# Characterizing Pore Structure of Coal under $CO_2$ Sequestration Conditions

Changjiang Liu, Geoff Wang, Huilin Xing, and Hans Muhlhaus

***Abstract*—High pressure supercritical $CO_2$ (HP-Sc$CO_2$) geochemical reactor was designed to study the interaction between coal and HP-Sc$CO_2$ in order to simulate the $CO_2$ geo-sequestration into and/or enhancement of coalbed methane recovery from deep coal, focusing on the characterization of the pore structure of coal and its changes. Four coal samples with different coal rank were chosen for the HP-Sc$CO_2$ tests using the geochemical reactor under around 40 ℃ and 9.8 MPa for 72 hours. The coal samples with and without the Sc$CO_2$-$H_2O$ treatment were further investigated using the mercury porosimetry, providing the mercury intrusion data for characterization of the pore structure of coals. Fractal analysis was used to distinguish inter- and intraparticle pores at lower mercury intrusion pressure and to define the initial pressure associated coal compressibility. The fractal dimension phenomena corresponding to three pressure ranges were observed associated with three different mercury intrusion processes. These fractal dimension phenomena can be described by means of the fractal dimensions. The fractal dimensions in relatively low pressure are not change much, mainly resulted from the accumulation mode of particle samples in the penetrometer and the roughness of samples which caused by crushing and grinding process. In the higher pressure range, the fractal dimensions decreases with increasing pressure as the coal rank increased, which probably related to the hardness of coal. In general, $CO_2$ sequestration process makes all the samples become easier to be compressed than the raw samples. Moreover, coal rank and ash content may play more important role in maintaining the pore structure. After reacted with HP-ScCO2, the higher rank samples exhibit larger pore structure changes than the lower rank ones.**

***Index Terms*—Coal, Sc$CO_2$-coal interaction, $CO_2$ geo-sequestration, pore structure, fractal dimension**

## I. Introduction

Sequestration of $CO_2$ into deep coal seam, as known as $CO_2$ geo-sequestration, is considered to be an attractive technology to enhance coalbed methane (CBM) recovery from deep coal and reduce greenhouse gas which cause global warming. With $CO_2$ sequestration in coal, $CO_2$ is mainly existed as a gas adsorbate bonded to coal surface. Under the reservoir temperature and pressure, $CO_2$ is likely to be presented as supercritical state ($T_c$ = 31.1 °C; $P_c$ = 7.38 MPa; $\rho_c$ = 0.47 g/cm$^3$). $CO_2$ is usually transported to sequestration site with pipelines for injection into coal seam either in the form as gas, a supercritical fluid or in the subcooled-liquid state. For instance, most $CO_2$ pipelines used for enhanced oil recovery transport $CO_2$ as a supercritical fluid (Sc$CO_2$) for both economical and effective concerns[1]. Thus, the growing interest in studies of the $CO_2$-$H_2O$-coal system has been received in recent years[2-5] and interactions between $CO_2$ and coal in supercritical $CO_2$-$H_2O$-coal system plays an important role in the $CO_2$ geo-sequestration process and $CO_2$-enhanced CBM recovery.

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This paper presents a study of interaction between coal and supercritical $CO_2$ to simulate the CO2 geo-sequestration and/or $CO_2$-enhanced CBM recovery from deep coal. Fractal dimension analysis was employed to investigate changes in the pore structure of coal under the conditions simulated $CO_2$ sequestration process. A high pressure supercritical $CO_2$ geochemical reactor was designed to simulate the $CO_2$ sequestration process with different coal rank samples, providing the Sc$CO_2$-$H_2O$ treated coal samples. The pore structure of various coal samples with and without Sc$CO_2$-$H_2O$ treatment have been comparatively discussed based on the fractal dimension analyses.

## II. Experiments

### *A. Samples*

Four different rank coal samples which are lignite, high volatile bituminous, low volatile bituminous and anthracite, named by $C_1$, $C_2$, $C_3$ and $C_4$ respectively, were chosen for investigation in this study. Before transported to laboratory, essential methods were applied to protect the samples from further oxidation. Table 1 is the key properties of the coal samples used in this study.

**Table 1** Typical properties of coals used in the experiments

| Samples | $R_o$, % | Proximate analysis, wt% | | | | Ultimate analysis, wt % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $M_{ad}$ | $A_d$ | $V_{daf}$ | $F_{Cd}$ | $O_{daf}$ | $C_{daf}$ | $H_{daf}$ | $N_{daf}$ |
| $C_1$ | 0.37 | 16.20 | 27.92 | 43.58 | 40.67 | 17.07 | 74.50 | 4.70 | 1.56 |
| $C_2$ | 0.71 | 2.14 | 7.34 | 43.15 | 52.68 | 10.72 | 79.59 | 5.43 | 1.42 |
| $C_3$ | 1.67 | 0.90 | 20.44 | 26.84 | 58.20 | 10.87 | 82.71 | 4.06 | 1.27 |
| $C_4$ | 3.09 | 1.59 | 6.87 | 13.54 | 80.52 | - | - | - | - |

Coal samples were crushed by hand and then grinded and sieved into 4-8 mm grain sizes. The grain sizes selected here mainly concern about the requirements for reaction equilibrium and limitation of apparatus. Theoretically, it is better to choose bigger bulk coal sample in the experiment simulating the *in situ* conditions in coal seams. However, for the laboratory experiments, using a large size coal sample will result in a very long reaction time to reach equilibrium and disallow efficient performance of the $ScCO_2$-$H_2O$ treatment test.

*B. Apparatus and methods*

To investigate the changes in pore structure of coal associated with $CO_2$ sequestration into deep coals, the high pressure supercritical $CO_2$ geochemical reactor (Figure 1) was introduced to mimic the $CO_2$ sequestration process at around 40 ℃ and 9.8 MPa for 72 hours, providing the $ScCO_2$-$H_2O$ treated samples. The $ScCO_2$-$H_2O$ treated coal samples were analyzed using mercury porosimetry with the same method used for the untreated coal samples. The results obtained from treated and untreated coal sample were then comparatively analyzed.

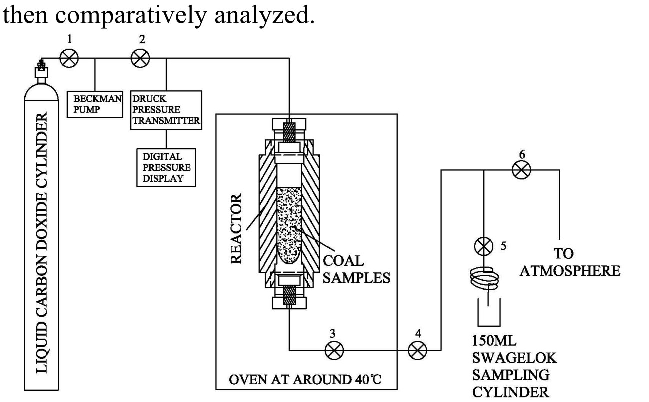


**Fig. 1** Sketch of high pressure supercritical $CO_2$ geochemical reactor

The study deals with supercritical $CO_2$ treatment test and mercury intrusion measurements using the coal samples with and without the supercritical $CO_2$ treatment. During sample preparation, all coal samples are divided into two parts. The first part, defined as reference part, is directly used for the mercury intrusion measurements. For these measurements, all the reference coal samples need to be dried in an air oven at 80-90 ℃ for at least 48 hours before the tests. The second part is firstly used for the $ScCO_2$-$H_2O$ treatment in the HP-$ScCO_2$ geochemical reactor (Figure 1), and then vacuum-dried for 24 hours at 50 ℃, providing the supercritical $CO_2$ treated sample for mercury intrusion measurements followed the same procedures as mentioned above.

Mercury porosimetry analysis was carried out with the AutoPore IV 9500, using the mercury filling at pressures from 0.0036 MPa to 387.4574 MPa permitting the pore diameter from 349317 nm to 3.2 nm calculated by the Washburn equation[6] in which the surface tension of 0.48 N/m and a contact angle of 130° between coal and mercury were used.

## III. Results and Discussion

The fractal analysis is becoming increasingly used in recent years to study of porous structures and surfaces[7, 8]. Mercury porosimetry data can be used to evaluate the fractal dimension of coal samples[9, 10] to study the pore structure. Assuming that $V$ denotes the pore metric volume which can be approximated by the cumulative intrusion volume ($cm^3/g$) and $P$ is applied mercury pressure (MPa), the fractal analysis results in the following correlation[11].

$$\log\left(\frac{dV}{dP}\right) \propto (D-4)\log P \qquad (1)$$

where $D$ is defined as the fractal dimension (-).

Figures 2 and 3 show results from fitting the mercury porosimetry data obtained from each coal sample with the correlation Eq. (1) above. The figures give the plots of Log ($dV/dP$) versus Log ($P$) which can be used for fractal dimensions analysis in logarithm scale. According to the correlations shown by the data, each data set of treated and untreated coal samples shows three regions distribution which reflects the three phases or stages of mercury intrusion process, i.e. interpore filling, intrapore filling and coal compressibility.

Each stage in Figures 2 and 3 represents the slope of the fitting line (i.e. $D$-4). Thus the values of fractal dimension ($D_1$, $D_2$, $D_3$) can be calculated, as shown in Table 2. $D_1$ can be interpreted as the fractal dimension for the crushed coal sample where mercury was intruded into the interparticle pores at low pressure. $D_2$ in the intermediate pressure range represents the surface fractal dimension. It is generally believed that the value of a fractal dimension larger than 3 i.e. $D_3$ no longer completely corresponds to pore filling but somewhat reflects the mechanical behavior of the sample (Friesen and Mikula, 1987; Friesen and Mikula, 1988), mainly the compressibility of coal.

**Table 2** Fractal dimensions of various coal samples

| Samples | Untreated | | |
|---|---|---|---|
| | $D_1$ | $D_2$ | $D_3$ |
| $C_1$ | 1.9654 | 2.4133 | 3.8959 |
| $C_2$ | 1.9709 | 2.9847 | 3.8191 |
| $C_3$ | 1.8501 | 2.9517 | 3.7689 |
| $C_4$ | 1.7559 | 2.6271 | 3.7611 |
| Samples | $ScCO_2$-treated | | |
| | $D'_1$ | $D'_2$ | $D'_3$ |
| $C_1$ | 1.9868 | 2.6048 | 3.9272 |
| $C_2$ | 1.8808 | 2.9355 | 3.9047 |
| $C_3$ | 1.9833 | 2.9500 | 3.8572 |
| $C_4$ | 1.7404 | 2.9778 | 3.8482 |

Since the value $D_3$ can be used as an index to measure the difficult level of coal compressibility, the difference between the values of untreated and $ScCO_2$-treated coal samples, i.e.

$$\Delta D_{3cj} = D_{3cj} - D'_{3cj}\ (j = 1, 2, 3, 4) \qquad (2)$$

can be employed to describe variability of the compressibility of coals with and without the $ScCO_2$-$H_2O$ treatment. The larger difference values of $\Delta D_3$ is, the easier the coal samples can be influenced by the $ScCO_2$-$H_2O$ treatment.

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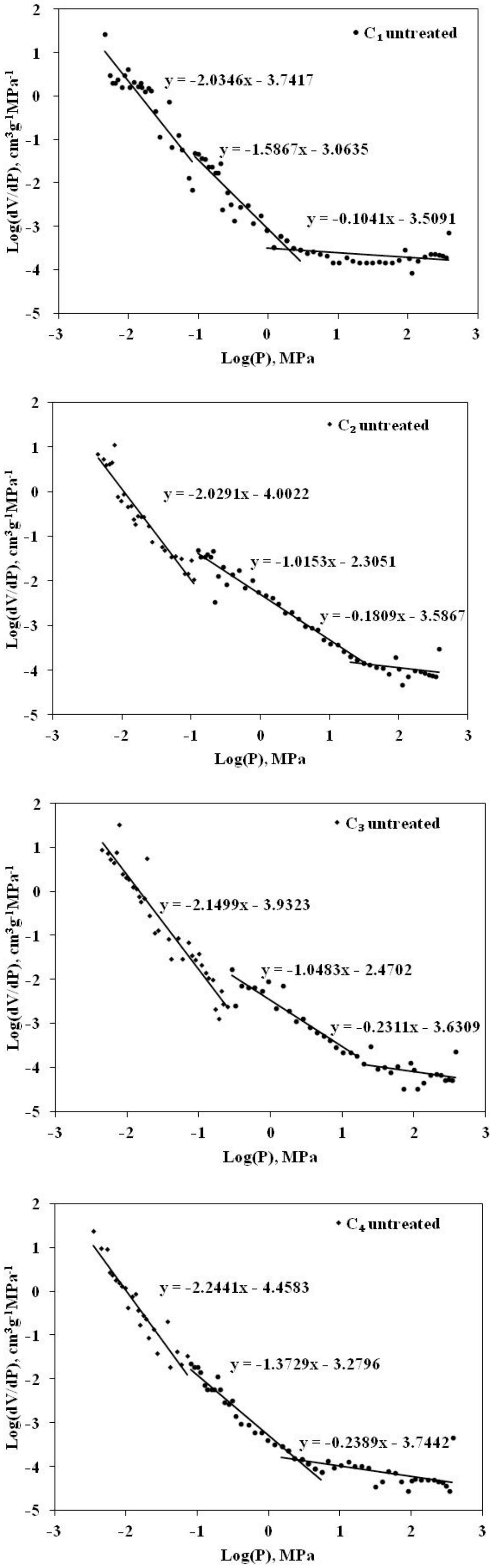


**Fig. 2** Plots of Log (dV/dP) versus Log (P) (A).

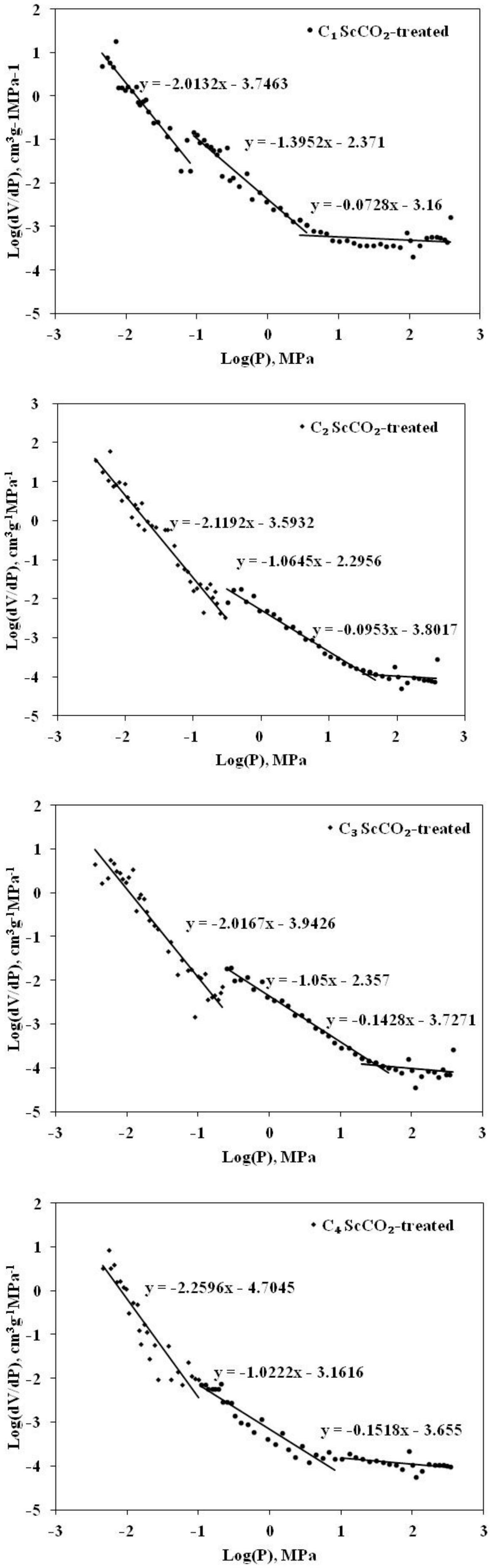


**Fig. 3** Plots of Log (dV/dP) versus Log (P) (B).

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As can be calculated, $\Delta D_{3c1}$=0.0313; $\Delta D_{3c2}$=0.0856; $\Delta D_{3c3}$=0.0883; $\Delta D_{3c4}$=0.0871. It shows that the coal sample $C_3$ exhibits the biggest difference value $\Delta D_{3cj}$, whilst there are no significant difference among $\Delta D_{3c2}$, $\Delta D_{3c3}$ and $\Delta D_{3c4}$. The reason of $\Delta D_{3c4}$ is smaller than $\Delta D_{3c3}$ is the same as aforementioned of highly developed micropores. The higher value of $\Delta D_{3c3}$ is probably because ash content is much high (20.44%). The higher content of ash implies that the more minerals will be involved in the $ScCO_2$-$H_2O$-Coal system which may make relatively lager changes of pore structure in this particular coal.

## IV. Conclusions

In this study, fractal analysis was employed to fitting with mercury intrusion data to investigate the changes of pore structure characteristics under the conditions simulated $CO_2$ sequestration process and $CO_2$-enhanced CBM recovery in laboratory with 4 different coal rank samples. The mimic $CO_2$ sequestration process was achieved by a high pressure supercritical $CO_2$ (HP-$ScCO_2$) geochemical reactor under around 40 °C and 9.8 MPa for 72 hours.

Fractal dimensions were calculated and further used to distinguish inter- and intraparticle voids at lower intrusion pressure and also to define the initial pressure when sample begin to be compressed. Three fractal dimensions $D_1$, $D_2$ and $D_3$ were identified corresponding to three pressure ranges of the mercury intrusion process, i.e. interpore filling, intrapore filling and coal compressibility. In the lower pressure range, the fractal dimensions are not changed largely because they are mainly depended on the accumulation mode of coal particles in penetrometer and the roughness of samples which caused by crushing and grinding process. In the higher pressure range, the fractal dimensions decrease while pressure is increasing as the coal rank increased which probably related to the hardness of coal.

The $ScCO_2$-$H_2O$ treatment has significant effects on different coal rank samples. Generally, treated coal samples become easier to be compressed than untreated ones. Coal rank is the most important factor in maintaining the pore structure. The HP-$ScCO_2$ caused more changes of pore volume of the higher rank coal samples compared with the lower coal rank samples. As the coal rank increased, micropores are highly developed, which makes the coal samples more easily reacted with HP-$ScCO_2$ and hence resulted more changes of pore volume during $CO_2$ sequestration. However, biggest changes of pore structure happened to the low volatile bituminous rather than anthracite due to its higher content of ash. Therefore coal rank and ash content are the two important factors that influence the changes of coal structure during the $CO_2$ sequestration.

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