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The chemical constitution of Pocahontas No. 3 coal

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A new method for the definition of the larger aromatic structural elements in high-rank coals has been developed. The procedure involves the oxidative decomposition of the coal with oxygen in basic solution and the subsequent decarboxylation of the aromatic carboxylic acids to yield a mixture of aromatic compounds that can readily be analyzed by conventional methods. This approach has been tested with pure compounds and applied to Pocahontas No. 3 coal.

1. INTRODUCTION

The Argonne National Laboratory Premium Coal Sample of Pocahontas No. 3 coal, a low-volatile bituminous coal that contains 89% vitrinite, 10% inertinite, and 1% liptinite, $C_{100}H_{57.5}O_{1.1}N_{1.2}S_{0.2}$, has been widely studied, and the information concerning its chemical constitution has been critically evaluated [1]. A structural representation that accommodates the available chemical and spectroscopic information has been described. It provides coal scientists with a guide to the chemistry of this highly aromatic coal with its abundant methyl groups and bridging biaryl and heterocyclic groups [1]. Whereas the aliphatic and heterocyclic constituents could be discussed with some confidence, it was recognized that it was impossible to specify the relative abundances of the aromatic components. Accordingly, we have attempted to address this deficiency by finding a suitable method to define the structures of these compounds in this coal.

2. RESULTS AND DISCUSSION

Ruthenium(VIII) oxidation, which is highly effective for the definition of the aliphatic structural elements of fossil fuels [2], also provides limited information about the aromatic compounds in Pocahontas No. 3 coal [3]. This oxidation reaction produced more benzenetri-, tetra-, and pentacarboxylic acids than benzenedicarboxylic acids, indicating that compounds with three or more rings predominated. Even more importantly, benzenepentacarboxylic acid and biphenyl-2,2',6,6'-tetracarboxylic acid, which are formed from compounds with five or more aromatic rings, were produced in the oxidation with ruthenium(VIII).

But, as already mentioned, this approach does not enable the definition of the structures of the large aromatic constituents, and we have investigated methods that might be suitable for the definition of the structures of these components through methods that were more selective for the oxidation of the structural elements on the periphery of the aromatic units. Inasmuch as these oxidation reactions provided a very complex mixture of carboxylic acids, we elected to decarboxylate the initial products to obtain a more manageable product distribution. Empirical work with a variety of reagents led to the conclusion that the highest yields could be obtained when the Pocahontas No. 3 coal was oxidized with oxygen in alkaline solution. This very old reaction [4] proved to be most effectively accomplished for the Pocahontas coal when barium hydroxide was used as the co-reagent. The methods for the decarboxylation of aromatic carboxylic acids were also explored by examining their effectiveness with representative pure compounds including naphthalene- and anthracenecarboxylic acids, and anthraquinonecarboxylic acids. We established that the decarboxylation reactions of these compounds proceeded most effectively with copper oxide in quinoline and N-methylpyrrolidinone. The researches of Cohen and his associates were extremely helpful in the selection and modification of this procedure [5]. When this procedure was applied to the oxidation products of the Pocahontas No. 3 coal, the conversion of the carboxylic acids to aromatic hydrocarbons was very successful.

The mixture of aromatic compounds from the Pocahontas No. 3 coal was examined by gas chromatography and mass spectroscopy. Dr. Jerry Hunt provided the desorption, electron impact, high-resolution mass spectrum that is shown in Figure 1.

Figure 1. Desorption, electron impact, high-resolution mass spectrum of decarboxylated oxidation products from Pocahontas (APCS 5).

The results indicate the broad array of products that are formed for the Pocahontas coal in the product-simplifying, oxidation-decarboxylation procedure. The qualitative ring-size scale, which is shown in the figure for convenient reference, does not distinguish between polycyclic molecules and biaryls. However, it is apparent that molecules with six to nine rings are rather abundant in the product mixture. The products contain hydrocarbons, heterocycles, and quinones.

3. CONCLUSION

A new method for the elaboration of the aromatic structural elements in coal has been investigated and applied to Pocahontas No. 3 coal. The results extend the conclusions of other investigations. For example, Solum, Pugmire, and Grant described a method by which the average aromatic cluster size could be deduced through solid state carbon magnetic resonance spectroscopy [6]. The application of their method to the most recent spectroscopic data for Pocahontas coal [1] suggests that the average cluster size could range from 17 (circular catenation) to 30 (linear catenation). The present results infer that the clusters are large and that molecules with six, seven, eight, and nine rings are abundant.

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