

# MODELING OF MOLECULAR STRUCTURE OF UPPER FREEPORT COAL BY USING $^{13}\text{C}$ NMR CHEMICAL SHIFT CALCULATION

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## INTRODUCTION

Many analytical techniques have been widely applied to structural analysis of coal. Solid-state  $^{13}\text{C}$  NMR is one of the attractive tools for characterization of coal since coal is hard to dissolve in ordinary organic solvents. Recently,  $^{13}\text{C}$  NMR chemical shift prediction software has been used to obtain information of chemical structure of various materials such as polymers. Thomas et al. calculated  $^{13}\text{C}$  chemical shift for some substituted pyridines using several NMR prediction programs and showed that the results of the prediction gave good agreement with the experimental values<sup>1</sup>.

Several structural models for coal have been based on analytical data obtained with the methods such as pyrolysis GC-MS,  $^{13}\text{C}$  NMR measurement<sup>2-4</sup> and hydrogenation HPLC/GC-MS<sup>5</sup>. However, original structures of coals may be broken by pyrolysis and hydrogenation reactions, and only volatile materials of coals may be detectable on the GC techniques. On the other hand, for extract fractions obtained from a room temperature extraction for Upper Freeport coal, the model structures based on the structural parameters obtained from  $^1\text{H}$  NMR and ultimate analysis were constructed<sup>6</sup>. Since no significant reaction such as bond breaking seemed to occur during the extractions, model structures based on original chemical structures could be constructed. However, information of types of carbon atom in the extract fractions was insufficient with  $^1\text{H}$  NMR, and furthermore the model structure for the extraction residue could not be obtained, since it was insoluble in solvents.

To get directly information of chemical structures of a whole coal including the extraction residue, solid state  $^{13}\text{C}$  NMR spectra were measured for several fractions which were obtained from extraction and fractionation at room temperature. The calculated  $^{13}\text{C}$  NMR spectra by using an NMR prediction software were determined<sup>7</sup> for the model structures of the extract fractions that have been suggested by Takanohashi and co-workers<sup>6</sup>. The model structures were improved to fit experimental spectra. In addition, a model structure of the extraction residue was constructed and revised by comparison between its calculated  $^{13}\text{C}$  NMR spectrum and the experimental one. Finally, a model structure of Upper Freeport coal including the extraction residue is suggested.

## EXPERIMENTAL

### *Sample Preparation*

Upper Freeport coal, which is an Argonne premium coal sample was obtained in ampoules (5 g of  $-150\ \mu\text{m}$ )<sup>8</sup>. The coal sample was extracted exhaustively with a carbon disulfide / *N*-methyl-2-pyrrolidone ( $\text{CS}_2$  / NMP) mixed solvent at room temperature<sup>9</sup>. The extract obtained was further fractionated by acetone and pyridine into three fractions, acetone-soluble (AS), acetone-insoluble and pyridine soluble (PS), and pyridine-insoluble (PI) fractions, as shown in Figure 1. The PS, PI and residue (the mixed solvent-insoluble (MI) fraction) were washed with acetone, and the AS was washed with acetone - water (1:4 by volume) solutions. All fractions were dried in a vacuum oven at  $80\ ^\circ\text{C}$  for 12 hr.

### *NMR measurements*

Solid state  $^{13}\text{C}$  NMR spectra were measured by both CP/MAS and SPE/MAS methods using a Chemmagnetics CMX-300 NMR spectrometer operating at a  $^{13}\text{C}$  frequency of 75.46 MHz. All spectra were acquired employing a  $^1\text{H}$   $90^\circ$  pulse length of 4  $\mu\text{s}$ . This was combined with a magic angle spinning rate of 10kHz. Repetition rates of 4s (CP/MAS) and 60s (SPE/MAS) were used

for all samples. For each spectrum, 4000 (CP/MAS) and 2000 (SPE/MAS) scans were accumulated. The contact time of CP/MAS was 1ms. The chemical shifts were calibrated with respect to tetramethylsilane using the peak of methyl group on hexamethylbenzene at 17.4 ppm as the external standard.

#### ***NMR chemical shift calculation***

Chemical shift calculations were carried out using a ACD laboratory C NMR predictor software. The software allows treatment of molecules containing up to 256 carbon atoms. The chemical shift of model structure is calculated by searching for similar sub-structural fragment with the corresponding experimental shift value in the database (600,000 chemical shifts of 50,000 compounds) and evaluating the chemical shift value taking into account intramolecular interactions. The calculated  $^{13}\text{C}$  NMR spectra of the model structures for the fractions were obtained by considering an adequate line width.

### **RESULTS AND DISCUSSION**

#### ***NMR spectra.***

The distributions of types of carbon atom obtained by deconvolution of  $^{13}\text{C}$  NMR spectra for each fraction are shown in Figures 2. For all spectra, SPE/MAS gave the lower ratios of  $\text{CH}_3$ ,  $\text{CH}_2$ , CH carbon and higher ones of aromatic and  $\text{CH}_2\text{-O-}$  carbon than CP/MAS. This is explained by that carbons with low CP efficiency such as non-protonated aromatic ones could be detected by SPE/MAS. Thus, for samples including many inner carbons like coal, SPE/MAS method may give more quantitative spectrum, although there are other problems such as background of spectrum. While, compared among fractions, the lighter fraction gave larger differences between both methods. Furthermore, the SPE/MAS data showed that except for AS fraction that is the lightest of all fractions here, all fractions including the extraction residue gave a similar distribution of carbon types. Nakamura et al. analyzed aromatic structures of several fractions obtained from mild hydrogenation and reported that ring structures for all fractions including an extraction residue were similar<sup>5</sup>. Iino et al. have also found<sup>10</sup> that addition of small amount (1%) of tetracyanoethylene (TCNE) to the  $\text{CS}_2/\text{NMP}$  mixed solvent enhanced greatly the extraction yield of Upper Freeport coal, i.e., the original MI became part of the PI fraction, and concluded that the effect of TCNE addition is attributed to dissolution of associates of the coal molecules. Therefore, the PS, PI and extraction residue (MI) have similar chemical structures and their difference may be due to the degree of association between coal molecules.

#### ***NMR Chemical Shift Calculation.***

The model structures for AS, PS and PI fractions based on the structural parameters obtained from  $^1\text{H}$  NMR and ultimate analysis have been suggested<sup>6</sup>. The calculated spectra for their model structures were obtained by using the prediction software. Next, the model structures were modified to fit the experimental spectra. Consequently, the modified model structures were obtained as shown in Figure 3. The calculated spectra of the modified models were compared with the experimental ones, which are shown in Figure 4. For all fractions, the calculated spectra were in excellent agreement with the experimentally obtained spectra. Table 1 shows ultimate analyses and structural parameters of each model, together with their experimental values. For AS fraction, which is the lightest of all fractions, there were differences in ultimate analysis. The model of AS fraction can be too small to express distribution of chemical structures. While, for PS, PI and MI, their ultimate analyses and structural parameters except for aromaticity,  $f_a$  were in good agreement with those of model. The  $f_a$  values of models except for AS were higher than those estimated from  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR measurements. This reason may be attributed to the inner carbons existed in the heavier fractions, which are hard to be relaxed even under SPE/MAS condition.

#### ***A Model Structure of Upper Freeport Coal.***

Nakamura et al. constructed<sup>5</sup> three-dimensionally a model structure of Zao Zhuang bituminous coal using computer-aided molecular design (CAMD) by assuming an anisotropic model structure formed from a periodic boundary cell. The same method was used to construct a model structure of Upper Freeport coal here since both coals have similar structural features<sup>9</sup>. The modified model structures for all fractions including the extraction residue were randomly placed in a rectangular cell, as shown in Figure 5. It is not required to connect between the models by covalent bonds, because all fractions were obtained from the room-temperature extraction and fractionation. The calculation procedure has been reported elsewhere<sup>5</sup>. Finally an associated model structure of Upper Freeport coal was suggested. The estimated density for the model structure was in agreement with the observed one.

## CONCLUSIONS

Upper Freeport coal was extracted and fractionated at room temperature, and for all fractions including the extraction residue,  $^{13}\text{C}$  NMR spectra were measured. The calculated  $^{13}\text{C}$  NMR spectra by using an NMR prediction software were determined for the model structures. The model structures were modified to fit experimental spectra. For all fractions, the spectra calculated for the modified models were in excellent agreement with the experimentally obtained spectra. Finally, by using computer-aided molecular design (CAMD), an anisotropic model structure of Upper Freeport coal was suggested.

## ACKNOWLEDGMENT

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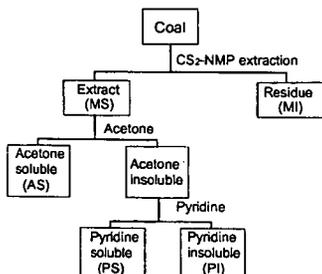


Figure 1 Procedures of Extraction and Fractionation

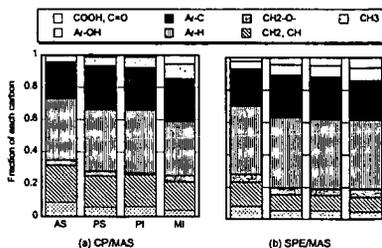


Figure 2 Solid state  $^{13}\text{C}$  NMR spectra of the fractions (AS, PS, PI and MI) by CP/MAS (a) and SPE/MAS (b) methods.

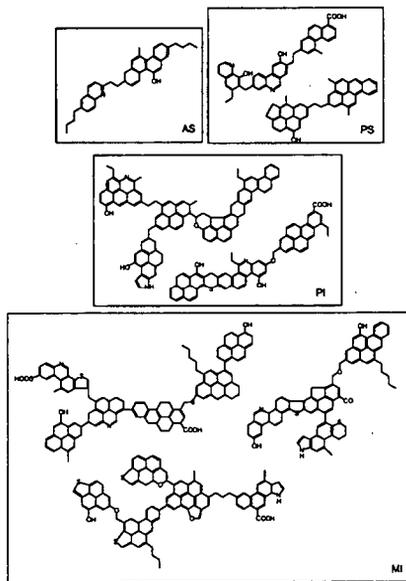


Figure 3 Modified Model Structures of Each Fraction

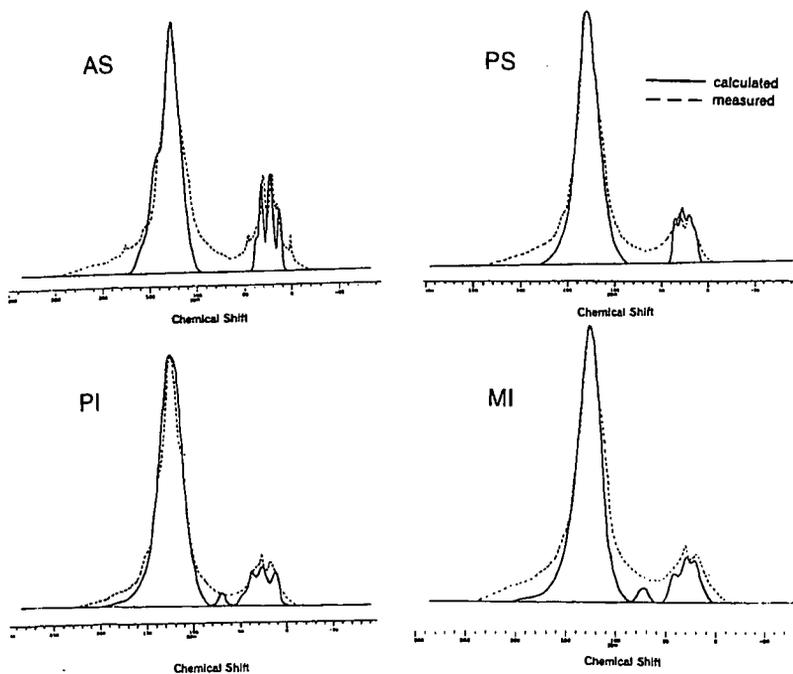
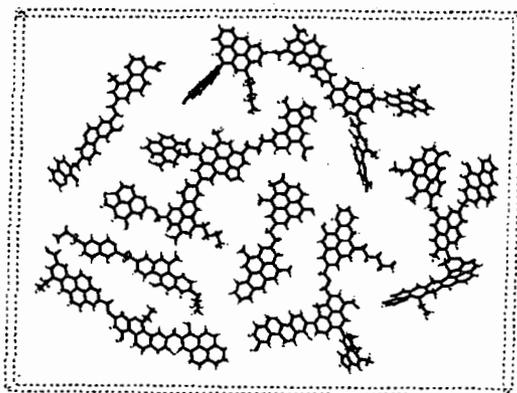


Figure 4 The measured  $^{13}\text{C}$  NMR spectra for all fractions, and their calculated spectra.

**Table 1** Ultimate Analyses and Structural Parameters for Each Fraction

fraction	C%	H%	N%	S%	O%	H/C	$f_a^a$
AS, observed	88.5	6.7	1.1	0.5	3.2	0.91	0.72 (0.71)
model	86.9	7.4	2.7	0.0	3.0	1.03	0.71
PS, observed	86.6	5.4	1.8	1.0	5.2	0.75	0.80 (0.78)
model	85.6	5.5	2.3	0.0	6.6	0.77	0.84
PI, observed	85.8	5.0	2.1	1.1	6.0	0.68	0.81 (0.79)
model	85.7	5.0	2.0	1.5	5.9	0.70	0.85
MI, observed	81.7	4.7	1.8	5.5	6.3	0.69	0.81
model	81.8	4.9	1.7	5.4	6.2	0.71	0.85

<sup>a</sup>The values in parenthesis are calculated from <sup>1</sup>H NMR measurement.



**Figure 5** Coal Molecules Put Randomly in a Rectangular Cell.