

CHARACTERISATION OF PITCH FRACTIONS BY QUANTITATIVE SOLID STATE ^{13}C NMR

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INTRODUCTION

Thermal and other pretreatments of pitch fractions are being widely investigated as a means to increase the extent of mesophase formation in relation to the production of high performance carbons ⁽¹⁻³⁾. The structural changes that occur can be assessed using carbon skeletal parameters but, although solid state ^{13}C NMR has been used for this purpose ⁽⁴⁻⁷⁾, the quantitative reliability of the technique has still to be established for pitch fractions. It was demonstrated previously ⁽⁷⁾ that, as for coals ⁽⁸⁾, cross-polarisation (CP) can vastly underestimate quaternary aromatic carbon concentrations. A combination of a low magnetic field strength to avoid problems with spinning sidebands and the simple Bloch decay or single pulse excitation (SPE) technique is now generally recognised as offering the most satisfactory approach for obtaining quantitative ^{13}C NMR results for coals and related materials ⁽⁸⁻¹¹⁾. In this study, single pulse excitation (SPE) and associated relaxation measurements have been conducted at low field on coal-derived pitches and their toluene-insoluble (TI) fractions, together with a biomass-derived pitch and the results compared with those from CP.

EXPERIMENTAL

The elemental compositions of the whole coal tar pitch (CTP), the TI fraction from a CTP and the biomass pitch prepared from Eucalyptus Saligna wood are listed in Table 1.

All the ^{13}C NMR measurements were carried out at 25 MHz on a Bruker MSL100 spectrometer with MAS at 5.0 kHz as described previously ⁽⁸⁾ to give spectra in which the sideband intensities are only *ca* 7-8% of the central aromatic bands. Typically, *ca* 250 mg of sample was packed into the zirconia rotors. The ^1H decoupling and spin-lock field was *ca* 60 kHz and, for SPE, the 90° ^{13}C pulse width was 3.3 μs . ^{13}C thermal relaxation times (T_1 s) of the pitch fractions were determined using the CP pulse sequence devised by Torchia ⁽¹²⁾ with a contact time of 5 ms in most cases. Tetrakis(trimethyl)silane (TKS) was added to the samples as an intensity standard. Variable contact time CP experiments were used to estimate ^1H rotating frame relaxation times ($T_{1\rho}$ s) and the characteristic time constant for CP (T_{CH}).

Table 1 Elemental compositions of the pitch samples investigated

	Whole CTP	Toluene-insolubles	Biomass pitch
%			
C	94.8	92.1	72.0
H	5.7	4.8	6.6
N	1.0	1.1	0.6
S	N.D.	0.4	N.D.
O ^(a)	<1	1.6	20.8
H/C	0.57	0.62	0.91

(a) = by difference. N.D. = not determined

Depending upon the ^{13}C T_{1s} , relaxation delays between 50 and 80 s were used for all the normal and variable delay dipolar dephasing (DD) SPE measurements. At least 5 dephasing periods in the range of 50 to 500 μs were used before the first rotational modulation and this was sufficient to allow an estimate of the decay constant of the non-protonated aromatic carbon. In order to allow for variations in tuning for the variable delay DD and CP experiments, blocks of 64 scans were successively accumulated for each delay, the total number of scans being 512. No background signal was evident in the SPE spectra from the Kel-F rotor caps. All the FIDs were processed using a line broadening factor of either 20 or 50 Hz. The measurement of the small aliphatic peak areas was conducted manually as this was found to be generally more precise than using the integrals generated by the spectrometer software.

RESULTS AND DISCUSSION

Quantitative reliability Table 2 summarises the relaxation parameters determined for the whole CTP and TI fraction. The variation of the aromatic carbon peak intensity in the Torchia ^{13}C T_1 method for the CTP is presented in Figure 1. The ^{13}C T_{1s} for the quaternary aromatic carbons (longer component where two are listed, Table 1) are *ca* 10 and 15 s, respectively for the whole CTP and TI fraction meaning that recycle delays of 50 and 75 s are required in SPE to ensure virtual complete relaxation of the ^{13}C spins between successive pulses. The hydrogen T_{1s} (T_{1H} , Table 1) and rotating frame relaxation times ($T_{1\rho H}$) are shorter for the TI fraction, mainly due to the presumed higher concentration of free radicals. The long T_{1H} for the whole CTP means that, even in CP, a recycle delay of *ca* 10-15 s is appropriate to ensure complete relaxation of the proton spins.

Table 2. Relaxation parameters for the coal tar pitch samples

Sample	T_{1H} /ms	$T_{CH}/\mu\text{s}$	$T_{1\rho}$ /ms	T_{1C} /s
Whole pitch	1100 (77%)	42 (44%)	5.4	15.2 (a)
	3200 (23%)	780 (56%)		
Toluene-insolubles	0.2 (59%)	27 (68%)	1.5 (68%)	1.0 (32%)
	60 (41%)	310 (32%)	11 (32%)	10.0 (68%)

(a) = for quaternary aromatic carbon only.

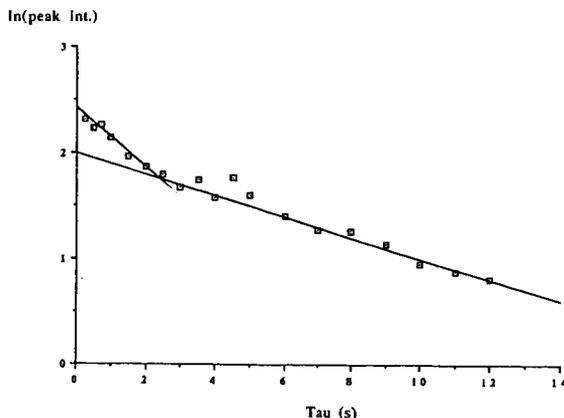


FIGURE 1 DECAY OF AROMATIC PEAK INTENSITY FOR THE TOLUENE-INSOLUBLE FRACTION IN DETERMINATION OF ^{13}C THERMAL RELAXATION TIMES

Figure 2 shows SPE spectra for the whole CTP and TI fraction. The use of TKS as an intensity standard has indicated that ca 90% of the carbon was observed by SPE in both fractions with a relaxation delay of 50 s (Table 3). As anticipated, the aromaticities are nearly 1 for both fractions but lower values (0.95-0.97 with a 1 ms contact) have been obtained by CP (Table 3).

Quaternary aromatic carbon Table 3 lists the aromaticities and fractions of quaternary carbon (C_q/C_A) derived from the SPE spectra for the whole CTP and TI fraction. Figure 3 compares the aromatic carbon intensity plots obtained from DD using SPE and CP with a 1 ms contact for the TI fraction. As for coals (8), CP grossly underestimates quaternary aromatic carbon concentrations. Although the value of 0.58 for C_q/C_A obtained with a contact time of 5 ms is significantly higher than that for 1 ms (0.40), it is still much lower than that 0.70 from SPE. The agreement between CP DD value of 0.58 for C_q/C_A and that of 0.68 for the slower relaxing carbon in the two component fit for the ^{13}C T_1 relaxation behaviour (Figure 1) is reasonably good, considering the experimental error for the latter.

As there is little aliphatic carbon and oxygen in the CTP samples (Tables 1 and 3), the errors involved in deducing the bridgehead aromatic carbon concentrations (C_{BR}/C) from the values for C_q/C_A are relatively small. The results obtained indicate that the average size of the aromatic nuclei correspond to 6/7 ring peri-condensed structures for the whole CTP and, as expected, considerably larger entities for the TI fraction

Aliphatic carbon Since the ^{13}C T_1 s of the aliphatic carbons are much shorter than those of the quaternary aromatic carbons, reasonably accurate results can thus be obtained with much shorter recycle times. Figure 4 compares the aliphatic

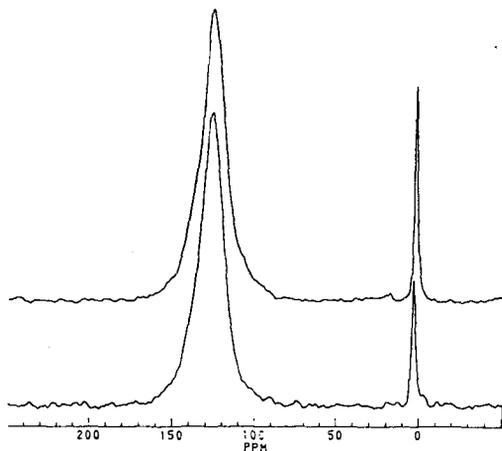


FIGURE 2 SPE ^{13}C NMR SPECTRA OF WHOLE CTP AND TOLUENE-INSOLUBLE FRACTION CONTAINING TKS

Table 3. Structural parameters for the coal tar pitch samples

Sample	Aromaticity, f_a	f_q	C_{BR}/C	% of C obs.
Whole pitch	0.98 (0.95)	0.52	0.50	93
Toluene-insolubles	>0.99 (0.97)	0.70	0.68	90

f_q = fraction of quaternary carbon of total aromatic carbon.
 C_{BR}/C = mole fraction of bridgehead aromatic carbon.

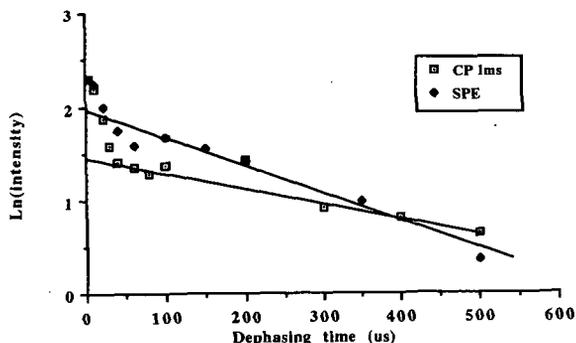


FIGURE 3 COMPARISON OF AROMATIC PEAK INTENSITIES FROM THE SPE AND CP (1 ms CONTACT) DIPOLAR DEPHASING EXPERIMENTS ON THE TOLUENE-INSOLUBLE FRACTION

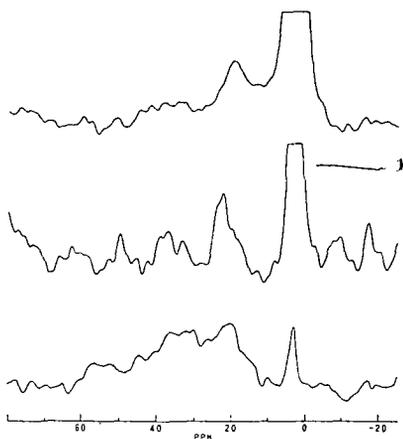


FIGURE 4 ALIPHATIC CARBON BANDS FROM SPE AND CP SPECTRA OF THE TOLUENE-INSOLUBLE FRACTION

regions from the SPE spectrum of the TI fraction obtained with a recycle delay of only 5 s with those from the CP spectra obtained with contact times of 0.5 and 2 ms. Although the signal to noise ratios are understandably low, the proportion of CH₃ (10-25 ppm) observed at the shorter contact time is only 30-40% of the aliphatic carbon due to the incomplete CP of the rotationally mobile CH₃. The proportion observed is higher at the longer contact time of 2 ms but the signal to noise ratio is less than in the SPE spectrum which indicates that CH₃ accounts for at least 60 to 70% of the aliphatic carbon.

Biomass pitch Figure 5 shows the spectra obtained by SPE with a 50 s relaxation time and by CP with a 1.5 ms contact time. Table 4 lists the relaxation parameters and the carbon aromaticity. As for the CTP, over 90% of the carbon was observed by SPE with a relaxation delay of approximately 5 times the ¹³C T₁ for quaternary aromatic carbons (ca 10 s, Table 4). The biomass pitch is structurally diverse with methoxyl groups (peak at 55 ppm, Figure 5) surviving the carbonisation which clearly indicates that tar evolves at relatively low temperatures. The carbon aromaticity of 0.60 obtained by SPE compares with that of 0.58 from CP suggesting that, as for wood and other lignocellulosic materials (13), the discrimination against aromatic carbon is not as great as for low-rank coals.

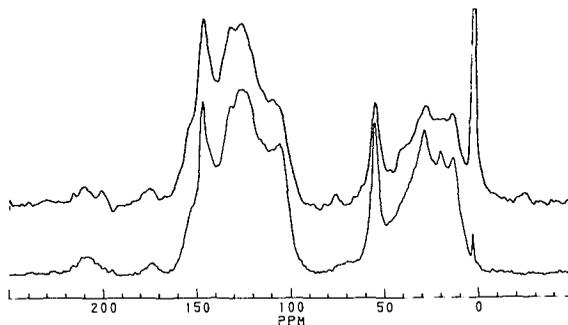


FIGURE 5 SPE AND CP (1 ms CONTACT) SPE ^{13}C NMR SPECTRA OF THE BIOMASS PITCH

Table 4. Structural and relaxation parameters for the biomass pitch.

T_1^H /ms	T_1^C aromatic /s	% C observed	Aromaticity, f_a
46 (80%)	9.8 (44%)	96	0.60
91 (20%)	0.8 (56%)		(0.58) (a)

(a) = CP value with a contact time of 1 ms.

CONCLUSIONS

^{13}C thermal relaxation times for quaternary aromatic carbons in coal tar and biomass pitches investigated are in the range 10-15 s and, provided that suitably long relaxation delays are used in SPE, over 90% of the carbon is observed. Further, the self-consistent quaternary aromatic carbon concentrations derived by SPE-DD are higher than those obtained from CP, even with long contact times. SPE has indicated that the aliphatic carbon present in the CTP T1 fraction investigated is predominately methyl.

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