

Comparison of oils and asphaltenes from extraction of bituminous coal and lignite with hydrogenated anthracene oil

Roberto Rosal, Fernando V. Díez, Herminio Sastre and Colin E. Snape*

Departamento de Ingeniería Química, Universidad de Oviedo, 33071 Oviedo, Spain

**Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK*

(Received 13 June 1994)

The application of ^1H n.m.r. spectroscopy and g.c.-m.s. to the analysis of aromatic fractions obtained in the liquefaction of two coals of different rank is described. The conversion and the yield of asphaltenes have been related to the proportion of aliphatic hydrogen in the extraction oils after liquefaction. The n.m.r. bands for asphaltenes are similar to those of recovered anthracene oils, but mass spectra show that a substantial amount of high-molecular-weight compounds is produced during the extraction of a bituminous coal, compounds not encountered in lignite liquefaction.

(Keywords: coal; liquefaction; asphaltenes)

Large-scale direct liquefaction processes are being developed to replace crude oil by high-quality liquids that could be processed in current refining facilities¹. However, it is not likely that coal-derived liquids will compete with petroleum in the near future. The needs for refining to meet environmental regulations may delay the implementation of these processes until dwindling petroleum resources have to be supplemented. None the less, there is considerable interest in the production of fractions as precursors for binder pitch for anodes, advanced carbon materials etc.²⁻⁵. Coal tar pitch from coke ovens is currently the major raw material for coal-based carbon fibres and other carbon materials. However, the amount and quality of coal tar are declining steadily while the demand for this product and most aromatic chemicals is rapidly increasing.

Subbituminous and low-rank bituminous coals have been recognized as major raw materials for liquefaction processes. However, some interest also remains in lower-rank coals. Lignite, for example, constitutes a major resource in the USA and Russia and a considerable fraction of the total reserves of fossil fuels in some European countries such as Germany and Spain.

The analysis of the liquid fractions from coal liquefaction is normally performed by chromatographic and spectroscopic methods. Most of the components of the light fractions are identified and quantified by gas chromatography and mass spectrometry. The analysis of heavier fractions is usually based on structural parameters derived from n.m.r. spectroscopy, providing information on bulk compositional properties of these extremely complex mixtures⁶⁻⁸. The determination of individual components is hindered by their lack of volatility and is generally limited to molecules of molecular weight ≤ 300 ,

which in the case of aromatic systems refers to compounds of up to five to six rings⁹.

This paper describes the application of ^1H n.m.r. and g.c.-m.s. using electron impact ionization to the analysis of the oils and asphaltenes obtained from the liquefaction of a lignite and a bituminous coal.

EXPERIMENTAL

Materials

A low-volatile bituminous coal (True Energy, Olga) and a lignite (Meirama, La Coruña) were used. Their proximate analysis are given in *Table 1*. Before reaction, the coals were ground to three particle size ranges: 0.030–0.100, 0.100–0.400 and 0.400–1.500 mm. The samples were dried at 110°C to constant weight before reaction.

The anthracene oil (90% recovered between 215 and 400°C) was hydrogenated over a sulfided nickel-molybdenum catalyst (BASF, M8-24) to obtain two fractions (denoted 1HAO and 2HAO) with different concentrations of hydroaromatic compounds. The hydrogenation procedure has been described previously¹⁰.

Microautoclave extraction

Batch hydrogen transfer extractions were conducted in 15 cm³ stainless steel bomb reactors shaken vertically in a fluidized bath of alumina sand at 600 cycles per minute and with an oscillation amplitude of 25 mm. Reaction conditions were monitored with a pressure transducer and a thermocouple. The device was similar to that described by Neavel¹¹. The coal (3 g) and the solvent (9 g) were accurately weighed, thoroughly mixed and transferred to the bomb. Reactions were carried out

Table 1 Properties of the coals used

	Meirama	Olga
Moisture (wt% as received)	57.4	7.8
Proximate analysis (wt% db)		
Ash	8.3	6.0
Volatile matter	51.1	19.6
Sulfur (wt% db)	1.3	0.6

under nitrogen (3 MPa at room temperature) to ensure the absence of hydrogen transfer from the gas phase. Liquefaction was performed at temperatures between 375 and 425°C and for reaction times between 20 and 60 min. Additional details are given elsewhere¹².

Analyses

After the reaction, the bomb was quenched with water, gas was vented and the rest of the products were separated by sequential extraction into tetrahydrofuran (THF)-insolubles, preasphaltenes (THF-soluble, toluene-insoluble), asphaltenes (toluene-soluble, *n*-hexane-insoluble) and oils (*n*-hexane soluble)¹³. The weight of the insoluble fractions was recorded after 2 h at 120°C. The amount of insoluble organic residue was calculated assuming a constant weight of mineral matter from the coal.

Anthracene oil and the *n*-hexane-soluble fractions were analysed by gas chromatography with a 50 m, 0.25 mm i.d. capillary column and OV-101 as stationary phase. Peaks were assigned by g.c.-m.s. Calibration factors were determined with pure standards whenever available; for other compounds the calibration factors were assumed to be unity, with acceptable accuracy¹⁴.

¹H n.m.r. spectra of the soluble fractions were recorded on a Bruker 300 MHz instrument. Deuteriochloroform was used as solvent and tetramethylsilane as internal standard. Chemical shifts were assigned as follows:

- 0.5–1.5 ppm CH₂ and CH in naphthenic rings and further than β from an aromatic ring; non-α-CH₃ groups (H_{β+})
- 1.5–2.0 ppm CH₂ and CH β to an aromatic ring and in naphthenic rings (H_n)
- 2.0–3.5 ppm CH₃, CH₂ and CH α to an aromatic ring (H_α)
- 3.5–4.5 ppm ring-joining methylene (H_{α2})
- 6.9–9.1 ppm aromatic protons (H_{ar})

The hydrogen aromaticity (f_{aH}) is defined as the fraction of total hydrogen bonded to aromatic carbon. For anthracene oil before hydrogenation, $f_{aH} = 0.755$, and for the hydrogenated fractions used in the extraction reactions, $f_{aH} = 0.689$ (1HAO) and $f_{aH} = 0.600$ (2HAO).

Analyses of oils were performed by gas chromatography on a capillary OV-101 column. Electron impact spectra were obtained at 70 eV.

RESULTS AND DISCUSSION

The yields of preasphaltenes, asphaltenes and oils were calculated relative to the initial weight of dry ash-free coal. The tetrahydrofuran-soluble conversion (THFSC) was calculated as follows:

$$\text{THFSC} = \frac{(\text{initial m.a.f. coal}) - (\text{THF ash-free insoluble})}{(\text{initial m.a.f. coal})}$$

Extractions were performed under conditions that did not favour the formation of light products. The yields of oils and gases was calculated by difference because the light fractions contained a substantial amount of volatile compounds, some of which were inevitably lost during solvent evaporation. The calculation ignored the possibility of formation of asphaltenes from the solvent and considered only the occurrence of progressive reactions¹². On this assumption, the amount of oils that could be attributed to coal-derived material was <5 and <10 wt% for Olga coal and Meirama lignite respectively. Most of the *n*-hexane-soluble fraction of the reaction products was a depleted anthracene oil.

Figure 1 shows that coal conversion (THFSC) is closely related to the amount of aliphatic hydrogen in the extraction oils. The hydrogen aromaticity is considerably higher in the oils from Olga bituminous coal ($f_{aH} > 0.56$) than in those from lignite extraction. This is due to the difference in composition of the *n*-hexane-soluble fraction obtained from the coal in the two cases and not in amount of oils relative to solvent. It was previously reported¹² that under the reaction conditions used in this work, the rate constant at 400°C for the reaction of asphaltenes to oils for Olga bituminous coal is more than 30 times that for Meirama lignite liquefaction. As a consequence, the difference in reactivity between the two coals results in a much greater yield of asphaltenes in lignite extraction, and a lower yield of liquefaction oils. Aliphatic chains make a significant contribution to overall hydrogen distribution. The disparity between the two sets of data should be attributed to the more aliphatic character of the reaction products from lignite. For both coals, but more clearly for the bituminous coal, a lower hydrogen aromaticity is observed in the oils from runs using the more hydrogenated solvent. The higher content of hydroaromatics results in a higher yield of light products from extraction and subsequently a higher content of aliphatic protons in the oils.

In the runs performed with Olga coal, different reactivities were observed for different particle sizes. The initial rate of coal dissolution for small particles (0.030–0.100 mm) was more than twice that for 0.400–1.500 mm particles. This led to differences in conversion which, however, resulted in a similar quantity of oils

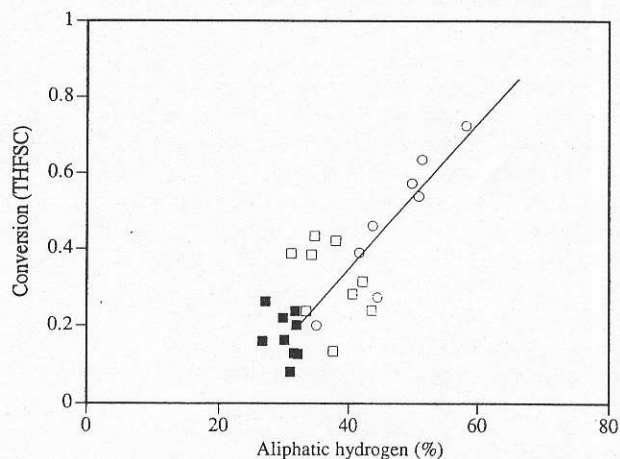


Figure 1 Conversion of coal to tetrahydrofuran-soluble fraction (THFSC) as a function of aliphatic hydrogen content of oils obtained in liquefaction. Meirama lignite (○); Olga bituminous extracted with 1HAO (□) and 2HAO (■)

because of the damping originating from the fact that oils are mainly a secondary reaction product and the rate of coal dissolution does not affect the rate constants for preasphaltene and asphaltene degradation. The points located above the line in Figure 1 represent runs performed with particles <0.100 mm; the remainder correspond to sizes of 0.100–0.400 and 0.400–1.500 mm. The distribution of points for the bituminous coal indicates that there is no significant correlation with the primary factors: particle size and aliphatic content of the HAO. For lignite reactions no difference was obtained with different particle sizes and there was no dispersion such as that encountered in the case of Olga bituminous coal. The most probable explanation for this behaviour is that the lignite underwent relatively rapid disintegration, masking any effect of different initial particle size^{15,16}.

The relative yields of asphaltenes are plotted in Figure 2 as a function of the amount of aliphatic hydrogen in the oils. The difference in slope for the two coals is a consequence of the difference in global rate of formation of asphaltenes. For Meirama lignite, the specific rate for the reaction of asphaltenes is two orders of magnitude lower than that of formation, and therefore they

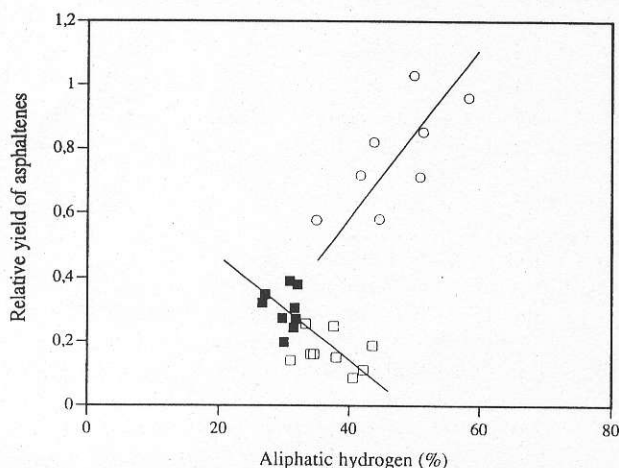


Figure 2 Yield of asphaltenes relative to the initial daf coal as a function of aliphatic hydrogen content of oils obtained in liquefaction. Symbols as in Figure 1

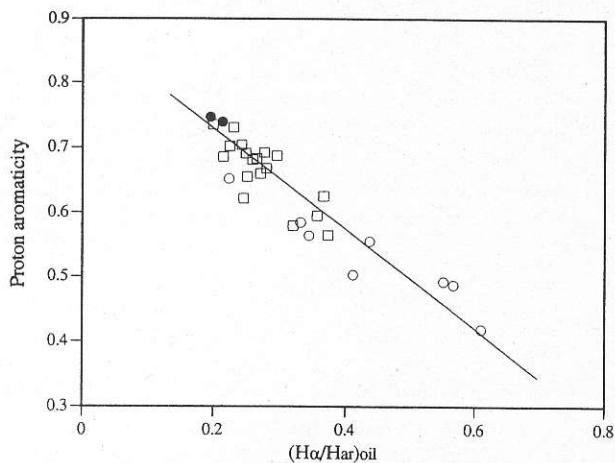


Figure 3 Proton aromaticity as a function of H_{α}/H_{ar} in liquefaction oils: ●, asphaltenes from extraction at 425°C; □, oils from Olga bituminous coal; ○, oils from Meirama lignite

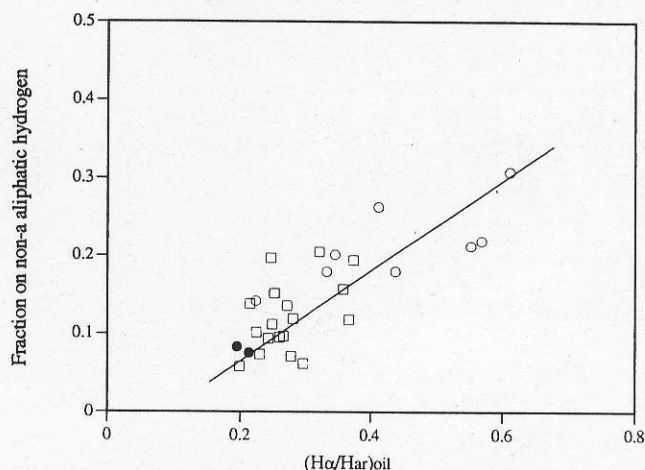


Figure 4 Non- α -aliphatic hydrogen as a function of H_{α}/H_{ar} in liquefaction oils. Symbols as in Figure 3

Table 2 Proton distribution in selected samples^a

	$H_{\alpha 2}/H_{ar}$	H_{α}/H_{ar}	H_n/H_{ar}	$H_{\beta+}/H_{ar}$
Fresh anthracene oil	0.058	0.176	0.008	0.083
1HAO	0.124	0.253	0.023	0.051
2HAO	0.067	0.336	0.072	0.192
Asphaltenes ^b				
Olga	0.037	0.195	0.033	0.077
Meirama	0.041	0.213	0.036	0.065
Liquefaction oils				
Olga, 1HAO	0.049	0.215	0.083	0.117
Olga, 2HAO	0.052	0.246	0.103	0.213
Meirama, 1HAO	0.062	0.412	0.145	0.379
Meirama, 2HAO	0.051	0.611	0.219	0.516

^a Liquefaction conditions: 425°C, 60 min

^b Using 2HAO

accumulate as the reaction proceeds. For Olga coal, however, the rate constant for the degradation reaction is higher than that of their formation from preasphaltenes¹².

Figures 3 and 4 relate the proton aromaticities and the proportions of non- α -aliphatic hydrogen of several samples of oils and asphaltenes to the proportion of H_{α} . The two samples of asphaltenes for which hydrogen data are reported were obtained from the liquefaction of Olga coal and Meirama lignite at 425°C for 60 min with the more hydrogenated solvent (2HAO). There is little or no difference between the hydrogen distributions for asphaltenes and oils from runs in which conversion was low. In such cases, the extraction oil was predominantly a spent anthracene oil and the composition of both systems is based on condensed aromatics. Full hydrogen distributions for selected samples are presented in Table 2. Figure 5 shows an example of a ¹H n.m.r. spectrum of an asphaltene sample from the processing of Olga coal at 425°C for 60 min.

The mass spectra of the asphaltenes from coal liquefaction revealed traces of the heavier components of the solvent, appearing in the *n*-hexane-insoluble fraction. Pyrene, fluoranthene, benzopyrenes and some other compounds that were previously detected in the solvent¹⁴ appeared in the EI mass spectra together with other compounds that presumably arose from anthracene oil, such as dibenzopyrenes and coronene. The reason is that no special precautions were taken to remove distillable material occluded in the asphaltenes. It should be also

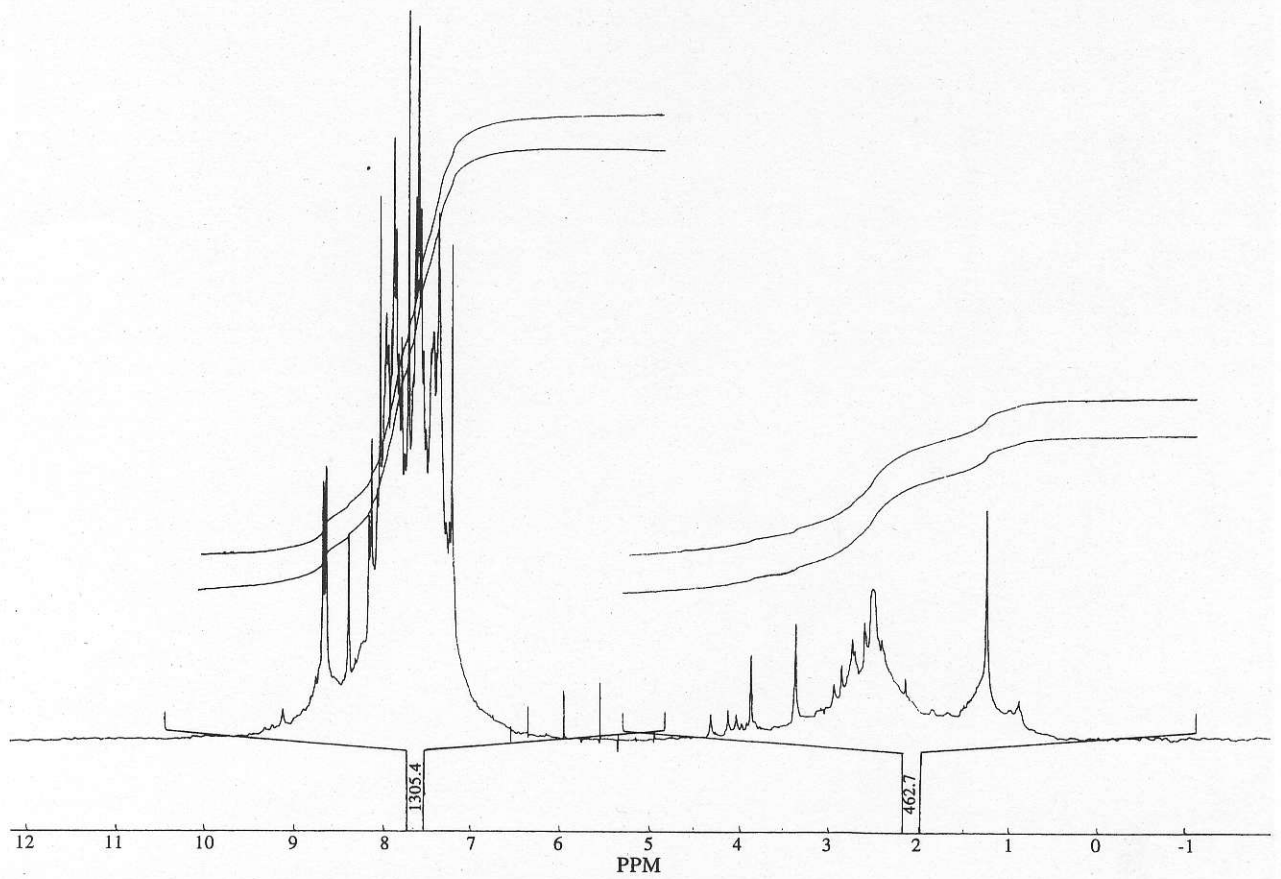


Figure 5 ^1H n.m.r. spectrum of an asphaltene sample obtained from Olga bituminous coal

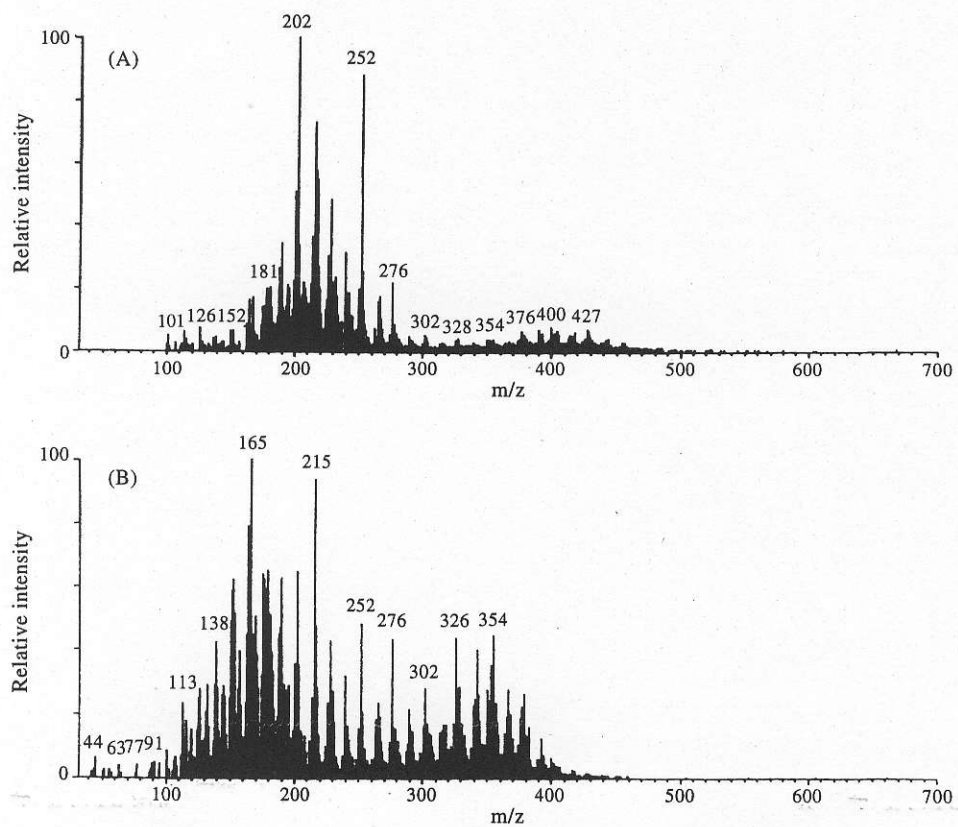


Figure 6 EI m.s. spectra of asphaltene samples from (A) Olga bituminous coal and (B) Meirama lignite

pointed out that the mass spectra are only qualitative, giving rise to fewer parent ions than softer techniques, particularly FI m.s. *Figure 6A* corresponds to an asphaltene from Olga coal whereas *B* shows EI mass spectra of an asphaltene fraction obtained from Meirama lignite. Hydrogen deficiency compared with alkanes, conventionally denoted by a number z defined as C_nH_{2n+z} , ranged from -20 to -40 for these highly condensed and unbranched compounds. The spectra showed the presence of longer alkyl chain homologues in the region of higher-molecular-weight substances, which could be attributed to coal fragments.

In the extractions with Olga bituminous coal, there were peaks for a significant number of masses representing $\geq 40\%$ of the total ion current (TIC) with masses up to 550. Lignite asphaltenes appeared to have a much narrower range, typically < 450 . A possible explanation for this behaviour is that lignite asphaltenes are more polar, so they are included in the asphaltene solubility class even though they have a lower molecular weight. The results indicated that the amount of asphaltenes generated during the extraction of lignite was higher than that obtained from Olga coal. The hydrogen distribution from n.m.r. analyses, however, was similar. Apparently, the molecular weight of fragments from the coal of higher rank was greater but the structures of the lignite products were not greatly different in alkyl substitution. Another effect that could partly explain the similarity between the n.m.r. bands is masking by the asphaltenic compounds from the anthracene oil. The fraction of asphaltenes that could be attributed to the solvent is in the range 20–40% for the lignite and up to 40% for the bituminous coal, depending on the extraction conditions.

ACKNOWLEDGEMENTS

This research was supported by FICYT (Foundation for the Support of Research in Applied Science and Technology, Asturias, Spain) and British Council –

Ministry of Education of Spain (Cooperative Research Projects). The authors are also grateful to the University of Swansea SERC mass spectrometry service, where the m.s. analyses were performed.

REFERENCES

- 1 Moroni, E. C. *Am. Chem. Soc. Div. Fuel Chem. Preprints* 1991, **36**, 433
- 2 Schultz, H. D. In 'Coal Liquefaction Products: NMR Spectroscopic Characterization and Production Processes' (Ed. H. D. Schultz), Wiley, New York, 1982
- 3 Marsh, H. (Ed.) 'New and traditional carbon materials from petroleum and coal sources', Paper presented at Information Transfer Session, Cooperative Program in Coal Research, Pennsylvania State University, November 1991
- 4 Donnet, J. B. and Bansal, R. P. 'Carbon Fibers', Dekker, New York, 1984
- 5 Walker, P. L. *Carbon* 1990, **28**, 261
- 6 Snape, C. E., Ladner, W. R. and Bartle, K. D. *Fuel* 1985, **64**, 1394
- 7 Snape, C. E. In 'Analytical NMR' (Eds L. D. Field and S. Sternhell), Wiley, New York, 1989
- 8 Snape, C. E., Ladner, W. R. and Bartle, K. D. In 'Coal Liquefaction Products: NMR Spectroscopic Characterization and Production Processes' (Ed. H. D. Schultz), Wiley, New York, 1982
- 9 Burchill, P., Herod, A. A. and James, R. G. In 'Carcinogenesis', Vol. 3, 'Polynuclear Aromatic Hydrocarbons' (Eds P. W. Jones and R. I. Freudenthal), Raven Press, New York, 1978, p. 35
- 10 Roasl, R., Diez, F. V. and Sastre, H. *Ind. Eng. Chem. Res.* 1992, **31**, 1007
- 11 Neavel, R. C. *Fuel* 1976, **55**, 237
- 12 Rosal, R., Diez, F. V. and Sastre, H. *Ind. Eng. Chem. Res.* 1992, **31**, 2407
- 13 Mima, M. J., Schulz, H. and McKinstry, W. E. 'Method for the determination of benzene insolubles, asphaltenes and oils in coal derived oil liquids', PERC/RI 76/6, US Energy R&D Administration, 1976
- 14 Rosal, R., Diez, F. V. and Sastre, H. *Fuel* 1992, **71**, 761
- 15 Whitehurst, D. D., Mitchell, T. O. and Farcasiu, M. 'Coal Liquefaction: the Chemistry and Technology of Thermal Processes', Academic Press, New York, 1980, pp. 108–112
- 16 Pradham, V. R., Holder, G. D., Wender, I. and Tierney, J. W. *Ind. Eng. Chem. Res.* 1992, **31**, 2051