The Influence of shales characteristics on CO_2 adsorption behaviour under sub-critical conditions

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Abstract. Shale gas has been an important source of natural gas and is expected to contribute 30% towards the global output by 2040. Shale formations also have CO_2 sequestration potential, which could be used to mitigate the greenhouse gas emissions. A quarter of Malaysian's sedimentary comprises of black shale formations. In this article, we evaluated the CO_2 sequestration potential of some of Malaysian's formation under sub-critical conditions, and we correlate shale's characteristics to CO_2 storage behaviour under sub-critical conditions. The evaluation is based on total organic carbon (TOC wt. %) contents, mineralogical compositions, particle size distribution PSD of mesopores and micropores. The results show that total organic carbon measured by TOC analyser ranges between 0.5wt. % to 12.1wt%. Bulk mineralogical composition was semi-quantified using X-ray Diffraction (XRD). Non-clay composition varies between ~35 wt.% to ~75 wt. %, which is dominated by quartz. All samples also contain clay minerals such as kaolinite and illite at different range. The CO_2 adsorption isotherm results show that KH sample adsorb the most while in contrast the KL samples adsorb the least of CO_2. Positive correlation between organic content and CO_2 adsorption was observed in most samples, indicating that formations with high organic content has higher CO_2 sequestration potential. Mineralogical composition also influence the CO2 adsorption, for instance, illite has lower surface area and pore volume compare with some other clays, subsequently, its presence reduced the CO2 storage potential on KL sample. However, the application of this observation may not fit to other formations due to the high degree of heterogeneity of shale formations.

1. Introduction

Shale is a common fine grained sedimentary rock laid below as consolidated mud and can be split easily into fragile slabs. It is usually comprises of organic matter and minerals such as quartz, and clays; illite, smectite and kaolinite and other minerals[1]. Shales occupy a large percentage of the world land. For example, black Palaeozoic shale rocks exist in Peninsular Malaysia, where they alone consistent 25% of the land area [2]. In addition to natural gas interest on shale formations, several studies have proven that shale formations can be used as CO_2 geological sinks. CO_2 sequestration in shales is identified by mass-transport paths and mechanisms simulation that micro-pores in organic matter acts as molecular sieves which allow only linear molecules for instance CO_2 to access their pore-spaces[3]. Furthermore, despite the ultra-low permeability shale have the capacity to store CO_2 approximately five times more than CH_4 storage capacity. Several authors have contributed to the literature by investigating experimentally the influencing factors on the adsorption behavior in shales. The factors are and not limited to; total organic carbon wt.%, micro and mesopores volume system,

mineral compositions[4]. Only few papers have published the characteristics of Malaysian's black shale formations regarding the aforementioned factor. In addition, to our knowledge, no publication has evaluated the CO_2 adsorption quantity for Malaysian's black shales and correlate shale's characteristics to CO_2 storage potential. In this paper, we characterized several shale samples collected from five locations of Malaysian's formations. TOC analyzer, X-ray diffraction (XRD), and N_2 low pressure adsorption were utilized in order to characterize the samples. The characterization is based on total organic carbon (TOC wt.%) contents mineralogical compositions and (pore size distribution PSD of mesopores and micropores). We also correlate the CO_2 volume adsorption capacity at sub-critical conditions to these characteristics. The evaluation may provide useful reference prospect in designing CO_2 Sequestration process in the future.

2. Sampling and Experiments

Eleven (11) shale samples were collected from five malaysian's shale formations locations namely; Batu Gaja (BG), Kenny Hill (KL), Dohol at Johor (J), Setap (S) at Sarawak, and Pending Kroh (KH). Longitude and latitude are described at table 1. The samples were collected from outcrops. Outcrops might have been affected by some degree of weathering. However, it is reported that collecting a newly outcrops from excavated engineering sites is recommended [5]. Therefore, this could reduce significantly the difference on the experimental results between drilling-cuttings and outcrops in the same formations. Around 30 grams of the each collected sample was crushed and sieved. All experimental tests, in this report were performed in crushed powder samples size between 200µm -300 µm.

2.1. Total Organic Carbon wt.%

TOC wt.% was determined based on the GB/T 19145-2003 standard [6]. 1.0 gram of each powdered samples were measured and place in beakers. The samples were acidified with HCL to remove inorganic carbon friction from samples. They were then left in the fume chamber combustion over 650°C before using rinsed with reverse osmosis water for 3 times and dried in the oven at 60 °C for 24 hours, after drying, 60mg of each samples were being weighted and placed in ceramic boats. Percentage of organic carbon is measured using Multi n/c 3100. The measurements were ran in duplicate and then results to be averaged, the precision reaches 0.6 ppm

2.2. Mineralogical Compositions

The X Ray Diffraction method allows mineralogical analysis of fine-grained shale samples with an absolute accuracy of 0.01_ of 2h. This process involves an analysis of the diffraction patterns that are produced when X-rays are passed through the sample to reveal the structural properties of crystalline solids.

2.3. The Microspores and Mesopores System

N_2 low pressure adsorption/desorption were conducted using Micromeritics ASAP 2020 at -196 °C on ~ 1 gram crushed sample. The pretreatment was carried out for 12 hours at 383.15 K to remove any moisture and volatile matters. The samples were also purged and degassed under vacuumed to eliminate any further residual moisture[7].

2.4. CO_2 Adsorption Measurement

Experimental studies of the CO_2 adsorption were conducted at subcritical conditions at relative pressure of 1bar and room temperature 293 K using BELSORP-mini II instrument (BEL Japan, Inc.). Before commencing the measurement, the samples were pre-treated and degassed at 383.15 K for at least 12 hours to remove the moisture and any volatile materials. Employing the volumetric technique, starting with measuring the dead volume of the reference cells and injecting CO_2. A target pressure is gradually increasing up to 1 bar, and at each pressure points, the amount of CO_2 is measured at each pressure segment.

3. Results and Discussion

3.1. Total Organic Carbon

The total organic carbon content results of the collected samples showed a wide range of variety between 0.52wt. % to12.13 wt. % table 1. The volume of stored gas is generally correlated with total organic carbon of the sample. The gases have high affinity to be stored in the organic matter small pores. Shale gas plays usually exhibits TOC higher than 2 wt.% [1]. However, TOC is not the only indicator of hydrocarbon storage potentiality, and rock eval pyrolysis analysis is needed to identify the more important details of the rock formations such as kerogen types, and thermal maturity [8].

Table 1. Location and coordinates of collected samples and toc contents (wt. %).

Formation	State	Sample ID	Longitude	Latitude	TOC%
Batu Caja	Perak	BG3	101°0'7.32"	4°47'35.25"	1.72
		BG4	101°0'7.32"	4°47'35.36"	2.02
		BG7	101°0'7.32"	4°47'36.06"	1.84
		BG9	101°0'7.32"	4°47'36.27"	2.06
		BG15	101°0'7.15"	4°47'55.28"	0.52
Kenny Hill	Kuala Lumpur	KL1	3.1745°	101.6798°	1.13
		KL5	3.1765°	101.6798°	1.71
		KL7	3.1765°	101.6795°	1.53
Dohol	Johor	JB	103 11.288'	01 55. 097'	1.81
Setap	Sarawak	S	114°00′30.7″	03°59′22.1″	2.61
Kroh	Kedah	KH	05° 36' 57"	101°01' 49"	12.10

TOC: Total organic carbon

3.2. Bulk Mineralogical Compositions

Five samples are analyzed using X-ray diffraction XRD that provides the possible mineralogical composition. We applied Bragg equation to determine the D-spacing. Semi quantitative mineralogical composition for the samples were estimated using USGS program RockJock to a degree less than 1 of the fitting between the measured and calculated pattern. Table 2 describes the mineralogical compositions approximation weight percent for the samples. KH bedrock contains the highest of quarts and Kspar compare to other samples. Similar trend is shown in S setap shale but with ~ 10 wt.% obsidian, and no Kspar content.   While BG9 and JB have lower quartz compositions (~ 29 wt. % and ~ 32 wt. % respectively), but they contain the highest clays such as illite, chlorite and muscovite.

Table 2. Mineralogical Compositions for Shales Samples.

Possible Minerals	Weight % & Sample ID				
	KH	**BG9**	**S**	**JB**	**KL5**
Quartz	65.9	29.3	48.0	32.5	46.6
Kspar	7.2	12.8	-	1.0	1.6
Plag	0.7	-	8.5	1.5	2
Calcite	0.8	1.3	1.5	-	1.3
Obsidian	-	-	10.6	0.5	-
Total non-clays	**74.5**	**43.4**	**68.6**	**35.5**	**51.5**
CLAYS					
Kaolinite	2.8	6.3	3.5	4.5	1.4
Smectite	9.7	12.7	5.1	6.7	-
Illite	9.7	21.1	9.1	9.0	41.5
Chlorite	1.9	5.0	-	7.8	1.6
Muscovite	-	9.5	7.3	30.7	-
Dickite	0.5	-	1	-	-
Others	1	2	5.5	5.8	4
Total clays	**25.5**	**56.6**	**31.5**	**64.5**	**48.5**

Clay minerals have the capacity to adsorb gases to their internal Pore structure, the amount is a clay type dependents. For example, Ross and Bustin [9] stated that the small nano-pore structure of 1-5 nm radius, which exists at our samples based on pore system analysis next section, between crystal layers of clay in such orders smectitie, kaolinite, illite provides adsorption sites for gases[10]. This makes the mineralogical composition important for gases adsorption capacity, subsequently the amount of CO_2 that might be sequestered in the formations.

3.3. Microspore and Mesoporous Systems

According to International Union of Pure and Applied Chemistry (IUPAC) classifications, Shale pores are classified into; micropores <2nm diameter, mesopore 2 nm<diameter<50 nm, and macropores that includes diamater >50 nm [4]. Figure.1 describes the incremental pore volume for five samples. micropore and mesopore volumes is determined using BJH model which can be found in the literature [7]. The smallest micropore size among the sample is 1.09nm in Setap shale S which also has the smallest average pore size 9.33nm comparing to all other samples. The smallest pores provide the sample with the largest surface area and total micro and meso pores volume. There is a noticeable positive correlation between TOC wt.% pore volume for samples. This suggests that the mesopores and micropore of these formations are created during the migration of organic matter or probably during the hydrocarbon generation[11]. The reason maybe that, KL is illite rich, and illite has the lowest surface area and pore volume comparing to other clays[5, 12]. KL exhibits the lowest pore volume among all samples using nitrogen adsorption. Another reason maybe due to the limitation of nitrogen molecules to access nanopores of specific type of organic matters. In the contrary of CO2 linear molecules structure which have higher potential to penetrate into all organic nanopores volumes. Consequently, it's recommended to investigate the reactive surface area with the adsorbate gas, and to [3]conduct pore system analysis using CO_2 adsorption-desorption [13]. Overall, micro and meso pores less than 5 nm is the major contributor to the bulk micropore and mesopores. volume which indicate, these pores would contribute significantly in providing volume for adsorption potential [7].
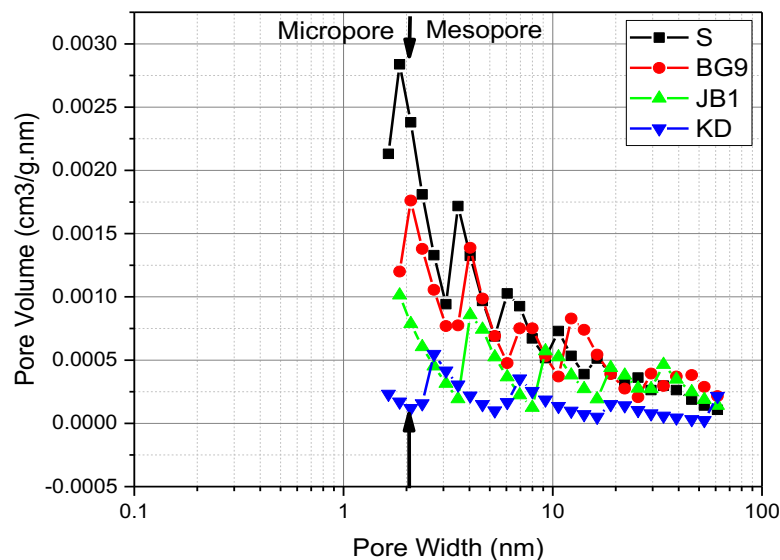
Figure 1. Pore-size distribution, pore volume using N2 adsorption analysis.
Pore diameter 1.09nm and 100nm

3.4. Carbon Dioxide Storage Potential of Shales

The amount of adsorbed CO_2 on all shale samples at constant temperature 298K increased with pressure. The adsorbed measured quantity is shown in figure.2. From the shape of the curves, we could mention the samples show different adsorption models. The highest adsorbent three samples KH JB and BG exhibits mono-layer adsorption property (Langmuir shape). The S and KL1 sample is showing a multi-layer adsorption (BET model)[14]. It is clearly that the amount of CO_2 adsorbed is highest at Kedah KH adsorbs ~ 0.8 cc/g where it has the highest TOC content. Organic rich shales has CO_2 wettability, while low organic shale has water-wet wettability[15] which is the reason KH has the highest CO_2 uptake. Moreover, KH contains higher micro and mesopore volume compare with other samples. Lowest CO_2 volume adsorbed for the both KL samples ~0.1 cc/g to ~ 0.22 cc/g at 1 bar. KL5 samples do not show any significant increase when increasing pressure. BG9 and JB samples adsorb almost similar amount of CO_2 over the course of pressure values. Both samples have also similar values of specific area and pore volume discussed in the previous section, which indicate the CO_2 adsorption characteristics is directly related to the pore system. The smaller pore size provides more volume and surface area for CO_2 molecules to be adsorbed. However, this trend seems to disagree with S that exhibits a relatively low CO_2 adsorption. This could be due to the CO_2 affinity to the mineral or the kerogen type comprised the bedrock[3].
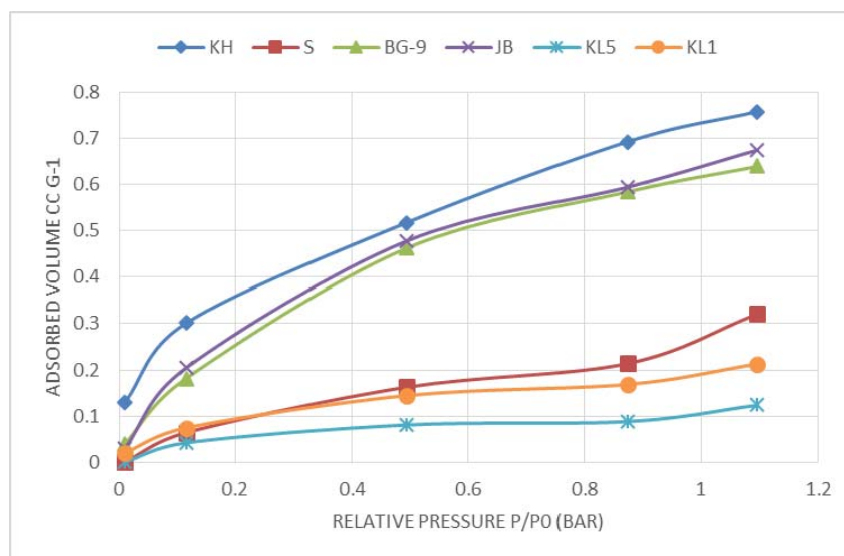
Figure 2. CO_2 adsorbed on Malaysian Shales at 298 K and at 1 bar.

4. Conclusion

TOC analyser, X-ray diffraction, N_2 experimental studies were utilized in order to characterize collected samples from different location of Malaysian's black shale formations and to correlate the shale's characteristic's to CO2 adsorption behavior. The characterizations include total organic carbon content, mineralogical composition, micro and meso pore distribution and CO_2 adsorption capacity under sub-critical conditions.

The sample's total organic carbon content is between 0.5 to 12.10 wt.%. Generally, the samples can be considered quartz rich shales. Clay minerals also present in all the samples mainly illite, kaolinite, and smectite. Micropores and mesopores size range between 1.1nm to pore size to more than 50nm. The specific surface area SSA as measured with BET is from ~ 2 m^2/g to ~ 12 m^2/g. All samples exhibit high volume contribution from pores within a dimeter of less than 5nm. KH sample adsorb the highest ~ 0.8 cc/g, and JB sample comes second ~ 0.7cc/g. KL5 and KL1 adsorb the lowest at ~0.1 cc/g to ~ 0.22 cc/g respectively.

There is a positive correlation between TOC content and pore volume for samples. This suggests that the mesopores and micropores of these formations may have been created during the migration of organic matter or probably during the hydrocarbon generation.

KH exhibits the highest organic content and pore volume, therefore it has the highest CO_2 adsorption capacity. There is a positive correlation between CO_2 adsorption capacity and total organic carbon content and pore volume for the samples (i.e. KH, JB, and BG-9). It is recommended for future work to evaluate CO_2 storage capacity under geological sub-surface conditions high pressure high temperature.

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