(特別講演1)

**CHANGES IN THE STRUCTURE OF NITROGEN SPECIES IN COAL DURING PYROLYSIS**

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**Synopsis:** X-ray Photoelectron Spectroscopy was used to characterize nitrogen forms in coals and their pyrolysis tars and chars. Transformations of nitrogen forms during various pyrolysis stages have been defined.

X-ray Photoelectron Spectroscopy (XPS) was used to identify and quantify the changes in organically bound nitrogen forms present in the tars and chars of coals after pyrolysis. The reproducibility and repeatability of the nitrogen curve resolution results (± 3 mole %) is the same as in a previous investigation of fresh Argonne premium coal samples [1]. For fresh Argonne Premium coals, pyrrolic nitrogen was found to be the most abundant form of organically bound nitrogen, followed by pyridinic, and quaternary types. The distributions were found to be rank-dependent, with the highest abundance of quaternary nitrogen in the lowest rank coals. Some of the quaternary nitrogen species initially present in these coals were lost upon mild pyrolysis, prior to hydrocarbon devolatilization. These quaternary species were attributed to pyridinic or basic nitrogen species associated with hydroxyl groups from carboxylic acids or phenols.

In this study, coals were pyrolyzed in a temperature programmed decomposition (TPD) apparatus [2] at 0.23 °C/sec up to a specified temperature then cooled. Several temperatures from 400-810 °C were chosen. Tars and chars from each pyrolysis
temperature were collected and analyzed for nitrogen forms distribution by XPS. A portion of the quaternary nitrogen species is lost at the very earliest stage of pyrolysis. Upon devolatilization (T<500 °C), the resultant tar and char contain mostly pyrrolic and pyridinic forms, however, a portion of the quaternary nitrogen initially present in the coal appears in the coal char and tar. This may be due to recombination of pyridines with phenols in the tars low rank coal or may indicate that relatively strong bonding interactions associated with quaternary species. For low rank coal, amino groups are preferentially released and concentrate in the tar.

Pyrolysis of the devolatilized char (T >600 °C) results in the appearance of an asymmetric carbon (1s) line shape in the XPS spectrum indicative of very large polynuclear “graphitic-like” units. This transformation is accompanied by a rise in the relative number of quaternary nitrogen forms in the chars, as first noted by Pels, et al. [3] and quaternary and pyridinic nitrogen forms become the dominant forms in severely pyrolyzed chars. These changes occurs over a relatively narrow temperature range (600-700 °C). The significant disappearance of pyrrolic nitrogen in these high temperature chars confirm the suggestion of Pels, et al., that pyrrolic nitrogen is partly converted into pyridinic nitrogen. Quaternary forms arise from incorporation of pyridinic nitrogen into the growing polynuclear aromatic structures.