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THE EXPERIMENTAL STUDY OF THE IMPACT ON SUPERCRITICAL CO₂ FROM CH₄ COMPOSITION IN COAL

Dongmei Wu, Yuanping Cheng

ABSTRACT: Carbon dioxide in a supercritical form can be stored in deep unmineable coal seams in great quantities than in the free state. However, other components of gases in coal seams can affect the storage conditions of the supercritical CO₂. Using the critical opalescence of carbon dioxide as a critical point criterion, with the experimental temperature 10~40 °C, and pressure 10 MPa, the critical points of ten groups of CH₄-CO₂ binary system and CH₄-CO₂+coal sample ternary system were measured with a high pressure visualization device with a sapphire window. The effects of different contents of CH₄ on the supercritical CO₂ were studied. The results show that, the critical temperature and critical pressure of the CH₄-CO₂ binary system varies with CH₄ content. When the CH₄ component concentration is less than 10%, the critical temperature range of the CO₂-CH₄ binary system is between the critical temperatures of the two components, it is lower than that of pure CO₂ and higher than that of pure CH₄. The critical pressure increases with the increase of CH₄. After adding coal, CO₂-CH₄ binary mixture critical opalescence phenomenon still occurs, but the critical temperature is slightly higher than that of the corresponding CH₄-CO₂ binary system, while the critical pressure is lower than that of the binary system.

INTRODUCTION

Supercritical CO₂ means the state over the critical temperature ($T_c = 31.02$ °C) and pressure ($P_c = 7.38$ MPa). The self-diffusion coefficient and viscosity of supercritical CO₂ are close to that of the gas, it has a similar flow behavior as the gas, similar density to liquid, and more kinetic energy than liquid (Zhang, 2000). Supercritical CO₂ can be captured and stored in coal seams because coal has a strong adsorption for it (IPCC, 2005; IPCC, 2007; Reeves, 2004). There are two positive reasons to inject supercritical carbon dioxide into coal seams: 1) it is one of the effective ways to reduce greenhouse gas emissions by storing supercritical carbon dioxide in the deep unmineable coal seams (Yu, *et al.*, 2008; Ye, *et al.*, 2007; Reeves, 2004). 2) During CO₂ injection and storage, the efficiency of coalbed methane (ECBM) can be effectively improved (Van Bergen, *et al.*, 2006; Yamaguchi, *et al.*, 2006; Mazzotti, *et al.*, 2009; Mazumder and Wolf, 2008, Gunter, *et al.*, 2004; Day, *et al.*, 2008). But it can also have a negative effect. There are a large number of unmineable coal seams in China, they can capture and store a large quantity of CO₂ from industrial production. Once the coal seams are mined in the future, serious coal and gas (CO₂) outbursts will be caused. The main gases in coal seams are CH₄ and CO₂, and the vast majority is CH₄. CH₄ and coal have great impact on the critical temperature and pressure of CO₂. Therefore the study of supercritical parameters of CO₂ in coal (critical temperature and critical pressure) and the impacts of other gases on the supercritical CO₂ is significant.

In general, the critical parameters of supercritical CO₂, CO₂ binary and multi-component systems can be measured by the fixed volume high visibility method (Belandria, *et al.*, 2010), variable volume high visibility method (Johannes, *et al.*, 1990; Nieuwoudt, *et al.*, 2002; Rand, *et al.*, 2001); supercritical fluid chromatography (SFC) (Zhao, *et al.*, 1996), and high-performance liquid chromatography (HPLC) (Lee, *et al.*, 1995; Cui, *et al.*, 1991, 1995). There are a few critical parameters of the CO₂-CH₄ two-phase system, and they were mentioned in Bezanek *et al.*, 2002. For example, the CO₂-CH₄ system P-V-T-X relations around the phase boundaries were researched (Arai, *et al.*, 1971). The pressure range covered was from 2.026 to 15.198 MPa and experimental temperatures were 288 K, 273 K, and 253 K. The values of the critical pressure and temperature for the CO₂-CH₄ system agreed well with those of Donnelly and Katz (1954). The phase equilibrium composition and critical properties of the CO₂-CH₄ system were measured at 298.1 K and 301.0 K by an improved high-pressure vapor-liquid equilibrium device (Bian, *et al.*, 1993). Thiéry *et al.* (1996) described that modified SRK EOS are successful for predicting near-critical conditions of nonpolar mixtures of CO₂-CH₄. The predicted results agreed with the experimental data (Al-Sahhaf *et al.*, 1983). Xu *et al.*, (1992) studied the vapor-liquid equilibrium of the CO₂-CH₄ binary system at 298.36 K using a static high-pressure equilibrium device. The parameters of critical region were measured and the interactive calculation of the experimental data were done with a modified

Peng-Robinson equation. The data and model can be used for gas separation process simulation calculations and engineering design. The above research was from the phase equilibrium properties of the CO₂-CH₄ binary system without involving the phase equilibrium state of the presence of coal.

Using the critical opalescence of carbon dioxide as a critical point criterion, the critical points of ten groups of CH₄-CO₂ binary system and CH₄-CO₂+coal sample ternary system were measured in the lab with a high pressure visualization device with a sapphire window. Based on the test data, the effects of different contents of CH₄ and coal samples on the supercritical CO₂ were studied. At the same time, this study provided the basis for testing supercritical CO₂ in the Haishiwan mining area of Yaojie Coal Mine.

The coal samples used for these measurements were collected from coal seam No.2 in the Yaojie Coal Mine, in Gansu province, China. The original carbon dioxide concentration in this mine ranges from 30% to 98%, which experienced violent outbursts of carbon dioxide in 1978 (Zhang, 1992). The currently measured temperature of coal seams in the mine is 31-38 °C, and gas pressure exceeds 7.5 MPa.

EXPERIMENTAL SECTION

Experimental reagent

The required high purity gas CO₂ (99.999%) and mixed gas 98.16% CO₂+1.84% CH₄; 96.50% CO₂+3.50% CH₄; 95.75% CO₂+4.25% CH₄; 90%CO₂+10%CH₄ were purchased from a Nanjing special gas plant.

Coal sample preparation

The crushed samples with moderate levels of metamorphism, were screened and divided into two groups, one of particle size 0.2 to 0.25 mm and the other with 1 to 3 mm particles, dried two hours under 105 °C vacuum. Parameters of the coal sample were determined according to China standards: GB/T212, DL/T 1030-2006 and GB/T 217-1996. Coal density was measured using the automated apparatus Micropore Structure Analysis Apparatus-Pore Sizer 9510, made in the USA (Table 1).

The samples, examined by petrographic methods, were cut parallel to the bedding plane. Petrographic analyses were performed with the use of a Jenapol polarising microscope, equipped with a 50×immersion lens and a 10×microscope eye-piece. Maceral analysis (see Table 1) indicated that the coal samples dominated by vitrinite and inertinite, where the amount of inertinite in coal sample was more than 47%. The moderately ranked coal was brittle and fissured. the vitrinite of the coal samples was mostly devoid of pores because its empty cells were filled with gelinite

Table 1 - Properties and petrographic analysis of coal samples (Wu, *et al.*, 2010)

Properties Parameters		Petrographic analysis	
Depth(top) (m)	1305	Vitrinite	48.68%
Mad (%)	1.01	Inertinite	47.35%
Aad (%)	3.35	Liptinite	2.85%
Vdaf (%)	30.1	Mineral substance	1.14%
Fcd (%)	69.43	Reflectivity R	0.9310
Porosity (%)	8.6%		

Experiment device

Based on literatures (Ye, *et al.*, 2007), we design a high pressure visualization device with a sapphire window to measure critical values of CH₄-CO₂ binary system and CH₄-CO₂+coal sample ternary system (see Figure 1). The experimental device mainly consists of a visual autoclave, pressure systems, constant-temperature system, vacuum system, data acquisition system, and fast imaging system. The experimental device schematic diagram is shown in Figure 2. A frontal view and cross section of the view cell are shown in Figures 3 and 4.

The visual autoclave is the core of the experimental device made in stainless steel. Its body cavity is an oval-shaped vessel, and the volume is 100 ml. A magneton equipped with the electromagnetic stirrer is set in the bottom of it.

Around the autoclave body is fitted a thermocouple, and in it are two high-precision four-wire PT-100 temperature control sensors which can accurately monitor the inside temperature. The experimental temperature range is 0 to 150 °C, digital temperature display instrument value: 0.01 °C; and control temperature sensor accuracy is ± 0.1 °C. There are pressure sensors in the air intake manifold line of the visual autoclave to accurately measure the inside pressure. The maximum pressure that can be measured is 30 MPa, the maximum pressure of the sensor is 40 MPa, and the measurement accuracy is ±0.02 MPa.

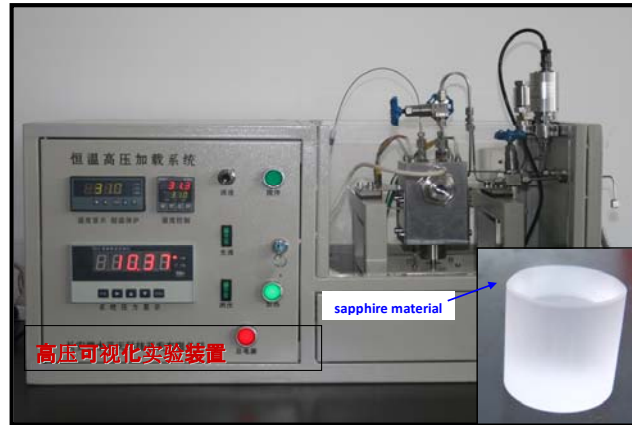
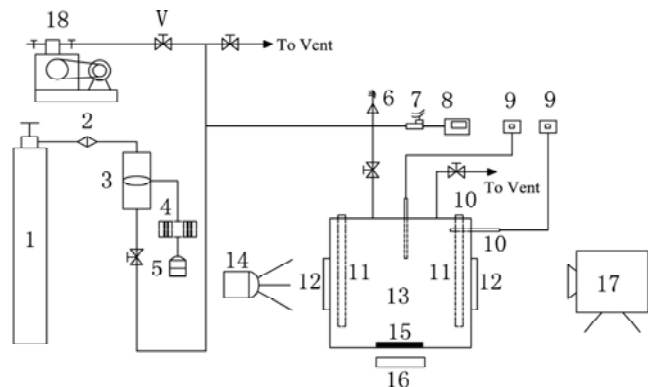


Figure 1 - High pressure visual



1 - gas cylinder; 2 - filter; 3 - booster pump; 4 - frozen compressed air dryer; 5 - air compressor; 6 - safety valve; 7 - pressure sensor; 8 - pressure digital display instruments; 9 - temperature display instruments; 10 - thermocouple; 11 - electric heat bar; 12 - visual transparent window; 13 - visual cell; 14 - light; 15 - magneton; 16 - electromagnetic stirrer; 17 - rapid imaging system; 18 - vacuum pump; V - cut-off valve

Figure 2 - Schematic diagram of the high pressure visual apparatus

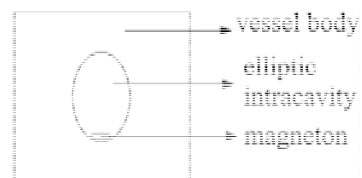
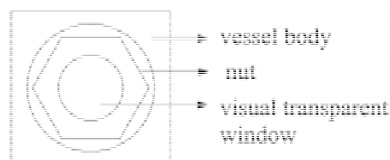


Figure 3 - Frontal view of the view cell Figure 4 - Cross section of the view cell

The visual autoclave window is made of analysis class sapphire material (h is 2.5 mm and d is 2 mm of sapphire cylinder). Through the sapphire window the sample state and transformation process under high pressure can be directly observed, and the gas-liquid interface disappearance and critical opalescence phenomenon can be clearly observed.

The experimental process

Gas test

To inject the tested gas into the autoclave body through the high-pressure pump (The air from the system was purged by pressurizing the system to 1MPa with the tested gas and then depressurizing the equilibrium cell. Before injection, the body of the autoclave was washed with the tested gas three times and then discharged to exclude air and other gases, and ensure the purity of the gas); to start magnetic stirring, adjust the temperature and pressure of the test equipment, observe the supercritical state of the phase process through the visual window. The temperature was then lowered slowly through the cooler, lower the pressure slowly by gas release, and carefully observe the state in the autoclave. Until the recurrence phase transition within the autoclave, the phenomenon of critical opalescence occurs, record the temperature and pressure at this time, which is the measured critical temperature and critical pressure. To ensure the accuracy of the results, each test is repeated five times measurements received and their average values calculated.

Testing with coal sample

Put 30 g dry coal sample with particle size about 1-3 mm into the autoclave reactor and keep the coal sample surface from exceeding one-third of the visual window to avoid the adsorption expansion of coal gas hindering the video window. After vacuum degassing of the coal sample for six to eight hours at 80 °C, the tested gas was injected. Critical parameters testing is the same with the pure gas testing.

RESULTS AND DISCUSSION

Using a high pressure visualization device with a sapphire window to measure critical values of CH₄-CO₂ binary system and CH₄-CO₂+coal sample ternary system, based on the critical opalescence of carbon dioxide as a critical point criterion, the critical points of the CH₄-CO₂ binary system and CH₄-CO₂+coal sample were measured. The effects of different contents of CH₄ on the supercritical CO₂ were studied. There is no literature reports regarding the critical point data of CH₄-CO₂+coal samples. In this test, the experimental temperature is 10~40 °C, pressure 10 MPa below, The critical temperature and pressure variation with the composition contents were measured and the results are shown in Table 2.

Table 2 - T_c and P_c experimental data of different systems with supercritical CO₂

Number	Components	T _c /K	P _c /MPa
1	CO ₂	31.05	7.35
2	98.16% CO ₂ +1.84%CH ₄	29.58	7.46
3	96.50% CO ₂ +3.50% CH ₄	28.74	7.49
4	95.75% CO ₂ +4.25%CH ₄	27.27	7.53
5	90% CO ₂ +10%CH ₄	15.21	8.13
1'	CO ₂ +coal	31.07	7.33
2'	98.16% CO ₂ +1.84%CH ₄ +coal	30.00	7.44
3'	96.50% CO ₂ +3.50% CH ₄ +coal	28.82	7.48
4'	95.75% CO ₂ +4.25%CH ₄ +coal	27.50	7.50
5'	90% CO ₂ +10%CH ₄ +coal	16.12	7.66

The results in Table 2 and Figure 5 show how the critical temperature and critical pressure of the CH₄-CO₂ + coal system vary with the CH₄ contents. When the CH₄ concentration is less than 10%, the critical temperature of the system is between the critical temperatures of CO₂ and CH₄, which are both lower than the CO₂ critical temperature and higher than the CH₄ critical temperature, the critical pressure increases with the increasing CH₄ contents (it agrees with the reported phase diagram, Swanenberg (1979), see Figure 6). The critical temperature of the CH₄-CO₂+coal system is slightly higher than that of the CH₄-CO₂ binary system, while the critical pressure is lower than that of the CH₄-CO₂ binary system, especially when the concentration of CH₄ component is equal to 10%, the critical pressure of the CH₄-CO₂+coal system is 7.66 MPa, significantly lower than that of the CH₄-CO₂ binary system (8.13 MPa).

It is difficult to measure the critical parameters, and the opalescence phenomenon of the critical points is difficult to capture, the colors of critical points of different components are also different, the experimental results show that (see Figure 6), the color of opalescence phenomenon of the CO₂-CH₄ binary system critical point is yellow-brown, the color becomes dark with the increase of methane content, and the color of pure CO₂ critical opalescence is light yellow. The color of opalescence phenomenon of the CO₂-CH₄ system critical point is lighter than that of the corresponding CO₂-CH₄ binary. With CO₂ phase transition,

the gas-liquid separation interfacial phenomena will occur near critical points, as shown in Figure 6D. When the pressure has an instant decrease to the critical points, the carbon dioxide ice inside the autoclave will block the window, as shown in Figure 6E, it is necessary to be careful to control the experimental pressure and temperature and thus the critical parameters may be measured.

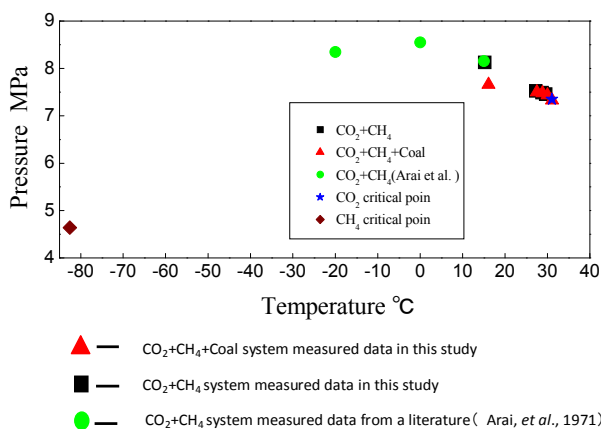
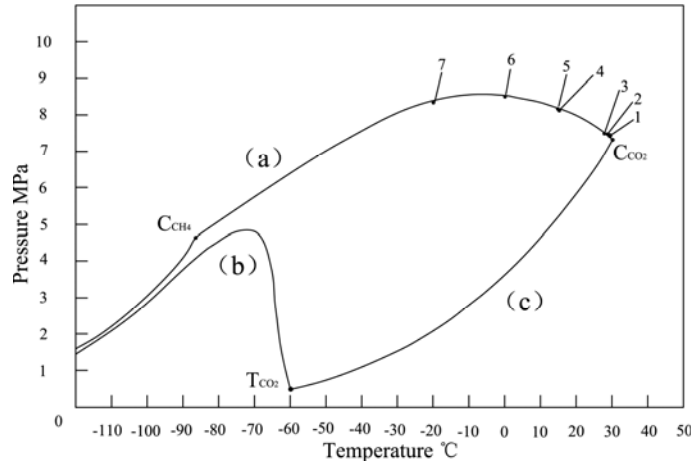


Figure 5 - The supercritical parameters of the CO₂-CH₄ system



Figure 6 - Pictures of critical points of different components of the CO₂-CH₄ binary system and CO₂-CH₄+coal system

In order to verify the accuracy of this test method, the critical values of pure CO₂ were measured, the measured critical temperature is 31.05 °C and pressure 7.35 MPa, which agrees with the theoretical values (Zhang, 2000). At the same time, comparing the critical pressure and critical temperature of the different component CO₂-CH₄ binary system and different component CH₄-CO₂ system phase diagrams (Swanenberg, 1979) (see Figure 7) with the test results of Arai (1971), there is good agreement. The locus of critical points for all bulk compositions is the so-called critical curve of the first order (a), connecting C_{CO₂} and C_{CH₄}, it shows that, in general, liquid-gas equilibria shift towards lower temperatures at increasing X_{CH₄} at the low –temperature side the two-phase liquid gas field intersects the univariant triple point (solid-liquid-gas equilibrium) curve^(b) between L and V. The triple point curve extends from the triple point of pure CO₂ (T_{CO₂}) to the quadruple point of the system CO₂-CH₄. The curves labeled (c) are the boiling curves of the unary systems CO₂ (Weast, 1975) and CH₄ (Zagoruchenko, *et al.*, 1969)



1 - 98.16%CO₂+1.84%CH₄; 2 - 96.5%CO₂+3.5%CH₄; 3 - 95.75%CO₂+4.25%CH₄;
4 - 90%CO₂+10%CH₄; 5 - 94% CO₂+6%CH₄; 6 - 89.1% CO₂+10.9%CH₄; 7 - 82.73%CO₂+17.27%CH₄

Figure 7 - Composite phase diagram of the system CO₂-CH₄. The dotted 5, 6, 7 is the experimental data are those of Arail *et al.* (1971) and dotted 1, 2, 3, 4 are data from this test.

CONCLUSIONS

The critical parameters of the CH₄-CO₂+coal system were studied with a high pressure visualization device with a sapphire window. The experimental temperature is 10~40 °C (equal to the actual temperature of coal seams), and pressures are all below 10 MPa. The critical temperature of the CO₂-CH₄+coal system is between the critical temperatures of CO₂ and CH₄, which are both lower than the CO₂ critical temperature and higher than the CH₄ critical temperature.

To compare the results and critical parameters of the CO₂-CH₄ system, the opalescence phenomenon is found, and the colour is lighter than that of the CO₂-CH₄ system. The critical temperature is higher than that of the CO₂-CH₄ system and the critical pressure is lower than that of the CO₂-CH₄ system. When CH₄ composition concentration is less than 10% and there are coal samples, the critical values of the CO₂-CH₄ system change on different levels, indicating that the coal has a certain influence on the critical parameters of the CO₂-CH₄ system. The critical values with coal samples become more complicated. This may be because the Yaojie Haishiwan coal is outburst coal, it has great adsorption capacity, the adsorption can change the ratio of gas components, the critical pressure becomes greater, and the possible reason may be the change of gas composition.

The critical parameters of CO₂-CH₄+coal system in this study can provide a reference to CO₂ storage in coal seams, and they are close to the related parameters in actual coal seams of Haishiwan Mine of Yaojie Coal and Electricity Company (the actual measured temperature is 31-38 °C, coal seam gas pressure exceeds 7.5 MPa, the highest CO₂ content in coal seams is up to 98%). According to that, there may be supercritical CO₂ in the coal seams of Yaojie Haishiwan Mine.

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