Gas generation from coal: taking Jurassic coal in the Minhe Basin as an example

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Abstract The gas generation features of coals at different maturities were studied by the anhydrous pyrolysis of Jurassic coal from the Minhe Basin in sealed gold tubes at 50 MPa. The gas component yields (C1, C2, C3, i-C4, n-C4, i-C5, n-C5, and CO2); the δ13C of C1, C2, C3, and CO2; and the mass of the liquid hydrocarbons (C6+) were measured. On the basis of these data, the stage changes of δ13C1, δ13C2, δ13C3, and δ13CO2 were calculated. The diagrams of δ13C1–δ13C2 vs ln (C1/C2) and δ13C2–δ13C1 vs δ13C3–δ13C2 were used to evaluate the gas generation features of the coal maturity stages. At the high maturity evolution stage (T > 527.6 °C at 2 °C/h), the stage change of δ13C1 and the CH4 yield are much higher than that of CO2, suggesting that high maturity coal could still generate methane. When T < 455 °C, CO2 is generated by breaking bonds between carbon and heteroatoms. The reaction between different sources of coke and water may be the reason for the complicated stage change in δ13C CO2 when the temperature was higher than 455 °C. With increasing pyrolysis temperature, δ13C1–δ13C2 vs ln (C1/C2) has four evolution stages corresponding to the early stage of breaking bonds between carbon and heteroatoms, the later stage of breaking bonds between carbon and heteroatoms, the cracking of C6+, and coal demethylation, and the cracking of C2–5. The δ13C2–δ13C1 vs δ13C3–δ13C2 has three evolution stages corresponding to the breaking bonds between carbon and heteroatoms, demethylation and cracking of C6+, and cracking of C2–5.

Keywords Jurassic coal • Pyrolysis • Gas generation • δ13C • Stage evolution

1 Introduction

The natural gas generated from different origins provides its formation characteristics during its evolution (Behar et al. 1992, 2008, 2010; Wang et al. 2013). Coal-formed gas has been an important field of natural gas and plays an important role in China’s natural gas resources (Dai et al. 2014). The heterogeneity of coal is strong, and the evolution features of coal-formed gas are more complex than those of other source rocks (Sun et al. 2013). The kinetics of hydrocarbon generation extend the hydrocarbon generation of coal under laboratory conditions to geologic history (Butala et al. 2000; Ping’an et al. 2009; Shuai et al. 2006), which simplifies the gas evolution of the coal. δ13C is one of the most important properties of natural gas. The δ13C of coal-formed methane has obvious evolution stage features (Cramer 2004; Cramer et al. 1998; Liu and Xu 1999), and the δ13C of natural gas could be used to trace the gas origin (Schoell 1980; Song and Xu 2005). The process of gas formation and evolution could be reflected by the δ13C relationship of different carbon numbers (Chung et al. 1988; Peng et al. 2009). The diagram of...
δ^{13}C_2–δ^{13}C_1 versus δ^{13}C_3–δ^{13}C_2 could reflect the maturity of natural gas (Jenden et al. 1993), and the diagrams of ln (C_2/C_3) vs ln (C_1/C_2) and δ^{13}C_1–δ^{13}C_2 vs ln (C_1/C_2) can be used to distinguish the gas origin (Prinzhofer and Huc 1995); these indicators are largely associated with thermal evolution (Tian 2006).

In recent years, there has been increasing attention on the CO_2 generated during the thermal evolution of coal (Fu et al. 2019a; Killops et al. 1996; Kotarba and Lewan 2004; Lewan and Kotarba 2014; Shuai et al. 2013a, b). CO_2 could be generated from organic matter at any maturity stage (Shuai et al. 2013b); at low maturity, CO_2 could be generated from the cracking of kerogen itself, and the disproportionation between organic matter and water could generate CO_2 at the high maturity stage (Seewald 2003; Seewald et al. 1998). The δ^{13}C of CO_2 in natural gas could be used for gas source contrast (Song and Xu 2005), and some post-reformation of natural gas can be reflected by δ^{13}CO_2 (Rice 1993; Zhang et al. 2004).

The evolution of coal-formed gas abundance and the δ^{13}C of gas can be measured by pyrolysis experiments (Behar et al. 1995; Hill et al. 2007; Lewan et al. 1985). Coal has a favorable gas generation ability and low oil adsorption property, liquid hydrocarbons can be generated when R_o% = 0.7, but oil expulsion cannot occur (Cook 1988; Johnston et al. 1991). Therefore, a closed system simulation experiment could reflect the gas generation process from coal, and anhydrous pyrolysis in sealed gold tubes under pressure could simulate the geological condition very well (Behar et al. 2008; Hill et al. 2007; Tang et al. 1996).

Previous hydrocarbon-generation kinetics research on Jurassic coal from the Minhe Basin shows that the mean values of the activation energies of CH_4 and C_{1–5} are 64.55 kcal/mol and 63.93 kcal/mol, respectively, with a frequency factor of 1.0 × 10^{14} s^{-1} (Fu et al. 2019b). However, the stage evolution characteristics of gas generation have not been studied. In this study, the anhydrous pyrolysis of Jurassic coal from the Minhe Basin in sealed gold tubes was simulated. The gas component yields (C_1, C_2, C_3, i-C_4, n-C_4, i-C_5, n-C_5, and CO_2); the δ^{13}C of C_1, C_2, C_3, and CO_2; and the mass of liquid hydrocarbons (C_{n–2}) were measured. Then, the stage δ^{13}C values of C_1, C_2, C_3, and CO_2 were calculated, and the diagrams of δ^{13}C_1–δ^{13}C_2 versus ln (C_1/C_2) and δ^{13}C_2–δ^{13}C_1 versus δ^{13}C_3–δ^{13}C_2 were obtained to study the gas evolution of coal.

2 Experimental

2.1 Sample and closed system pyrolysis

The immature Jurassic coal used in this study was from the Minhe Basin, Gansu Province, China (Fig. 1), and the basic geochemical characterization of the sample is listed in Table 1.

The coal was pulverized via a 100 mesh, and no other chemical treatment was conducted. The pyrolysis experiments were conducted in sealed gold tubes (40 mm × 5 mm). The sample (15–60 mg) was loaded in a gold tube with one end welded closed, and the air was replaced by argon. The open end was then welded closed by TIG (Pulse arc welding) with the closed end protected in room temperature water. The samples in sealed gold tubes were heated in one furnace in 12 separated stainless steel autoclaves. To avoid the influence of phase differentiation, the experiment was conducted at a constant pressure of 50 MPa, in which the fluid phase is basically in a single phase (Fu et al. 2019a, b). Two series of experiments were conducted, and the gold tubes were heated for 10 h from room temperature to 250 °C and then heated to 600 °C with heating rates of 20 °C/h and 2 °C/h. Additional descriptions of the experimental procedure can be found in (Pan et al. 2007; Shuai et al. 2013b; Wang et al. 2013).

2.2 Gas analysis

After the pyrolysis experiment, the gold tube was punctured in a closed system and connected to an Agilent 7890A gas chromatograph (GC) that has a Wasson ECE module for analyzing the gas composition (C_{1–5}, CO_2) using the external standard method to calculate the quantities of each gas component. The GC employed an HP-AL/S capillary column (25 m × 0.32 mm × 0.8 μm) and used helium as the carrier gas. The column temperature was programmed from 60 °C (held for 3 min) to 190 °C (held for 3 min) at 25 °C/min.

2.3 Stable carbon isotope analysis

The δ^{13}C levels of C_1, C_2, C_3, and CO_2 analysis were conducted on an Isoprime 100 mass spectrometer that interfaced an Agilent 6890 GC. The GC was equipped with a CP-Poraplot Q column (27.5 m × 0.32 mm × 10 μm), and helium was used as the carrier gas. The column temperature was programmed from 50 °C (held for 3 min) to 190 °C (held for 5 min) at 25 °C/min. The δ^{13}C of each sample was measured twice, and the average deviation was less than 0.3‰.
The C$_{6-14}$ composition was separated to C$_{6-14}$ and C$_{14+}$ for analysis. After the gas composition was analyzed, the C$_{6-14}$ liquids were collected by a liquid nitrogen cold trap (4 mL, quartz bottle) (Behar et al. 1995) and injected with 3 mL of n-hexane. Then, the gold tube was cut into pieces and put into the bottle to ensure that the C$_{6}$ liquids could be dissolved completely. Deuterated-24-alkanes were used as the internal standard to determine the quantities of the liquids. The analysis was conducted on an Agilent 7890A GC that employed a DM-5 capillary column (30 mm × 0.32 mm × 0.25 µm) and used helium as the carrier gas. The initial oven temperature was 40 °C and held for 5 min, after which the oven was heated to 290 °C with a heating rate of 4 °C/min and held at 290 °C for 15 min. The C$_{14+}$
was ultrasonically extracted by dichloromethane and weighed.

## 3 Results

### 3.1 Liquid (C₆⁺) yield

The yields of C₆⁺ should be the sum of C₆–14 and C₁₄⁺. Table 2 and Fig. 2a show the cumulative yields of the liquid hydrocarbons (C₆⁺) in the experiments. As Fig. 2a shows, the yields of C₆⁺ increased rapidly at low temperature (T < 410 °C), and the maximum yield was 78.17 mg/g TOC (20 °C/h, 406.9 °C). The yield began to decrease rapidly when the temperature > 410 °C because of cracking.

### 3.2 Gas yields

The yields of C₁, C₂, C₃, C₄, C₅, and CO₂ generated from coal pyrolysis are shown in Fig. 2 and Table 2. As a whole, C₂–₅ (Fig. 2b) peaked at 431 °C (2 °C/h) and 478 °C (20 °C/h), which is close to the end of the C₆⁺ liquids cracking. The volumetric productivities of C₂, C₃, C₄ and C₅ were in descending order, and the relationship with temperature was similar. However, the cracking temperature was different and decreased with increasing carbon number; in addition, the cracking temperature was different at different heating rates, which manifested as the temperature became lower during the slow heating rate than during the rapid heating rate.

The yields of methane were low before 410 °C and increased rapidly after 410 °C, which was close to the cracking temperature of the C₆⁺ liquids. The maximum yield of methane was 257.35 mL/g TOC (599.3 °C, 2 °C/h), which was much higher than that of all the other gases. At the same temperature, the gas yield during the slow heating rate was higher than during the rapid heating rate, which was the result of the complementary relationship between time and temperature on the chemical kinetics (Connan 1974).

CO₂ is the most important nonhydrocarbon gas of the coal thermal maturity process (Shuai et al. 2013b; Tang et al. 1996). Figure 2h shows that the yield of CO₂ was significant at 336 °C and much higher than that of the hydrocarbon gases. The yield of methane exceeded that of CO₂ when the temperature was higher than 455 °C (20 °C/h) and 431 °C (2 °C/h), and the maximum CO₂ was

### Table 2 Yields of gases and their δ¹³C value and liquid hydrocarbon generated by pyrolysis experiment

| T(°C) | Rate °C/h | CO₂ (g) | C₁ | C₂ | C₃ | C₄ | C₅ | C₂–₅ (ml/g) | C₆⁺ (mg/g) | δ¹³C₁ (%) | δ¹³C₂ (%) | δ¹³C₃ (%) | δ¹³C₄ (%) |
|-------|-----------|---------|----|----|----|----|----|-------------|-------------|------------|------------|------------|------------|
| 334.8 | 20        | 10.41   | 0.44| 0.04| 0.01| 0.02|   | 0.08        | 8.86        | -31.58     | -24.03     | -24.03     | -24.03     |
| 358.9 | 20        | 18.34   | 1.74| 0.31| 0.11| 0.05|   | 0.01        | 11.47       | -32.52     | -27.69     | -26.23     | -22.27     |
| 382.8 | 20        | 26.41   | 4.79| 1.45| 0.63| 0.16|   | 0.06        | 30.09       | -35.21     | -29.05     | -26.59     | -21.08     |
| 406.9 | 20        | 36.07   | 12.37|4.48| 2.00| 0.28|   | 0.25        | 7.12        | 37.39      | 28.23      | 25.67      | 20.88      |
| 431.0 | 20        | 42.14   | 25.43|8.12| 3.31| 0.49|   | 0.48        | 43.48       | -37.12     | -27.23     | -24.92     | -20.69     |
| 454.9 | 20        | 47.71   | 48.12|12.37|4.42| 0.59|   | 0.60        | 23.64       | -35.42     | -25.92     | -23.79     | -20.60     |
| 478.7 | 20        | 50.18   | 77.78|14.54|3.53| 0.61|   | 0.26        | 18.94       | -33.58     | -24.48     | -21.37     | -21.41     |
| 503.0 | 20        | 54.69   | 116.99|12.53|1.28| 0.19|   | 0.01        | 13.94       | -31.38     | -20.36     | -13.64     | -21.26     |
| 525.0 | 20        | 56.92   | 147.03|7.53| 0.22| 0.01|   | -           | 7.81        | -29.92     | -15.23     | -20.85     | -21.37     |
| 544.0 | 20        | 60.72   | 167.92|3.57| 0.02| -   |   | -           | 6.02        | -29.11     | -9.60      | -21.55     | -21.37     |
| 562.0 | 20        | 68.46   | 187.78|1.62| -   | -   |   | -           | 5.65        | -27.76     | -          | -22.33     | -22.33     |
| 585.0 | 20        | 73.09   | 205.67|0.88| -   | -   |   | -           | 5.65        | -26.96     | -          | -22.33     | -22.33     |

“--” indicates not detected.

(Connan 1974).
Fig. 2 The C_{6+} yields of (a), C_{2,5} (b), C_{5} (c), C_{4} (d), C_{3} (e), C_{2} (f), C_{1} (g), and CO_{2} (h) during the pyrolysis experiments.
112.13 mL/g TOC (599.3 °C, 2 °C/h). The XRD results (Table 3) indicated that the sample contains very small amounts of carbonate minerals, and the detection of liquid HCl showed the same results. The carbonate minerals contained in the sample could not generate such a large amount of CO₂, which means that the CO₂ was mainly from an organic origin.

| Mineral         | Content (%) | Mineral   | Content (%) |
|-----------------|-------------|-----------|-------------|
| Quartz          | 7.19        | Dolomite  | 0.68        |
| Calcite         | 2.05        | Gypsum    | 1.09        |
| montmorillonite | 12.79       | Pyrite    | 3.14        |
| Illite          | 35.00       | Siderite  | 0.75        |
| Kaolinite       | 14.24       | Orthoclase| 1.01        |
| Chlorite        | 19.03       | Hematite  | 1.46        |
| Anorthoclase    | 1.57        |           |             |

### 3.3 The δ¹³C of gases

The δ¹³C values of C₁, C₂, C₃, and CO₂ are shown in Fig. 3 and Table 2. The δ¹³C of C₁–3 decreased with increasing pyrolysis temperature and then began to enrich ¹³C, manifesting as δ¹³C₁ < δ¹³C₂ < δ¹³C₃ at the same temperature and heating rate. Taking 2 °C/h as an example, the δ¹³C₁ decreased over the range of 334.8–383.5 °C and began to enrich the ¹³C after 383.5 °C and the lightest δ¹³C₁ was –37.71‰. Many other pyrolysis experiments of kerogen and crude oil samples have similar changes (Tang et al. 2000; Tian et al. 2007; Wang et al. 2013; Xiong et al. 2004). The δ¹³C of CO₂ ranged from –24.03‰ to 20.62‰, and this is much less than that of hydrocarbon gases and is different from the report of Shuai et al. (2013b), showing that CO₂ became enriched in ¹³C with increasing temperature but increased to –20.74‰ at 358.7 °C and then fluctuated between –20.63‰ and –21.03‰ to 479.0 °C; in addition, with increasing temperature, it became lighter after 479.0 °C.

![Fig. 3 δ¹³C of C₁, C₂, C₃, and CO₂ during the pyrolysis experiment](image-url)
4 Discussion

4.1 Stage $\delta^{13}C$ values of C$_1$, C$_2$, C$_3$, and CO$_2$

The instantaneous changes in $\delta^{13}C$ could not be obtained because of the closed pyrolysis system. To solve this problem, the following formula was used to calculate the stage value of $\delta^{13}C$ according to the law of isotopic conservation and based on the gas yields and $\delta^{13}C$ (Shuai et al. 2013b): 

$$
\delta^{13}C_{Ti} = \frac{(\delta^{13}C_{Ti} \times V_{Ti} - \delta^{13}C_{Ti-1} \times V_{Ti-1})}{(V_{Ti} - V_{Ti-1})}
$$

(1)

where, $\delta^{13}C_{Ti}$ is the stage value of $\delta^{13}C$ from temperature $T_{i-1}$ to $T_i$; $\delta^{13}C_{Ti}$ and $\delta^{13}C_{Ti-1}$ are the cumulative $\delta^{13}C$ values of gases at temperatures $T_i$ and $T_{i-1}$, respectively; and $V_{Ti}$ and $V_{Ti-1}$ are the cumulative volumetric yields of gases at temperature $T_i$ and $T_{i-1}$, respectively.

The stage $\delta^{13}C$ values of C$_1$, C$_2$, C$_3$, and CO$_2$ are shown in Fig. 4. Ethane and propane are generated and cracked during pyrolysis, so $\delta^{13}C_{Ti}$, calculated by Eq. (1), can be divided into two processes. There is a certain temperature
overlap between ethane and propane at the end of the formation and at the beginning of the cracking (Shuai et al. 2006; Tian 2006), so the calculated values that were close to the temperature when cracking began were discarded. As shown in Fig. 4, with increasing pyrolysis temperature, the stage $\delta^{13}$C values of C2 and C3 first decreased and then increased during the generation stage. During the cracking processes, the light carbon ethane and propane were cracked prior because the bond energy of $^{13}$C–$^{13}$C is higher than that of $^{12}$C–$^{13}$C (Arneth and Matzigkeit 1986; Stevenson et al. 1948; Tang et al. 2000). Therefore, the cumulative values of $\delta^{13}$C2 and $\delta^{13}$C3 in Fig. 3 began to increase when the cracking temperature was reached.

The stage $\delta^{13}$C value of C1 is significantly different from its cumulative value. Cramer (2004) explained the evolution of the $\delta^{13}$C value of coal-generated methane according to kinetics and divided methane generation into the following four reaction stages: (1) cleavage of heteroatoms, (2) demethylation reactions, (3) second cracking of long-chain alkanes and cyclic compounds generated, and (4) polycondensation reactions. Taking 2 °C/h as an example, with the increase of pyrolysis temperature, the stage $\delta^{13}$C1 value decreased to −38.85% at 383.5 °C, which means it was close to the end of the reaction stage (1) (Cramer 2004; Liao et al. 2007). After that, the stage value of $\delta^{13}$C1 began to increase, and the peak value of −17.59% was reached at 527.6 °C. This stage corresponded to the second cracking of liquid hydrocarbon ($C_{6+}$) and wet gas ($C_{2.5}$) one after another (Fig. 2a, b), which reflects that reactions stage (2) and (3) occurred (Cramer 2004). Then, the stage value of $\delta^{13}$C1 started to decrease with increasing temperature, and the yield continued to increase which corresponding to the reaction stage (4). However, the changes in $\delta^{13}$C2 and $\delta^{13}$C3 (Figs. 3, 4) and their remaining amounts (Fig. 2) showed that the cracked gases were almost complete and that $\delta^{13}$C became heavier, which means that the methane generated at this stage came from not only the cracking of $C_{2.5}$ but also other reactions that may be the main source of methane. The reaction between water and coke in the higher evolution stage could generate some of the CH4, but as Eq. (2) below shows

$$2H_2O + 2C = CO_2 + CH_4.$$  

(2)

The gas generation yields of CO2 and CH4 of this evolution stage should be equal; however, as Table 2 shows, the increase in CH4 is much higher than that in CO2. Therefore, there must be another origin of CH4. Cramer (2004) points out that the polycondensation reaction is the reason that $\delta^{13}$C1 decreases during this stage and that coal has gas generation potential at this stage.

The stage $\delta^{13}$C value of CO2 was complex and changed between −37.04‰ and −10.67‰, and it is generally believed that the $\delta^{13}$CO2 of an organic origin is less than −10‰ (Dai et al. 1996; Wycherley et al. 1999); in addition, the calculated stage $\delta^{13}$C value of CO2 shows that the CO2 in the experiment was of an organic origin and that the XRD result (Table 3) also supported this view. Shuai et al. (2013b) suggest that the $\delta^{13}$C of organic origin CO2 could be as high as 18‰. However, in this paper, the data do not support this conclusion, which may be due to the complex composition of coal. The stage $\delta^{13}$C value of CO2 changed smoothly before 455 °C (remaining at approximately −20‰), which was significantly higher than the stage $\delta^{13}$C value of methane at the same stage. This is because during this stage, the CO2 is mainly sourced from the cleavage of the heteroatom reaction of coal (Seewald et al. 1998), and the carbon that is attached to the heteroatom is more enriched in $^{13}$C than the aliphatic side chains (Cheng et al. 2009). At the high maturity stage, CO2 is generated from the reaction between H2O and organic matter (Lewan 1997; Seewald et al. 1998). Because of anhydrous pyrolysis, H2O may originate from the pyrolysis of coal or from the bond water in clay minerals (Wang et al. 2013). When the temperature was higher than 455 °C, the stage $\delta^{13}$C value of CO2 changed substantially, which may be related to the different causes of coke (cracking of aromatization carbon or liner carbon) reacting with H2O. In fact, as the experimental temperature increases, the number of free radicals in the reaction system increases accordingly. The generated CO2 should result of the reaction of oxygen free radicals and carbon free radicals. The oxygen free radicals and carbon free radicals here are from the cracking of H2O and coal, respectively. At the same time, we believe that the production of C radicals is mainly affected by temperature and pressure, and the isotope fractionation process is more complicated, which directly leads to the complex characteristics of the $\delta^{13}$C value of CO2.

![Fig. 5 $\delta^{13}$C2–$\delta^{13}$C1 vs. ln C2/C3](image_url)
4.2 $\delta^{13}C_i - \delta^{13}C_j$ vs $\ln C_i/C_j$

The $\delta^{13}C$ of hydrocarbon gases has a good correlation with thermal maturity and source rock (Dai and Qi 1989; Schoell 1983), and the gas composition is very sensitive to thermal maturity (Wang et al. 2013). Therefore, the $\delta^{13}C_i - \delta^{13}C_j$ vs $\ln C_i/C_j$ diagram can be used to indicate the thermal maturity and source rock of natural gas (Hill et al. 2003; Prinzhofer and Huc 1995; Tian et al. 2010). The $\delta^{13}C_2 - \delta^{13}C_3$ vs $\ln C_2/C_3$ diagram based on the pyrolysis experimental data (Fig. 5) shows a significant feature of kerogen pyrolysis gas (Prinzhofer and Huc 1995), which is characteristic of coal.

The $\delta^{13}C_1 - \delta^{13}C_2$ versus $\ln C_1/C_2$ diagram could be used to reflect the maturity of natural gas, the leakage of natural gas and the mixing of thermogenic gas and biogenic gas (Jenden et al. 1993; Prinzhofer and Huc 1995). The closed system pyrolysis experiment could exclude the influences of leakage and biogenic gas, which should only be correlated with the thermal maturity and the sample. The $\delta^{13}C_1 - \delta^{13}C_2$ versus $\ln C_1/C_2$ diagram based on the pyrolysis experimental data (Fig. 6) shows obvious stage changes. Taking 2 °C/h as an example, the first stage was 334.8–358.7 °C, and $C_1/C_2$ decreased with increasing temperature, which means that the increasing ratio of ethane was higher than that of methane (Wang et al. 2013). The $\delta^{13}C_1 - \delta^{13}C_2$ decreased slightly, which was possibly because both methane and ethane were generated from cleavage of the heteroatom side chain, and the isotope fractionation effect of methane was higher than that of ethane. The second stage was from 358.7 to 407.2 °C, corresponding to the end of the cleavage heteroatom reaction. The $C_1/C_2$ almost remained unchanged, and the $\delta^{13}C_1 - \delta^{13}C_2$ decreased rapidly because of high heredibility from the source rock of ethane (James 1983; Xie et al. 1999). The next stage was from 407.2 to 455.3 °C, both the methane and ethane yields were increased because of the cracking of $C_6+$ (Fig. 2) during this interval, and the $\delta^{13}C_1$ and $\delta^{13}C_2$ were also increased. $C_1/C_2$ increased, which means that the increase ratio of methane was higher than that of ethane, and the $\delta^{13}C_2$ increased slightly, showing that the degree of increasing $\delta^{13}C_1$ heaviness was larger than that of $\delta^{13}C_2$. When the temperature was higher than 455.3 °C, ethane began to crack (Fig. 2), and $C_1/C_2$ increased rapidly with decreasing $\delta^{13}C_1 - \delta^{13}C_2$.

4.3 $\delta^{13}C_3 - \delta^{13}C_2$ vs $\delta^{13}C_2 - \delta^{13}C_1$

The $\delta^{13}C_3 - \delta^{13}C_2$ and $\delta^{13}C_2 - \delta^{13}C_1$ values decrease with increasing thermal maturity (Jenden et al. 1993; Prinzhofer and Huc 1995), so the $\delta^{13}C_3 - \delta^{13}C_2$ vs $\delta^{13}C_2 - \delta^{13}C_1$ diagram can be used to reflect the maturity of natural gas (Jenden et al. 1993). However, many simulation experiments show the opposite change (Guo et al. 2009, 2011; Tian 2006). The indexes above largely depend on the maturity of natural gas (Tian 2006). As Fig. 7 shows, in this experiment, the $\delta^{13}C_3 - \delta^{13}C_2$ vs $\delta^{13}C_2 - \delta^{13}C_1$ diagram shows obvious stage changes. Taking 2 °C/h as an example, when the temperature was lower than 383.5 °C, the $\delta^{13}C_3 - \delta^{13}C_2$ increased slightly from 2.16‰ to 2.94‰, and
the \( \delta^{13}C_2 - \delta^{13}C_1 \) increased rapidly from 5.36\% to 9.82\%. This is because during this stage, \( \delta^{13}C_1 \) decreased, but \( \delta^{13}C_2 \) first decreased and then increased, and \( \delta^{13}C_3 \) remained almost unchanged (Figs. 2, 3). Then, when the temperature was between 383.5 and 431.2 °C, the \( \delta^{13}C_3 - \delta^{13}C_2 \) first decreased and then increased, changing over the range of 2\% to 3\%, and the \( \delta^{13}C_2 - \delta^{13}C_1 \) remained almost unchanged. This result indicates that the variations in \( \delta^{13}C_1, \delta^{13}C_2 \) and \( \delta^{13}C_3 \) were basically the same, and the main sources of these gases were the same during this stage. In contrast to Fig. 2, we conclude that the cracking of \( C_{6+} \) was the main source of these gases. The last stage was from 431.2 to 455.3 °C, where \( \delta^{13}C_2 - \delta^{13}C_1 \) remained at approximately 10\% and \( \delta^{13}C_3 - \delta^{13}C_2 \) increased rapidly from 1.95\% to 5.08\% because of propane undergoing cracking before ethane.

5 Conclusions

Anhydrous pyrolysis experiments were conducted in sealed gold tubes with Jurassic coal from the Minhe Basin. The hydrocarbon composition and \( CO_2 \) yields and the \( \delta^{13}C \) of gas compositions were obtained. The following conclusions were drawn:

The stage \( \delta^{13}C \) value of methane shows a change trend of the “S” type that first decreased, then increased and finally decreased. The stage \( \delta^{13}C \) values of ethane and propane first decreased and then increased during the generating stage and became enriched in \( ^{13}C \) during the cracking stage because the bond energy of \( ^{12}C - ^{13}C \) was higher than that of \( ^{12}C - ^{12}C \). The stage \( \delta^{13}C \) value of \( CH_4 \) decreased when \( T > 520 °C \), but the \( \delta^{13}C \) values of cracked ethane and propane increased, which proved that coal still had the potential to generate \( CH_4 \) at high maturity. The stage \( \delta^{13}C \) value of \( CO_2 \) changes when \( T > 455 °C \) since the difference caused coke to be reacted with \( H_2O \).

According to the diagram of \( \delta^{13}C_1 - \delta^{13}C_2 \) versus \( C_1/C_2 \) and \( \delta^{13}C_3 - \delta^{13}C_2 \) versus \( \delta^{13}C_2 - \delta^{13}C_1 \), five stages of coal gas generation could be determined: (1) early stage of heteroatom cleavage reaction, (2) later stage of heteroatom cleavage reaction, (3) demethylation reaction and second cracking of \( C_{6+} \), (4) cracking of wet gases (\( C_2 - 5 \)), and (5) polycondensation reaction.

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