



Interlaboratory comparisons of petrography of liquefaction residues from three Argonne Premium coals

JAMES C. HOWER,¹ KEN B. ANDERSON,² GLENDA MACKAY,³ HENRIQUE PINHEIRO,⁴
DEOLINDA FLORES⁴ and MANUEL J. LEMOS DE SOUSA⁴

¹University of Kentucky, Center for Applied Energy Research, Lexington, KY 40511, U.S.A.

²Amoco Oil Co., Research and Development Department, Naperville, IL 60566, U.S.A.

³Swinburne University of Technology, Hawthorn, Victoria 3122, Australia

⁴Organic Petrology Unit, University of Porto, 4000 Porto, Portugal

Abstract—Three Argonne Premium coal samples, the Beulah-Zap lignite (North Dakota), the high volatile A bituminous Stockton (West Virginia), and the low volatile Pocahontas No. 3 (Virginia), were ground to three initial sizes: –20 mesh, –100 mesh, and “micronized”. The samples were each subjected to liquefaction at 673 K for 30 min at a 2:1 tetralin:coal ratio and in an H₂ atmosphere at 13.79 MPa (~2000 psi). Polished pellets of the unconverted residues were circulated to three laboratories for a study designed to determine, albeit on a limited scale, the interlaboratory consistency in constituent identification and the problem areas in maceral/neo-maceral/mineral recognition. Within broad categories, the agreement for the Beulah-Zap and Pocahontas No. 3 residues is good. The high volatile A bituminous Stockton coal was the most plastic and most altered, resulting in a residue lending itself to more subjective interpretations. The biggest discrepancy between the laboratories is in the distinction of granular residue and mineral matter and in the transitions between “partially reacted macerals” and “vitroplast” and between “vitroplast” and “granular residue”. The initial size of the feed coal appears to influence the recognition of material in the residue.

Key words—Argonne Premium coals, liquefaction, liquefaction residues, macerals

INTRODUCTION

The study of the insoluble residues from coal liquefaction adds to the understanding of the interaction between processing conditions and coal characteristics. Some effort has been expended in developing consistent nomenclature to describe the residues (ICCP, 1993) but, as the number of laboratories conducting such studies is considerably more limited than the number of organic petrology laboratories, the opportunities for interlaboratory comparisons have been limited. This study developed as a research committee project of The Society for Organic Petrology (TSOP) and was conducted from 1991 to 1993. The sole objective of the study was to investigate the level of agreement between different laboratories. Studies of the development of residues through variations in processing conditions, studies which are beyond the scope of this project, have been conducted by Hower *et al.* (1992, 1993) and Keogh *et al.* (1992) on high volatile bituminous coals.

PROCEDURE

Three Argonne Premium coals: the Beulah-Zap (North Dakota) lignite (APCS #8), the high volatile A bituminous Stockton coal (West Virginia) (APCS #7), and the low volatile bituminous Pocahontas No. 3 coal (Virginia) (APCS #5), were ground to

three sizes each: –20 mesh, –100 mesh, and “micronized” (–325 mesh). Liquefaction was conducted at 673 K for 30 min at 2:1 tetralin:coal and 13.79 MPa (~2000 psi) H₂ in agitated tubing bombs heated in a fluidized-bed sand bath. Liquefaction products were then Soxhlet extracted (sequentially) with hexane, toluene, and tetrahydrofuran (THF) to remove oils, asphaltenes, and pre-asphaltenes, respectively. The residues were then dried overnight under vacuum at 60°C.

Each of the nine insoluble residues was prepared as epoxy-bound polished pellets and complete sets were distributed to the participating laboratories. The participants were also provided with particulate pellets of the original –20 mesh coal. As noted, there are a limited number of laboratories worldwide conducting this type of analysis. Several additional laboratories were solicited but declined to participate. Petrographic description of the residues followed guidelines established in the ICCP report (1993). A draft form of the ICCP report was distributed to the participants.

DISCUSSION

The proximate and ultimate analyses and petrographic analyses of the three coals are given on Tables 1 and 2. The percent conversion of each of the samples is given on Table 3. Decreased conversion in

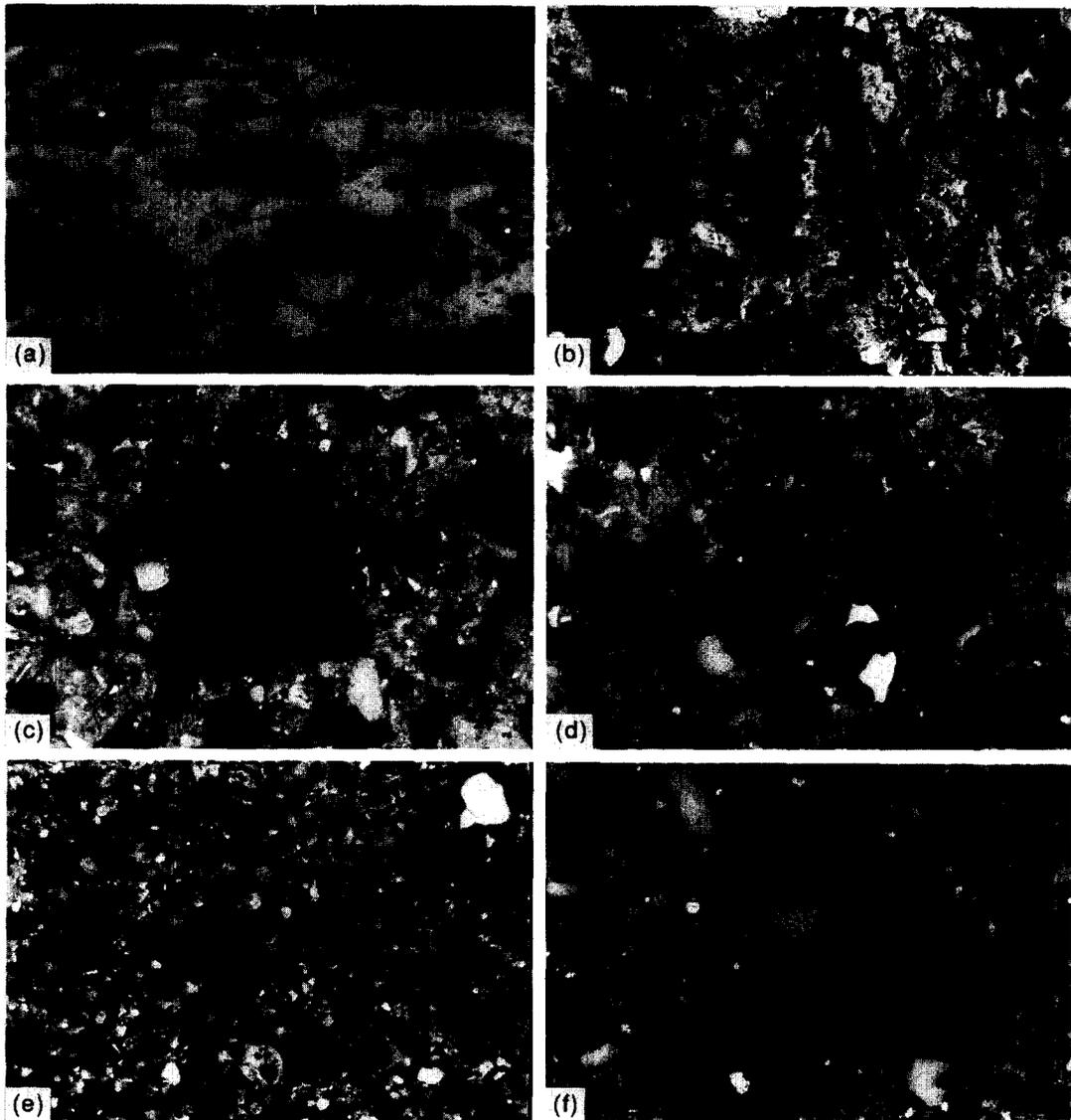


Fig. 1. Liquefaction residues from the Beulah-Zap lignite (all photos $330\ \mu\text{m}$ on long axis). (a, b) -20 mesh feed coal. Note unreacted semifusinite (a) and partially reacted humic macerals (b). (c, d) -100 mesh feed coal. Both fields are dominated by partially reacted, fused humic macerals. (e, f) Micronized feed coal. Evidence of reactions is seen in the devolatilization vacuoles and in the partial fusion of particles.

recognizing more unreacted macerals, usually fusinite and semifusinite.

The appearance of the Beulah-Zap residues in reflected light, oil immersion is illustrated in Fig. 1. The residue particle size strongly reflects the size of the original coal particles. There is evidence of at least partial melting of the huminite macerals as seen in the rounded corners of particles and the apparent welding of particles. The decision whether to place such material in the "partially reacted maceral" or "vitroplast" categories was a point on which the three laboratories differed. Devolatilization of the reacted huminite is evident in Fig. 1(b)-(f).

Stockton

The results for the high volatile A bituminous

Stockton coal are shown on Table 5. In comparison to the Beulah-Zap residues, discussed above, and the Pocahontas No. 3 residues, to be discussed below, the interpretation of the Stockton residues differed considerably between laboratories. The coal was obviously highly plastic (see Fig. 2) and altered, factors leading to problems in the recognition of residue forms. The biggest discrepancy lies in the transition from "vitroplast" to "granular residue". In addition, the distinction between "granular residue" and fine clay minerals was noted to be difficult and, consequently, some of the laboratory 2 "granular residue" may actually be unreacted mineral matter. The apparent increase in "granular residue" with a decrease in initial particle size as seen by both laboratories 1 and 2 may be a function of greater dispersion of fine

Table 5. Petrography of liquefaction residues from the Stockton coal (vol. %). Blanks imply that laboratory did not seek that maceral or neomaceral

Mesh Laboratory	-20 1 (vol. %)	-20 2 (vol. %)	-20 3 (vol. %)	-100 1 (vol. %)	-100 2 (vol. %)	-100 3 (vol. %)	Micronized 1 (vol. %)	Micronized 2 (vol. %)	Micronized 3 (vol. %)
Vitrinite									
Fusinite	9.5			10.0			8.7		
Semifusinite	6.5			8.2			8.2		
Micrinite	0.2								
Liptinite	0.2			0.5			0.5		
Subtotal: unreacted macerals	16.4	2.4	13.0	18.7	5.8	10.0	17.4	0.4	7.0
Partially reacted macerals (pr)		15.8	53.0		9.0	40.0		7.0	34.0
Vitroplast (vp)	56.3	19.8	26.0	50.3	15.2	45.0	54.5	6.2	55.0
Cenosphere (cs)						1.0			Trace
Subtotal: pr + vp + cs	56.3	35.6	79.0	50.3	24.2	86.0	54.5	13.2	89.0
Primary semicoke	0.5	0.8		0.3	0.4		0.3	1.0	
Secondary semicoke	3.5	0.6		2.7			1.8		
Granular residue	4.0	60.0	Trace	8.4	67.2	1.0	9.7	84.8	Trace
Unaltered minerals	17.9		8.0	18.0	0.4	3.0	14.1		4.0
Altered minerals					0.2			0.2	
Sulfides	1.5			1.6					
Neominerals					1.2		2.0	0.4	

clays, leading to increased confusion in the distinction between organics and minerals. It is also possible that finer particles reacted more completely, leading to the increase in "granular residue". The latter scenario could be tested better through kinetic studies in which both reaction time and temperature are varied.

Problems inherent in the recognition of residue phases can be seen in the photographs in Fig. 2. Thorough melting of the vitrinite to a "partially reacted maceral/vitroplast" is evident on all of the photographs. In some of the fields, particularly Fig. 2(c) and (d), there is a broad homogeneity to the fields in the sense that residual inertinites and minerals are evenly dispersed throughout the "vitroplast".

Pocahontas No. 3

The analysis of the residues from the low bituminous Pocahontas No. 3 coal provided the best inter-

laboratory comparisons. The consistency in identification, as seen on Table 6, is evident in the "unreacted macerals" and "partially reacted macerals" plus "vitroplast" categories. The partially-reacted vitrinite-derived macerals consist largely of cracked, thermally-altered vitrinite [Fig. 3, particularly (a) and (b)]. In the residues derived from the -100 mesh and "micronized" coals there is some evidence of welding of particles, indicating slight plasticity [Fig. 3(d)-(f)].

CONCLUSIONS AND RECOMMENDATIONS

When considering broad categories, the interlaboratory comparisons of the petrography of the Beulah-Zap and Pocahontas No. 3 residues are relatively good. The high volatile A bituminous Stockton coal was the most plastic (although the Beulah-Zap lignite

Table 6. Petrography of liquefaction residues from the Pocahontas No. 3 coal (vol. %). Blanks imply that laboratory did not seek that maceral or neomaceral

Mesh Laboratory	-20 1 (vol. %)	-20 2 (vol. %)	-20 3 (vol. %)	-100 1 (vol. %)	-100 2 (vol. %)	-100 3 (vol. %)	Micronized 1 (vol. %)	Micronized 2 (vol. %)	Micronized 3 (vol. %)
Vitrinite									
Fusinite	8.9			6.9			8.0		
Semifusinite	4.1			3.7			4.0		
Micrinite									
Liptinite									
Subtotal: unreacted macerals	13.0	18.6	18.0	10.6	9.4	13.0	12.0	9.8	15.0
Partially reacted macerals (pr)	82.9	78.4	81.0	85.6	88.0	86.0	85.9	88.4	84.0
Vitroplast (vp)	2.2	0.4		2.2	0.6		1.4		
Cenosphere (cs)		1.8	Trace		2.0			1.2	
Subtotal: pr + vp + cs	85.1	80.6	81.0	87.8	90.6	86.0	87.3	89.6	84.0
Primary semicoke									
Secondary semicoke									
Granular residue	0.2	0.2		0.2			0.2	0.6	
Unaltered minerals	1.0	0.4	1.0	1.2		1.0	0.4		1.0
Altered minerals									
Sulfides	0.4			0.2			0.2		
Neominerals		0.2							

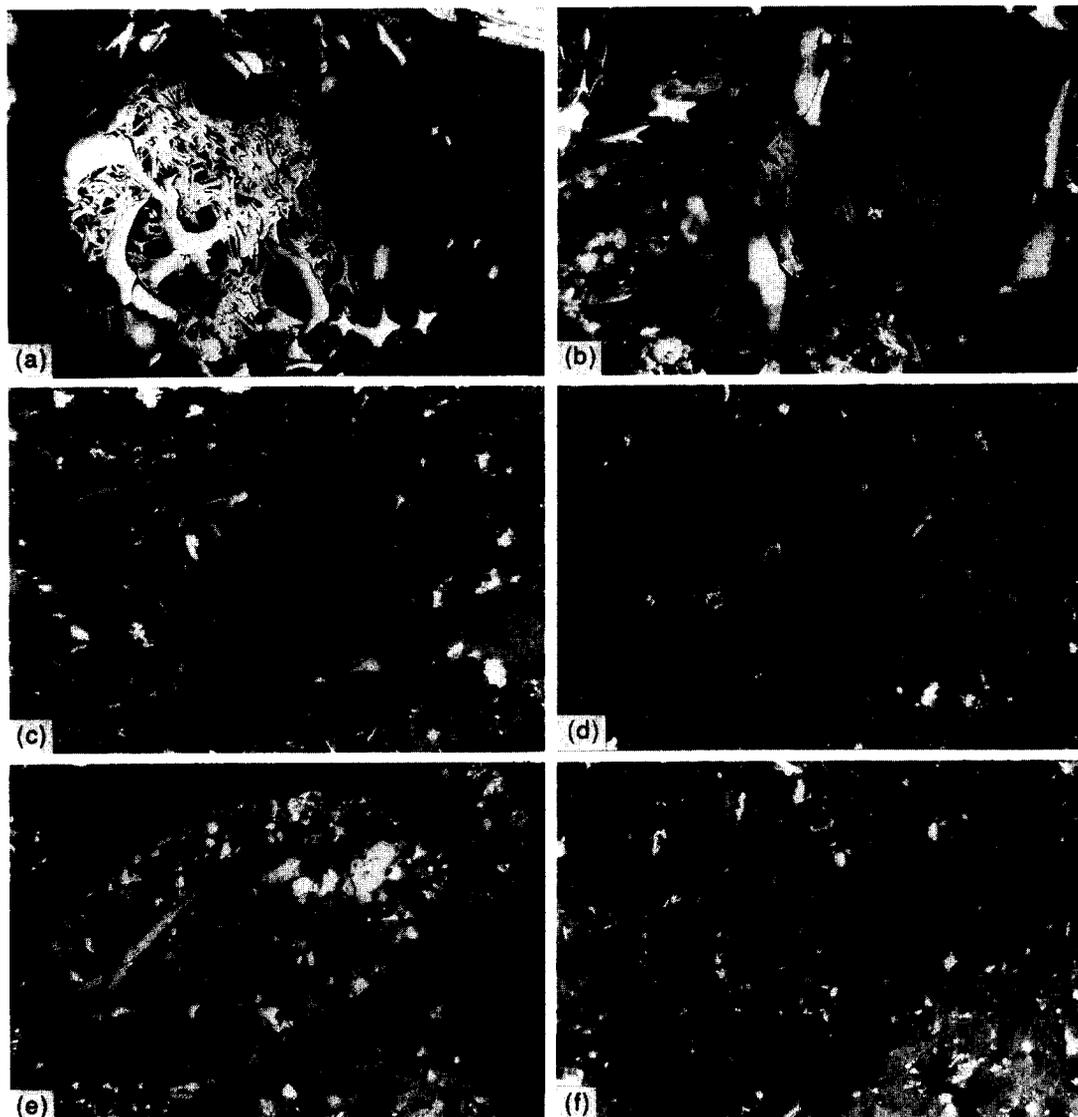


Fig. 2. Liquefaction residues from the Stockton coal (all photos $330\ \mu\text{m}$ on long axis). (a, b) -20 mesh feed coal. Inertinites (a) and partially reacted coal (b) within spherical masses which provide evidence of plasticity of coal mass. (c, d) -100 mesh feed coal. Inertinites in vitroplast. Evidence for plasticity provided by the random distribution of fine inertinites within vitroplast and by the size of the vitroplast masses—considerably larger than the -100 mesh particle size of the feed coal. (e, f) Micronized feed coal. The appearance of the residues is similar to those in Fig. 2(a), (b) and (e) and in Fig. (c), (d) and (f), the difference being in the size of the inertinite particles (at least in contrast to the -20 mesh feed).

was more reactive), resulting in a residue lending itself to more subjective interpretations. The biggest discrepancy between the laboratories is in the distinction of granular residue and mineral matter and in the transitions between “partially reacted macerals” and “vitroplast” and between “vitroplast” and “granular residue”.

Comparisons between initial sizes, even within one laboratory, are more difficult. Although we would expect that the respective splits from the original coal would have virtually identical maceral and mineral compositions, experience tells us that differences will arise between the size fractions. These differences will

be passed on in the residues and be further compounded by differences in reactivity due to the original size consist.

One approach to the problem of recognition of phases from highly thermoplastic coals such as the Stockton, as well as to the question of differences in reactivity of different size starting materials would be a kinetic study. In this type of investigation the three initial sizes could each be subjected to a matrix of several temperatures and several reaction times. In this manner questions regarding the rate of formation of various residue phases could be addressed. An interlaboratory study of such residues would also

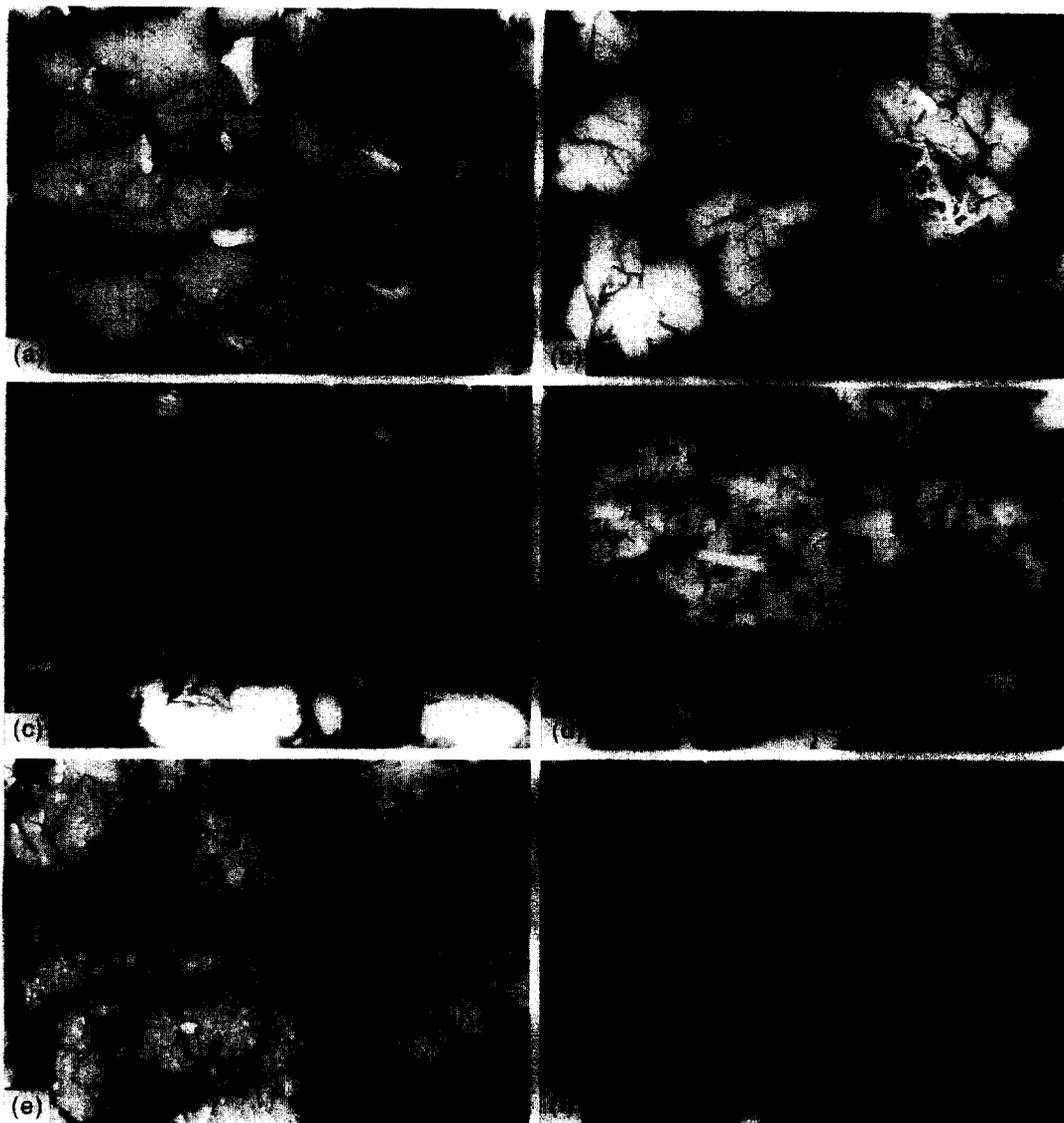


Fig. 3. Liquefaction residues from the Pocahontas No. 3 coal (all photos 330 μm on long axis). (a, b) -20 mesh feed coal. Vitroplast/partially reacted vitrinite showing signs of plasticity and devolatilization (b). (c, d) -100 mesh feed coal. Sulfides and carbonates in residue (c) and welded mass showing devolatilization. (e, f) Micronized feed coal. Vitroplast with fine dispersed inertinites.

more thoroughly address the problems in identifying complex species in residues from highly reactive coals.

Acknowledgements—John Lesko, Amoco, provided technical assistance in the preparation of the residues. The research was conducted under the guidance of The Society for Organic Petrology research committee. Rui Lin and G. Mitchell provided thorough reviews of the manuscript.

REFERENCES

- Hower J. C., Keogh R. A. and Davis B. H. (1992) Petrography of liquefaction residues. High-vitrinite, high-sulfur Davis (Western Kentucky No. 6) coal. *Energy & Fuels* **6**, 609–613.
- Hower J. C., Keogh R. A., Taulbee D. N. and Rathbone R. F. (1993) Petrography of liquefaction residues: semifusinite concentrates from a Peach Orchard coal lithotype, Magoffin County, Kentucky. *Org. Geochem.* **20**, 167–176.
- International Committee for Coal Petrology (1993) *International Handbook of Coal Petrography*, 3rd supplement, 2nd edition. University of Newcastle-upon-Tyne.
- Keogh R. A., Taulbee D. N., Hower J. C., Chawla B. and Davis B. H. (1992) Liquefaction characteristics of the three major maceral groups separated from a single coal. *Energy Fuels* **6**, 614–618.
- Vorres K. S. (1990a) *User's Handbook for Argonne Premium Coal Sample Program*. Argonne National Laboratory Report ANL/PCSP-89/1.
- Vorres K. S. (1990b) The Argonne Premium coal sample program. *Energy Fuels* **4**, 420–426.