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Effect of inorganic matter removal from coals and chars on their surface areas

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Removal of inorganic matter from coals by acid treatment brings about random and, in some cases, significant changes in surface areas measured by adsorption of N_2 and CO_2 . Changes in surface areas of chars are generally more pronounced than those found in coals. However, the surface area changes in chars are markedly dependent upon whether the acid treatment is given to the coal precursor prior to charring or to the char produced from the raw coal. Changes in surface areas of raw coals and chars produced therefrom have been attributed to: (i) 'physical' removal of inorganic matter from the aperture-cavity system, (ii) bonding of HCl to basic nitrogen present in pyridine-like structures, and (iii) adsorption of acid. Results suggest that the removal of inorganic matter from coals prior to charring affects the carbonization process and, hence, the surface area of the resultant char.

Coals are associated with two broad classes of inorganic impurities — the discrete mineral matter which is usually present as particles greater than $1\ \mu m$ in size and minor and trace elements which are more or less associated with the organic phase or mineral phase of the coal. It is well known that most inorganic impurities catalyse gasification rates of carbons^{1,2}. In this laboratory, we have studied extensively the reactivities of a wide spectrum of chars in air³, CO_2 ⁴, H_2 ⁵, and steam⁶. It was found that in each gasification atmosphere partial or complete removal of inorganic impurities (by acid treatment) from raw coals prior to charring or from chars produced from raw coals usually decreased resultant char reactivity. It was not clear that this behaviour could be attributed solely to the removal of catalytically active inorganic impurities because it was found that, concomitant with changes in reactivities, chars produced from acid washing had surface areas which were markedly different from those for the chars produced from processes involving no acid treatment. Since there is a growing interest in better understanding the various factors which govern char reactivity, it is desirable to investigate systematically the effect of inorganic matter removal on surface areas of coals and chars. The present paper describes results of such a study.

Results of the present study should also have relevance to coal liquefaction studies. It is not well understood what effect, if any, the inorganic matter present in coals has on the kinetics of hydrogen transfer from the vehicle (hydrogen-donor solvent) to coal or on the yield and composition of the liquid products. The possibility of a catalytic effect is usually ascertained from the difference in results obtained on raw and acid-washed coals. However, acid treatment affects the porosity in coals. Since the initial step in the overall liquefaction process is the adsorption of vehicle by the coal particles, changes in porosity may affect the overall rate of coal liquefaction.

EXPERIMENTAL

Coals studied

Coals (40 × 70 U.S. mesh) varying in rank from anthracite to lignite were used in the present study. Important properties of the coals are given in *Table 1*. Inorganic matter contents of coals were estimated by the modified version of the Parr formula proposed by Given *et al.*⁷. In some cases, inorganic matter contents of coals were also determined by acid treatment (with HCl and HF) in the manner suggested by Bishop and Ward⁸. Inorganic matter contents of coals determined by this procedure (given in parenthesis in column 4, *Table 1*) agree well with those estimated from the modified Parr formula.

Partial removal of inorganic matter from coals was accomplished by acid washing with 10 vol % HCl at 333 K for 48 h. The treated coals were then washed thoroughly with hot distilled water. The inorganic matter content of some of the acid-washed coals was further reduced by treatment with a 1:1 concentrated HCl-HF mixture at 333 K, followed by thorough washing with hot distilled water. These coals are referred to as demineralized (Dem) coals in the text.

Inorganic matter content of acid-washed and some Dem coals was determined by low-temperature ashing (LTA) in an oxygen plasma⁹. The LTA technique suffers from the drawback that some of the sulphur in pyrite and some organic sulphur are oxidized to SO_3 which forms H_2SO_4 in the presence of moisture¹⁰. The acid can then react with carbonate minerals or in the case of low-rank coals (sub-bituminous and lignites) with exchangeable cations associated with carboxylic acid groups. Treatment of coals with acids will decompose the carbonates and replace the metal cations by H ions, thus minimizing the fixation of organic sulphur as sulphates. Inorganic matter contents of

Table 1 Surface areas of coals

Coal No. (1)	ASTM rank (2)	State (3)	Inorganic matter (% dry basis) (4)	C ^a (5)	N ^a (6)	N ₂ surface area (m ² /g)			CO ₂ surface area (m ² /g)		
						Raw (7)	Acid- washed (8)	Dem (9)	Raw (10)	Acid- washed (11)	Dem (12)
91	Lignite	Mont.	8.8 (8.2)	71.5	0.81	23	—	7	315	239 (1.3%)	273
87	Lignite	N.D.	9.3 (10.6)	72.1	0.56	8	20 (0.76%)	26 (0.14%)	211	220	184
245	Lignite	N.D.	15.4	73.6	0.13	18	—	14	169	—	239
100	Sbb-C	Wyo.	5.7 (5.4)	72.6	0.82	15	—	17	261	—	184
138	Lignite	Tex.	11.7 (11.2)	75.5	0.37	10	11 (6.7%)	16	216	191	184
101	Sbb-C	Wyo.	6.9 (7.2)	75.5	0.90	—	—	—	—	—	—
230	Sbb-B	Mont.	10.5	76.4	1.1	37	—	14	297	—	256
232	HVC	Ky.	13.5	77.6	1.4	14	—	17	229	—	239
127	LV	Pa.	6.6	90.4	1.0	<1	—	10 (0.57%)	248	—	239

^a Expressed as wt %, dry-inorganic-matter-free basis

acid-washed and some Dem coals are given in parentheses in columns 8, 9 and 11, Table 1.

Char preparation

Chars were prepared from selected raw, acid-washed, and demineralized coals. One of the selected coals, PSOC-127, was a caking coal. This coal was carbonized in a horizontal-tube reactor while held in a boat. The non-caking coals were carbonized in a fluidized-bed reactor. In each case, coal was heated in a N₂ atmosphere at a rate of 10 K/min up to 1273 K. Soak time at 1273 K was 2 h. Chars prepared from PSOC-127 were reground and 40 × 100 mesh fractions used for surface-area measurements.

In a few cases, chars produced from raw coals were acid-washed with HCl. Chars produced from acid-washed coals are referred to as AW in the text, the acid-washed chars are referred to as AW*, and chars produced from Dem coals are referred to as Dem chars.

In the present study the acid treatment was carried out in an air (ambient pressure) atmosphere. Therefore, it may be argued that the coals have undergone some oxidation during acid treatment. However, this possibility is ruled out by the work of Bishop and Ward⁶. These workers treated a sample of low-rank vitrain with an oxygen-free mixture of HCl and HF at 328–333 K in an inert atmosphere, while a duplicate sample was treated without using these precautions. The carbon and hydrogen contents of the acid-washed vitrain in the two cases were found to be essentially the same. Therefore, Bishop and Ward concluded that no significant coal oxidation had occurred during acid treatment in an air atmosphere.

Surface area

Surface areas of coals and chars were determined from N₂ adsorption at 77 K using the BET equation and from CO₂ adsorption at 298 K using the Polanyi–Dubinin equation¹¹. Prior to making an adsorption run, coals were out-gassed at 383 K and chars at 773 K for 16 h at a pressure of 1.33 × 10⁻³ Pa⁵. For each adsorption point on the N₂ and CO₂ isotherms, an arbitrary adsorption time of 30 min was allowed.

Surface areas of coals and chars in most cases have been expressed on a dry-inorganic-matter-free basis. It has been

assumed that inorganic matter present in coals has a negligible surface area. In the case of the chars, the ash yields have been assumed to approximate the inorganic matter contents. For the Dem coals for which the inorganic matter contents are not listed in Table 1, surface areas have been expressed on a dry-inorganic-matter-containing basis. Because of the very small amounts of inorganic matter expected to be contained in these coals, it is reasonable to assume that their surface areas will increase minimally if expressed on a dry-inorganic-matter-free basis. In any case, such increases are likely to be well within the experimental error involved in measuring surface areas of coals and chars.

RESULTS

Surface areas of coals

The effect of inorganic matter removal on the N₂ and CO₂ areas of coals is illustrated by the data given in Table 1. These results show that acid treatment of coals does not always bring about significant changes in their N₂ and CO₂ areas. Further, there is no obvious correlation between the effect of acid treatment and coal rank. Considering the N₂ areas, it is seen that for the PSOC-100 and 232 coals, N₂ areas remain essentially unchanged upon demineralization, that of PSOC-91 decreases by a factor of three, whereas the surface area of PSOC-127 increases by an order of magnitude. The remainder of the coals exhibit an intermediate behaviour. In contrast, the relative changes in CO₂ areas of coals brought about by inorganic matter removal are less pronounced. The maximum increase in CO₂ area (41%) upon demineralization occurs for PSOC-245 coal, whereas the maximum decrease (30%) is observed for PSOC-100 coal. Removal of inorganic matter from a given coal does not necessarily change both the N₂ and CO₂ areas. In those cases where the two areas do change, the relative magnitude of the change is not similar.

The effect of demineralizing the acid-washed coals on the N₂ and CO₂ areas is different in the two coals studied (PSOC-87 and 138). The N₂ area of both the coals increases; the CO₂ area of one coal (PSOC-87) decreases while that of the other (PSOC-138) remains essentially unchanged.

Table 2 Surface areas of chars

PSOC Sample No.	ASTM rank of parent coal	Char ash (wt %)	Surface area (m ² /g)	
			N ₂	CO ₂
91	Lignite	10.9	35	471
91 AW*		7.2	18	506
91 AW		1.3	89	924
87	Lignite	13.1	107	299
87 AW*		6.0	113	532
87 AW		2.6	11	626
87 DEM		0.0	1	600
138	Lignite	16.0	143	667
138 AW*		11.6	12	562
138 AW		9.6	4	752
138 DEM		0.9	47	116
101	Sbb-C	8.2	68	501
101 AW*		5.4	18	379
101 AW		1.1	3	677
127	LV	6.7	2	13
127 DEM		0.0	4	38
81	Anthracite	6.4	1	42
81 AW*		6.1	<1	50
81 AW		5.8	<1	42
81 DEM		0.9	<1	57

Surface area of chars

Surface areas of various char samples are given in Table 2. Conversion of raw coals to chars appreciably increases the N₂ area in every case. However, increases in CO₂ areas are observed for the lower-rank samples only; and in these cases fractional increases are less pronounced than found for the N₂ areas. The CO₂ area of a higher-rank LV bituminous coal (PSOC-127) is sharply reduced upon charring at 1273 K. The conversion of acid-washed coals to AW chars decreases the N₂ area but increases the CO₂ area. On the other hand, the conversion of demineralized coals to chars brings about random changes in N₂ and CO₂ areas.

The CO₂ areas of the AW chars produced from lignites and sub-bituminous coal are higher (as much as 104%) than those of the raw chars. Although differences in the N₂ areas of the raw and AW chars are more pronounced than are differences in the CO₂ areas, these differences do not follow the same trend in all cases. For example, the N₂ area of the raw char produced from PSOC-91 is 40% of the area of the AW char; whereas the areas of the remainder of the lower-rank raw chars are higher (as much as 36 times) than those of the corresponding AW chars.

The N₂ and/or CO₂ areas of the lower rank Dem chars show major differences from those of the corresponding AW chars. The N₂ area of PSOC-87 AW char is an order of magnitude higher than that of the Dem char, but the CO₂ areas in the two cases are essentially the same. On the other hand, in the case of PSOC-138 Dem char the N₂ area is appreciably higher and the CO₂ area is appreciably lower than that of the AW sample.

Acid treatment of the raw chars brings about random variations in the N₂ and CO₂ areas. With the exception of PSOC-87 AW* char, the N₂ areas of the remainder of the lower-rank AW* chars are significantly lower than those of the raw chars. On the other hand, the CO₂ areas of the PSOC-91 and 87 AW* chars are higher, while those of the PSOC-138 and 101 AW* chars are lower than those of the

raw chars. It is noteworthy that with the exception of PSOC-91 char, the N₂ areas of the remainder of the lignite and sub-bituminous AW chars are lower than those of the corresponding AW* chars. However, the CO₂ areas of the AW chars are consistently higher. These results thus show that changes in char surface areas are markedly dependent upon the manner in which the inorganic matter is removed, that is whether the acid treatment is given to the coal precursor prior to charring or to the char produced from the raw coal.

Considering the results for higher-rank chars, it is seen that the removal of inorganic matter has a minimal effect on the N₂ and CO₂ areas of the anthracite char (PSOC-81), while the N₂ and CO₂ areas of the LV bituminous char (PSOC-127) increase by factors of 2 and 3, respectively.

DISCUSSION

Coals and chars are highly microporous materials. Their porosity is of the aperture-cavity type and a large proportion of the total surface area and pore volume is accessible through apertures 0.49–0.52 nm in size¹². Slight changes in aperture openings can have a profound effect on the surface area and porosity of such materials^{12,13}. Since the minimum dimension of a N₂ molecule (0.365 nm) is larger than that of a CO₂ molecule (0.33 nm), N₂ areas are more sensitive to slight changes in aperture sizes. With this brief introduction, the possible reasons for the observed surface area changes upon acid treatment can be considered.

Removal of inorganic matter

Changes in surface areas of coals and chars upon acid treatment can be due to the 'physical' removal of inorganic matter. In this context, two extreme cases can be considered. Consider one extreme case. The presence of inorganic matter in the apertures of coals and chars can decrease the aperture size to an extent that the area and volume contained in the aperture-cavity system are inaccessible to N₂ and CO₂ molecules. Removal of inorganic matter from the apertures, in such cases, can increase the available surface area.

Consider now the other extreme case. When raw coals and chars produced from them are treated with HCl, a part of the inorganic matter present (such as quartz and pyrite) is not extracted by the acid. The amount of the unextractable material is expected to be greater in chars than in the coal precursors. This is because most of the inorganic impurities initially present in the coal precursors undergo changes in their chemical form upon heat treatment to the maximum temperature (1273 K) used in this study for the preparation of chars^{14,15}. As a result of heat treatment, some of the inorganic matter which is initially soluble in HCl is converted to an insoluble form either because of a change in its chemical form or because of combination with some other constituent(s) of the inorganic matter. This is reflected in the higher ash yields of the AW* char samples compared to the AW chars (Table 2). If the insoluble inorganic impurities in coals and chars are present in the cavities as an admixture with the soluble impurities, it is possible that when soluble impurities are leached out upon acid treatment, the insoluble inorganic matter might be displaced from the cavities (in which most of the area and porosity are contained) and become trapped within the apertures. The apertures can thus become effectively

blocked or reduced in size and result in a decrease in accessible surface area.

Retention of acids

Changes in surface area can also be due, at least in part, to retention of acids in the microporous structure of coals and chars. In this context, it has been observed that in the case of coals associated with small amounts of inorganic matter, acid treatment results in an increase in weight^{16,17}. This increase has been attributed to the retention of acids. Uptake of acids on coals and chars can be due to the following causes. In the present study, the coals contain up to a maximum of 1.4 wt % nitrogen (Table I). It is generally agreed that nitrogen in coals occurs almost completely in heterocyclic ring structures¹⁸. Although quantitative information on the functionality of nitrogen in coals is lacking in the literature, it is now believed that a part of the nitrogen is present as basic nitrogen (as in pyridine structures) and a part is present in acidic nitrogen (as in pyrrole structures)¹⁹. The acidic nitrogen is not expected to partake in reaction with HCl whereas the basic nitrogen can bind HCl in the form of hydrochloride structures. Upon washing with water (following acid treatment), the hydrochlorides are expected to undergo hydrolysis but some HCl may be retained on the more basic nitrogen groups.

Since during coal pyrolysis nitrogen comes off in the gas phase as ammonia and HCN, and in the tar as derivatives of pyridine, aniline, quinoline, etc.²⁰, the nitrogen contents of chars (produced at 1273 K) and, hence, the amounts of HCl bound to nitrogen, are expected to be less than the amounts present in the coal precursors. It is not expected that the entire nitrogen content of coals will be eliminated upon heat treatment up to 1273 K. In this context, Issacs carbonized anthracene, phenanthrene and several nitrogen heterocyclic derivatives of these compounds with the same ring structure but containing one or two nitrogen atoms in place of carbon²¹. He found that in all cases the 873 K chars had essentially the same nitrogen contents as those of the original compounds and that all of the nitrogen was not eliminated up to 1573 K.

Even in the absence of basic nitrogen groups, coals and chars can adsorb mineral acids. This, in turn, can affect aperture size and surface area. From fundamental studies on relatively pure carbons, it is known that carbons can adsorb both acids and alkalis^{22,23}. Carbons associated with acidic surface oxygen groups, such as carboxylic and phenolic, preferentially adsorb alkalis. Further, carbons showing higher adsorption capacities for alkalis are poor adsorbents for acids and vice versa. Adsorption of mineral acids on carbons does not involve dispersive forces because the anion of an adsorbed acid can be exchanged for a different anion from an added neutral salt²².

The concentration of acidic surface oxygen complexes (carboxyl and/or phenol) on coal surfaces decreases with increase in coal rank¹⁸. In light of the above discussion, it is to be expected that the adsorption of acids on coals devoid of inorganic matter should increase with increase in coal rank. Since heat treatment of microcrystalline carbons in an inert atmosphere up to 1273 K results in the elimination of essentially all the oxygen complexes²³, the chars in the present study are expected to be better adsorbents for the acids than the precursor coals. Coals and chars are always associated with inorganic matter, part of which is soluble in HCl. The presence of soluble chlorides of multivalent cations can increase the ionic strength of the

acid and, hence, the extent of acid uptake²².

It is concluded that observed changes in surface areas of raw coals and AW* chars upon acid treatment are due primarily to two effects — removal of inorganic matter and retention of acids. Because of the complexity of these effects, it is not surprising that changes in surface areas do not follow a regular pattern.

Effect of acid treatment of coal on subsequent carbonization mechanism

The structure of a char produced by the heat treatment of a coal is determined by a number of complex reactions such as rupture of bonds, ring closure, condensation, unsaturation, and aromatization. The addition of selected catalysts to the coal can accelerate one or more of these reactions during subsequent pyrolysis and thus affect the yields (and possibly composition as well) of gas, tar and coke²⁴. To what extent, if any, the inorganic constituents contained in different coals have catalytic effects is open to speculation. Some clays at elevated temperatures catalyze organic reactions, particularly those that proceed by a carbonium ion mechanism, such as the cracking of hydrocarbons. In this context, the addition of certain active clays to coals has been shown to bring about a significant decrease in the yield of tar and a corresponding increase in char yield²⁴. It was concluded that the active clays can change the carbonization process by modifying the cleavage, polymerization and alkylation reactions. The catalytic sites in clays are the acidic OH groups. They are capable of exchanging protons for metal cations with a drop in catalytic activity. Conversely, replacement of metal cations in clays (contained in coals) by protons upon acid washing with HCl is expected to increase their catalytic activity.

Tar produced during coal pyrolysis contains, among other constituents, aromatics, saturated hydrocarbons and olefins²⁰. These molecules, along with those of the hydrocarbon gases evolved, are potentially capable of cracking at carbon surfaces depositing carbon^{25,26} as they diffuse out of the microporous structure of coals. Even small amounts of inorganic impurities can have a marked catalytic effect on the cracking of hydrocarbons²⁷. Kamishita *et al.* have recently shown that the partial removal of inorganic matter from a 1273 K lignite char by acid treatment decreases both the rate of and the extent of carbon deposition from the cracking of methane¹³. Upon heat treatment to 1273 K, the 'active' clays, if present in the lignite precursor, are expected to lose their catalytic activity for cracking because of the breakdown of their structure. Thus, the results of Kamishita *et al.*¹³ show that inorganic impurities other than active clays present in coals also possess catalytic activity for the cracking of hydrocarbons. Because of the aperture-cavity type porosity in coals and chars, even small amounts of carbon deposition can markedly affect the aperture size and, hence, surface area and porosity. For instance, addition of only 2.6%, by weight, of deposited carbon to a 1273 K lignite char reduced the N₂ area from 241 to 33 m²/g¹⁸.

Lower-rank coals contain significant amounts of carboxylic acid groups¹⁸. It has recently been observed that the replacement of H⁺ ions of carboxyl groups of brown coals by metal cations affects the mechanism of release of oxygen complexes (CO₂, CO and H₂O)²⁸. For instance, the amount of CO₂ evolved from the acid form of brown coals (that is, the acid-washed coals) upon heat treatment up to 1173 K corresponds to the carboxyl content of coals. In contrast,

the cation-exchanged samples evolve significantly larger amounts of CO₂. The change in the mechanism of release of oxygen complexes resulting from the acid treatment of lower-rank coals can possibly affect the resultant char structure and, hence, their surface area.

It is difficult to ascertain the manner in which HCl retained in the coal as a result of acid treatment will affect subsequent carbonization and, hence, the char structure produced. This will largely depend upon the manner in which it is desorbed upon heat treatment, that is whether it comes off as HCl or Cl₂, and the temperature range over which it is desorbed. HCl is a polymerization catalyst and thus can affect the conversion of coal to char. If, on the other hand, HCl is desorbed as Cl₂, then depending upon the temperature at which it is evolved it may react with the coal and some may be chemisorbed on the surface. It is known that microcrystalline carbons can chemisorb chlorine over a fairly large temperature range²³. Macrae and Oxtoby have shown that the uptake of small amounts of chlorine by a strongly caking coal completely destroyed its caking properties²⁹. They found that the char produced from the chlorinated coal had a more disordered structure and greater available surface area than that prepared from the untreated coal. Pinchin has reported that carbonization of chlorinated coals does not produce chlorinated tars but only HCl along with reduced amounts of volatile matter³⁰. It was suggested that this reagent promotes condensation and molecular growth through elimination of HCl rather than degradation reactions. Chlorine can also react with some constituents of the inorganic matter to give volatile chlorides. In this context, Imperial³¹ has shown that treatment of an anthracite with Cl₂ at temperatures ≥ 873 K results in the removal of significant amounts of inorganic matter as volatile chlorides.

It is possible that some constituents of the inorganic matter present in caking coals may reduce or destroy the softening and swelling of these coals upon heat treatment. Impurities may then change, partly or wholly, caking coals from thermoplastic to thermosetting precursors for the production of chars. The chars thus produced will have a higher surface area.

In conclusion, acid treatment of coals and chars does remove inorganic constituents; but it also, in many cases, alters the micropore structure of the material. Thus, when such treatment alters coal or char reactivity, interpretation of the results is not always straightforward.

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REFERENCES

- 1 Walker, P. L. Jr, Rusinko, F. Jr and Austin, L. G. In *Advances in Catalysis*, Vol. 11 (Eds. D. D. Eley, P. W. Selwood and P. B. Weisz), Academic Press, New York, 1959, pp 134–221
- 2 Walker, P. L. Jr, Shelef, M. and Anderson, R. A. In *Chemistry and Physics of Carbon*, vol. 4 (Ed. P. L. Walker Jr), Marcel Dekker, New York, 1958, pp 287–830
- 3 Jenkins, R. G., Nandi, S. P. and Walker, P. L. Jr *Fuel* 1973, 52, 288
- 4 Hippo, E. and Walker, P. L. Jr *Fuel* 1975, 54, 245
- 5 Tomita, A., Mahajan, O. P. and Walker, P. L. Jr *Fuel* 1977, 56, 137
- 6 Linares-Solano, A., Mahajan, O. P. and Walker, P. L. Jr *Fuel*, 1978, 58, 327
- 7 Given, P. H., Cronauer, D. C., Spackman, W., Lovell, H. L., Davis, A. and Biswas, B. *Fuel* 1975, 54, 48
- 8 Bishop, M. and Ward, D. L. *Fuel* 1958, 37, 191
- 9 Gluskoter, H. J. *Fuel* 1965, 44, 285
- 10 Miller, R. N., *PhD Thesis*, The Pennsylvania State University, 1977
- 11 Gan, H., Nandi, S. P. and Walker, P. L. Jr *Fuel* 1972, 51, 272
- 12 Walker, P. L. Jr, Austin, L. G. and Nandi, S. P. In *Chemistry and Physics of Carbon*, vol. 2 (Ed. P. L. Walker Jr), Marcel Dekker, New York, 1966, pp 257–371
- 13 Kamishita, M., Mahajan, O. P. and Walker, P. L. Jr *Fuel* 1977, 56, 444
- 14 Mitchell, R. S. and Gluskoter, H. J. *Fuel* 1976, 55, 90
- 15 O'Gorman, J. V. and Walker, P. L. Jr *Fuel* 1973, 52, 71
- 16 Mayer, K. *Brennst. Chemie* 1929, 10, 381
- 17 Redmacher, W. and Mohrhauer, P. *Brennst.-Chem.* 1955, 36, 236
- 18 Van Krevelen, D. W., *Coal*, Elsevier, Amsterdam, 1961
- 19 Sternberg, H. W., Raymond, R. and Schwieghardt, F. K. *Science* 1975, 188, 49
- 20 Karr, C. Jr. In *Chemistry of Coal Utilization*, Suppl. Vol. (Ed. H. H. Lowry), Wiley, New York, 1963, pp 539–579
- 21 Issacs, L. G. *Carbon* 1970, 8, 1
- 22 Mattson, J. S. and Mark, H. B. Jr, *Activated Carbon*, Marcel Dekker, New York, 1971
- 23 Puri, B. R. In *Chemistry and Physics of Carbon*, Vol. 6 (Ed. P. L. Walker Jr), Marcel Dekker, New York, 1970, pp 191–282
- 24 Howard, H. C. In *Chemistry of Coal Utilization*, Suppl. Vol. (Ed. H. H. Lowry), Wiley, New York, 1963, pp 340–394
- 25 Palmer, H. B. and Cullis, C. F. In *Chemistry and Physics of Carbon*, Vol. 1 (Ed. P. L. Walker Jr), Marcel Dekker, New York, 1965, pp 265–325
- 26 Bokros, J. C. In *Chemistry and Physics of Carbon*, Vol. 5 (Ed. P. L. Walker Jr), Marcel Dekker, 1969, pp 1–118
- 27 Hoffman, W. P., *PhD Thesis*, The Pennsylvania State University, 1978
- 28 Durie, R. A. Private communication to P. H. Given
- 29 Macrae, J. C. and Oxtoby, R. *Fuel* 1965, 44, 409
- 30 Pinchin, F. J. *Fuel* 1958, 37, 293
- 31 Imperial, G. R., *PhD thesis*, The Pennsylvania State University, 1962