CHARACTERIZATION AND REACTIVITY OF ORGANICALLY BOUND SULFUR AND NITROGEN IN FOSSIL FUELS

Martin L. Gorbaty and Simon R. Kelemen
Exxon Research and Engineering Company
Rt. 22 East; Clinton Twp.
Annandale, NJ 08801

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Introduction

The chemistries of organically bound sulfur and nitrogen forms impact significantly on the reactivity of and utilization strategy for fossil fuels. Previous inability to speciate and quantify the chemical forms of these heteroatoms coupled with the lack of a suite of standardized, well preserved, well characterized coals of varying rank limited the gaining of understanding of important fundamental chemical mechanisms. Advances in X-ray instrumentation over the last decade, along with the establishment of the Argonne Premium Coal Sample Program have allowed the determination and quantification of organically bound sulfur and nitrogen forms in fossil fuels and has led to deeper understanding of their reactivities. This paper reviews recent technical advances in this area and highlights several areas were significant progress in chemical understanding has been achieved and speculates about future trends.

Organically Bound Sulfur Characterization

In the last decade, major advances have been made in speciating and quantifying forms of organically bound sulfur in fossil fuels, involving both reactive and direct measurements. One reactive method uses flash pyrolysis[1], while the direct measurements involve XPS[2], K-Edge X-ray Absorption Near Edge Structure Spectroscopy (XANES)[3, 4] and L-Edge XANES[5]. The XPS and sulfur K-edge XANES methods were used to determine the forms of sulfur in the suite of Argonne Premium coals[6], and the results from XPS and two different K-edge XANES methods are plotted together in Figure 1. The accuracy of the latter methods is reported to be ±10 mole%. It was concluded that in low rank coals there are significant amounts of aliphatic sulfur (i.e., dialkylsulfides), and that levels of aromatic sulfur (i.e., thiophenes and diarylsulfides) increase directly as a function of increasing rank [3, 4]. The X-ray methods have been used to follow the chemistry of organically bound sulfur under mild oxidation in air[7], where it was shown that the aliphatic sulfur oxidizes in air much more rapidly than the aromatic sulfur, pyrolysis [8, 9], single electron transfer and strong base[10] conditions. Recently, results from the XPS and K-edge XANES methods have been shown to compare favorably with those from flash pyrolysis[11], mass spectrometry[12], and temperature programmed reduction (TPR)[13, 14]. This is a particularly important development since an approach to sulfur speciation using these techniques may be much more readily available than X-ray methods. In the future, speciation and quantification of organically bound sulfur by a pyrolysis GC/MS analysis or TPR approach may develop into a standard laboratory method.

Organically Bound Nitrogen Characterization

It is necessary to know how nitrogen is incorporated in the organic matrix, since it has been apparent for some time that nitrogen species play a role in coal asphaltene behavior[15] and in coal conversion chemistry[16]. X-Ray Photoelectron Spectroscopy (XPS) was used to speciate and quantify accurately the forms of organically bound nitrogen[17, 18], including the basic pyridines and quinolines and the weakly acidic or neutral indoles and carbazoles. These measurements, done on a suite of UK coals containing 80wt% or more carbon, indicate that basic nitrogen increases as pyrrolic nitrogen decreases as a function of carbon content. The organically bound nitrogen forms in the Argonne Premium coal samples[6] were determined by XPS[19]. The quantitative distributions of nitrogen types in Argonne Premium coals from XPS analyses are plotted in Figure 2 as a function of wt% Carbon. 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. It is clear from Figure 2 that the distributions are rank-dependent, with the highest abundance of quaternary nitrogen in the lowest rank coals. The concentrations of this form decrease while pyridinic, or basic nitrogen forms appear to increase correspondingly as a function of increasing rank. The quaternary species were attributed to protonated pyridinic or basic nitrogen species associated with hydroxyl groups from carboxylic acids or phenols[19]. Similar distributions from XPS analysis of coal as a function of rank were independently confirmed [32]. The predominance of pyrrolic and pyridinic nitrogen forms in Argonne

Premium coal was verified by recent desorption high-resolution mass spectrometry both with whole coals and their pyridine extracts [33]. The sensitivity of the XPS approach for amino nitrogen species in fossil material has been established [28, 29]. Samples of recent sediments with up to 45% amino nitrogen [29] and pyrolysis tars of kerogen with up to 33% amino nitrogen [28] have been reported.

X-ray Absorption Near Edge Structure spectroscopy (XANES) has also been used for characterization of nitrogen forms in petroleum asphaltenes[20a] and Argonne Premium coals[20b]. These early nitrogen XANES results are not in total accord with those from XPS. Pyrrolic nitrogen appears to be the major form of organically bound nitrogen measured by both techniques. However, the XANES results report, in addition to pyrrolic and pyridinic nitrogen, the presence of aromatic amines and also pyridone forms, the latter in amounts similar to pyridinic nitrogen. In addition, the XANES results do not report the presence of quaternary nitrogen. While the XPS results were largely confirmed by high resolution mass spectrometry[33], opportunities remain for further development of an XANES approach for nitrogen speciation.

Solid state ^{15}N nmr offers much promise for characterizing nitrogen forms. The difficulties in developing a solid state ^{15}N nmr technique for the characterization of nitrogen forms in coals have been discussed, and progress is being made[21]. An earlier attempt to characterize the nitrogen forms in three Penn State coal bank coals by solid state ^{15}N nmr reported the observation of pyrrolic but not pyridinic nitrogen forms[22]. This appeared to be in contradiction with XPS and XANES data, however more careful work on Argonne Premium coals and their acidified derivatives showed the presence of pyridinic nitrogens. In the future, it is expected that the current hurdles will be overcome and that the technique will be used almost routinely for characterizing organically bound nitrogen forms.

X-ray Photoelectron Spectroscopy (XPS) was used to help define the possible correlation between the functional forms of nitrogen in coals and the formation of NO_x precursors during combustion processes [23, 30, 31]. These studies showed that the impact of structural variation in nitrogen forms initially present in coal was secondary to the effect of other coal combustion factors [30, 31]. XPS has also been used to characterize the forms of nitrogen found on carbon surfaces after treatment with NO_x [24]. XPS was used to identify and quantify the changes in organically bound nitrogen forms initially present in the Argonne coals in their tars and chars after pyrolysis[25]. In that study, coals were pyrolyzed in a temperature programmed decomposition (TPD) apparatus[26] at 0.23°C per second 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. 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[19]. Representative changes in the nitrogen forms in two Argonne coal chars as a function of temperature are shown in Figure 3. Some of the quaternary nitrogen species are lost at the very earliest stage of pyrolysis, however, the major changes occur over a relatively narrow temperature range (600-700°C). Above 600°C the loss of pyrrolic forms is accompanied by a rise in the relative number of quaternary nitrogen forms in the chars, as noted by Pels, *et al.*[27] and Kambara, *et al.*,[23], and the quaternary and pyridinic nitrogen forms become the dominant forms in severely pyrolyzed chars. The significant disappearance of pyrrolic nitrogen in these high temperature chars confirms the suggestion of Pels, *et al.*[27], that pyrrolic nitrogen is partly converted into pyridinic nitrogen. Quaternary forms are proposed to arise from incorporation of pyridinic nitrogen into the growing polynuclear aromatic structures.

Future Outlook

In summary, methods are available today to get the kind of detailed information on important coal structural features that was not available just a few years ago. They are been applied to a standard suite of coals, and this represents an important advance in order to define the parametric variations as a function of coal rank. Exciting new opportunities now exist for elucidating and understanding the detailed chemistry taking place during conversion procedures by using these methods to characterize the reaction products as well as the starting coals. Mechanistic inferences and structure-reactivity relationships can be built based on this information.

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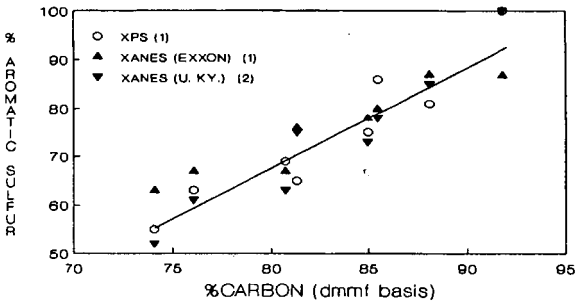

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2) *Energy Fuels*, **1991**, *5*, 574.

Figure 1. Organic Sulfur Speciation and Quantification by S-XANES (refs. 3, 4)

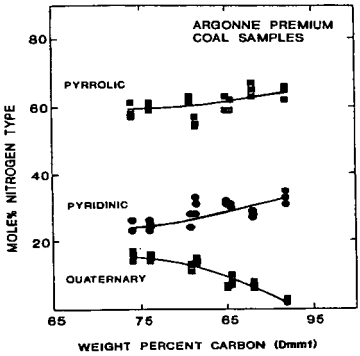

Figure 2. Organic Nitrogen Speciation and Quantification by XPS. (ref. 19)

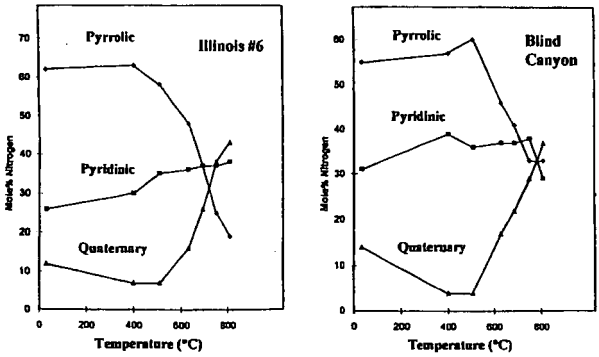

Figure 3. Tracking the Reactivity of Organically Bound Nitrogen Species (ref. 25)