Evolution of pore structure, submaceral composition and produced gases of two Chinese coals during thermal treatment

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Abstract:

To better understand coal performance during underground coal gasification, coal combustion and in-situ enhancement of coalbed methane recovery by heating, the variable gases generation and pore structure of subbituminous coal and bituminous coal with thermal treatment related to organic petrology are investigated. Multiple experiments including organic petrology analysis from an optical microscope, gases analysis from thermogravimetry coupled with mass spectrometry (TG-MS), pore structure analysis using scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and nuclear magnetic resonance (NMR) were constructed to simulate the thermal treatment of coal at elevated temperatures. The coal petrology results exhibit that the submacerals that contribute to the gases generation were significantly reduced when temperature was over 400 °C, especially for collinite, cutinite, resinite and telalginite. And there was only a slight difference in CO_2 content between subbituminous coal and bituminous coal, which was reduced in the bituminous coal. On the other hand, thermal decomposition of

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functional groups of submacerals at over 400 °C also creates more seepage pores and fractures. Pore structure analysis indicates that the adsorption pores were observed with aggregates of plate-like particles leading to slit-shaped pores below 200 °C. However, the massive seepage pores and fissures (over 35.42% in volume) were created in the high-temperature-treated coals, especially between 400 °C and 600 °C. Furthermore, the dominant seepage pores and fissures formed at high temperature (>400 °C) are due to the pyrolysis of semifusinite and collinite submacerals. These investigations may serve to characterize gases generation and pore evolution of coal during thermal treatment.

Keywords: gas generation; pore structure; coal; thermal treatment; coal petrology

Nomenclature

TG-MS	thermogravimetry coupled with mass spectrometry
SEM	scanning electron microscopy
MIP	mercury intrusion porosimetry
NMR	nuclear magnetic resonance
C	collinite
Cu	cutinite
R	resinite
Ta	telalginite
MiS	microsporinite
MaS	macrosporinite
LD	liptodetrinite

CBM	coalbed methane
UCG	underground coal gasification
T_E	time interval of echoes, ms
T_W	a waiting time, ms
T_2	transverse relaxation time, ms

1. Introduction

Currently, China has a vast amount of unrecoverable coal resources due to depth, access and other factors, which may provide an opportunity for an in situ technology to exploit potential energy (e.g., coalbed methane) from coal. Coalbed methane (CBM) recovery, which produces less than 1% of the total coal seam's energy, is feasible in this environment [1]. Although CBM has less contribution to energy, it is essential in the context of reducing greenhouse gas emissions, contributing to the development of the gas industry and maintaining the safety and economic advantages of mining [2]. Furthermore, enhancing CBM recovery from underground coal with in situ thermal treatment may provide the possibility for more massive gases recovery [3] and [4]. For the past decade, thermal treatment technology has observed promising acceptance as an effective tool for improving reservoir properties and increasing gases content in coal seams. Existing researches [4] and [5] have been conducted to simulate coal thermal treatment with the goal of improving reservoir properties and increasing gases content, which differs significantly from underground coal gasification (UCG) [6], [7] and [8]; it indirectly heats the coal to pyrolysis temperatures rather than injecting air/oxygen mixtures to directly gasify the coal. This process produces CH_4, H_2 and CO_2 due to the thermochemical decomposition reaction and gasification of organics without oxygen as Kerogen pyrolysis [9]. Therefore, an improved capability for suspending operations and reducing the risk of subsidence for in situ coal thermal treatment offers substantial merits, compared with UCG. By heating coal in situ, the coal is decomposed from long chain organics to synthetic gases, liquids, and char. This process has the potential to produce large portions of the available fuels from the coal in situ. Although in situ coal thermal treatment requires extra energy [4], [10] and [11], these additional energy resources may prove that this process is worthwhile. Different property transformations occur during coal pyrolysis: (1) the first stage (25-300 °C) is the dry gas stage. In this stage, moisture and adsorbed gases are desorbed until ~200 °C. The coal structure keeps steady. When the temperature is increased from 200 °C to 300 °C, thermal decomposition occurs for the low-rank coals; (2) the second stage (300-550 °C) is the coal pyrolysis stage, which involves forming gases and tars. Before 400 °C, the coal turned softer and congealed into a viscous mass. In the range of 400 to 550 °C, gases increase and coal tar precipitates. The residual coal mass increasingly stiffens and solidifies just as char. Gas produced during 450-550 °C includes light aromatic hydrocarbon and a long chain fatty substance. The petrophysical properties of coals (including pore fractures, adsorption and permeability, etc.) significantly change in this stage [5], [12], [13] and [14]. The condensation reaction is not common (3) in the third stage (550-1000 °C) or the carbocoal stage [15], in which polycondensation reactions occur. The aromatic layers often become even more ordered, realistic density increases and a breakthrough degree of aromatization exists. The gas generation is due to thermal decomposition of the functional groups. Generated gases will flow/burst out of the mass, which produce more gas-burst pores. The gases/liquids generation and petrophysical variation are the keys for energy extraction. Although existing research has investigated the process of gases generation and petrophysical variation during coal pyrolysis [4], [5], [6], [7], [13] and [14], the pore changes and gases generation related to coal submacerals are still unclear.

In response to the findings above, the objective of the research presented here is to investigate the pores and gases change of the coals (a subbituminous coal and a low volatile bituminous coal) with thermal treatment related to coal submacerals. The NMR and modified MIP could be the promising methods to investigate the pore structure. Pore structure is the key to CBM preservation and production. Therefore we put a lot of work into understanding the pore development. Recently, a few researchers [11], [13] and [14] have conducted the experiments of heating on coal reservoir from the perspective of enhancing CBM production. In this research, thermogravimetry coupled with mass spectrometry (TG-MS) was employed to investigate the decomposed products from these two rank coals during pyrolysis (25-1200 °C) as related to coal petrology. Although only two Chinese coals (a subbituminous coal and a low volatile bituminous coal) were analyzed, the detailed and systematic investigations would provide a better way to understand the variable gases generation, pores development and submacerals evolution of two Chinese coals with thermal treatment. Therefore, it is meaningful to know well the effects of submacerals on pore development and valuable gases generation. Secondly, the pathways including pores (e.g., pore shape, pore surface, pore volume/size distribution) and fractures features of coals during pyrolysis were studied with raising temperatures up to 600 °C. An investigation into petrophysics of the two thermal treated coals by multiple methods (SEM, MIP, N_2 adsorption, NMR etc.) were systematically and detailed conducted. Finally, the effects of the parameters (coal rank, particle size, pyrolysis temperature, and coal submacerals) from the adopted experiments on pore structure development of coals with varying ranks were discussed.

2. Experiment and methodology

2.1. Samples and coal basic analyses

A subbituminous coal ($R_{o,\ m}$ 0.57%) from the southern Junggar Basin and a low volatile bituminous coal ($R_{o,\ m}$ 1.68%) from the eastern Ordos Basin were gathered from active mines (Table 1). Blocks of these two samples, which were approximately 3 kg each, were carefully collected and wrapped and then delivered immediately to the laboratory. The standard coal analysis, optical microscope analysis and TG-MS analysis were executed for both of these two samples. SEM, MIP, N_2 adsorption and NMR analyses were conducted for the low volatile bituminous coal to investigate the pore changes by thermal treatment targeted at 25 °C, 200 °C, 400 °C and 600 °C. The maximum vitrinite reflectance ($R_{o,\ m}$), proximate analysis and macerals analysis for these two thermal treated coals were measured in a previous study [16], and these figures were provided in Table 2.

2.2. Pyrolysis with TG-MS

TG-MS analysis was used by a Rigaku TG-DTA coupling with an Omnistar MS, which were connected by a conduit from the TG to the MS. The TG conditions, as explained in our previous research [5] and [14] have a 10 °C/min heating rate at 25-1200 °C; sweep nitrogen, 60 cm^3/min and constant sample weight 25-50 mg. Small fractions of gases will be used for MS analysis [17]. The MS was scanned over a mass to charge ratio (m/z) of 1 to 100 amu with metering intervals of approximately 19 s. The products of coal pyrolysis were determined and compared with the temperatures in the multiple ion detection modes (Fig. 1).

2.3. Pore characterization for thermal treated coal

MIP is an important and widely used technique for quantitatively characterizing porous materials

[18], [19] and [20]. In this study, the measurements range in pressure up to 206 MPa with an accessible pore throat as small as 3.6 nm. N_2 adsorption/desorption was performed using an ASAP 2020 rig at 77 K with the range of $0.01 \leq P/P_0 \leq 0.996$ and an equilibrium time of 6 min. Experimental and data processing procedures for N_2 adsorption and MIP parameters were the same as in previous research [19] as listed in Table 3.

NMR experiments were designed as follows: first, one block of the coal sample was prepared for thermal treatment and separated into four groups corresponding to 25 °C, 200 °C, 400 °C and 600 °C. After finishing thermal treatment, the samples were prepared for NMR experiments. NMR measurements adopted a MiniMR-60 rig with a resonance frequency of 23.1 MHz. The parameters consisted of time interval of echoes (T_E) of 0.3 ms, a waiting time (T_W) of 4 s, echo numbers of 3000, scanning numbers of 128, and an environment temperature of 25 °C. The NMR results are provided in Table 4.

3. Results and Discussions

3.1 Gases release related to coal submacerals

For CBM recovery in China, the CBM production in low rank coal normally can reach over 10000 m^3 per day but the duration can not last long. However the CBM production in high rank coal lower than 1000 m^3 per day is common and it normally lasts more than ten years. Therefore when a coal reservoir is more or less suitable for CBM recovery, pyrolysis modeling should be linked to submacerals. Figure 1 depicts mass loss and gas generation of subbituminous coal and low volatile bituminous coal during pyrolysis at 25-1200 °C under the flow of nitrogen. Based on TG-MS, the weight change can be negligible during this low heating stage. Previous researches [7] and [21] have confirmed that dehydration mainly occurs at temperatures lower than 350 °C, together with small fractions of gases. In this study, the ion current from MS of subbituminous coal (Fig. 1a) is in the range of 0.93 to 1.41×10^{-10}A with the mass to charge ratio (M/Z) of 18, which indicates that partial moistures were released at a low heating stage, especially at temperatures between 110 and 200 °C. For the bituminous coal, this process occurred after the temperatures reached 180 °C (Fig. 1b). For the original coal, the main submacerals in subbituminous coal are collinite (C), cutinite (Cu), microsporinite (MiS), liptodetrinite (LD), resinite (R), macrosporinite (MaS) and telalginite (Ta) (Fig. 2a_1, a_2; Table 5). Most of these submacerals were well preserved and without breakage; however, a small part of coal submacerals had changed somewhere, which is confirmed by the reflected fluorescence microscopy (Fig. 2b_1, b_2). First, oil stains appeared in this low heating stage, which may indicate that some oil-prone submacerals (e.g., telalginite, microsporinite, macrosporinite and resinite) should be decomposed. Second, the response intensity of reflected fluorescence was reduced and pores (the black area in Fig. 2b_1, b_2) have been generated during this low heating stage. This indicates that the heating process dislodged volatiles and moistures and caused alterations to the pore structure in the low heating procedure (lower than 200 °C) and shows that the escape of volatiles and moistures created more micropores [5]. When the temperature is over 300 °C, a drastic evolution of gases takes place. The massive gases generated during elevated thermal treatment contain H_2O, CH_4, CO_x, C_nH_m, H_2 (Fig. 1). The TG-MS of the subbituminous coal shows that the main gases produced at temperatures between 300-400 °C are H_2O, CH_4, CO and C_2H_4. There was a slight difference in CO_2, which was reduced in the bituminous coal. The methane discharge increased with ascending temperature from 300 °C, arriving a peak at ~400 °C and making up 50-60% of the mass. The gases released from the coals caused the stacking in coal structure [22]. Figure 2c_1, c_2 shows that more oil stains are present in this stage. The massive content of submacerals has been vastly reduced, especially for collinite (C) and cutinite (Cu). Some of the submacerals, such as resinite (R) and telalginite (Ta), have disappeared during this stage. In other words, these submacerals may contribute to the massive gases release. Although heating can partially improve pore accessibility and produce more gas, the tar that is produced could condense and may block the flow paths of the pores [23]; thus the technique of thermal treatment for enhancing CBM recovery is constrained by the temperature. When the temperature reached 600 °C, polycondensation reactions occurred, which is also evidenced by the secondary gases generated during carbocoal transition [5]. The gas generation is closely related to the thermal decomposition of functional groups of organics in coals. The organic masses are pyrolyzed into significant liquid fuels and gases, which can burst out of the mass and then create more pores and fractures as shown in Fig. 2d. At this stage, the main submacerals (such as cutinite (Cu), microsporinite (MiS), liptodetrinite (LD), resinite (R), macrosporinite (MaS), telalginite (Ta)) have been totally decomposed and as a result, generated oil stains. Only partial collinite (C) was saved. Much of the generated gases escaped from the submacerals, which produced multiple gas pores with a diameter of 10-20 micrometers. Figure 2e shows the submacerals, pores and fissures in the original bituminous coal, which indicates that the bituminous coal had gone through a relatively deep coalification process. As a result of this process, many of the submacerals that had existed in the original form had now vanished, especially for the exinite submacerals. From the perspective of produced gases, the subbituminous coal may have advantage in produced gases than the bituminous coal (see tables S1 and S2 in appendix), which indicates that the low rank coal in the southern Junggar Basin should be promising in enhanced CBM recovery by thermal treatment.

3.2 Effect of coal lump/grain/powder size on pore structure

Previous researches [24] and [25] confirm that particle size has an effect on the variation of pore structure during thermal treatment, especially at high temperatures. The Sabine lignite with granular and powder grain sizes was adopted to investigate the probable mechanism of the coal sample size effect for pore structure development in the TG at 800 °C (Fig. 3). This showed that pore volume decreased drastically with an increase of grain size. The pore volume development in both of these two grain sizes has two distinct stages [25]: a fast increasing stage for cumulative pore volume that occurs before 2 nm of pore diameter followed by a steady increment as presented in Fig. 4. Although the boundaries have a discrepancy with 2 nm and 40 nm, there is a consistent trend of pore volume development within the two stages. One assumption is that the transport of volatiles from the interior of the coal to the exterior is constrained in larger grain coals [26], which could cause limited weight loss and pore generation for the granular coal or lump coal than for the powdered coal. The weight loss features of both coal sample sizes during pyrolysis were substantially identical. Nonetheless, in contrast, the TG-MS features of granular and powder lignite from previous research [25] reveal that the higher ion currents that were produced contained small molecular compounds, including H_2O, CO_2, and CH_4. The escape of small molecular compounds corresponds to fundamental changes in the pores during high-temperature thermal treatment (e.g., the loss of functional groups and graphitization) [5].

3.3 Effect of temperature on pore structure

3.3.1 Pore size distribution and coal mass variation

For this study, previous coal pore size classification [27] and [28] was adopted: adsorption pores (<100 nm) and seepage-pores (>100 nm). When mercury intrusion pressure was over 20 MPa, coal pore compressibility had a significant effect on MIP results [29]. The calculation of coal pore compressibility has been documented in existing research [14]; therefore, it will be briefly summarized below. The coal pore compressibility [14], [30] and [31] is defined as:

$$\omega_p = \frac{b(D-3)P^{D-4}}{a+bP^{D-3}} \tag{1}$$

where a and b are constants, P is mercury intrusion pressure, and D is the pore fractal dimension. The MIP result was reevaluated with the coal pore compressibility. Table 6 indicates that pore compressibility decreases with increasing mercury intrusion pressure and thermal-treated temperature. Previous research [14] reveals that the change of organic matter decomposition and the pore structure of coal may have a significant impact on pore compressibility. For the bituminous coal at low temperatures (< 200 °C), pore compressibility greatly changes when the pressure is less than 75 MPa. The compressibility for bituminous coal at 200°C decreases from 20.6×10^{-9} m^2/N to 4.96×10^{-9} m^2/N, which may indicate that the unsound pore structure has an important impact on pore compression. Pore compressibility reaches the maximum for the bituminous coal at 400°C, whereas it decreases when the coal reached 600°C. This could be related to the tar that had been produced and blocked the micropores less than 100 nm.

3.3.2 Pore surface morphology from SEM

Figure 5 demonstrates that there are scattered original pores and fissures within the original state of the coals. When the temperature reached 200 °C, this resulted in partially generated pores and fissures due to thermal expansion and volatile release. During this process, pore surface morphology remained stable, contributing to the upcoming gas burst pore performance. At this point, the closure or segmental closure of pores because of the thermal expansion at low temperatures (<200 °C) may occur [21]. Most of the pores are less than 2 micrometers; however, the pore surface and volume were enlarged due to the removal of volatiles and moistures [14]. When the temperature reached 400°C, massive cylindrical pores were generated due to partial submacerals pyrolysis. The pore morphology of the subbituminous coal changed and was now smooth and regular and in a cylindrical structure with the pore diameter having significantly increased. Residual minerals existed in the cellular structure, which indicates that a chemical sedimentation occurred. The pore morphology of the subbituminous coal treated at 600°C is faveolate, which was created by the decomposition of all of the exinite submacerals as listed in Table 5. Therefore, the pores are mostly gas burst pores, which will produce well connected pathway for gas flow.

3.3.3 Adsorption pores by N_2 adsorption/desorption

Pore-specific surface area and pore size/volume distribution of adsorption pores can be detected by using N_2 adsorption/desorption at 77K [19] and [32]. The results for subbituminous coal indicate that the Brunauer, Emmett and Teller (BET method) pore surface area with elevated temperatures ranges from 0.667 to 0.845 m^2/g and the total pore volume by the Barrett, Joyner and Halenda model (BJH model) is in the range of 3.494×10^{-3}~6.359×10^{-3} cm^3/g. The coals would be soft, and the thermal shrinkage would take place after 400 °C due to the decomposition of organic materials and heat-solid reaction [33]. Therefore, the proportion of adsorption pores decreases significantly after 400 °C, which results in the vast reduction of pore surface area and pore volume, as shown in Table 3. However, the open pores will be increased with the decomposition of the organic matter [5]. The average adsorption pore diameter ranges from 52.07 nm to 81.87 nm when the temperature rises from 25 to 600 °C as shown in Table 3. Hysteresis loops in Fig. 6 show that the precipitous region of the desorption branch resulting in the lower closure point occurs at relative pressure, which is usually an independent innate quality of the poriferous adsorbent but mainly due to the adsorptive nature (e.g., for nitrogen at its boiling point at p/p_0 0.42) [34]. Although the effect of several factors on hysteresis was not completely comprehended, the shapes of hysteresis loops have normally been identified with particular pore structures. The adsorption/desorption isotherms for the samples at temperatures of 25, 200 and 400 °C belong to the Type H3 loop based on the IUPAC classification [34], which does not present any constrained adsorption at high relative p/p_0 and is evidenced by clusters of plate-like particles leading to slit-shaped pores. In contrast, the N_2 adsorption/desorption isotherm of the bituminous coal treated at 600°C belongs to an abnormal type, which may contribute to the adsorbents that tend to non-adsorptive mass and the tar that is produced.

3.3.4 Seepage pores by MIP and NMR

Table 3 exhibits the parameters of MIP at elevated treated temperatures. An interesting phenomenon is that the parameters of MIP at 25 °C are similar with those at 400 °C, whereas the parameters of MIP at 200 °C are similar with those at 600 °C. Although there are similar parameters at different temperatures, a discrepancy still exists. The pore throat radius at 400 °C is the smallest one (88 nm), which should contribute to the massive micropore generation at this stage. The multiple micropores that are generated normally produce low mercury porosimetry saturation. In this study, the massive micropore generation at 400 °C can be confirmed by the lowest maximum mercury intrusion saturation (76.72%) as presented in Fig. 7. The mercury intrusion/extrusion curves are distinct at 200 °C as with other temperatures, which show a well-connected pore size distribution. The pore size distribution remains well connected from 25 to 200 °C, and then becomes complex again. Normally, the seepage pores improved when the temperature reached 200 °C due to the loss of moistures and volatiles. When the temperature reached 400 °C, the amount of seepage pores dropped due to the massive adsorption pores that are generated; however, the seepage pores were promoted again because of the heat cracking of coal macromolecules when the temperature increased to 600 °C.

Pore size distribution of coals can be evaluated by NMR T_2 values (the transverse relaxation time) with water-saturated cores [35] and [36]. The T_2 spectrum, which normally distributes from 0.1 ms to 10,000 ms, offers the PS/VD as seen in Fig. 8. The T_2 spectrum, including the size, number and peak position of the T_2 spectrum can be adopted to investigate coal pores: the T_2 less than 4.04 ms corresponds to adsorption pores; the T_2 over 4.04 ms corresponds to seepage pores; which include the possible microfractures (T_2 over 37.65 ms) in coals. Although the results show that there are variable T_2 spectrums for coals treated at different temperatures, there is a typical trimodal pore size distribution (Fig. 8). The T_2 of adsorption pores is in the range of 0.01 to 0.87ms, 0.01-1.52ms, 0.01-2.01 ms and 0.01-4.04ms corresponding to 25, 200, 400, and 600 °C, respectively (Table 3). There is a clear increase with raising thermal-treated temperatures, which means that heat is an effective tool for improving the adsorption pore size. Previous research [11] has reported a similar trend for coals that had been treated by microwave, which claimed that when the treatment time increases from 0 to 30 s, the peak P1 enlarges and the origin of the spectra moves toward a shorter transverse relaxation time corresponding to a smaller pore size. In contrast, in our study, the seepage pore size had gone through the decrease process and then risen. The T_2 of seepage pores was 5.34-100ms, 1.75-32.75ms, 2.31-86.97 ms and 4.64-100ms. The same situation occurs to the microfractures. The pore/microfractures volume distribution had also changed vastly with the raising treated temperatures. The lowest adsorption pore volume ratio is

15.13 % due to the existence of massive oil stains as demonstrated in Fig. $2c_1$, $2c_2$. The lowest seepage pore volume ratio was 35.42% (600 °C), which indicates that the seepage volume may change to microfractures with a steady increase of 7.91%-29.11%. The total pore volume (represented by T_2 spectrum area) at 25-400 °C increased from 1527.54 to 8630, and then decreased to 7100.13, which means that the pore volume increase mainly contributes to seepage pores and microfractures when the temperature reaches 400 °C. Previous research [5] and [37] reveal that the micropore size distribution of low-rank coal with low temperature treatment was not significantly changed, whereas an immediate increase of the microporosity in coals with high-temperature treatment was observed because of the release of inorganic gases after forming the tar, which is consistent with this study’s findings. When the temperature reached 600 °C, massive adsorption pore volume was generated, occupying 35.47% of the total pore volume (Table 4).

3.4 Pores evolution related to coal submacerals

Table 5 identifies the variation of coal submacerals composition at elevated treated temperatures for both subbituminous coal and bituminous coal. For subbituminous coal, the exinite becomes extinct when the temperature reaches 400 °C. For subbituminous coal, no exinite exists due to the relatively deep coalification with maximum vitrinite reflectance of 1.68%, as shown in Table 1. Although there is no obvious variation of submacerals from optical microscopy (Fig. 9), the TG-MS has revealed that partial volatiles and moistures were released during a low heating procedure (lower than 200 °C), which resulted in changes to the pore structure with more micropores produced (e.g., the P1 peak ratio increased from 33.76% to 44.34% in Table 4). For exinite, a slight volume decrease occurs to resinite, sporinite and exodetrinite when the temperature rises to 200 °C, which corresponds to the minor increase of cutinite. The content of inertinite relatively increases [38]. Resinite was exhausted at a temperature of 400 °C due to pyrolysis. Other submacerals also exhibit an obvious reduction in volume. When the temperature reaches 600 °C and all submacerals of exinite have been decomposed, this may result in average pore radius, pore size/volume and a marked increase in porosity. Previous research [5] has found a significant increase in the pore size/volume and porosity with raising high temperatures, which indicates that a strong expansion of the fractures and pore size/volume took place. For vitrinite in both subbituminous coal and bituminous coal, the general trend is a decrease in volume for telinite and collinite, which indicates that there is a substantial increase in pore volume as the result of raising temperatures. The Fig. 9b shows the newly generated pores in collinite when the temperature reached 400 °C. For inertinite in both subbituminous coal and bituminous coal, semifusinite and fusinite have a relative increase in volume due to the disappearance of exinite and loss of vitrinite. Massive seepages and fissures (or microfractures) were created in the high-temperature-treated coals, especially between 400 °C and 600 °C. The diameters of part pores are over 50 micrometers, as demonstrated in Fig. 9 and are generally present in semifusinite and collinite. However, the mechanism of pore evolution with submacerals structure is still unclear; thus, more research may be necessary to achieve a better understanding of this phenomenon. Therefore, from the perspective of pore evolution, many of adsorption pores were generated below 200 °C, and most of seepage pores or fissures were created at high temperatures over 400 °C when the temperature was constrained below 600°C.

4. Conclusions

In this study, fundamental standard coal analysis, optical microscope analysis and TG-MS analysis combined with pore structure analysis have been conducted on subbituminous coal and bituminous coal during thermal treatment at elevated temperatures to ascertain the effect of temperatures on gases generation, pore structure properties, submacerals and their relations. The following conclusions can be made:

(1) The extensive evolution of gases takes place when the temperature is over 300 °C. The major gases generated during elevated thermal treatment are: H_2O, CH_4, CO_x, C_nH_m and H_2. In this stage, oil stains are also present due to the massive reduction of submacerals contents, especially for collinite (C), cutinite (Cu), resinite (R) and telalginite (Ta). In other words, these submacerals should contribute to the massive gases release.

(2) Pore compressibility decreased with increasing pressure, indicating that unsound pore structure has an important impact on pore compression. Pore compressibility reaches its maximum at 400 °C for the bituminous coal and then decreases until 600 °C, which could be related to the tar that is produced and subsequently blocks the adsorption pores.

(3) The T_2 values of adsorption pores are in the range of 0.01 to 0.87ms, 0.01-1.52ms, 0.01-2.01 ms and 0.01-4.04ms corresponding to 25 °C, 200 °C, 400 °C, and 600 °C, respectively. There is a clear increase in T_2 spectrum with raising thermal-treated temperatures, which means that heat is an effective tool for improving adsorption pore size.

(4) The massive seepage pores and fissures (or microfractures) that were created in the high temperature-treated coals, especially between 400 °C and 600 °C, resulted from the predominant amount of semifusinite and collinite.

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References

[1] R.M. Flores, Coalbed methane: from hazard to resource. International Journal of Coal Geology, 35(1998), 3-26.

[2] C.Ö. Karacan, F.A. Ruiz, M. Cote, S. Phipps, Coal mine methane: a review of capture and utilization practices with benefits to mining safety and to greenhouse gas reduction. International Journal of Coal Geology, 86(2011), 121-156.

[3] K.U. Takahashi, N. Suzuki, H. Saito, Compositional and isotopic changes in expelled and residual gases during anhydrous closed-system pyrolysis of hydrogen-rich Eocene subbituminous coal. International Journal of Coal Geology, 127(2014), 14-23.

[4] K.E. Kelly, D. Wang, M. Hradisky, G.D. Silcox, P.J. Smith, E.G. Eddings, D.W. Pershin, Underground coal thermal treatment as a potential low-carbon energy source. Fuel Processing Technology, 144(2016), 8-19.

[5] Y. Cai, D. Liu, Y. Yao, Z. Li, Z. Pan, Partial coal pyrolysis and its implication to enhance coalbed methane recovery, Part I: An experimental investigation. Fuel, 132(2014), 12-19.

[6] K. Stanczyk, N. Howaniec, J. Smolinski, K. Kapusta, J. Grabowski, J. Rogut, Gasification of lignite and hard coal with air and oxygen enriched air in a pilot scale ex situ reactor for

underground gasification. Fuel, 90(2011), 1953-1962.

[7] A.W. Bhutto, A.A. Bazmi, G. Zahedi, Underground coal gasification: from fundamentals to applications. Progress in Energy and Combustion Science, 39(2013), 189-214.

[8] H. Akbarzadeh, R.J. Chalaturnyk, Structural changes in coal at elevated temperature pertinent to underground coal gasification: A review. International Journal of Coal Geology, 131(2014), 126-146

[9] T.I. Eglinton, S.R. Larter, J.J. Boon, Characterisation of kerogens, coals and asphaltenes by quantitative pyrolysis—mass spectrometry. Journal of Analytical and Applied Pyrolysis, 20(1991), 25-45.

[10] A.A. Eftekhari, K.H. Wolf, J. Rogut, H. Bruining, Mathematical modeling of alternating injection of oxygen and steam in underground coal gasification. International Journal of Coal Geology, 150-151(2015), 154-165.

[11] H. Li, B. Lin, W. Yang, C. Zheng, Y. Hong, Y. Gao, T. Liu, S. Wu, Experimental study on the petrophysical variation of different rank coals with microwave treatment. International Journal of Coal Geology, 154-155(2016), 82-91.

[12] Y.S. Zhao, F. Qu, Z.J. Wan, Y. Zhang, W.G. Liang, Q.R. Meng, Experimental investigation on correlation between permeability variation and pore structure during coal pyrolysis. Transport in Porous Media, 82(2010), 401-412.

[13] Y.Y. Feng, C.F. Jiang, D.J. Liu, W. Chu, Experimental investigations on microstructure and adsorption property of heat-treated coal chars. Journal of Analytical and Applied Pyrolysis, 104(2013), 559-566.

[14] Z. Li, D. Liu, Y. Cai, Y. Yao, H. Wang, Pore structure and compressibility of coal matrix with

elevated temperatures by mercury intrusion porosimetry. Energy Exploration & Exploitation, 33(2015), 809-826.

[15] A. Guerrero, M.A. Diez, A.G. Borrego, Effect of volatile matter release on optical properties of macerals from different rank coals. Fuel, 114(2013), 21-30.

[16] Y. Cai, D. Liu, Y. Yao, J. Li, Y. Qiu, Geological controls on prediction of coalbed methane of No. 3 coal seam in Southern Qinshui Basin, North China. International Journal of Coal Geology, 88(2011), 101-112.

[17] A.M. Rubel, M. Jagtoyen, J.M. Stencel, S.N. Ahmed, F.J. Derbyshire. TG-MS for characterization of activated carbons from coal. In: Symposium on analytical techniques for characterizing coal and coal conversion products American Chemical Society Washington DC, Mefling, August 23-28, 1992. pp. 1206-1213.

[18] M. Mahamud, Ó. López, J.J. Pis, J.A. Pajares, Textural characterization of coals using fractal analysis. Fuel Processing Technology, 81(2003), 127-142.

[19] Y. Cai, D. Liu, Z. Pan, Y. Yao, J. Li, Y. Qiu, Pore structure and its impact on CH4 adsorption capacity and flow capability of bituminous and subbituminous coals from Northeast China. Fuel, 103(2013), 258-268.

[20] Y. Cai, D. Liu, Z. Pan, Y. Che, Z. Liu, Investigating the effects of seepage-pores and fractures on coal permeability by fractal analysis. Transport in Porous Media, 111(2016), 479-497.

[21] Y.M. Yu, W.G. Liang, Y.Q. Hu, Q.R. Meng, Study of micro-pores development in lean coal with temperature. International Journal of Rock Mechanics and Mining Sciences, 51(2012), 91-96.

[22] A. Arenillas, F. Rubiera, J.J. Pis, M.J. Cuesta, M.J. Iglesias, A. Jiménez, I. Suárez-Ruiz,

Thermal behaviour during the pyrolysis of low rank perhydrous coals. Journal of Analytical and Applied Pyrolysis, 68-69(2003), 371-385.

[23] J.S. Bae, S.K. Bhatia, V. Rudolph, P. Massarotto, Pore accessibility of methane and carbon dioxide in coals. Energy & Fuels, 23(2009), 3319-3327.

[24] N.Y. Nsakala, R.H. Essenhigh, P.L. Walker, Characteristics of chars produced from lignites by pyrolysis at 808 °C following rapid heating, Fuel, 57(1978), 605-611.

[25] H. Huang, Y. Wang, F.S. Cannon, Pore structure development of in-situ pyrolyzed coals for pollution prevention in iron foundries. Fuel Processing Technology, 90(2009), 1183-1191.

[26] G.R. Gavalas, Coal Pyrolysis. Elsevier Scientific Publishing Company, Amsterdam, 1982.

[27] Y. Yao, D. Liu, D. Tang, S. Tang, W. Huang, Fractal characterization of adsorption pores of coals from North China: an investigation on CH_4 adsorption capacity of coals. International Journal of Coal Geology, 73(2008), 27-42.

[28] Y. Yao, D. Liu, D. Tang, S. Tang, W. Huang, Z. Liu, Y. Che, Fractal characterization of seepage-pores of coals from China: an investigation on permeability of coals. Computers & Geosciences, 35(2009), 1159-1166.

[29] J.T., Comisky, M., Santiago, B., McCollom, A., Buddhala, K.E. Newsham, Sample size effects on the application of mercury injection capillary pressure for determining the storage capacity of tight gas and oil shales. CSUG/SPE, 149432(2011), 1-23.

[30] W.I. Friesen, R.J. Mikula, Mercury porosimetry of coals: pore volume distribution and compressibility. Fuel, 67(1988), 1516-1520.

[31] Z.H. Qu, G.X. Wang, B. Jiang, V. Rudolph, X.Z. Dou, M. Li, Experimental study on the porous structure and compressibility of tectonized coals. Energy & Fuels, 24(2010),

2964-2973.

[32] M. Firouzi, E.C. Rupp, C.W. Liu, J. Wilcox, Molecular simulation and experimental characterization of the nanoporous structures of coal and gas shale. International Journal of Coal Geology, 121(2014), 123-128.

[33] E.M. Suuberg, S.C. Deevi, Y. Yun, Elastic behaviour of coals studied by mercury porosimetry. Fuel, 74(1995), 1522-1530.

[34] IUPAC, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure and Applied Chemistry, 54(1982), 2201-2218.

[35] R.L. Kleinberg, W.E. Kenyon, P.P. Mitra, Mechanism of NMR relaxation of fluids in rock. Journal of Magnetic Resonance , Series A, 108(1994), 206-214.

[36] A. Dillinger, L. Esteban, Experimental evaluation of reservoir quality in Mesozoic formations of the Perth Basin (Western Australia) by using a laboratory low field Nuclear Magnetic Resonance. Marine and Petroleum Geology, 57(2014), 455-469.

[37] Y. Matsuo, J-i. Hayashi, K. Kusakabe, S. Morooka, Proceedings of the Eighth International Conference on Coal Science, Oviedo. Amsterdam: Elsevier, 1995.

[38] N. Vuković, D. Životić, J.G.M. Filho, T. Kravić-Stevović, M. Hámor-Vidó, J.O. Mendonça, K. Stojanović, The assessment of maturation changes of humic coal organic matter — Insights from closed-system pyrolysis experiments. International Journal of Coal Geology, 154-155(2016), 213-239.

Captions for figures and tables

Fig. 1 TG-MS recorded mass loss and gas generation of subbituminous coal ((a_1) for mass loss and (a_2) for gas generation) and bituminous coal ((b_1) for mass loss and (b_2) for gas generation) during pyrolysis at a rate of 10 °C/min at temperatures between 25-1200 °C.

Fig. 2 The submaceral composition of subbituminous coal and bituminous coal at elevated temperatures form 25 °C to 600 °C (reflection fluorescence with blue light excitation). (a_1): Cutinite (Cu), microsporophyte (MiS), liptodetrinite (LD) and sparse resinite (R) had parallel distribution within collinite (C); (a_2): Cutinite (Cu), Telalginite (Ta), microsporophyte (MiS) and liptodetrinite (LD) had parallel distribution within collinite (C); Telalginite (Ta) is spherical, which has strong fluorescence; (b_1): Cutinite (Cu), liptodetrinite (LD) and sparse resinite (R) had parallel distribution within collinite (C); the fluorescent color of part liptodetrinite (LD) transfer to sepia; (b_2): cutinite (Cu), suberinite (Sub), microsporophyte (MiS), sparse resinite (R) and oil stains (O) had parallel distribution within collinite (C); (c_1): Cutinite (Cu) presents in promiscuous structure in collinite (C), which shows many structures (e.g., straight, curved, ringed). The inside serrated glandular structure vanished. Liptodetrinite (LD) and oil stains (O) exhibited in collinite (C); (c_2): cutinite (Cu) locally concentrates in collinite (C), which presents in many forms (e.g., straight, curved and serrated); liptodetrinite (LD) and occasional oil stains (O) appeared; (d): gas pores (Po) were created in elliptical shape with the diameter ranging from 10 to 100 micrometers. Generally, the direction of macroaxis is roughly consistent throughout. They (Po) distribute in an isolated mode within collinite (C), which were less connected to each other. Little fissures (Fi) were created; (e): No fluorescent components were found in the organics, which should be related to the deep coalification. Massive fissures (Fi) and less pores (Po) were presented within collinite (C), the fluorescence in pores and fissures is from gelatin (J).

Fig. 3 (a): Pore volume distribution of powder and granular Sabine lignite and (b): mass loss of powder and granular Sabine lignite with a heating rate at 50 °C/min (Redrafted from Huang et al., 2009).

Fig. 4 The incremental pore volume with pore size distribution of subbituminous coal at elevated temperatures by N_2 adsorption at 77K

Fig. 5 The pore evolution of subbituminous coal at elevated thermal treatment (scattered original pores and cavity at 25 °C; partial generated pores and fissures due to thermal expansion and volatile release at 200 °C; massive cylindrical pores generated due to partial macerals pyrolysis at 400 °C; faveolate pores created due to the decomposition of all exinite submacerals at 600 °C)

Fig. 6 The adsorption/desorption isotherm for each temperature and the hysteresis loops

Fig. 7 Mercury intrusion/extrusion curves and mercury saturation with pore throat width distribution at each temperature

Fig. 8 The change of trimodal pore size distribution by T_2 spectrums for coals treated at different temperatures

Fig. 9. The submacerals composition of subbituminous coal ((a_1), (a_2), (a_3) and (a_4) for 25 °C, 200 °C, 400 °C and 600 °C, respectively) and bituminous coal ((b_1), (b_2), (b_3) and (b_4) for 25 °C, 200 °C, 400 °C and 600 °C, respectively) after being treated at elevated temperatures (reflection single polarization with oil immersion). (a_1): semifusinite (Sf) existing between collinite (C) and telinite (T), the woody structure was preserved. The cell wall was acutely swelled. Clay fills the cellular cavity. Fissures well developed and disorderly distributed; (a_2): collinite (C) was presented in banded distribution and uniform, which belongs to telocollinite. Telinite (T) and semifusinite (Sf) existed in the band. Clay fills the cellular cavity; (a_3): Fragment of semifusinite (Sf) presents within the mixture of collinite (C) and telinite (T). The cell wall is thick and in square form. The gas pores (Po) exist in semifusinite (Sf). Clays were massively distributed within collinite (C) and telinite (T); (a_4): Semifusinite (Sf) fragment and telinite (T) lenticle appear within collinite (C) with weak reflection color. The gas pores (Po) were massively created, which presented in moniliform distribution. Fissures (Fi) were created in collinite (C); (b_1):

Coal structure was locally mylonitized. Collinite (C) was obviously crushed. A little inertodetrinite (ID) was presented in collinite (C). Fissures (Fi) and gas pores (Po) developed; (b_2): telinite (T) and collinite (C) are in the transformation. Lenticle semifusinite (Sf) presented between them. Most of the woody structures were crushed into small pieces. Clays filled in the residual cellular cavity. Fissures (Fi) and gas pores (Po) were occasionally created; (b_3): Collinite (C) and telinite (T) were presented in hidden banded distribution. Inertodetrinite (ID) was parallel with the band. Fissures (Fi) and gas pores (Po) were created, which were normally less than 10 micrometers; (b_4) The reflection color of the submacerals tends to be uniform after going through high-temperature thermal treatment. The residual submacerals are telinite (T) and a little collinite (C). The gas pores (Po) were extensively created with a general diameter over 50 micrometers.

Table 1 Variation of coal composition at elevated temperatures

Table 2 Proximate analysis of the subbituminous coal and bituminous coal at elevated temperatures

Table 3 N_2 adsorption parameters and mercury porosimetry of bituminous coal at elevated temperatures

Table 4 Nuclear magnetic resonance characterization of bituminous coal at elevated temperatures

Table 5 Variation of coal submacerals composition of subbituminous coal and bituminous coal at elevated temperatures

Table 6 Coal pore compressibility of bituminous coal at elevated temperatures

Table S1 The generated gases and average composition from TG-MS results of subbituminous coal

Table S2 The generated gases and average composition from TG-MS results of bituminous coal