Characterization of Malaysian coals for carbon dioxide sequestration

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Abstract. Coal samples from Mukah-Balingian and Merit-Pila coal mines were characterized with ultimate, approximate, petrographic analysis, FT-IR spectra patterns, FESEM images and BET measurements to obtain information on the chemical composition and chemical structure in the samples. Two coal samples were obtained from Merit-Pila coal mine namely sample1 (S1) and sample2 (S2). The other two coal samples were obtained from Mukah-Balingian coal mine namely sample3 (S3) and sample4 (S4), Sarawak, Malaysia. The results of ultimate analysis show that coal S1 has the highest carbon percentage by 54.47%, the highest hydrogen percentage by 10.56% and the lowest sulfur percentage by 0.19% and the coal S4 has the highest moisture content by 31.5%. The coal S1 has the highest fixed carbon percentage by 42.6%. The coal S4 has BET surface area by 2.39 m²/g and Langmuir surface area by 3.0684 m²/g respectively. Fourier-Transform Infrared (FT-IR) spectroscopy analysis of all coal samples shows a presence of oxygen containing functional groups which considered are as active sites on coal surface. The oxygen functional groups are mainly carboxyl (−COOH), hydroxyl (−OH), alky (−CH, −CH₂, −CH₃), aliphatic (C−O−C stretching associated with −OH), amino (−NH stretching vibrations), (−NH stretching vibrations), aromatic (C=C), vinylc (C=C) and clay minerals. In all FE-SEM images of coal samples matrix, it can be seen that there are luminous and as non luminous features which refer to the existence of various minerals types distributed in the coal organic matrix. The bright luminosity is due to the presence of sodium, potassium or aluminium. According to petrographic analysis, all coal sample samples are range in vitrinite reflectance from 0.38% to 56% (VRr) are sub-bituminous coals.

1. Introduction
Geological sequestration of carbon dioxide (CO₂) in deep unmineable coal bed seams considered as one of promising geologic reservoirs [1] because coal bed seams have large capacity of CO₂ and the worldwide unmineable coal bed seams capacity of CO₂ storage ranges between 140 and 3000 Gt [2] and it is calculated that one ton of coal could adsorb about 30 – 35 m³ of CO₂ at pressure range 5 to 8

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In addition to that coal usually holds in its micropores methane (CH$_4$). Thus, unmineable coal bed seam could be utilized for enhanced coal bed methane recovery (CBM) and CO$_2$ storage. Since coal has high affinity to CO$_2$, the injected CO$_2$ displaces the preadsorbed CH$_4$ in the coal seam [4]. However, the laboratory experiments of CO$_2$ adsorption isotherms on coal has been considered as one of the basic steps for the evaluation of CO$_2$ geological storage as well as enhanced coal bed methane recovery (CBM) [5].

The fact that the structure of coal is a mixture of inorganic and organic materials in a complex, three-dimensional network, that may change during the adsorption or desorption process, can complicate matters considerably. However, coal being highly heterogeneous from basin to basin, seam to seam, and those within the seam, it is difficult to determine the properties of the complete seam. This makes it difficult to characterize and understand the coal properties for developing ideal models for optimization of sequestration process and generating useful correlations [6].

One of the main the coal physical properties is surface area. Coal surface area is originally measured by the adsorption of N$_2$ at -196 °C. The Brunauer-Emmett-Teller (BET) equation was generally used to determine the surface area. However N$_2$ surface areas of coals are varying in the range of 1-9 m$^2$/g and lower than expected. It was concluded that the surface area, as measured with N$_2$, is a measure of the macroporosity of coals [7] because N$_2$ molecules at -196 °C are not completely accessible to micropores in coals. However, the micropore in coal has large micropore surface area, and accounts for 97.3% of whole area, which is about 200 m$^2$/g calculated using Dubinin-Polanyi equation and such a big area determine the adsorption volume of the coal [8–11]. Fourier transform infrared spectroscopy (FTIR), a non-destructive technique, is one the most powerful techniques to characterize the chemical structure of coals. The FTIR technique focuses on determining information on the functional groups on coal [12].

The porous carbon materials such as coal usually include its structure of oxygen containing functional groups for example carboxyl and hydroxyl surface functional groups. This could lead to complex CO$_2$ functional group–surface interactions. Rather than interacting directly with a surface, CO$_2$ may react indirectly via a shared proton. These embedded functional groups will change the electrostatic properties of the adsorbent surface and thus are expected to play a significant role in the adsorption mechanisms associated with CO$_2$ in these systems depending on the temperature and pressure conditions [13]. Coal samples from different coal bed seams vary based on a number of factors, including coal rank and moisture and carbon content, organic and inorganic matters and oxygen containing functional groups. Hence, coal characterization analysis is necessary before and after any gas adsorption measurements.

In this work, the objectives were to characterize the structural features of the coal samples using ultimate analysis, approximate analysis, Brunauer-Emmett-Teller (BET) technique, Fourier-Transform Infrared (FT-IR) Spectroscopy, Powder X-ray diffraction (XRD), Field-Emission Scanning Electron Microscope (FE-SEM) and petrographic analysis.

2. Material and Methods

2.1 Coal specimens
The coal specimens were obtained from two locations. First location is Merit-Pila coal mine and second location is Mukah-Balingian coal mine, Sarawak. From Merit-Pila coal mine, we obtained coal sample1 (S1) and coal sample2 (S2). From Mukah-Balingian mine, we obtained sample3 (S3) and sample 4 (S4). Merit-Pila and Mukah-Balingian mines are at depth 16 to 20 m below existing ground and seam thickness is generally about 1.2 to 1.4 m.

2.2 Methods
Four coals, S1, S2, S3, and S4, were grinded and dried for the characterization. The techniques were used to characterize the micro-texture of the coal samples. The methods are ultimate analysis where characterized by CHNS-932 analyzer, approximate analysis where made by thermal gravimetric
analysis (TGA), Brunauer-Emmett-Teller (BET) technique and Langmuir were performed with N\textsubscript{2}(g) at 77 K (-196 °C), determining functional groups by Fourier-Transform Infrared (FT-IR) Spectroscopy, coal surface morphology by powder X-ray diffraction (XRD), Field-Emission Scanning Electron Microscope (FE-SEM) and coal maturity (rank) by petrographic analysis.

3. Characterization of coal samples

3.1 Ultimate analysis

Ultimate analysis tests produce more comprehensive results than the proximate analyses. The ultimate test was conducted using CHNS-932 elemental analyzer (ASTM5373, Truspec, Leco, USA). The analysis was performed to determine percentages of basic elements namely carbon, hydrogen, nitrogen and sulphur (CHNS) on dry coal samples basis. As shown in Table 1, the coal sample 2 has the highest carbon percentage by 54.47%, the highest hydrogen percentage by 10.56% and the lowest sulfur percentage by 0.19%.

| Coal sample | Carbon% | Hydrogen% | Nitrogen% | Sulfur% |
|-------------|---------|-----------|-----------|---------|
| Sample 1    | 32.81   | 4.25      | 0.0       | 0.25    |
| Sample 2    | 54.47   | 10.56     | 0.832     | 0.19    |
| Sample 3    | 44.00   | 5.85      | 1.52      | 0.34    |
| Sample 4    | 34.07   | 6.66      | 0.83      | 0.28    |

3.2 Proximate analysis

The approximate analysis signifies the percentage by weight of the fixed carbon, volatiles, ash, and moisture content in coal. It was performed using thermal gravimetric analysis (TGA, PerkinElmer, Thermal Analysis, STA 6000, USA). Raw sample of crushed coal is weighed and placed in crucible of TGA and heated up to 900±15°C. The fixed carbon is a solid combustible matter (carbon in its free state) without the light and volatile compounds. It is a value obtained from by abstracting the sun of ash, moisture and volatile matter from 100 where all values are on the same moisture reference base. However, coal S4 has the highest moisture content by 21.5% and coal S2 has the highest fixed carbon percentage by 42.6%. Hence, it is essential to measure the moisture in coal samples to evaluate the potential moisture effect on CO\textsubscript{2} sorption on coal.

| Coal sample | Moisture% | Volatiles% | Fixed carbon% | Ash% |
|-------------|-----------|------------|---------------|------|
| Sample 1    | 11.3      | 26.8       | 42.6          | 19.2 |
| Sample 2    | 13.4      | 43.3       | 36.7          | 6.6  |
| Sample 3    | 21.3      | 25.4       | 32.6          | 10.5 |
| Sample 4    | 21.5      | 22.2       | 35.8          | 10.5 |

3.3 Brunauer-Emmett-Teller (BET) technique

The BET surface area measurement was proposed by Brunauer, Emmett and Taylor. It was built on subsequent assumptions. First, the adsorbate molecules physically adsorb on a adsorbent surface, the adsorbent surface is uniform and identical, the interaction between the adsorbent and adsorbate molecules are stronger than the interaction between the adsorbate molecules, the interactions of adsorbent molecules are considered only in the vertical to the adsorbent surface, and is accounted as condensation [14].

Micromeritics (3Flex 3.00) analyzer utilized measure BET and Langmuir surface area analysis (GAT scientific Sdn Bhd in Selangor, Malaysia). Nitrogen pressures were varies and introduced onto the coal samples and quantify the amount of N\textsubscript{2} gas adsorbed at each target pressures. The surface area
was determined for relative pressure target range from 0.05-0.35 \( P/P_0 \). It is figured out that the surface area measured using \( \text{N}_2 \) gas is a measure of macroporosity range [7] because \( \text{N}_2 \) molecules at -196 °C could not manage completely to access micro pores in coals. Micropore in coal has an enormous internal surface area is about 200 m\(^2\)/g, and it represents 97.3% of entire area and this huge surface area determine gas adsorption on coal [8].

The surface area of all coal samples were obtained by measuring BET and Langmuir surface areas of the coal samples as shown in Table 1, Table 2. The sample 4 has the highest BET surface area by 2.3988 m\(^2\)/g and Langmuir surface area by 3.0684 m\(^2\)/g respectively.

### 3.4 Fourier transform infrared spectroscopy (FT-IR)

Fourier-Transform Infrared (FT-IR) spectroscopy was performed to investigate the variation in functional groups and their properties change and the FT-IR spectrum for every single sample was tested and recorded in FT-IR spectrophotometer (Perkin Elmer, Spectrum One/BX) with KBr pellet.

The FT-IR spectra of functional groups in coals S1, S2, S3 and S4 are demonstrated in Figure 1. The distinct peak in all coal samples at 1078 cm\(^{-1}\), 1031 cm\(^{-1}\), 1008 cm\(^{-1}\) and 471 cm\(^{-1}\) are ascribed to clay minerals such as quarts, kaolinite, illite and momtmorillonite. The silicate minerals (Si–O–Si) stretching vibration causes absorption at 1031 cm\(^{-1}\) and 1008 cm\(^{-1}\). The silicates (Si–O) bending vibration in coal S3 attributes to stretch at 533 and 471 cm\(^{-1}\) and both peaks can also be due to the presence of ionic sulphates. A small peak of absorption at 1149 cm\(^{-1}\) in S1, S2 and S4 can be attributed to the existance of mineral quartz.

There is small but visible band at 695 cm\(^{-1}\) in coal S3 may possibly be due to magnetite (Fe\(_2\)O\(_3\)). Mediaum peak at 2375 cm\(^{-1}\) in the FT-IR peaks of sample1, S2 and S4 can be attributed to isocyanate functional group (–N=O). Strong peak at 2969 cm\(^{-1}\) in the FT-IR of S2 and sample4 coals can be attributed to C–H stretch (alkanes) or CH\(_3\) (aliphatic). The peaks in coal sample1, sample2 and sample 4 at 3202 cm\(^{-1}\), 3305 cm\(^{-1}\), 3466 cm\(^{-1}\) and 3530 cm\(^{-1}\) is assigned to alcohols (O–H stretch) and phenols (H–bonded).

Table 4 describes FTIR band assignments of all coal samples. The peak of 1624 cm\(^{-1}\) in coal sample3 and the tiny peak of 1627 cm\(^{-1}\) are assigned to amines functional group (N–H bend). The peaks of 1082 cm\(^{-1}\) and 1152 cm\(^{-1}\) in all coal samples assigned to C–O peak which represent alcohols, carboxylic acids, esters and ethers functional groups. These functional groups are considered as oxygen-containing functional groups.

| Bands (cm\(^{-1}\)) | Assignments |
|---------------------|-------------|
| 400-690             | Clay and silicate minerals |
| 530-580 (s)         | C–C (cycloalkanes) and C–C–CN (nitriles) |
| 1082-1150 (s)       | C–O (alcohols, carboxylic, acids, esters and ethers) |
| 1580-1650           | C=C (aromatic) and C=O (esters) and NH\(_3\) and NH\(_2\) (primary amines) |
| 2000-2500           | –N=C=O (isocyanate functional group) |
| 2350-2780           | –OH strongly hydrogen-bonded and NH stretching mode |
| 2850-2960 (s)       | C–H stretch (alkanes) and CH\(_3\) (aliphatic) |
| 2500-3300 (s,b)     | O–H stretch (carboxylic acids) |
| 3200-3600           | O–H stretch, H–bonded (alcohols and phenols) |

s=strong, m=medium, b=broad.
3.5 Powder X-ray diffraction (XRD)

X-ray diffraction analysis was conducted using Bruker D8 instrument. XRD is a qualitative and quantitative method conducted to identify crystal structure of various minerals in powder materials and provide information about mineralogical composition. Hence, the coal samples were subjected to XRD inspection. All coal samples were scanned 10 to 80° using CuKα radiation with step scan mode (step size 0.0173°).

The XRD patterns of all coal samples are presented in Table 5. There are two main major diffraction peaks of quartz are located around 21° and 26° in all the samples. As shown in Figure 2., XRD patterns of all coal samples show a dominance of quartz with a small percentage of kaolinite, calcite, priyite, hematite and aluminium silicate identified asandalusite (Al₂SiO₅).
### Table 5. Percentage of minerals in S1, S2, S3 and S4 coal samples.

| Compound Name | S1    | S2    | S3    | S4    |
|---------------|-------|-------|-------|-------|
| Quartz        | 44.14%| 13.90%| 54.03%| 19.85%|
| Kaolinite     | 15.64%| 25.22%| 11.35%| 28.62%|
| Hematite      | -     | 3.31% | 2.57% | 3.14% |
| Anatase       | -     | 3.79% | 1.37% | 4.22% |
| Pyrite        | 1.65% | 5.11% | -     | 8.65% |
| Illite        | 33.67%| 39.98%| 19.72%| 21.64%|
| Dolomite      | 4.90% | 8.68% | 10.96%| 13.88%|

### 3.6 Field emission scanning electron microscopy (FE-SEM)

FE-SEM imaging was utilized to provide surface morphology as well as information about elements at magnifications of 10x to 300,000x with virtually at magnifications of 10x to 300,000x with virtually infinite depth of field. The intact and unpolished coal samples were investigated with FE-SEM instrument (SUPRA 55VP, Carl Zeiss AG, Germany). All coal specimens were scanned using high voltage with extra high tension (EHT) of 20 kV and magnification of 1.00 kX.

FE-SEM analysis was performed at effective distance of around 8 mm, utilizing derived electron imaging. The coal sample was placed on SEM stubs using double-sided conductive carbon tape. The bulk microstructure composed of homogeneously distributed network of small crystallites demonstrated existence of minerals. In all coal samples, it can be seen that there are luminous and as non-luminous features as depicted in FE-SEM images in Figure 3. Those features signify the presence of minerals distributed in the organic coal matrix. The brightness sites are due to existence of aluminum, potassium or sodium. The dark sites are due to the presence of chalcophiles [1].

![FE-SEM images of coal S1, S2, S3 and S4.](image-url)
3.7 Petrographic analysis

Coal is often classified according to its rank, or thermal maturity. The three main classifications of coal rank from low-rank to high-rank are lignite, bituminous, and anthracite. Carbon content is often used as a measure of rank. As the carbon content of the coal increases, rank increases. Coal petrography is a microscopic method conducted to determine coal rank (degree of coalification) as well as amount and type of macerals on polished specimens of minus 20 mesh prepared coal.

Vitrinite reflectance (VRo) usually utilized as an indicator of coal thermal maturity. Petrographic analysis measurements were conducted according to Australian standard AS 2856.3. The maximum reflectance (Rmax) was measured in a green light with reflected light microscope-photometer using Leitz-Orthoplan. As shown in Table 6, the Vitrinite reflectance of coal samples range in vitrinite reflectance from 0.38% to 56% VRr. According to the classification of coal types based on vitrinite reflectance, sub-bituminous coals range between 0.3–0.7 of vitrinite reflectance [16,17]. These coal samples range in vitrinite reflectance from 0.38% to 56% VRr which are sub-bituminous coals.

| Petrographic analysis          | S1    | S2    | S3    | S4    |
|-------------------------------|-------|-------|-------|-------|
| Mean maximum reflectance[%]   | 0.38  | 0.38  | 0.56  | 0.51  |
| Vitrinite                     | 76.1  | 81.3  | 80.1  | 84.5  |
| Liptinite                     | 13.9  | 8.7   | 4.3   | 3.7   |
| Inertinite                    | 3.5   | 2.3   | 7.4   | 5.2   |
| Minerals                      | 6.5   | 7.8   | 8.2   | 6.6   |

4. Conclusions

The characterization study is a first step that requires to be performed before and after conducting CO₂ sorption capacity on coal. Thus, ultimate, approximate, petrographic analysis, FT-IR spectra patterns, FESEM images and BET measurements are the main basic characterization techniques. All coal samples are range in vitrinite reflectance from 0.38% to 56% (VRr) which are sub-bituminous coals. It is obtained that coal S2 has the highest carbon percentage by 54.47%, the highest hydrogen percentage by 10.56% and the lowest sulfur percentage by 0.19%. Coal S4 has the highest moisture content by 21.5% and coal sample1 has highest fixed carbon percentage by 42.6%. The FT-IR spectra for all coal specimens demonstrate the presence of alkanes (–CH, –CH₂ and –CH₃ groups), aliphatic (C−O−C stretching associated with −OH), amine (−NH stretching vibrations), aromatic (C=C), and clay minerals. In all coal samples morphology, there are luminous and as dark features. Those features signify the existence of organic minerals distributed in the organic matrix of coal. The bright luminosity is due to the presence of aluminium, potassium or sodium. The presence of moisture, minerals and oxygen functional groups do play a crucial on CO₂ sorption onto coal.

5. References

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