

## DETERMINATION OF NITROGEN AND SULPHUR FUNCTIONALITY IN COAL AND COAL LIQUIDS

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### INTRODUCTION

The type and distribution of nitrogen and sulphur functional groups in raw coal and their fate during processing have vital implications for the environmental impact of coal utilisation, as well as for the mechanism of the processes themselves. The combustion of nitrogen and sulphur rich fuels is known to release many hetero-PAC's, NO, and SO<sub>x</sub> compounds into the atmosphere. NO and SO<sub>x</sub> can be formed from the oxidation of nitrogen and sulphur compounds present in the fuel and, in the case of NO<sub>x</sub>, also from atmospheric nitrogen (thermal NO<sub>x</sub>). Whilst conventional petroleum derived fuels contain low enough heteroatom concentrations for thermal NO<sub>x</sub> to predominate, in typical liquid fuels derived from coal, which have much higher heteroatom contents, fuel derived NO<sub>x</sub> and SO<sub>x</sub> are dominant<sup>1</sup>. Furthermore, combustion of fuel bound nitrogen under fuel rich conditions can lead to the formation of HCN and NH<sub>3</sub>, as well as NO<sub>x</sub>.

The ultimate fate of the nitrogen and sulphur functional groups in coals and coal derived liquids is, however, dependent on the types of functional groups in which they are present. Non-basic nitrogen functions are thought to be the major source of NO<sub>x</sub> emissions during combustion whilst reactive sulphur compounds, such as mercaptans, cause excessive metal corrosion during processing. In addition, some nitrogen and sulphur compounds (e.g. nitrogen bases) are known to reduce the useful lifetime of the catalysts used during the refining processes<sup>2</sup>.

In this paper we report on methods which allow the analysis of nitrogen and sulphur functional groups in samples ranging from raw coals to process derived liquids and solids. X-ray photoelectron spectroscopy (XPS) has been combined with potentiometric titration and infra-red spectroscopy to provide a self consistent quantitative analysis of nitrogen functionality. Sulphur functional group distributions have been determined by temperature programmed reduction (TPR) and the method has been applied to study the hydrogen donor liquefaction of coal. The potential of using XPS as a method for the study of sulphur functional groups is also discussed.

### EXPERIMENTAL

#### 1) Materials

Two SRC process solvent residues (A, 397 °C; B, 351 °C), a coal liquid produced in a tubing bomb shaking autoclave from Burning Star coal, a Belgian (Beringen) coal and its SRC product were

studied. To facilitate nitrogen functional group determination, the samples were separated into n-pentane soluble, asphaltene and preasphaltene fractions<sup>3</sup>. The asphaltenes were further separated by a fractionation scheme outlined elsewhere<sup>4,5</sup>. The scheme produced three nitrogen-rich fractions consisting of strong bases, weak bases (as quaternary salts) and neutrals. The fractions were then analysed by the methods outlined below.

## 2) X-Ray photoelectron spectroscopy

Photoelectron spectra were recorded on a Kratos ES300 spectrometer using AlK<sub>α</sub> radiation. The spectrometer was run in fixed analyser transmission mode at a pass energy of 65eV, slit width 1.75 mm with an X-ray source power of 300 W. Powdered samples were mounted by pressing onto double sided adhesive tape and introduced into the spectrometer via a rapid insertion probe. Coal samples were ground under heptane in a ball mill to < 5µm and stored under heptane before use to minimise the effects of surface oxidation. Spectra were recorded at a pressure of less than  $1 \times 10^{-5}$  Pa. Data acquisition was controlled by a Kratos DS300 data system which was also used for spectral quantification and analysis. In order to obtain N(1s) spectra of sufficient quality to permit resolution of the different nitrogen components, long data acquisition times were required. For samples of the lowest nitrogen concentration this amounted to several hours of data accumulation. The nitrogen peak was resolved using a peak synthesis routine employing symmetric components of Gaussian line shape at fixed binding energies determined from model compound studies<sup>5</sup>. The intensities of the components were varied in order to obtain the best fit to the experimental spectrum while constraining the full widths at half maximum of all the components to be within the limits 1.8 to 2.0eV.

## 3) Infra-Red Spectroscopy

Quantitative infra-red spectra were recorded to determine the amount of nitrogen present as non-basic N-H. Spectra were recorded on a Perkin Elmer 1750 Fourier Transform Infra-red Spectrometer. Samples were dissolved in deuteriochloroform at low concentration (<30mg/10ml), to reduce hydrogen bonding, and spectra recorded in a 1 cm quartz cell.

Quantification of the N-H stretch ( $3460-3480 \text{ cm}^{-1}$ ), for fossil fuel derived samples, was achieved from a calibration graph of absorbance at this wavelength versus NH concentration determined, by XPS. In all cases samples were methylated using diazomethane<sup>7</sup> before analysis to remove the interfering OH absorptions.

## 4) Potentiometric Titration

Non-aqueous potentiometric titration was used to determine the basic nitrogen content of soluble samples<sup>6</sup>, including those samples of low molecular mass which were not amenable to study by XPS because of higher vapour pressure. Between 100mg and 500mg (depending on nitrogen content) of the sample was dissolved in a small quantity of benzene or chloroform before the addition of 50-75cm<sup>3</sup> of the titration medium, glacial acetic acid. The titrant, 0.05M perchloric acid in glacial acetic acid, was added

via an automatic titration system and the end point detected using a combined glass and a calomel electrode.

#### 5) Temperature Programmed Reduction

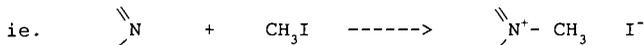
Temperature programmed reduction experiments were performed in a 3ml stainless steel reactor designed to give optimum recovery of sulphur. The samples (between 5mg and 75mg depending on sulphur content) were mixed with a reducing solvent mixture (phenanthrene, resorcinol, 9,10 dihydrophenanthrene, tetralin and pyrogallol) in the reaction vessel and sonicated for one hour. The reduction experiment was performed by fitting the reaction vessel to a stainless steel condenser arrangement and applying a temperature ramp of 7 °C/min to the cell. Any H<sub>2</sub>S evolved was flushed from the cell by a stream of preheated nitrogen (30 ml/min) and make-up nitrogen was added (30 ml/min) to the gas stream immediately following the condenser system. The H<sub>2</sub>S was detected by measuring the sulphide ion in an alkaline sulphur antioxidant buffer (SAOB) using a sulphur-specific electrode system. The sulphide electrode was calibrated by adding small amounts of sodium sulphide to the SOAB solution via an automatic burette. The electrode response was checked at the beginning and end of each run by adding a known concentration of sodium sulphide. Changes in the cell potential and reactor temperature were recorded by a computer data capture system and the data were subsequently output as plots of sulphur concentration versus temperature or as the integrated signal.

### RESULTS AND DISCUSSION

#### 1) Quantification of Nitrogen Functional groups

##### i) XPS of Nitrogen Containing Functional Groups

Table I shows the ultimate analysis data for the coal and coal derived products studied. In every case these products gave rise to a single, broad, N(1s) peak in their XPS spectra. In all cases, except for the quaternarised samples, the N(1s) spectra could be resolved into two major components at binding energies of 400.2eV and 398.8eV corresponding to nitrogen in pyrrole and pyridine type structures respectively<sup>5</sup>. The proportions of the two components were calculated for each fraction and are shown in Table I. The XPS spectra of the fractions quaternarised with methyl iodide are more complex since the reaction produces a pyridinium ion



This produces a shift in the pyridine N(1s) binding energy from 398.8eV to 401.4eV and the associated iodine concentration provides a further quantification of the pyridine groups. Since the pyridinium ion is unstable in the X-ray beam, however, the N(1s) spectrum consists of four components. From model compound studies using quaternarised phenanthridine, these were found to be, in order of decreasing binding energy, the quaternary salt

(401.4eV), pyrrole types (400.2eV), the degradation peak (399.5eV), and a small component due to residual pyridine types. The peak synthesis is simplified, however, because the quaternary and degradation product peaks are coupled and their ratios may be determined by analysis of the I(3d<sub>5/2</sub>) peak. The result of N(1s) peak synthesis on the quaternarised Burning Star asphaltene is shown in Figure 1. The amount of pyridinium ion calculated from the iodine peak is in excellent agreement with that calculated by N(1s) peak synthesis alone, validating the N(1s) peak assignments. As a check of the XPS results, the basic nitrogen contents of some of the asphaltene fractions were determined by potentiometric titration. The amount of basic nitrogen determined directly agrees well with the XPS results (correlation coefficient 0.95), further confirming the validity of the XPS procedure. XPS, however, unlike the titration method, is not limited by the solubility of the samples.

#### ii) Infra-Red Spectroscopy

Since a simple two component model was found to fit the XPS data for all samples, the pyrrole to pyridine ratios obtained in this way can be viewed with some certainty. The volatile nature of some of the lower molecular mass coal derived fractions, however, makes them difficult to study by XPS. Because of this, the pyrrole contents, as determined by XPS, were used to calibrate the infra-red NH stretch (3480cm<sup>-1</sup>). Figure 2 shows the plot of absorbance versus the XPS determined NH concentration for the range of coal derived asphaltene fractions studied. Several of the samples were recorded over a range of concentrations to establish the validity of the Beer-Lambert relationship for these materials. The linearity of these plots indicates that the solutions were sufficiently dilute to prevent significant intermolecular hydrogen bonding. Using the Beer-Lambert law the specific absorption coefficient per gram of NH was calculated to be  $6.9 \pm 0.4 \text{ dm}^3\text{g}^{-1}\text{cm}^{-1}$ . With this value it is possible to use infra-red spectroscopy as an independent method of calculating [NH]. Furthermore, comparison of the XPS and FT-IR data obtained from shale oil asphaltene suggests that the extinction coefficient may be generally applicable to high molecular mass fossil fuel samples.

## 2) Analysis of Sulphur Containing Functional Groups

### i) Temperature Programmed Reduction of Sulphur Functional Groups

The Beringen coal and its SRC product were analysed by temperature programmed reduction (TPR). The TPR kinetogram of the coal showed two resolved peaks at 380°C and 420°C, corresponding to the reduction of organic sulphur functional groups and pyrite respectively. In contrast to this, the TPR kinetogram of the SRC product obtained from the same coal contained no pyrite peak and the peak due to the reduction of the organic components was shifted to lower temperatures, consistent with a change in sulphur functional group distributions. From model compound data, this peak shift suggests the formation of aromatic sulphide groups from thiophene structures.

### ii) XPS of sulphur containing functional groups

Since XPS can analyse for all elements except hydrogen and helium, it offers a potential method for the determination of sulphur functional groups in fossil fuels. Frost et al<sup>7</sup> and Perry and Grint<sup>8</sup> demonstrated that there was a correlation between surface and bulk sulphur contents over a range of coals. XPS has also been applied to the study of sulphur in diesel particulates<sup>9</sup>, and, more recently, to determine the role of sulphur compounds in liquid fuel stability<sup>10</sup>.

Analysis of the S(2p) spectra of of the coal-derived samples discussed in section 1 above reveals that in most cases sulphur is present in one valence state, with binding energies centred at between 162.4eV and 164.7eV, depending on the individual sample, and corresponding to various organic sulphur (II) types (i.e. thiols, sulphides, disulphides or thiophenes). As shown in Figure 3a, however, in some samples, two peaks were observed, one centred at 164.5eV and the other at 169.3eV. These correspond respectively to organic sulphur (II) and oxidised sulphur (IV and VI) species. Comparison of the binding energy of the oxidised sulphur peak (169.3eV) with those for model compounds<sup>11-13</sup> reveals that this peak is probably due to sulphones (R-SO<sub>2</sub>-R). Jones et al<sup>11</sup> showed that the performic acid/ methanol oxidation of thiophene structures yields sulphones in a two step process which goes via the sulphoxide. The sulphur peak at 169.3eV may, therefore, be tentatively assigned to the oxidation products of thiophenes (or sulphides) in the original asphaltene.

From consideration of the chemical shift data for sulphur containing model compounds, it is apparent that the chemical shift range for the possible fossil fuel sulphur types is not as great as was observed for nitrogen species. Furthermore, the larger number of possible functional groups would complicate the analysis. It is unlikely, therefore that a simple analysis by peak synthesis methods will be as effective as it was for nitrogen functional groups. As sulphur can exist in several different stable oxidation states, however, there is a potentially greater S(2p) chemical shift range accessible. Figure 3b shows the S(2p) spectrum of the SRC asphaltene 'A', after reaction with methyl iodide in which sulphur (II) is converted to sulphur (IV). As with the nitrogen compounds, an obvious peak shift to higher binding energies is evident. This shift is consistent with the formation of a sulphonium salt of the form RR'S<sup>+</sup>Me I<sup>-</sup>. Clearly, derivatisation reactions of this type can be readily followed by XPS. If XPS analysis is combined with a suitable fractionation scheme, or a series of selective derivatisation/oxidation reactions, it will provide a method from which valuable information about the distribution of sulphur types in coal and its derivatives may be obtained.

### ACKNOWLEDGEMENTS

The authors thank the Science and Engineering Research Council for support of this work through grants and CASE studentships (S. Wallace and M. Baxby).

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**TABLE I**  
Distribution of Nitrogen Functional Groups

	SRC Asph. 'A'		SCR Asph. 'B'		Burning Star Coal Liquid Asph.				
	Asph. Bases	Asph. Bases	Asph. Bases	Asph. Bases	Raw Coal (dmmf)	Asph. Bases	Quat. Bases	Non-Basic N	
C	85.3	67.3	82.8	79.4	81.7	84.1	48.0	65.1	81.0
H	6.9	7.1	6.2	6.2	5.7	6.4	4.3	4.2	6.1
N	3.1	5.7	2.5	6.7	1.5	1.7	2.8	1.9	1.6
S	-	-	-	-	2.0	2.1	4.4	2.9	1.7
H/C	0.97	1.27	0.90	0.94	0.84	0.91	1.06	0.77	0.90
N/C	0.03	0.07	0.03	0.07	0.02	0.02	0.05	0.03	0.02
% Pyrrolic	62	30	49	35	58	58	35	40	65
% Pyridinic	40	62	50	63	31	34	62	60	33

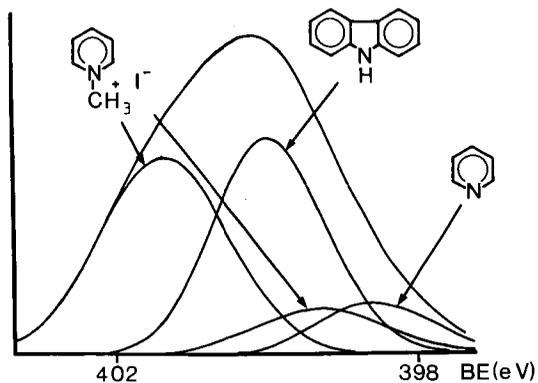


Figure 1. Synthesised N(1s) Spectrum of the Quaternarised Burning Star Asphaltene

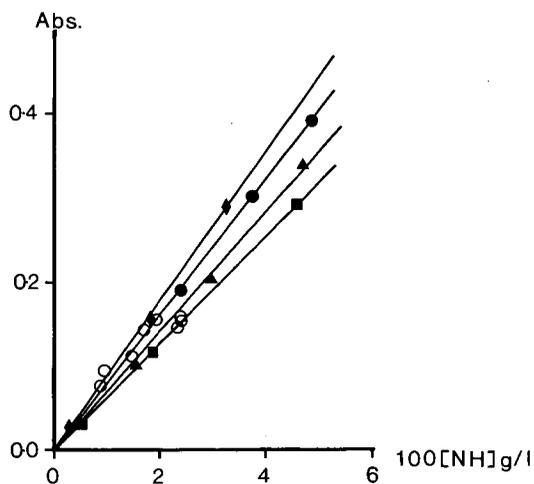


Figure 2. Plot of Absorbance Versus [NH] (Determined by XPS) for a Range of Coal Derived Asphaltene Fractions

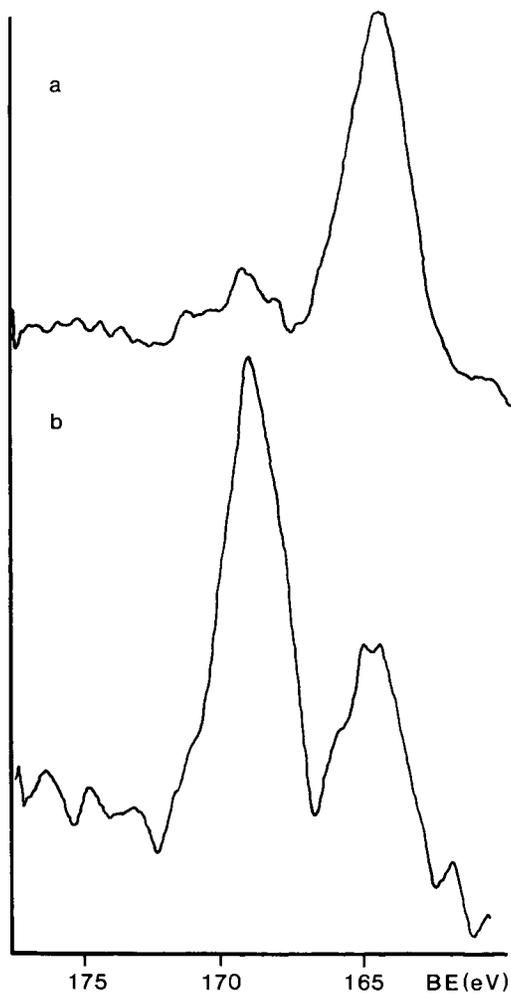


Figure 3. S(2p) Spectra of a) Asphaltenes and b) Quaternarised Asphaltenes