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Impact of CO₂ injection on wettability of coal at elevated pressure and temperature

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Abstract: Injection of carbon dioxide (CO₂) into coal seams has been demonstrated as an effective technology for enhanced methane recovery and CO₂ storage. However, the impacts of the geochemical reactions between CO₂ and coal on the wettability of coal pore surfaces, which influences immiscible multiphase displacement, are not yet well understood. We studied wettability alterations of coal surfaces resulting from reactions with gas, liquid and supercritical (sc)CO₂ under varied pressure (1-141 bar) and temperatures (~25 - 60 °C) through measuring static and dynamic contact angles with anthracite coal plates. We found that reactions with gas CO₂ only slightly changed the wettability of coal surfaces from water-wet to intermediate-wet with static contact angles from ~60° to 70°-90°. However, reactions with liquid and scCO₂ altered the coal surfaces to strongly CO₂-wet, with the contact angles up to 115-180°. We also found that both static and dynamic contact angles increase significantly with increasing pressure. Temperature affects the contact angles reversely especially under supercritical pressure conditions. These relationships of contact angles with pressure and temperature may be explained by the CO₂ density dependence on pressure and temperature.

Keywords: Coalbed methane, Carbon dioxide, Wettability, Supercritical CO₂, Contact angle, Temperature, Pressure.

1 Introduction

The technology of carbon dioxide (CO₂) enhanced coalbed methane recovery (CO₂-ECBM, a method involving CO₂ injection and storage into coal seams) has been advanced greatly since it was proposed by Puri and Lee (Puri and Yee, 1990) and Gunter (Gunter, et al., 1997). CO₂ injection into coal seams involves several complex

1 steps, including the mixture of gas and liquid advection and
2 diffusion in fractures or cleats, and CO₂ competitive adsorption with
3 water and methane, which have been extensively studied by many
4 researchers (Busch and Gensterblum, 2011; Masoudian, 2016;
5 Mukherjee and Misra, 2018). Given the presence of water in CBM
6 reservoirs, wettability of coal surfaces is a fundamental factor
7 controlling CO₂ injection, adsorption, and sequestration (Arif, et al.,
8 2017).

9 The wettability of a solid surface is commonly characterized by
10 static and dynamic water contact angles. The wettabilities of
11 varieties of rock and mineral surfaces in CO₂ and brine systems
12 relevant to CO₂ storage and enhanced oil and gas recoveries have
13 been studied, including substrates such as shales, mica, quartz,
14 phyllosilicate, and calcite (Bikkina, 2011; Chen, et al., 2015; Jung
15 and Wan, 2012; Pan, et al., 2018; Wan, et al., 2014; Wan, et al.,
16 2018). Wettability of coals with respect to water and other fluids has
17 also been reported (Eissler and Holde, 1962; Jańczuk, et al., 1988;
18 Kilau, 1993; Saghafi, et al., 2014). Kaveh et al. (Kaveh, et al., 2011)
19 measured the contact angles of synthetic flue gas (80/20 of N₂/CO₂
20 mixture) and pure CO₂ on a Warndt Luisenthal coal (high volatile
21 bituminous (hvBb) medium rank coal). They reported that the static
22 contact angles (SCA) linearly increased with pressure, and the coal
23 surface became hydrophobic under pressures higher than 85 bar at
24 45 °C. Sakurovs and Lavrencic (Sakurovs and Lavrencic, 2011)
25 measured contact angles in a coal-water-scCO₂ system at 40 °C and
26 pressures up to 150 bar and found that contact angles for the coals
27 ranging between 80° to 100°, except for one coal with a contact
28 angle of 115°. Mahoney et al. (Mahoney, et al., 2017) measured
29 contact angles (H₂O phase) in a water-CO₂-anthracite coal system
30 for pressures ranging from atmospheric pressure to 140 bar. They
31 reported that the coals remained water-wet with contact angles of
32 85° at atmospheric pressure, while the coal sample became CO₂-wet
33 as the pressure increased above 2.6 bar. Recently, Arif et al. (Arif, et
34 al., 2016; Arif, et al., 2017) measured the CO₂-wettability of coals
35 from low to high ranks using the pendant drop tilted plate
36 technique. They found that the high-rank coals were strongly CO₂-
37 wet, medium-rank coals are weakly CO₂-wet, and low-rank coals are
38 intermediate-wet at typical coal reservoir conditions. In addition, the
39 CO₂-wettability of coals increased with pressure and salinity, and
40 decreased with temperature irrespective of the coal rank.

41 However, most of the previous researches focused on static
42 contact angles only except Arif et al (2016), and the measurements
43 were conducted with single CO₂ phase (gas or supercritical phase),

despite the fact that CO₂ injection into coalbeds usually encounters different reservoir temperatures and pressure, so that the CO₂ may exist as gas, liquid or supercritical phases. In order to examine wettability (For consistent, the single word “wettability” in the present work means water wettability) over the range of typical reservoir conditions, we measured SCAs on coals at different temperatures and pressures. Given that coalbeds commonly contain abundant water, dynamic contact angles (DCAs) were measured by using CO₂ bubbles surrounded by the water in the present work, just as DCAs have been measured on other minerals in many previous studies. This approach mimics CO₂ injection into water-saturated coals, with CO₂ initially displacing water. In Arif et al.’s experiments, water droplets were released into CO₂-saturated coals, such that water is initially displacing CO₂. Thus, the present study includes DCA measurements that are complementary to those of Arif et al.

2 Experiments

2.1 Coal sample and preparation

Although low-rank coals with lower mining value have been considered to be most beneficial for CO₂-ECBM and CO₂ storage (Leung, et al., 2014; White, et al., 2003), in recent years, China has been shutting down many coal mines, some with thin coal seams and many with high-rank coals, because of safety concerns (State Administration of Work Safety et al., (2014). It is worth noting that CO₂ injection into high-rank coals with greater hardness usually does not cause coal and gas outbursts (State Administration of Work Safety, et al., (2006). Therefore, there may be a great potential to inject CO₂ into high-rank coal seams to enhance coalbed methane recovery, and high-rank anthracite coal was collected from a coal mine in China for testing in this study. Proximate analysis results of the coal are shown in Table 1. The pore size distribution and a scanning electron micrograph (SEM) image are shown in Figure 1.

Table 1. Proximate analysis results of the coal sample

Index	Value by mass (%)
Moisture (air dry basis)	2.14
Ash (dry basis)	11.04
Volatile (dry and ash free basis)	5.81
Fixed carbon (dry and ash free basis)	83.8
Maximum vitrinite reflectance (R _{max})	2.41

Figure 1 Pore size distribution and SEM image of the coal sample (not polished). (a) Pore size distribution, (b) SEM image.

There are two different methods to prepare coal substrates. The first method uses high-pressure compressed discs (with artificial surfaces) made from the powdered coal, which may average the surface of the coal substrate with different organic and inorganic compositions (Sun, et al., 2018). However, this method may be more suitable for substrates contacting with air (or other gases) at atmospheric pressure or low pressures. In our study, we also tried to use compressed discs but failed due to coal substrates dissolved gradually in water even at atmospheric pressure. Therefore, we used the other method involving cutting coal slices from large coal blocks. In our experiments, coal samples were cut into square slices with a dimension of $\sim 21 \text{ mm} \times 21 \text{ mm} \times 3\text{-}4 \text{ mm}$ (thickness).

Surface roughness is one of the important factors influencing the contact angle measurement (Letellier, et al., 2007; Marmur, 2006). Therefore, the surface treatment of the coal sample is very important. However, there is no standard criterion for treating coal surfaces. Siemons et al. and Kaveh et al. polished coal surfaces with a series of abrasive papers of grits from 60 to 1200, followed by polishing with 0.5- μm abrasive alumina powder and a fibrous cloth (Drelich, et al., 1997; Kaveh, et al., 2011; Siemons, et al., 2006).

In our experiments, coal surfaces were polished with a series of silicon carbide sandpapers (220 to 10,000 grit). 220 to 320-grit sandpapers were first used to remove small scratches. Surfaces were finished by use of 400 to 10,000-grit sandpapers in turn for carefully wet polishing (washed with water during the polishing operations). Then the coal samples were dried for at least 72 h at room temperature and then cleaned with Accuduster III 2510 (widely used in surface cleaning) before experiments. The surface roughness was measured using atomic force microscopy (AFM) and

1 the example AFM images are shown in **Figure 2**, indicating
 2 reasonable coal surface roughness. The contact angle of the
 3 polished coal substrate with distilled water at atmospheric pressure
 4 and temperature is $57 \pm 5.2^\circ$ as shown in **Figure 3**, which indicates
 5 that the coal surface is water-wet at atmospheric pressure and room
 6 temperature.

7

8

9 Figure 2 AFM images taken at three different positions of the coal
 10 surface after polishing. The arithmetic average (R_a) and root mean
 11 square(R_q) roughness of the coal sample are 10.1-14.1 nm and 12.9-
 12 19.4 nm, respectively.

13

14

15 Figure 3 The contact angle of a polished coal substrate with distilled
 16 water droplet at atmosphere pressure and room temperature.

17

18 2.2 Experiment setup

19 The experiment system (**Figure 4**) was modified from that used
 20 in previous studies ([Chen, et al., 2015](#); [Wan, et al., 2014](#)). The
 21 maximum working pressure and temperature of the H-P-T (high-
 22 pressure and temperature) chamber (IFT-10-P, Core Laboratories)
 23 are 10,000 psi and 177 °C, respectively. The chamber has an upper
 24 inlet hole connected to a two-stem BuTech manifold (A) with one

1 stem connected to an ISCO pump (A) providing back pressure and
 2 the other stem connected to an exhaust tube to expel CO₂ safely
 3 into a fume hood. On the bottom side of the chamber, there is also a
 4 lower inlet hole connected to a needle system to generate CO₂
 5 bubbles. The needle system is connected to a 3-way valve by a
 6 needle valve used to control the flow rate of CO₂. Another port near
 7 the lower inlet hole is connected to a Parr stirred reactor (Parr 4848)
 8 via another two-stem BuTech manifold (B) with one stem connected
 9 to a water tank for collecting wastewater after experiments. The
 10 other ISCO pump (B) was used to provide CO₂ to the Parr stirred
 11 reactor.

12 A stainless plate holds coal substrates near the top side of the
 13 chamber. Two high temperature and pressure resistant glass
 14 windows installed on opposite sides of the chamber allowing light
 15 from an illuminator to pass through the chamber and imaging of
 16 droplets (Nikon D7000, 24 fps at resolution of 1920×1080). The
 17 temperature in the chamber was controlled by a temperature
 18 controller (Digi Sense R/S, used up to 60 °C, well below the
 19 Max.maximum thermocouple input temperature of 1000 °C) which
 20 regulated heat circulated from heat lamps with a mixing fan. The
 21 whole experiment system was surrounded by thermally insulated
 22 walls to maintain environment temperatures controlled by another
 23 temperature controller. The space surrounded by thermally insulated
 24 walls will be referred to as the thermally insulated box.

1

(a)

(b)

Figure 4 High-pressure and temperature contact angle measurement system, (a) Schematic diagram of the system; (b) Photo of the system.

2.3 Experimental procedure

The static and dynamic contact angles can be measured by sessile drop method (Drelich, 2013), pendant drop method (Bhutani, et al., 2012) or captive bubble method (Taggart, et al., 1930). The former two methods are widely used in the contact angle measurement of a liquid droplet resting on a solid surface, while the captive bubble method is more convenient for measuring the contact angle of a CO₂ bubble beneath a solid substrate immersed in a liquid. In our study, the captive bubble method was used. A schematic of the contact angles of gas bubbles beneath a solid substrate is shown in **Figure 5**. The main operations in our experiments are described below.

Figure 5. Schematic of the contact angle on a solid substrate immersed in water. Young's contact angle = θ_0 , advancing contact angle = θ_A , receding contact angle = θ_R . Usually $\theta_A > \theta_0 > \theta_R$. The left and right advancing or receding contact angles are usually

different and measured individually due to inhomogeneity of physical and chemical properties of the substrate surface. Young's contact angle is impossible to be directly measured, and the static or stable contact angle is measured instead, which usually fluctuates within a range. Note that in this paper we define contact angle as the water contact angle, that is measured through the water phase.

(1) A coal substrate was first clipped onto the stainless plate inside the chamber. The coal substrate was then submersed in high-pressure deionized water (20 bar) for at least 48 h to allow the water to penetrate the coal pores.

(2) The thermally insulated box and the chamber were heated to the desired experimental temperature. The chamber was then filled with CO₂ and pressurized to desired pressure using the ISCO pump (A).

(3) The stirred Parr reactor pre-filled with deionized water was set to the desired temperature and pressurized to slightly higher than the desired pressure using the ISCO pump (B) filled with CO₂. Solubility equilibrium between CO₂ and H₂O was established over a period of 4 h, followed with further stirring for 30 min before injection into the chamber.

(4) The valves between the stirred Parr reactor and the chamber were opened allowing the CO₂-saturated deionized water to flow into the chamber to replace about 90% of the fluid volume of the chamber. During this process, the ISCO pump (A) and (B) were set in constant pressure mode. Further solubility equilibration for ~1 h was performed, considering the pressure difference between injection pressure and back pressure (5 bar at pressures lower than 90 bar, 10 bar at high pressures) between injection pressure and back pressure.

(5) A CO₂ bubble was then released from the stirred Parr reactor via the needle and captured onto the coal substrate. For the dynamic contact angle, the CO₂ bubbles advanced under the pressure difference between the Parr reactor and the H-P-T chamber and receded under the differential pressure between the ISCO pump (B) (pre-depressurized to a lower pressure) and the H-P-T chamber. The bubble expansion and contraction speed (as slow as possible) were controlled by a needle valve. The whole process was recorded by a video, and the images were extracted for contact angle measurements. The static contact bubble was immediately recorded as a photo when contacting the coal substrate (the needle was pulled down and separated from the bubble).

3 Results

3.1 Static contact angles

In our experiments, the contact angles were measured at different combinations of temperatures ($\sim 25, 30, 40, 50$, and 60°C) and pressures (1, 21, 41, 61, 91, and 141 bar, absolute pressure), covering gas, liquid and supercritical phases of CO_2 as shown in **Figure 6**. For each experimental point, the contact angle was measured at least 5 times. We also tried to measure the static contact angles at 181 bar, but it is 180° even at 60°C , suggesting that it was not necessary to measure both the static and dynamic contact angles at such high pressure.

Figure 6. CO_2 phase diagram and a schematic of designed experimental points (green dots) in our experiments.

Figure 7 shows results measured by the static method, i.e. the CO_2 bubble was first generated on the injection needle tip and then contacted the coal surface before the bubble detached and floated to the coal surface. It can be seen that the effect of temperature on the static contact angles at pressures lower than 61 bar (CO_2 in the gas phase) is negligible. However, when the pressure was increased to 91 and 141 bar, the static contact angles decreased significantly with increasing temperature. The static contact angles clearly increased with the increase of pressure, especially for CO_2 transforming from gas to condensed phases. Most of the static contact angles lie between 70° and 90° when the pressures are

1 between 1 and 61 bar, which indicates that the coal surface is
 2 weakly water-wet or intermediate-wet according to Anderson's
 3 criteria (Anderson, 1986). Above the critical pressure of CO₂ (73.8
 4 bar), the coal surfaces became strongly CO₂-wet (115-180°),
 5 especially below the critical temperature (31.1 °C). The static
 6 contact angles at 91 bar are ~161°–162° when the temperatures
 7 are 25 and 30 °C. They are even higher when the pressure
 8 increased to 141 bar (≈ 180°). At both higher pressures and
 9 temperatures when CO₂ became supercritical, the static contact
 10 angles are lower than those in the liquid phase.
 11

12

13 Figure 7 Pressure- and temperature-dependence of static contact
 14 angles. Blue dot line – CO₂ in liquid phase, red dash line – CO₂ in
 15 supercritical phase, others in gas phase.
 16

17 3.2 Dynamic contact angles

18 The dynamic contact angles resulted from the processes of
 19 water-advancing (θ_A) or water-receding (θ_R) are important
 20 parameters, because that they are in fact the contact angles govern
 21 the capillary pressure therefore are relevant during flow. Our DCAs
 22 were measured over the same combinations of temperatures and
 23 pressures used in our SCA experiments. The DCAs measured on coal
 24 substrates in our experiments are shown in **Figure 8**. When the
 25 pressure was lower than 61 bar, the advancing and receding contact
 26 angles were insensitive to temperature variations. The advancing
 27 contact angles varied from 87° to 108° (average values), implying
 28 that the coals varied from intermediate-wet to CO₂-wet. The
 29 receding contact angles at pressures ≤ 61 bar at a constant
 30 temperature are also very close except the ones at 1 bar, which are

1 slightly lower than those at higher pressures. These receding
 2 contact angles lay between 62° and 84° (average values), indicating
 3 that the coals became water-wet or intermediate-wet (at 1, 21, 41,
 4 61 bar).
 5

7
 8 Figure 8 Measured pressure and temperature dependence of DCAs.
 9 “L” and “R” refer to measured values on the left and right sides of
 10 the bubble, respectively. Range bars represent standard deviations.

11
 12 At the higher pressures of 91 bar and 141 bar, the coal became
 13 strongly CO₂-wet and the DCAs became very large. At these higher
 14 pressures, both the advancing and receding contact angles
 15 decreased significantly with increased temperature. At room
 16 temperature (~25 °C), the mean advancing and receding contact
 17 angles at 91 bar are as large as 168° and 155°, respectively. The
 18 dynamic contact angles at 141 bar were much larger than those at
 19 91 bar, and they are even as high as ~180° when the temperature

decreased to 40 °C and lower. Arif et al. reported a similar trend in their experiments (Arif, et al., 2016), i.e. both the advancing and receding contact angles slightly decreased with temperature (35, 50, and 70 °C) and increased with pressure.

4 Discussion

4.1 Comparisons of our measured contact angles with the literature values

Figure 9 summarizes static contact angles measured by some previous researchers. Coal types of the samples used in their experiments varied from bituminous coal to anthracite coal. Proximate analysis results of these coal samples mentioned in the literatures were given in Table 2. A comparison between our measurements and previous results was made and the main findings are as follows:

(1) Our findings are similar to the overall increasing trend of SCAs with increased pressure of CO₂ bubbles reported in the literatures. This trend was also found in other types of rocks (Ameri, et al., 2013; Iglauder, et al., 2014; Wan, et al., 2014).

Figure 9. Comparison of static contact angles (measured from water phase) on the coal surfaces in the literatures with that from the present work. □, △, ◇, ▽, ●, contact angles were measured from water phase. ○, ☆, □, ×, |, contact angles were measured from CO₂ phase (θ_{CO_2}) and converted here to SCAs measured through water by equation $(180 - \theta_{CO_2})$. WL, SC, B, C, G, M, and W are symbols indicating coal types in the literatures.

Table 2 Proximate analysis results of coal samples given in the literatures.

Literature	Moisture (%)	Ash (%)	Volatile (%)	Carbon (%)	R _{max} (%)	t (°C)	Coal type
Siemons et al., 2006	1.3	3.9	10.4	85.68	2.41	45	anthracite
Kaveh et al., 2011 (WL)	N/A	2.77	40.5	58.36	0.71	45	hvbB
Kaveh et al., 2012 (SC)	N/A	3.94-5.5	10.4	89.27	2.41	45	semi-anthracite
Ibrahim et al., 2016	0.2	2	47	50.8	N/A	40	hvAb
Sakurovs et al., 2011 (B)	N/A	7.7	31.7	83.0	0.69	40	N/A
Sakurovs et al., 2011 (C)	N/A	20.3	31.2	80.7	0.62	40	N/A
Sakurovs et al., 2011 (G)	N/A	5.6	36.1	84.1	0.95	40	N/A
Sakurovs et al., 2011 (M)	N/A	16.9	21.7	88.9	1.4	40	N/A
Sakurovs et al., 2011 (W)	N/A	8.9	24.3	88.4	1.31	40	N/A
In the present work	8.68	10.6	35.36	57.79	0.49	40	Sub-bituminous

* hvbB = high volatile bituminous coal, hvAb = high volatile A bitumen coal, N/A = not available.

(2) Although most coals were intermediate-wet or CO₂-wet (except Ibrahim et al. (Ibrahim and Nasr-El-Din, 2016) and Sakurovs et al.'s experiments (Sakurovs and Lavrencic, 2011)), the SCAs measured by different researchers are quite different, even at the same pressure and similar temperature. For example, the SCAs varied from ~30° to ~120° at atmospheric pressure, indicating that the coals varied from water-wet to CO₂-wet. The primary reasons are attributable to differences in coal types as shown in Table 2. The treatment of the coal surface may be another important factor. Kaveh et al. and Siemons et al. polished the coal surface using a series of abrasive papers (60 to 1200 grid) and 0.5-μm abrasive alumina powder as mentioned above (Kaveh, et al., 2011; Kaveh, et al., 2012; Siemons, et al., 2006), and Ibrahim et al. polished the coal surface using a series of sandpapers with average particle diameter 35, 58.5, 100, and 125μm) (Ibrahim and Nasr-El-Din, 2016). Sakurovs polished with a worn P220 silicon carbide paper (Sakurovs and Lavrencic, 2011). The experiment procedures may be different as well, and can contribute to the differences in experimental results. The SCAs in the experiments of Ibrahim et al. (2016) and

1 Sakurovs et al. (2011) were measured from CO₂ bubbles that were
 2 released from the injection needle and buoyantly rose up to the coal
 3 surfaces. Siemons et al. (2006) let the CO₂ bubble grow until it hit
 4 coal surfaces and then measured the SCAs (the bubble contacted on
 5 both the needle and the coal surface during the process).
 6 (3) The coal type used in our experiments is similar to that used by
 7 Kaveh et al. (Kaveh, et al., 2011), and the SCAs are also similar
 8 when CO₂ is in the gas phase. However, the SCAs increased more
 9 dramatically when CO₂ became supercritical in our experiments. Our
 10 results are more similar to those in Sakurovs et al's experiments
 11 despite the large differences in the coal types (Sakurovs and
 12 Lavrencic, 2011), i.e. the SCAs showed a slight increase when CO₂ is
 13 in the gas phase and followed by a sharp increase when CO₂
 14 became supercritical.

15 DCAs on coal surfaces have seldom been reported in the
 16 literature, with the exception of the recent work by Arif et al. (Arif, et
 17 al., 2016). A comparison of DCAs obtained in our experiments with
 18 theirs is shown in **Figure 10**. The DCAs from both studies increased
 19 with pressures and were close in gas CO₂ phase, except for the
 20 nearly constant advancing contact angles in the present work. When
 21 the CO₂ became supercritical, the DCAs in our experiments kept
 22 increasing until up to ~180°. However, the DCAs obtained by Arif et
 23 al. tended to stabilize, indicating a weaker CO₂ wettability.

24
 25 Figure 10. Comparison of pressure-dependence of DCAs measured
 26 by Arif et al (2016) with that from the present work. The vertical
 27 dashed line indicates the critical pressure for CO₂ (73.8 bar).
 28

29 4.2 Effect of temperature on contact angles

30 In our experiments, both the SCAs and DCAs decreased distinctly
 31 with increase of temperature when the CO₂ became supercritical.

1 Villa et al. proposed a model derived from the Decreasing Trend
 2 Model for polar liquid (water in the present work) developed by
 3 Owens and Wendt (Owens and Wendt, 1969) to calculate the
 4 contact angle (Villa, et al., 2018):

$$\cos(\theta) = -1 + \frac{2}{\sqrt{\gamma_{LV,0}(1-aT)}} \sqrt{c} \quad (20^\circ\text{C} < T < 90^\circ\text{C}) \quad (1)$$

6 Where, θ is the contact angle; $\gamma_{LV,0}$ is the surface tension of water at
 7 a reference temperature T_0 (normally $T_0 = 20^\circ\text{C}$); a is the
 8 temperature coefficient that is positive for one phase substance; c
 9 can be calculated by:

$$c = \sqrt{\gamma_{sg}^D \frac{\gamma_{lg}^D}{\gamma_{lg}} + \gamma_{sg}^P \frac{\gamma_{lg}^P}{\gamma_{lg}}} \quad (2)$$

12 where γ_{sg} and γ_{lg} are solid-gas interfacial tension and liquid-gas
 13 interfacial tension, respectively, D is the dispersion force (van der
 14 Waals interaction) and P is the combined polar force (e.g. dipole-
 15 dipole interactions and hydrogen bonding). Due to the negligible
 16 variation of γ_{sg} and γ_{sl} in the temperature range $20^\circ\text{C} < T < 90^\circ\text{C}$, the
 17 c is considered constant (Frolov and Mishin, 2009; Villa, et al., 2018).
 18 Thus, the temperature T is the only variable term in the formula.
 19 Therefore, the contact angle (always in the range of 0° to 180°) will
 20 decrease with the increase of the experiment temperature.

21 At constant pressure, the intermolecular distance among H_2O
 22 molecules will be enlarged due to the increase of temperature,
 23 which weakens the intermolecular attraction ($F_{\text{H}_2\text{O}-\text{H}_2\text{O}}$) among H_2O
 24 molecules on the interface between H_2O phase and CO_2 phase
 25 (**Figure 11**). Meanwhile, the intermolecular attraction between CO_2
 26 and H_2O molecule ($F_{\text{CO}_2-\text{H}_2\text{O}}$) decreases. The surface tension of water-
 27 CO_2 will decrease as a result. This has been experimentally validated
 28 by many researchers. For example, the surface tension of water at
 29 25, 30, 40, 50, and 60°C under atmospheric pressure is 71.99×10^{-3} ,
 30 71.20×10^{-3} , 69.60×10^{-3} , 67.94×10^{-3} , and 66.24×10^{-3} N/m,
 31 respectively (Vargaftik, et al., 1983), which shows a slight decrease
 32 as temperature is increased. Thus, the contact angle on a given
 33 solid surface will also decrease with increased temperature at
 34 constant pressure. Meanwhile,

35

1

2 Figure 11 Schematic of the relationship between the contact angle,
 3 interfacial tension, and intermolecular attraction or force (IMF). $F_{\text{CO}_2\text{-H}_2\text{O}}$
 4 H_2O is the IMF between CO_2 and H_2O molecule at water- CO_2 interface,
 5 and $F_{\text{H}_2\text{O-H}_2\text{O}}$ is the IMF among H_2O molecules. F_1 is the inward force
 6 due to missing cohesive forces to neighboring H_2O molecule, which
 7 is directed toward the internal water.

8

9 However, the contact angles showed no obvious decreases with
 10 increasing temperature at pressures below 61 bar. **Figure 12** gives
 11 pressure-dependent CO_2 density for the present experimental
 12 conditions. The gas CO_2 densities at different temperatures are very
 13 close for pressures below 61 bar. Thus, the $F_{\text{CO}_2\text{-H}_2\text{O}}$ differs little with
 14 temperature, and the surface tension of water- CO_2 will not vary
 15 much. This explains why the effect of temperature on contact angles
 16 was minor at pressures below 61 bar. The differences in sc CO_2
 17 densities among different temperatures become larger as the
 18 pressure increased, which led to a more obvious decrease of
 19 temperature-dependent contact angles.

20

21

22 Figure 12 Pressure-dependence of CO_2 density for different
 23 temperatures. Calculated with "Thermophysical Properties of Fluid

Systems" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Lemmon, et al., 2018).

4.3 Effect of pressure on contact angles

The above results show that both static and dynamic contact angles increased slightly at pressures below 61 bar and showed a distinct increase when CO₂ transformed from gas phase to liquid and supercritical phase. When the pressure increases, the density of the CO₂ phase will increase, which magnifies the intermolecular attraction forces $F_{\text{CO}_2\text{-H}_2\text{O}}$ and $F_{\text{H}_2\text{O-H}_2\text{O}}$ (**Figure 11**). Given that the change in water density is small in our experimental condition (Cho, et al., 2002), the contact angle will then increase as a result. This phenomenon is not obvious at low pressures, but it will be more significant at high pressures.

Some researchers also suggested that the effect of pressure on contact angles was mainly related to the variation in CO₂ density (Arif, et al., 2016; Kaveh, et al., 2011; Kaveh, et al., 2012). **Figure 13** gives the pressure-dependence of advancing and receding CAs (average values of the left and right DCAs) at different temperatures. It shows that there is a good correspondence between CO₂ densities and the DCAs as shown in subordinate figures in **Figure 13** (25 °C for example).

(1) When the pressure is lower than 61 bar, the CO₂ densities increase smoothly as shown in Figure 12, and they are very close at different temperatures varying from ~25 °C to 60 °C. The advancing CAs shows no obvious increase, while the receding CAs indicates a slight increase.

(2) As the pressure rises above 61 bar, the CO₂ densities increase sharply, especially at the lower temperatures. This explains why the differences in the contact angles between lower pressures (1, 21, 41, 61 bar) and larger pressures (91 bar and 141 bar) are larger as shown in **Figure 13**.

(3) When the pressure keeps increasing, the CO₂ densities for different temperatures become stabilized. When the pressure is larger than 141 bar in our experiments, the contact angles in **Figure 7** and **Figure 13** became very large or even increase up to 180° at lower temperatures, indicative of stable hydrophobic conditions. The stabilized pressure also depends on temperature and solid surface types. For example, in the experiments of Arif. et al., the DCAs showed a distinct flatness when the pressure was larger than ~100 bar (Arif, et al., 2017). Espinoza et al. found that the contact angles on both hydrophobic substrates (oil-wet quartz and PTFE) and hydrophilic substrates (quartz and calcite) remained

1 constant after the pressure exceeds the CO₂ liquid-vapor phase
 2 boundary (~64.33 bar at 298K) (Espinoza and Santamarina, 2010).
 3

4

5

6 Figure 13. Pressure-dependence of the advancing and receding
 7 DCAs at different temperatures. The vertical dashed line indicates
 8 the critical pressure for CO₂ (73.8 bar). The abscissa of the
 9 subordinate figure is the CO₂ density (ρ , kg·m⁻³), and the ordinate is
 10 the dynamic contact angle (θ).
 11

12 As discussed in previous section, when the pressure increases,
 13 CO₂ adsorption on coal surfaces is enhanced, which also leads to the
 14 decrease of interfacial tension between CO₂ and the solid surface,
 15 and the increase in contact angles (Espinoza and Santamarina,
 16 2010; Ibrahim and Nasr-El-Din, 2016). However, this may be not as
 17 significant as the effect of CO₂ density variation. In our experiments,
 18 the coal sample was completely immersed in water, and water
 19 molecules occupied most of the adsorption sites on the coal
 20 surfaces before the CO₂ bubble contact. As is known, water has
 21 higher adsorption capacity than CO₂ (Merkel, et al., 2015), so the
 22 coal surface sites will uptake low amounts of CO₂ during the contact

process, especially within short times. Further studies are needed to measure CO₂ uptake amount on water-immersed coal surfaces at different pressures and temperatures.

5 Conclusions

We experimentally investigated the wettability of coals by measuring both static and dynamic contact angles over wide ranges of pressures and temperatures. The main findings are as follows:

(1) The coal surface is weakly water-wet (57°) before contacting with CO₂. The reactions with gas-CO₂ slightly altered the coal surfaces to become intermediate-wet (SCAs increased to 70°-90°). The reactions with scCO₂ strongly altered the coal surfaces to become CO₂-wet (~115-180°).

(2) The effect of temperature on both static and dynamic contact angles is negligible in gas-CO₂. However, when the pressure increased above the critical pressure, the contact angles decreased with the increased temperature.

(3) For gas-CO₂, both static and dynamic contact angles increased slightly with increase of pressures. For liquid-CO₂ and scCO₂, the static and dynamic contact angles on coal surface increased greatly with the increase of pressures.

(4) The contact angles for water on coals were strongly positively correlated to CO₂ densities.

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References

- Specification for Identification of Coal and Gas Outburst Coal Mine. In: Safety, S.A.o.W., editor. Beijing: China Coal Industry Publishing House; 2006.
- Notice on speeding up the closure and withdrawal of small coal mines. In: State Administration of Work Safety, N.C.M.S.A., National Development and Reform Commission, Ministry of Public Security, Ministry of Finance,

1 Ministry of Human Resources and Social Security, Ministry of Land and
2 Resources, Ministry of Environmental Protection, State-owned Assets
3 Supervision and Administration Commission, State Administration for
4 Industry and Commerce, National Energy Administration, All-China
5 Federation of Trade Unions, editor. Beijing; 2014.

6 Ameri, A., *et al.* Investigation on Interfacial Interactions among Crude
7 Oil–Brine–Sandstone Rock–CO₂ by Contact Angle Measurements.
8 *Energy & Fuels* 2013;27:1015–1025.

9 Anderson, W.G. Wettability literature survey - Part 2: Wettability
10 measurement. *Journal of Petroleum Technology* 1986;38(11):1246-
11 1262.

12 Arif, M., *et al.* CO₂-wettability of low to high rank coal seams: Implications
13 for carbon sequestration and enhanced methane recovery. *Fuel*
14 2016;181:680-689.

15 Arif, M., *et al.* Influence of surface chemistry on interfacial properties of
16 low to high rank coal seams. *Fuel* 2017;194:211-221.

17 Bhutani, G., Khandekar, S. and Muralidhar, K. Contact Angles of Pendant
18 Drops on Rough Surfaces. In, *Proceedings of the Thirty Ninth National*
19 *Conference on Fluid Mechanics and Fluid Power*. Gujarat, India: SVNIT
20 Surat; 2012. p. 1-10.

21 Bikkina, P.K. Contact angle measurements of CO₂-water-quartz/calcite
22 systems in the perspective of carbon sequestration. *International*
23 *Journal of Greenhouse Gas Control* 2011;5:1259-1271.

24 Busch, A. and Gensterblum, Y. CBM and CO₂-ECBM related sorption
25 processes in coal: A review. *International Journal of Coal Geology*
26 2011;87:49-71.

27 Chen, C., *et al.* Water contact angles on quartz surfaces under supercritical
28 CO₂ sequestration conditions: Experimental and molecular dynamics
29 simulation studies. *International Journal of Greenhouse Gas Control*
30 2015;42:655-665.

31 Cho, C.H., *et al.* Pressure Effect on the Density of Water. *The Journal of*
32 *Physical Chemistry A* 2002;106:7557-7561.

33 Drelich, J. Guidelines to measurements of reproducible contact angles
34 using a sessile-drop technique. *Surface Innovations* 2013;1(4):248-254.

35 Drelich, J., *et al.* Preparation of a coal surface for contact angle
36 measurements. *Journal of Adhesion Science and Technology*
37 1997;11(11):1399-1431.

38 Eissler, R.L. and Holde, K.E.V. Wettability of coal, graphite, and
39 Naphthalene as measured by contact angles. In. Urbana: Illinois State
40 Geological Survey 1962.

41 Espinoza, D.N. and Santamarina, J.C. Water-CO₂-mineral systems:
42 Interfacial tension, contact angle, and diffusion—Implications to CO₂
43 geological storage. *Water Resoures Research* 2010;46(7).

- 1 Frolov, T. and Mishin, Y. Temperature dependence of the surface free
2 energy and surface stress: An atomistic calculation for Cu(110).
3 *Physical review B* 2009;79(4):045430.
- 4 Gunter, W.D., et al. Deep coalbed methane in Alberta, Canada: A fuel
5 resource with the potential of zero greenhouse gas emissions. *Energy*
6 *Conversion and Management* 1997;38(Supplement):S217-S222.
- 7 Ibrahim, A.F. and Nasr-El-Din, H.A. Effect of Water Salinity on Coal
8 Wettability During CO₂ Sequestration in Coal Seams. *Energy & Fuels*
9 2016;30:7532–7542.
- 10 Iglauer, S., et al. Contamination of silica surfaces: Impact on water-CO₂-
11 quartz and glass contact angle measurements. *International Journal of*
12 *Greenhouse Gas Control* 2014;22:325-328.
- 13 Jańczuk, B., Wójcik, W. and Bialopiotrowicz, T. Wettability of Coal Surface
14 and its Surface Free Energy Components. *Croatica Chemica Acta*
15 1988;61(1):51-63.
- 16 Jung, J.W. and Wan, J. Supercritical CO₂ and Ionic Strength Effects on
17 Wettability of Silica Surfaces: Equilibrium Contact Angle Measurements.
18 *Energy & Fuels* 2012;26:6053–6059.
- 19 Kaveh, N.S., et al. Wettability determination by contact angle
20 measurements: hvbB coal-water system with injection of synthetic flue
21 gas and CO₂. *Journal of Colloid and Interface Science* 2011;364:237-
22 247.
- 23 Kaveh, N.S., et al. Effect of coal petrology and pressure on wetting
24 properties of wet coal for CO₂ and flue gas storage. *International Journal*
25 *of Greenhouse Gas Control* 2012;11(Supplement):S91-S101.
- 26 Kilau, H.W. The wettability of coal and its relevance to the control of dust
27 during coal mining. *Journal of Adhesion Science and Technology*
28 1993;7(6):649-667.
- 29 Lemmon, E.W., McLinden, M.O. and Friend, D.G. Thermophysical Properties
30 of Fluid Systems. In. Gaithersburg MD: National Institute of Standards
31 and Technology; 2018.
- 32 Letellier, P., Mayaffre, A. and Turmine, M. Drop size effect on contact angle
33 explained by nonextensive thermodynamics. Young's equation
34 revisited. *Journal of Colloid and Interface Science* 2007;314:604-614.
- 35 Leung, D.Y.C., Caramanna, G. and Maroto-Valer, M.M. An overview of
36 current status of carbon dioxide capture and storage technologies.
37 *Renewable and Sustainable Energy Reviews* 2014;39:426-443.
- 38 Mahoney, S.A., et al. The effect of rank, lithotype and roughness on
39 contact angle measurements in coal cleats. *International Journal of Coal*
40 *Geology* 2017;179:302-315.
- 41 Marmur, A. Soft contact: measurement and interpretation of contact
42 angles. *Soft Matter* 2006;2:12-17.
- 43 Masoudian, M.S. Multiphysics of carbon dioxide sequestration in coalbeds:

1 A review with a focus on geomechanical characteristics of coal. *Journal*
2 *of Rock Mechanics and Geotechnical Engineering* 2016;8:93-112.

3 Merkel, A., et al. Competitive sorption of CH₄, CO₂ and H₂O on natural coals
4 of different rank. *International Journal of Coal Geology* 2015;150-
5 151:181-192.

6 Mukherjee, M. and Misra, S. A review of experimental research on
7 Enhanced Coal Bed Methane (ECBM) recovery via CO₂ sequestration.
8 *Earth-Science Reviews* 2018;179:392-410.

9 Owens, D.K. and Wendt, R.C. Estimation of the Surface Free Energy of
10 Polymers. *Journal of Applied Polymer Science* 1969;13:1741-1747.

11 Pan, B., et al. CO₂ and CH₄ Wettabilities of Organic-Rich Shale. *Energy &*
12 *Fuels* 2018;32:1914-1922.

13 Puri, R. and Yee, D. Enhanced coalbed methane recovery. In, *65th Annual*
14 *Technical Conference and Exhibition*. New Orleans, LA: Society of
15 Petroleum Engineers; 1990.

16 Saghafi, A., Pinetown, K. and Javanmard, H. Gas Wettability of Coal and
17 Implications for Gas Desorption and Drainage. In, *14th Coal Operators'*
18 *Conference*. University of Wollongong: The Australasian Institute of
19 Mining and Metallurgy & Mine Managers Association of Australia; 2014.
20 p. 266-273.

21 Sakurovs, R. and Lavrencic, S. Contact angles in CO₂-water-coal systems at
22 elevated pressures. *International Journal of Coal Geology*
23 2011;87(1):26-32.

24 Siemons, N., et al. Pressure dependence of the contact angle in a CO₂-
25 H₂O-coal system. *Journal of Colloid and Interface Science*
26 2006;297:755-761.

27 Sun, X.-x., et al. Investigations of CO₂-water wettability of coal: NMR
28 relaxation method. *International Journal of Coal Geology* 2018;188:38-
29 50.

30 Taggart, A.F., Taylor, T.C. and Ince, C.R. Experiments with Flotation
31 Reagents. *Transactions of the American Institute of Mining,*
32 *Metallurgical, and Petroleum Engineers* 1930;87:285-289.

33 Vargaftik, N.B., Volkov, B.N. and Voljak, L.D. International Tables of the
34 Surface Tension of Water. *Journal of Physical and Chemical Reference*
35 *Data* 1983;12(3):817-820.

36 Villa, F., Marengo, M. and De Coninck, J. A new model to predict the
37 influence of surface temperature on contact angle. *Scientific Reports*
38 2018;8(1):6549.

39 Wan, J., Kim, Y. and Tokunaga, T.K. Contact angle measurement ambiguity
40 in supercritical CO₂-water-mineral systems: Mica as an example.
41 *International Journal of Greenhouse Gas Control* 2014;31:128-137.

42 Wan, J., et al. Supercritical CO₂ uptake by nonswelling phyllosilicates.
43 *Proceedings of the National Academy of Sciences* 2018;115(5):873-878.

- 1 White, C.M., et al. Separation and Capture of CO₂ from Large Stationary
- 2 Sources and Sequestration in Geological Formations—Coalbeds and
- 3 Deep Saline Aquifers. *Journal of the Air & Waste Management*
- 4 *Association* 2003;53:645-715.
- 5