STRUCTURAL CHARACTERIZATION OF ANODE BINDER PITCHES

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Introduction

The unique properties of coal tar pitches have resulted in numerous applications for carbon products, such as binders for anodes. However, as the number of by-product coke ovens is diminishing, the design of superior binders from alternative materials or processes is sought by the carbon industry [1]. Accordingly, structural characterization of coal tar pitches and their solvent fractions, using quantitative analytical techniques is required to successfully obtain this goal. Quantitative solid state ^{13}C NMR has previously been shown to be a powerful tool to study the overall aromatic ring-size for coal tar pitches and their toluene insoluble (TI) fractions [2, 3]. The TI fraction can further be separated into its quinoline soluble part (beta-resin) and insoluble fraction (QI). Both these fractionsaffect the overall fluidity and coking yield of the pitches. Correspondingly, this paper correlates the structural differences in the aromatic nature of the whole pitches and their solvent fractions.

Experimental

Five coal tar pitches, A to E, were extracted in quinoline (ASTM D2318) to generate the QI fraction. Quinoline was distilled from the soluble fraction, which was further extracted in toluene (ASTM D5294) to generate the beta-resin and TS fractions. Generally, there was good agreement between the beta-resin yield obtained by the above procedure and that obtained by subtracting the QI from the TI, which was based on a separate ASTM D5294 extraction on the whole pitches. The elemental analyses were carried out using a CHN-600 Leco. The solid state ^{13}C NMR was conducted on a Chemagnetics M-100 with a field of 2.4 T and a spinning speed of 3.5 kHz. For the CP measurements around 10k-20k scans were accumulated using 1 ms contact time and 1 sec recycle delay. For the quantitative single pulse excitation experiments, SPE, about 1000-5000 scans were acquired with recycle delays ranging from 60-300 seconds.

Results and Discussion

Table 1 lists the extraction data for the five pitches investigated, showing distinctive QI contents, ranging from 13 to 21 wt%, and a correspondingly range of TS from 71 to 61 wt%. The atomic H/C ratios are listed in Table 2 for the whole coal tar pitches (CTP) and their TS, beta-resin and QI fractions. The whole CTPs show similar H/C ratio from 0.54 for the CTP with the lowest QI content to 0.51 for the one with the highest QI. The H/C ratios of the different solvent fractions are strikingly similar, where the TS fraction have H/C atomic ratios between 0.64 to 0.66, the beta-resin within 0.46 to 0.48 and the QI between 0.21 to 0.30. This indicates that the overall structure of pitches may follow some general pattern that will allow a design of superior pitches from alternative carbonaceous sources. Further, the weighed sum of the TS, beta-resin and QI fractions, based on their extraction yields and individual H/C atomic ratios (Table 2), are close to those of the whole pitches. Figure 1 shows the solid state ^{13}C NMR spectrum of CTP A using the quantitative SPE method. The spectrum is dominated by the aromatic peak centered at 125 ppm, giving spinning sidebands out of the region of interest. The aliphatic carbon accounts for less than 1%, supported by measurements using the qualitative CP technique. The aromatic peak contains signals from two main carbon types: those directly bound to hydrogen and those that are not, described as protonated and non-protonated aromatic carbon, respectively. The ratio of protonated over total aromatic carbon can be found from the dipolar dephasing technique as illustrated for the QI fraction of CTP D in Figure 2. With no dephasing time, the total carbon signal is detected in the aromatic peak. As the dephasing time is increased, the protonated carbon signal decays (Gaussian distributed), leaving only the non-protonated signal (Lorentzian distributed). The ^{13}C NMR structural data will be correlated with X-ray data and H/C atomic ratios.

Conclusions

Coal tar binder pitches and their three solvent fractions, TS, beta-resin and QI, have been studied by quantitative SPE ^{13}C NMR, where the results obtained have been correlated with elemental analysis. The overall structural uniformity indicates the possibility of pitch design.

References

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Table 1. Solubility parameters for the coal tar pitches investigated.

Pitch	Toluene soluble / wt%	Beta-resin / wt%	Quinoline insoluble / wt%
A	71.1	15.3	13.6
B	69.8	15.0	15.2
C	69.2	12.9	17.9
D	64.0	16.6	19.4
E	60.5	18.4	21.1

Table 2. Atomic H/C ratios for the whole pitches and their TS, beta-resin and QI fractions.

Pitch	Whole	TS	Beta-resin	QI	Weighed sum of fractions
A	0.54	0.66	0.48	0.22	0.57
B	n.d.	n.d.	n.d.	n.d.	n.d.
C	0.51	0.64	0.47	0.21	0.54
D	0.53	0.65	0.46	0.30	0.55
E	0.51	0.64	0.47	0.27	0.53

n.d. = Not determined.

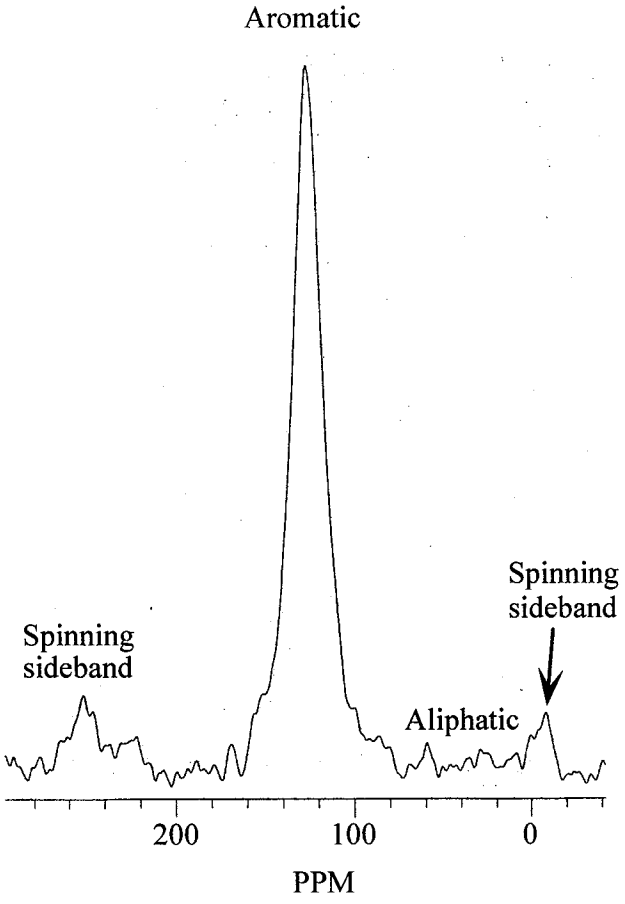

Figure 1. Solid state ^{13}C NMR spectrum of the whole binder pitch A, using the quantitative single pulse excitation technique.

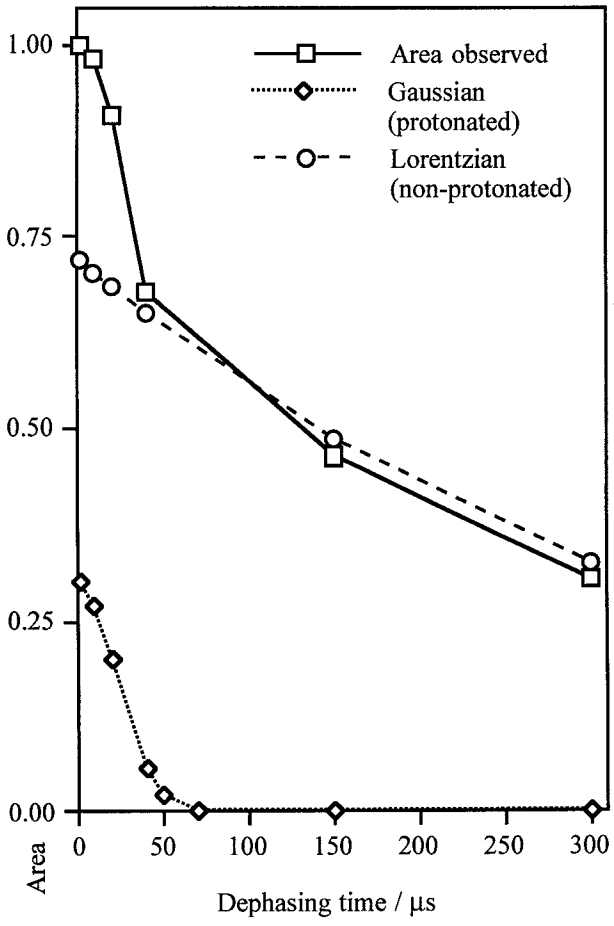

Figure 2. Variation in area observed for the aromatic peak with respect to the dephasing time for the quinoline insoluble fraction of coal tar pitch D.