

AN INVESTIGATION OF THE OXYGEN AND NITROGEN GROUPS IN
SUPERCRITICAL GAS EXTRACTS OF COAL BY NMR

T.G. Martin and C.E. Snape

National Coal Board, Coal Research Establishment
Stoke Orchard, Cheltenham, Glos., GL52 4RZ, England.

K.D. Bartle

Department of Physical Chemistry, University of Leeds
Leeds, LS2 9JT, England.

ABSTRACT

In the liquefaction processes under development by the National Coal Board coal extracts, including supercritical gas extracts, are subjected to catalytic hydrocracking. Thus, characterisation of heteroatoms in these extracts is important for identifying species which may give rise to catalyst poisoning. NMR methods are described for nitrogen and oxygen group determinations. Hydroxyl groups in extracts may be completely silylated so that they can be estimated from the OSi(CH₃)₃ band in the ¹H NMR spectrum. The solubility of benzene-insoluble fractions is also significantly increased by silylation so that they can be easily studied by NMR. The ¹⁹F nucleus provides a magnetic label for hydroxyl via reagents such as hexafluoroacetone, and may allow identification of different environments for such groups. ¹³C NMR is suitable for characterising non-phenolic oxygen groups, since the resonances of carbon in carbonyl and aromatic ether groups are well separated. Basic nitrogen can be studied by ¹H and ¹⁹F NMR via hydrogen-bonding interactions with model phenols such as 2,6-xylenol and p-fluorophenol. For neutral nitrogen, labelling with ¹⁹F, using e.g. trifluoroacetyl imidazole, shows promise.

1. INTRODUCTION

Supercritical gas (SCG) extraction of coal with aromatic solvents, such as toluene, at temperatures around 690 K and pressures of about 200 bar (1) gives up to 50% d.a.f. coal as a homogeneous extract, which is then subjected to catalytic hydrocracking to produce liquid products. Characterisation of heteroatoms in the extract is important in helping to identify species which may contribute to catalyst poisoning.

Established titrimetric methods for hydroxyl group (2,3) and basic nitrogen group (4,5) determinations are of great value in structural characterisation of extracts. There are, however, no established procedures for the measurement of non-hydroxylic functions or neutral nitrogen functions. We describe here our attempts to compliment and extend existing functional group methods by utilising the NMR spectroscopic methods which are summarised in Table 1. Hydroxyl groups have been determined by ¹H and ¹⁹F spectroscopy following derivatisation with trimethylsilyl (groups) and adduction with hexafluoroacetone (HFA). Non-hydroxyl groups have been determined directly from ¹³C NMR spectroscopy. Basic nitrogen groups have been estimated from their interaction with 2,6-xylenol by observing the changes in the -OH chemical shift. Preliminary results using an alternative ¹⁹F NMR method with p-fluorophenol have been obtained. Derivatisation with trifluoroacetyl imidazole, which acts as an ¹⁹F magnetic label, is under investigation as a possible route for estimating neutral nitrogen directly.

2. EXPERIMENTAL

The SCG extracts were fractionated by solvent separation and silica gel adsorption chromatography, as previously described (6). Asphaltenes and methylated asphaltenes (prepared by the method used by Liotta (7)) were separated by Sternberg's acid/base procedure (8). Silylation of the extract fractions was carried out as previously (9), and HFA adducts of some asphaltene fractions were prepared by bubbling the gas into ethyl acetate solutions (10). Also, trifluoroacetyl esters of carbazole and indole were prepared by warming at 80°C in pyridine with trifluoroacetyl imidazole for 30 minutes.

¹H NMR spectra were obtained at 60 and 220 MHz using Perkin-Elmer R24B and R34 instruments respectively. For the ¹H NMR studies of basic nitrogen, silylated extract fractions were added to 0.2 molar 2,6-xyleneol in carbon tetrachloride, and changes in the hydroxyl chemical shift were observed. ¹³C NMR spectra were obtained at 45 MHz in chloroform-d using a Bruker WH 180WB instrument under experimental conditions which have been shown to yield quantitative data (11). ¹⁹F NMR spectra were obtained at 84.6 MHz using a Bruker WH90 instrument; furfuryl alcohol was used as an external standard for determination of -OH contents from the spectra of HFA adducts. The procedure described by Gurka and Taft (12) was followed for studying basic nitrogen using 0.01 molar p-fluorophenol where p-fluoroanisole is employed as an internal standard.

Basic nitrogen contents were also determined by non-aqueous potentiometric titration (4,5) and acidic hydroxyl contents were measured by enthalpimetric titration (3,6). Gas chromatographic analysis was carried out on the trifluoroacetyl esters of indole and carbazole.

3. RESULTS AND DISCUSSION

3.1 Hydroxyl Oxygen

The hydroxyl contents determined from the intensity of the -OSi(CH₃)₃ band in the ¹H NMR spectra of extract fractions were in reasonable agreement with the values obtained by enthalpimetric titration (see Table 2), indicating that all the hydroxyl groups in the extracts have been silylated. In addition, silylation gives a significant enhancement of extract solubility (9). The presence of non-acidic (alcoholic) hydroxyl groups was discounted since there was no evidence of -OCH₂ resonances in the ¹³C NMR spectra. Figure 1 is the ¹H NMR spectrum of the silylated benzene-insolubles from an SCG extract of bituminous coal. It shows that the -OSi(CH₃)₃ band, which is well separated from the other aliphatic resonances, has a maximum at 0.3 ppm with a broad shoulder extending to -1 ppm indicative of the presence of both unhindered (meta- and para-substituted) and hindered (ortho-substituted) phenolic groups (13). Unlike the spectra of Synthoil products (14), no splitting of the -OSi(CH₃)₃ band was observed at 220 MHz. The two sharp peaks between 0 and 0.2 ppm are attributable to a little hexamethyldisiloxane (hydrolysis product) and silylating reagent (hexamethyldisilazane). Methylation (7) and acetylation (15) are alternatives to silylation for measurement of hydroxyl groups, but both these methods have much longer preparation times (1 day) than silylation (1-2 hours). Also, there is an overlap of -OCH₃ resonances with ring-joining methylene resonances between 3.4 and 4.2 ppm in coal extracts (6).

Silylation, which gives a reliable measure of the total hydroxyl content, provides little information on the distribution of hydroxyl groups. On the other hand, HFA adducts considerably less than half the total number of hydroxyl groups (see Table 2), but gives a good separation in the ¹⁹F NMR spectra between hindered and unhindered phenolic hydroxyl groups. The evidence

obtained so far suggests that there are similar numbers of hindered and unhindered groups in an asphaltene SCG extract fraction of a bituminous coal.

3.2 Non-Hydroxyl Oxygen

^{13}C NMR spectroscopy is particularly useful for assessing the environments of non-hydroxyl groups because the resonances due to carbonyl groups, which lie between 170 and 210 ppm, are well separated from those due to aromatic ethers (148-168 ppm) and aliphatic ethers (55-70 ppm) (16), although the resonances of aromatic ether groups partially overlap with those of phenolic hydroxyl groups (148-158 ppm). Figure 2 shows that no carbonyl and aliphatic ether resonances are discernible in the spectrum of the asphaltene fraction of an SCG extract of bituminous coal, but the distinct band between 158 and 168 ppm is solely attributed to aromatic ether groups. From silylation and integration of the CAR-O band between 148 and 168 ppm, the aromatic ether groups were estimated to account for 30% of the total oxygen content in SCG extracts of bituminous coal.

3.3 Basic Nitrogen

The changes observed in the position of the hydroxyl band in the ^1H NMR spectrum of 0.2 molar 2,6-xyleneol when (a) model compounds and (b) silylated coal extracts were added are shown in Table 3. Linear plots of the concentration of the basic species against shift in the spectrum were found up to a concentration of about 0.15 molar of the basic species and the values shown in Table 3 were taken from those graphs. A similar correlation was found by Tewari et al (17) who used o-phenyl phenol, but in the present work 2,6-xyleneol was preferred because it gives a sharp hydroxyl resonance in CCl_4 . The hydroxyl chemical shift of 2,6-xyleneol on its own remains constant at 4.3 ppm for concentrations 0.2 molar, which indicates that hydrogen bonding of 2,6-xyleneol itself ceases to be significant at these concentrations. For the SCG extract fractions prior silylation was required to prevent exchange of hydroxyl hydrogen between the extract and 2,6-xyleneol.

The results of the studies on model compounds (Table 3) show that little change in chemical shift for non-basic species, such as dibenzofuran and indole occurs while changes between 0.8 and 1.2 ppm/0.1 mole were obtained for alkyl substituted pyridines and quinolines. The changes in hydroxyl chemical shift generally increased with increasing degree of alkyl substitution and it is thought that di- and trisubstituted pyridines are the most realistic models for basic nitrogen environments in SCG extracts. The changes in chemical shift were found to vary greatly for the silylated SCG extract fractions and an encouraging correlation, shown in Figure 3, was obtained with basic nitrogen contents determined by non-aqueous potentiometric titration.

In an alternative approach, ^{19}F NMR was utilised and preliminary results obtained with 0.01 molar p-fluorophenol suggest that some correlation may exist between the ^{19}F chemical shift titration curves obtained for silylated SCG extract fraction and basic nitrogen content. For model bases, the change in ^{19}F chemical shift reaches a maximum value, e.g. 2.5 ppm for pyridine, when large concentrations (0.4 molar) have been added. However, for extract fractions, this maximum value cannot be measured directly because of their limited solubility in CCl_4 , and therefore information has to be derived from the titration curves obtained for low (0.2 molar) extract concentrations.

To isolate basic fractions for the studies described above, Sternberg's acid/base procedure (8) was employed for the asphaltenes of a bituminous coal SCG extract. This gave 60% bases which is significantly larger than the amounts thought to be present by the -OH chemical shift method (30%) and by

non-aqueous potentiometric titration (20%). The analysis of the base-hydrochloride salt suggested that not every molecule contained a basic nitrogen group. To help to resolve this issue, methylated asphaltenes were separated by the same acid/base procedure, but only 20% of bases was obtained, indicating that the acid/base procedure is inappropriate for SCG extracts of bituminous coals, probably due to the relatively low basic nitrogen contents and high phenolic hydroxyl contents.

3.4 Non-Basic Nitrogen

Recently, trifluoroacetyl derivatives of indole and carbazole (50% yield) have been prepared with trifluoroacetyl chloride (18). This is an important development since most non-basic nitrogen in extracts of bituminous coal is thought to be in the form of aromatic secondary amines. In the present work, we found that 90% of indole and carbazole can be derivatised using trifluoroacetyl imidazole. In an attempt to measure non-basic nitrogen in SCG extracts, methylation prior to esterification with this reagent and detection by ¹⁹F NMR is being carried out.

4. CONCLUSIONS

The results of this investigation demonstrate that NMR methods (¹H, ¹³C, ¹⁹F) offer viable alternatives to existing titration techniques for determining phenolic hydroxyl and basic nitrogen in coal extracts and provide ways for the direct measurement of non-hydroxyl and non-basic nitrogen groups.

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Table 1 Summary of NMR Methods for Heteroatoms

Group	NMR Nucleus	Method
Hydroxyl oxygen	¹ H ¹⁹ F	Silylation Adduction with hexafluoroacetone
Non-hydroxyl oxygen	¹³ C	Observation of ¹³ C chemical shifts
Basic nitrogen	¹ H ¹⁹ F	Observation of change in hydroxyl chemical shift of 0.2 molar 2,6-xylenol Observation of change in chemical shift of 0.01 molar p-fluorophenol
Neutral nitrogen	¹⁹ F	Esterification with trifluoroacetyl imidazole

Table 2 Hydroxyl Contents of SCG Extract Fractions

Fraction	% Hydroxyl		
	Enthalpimetry	Silylation	HFA Adduction
Asphaltenes, bituminous coal	6.3	6.3	1.4
Benzene-insolubles, bituminous coal	6.6	7.2	N.D.
Acid asphaltenes, bituminous coal	6.0	5.3	N.D.
Asphaltenes, perhydrous coal	4.7	4.6	N.D.

N.D. = Not Determined

Table 3 Hydroxyl Chemical Shift Changes of 0.2 molar 2,6-xyleneol on the Addition of 0.1 moles of (a) model compounds and (b) silylated SCG extract fractions

Model Compound (a)	Chemical Shift Change ppm (from 4.3 ppm)	Silylated SCG Extract Fraction (b)	Chemical Shift Change ppm (from 4.3 ppm)
Indole	0.02	<u>Bituminous coal</u>	
Dibenzofuran	0.02	Aromatic fraction,	0.05
Anisole	0.02	n-pentane solubles	
Tetrahydrofuran	0.15		
Quinoline	0.87	Polar fraction,	0.24
Pyridine	0.82	n-pentane solubles	
2-methyl pyridine	0.96	Asphaltenes	0.35
3-methyl pyridine	1.10		
4-methyl pyridine	1.00	<u>Perhydrous coal</u>	
2-ethyl pyridine	0.85	Asphaltenes	0.35
4-ethyl pyridine	0.85		
2,3-dimethyl pyridine	1.00	<u>Lignite</u>	
2,5-dimethyl pyridine	0.97	Asphaltenes	1.2
2,6-dimethyl pyridine	0.90		
3,4-dimethyl pyridine	1.08		
2,4,6-trimethyl pyridine	1.16		
4-methyl quinoline	1.16		

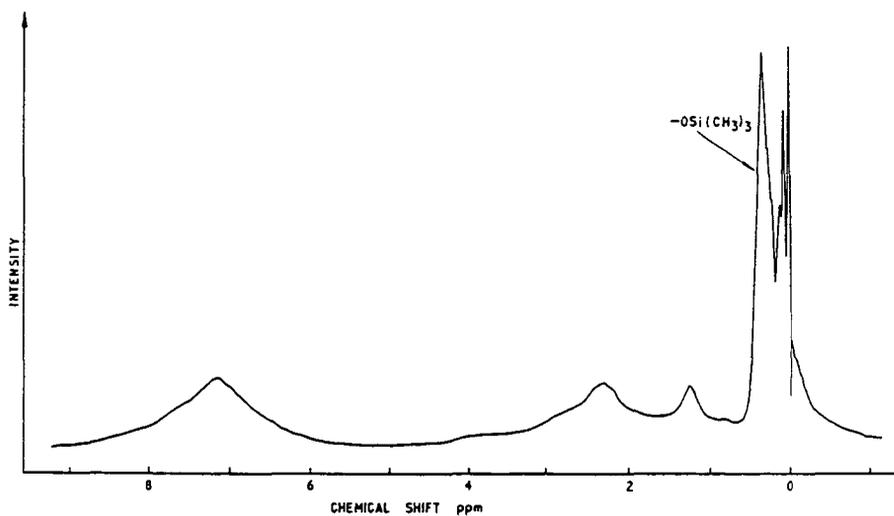


FIGURE 1. ^1H NMR SPECTRUM OF SILYLATED BENZENE INSOLUBLES FROM SCG EXTRACT.

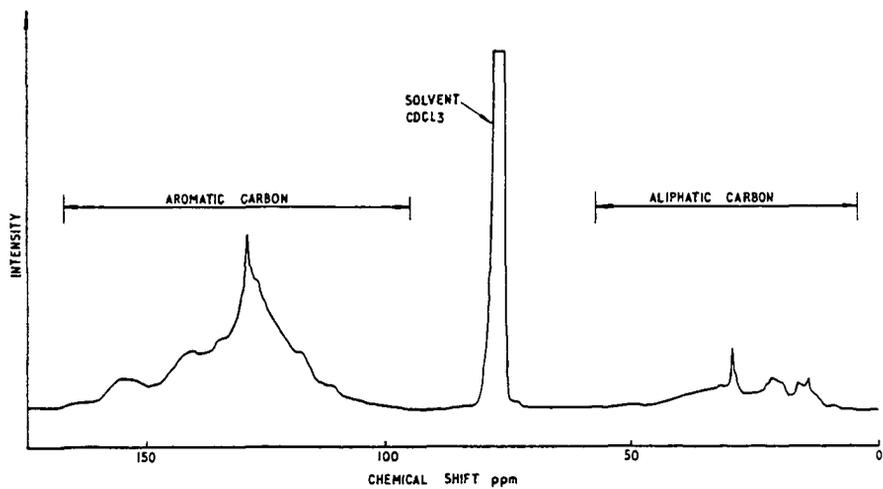


FIGURE 2. ^{13}C NMR SPECTRUM OF ASPHALTENES FROM SCG EXTRACT.

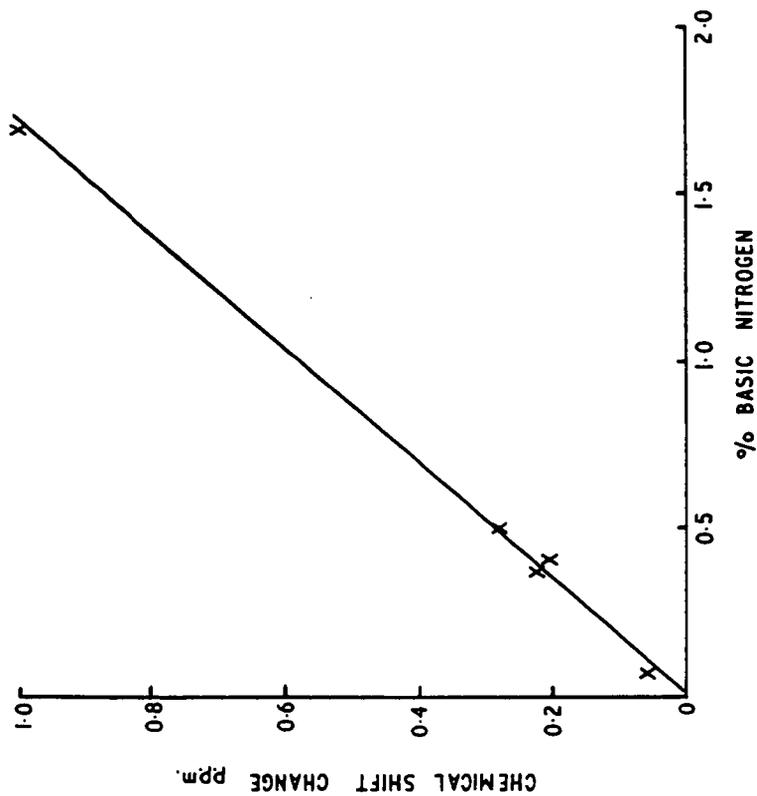


FIGURE 3. PLOT OF HYDROXYL CHEMICAL SHIFT CHANGES FOR 0.2 MOLAR 2,6 XYLENOL ON ADDITION OF 50mg SAMPLE vs % BASIC NITROGEN FOR SCG EXTRACT FRACTIONS.