HIGH TEMPERATURE IN-SITU ^{1}H NMR STUDIES ON THE FLUIDITY INTERACTIONS BETWEEN SOLVENT FRACTIONS OF COAL TAR PITCH

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Introduction

The assessment of fluidity interactions between coal tar pitch solvent fractions during heating is important for the future design of pitches from untraditional sources or processes. High temperature ^{1}H NMR has been a useful tool to investigate the fluid and rigid components of pitches, especially with its interaction with coal [1] and to quantify mesophase in pitch [2]. However, very little work has been performed to correlate the fluidity behavior of pitch with the mobility of its differentsolubility fractions. Accordingly, this paper addresses the fluidity interactions between different pitch solvent fractions (TS, beta-resin and QI) by high temperature ^{1}H NMR. Particularly, the fluidity studies on the beta-resin alone can verify whether this fraction becomes plastic during heating.

Experimental

Two binder pitches, A and B, were used and they are described elsewhere [3]. A Bruker MSL100 spectrometer at a field strength of *ca.* 2.4 Tesla was used for the in-situ ^{1}H NMR measurements, together with a Doty probe. The solid echo pulse sequence with a refocusing time of 5 μs was used. The selected spectra obtained were fitted numerically to Lorentzian and Gaussian components, as previously described [1, 2].

Results and Discussion

Figure 1 shows three spectra of binder pitch B during softening. The top spectrum is at ambient temperatures, where no softening has taken place. This peak is broad and typical for non-softened or rigid materials. The shape is flat on top and decaying rapidly down to the baseline, typical for Gaussian distributed peaks. As the temperature is increased to 80°C, some of the material becomes fluid as the pitch softens, illustrated by the introduction of a narrower line-shape in the middle spectrum. This spectrum consist of two components, one broad Gaussian deriving from the non-softened material and one sharp Lorentzian component from the fluid or mobile phase. With a further rise in temperature, the pitch becomes fully softened as illustrated in the bottom spectrum at 150°C in Figure 1, and it is described by one single Lorentzian component. A common parameter used to describe the NMR signal is the peak half-width, which is given by the width in Hertz at half the height of the overall spectrum. This parameter has been plotted versus temperature for the whole binder pitch A and its TS, beta-resin and QI fractions. All samples have a rigid character at ambient temperature with a half-width of 30kHz. As the temperature is increased, the half-width is rapidly decreasing for the whole pitch, corresponding to a softening temperature of 105-110°C. The TS fraction shows a similar behavior, but with a lower softening point (~80°C). Both pitches A and B and their TS fraction become totally fluid. However, the QI fraction only shows a slight drop in the half-width around 150°C due to vibrations in the methyl groups not associated with softening, and stays rigid up to 500°C. The beta-resin follows the pattern of the QI up to 400°C, where it starts to partially soften, indicated by a drop in the half-width to ~8000Hz at 475°C. Figure 3 shows the deconvolution of the spectrum at this temperature into its fluid or Lorentzian and rigid or Gaussian components, indicating that 24% of the beta-resin becomes mobile. This indicates a plastic behavior of the beta-resin at temperatures above 350°C, which can contribute significantly to the overall fluidity of the pitch at these temperatures depending on the volatility of the TS fraction during heating.

Conclusions

High temperature ^{1}H NMR has shown that the softening of a pitch is closely related to the TS part, but that the beta-resin indeed becomes plastic on its own and can significantly contribute to the total mobility of the pitch.

References

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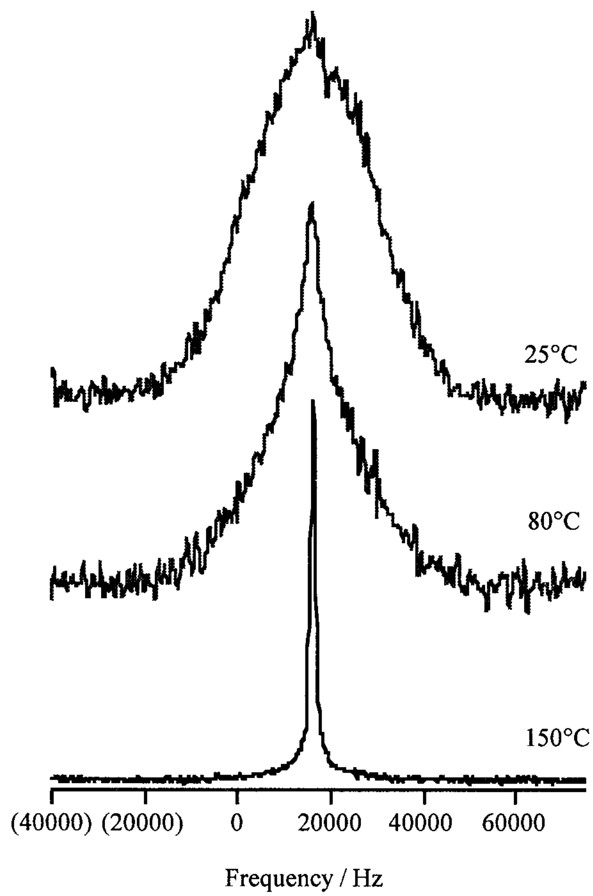

Figure 1. High temperature ^{1}H NMR spectra of the binder pitch B at ambient temperature (25°C, top), 80°C (middle) and 150°C (bottom) showing the effect of softening upon the NMR signal.

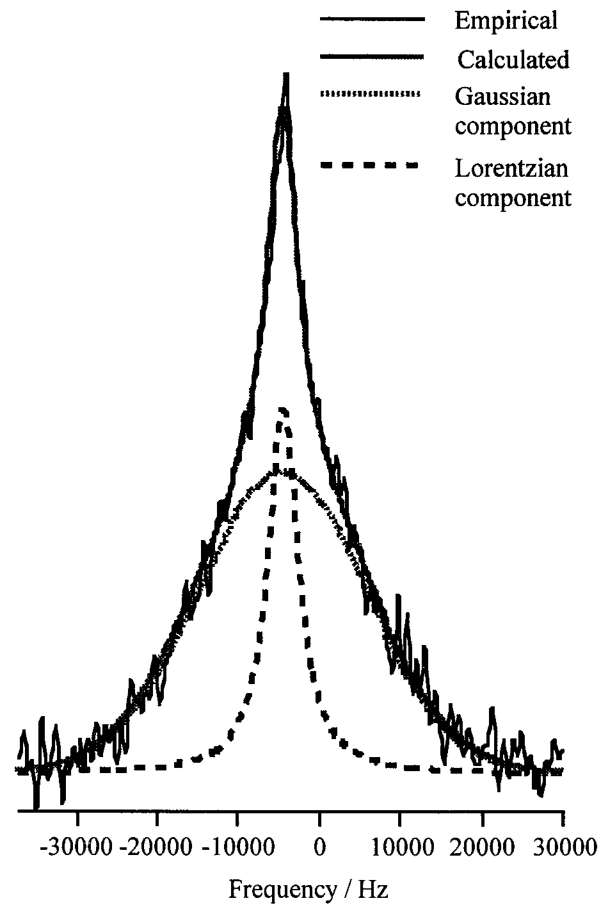

Figure 3. High temperature ^{1}H NMR spectrum of the beta-resin fraction of binder pitch A at maximum fluidity at 475°C deconvoluted into its fluid or Lorentzian component, and its rigid or Gaussian component.

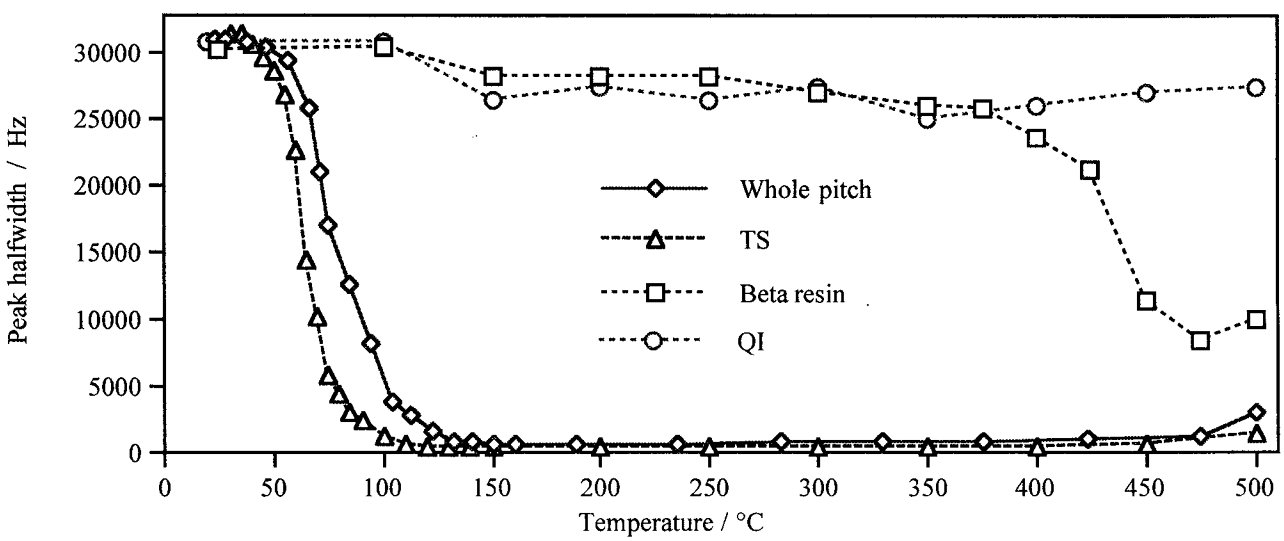

Figure 2. Variation in the peak half-width for binder pitch A and its TS, beta resin and QI fractions with temperature.