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Supercritical CO_2 extraction of organic matter from coal based on CO_2 sequestration in deep coal seams

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To evaluate the potential for mobilizing organic matter in coal during CO_2 sequestration into deep coal beds, three coal samples of different rank were extracted with supercritical CO_2 (Sc-CO_2) using a self-assembled experimental device. The results showed that the extract yields decrease with the increase in coal rank, extraction temperature or coal particle size. Sc-CO_2 extraction yields of lignite, bituminous and anthracite coal sample with a size less than 0.2 mm were 749, 218 and 201 mg/kg on a dry, ash-free basis at 40 ℃, respectively. Most of the small molecular organics in coal could be extracted at 40 ℃ with Sc-CO_2, especially for low-rank lignite and high-rank anthracite. Although Sc-CO_2 has a strong dissolution effect on small coal molecules, medium and high pressure (> 7 MPa) did not favor the diffusion of the extract from coal into the CO_2-free phase. The main control factors in Sc-CO_2 extraction of different rank coals may be different, e.g., the dissolved-organics quantity for lignite, the extraction temperature for bituminous coal, and the pore structure of coal for anthracite. These results demonstrate that Sc-CO_2 dissolved small organic molecules trapped within coal will be mobilized with CO_2, which is important to evaluate CO_2 sequestration into deep coal seams.

Key words: Supercritical, CO_2, Extraction, Coal, Sequestration.

INTRODUCTION

The injection of CO_2 into deep coal seams can not only enhance the recovery of coal bed methane, but also sequestrate CO_2 [1-3]. However, there are many unknowns and gaps in our knowledge to understand sequestration process [4]. This gap of knowledge is due in part to an incomplete understanding of the physical and chemical interactions between CO_2 and coal [5,6]. The possible effect of CO_2 sequestration on environmental quality is not known due to the interactions. For example, CO_2 injected into coal seams may mobilize organic matter from the coal matrix. In the event of CO_2 leakage from the coal bed, this organic matter may be transported into adjacent aquifer units and compromise water quality [7-9].

Solvent extraction of coal has been used to obtain valuable information about coal structure and organic matter in coal [10,11]. Supercritical CO_2 (Sc-CO_2) can extract some valuable compounds from plant matter to replace conventional organic solvents [12-14]. Sc-CO_2 can dissolve small organic molecules and their presence in the coal makes it necessary for researchers to consider Sc-CO_2 extraction of coal [8, 15]. Soluble small molecules from coal not only affect the migration of CO_2 in coal seams [16], but also pollute groundwater [17], causing serious environmental safety and health (ES&H) problems [1].

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There have been some works on Sc-CO_2 extraction of coal. Reucroft *et al*. [18] and Larsen [19] reported that CO_2 storage in coal is not a simple adsorption, but is dissolution. Kolak and Robert [8] reported that the total measured alkane concentrations extracted from the coal samples ranged from 3.0 mg/kg (anthracite) to 64 mg/kg (lignite) of dry coal. Karacan [20] reported that some organic matter in coal can be dissolved in CO_2 at long-term contact of coal with CO_2.

In this paper, Sc-CO_2 extraction of coal samples with different rank was carried out with a self-assembled extraction device at a given pressure and temperature. The dissolution by Sc-CO_2 of small organic molecules involved in CO_2 injection in coal seams was discussed. The results can lay the foundation for studying CO_2 migration in coal reservoirs, prediction of reservoir pressure change, coal seam permeability and ES&H problems.

EXPERIMENTAL

Experimental apparatus and materials

Experimental apparatus

The basic configuration of the self-assembled device for Sc-CO_2 extraction, built on the basis of the classical Sc-CO_2 extraction system, is shown in Fig. 1 [21-25].

The essential parts of the experimental device mainly include pressurization for CO_2 injection, coal extraction, collection and enrichment of extracts, and extraction yield measurement. (1) The part of Sc-CO_2 pressurization and injection provides clean Sc-

CO_2. This part includes a CO_2-cylinder, a booster pump for CO_2 pressurization, a needle valve to open/cut off CO_2 access to the extraction cell, a CO_2 storage tank to remove organic matter from CO_2, and an air-compressor for driving the booster pump. (2) The extraction part can be used to extract organic molecules from coal with Sc-CO_2, including an extraction cell (using a dust filter paper), a manometer for determiation of CO_2 pressure in the extraction cell, a needle valve to control CO_2 flow yield, and a water bath for constant extract temperature. (3) Extracts collection part mainly includes a needle valve, two collection vessels, a restrictor to keep the flow-rate constant, an anti-volatilization conduit to avoid extracts volatilization with CO_2, a solvent for trapping extracts, and an ice bath for keeping extracts at low temperature. (4) In the Extracts measurement part the extracts are separated from the solvents and their quantity is determined using a nitrogen blowing system to remove the solvent and an analytical balance to obtain the extract mass.

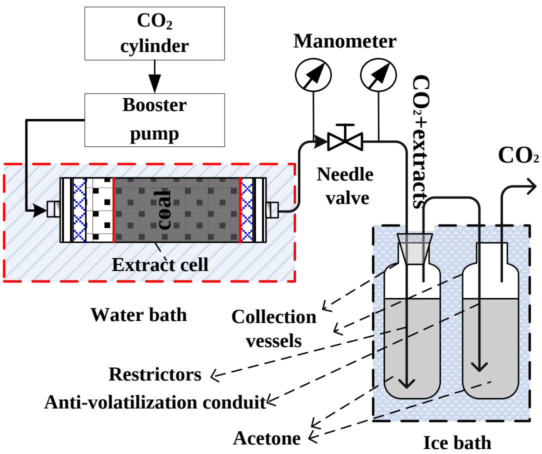

Fig. 1. Simplified diagram of the experimental apparatus

Materials

To investigate the effect of coal rank on Sc-CO_2 extraction, the extraction experiments were carried out using Neimeng bituminous coal, Shanxi anthracite and Yinni lignite. The quality indices of the three coals are shown in Table 1.

The main experimental procedures are shown in Fig. 2, including sample preparation, CO_2 injection and its leak detection, extraction of coal, collection of extract, solvent removal and determination of extraction yield.

Experimental procedure

About 100 g of air-dry coal sample was put into an extraction cell. The temperature of the water bath was set to the adopted value, the pressure in the gas storage tank was increased to about 20 MPa by the booster pump.

Table 1. Coal quality indices of coal samples

Coal sample	Proximate analysis (wt %)			
	Moisture M_{ad}	Ash A_{ad}	Volatile matter V_{ad}	Fixed carbon FC_{ad}
Yinni	6.89	9.06	42.09	41.96
Neimeng	3.87	7.51	32.65	55.97
Shanxi	2.87	10.51	8.29	78.33

After about 10 min, CO_2 was injected into the extraction cell. The pressurized CO_2 injection operation was completed when the pressure in the extraction cell was stabilized to a set value (10 MPa) for 2 h with repeatedly pressurized CO_2, which means 2 h of static extraction.

Two 5 mL portions of acetone were added to the two collection vessels, respectively, the restrictor was inserted into the first solvent vessel, and the anti-volatilization conduit was inserted into the second vessel.

The extraction program consisted of a 2-h static (no-flow) step followed by a dynamic (flow) step at a flow rate of approximately 5 mL/min. After the extraction, the solvent was transferred into a weighing vial, and was evaporated under a gentle stream of nitrogen. The extract in the vial was weighed and Sc-CO_2 extraction yield of coal was calculated by Eq. (1).

$$\eta_{daf} = \frac{100 m_E}{m_C\left(100 - M_{ad} - A_{ad}\right)} \times 10^6 \tag{1}$$

where η_{daf} is the extraction yield of coal expressed on a dry, ash-free basis, mg/kg; m_E is the mass of the extract, g; m_C is the mass of experimental coal sample, g; M_{ad} and A_{ad} are the moisture and ash content on an air-dry basis in coal, respectively (Table 1), %.

The process of Sc-CO_2 extraction included extraction of raw coal and re-extraction of the extracted coal. Sc-CO_2 extraction of raw coal was carried out at 40, 60 and 80°C. The extracted raw-coal residue at 40°C (EC40) was re-extracted with Sc-CO_2 at 60°C and the extracted EC40 residue at 60°C (EC60) was re-extracted with Sc-CO_2 at 80 °C.

The collection of extracts includes one-stage extraction and multi-stage extraction. The one-stage extraction means that the extracts are continuously collected without replacement of the solvent during the whole extraction process, and multi-stage extraction means replacement of the solvent at different pressure drop stages.

RESULTS AND DISCUSSION

Single-stage extraction of Raw Coal

In order to comprehensively understand the effect of coal rank and temperature on CO_2 extraction, the extraction was carried out under static conditions at 10 MPa for 2 h, followed by dynamic extraction of raw coal at 40, 60 and 80 °C. To ensure that the Sc-CO_2 extract can be completely removed from the coal voids by CO_2, the CO_2 pressure in the extraction cell was continuously reduced from 10 MPa to atmospheric pressure with a flow rate of 5 mL/min. The ratio of extraction yield to CO_2 density (η_{daf}/D) was used to explain the effect of CO_2 density (D) on the extraction. CO_2 density (D) at 40, 60 and 80 °C at 10 MPa was 628.61, 289.95 and 221.60 kg/m^3, respectively, calculated by the SW equation [26].

Extraction yields of coal and ratio of yield to CO_2 density (η_{daf}/D) for Yinni, Neimeng and Shanxi coals are shown in Table 2. It can be seen from Table 2 that under the same temperature conditions, the yield decreases with the increase in coal rank, e.g., at 40 °C the η_{daf} value of Yinni lignite is nearly 3.5 times that of Neimeng bituminous coal, and 3.7 times that of Shanxi anthracite. Lignite contains a large number of small organic molecules and a larger pore size while anthracite has a lower number of free small molecules and smaller pore size structures [27].

Table 2. Sc-CO_2 extraction yield and ratio of the yield to CO_2 density (η_{daf}/D) for raw coal

T (°C)	Extraction yield η_{daf} (mg·kg^{-1})			η_{daf}/D (kg·mg·kg^{-1}·m^{-3})		
	Yinni	Neimeng	Shanxi	Yinni	Neimeng	Shanxi
40	749	218	201	1.19	0.35	0.32
60	648	191	172	2.23	0.66	0.59
80	528	154	150	2.38	0.69	0.68

It can be seen from Table 2 that the extraction yield of all coals decreases and the η_{daf}/D value increases with the increase in temperature. This is consistent with the inversely proportional solubility of small molecules to the CO_2 density [28]. The acting force between small organic molecules in coal and the coal matrix decreases when the temperature is raised, which helps extracts to dissociate from coal and be extracted by CO_2. On the other hand, elevated temperature favors the expansion of coal pores and the diffusion of small organic molecules into the free phase of the coal matrix. The decrease in extraction yield with the increase in temperature indicates that the dissolution of small organic molecules in coal is an important factor to control Sc-CO_2 extraction of coal, rather than the interaction of CO_2 with the coal matrix and the pore structure of coal.

Single-stage re-extraction of extracted coal

In order to assess the remaining extracts in Sc-CO_2 extracted coal, the extracted coal from raw coal at 40 °C (EC40) and the residual coal of EC40 at 60 °C (EC60) were re-extracted with Sc-CO_2 at 60 and 80 °C, respectively. Just like the raw coal, EC40 and EC60 were extracted at 10 MPa, and the extracts were continuously collected at a flow rate of 5 mL/min until depressurized to 0 MPa. Table 3 shows the extraction yield of raw coal, EC40 and EC60 and their distribution for Yinni, Neimeng and Shanxi coal.

Table 3. Sc-CO_2 extraction yields of extracted coals and their proportion at different temperatures

T (°C)	Coal	η_{daf} (mg.kg^{-1})			Proportion (%)		
		Yini	Neimeng	Shanxi	Yinni	Neimeng	Shanxi
40	Raw coal	749	218	201	83.61	48.14	71.86
60	EC40	36	179	66	3.99	39.51	23.53
80	EC60	111	56	13	12.4	12.35	4.61
Total	-	896	453	280	100	100	100

It can be seen from Table 3 that the Yinni coal has the highest total-extraction yield (896 mg/kg), Neimeng coal takes the second place (453 mg/kg), and Shanxi has the lowest extraction yield (280 mg/kg). The total extraction yield of Yinni coal is nearly 2 times that of Neimeng bituminous coal and 3.2 times that of Shanxi anthracite.

The extraction yield of raw coal at 40 °C is higher than that of re-extraction for EC40 at 60 °C and EC60 at 80 °C, and the percentage of the extraction yield of raw coal in Yinni, Neimeng and Shanxi coal is 83.61%, 48.14% and 71.86% at 40 °C, respectively. Comparing the extraction yields of raw coal and extracted coal (EC40 and EC60), it can be found that most of the small organic molecules dissolved in Sc-CO_2 can be extracted, especially for Yinni lignite.

For the extraction yield of extracted coal (EC40) at 60 °C, Neimeng coal has the highest re-extraction yield (179 mg/kg), Shanxi coal takes the second place (66 mg/kg), and Yinni lignite has the lowest extraction yield (36 mg/kg). The percentage of the extraction yield of EC40 in Neimeng, Shanxi and Yinni coal is 39.51%, 23.53% and 3.99 % at 60 °C, respectively. The re-extraction yields of EC60 at 80 °C are 111, 56 and 13 mg/kg for Yinni lignite, Neimeng coal and Shanxi anthracite at 80 °C, accounting for 12.40%, 12.35% and 4.61% of the total extraction yield, respectively.

Sc-CO_2 extraction depends not only on temperature, pressure [29] and nature of the extract [30], but also on the pore characteristics of coal [31,32], the existing forms of extracts and the force between the extracts and the coal matrix [33,34].

Less than 50% of the Sc-CO_2 extract is extracted from Neimeng raw-coal at 40°C. So, small molecules in Neimeng coal are difficult to extract from coal. The vapor pressure of small molecules in the coal matrix and the pore size in coal increase with temperature increase, the elevated temperature is favorable for the extraction of small molecules in bituminous coal with medium pore size. The elevated temperature is favorable for extraction of Neimeng bituminous coal.

Up to 83.61% of the Sc-CO_2 extract is extracted from Yinni lignite at 40 °C and only 3.69% and 12.40% of the extractable extract from the coal is extracted frm the EC40 and EC60 at 60 and 80 °C, respectively. The small organic molecules of Yinni lignite are easily extracted by Sc-CO_2 at 40 °C and the molecules being not easily extracted in the EC60, are extracted by Sc-CO_2 at 80 °C due to the increased vapor pressure of the small organic molecules. The effect of elevated temperature on Yinni lignite is not significant, and most of the extracts can be extracted at 40 °C.

With increasing coalification (progressing from lignite to bituminous coal to anthracite), the amount of lower-molecular-weight species (guest molecules) in coal and the quantity of micropores both increase, but the quantity of macropores and functional groups decreases. The increase in rank is accompanied by a conversion of alicyclic structures to aromatic layer. So, Shanxi anthracite displays the lowest extraction yield and is at the second place as regards extraction difficulty.

Small organic molecules in lignite are easily extracted at 40 °C, the main controlling factor being the quantity of such molecules in coal. Raw coal and extracted coal (EC40 and EC60) for Neimeng coal both have certain amounts of extracts at all extraction temperatures, which indicates that the temperature is the main controlling factor for bituminous coal. Anthracite is also easily extracted at 40 °C, but the main controlling factors of the extraction are the coal pore structure and the force between CO_2 and coal for anthracite.

Multiple extraction with single-stage

Single-stage extraction yield of Yinni lignite is the highest, so this coal was used to investigate the residual extracts obtained by multiple extraction. The raw coal with size less than 0.2 mm was extracted 3 times at 40 °C; the extracted coal at 40 °C (EC40) was re-extracted 2 times at 60 °C, and the extracted coal at 60 °C (EC60) was re-extracted 2 times at 80 °C. The extracts were continuously collected at a flow rate of 5 mL/min until depressurized to 0 MPa, just like the single-stage above. Table 4 shows the yield of multiple extraction with single-stage and its distribution.

Table 4. Extraction yield of multiple-stage extractions with single-stage and their proportion of raw-coal and extracted-coal samples for Yinni coal

T (°C)	Coal	No.	η_{daf} (mg.kg^{-1})			Proportion (%)	
			Each	Subtotal	Total	Each	Subtotal
40	Raw coal	1	753	801	979	94.01	81.82
		2	20			2.50	
		3	28			3.49	
60	EC40	1	35	55		63.64	5.62
		2	20			36.36	
80	EC60	1	84	123		68.29	12.56
		2	39			31.71	

Multi-stage extraction

The main aim of this part was to investigate whether the extract exists at pressures below CO_2 critical pressure of 7.38 MPa. In order to dynamically understand the change in extraction yield, coal extraction experiments were carried out by collecting extracts at different pressure stages, called multi-stage extraction in the following text. Neimeng and Shanxi coals were selected for multi-stage extraction because Neimeng coal only has 48.14% extraction yield (Table 3) at 40 °C and Shanxi coal is anthracite with smaller pore size.

Neimeng coal

Table 5 shows the extraction yield of Neimeng coal at different pressure drop stages. 3 depressurization stages of extraction (10-9 MPa, 9-7 MPa and 7-0 MPa) were carried out for raw coal at 40 °C. The extraction yield of raw coal with a depressurization stage of 7-0 MPa was the highest, and that at 9-7 MPa the lowest. Although CO_2 at a pressure below 7 MPa is in non-supercritical state, the extraction yield was the highest in the depressurization stage at 7-0 MPa. This indicates that there are extracts in the non-supercritical CO_2, which are easy to diffuse into free phase of CO_2 at a lower pressure. In addition, the total extraction yield, , 197 mg/kg with the pressure drop of 3 times (solvent removal), is lower than the 218 mg/kg (Table 2) with the single-stage extraction (one solvent-removal). This may be caused by the loss of extracts during nitrogen blowing and natural solvent removal.

EC40 was extracted with CO_2 two times at 60 °C, the first extraction being carried out with 3 depressurization stages (10-8 MPa, 8-6.5 MPa and 6.5-0 MPa), and the second with 2 stages (10-6.5 MPa and 6.5-0 MPa). The re-extraction yield at high pressure (10~8 MPa for the first time and 10-6.5 MPa for the second time) was zero, and the second extraction yield (20 mg/kg) of EC40 was significantly lower than the first one (161 mg/kg). This means that most of the extracts in EC40 can be extracted with one extraction.

To investigate whether CO_2 has a high extraction yield of Neimeng coal at a lower pressure, CO_2 extraction of Neimeng coal was carried out at a pressure below 7 MPa at 40 °C. The extraction yield was about 3 mg/kg, which indicates that CO_2 in non-supercritical state has a very low extraction capacity for Neimeng coal.

Table 5. Sc-CO_2 extraction yields of raw coal and extracted coal for Neimeng coal under different depressurization stages

T (℃)	Coal	No.	Pressure (MPa)	η_{daf} (mg.kg^{-1}) Each	Subtotal	Total
40	Raw coal	1	10～9	25	197	423
			9～7	20		
			7～0	152		
60	EC40	1	10～8	0	161	
			8～6.5	25		
			6.5～0	136		
		2	10～6.5	0	20	
			6.5～0	20		
80	EC60	1	10～7	10	45	
			7～5.5	25		
			5.5～0	10		

The re-extraction of EC60 is divided into three depressurization stages (10-7 MPa, 7-5.5 MPa and 5.5-0 MPa) at 80 °C. It can be seen from Table 5 that the extraction yield of EC60 at 80 °C is lower. The extraction yield of Neimeng coal is 423 mg/kg with 4-fold extraction and 11 depressurization stages, which is lower than that of the three-fold extraction (453 mg/kg). This may be due to the loss of extracts during solvent removal mentioned above.

Shanxi coal

The extraction yield with a 10-7.5 MPa depressurization stage was the highest and that at 7.5-5.5 MPa the lowest.

The extraction of EC40 was carried out at 60 ℃ with 2-fold depressurization (10-7.5 MPa and 7.5-0 MPa). It can be seen from Table 6 that the extraction yield at a depressurization of 10-7.5 MPa is obviously higher than that at depressurization stage of 7.5-0 MPa.

Just like EC40 extraction, the extraction of EC60 was carried out at 80 ℃ with 2-fold depressurization (10-7.5 MPa and 7.5-0 MPa). No extracts were detected at depressurization stage of 10-7.5 MPa, and the extraction yield of EC60 was very low at a depressurization stage of 7.5-0 MPa.

The extraction yield of Shanxi coal is 264 mg/kg with 7-fold depressurization, which is lower than that of the 3-fold extraction (280 mg/kg). Similar to that of Neimeng coal, the loss of extract during solvent removal will result in a lower extraction yield for the multi-stage extraction.

Table 6. Sc-CO_2 extraction yields of raw coal and extracted coal for Shanxi coal under different depressurization stages

T (°C)	Coal sample	Pressure (MPa)	η_{daf} (mg.kg^{-1}) Each	Subtotal	Total
40	Raw coal	10-7.5	95	190	264
		7.5-5.5	27		
		5.5-0	68		
60	EC40	10-7.5	50	62	
		7.5-0	12		
80	EC60	10-7.5	0	12	
		7.5-0	12		

Effect of coal size on extraction

In order to investigate the effect of coal size on the extraction, Neimeng raw coal with coal size less than 6 mm was extracted 3 times at 40 ℃, EC40 and EC60 were extracted 2 times at 60 ℃ and 80 ℃, respectively. Table 7 shows the extraction yield of Neimeng coal with coal size less than 6 mm.

Table 7. Sc-CO_2 extraction yields of raw coal and extracted coal samples of Neimeng coal (<6mm)

T (°C)	Coal	No.	η_{daf} (mg/kg) Each	Subtotal	Total
40	Raw coal	1	22	53	152
		2	13		
		3	18		
60	EC40	1	11	24	
		2	13		
80	EC60	1	40	75	
		2	35		

As can be seen from Table 7, Sc-CO_2 extraction yield of Neimeng coal with size less than 6 mm is much lower than that sized below 0.2 mm. The coal particle size significantly affects the extraction yield and the latter decreases when the coal particle size increases. Coal with a lower particle size is favorable for the diffusion of CO_2 into the coal pores, but also will favor the diffusion of small organic molecules dissolved in CO_2 into CO_2-free phase.

The extraction yield of EC60 at 80 °C (75 mg/kg) is higher than that of EC40 at 60 °C (24 mg/kg). The increase in temperature could effectively expand the micropores of coal and increase the vapor pressure of small organic molecules. Elevated temperature results in that CO_2 more easily diffuses into the micropores of coal, dissolves the small molecules in coal, and extracts are more favorable for entering CO_2 free phase.

CONCLUSIONS

Sc-CO_2 extraction yield of coal decreases with the increase in coal rank. The extraction yield of Yinni lignite, Neimeng bituminous and Shanxi anthracite coal samples with particle size less than 0.2 mm is 749, 218 and 201 mg/kg on a dry, ash-free basis at 40 ℃, respectively. With the increase in extraction temperature, the extraction yield of coal decreases. The main small molecular organics in coal could be extracted at 40 ºC with Sc-CO_2, especially for low-rank lignite and high-rank anthracite. The extract yield of coal with non-supercritical CO_2 was very low, but the highest quantity of Sc-CO_2 extracts was collected at a pressure below 7 MPa. The shrinkage of the coal matrix facilitates the diffusion of the extracts into CO_2 free phase and a higher yield of extract will be obtained at a lower pressure (<7 MPa). The extraction yield increases with the decrease in coal size. The main controlling factors of Sc-CO_2 extraction of coal rank are different. Under the present experimental conditions, the main controlling factor for Inni lignite is the amount of small organic molecules, for Neimeng bituminous coal - the extraction temperature and for Shanxi anthracite - the micropore structure in coal.

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