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

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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 hva 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}C and ^{15}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 (900 K, 160 ms) were performed on three bituminous coals. The coal and char were analyzed with solid-state ^{13}C NMR. The tar was partially dissolved in deuterated methylene chloride (CD_2Cl_2). The nonsoluble tar portion was analyzed in the same manner as the coal and char, while the soluble portion was analyzed using a recently developed high-resolution 13C NMR technique developed for liquid phases. This is the first time these kind of data have been available.
- In these analyses, the tar structure was found to be significantly different from the structure of the char and coal. The number of bridges and loop per cluster in the tar was up to 65% lower than in the char. In addition, the number of aromatic carbons per cluster in the tar was significantly lower than that found in either the coal of the char. Since 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).

- Additionally, the mass of nitrogen per cluster in the tar was found to be significantly lower in the tar than in either the coal or the char. These experimental findings suggest that changes may be necessary in current network devolatilization models to accurately describe the changes in chemical structure.
- The Argonne Premium Coal (APC) samples were analyzed using ^{15}N NMR; these are the first published ^{15}N NMR data on the APC samples.
- The Argonne Premium Coal (APC) samples were treated with strong acid and analyzed using ^{15}N NMR. This resulted in an increase in the signal from the pyridinium (quaternary) type nitrogens, thus implying that pyridine type nitrogens are present in the coal but are undetectable by standard solid state NMR techniques. These experimental results indicate that ^{15}N NMR analyses are now in general agreement with XPS data which indicate that approximately 25% of the nitrogens are present as pyridine types.
- A preliminary nitrogen-specific chromatography analysis of coal tars was completed. This analysis showed that there are extremely complex mixtures of nitrogen-containing compounds in coal tar. Due to this extreme complexity, the quantitative resolution of the resulting chromatograms was poor. However, despite the lack of good resolution, thirty nitrogen-containing polycyclic aromatic compounds were tentatively identified in these tars. These compounds were mainly pyridinic and pyrrolic, with numbers of fused aromatic rings ranging from 2 to 5.