Porosity and gas sorption capacity of some eastern Australian coals in relation to coal rank and composition

by

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ABSTRACT

The porosity, pore-size distributions, methane sorption and carbon-dioxide sorption capacities of a suite of coals selected from the southern Sydney and Bowen Basins were studied. The total open pore volumes of these coals range from 2.9 to 7.4 x 10^{-2} cm^3/g with mineral matter causing a relative increase in the macro-pore volume. Most of the gas uptake in coals appears to take place in meso- and micro-pores which are the dominant porosity in the coals.

At a temperature of 25^0C and pressure of approximately 4000 kPa the volume of CH_4 and CO_2 sorbed by the southern Sydney and Bowen Basin coals studied ranges from 10.7 to 16.9 cm^3/g and 22.6 to 29.7 cm^3/g respectively. The sorption capacity shows a positive correlation with coal rank and surface area, and a negative correlation with the minerals content. Fixed carbon content of the coal is linearly related to the sorption capacity and can be used to model sorption isotherms at a given temperature. Variations in maceral composition do not show any significant influence on the gas sorption capacity

INTRODUCTION

Coal has a capacity for storing large volumes of gas relative to conventional clastic or carbonate reservoirs. Permian coals along the eastern coast of Australia are no exception and contain up to 30 m^3/t methane and carbon-dioxide gas. The amount of gas retained in a coal seam is controlled by many geological factors including coal rank, maceral and mineral composition, porosity, pressure, temperature, tectonic history and geological structure. The aim of this study was to determine the influence of coal rank, composition, porosity, type of gas and pressure on the gas storage capacity of a suite of coal samples selected from the Southern Sydney and Bowen Basins. Samples for this study were obtained from the Bulli and Wongawilli seams of the southern Sydney Basin and Castor, Dysart, Garrick and German Creek seams of the Bowen Basin. Petrographic and chemical properties of these samples are summarised in Table 1.

GAS RETENTION IN COAL

The three modes of gas retention in coals (Rightmire, 1984) are as:

1. sorbed molecules on pore surfaces;
2. free gas held within the matrix porosity (macro-and micro-porosity); and
3. gas dissolved in groundwater within the coal seam.

The first of these modes, sorption, accounts for more than 90% of the gas held in coal.

It has been well established that the gas sorption capacity of coal increases with increasing pressure and coal rank, and decreases with increasing temperature (Kim, 1978). The influence of the maceral composition of coal on the sorption capacity, however, is poorly understood. Previous work carried out in this areas by various workers have indicated contradictory results. Ettinger *et al.* (1966) concluded that at low and medium ranks, inertinite-rich coals have a higher CH_4 sorption capacity than vitrinite-rich coals, whereas at higher ranks, both coal types sorb similar amounts. In contrast works of Patteisky and Coppens (1961; cited in Ettinger *et al.*, 1966), and Creedy (1979) concluded that CH_4 sorption capacity of vitrinite is greater than inertinite. To further complicate matters, the work of Swietoslawsky (1942) and Schwarzer and Byrer (1983) indicated that the quantity of CH_4 sorbed **does not** vary in any systematic manner relative to the maceral composition. It is worth noting all of these works were concentrated on coals of the Northern Hemisphere. Such work on coals of the Southern Hemisphere, more importantly Gondwana coals, is lacking and extrapolation of Northern Hemisphere data to Gondwana coals may be erroneous.

POROSITY, SURFACE AREAS AND PORE SIZE DISTRIBUTIONS

Electron microscopic studies have indicated the presence of a wide range of pores in coals and the size range categories as defined by the IUPAC (1972) are; macro-pores (> 50 nm), meso-pores (2-50 nm) and micro-pores (< 2 nm). An estimation of the porosity and pore volumes of coal is conveniently made using fluid displacement methods (Mahajan and Walker, 1978) and the total open pore volume of coal is determined from the difference in the reciprocal values of the densities between He (d_{He}) and Hg (d_{Hg}):

total open pore volume,

$$V_T = \left(\frac{1}{d_{He}} - \frac{1}{d_{Hg}}\right)$$

total porosity,

$$P = 100d_{Hg}\left(\frac{1}{d_{He}} - \frac{1}{d_{Hg}}\right)$$

In these calculations it is assumed that the He molecule does not react with the surface of the coal and does penetrate the open pores; that is, pores of greater than 0.42 nm.

Table 2 summarises He and Hg densities and estimated porosities of the coals tested.

Pore size distributions in the coal samples were estimated by the intrusion of Hg at increasing pressures up to 41.3 MPa (6000 psi). Two typical curves showing the pore size distributions of coals as determined by Hg intrusion are shown in Figure 1. All the samples tested show similar patterns of pore-size distributions. This pattern indicates: a very high frequency of pores with a size less than 10 nm, a very low frequency of pores in the range between 10 nm and 500 nm and a moderate number of pores with a size greater than 500 nm.

The use of Hg intrusion to estimate micropores and the smaller range of meso-pores by applying very high Hg pressures is not reliable for two reasons (Deblek and Schrodt, 1979; Unsworth *et al.*, 1989):

- opening up of closed pores due to high pressures, and
- volume reduction due to coal compressibility at high pressures.

Micro- and meso-pore volumes in coals and coal surface areas are more reliably estimated by the gas adsorption-desorption techniques and in this study pore volumes of the coal samples were determined by CO_2 adsorption at 0^0C using the Dubinin-Radushkevich equation. The surface area was then determined by multiplying the pore volume by the CO_2 cross-sectional area (0.253 nm^2).

On the basis of the pore volume distributions obtained from Hg intrusion and CO_2 adsorption data, it is possible to differentiate pore volumes according to their size ranges. A summary of these values are shown in Table 3.

The volume of macro-pores (50 nm) of the coals studied varies between 0.007 and 0.024 ml/g. For the majority of the coals, percentage of macro-pores accounts for less than 25% of the total pore volume although some samples gave values outside this range. Macro-pore volume of the samples CK-1 and T-2 accounted for about 35% of the total open pore volume. In contrast, the lowest macro-pore volumes were observed in samples TH-1 and GK-1. It is interesting to note that of the coals studied TH-1 and GK-1 had the lowest mineral matter content and CK-1 and T-2 had the highest. The relationship between the mineral matter content and the macro-pore volumes (Fig. 2a) indicates that the volume of macro-pores increases with increasing mineral matter content. This relationship, therefore, clearly indicates that the occurrence of mineral matter contributes to the abundance of large pores in the suite of coals studied. However, porosity and pore sizes in mineral-rich layers in coal could vary significantly with the type of mineral matter and this needs further study.

Plots of the volumes of different pore sizes (that is, V_{50}, $V_{(T-50)}$ and $V_{(T-10)}$) against the pore volume determined by CO_2 adsorption (V_{CO_2}) are shown in Figures 2b, 2c and 2d. These plots indicate that $V_{(CO_2)}$ shows strong positive correlations with meso- and finer sized pores ($V_{(T-50)}$ and $V_{(T-10)}$) while it shows no significant correlation with macro-pores (V_{50}). Therefore, indications are that no significant CO_2 uptake occurs in macro-pores and most of it occurs in the pores of much finer dimensions, that is, in meso- and micro-pores.

CH_4 AND CO_2 SORPTION CAPACITY

CH_4 and CO_2 sorption capacities of the coal samples were tested using a gravimetric gas sorption method as described by Lama (1982). The experiments were carried out at 25°C using coal samples of particle size 2.5 to 4.5 mm. The volumes of sorbed CH_4 and CO_2 on a known weight of coal were measured at absolute pressures of 300, 600, 1100, 2100, 3100 and 4100 kPa and sorption isotherms were drawn for each coal sample (Fig. 3). For the suite of coals tested the amount of CH_4 sorbed at 4100 kPa and 25°C varied from 10.7 cm^3/g to 16.9 cm^3/g, whereas CO_2 varied from 22.6 cm^3/g to 29.7 cm^3/g. These data indicate that the amount of CO_2 sorbed by a coal is far greater than the amount of CH_4 sorbed under similar temperature and pressure conditions. At a pressure of approximately 4000 kPa the volume of CO_2 sorbed by a coal is approximately 180 to 220% greater than the amount of CH_4 sorbed. At lower pressures this ratio is even greater. For example, at 1000 kPa this ratio varies from approximately 220 to 270%. In this study tests using gas mixtures of CH_4 and CO_2 were not conducted. However, previous studies indicated that the amount of mixed gases (CH_4 and CO_2 mixtures) sorbed by a coal is intermediate between the amount of CO_2 and CH_4 sorbed (Lama and Bartosiewicz, 1982; Siahaan, 1990).

Gas sorption isotherms are best described by the Langmuir equation (Ruppel *et al.*, 1974) of which the commonly written form is:

$$V = \frac{V_m bP}{(1+bP)}$$

where,

P = pressure,

V = volume of adsorbate adsorbed at pressure P,

V_m = monolayer saturation volume (quantity of gas adsorbed per gram of coal to form a saturated monomolecular layer),

b = constant.

The plot of P/V against P for the experimentally-derived data form a least squares straight line and the slope of this line gives the reciprocal of the Langmuir volume (V_m).

According to the Langmuir theory the value of V_m, ideally, represents the maximum gas holding capacity of the coal. For the coals studied the calculated V_m values for CH_4 varies from 16.7 to 22.7 cm^3/g and for CO_2 from 27.8 to 36.2 cm^3/g.

EFFECT OF COAL COMPOSITION AND RANK ON SORPTION CAPACITY

To investigate coherence patterns among gas sorption capacity, porosity and coal properties, an R-mode cluster analysis technique was used. According to the dendrogram shown in Figure 4 it is evident that the Langmuir volumes are strongly positively related to vitrinite reflectance ($R_v max$), fixed carbon content (FC%), surface area and porosity of coal. As shown Figures 5a and 5b Langmuir volumes also show strong negative correlations with ash content (M%) and mineral content (M%). These relationships, therefore, indicate that mineral matter does not contribute significantly to the amount of gas sorbed in coal. As noted previously the occurrence of mineral matter in coal mainly contributes to its macro-pore (50 nm) volume and the amount of gas stored in these pores is relatively small and mainly occurs as free gas. Therefore, it is postulated an increase in mineral matter in coal causes a relative decrease in the meso- and macro-pore volumes and consequently decreases the gas sorption capacity of the coal.

Langmuir volumes show the strongest correlation with fixed carbon content (Figs. 4 & 5c). As fixed carbon is a measure of the material (mainly C) that is devoid of volatile matter, mineral matter and moisture (i.e. FC = 100-IM-A-VM) it is virtually a measure of the combined effects of rank, moisture and mineral matter content of coal. Thus, the strong positive correlation between FC% and Langmuir volumes reflects the combined effects of rank, moisture and ash contents on the gas sorption capacity.

As the inorganic phase of the coal suggested a negative effect on the sorption capacity, to gain a better understanding of the effect of maceral composition and rank it is necessary to compare these variables on a basis independent of inorganic matter. For this purpose, Langmuir volumes and volatile matter were converted to a dry ash free basis whereas coal maceral volumes were converted to a minerals free basis. Bivariate plots showing the relationships between Langmuir volumes (daf, dry ash free basis), $R_v$max, VM% (daf) and inertinite (mf), minerals free basis) are shown in Figures 5d - 5f. Relationships indicated in these graphs clearly show that the gas sorption capacity linearly increases with increasing rank. The relationship between the Langmuir volumes and inertinite contents shown in Figure 5f indicates a vague negative correlation, but, it is not significant enough to suggest that inertinite has a lower gas sorption capacity than vitrinite. It is worth noting, however, that due to the strong dependence of the sorption capacity on coal rank, the effect of the maceral composition, if any, could be masked.

As discussed previously, of all the coal properties, fixed carbon is most strongly related to the sorption capacity of raw coals. Therefore, using least squares regression technique sorption isotherms for CH_4 and CO_2 are modelled (Fig. 6) showing the sorption capacities of these coals at 25^{0}C and varying pressures.

CONCLUSIONS

Approximately 75% of the pores in the suite of coals studied fall into the size range of meso- and micro-pores (< 50 nm). The presence of mineral matter in coal mainly contributes to the volume of macro-pores, hence the macro-pore volume increases with increasing mineral matter content. Micro- and meso-porosity accounts for most of the gas retained in coal. The CO_2 sorption capacity of the coals studied is approximately two times higher than that of CH_4 and the quantity of gas sorbed by coal increases with increasing rank and decreases with increasing mineral matter content. The decrease in the volume of gas sorbed with increasing mineral matter content could be attributed to the relative decrease in the meso- and micro-porosity.

For the suite of Australian coals studied, no significant variations in the gas sorption capacity of different coal types were observed. Due to the combined effects of rank and mineral matter, the gas sorption capacity is proportional to the fixed carbon content of the coal and the volume of gas in the coal can be modelled with a reasonable degree of confidence using the fixed carbon content at any nominated pressure and temperature conditions.

ACKNOWLEDGMENTS

The authors wish to thank geologists and management of Cordeaux, Metropolitan, Tahmoor, Tower and Wongawilli Collieries in N.S.W. and Collinsville, Cook, German Creek, Norwich Park and Peak Downs Collieries in Queensland for providing coal samples used in this study.

Special thanks are due to Dr. Tony Pandolfo CSIRO Division of Coal and Energy Technology, Lucas Heights, Prof. A.C. Cook and Mr. Aivars Depers for their assistance.

Technical assistance with gas sorption measurements was rendered by Mr. Ian Laird and is greatly appreciated. The assistance of the academic and technical staff of the Geology and Civil and Mining Engineering Departments of University of Wollongong are greatly acknowledged.

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Sample number	V %	I %	L %	M %	$R_v$max %	IM %	ASH %	VM %	FC %
T-2	33.4	57.6	0.5	8.5	1.11	1.0	16.2	21.7	60.8
CD-1	23.9	70.8	tr.	5.3	1.27	1.0	8.2	20.0	70.8
MP-1	21.6	70.5	tr.	7.9	1.35	1.0	12.2	18.4	68.4
MP-2	40.2	54.4	tr.	5.3	1.38	1.0	9.6	19.6	69.8
TH-1	40.8	53.4	2.1	3.7	1.04	1.3	7.3	26.1	65.3
W-1	57.8	27.7	tr.	14.5	1.27	1.0	24.4	18.9	52.7
CK-1	74.5	14.5	1.7	9.3	1.04	1.6	10.6	30.0	57.8
G-1	53.0	23.9	2.9	20.2	0.93	1.4	18.2	27.4	53.0
GK-1	80.7	16.0	tr.	3.3	1.42	0.9	4.8	22.2	72.1
NP-1	82.8	11.1	tr.	6.1	1.67	1.1	10.1	16.6	72.2
PD-1	55.1	37.1	0.2	7.6	1.32	1.2	9.7	22.9	66.2

V - vitrinite I - inertinite L - Liptinite M - minerals
IM - inherent moisture A - ash content VM - volatile matter FC - fixed carbon
tr. - trace amounts $R_v$max - mean maximum reflectance of vitrinite

Note: Proximate analyses data on air dried basis.

Table 1. Results of petrographic and proximate analyses of the samples tested.

SAMPLE	d_{He} (g/cm^3)	d_{Hg} (g/cm^3)	$V_T(10^{-2})$ (cm^3/g)	P (%)
T-2	1.42	1.35	3.65	4.93
CD-1	1.41	-	-	-
MP-1	1.44	-	-	-
MP-2	1.35	1.28	4.05	5.19
TH-1	1.34	1.29	2.89	3.73
W-1	1.57	-	-	-
CK-1	1.39	1.27	7.42	8.63
G-1	1.57	-	-	-
GK-1	1.32	1.23	5.54	6.84
NP-1	1.38	1.28	5.66	7.24
PD-1	1.36	1.28	4.60	5.88

d_{He} - helium density, d_{Hg} - mercury density P - porosity
V_T - open pore volume estimated from He and Hg densities

Table 2. Densities, pore volumes and porosities of selected coals.

SAMPLE No.	S_{CO2} m^2/g	V_{CO2} (cm^3/g)	V_T (cm^3/g)	V_{50} (cm^3/g)	V_{10} (cm^3/g)	$V_{(T-50)}$ (cm^3/g)
T-2	161	0.0408	0.0365	0.012	0.019	0.025
MP-2	187	0.0472	0.0405	0.011	0.019	0.030
TH-1	160	0.0405	0.0289	0.007	0.014	0.022
CK-1	183	0.0463	0.0680	0.024	0.035	0.044
GK-1	201	0.0510	0.0554	0.009	0.017	0.046
NP-1	212	0.0536	0.0566	0.013	0.020	0.044
PD-1	201	0.0507	0.0521	0.013	0.021	0.034

S_{CO2} = surface area estimated from CO_2 adsorption
V_{CO2} = pore volume estimated from CO_2 adsorption
V_T = volume of total open pores (accessible to He) > 0.42nm
V_{50} = volume of pores > 50nm
V_{10} = volume of pores > 10nm
$V_{(T-50)}$ = volume of pores between 0.42 and 50nm

Table 3. Pore volumes estimated from different methods.

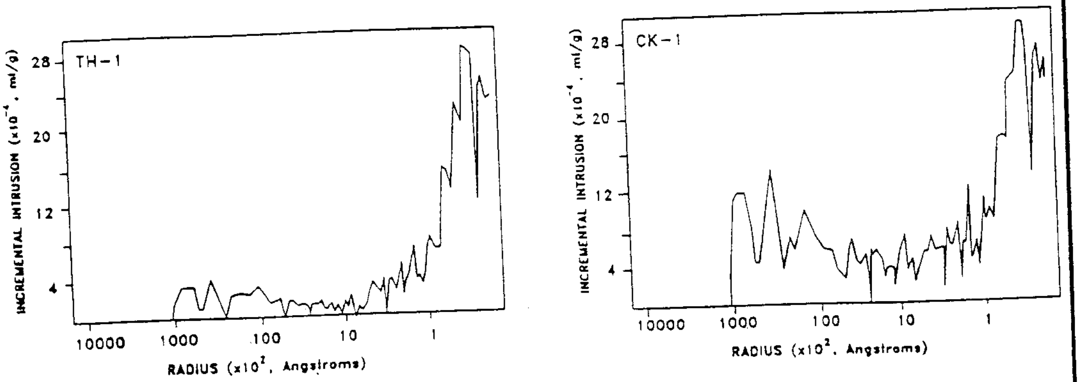
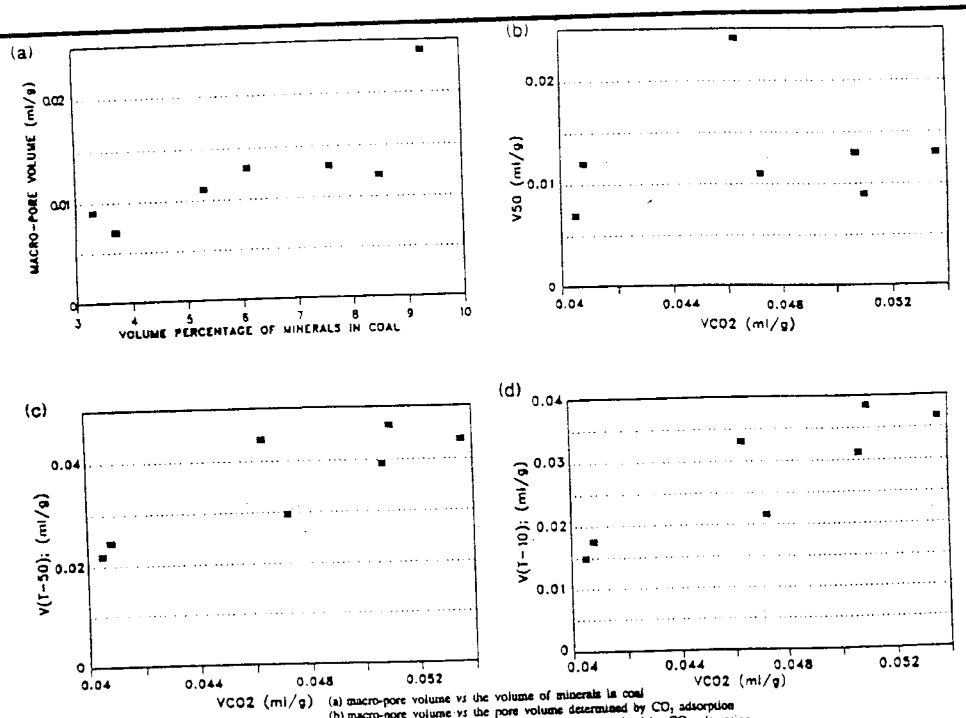


Figure 1. Pore size distributions in coal determined by mercury intrusion.



(a) macro-pore volume *vs* the volume of minerals in coal
(b) macro-pore volume *vs* the pore volume determined by CO_2 adsorption
(c) volume of pores < 50 nm *vs* pore volume determined by CO_2 adsorption
(d) volume of pores < 10 nm *vs* pore volume determined by CO_2 adsorption

Figure 2. Relationships between volumes of various pore-sizes and minerals content.

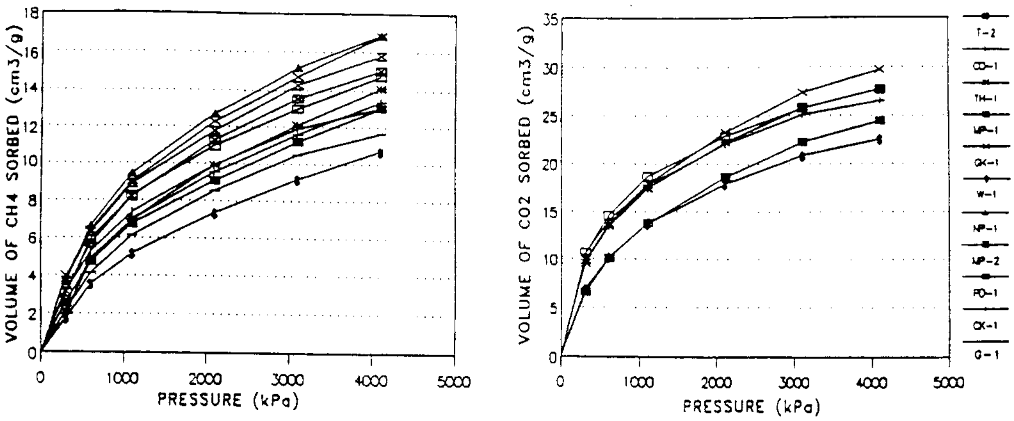
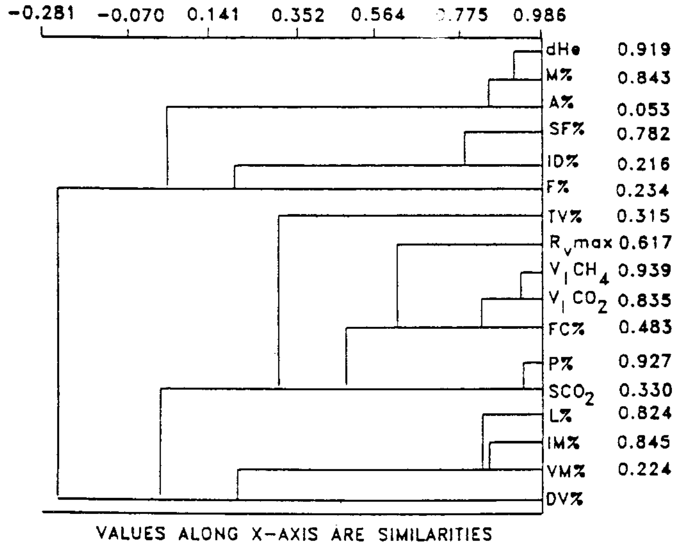


Figure 3. CH_4 and CO_2 sorption isotherms at 25°C.



dHe - He density, TV - telovitrinite, DV - detrovitrinite,
SF - semifusinite, F - fusinite, ID - inertodetrinite,
L - liptinite, M - minerals, IM - inherent moisture,
A - ash, VM - volatile matter, FC - fixed carbon,
$R_v$max - % mean maximum reflectance of vitrinite, SCO_2 - surface area determined by CO_2 adsorption,
V_lCH_4 - Langmuir volume for methane, V_lCO_2 - Langmuir volume for carbon-dioxide,
P - porosity

Figure 4. R-mode cluster analyses dendogram showing the similarity levels between the variables.

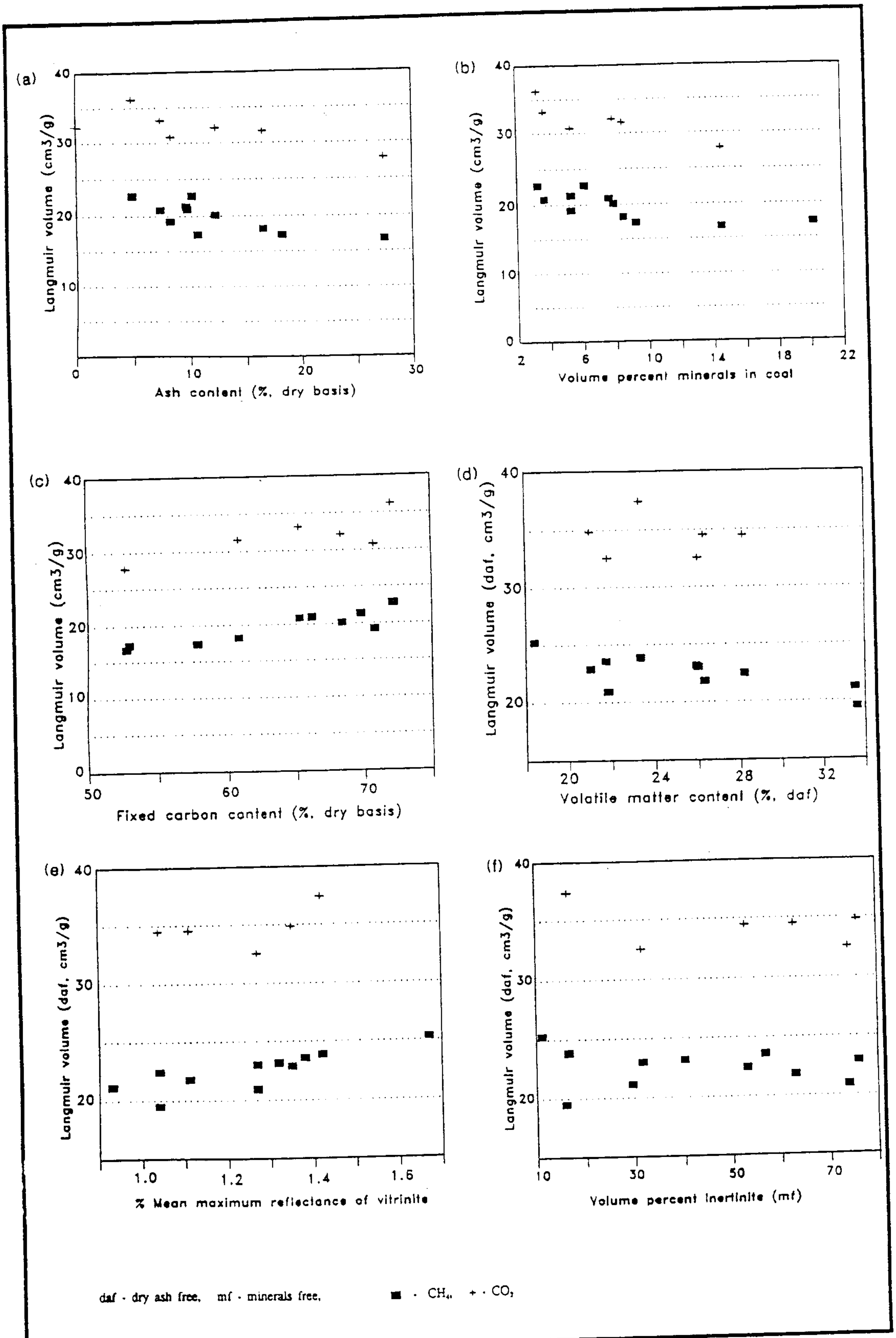
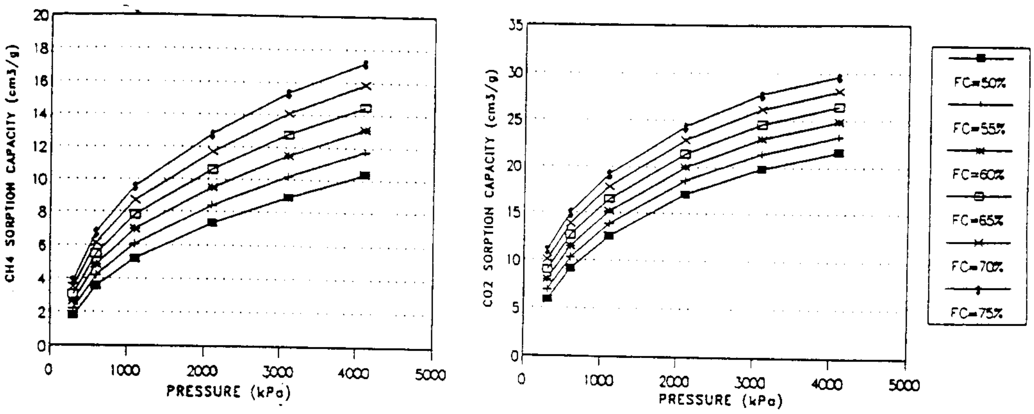


Figure 5. Relationships between the gas sorption capacity, coal composition and rank.



FC - fixed carbon content (%, dry basis)

Figure 6. Modelled CH_4 sorption isotherms as a function of fixed carbon content.