Materials Research Express

PAPER

Thermogravimetric study of the kinetics and characteristics of the pyrolysis of pulverized coal

Zhang Shi-Xin 1,2,3, Li Chang-Rong 1,2,4, Huang Run 1,2, Xiao Yang-Wu 1, Mao Rui 1, Huang Jun 1 and Zhou Cheng-Lin 3

1 College of Materials and Metallurgy, Guizhou University, Guiyang 550025, People’s Republic of China
2 Key Laboratory for Metallurgical Engineering and Process Energy Saving, Guiyang 550025, People’s Republic of China
3 Industrial Department of Ironmaking and Coking, Shougang Shuicheng Iron & Steel (Group) Co., Ltd, Liupanshui 553028, People’s Republic of China
4 Author to whom any correspondence should be addressed.

E-mail: crlc@gzu.edu.cn

Keywords: coal, TG-MS, pyrolysis, activation energy

Abstract

Simultaneous thermogravimetric-mass spectrometric (TG-MS) analyzer was used to investigate the pyrolysis characteristics and gas generation rule of three coal samples. Results indicated that Jing-mei (JM), Xinjiang-mei (XM), and Yan-mei (YM) coals had similar pyrolysis characteristics and gas generation law. Their pyrolysis process could be roughly divided into three stages. JM had the highest weight loss and gas generation rates among all the samples. CO and CO2 components in the escaping gas continued to increase when the temperature reached 800 °C. Coats–Redfern method was employed to calculate the activation energy of three kinds of coal at four temperature stages with different mode functions. The activation energy of the four stages of JM pyrolysis was 33.3 kJ mol⁻¹, 2.66kJ mol⁻¹, 88.51kJ mol⁻¹, and 33.26 kJ mol⁻¹. The result of XM pyrolysis was 51.29 kJ mol⁻¹, 6.84 kJ mol⁻¹, 47.38 kJ mol⁻¹, and 15.65 kJ mol⁻¹. Calculations of YM pyrolysis were 51.35 kJ mol⁻¹, 5.11 kJ mol⁻¹, and 117.49 kJ mol⁻¹ respectively.

1. Introduction

The world pig iron is on the rise, as shown in table 1 [1]. Coal is an important raw material in blast furnace production making a great difference in coal injection and coking system. Pyrolysis is the primary stage of coal combustion and coking, which is of great reference significance to the study of the subsequent process of coal conversion [2, 3]. Classification conversion of coal is an important means for improving the utilization rate and coal cleaning conversion [4, 5]. The law and kinetics of product release at different stages of coal pyrolysis are important angles to improve coal classification conversion.

TG-MS combines the thermogravimetry with mass spectrometry and computer system online analysis by using the characteristics and functions of a thermal analyzer and other instruments. TG-MS analyzer is widely used in the study of coal pyrolysis of its high sensitivity.

Due to the environmental diversity in different regions, many researchers have focused on exploring the pyrolysis differences among different types of coal [6–9]. The pyrolysis products contain pollutants such as N and S, which have also received extensive attention [10–12]. The structure of coal is complex and the pyrolysis of different functional groups is closely related to gas precipitation [13, 14].

Meanwhile, many researchers have tried to develop different methods to describe the pyrolysis of coal from the perspective of kinetics. Some researchers have made dynamic calculations from the Angle of the weight change of coal samples [14–16]. Several researchers have conducted the thermodynamic analysis from the perspective of gas changes generated by coal pyrolysis [17, 18].

In this study, three raw coals, namely, Jing-mei (JM), Xinjiang-mei (XM), and Yan-mei (YM) came from an ironworks and were analyzed by TG-MS. The research focuses on the differences in gas precipitation during the
thermal process of the three kinds of coal, as well as the kinetic analysis of their pyrolysis at different stages. This research is aimed at providing references for other working procedures in ironworks.

2. Materials and methods

2.1. Raw materials

Tables 2 and 3 show the blast furnace injection of JM, XM, and YM proximate and ultimate analyses. According to the volatile and sulfur contents, YM belonged to high volatile coal and all coals were low-sulfur coal, which met the requirements of blast furnace production. The samples were dried for 4h and ball milled to a 200 mesh sieve before the TG-MS experiment. As shown in figures 1 and 2, XM had the highest average particle size among the three coal samples. X-ray diffraction patterns of the pdf cards and coal samples showed that mullite, calcite, and hematite existed in the three kinds of coal as shown in figure 3.

2.2. TG-MS analysis

Pyrolysis experiments were conducted with a high-temperature thermal analyzer (Setaram Setys Evolution 16/18, France) and mass spectrograph (Pfeiffer, Germany). The samples were heated to approximately 970 °C at a rate of 10 °C min⁻¹ under a nitrogen flow of 60 ml min⁻¹. Mass spectrograph worked under high vacuum (8–10 Pa) conditions to detect gas products with a mass range of 1–300 molecular weight. The precipitation curves of 16, 2, 18, and 44 m z⁻¹, CH₄, H₂, CO, and CO₂, were got on-line respectively.

Table 1. World pig iron production in the last decade (Million tons).

| Year | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 |
|------|------|------|------|------|------|------|------|------|------|------|
| Output | 1034 | 1104 | 1123 | 1170 | 1187 | 1161 | 1174 | 1186 | 1253 | 1278 |

Table 2. Proximate analysis of JM, XM, and YM.

| Moisture ad (%) | Volatile matter ad (%) | Ash ad (%) | Fixed Carbon ad (%) |
|----------------|------------------------|------------|---------------------|
| JM 3.14        | 10.18                  | 12.96      | 71.84               |
| XM 8.5         | 9.85                   | 10.90      | 70.86               |
| YM 5.42        | 25.71                  | 8.59       | 58.79               |

a ad indicates ‘air dry basis’.

Table 3. Ultimate analysis of JM, XM, and YM.

| Carbon ar (%) | Hydrogen ar (%) | Oxygen ar (%) | Nitrogen ar (%) | Sulphur t.ar (%) |
|---------------|-----------------|---------------|-----------------|-----------------|
| JM 66.71      | 2.57            | 0.69          | 1.13            | 0.54            |
| XM 68.02      | 1.43            | 3.45          | 0.73            | 0.27            |
| YM 68.98      | 3.58            | 7.53          | 0.89            | 0.30            |

a ar indicates ‘as the received basis’.
b t.ar indicates ‘total sulfur as received basis’.

Figure 1. SEM images of the three kinds of coal samples.
3. Results and discussion

3.1. TG/DTG characteristics

Figure 4 shows the TG and DTG curves of the pyrolysis of the three kinds of raw coal samples. Three weightlessness peaks were divided into three stages of dry degassing, cracking and condensation polymerization, and polycondensation. This result was similar to those in other works [12, 19].

In the first stage, water and physically-adsorbed gases were mainly removed from the three coal samples. The weak bonds in the coal were broken to form small gas molecules, and CO₂ was generated when the functional groups containing carboxyl groups were broken. The second stage involved the main pyrolysis temperature range of the coal samples, where the mass change rate was the fastest. The DTG curves of the coal samples all showed the maximum weight loss peak, generating semicoke and a large number of volatile components. The following characteristic parameters were obtained [20, 21]: temperature of initial weight loss ($T_i$), the temperature at the end of the reaction ($T_f$), the maximum weight loss rates ($R_{max}$), and the corresponding peak temperature ($T_{max}$). $T_i$ was defined as the temperature at $\alpha = 5\%$, and $T_f$ was calculated at $\alpha = 85\%$ similarly as $T_i$. The TG properties of the coal samples are provided in table 4.

The TG curve showed that YM had the largest weight loss rate of YM, followed by XM and JM had the smallest. The mass change rate of YM was also the highest because volatiles were the main extruded substances during coal pyrolysis. Table 4 also shows that YM contained more volatile content than the other two coal types. The main mass drastic reduction stage of JM occurred at 400 °C–600 °C, whereas that of XM and YM was at 400 °C–500 °C, indicating that the functional groups of the three coal samples were different and that JM was more stable than the other two coals. At 400 °C–500 °C, XM, and YM produced more pyrolysis products than JM. The burnout temperature of YM was more than 100 °C different from that of JM and XM, indicating that the burnout performance of YM was better than that of the other two. Moreover, more pyrolysis products were obtained under low-temperature range. Therefore, the thermal stability of JM, XM, and YM coal decreased continuously.
3.2. Gaseous product evolution during pyrolysis

The mass spectrometer examined the components of gases that escaped during pyrolysis by recording the strength of the mass-to-charge ratio of different gases. The analysis and comparison of different components of the escaped gas showed the relationship between the different kinds of samples and volatile content. Figure 5 shows the escape curve of gases generated in the pyrolysis process of the three kinds of coal.

Figure 5. Evolution of (a) CH$_4$, (b) H$_2$, (c) CO, (d) CO$_2$, and (e) H$_2$S during JM, XM, and YM pyrolysis.

Table 4. TG/DTG characteristic of three kinds of coal samples.

| Coal samples | $T_i$/°C | $T_{max}$/°C | $T_f$/°C | $R_{max}$(%) |
|--------------|----------|--------------|----------|--------------|
| JM           | 179      | 508          | 810      | 12.5         |
| XM           | 94       | 434          | 806      | 14.9         |
| YM           | 304      | 438          | 671      | 29           |

3.2. Gaseous product evolution during pyrolysis

Figure 4. TG/DTG curves of JM, XM, and YM.

The mass spectrometer examined the components of gases that escaped during pyrolysis by recording the strength of the mass-to-charge ratio of different gases. The analysis and comparison of different components of the escaped gas showed the relationship between the different kinds of samples and volatile content. Figure 5 shows the escape curve of gases generated in the pyrolysis process of the three kinds of coal.

Figure 5(a) shows that JM, XM, and YM coal start to generate CH$_4$ at about 400°C and reach a peak between 500°C and 600°C, and their sources are mainly aromatic hydrocarbon and methyl fracture. The CH$_4$ escape curve of the three types of coal presented a relatively wide single peak, which is similar to Shenhua and Neimongol coals [22] and four different rank coals. A previous study [18] showed that CH$_4$ precipitation at low
temperature was mainly due to the desorption of \( \text{CH}_4 \) naturally adsorbed in coal structure. The peak temperature increases with the increase in coal grade due to the reaction of the multi-component structure. In coal, the macromolecular network breaks down and pyrolysis reaction occurs. At high temperatures, coals are mainly derived from the condensation reaction of aromatic hydrocarbon or decomposition reaction of heterocyclic compounds.

Figure 5(b) shows the variation rules of \( \text{CO} \) in the three kinds of coal samples pyrolysis gas. The measurement of \( \text{CO} \) in low temperature with the same mass-to-charge ratio of 28 is affected to a certain extent due to the use of a nitrogen atmosphere. Compared with Zhaotong lignite, Shenhua bituminous coal, and Zunyi anthracite [6], there is one more peak per curve. The relative intensity of \( \text{CO} \) reached the first peak at almost 400 °C and the second peak at about 780 °C. According to the related experiment of ash removal coal [18], \( \text{CO} \) may come from the product of \( \text{CO}_2 \) reaction with semicoke pyrolysis.

Figure 5(c) shows that the changing trend of \( \text{H}_2 \) produced by the pyrolysis of the three kinds of pulverized coal was roughly the same, that is, all start to be generated at about 500 °C. JM and YM reach their maximum value at about 900 °C. XM reached its maximum value at about 780 °C. In the present study, the relative strength of \( \text{H}_2 \) was higher than that of the other three gas products, and the change rate of XM was lower than that of the other two coals. These findings indicated that the temperature of the third shoulder peak of XM in the DTG curve (figure 3) was lower than that of the other two coals.

As shown in figure 5(d), the precipitation of \( \text{CO}_2 \) is similar to that of \( \text{CO} \), and the reaction of \( \text{CO}_2 \) formation occurred in the whole temperature range. The temperatures corresponding to the first peak relative intensity were approximate between 400 °C and 500 °C. \( \text{CO}_2 \) came from decarbonization within macromolecules. At high temperatures, the decomposition of stable oxygen-containing function groups produces \( \text{CO}_2 \) [24, 25]. In the present study, the second peak intensity of XM was lower than that of the other two coals.

Two main stages of \( \text{H}_2\text{S} \) evolution during coal pyrolysis are shown in figure 5(e). At the first stage (200 °C–500 °C), shoulder peaks possibly come from the breakage of unstable sulfur-containing aliphatic hydrocarbons. \( \text{H}_2\text{S} \) continues to be released owing to the decomposition of iron pyrite and organic sulfur of high bond energy at the second stage [26, 27]. The end temperatures of three coals at the first stage also indicate different content of organic sulfur and shoulder peaks from 400 °C to 800 °C in figure 4.

### 3.3. Kinetic analysis of coal sample pyrolysis

Coats–Redfern method [21, 28] was applied to solve the activation energy of the three kinds of coal. According to the chemical reaction kinetics theory, the reaction rate of coal pyrolysis could be expressed by Arrhenius formula, as shown in equation (1)

\[
\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha)
\]

where \( T \) is the absolute temperature, K; \( A \) is the pre-exponential factor, \( \text{min}^{-1} \); \( E \) is the activation energy, \( \text{kJ} \cdot \text{mol}^{-1} \); \( R \) is the universal gas constant, 8.314 J/(K·mol·K); \( \alpha \) is the mass fraction at time \( t \), %.

For MS measurement, the degree of conversion \( \alpha \) of the pyrolysis process, which describes the change in evolved gas, can be expressed as follows:

---

Figure 6. Activation energy solution curves of JM, XM, and YM.
Table 5. Pyrolysis kinetics of coal samples.

| JM   | 60°C–120°C | 120°C–360°C | 360°C–540°C | 540°C–850°C |
|------|-------------|-------------|-------------|-------------|
|      | E/R | r | E/kl/mol | E/R | r | E/kl/mol | E/R | r | E/kl/mol | E/R | r | E/kl/mol |
| A    |    |   |          |    |   |          |    |   |          |    |   |          |
| B    | 1665.624 | 0.99445 | 13.848    | 314.174 | 0.90186 | —        | 503.476 | 0.93535 | 41.85899 | 2441.331 | 0.99429 | 20.29723 |
| C    |    |   |          |    |   |          |    |   |          |    |   |          |
| D    | 862.7206 | 0.98426 | 8.000459  | 9.96949 | —        | —        | 335.846 | 0.92399 | 36.21986 | 3525.952 | 0.94451 | 29.31477 |
| E    | 1723.916 | 0.99386 | 14.33264  | 130.733 | 0.86291 | —        | 6678.383 | 0.94912 | 55.24084 | 9291.043 | 0.95548 | 77.24573 |
| F    | 4750.917 | 0.99587 | 33.31685  | 49.99242 | 0.76038 | 2.37875  | 10170.2 | 0.97825 | 84.55505 | 2828.618 | 0.97651 | 23.51713 |
| G    | 4009.566 | 0.99583 | 33.33553  | 0.57391 | 2.492174 | 10623.59 | 0.97624 | 88.32435 | 3851.03 | 0.99287 | 32.01746 |
| H    | 0.99578 | 33.50826 | 313.5936 | 0.58993 | 2.607231 | 11105.23 | 0.97402 | 92.3289 | 5252.067 | 0.99825 | 43.66569 |
| Average | (D E G) | 33.3 | (F H) | 2.66 | (D E G) | 87.51 | (A F G) | 33.26 |          |          |          |          |

| XM   | 50°C–120°C | 120°C–390°C | 39°C–600°C | 600°C–850°C |
|------|-------------|-------------|-------------|-------------|
|      | E/R | r | E/kl/mol | E/R | r | E/kl/mol | E/R | r | E/kl/mol | E/R | r | E/kl/mol |
| A    |    |   |          |    |   |          |    |   |          |    |   |          |
| B    | 1665.624 | 0.99445 | 13.848    | 314.174 | 0.90186 | —        | 503.476 | 0.93535 | 41.85899 | 2441.331 | 0.99429 | 20.29723 |
| C    |    |   |          |    |   |          |    |   |          |    |   |          |
| D    | 862.7206 | 0.98426 | 8.000459  | 9.96949 | —        | —        | 335.846 | 0.92399 | 36.21986 | 3525.952 | 0.94451 | 29.31477 |
| E    | 1723.916 | 0.99386 | 14.33264  | 130.733 | 0.86291 | —        | 6678.383 | 0.94912 | 55.24084 | 9291.043 | 0.95548 | 77.24573 |
| F    | 4750.917 | 0.99587 | 33.31685  | 49.99242 | 0.76038 | 2.37875  | 10170.2 | 0.97825 | 84.55505 | 2828.618 | 0.97651 | 23.51713 |
| G    | 4009.566 | 0.99583 | 33.33553  | 0.57391 | 2.492174 | 10623.59 | 0.97624 | 88.32435 | 3851.03 | 0.99287 | 32.01746 |
| H    | 0.99578 | 33.50826 | 313.5936 | 0.58993 | 2.607231 | 11105.23 | 0.97402 | 92.3289 | 5252.067 | 0.99825 | 43.66569 |
| Average | (D E G) | 33.3 | (F H) | 2.66 | (D E G) | 87.51 | (A F G) | 33.26 |          |          |          |          |

| YM   | 60°C–120°C | 120°C–330°C | 330°C–460°C | 460°C–850°C |
|------|-------------|-------------|-------------|-------------|
|      | E/R | r | E/kl/mol | E/R | r | E/kl/mol | E/R | r | E/kl/mol | E/R | r | E/kl/mol |
| A    |    |   |          |    |   |          |    |   |          |    |   |          |
| B    | 1665.624 | 0.99445 | 13.848    | 314.174 | 0.90186 | —        | 503.476 | 0.93535 | 41.85899 | 2441.331 | 0.99429 | 20.29723 |
| C    |    |   |          |    |   |          |    |   |          |    |   |          |
| D    | 862.7206 | 0.98426 | 8.000459  | 9.96949 | —        | —        | 335.846 | 0.92399 | 36.21986 | 3525.952 | 0.94451 | 29.31477 |
| E    | 1723.916 | 0.99386 | 14.33264  | 130.733 | 0.86291 | —        | 6678.383 | 0.94912 | 55.24084 | 9291.043 | 0.95548 | 77.24573 |
| F    | 4750.917 | 0.99587 | 33.31685  | 49.99242 | 0.76038 | 2.37875  | 10170.2 | 0.97825 | 84.55505 | 2828.618 | 0.97651 | 23.51713 |
| G    | 4009.566 | 0.99583 | 33.33553  | 0.57391 | 2.492174 | 10623.59 | 0.97624 | 88.32435 | 3851.03 | 0.99287 | 32.01746 |
| H    | 0.99578 | 33.50826 | 313.5936 | 0.58993 | 2.607231 | 11105.23 | 0.97402 | 92.3289 | 5252.067 | 0.99825 | 43.66569 |
| Average | (D E G) | 33.3 | (F H) | 2.66 | (D E G) | 87.51 | (A F G) | 33.26 |          |          |          |          |
Table 6. Partial mode function commonly used in the solid-phase reaction.

| First-order reaction (A) | Second-order reaction (B) | Third-order reaction (C) | 1D diffusion (D) |
|--------------------------|---------------------------|--------------------------|-----------------|
| $g(\alpha)$              | $(1-\alpha)^{-1}$         | $1/2(1-\alpha)^{-2}$    | $\alpha^2$      |
| $2D$ diffusion (E)        | $3D$ Hagen diffusion (F)  | $3D$ G-B diffusion (G)   | $3D$ Z-L-T diffusion (H) |
| $g(\alpha)$              | $(1-\alpha)\ln(1-\alpha) + \alpha$ | $1-(1-(\alpha)^{1/3})^2$ | $1-2\alpha/(1-\alpha)^{3/4}$ |
|                          |                           | $1+2\alpha/(1-\alpha)^{3/4} - (1-(\alpha)^{1/3})^2$ |                 |

$$\alpha = (M_0 - M_i)/(M_0 - M_{\infty})$$ (2)

where, $M_0$ is the initial sample mass, mg; $M_i$ is the actual sample mass at time $t_i$, mg; and $M_{\infty}$ is the sample mass after pyrolysis, mg.

The samples were heated at a constant rate, $\beta = dT/dt$. According to Coats–Redfern (equations (3) and (1)), the kinetic expression of pyrolysis is as follows:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{ART^2}{E\beta} \exp \left( -\frac{E}{RT} \right)$$ (3)

$$G(\alpha) = \frac{RT^2}{E\beta} \frac{d\alpha}{dt} \frac{1}{f(\alpha)}$$ (4)

With the logarithm of equations (3), (5) can be expressed as follows:

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \frac{AE}{\beta R} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT}$$ (5)

Under normal conditions, $E/RT \gg 1$, the corresponding $E$ and $A$ can be obtained from the slopes and intercepts of $\ln [g(\alpha)/T^2]$ versus $1/T$. Table 4 shows some commonly used mode functions in a solid-phase reaction [18] to study complicated the pyrolysis of coals.

According to the distribution law of $\ln [g(\alpha)/T^2]$, the calculation of activation energy is roughly divided into four stages, as shown in figure 6 and table 5. At each stage, three functions with the best fit are selected to obtain the average activation energy. The calculated results are obtained by different mode functions shown in table 6 shown. The activation energy of stage one and three was higher than that of stage two and four among three coals.

It can be inferred from the above gas precipitation rule that the second stage is the fracture of the side chain of small molecules and the third stage is the cleavage of the main chain. The value of the activation energy also increases as the reaction becomes more difficult. Results of studies [29, 30] also show that the activation energy calculated by the Starink method decreased with the increasing conversion.

The pyrolysis reaction of coal volatiles is the most intense in the third stage, where the activation energy required is the highest. It can be observed that activation energy rises with the growth of volatile content.

4. Conclusions

The pyrolysis characteristics and kinetics of three kinds of coals (JM, XM, and YM) were studied by TG–MS. The main conclusions are as follows:

1. The pyrolysis of the three kinds of pulverized coal can be roughly divided into three stages: dry degassing, cracking, and polycondensation. Volatile matter is the main substance to be removed.

2. The gas formation mechanism during pyrolysis is roughly similar for the three kinds of pulverized coal. According to relative intensity distribution, H2 and CH4 are the two principal pyrolysis gas products. Pyrolysis contributes to removing some of the sulfur from the coal.

3. The activation energy of the four stages of JM pyrolysis was 33.34 kJ mol\(^{-1}\), 2.66 kJ mol\(^{-1}\), 88.40 kJ mol\(^{-1}\), and 33.26 kJ mol\(^{-1}\). The result of XM pyrolysis was 51.29 kJ mol\(^{-1}\), 6.84 kJ mol\(^{-1}\), 47.38 kJ mol\(^{-1}\), and 15.26 kJ mol\(^{-1}\). Calculations of YM pyrolysis were 51.35 kJ mol\(^{-1}\), 5.11 kJ mol\(^{-1}\), and 77.59 kJ mol\(^{-1}\), 31.15 kJ mol\(^{-1}\), respectively. The second stage between 330 °C–360 °C and 460 °C–600 °C is the main pyrolysis stage of coal volatiles. The increasing difficulty of pyrolysis reaction also leads to an increase in activation energy.
Acknowledgments

The authors acknowledge the support from the National Natural Science Foundation of China(51864013) and the Shougang Shuicheng Iron & Steel Industry(Group) Company, Ltd.

ORCID iDs

Zhang Shi-Xin  https://orcid.org/0000-0001-6248-0773

References

[1] World Steel Association AISBL Production of Pig Iron DB/ON (https://www.worldsteel.org)
[2] Wu H, Zou C, He J Y, Wang W A, Liu Z W and Shi S J 2020 Difference of combustion between different pyrolytic char and pulverized coal injection in blast furnace iron and steel S 12–9
[3] Niu Z, Liu G, Yin H and Zhou C J 2018 Devolatilization behavior and pyrolysis kinetics of coking coal based on the evolution of functional groups J. Anal. Appl. Pyrolysis 134 351–61
[4] Yu J et al 2018 Conversion of low-grade coals in sub- and supercritical water: a review Fuel 217 275–84
[5] Sharma D K J 2010 Enhancing the steam gasification reactivity of coal by boosting the factors affecting the gasification reactions in the stepwise coal conversion Energy Sources Part A 40 2963–9
[6] Wei J et al 2018 A Comparative study on pyrolysis reactivity and gas release characteristics of biomass and coal using TG-MS analysis Energy Sources Part A 40 155–62
[7] Zhou F et al 2018 The pyrolysis characteristics and gas generation law of coal used in COREX process Journal of China Society 38 211–6
[8] Han F et al 2016 Thermal decomposition and evolved gas analysis (TG-MS) of lignite coals from southwest china J. Energy Inst. 89 94–100
[9] Wu D, Liu G and Sun R J 2014 Investigation on structural and thermodynamic characteristics of perhydrous bituminous coal by fourier transform infrared spectroscopy and Thermogravimetry/Mass Spectrometry Energy & Fuels 28 3024–35
[10] Hou J et al 2018 Transformation of sulfur and nitrogen during shennu coal pyrolysis Fuel 231 134–44
[11] Li C, Wang X H, Wang X L and Liu L J 2013 Study on the pyrolysis of coal from Xinjiang by application of DSC-TG in hyphenation with FTIR-MS Physical Testing and Chemical Analysis (Part B: Chemical Analysis) 49 1284–90
[12] Liu Q F et al 2015 Release behavior of nitrogen in different rank coals during pyrolysis Journal of China Coal Society 40 450–5
[13] Zeng F G and Lia B J 2009 Reaction types and kinetics of methane generation from huolinhe coal lignite pyrolysis by TG/MS experiment and quantum chemical calculations Acta Phys. Chim. Sin. 25 1117–24
[14] Chen L H, Chen X, Wu Y Y, Zhou H and Cen K F J 2016 Quantitative analysis of gaseous products evolved by coal combustion using TG-FITR-MS technique Journal of Zhejiang University (Engineering Science) 50 961–9
[15] Jiang G D, Wei I P, Teng H P and Hao H D J 2017 A kinetic model based on TGA data for pyrolysis of Zhundong coal CIESC Journal 68 1415–22
[16] Jeong H M et al 2014 Pyrolysis kinetics of coking coal mixed with biomass under non-isothermal and isothermal conditions Bioresour. Technol. 155 442–5
[17] Zou C et al 2017 Characterization and non-isothermal kinetics of shennu bituminous coal devolatilization by tg-ms J. Anal. Appl. Pyrolysis 127 309–20
[18] Liu J et al 2014 Pyrolysis of superfine pulverized coal Part 1. Mechanisms of methane formation Energy Convers. Manage. 87 1027–38
[19] Lu Z F, Wang Y F, Li J L, Wang F C and Yu G S J 2016 Evolution characteristics of gas from pyrolysis of typical coals Journal of East China University of Science and Technology 42 764–70
[20] Gaol S 2010 Coal Pyrolysis, Coking, and Coal Tar Processing (Beijing: Chemical Industry Press)
[21] Xu Y et al 2013 Thermogravimetric study of the kinetics and characteristics of the pyrolysis of lignite reaction kinetics Mechanisms and Catalysis 110 225–35
[22] Luo L et al 2017 TG-MS-FITR Study on Pyrolysis Behavior of Superfine Pulverized Coal J. Anal. Appl. Pyrolysis 128 64–74
[23] Arenillas A, Rubiera F and Pis J J 1999 Simultaneous thermogravimetric-mass spectrometric study on the pyrolysis behavior of different rank coals J. Anal. Appl. Pyrolysis 50 31–46
[24] Yan J D, Cui H, Yang J L and Liu Z Y J 2003 Study on pyrolysis behavior of yunzhou coal by TG-MS Journal of China University of Mining & Technology 32 311–5
[25] Fan D M, Zhu Z P and Lv Q G J 2014 TG-MS study on gas release characteristics during pyrolysis of bituminous coal Coal Conversion 037 5–10
[26] Calkins W H J 1987 Investigation of organic sulfur-containing structures in coals by pyrolysis experiment Energy Fuels 1 59–64
[27] Yao Q X, Du M I and Wang S L J 2012 Characteristics of sulfur forms transformation in high sulfur coal pyrolysis Coal Conversion 35 17–21
[28] Zhao Y, Liu L, Qui P H, Xie X, Sun S Z, Liu H P and Chen L Z J 2016 Application limitations of single scanning rate method in pyrolysis kinetics of zhundong coal Journal of Harbin Institute of Technology 48 58–66
[29] Hu Y J, Wang Z Q, Cheng X X and Ma C Y J 2018 Non-isothermal TGA study on the combustion reaction kinetics and mechanism of low-rank coal char RSC Adv. 8 22909–16
[30] Shirvani S and Mohammad G J 2018 Combined effect of nanoporous diluent and steam on catalytic upgrading of fuel oil to olefins and fuels over USY Catalyst Pet. Sci. Technol. 36 750–5