Experimental Study of the Wettability Characteristic of Thermally Treated Shale

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ABSTRACT: Extraction of shale gas from shale reservoirs is significantly affected by shale wettability. Recently, thermal recovery technologies (e.g., combustion) have been tested for shale gas recovery. This requires an understanding of the wettability change mechanism for thermally treated shale samples. In this study, the effect of combustion on shale wettability was investigated. Shale samples were first processed to obtain smooth surfaces and then combusted at temperatures of 200, 400, and 800 °C. The initial contact angles and dynamic behavior of water droplets on shale surfaces were recorded using the sessile drop method. It was found that pores and fractures were generated on the shale surfaces following high-temperature combustion. The pore volume and diameter increased with increasing combustion temperature, which improved the connectivity of hydrophilic pore networks. Compared to a raw shale sample, the shale sample combusted at 400 °C showed a smaller initial water contact angle and a more rapid decrease in the contact angle because of the oxidation of organic matter and generation of pore structures. Water droplets were found to completely spread over the surface of the shale sample combusted at 800 °C because of the generation of fractures. Moreover, the van der Waals potential between water droplets and combusted shale samples was determined to be stronger. However, the initial contact angle and dynamic behavior of water droplets did not show a significant change for the shale sample combusted at 200 °C. As a result, high-temperature combustion (≥400 °C) can be used to significantly improve the hydrophilicity of shale.

1. INTRODUCTION

The successful exploitation of unconventional oil and gas resources (e.g., shale gas) in North America has inspired an energy revolution because of a rapid increase in energy demand on a worldwide scale.1−4 It has been reported that China has approximately 36 trillion cubic meters of recoverable shale gas resources and has made an ambitious plan for large-scale gas extraction.5,6 Wettability is an important parameter for defining the affinity of a fluid to a shale surface in the presence of another fluid. Generally, the wettability of shale is divided into three states: (1) water-wet, (2) mixed-wet, and (3) oil-wet.7 The shale gas recovery efficiency is affected by the relative permeability and capillary pressure, which are strongly dependent on the shale wettability.8−11 Thus, the wettability of shale reservoirs has received considerable attention. Methods such as Amott and the United States Bureau of Mines (USBM) wettability index have been used to characterize the wettability of conventional natural gas formations.12 However, one obvious characteristic of tight shale formation is its low matrix permeability, which is six orders of magnitude lower than that found in conventional gas reservoirs.13−16 Most of the pores within a shale matrix are micrometer- to nanometer-scaled pores.17 The ultralow permeability and small pore structures limit the application of Amott and USBM methods for characterization of the shale wettability.18 In addition, the high level of heterogeneity of the compositions inside the shale also limits applications of these methods.19 Today, contact angle measurement is a feasible method that is widely employed to analyze the wettability of tight shale rocks with ultralow permeability.20

Previous studies reported that oil droplets (e.g., kerosene) were found to completely spread out on the shale surface, and the contact angles of water droplets were more accurate.21 However, the initial contact angle and dynamic behavior of water droplets did not show a significant change for the shale sample combusted at 200 °C. As a result, high-temperature combustion (≥400 °C) can be used to significantly improve the hydrophilicity of shale.
of air. Pan et al. also found that the water contact angle had a positive correlation with pressure in CH₄ and CO₂ environments. Yaseri et al. attributed the positive correlation to the less density difference between two fluid phases (gas and liquid phases). Some researchers have reported that the contact angle decreased with increasing temperature. The contact angles showed a negative correlation with maturity. However, the effect of the content of total organic matter (TOC) on the water contact angles is more complicated. In the air/brine/shale system, the contact angles were found to decrease first (TOC<1.5%) and then increase (TOC>1.5%) with the increase of the content of TOC. The tendency to decrease first and then increase was mainly controlled by the development and distribution of migratory organic matter and the illite/smectite mixed layer. In addition, the dynamic behavior of water droplets is crucial for multiphase flow and transport in the subsurface, although the dynamic behavior of water droplets on shale samples does not get enough attention. Because of the spreading of water droplets over the shale surface and infiltration of droplets into a porous shale matrix, some researchers found that the contact angle decreased as time went on, but they did not carry out further research. Shang et al. recorded the temporal changes in the droplet diameter in their study. Gates et al. developed a systematic method for calculating the contact angle and directly visualized droplet infiltration into the porous shale matrix. Water droplets can more easily infiltrate into shale samples that exhibit better connectivity of hydrophilic pore networks, which increases the rate of decrease in the contact angle.

Recently, thermal recovery technologies (e.g., combustion) have been used to improve gas recovery from tight shale rocks. During combustion, organic matter and parts of inorganic minerals inside shale are oxidized. Meanwhile, the permeability of shale is also increased after combustion. These changes in the composition and structure can have a great effect on the shale wettability. Because the wettability of combusted shale samples has not been well studied, it is essential to investigate the effect of combustion on the shale wettability for the development of thermal recovery technologies.

In this study, shale rocks collected from Wenjiaba, Guizhou Province, China were employed as samples for wettability tests. The effect of combustion on the shale wettability was analyzed by recording the initial contact angles and dynamic behavior of water droplets on raw and combusted shale samples. The van der Waals potential between water droplets and shale surfaces was also investigated. Moreover, the pore structure and surface condition for raw and combusted shale samples were investigated by means of a liquid nitrogen adsorption and desorption test and scanning electron microscopy (SEM).

2. RESULTS AND DISCUSSION

2.1. Shale Properties. Based on the proximate and ultimate analysis (Table 1), the TOC (e.g., volatile matter (VM) and fixed carbon (FC)) in the Wenjiaba shale is determined to be close to 10%. The shale is found to be thermally mature with Rₒ = 2.7% and contained type II kerogen. The well-developed pore system inside the organic matter can provide significant sites for gas-molecule absorption. Thus, Wenjiaba shale has high gas-adsorption capacity and a large amount of gas stored in the pore system.

Table 1. Proximate and Ultimate Analysis of Wenjiaba Shale

| Component | Raw Shale (%) |
|-----------|---------------|
| moisture  | 2.59          |
| ash       | 87.58         |
| VM        | 7.44          |
| FC        | 2.39          |
| carbon    | 5.36          |
| oxygen    | 1.04          |
| hydrogen  | 0.48          |
| nitrogen  | 0.26          |
| sulfur    | 5.36          |
| Rₒ        | 2.7           |
| kerogen type | II          |

The mineral composition has a significant effect on shale wettability. As shown in Figure 1, the main minerals identified within the raw Wenjiaba shale sample are quartz, feldspar, illite, kaolinite, magnetite, pyrite, and quartz.

![Figure 1. XRD spectrograms of the raw and combusted shale samples (F- feldspar, I- illite, K- kaolinite, M- magnetite, P- pyrite, and Q- quartz).](https://dx.doi.org/10.1021/acsomega.0c03258)
CS2 samples have the same mineral compositions. The mineral composition of the shale did not change significantly at temperatures of 200 and 400 °C in an air environment. However, all the pyrite (P) is oxidized and transformed into magnetite (M) at 800 °C.

2.2. Pore Volume and Diameter of Combusted Shale Samples. The characteristic of shale such as low porosity and low permeability is not conducive to the flow of water inside the shale matrix. During combustion, the pore structure change, such as the pore size and pore shape, has a huge impact on the shale wettability. In addition, because organic matter is one of the components of the shale matrix, the removal of organic pores caused by the oxidation of organic matter also influences the shale wettability. Figure 2 shows the liquid nitrogen adsorption and desorption isotherms of the raw and combusted shale samples.

![Figure 2. Liquid nitrogen adsorption and desorption isotherms of the raw and combusted shale samples.](image)

According to the International Union of Pure and Applied Chemistry, the isotherms of the raw, CS1, and CS2 samples belong to type IV isotherms with type H4 hysteresis loops. The isotherm of the CS3 sample is similar to the type IV isotherm with a type H3 hysteresis loop. Based on a previous study, the pores in raw, CS1, and CS2 samples with H4 hysteresis loops belong to narrow slitlike pores. The CS3 sample with a H3 hysteresis loop contains slit-shaped pores. The amount of N2 adsorbed at a relative pressure of P/P0 = 0.98 corresponds to the pore volume. It can be seen that the pore volume is larger for the shale samples combusted at higher temperature, with the following correlation: CS3 > CS2 > CS1 ≈ Raw. The adsorption and desorption isotherms of the raw and CS1 samples are similar, indicating that the pore structure of the CS1 sample did not change significantly at low temperature (200 °C). However, the CS2 and CS3 samples with steeper isotherm slopes at a higher relative pressure show larger pore volumes after high-temperature combustion. Thus, the capacity of the CS2 and CS3 samples to store water molecules was improved.

Figure 3 shows the comparison of the mean pore diameters of the raw and combusted shale samples. In this study, the liquid nitrogen adsorption and desorption tests were conducted on each shale sample three times in order to obtain more precise data about the pore size. As shown in Figure 6, the mean pore diameters of the raw, CS1, CS2, and CS3 samples are 7.15, 7.45, 9.07, and 17.06 nm, respectively. It can be seen that mesopores (2−50 nm) are dominated inside these shale samples. The mean pore diameter increased with increasing combustion temperature, especially for the shale samples heated at 800 °C. The increase in the pore volume and diameter increased the permeability of the shale and provided more efficient channels for water molecules to enter the shale matrix. The connectivity of hydrophilic pore networks was also effectively improved. Meanwhile, CS2 and CS3 samples with larger pore volumes allowed more water molecules to enter the shale matrix.

2.3. Surface Condition Analyses Based on SEM Images. The surface condition plays an important role in the shale wettability. The change in the surface condition after combustion is observed by comparing the SEM images of the raw and combusted shale samples (Figure 4). The SEM images demonstrate that many clay minerals (granular shape) are distributed on the raw shale surface (Figure 4a). As shown in Figures 4a and b, the surface conditions for the raw and CS1 samples are similar, which is consistent with the similar pore volume and diameter. Because only the moisture and a small amount of volatile are released, there are no obvious pores and fractures observed on the surfaces of raw and CS1 samples. Some pores and fractures generated on the surfaces of CS2 and CS3 samples were observed (Figure 4c and d). Complex physical and chemical reactions occurred at high combustion temperature (≥2400 °C). When the combustion temperature increased to 400 °C, a part of the organic matter was oxidized.
and released as crude oil or natural gas.\textsuperscript{33,37,47} Meanwhile, parts of blocked pore throats were reopened during combustion.\textsuperscript{33} When the shale samples were heated up to 800 °C, parts of minerals (e.g., pyrite and carbonate minerals) were decomposed.\textsuperscript{37,43} Thus, pores and fractures were generated because of the oxidation of organic matter and decomposition and collapse of minerals. The generation of pores and fractures effectively enhanced the flow transportation capacity.\textsuperscript{48} In addition, the removal of hydrophobic organic matter enhanced the affinity of the combusted shale samples to water molecules. As a result, water droplets on the CS2 and CS3 samples can show different initial contact angles and dynamic behavior compared to water droplets on the raw shale sample. For gas extraction, these generated structures such as pores and fractures during combustion provided more channels for gas flow and effectively improved the production rate of gas from reservoirs.\textsuperscript{33}

2.4. Effect of Combustion on the Initial Contact Angle. The initial contact angle measured at 0 s is suggested to be accurate characterization to estimate the shale wettability.\textsuperscript{20} Figure 5 presents the initial contact angles of water droplets measured on raw, CS1, and CS2 samples. The contact angles measured on the CS1, CS2, and CS3 samples before combustion were all similar to the angle on the raw shale sample (raw CS1=66 °, raw CS2=64 °, and raw CS3=66 °). Therefore, only the contact angle on the raw shale sample (Figure 7a) was presented in this study. All the initial contact angles are smaller than 90 ° because of the existence of hydrophilic inorganic minerals,\textsuperscript{30} indicating that the raw Weniiba shale sample is overall hydrophilic. As discussed before, the pore structure and surface condition for the CS1 sample did not show a great change, so the initial contact angles for the raw and CS1 samples are similar. Low-temperature combustion (≤200 °C) did not lead to a significant effect on the initial contact angles for the combusted shale samples. The initial contact angle for the CS2 sample is obviously smaller than the corresponding contact angles for raw and CS1 samples. Considering that the spreading of a water droplet on the shale surface is mainly controlled by the affinity of the shale sample to water molecules,\textsuperscript{29} the smaller initial contact angle indicates that the CS2 sample has a higher affinity to water molecules. During combustion, the hydrophobic organic matter distributed on the shale surface was oxidized,\textsuperscript{37,47} leading to the exposure of more hydrophilic inorganic minerals with a stronger affinity to water molecules on the shale surface. The pore structures generated in the CS2 sample also prompted the spreading of the water droplet. In addition, many oxygen-containing functional groups were added on the shale surface during combustion,\textsuperscript{30} which effectively increased the affinity of shale to water molecules. The water droplets were observed to completely spread over the surface of the CS3 sample and did not maintain certain shapes because of the generation of large fractures. Accordingly, the shape of a water droplet on the CS3 sample is not provided in Figure 5. High-temperature combustion (≥400 °C) resulted in an obvious decrease in the initial contact angle.

2.5. Effect of Combustion on the Dynamic Behavior of Water Droplets. The contact angles of water droplets on raw and combusted shale samples as a function of time are presented in Figure 6. As mentioned previously, Figure 6 does not show the dynamic behavior of a water droplet on the CS3 sample because the water droplet was found to completely spread over the surface of the CS3 sample. Because all the measurements were conducted in the same experimental environment (T = 25 °C, P = 101.325 kPa, and relative humidity (RH) = 75%), the effect of water evaporation on the observed decrease in the contact angle can be ignored.\textsuperscript{30} The difference in the rate of decrease in the contact angle was mainly affected by the difference in the water infiltration rate.\textsuperscript{30} As shown in Figure 6, the dynamic behavior of the water droplets exhibits two distinct phases: a rapid decrease followed by a less rapid decline. In the initial stage, water droplets spread over the shale surface, which rapidly lowers the contact angle.\textsuperscript{29} Moreover, the water molecules enter the pore structure quickly because of the presence of capillary pressure,\textsuperscript{7} which also leads to a large rate of decrease in the contact angle. With increasing time, the infiltration of water droplets becomes the main reason why the contact angles are observed to still decrease, although the water droplets stop spreading over the shale surface. Meanwhile, clay minerals (e.g., kaolinite and illite) detached from the shale surface tend to block parts of pore throat restrictions.\textsuperscript{54} Accordingly, the rate of decrease in the contact angle was lowered in the second stage to some extent.

Because of the similar pore structure and surface condition, the dynamic behavior of water droplets on raw and CS1 samples was found to be similar. Low-temperature combustion (≤200 °C) did not obviously impact the dynamic behavior of the water droplets. A significant departure between the dynamic behavior of the water droplets on raw and CS2 samples was identified in which the contact angle was observed to decrease faster in the second stage for the CS2 sample. When the experiment was carried out for 11 min, the contact angle for the CS2 sample decreased to 10 °. On the one hand, infiltration of water droplets is inhibited by the hydrophobic
organic matter inside raw and CS1 samples, while such inhibition does not occur in the CS2 sample. On the other hand, pore structures observed in SEM images of the CS2 sample show an improved connectivity of hydrophilic pore networks.\textsuperscript{35} This reveals that high-temperature combustion (≥400 °C) can effectively promote water molecules to enter the shale matrix and obviously enhance the rate of decrease in the contact angle.

2.6. van der Waals Potential between the Water Droplets and Shale Surface. The contact angle was employed to evaluate the van der Waals potential (V) between the water droplet and shale surface based on eq 2.\textsuperscript{56} Garcia et al. pointed out that the van der Waals potential described the net preference of water molecules for wetting shale samples.\textsuperscript{56} Considering that all the contact angle measurements in this work were conducted under the same conditions, the differences in Δρ and γₜₗ were ignored. The smaller initial contact angle measured on the CS2 sample indicates that the van der Waals potential and the net preference of the water molecules for wetting the combusted shale samples are stronger. The shale samples became more hydrophilic after combustion.

3. CONCLUSIONS

The primary objective of this study was to investigate the effect of combustion on the shale wettability by recording the initial contact angles and dynamic behavior of water droplets. The conclusions are listed as follows:

(1) The TOC in the Wenjiaba shale sample was determined to be approximately 10%, and the shale was found to be thermally mature with Rₒ = 2.7. The main minerals inside the shale matrix were found to be quartz, feldspar, illite, kaolinite, magnetite, and pyrite. Pyrite was decomposed at a temperature of 800 °C.

(2) According to a liquid nitrogen adsorption and desorption test, the pore volume and diameter increased with increasing combustion temperature and showed the following correlation: CS3>CS2>CS1 ≈ Raw. Because of the oxidation of organic matter at 400 °C and decomposition of parts of the minerals at 800 °C, large pores and fractures were generated in the CS2 and CS3 samples. The connectivity of hydrophilic pore networks inside the shale was found to be effectively improved after combustion.

(3) With the removal of hydrophobic organic matter distributed on the shale surface, a water droplet on the CS2 sample shows a smaller initial contact angle. Moreover, water droplets were observed to completely spread over the surface of the CS3 sample and did not maintain certain shapes. High-temperature combustion effectively decreased the initial contact angle for the shale samples.

(4) The dynamic behavior of the water droplets exhibited two distinct stages: a rapid decrease followed by a less rapid decline. A water droplet on the CS2 sample showed a larger rate of decrease in the contact angle in the second stage caused by the well-developed connectivity of hydrophilic pore networks. High-temperature combustion was beneficial to the infiltration of the water droplet into the shale matrix.

(5) The water droplets showed a stronger net preference for wetting combusted shale samples because of the stronger van der Waals potential between water droplets and combusted shale samples. As a result, the hydrophilicity of the combusted shale samples was significantly improved.

4. SAMPLES AND EXPERIMENTS

4.1. Shale Properties. In this study, gray shale samples with a cylindrical shape (Figure 7a) collected from Wenjiaba, Guizhou Province, China were used to analyze the wettability change mechanism for combusted shale samples. Before the experiments, fresh raw shale samples were sent to a commercial laboratory for proximate, ultimate, and maturity analyses. The contents of moisture, ash, VM, and FC were measured in proximate analysis. The elemental compositions of the shale including carbon, hydrogen, nitrogen, sulfur, and oxygen were determined in ultimate analysis. The vitrinite reflectance (Rₒ) was also measured. These physical properties are provided in Table 1.\textsuperscript{35} More detailed information about the proximate, ultimate, and maturity analyses is provided in the appendix.

4.2. Sample Preparation. Before the contact angle measurements, the gas shale samples (as received) were first processed in air to obtain the desired flat surfaces (Figure 7b). Then, the shale surfaces were polished using sandpaper (2000 mesh). Afterward, the samples were cleaned in an ultrasonic water bath (deionized water) for 30 seconds to remove contaminants and reduce the uncertainty.\textsuperscript{30} Finally, the cleaned samples were dried in a drying oven at 100 °C, and the surfaces were flushed using high-pressure nitrogen. The cleaning method for the contact angle measurement used in this study is consistent with the one developed by Yuan et al.\textsuperscript{30}

The weight-loss curve for the Wenjiaba shale samples showed that weight was lost rapidly when the temperature was increased to 400 °C and that the weight tended to be stable when the shale sample was heated up to 800 °C.\textsuperscript{51} Thus, temperatures of 200, 400, and 800 °C were selected as combustion temperatures to investigate the effect of combustion on the shale wettability. Finally, the shale samples (CS1, CS2, and CS3) were combusted in a tube furnace with a constant air flow at 200, 400, and 800 °C for 30 min, respectively.

4.3. Contact Angle Measurement. In this study, a sessile drop method was conducted in the air/deionized water/shale system to test the shale wettability.\textsuperscript{30} A constant volume (5 μL) of deionized water was dispensed onto the flat shale surface using a fixed volume microsyringe under an ambient condition (25 °C and 101.325 kPa), as shown in Figure 8. The RH is maintained at a high level (75%) during the contact
samples were combusted at a temperature of 200, 400, and 800°C and sieved to a mesh size of 0.088 mm. Preparation requirements, all the shale samples were crushed and sieved to a mesh size of 0.088 mm. The crushed shale samples were dried and degassed at 110°C for 6 h to remove bound water and adsorbed gases. The analytical data were obtained under relative pressure (P/P₀) ranging from 0.050 to 0.995 and at a temperature of 77 K.

4.6. SEM Test. To observe the change in the surface condition for shale samples combusted at different temperatures, SEM images of raw and combusted shale samples were obtained using a scanning electron microscope. The equipment (HITACHI SU8010, Tokyo, Japan) was operated under an acceleration voltage of 1 kV and a beam current of 10 μA. Before the SEM tests, all the shale samples were gold-plated to increase the electrical conductivity and therefore improve the sharpness of SEM images. All the shale samples were observed under low magnification (2.00 k) to provide more useful information within a limited image.

4.7. Evaluation of van der Waals Potential. Young’s equation relates the contact angle of a water droplet to the gas—solid interfacial tension (γₛₐ), liquid—solid interfacial tension (γₛₗ), and liquid—gas interfacial tension (γₗ₉), which can be expressed as follows:

$$\cos \theta = \frac{(\gamma_{sl} - \gamma_{sq})}{\gamma_{lg}}$$  

(1)

However, it is difficult to measure the gas—solid and liquid—solid interfacial tensions, which limits the applicability of Young’s equation. Based on the sharp-kink approximation, it is possible to introduce the van der Waals potential by replacing the gas—solid and liquid—solid interfacial tensions to obtain the following expression:

$$\cos \theta = \frac{\Delta \rho}{\gamma_{lg}} I - 1$$  

(2)

where \( \Delta \rho = \rho_l - \rho_s \) (\( \rho_l \) and \( \rho_s \) are the densities of the liquid and gas, respectively) and \( I = -\int_{-\infty}^{\infty} V(z) \) is the van der Waals potential integral.

APPENDIX

In proximate analysis, the moisture content is determined by the mass loss of the shale sample below 110°C, using an air drying oven (101-2ES) and an electronic balance (Mettler Toledo AE100, Columbus, USA). The VM content corresponds to the volatile products evolved between 110 and 900°C in a N₂ environment as a result of thermal decomposition. Ash is the residue that remains after complete combustion of the shale sample at 815 ± 10°C in air. The FC content of shale is determined by subtracting the percentages of moisture, VM, and ash from the original mass of the shale sample.

In ultimate analysis, each element is expressed as a percentage of the total mass of the original shale sample on an-as-received basis. In ultimate analysis, carbon and hydrogen are determined using a carbon—hydrogen analyzer (CTCH500, Hunan, China) based on GB/T476—2008; sulfur is determined using an automatic sulfur analyzer (XH34-ZCL-3, Beijing, China) based on GB/T214—2007; oxygen is calculated by difference. The vitrinite reflectance (Rᵥ) is measured using a microscope photometer (Leitz ORTHOLUX-II POL-BK, Wetzlar, Germany).
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Notes
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