

# Title: **Determination of the Forms of Nitrogen Released in Coal Tar During Rapid Devolatilization**

**Authors:** Thomas H. Fletcher  
tom@harvey.et.byu.edu  
Tel.: (801) 378-6236  
Fax: (801) 378-7799  
Brigham Young University  
Chemical Engineering Dept.  
350 Clyde Building  
Provo, UT 84602

## **ABSTRACT**

**OBJECTIVE:** The primary objective of this project is to determine the forms of nitrogen in coal that lead to nitrogen release during devolatilization. Specific questions to be addressed are:

1. Why do low rank coals (i.e., lignites) release as much nitrogen during devolatilization as high volatile bituminous coals when the tar yields are markedly different?
2. Why do coals of similar rank and elemental composition release different amounts of nitrogen during devolatilization?

It is thought that these questions can be answered in terms of the chemical structural features of the coal. This work focuses on determining the chemical structural features of coal tar and char at varying degrees of devolatilization. These features are determined through the use of  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR and XPS. Two reactor systems are utilized in this project. A drop tube reactor (HPCP) is used to produce partially devolatilized samples and a flat flame burner (FFB) is used to provide high temperature, high heating rate pyrolysis products.

## **ACCOMPLISHMENTS AND CONCLUSIONS:**

- Mild pyrolysis experiments (820 to 1200 K, 170 to 412 ms) were performed on four coals (ranging in rank from subbituminous A to low volatile bituminous) and one lignite. The coal, char and tar samples from one pyrolysis condition were analyzed with solid-state  $^{13}\text{C}$  NMR. These NMR data represent the first set of matched coal/char/tar chemical structural data obtained using solid-state  $^{13}\text{C}$  NMR.
- In these analyses, the tar structure was found to be significantly different from the structure of the coal. The carbon aromaticity of the tar was found to be 14 to 53 percent higher than that of the parent coal. This increase in aromaticity in the tars is due to the decrease in the number and size of side chains attached to the aromatic cluster. The average number of aromatic carbons per cluster ( $C_{Cl}$ ) in the tar is similar to  $C_{Cl}$  in the parent coal. The number of side chains per cluster (S.C.) in the tar is 56 to 82 percent lower than the coal on a relative basis. The molecular weight of attachments

(MW) in the tar is observed to be 57 to 68 percent lower than the coal on a relative basis. The fact that  $C_{Cl}$  in the tar and coal are similar and that S.C. and MW are greatly lower in the tar, is consistent with the increased aromaticity of the tars as compared to the parent coals.

- Additionally, the molecular weight per cluster in the tar is lower than reported average tar molecular weights, these data imply that tar is made up of a number of multiple clusters (dimers, trimers, etc.) as well as single clusters (i.e., monomers).
- In these analyses, the char structure was found to be similar to the char structure in many respects. The only major differences between the structures of the char and tar were seen in the cluster attachments (B.L. and S.C.). The number bridges and loops per cluster (B.L.) in the char is generally much larger than B.L. in the tar (0 to 41 percent larger). The number of side chains per cluster (S.C.) in the char is generally lower than S.C. in the tar (28 to 80 percent).
- The mass of nitrogen per cluster in the tar was found to be similar to the mass of nitrogen in the char for the three highest rank coals. This finding and the finding that  $C_{Cl,tar} \approx C_{Cl,coal}$  indicate that several assumptions that are commonly made in coal nitrogen devolatilization models may be reasonable.
- An Argonne Premium Coal (APC) sample of Pocahontas #3 coal was analyzed using  $^{15}N$  NMR with Dynamic Nuclear Polarization (DNP) techniques; this analysis indicates that significant enhancements may be gained with DNP techniques.

## List of Publications, Presentations, and Students

### DOE Contract DE-FG22-95PC95215

#### A. Publications

##### Sponsored by Contract

- Genetti, D., T.H. Fletcher, and R.J. Pugmire, "Predicting  $^{13}\text{C}$  NMR Measurements of the Chemical Structure of Coal Based on Elemental Composition and Volatile Matter Content," submitted to *Energy and Fuels* (April, 1998).
- Hamby, E.M., T.H. Fletcher, M.S. Solum, and R.J. Pugmire, "Chemical Structure of Coal Tar during Devolatilization Using Solid-State  $^{13}\text{C}$  NMR," submitted to the *27th Symposium (International) on Combustion* (December, 1997).
- Kelemen, S.R., M.L. Gorbaty, P.J. Kwiatek, T.H. Fletcher, M. Watt, M.S. Solum, and R.J. Pugmire, "Nitrogen Transformations in Coal during Pyrolysis," *Energy and Fuels*, **12**, 159-173 (1998). (partially sponsored by contract)
- Watt, M., T.H. Fletcher, S. Bai, M.S. Solum, and R.J. Pugmire, "Chemical Structure of Coal Tar During Devolatilization," *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 3153-3160 (1996).

##### Related to Contract

- Brown, A.L. and T.H. Fletcher, "Modeling Soot Derived from Pulverized Coal," accepted for publication in *Energy and Fuels* (1998).
- Fletcher, T.H., J. Ma, J.R. Rigby, A.L. Brown, and B.W. Webb, "Soot in Coal Combustion Systems," *Progress in Energy and Combustion Science*, **23**, 283-301 (1997).
- Baxter, L.L., R.E. Mitchell, and T.H. Fletcher, "Release of Inorganic Material During Coal Devolatilization," *Combustion & Flame*, **4**, 494-502 (1997).
- Ma, J., T.H. Fletcher, and B.W. Webb, "Conversion of Coal Tar to Soot During Coal Pyrolysis in a Post-Flame Environment," *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 3161-3167 (1996).

#### B. Presentations

##### Sponsored by Contract (or cost-sharing on contract)

- Hambly, E.M., Fletcher, T.H., Pugmire, R.J., "Solid-State  $^{13}\text{C}$  NMR Analysis of Coal Tar and Char," accepted for presentation at the National ACS Meeting, Dallas, TX (March 1998).
- Pugmire, R.J., M.S. Solum, D.M. Grant, T.H. Fletcher, and R.A. Wind, " $^{15}\text{N}$  NMR Spectroscopy of Coals and Pyrolysis Products," proceedings of the 9th International Conference on Coal Science, 1:417-420, Essen, Germany (September 7-12, 1997).

- Genetti, D.B., T.H. Fletcher, and R.J. Pugmire, "Predicting  $^{13}\text{C}$  NMR Measurements Based on Coal Elemental Composition," presented at the 8th International Conference on Coal Science, Oviedo, Spain (September 10-15, 1995); in Coal Science, edited by J.A. Pajares and J.M.D. Tascon, **1**, 331-334, Elsevier, New York, (1995).
- Fletcher, T.H., W. Watt, S. Bai, M.S. Solum, and R.J. Pugmire, "Chemical Structure of Coal Tar During Devolatilization," ACS Division of Fuel Chemistry preprints, **41**(2), 752-755, New Orleans, LA (March, 1996).
- Watt, M., T.H. Fletcher, S. Bai, M.S. Solum, and R.J. Pugmire, "Chemical Structure of Coal Tar During Devolatilization," presented at the Twenty-Sixth Symposium (International) on Combustion, Naples, Italy (July, 1996).
- Genetti, D. And T.H. Fletcher, "Predicting  $^{13}\text{C}$  NMR Measurements of Chemical Structure of Coal Based on Elemental Composition Volatile Matter Content," ACS Division of Fuel Chemistry Preprints, **42**:1, 194-198 (April, 1997).

### Related to Contract

- Perry, S. T., T.H. Fletcher, "Modeling of Nitrogen Release during Rapid Coal Devolatilization Based on Detailed Chemical Structural Changes in the Char," accepted for presentation at the National ACS Meeting, Dallas, TX (March, 1998).
- Rigby, J.R., B.W. Webb, and T.H. Fletcher, "Measurement of the Optical Properties of Coal-Derived and Propane-Derived Soot," presented at the Spring Meeting of the Western States Section of the Combustion Institute, Tempe, Arizona, March 11-12 (1996).
- Ma, J., T.H. Fletcher, and B.W. Webb, "Conversion of Coal Tar to Soot During Coal Pyrolysis in a Post-Flame Environment," presented at the Twenty-Sixth Symposium (International) on combustion, Naples, Italy (July, 1996).
- Brown, Alexander L. And T.H. Fletcher, "Modeling Soot in Coal Combustion Flames," presented at the Fall Meeting of the Western States Section of the Combustion Institute, University of Southern California, Los Angeles, CA (October 28-29, 1996).

### **C. Students Receiving Financial Support from Grant**

<i>Name</i>	<i>Degree Sought</i>	<i>Major</i>
James Anderson	BS	Chem Eng
Michael Busse	BS	Chem Eng
Dominic Genetti	BS	Chem Eng
Hugh Palmer	BS	Chem Eng
Catherine Poulos	BS	Chem Eng
Todd Salisbury	BS	Chem Eng
Daniel Sullivan	BS	Chem Eng
Eric Hambly	MS	Chem Eng
Mathew Watt	MS (graduated)	Chem Eng
Steve Perry	PhD	Chem Eng

## **D. Student Theses and Dissertations**

### Sponsored by Contract (or cost-sharing contract)

- Watt, M., "The Chemical Structure of Coal Tar and Char During Devolatilization," M.S. Thesis, Chemical Engineering Department, Brigham Young University (August, 1996).
- Hambly, Eric M. "The Chemical Structure of Coal Char and Tar during Devolatilization," M.S. Thesis, Chemical Engineering Department, Brigham Young University (April, 1998).

### Related to Contract

- Ma, J. , "Soot Formation During Coal Pyrolysis, "Ph.D. Dissertation, Chemical Engineering Department, Brigham Young University (August, 1996).
- Brown, Alexander L., "Modeling Soot in Pulverized Coal Flames, "M.S. Thesis, Mechanical Engineering Department, Brigham Young University (August, 1997).