

## Changes of reactive functional groups in coal with the release of small molecule gases during pyrolysis

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### Abstract

Active functional groups play an extremely crucial role in the formation and release of small molecule gases during the pyrolysis of coal. In this paper, the formation and release of small molecule gases and the changes of active functional groups during the pyrolysis of coal at 30–1000 °C were investigated by Fourier infrared spectroscopy (FTIR), thermogravimetric and Fourier infrared spectroscopy (TG-IR). The results manifested that the pyrolysis of coal can produce a large amount of gas only at middle and high temperatures, and the coal contains more  $-\text{CH}_2-$ ,  $-\text{C}=\text{O}$ ,  $-\text{COOH}$  and  $-\text{OH}$  functional groups, which can produce more gas during pyrolysis. Coal pyrolysis is divided into three stages, the dry desorption stage, the medium-temperature pyrolysis stage, and the high-temperature pyrolysis stage. The results of this examine established the relationship between the macroscopic changes of gases and the microscopic changes of functional groups during the pyrolysis of coal, which provided research ideas for understanding the pyrolysis process of low-rank coal and revealing the mechanism of pyrolysis gas production.

### Keywords

Pyrolysis; TG-IR; TG-MS; Active functional groups; Small molecule gases.

### 1. Introduction

Coal is a organic matter with a complex pore structure and a high molecular weight carbon structure [1], where the fracture and condensation of reactive functional groups in the carbon structure provide a source of material for the formation and release of small molecule gases, and the pore structure provides storage space for the small molecule gases. Pyrolysis is an initial concomitant reaction of many conversion processes such as hydrogenation, combustion, and gasification [2], yet the complexity and non-homogeneity of coal and the overlapping temperature ranges of the different decomposition phases [3] pose a great challenge in describing the pyrolysis process in detail. Therefore, it is exceedingly indispensable to focus on the changes in reactive functional groups during pyrolysis in order to understand the effect of reactive functional groups on the release of small molecule gases.

Thermogravimetric analysis (TG) has been demonstrated to research the thermal behavior of various solid samples in air or inert gases in terms of the change in the rate of mass loss with increasing temperature [3,6], and mass spectrometry (MS) and Fourier Transform Infrared Spectroscopy (FTIR) are often used to carry out the analysis of pyrolysis and gas evolution at the same time, and they can be used to identify the samples that emit, on the basis of their mass

or vibrational spectra, the of gaseous substances. Thermogravimetric and Fourier Infrared Spectroscopy (TG-IR) data were utilized to research coal pyrolysis product distribution, decomposition kinetics, and functional group composition [7,11]. Thermogravimetry coupled with mass spectrometry (TG-MS) has additionally been applied to the examine of pyrolysis gas evolution of coal [2, 3, 12]. Based on infrared spectra, A. Arenillas [2, 3] et al. Established a correspondence between absorption bands and functional groups, and absorption bands arising from O–H bonds were observed in spectra with wavelengths of 3700–2800  $\text{cm}^{-1}$ ; Absorption bands of aromatic and aliphatic C–H bonds were observed in the spectra at wavelengths of 3050–2850  $\text{cm}^{-1}$ ; the region of 1800–1700  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$  were the absorption bands of the anhydride groups; the wavelengths at 1600  $\text{cm}^{-1}$  manifests a strong absorption band, which is typical of the C=O stretching of amides; there are several bands between 1650–1200  $\text{cm}^{-1}$ , which are characteristic of the cyclic respiratory vibrations of pyridine analogs; the benzene respiratory vibration bands are additionally shown in the region of 1600–1500  $\text{cm}^{-1}$ ; and the a large number of bands of O–H deformation and C–O stretching vibrations are present at 1350–1000  $\text{cm}^{-1}$ .

The generation of oil and natural gas represents the production of hydrocarbons over a range of temperatures [13]. During pyrolysis, the evolution of gaseous products can be measured by TG / MS [14, 15], and the maximum evolution peaks of  $\text{CO}_2$ , CO, and  $\text{H}_2\text{O}$  correspond to the maximum rate of weight loss over a range of temperatures [15]. By correlation analysis, –OH, –COOH, and – $\text{CH}_2$ – demonstrated favorable temperature correlation with indicator gas emissions.

Currently, most researchers have focused on the oxidation and spontaneous combustion of coal, and few detailed studies have been conducted to reveal the differences in the gas production mechanisms of coal pyrolysis in an inert atmosphere. In this work, pyrolysis of low-ranked coal extracted from low-evolved shale was investigated. The mass loss in the pyrolysis of the samples was obtained by TG-DTG measurements, and the gases produced by TG-MS measurements, and the TG- IR analyzed the changes in active functional groups. By analyzing the pyrolysis process, the effect of coal active functional groups on the release of small molecule gases was investigated.

## 2. Experiments and methods

### 2.1. Sample

#### 2.1.1 Collection and preparation of coal and shale samples

The Fukang Area at the southern margin of the Junggar Basin in Northwest China is a major low-rank coal coalbed methane production area, and sample of low rank coal from the Middle and Lower Jurassic Xishanyao Formation was collected from the CBM drilling well. Fresh core sample was wrapped in cling film and numbered. Coal sample from the Xishanyao Formation was numbered as FXC. The geochemical parameters of the coal-derived hydrocarbon rocks are shown in Table 1. All the samples were crushed first, and were ground to fine particles with agate mortar and sieved to 20–25 mesh. Coal sample was continued to be ground to fine particles with agate mortar, sieved to 200 mesh, and dried with a fan at 105 °C for 24 hours.

#### 2.2. FTIR measurements.

To compare the active functional groups of the samples before pyrolysis, FTIR spectroscopy experiment was performed on the sample [8]. The sample was ground, sieved into particles with sizes less than 0.075 mm, and placed in a vacuum drying oven at 60 °C for 12 h to minimize the interference of external water in the test. 0.1 g of the sample and potassium bromide was mixed homogeneously in the ratio of 1:100 and then ground thoroughly with a grinder for 10 min to ensure that they were well mixed. The experiments were performed using a NICOLET

6700 Fourier transform infrared spectrometer manufactured by Thermo Fisher Scientific, USA, with a room temperature of 23 °C and a humidity of less than 20%, and 32 scans were performed for each spectrum with a resolution of 4.000 cm<sup>-1</sup>, and all the spectra were obtained in the wave number range of 4000–650 cm<sup>-1</sup>, and corrected for the treatment of multiple small peaks and baselines in different regions of the spectrogram.

### 3. Results and discussion

#### 3.1. Main characteristics of coal and shale

The main characteristics and geochemical parameters of the coal and shale in this work are shown in Tables 1 and 2. The low degree of metamorphism of the coal, which belongs to the low-rank coal, and the low degree of thermal evolution of the shale can be seen from the reflectivity of the sample specimens.

Table 1 Property analyses of the coals

Sample	M <sub>ad</sub> (%)	A <sub>ad</sub> (%)	V <sub>ad</sub> (%)	FC <sub>ad</sub> (%)	C (wt%)	H (wt%)	O (wt%)	N (wt%)	S (wt%)
FBC	3.52	15.37	29.04	52.07	81.25	5.66	10.99	1.89	0.21

Table 2 Geochemical parameters of coal and shale

Sample	TOC (%)	S <sub>1</sub> +S <sub>2</sub> (mg/g)	I <sub>H</sub> (mg/g)	I <sub>O</sub> (mg/g)	T <sub>max</sub> (°C)	H/C	O/C	Ro (%)
FBC	64.55	165.49	242	53	443	0.96	0.24	0.87

#### 3.2. FTIR properties of coal

FTIR can be used to characterize functional groups in coals and shales [13], and thus the technique was utilized to analyze the reactive groups in coals and shales. According to previous research [10], the absorption bands in the infrared spectra were categorized into aromatic ring structures (900–700 cm<sup>-1</sup>), oxygen-functional structures (1800–1000 cm<sup>-1</sup>), aliphatic structures (3000–2700 cm<sup>-1</sup>), and hydroxyl structures (3600–3000 cm<sup>-1</sup>).

#### 3.3. TG/DTG results

Pyrolysis experiments was carried out on FBC coal, and the mass loss curves (TG) and derivative (DTG) versus the reaction temperature is shown in Fig. 1. The pyrolysis of coal can be divided into four stages, the first stage of coal pyrolysis, with temperatures from 30 °C to 166 °C, has a mass loss rate of 1.6%; the second stage, with temperatures from 166 °C to 572 °C, has a mass loss rate of 15.5%, and a mass loss peak occurs at the temperature of 454 °C, which is mainly due to the large amount of light hydrocarbons, carbon dioxide, and water produced in this stage causing mass loss [13]; In the third stage, the temperature is from 572 °C to 902 °C, the mass loss rate is 9.7%, and the mass loss peak occurs at the temperature of 647 °C. This is due to the gradual increase of the breakage of the unstable heterocycles in the pyrolysis process, and the further increase of the temperature, the condensation of some of the aromatic rings and the decomposition of the mineral substances (kaolinite, silicate minerals, etc.) [15], which is more favorable to the generation of free radicals, the release of hydrogen, methane, carbon dioxide and carbon monoxide [12]; and the fourth stage, with temperatures ranging from 902 °C to 1000 °C, with a mass loss of 1.1%; the weight of the coal was reduced by 27.9% after pyrolysis.

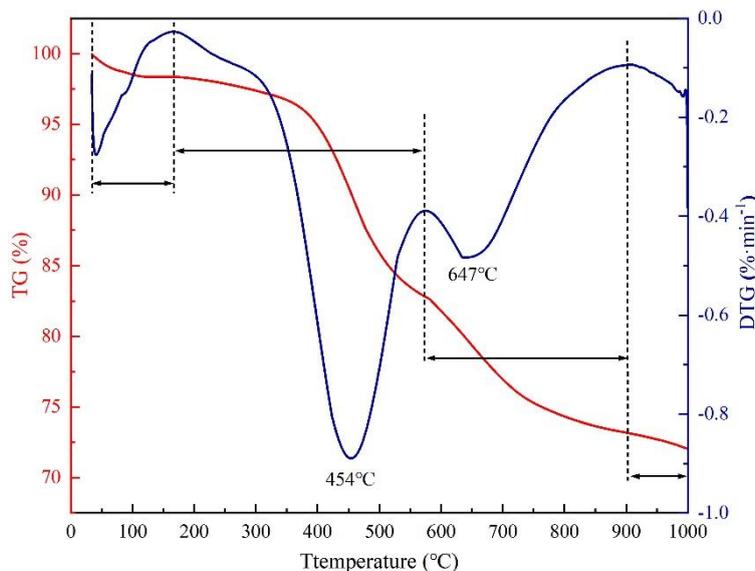


Fig. 1. TG/DTG curves during the pyrolysis of FBC coal sample.

### 3.4. Changes of active functional groups during pyrolysis

According to the literature [7], the absorbance peaks at wave numbers of 1680–1720  $\text{cm}^{-1}$  indicate the presence of oxygen-based compounds, the bands at wave numbers of 2060–2240  $\text{cm}^{-1}$  are characteristic peaks of CO, and the wave numbers of 2240–2400  $\text{cm}^{-1}$  corresponds to the formation of  $\text{CO}_2$ , while the band at 3500–4000  $\text{cm}^{-1}$  is caused by the stretching of the O–H bond, indicating the production of  $\text{H}_2\text{O}$ .

The main gaseous products during pyrolysis of coal is hydrocarbons and non-hydrocarbons [2]. Pyrolysis of coal leads to the breaking of chemical bonds and decomposition of the macromolecular structure, yielding smaller fragments, and information on this can be obtained from the regularity of the gas evolution by mass spectrometry [15]. Each compound detected by mass spectrum has its own unique response factor, and by semi quantitative analysis it is feasible to compare the amount of the same compound released from different samples and additionally the amount of different compounds released from the same sample [2]. Previous research [2, 15] have demonstrated that the products of coal pyrolysis are mainly  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , CO (or  $\text{N}_2$ ), and  $\text{CO}_2$ , corresponding to  $m/z$  values of 2, 16, 18, 28, and 44, respectively. Fig. 2. manifests the variation of gas products with temperature during pyrolysis of FBC coal, and for the pyrolysis of the FBC coal (Fig. 2a), the drastic change in the gas absorbance is mainly from about 400°C and increases exponentially. The absorbance of  $\text{H}_2$  was significantly higher than that of other gases, and the peak areas of  $\text{H}_2$  and  $\text{H}_2\text{O}$  were the largest, followed by CO and  $\text{CH}_4$ , and the peak area of  $\text{CO}_2$  was the smallest, indicating that the main gases produced by pyrolysis of FBC coal were  $\text{H}_2$  and  $\text{H}_2\text{O}$ .

Previous research [12, 15] have suggested that the production of  $\text{H}_2$  from coal during pyrolysis at 300–600°C is mainly due to polycondensation and dehydrogenation reactions of cyclization, aromatization, and hydrogenation structures of alkanes.  $\text{CH}_4$  is an important product of coal pyrolysis of aliphatics, and the fragment ions  $m/z$  of  $\text{CH}_4$  in mass spectra are 15 and 16, respectively [12]. Fig. 2c manifest the evolution of  $\text{H}_2\text{O}$ , the evolution of  $\text{H}_2\text{O}$  is usually related to the presence of  $\text{H}_2\text{O}$  and hydroxyl groups in the samples [12], the  $\text{H}_2\text{O}$  produced by low-temperature pyrolysis is mainly from adsorbed and free  $\text{H}_2\text{O}$  in the pores of the samples, while the  $\text{H}_2\text{O}$  produced by high-temperature pyrolysis is mainly from the decomposition of oxygen-containing functional groups dominated by hydroxyl groups [12]. CO is an important product of coal pyrolysis, and CO and  $\text{N}_2$  have the same  $m/z$  value (28) and both can be formed during pyrolysis [12]. CO needs to be detected in medium-high temperature pyrolysis, whereas low-

temperature detection should be for the desorption of  $N_2$  adsorbed on the pore walls of the sample.

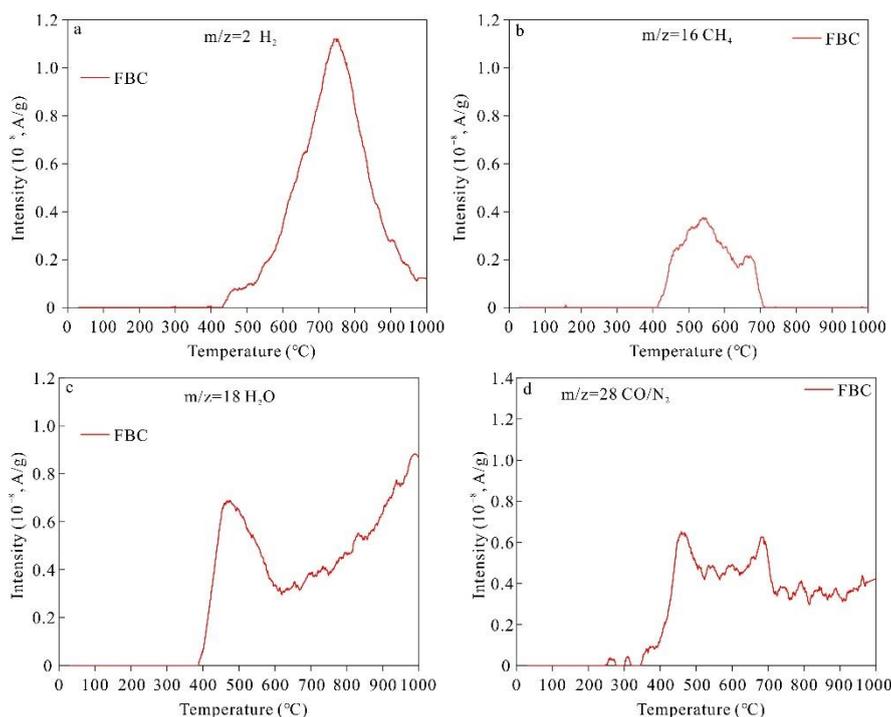


Fig. 2. Gas evolution during the pyrolysis of FBC coal.

#### 4. Conclusion

In this work, a comparative investigate of gas production from pyrolysis was carried out by selecting samples of low-rank coal, and the following conclusions were drawn in detail:

(1) According to the mass loss of pyrolysis process of coal can be divided into 4 stages, the mass loss of coal pyrolysis in each stage varies greatly. The maximum mass loss of coal pyrolysis occurs in the second stage, with the temperature ranging from 166°C to 572°C, and the mass loss rate is 15.5%, which generates a large number of light hydrocarbons, carbon dioxide and water.

(2) Aliphatic hydrocarbons in coal manifested high levels of activity at wave numbers of 3100–2800  $cm^{-1}$ . The absorbance of coal increased and then decreased during the pyrolysis process.

(3) Coal has more reactive hydrogen radicals, which can produce more  $H_2$ .

#### Acknowledgements

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#### References

- [1] C. B. Cockreham, X. Zhang, M. L. Lau, et al. Thermal Evolutions and Resulting Microstructural Changes in Kerogen-Rich Marcellus Shale, *ACS Earth Space Chemistry*. vol. 4 (2020), 2461–2469.
- [2] A. Arenillas, C. Pevida, F. Rubiera, et al. Characterisation of Model Compounds and a Synthetic Coal by TG/MS/FTIR to Represent the Pyrolysis Behaviour of Coal, *Journal of Analytical and Applied Pyrolysis*. vol. 71 (2004), 747–763.
- [3] A. Arenillas, F. Rubiera, J. J. Pis: Simultaneous Thermogravimetric–Mass Spectrometric Study On the Pyrolysis Behaviour of Different Rank Coals, *Journal of Analytical and Applied Pyrolysis*. vol. 1 (1999), 31–46.

- [4] J. Cai, Y. Wang, L. Zhou, et al. Thermogravimetric Analysis and Kinetics of Coal/Plastic Blends During Co-Pyrolysis in Nitrogen Atmosphere, *Fuel Processing Technology*. vol. 89 (2008), 21–27.
- [5] K. Miura, H. Ohgaki, N. Sato, et al. Formulation of the Heat Generation Rate of Low-Temperature Oxidation of Coal by Measuring Heat Flow and Weight Change at Constant Temperatures Using Thermogravimetry-Differential Scanning Calorimetry, *Energy Fuels*. vol. 31 (2017), 11669–11680.
- [6] M. Safaei-Farouji, M. Jafari, A. Semnani, et al. TGA and Elemental Analysis of Type II Kerogen From the Bakken Supported by Hrtem, *Journal of Natural Gas Science and Engineering*. vol. 103 (2022), 104606.
- [7] B. Baruah, P. Tiwari: Compositional and Kinetic Study of Thermal Degradation of Kerogen Using FTIR, NMR, and Microscopic Study, *AIChE Journal*. vol. 68 (2022), 1–16.
- [8] D. Gao, L. Guo, F. Wang, et al. Investigation On Thermal Analysis and FTIR Microscopic Characteristics of Artificially-Oxidized Coal and Chronic Naturally-Oxidized Coal During Secondary Oxidation, *Fuel*, vol. 1 (2022), 125151.
- [9] M. Labus, I. Matyasik, K. Ziemianin: Thermal Decomposition Processes in Relation to the Type of Organic Matter, Mineral and Maceral Composition of Menilite Shales, *Energies*, vol. 16 (2023), 4500.
- [10] M. Chi, X. Xu, D. Cui, et al. A TG-FTIR Investigation and Kinetic Analysis of Oil Shale Kerogen Pyrolysis Using the Distributed Activation Energy Model, *Oil Shale*, vol. 33 (2016), 228.
- [11] X. Qi, D. Wang, H. Xin, et al. In Situ FTIR Study of Real-Time Changes of Active Groups During Oxygen-Free Reaction of Coal, *Energy Fuels*, vol. 27 (2013), 3130–3136.
- [12] N. Kundu, P. Biswas, P. Bhunia, et al. Evolution Characteristics of Metallurgical Coals for Coke Making through Thermogravimetric-Mass Spectroscopic Measurements, *Journal of Environmental Chemical Engineering*, vol. 9 (2021), 106874.