

## The Use of Acetylation to Quantitate Acid Groups in Coal Derived Liquids

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The determination of types of nitrogen and oxygen species in coal derived products is an important problem to be solved in liquefaction research. Methods are needed which can rapidly isolate or characterize the nitrogen and oxygen heteromolecules in complex mixtures. Two major types of problems need to be solved. First, the types of functional groups can be identified by specific chemical reactions, but such reactions must be quantitative to be of use. Secondly, a large portion of coal derived products formed in the early stages of a liquefaction process are preasphaltenes, which limit any subsequent chromatographic procedures used to isolate compound types or molecular fractions. In this paper we shall describe the use of acetylation as a means of measuring quantitatively the fraction of acidic protons in coal derived products.

The similarity of the fractions of acidic protons measured by acetylation techniques with those of acid-base titration data suggest that no alcoholic groups are present in the SRL and SRC samples selected for this study. In addition, the acetylation process greatly increased the dissolubility of the coal derived substances in benzene and chloroform. Such dissolubility would give the opportunity for studies not accessible in pyridine. For example, the use of NMR shift reagents in chloroform could be employed in structural analysis.

### Experimental

#### Materials

Three solvent refined lignite (M11-A, M34-A and M39-A) and two solvent refined coal (AMAX and Tacoma) samples were obtained and ground to about 40 mesh for this study (1). Elemental analysis of the samples was performed by Spang Micro-Analytical Laboratory.

### NMR Spectra

Proton NMR spectra were obtained using a Varian EM-390 spectrometer. Samples were dissolved in pyridine- $d_5$  containing a calibrated amount of s-trioxane as standard. Correction for pyridine was based on a standard versus residual pyridine integration. Generally, seven integrations were run and averaged. Carbon 13 PFT-NMR were measured in a JOEL JNM-FX60 spectrometer. Chloroform- $d_1$  was used as the solvent with TMS as an internal standard.

### Non Aqueous Titration

Non-aqueous potentiometric titration of the acidic groups was carried out in pyridine using 0.05 M of tetra-n-butylammonium hydroxide in benzene as the titrant (2). The emf was measured by a Beckman Zeromatic -pH meter with a glass electrode and a simple side arm column reference electrode connected by a salt bridge of KCl-dry methanol through a medium porosity filter to the titration solution (3).

### Acetylation

Samples of SRL or SRC (1.0 g) were acetylated by refluxing for 24 h with 15 ml acetic anhydride-pyridine mixture (1:3) under an inert atmosphere of argon. Subsequently, the reaction mixture was concentrated by rotovap to about 5 ml. The mixture was added to 250 ml water and the precipitated derivative filtered. The residue on the filter was washed with water until the effluent was free of acid. The acetylated sample was freeze dried with benzene to remove the last portion of residual pyridine. Finally, the sample was vacuum dried at 80° in an abderhalden apparatus.

### Acidic Proton Analyses

The acetylated samples were analyzed for acidic proton content by saponification-titration, and by NMR measurement. The saponification of a dried acetylated sample was carried out with 1.5 g potassium hydroxide in 100 ml water-pyridine (3:1) by refluxing for 20 h. The mixture was then acidified (pH 3.0) with concentrated sulfuric acid. The liberated acetic acid was collected by distillation and titrated with standard sodium hydroxide.

Proton NMR measurements of the sample in pyridine- $d_5$  before and after acetylation were used to measure the fraction of acid groups in the sample. Prior to acetylation the acidic proton signals are located under the aromatic region. After acetylation the methyl group of the acetyl group signals are in the aliphatic region. The percentage H as acidic hydrogens can be calculated

from (equation 1),

$$\% \text{H as acidic H} = \frac{R_2 - R_1}{2R_1 + 1} \times 10^2 \quad (1)$$

where  $R_1$  is the fraction of the aromatic protons (area) in the acetylated SRC and SRL samples and  $R_2$  is the fraction of aromatic protons (area) in the non-acetylated samples.

Measurement of the percentages of acidic protons by  $C^{13}$  NMR was calculated from the relative area of the carbonyl carbon (169 ppm) to the total carbon atoms and from the carbon-hydrogen elemental analysis (equation 2).

$$\% \text{H as acidic H} = \frac{(\text{C=O Area}) \times (\text{Wt \% C}) \times 10^2}{[\text{Total Carbon Area} - 2 (\text{C=O Area})] \times 12 \times (\text{Wt \% H})} \quad (2)$$

## Results and Discussion

### Dissolubility

Table I shows the chemical analysis of the SRL and SRC samples studied in this work. The increased dissolubility of the coal derived products in several solvents due to acetylation is shown in Table 2. The dissolubility in this work was not run in the necessary manner to define the percentage of pre-asphaltenes, asphaltenes and oils in the samples, but rather to demonstrate the increased dissolubility obtained through the acetylation reactions. The dissolubility was measured by mixing 1 gm of sample in 10 ml of solvent for 20h at room temperature. The mixture was filtered through Whatman number one filter paper. The resulting filtrate and residue was dried and weighed. The total recovery varied from 97 to 99%. One immediate benefit of this increased dissolubility is that  $C^{13}$  NMR techniques could be used to measure the percentage of acetyl groups using chloroform- $d_1$  as the solvent. The remarkable increase in dissolubility after derivatization of the acidic groups can be attributed to the breaking of intermolecular hydrogen bonding (4,5). Gould, *et. al.* have recently reported the silylation of coal liquefaction bottoms which resulted in a four to seven fold decrease in viscosity and 0 to 26% increase in extrability in heptane (6).

### Acid Content

Nonaqueous titration for acidity gave a range of 1.34 to 2.22 meq/gm for the corresponding to 2.5 to 4.0% protons as acidic protons. The pure com-

pounds, carbazole and phenol, can be titrated with a precision of  $\pm 3\%$ . The actual SRL and SRC samples give a wider range of uncertainty as shown in Table 3. This is due to the presence of a wide range of weak acids which give a poor titration break.

The acetyl group content of a derivatized sample was measured by different methods. The saponification-titration procedure gave the same meq/gm as the nonaqueous titration results. The results were converted to %H as acidic H in Table 3 for comparison. The number of acetyl groups determined by proton NMR (equation 1) agreed with both types of titration data. Acetylation of model compounds (phenol, carbazole, and several hindered phenols) gave complete acetylation of the acidic groups as determined by NMR measurement of the products. The agreement between the three types of data would be consistent with the following. 1) No acylation of the aromatic carbon of the aromatic rings in coal was apparent. The acylation of an aromatic carbon seems remote under the reaction conditions, but in any case the agreement between the saponification-titration and proton NMR data eliminates that possibility. 2) The presence of alcoholic hydrogens in the samples can be ruled out because of the agreement between the acetylation and nonaqueous titration data. If alcohol acetylation had occurred a similar quantity of phenolic groups would have to remain unreacted for comparable results. That this would occur to the same extent to agree with the nonaqueous titration seems extremely remote. To check this point we are planning to measure total replaceable hydrogen content by LAH reduction in pyridine. 3) The location of the acidic protons lies under the aromatic portion of NMR spectra when the samples are dissolved in pyridine. In our study of several model compounds, the chemical shifts of OH (phenols) and NH (carbazole) hydrogens in pyridine- $d_5$  are generally downfield (between 9.5 to 6.3 ppm, aromatic region) depending upon the concentration (7).

Carbon-13 NMR integration data were generally lower than the other two types of acetyl analyses as shown in Table 3. The precision also is poorer as noted in Table 3. The reason for this is due to the small percentage of C=O groups relative to the total number of carbons and the inability to properly phase the baseline in the C=O region of the NMR experiment.

#### Acknowledgement

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### References

1. Samples were obtained as follows:  
M11-A prepared by the University of North Dakota Chemical Engineering Department under Project Lignite, from North Dakota Lignite. Conditions: 2500 psi of 1:1 CO; H<sub>2</sub> at 479°C (max); M34-A, 2500 psi of 1:1 CO; H<sub>2</sub> at 426°C (max); M39-A, 2500 psi of hydrogen at 426°C (max).  
Tacoma prepared by Pittsburg and Midway Coal Co. at their Fort Lewis PDU from a blend of Kentucky No. 9 and No. 14 bituminous coals from the Colonial Mine. Conditions: 1500 psi of H<sub>2</sub> (85% min) at 450°C (max) using recycle solvent.  
Amax Catalytic Inc., Wilsonville, Alabama from Amax subbituminous coal from Bel Ayr Mine, Wyoming. Conditions: 2500 psi H<sub>2</sub> and recycle gases at 460°C (max) using recycle solvent heavy in phenols and 1,2 and 3 ring aromatics.
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6. Gould, K. A., Gorbaty, M. L., and Miller, S. D., Fuel, 57, 510 (1978).
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Table 1

## Comparison of Coal and Lignite Derived Samples

	<u>M11-A</u>	<u>M34-A</u>	<u>M39-A</u>	<u>Tacoma</u>	<u>Amax</u>
C%	89.31	86.74	87.47	87.31	88.29
H%	5.80	6.73	6.09	5.59	5.65
N%	1.11	1.63	1.11	2.36	1.65
S%	0.86	1.15	0.74	0.30	< 0.1
O%	2.35 <sup>a</sup>	2.10 <sup>b</sup>	3.57 <sup>b</sup>	3.22 <sup>a</sup>	3.37 <sup>a</sup>
H% (Acid)	2.6	2.70	3.3	3.7	4.0
Ash %	< 0.1	1.7	1.0	< 0.1	< 0.1

<sup>a</sup> measured by neutron activation analysis<sup>b</sup> measured by difference

Table 2

## Dissolubility in Various Solvents

	<u>Pyridine</u>	<u>Benzene</u>	<u>Chloroform</u>
M11-A	96.8	50 (90) <sup>a</sup>	60 (100) <sup>a</sup>
Tacoma	95.4	25 (80)	40 (100)
M39-A	96.5	48 (85)	62 (99)

<sup>a</sup> The number in parenthesis indicates the dissolubility after acetylation.

Table 3

## Acid Proton Contents of Various Samples

Samples	Acetylated Samples and		Saponification/ Titration	Direct Nonaqueous Titration
	$^1\text{H}$ - nmr	$^{13}\text{C}$ nmr		
M11-A	$2.65 \pm 0.06\%$ <sup>a</sup>	2.0, 2.3 %	$2.57 \pm 0.05\%$ <sup>a</sup>	$2.6 \pm 0.3\%$ <sup>a</sup>
M34-A	$2.7 \pm 0.2$	2.8	$2.7 \pm 0.2$	$2.5 \pm 0.2$
M39-A	$3.1 \pm 0.2$	3.1, 3.3	$3.3 \pm 0.1$	$3.3 \pm 0.1$
Tacoma II	$3.9 \pm 0.2$	3.1, 3.4, 3.5, 3.7	$3.7 \pm 0.2$	$3.7 \pm 0.1$
AMAX	$4.1 \pm 0.2$	3.6, 3.9	$4.0 \pm 0.2$	$4.0 \pm 0.2$

<sup>a</sup> The uncertainty reported is the standard derivation ( $1\sigma$ ) for four to five determinations.