

# High Resolution $^{13}\text{C}$ -NMR Spectroscopy of Neat Coal Extracts and Coal Tar Pitches

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**Abstract.** The improved method of C-13 NMR for structural investigation of coal extracts and coal tar pitches is proposed in this paper. The new method is characterized by direct heating of samples over the softening point into the melted state. Some advantages which make it possible to get high resolution spectra in high S/N ratio for a short period are discussed.

## Introduction

Carbon-13 Fourier Transform Nuclear Magnetic Resonance (CMR) can be a useful technique to delineate the carbon backbones of complex coal-derived materials. Its measurement may be used in both liquid and solid states. However, the method of CMR in solids (CP/MAS method) lacks sufficient resolution to deduce the structural composition. In liquid state measurements, the main problem is the fact that many coal-derived materials are not soluble enough in solvents suitable for CMR. Remarkable spectrum of hard-coal-tar pitch using  $^{12}\text{C}$  enriched  $\text{CDCl}_3$  as a solvent was reported.<sup>1</sup> However, the method is impractical for the routine use, because of 5-day time period needed for measurement due to sample dilution and the use of the precious solvent.

In this paper, the improved CMR technique which is characterized by direct heating of samples over the softening point into the melted state is described. The results show that the structural information of coal extracts and coal tar pitches can be obtained for a short period.<sup>2</sup>

## Experimental

CMR measurements were made on the specimens at a resonance frequency of 15 MHz using a JEOL FX-60Q spectrometer equipped with a variable temperature accessory.  $\text{DMSO-d}_6$  was used as the reference for all the melted state spectra.  $\text{Cr(III)(acac)}_3$

was added to  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$ .  $\text{CDCl}_3$  was used as the solvent for the liquid state spectrum. Solid state measurement employed cross polarization, high power  $^1\text{H}$  decoupling, and magic angle spinning (CP/MAS).

The sample for the melted state measurement was put in an NMR sample tube with 10 mm diameter which coaxially contained a capillary filled with the  $\text{DMSO-d}_6$  reference.

The standard CMR measurement conditions are as follows.

Lock: External Lock (D-Lock)  
( $\text{d}_6$ -DMSO +  $\text{Cr(acac)}_3$  in 5 mm $\phi$  capillary)

Reference Signal: Methyl carbons of  $\text{d}_6$ -DMSO

Pulse Width: 45°

Pulse Repetition Time: 2 sec

Accumulation: 10,000 ~ 30,000 times

Total Time Period: 6 ~ 17 hours

Temperature : 120 ~ 190°C

## Results and Discussion

Figure 1 shows the CMR spectrum of the saturated  $\text{CDCl}_3$  solution of the toluene soluble fraction of coal extract (Pitch A, SP 47°C). Figure 2 shows that of neat pitch A in melted state at 120°C.

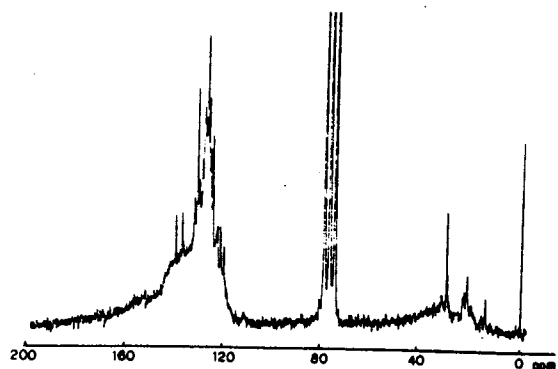


Fig. 1 CMR spectrum of saturated  $\text{CDCl}_3$  solution of pitch A.  
Pulse width: 4  $\mu\text{sec}$  (flip angle  $25^\circ$ )  
Pulse repetition time: 4 sec

Visual comparison of the spectrum in figure 1 and the lower spectrum in figure 2 suggests that, even with the longer pulse width and the shorter pulse repetition time, the melted state spectrum shows a much higher S/N ratio than the liquid state spectrum. Apparently, solid state  $^{13}\text{C}$ -NMR has insufficient resolution for structural investigation.

As for pulse repetition time, two seconds which consist of acquisition time of 1.365 sec and interval of 0.635 sec are long enough for quantitative measurements in melted state. This is proven by coincidence of ratios between aromatic and aliphatic carbon atoms of the 10-sec repetition time spectrum (center in fig. 2).  $^1\text{H}$  gated decoupling in Nuclear Overhauser Effect (NOE) suppressed mode is necessary for quantitative measurement of quaternary aromatic carbons (fig. 2, table 1).

Two-second repetition time is surprisingly short for the relaxation of quaternary aromatic carbons. However, it is sufficiently long for the melted method measurement. This might suggest that aromatic free radicals, which are contained in carbonaceous pitches with  $10^{18}$ – $10^{19}$  spins/g concentration, play an important role in relaxation.

Additionally, pitch concentration in melted method is much greater than that in liquid method. These advantages make it possible to get high resolution CMR spectra of coal-derived materials in high S/N ratio for a short period. We also found that this

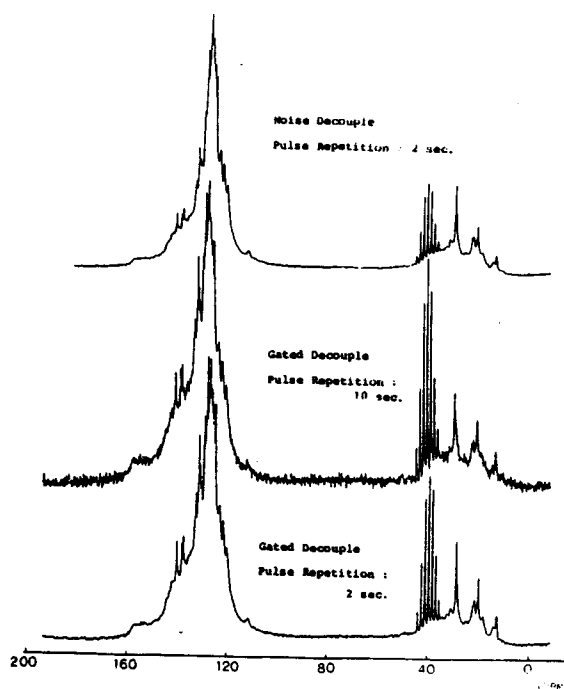


Fig. 2 CMR spectra of pitch A at  $120^\circ\text{C}$  at various pulse conditions.

Table 1 Carbon Determination by CMR.

Method	Pulse Repetition (sec.)	$C_{ar} / C_{al}$	$f_a$
Gated Decouple	10	4.21	0.808
Gated Decouple	2	4.13	0.805
Noise Decouple	2	3.73	0.789
Non-decouple	2	4.06	0.802

new method is applicable to other types of pitches, such as petroleum pitches or coal liquefaction products.

#### References

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