

CHARACTERIZATION OF COAL CHARs FROM A FLASH PYROLYSIS PROCESS BY  
CROSS POLARIZATION / MAGIC ANGLE SPINNING  $^{13}\text{C}$  NMR

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INTRODUCTION

In the last two decades, flash pyrolysis has been used to investigate the structure of coal and shale (1-4). Several coal conversion processes based on flash pyrolysis are under investigation in the United States (5-8), West Germany (9), and Australia (10,11,12). Studies of the molecular properties of the flash pyrolysis products have been confined to the liberated organic matter: volatile liquids and gases. Changes occurring in the organic structure of the chars are poorly understood.

The development of  $^{13}\text{C}$  cross polarization (CP) (13) and Magic Angle Spinning (MAS) (14) Nuclear Magnetic Resonance (NMR) spectroscopy with high-power proton decoupling has allowed investigators to obtain spectra of the organic matter in solid coal (15-25). Sullivan and Maciel (26) and Dudley and Fyfe (27) have verified the quantitative reliability of this technique as applied to coal.  $^{13}\text{C}$  NMR spectra of coal demonstrating the utility of both CP and MAS have been reported previously (15,16,18,21,22), however, there has been no reported investigation of  $^{13}\text{C}$  CP/MAS NMR spectra of the chars produced by flash pyrolysis.

This paper reports the results of this technique applied to the study of chars produced by the flash pyrolysis of coal at progressively higher temperatures. The investigation has given valuable insight into the changes of organic composition of coal during carbonization as well as the optimum temperature for efficient conversion of coal into liquids and gases.

EXPERIMENTAL

A high-volatile C bituminous (HVCB) Illinois Harrisburg (No. 5) coal was used. The analyses of the raw coal sample are given in Table 1. The coal was flash pyrolyzed in a quartz tube under a flow of helium. The tube was heated at a ramp-rate of  $75^\circ\text{C}/\text{msec}$  to the desired final temperature with a 20 sec hold at the final temperature. Since only small quantities of coal were used for each run, a sample of sufficient size for NMR analysis and elemental analysis at each temperature was prepared by combining the products of replicate preparations.

Chars produced at  $300^\circ$ ,  $400^\circ$ ,  $500^\circ$ ,  $600^\circ$ ,  $700^\circ$ , and  $800^\circ\text{C}$  were studied. The  $^{13}\text{C}$  CP/MAS NMR measurements of the chars were made on a JEOL FX60Q NMR spectrometer modified for CP and MAS. The spectra were recorded under standard conditions that have been described previously (26).

For the volatile analysis, the same sample of coal was heated in steps; first to  $300^\circ\text{C}$ , then successively to  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $700^\circ\text{C}$ , and to  $800^\circ\text{C}$ . The volatile matter was entrained in a helium flow of  $35\text{ ml}/\text{min}$  and was analyzed by gas chromatography (GC) using a  $2.5\text{ m} \times 3\text{ mm}$  stainless steel column packed with 3%

Table 1. Proximate and ultimate composition of the Illinois No. 5 (HVCB) coal sample. (moisture-free basis).

Proximate analysis	%	Ultimate analysis	%
Volatile matter	43.3	Hydrogen	4.72
Fixed carbon	44.3	Carbon	65.45
Ash	12.4	Nitrogen	1.13
		Oxygen (by diff.)	11.52
		Sulfur	3.91
		Low Temp. Ash	13.27

Dexsil 300 on 80/100 Chromosorb WHP connected to a flame ionization detector (FID). The column temperature was programmed from 50°C to 250°C at 8°C/min and held at the final temperature for 15 min.

#### RESULTS AND DISCUSSION

The GC traces of volatile products evolved at each charring temperature are shown in Figure 1. The evolution of decomposition products, gases and liquids, starts at 500°C, maximizes at 600°C, and completes at 700°C. At 800°C the main volatiles evolved are hydrogen and light hydrocarbon gases. The hydrogen to carbon atom ratios (H/C) of the coal and chars at each temperature are given in Table 2. There is little change in the H/C ratios at temperatures below 500°C. Above 500°C, the H/C ratios decrease as the temperature is increased. The data show a change in H/C value from 0.82 (highly benzenoid) at 500°C to 0.36 (highly graphitic) at 800°C. Based on similar results, polycondensation of the aromatic ring system occurring at the same time as dehydrogenation of the hydroaromatic and alicyclic systems has been suggested as a model for carbonization by early coal workers (28). However, <sup>13</sup>C CP/MAS NMR results give an insight into the changes of the organic matter of chars.

Table 2. The atomic ratio of hydrogen to carbon (H/C) for coal and chars at each temperature step.

Temperature (°C)	Raw coal	300	400	500	600	700	800
H/C	0.87	0.87	0.85	0.82	0.57	0.54	0.36

<sup>13</sup>C CP/MAS NMR spectra of the raw coal and the six chars are illustrated in Figure 2. In general, the spectra exhibit two broad characteristic peaks. The chemical shifts are referenced to tetramethylsilane (TMS) with hexamethylbenzene (HMB) used as a secondary external standard. The chemical shift of the aromatic peak of HMB is taken to be 132.3 ppm relative to TMS. The peak at 129 ppm is assigned to sp<sup>2</sup> (mainly aromatic) carbon and the peak at 30 ppm is assigned to sp<sup>3</sup> (saturated) carbon.

The <sup>13</sup>C CP/MAS NMR spectra show (fig. 2) that the aliphatic carbon peak is progressively decreasing as the temperature is increased; while the aromatic carbon peak retains approximately the same height and shape. The peaks at 298 ppm and -37 ppm are spinning side bands (SSB). For a given temperature the NMR spectra provide a measure of the relative carbon distribution of the organic material remaining in the char. The relative percentages of aromatic ( $f_{ar}$ ) and of aliphatic ( $f_{al}$ ) carbons are calculated by dividing the integrated area of each individual carbon peak by the sum of the areas of the peaks. The  $f_{al}$  values of chars are shown in Figure 2. The  $f_{ar}$  of the raw coal is 67%. The initial stage

of heating (300°C) produces a char with 68% of  $f_{ar}$ , and successive heatings give chars with  $f_{ar}$  of 70% (400°C), 73% (500°C), 89% (600°C), 95% (700°C), and 96% (800°C). However, the actual amount of aromatic ( $w_{ar}$ ) and aliphatic ( $w_{al}$ ) carbon in char can be calculated by using the NMR measurements ( $f_{ar}$ ;  $f_{al}$ ), the organic carbon content of the char ( $\%C_{org}$ ), and the weight of the char ( $w_{char}$ ).

$$w_{ar} = \%C_{org} \times f_{ar} \times w_{char}; w_{al} = \%C_{org} \times f_{al} \times w_{char}$$

Figure 3 shows the calculated values and the weight of char based on 100 g of raw coal used in relation to temperature: the amount of aromatic carbon in char ( $w_{ar}$ ) remains relatively constant at each temperature, while the amount of aliphatic carbon in char ( $w_{al}$ ) is reduced during higher temperature charring. At 600°C, both a large reduction of the aliphatic-carbon content and a maximum weight loss occur.

This study shows that the aliphatic part of the organic matter in coal is substantially lost during pyrolysis at temperature greater than 500°C. Although, the loss of aliphatic-bound carbon from coal may involve several mechanisms, it may have been volatilized directly or it may have been converted to an aromatic form from which it could volatilize or could become fixed as part of the char. The maximum temperature for efficient evolution of volatiles from coal by heat is at 600°C to 700°C. Also, the amount of carbonaceous residue at 800°C can be estimated from the aromatic-bound carbon of raw coal. The usefulness of the  $^{13}C$  CP/MAS NMR technique as a tool for coal process research is clearly demonstrated.

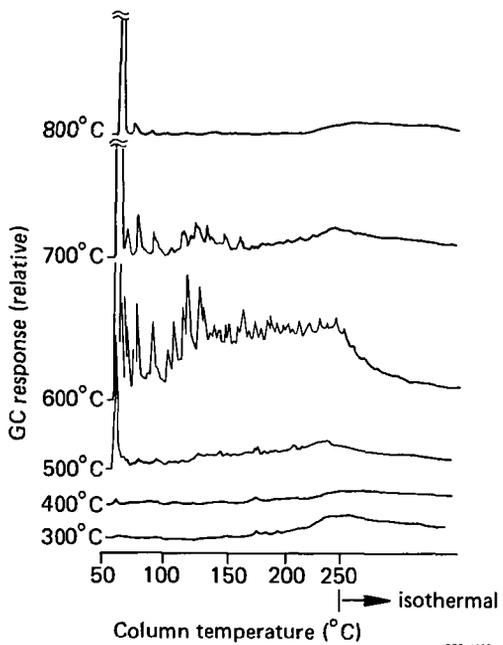
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Fig. 1. The GC traces of volatile products produced at each charring temperature.

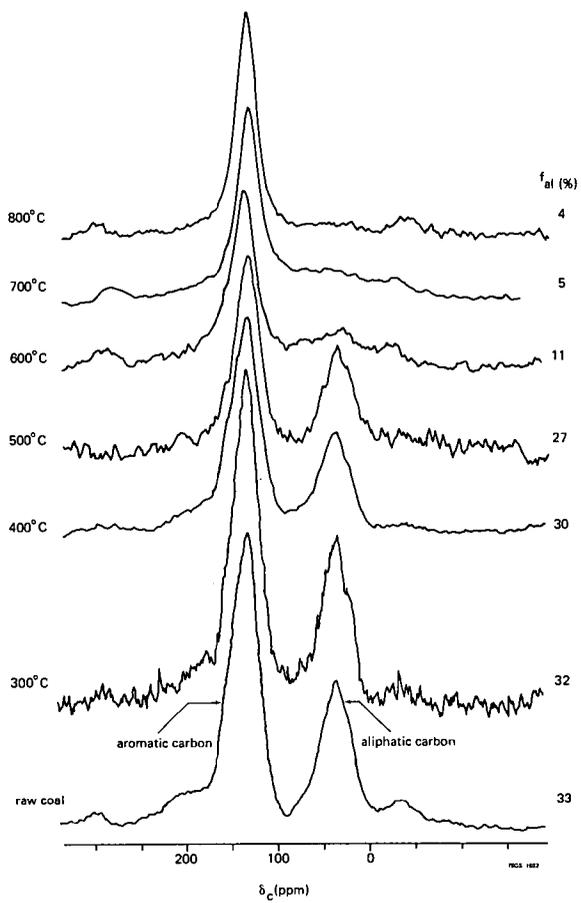


Fig. 2.  $^{13}\text{C}$  CP/MAS NMR spectra of the raw coal and of the chars at the various charring temperatures.

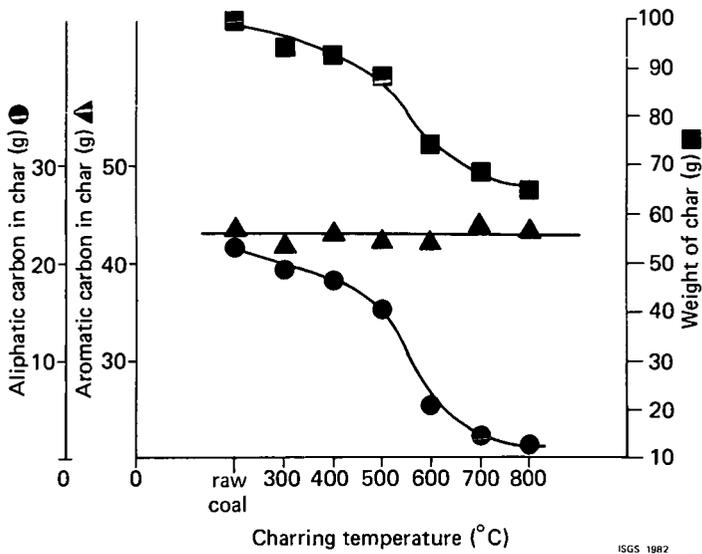


Fig. 3. The calculated amounts of aliphatic and aromatic carbon in char in relation to temperature and the weight of char based on 100 g of raw coal used.