

Variation of functional groups in coal oxidation process at low temperature based on TG and infrared spectra

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Abstract

Structure of coal is quite complex. In order to study the variation of the functional groups in coal at low temperature, Fourier transform infrared spectroscopy and sub-peaks technology were used in this paper to do scanning experiments on three different metamorphic grade coal samples which were lignite, bituminous coal and anthracite coal, respectively. The peak area values of different functional groups in three kinds of those coal samples were obtained at 50 - 200°C. The coal samples were isothermal in thermogravimetric analyzer. It indicates that for one same coal sample, the peak area values of different functional groups have different trends with temperature varying, and for one same functional group in different coal samples, the peak area values also have different trends. The trends of different functional groups with temperature in different coal samples and temperature turning points were obtained. And this provides the basis of microscopic aspects for macroscopically determining the feature point temperatures of coal oxidation and combustion.

Key words: FOURIER TRANSFORM INFRARED SPECTROSCOPY; FUNCTIONAL GROUP; PEAK AREA VALUE; LOW TEMPERATURE; METAMORPHIC GRADE

Introduction

Coal spontaneous combustion is one of the main disasters in domestic and foreign coal mines. About 20 percentage of mine fires are caused by coal spontaneous combustion in the United States [1]. In the 1970s, there would be 7-8 fires caused by coal spontaneous combustion every year in France and Britain. From 1970 to 1990, more than 1/3 of 254 coal fires were caused by coal spontaneous combustion [2]. In Australia, there were 125 coal spontaneous combustion disasters only in New South Wales during 1960-1991 [3]. And in China, coal spontaneous combustion is particularly serious, 51.3 percentage of state-owned key coal mines have the risk of spontaneous combustion and 90 percentage of coal fires are caused by spontaneous combustion. In the process

of coal spontaneous combustion, at low temperature which is about 0-300°C, physical adsorption and chemical adsorption occurs firstly when coal meets oxygen. These adsorptions between coal and oxygen release a certain amount of heat and the accumulation of heat increases the temperature of coal, thus promote the adsorption between coal and oxygen further until the chemical reaction happens [4-6]. The chemical reaction of coal oxidation is mainly the reaction of side chain groups of organic molecules with low molecular compounds in coal and oxygen molecules [7-9]. The interaction of these organic molecules with organic low molecular compounds constitutes a variety of functional groups and chemical bonds in coal. According to the difference of analysis methods, the structure models of coal molecules

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are also different. There are mainly two kinds of structure models: chemical model and physical model. The German W·Fuchs proposed Fuchs Model [10] which belongs to the chemical structure model. This model shows that coal is consist of cellular condensation of aromatic ring and arbitrary distribution of oxygen containing functional groups on its edge. The model was modified to become the chemical structure of coal by Krevenlen in 1957. In addition, the Given Model [11] proposed by the British P·H·Given, Wisser Model [12] proposed by American W·H·Wisser, Honda Model [13] and Shinn Model [14] reflect researchers' understandings of coal macromolecular in different periods. The physical structure models mainly include Hirsch Model and the Two-phase Model [15]. In recent years, the Oberlin Model and Sphere Model [16] which embody the integrated structure of coal molecular are representative. In this paper, thermogravimetric analyzer and Fourier transform infrared spectroscopy (FTIR) technique [17] were utilized to analyze the distribution and variation of functional groups in the min-infrared region as well as turning point temperatures of functional group peak area values in coal when coal reacts with oxygen at low temperature. It has great significance for study on the molecular structure of coal, and for determination the ignition point of coal as well as fire prevention in underground coal mine.

Instruments and experiments

Fourier transform infrared spectrometer

In coal molecule, different energy is needed when inspiring functional groups from ground state to excitation state. Thus leads to different energy absorption during excitation. Different absorption peaks were formed when infrared energy was absorbed by different functional groups, here and now the infrared spectra were formed. TENSOR 27 Fourier transform infrared spectrometer and its working principle are showed in Fig.1 and Fig.2, respectively.

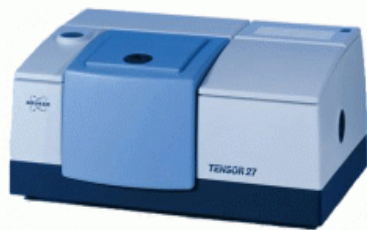


Figure 1. TENSOR 27 Fourier transform infrared spectrometer

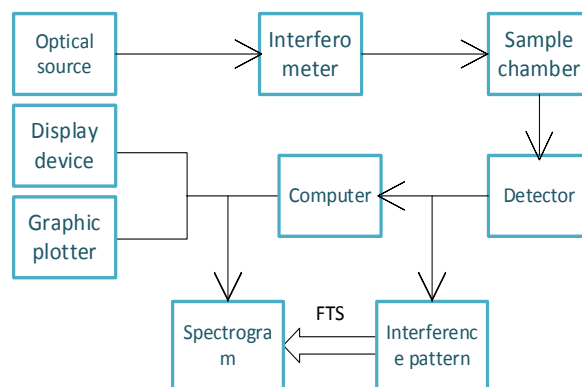


Figure 2. Working principle of Fourier transform infrared spectrometer

Process of experiments

Lignite, anthracite and bituminous coal are tested in this paper. Coal samples are shattered to the diameter of 180~250 μm and then put in a vacuum drying oven for drying. STA449F3 simultaneous thermal analyzer is utilized for isothermal oxidation experiments after coal samples are cooled down. The atmosphere of isothermal oxidation is air, in which the volume ratio of nitrogen and oxygen is 79:21. The airflow velocity is 100 ml min^{-1} . The temperature range of isothermal oxidation is from 50°C to 200°C, the temperature interval is 10 °C, and the objective temperatures are kept for 1 hour. That means when the temperature is 50°C, 60°C, 70°C, ..., 200°C, respectively, coal samples will be kept in each above-mentioned temperature for 1 hour. The heating rate is 10 °C min^{-1} . In room temperature, the reaction furnace is passed into nitrogen only, and then switch to air when reaching the objective temperatures. After isothermal period, coal samples are taken out from reaction oven and grinded with potassium bromide (KBr) powder. The mass ratio of coal sample and potassium bromide is 1:159 when they are blended. After coal and potassium bromide powder are blend evenly, the mixture will be put into the bead machine and pressurized to 10 MPa for about 1 minute. The circular translucent diaphragm with a diameter 9 mm and thickness 0.1 mm is prepared after unloading. Finally the translucent diaphragm is put into the sample room of the Fourier transform infrared spectrometer for scan. The wave-number range of the apparatus is 4000-600 cm^{-1} with a resolution of 4.0 cm^{-1} . Scan time is about 1 minute for 16 times totally. The proximate analysis and ultimate analysis of 3 coal samples are showed in Table 1.

Table 1. Proximate and ultimate analysis of coal samples

Coal samples	Proximate analysis/%				Ultimate analysis/%				
	Moisture	Ash	Volatile matter	Fixed carbon	C	O	S	N	H
Lignite	8.62	30.51	2.13	58.75	72.96	14.58	0.401	0.944	5.079
Bituminous coal	3.91	30.92	3.74	61.43	74.77	9.587	0.728	1.305	3.926
Anthracite	2.13	4.36	13.09	80.42	81.64	3.314	2.889	0.625	1.339

Results and discussion

Among the formed infrared spectrums, the intensity of each absorption peak of 3 coal samples is different but the peaks are in the similar shape [18, 19]. This is probably because various different metamorphic grade coal has similar types of functional groups but the number of which is different. The main types of IR spectrum peak of coal include aliphatic hydrocarbon, aromatic hydrocarbon and oxygen-containing functional groups. And among them, oxygen-containing groups mainly exist in three forms: carboxyl (-COOH), hydroxyl, carbonyl (-CO) and ether bond (-C-O-). Through experiment test, it indicates that the total oxygen content of coal is basically consistent with the total oxygen content of the three groups. The type of oxygen-containing functional groups varies along with the different metamorphic grade of coal. Bituminous coal, for example, Fig.3 shows its infrared spectra at different temperatures.

For aliphatic hydrocarbons, from 50-200°C, The spectrum peaks of 2858-2878cm⁻¹ and 2915-2975cm⁻¹ have the same variation, which are bimodal peaks throughout the course of oxidation. As the temperature increases, the intensity of the bimodal peaks was reduced and the increased but at last decreased. Peak intensity of 1439-1449 cm⁻¹ decreases with increasing temperature, but reaches a high point at 160 °C. No 1373-1379 cm⁻¹ peak exists in the bituminous coal sample. For aromatic hydrocarbon, at 3030-3050 cm⁻¹, the peak is higher at 50-80 °C than at 80-200°C. After 80°C, there is little change in spectrum peak. At 1599-1604cm⁻¹, as temperature increases, the spectrum peak decreases firstly and then increases and decreases again. For oxygen-containing functional groups, the corresponding peak position is 1000-1800 cm⁻¹. The tendency of oxygen-containing functional groups is decreasing with temperature increasing from 50°C to 200°C.

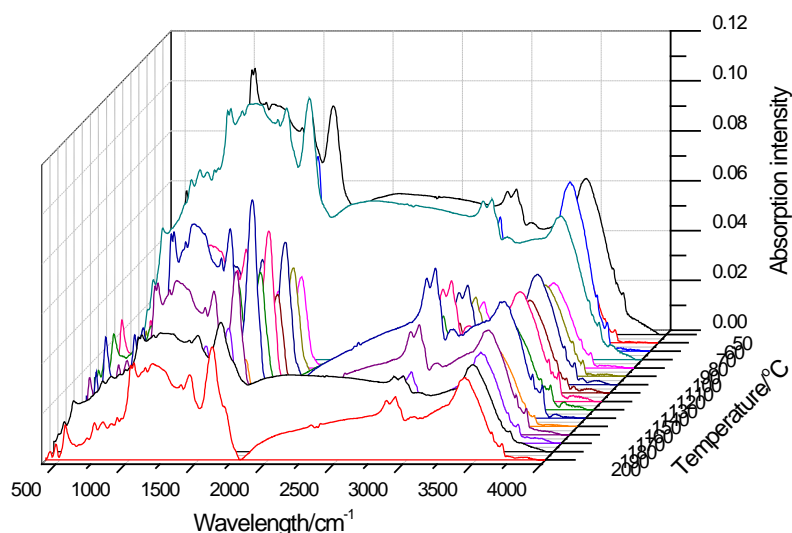


Figure 3. Absorption of bituminous coal verse wavelength at different temperatures

In order to analysis the variation tendency of functional groups in different metamorphic degree of coal further, peak separation software PeakFit is utilized to analyze the changes of functional groups in coal samples during

isothermal oxidation in a quantitative way in this paper. According to rule of Lambert-Beer, when the light beam passes through the prepared diaphragm made by pressed tablet, for any wavelength of light, the absorption intensity is in proporti on to both the

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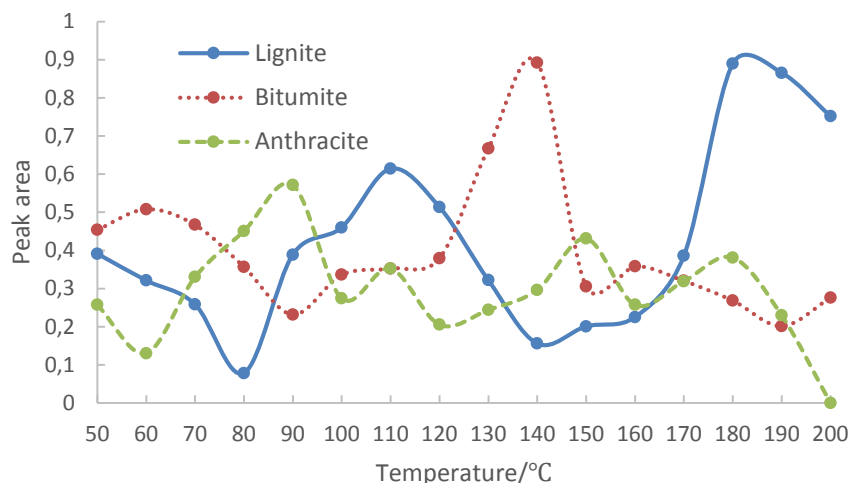
concentration of each component in the diaphragm and optical length [20]. The formula can be expressed as:

$$A(\nu) = \lg \frac{1}{T(\nu)} = a(\nu)bc$$

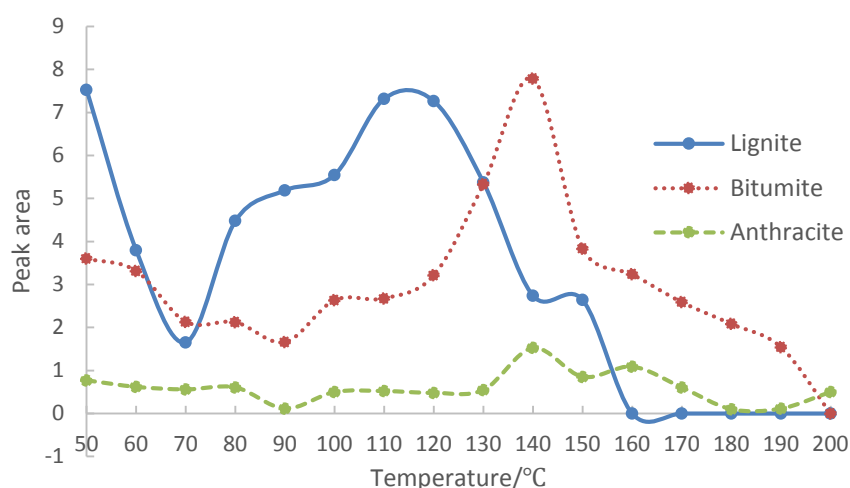
Where, at wave-number of ν , $A(\nu)$ is

absorption intensity; $T(\nu)$ is transmittance; $a(\nu)$ is absorption intensity coefficient; b is optical length; c is concentration of component in the diaphragm.

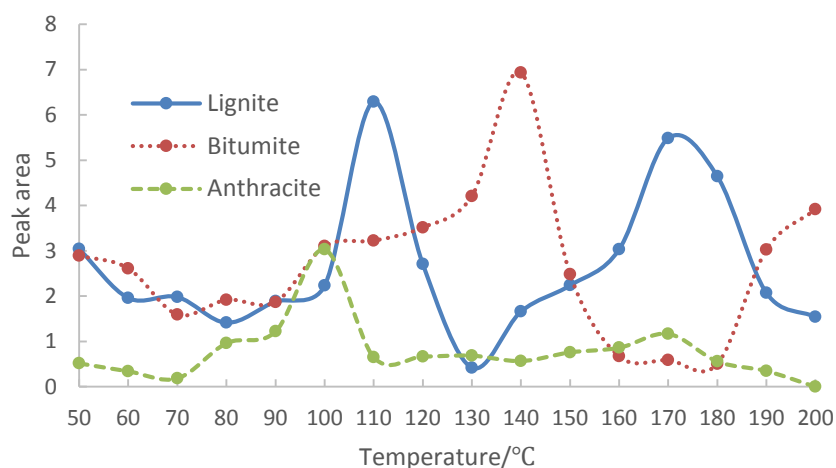
In the experimental process from 50 °C to 200 °C, the variations of functional group peak area values in three coal samples are shown in Fig.3.



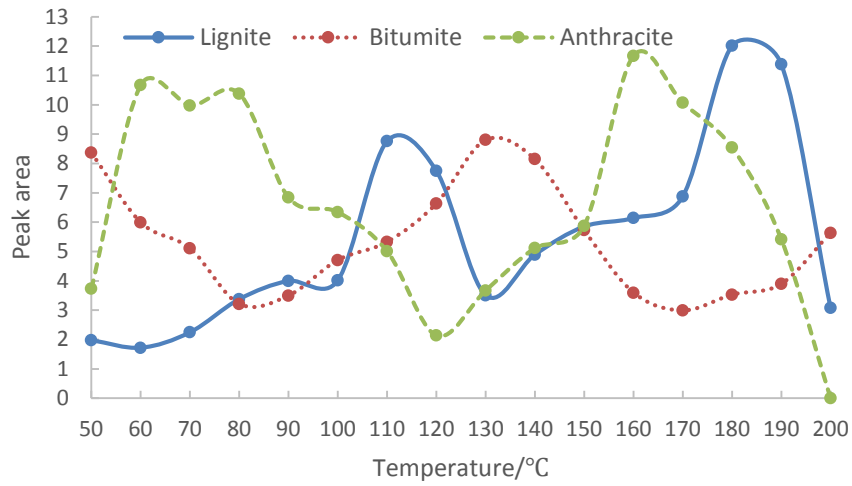
(a) Variation trend of aromatic hydrocarbon verse temperature



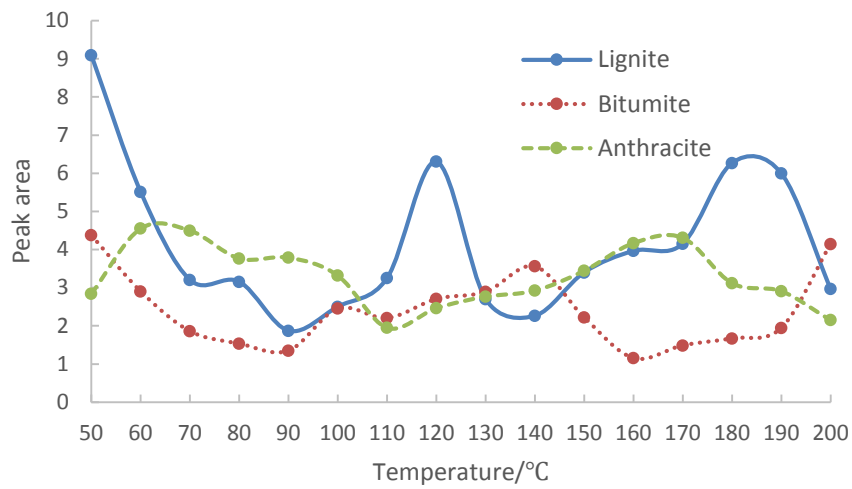
(b) Variation trend of aromatic ring verse temperature



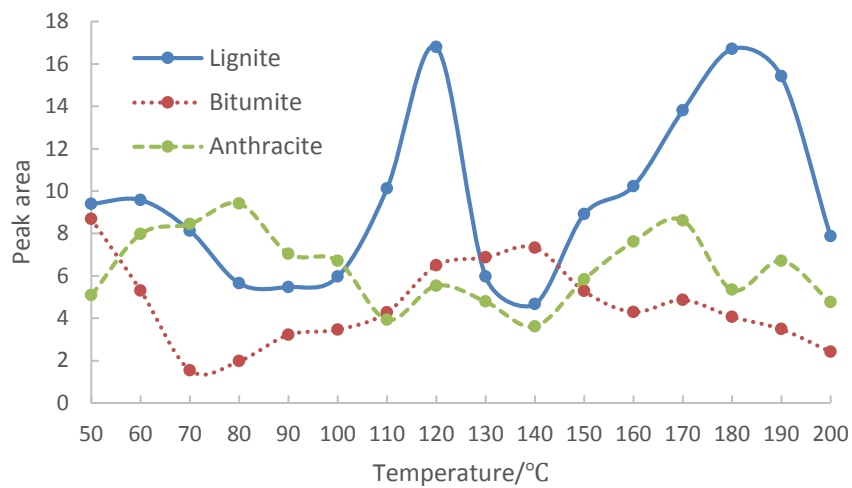
(c) Variation trend of methyl (-CH₃) and methylene (-CH₂-) verse temperature



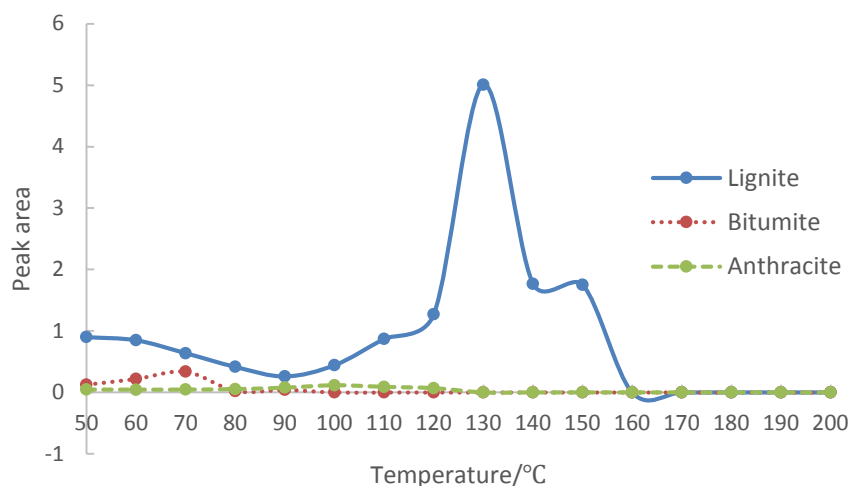
(d) Variation trend of hydroxyl (-OH) verse temperature



(e) Variation trend of substituted benzene verse temperature



(f) Variation trend of ether bond (-CO) verse temperature



(g) Variation trend of ester (-COO) verse temperature

Figure 4. Variation of functional groups in coal verse temperature

Fig.4 (a) shows that in lignite, the turning temperature of peak area of aromatic hydrocarbon is 80 °C,120 °C and 140 °C, respectively. Overall change trend of peak area experienced two decreases and two increases; the turning temperature in bituminous coal is 90 °C and 140 °C, the overall trend has two decreases and one increases; but in anthracite, the turning temperature is 90 °C, the peak area increases when temperature is below 90 °C and decreases when temperature is higher than 90 °C. In general, peak area of aromatic hydrocarbon in anthracite is lower than in lignite and bituminous coal. This means that concentration of aromatic hydrocarbon in anthracite is lower than the concentrations in lignite and bituminous coal, respectively. In Fig.4 (b), aromatic ring (C=C) in lignite experiences two decreases and one increase, the correspondent turning temperature is 70 °C and 120 °C, respectively; the tendency of peak area of aromatic ring (C=C) in bituminous coal is about similar with lignite and the temperature of turning point is 90 °C and 150 °C, higher than turning temperature of lignite; but the peak area of aromatic ring (C=C) in anthracite is very small, and there is no significant trend of increase or decrease. It can be seen in Fig.4 (c) that in lignite, peak area of functional methyl (-CH₃) and methylene (-CH₂-) experienced three decreases and two increases during isothermal oxidation. The temperature of turning point is 80 °C, 110 °C, 130 °C and 170 °C; in bituminous coal, the turning temperature is 70 °C,140 °C and 180 °C; in anthracite, value of peak area changes to decrease trend from increase trend at 100 °C.

Similar with aromatic hydrocarbon, value of peak area in anthracite is smaller than in lignite and bituminous coal. In Fig.4 (d), turning

temperature can be found out in three coal samples: in lignite, it is 110 °C,130 °C and 180 °C, respectively; in bituminous coal, it is 80 °C, 130 °C and 170 °C, respectively and in anthracite 60 °C, 120 °C and 160°C, respectively. In Fig.4 (e) and Fig.4 (f), turning temperature and trend of peak area value can be found out easily. In Fig.4 (g), value of peak area of ester (-COO) in lignite is larger than both in bituminous coal and anthracite which is quite small, about 0. For comparing and accessing, the trend of peak area values of different functional groups in three coal samples and the turning point temperatures are listed in Table 2.

In brief, aromatic hydrocarbon, aromatic ring (C=C), methyl (-CH₃) and methylene (-CH₂-), substituted benzene and other functional groups in lignite and bituminous coal are in similar trends, the difference is the temperature at which the transitions occur. But change trends of peak area of functional groups in anthracite are not consistent even opposite with lignite and bituminous coal. Different ranks of coal leads to this phenomenon. Metamorphism of lignite and bituminous coal is similar to each other, Table 1 have also reflected this. At low temperature, some groups just react with oxygen, thus the groups will be gradually reduced, such an aromatic hydrocarbon, aromatic ring, substituted benzene and so on. At relatively high temperature, some other functional groups in coal will react with oxygen to generate those groups which have reacted with oxygen at lower temperature before, thus the quantity of above groups will be increased again in the trend. The variation of internal structure in coal molecule contributes to the fluctuations of functional groups quantity in coal, which reflects in the peak area value of functional groups. The different rank of

lignite, bituminous coal and anthracite leads to the difference of internal structure inevitably, so for some functional groups, there will be an decreasing trend in lignite and bituminous coal but an increasing trend in anthracite, such as aromatic hydrocarbon, aromatic ring, methyl (-CH₃) and

methylene (-CH₂-), and substituted benzenes. Fig.3 also indicates that the activation temperatures of different functional groups in coal are different, the order of their appearance in coal oxidation is also different. The active functional groups will change as temperature changes.

Table 2. Trends of peak area values of different functional groups and turning temperatures/°C

Coal samples	Lignite	Bituminous coal	Anthracite
Aromatic hydrocarbon	80,120, 140	90, 140	90
Aromatic ring	70, 120	90, 150	—
Methyl and methylene	80,110,130,170	70,140,180	100
hydroxyl	110,130,180	80,130,170	60,120,160
Substituted benzenes	90,120,140,180	90,140,160	60,110,170
Ether bond	90,120,140,180	70,140	80,140,170
Ester	90,130	—	—

Conclusions

Three coal samples of different rank are scanned and tested by Fourier transform infrared spectroscopy, and peak area values of different functional groups are calculated by software PeakFit. It is found that for one single coal sample, the peak area values of one single functional group are different at different temperature. And for different coal samples, at the same temperature, the peak area values of the same functional group are not the same either. This is due to the different rank of coal samples and the order in which the functional groups are activated during coal oxidation at low temperature. Variation of peak area values of each functional group along with temperature in coal are identified, and temperatures of turning points are also found out. The trends of peak area values of different functional groups in different rank of coal samples are analyzed and compared with each other. This paper provides a microcosmic basis for characteristic temperatures of oxidation during coal spontaneous combustion, and provides a basis for the control and prevention of spontaneous combustion to ensure the safety in coal mine.

References

1. Alex C. Smith, Yael Miron, Charles P. Lazzara, 1991. Large-scale studies of spontaneous combustion of coal. United States Department of the Interior, Bureau of Mines.
2. J. M. Kuchta, V. R. Rowe, D.S. Burgess, 1980. Spontaneous Combustion Susceptibility of U.S. Coal. United States Department of the Interior, Bureau of Mines.
3. Cliff D, Rowlands D, Sleeman J,

1996. Spontaneous combustion in Australian Underground Coal Mines. Queensland, Australia, SIMTARS.
4. Carpenter D.L. and Giddings D.S., 1964. The initial stage of the oxidation of coal with molecular oxygen. *Fuel* 43(4), 247.
5. Kathy E. Benfell, B. Basil Beamish, K. A. Rodgers, 1997. Aspects of combustion behavior of coals from some New Zealand lignite-coal regions determined by thermogravimetry. *Thermochimica Acta* 297, 79-84.
6. B. Basil Beamish, J. D. ST. George, M. A. Barakat, 2003. Kinetic parameters associated with self heating of New Zealand coals under adiabatic conditions. *Mineralogical Magazine* 67 (4), 665-670.
7. Krishnaswamy S K, Bhat S, Gunn R D, et al.,1996. Low-temperature oxidation of coal-2: An experimental and model investigation using a fixed-bed isothermal flow reactor. *Fuel* 75(3), 344-352.
8. Beamish B B, Barakat M A, 2001. Spontaneous-combustion propensity of New Zealand coals under adiabatic conditions. *International Journal of Coal Geology* 45, 217-224.
9. Wang H, Dlugogorski B Z, Kennedy E M, 2002. Kinetic modeling of low-temperature oxidation of coal. *Combust Flame* 131(4), 452-469.
10. Jishun, Yu, 2005. *Coal Chemistry*. Metallurgical Industry Press, Beijing.
11. Giver P.H., 1960. The distribution of hydroxyl in coal and its relation to coal structure. *Fuel* 39, 147.
12. Wisner W H., 1975. *Anl Chem Soc Div.*

Thermal technology

- Fuel Chem, Preprint 20, 733.
13. Peizhi Zhu, Jinsheng Gao, 1984. Coal Chemistry. Science and Technology Press, Shanghai.
 14. Shinn J.H., 1984. Towards an understanding of the coal structure. Fuel 63, 483-497.
 15. Kovac J, Larsen J W, Prep Pap, 1975. Am Chem Soc. Div Fuel Chem 20(2), 122.
 16. Kechang Xie, 2001. Structure and reactivity of coal. Science Press, Beijing.
 17. Satoru Murata, Masahiro Hosokawa, Koh Kidena, et al., 2000. Analysis of oxygen-functional groups in brown coals. Fuel Processing Technology 67, 231-243.
 18. Aidong Guo, 2011. Stage characteristics of coal spontaneous combustion and zone variation law of goaf spontaneous combustion. China University of Mining and Technology (Beijing).
 19. Lanyun Wang, Shuguang Jiang, Hao Shao, et al., 2011. Study on self oxidation temperature of coal during spontaneous combustion. Journal of China Coal Science 36(6), 989-992.
 20. Geng W H, Nakajima T, Takanashi H, et al., 2009. Analysis of carbonyl group in coal and coal aromaticity by Fourier transform infrared (FT-IR) spectrometry. Fuel 88 (1), 139-144.

