

values of  $V_{mic}$ ,  $V_m$ , and  $V_{mic}^t$ , and (b) with the calorimetrically determined heats of immersion—the values of  $(-\Delta H_i)_{\beta E_0}$  are very close to respective values of  $[(-\Delta H_i)_{calor} - (-\Delta H_i)_{S_{mes}}]$ .

This agreement was achieved (a) if the values of  $S_{mes}$ , necessary for the construction of the corrected adsorption isotherms, were obtained from the calculations of the pore-size distributions of the mesopores and (b) if in the applied DA equation the exponent  $n = 2$  was assumed, even though other values of  $n$  may sometimes give better formal correlation of the experimental data with the DA equation.

It seems that these parameters  $W_0$  and  $\beta E_0$  are closely related to the real properties of the capillary structure of

the chars—their micropore volumes and the integral enthalpies of immersion, respectively.

These conclusions were obtained for micro- and mesoporous carbonaceous materials and so should be applicable to the evaluation of adsorption data on other active carbons characterized by similar capillary structures.

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**Registry No.** Benzene, 71-43-2; cyclohexane, 110-82-7.

## Test of the Proposed Two-Phase Model for High-Volatile Bituminous Coal

Masaharu Nishioka\*<sup>†</sup> and Martin L. Gorbaty

Corporate Research Science Laboratories, Exxon Research and Engineering Company,  
Clinton Township, Annandale, New Jersey 08801

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The two-phase model for coal states that relatively large amounts of low-molecular-weight compounds are physically trapped in the macromolecular network. This model was tested by studying tetrahydrofuran (THF) extracts of original and *n*-butylamine-treated Illinois No. 6 coal and a heat-treated sample of the *n*-butylamine-treated coal's THF extract. Major portions of high-volatile bituminous coals are rendered THF soluble by heating in *n*-butylamine and should release any physically trapped low-molecular-weight molecules. These molecules were not released by *n*-butylamine treatment but were released by thermal degradation of the extracts of the *n*-butylamine-treated coal. It is concluded that the two-phase model is not applicable for this high-volatile bituminous coal. A monophasic model is proposed in this paper, which postulates that (1) large amounts of neutral small molecules are not tightly occluded inside the coal network and (2) the "mobile phase" consists largely of partial constituents of macromolecules.

### Introduction

It has been proposed that coal is composed of macromolecular networks with relatively small molecules occluded in these networks.<sup>1,2</sup> This idea is known as the two-phase or host-guest model. The essence of this model is that a large amount of a mobile (molecular) phase or a "guest" of relatively low-molecular-weight, such as a pentacyclic triterpane and various long-chain alkyl aromatics, is physically trapped inside an immobile (macromolecular) phase, or host, of relatively high molecular weight. A similar model is one in which some portions of the mobile phase are bonded to the immobile phase; however, the key feature is still that a substantial portion of the mobile phase is clathrated within the immobile phase.<sup>3,4</sup>

Extraction of low-molecular-weight compounds was extensively investigated from 1960 to the early 1970s,<sup>5,6</sup> and their complete extraction was difficult. In the late 1970s to early 1980s, the amount of mobile phase was reestimated by using NMR techniques when the <sup>1</sup>H NMR free-induction decay was applied for coal to distinguish between

mobile protons and immobile protons.<sup>7-13</sup> Many workers have attempted to validate the two-phase model,<sup>14-20</sup> and

(1) Given, P. H. In *Coal Science*; Gorbaty, M. L., Larsen, J. W., Wender, I., Eds.; Academic Press: New York, NY, 1984; Vol. 3, pp 190-204.

(2) Given, P. H.; Marzec, A.; Barton, W. A.; Lynch, L. J.; Gernstein, B. C. *Fuel* 1986, 65, 155-163.

(3) Lin, R.; Davis, A.; Bensley, D. F.; Derbyshire, F. J. *Org. Geochem.* 1987, 11, 393-399.

(4) Given, P. H.; Marzec, A. *Fuel* 1988, 67, 242-244.

(5) Holden, H. W.; Robb, J. C. *Fuel* 1960, 39, 39-46, 485-494.

(6) Vahrman, M. *Fuel* 1970, 49, 5-16. Spence, J. A.; Vahrman, M. *Fuel* 1970, 49, 395-408. Rahman, M.; Vahrman, M. *Fuel* 1971, 50, 318-328. Palmer, T. J.; Vahrman, M. *Fuel* 1972, 51, 14-21, 22-26. Vahrman, M.; Watts, R. H. *Fuel* 1972, 51, 130-134, 235-241. Vahrman, M. *Chem. Br.* 1972, 8, 16-24.

(7) Yokono, T.; Sanada, Y. *Fuel* 1978, 57, 334-336.

(8) Lynch, L. J.; Webster, D. S. *Fuel* 1979, 58, 235-237.

(9) Jurkiewicz, A.; Marzec, A.; Idziak, S. *Fuel* 1981, 60, 1167-1168.

(10) Jurkiewicz, A.; Marzec, A.; Pislewski, N. *Fuel* 1982, 61, 647-650.

(11) Marzec, A.; Jurkiewicz, A.; Pislewski, N. *Fuel* 1983, 62, 996-998.

(12) Barton, W. A.; Lynch, L. J.; Webster, D. S. *Fuel* 1984, 63, 1262-1268.

(13) Jurkiewicz, A. *Fuel* 1986, 65, 1022-1024.

(14) Redlich, P.; Jackson, W. R.; Larkins, F. P. *Fuel* 1985, 64, 1383-1390.

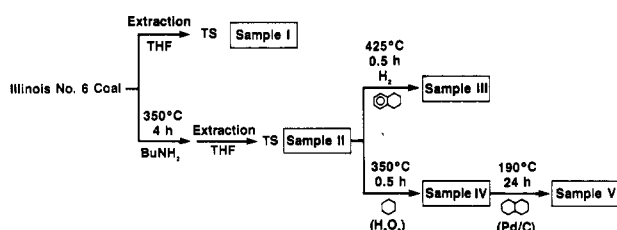
(15) Schulten, H. R.; Marzec, A. *Fuel* 1986, 65, 855-860.

(16) Marzec, A. *Fuel Process. Technol.* 1986, 14, 39-46.

(17) Kamiński, B.; Pruski, M.; Gerstein, B. C.; Given, P. H. *Energy Fuels* 1987, 1, 45-50.

\*To whom correspondence should be addressed.

<sup>†</sup>Present address: BCR National Laboratory, 500 William Pitt Way, Pittsburgh, PA 15238.



**Figure 1.** Solvent treatment and reaction scheme of Illinois No. 6 coal.

there seems to be consensus by them that only some portion of a mobile phase can be extracted by using conventional extraction procedures because of restricted orifice sizes of the immobile phases or networks. However, there is no direct evidence to prove the two-phase model.

It was shown in a previous paper<sup>21</sup> that low-molecular-weight compounds such as *n*-alkanes, naphthalene, phenanthrene, and alkylpentacyclic hydrocarbons were produced from high-molecular-weight coal extract fractions by very mild heating (250 °C, 24 h). This result implies that some low-molecular-weight compounds usually found in solvent extracts are also partial constituents of high-molecular-weight compounds and are not always trapped inside the immobile phase.

However, since very mild pyrolytic conditions were employed in the previous work, only small amounts (less than a few percent) of low-molecular-weight compounds were produced. Thus, only partial amounts of the whole coals were examined in that study. Larger portions of coals and quantitation of the compounds produced by a pyrolysis are required in order to clarify the mobile and immobile states in coal.

Recently, it was reported by Tagaya et al.<sup>22</sup> that greater than 70% of the organic portion of high-volatile bituminous coals could be solubilized in tetrahydrofuran (THF) after heating in *n*-butylamine at 200–300 °C. The two-phase model predicts that most of the physically trapped small molecules would be released during this procedure.

To test the two-phase model, THF extracts obtained after treating coals with *n*-butylamine were examined and also further pyrolyzed in two different ways. The THF extracts from the original coal and the *n*-butylamine-treated coal and the pyrolyzed extracts were fractionated into chemical classes. Representative "mobile-phase" compounds, *n*-alkanes and polycyclic aromatic hydrocarbons (PAH), were semiquantitated and compared. If the two-phase model is valid, roughly equal amounts of these low-molecular-weight species should be detected in the *n*-butylamine-treated coal and the pyrolyzed extracts and the amounts should be higher than in the extract from the untreated coal.

### Experimental Section

High-volatile C bituminous Illinois No. 6 coal (Exxon Research and Engineering Co.) was used in this study. The elemental analysis and sample preparations were reported in a previous paper.<sup>21</sup> ACS reagent and HPLC grade solvents were used. Palladium on activated carbon (10%) was obtained from Alfa Products (Danvers, MA). THF was distilled before use, but other materials were used without purification.

Coal was treated as outlined in Figure 1. The coal (6 g) was charged into the Pyrex liner of a 300-mL autoclave (Parr Instrument Co., Moline, IL). After adding *n*-butylamine (25 mL), evacuating, and purging with nitrogen five times, the autoclave was heated to 350 °C within 10 min with a Parr bomb heater and held at 350 ± 3 °C for 4 h with agitation provided by magnetic stirring. The products were washed out with THF, filtered, and Soxhlet extracted with THF (sample II).

One part of the THF extract was hydrotreated following the procedure of Mudamburi and Given.<sup>23,24</sup> A sample (2 g) was heated with tetralin (5.6 mL) and H<sub>2</sub> (initial pressure 6.5 MPa) in a tubing bomb heated by immersion in a preheated fluidized bed sand bath at 425 °C for 30 min (sample III). Another sample (2 g) was heated in cyclohexane (30 mL) and 3% aqueous H<sub>2</sub>O<sub>2</sub> (3 mL) at 350 °C for 30 min in the autoclave (sample IV).<sup>25</sup> The product (0.3 g) after H<sub>2</sub>O<sub>2</sub> treatment was further refluxed in decalin (50 mL) with Pd (10%) on activated carbon (300 mg) at 190 °C for 24 h (sample V).

The starting coal and the *n*-butylamine-treated samples (2–3 g) were extracted with 200 mL of THF for 24 h in a Soxhlet apparatus under a N<sub>2</sub> atmosphere, and the extracts fractionated into chemical classes by column adsorption chromatography on neutral alumina.<sup>26</sup> The aliphatic and neutral aromatic fractions were analyzed in this study using a Hewlett-Packard Model 5840A gas chromatograph (GC) equipped with a flame ionization detector. Sample injection was made in the splitless mode, and the helium carrier gas was set at a linear velocity of 50–60 cm s<sup>-1</sup>. The fused silica capillary column (30 m × 0.25 mm i.d.) coated with SE-54 (film thickness of 0.25 μm) was obtained from SUPELCO, INC. (Bellefonte, PA). Compounds were identified by comparison of sample component retention data with those of pure standards and by gas chromatography/mass spectrometry (GC/MS). Mass spectral data were collected with a Hewlett-Packard 5970 mass spectrometer system operated in the electron-impact mode at 70 eV with the ion source and analyzer temperature held at 250 and 280 °C, respectively, and with the scan speed set at 300 amu s<sup>-1</sup>.

### Results and Discussion

Given et al.<sup>23,24,27</sup> reported that the yield of *n*-alkanes and *n*-alkyl aromatics released from coals by liquefaction in tetralin at 400–425 °C was 6–10 times greater than the yield obtained by Soxhlet extraction. They found it difficult to conceive of such homologous series being released from the macromolecular network by thermal reactions and inferred that the compounds were clathrated inside the network. It is, however, impossible to distinguish the breaking of covalent bonds from disruption of physical interactions using their data.

Since most of the organic matter of high-volatile bituminous coals could be solubilized in THF after mildly heating in *n*-butylamine, use of the two-phase model would predict the observation of larger amounts of low-molecular-weight compounds in the THF extract of the *n*-butylamine-treated coal relative to that found in the THF extract from untreated coal. Thus, representative "mobile-phase" compounds, *n*-alkanes and PAH, in the THF extracts from the *n*-butylamine-treated coal were compared to that found in the THF extracts of the untreated coal. The THF extract from the *n*-butylamine heated coal was further treated according to Given's procedure as well as another method to differentiate between breaking covalent bonds and physical forces (Figure 1). Although the detailed solvation mechanism in *n*-butylamine is not clear, increases in abundance of low-molecular-weight compounds in samples III and IV compared

(18) Singleton, K. E.; Cooks, R. G.; Wood, K. V.; Rabinovich, A.; Given, P. H. *Fuel* 1987, 66, 74–82.

(19) Monthieux, M.; Landais, P. *Fuel* 1987, 66, 1703–1708.

(20) Lynch, L. J.; Sakurovs, R.; Webster, D. S.; Redlich, P. J. *Fuel* 1988, 67, 1036–1041.

(21) Nishioka, M.; Larsen, J. W. *Energy Fuels* 1988, 2, 351–355.

(22) Tagaya, H.; Sugai, J.; Onuki, M.; Chiba, K. *Energy Fuels* 1987, 1, 397–401.

(23) Mudamburi, Z.; Given, P. H. *Org. Geochem.* 1985, 8, 221–231.

(24) Mudamburi, Z.; Given, P. H. *Org. Geochem.* 1985, 8, 441–453.

(25) Gurdzinska, E.; Bukowski, A. *Fuel* 1982, 61, 867–871.

(26) Later, D. W.; Lee, M. L.; Bartle, K. D.; Kong, R. C.; Vassilaros, D. L. *Anal. Chem.* 1981, 53, 1612–1620.

(27) Youtcheff, J. S.; Given, P. H.; Baset, Z.; Sundaram, M. S. *Org. Geochem.* 1983, 5, 157–164.

**Table I. Approximate Weight Percent of Each Fraction of the Samples I-V for the Starting Whole Coal by the Neutral Alumina Adsorption Fractionation<sup>12</sup>**

fraction	sample				
	I	II	III	IV	V
A-1 (aliphatics)	0.69	1.7	<i>a</i>	1.9	<i>a</i>
A-2 (aromatics)	0.29	0.60	3.8	2.8	2.8
A-3 (weak basics)	0.77	20	25	18	17
A-4 (weak acidics)	2.3	53	29	12	10

<sup>a</sup> Not obtained because of difficulty of solvent removal.

**Table II. Approximate Relative Abundances of Selected Compounds in Each Sample**

	sample <sup>a</sup>				
	I	II	III	IV	V
<i>n</i> -C <sub>17</sub> H <sub>36</sub>	1	4	40	110	40
<i>n</i> -C <sub>18</sub> H <sub>38</sub>	2	5	40	70	70
<i>n</i> -C <sub>19</sub> H <sub>40</sub>	2	4	50	30	30
<i>n</i> -C <sub>20</sub> H <sub>42</sub>	1	3	40	20	20
<i>n</i> -C <sub>21</sub> H <sub>44</sub>	2	6	80	20	20
<i>n</i> -C <sub>22</sub> H <sub>42</sub>	0.3	0.5	30	10	10
naphthalene	<i>b</i>	<i>b</i>	3	4	10
fluorene	<i>b</i>	<i>b</i>	0.2	5	5
phenanthrene	1	1	3	10	20
anthracene	0.05	0.05	0.1	1	4
fluoranthene	<i>b</i>	<i>b</i>	2	4	5
pyrene	0.1	0.1	2	3	4
benzo[ <i>b</i> ]fluorene	<i>b</i>	<i>b</i>	0.4	0.5	0.05
benz[ <i>a</i> ]anthracene	<i>b</i>	<i>b</i>	2	0.03	0.06
chrysene	<i>b</i>	<i>b</i>	2	0.1	0.01

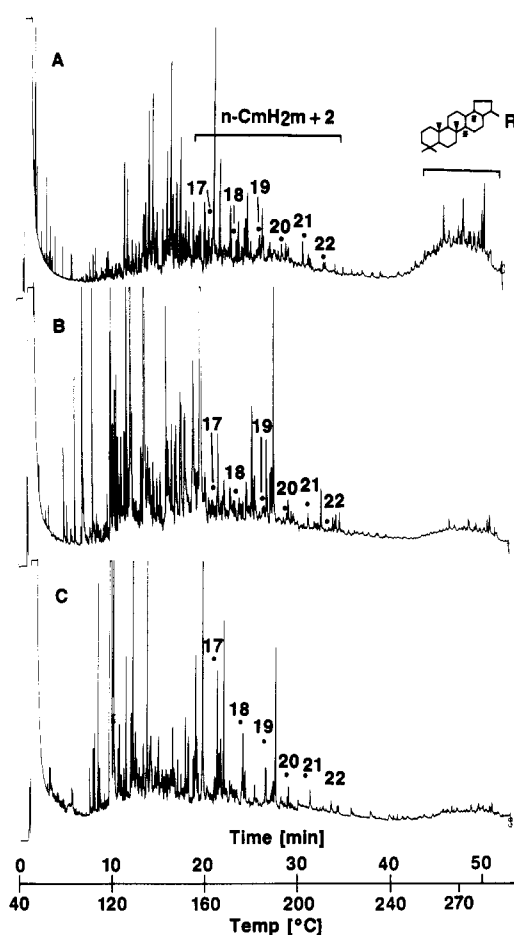
<sup>a</sup> Relative abundances are shown as *n*-C<sub>20</sub>H<sub>42</sub> = 1 in sample I for aliphatics and phenanthrene = 1 in sample I for aromatics (wt ratio). <sup>b</sup> <0.01.

to samples I and II would unequivocally show that this is due to breaking of chemical bonds. (See Figure 1.)

The yield of sample II from the Illinois No. 6 coal was approximately 85 wt %, which was normalized for the extract and the nonextract because of an 18 wt % weight gain after heating in *n*-butylamine (the yield of sample I was 11.2 wt %<sup>21</sup>). Approximate weight percent of each fraction by column adsorption chromatography is listed in Table I. Relative abundances of *n*-alkanes in the samples were semiquantitatively analyzed by GC. The results are shown in Table II relative to *n*-C<sub>20</sub>H<sub>42</sub> in sample I. It is obvious that the yields of these compounds in samples III and IV are 10 times greater than those in samples I and II, while the yields of these compounds in samples I and II are nearly comparable. From this, it can be concluded that the increased amounts of these compounds in samples III and IV are due to the thermal degradation of macromolecules and were not released from physically trapped or clathrated compounds inside the network or immobile phase.

Figure 2 shows the gas chromatograms of the aliphatic fractions of samples I, II, and IV. It is clear that *n*-alkanes with carbon numbers 17–22 were relatively increased from samples II to IV by the heat treatments. Since the abundances of pentacyclic triterpanes decreased in the order of more heat-treated samples I, II, and IV, they are presumably thermally labile compared with *n*-alkanes.

Since the great increase of *n*-alkanes in the product obtained by this study is due to the degradation of coal macromolecules, it is proposed that *n*-alkyl groups are important substituents of Illinois No. 6 coal macromolecules, and most of the *n*-alkanes in its derived products are formed from breakdown of high-molecular-weight compounds. Previously, it was shown<sup>21</sup> that low-molecular-weight compounds containing *n*-alkanes are not always physically trapped in the coal but are produced by the



**Figure 2.** Gas chromatograms of aliphatic fractions of (A) sample I, (B) sample II, and (C) sample IV. Conditions are as follows: 40–120 °C at 10 °C min<sup>-1</sup> and 120–270 °C at 4 °C min<sup>-1</sup> after an initial 2-min isothermal period. Numbers denote the number of carbons of *n*-alkanes.

decomposition of higher molecular weight compounds. Both results, obtained by different experimental procedures, are consistent.

The relative abundances of the major PAH in samples I–V are also shown in Table II relative to phenanthrene in sample I. The compounds in samples III–V were noticeably increased after thermal reactions, similar to the *n*-alkanes. Therefore, they are also apparently important partial constituents of coal macromolecules, or derived from macromolecules during heat treatment. Gas chromatograms of aromatics of samples I, IV, and V and their possible identifications are shown in Figure 3 and Table III. The identifications of hydroaromatics were based on the retention indices and mass fragmentation patterns reported by Wozniak and Hites.<sup>28</sup>

There were two purposes for the reaction leading to sample V. One was to confirm the identification of the hydroaromatics, because it is known most of the hydroaromatics are dehydrogenated by Pd on activated carbon at the low temperature used in this study. It was confirmed in this work that more than 95% of 9,10-dihydroanthracene and 1,2,3,6,7,8-hexahydropyrene were dehydrogenated and produced anthracene and pyrene. The second purpose was to investigate the effect of aromatization by dehydrogenation during coal liquefaction.

Some structural characteristics were found for low-molecular-weight compounds in the heat-treated samples.

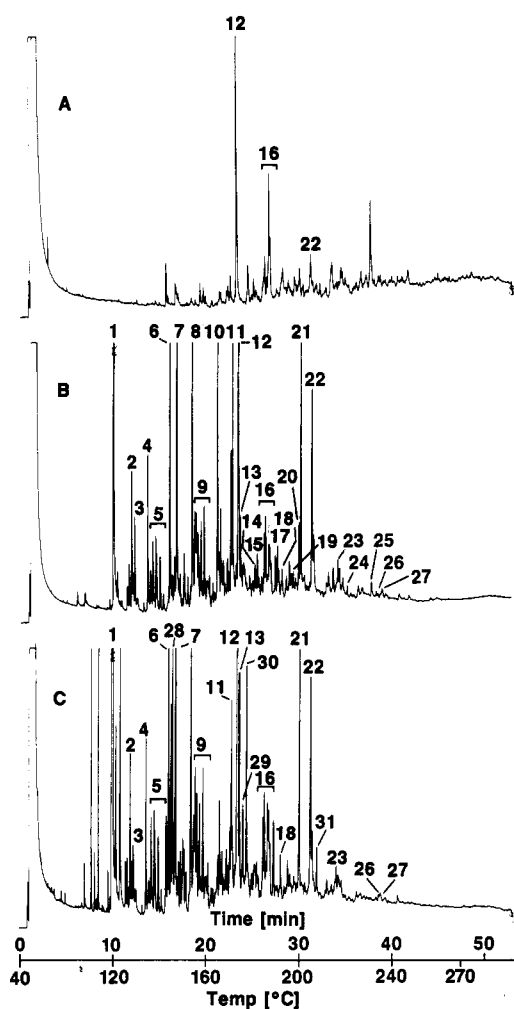


Figure 3. Gas chromatograms of the aromatic fractions of (A) sample I, (B) sample IV, and (C) sample V. Conditions were as in Figure 2. Peak assignments are listed in Table III.

Hydroaromatics such as hydroanthracenes, hydrophenanthrenes, and hydroxyrenes were abundant in sample IV compared to sample III, while 4- and 5-ring PAH such as chrysene and benzopyrenes were abundant in sample III (Table II). Since it is thought that the major reaction producing sample IV from sample II is a mild radical cracking while the major reaction involved in forming sample III from sample II is hydrocracking including thermal aromatizations at high temperature, hydroaromatics seem to be important constituents of coal macromolecules. Although phenyl-substituted aromatics such as biphenyls and phenylnaphthalenes are abundant in samples III and IV, carbon-linked aromatics such as diphenylmethane and bibenzyl were not found in these samples at a significant level. The relative abundances of the aliphatics and aromatics in sample V are approximately similar to other coal liquids such as the solvent-refined coal II heavy distillate (SRC II HD),<sup>29</sup> although the feedstock was a different coal.

From the above results, we can infer the following. Distribution of coal functionalities are quite uniform in

Table III. Neutral Aromatics Identified in Original and Pyrolyzed Illinois No. 6 Samples

peak no.	molecular mass and/or major fragments, <sup>a</sup> <i>m/z</i>	possible structure
1	128	naphthalene
2	142	2-methylnaphthalene
3	142	1-methylnaphthalene
4	154	biphenyl
5	156	C <sub>2</sub> -naphthalene
6	154	acenaphthene
7	168	C <sub>1</sub> -biphenyl
8	166	fluorene
9	168, 182, 180	C <sub>1</sub> -acenaphthene, tetrahydroanthracene, dihydroanthracene
10	180 (100), 179 (71), 178 (48)	9,10-dihydrophenanthrene
11	182	tetrahydrophenanthrene
12	178	phenanthrene
13	178	anthracene
14	204	1-phenylnaphthalene
15	196 (100), 181 (73), 168 (54), 165 (56)	C <sub>3</sub> -biphenyl or C <sub>1</sub> -tetrahydrophenanthrene
16	192	C <sub>1</sub> -phenanthrene
17	206 (100), 178 (212)	4,5,9,10-tetrahydropyrene
18	204	2-phenylnaphthalene
19	208 (100), 207 (83), 206 (51), 178 (46)	1,2,3,6,7,8-hexahydropyrene
20	204 (100), 203 (100), 202 (75)	4,5-dihydropyrene
21	202	fluoranthene
22	202	pyrene
23	216	benzo[ <i>b</i> ]fluorene
24	216	C <sub>1</sub> -pyrene
25	232 (100), 207 (67), 204 (57)	tetrahydrobenz[ <i>a</i> ]anthracene
26	228	benz[ <i>a</i> ]anthracene
27	228	chrysene
28	220 (100), 205 (479)	unknown
29	196 (100), 195 (76), 181 (133), 167 (71)	C <sub>2</sub> -fluorene
30	233 (100), 181 (55)	unknown
31	216 (100), 215 (66)	C <sub>1</sub> -fluoranthrene

<sup>a</sup>Numbers in parentheses denote relative abundances in mass spectrum.

the extractables and nonextractables. Most *n*-alkanes and PAH are not physically tightly trapped inside networks and can be extracted by conventional procedures such as a Soxhlet extraction. They exist as both free molecules and partial constituents of macromolecules or are derived from macromolecules during heat treatment. Consequently, since the two-phase model requiring large amounts of trapped low-molecular-weight molecules does not appear to be appropriate for Illinois No. 6 coal, the coal should be considered as being more like a monophasic.

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(29) Nishioka, M.; Lee, M. L. In *Polynuclear Aromatic Compounds; Advances in Chemistry* 217; American Chemical Society: Washington, DC, 1988; Chapter 14, and references cited in the paper.