

LEI ZHANG\*<sup>1</sup>, NAJ AZIZ\*\*, TING REN\*\*, JAN NEMCIK\*\*, SHIHAO TU\***INFLUENCE OF COAL PARTICLE SIZE ON COAL ADSORPTION AND DESORPTION CHARACTERISTICS****WPLYW WIELKOŚCI ZIAREN WĘGLA NA CHARAKTERYSTYKI ADSORPCJI I DESORPCJI NA WĘGLU**

Accurate testing coal isotherm can play a significant role in the areas of coal seam gas drainage, outburst control, CO<sub>2</sub> geo-sequestration, coalbed methane (CBM) and enhanced coalbed methane recovery (ECBM) etc. The effect of particle size on the CO<sub>2</sub> and CH<sub>4</sub> sorption capacity of bituminous coal from Illawarra, Australia was investigated at 35°C and at pressure up to 4 MPa. A unique indirect gravimetric apparatus was used to measure the gas adsorption and desorption isotherms of coal of different particle sizes ranging from around 150 μm to 16 mm. Langmuir model was used to analysis the experimental results of all gases. Coal particle size was found to have an apparent effect on the coal ash content and helium density results. Coal with larger particle size had higher ash content and higher helium density. The sorption isotherm was found to be highly sensitive with helium density of coal which was determined in the procedure of testing the void volume of sample cell. Hence, coal particle size had a significant influence on the coal sorption characteristics including sorption capacity and desorption hysteresis for CO<sub>2</sub> and CH<sub>4</sub>, especially calculated with dry basis of coal. In this study, the 150-212 μm (150 μm) coal samples achieved higher sorption capacity and followed by 2.36-3.35 mm (2.4 mm), 8-9.5 mm (8 mm) and 16-19 mm (16 mm) particle size samples. However, the differences between different coal particles were getting smaller when the sorption isotherms are calculated with dry ash free basis. Test with 150 μm coal samples were also found to have relatively smaller desorption hysteresis compared with the other larger particle size samples. The different results including adsorption/desorption isotherm, Langmuir parameters and coal hysteresis were all analysed with the CO<sub>2</sub> and CH<sub>4</sub> gases.

**Keywords:** coal adsorption, desorption, coal particle size, isotherm, Langmuir volume

Dokładne zbadanie izoterm sorpcji na węglu odgrywa kluczową rolę w takich dziedzinach jak odgazowanie pokładów węgla, zapobieganie wybuchom, sekwestracja geologiczna CO<sub>2</sub>, odzysk metanu ze złoża. Wpływ wielkości ziaren na pojemność sorpcyjną bitumicznego węgla z Illawara (Australia)

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względem CO<sub>2</sub> i CH<sub>4</sub> zbadano w temperaturze 35°C przy ciśnieniu do 4 MPa. Wykorzystano oryginalną aparaturę do badań grawimetrycznych do zmierzenia izoterm adsorpcji i desorpcji na węglu w którym rozmiar ziaren wahał się od 150 µm do 16 mm. Analizę wyników doświadczalnych dla wszystkich gazów przeprowadzono w oparciu o model Langmuira. Stwierdzono, że rozmiary ziaren węglowych w znacznym stopniu warunkują zawartość popiołu i gęstość helową. Węgiel grubiej uziarniony charakteryzował się wyższą zawartością popiołu i większą gęstością helową. Wykazano, że izoterma sorpcji wykazuje wysoką wrażliwość na zmiany gęstości helowej, co stwierdzono na podstawie badania martwej przestrzeni ampulki w której umieszczono próbkę. Wnioskować stąd można, że rozmiar ziaren węgla w dużym stopniu wpływa na charakterystyki sorpcyjne węgla, w tym także na chłonność sorpcyjną i histerezy desorpcji dla CO<sub>2</sub> i CH<sub>4</sub>, zwłaszcza w badaniach na węglu suchym. W trakcie badań próbki węgla z ziarnami o wymiarach 150-212 µm (150 µm) wykazywały wyższą chłonność sorpcyjną, w dalszej kolejności plasowały się próbki o wymiarach ziaren: 2.36-3.35 mm (2.4 mm), 8-9.5 mm (8 mm) i 16-19 (16 mm). Jednakże różnice pomiędzy różnymi ziarnami węgla stawały się mniej wyraźne gdy izotermy sorpcji obliczane były w odniesieniu do próbki suchej, pozbawionej popiołu. Badania próbek o wymiarach ziaren 150 µm wykazały, że w ich przypadku histereza desorpcji jest stosunkowo mniejsza w porównaniu z próbkami gruboziarnistymi. Wszystkie wyniki: izotermy adsorpcji i desorpcji, parametry Langmuira oraz histerezy węgla badano przy użyciu dwóch gazów: CO<sub>2</sub> i CH<sub>4</sub>.

**Słowa kluczowe:** adsorpcja i desorpcja na węglu, wymiary ziaren węgla, izoterma, objętość Langmuira

## 1. Introduction

Better understanding the coal relationship with gas sorption capacity, gas content, gas pressure can play a significant role in the various areas of coal mining industry and coalbed methane (CBM) industry (Gamson & Beamish, 1992; Aziz & Li, 1999; Black, 2012; Vlastimil et al., 2013). Experimental results can still vary widely although sorption isotherm experiments have been used for many years to estimate the storage capacity of methane and other gases of the coal matrix. The most significant causes of errors are believed to the use of gas composition and coal moisture content that are not representative of the *in situ* conditions, oxidation of the coal, and the use of crushed samples (Mavor et al., 1992). In their test, Mavor et al. (1992) suggested the grain size of coal used in adsorption testing affected the measured gas storage capacity with the adsorption capacity of coal samples 25 mm long and 38 mm in diameter having a greater adsorption capacity than crushed samples, which indicated a possible reason why they observed canister desorption derived estimates of gas content that were greater than sorption isotherm storage capacity estimates obtained with methane on crushed samples.

Result reported by Yalcin and Durucan (1991), the tests of effect of coal particle size on methane adsorption is carried with three different coal particle size, 500-707 µm, 149-250 µm and 88-125 µm. And for each size range, adsorption experiment were carried out for three samples at five different pressures and the average volume of methane adsorbed was calculated for each pressure and a mean adsorption isotherm was plotted. The results showed that the size of the coal sample does not affect the methane adsorption capacity of coal if the sample can be fully penetrated by methane and fully equilibrated. However, according to the three mean isotherms, the larger particle size of 500-707 µm isotherm did apparently lie under the other two particle isotherms, the 149-250 µm and 88-125 µm isotherms were very close.

Gamson and Beamish (1992) reported that sorption testing using both small, solid (1 g) blocks and crushed (–250 µm) coal samples, they confirmed the that the crushed size fraction has a more rapid methane uptake and reaches equilibrium more quickly than their solid samples, the similar relationship was reported by Perkins and Cervik (1969). Gamson and Beamish (1992)

indicated although this indicates that the higher uptake of methane observed in the crushed coal is more representative of the coals' maximum gas storage capacity, the rapid uptake of methane shown by the crushed size fraction, tells little about the time it takes for methane to flow through a solid coal i.e. the coals diffusivity.

Among all the researches and discussions, Black (2012) recently suggested that commercial laboratories prefer using coal of smaller particle size due to the reduced time required to achieve saturation. A potential issue associated with the use of finely ground coal samples in sorption testing is the risk of overstating the sorption capacity of the coal. Black (2012) examined that the two reasons where sorption capacity may be overstated are (i) loss of coal material during desorption/depressurisation resulting in reduced coal mass relative to the measured adsorbed gas volume, thereby overstating the adsorbed gas content, and (ii) the surface area of coal crushed to less than 212  $\mu\text{m}$  is significantly greater than coal in its natural state allowing greater total gas adsorption than would be practically achieved by *in situ* coal. The relatively small coal sample mass used by commercial testing laboratories is also considered a risk to obtaining accurate results from sorption testing as the percentage error inherent in the measurement of the adsorbed gas volume will be greater than for larger sample sizes.

## 2. Experimental methods and procedures

### 2.1. Sample preparation

Coal samples tested in this experiment were collected from a longwall, panel (520) extracting from the Bulli Seam of the Sydney Basin, Australia. The coal samples used in the study consisted of the borehole cores as well as large coal lump samples freshly collected the development headings. The retrieved large coal samples were wrapped in plastic sheet and taken to the laboratory. Coal fragments were later crushed and sieved to obtain the appropriate particle sizes for the test. Coal fragments of 2.36-3.35 mm (2.4 mm), 8-9.5 mm (8 mm) and 16-19 mm (16 mm) particle size samples and coal powder, 150-212  $\mu\text{m}$  (150  $\mu\text{m}$ ) were used in the study. The preliminary information about this type of coal was shown in Table 1 and Table 2, tested by Saghafi and Roberts (2008) from CSIRO.

TABLE 1

Coal density and proximate analysis

Sample Code	Depth (m)	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Volatile Matter (% <sub>daf</sub> )	Coal Density (g/cm <sup>3</sup> )
520	450	1.3	21.7	71.4	23.3	1.43

TABLE 2

Coal Petrography

Sample Code	Vitrinite Reflectance (%)	Maceral (%)			Maceral (% <sub>mineral free</sub> )			
		Vitrinite	Liptinite	Inertinite	Mineral	Vitrinite	Liptinite	Inertinite
520	1.28	41.6	0.1	55.3	3.0	42.9	0.1	57.0

It is widely recognised that thermal drying of low rank coals can cause irreversible coal structure changes and these effects can be diminished with increasing rank and it has been reported that drying does not significantly change the structure of bituminous coals (Miknis et al., 1996). The bituminous coal from Bulli Seam of the Sydney Basin is suitable to carry the test to avoid the effects of structural change induced by drying, which may affect the isotherm results of this study.

Prior to sorption testing, the coal samples were dried in a desiccator containing water sorbing material. The desiccator was vacuumed to keep the coal from the air and prevent coal sample oxidation. The desiccator was then kept in a heated oven at 60°C. The coal sample moisture content was checked regularly to achieve a total dry condition (zero moisture content).

## 2.2. Sorption apparatus

The gravimetric method with only sample cell, also referred to the indirect gravimetric method, was first reported by Lama and Bartosiewicz (1982), and later by Aziz and Li (1999) and Sereshki (2005). Fig. 1 shows the modified version of the apparatus currently being used in the gas laboratory, University of Wollongong. The new and more accurate sorption testing and calculation method regarding this apparatus were developed for this study recently.

In this apparatus, each cell known as “bomb”, has its own pressure transducer connected to the data logger so that the sorption process and pressure changes in the bomb can be readily determined. These bombs are immersed in the automatic temperature-controlled water bath, which allows the tests of coal isotherm at different temperatures. Approximately 200 g of coal ranging from powder size to standard coal core size can be used in the test. A high accuracy balance is

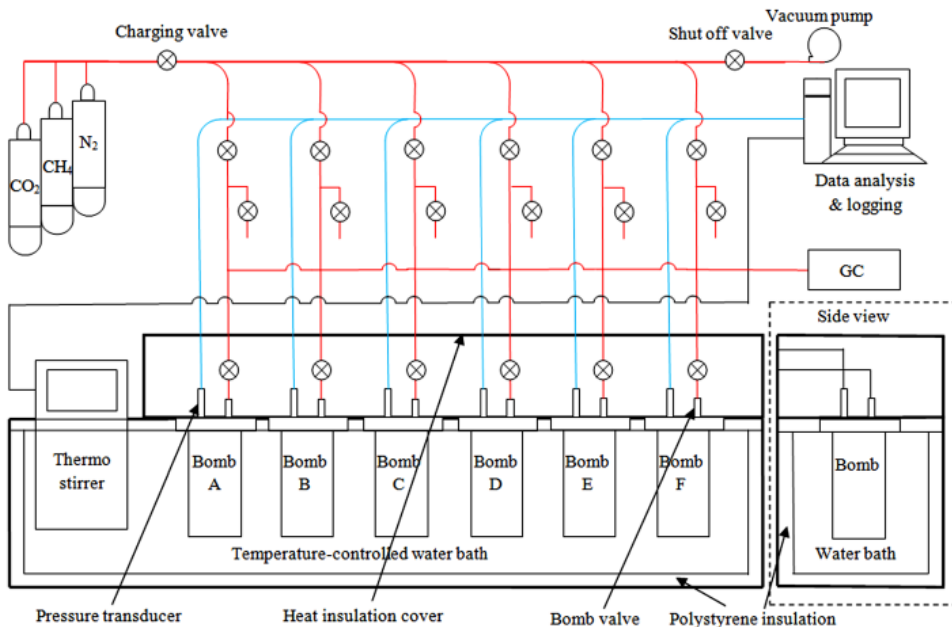


Fig. 1. Schematic diagram of the gravimetric method with sample cells

used to weigh the bomb weight. The equipment has recently been modified to accommodate increases in temperature up to 100°C. The addition of a heat isolation jacket outside the water bath as well as the insulation cover enabled the sample bombs to maintain the desired experimental temperature with an accuracy of 0.1°C.

## 2.3. Experiment procedure

### 2.3.1. Sorption procedure and helium density measurement procedure

- (1) Empty adsorption isotherm bomb is weighed;
- (2) Coal sample is prepared and subsequently charged in the bomb and weighed;
- (3) Bomb with coal sample is placed in the water bath and brought to desired test temperature;
- (4) Bomb is evacuated to make sure there is no air inside the bomb;
- (5) Helium is introduced into the bomb and allowed to equilibrate until the pressure becomes constant;
- (6) After equilibrium, the constant pressure is recorded and bomb is weighed again;
- (7) Repeat Steps 5 and 6, charging at different pressure steps of approximately 1, 2, 3, 4 MPa; this data is used to calculate the free volume (void volume) of the bomb and consequently the helium density of the coal;
- (8) After determination of the void volume, the bomb is evacuated;
- (9) The test gas is introduced into the bomb and allowed to equilibrate until the pressure becomes constant;
- (10) After equilibrium, the constant pressure is recorded and bomb is weighed again;
- (11) Repeat steps 9 and 10 at different pressure steps to obtain final isotherm at approximate pressures of 0.5, 1, 2, 3, 4 MPa;
- (12) The isotherm results are calculated as adsorbed volume per mass of coal at normal temperature and pressure condition (NTP) which is 20°C and 1 atm (101.325kPa), the Australia standard condition.

### 2.3.2. Ash content test

For each of the coal samples tested with the isotherm, the ash content test was carried out in accordance with the Australian Standard (AS 1038.3-1989). The only variation from this standard was that different particle size coal samples were directly used in the ash content test, instead that usually powder coal sample was used in the standard. The percentage of ash was calculated from the mass of residue remaining after incineration. For the larger particle size sample ash content test, the heating time at 815°C took longer to achieve the constant mass to ensure that the coal samples were totally incinerated. It should be noted that in this study all the residual material for each particle size tests which were not incinerated in the above condition could be treated as ash content.

## 2.4. Calculation method

In the indirect gravimetric method, at each of the pressure steps, the total mass of gas in the bomb is directly weighed and the total gas in the bomb can be calculated by:

$$n_{total} = \frac{M_{total}}{M_{gas}} \quad (1)$$

where  $n_{total}$  is the total amount-of-substance of gas,  $M_{total}$  is the total gas weight in bomb and  $M_{gas}$  is the mole mass of gas. The amount-of-substance of gas in the void space can thus be calculated using the following SRK equation:

$$PV_{void} = n_{void} Z_{SRK} RT \quad (2)$$

where  $n_{void}$  is the void volume of the bomb,  $V_{void}$  is the void volume, calculated with the helium expansion,  $P$  is the equilibrium gas pressure inside the bomb, which can be measured with the transducer,  $T$  is the experiment temperature,  $R$  is universal gas constant,  $Z_{SRK}$  is the compressibility factor of the tested gas calculated with SRK equation at the pressure  $P$  and temperature  $T$ . Using  $n_{total}$  and  $n_{void}$ , the Gibbs (Excess) amount of adsorbed gas can be calculated as:

$$n_{adsorbed} = n_{total} - n_{void} \quad (3)$$

The adsorption isotherm is expressed in terms of volume in standard condition, hence the adsorbed volume is:

$$v_{adsorbed} = n_{adsorbed} V_m \quad (4)$$

where  $V_{adsorbed}$  is the adsorbed volume of gas and  $V_m$  is the mole volume of gas at standard condition (NTP). For each of the pressure steps, the Gibbs adsorbed gas for the isotherm is calculated by dividing Gibbs  $v_{adsorbed}$  by the mass of coal in the cell.

## 3. Results and discussions

### 3.1. Coal particle size influence on coal ash content and helium density

Before commencing the sorption isotherm experiments, the moisture content, ash content and helium tests for the different particle size coal samples were carried out to fully understand the basic parameters of tested coal samples. The moisture content of tested coal samples at different particle size was nearly zero to make sure the samples were totally dry. The ash content of coal was treated as a key parameter in the sorption experiment especially with different particle size samples and isotherms calculated on dry basis. This is confirmed by the results from Massarotto et al. (2010) who recommended measuring the ash content of the chosen particle size range to represent the original coal block. Fig. 2 and Fig. 3 show coal ash content test samples before and after incineration.

As shown in Fig. 4, ash content of coal samples increased with increasing coal particle size. The ash content was 27.0% for the 16 mm particle size while the ash content of the 150  $\mu\text{m}$  was

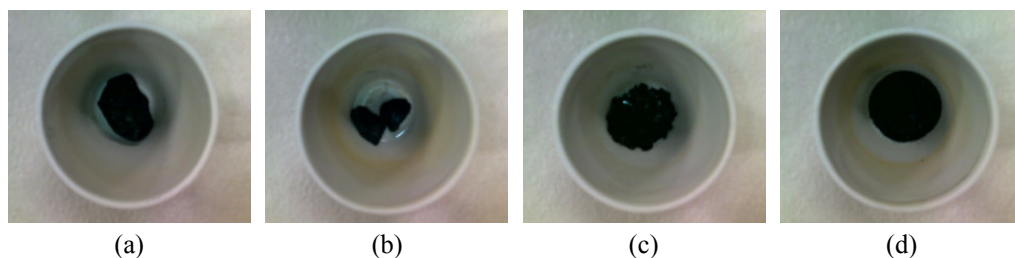


Fig. 2. Coal samples before the ash content test (a) 16 mm, (b) 8 mm, (c) 2.4 mm, (d) 150  $\mu\text{m}$

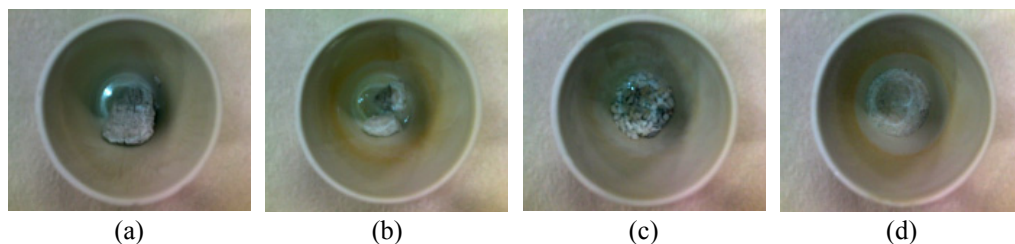


Fig. 3. Coal samples after the ash content test (a) 16 mm, (b) 8 mm, (c) 2.4 mm, (d) 150  $\mu\text{m}$

around 11.3%. With linear fitting of the ash content results, the relationship between the ash content and coal particle size is  $y_1 = 0.9525x + 10.7870$  with  $R^2 = 0.866$ . The ash contents of cube samples of 15 mm were apparently larger than finer particle samples (200  $\mu\text{m}$ ). The difference in the ash content with particle size indicates that some ash content materials were lost during the powder sample preparation as some pore and matrix is the storage space for the mineral matter which is opened in the grinding process.

As also shown in Fig. 4, the helium density of coal also increases with the increasing coal particle size. The helium density of 16 mm sample achieves 1.39  $\text{g}/\text{cm}^3$  while the helium

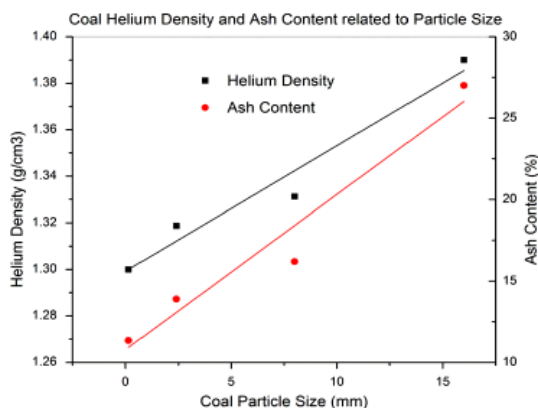


Fig. 4. Coal helium density and ash content test results

density of 150  $\mu\text{m}$  is lowest which is 1.30  $\text{g}/\text{cm}^3$  and the linear relationship between them is  $y_2 = 0.0054x + 1.2992$  with  $R^2 = 0.882$ . One of the reasons why larger particle size coal samples have higher helium density is because they have higher ash content, which contains higher mineral matters with higher density than organic matters (i.e. macerals). In the process of grinding, coal is likely to lose the higher density material component and concurrently increase the pore accessibility indicating that when coal is being ground, coal mass relatively decreases and coal volume increases resulting in the helium density decrease.

The linear relationship between the helium density of tested coal and the ash content is  $y_2 = 0.0057y_1 + 1.2380$ , coal helium density increases with the increasing ash content. As there is an apparent difference in the ash content between the different coal particle samples, it is important to report the ash content of the particle size range that is used for determining accurate adsorption measurements.

### 3.2. Coal adsorption isotherms

The  $\text{CO}_2$  adsorption isotherm in Fig. 5 shows coal sorbed volume decreases with increasing coal particle size, both on a dry basis and on a dry ash free basis. This is similar to the results reported by Bae and Bhatia (2006), the fact that the larger particle size coal samples are ground down to finer particles, which possibly opens some otherwise closed pores, thus leading to an increased pore accessibility and consequently an increase in the  $\text{CO}_2$  amount adsorbed. Another possible reason is that larger particle size samples need much longer time period for diffusion process to achieve complete saturation. By comparison of Fig. 5(a) with Fig. 5(b), the difference of  $\text{CO}_2$  adsorption isotherms of different particle size coal sample calculated on a dry ash free basis is smaller than on a dry basis.

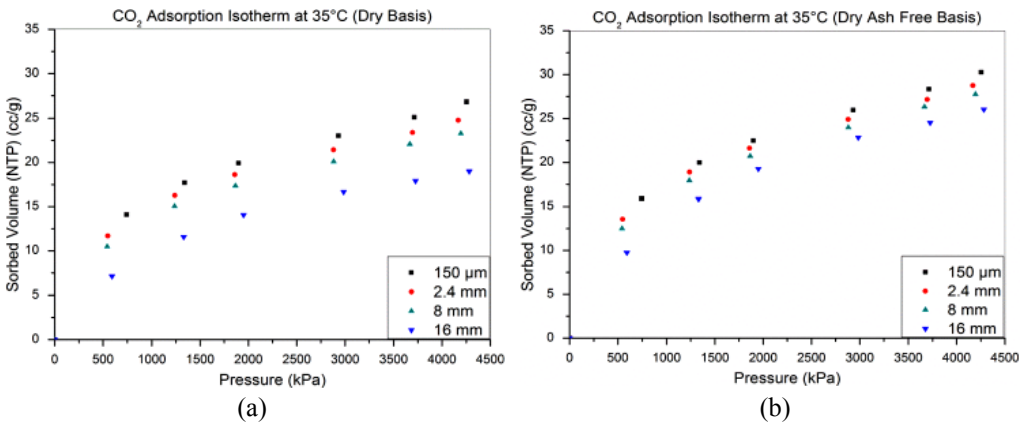


Fig. 5. Coal adsorption isotherm results with  $\text{CO}_2$

$\text{CH}_4$  adsorption isotherms in Fig. 6 follow the same trend as the  $\text{CO}_2$  isotherms, showing the coal sorbed volume decreases with increasing coal particle size, both on a dry basis and dry ash free basis and the isotherm difference is smaller with dry ash free basis than dry basis. Results



are similar to Beamish and O'Donnell (1992) who researched particle size on gas sorption capacity and claimed that reducing coal particle size to speed up the sorption process has often been confused as a possible source of falsely increasing storage capacity (Perkins & Cervik, 1969; Beamish & O'Donnell, 1992; Gamson & Beamish, 1992). A constant difference of isotherm with coal particle size results is also observed (Busch et al., 2004). Busch et al. (2004) found that obvious variations existed in the isotherms for different particle size coal samples, but no specific trend was claimed in terms of shape or maximum sorption capacity.

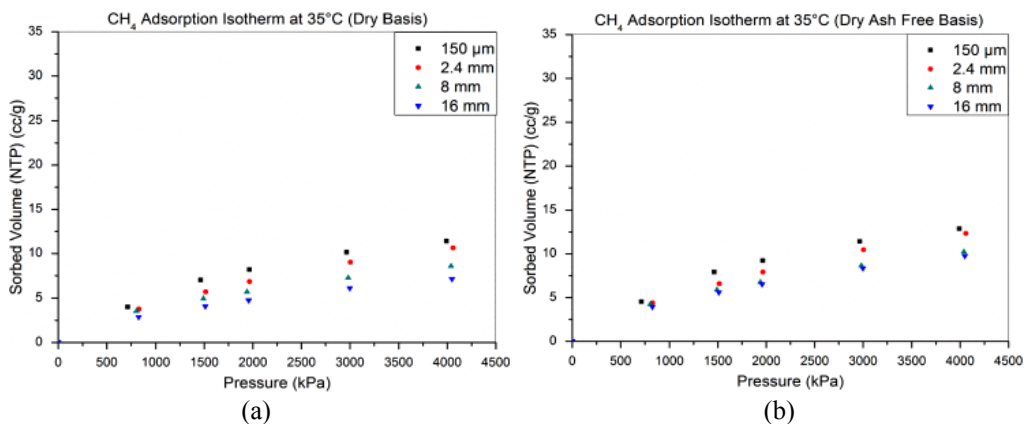


Fig. 6. Coal adsorption isotherm results with CH<sub>4</sub>

### 3.3. Coal adsorption capacity

After the Langmuir parameters for each isotherm are calculated, the average Langmuir pressure is used to recalculate the Langmuir volume, ensuring that Langmuir volume for each isotherm is estimated under the same Langmuir pressure. As shown in Fig. 7, the Langmuir volume decreases with the increasing coal particle size. The Langmuir volume of CO<sub>2</sub> adsorption follows the trend line:  $y = -0.3911x + 35.9134$  ( $R^2 = 0.929$ ) for dry ash free basis and  $y = -0.6238x + 31.8565$  ( $R^2 = 0.917$ ) for dry basis. The Langmuir volume of CH<sub>4</sub> adsorption follows the trend line:  $y = -0.2969x + 18.3335$  ( $R^2 = 0.696$ ) for dry ash free basis and  $y = -0.3964x + 16.2932$  for dry basis ( $R^2 = 0.849$ ). It can be seen that the Langmuir volume difference becomes larger between dry ash free basis and dry basis with the increasing coal particle size, especially for the CO<sub>2</sub> adsorption isotherm. The CO<sub>2</sub> adsorption capacity of this bituminous coal with 150 μm coal size is 1.85 times larger than the CH<sub>4</sub> adsorption capacity (daf).

Beamish and O'Donnell (1992) calculated the percentage change in the increasing surface area by crushing a bituminous coal to 250 μm is of the order of 0.02%, which indicated the sum of external surface area of coal particles is progressively smaller as compared to the internal surface area of the pores available for sorption. Thus increased accessibility to the new opened pore space is a more important reason than the increased coal surface area. It can also be concluded to some extent, that removing some of the ash content creates extra gas adsorption capacity. The similar decreasing trend of coal sorption of ethane gas with increasing coal size is also reported

(Żyła et al., 2013). Different results are obtained between the results from this study and some other researches, as referring to the low degree of statistical difference results of testing by Bielicki et al. (1972) and Ruppel et al. (1974) with the storage capacities of coals tested at particle sizes ranging from 3.36 mm-44  $\mu$ m and 12.7 mm-74  $\mu$ m respectively.

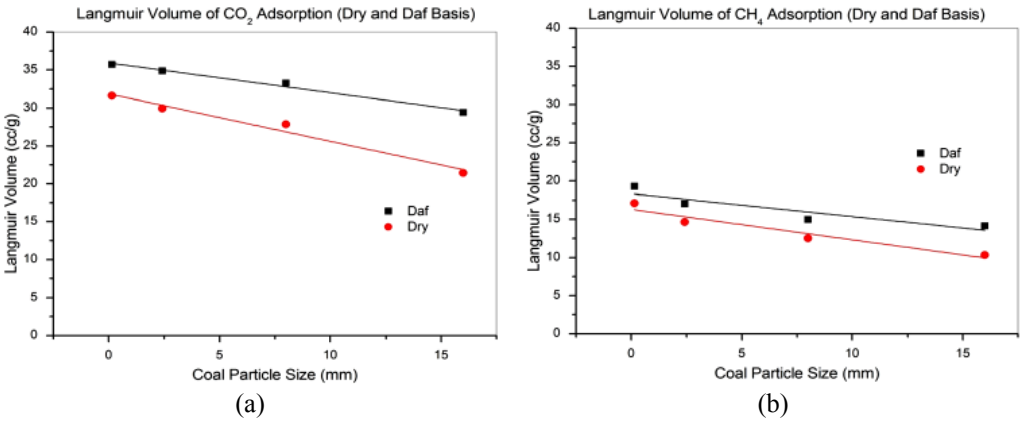


Fig. 7. Langmuir volume of adsorption isotherm with CO<sub>2</sub> and CH<sub>4</sub>

### 3.4. Coal desorption isotherms

Fig. 8 shows the tested coal isotherms have apparent hysteresis for both CO<sub>2</sub> and CH<sub>4</sub> and all coal particle sizes. The phenomenon that desorption isotherms generally lie above the sorption isotherms represents the sorption hysteresis which is associated with the sorption/desorption process. Coal as a sorbate, when coal adsorbs and desorbs the sorbent, it has the hysteresis, which not only happens with gas which is widely observed (Dudzińska et al., 2013;

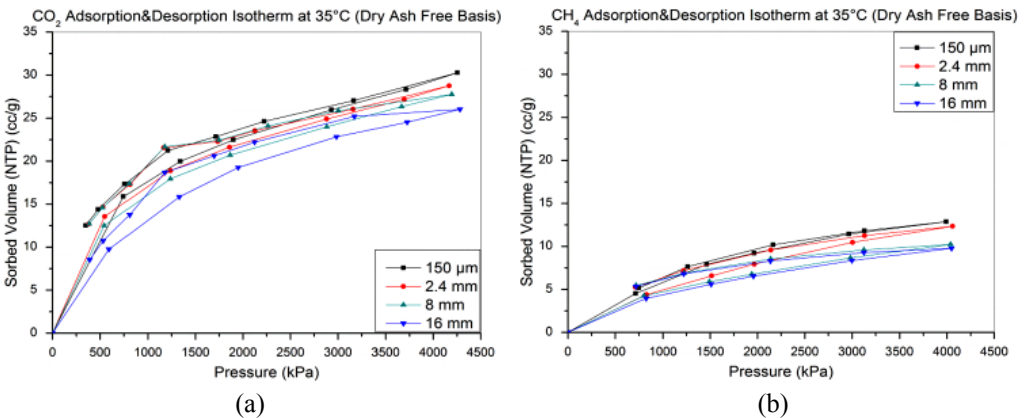


Fig. 8. Coal desorption isotherm results with CO<sub>2</sub> and CH<sub>4</sub>

Goodman et al., 2004; Medek et al., 2006; He et al., 2010), but also with water (McCutcheon & Barton, 1998; McCutcheon et al., 2002; Charrière & Behra, 2010). The hysteresis effect indicates that the sorbent/ sorbate system is in a metastable state and at decreasing pressure the gas is not readily released to the extent corresponding to the thermodynamic equilibrium value (Busch et al., 2003).

The study from Dutta et al. (2011), indicated that there were explanations other than those cited above for adsorption/desorption hysteresis, the nature of sorption of CO<sub>2</sub> molecules on coal may well be a reason for the hysteresis. The hysteresis due to this reason may get relatively smaller with a longer term desorption process. As shown in Fig. 8(a), larger particle size coals show a larger hysteresis, CO<sub>2</sub> may also be absorbed/dissolved into the coal structure and during desorption, only the adsorbed molecules come out of the pore-spaces leaving behind the dissolved molecules in the coal structure. This was also confirmed by Ozdemir et al. (2004), where the positive deviation of CO<sub>2</sub> desorption was attributed to the swelling of the coal matrix. Shrinkage/swelling of coal matrix is believed to be associated with the desorption/adsorption process. Coal with larger particle size has a better chance to trap the gas molecules as it has more pore system and longer path distances for gas to desorb from the internal surface.

The desorption hysteresis on coal or any adsorbent may occur due to two different reasons, which are the changes in the adsorbent properties/structures and/or the capillary condensation in the adsorbent micropores (Harpalani et al., 2006). Tang et al. (2005) postulated that the surface geometry heterogeneity may account for the adsorption-desorption hysteresis. They mentioned the work of Seri-Levy and Avnir (1993) who used Monte-Carlo simulations of gas-solid systems to examine gas adsorption on rough surfaces of various geometries and computed significant hysteresis in equilibrium isotherms as a result of path dependent configurations of adsorbed molecules.

### 3.5. Coal desorption capacity

As the same calculation procedure with adsorption analysis, the Langmuir volume is recalculated with the average Langmuir pressure. As shown in Fig. 9, Langmuir volume decreases with the increasing coal particle size. The Langmuir volume of CO<sub>2</sub> desorption follows the trend

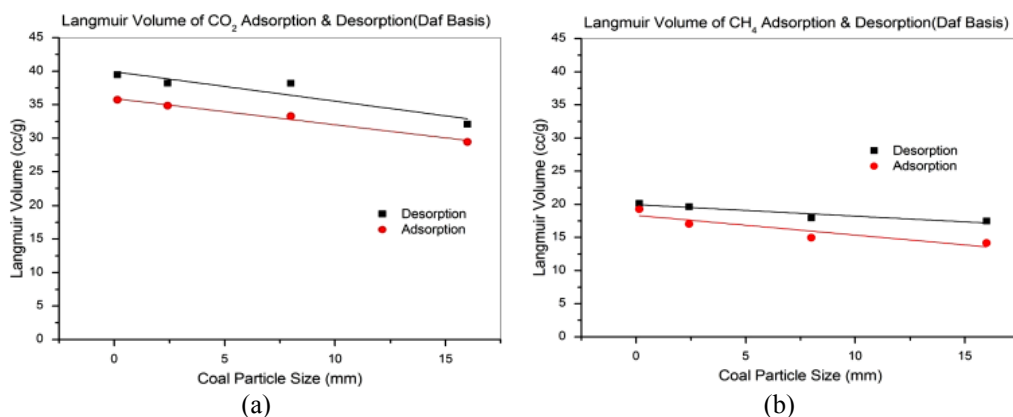


Fig. 9. Langmuir volume of desorption isotherm with CO<sub>2</sub> and CH<sub>4</sub>

line:  $y = -0.4387x + 39.9164$  ( $R^2 = 0.755$ ) for dry ash free basis and the Langmuir volume of  $\text{CH}_4$  adsorption follows the trend line:  $y = -0.1725x + 19.9469$  ( $R^2 = 0.797$ ) for dry ash free basis. It can be seen that the Langmuir volume difference becomes larger between adsorption and desorption isotherms with the increasing coal particle size, especially for  $\text{CH}_4$  tests.

## 4. Conclusions

A modified gravimetric apparatus with single sample cell which is also called the indirect gravimetric method apparatus including its setup, operation procedure and calculation method are introduced.

Ash content of coal samples increase with the increasing coal particle size. The ash content achieves 27.0% for the 16 mm particle size while the ash content of the 150  $\mu\text{m}$  is around 11.3%. The difference in the ash content with particle size indicates that some ash content materials were lost during the powder sample preparation.

The helium density of coal also increases with the increasing coal particle size and coal ash content. It can be concluded that in the process of grinding, with the decreasing coal particle size, coal is losing the higher density component and at the same time increasing the pore accessibility finally results coal volume relatively increasing and the helium density decreasing.

Coal sorbed volume decreases with the increasing coal particle size, both in dry basis and dry ash free basis. The difference of  $\text{CO}_2$  and  $\text{CH}_4$  adsorption isotherms of different particle size coal sample calculated with dry ash free basis is smaller than dry basis.

Langmuir volume decreases with the increasing coal particle size for  $\text{CO}_2$  and  $\text{CH}_4$  adsorption and desorption. Langmuir volume difference is found to become larger between dry ash free basis and dry basis with the increasing coal particle size, especially for  $\text{CO}_2$  adsorption isotherm.

The tested coal isotherms have apparent hysteresis for both  $\text{CO}_2$  and  $\text{CH}_4$  and all range of coal particle sizes and larger particle size coals show a larger hysteresis. Langmuir volume decreases with the increasing coal particle size. Langmuir volume differences become larger between adsorption and desorption, with the increasing coal particle size, especially for  $\text{CH}_4$  adsorption and desorption isotherms.

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