

STRUCTURAL DETERMINATIONS OF PENNSYLVANIA ANTHRACITES

Peter J. Pappano, Jonathan P. Mathews, Harold H. Schobert
The Energy Institute
The Pennsylvania State University
University Park, PA 16802

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INTRODUCTION

Four Pennsylvania anthracites were selected for analysis, based on their availability from currently active mines and presumed geological differences. A battery of experiments was performed on these samples to determine their physical and chemical properties. The data collected from these experiments was used as input for modeling the structure of anthracite using Cerius², a Molecular Simulations Incorporated (MSI) software package. Visualization of anthracite structure is useful in visualizing the reactions necessary to produce advanced carbon materials, such as graphite, from anthracite.

EXPERIMENTAL

The anthracites come from the Harmony, Jeddo, LCNN, and Summit mines, all of which mine the Eastern Middle Field of Pennsylvania. LCNN and Jeddo mine the Mammoth vein; Harmony, the Lykens Valley #2; and Summit, the Tracey vein. No blending of coals is done at these plants, ensuring repeatability of data collected on the anthracites. Approximately 1000 lbs. of each anthracite were collected and a subset homogenized using techniques outlined by Glick and Davis of the Penn State Coal Sample Bank and Data Base [1]. The end products of this process were aliquots of -20 and -60 (U.S. Standard Sieve) mesh anthracite stored in foil laminate bags under an argon atmosphere [1]. Next, chemical and physical data were collected using X-ray diffraction, ¹³C NMR, proximate and ultimate analysis, maceral point counts, CO₂ surface area, and helium density. Values for aromaticity, H/C ratio, and interlayer spacing were used in generating possible anthracite structures using MSI software [2].

RESULTS

Ultimate and proximate analysis results are presented in Table 1 and Table 2, respectively. With increasing carbon content there is a decrease in the hydrogen content, as expected. This is indicative of ring condensation with concurrent loss of hydrogen. When normalized to 100 carbon atoms, Summit has the highest hydrogen content with 32 hydrogens per 100 carbon atoms while LCNN has the lowest with 19 hydrogen atoms per 100 carbon atoms. Table 2 shows relatively equal amounts of ash and volatile matter, except for the Summit anthracite, which has nearly twice the levels of ash in comparison to the other samples. High levels of mineral matter, as indicated by high levels of ash, are undesirable for graphite production [3]. The maceral compositions are shown in Table 3. The category "other inertinite" was used when the optical differences between fusinite and semi-fusinite could not be distinguished. Maceral composition is usually an important parameter as macerals are known to have different chemical structures which may lead to different levels graphitizability [4]. X-ray diffraction, diffractogram shown in Figure 1, was used to determine the distance between aromatic sheets in d-spacing. The XRD diffractogram of the Jeddo sample indicates d-spacings range from 12.91 to 2.57 nm in the identifiable peaks. ¹³C Single Pulse NMR, Figures 2, was used to determine the aromaticity of the samples. All the anthracites studied were found to be 100% aromatic.

DISCUSSION

Using the chemical data, a hypothetical structure for the Jeddo anthracite was generated and minimized using molecular mechanics (Drying force-field [5]), see Figure 3. The parameters utilized in generation of the model were %H, %N, %O, d-spacing, aromaticity, and number of rings in an aromatic, or pre-graphitic sheet. The atomic H/C ratio determined from the ultimate analysis (H/C=0.22) and calculated from the model (H/C=0.22) are in agreement. Unfortunately, the relative proportions of quarternary, pyrrolic, and pyridinic nitrogen have not been determined for anthracite. Therefore it was assumed the nitrogen was present primarily in the quarternary form (9 of the 11 nitrogens are quarternary in Figure 3), presumably from the condensation of smaller pyridinic containing sheets. Oxygen was assumed to be in open or closed ethers with perhaps some carbonyl. As there are only 18 heteroatoms per 1010 carbons in the proposed anthracite, any errors in their assignments will have a minimal impact on the gross structure of the model. However, their assignments and placements may well have a bearing on the reactivity of the structure.

Past research has shown graphitized anthracites have crystallite heights of <36.8 nm, therefore the raw anthracite modeled here was generated with heights significantly lower than 36.8 nm [6]. The anthracite model shown in Figure 3 is approximately 45 Å across (plan view) and approximately 15 Å high. Average d-spacings between the sheets fall within the acceptable experimentally determined range, approximately 4 Å. However, the structure shown has not been subjected to molecular dynamics (thus may be trapped in a local minimum) nor does the force-field used contain an implicit $\pi - \pi$ interaction term. Furthermore, the model was minimized in a vacuum and has not experienced high pressures or interactions with neighboring sheets, which may be important in the overall structural alignment. Hence the structural representation is a product of less accurate modeling methods (due to model size restrictions on quantum mechanics and computational expense).

Ring condensation in anthracite is believed to be between >10 and 100 (rings per sheet) [7], so the number of rings in a polycyclic sheets shown in Figure 3 is a maximum of 91 and minimum of 47 rings. Combining the chemical data with stated assumptions resulted in a simplistic structure for the Jeddo anthracite, Figure 3. The model contains five pre-graphitic planes with an average of 81 rings comprising a sheet. The beginnings of graphitic stacking are apparent, Figure 3. The aromaticity of the model is 99%, while the experimentally determined aromaticity is 100%. Recall that the model is in agreement with the elemental composition. Hence the model is in close agreement with the chemical data determined to date. Incorporation of physical data, such as helium density, and additional chemical data will further refine the structure [8].

CONCLUSIONS

The coals selected for this research are all in the anthracite range, yet exhibit varied chemical properties (mostly hydrogen content, maceral composition and degree of crystallinity) presumably as a result of different geological histories. It may be assumed that the graphitizability of these samples will vary with their constitution. These differences can be better presented through visualization of the anthracite's structure and its changes upon carbonization. A model structure for Jeddo anthracite is presented. Incorporation of additional physical and chemical data will further refine the proposed model.

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Table 1. Ultimate Analysis Of Anthracite Samples*

Anthracite	% C	% H	% N	% S	% O (by diff.)
LCNN	95.7	1.5	1.2	0.5	1.0
Jeddo	95.2	1.8	1.1	0.6	1.3
Harmony	94.0	2.2	1.0	0.5	2.3
Summit	93.2	2.5	1.6	0.6	2.2

*dry ash-free basis

Table 2. Proximate Analysis Of Anthracite Samples

Anthracite	% Moisture	% Volatiles	% Ash	Fixed Carbon
LCNN	3.3	4.5	6.7	88.3
Jeddo	4.7	6.1	8.1	85.9
Harmony	4.6	7.5	6.6	86.2
Summit	2.6	11.1	17.6	71.2

Table 3. Maceral Percentages (from point counts)

Anthracite	Vitrinite	Fusinite	Semi-fusinite	Other Inertinite	Liptinite
LCNN	80	10	7	2	1
Jeddo	86	6	5	2	1
Harmony	60	24	14	1	1
Summit	80	15	4	0.5	0.5

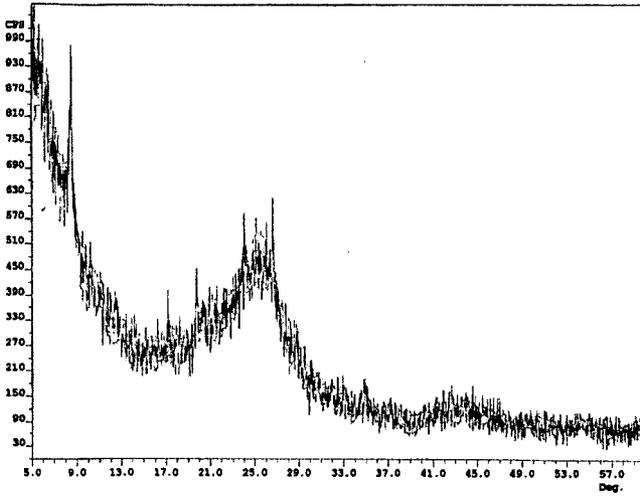


Figure 1. XRD Diffractogram Of Jeddo Anthracite

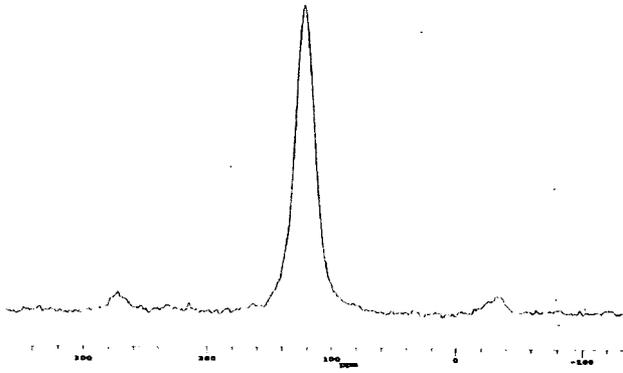


Figure 2. ¹³C CPMAS Spectra Of Jeddo Anthracite

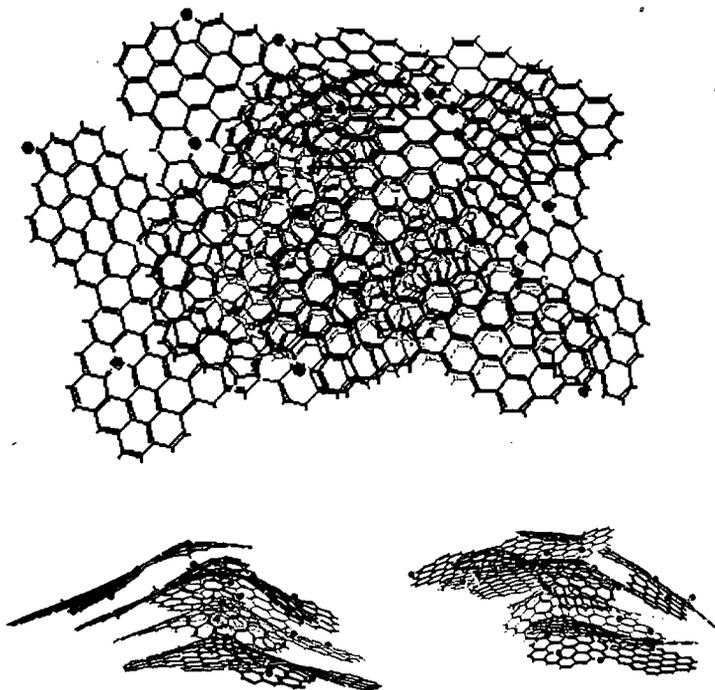


Figure 3. Plan And Side Views Of A Simplistic Model Of Jeddo Anthracite. $C_{1016}H_{2223}O_9N_9$
Heteroatoms shown as spheres.