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Characterization of gases and solid residues from closed system pyrolysis of peat and coals at two heating rates

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ABSTRACT

Closed system gold-tube pyrolysis experiments were performed on a peat and two coals (TY: $R_0 = 0.51\%$; SX: $R_{\rm o}$ = 0.94%) at temperatures ranging from 337 to 600 °C and a pressure of 50 MPa with heating rates of 2 and/or 20 -C/h. Solid reaction residues were analyzed microscopically. Yields and chemical and isotopic compositions of the generated gases were also determined. All three samples had similar thermal evolution pathways. With increasing heating temperature, vitrinite reflectances (VR_r) of the residues increased linearly from 0.72% to 4.50%. This increase was lesser for the sample with a higher hydrocarbon generation potential and at faster heating rates. Gas compositions are dominated by $CO₂$ and $CH₄$ throughout the experimental process. Total gas and CH4 yields gradually increase with pyrolysis temperature for all samples. The carbon isotopic compositions of CH_4 generated from the peat are lighter than those from the coals. The $\delta^{13}C_{\text{CH}_4}$ values exhibit a generic evolution pattern which the initial CH₄ is isotopically heavy, then becomes lighter at moderate temperatures, and finally becomes heavier again. Methane produced from the samples at low heating rate has higher transformation ratio than that at high heating rate under the same temperature, so tends to be isotopically heavy after pyrolysis temperature of more than 408 °C.

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1. Introduction

Many researches on coals as a major gas source rock have been carried out [\[1,2\]](#page-4-0), even though coals are now also recognized as potential sources of oil [\[3\].](#page-4-0) The gas generation mechanism and potential of coals are a main aspect of this research. Experimental simulations have been used to determine the gas generation mechanisms and assess the gas generation potential of coals [\[4–17\].](#page-4-0) These studies are mainly based on the cognition that organic matter exposed to higher temperature for a shorter period of time has the same maturity as organic matter exposed to lower temperature for a longer period of time [\[18\],](#page-4-0) suggesting that temperature and time compensate for each other as effects on organic matter maturity. Therefore, it seems to be valid to simulate the natural maturation process in the laboratory by increasing temperature during a short period of time [\[14\]](#page-4-0).

Many simulation experiments on coal have been performed to demonstrate the mechanism of hydrocarbon generation and coalification process (e.g. [\[1–3,14,15\]](#page-4-0)). These simulations have been used in both open and closed systems, and it is found that opensystem pyrolysis is not a good simulation of natural conditions [\[19\]](#page-4-0). The samples adopted in these simulation studies include different coals (e.g. brown coal, bituminous coal and torbanite) and maceral components (vitrinite, exinite and inertinite) of coal [\[14,15,20\],](#page-4-0) the gas generation potential of which is obvious. However, these simulation results are often inconsistent due to the differences of approaches and samples. For example, Behar et al. noticed by pyrolysis experiment that gas generations of coal differ significantly between open and closed systems [\[21\]](#page-4-0). The data obtained using simulation experiment by Yao et al. showed that the yield of gas vary among pyrolysis coal samples [\[15\].](#page-4-0) Therefore, more simulation experiments on coal should be made using different approaches and samples to understand the hydrocarbon generation of coal and provide the basis data for the application study in natural systems. It is also important to understand how small variations in maceral proportion and chemical composition will influence the generation of gas from coals because it would assist in predicting the gas generation potential of the coal that is widely distributed in the natural environment. Nevertheless this simulation comparative study is also not performed. Peat is considered as the original matter of coal and has not undergone deep burial and strong degradation, which normally contains abundant original organic matters. On the other hand, sedimentary environments also affect the initial composition and extent of biodegradation of peat. At present, the simulation experiment is lacked on peat formed under cold climate. So far, many previous simulations have been performed under normal pressures. However, gas from coal is

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generally generated under certain pressure even though there are some disputes about the influence of pressure on gas generation. Therefore, the pyrolysis experiment under high pressure would be better suitable to simulate natural conditions. Furthermore, gas generation and vitrinite reflectance of coal are sensitive to heating time. The most attentive problem at present is the level of the influence of a certain difference of heating time on gas generation and vitrinite reflectance of coal although the effect heating time is well known.

In this study, a peat formed under cold climate and two coals representing slightly different maceral compositions and distinctly different depositional settings were subjected to pyrolysis in a sealed gold tube at temperatures ranging from 337 to 60 °C with heating rates of 2 or 20 °C/h and a pressure of 50 MPa consistently. The kinetic parameters of hydrocarbon gas generation of these samples and the history of hydrocarbon gas generation in the Qinshui Basin were reported previously [\[22\].](#page-4-0) The objectives of this work were to investigate the evolutional features of the gas and vitrinite reflectances during coalification from peat to anthracite stage. Furthermore it aimed at an improved understanding of the influence of slight differences in maceral compositions on these features. The results provide important evidence for understanding the potential and genesis of natural gas derived from coals.

2. Samples and experiments

Two coals and a peat were used for the simulation experiment. The coals were collected from the Late Carboniferous Taiyuan Formation (TY) formed in a shallow epicontinental sea delta environment from Tanggongta Coal Mine of Inner Mongolia Autonomous Region, and the Early Permian Shanxi formation (SX) formed in an epicontinental carbonate platform environment from Liyazhuang Coal Mine of Shanxi Province, China, respectively. The peat was collected at a depth of 3.0–3.2 m from Ruoergai Marsh located in the eastern part of Chinese Qinghai-Tibet plateau with a cold and moist climate. Prior to simulation experiments, the vitrinite reflectance, total organic carbon (TOC), and maceral and elemental compositions in the samples were analyzed. The analytical results are listed in Table 1. The original vitrinite reflectances (R_0) of the two coals are 0.51% and 0.94%, respectively, corresponding to an early stage of coal maturation. The exinite content of the SX coal is slightly higher than that of the TY coal. The H/C atomic ratios indicate that the coals and peat are classified as type III kerogens [\[23\].](#page-4-0)

The samples were first crushed to 120 mesh and then treated with hydrofluoric and hydrochloric acid according to a standard procedure [\[24\]](#page-4-0) in order to remove inorganic matter, and then extracted using a Soxhlet apparatus with a mixture of methanol– acetone–benzene $(1:2.5:2.5, v/v)$.

The treated samples were pyrolyzed in a set of gold tubes with a 40 mm length, 5 mm i.d. and 0.5 mm thick. The gold tubes were welded at one end and 25–50 mg of sample was put in each gold tube. Then, the open end of each gold tube was welded in the presence of argon. The 13 gold tubes were separately placed into 13 high pressure vessels with a 180 mm length, 10 mm i.d. and

Table 1

28 mm thick and heated in a temperature-programmed round furnace [\[25\].](#page-4-0) A 1/8 in. stainless steel tube leads to inside of a vessel to inject high pressure water into the vessel. The internal pressure of the vessels, which were connected to each other with pipelines, was adjusted to 50 MPa by pumping water into the vessels before heating. It maintained automatically by pumping water into or out of the vessels during pyrolysis experiments. The pressure acted on powdered samples through the deformed gold tube. The pyrolysis experiments were performed at heating rates of 2 and 20 C/h in the range of 337–600 \degree C. Two heating rates represent different heating times in the pyrolysis experiments. Namely, pyrolysis time spent at heating rates of 2 C/h is 10 times more than that at heating rates of 2 °C/h. There is a fan at the bottom of the furnace to disturb air in the furnace to maintained uniform temperature in the vessels during the experiment. Two thermal couples were used to control temperature. One was put inside a testing vessel which has the sample size as the other 13 vessels to measure inside temperature of the vessel, and the other was put in air near the testing vessel to control temperature of the furnace. We also put a thermal couple into a small hole in wall of each vessel to measure its individual temperature. So in the system, 15 thermal couple was used to measure temperature of inside testing vessel, air in the furnace and individual temperature of each vessel. By all the measures we made temperature errors among the vessels less than 1 ° C.

At defined temperatures, the vessels were quenched to room temperature in cold water and the pressure inside the vessel was gradually reduced to the atmosphere pressure. Then, individual gold tubes were taken out of the furnace and placed in a vacuum line with an internal pressure of less than 1×10^{-4} Pa. The gold tube was carefully pierced using a steel needle put inside the vacuum line to release gases and total gas was measured quantitatively. Molecular characterization and relative quantification of the total gas fraction were carried out with a HP8890 gas chromatograph with an external calibration. Individual gas amounts were then lumped into C_1 , C_{2-5} , and non-hydrocarbons.

The carbon isotopic compositions of $CH₄$ were measured by GC-combustion IRMS with a VG Isochrom II instrument. The GC was equipped with a Poraplot Q column (30 m length \times 0.32 mm i.d.). Helium was used as the carrier gas. The temperature was programmed from 50 to 180 °C at a heating rate of 25 °C/min, and then held at 180 °C for 8 min. Each pyrolysate fraction was measured 2–3 times. The analytical error was less than 0.3‰. The isotopic compositions of the samples being measured are expressed as δ^{13} C values as follows:

$$
\delta^{13}C(\%)=[(^{13}C/^{12}C_{sample}-^{13}C/^{12}C_{standard})/(^{13}C/^{12}C_{standard})]\times1000
$$

All carbon isotopic values were reported in permil $(\%_{o})$ relative to the PDB standard. PDB refers to the belemnite carbonate from the Cretaceous Peedee formation, SC, USA.

The solid residues were recovered and mounted with epoxy into drilled holes on plastic rods. The mounted sample plugs were polished and analyzed for vitrinite reflectance using a Leitz MVP III microscopic photometer system [\[26\]](#page-4-0).

TOC for the starting samples was measured with a LECO CS-334 elemental analyzer. Prior to analysis, the samples were acidified by HCl to remove the inorganic carbon and washed with distilled water followed by drying at low temperature. All TOC values were reported in percent (%) relative to dry weight of the sample.

3. Results and discussion

3.1. Distribution and evolution of vitrinite reflectance

As shown in [Fig. 1,](#page-2-0) the vitrinite reflectance values (R_o) of pyrolysis residues exhibit different distributions among the SX coal, the

Fig. 1. Evolution of the vitrinite reflectance as a function of pyrolysis temperature.

TY coal and the peat. At 20 °C/h and temperature of 337–600 °C, their R_0 values increased from 0.80% to 4.05%, 0.83% to 3.97% and 0.72% to 3.72%, respectively. However, at 2 °C/h and the same temperature scope, their R_0 values increased from 0.98% to 4.49%, 1.07% to 4.5% and 0.96% to 4.19%, respectively. Here the heating rate reflects heating time that affects the vitrinite reflectance values of pyrolyzed residues on the basis of the principle of temperature and time compensate [\[27–30\].](#page-4-0) The low heating rate means that the sample reaching at a given temperature keeps longer heating time compared to high heating rate. The studied results show that 10 fold increase in heating time leads to the differences in R_o values of pyrolyzed residues at temperature of 337–600 °C ranging from 0.18% to 0.44% for the SX coal, 0.24% to 0.53% for the TY coal and 0.24% to 0.47% for the peat (Fig. 1). As temperature rises from 337 to 600 °C, the vitrinite reflectance values of all three samples increase systematically (Fig. 1). This is in agreement with previous simulation works [\[11,27\]](#page-4-0) and many observations in natural samples from various sedimentary basins [\[31\].](#page-5-0) The vitrinite reflectances of pyrolyzed residues from these three samples exhibit an approximately linear increase with pyrolysis temperature (Fig. 1), although Han et al. and Yao et al. reported that the alteration trend of vitrinite reflectance vs. temperature was nonlinear and characterized by four phases [\[14,15\]](#page-4-0). At the same heating rate, there are considerable differences in the vitrinite reflectance among different samples. At the temperatures between 337 and 504 °C with a heating rate of 20 °C/h, the vitrinite reflectances of the peat and SX coal are lower than those of the TY coal, but the vitrinite reflectance of the SX coal exceeds the peat and TY coal at 529 °C. However, at 2 °C/h heating rate the vitrinite reflectances of the peat and SX coal are always lower than those of the TY coal throughout the whole simulation experiment. This phenomenon is possibly related to the nature of the samples, because the SX coal contains higher exinite compared to the TY coal, and the peat has higher H/C value than the coals [\(Table 1](#page-1-0)). The presence of higher exinite and H/C value shows that these samples have a higher hydrocarbon generation potential. It was believed in previous studies that vitrinite reflectance decreased with increasing Rock–Eval hydrogen index (HI = pyrolysis hydrocarbon amount/total organic carbon) in coal [\[32\]](#page-5-0). The results obtained by thermal simulation experiment of lignite also showed that the higher the original hydrogen content in the sample, the slower rate of vitrinite reflectance change [\[33\]](#page-5-0). The results in the present study further confirmed the influence of hydrocarbon generation potential of sample on vitrinite

reflectance [\[32\]](#page-5-0). The results of the artificial simulation experiments performed in this study also demonstrated the thermal evolution process of vitrinite reflectance from peat to anthracite stage.

3.2. Yield of gaseous products

The yields of gaseous products are shown in [Table 2.](#page-3-0) Under the same pyrolysis conditions, the overall yield of gas product from the peat is much higher than that of the coals, and the TY coal higher than that of the SX coal. At the beginning of the experiment, the total yield of gas is high and reaches 314 ml/g Corg at 2 C/h for the peat, but low for the coals. As the pyrolysis temperatures increase, the yield of gas gradually increases for all samples and for the peat at a relatively higher rate compared to the coals. At the end of the heating process (600 °C) and the 2 °C/h heating rate, a total of 1059 ml gaseous products/g Corg is generated from the peat, 352 ml from the TY coal and 247 ml from the SX coal. These results show that the total yield of gas is closely related to the original maturity level of the samples studied under the same pyrolysis conditions. The heating time influence on the total yield of gas was also observed and the total yield of gas is higher at the 2 \degree C/ h heating rate. Ten fold increase in heating time results in that the differences in the total yield of gas at temperature of 337– 600 °C are from 1 to 52 ml/g Corg for the SX coal, 15 to 95 ml/g Corg for the TY coal and 18 to 197 ml/g Corg for the peat.

The variation of $CO₂$ is similar to that of total gas as above, but the variation of hydrocarbon gas is not fully the same [\(Table 2](#page-3-0)). The yield of CH₄ slowly rises below 400 °C and then increases rapidly above 400 °C. The peat has the fastest rate of CH_4 generation and the TY coal the slowest rate; the SX coal has an intermediate rate of CH₄ production. At the end of the heating process (600 °C) with the $2 °C/h$ heating rate, the peat has the highest yield of CH₄ (411 ml/g Corg), the SX coal the second (201 ml/g Corg), and the TY coal the lowest (198 ml/g Corg). At the same time, the yield of CH₄ at the 2 C/h heating rate is higher than that at the 20 C/h heating rate. Thus 10 fold increase in heating time causes that the differences in the yield of CH₄ at temperature of 337–600 \degree C are from 1 to 53 ml/g Corg for the SX coal, 2 to 58 ml/g Corg for the TY coal and 3 to 116 ml/g Corg for the peat.

The yield of C_{2-5} gases firstly increases to the temperature of maximum rate around 430–500 $\mathrm{C}(T)$ peak) and then decreases un-til 600 °C [\(Table 2](#page-3-0)) as a result of their cracking. The difference in the yield of C_{2-5} gases is obvious among these three samples. At the same pyrolysis temperature, the yield of C_{2-5} gases is the highest for the peat, medium for the SX coal, and the lowest for the TY coal. The peak values are about 83 ml/g Corg for the peat and about 11–17 ml/g Corg for the coals. It is also observed that for a given pyrolysis temperature the yield of C_{2-5} gases at the 2 C/h heating rate is higher than that at the 20 \degree C/h heating rate below the peak temperature, whereas it reverses above the peak temperature. This also reflects the influence of heating time on the generation of C_{2-5} gases.

These results above show that the peat yields more volatile components including hydrocarbons, so that it can generate more total gas, CH₄ and C₂₋₅ gases compared to the coals. In addition, the SX coal with slightly higher exinite component compared to the TY coal generated more CH₄ and C₂₋₅ gases, although it has a relative higher maturity. This is consistent with the results obtained by other simulation experiment of maceral components of Tarim coals [\[20\]](#page-4-0).

3.3. Carbon isotopes of CH4

The carbon isotope composition $(^{13}C/^{12}C$ value) of CH₄ in gas from coal is related to the process of formation, thermal maturation, and the maceral composition of coal. For example, $CH₄$

becomes enriched in 13 C with increasing maturation due to the kinetic effect. The carbon isotope composition of $CH₄$ also depends on the maceral type. In general, the exinite-derived CH4 has lighter carbon isotope composition. The carbon isotope compositions of $CH₄$ in the gaseous product from the samples studied are presented in Fig. 2. At 20 °C/h and the same pyrolysis temperature, the carbon

Fig. 2. Changes in isotopic compositions of the gaseous product $CH₄$ as a function of pyrolysis temperature.

isotope compositions of $CH₄$ in the gaseous product range from $-40.9%$ to $-35.2%$ for the peat, $-41.2%$ to $-29.0%$ for the SX coal and -37.6% to -28.6% for the TY coal, respectively. Their average values are -40.0% , -36.0% and -34.0% , respectively. These data indicate that the peat produces the lightest methane of all studied samples, reflecting the peat with more original light isotopic components compared to the two coals. On the other hand, methane produced from the SX coal has lighter carbon isotopic compositions than that from the TY coal, although the SX coal has higher maturity than the TY coal. Previous results showed that coals with high exinite content could generate methane with lighter carbon isotopic values whereas coals with high inertinite content yield methane with heavier carbon isotopic values at the equivalent maturity [\[20\].](#page-4-0) In this study, the SX coal contains slightly higher exinite content and slightly lower inertinite content compared to the TY coal ([Table 1](#page-1-0)). The difference in the carbon isotopic compositions of methane produced by the SX and the TY coals is consistent with previous studies [\[20\]](#page-4-0). The carbon isotopic composition of $CH₄$ from this pyrolysis experiment is initially heavy at low temperature, and then becomes light with increasing temperature, reaches the lightest at temperatures of 360–432 \degree C, and finally becomes heavy again with increasing pyrolysis temperature (Fig. 2). This variety in the carbon isotopic composition of $CH₄$ with increasing pyrolysis temperature is similar to previous studies [\[4,20,34\].](#page-4-0)

On the other hand, relative methane transformation ratio (MTR) for the samples were calculated by normalizing to the highest $CH₄$ yield obtained from the sample at the highest temperature of the $2 °C/h$ heating experiment ([Table 3](#page-4-0)). The obtained MTR results

TR = amount of CH₄/the highest CH₄ yield obtained from the sample at the highest temperature of the 2 °C/h heating.

indicate that the relative amount of CH₄ generated from the 2 °C/h experiment is always significantly higher than for the 20 °C/h experiment at the same temperature owing to the sample keeping longer heating time at low heating rate as discussed above. Thus, methane produced from the 2 °C/h experiment appears to contain more 13 C-enriched components after more than 408 °C and more 12 C-enriched ones before 408 °C, so has a cumulativeness of heavier isotope signal after more than 408 °C and light isotope one before 408 °C compared to the 20 °C/h experiment at the same temperature. These results further demonstrate that the carbon isotopic composition of coal-derived gas in the natural environment is controlled mainly by the nature and maturity of coal and geological time during coalification.

4. Conclusions

The results of this artificial simulation experiments demonstrated the thermal evolution process of gas and vitrinite reflectance from peat to anthracite stage. With increasing heating temperature, total gas and $CH₄$ yields gradually increases for all samples, and the vitrinite reflectances of the samples show a linear increasing trend. In whole pyrolysis process the peat has lower vitrinite reflectance values and yields more hydrocarbon gases compared to the coals, and the slight differences in maceral compositions of the coals obviously influence the vitrinite reflectance values and the generation rate of hydrocarbon gases. The peat also produces lighter methane than the coals, and methane generated from the coal containing slightly higher exinite content and slightly lower inertinite content has evidently light carbon isotopic composition. Results of this comparative study enhanced our understanding of the effects of original evolution levels of coalformed material and slight variance in coal maceral compositions on the generation gas and vitrinite reflectance characteristics.

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