that more accurate

methods can be produced in order to better describe the effects of coal type and to use these models in other applications, such as coal liquefaction.

Some investigators have attempted to expand on the pyrolysis models to include predictions of the evolution of nitrogen in the tar and light gases.^{32, 60, 61} At this time the scientific basis of these attempts is still questionable. Further understanding of the nitrogen chemistry in coal is needed as the power industry tries to reduce nitrogen pollution species. More detailed analysis of nitrogen in coal, char and tar is desired on matching sets of samples. By coupling the ¹³C NMR data with elemental nitrogen analysis a more complete understanding of nitrogen chemistry is possible.

To obtain more accurate models of the coal and the pyrolysis process it is necessary to obtain good information on the changing chemical structure of the coal and the pyrolysis products during devolatilization. Previous studies have used ¹³C and ¹H NMR of the char and tar structure.^{15, 48, 49, 62} Other chemical methods, such as mass spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, gas chromatography have also been used.^{19, 50, 51, 63}

The limit with many of these methods has been the inability to quantitatively analyze the chemical structure of coal, along with matching samples of char and tar produced from the same devolatilization experiment. It has been shown that ¹³C NMR is an excellent method of obtaining quantitative chemical structural data. Detailed chemical analysis of matching coal, char and tar sets has been performed with the use of ¹³C NMR for the coal and char and ¹H NMR for the tar. The ¹H NMR data are limited with regards to the available chemical structure information obtained. With the use of a new high resolution ¹³C NMR technique developed for liquid phases it is now possible to obtain ¹³C NMR data on matching sets of coal, char and tar. In this study matching samples of coal, char and tar were produced and analyzed by ¹³C NMR. It is felt that this quantitative analysis will improved understanding of the chemical pyrolysis process. In addition, elemental analysis

and limited XPS analysis were performed. The results from this study help improve the understanding of the chemical processes that occur during devolatilization with an emphasis on the nitrogen chemistry. This improved understanding will hopefully lead to better rank-dependent devolatilization models that will include accurate nitrogen evolution information.

3. Objectives and Approach

The objective of this study is to improve the understanding of coal structure and the chemical processes that occur during pyrolysis. Emphasis will be placed on the nitrogen in the coal and the pyrolysis products. This was done by performing pyrolysis experiments and collecting char and tar sets, while working with renowned chemists in the areas of NMR and XPS spectroscopy to analyze for the chemical structural features of the matching samples.

Pyrolysis experiments were performed in a drop tube furnace at low to moderate temperatures. The temperatures were kept below 1300 K to avoid excessive secondary tar reactions. The maximum heating rate in the entrained flow system was on the order of ~ 10^4 K/s, approaching heating rates expected in pulverized coal furnaces (~ 10^5 to 10^6 K/s).

Further devolatilization experiments were performed using a methane air flat-flame burner (FFB). The FFB temperatures are on the order of 1600 K and higher while the heating rate reaches 10⁵ K/s, allowing data comparisons to the lower temperatures and heating rates of the drop tube furnace. All experiments in the drop tube furnace and the FFB were performed at atmospheric pressures.

Six coals that span a range of rank, from lignite to low-volatile bituminous, were pyrolyzed in both the FFB and the drop tube reactor. The coals were pyrolyzed at a number of different conditions to provide matching sets of char and tar that were pyrolyzed to different degrees. Analysis is performed that provides a comparison of data as a function of both rank and degree of pyrolysis.

4. Description of Experiments

Two different reactors were used to pyrolyze the coal particles, a drop tube entrained flow system known as the High Pressure Controlled-Profile drop tube furnace and a methane-air flat flame burner. The different reactors allowed for the pyrolysis of samples at different temperatures, particle heating rates and extents of devolatilization. A description of the experimental equipment, chemical analysis techniques, and experimental procedure is found below.

Apparatus

High Pressure Controlled-Profile (HPCP) Drop Tube Furnace

The High Pressure Controlled-Profile (HPCP) drop tube reactor^{64, 65} was designed specifically to determine rates and kinetics for pyrolysis and oxidation of solid fuels at both atmospheric and high pressure. It is a laminar flow furnace with a computer-controlled wall temperature profile to create controlled profile conditions for reactivity tests. Solid and gaseous products are separated aerodynamically and collected for analysis.

A schematic diagram of the HPCP system is shown in Fig. 4.1. Particles are fed with the primary gas through a water-cooled injector, which is moveable in order to vary particle residence times. The secondary gas flows into a preheater prior to entering the reactor. Wall heaters maintain an isothermal temperature profile. Four optical access windows are located near the bottom of the reactor. The collection probe collects the entire mass flow and quenches the particle reaction just below the optical access windows.



Figure 4.1. Schematic of the High Pressure Controlled Profile (HPCP) drop tube reactor⁶⁴.

The collection probe is water-cooled with gas quench jets in the probe tip. A permeable liner inside the main probe tube allows quench gas to be injected radially along the length of the probe to reduce particle and tar deposition inside the probe. A virtual impactor follows in-line with the collection probe to aerodynamically separate the gases from the heavier particles. A cyclone follows the virtual impactor to further separate the aerosols from the heavier char particles. The char particles are captured in the cyclone and the tars are collected on polycarbonate filters that are located after the virtual impactor and the cyclone (see Fig 4.3 for a flow diagram). The tar is scraped from the filters rather than removed using a solvent. The light gases pass through the filters and are saved for analysis or vented from the system. Detailed design information is found elsewhere.⁶⁶



Figure 4.2. Flow diagram of the HPCP collection system.⁶⁶

This reactor has been used for (a) char oxidation research as a function of pressure for both small particles (~50 μ m diameter)^{64, 65} and large particles (~5 mm diameter);⁶⁷ and (b) devolatilization experiments at atmospheric pressure as a function of coal type, heating rate, and oxidation environment.^{68, 69}

It was found that the filters system for the tar was originally placed too far from the reactor exit. This allowed for the tar to cool and deposit on the tube walls, creating substantial tar losses (> 80%). The filter system was redesigned to correct this problem. The full explanation can be found in Appendix D. After the redesign was implemented, an analysis was performed to determine the amount of tar deposition on the inner walls of the collection system (i.e., the virtual impactor, cyclone, and associated tubing, but not in the collection probe). For a set of pyrolysis experiments, the tar was scraped from the collection system and weighed. The deposition per unit surface area was obtained and applied to surfaces where it was impossible to scrape, such as in some of the tubing. Based on this analysis, the mass of tar collected is corrected by 20% to account for deposition on the walls of the collection system. This is similar to the correction factors of ~10% used by Chen⁷⁰ and 15% used by Ma^{71, 72} in similar experiments.

Methane Flat Flame Burner System (FFB)

A schematic of the flat-flame flow reactor system is shown in Fig. 4.3. It consists of a Hencken flat flame burner, similar to that used at Sandia,^{42, 73} and several designs of towers to confine the flame. The air, methane and hydrogen burn to provide a high-temperature flame environment for coal pyrolysis. The outlet of the burner is a 2" by 2" square. The flow rates of air, methane and hydrogen are adjusted to obtain a horizontally uniform flame. The velocity of the hot gas above the burner is approximately 2 m/s (i.e., laminar flow). The coal particles are fed into the burner by a syringe particle feeder, driven



Figure 4.3. Schematic of the methane-air flat flame burner (FFB).

by a stepping motor. The pulse signal used for driving the stepping motor is generated by a computer. The feed rate of coal particles can be adjusted by changing the frequency of the pulse signal (i.e., the stepping rate of the motor). The coal particles are entrained by a stream of carrier nitrogen gas. The hot combustion products from the methane/hydrogen/ air flame heat the coal particles which are injected along the centerline of the laminar flow reactor. The flat flame can be operated under either fuel-rich or fuel-lean conditions so that the post-flame gases provide a reducing or oxidizing atmosphere for coal devolatilization and/or oxidation. Fuel-rich conditions with no post-flame oxygen were used in these experiments. The flame temperature can be adjusted by changing the flow rates of inert gas, fuel and oxidizer. Flame temperatures along the height of the tower are measured in the absence of particles using a fine-wire silica-coated type B thermocouple, and then

correcting the thermocouple reading for radiation heat loss. The particle feed rate used is ~ 1 g/hr., which is small enough to achieve single particle behavior.

The FFB is equipped with a water-cooled, gas-quench probe with porous liner for reduced deposition, and the probe is followed by a virtual impactor, cyclone, and filter system patterned after the collection system described above in the HPCP. The FFB experiments performed in this research provide char and soot samples from a high temperature, high heating rate environment, with products of hydrocarbon combustion present. The FFB environment is closer to industrial combustor environments than conventional drop tube furnaces, due to higher particle heating rates, temperatures and gas composition. The FFB experiments give data regarding complete devolatilization, while the HPCP experiments can be used to study the intermediate char and tar products of devolatilization.

Chemical Analysis Techniques

A number of analysis techniques were used to study the char and tar samples that were produced in this study. A full explanation of the different methods are found below.

Proximate and Ultimate Analysis

Proximate analysis was performed on the coal and char samples following ASTM standard procedures. Proximate analysis is the term used when the amount of moisture and non-combustible material (i.e. ash) in the samples is measured. The analysis is carried out by using an oven that dries and then burns the sample down to the ash. Samples are weighed at the appropriate intervals to determine the ash and moisture content.

Elemental (i.e. ultimate analysis) was performed for the samples of coal, char, and tar. Carbon, hydrogen, and nitrogen contents were determined using different laboratories. A number of samples were tested at BYU with the use of a LECO 800 analyzer. The

analyzer was calibrated with several standard compounds with known compositions. A high-precision balance with a 0.01 mg readability was used to determine sample mass. Other samples were sent for independent analysis to LECO (St. Joseph, MI) and Huffman Laboratories (Golden, CO). Since this is a fairly routine analysis technique the data from all three laboratories were similar, usually within 1%.

ICP Analysis

Inductively coupled plasma (ICP) atomic emission spectroscopy was used to determine the mass fraction of Titanium (Ti) in the parent coal and char samples. The ICP analysis was performed at the BYU chemistry department with the use of a Perkin Elmer Plasma 2 ICP machine. Titanium was then used as a tracer to determine the extent of mass release due to devolatilization. Assuming no Ti loss in the pyrolysis and ashing processes, the mass fractions of Ti in parent dry coal (f_{Ti}^{coal}) , in dry char (f_{Ti}^{char}) and in ash (f_{Ti}^{ash}) are related to the masses of the coal (m_{coal}) , char (m_{char}) and ash (m_{ash}) by:

$$m_{coal} f_{Ti}^{coal} = m_{char} f_{Ti}^{char} = m_{ash} f_{Ti}^{ash}$$

$$\tag{4.1}$$

The percentage mass release or total volatile yield Y_{vol} (on dry ash free basis) during pyrolysis can then be calculated:

$$Y_{vol} = \frac{m_{coal} - m_{char}}{m_{coal} - m_{ash}} = \frac{m_{coal} - \frac{f_{Ti}^{coal}}{f_{Ti}^{coal}}}{m_{coal} - \frac{f_{Ti}^{coal}}{f_{Ti}^{ash}} m_{coal}} = \frac{f_{Ti}^{char} - f_{Ti}^{coal}}{f_{Ti}^{ash} - f_{Ti}^{coal}} - \frac{f_{Ti}^{ash}}{f_{Ti}^{ash}}$$
(4.2)

The mass release determined from the Ti-tracer technique is compared to the ash tracer technique (from proximate analysis) and to the mass balance (mass of coal fed to the reactor compared with the mass of char collected). In most cases the mass balance and the Ti-tracer technique gave results within a 5% difference. It has been shown that at high

temperatures, ash and even Ti can volatilize, giving incorrect mass loss values.⁷⁴ In the case of the experiments performed for this study, the temperatures are not high enough to be affected by Ti volatilization to any significant degree.

NMR Analyses

Standard solid-state ¹³C NMR spectroscopic techniques were employed to examine the coal and the partially-devolatilized char. Cross-polarization (CP), magic angle spinning (MAS), and dipolar decoupling techniques permit direct measurement of the number and diversity of aromatic and nonaromatic carbons present in the sample. It has been shown that carbon aromaticities obtained from this technique compare favorably with carbon aromaticities obtained from the Bloch decay experiments.⁷⁵

A newly developed high resolution ¹³C NMR technique¹⁴ was used to analyze the tar products of devolatilization. This technique uses spin-lattice relaxation to differentiate protonated from nonprotonated carbons in liquids, based on relaxation differences arising from direct CH dipolar interactions. Once the ratio of protonated to nonprotonated carbons is determined, many of the structural features can be calculated by comparing the data to numerous model compounds. Comparison studies have been performed on model compounds between the liquid NMR and the solid-state NMR methods.¹⁴ It was found that both methods resulted in the same quantitative information regarding the carbon skeletal structure.

Tar samples were dissolved in deuterated methylene chloride (CD_2Cl_2) and then filtered. A significant amount of insoluble residue was obtained for each tar. This tar residue was subsequently analyzed using the same solid-state ¹³C NMR technique as that used for coal char, while the dissolved tar was analyzed with liquid ¹³C NMR.

XPS Analyses

X-Ray Photoelectron Spectroscopy (XPS) is a surface spectroscopic technique that can provide broad groupings of the forms of nitrogen and oxygen in coals. High resolution is required to separate noise from actual spectra. This high resolution requires that the sample be very pure. Through our ACERC interaction with Dr. Simon Kelemen at Exxon, several samples of partially and fully-devolatilized char and tar samples were analyzed. XPS curves are resolved based on XPS data from model compounds. This method has shown excellent reproducibility in the ability to resolve the spectroscopy curves.^{19, 22}

Experimental Procedure

Experimental Variables

In order to study how pyrolysis effects the chemical structure of coal and tar as a function of rank and degree of pyrolysis, coals were pyrolyzed in either the HPCP and/or FFB. Five coals were obtained from the suite of coals selected by the DOE Pittsburgh Energy Technology Center's Direct Utilization/AR&TD (PETC) program, and one coal was obtained from the Argonne National Laboratory Premium Coal Sample Bank. Properties of these six coals are located in Table 4.1.

Coal	PSOC #	Rank	%C(daf)	%H(daf)	%N(daf)	%Ash(mf)
Beulah Zap	1507 D	ligA	69.99	5.59	1.17	15.31
Wyodak	Argonne	subC	75.01	5.35	1.12	8.77
Blue #1	1445 D	hvCb	77.29	5.69	1.27	3.62
Illinois #6	1493 D	hvCb	76.65	4.93	1.47	15.13
Pittsburgh #8	1451 D	hvAb	84.70	5.40	1.71	4.11
Pocahontas #3	1508 D	lvb	90.52	4.60	1.60	11.65

Table 4.1Experimental Coals and Properties

The five PETC coals were crushed and aerodynamically classified to the 63 - 75 μ m size range. The Argonne Premium Wyodak Anderson coal was received with a wide size distribution. A theoretical analysis was performed with the use of the CPD devolatilization model to determine how different size fractions would heat up and pyrolyze in an entrained-flow reactor. This analysis indicated that the larger fractions, above approximately 75 μ m, would devolatilize differently than the size fraction below the 75 μ m level. Due to this the coal was sieved to eliminate the larger size fractions above 75 μ m.

These six coals were chosen for a number of reasons: 1)All six coals have been well characterized and studied by numerous other researchers; 2) the coals span a range of rank; 3) each exhibits different pyrolysis evolution characteristics with respect to total volatiles released and the amount of total nitrogen evolution; and 4) all six coals are commonly used in industry.

The six coals were pyrolyzed in both the HPCP and FFB under a range of different gas temperatures and residence times in order to obtain different degrees of devolatilization. The coals were pyrolyzed in the HPCP using pure nitrogen as the flow gas. The maximum particle heating rates in the furnace are on the order of 10^4 K/s. Pyrolysis conditions in the FFB consisted of operating the burner using excess methane fuel to eliminate all oxygen from the pyrolysis zone. The maximum particle heating rates in the FFB are on the order of 10^5 K/s. The general conditions for the experiments performed on the five PETC coals are given in Table 4.2. Experimental conditions for the Wyodak coal are listed in Table 4.3.

Temperature Profiles

It is important to know the in-situ temperature of HPCP and the FFB during the experiments. With the in-situ temperature, also refered to as the gas temperature, known

calculations can be performed to determine the temperature of the coal particles as they traverse the length of the HPCP or FFB.

Equipment	Maximum Gas Temp. (K)	Residence Time(ms)	Gas Atmosphere
HPCP	850	140	N2
HPCP	900	160	N2
HPCP	1050	210	N2
НРСР	1220	230	N2
FFB	1650	15	0% O ₂

Table 4.2Experimental Conditions for the Five PETC Coals

Table 4.3
e (1)

]	Expei	rime	ntal	Cond	litior	ns for t	he Arg	gonne	Premiu	$\mathbf{m} \mathbf{W}_{1}$	yodak	Coal
	1					0		5			2	

Equipment	Maximum Gas Temp. (K)	Residence Time(ms)	Gas Atmosphere
HPCP	850	110	N2
HPCP	900	130	N2
HPCP	920	110	N2
FFB	1650	15	0% O ₂
FFB	1650	30	0% O ₂

The centerline gas temperature of the HPCP was measured by inserting a very small type S microbead thermocouple (76.2 μ m diameter bead) into the bottom of the furnace and aligning the bead to the center of the furnace muffle tube. The thermocouple was raised into the reactor, and temperature measurements were taken along the centerline of the reactor as a function of distance. The measurements are taken with the appropriate furnace wall temperatures and gas flows that correspond to the known experimental conditions.

Since the readings were actually the temperature of the thermocouple bead T_b , the thermocouple temperature measurements were corrected for radiation effects to obtain the correct gas temperatures T_g . The emissivity for the type S thermocouple ε was assumed to be 0.13.⁷⁶ The temperature of the walls T_s was taken from measurements in the HPCP. The energy balance between convective and radiative heat interactions can be expressed as

$$h\left(T_{g}-T_{b}\right)=\varepsilon\sigma\left(T_{b}^{4}-T_{s}^{4}\right)$$

$$(4.3)$$

where σ is the Stefan-Boltzmann constant and *h* is the convective heat transfer coefficient, which is related to the Nusselt number (Nu). The Nusselt number was correlated with the use of the following equation:

$$Nu = 2.0 + 0.60 \frac{D_p v \rho_g}{\mu_g} \frac{1/2}{k} \frac{C_p \mu}{k} \frac{1/3}{g}$$
(4.4)

Combining the equations and solving for T_g gives the following:

$$T_g = T_b + \frac{\varepsilon \sigma D_b \left(T_b^4 - T_s^4 \right)}{N u \, k_g} \tag{4.5}$$

Figure 4.4 shows the centerline gas temperature profiles in the HPCP for the four experimental conditions at which the Pittsburgh #8 coal was pyrolyzed. The graph labels are the approximate maximum gas temperatures of the four experiments. Future references to these experimental conditions will be by the approximate maximum gas temperatures and the appropriate coal. The gas temperature profiles for the experimental conditions at which the other four PETC coals were pyrolyzed are found in Appendix A. These temperature profiles are similar to those for the Pittsburgh #8 coal. Three experiments were performed on the Argonne Premium Wyodak coal in the HPCP; the three temperature profiles are shown in Fig. 4.5.

Large gas temperature gradients are observed near the injection point (distance = 0). This is due to the water-cooled injection probe and the cold nitrogen gas that is used as the entrainment gas for the coal particles. It should also be noted that the temperature profiles of the 1050 K and the 1220 K experiments dip slightly near the reactor exit. The cooling near the exit is caused by the water-cooled collection probe and the quartz windows in the HPCP. The low flow rates of the hot gases that are peculiar to these two experimental



Figure 4.4. Gas Temperature profiles for the experiments performed on Pittsburgh #8 coal.



Figure 4.5. Gas Temperature profiles for the experiments performed on the Argonne Premium Wyodak coal.

conditions increase the cooling effects compared to the higher gas flows used for the 850 K and the 900 K experiments.

Experimental conditions in the FFB are somewhat different than those in the HPCP. The flame conditions in the FFB were analyzed by Ma.⁷² The five PETC coals were all pyrolyzed at the same condition. The Argonne Wyodak coal was pyrolyzed in the FFB at two conditions: one condition that corresponds to the condition at which the five PETC coals were pyrolyzed and one additional condition. The maximum centerline gas temperature for all the experiments in the FFB was 1640K. The centerline gas temperature profile for the FFB experiments is shown in Fig. 4.6. It is noted that the temperature decreases slightly near the burner, due to a small amount of ambient temperature nitrogen gas used to carry the coal particles to be injected into the flame.



Figure 4.6. Gas temperature measurements for the experiments performed on the five PETC coals and the Wyodak Anderson coal in the FFB.

Pyrolysis was stopped by rapidly quenching the pyrolysis products with cold nitrogen gas at the tip of the collection probe. The five PETC coals and the Wyodak coal were all quenched at a distance of 2.5 cm above the burner, corresponding to a residence time of 15 ms. The Wyodak coal was pyrolyzed at an additional distance of 3.8 cm (residence time of 30 ms).

Residence Times and Heating Rate

Since it is known that many factors in devolatilization are dependent on the time that the coal spends in the reaction zone of the furnace, accurate particle residence time calculations are needed for each of the experimental conditions. The heat and mass transfer code FLUENT 4.31⁷⁷ was used to model temperature and flow characteristics of the HPCP. The temperature predictions of the FLUENT model were compared to actual temperature profiles. In most cases the temperatures differences were less than 50 K. However, in a few cases the differences did reach close to 150 K due to the difficulty in specifying boundary conditions.

Since gas velocity is a strong function of the gas temperature, corrections were made to the calculated velocities to account for the temperature differences. This was done by first assuming the mass flow rate is constant. If such is the case then Eq. 4.6 is valid:

$$\rho_1 A v_1 = \rho_2 A v_2 \tag{4.6}$$

By assuming that the ideal gas law applies, and that the areas are equal for condition 1 and condition 2, Eq. 4.6 can be modified to:

$$v_2 = \frac{T_2}{T_1} v_1 \tag{4.7}$$

In this manner the predicted gas velocities (v_1) from the FLUENT models were corrected to account for the differences between the experimental temperature profiles and the predicted

FLUENT gas temperatures. A more detailed explanation can be found in Appendix B. This produced a gas velocity profile for the HPCP.

With the gas velocity profile, and assuming the coal particle is a sphere with a diameter D_p and density ρ_p , the drag force acting on the particle is

$$F_{k} = \frac{\pi D_{p}^{2}}{4} \quad \frac{1}{2} \rho_{g} v^{2} \quad \frac{24}{\text{Re}}$$
$$= \frac{\pi D_{p}^{2}}{4} \quad \frac{1}{2} \rho_{g} v^{2} \quad \frac{24\mu_{g}}{D_{p} v \rho_{g}}$$
$$= 3\pi \mu_{g} D_{p} v \qquad (4.8)$$

where μ_g , ρ_g , and v are gas viscosity, gas density, and slip velocity between the particle and entraining gas, respectively. The force of gravity on the particle is

$$F_g = \frac{\pi}{6} D_p^3 \left(\rho_p - \rho_g \right) g \tag{4.9}$$

The momentum equation can then be expressed as:

$$m\frac{dv}{dt} = F_k - F_g \tag{4.10}$$

Equation 4.10 can then be solved using a finite differencing method.

The heating rate and particle temperature were modeled in the HPCP using a singleparticle transient mass and energy balance.⁷⁸ The energy conservation equation used to describe the particle temperature history is as follows:

$$m_p C_p \frac{dT_p}{dt} = h A_p (T_g - T_p) \frac{B}{e^B - 1} - \sigma \varepsilon_p A_p (T_p^4 - T_s^4) - \frac{dm_p}{dt} H \quad (4.11)$$

The equation represents the convective heat transfer from the surrounding gas, radiative heat transfer, and the global heat of reaction of devolatilization. The convective term is corrected for high mass transfer with a blowing parameter that is modeled as:⁷⁹

$$B = \frac{C_{p_g}}{2\pi D_p k_g} \frac{-dm_p}{dt}$$
(4.12)

The Chemical Percolation Devolatilization (CPD) model was used to model the devolatilization rate for the energy conservation equation. Since the CPD model needs the particle velocity as an input parameter and due to the fact that the CPD and energy conservation equations are interdependent, the above momentum and energy equations were used in conjunction with the CPD code to provide the necessary temperature history and residence times. The NMR parameters needed for the CPD model were obtained from the literature.^{12, 15, 78} The data from the literature generally corresponded directly to coals that were used in this study.

Figure 4.7 shows the particle temperature histories for the experiments performed on the Pittsburgh #8 coal; the particle temperature histories for the other four PETC coals and experiments are similar and can be found in Appendix C. The experiments performed on the Wyodak coal were slightly different as shown by the temperature histories in Fig. 4.8.

The particle temperatures are very low for the first 5 to 10 ms. This is due to the cold injection gas and the initial heating of the particle which causes the moisture in the coal to vaporize, maintaining a low particle temperature. Only when the water is fully vaporized does the temperature of the particle begin to increase dramatically.

Residence times in the FFB were calculated in a slightly different manner. The FFB allows for optical access to the reaction zone. Using a high speed camera, particle velocities were calculated by comparing times between camera exposures and the distance traveled by a single coal particle. A full description of the determination of particle residence time in the FFB is found elsewhere.⁷²



Figure 4.7. Particle temperature history and particle heating rate for Pittsburgh #8 coal in the HPCP. Graph (a) is the 850 K condition, (b) 900 K, (c) 1050 K and (d) 1220 K.



Figure 4.8. Particle temperature history and particle heating rate for the Argonne Wyodak coal in the HPCP.

Reliability of the HPCP

The errors involved in the experiment are important in order to determine the ability of the experimental method and equipment to produce reliable results. To test the reproducibility of the experiments performed in the HPCP a number of experiments were performed three times. After each experiment, the percent mass release of the parent coal was calculated by comparing the collected char weight to the original weight of the coal. If large differences occurred in the mass balance data then inconsistencies would be present in the equipment or the experimental method.

Reliability experiments were performed on four of the research coals in this study. Each of the experiments was repeated three times, and mass release data based on a mass balance were compared. One of the three experimental samples was analyzed with the ICP, and the mass release was calculated by the titanium tracer method. This allowed for a comparison of ICP data with the mass balance data. Table 4.4 shows conditions for each of the experiments. The mass release data are found in Table 4.5.

It is noted from Table 4.5 that the experimental mass release values are fairly consistent, the average and the standard deviation are also shown for the three experimental runs at each condition. The last row in Table 4.5 is the data obtained by the use of the ICP using the titanium tracer method. The ICP analysis was performed on the sample from the third experiment at each condition and can be compared directly this value. It can be seen that most of the experiments show consistent behavior with only a few deviations.

One factor that greatly affects reproducibility is the gas temperature. The HPCP is prone to periodic down-times due to fractures of the ceramic liners and breaking of the Kanthal heating elements. It was found early on that measured gas temperatures showed inconsistent behavior in the HPCP before and after these down times. During a single operational period the HPCP temperature profiles were relatively consistent. It was only after a non-operational period that slightly different gas temperature profiles were observed

for the same heater and gas settings. To minimize the effects of changing furnace conditions, gas temperature profiles were measured before sampling experiments were performed at each temperature condition and after each non-operational period.

 Table 4.4

 Experimental Conditions for Reliability Analysis

Experiment	Α	В	С	D	Ē	F	G
Coal	Blue #1	Blue #1	Ill #6	Ill #6	Pitt #8	Poc #3	Poc #3
Max Particle T.(K)	920	920	920	920	920	920	940
Residence Time(ms)	140	320	140	320	320	140	310

Table 4.5 Comparison of Mass Release Values

Comparison of Links Release (undes										
Experiment	Α	B	С	D	Ε	F	G			
%M. R.	12.1	25.7	6.8	35.5	45.3	9.2	21.7			
%M. R.	12.1	26.9	5.7	35.7	42.8	9.0	24.5			
%M. R.	12.5*	28.0*	11.0*	34.6*	48.2*	6.5*	24.9*			
Average	12.2	26.9	7.9	35.3	45.4	8.2	23.7			
σ	0.2	1.2	2.9	0.6	2.7	1.5	1.7			
%M.R.(Ti)	17.6*	29.0*	8.9*	30.8*	42.4*	6.5*	20.6*			

* corresponding samples

5. Experimental Results

Ultimate and Proximate Analysis Results

All chars were analyzed for carbon, hydrogen, and nitrogen content, as shown in Table 5.1 for the chars from the five PETC coals and the Argonne Wyodak coal. This table also lists the percent mass release on a dry ash-free basis and the tar yield. The "FFB" in the table indicates the experiments performed on the flat flame burner with the listed coal. The tar release was not measured in the flat flame burner experiments since secondary reactions are known to be present and the tar reacts to soot and light gases.⁷²

As expected, the amount of carbon in the char increases as the total mass release increases. The more unstable bonds tend to be the aliphatic carbon bonds and heteroatoms, which are rich in hydrogen and oxygen. These aliphatic compounds are released to a much higher degree than the more stable aromatic carbon structures. The fact that the char becomes more concentrated in carbon and less concentrated in hydrogen is consistent with this trend. The nitrogen, for most of the coals, appears to increase in the char as the mass release increases. It is not certain if this is an actual trend or simply scatter in the data. The amount of nitrogen in the samples is small which could create large errors in the values on a percentage basis.

The amount of tar that is released exhibits a maximum in most of the coals at the 1050 K temperature condition. At the 1220 K temperature a slight drop in the tar is noted. This drop is likely due to secondary reactions that take place at higher temperatures. The secondary reactions break apart some of the tar structures to smaller groups that then exit the reactor as light gases and smaller structural units. It should also be noted that the total

Table 5.1

Ultimate Analysis Data of the Chars from the Five PETC Coals and the Argonne Wyodak Coal, the Percent Mass Release (%M.R. of daf coal), and the Tar Yield (% of daf coal) During Pyrolysis

the	I al I l		or uur co	Jul) Dul	<u> </u>	01,515	
	Temp (K)	Time (ms)	%C (daf)	%H (daf)	%N (daf)	%M.R.	%Tar
Beulah Zap	850	140	73.79	4.35	0.92	23.01	1.13
^	900	160	76.34	3.62	1.29	38.18	4.43
	1050	210	80.89	3.01	1.49	44.75	3.31
	1220	230	92.94	2.27	1.50	54.73	1.53
FFB	1650	15	85.95	1.91	1.33	53.20	n/a
Wyodak	850	110	75.34	4.78	1.34	17.92	n/a
	900	130	76.86	4.34	1.49	26.15	n/a
	920	110	76.70	4.74	1.23	31.67	n/a
FFB	1650	15	80.18	3.85	1.61	49.05	n/a
FFB	1650	30	78.89	3.77	1.36	58.84	n/a
Blue #1	850	140	78.98	5.05	1.44	17.68	2.94
	900	160	79.30	4.83	1.28	23.16	8.41
	1050	210	83.80	3.24	1.83	47.06	15.79
	1220	230	90.09	2.96	1.78	53.85	10.76
FFB	1650	15	91.79	1.71	1.48	59.30	n/a
Illinois #6	850	140	76.77	4.67	1.90	8.95	1.86
	900	160	77.21	4.39	1.56	37.50	9.81
	1050	210	82.16	3.26	1.93	45.51	20.71
	1220	230	93.72	2.63	2.00	53.83	16.22
FFB	1650	15	88.39	1.54	1.62	58.86	n/a
Pittsburgh #8	850	140	84.93	5.43	1.25	21.50	3.09
	900	160	83.73	3.90	1.86	45.90	26.08
	1050	210	88.11	3.32	1.91	45.03	28.36
	1220	230	91.36	2.51	2.06	49.23	21.12
FFB	1650	15	92.44	1.55	1.69	53.80	n/a
Pocahontas #3	850	140	93.46	4.38	1.14	6.60	1.61
	900	160	89.89	4.25	1.13	11.84	2.42
	1050	210	90.16	3.35	1.18	12.96	11.62
	1220	230	95.38	2.77	1.49	16.59	9.54
FFB	1650	15	94.95	1.45	1.12	22.52	n/a

amount of tar that is released is also a function of coal rank. Only a very low amount of tar is produced from the Beulah Zap lignite, while as the rank goes up the amount of tar increases to a maximum with the Pittsburgh #8 high volatile bituminous coal. The higher ranked Pocahontas #3 low volatile bituminous coal shows a drop in tar release compared to the high volatile bituminous coal. The volatiles and tar release as a function of rank for the five coals in this study pyrolyzed at the 1220 K temperature condition, shown in Fig. 5.1 is similar to that shown previously in Fig. 2.4. This indicates that the tar and volatile release data follow the same trends shown in the literature. For the Wyodak coal experiments the amount of tar sample collected was minimal; this caused the reliability of the tar yield from the Wyodak to be suspect. For this reason the percent tar is not reported for the Wyodak coal.



Figure 5.1. Percent of total volatiles and tar volatiles as a function of rank. Lines were placed in graph for emphasis of trends only.

The tar samples for each of the experiments in Table 5.1 were also analyzed for percent carbon, hydrogen and nitrogen, as shown in Table 5.2. Some of the samples were

not tested due to the limited amount of sample, or if tested the accuracy of certain values are questionable. Since the FFB does not produce tar the soot has been analyzed.

	Temp(K)	%C(daf)	%H(daf)	%N(daf)	%M.R.
Beulah Zap	850	70.40	8.17	0.4*	23.01
	900	76.29	6.95	0.94	38.18
	1050	73.61	5.02	1.23	44.75
	1220	76.38	3.81	1.04	54.73
FFB**	1650	85.13	2.82	0.9*	53.20
Blue #1	850	77.93	7.62	0.9*	17.68
	900	79.07	7.07	1.22	23.16
	1050	80.49	4.98	1.74	47.06
	1220	90.57	4.22	1.72	53.85
FFB**	1650	95.78	2.07	0.37	59.30
Illinois #6	850	68.54	5.35	1.38	8.95
	900	79.36	5.66	1.27	37.50
	1050	81.645	4.92	1.77	45.51
	1220	88.98	4.14	1.78	53.83
FFB**	1650	95.34	1.34	0.47	58.86
Pittsburgh #8	850	82.50	6.13	1.50	21.50
	900	86.61	5.48	2.12	45.90
	1050	85.46	4.95	1.94	45.03
	1220	90.53	3.95	1.94	49.23
FFB**	1650	95.56	1.39	0.45	53.80
Pocahontas #3	850	74*	7*	0.4*	6.60
	900	80.63	4.97	1.05	11.84
	1050	89.98	4.90	1.25	12.96
	1220	92.25	4.30	1.24	16.59
FFB**	1650	96.11	1.09	0.45	22.52

Table 5.2 Ultimate Analysis Data of the Tars from the Five PETC Coals

* Due to the limited size of the sample the accuracy of the value is very questionable. ** The "tar" samples collected in the FFB experiments were actually soot.

The amount of carbon in the tar tends to increase (with some minor discrepancies) as the total mass release increases. The hydrogen content in the tar tends to follow the

trends in the char and decreases as mass release increases. As with the char the more unstable bonds in the tar tend to be the aliphatic carbon bonds and heteroatoms, which are rich in hydrogen and oxygen. These aliphatic compounds and heteroatom structures detach from the tar structure at higher temperatures and residence times to be released as light gases. The fact that the tar becomes more concentrated in carbon and less concentrated in hydrogen is consistent with this trend.

The nitrogen appeared to reach a maximum in at the 1050 or 1220 K condition and then decreased dramatically in the soot. The higher temperatures of the FFB appeared to break the heteroatom structures containing nitrogen, causing the loss of nitrogen as a secondary pyrolysis product. At the higher temperatures of the FFB the nitrogen would be released from the tar and soot structure as HCN, and possibly NH₃.

The elemental analysis data for the coal tars presented in Table 5.2 are compared to data from Freihaut, et al.⁸⁰ and Chen⁷⁰ in Fig. 5.2 and 5.3. Due to the presence of secondary tar reactions the data presented in the figures, from this thesis, does not include the FFB values or the values from the 1220 K condition in the HPCP. Freihaut and coworkers devolatilized coal in an entrained flow reactor at different gas temperatures and residence times. Chen used a radiant entrained flow reactor to devolatilize a number of coals at different temperatures. The experimental conditions used by both Freihaut and coworkers, and Chen were designed to minimize secondary tar reactions. The data from these investigators is in Appendix F.

Figure 5.2 shows hydrogen to carbon ratios (mass basis) in the tar plotted as a function of carbon in the parent coal. The trend appears to show a slight decrease as a function of rank, while the values are within the bounds of the literature data. The data in Fig. 5.3 shows that for the mass percent of nitrogen in the tar, a maximum is present at approximately 85% carbon in the parent coal. The data from this thesis follows the trend in the literature.



Figure 5.2: Ratio of hydrogen to carbon in the tar as a function of carbon in the parent coal. The marker is the average of the data and the error bars shows the maximum and minimum values of the data.



Figure 5.3: Mass of nitrogen in the tar as a function of carbon in the parent coal. The marker is the average of the data and the error bars shows the maximum and minimum values of the data.

XPS Analysis of Wyodak Samples

High resolution XPS is required for nitrogen analysis in coals because of the low nitrogen content (1-2%). XPS analysis was performed on the Wyodak chars by Dr. Simon Kelemen at Exxon Research on one of the highest resolution instruments available. XPS only has the ability to determine general structural nitrogens forms and is known to have limitations on accuracy. However, the technique was used since the method is one of the few currently available that can independently determine nitrogen structure.

This is the first known study where high temperature, high heating rate chars have been analyzed with the use of high resolution XPS in order to determine how the nitrogen functionalities change as a function of devolatilization. As noted in Fig. 5.4, for the Wyodak chars, the forms of nitrogen found by XPS do not change much as a function of mass release. The only changes observed as a function of mass release are that the pyridinic forms of nitrogen increase slightly while the quaternary forms decrease slightly. It has been suggested²² that a portion of the quaternary nitrogens are protonated pyridinic groups. As pyrolysis proceeds, it is possible that the hydrogen is scavenged from the protonated pyridinic nitrogens leaving a pyridinic nitrogen form. This reaction would increase pyridinic nitrogen and decrease quaternary nitrogen, as analyzed by XPS.

It is interesting to note that quaternary forms of nitrogen are present in all of the chars. Some forms of quaternary nitrogen must be relatively stable, since pyrolysis conditions for these samples were relatively harsh. As such, the quaternary nitrogen may not be only protonated pyridines, but other forms as well. If the quaternary nitrogen were only protonated pyridines, the protons would have been easily scavenged by other molecular groups at the high heating rate and temperature conditions of the FFB experiments, and only limited amounts of quaternary nitrogen groups would be left in the char with 60% mass release.



Figure 5.4. Forms of nitrogen determined in Wyodak chars as a function of mass release using XPS.

In XPS studies that pyrolyzed coal at slow heating rates (~0.5 °C/sec) and low temperatures (400 °C) it was reported that the quaternary forms of nitrogen were almost completely eliminated.^{19, 22} This result is in contrast to this study, where a significant amount of quaternary nitrogen is still present at comparable mass release levels. It is postulated that the differences in the residence times and heating rate may influence the quaternary nitrogen; further experiments are needed to verify this hypothesis.

Oxygen analysis was also performed on the Wyodak char samples using XPS (see Fig. 5.5), it shows that oxygen is lost preferentially at the beginning of pyrolysis and then is released at the same rate as total mass is released. It is possible that the oxygen chemistry is somehow coupled to the nitrogen volatile chemistry in some form. Oxygen has a strong affinity for hydrogen, and pyrolysis products could include species such as

H₂O and phenols. Further investigation of the solid phase chemistry is necessary before any such speculated mechanisms can be verified.



Figure 5.5. Percent organic oxygen present in the Wyodak chars as a function of mass release.

As discussed earlier in Section 2, nitrogen release during pyrolysis is known to be a strong function of coal rank. The fact that XPS is only able to determine the general nitrogen chemical forms limits the ability of XPS to indicate reasons for the variability of nitrogen release. It was hoped that the data presented here on partially-devolatilized chars would indicate reasons for nitrogen losses to the tar and light gases. The limited changes in nitrogen groups as a function of mass release imply that mechanisms that are not indicated by XPS are involved in nitrogen loss. Therefore, other techniques will have to be used to give a more insightful picture of the coal chemistry that occurs during pyrolysis.
¹³C NMR Analysis

The char and tar samples of the three PETC coals (Pittsburgh #8, Illinois #6, and Blue #1) pyrolyzed in the HPCP at 900 K temperature and 160 ms residence time were analyzed with the use of ¹³C NMR. The tars were analyzed using the high resolution ¹³C NMR spin-lattice relaxation technique;¹⁴ this is the first time that detailed solid-state and high resolution ¹³C NMR spectroscopy techniques have been applied to common sets of coal tar and char samples. The ¹³C NMR data presented here on coal tars contain more useful chemical structural information than has been previously available from ¹H NMR data presented in the literature. Data for the char, tars and the parent coals are presented in Tables 5.3 and 5.4. As seen in Table 5.4, 12 to 42% of the tar sample collected was insoluble in CD_2Cl_2 and was deposited on the filter as residue; this insoluble tar fraction is designated as tar residue. The average values of the chemical structure features for the composite tar were determined by combining the values for the dissolved tar and tar residue, according to the relative weight fractions of soluble tar and tar residue. These combined tar data are also presented in Tables 5.3 and 5.4 and labeled "tar." Information on a preliminary set of coal, char and tar are presented in Appendix H. The information in Appendix H helps to substantiate the more complete findings discussed in this thesis. The data presented in Appendix H are a preliminary set that was used to determine the validity of the high resolution liquid ¹³C NMR analysis process on coal tars, and therefore is not presented here in the text.

Carbon Aromaticity

Comparing the NMR data for the tar, tar residue and char with that for the coal gives some interesting insight into the changing structure of coal during pyrolysis. The carbon aromaticity $(f_{a'})$ of the char is 11 to 32% higher than in the parent coal (see Fig. 5.6), which is a smaller difference between char and coal than reported previously for

experiments at 1250 K.^{48, 49, 54} This difference is most likely due to the fact that the data shown here are from lower temperature experiments (900 K) and represent an intermediate stage of devolatilization. This fact is verified by comparing the total volatiles yields for all three of these coals with the experiments in the literature at 1250 K.^{48, 49, 54} The literature showed total volatiles release were 52 to 54% (daf) at 1250 K as compared to the 23 to 45%(daf) for the coals in this study (at 900 K).

Coal	Sample	fa	f_a^C	f _{a'}	f_a^{H}	f_a^{N}	f_a^{P}	$f_a^{\ S}$	$f_a^{\ B}$	fal	f_{al}^{H}	f_{al}^{*}	falO
Pitt #8	coal	65	3	62	23	39	5	16	18	35	24	11	7
Pitt #8	char	87	5	82	27	55	6	19	30	13	7	6	3
Pitt #8	tar dis.	69	2	67	38	29	5	15	9	31	20	11	na
Pitt #8	tar res.	83	3	80	34	46	8	18	20	17	10	7	2
Pitt #8	tar	73	2	70	37	33	6	16	12	28	18	10	na
Illinois #6	coal	66	3	63	21	42	7	16	19	34	24	10	8
Illinois #6	char	74	4	70	23	47	7	18	22	26	17	9	4
Illinois #6	tar dis.	70	1	69	40	29	4	15	10	30	20	10	na
Illinois #6	tar res.	80	6	74	28	46	8	18	20	20	12	8	3
Illinois #6	tar	74	3	71	35	36	6	16	14	26	17	9	na
Blue #1	coal	60	5	55	19	36	8	13	15	40	29	11	7
Blue #1	char	71	7	64	20	44	8	14	22	29	21	8	4
Blue #1	tar dis.	63	7	56	27	29	8	16	5	37	27	10	na
Blue #1	tar res.	72	6	66	24	42	9	15	18	28	17	11	12
Blue #1	tar	64	7	57	27	31	8	16	7	36	26	10	na

Table 5.3¹³C NMR Analysis of Coals, Tars, and Chars^a (160 ms at 900 K)

^aPercentage carbon (error): $f_a = total sp^2$ -hybridized carbon (±3); $f_{a'} = aromatic carbon$ (±4); $f_a^C = carbonyl, > 165 ppm (\pm 2)$; $f_a^H = aromatic with proton attachment (\pm 3)$; $f_a^N = nonprotonated aromatic (\pm 3)$; $f_a^P = phenolic or phenolic ether, = 150-165 ppm (\pm 2)$; $f_a^S = alkylated aromatic = 135-150 ppm(\pm 3)$; $f_a^B = aromatic bridgehead (\pm 4)$; $f_{al} = aliphatic carbon (\pm 2)$; $f_{al}^H = CH$ or $CH_2 (\pm 2)$; $f_{al}^* = CH_3$ or nonprotonated (\pm 2); $f_{al}^O = bonded$ to oxygen, = 50-90 ppm (±2), tar dis. = tar that dissolved in CD_2Cl_2 , tar res. = fraction of collected tar that did not dissolve in CD_2Cl_2 , tar = weighted combined values of the tar res. and tar dis.

a 1	a 1		à				aa			
Coal	Sample	Xb	C _{cl}	σ+ 1	Po	B.L.	S.C.	MW _{cl}	MW _{att}	tar
				011						res.
Pitt #8	coal	0.290	14	4.8	0.48	2.3	2.5	323	32	
Pitt #8	char	0.366	18	5.4	0.76	4.1	1.3	315	18	
Pitt #8	tar dis.	0.134	8	2.4	0.45	1.0	1.4			
Pitt #8	tar res.	0.250	12	3.9	0.73	2.8	1.1			0.25
Pitt #8	tar	0.163	9	2.8	0.52	1.5	1.3	178	25	
Illinois #6	coal	0.300	15	5.5	0.52	2.9	2.6	368	35	
Illinois #6	char	0.314	15	5.3	0.64	3.4	1.9	326	29	
Illinois #6	tar dis.	0.144	9	2.5	0.47	1.2	1.3			
Illinois #6	tar res.	0.270	13	4.6	0.69	3.2	1.4			0.42
Illinois #6	tar	0.197	11	3.4	0.56	2.0	1.3	228	30	
Blue #1	coal	0.270	13	5.0	0.48	2.4	2.6	371	42	
Blue #1	char	0.344	17	5.8	0.64	3.7	2.1	402	34	
Blue #1	tar dis.	0.090	7	3.0	0.58	1.7	1.3			
Blue #1	tar res.	0.273	13	4.7	0.54	2.5	2.2			0.12
Blue #1	tar	0.112	8	3.2	0.58	1.8	1.4	205	35	

Derived Properties of Coal, Tar, and Char from the ¹³C NMR analysis^b (160 ms at 900 K)

Table 5.4

 ${}^{b}X_{b}$ = fraction of bridgehead carbons, C_{cl} = aromatic carbons per cluster, +1 = total attachments per cluster, P_{o} = 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_{att} = the average molecular weight of the cluster attachments, V = total volatiles yield, Tar = tar collected on filters and corrected for the tar deposited on sampling apparatus, tar dis. = tar that dissolved in CD₂Cl₂, tar res. = fraction of collected tar that did not dissolve in CD₂Cl₂, tar = weighted combined values of the tar res. and tar dis.

Carbon aromaticities (f_a) in the dissolved tar are similar to those of the parent coal for Blue #1 coal, but values of f_a in the tars from the other two coals are 8 to 10% higher (on a relative basis) than in the parent coal. For the Illinois #6 coal, the value of f_a in the dissolved tar was similar to that of the corresponding char rather than that of the parent coal. The f_a values of the tar residues of all three coals are close to the corresponding values in the chars.



Figure 5.6. Carbon aromaticity of the coal, char, dissolved tar (Tar dis.), tar residue (Tar res.), and the combined tar (Tar).

Cluster Attachments

The number of attachments per cluster (+1) and the number of bridges and loops per cluster (B.L.) in the dissolved tar are significantly lower than in the coal (Fig. 5.7 and Fig. 5.8). In the tar residue, +1 is only slightly less than in the coal, while the bridges and loops parameter (B.L.) is slightly higher. This indicates that there is cross-linking in a portion of the tar that was liberated from the coal lattice. The combined tar values of +1 and B.L. are still significantly less than in both the coal and the char. The values of B.L. in the chars are higher than in the parent coals, which also indicates cross-linking. The low values of side chains per cluster (S.C.) in the char, compared to the coal, indicates that side chains have been broken from the aromatic clusters. These broken side chains produce light gases. Light gas yield is indicated by the difference between the total volatiles yield and tar yield in Fig. 5.1. The average molecular weight of the side chains (MW_{att}) for the coal, char and the combined tar are presented in Fig. 5.9. The MW_{att} of the coals increases as rank decreases. The average molecular weight of the side chains (MW_{att}) in the tars are lower than in the coals by 5 to 7 daltons. The MW_{att} of the chars show a small decrease (6 to 8 daltons) for the Blue and Illinois chars and a large decrease (16 daltons) for the Pittsburgh char when compared to the original coal values. It is also noted that the molecular weight of the side chains (MW_{att}) in the char are less then the MW_{att} in the tar. The Pittsburgh char value is in agreement with previous pyrolysis data at 1250K in an inert atmosphere (11 to 18 daltons).^{48, 49, 54} This agreement seems to indicate that the Pittsburgh char is much further pyrolyzed than the other two chars in this study, and is consistent with the higher volatiles yield for this coal. The other chars are not in agreement with the previous studies, indicative of the low degree of pyrolysis for the Illinois and Blue chars.



Figure 5.7. Total attachments per aromatic cluster (+1) of the coal, char, dissolved tar (Tar dis.), tar residue (Tar res.), and the combined tar (Tar).



Figure 5.8. Bridges and loops per cluster in the coal, char, dissolved tar (Tar dis.), tar residue (Tar res.), and the combined tar (Tar).



Figure 5.9. Molecular weight of attachments in the coal, char and tar.

Aromatic Cluster Size

The average number of aromatic carbons per cluster (C_{cl}) in the coal is 13 to 15, which corresponds to structures with 3 to 4 aromatic rings. The values of C_{cl} in the tar residue are similar to those found in the coal (see Fig. 5.10). Perhaps the most interesting finding is that the average cluster size of the dissolved tar ranges from 7 to 9 aromatic carbons. This is significantly lower than the values of 12 to 15 aromatic carbons per cluster found in the coal and tar residue (and the value of 15 to 18 in the char). The average number of aromatic carbons per cluster (Ccl) in the coals are in agreement with previous data $^{\rm 54}$ that showed values of C_{cl} in coals ranging from 10 to 18 with rank ranging from lignite to lv bituminous. The values of Ccl of the char increased slightly from that found in the parent coal to values of 15 to 18. In previous studies, it has been shown with repeated data sets that the number of aromatic carbons per cluster in the char does not increase substantially during devolatilization, generally staying within the 12 to 16 range.^{47-49, 54} The difference between this study and previous studies is not extreme. One possible reason for the discrepancy may be the intermediate stage of pyrolysis for the coals in this study. This, however, would need to be tested further with other intermediate devolatilization experiments.

The data for the combined tar, obtained from the weighted average parameters of the dissolved and residual tars, show that the average number of aromatic carbons per cluster (C_{cl}) in the tar are around 8 to 11. As illustrated in Fig. 5.10, the values of C_{cl} in the combined tar from all three coals are significantly (30 to 50%) lower than the corresponding values for the coal. According to these data, tar contains a lower average number of aromatic carbons per cluster than was previously supposed. It is likely that the vapor pressures of the higher molecular weight structures that are freed from the coal may not be high enough to permit vaporization from the metaplast to form tar. Another concept

is only the tar molecules with small sizes are preferentially freed from the coal macromolecule.



Figure 5.10. Average number of aromatic carbons per cluster (C_{cl}) in the coal, char and combined tar.

These explanations may seem reasonable, but it has been shown that a distribution of tar structures with molecular weights as high as 800 daltons have been detached from the coal macromolecule and released at relatively low temperatures (800 K).⁵² Several sets of data indicate that tar molecular weight distributions peak in the 250 to 400 dalton range.^{35, 52, 80} The current experiments were performed at higher temperatures and heating rates than used by Simmleit, et al.,⁵² and hence large molecular weight structures (up to 800 daltons) would be expected to vaporize from the metaplast to form tar. Therefore, the explanations for small cluster sizes listed above are not sufficient to explain these data.

To further analyze the cluster size distribution of the tars, the average number of aromatic carbons per cluster (C_{cl}) in the tar (8 to 11) are used to predict the molecular weight per cluster (MW_{cl}) of approximately 200, listed in Table 5.4., and shown in Fig.

5.11. The cluster molecular weight (MW_{cl}) accounts for the non-aromatic portion of the cluster, such as side chains and bridges, as well as the aromatic portion.^{12, 15} It is seen from Fig. 5.11 that the coal and char values are nearly equivalent. The differences are most likely attributed to variability in the data and experimental sampling procedure. The molecular weight per aromatic cluster in the tar is significantly less than the values for the coal and the char; the difference is 38 to 44% less than the coal. If the average tar molecular weights are in the range of 250 to 400 (as stated by Simmleit, et al. and others^{35, 52, 80}), then a significant fraction of tar molecules must contain multiple clusters (i.e., dimers and trimers). This is also confirmed by the number of bridges and loops per cluster (B.L. in Table 5.4, and Fig. 5.8), which is greater than or equal to 1.0 in all of the tar and tar residue samples; monomers have no bridges.



Figure 5.11. Comparison of average molecular weight per aromatic cluster. Tar is the combined tar.

6. Discussion

The implications of the findings in this thesis and how they relate to coal, char and tar structure will be discussed. Possible explanations will be covered, as well as implications to present coal devolatilization models. Methods to model nitrogen evolution during devolatilization are presently emphasized in the literature. Due to this a model of nitrogen release will be discussed and the implications of the findings from this study on the model will be discussed.

Chemical Structure

A significant finding from this study is that the average number of aromatic carbons per cluster (C_{cl}) in the tar residue is higher than in the dissolved tar. This suggests that a wide distribution of species occurs in tar. Other investigators have previously shown that large molecular weight distributions are present in tar.^{35, 52, 80} However, in the network models, this distribution is only treated by assuming a distribution of oligimers (monomers, dimers, etc.) with a fixed cluster size. The data presented here suggest that it may be necessary to use a distribution of cluster sizes in the network devolatilization models.

Another important finding of this study has been that the average number of aromatic carbons per clusters (C_{cl}) in the tar is much lower than the C_{cl} in the coal and the char. These new data on tar bring into question 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. More accurate coal pyrolysis models may be obtained by modifying the models to account for different values of C_{cl} in tar.

Cluster Balance

The average number of aromatic carbons per clusters (C_{cl}) in the char increased from that found in the parent coal to values of 15 to 18. This may imply that the decrease in the value of C_{cl} in the tar is compensated by a corresponding increase in C_{cl} in the char. It is also possible that ring opening and/or ring condensation reactions occur in the char and the tar. The ¹³C NMR data presented here can be used to perform a balance on the number of clusters in the coal, char and tar. This is the first time that this type of balance has been possible to calculate. The number of moles of clusters per kilogram of parent coal (n_{cl}) is calculated in the following manner:

$$n_{cl}^{i} = \frac{m_{i}}{MW_{cl,i}} \tag{6.1}$$

where m_i is the mass (per kilogram of unreacted daf coal), *i* represents the coal, char or tar and $MW_{cl,i}$ is the average molecular weight of the cluster. If the assumptions are made that no aromatic clusters are included in light gases, and that the number of aromatic clusters is conserved (i.e., no ring opening or condensation), then the number of moles of cluster in the coal (n_{cl}^{coal}) should be equal to the number of moles of cluster in the char (n_{cl}^{char}) and the tar (n_{cl}^{tar}) , as shown:

$$n_{cl}^{coal} = n_{cl}^{char} + n_{cl}^{tar}$$
(6.2)

Results of the cluster balance (Eqs. 6.1 and 6.2) are shown in Fig. 6.1. The moles of aromatic clusters per kilogram of parent coal in the tars from both the Illinois #6 and the Blue #1 coals are significantly lower than in their respective chars, consistent with the low

tar yields observed for these coals. The values of n_{cl} in the tar and char from the Pittsburgh #8 coal are approximately equal. The close agreement in the n_{cl} in the tar and the char for the Pittsburgh #8 coal is most likely due to the higher degree of pyrolysis and higher tar yields for the Pittsburgh sample than for the Illinois and Blue samples (see Table 5.1).



Figure 6.1. Number of moles of aromatic clusters per kilogram of the parent coal for the coal, tar, and char.

The lower rank Blue #1 and Illinois #6 coals have slightly more aromatic clusters than are accounted for in the tar and char (a difference of ~14%) as seen in Fig. 6.2. The number of clusters in the Pittsburgh #8 coal is slightly lower than accounted for in the combined tar and char (a difference of ~8%). These differences are most likely within the combined experimental error of the tar yield and NMR data, and seem to indicate that the degree of ring opening and/or ring condensation in these experiments is small.



Figure 6.2. Difference in the number of moles of aromatic clusters per kilogram of the parent coal.

Ring Opening Reactions

The occurance of ring opening reactions during devolatilization has been recently suggested.³³ It is known that the aromatic ring structure is very stable, but it is postulated that the ring structure may open at the weaker bonded heteroatoms, such as oxygen and nitrogen. Figure 6.3 shows how this might occur.



Figure 6.3. Possible ring opening reactions.

As shown in Fig. 6.3 the beginning ring structure of both reaction A and B may be interpreted by ¹³C NMR as a single aromatic ring. After the ring opening takes place two

rings are present, with a side chain attachment on one of the rings. This postulated mechanism would keep the molecular weight of the tar molecule fairly constant, but would lower the molecular weight per cluster by an approximate factor of two. However, if this was a dominant mechanism, the following changes in chemical structure would be observed: (1) the number of aromatic rings would increase, (2) the size of the aromatic clusters would decrease and (3) the number of attachments would increase.

The number balance performed earlier on the number of aromatic rings (see Fig. 6.1 and 6.2), showed that for the samples collected in this study the total number of rings did not increase significantly. It was shown that the number of rings in the char and tar are different for the lower ranked coals, but that the overall balance in ring numbers did not change significantly.

The size of the aromatic clusters can be seen in the aromatic carbons per cluster (C_{cl}) and the average molecular weight of a cluster (MW_{cl}) , shown in Fig. 5.10 and 5.11. It is noted in both values that the tar is significantly less than the coal and the char. The C_{cl} of the char is higher for two of the coals. The ring opening reaction may be a possible explanation for the low values of the tar, based on the low values of C_{cl} . Further evidence of the ring opening reaction occurring in the tar is the low molecular weight of the aromatic clusters in the tar coupled with the evidence that tar molecules average between 250 to 400 daltons. This seems to indicate that dimers and trimers are present in tar. The ring opening reaction may be an explanation for the presence of these cluster polymers. The NMR parameters for the char, however, seem to indicate that the ring-opening behavior is not present in the char.

The number of attachments per cluster (+1) are shown in Fig. 5.7. As was noted earlier the attachments decrease for the tar while the char values remain similar to the parent coal. Other indicators of attachments include the value of the side chains (S.C.) and the

bridges and loops (B.L.). The number of side chains decrease from the parent coal in the char and the tar. The bridges and loops decrease for the tar and increase for the char.

The proposed ring opening reaction should increase the attachments of a cluster. All the values that deal with attachment, however, show decreases for the tar, while the char values give inconsistent results. This would seem to indicate that ring-opening reactions are not present at these conditions of devolatilization. The problem with attachment data as an indicator of ring-opening reactions is that the side-chains that would be formed in a ring-opening reaction may be lost to the the light gases during pyrolysis. Also the bridges are known to break and recombine during pyrolysis. In conclusion, to determine which portion of the cluster attachments are part of the formed attachments from the ring-opening reactions and which are lost due to pyrolysis would be difficult to ascertain. The fact that attachments, and side chains are still prominent in the pyrolysis samples of tar and char may indicate the formation of side chains by ring-opening reactions.

The evidence from this study is not yet strong enough to confirm the conjecture of ring-opening reactions. It is possible that the reactions are present in the tar, but may be very limited in the char. The weak indications of the ring-opening reactions, from this study, may be due to the low devolatilization temperatures and the intermediate degree of devolatilization of these samples. Further NMR studies should be made on chars and tars produced at higher temperatures and at a greater degree of pyrolysis. Samples of that nature may give stronger evidence of the ring-opening reactions.

Model of Coal Nitrogen Release

An important aspect of this study is to help resolve the question of nitrogen release during devolatilization as a function of coal type, as shown earlier in Fig. 2.6. It is also known, as indicated in Fig. 2.7, that during pyrolysis nitrogen is released from coal as

(a) part of the tar structure and (b) in the light gases, generally as hydrogen cyanide (HCN).^{1-3, 38, 80} A general nitrogen model approach that is used by other investigators,^{60, 61} and has been modified will be covered in this section. It is presented to help provide a basis for further analysis of the coal tar structure.

As tar leaves the coal during pyrolysis, nitrogen is carried with the tar as part of the aromatic cluster groups. It is helpful then to know the average amount of nitrogen in the clusters of the tar. To model the nitrogen that is released from the coal in the aromatic clusters of the tar, the mass of nitrogen per cluster (M_{cl}^N) is defined as:

$$M_{cl}^{N} = \frac{\text{mass of nitrogen}}{\text{aromatic cluster}}$$
(6.3)

The value M_{cl}^N can be calculated from known coal properties in the following manner:

$$M_{cl}^{N} = \frac{x_{N}}{x_{C}} M W_{C} \frac{C_{cl}}{f_{a}}$$
(6.4)

The units to this equation are:

$$= \frac{\text{mass of N/mass of coal}}{\text{mass of C/mass of coal}} \frac{\text{mass of C}}{\text{moles of C}} \frac{\text{moles of aromatic C/cluster}}{\text{moles of aromatic C/moles of C}}$$

Where x_N = weight percent of nitrogen in the coal (daf)

 x_C = weight percent of carbon in the coal (daf)

 MW_C = molecular weight of carbon

 C_{cl} = number of aromatic carbons per cluster

 f_a = carbon aromaticity (ratio of aromatic carbons to total carbons).

It is possible that nitrogen, at some point in the devolatilization process, is simultaneously released with the tar structure and as HCN. Since nitrogen is released as HCN, the variable M_{cl}^{N} will change with time. This necessitates the continuous calculation of M_{cl}^{N} on a time-dependent basis. To help in this process, Eq. 6.4 must be

modified to include variables that are more easily obtained. The average cluster molecular weight is calculated by:

$$MW_{cl} = \frac{MW_C C_{cl}}{x_C f_a} \tag{6.5}$$

This equation for MW_{cl} can be substituted into Eq. 6.1 to obtain

$$M_{cl}^{N} = M W_{cl} x_{N} \tag{6.6}$$

The three major devolatilization models calculate MW_{cl} , which can then be used in Eq. 6.6 to determine the M_{cl}^N . That leaves the value of x_N to still be calculated to complete Eq. 6.6.

To find x_N it is first assumed, as other investigators have,^{60, 61} that the mass of nitrogen per cluster is a constant at any moment of time. This assumption gives the following equation:

$$M_{cl,char,t}^{N} = M_{cl,tar,t}^{N}$$
(6.7)

where:

 $M_{cl,char,t}^{N}$ = mass of nitrogen per aromatic cluster in the char at time 't' $M_{cl,tar,t}^{N}$ = mass of nitrogen per aromatic cluster in the tar at time 't'

The assumption of Eq. 6.7 allows for the calculation of x_N from either the char or the tar, without having to calculate both values. x_N is defined as:

$$x_N = \frac{\text{mass of nitrogen}}{\text{total mass}}$$
(6.8)

The total mass of the char, and the tar are calculated in the devolatilization models. This leaves the mass of nitrogen to be determined to satisfy Eq. 6.8.

A mass balance on the nitrogen is performed to calculate the mass of nitrogen in the char. If m_{HCN}^N is the mass of nitrogen released as HCN and m_{char}^N is the mass of N remaining in the char, the value m_{char}^N can be calculated from a mass balance:

$$m_{char}^{N} = m_{coal}^{N} - m_{tar}^{N} - m_{HCN}^{N}$$
(6.9)

where m_{coal}^{N} and m_{tar}^{N} are the mass of nitrogen in the coal and tar respectively.

To provide a relation between m_{HCN}^N and m_{char}^N , HCN release during pyrolysis has commonly been modeled using an empirical first order kinetic mechanism.^{46, 60} The equation is generally of the form:

$$\frac{dm_{HCN}^{N}}{dt} = k_{HCN}m_{char}^{N}$$
(6.10)

To provide a relationship between the tar and the char, the nitrogen released in the tar can be modeled as the incremental tar release times the fraction of nitrogen in the tar, as follows:

$$\delta m_{tar,n}^{N} = \delta m_{tar,n} \frac{n M_{cl}^{N}}{M_{mer,n}}$$
(6.11)

where the units work out as:

and:

$$nM_{cl,n} = M_{mer,n} \tag{6.12}$$

The definitions are as follows:

 δm_{tar}^N = differential mass of nitrogen released with the tar

 δm_{tar} = differential mass of tar

 M_{cl} = mass of a cluster

 M_{mer} = mass of a polymer of clusters crosslinked together

The subscript *n* denotes the number of clusters of the tar molecule. With some rearrangement, and adding all the polymer clusters together the following equation applies:

$$\delta m_{tar}^{N} = \int_{n=1}^{N} \delta m_{tar,n}^{N} = M_{cl}^{N} \frac{n \delta m_{tar,n}}{m_{el}}$$
(6.13)

It is now possible to model the nitrogen release during coal devolatilization with the use of the above equations and a coal devolatilization model.^{28, 32, 58} The calculational procedure requires a time-step process starting at t=0, where the input values begin with the coal input parameters. In the above equations only the kinetic data of HCN release is needed to complete the model. Other investigators have attempted to calculate kinetic parameters for HCN release,^{46, 61} but the accuracy and success of the measurements are still unknown.

Analysis of Model Assumptions

The following assumption is inherent in the above nitrogen model:

$$M_{cl,char,t}^{N} = M_{cl,tar,t}^{N}$$
(6.7)

To determine the validity of this assumption both sides of Eq. 6.4 are divided by the molecular weight of nitrogen. This equation then describes the nitrogens per aromatic cluster (N_{cl}). With the assumption of Eq. 6.7, the N_{cl} of the coal, char and tar should also be equal at any specific time. It is known, however, that HCN is both a secondary reaction product and a product that occurs at higher temperatures than tar release.^{43, 80} The nitrogens per cluster of the coal, char and tar should therefore remain constant during the primary devolatilization step.

Data on elemental composition of coal tar are available in the literature for numerous coals of different rank and under a number of different experimental conditions. Experimental studies by Freihaut et al.^{44, 80} used an entrained-flow reactor to devolatilize three different coals at a number of different gas temperatures ranging from 780 K to 1325 K. The entrained flow reactor was designed to minimize secondary pyrolysis reactions. Chen and Niksa used a radiant entrained-flow reactor to pyrolyze four coals of different rank. All four coals were pyrolyzed at more than five different residence times in the reactor.

Many of the same coals that were used in the studies by Freihaut and by Chen were also analyzed by solid state ¹³C NMR by other investigators.^{12, 15, 47, 49} These additional NMR data provide the necessary information needed to calculate nitrogens per aromatic cluster (N_{cl}) with the use of Eq. 6.4. For the coals that had not been analyzed with ¹³C NMR, information was extrapolated from coals of similar rank and coal type.

The data from all of these investigators^{12, 15, 44, 47, 49, 70, 80} were used and the nitrogens per cluster (N_{cl}) of the tar and coal were calculated. The results of this analysis are plotted in Fig. 6.4. The data should fall on the 45 degree line if the assumption that the mass of nitrogen per cluster (M_{cl}^N) in the tars equals the mass of nitrogen per cluster in the parent coal. This analysis indicates that the mass of nitrogen per cluster in the tar does not equal that in the coal.

Since the results in Fig. 6.4 were assembled from data reported in several experiments;^{44, 70, 80} the use of several different data sets may have caused some error in the analysis. It may also be possible that the assumptions in the analysis were in error, namely (a) that the average number of carbons per aromatic cluster (C_{cl}) in the tar is *not* equal to that in the coal, (b) that the carbon aromaticity (f_a ') of the tar *does not* equal that of the coal, and/or (c) the reported tar data were skewed by concurrent HCN release.

To test whether the differences in the nitrogens per cluster (N_{cl}) of the coal and the tar may be attributed to the different studies, an analysis of the data obtained in this study from a matching sample set of coal, char and tar in this study was performed to calculate the mass of nitrogen per aromatic cluster (M_{cl}^N) . Using Eq. 6.4, along with the chemical

composition and structural data obtained in this study (i.e., x_C , x_N , f_a , and C_{cl}), the nitrogen per cluster value can be compared for the coals, chars and tars. Although HCN was not measured in these experiments, the moderate temperatures (900 K) would likely minimize HCN release.^{44, 80} Figure 6.5 shows that the mass of nitrogen per cluster in the tar collected in these current experiments is much lower than in either the char or the parent coal (a difference of ~30 to 50%). The values of M_{cl}^N in the char, however, are similar to that in the coals. This confirms the earlier analysis, using literature data from several sources, that showed that the nitrogens per cluster (N_{cl}) were not equal for the coal and the tar.



Figure 6.4. Comparison of the nitrogens per cluster in the coal and tar.

Since the assumption of Eq. 6.7 appears to be incorrect, the earlier assumptions of (a) that the number of carbons per aromatic cluster in the tar is *not* equal to that in the coal, and/or (b) that the carbon aromaticity of the tar *does not* equal that of the coal must be examined.



Figure 6.5. Mass of nitrogen per cluster (M_{cl}^N) for the coal, char and combined tar.

It was shown earlier in Fig. 5.10 that the aromatic carbons per cluster (C_{cl}) in the char are slightly higher than the coal, and that the carbons per cluster in the tar are much lower than both the char and coal. The comparison of carbon aromaticity (f_a ') for the coal, char and tar is shown in Fig. 5.6. As noted in the results section, both the char and tar aromaticities are slightly higher than the coal. The tar aromaticity is much closer to the value of the coal than the char though there is still a significant difference. The major break down with the assumptions in the proposed model appears to be with the aromatic carbons per cluster and tar.

Nitrogen Balance

The loss of nitrogen to the light gases as HCN may be another explanation for the low value of the mass of nitrogen per cluster (M_{cl}^N) in the tar. To determine the possibility of nitrogen being lost from the tar to the light gases a mass balance was performed on the

nitrogen in the coal and compared to the nitrogen in the pyrolysis products of char and the tar. The difference between the nitrogen in the coal compared to the nitrogen in char and tar was assumed to have escaped to the light gases. The values are listed in Table 6.1, with the percent nitrogen on a dry ash free basis of the coal.

Disti	IDUIIOII		ogen m	the Lyr	101ysis 110uucis				
	Temp	Time	f_N^{\dagger}	f _N †	f _N †	%M.R.	%Tar		
	(K)	(ms)	(char)	(tar)	(L.G.)				
Beulah Zap	850	140	60.5	0.4*	39.1*	23.01	1.13		
	900	160	68.1	3.6	28.3	38.18	4.43		
	1050	210	70.4	3.5	26.2	44.75	3.31		
	1220	230	58.1	1.4	40.5	54.73	1.53		
Blue #1	850	140	93.3	2.1*	4.6*	17.68	2.94		
	900	160	77.3	8.1	14.7	23.16	8.41		
	1050	210	76.1	21.6	2.3	47.06	15.79		
	1220	230	64.8	14.6	20.6	53.85	10.76		
Illinois #6	850	140	117.6	1.7	*	8.95	1.86		
	900	160	66.3	8.5	25.3	37.50	9.81		
	1050	210	71.4	24.9	3.7	45.51	20.71		
	1220	230	62.9	19.6	17.4	53.83	16.22		
Pittsburgh #8	850	140	57.5	2.7	39.8	21.50	3.09		
	900	160	58.8	32.3	8.9	45.90	26.08		
	1050	210	61.3	32.2	6.5	45.03	28.36		
	1220	230	61.1	24.0	14.9	49.23	21.12		
Pocahontas #3	850	140	66.5	0.4*	33.1*	6.60	1.61		
	900	160	62.3	1.6	36.1	11.84	2.42		
	1050	210	64.2	9.1	26.7	12.96	11.62		
	1220	230	77.8	7.4	14.9	16.59	9.54		

Table 6.1Distribution of Nitrogen in the Pyrolysis Products

 $\dagger f_N$ = fraction of nitrogen from the coal in the char, tar, or light gases.

* = values known to be inaccurate.

Since there is very little nitrogen in the coal and subsequently in the pyrolysis products, small errors in experimentation can produce large significant errors on a percentage basis. Due to this, the nitrogen data in the table are not completely reliably. The values that are known to be inaccurate are marked (*). Other values may also be inaccurate but are not marked since the accuracy in unknown. It can be seen that some of the samples have significant losses of nitrogen to the gas. This gaseous nitrogen may come from the the char and/or the tar. The limited value of the mass of nitrogen per cluster (M_{cl}^N) in the tar seems to indicate that the nitrogen in the gas may be from the tar structure. The jump in the percent of nitrogen in the light gases at the 1220 K condition also indicates the presence of secondary reactions breaking up the tar structure. The low rank Beulah Zap coal shows a much higher proportion of the nitrogen in the light gases than the other coals. This may indicating that a significant fraction of nitrogen is escaping from the lignite via light gas release in addition to that released in the tar.

This analysis seems to indicate that some nitrogen is escaping via the light gases, even at the moderate temperature (900 K) used in these experiments. The proportion of nitrogen released in the light gas is rank dependent as expected, with the low rank coals releasing the most nitrogen as light gas. This may be a reason for the low value of the mass of nitrogen per cluster (M_{cl}^N) in the tar. The proportion of nitrogen released in the tar and light gases also seems to be a slight function of rank. It is suggested that (a) the quality of the CHN analysis be improved, and (b) the amount of HCN released be measured in future experiments to verify this hypothesis.

7. Conclusions & Recommendations

Coal pyrolysis is an important step in understanding coal combustion. Pyrolysis is known to affect the physical and chemical structure of the coal particle, which eventually burns. A number of complicated network models have been developed which predict, to a reasonable degree of accuracy, the volatile and tar release that occurs during devolatilization. Some of these models have attempted to predict how certain species evolve during pyrolysis. Some of the species of interest are those that are known to be pollutants, such as nitrogen and sulfur.

To accurately predict devolatilization, network models use an understanding of the physical and chemical properties of coal, char and tar. To help in the development of these network models it is important that a more complete understanding of devolatilization be developed.

In this study, six well established research coals were pyrolyzed, in a drop tube reactor and in a methane-air flat flame burner. The coals were analyzed with both established and recently developed techniques by other investigators to obtain a better understanding of coal devolatilization.

X-ray photoelectron spectroscopy (XPS) was used for the first time to analyze chars that were prepared at high temperatures (850-1650 K) and heating rates ($\sim 10^4$ - 10^5 K/s). The data show that as the degree of devolatilization increases the amount of quaternary nitrogen decreases and pyridinic nitrogen increases. This may indicate that some of the quaternary nitrogen groups are protonated pyridinic groups. It was also shown that XPS appears to be a limited technique for the study of nitrogen functional

groups and that other methods will need to be used to further quantify the forms of nitrogen in coal.

Samples of coal and char were analyzed with the use of solid-state ¹³C NMR. This technique has been shown to be both effective and reliable. The solid-state ¹³C NMR data presented here are consistent with available literature data, and serve to expand the database.

Matching tar samples for the coal and char, obtained during pyrolysis at moderate temperatures (900 K), were analyzed using a new high resolution ¹³C NMR technique developed for the analysis of liquid samples. This allowed, for the first time, the comparison of the complete ¹³C NMR chemical structural data between matching sets of coal, char and tar.

It was found that the carbon aromaticities in the char and tar are higher than in the coal. The aromaticity value in the tar residue was closer to the char value than the coal value, while the aromaticity of the dissolved tar was closer to the coal than the char. The number of attachments and the bridges and loops per cluster showed that significant cross-linking reactions occurred in the char. The average number of aromatic carbons per cluster (C_{cl}) in the tar was much smaller than found in the coal, whereas C_{cl} in the char increased slightly in comparison to the coal. Along with the decrease in the cluster size of the tar was a decrease in the average molecular weight of aromatic clusters in the tar. All of these data indicate that there are significant differences in the chemical structures of the tar compared to the char and the coal.

Some of the data presented here contradicts common assumptions used in network devolatilization models. These data show that the aromatic carbons per cluster in the coal, char and tar are not equivalent, as assumed in the current models. The average number of aromatic carbons per cluster (C_{cl}) determined for the tar is significantly lower than that in the coal and in the char, while the char values are slightly higher than in the coal. More

accurate models may be obtained by implementing these findings into current devolatilization models.

A balance was performed on the number of aromatic clusters in the coal versus the number in the char and tar. The number of aromatic clusters per kilogram of parent coal remained relatively constant during pyrolysis. This indicates that the degree of ring opening and/or ring condensation is minimal in the samples that were analyzed in this study.

Some investigators have attempted to develop models that predict nitrogen evolution during devolatilization. One method has been to assume that the mass of nitrogen per aromatic cluster (M_{cl}^N) is equal for the coal and the tar. With the data obtained from this study, the mass of nitrogen per aromatic cluster was determined for a matching set of coal, char and tar. It was shown that values of M_{cl}^N for the tar were much lower than in the coal and the char. The nitrogens per cluster in the coal and the char were approximately equal. The primary cause of this phenomenon is the low value of C_{cl} in the tar. This may have implications on proposed mechanisms used to model nitrogen release during coal devolatilization.

To obtain a more adequate method to model nitrogen release during devolatilization, a more accurate picture of devolatilization, and the nitrogen structure in the coal, char and tar is needed. It is felt that a more extensive study of ¹³C NMR analysis of matching sets of coal, char, and tar should be performed to provide a more complete understanding. This could be done by analyzing matching sets of chars and tars produced at different conditions than the ones studied here. The tars analyzed in this study were from moderate temperature experiments and represent an intermediate stage of devolatilization. Higher temperature experiments are recommended.

It has also been noted that ¹³C NMR may not be the most effective tool to determine the existence of ring-opening reactions. Analysis of tar structure with the use of nitrogen

specific gas chromatography may be a method whereby ring-opening reactions can more easily be verified. The use of nitrogen specific gas chromatography may also be an excellent method to give a more accurate concept of the processes that lead to nitrogen release during pyrolysis.

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Appendix A

Gas Temperature Profiles

The following gas temperature profiles were measured in the HPCP drop tube furnace and corrected for radiation effects.

1. Wyodak

Gas remperature Profiles for wyodak										
Temp 850K			Temp 900K			Temp 920K				
Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)			
0	323		0	323		0	323			
0.8	488		0.8	490		0.8	529			
1.8	535		1.8	538		1.8	590			
2.8	673		2.8	674		2.8	704			
4.8	723		4.8	726		4.8	825			
6.8	824		6.8	856		6.8	889			
8.8	852		8.8	902		8.8	915			
10.8	818		10.8	878		10.8	849			
11.8	823		12.8	814		11.8	852			
			13.8	817						

Table A.1Gas Temperature Profiles for Wyodak



Figure A.1. Measured gas temperature profiles for Wyodak pyrolysis experiments.
2. Beulah Zap

remperature ritornes for beuran Zap											
Temp	850K		Temp 900K			Temp 1050K			Temp 1220K		
Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)	
0	323		0	323		0	323		0	323	
0.8	468		0.8	516		0.8	875		0.8	878	
1.8	571		1.8	692		1.8	914		1.8	977	
2.8	643		2.8	768		3.8	976.		3.8	1094	
4.8	697		4.8	836		5.8	1013		5.8	1155	
6.8	717		6.8	865		7.8	1040		7.8	1191	
8.8	754		8.8	881		9.8	1057		9.8	1212	
10.8	866		10.8	902		11.8	1063		11.8	1222	
11.8	880		12.8	904		13.8	1063		13.8	1223	
			14.8	901		15.8	1058		15.8	1218	
			15.8	917		17.8	936		17.8	1199	
						19.8	959		19.8	1049	
						20.8	968		20.8	1056	

Table A.2Temperature Profiles for Beulah Zap



Figure A.2. Measured gas temperature profiles for Beulah Zap pyrolysis experiments.

3. Blue #1

Sus remperature rionnes for Blue #1										
Temp	850K		Temp 900K			Temp 1050K			Temp 1220K	
Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)
0	323		0	323		0	323		0	323
0.8	428		0.8	556		0.8	875		0.8	878
1.8	528		1.8	693		1.8	914		1.8	977
2.8	679		2.8	754		3.8	976.		3.8	1094
4.8	763		4.8	805		5.8	1013		5.8	1155
6.8	763		6.8	833		7.8	1040		7.8	1191
8.8	784		8.8	845		9.8	1057		9.8	1212
10.8	853		10.8	830		11.8	1063		11.8	1222
11.8	864		12.8	832		13.8	1063		13.8	1223
			14.8	905		15.8	1058		15.8	1218
			15.8	919		17.8	936		17.8	1199
						19.8	959		19.8	1049
						20.8	968		20.8	1056

Table A.3Gas Temperature Profiles for Blue #1



Figure A.3. Measured gas temperature profiles for Blue #1 pyrolysis experiments.

4. Illinois #6

Temp	850K		Тетр 900К			Temp 1050K			Temp 1220K		
Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)	
0	323		0	323		0			0		
0.8	428		0.8	556		0.8	875		0.8	878	
1.8	528		1.8	693		1.8	914		1.8	977	
2.8	679		2.8	754		3.8	976.		3.8	1094	
4.8	763		4.8	805		5.8	1013		5.8	1155	
6.8	763		6.8	833		7.8	1040		7.8	1191	
8.8	784		8.8	845		9.8	1057		9.8	1212	
10.8	853		10.8	830		11.8	1063		11.8	1222	
11.8	864		12.8	832		13.8	1063		13.8	1223	
			14.8	905		15.8	1058		15.8	1218	
			15.8	919		17.8	936		17.8	1199	
						19.8	959		19.8	1049	
						20.8	968		20.8	1056	

Table A.4Gas Temperature Profiles for Illinois #6



Figure A.4. Measured gas temperature profiles for Illinois #6 pyrolysis experiments.

5. Pittsburgh #8

Temp	850K		Temp 900K			Temp	1050K		Temp	1220K	
Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)	
0	323		0	323		0			0		
0.8	428		0.8	516		0.8	875		0.8	878	
1.8	528		1.8	692		1.8	914		1.8	977	
2.8	679		2.8	768		3.8	976.		3.8	1094	
4.8	763		4.8	836		5.8	1013		5.8	1155	
6.8	763		6.8	865		7.8	1040		7.8	1191	
8.8	784		8.8	881		9.8	1057		9.8	1212	
10.8	853		10.8	902		11.8	1063		11.8	1222	
11.8	864		12.8	904		13.8	1063		13.8	1223	
			14.8	901		15.8	1058		15.8	1218	
			15.8	917		17.8	936		17.8	1199	
						19.8	959		19.8	1049	
						20.8	968		20.8	1056	

Table A.5Gas Temperature Profiles for Pittsburgh #8



Figure A.5. Measured gas temperature profiles for Pittsburgh #8 pyrolysis experiments.

6. Pocahontas #3

Temp	850K		Temp 900K			Temp 1050K			Temp 1220K			
Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		Dist(cm)	Temp(K)		
0	323		0	323		0	323		0	323		
0.8	428		0.8	516		0.8	875		0.8	878		
1.8	528		1.8	692		1.8	914		1.8	977		
2.8	679		2.8	768		3.8	976.		3.8	1094		
4.8	763		4.8	836		5.8	1013		5.8	1155		
6.8	763		6.8	865		7.8	1040		7.8	1191		
8.8	784		8.8	881		9.8	1057		9.8	1212		
10.8	853		10.8	902		11.8	1063		11.8	1222		
11.8	864		12.8	904		13.8	1063		13.8	1223		
			14.8	901		15.8	1058		15.8	1218		
			15.8	917		17.8	936		17.8	1199		
						19.8	959		19.8	1049		
						20.8	968		20.8	1056		

Table A.6Gas Temperature Profiles for Pocahontas #3



Figure A.6. Measured gas temperature profiles for Pocahontas #3 pyrolysis experiments.

Appendix **B**

Velocity Profile Calculations

To determine the residence time of particles in the HPCP reactor it was necessary to calculate gas velocity profiles. The program FLUENT 4.3.1 was used to model the HPCP reactor and simulate the temperature and gas velocities. The HPCP uses a cylindrical tube to act as a reaction zone. To model this system the reaction zone was modeled using cylindrical coordinates on an axi-symmetric system.

FLUENT uses finite difference modeling to converge a solution. To obtain the grid the radial direction was divided into 58 sections and the length was divided into 158 sections. This gave a total of over 9000 separate elements. To simplify the calculations it was assumed that the reaction section was symmetrical about the center of the HPCP reaction tube.

Seven different temperature boundary conditions were used for different areas of the reactor wall. The seven temperatures made it possible to more accurately model the true wall temperatures of the HPCP. The wall temperatures were obtained from thermocouples in the HPCP. The injection area was modeled as an annulus with the interior annulus wall having an appropriate size dimension of 3.175 mm.

The temperature of the secondary injection gases were modeled by obtaining gas temperatures with the use of a thermocouple placed down the top of the HPCP. This procedure was able to obtain temperatures for the secondary gases at the locations needed in the reaction zone. The primary gas temperatures were assumed to be 323 K in all cases.

The initial gas velocities were calculated assuming ideal gas behavior and an appropriate area of flow. For the secondary gases the area was an annulus with the injection probe being the area of the annulus interior. The primary gas area was calculated from the inner diameter of the injection nozzle.

Since devolatilization was performed in pure nitrogen the thermophysical properties of the gas were needed for the model. These were obtained from published data⁸¹ and then fit to a polynomial to obtain the data as a function of temperature. The equations were then added to the FLUENT model.

Three simulations were performed for the this study. This study used more than the three experimental conditions that were modeled in FLUENT. However, a number of the experimental conditions were very similar. It was therefore assumed that three FLUENT predictions could adequately represent all the experimental conditions in the HPCP with only minor extrapolations.

The temperatures from the FLUENT model calculations and the experimental temperature results were not in perfect agreement. Since gas velocity is a strong function of the gas temperature, corrections were made to the calculated gas velocities to account for the temperature differences. If it is assumed that the mass flow rate must be a constant then the following applies:

Equation B.1 is equivalent to Eq. B.2 if the area terms are equal for both conditions.

$$\rho_2 A v_2 = \rho_1 A v_1 \tag{B.2}$$

Assuming ideal gas and dividing out terms one obtains the velocity equation shown in Eq. B.3.

$$v_2 = \frac{T_2}{T_1} v_1 \tag{B.3}$$

In this manner the new gas velocity was obtained. The difference between the modeled temperatures and the experimentally measured temperatures were generally less than 50 degrees. In some minor cases the temperature difference did reach slightly higher than 150 degrees.

Appendix C

Particle Temperature History

Graphs of the particle temperature profiles produced with the modified CPD model and the gas velocity profiles modeled in FLUENT 4.3.1.

1. Wyodak



Figure C.1. Particle temperature history and particle heating rate of Wyodak coal in the HPCP.

2. Beulah Zap



Figure C.2. Particle temperature history and particle heating rate of Beulah Zap coal in the HPCP. Graph (a) is the 850 K condition, (b) 900 K, (c) 1050 K and (d) 1220 K.



Figure C.3. Particle temperature history and particle heating rate of Blue #1 coal in the HPCP. Graph (a) is the 850 K condition, (b) 900 K, (c) 1050 K and (d) 1220 K.

4. Illinois #6



Figure C.4. Particle temperature history and particle heating rate of Illinois #6 coal in the HPCP. Graph (a) is the 850 K condition, (b) 900 K, (c) 1050 K and (d) 1220 K.

5. Pittsburgh #8



Figure C.5. Particle temperature history and particle heating rate of Pittsburgh #8 coal in the HPCP. Graph (a) is the 850 K condition, (b) 900 K, (c) 1050 K and (d) 1220 K.

6. Pocahontas #3



Figure C.6. Particle temperature history and particle heating rate of Pocahontas #3 coal in the HPCP. Graph (a) is the 850 K condition, (b) 900 K, (c) 1050 K and (d) 1220 K.

Appendix D

Tar Filter Modifications

It was found that the filters system for the tar was originally placed too far from the reactor exit. This allowed for the tar to cool and deposit on the tube walls, creating substantial tar losses(> 80%). The filter system was redesigned to correct this problem. To provide an in-depth analysis of the situation a series of tests were performed that measured temperatures of key components of the collection system while varying the temperature and pressure of the HPCP drop tube furnace.

Thermocouples were placed at the outlet from the virtual impactor and at 7.5 cm below the optical ports, but before the virtual impactor. Temperature measurements were also made along the tubing system after the leaving the impactor. Figure D.1 shows the temperature of gases just after the virtual impactor as a function of reactor temperature and pressure.



Figure D.1. Temperature measurements taken just after the virtual impactor as a function of reactor temperature and pressure.

The temperature leaving the impactor is low, which leads to the conclusion that any significant cooling before the filters would only increase tar deposition in the copper tubing. It was decided that cooling should take place in the filters to insure maximum temperature in the tubing. As noted in the Fig. D.1 the most severe conditions occur at 5 atm for the three temperature ranges tested. The decrease in temperature for the 10 and 15 atm cases is due to the loss of heat through the refractory lining of the reactor. ⁶⁴

The new design of the filter plates is shown in Fig. D.2 to D.5. The filters were moved from the previous location of over 10 ft from the collection system to just under one foot. Water cooling was also placed directly in the filter plates to maximize the cooling of the tar at the filters with minimal tar losses in the collection system.

I would like to acknowledge Boyd Bishcoff who did all the work involved with the filter redesign.



Figure D.2. Side view of filter holder



Figure D.3. Top inside view of filter holder



Figure D.4. Side view of filter lid.





Appendix E

Modification of the HPCP Preheater

Before experiments were performed, gas temperature profiles were measured to check the temperatures in the reactor. It was found that the furnace had a difficult time reaching the higher experimental temperature conditions(1220K). Further analysis indicated that the secondary gas temperature from the preheater was too low. Temperatures were measured by thermocouples placed at the gas exit of the preheater while varying secondary gas flows in the preheater. Temperatures generally ranged from 500 to 600 K. These temperatures were far too low to obtain the gas temperatures desired for the experiments.

Another problem with the preheater is that the U shaped heating element bows out due to opposing electromagnetic forces on each leg of the heater. When the heater element bowed with the original design it tended to come in contact with the inner walls of the heating element housing. This contact caused the element to stick to the walls and eventually break due to physical stresses. During a three month period three heating elements were broken, causing down time and increasing expenses.

Due to these two problems it was decided to redesign the preheater section of the HPCP. The preheater cast iron housing limited the redesign. The interior diameter of the preheater was increased in size and improved insulation was used to compensate for the loss of insulation volume from the original design. The original top cross-section is shown in Fig. E.1 and the redesigned top cross-section is shown in Fig. E.2.

The length of the preheater was also shortened from the original to help limit the bowing effect of the heating element. The bowing is a function of the heater length and by decreasing the length of the heater the bowing would be decreased. The original length was 41 inches and the design is shown in Fig. E.3. The new design is shown in Fig. E.4 and indicates the new heater length of 37 inches.

The lack of gas temperature in the original design was due to channeling problems within the preheater. It was found, upon opening the preheater, that the packed bed of the reactor was too dense. This created a need for large pressure differences across the bed to cause the gases to flow through the packing. The gases would bypass the packed bed by leaking into insulation layer. The gases then traveled down the preheater on the outside of the insulation and the inside of the cast iron preheater shell. This by-passing of the packed bed created the low gas temperatures of the preheater. The packed bed was taken out of the preheater and added material was placed in strategic locations to help eliminate the possibility of gas leakages through the insulation layer.

After all the redesign work was accomplished further tests revealed that the gas preheater temperatures had increased to approximately 900 K. This temperature increase helped to obtain the necessary experimental conditions needed for this study. The life of the preheater also increased from 1 month to over 14 months. Additional preheater modifications are recommended to increase the maximum temperature.



Figure E.1. Top cross section of the original preheater for the HPCP



Figure E.2. Top cross section of the preheater for the HPCP







Figure E.4. Side cross section of preheater

Appendix F Nitrogens per Cluster Analysis

The following is a summary of the data used for the literature analysis on the nitrogens per aromatic cluster in the coal and tar. The tables show information taken from the literature, as well as the NMR parameters used for the calculations. Freihaut et al.^{44, 80} used an entrained-flow reactor to devolatilize three different coals at a number of different gas temperatures ranging from 780 K to 1325 K. The entrained flow reactor was designed to minimize secondary pyrolysis reactions. Chen⁷⁰ used a radiant entrained-flow reactor to pyrolyze four coals of different rank. The temperatures listed in Table F.2 for Chen's data correspond to the wall temperature of the reactor, since the gas temperature was not measured. All four coals used in the study by Chen were pyrolyzed at more than five different residence times.

Table	F.	1
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Summary of Tar Data from Freihaut^{44, 80} Used to Calculate M_{cl}^{N} .*

					Coal	(daf)	Tar	(daf)			N/C	luster
Coal	ID #	Size	Tg	Time	%C	%N	%C	%N	C _{cl}	f _a '	Coal	Tar
		(µm)	(°Č)	(ms)								
Pitt #8	1451	20-30	507	580	83.98	1.67	84.05	1.64	14	0.61	0.39	0.38
Pitt #8	1451	20-30	569	545	83.98	1.67	84.07	1.67	14	0.61	0.39	0.39
Pitt #8	1451	20-30	660	515	83.98	1.67	84.37	1.68	14	0.61	0.39	0.39
Pitt #8	1451	20-30	660	515	83.98	1.67	84.46	1.76	14	0.61	0.39	0.41
Pitt #8	1451	20-30	796	450	83.98	1.67	84.62	1.69	14	0.61	0.39	0.39
Pitt #8	1451	20-30	895	410	83.98	1.67	85.22	1.73	14	0.61	0.39	0.40
Pitt #8	1451	20-30	969	355	83.98	1.67	85.55	1.74	14	0.61	0.39	0.40
Pitt #8	1451	20-30	1053	335	83.98	1.67	86	1.73	14	0.61	0.39	0.40
Pitt #8	1451	63-75	507	580	84.7	1.71	83.97	1.64	14	0.61	0.40	0.38
Pitt #8	1451	63-75	660	515	84.7	1.71	84.47	1.72	14	0.61	0.40	0.40
Pitt #8	1451	63-75	660	515	84.7	1.71	84.16	1.74	14	0.61	0.40	0.41
Pitt #8	1451	63-75	1053	335	84.7	1.71	85.5	1.76	14	0.61	0.40	0.40
S.Rol	1520	20-30	507	580	73.67	1.11	78.21	0.63	12	0.55	0.28	0.15
S.Rol	1520	20-30	569	545	73.67	1.11	78.53	0.68	12	0.55	0.28	0.16
S.Rol	1520	20-30	660	515	73.67	1.11	78.15	0.79	12	0.55	0.28	0.19
S.Rol	1520	20-30	660	515	73.67	1.11	77.78	0.81	12	0.55	0.28	0.19
S.Rol	1520	20-30	895	410	73.67	1.11	78.5	0.82	12	0.55	0.28	0.20
S.Rol	1520	20-30	1053	335	73.67	1.11	78.92	0.98	12	0.55	0.28	0.23
L.Kitt	1516	20-30	569	545	88.88	1.49	89.38	1.39	15	0.8	0.27	0.25
L.Kitt	1516	20-30	660	515	88.88	1.49	88.78	1.29	15	0.8	0.27	0.23
L.Kitt	1516	20-30	796	450	88.88	1.49	89.6	1.44	15	0.8	0.27	0.26
L.Kitt	1516	20-30	796	450	88.88	1.49	89.75	1.46	15	0.8	0.27	0.26
L.Kitt	1516	20-30	895	410	88.88	1.49	90.12	1.48	15	0.8	0.27	0.26

* NMR data taken from Fletcher, et al.⁵⁴

Table	F.	2
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Summary of Tar Data from Chen⁷⁰ Used to Calculate M_{cl}^{N} .*

					Coal (daf)		Tar	(daf)			N/Cluster	
Coal	ID #	Size	Time	Tw	%C	%N	%C	%N	C _{cl}	f _a '	Coal	Tar
		(µm)	(ms)	(°C)								
Dietz	1488	75-106	61	1567	69.5	0.97	57.2	0.6	12	0.55	0.26	0.20
Dietz	1488	75-106	66	1567	69.5	0.97	71.4	0.78	12	0.55	0.26	0.20
Dietz	1488	75-106	72	1567	69.5	0.97	69.5	0.77	12	0.55	0.26	0.21
Dietz	1488	75-106	77	1567	69.5	0.97	70.1	0.79	12	0.55	0.26	0.21
Dietz	1488	75-106	83	1567	69.5	0.97	74.5	0.83	12	0.55	0.26	0.21
Dietz	1488	75-106	83	1567	69.5	0.97	69.4	0.7	12	0.55	0.26	0.19
Dietz	1488	75-106	83	1567	69.5	0.97	75.1	0.81	12	0.55	0.26	0.20
Dietz	1488	75-106	86.5	1567	69.5	0.97	74.5	0.86	12	0.55	0.26	0.22
Dietz	1488	75-106	89	1567	69.5	0.97	79.4	1.05	12	0.55	0.26	0.25
Dietz	1488	75-106	89	1567	69.5	0.97	71	0.84	12	0.55	0.26	0.22
Dietz	1488	75-106	89	1567	69.5	0.97	75.9	0.99	12	0.55	0.26	0.24
Ill #6	1493	75-106	61	1567	74.1	1.52	73.4	1.13	13	0.65	0.35	0.26
Ill #6	1493	75-106	66	1567	74.1	1.52	72.3	1.12	13	0.65	0.35	0.27
Ill #6	1493	75-106	72	1567	74.1	1.52	74.4	1.18	13	0.65	0.35	0.27
Ill #6	1493	75-106	72	1567	74.1	1.52	75.8	1.26	13	0.65	0.35	0.28
Ill #6	1493	75-106	77	1567	74.1	1.52	76.1	1.26	13	0.65	0.35	0.28
Ill #6	1493	75-106	77	1567	74.1	1.52	75.4	1.27	13	0.65	0.35	0.29
Ill #6	1493	75-106	83	1567	74.1	1.52	76.5	1.27	13	0.65	0.35	0.28
Ill #6	1493	75-106	83	1567	74.1	1.52	75.9	1.27	13	0.65	0.35	0.29
Ill #6	1493	75-106	83	1567	74.1	1.52	75.8	1.25	13	0.65	0.35	0.28
Ill #6	1493	75-106	86.5	1567	74.1	1.52	75.4	1.29	13	0.65	0.35	0.29
Ill #6	1493	75-106	86.5	1567	74.1	1.52	75.6	1.31	13	0.65	0.35	0.30
Ill #6	1493	75-106	89	1567	74.1	1.52	78.3	1.39	13	0.65	0.35	0.30
Ill #6	1493	75-106	89	1567	74.1	1.52	80.7	1.5	13	0.65	0.35	0.32
Ill #6	1493	75-106	89	1567	74.1	1.52	78.3	1.4	13	0.65	0.35	0.31

* NMR data taken from Fletcher, et al.⁵⁴ (cont. on next page)

~ j - - - - - - - - 					-			-				
					Coal	(daf)	Tar	(daf)			N/Cluster	
Coal	ID #	Size	Time	Tw	%C	%N	%C	%N	C _{cl}	f _a '	Coal	Tar
		(µm)	(ms)	(°C)								
Pitt #8	1451	75-106	56	1567	82.5	1.77	74.2	1.2	13	0.61	0.39	0.30
Pitt #8	1451	75-106	61	1567	82.5	1.77	78.9	1.34	13	0.61	0.39	0.31
Pitt #8	1451	75-106	66	1567	82.5	1.77	76.1	1.26	13	0.61	0.39	0.30
Pitt #8	1451	75-106	66	1567	82.5	1.77	77	1.32	13	0.61	0.39	0.31
Pitt #8	1451	75-106	72	1567	82.5	1.77	78.9	1.39	13	0.61	0.39	0.32
Pitt #8	1451	75-106	77	1567	82.5	1.77	78.6	1.39	13	0.61	0.39	0.32
Pitt #8	1451	75-106	77	1567	82.5	1.77	77.7	1.37	13	0.61	0.39	0.32
Pitt #8	1451	75-106	83	1567	82.5	1.77	81.7	2.05	13	0.61	0.39	0.46
Pitt #8	1451	75-106	83	1567	82.5	1.77	77.6	1.39	13	0.61	0.39	0.33
Pitt #8	1451	75-106	83	1567	82.5	1.77	77.1	1.4	13	0.61	0.39	0.33
Pitt #8	1451	75-106	86.5	1567	82.5	1.77	81.2	1.89	13	0.61	0.39	0.43
Pitt #8	1451	75-106	86.5	1567	82.5	1.77	82	1.6	13	0.61	0.39	0.36
Pitt #8	1451	75-106	86.5	1567	82.5	1.77	77.5	1.38	13	0.61	0.39	0.33
Pitt #8	1451	75-106	86.5	1567	82.5	1.77	79.3	1.46	13	0.61	0.39	0.34
Pitt #8	1451	75-106	89	1567	82.5	1.77	84	1.59	13	0.61	0.39	0.35
Pitt #8	1451	75-106	89	1567	82.5	1.77	77.5	1.34	13	0.61	0.39	0.32
Pitt #8	1451	75-106	89	1567	82.5	1.77	79	1.46	13	0.61	0.39	0.34
L.Kitt	1516	75-106	61	1567	88.7	1.72	70.1	0.81	15	0.8	0.31	0.19
L.Kitt	1516	75-106	66	1567	88.7	1.72	79.2	1.12	15	0.8	0.31	0.23
L.Kitt	1516	75-106	72	1567	88.7	1.72	81.1	1.21	15	0.8	0.31	0.24
L.Kitt	1516	75-106	77	1567	88.7	1.72	82.3	1.23	15	0.8	0.31	0.24
L.Kitt	1516	75-106	83	1567	88.7	1.72	84.8	1.25	15	0.8	0.31	0.24
L.Kitt	1516	75-106	83	1567	88.7	1.72	73.5	1.04	15	0.8	0.31	0.23
L.Kitt	1516	75-106	83	1567	88.7	1.72	83	1.25	15	0.8	0.31	0.24
L.Kitt	1516	75-106	86.5	1567	88.7	1.72	77.5	1.26	15	0.8	0.31	0.26
L.Kitt	1516	75-106	86.5	1567	88.7	1.72	82.8	1.19	15	0.8	0.31	0.23
L.Kitt	1516	75-106	89	1567	88.7	1.72	80.8	1.17	15	0.8	0.31	0.23
L.Kitt	1516	75-106	89	1567	88.7	1.72	80.8	1.17	15	0.8	0.31	0.23
L.Kitt	1516	75-106	89	1567	88.7	1.72	84	1.23	15	0.8	0.31	0.24

Table F.2(continued)

Summary of Tar Data from Chen⁷⁰ Used to Calculate M_{cl}^{N} .*

* NMR data taken from Fletcher, et al.⁵⁴

Appendix G

Summary of Coal, Char and Tar Data

The following is a summary of the coal, char and tar data that appears in the written portion of the thesis. This is for reference purposes only.

1. Coal

Experimental Coals and Froperties										
Coal	PSOC #	Rank	%C(daf)	%H(daf)	%N(daf)	%Ash(mf)				
Beulah Zap	1507 D	ligA	69.99	5.59	1.17	15.31				
Wyodak	Argonne	subC	75.01	5.35	1.12	8.77				
Blue #1	1445 D	hvCb	77.29	5.69	1.27	3.62				
Illinois #6	1493 D	hvCb	76.65	4.93	1.47	15.13				
Pittsburgh #8	1451 D	hvAb	84.70	5.40	1.71	4.11				
Pocahontas #3	1508 D	lvb	90.52	4.60	1.60	11.65				

Table G.1.Experimental Coals and Properties

2. Experimental Conditions

Equipment	Maximum Gas Temp. (K)	Residence Time(ms)	Gas Atmosphere
HPCP	850	140	N2
HPCP	900	160	N2
HPCP	1050	210	N2
HPCP	1220	230	N2
FFB	1650	15	0% O ₂

Table G.2Experimental Conditions for the Five PETC Coals

Table G.3Experimental Conditions for the Argonne Premium Wyodak Coal

Equipment	Maximum Gas Temp. (K)	Residence Time(ms)	Gas Atmosphere
HPCP	850	110	N2
HPCP	900	130	N2
HPCP	920	110	N2
FFB	1650	15	0% O ₂
FFB	1650	30	0% O ₂

3. Char Analysis

Table G.4Ultimate Analysis Data of the Chars from the Five PETC Coals and theArgonne Wyodak Coal, the Percent Mass Release (%M.R. of daf coal),
and the Tar Yield (% of daf coal) During Pyrolysis

		(,	. 0	J - J	
	Temp	Time	%C	%Н	%N	%M.R.	%Tar
	(K)	(ms)	(daf)	(daf)	(daf)		
Beulah Zap	850	140	73.79	4.35	0.92	23.01	1.13
	900	160	76.34	3.62	1.29	38.18	4.43
	1050	210	80.89	3.01	1.49	44.75	3.31
	1220	230	92.94	2.27	1.50	54.73	1.53
FFB	1650	15	85.95	1.91	1.33	53.20	n/a
Wyodak	850	110	75.34	4.78	1.34	17.92	n/a
	900	130	76.86	4.34	1.49	26.15	n/a
	920	110	76.70	4.74	1.23	31.67	n/a
FFB	1650	15	80.18	3.85	1.61	49.05	n/a
FFB	1650	30	78.89	3.77	1.36	58.84	n/a
Blue #1	850	140	78.98	5.05	1.44	17.68	2.94
	900	160	79.30	4.83	1.28	23.16	8.41
	1050	210	83.80	3.24	1.83	47.06	15.79
	1220	230	90.09	2.96	1.78	53.85	10.76
FFB	1650	15	91.79	1.71	1.48	59.30	n/a
Illinois #6	850	140	76.77	4.67	1.90	8.95	1.86
	900	160	77.21	4.39	1.56	37.50	9.81
	1050	210	82.16	3.26	1.93	45.51	20.71
	1220	230	93.72	2.63	2.00	53.83	16.22
FFB	1650	15	88.39	1.54	1.62	58.86	n/a
Pittsburgh #8	850	140	84.93	5.43	1.25	21.50	3.09
	900	160	83.73	3.90	1.86	45.90	26.08
	1050	210	88.11	3.32	1.91	45.03	28.36
	1220	230	91.36	2.51	2.06	49.23	21.12
FFB	1650	15	92.44	1.55	1.69	53.80	n/a
Pocahontas #3	850	140	93.46	4.38	1.14	6.60	1.61
	900	160	89.89	4.25	1.13	11.84	2.42
	1050	210	90.16	3.35	1.18	12.96	11.62
	1220	230	95.38	2.77	1.49	16.59	9.54
FFB	1650	15	94.95	1.45	1.12	22.52	n/a

4. Tar Analysis

Jumate Analysi	s Data of th	ie lars iro	m the Five	PEIC COa
	Temp(K)	%C(daf)	%H(daf)	%N(daf)
Beulah Zap	850	70.40	8.17	0.4*
	900	76.29	6.95	0.94
	1050	73.61	5.02	1.23
	1220	76.38	3.81	1.04
FFB	1650	85.13	2.82	0.9*
Blue #1	850	77.03	7.62	0.0*
	900	79.07	7.02	1.22
	1050	80.49	/.07	1.22
	1030	00.47	4.20	1.74
FFB	1650	95.78	2.07	0.37
			,	
Illinois #6	850	68.54	5.35	1.38
	900	79.36	5.66	1.27
	1050	81.645	4.92	1.77
	1220	88.98	4.14	1.78
FFB	1650	95.34	1.34	0.47
Pittsburgh #8	850	82.50	6.13	1.50
	900	86.61	5.48	2.12
	1050	85.46	4.95	1.94
	1220	90.53	3.95	1.94
FFB	1650	95.56	1.39	0.45
Pocahontas #3	850	74*	7*	0.4*
i scanonias #3	900	80.63	4 97	1.05
	1050	89.98	4.90	1.05
	1220	92.25	4.30	1.24
FFB	1650	96.11	1.09	0.45

Table G.5Ultimate Analysis Data of the Tars from the Five PETC Coals

* Due to the limited size of the sample the accuracy of the value is very questionable.

The limited sample size of the Wyodak tars precluded the ability to analyze the tars using CHN techniques.

5. XPS Analysis

XPS	XPS Analysis of Wyodak Chars on a Mole Percent Basis												
Experiment	Temp(K)	Pyridinic	Pyrrolic	Quaternary	Organic O ₂								
HPCP	850	29	58	13	10.8								
HPCP	900	32	56	12	10.0								
HPCP	920	31	57	12	9.8								
FFB 1	1650	31	58	11	11.1								
FFB 2	1650	31	57	12	9.7								

Table G.6XPS Analysis of Wyodak Chars on a Mole Percent Basis

6. ¹³C NMR Analysis

Table G.713C NMR Analysis of Coals, Tars, and Charsa (160 ms at 900 K)

Coal	Sample	fa	f_a^C	f _{a'}	f_a^{H}	f_a^{N}	f_a^{P}	f_a^S	f_a^{B}	fal	f_{al}^{H}	f_{al}^{*}	f _{al} O
Pitt #8	coal	65	3	62	23	39	5	16	18	35	24	11	7
Pitt #8	char	87	5	82	27	55	6	19	30	13	7	6	3
Pitt #8	tar dis.	69	2	67	38	29	5	15	9	31	20	11	na
Pitt #8	tar res.	83	3	80	34	46	8	18	20	17	10	7	2
Pitt #8	tar	73	2	70	37	33	6	16	12	28	18	10	na
Illinois #6	coal	66	3	63	21	42	7	16	19	34	24	1	8
Illinois #6	char	74	4	70	23	47	7	18	22	26	17	9	4
Illinois #6	tar dis.	70	1	69	40	29	4	15	10	30	20	10	na
Illinois #6	tar res.	80	6	74	28	46	8	18	20	20	12	8	3
Illinois #6	tar	74	3	71	35	36	6	16	14	26	17	9	na
Blue #1	coal	60	5	55	19	36	8	13	15	40	29	11	7
Blue #1	char	71	7	64	20	44	8	14	22	29	21	8	4
Blue #1	tar dis.	63	7	56	27	29	8	16	5	37	27	10	na
Blue #1	tar res.	72	6	66	24	42	9	15	18	28	17	11	12
Blue #1	tar	64	7	57	27	31	8	16	7	36	27	10	na

^aPercentage carbon (error): $f_a = total sp^2$ -hybridized carbon (±3); $f_{a'} = aromatic carbon$ (±4); $f_a^C = carbonyl, > 165 ppm (±2); f_a^H = aromatic with proton attachment (±3); <math>f_a^N =$ nonprotonated aromatic (±3); $f_a^P =$ phenolic or phenolic ether, = 150-165 ppm (±2); $f_a^S =$ alkylated aromatic = 135-150 ppm(±3); $f_a^B =$ aromatic bridgehead (±4); $f_{al} =$ aliphatic carbon (±2); $f_{al}^H =$ CH or CH₂ (±2); $f_{al}^* =$ CH₃ or nonprotonated (±2); $f_{al}^O =$ bonded to oxygen, = 50-90 ppm (±2), tar dis. = tar that dissolved in CD₂Cl₂, tar res. = fraction of collected tar that did not dissolve in CD₂Cl₂, tar = weighted combined values of the tar res. and tar dis.

Coal	Sample	Xb	C _{cl}	σ+1	Po	B.L.	S.C.	MW _{cl}	MW _{att}	tar		
										res.		
Pitt #8	coal	0.29	14	4.8	0.48	2.3	2.5	323	32			
Pitt #8	char	0.366	18	5.4	0.76	4.1	1.3	315	18			
Pitt #8	tar dis.	0.134	8	2.4	0.45	1.0	1.4					
Pitt #8	tar res.	0.25	12	3.9	0.73	2.8	1.1			0.25		
Pitt #8	tar	0.163	9	2.8	0.52	1.5	1.3	178	25			
Illinois #6	coal	0.30	15	5.5	0.52	2.9	2.6	368	35			
Illinois #6	char	0.314	15	5.3	0.64	3.4	1.9	326	29			
Illinois #6	tar dis.	0.144	9	2.5	0.47	1.2	1.3					
Illinois #6	tar res.	0.27	13	4.6	0.69	3.2	1.4			0.42		
Illinois #6	tar	0.197	11	3.4	0.56	2.0	1.3	228	30			
Blue #1	coal	0.27	13	5.0	0.48	2.4	2.6	371	42			
Blue #1	char	0.344	17	5.8	0.64	3.7	2.1	402	34			
Blue #1	tar dis.	0.09	7	3.0	0.58	1.7	1.3					
Blue #1	tar res.	0.273	13	4.7	0.54	2.5	2.2			0.12		
Blue #1	tar	0.112	8	3.2	0.58	1.8	1.4	205	35			

Table G.8Derived Properties of Coal, Tar, and Char from the ¹³C NMR analysis^b(160 ms at 900 K)

 ${}^{b}X_{b}$ = fraction of bridgehead carbons, C_{cl} = aromatic carbons per cluster, +1 = total attachments per cluster, P_{o} = 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_{att} = the average molecular weight of the cluster attachments, V = total volatiles yield, Tar = tar collected on filters and corrected for the tar deposited on sampling apparatus, tar dis. = tar that dissolved in CD₂Cl₂, tar res. = fraction of collected tar that did not dissolve in CD₂Cl₂, tar = weighted combined values of the tar res. and tar dis.

Appendix H

Preliminary ¹³C NMR Data

The data presented here are a preliminary set that was used to determine the validity of the high resolution liquid ¹³C NMR analysis process on coal tars. The coals and the conditions at which pyrolysis experiments were performed are found in Table H.1 and H.2. The three coals used in this preliminary study were the same coals described in Table 4.1. The residence times are slightly higher than the experiments described in the thesis, but the maximum gas temperature is similar.

Table H.1.Experimental Coals and Properties

Coal	PSOC #	Rank	%C (daf)	%H (daf)	%N (daf)	%Ash (mf)	%M.R. (daf)
Blue #1	1445 D	hvCb	77.29	5.69	1.27	3.62	29.0
Illinois #6	1493 D	hvCb	76.65	4.93	1.47	15.13	30.8
Pittsburgh #8	1451 D	hvAb	84.70	5.40	1.71	4.11	42.4

Table H.2Experimental Conditions for the Preliminary Study

Equipment	Maximum Gas	Residence	Gas
	Temp. (K)	Time(ms)	Atmosphere
HPCP	920	320	N2

The coal and the char were analyzed with the use of solid-state ¹³C NMR. The tar was dissolved in deuterated methylene chloride and the dissolved portion was analyzed with the use of high resolution liquid ¹³C NMR. This preliminary analysis technique for coal tars did not account for a nonsoluble portion. Therefore the tar residues of this analysis were not analyzed. The analysis method was later modified to account for the tar

residue portion in subsequent samples. This allowed for a more complete analysis of the tar, which is presented in the text.

The results of the ¹³C NMR analysis are shown in Tables H.3 and H.4. Many of the trends from the more complete study in the thesis are also present in these data. Specifically, these data show (a) the low number of aromatic carbons per cluster (C_{cl}) in the dissolved tar; (b) the similar values of aromaticity between the coal, char and dissolved tar; and (c) the lower values of bridges and loops and attachments in the tar when compared to the coal.

0 1	G 1	С	_	C		, 	_		<u> </u>	C	·		-
Coal	Sample	t _a	f_a^C	t _{a'}	f_a^H	f _a N	f _a P	f_a^S	f _a B	t _{al}	f _{al} H	f _{al} *	f _{al} O
Pitt #8	coal	65	3	62	23	39	5	16	18	35	24	11	7
Pitt #8	char	81	5	76	24	52	6	18	28	19	11	8	6
Pitt #8	tar dis.	76	5	71	35	36	10	19	7	24	9	15	na
Illinois #6	coal	66	3	63	21	42	7	16	19	34	24	10	8
Illinois #6	char	78	6	72	25	47	8	19	20	22	13	9	4
Illinois #6	tar dis.	76	6	70	32	38	10	19	9	24	7	14	na
Blue #1	coal	60	5	55	19	36	8	13	15	40	29	11	7
Blue #1	char	77	5	72	24	48	9	20	19	23	15	8	4
Blue #1	tar dis.	62	7	55	24	31	9	15	7	38	9	29	na

Table H.3¹³C NMR Analysis of Coals, Tars, and Chars^a(320 ms, 920 K)

^aPercentage carbon (error): $f_a = total sp^2$ -hybridized carbon (±3); $f_{a'} = aromatic carbon$ (±4); $f_a^C = carbonyl, d > 165 ppm (\pm 2); f_a^H = aromatic with proton attachment (±3); f_a^N = nonprotonated aromatic (±3); <math>f_a^P =$ phenolic or phenolic ether, d = 150-165 ppm (±2); $f_a^S =$ alkylated aromatic d = 135-150 ppm(±3); $f_a^B =$ aromatic bridgehead (±4); $f_{al} =$ aliphatic carbon (±2); $f_{al}^H =$ CH or CH₂ (±2); $f_{al}^* =$ CH₃ or nonprotonated (±2); $f_{al}^O =$ bonded to oxygen, d = 50-90 ppm (±2), tar dis. = tar that dissolved in CD₂Cl₂

Table H.4

Coal Sample Xb P₀ B.L S.C. MW_{cl} **MW**_{att} C_{cl} $\sigma + 1$ 0.290 4.8 0.48 323 32 Pitt #8 coal 14 2.3 2.5 Pitt #8 0.368 5.7 332 20 char 18 0.67 3.8 1.9 Pitt #8 tar dis. 0.100 8 3.3 0.69 2.3 1.0 na na Illinois #6 0.300 15 5.5 0.52 2.9 368 35 coal 2.6 Illinois #6 char 0.278 13 4.9 0.67 3.3 1.6 27123 0.130 8 3.3 2.5 Illinois #6 tar dis. 0.76 0.8 na na Blue #1 0.270 13 5.0 0.48 2.4 2.6 371 42 coal Blue #1 char 0.344 17 5.8 0.64 3.7 2.1 402 34 Blue #1 8 0.63 tar dis. 0.130 3.5 2.2 1.3 na na

Derived Properties of Coal, Tar, and Char from the ¹³C NMR analysis^b

 ${}^{b}X_{b}$ = fraction of bridgehead carbons, C_{cl} = aromatic carbons per cluster, s+1 = total attachments per cluster, P_{o} = 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_{att} = the average molecular weight of the cluster attachments, Tar = tar collected on filters and corrected for the tar deposited on sampling apparatus, tar dis. = tar that dissolved in CD₂Cl₂