



CO₂ emission of coal spontaneous combustion and its relation with coal microstructure, China

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Abstract

Coal spontaneous combustion is widely distributed all over the world. CO₂ is the main greenhouse gas emitted by coal spontaneous combustion. In the present study characters of CO₂ emitted by 10 typical Chinese coal spontaneous combustion and the influence of raw coal functional group on CO₂ was studied. CO₂ already exists under normal temperature as coal exposed in atmosphere. Under low temperature, the quality of CO₂ released by coal spontaneous combustion is relatively small, but tends to increase. And corresponding with it, the oxygen consumption amount is also small. At medium temperature, the oxygen consumption increases rapidly and CO₂ mass release rate begins to increase rapidly. Then, CO₂ release rate increase rapidly under relatively high temperature (higher than 673K). Over 873K, concentration of O₂ is 6% and release rate of CO₂ tends to be steady. It also concluded that mass ratio of CO to CO₂ (CO/CO₂) during coal spontaneous combustion was lower than 0.10 at low temperature. And then, it increased rapidly at medium temperature and reached to top at about 673K. At 673-873K, the ratio decreased again, and did not decrease evidently at about 873K. At temperature higher than 873K, the ratio was about 0.13. During the whole testing temperature range, CO/CO₂ was not be higher than 0.26, lower than 0.2. This means that release rate of CO₂ was much higher than CO during the whole process of coal spontaneous combustion. Moreover, the gas release quantity of CO₂ is positively related with carbonyl content in raw coal. Carbonyl and carboxyl were both material basis of CO₂.

Key words

Coal, Functional group, Greenhouse gas, Mass release rate, Spontaneous combustion

Introduction

Coal is a kind of combustible solid, containing carbonic material with over 50% mass and 70% volume. Under natural state, coal that is in the deposition layer does not take part in the process of atmospheric carbon cycle. With exploitation and application of coal, carbon of coal is transformed into gas material, and is then emitted into the atmosphere. There are mainly three types of coal participation in atmosphere carbon cycle. The first type is that the gas stored in coal directly escape into the atmosphere during mining, such as direct emission of CH₄ (Cheng *et al.*, 2011; Noim *et al.*, 2015); second type is that, after solid coal is mined, when it is burned during the industrial or civil use process, the combustible component of coal transfers into CO₂, H₂O, etc. and escapes into the atmosphere, participating in carbon cycle (Wei, 2007); third type is slow oxidation of coal

produces gases like CO₂, CH₄, CO (Stracher, 2004) under natural condition and escapes to the atmosphere. For first type, the gaseous product quantity can be estimated by measuring the gas amount of mining and recycling (Yang *et al.*, 2014; Yue *et al.*, 2012). And for second type, it can be estimated by chemical reacting process under complete combustion condition (fully oxygen supply) (Darío *et al.*, 2006). But in third type, which is different from the second for oxidization condition, is coal oxidation process under inadequacy oxygen supply (oxygen deficient). Thus, formation character of the product is also different from the second due to slow oxidation process. This kind of oxidation generally occurs during underground coal spontaneous combustion, coal field fire, gangue spontaneous combustion, coal dump burning, etc (Sipiä *et al.*, 2012; Pan *et al.*, 2013; Sokol *et al.*, 2014). However for release of greenhouse gas due to coal spontaneous combustion, literature meagre.

In the field of coal spontaneous combustion caused by underground mining, the main concern is about selection and measurement of coal spontaneous combustion early-warning index gas (PDEP, 2001; Xiao *et al.*, 2007). The measuring standards mainly include CO, C₂H₄ etc (Deng *et al.*, 2014). Volume concentration is selected as measuring unit of these indexes, and the change of gas volume concentration at low temperature is also considered. The coalfield fires are widely distributed with large environmental damage (Stracher, 2004), so it is more eye-catching among the greenhouse gas release caused by third type of coal spontaneous combustion. But the current achievements on it are only limited to regional simple site testing for measurement of gas release rule (Mark *et al.*, 2013). In addition, coal spontaneous combustion process is more complicated than the coal oxidation process at oxygen enrichment condition. Three factors, namely various coal types, large range of coal spontaneous combustion temperature (it can be as high as 1000°C (Zhang, 2008)), diversified forms of air leakage, have made the greenhouse gas released by spontaneous combustion different from that released by oxygen enriched combustion of coal completely.

Gases emitted by coal spontaneous combustion include CO₂, CO, CH₄, C₂H₄, C₂H₆, among which, formation amount of CO₂ is much higher than other gases (Glenn *et al.*, 2010), and therefore, it is the main greenhouse gas of coal spontaneous combustion. Therefore, analyzing CO₂ release characters by quantity is significant in weighing the contribution of coal spontaneous combustion on atmosphere carbon cycling. Wang *et al.* (2002) applied non-isothermal continuous reactor to quantify the feature of oxidative product generation quality and oxygen consumption rate of bitumite at low temperature. The experiment indicated that CO₂ output was much higher than CO, and molar ratio was about 3:1. Yuan *et al.* (2013) tested the volume fraction of CO₂ released by spontaneous combustion of three kinds of American coal samples under four kinds of oxygen concentration at temperature of 50-110°C. John *et al.* (2009) experimented the release flux of CO₂ when low temperature oxidation of coal gangue and fat coal from 11 open-pit mines in Australia, and got the average release rate of CO₂ according to the spontaneous combustion degree. Baris *et al.* (2012) obtained the formation rate of CO₂ released by four different kinds of Turkey coal at 40°C, 60°C and 90°C. The results indicated that formation rate of CO₂ increased with increase of coal temperature. But the present researches on coal spontaneous combustion are mainly laboratory analysis at low coal temperature and simple measurement of specific coal field fire. There is rarely laboratory gaseous product analysis (especially for greenhouse gases) on the whole coal spontaneous combustion process from low temperature to high temperature.

Besides, during coal spontaneous combustion as such as coal field fire and underground coal spontaneous combustion, the production rate of CO₂ is not only controlled by coal natural

character, but also by coal body occurrence condition, air leakage, inorganic matter content of coal etc. Undoubtedly, when the coal natural character is different and the rest conditions are same, CO₂ release rate during oxidation process will be different. Related research has shown that the coal microstructure can directly influence coal pyrolysis and oxidative products. During coal oxidation process, the generating process of micromolecule products such as CO₂ is related with coal functional group and molecular structure (Xin *et al.*, 2014). At the field of coal spontaneous combustion with low temperature, some literatures about relation of functional group with CO₂ can be found. Yuan *et al.* (2014) analyzed the composition of functional group during coal oxidation process at different temperature by Fourier transform infrared spectroscopy, and then acquired its influence on oxidation products that include CO₂. Qi (2014) proposed chemical reaction processes which generated CO, CO₂ and H₂O. He pointed out that primary (secondary) carbonyl, carboxyl and hydroxy in coal were the main material basis of their formation respectively. Combining FTIR with low temperature oxidation experiment, Wang *et al.* (2010) concluded that unstable carbon and oxygen complex would be generated after aliphatic hydrocarbon was attacked by oxygen atom and then broke up into CO, CO₂ and stable complex. At accelerating oxidation stage, the stage complex would break down in large amount, providing active center for further oxidation. The researches above were important to find out the mechanics of coal spontaneous combustion, but did not mentioned how to assess the influence of primary functional group on CO₂ emitted in the whole spontaneous combustion process.

The objective of the study was to analyze the release characters of CO₂ on coal spontaneous combustion at 30-800 °C and oxygen deficient conditions, using FTIR and spontaneous combustion modeling technology.

Materials and Methods

10 kinds of coal (from lignite to anthracite) were selected from north and northwest of China. Once the fresh raw coals were collected in situ, they were put into sealed container and taken back to laboratory. Then, they were broken into specific size according to need. After that, samples made were put into sealed wide-mouth bottle and set aside. The screening particle sizes included 1-3mm, 3-5mm, 5-7mm and 7-10mm. The basic information of 10 kinds of coal sample and basic industrial and elemental analysis are shown in Table 1.

Fourier transform infrared spectroscopy : Similar to nuclear magnetic resonance spectroscopy, mass spectra and ultraviolet spectrum, infrared spectroscopy is an efficient way to determine molecular organization and structure. FTIR can detect special properties of different coals according to strength, location and formation of infrared spectral analysis peak. A NICOLET iS10 thermofisher fourier transform infrared spectrometer, which had spectral resolution of 0.4 cm⁻¹ and noise value of 1.24×10⁻⁵ AU,

Table 1 : Industrial and elemental analysis of coal samples

Number	Coal rank	M _{ad} (%)	A _{ad} (%)	V _{ad} (%)	FC _{ad} (%)	C _{ad} (%)	H _{ad} (%)	O _{ad} (%)	N _{ad} (%)	S _{ad} (%)
SAM-1	lignite	16.0	34.8	33.5	31.7	39.1	4.8	24.9	0.83	1.51
SAM-2	jet coal	4.6	18.5	20.5	61.0	64.4	3.9	12.9	1.29	0.36
SAM-3	non-caking coal	12.8	13.2	29.9	56.8	61.5	6.0	23.2	0.82	1.19
SAM-4	weakly caking coal	3.3	4.7	28.8	66.5	62.2	0.5	8.8	0.51	0.28
SAM-5	gas coal	2.9	25.8	29.5	44.7	57.1	4.7	12.5	1.28	0.74
SAM-6	fat coal	1.4	12.6	32.5	54.9	73.6	5.7	8.7	1.11	0.34
SAM-7	coking coal	1.1	6.2	24.5	69.1	82.7	6.7	5.5	1.63	0.83
SAM-8	lean coal	0.8	10.4	13.5	76.5	81.3	4.5	4.0	1.66	0.4
SAM-9	meagre coal	1.3	10.6	11.5	77.8	80.8	4.1	4.3	1.61	0.41
SAM-10	anthracite	3.3	35.2	7.8	57.0	89.0	0.9	4.5	0.54	0.22

was used of FTIR experiment of coals. Its fast scan can reach 40 spectrums each second. After breaking the fresh raw coal was screened by 200 mesh standard, dried 24 hrs in vacuum condition and then 5 mg was for taken FTIR experiment. Coal sample was mixed with pure potassium bromide in 1:160 ratio and grounded evenly in agate mortar; the mixture was taken out and put it into the mould. Then, used tableting machine to make mixture into transparent slice and dried for 30 min in infrared lamp. After that, it was put in the sample room for testing. The testing wave number was 4500-400 cm⁻¹, resolution ratio was 4.0cm⁻¹, and sample scan times were 32. Scanned KBr background for 16 times to get high quality spectrum. Fig. 1 shows primary infrared transmission spectra of 10 coals.

Coal spontaneous combustion experiment : Greenhouse gas experiment of coal spontaneous combustion adopted the whole stage coal spontaneous combustion experiment system. The experiment system included spontaneous combustion experiment platform, computer monitoring and controlling subsystem, gas analysis and collection subsystem. Spontaneous

combustion experiment platform was mainly composed of air generator, coal oxidation reactor, furnace, tar and gas separator, water tank, flow meter, thermocouples and pressure sensors, etc. Computer monitoring and controlling subsystem consisted of hardware system which was responsible for collecting and handling signals and software system doing process control on experimental furnace. Spontaneous combustion experiment process is shown in Fig. 2.

The experimented coal quantity was 200g made of particles of 1-3mm, 3-5mm, 5-7mm, 7-10mm. The composition of coal oxidation product was analyzed by gas collecting and analyzing system. The experimental coal temperature range was set as 30-800°C (that is, 303-1073K). During experiment process, spontaneous combustion gaseous product was tested every 20K in coal temperature of 303-573K and tested every 30K from 573K to 1073K. Considering the influence of non-uniformity of actual air leakage on CO₂ output, the experiment at air supply was made of four states, *i.e.*, 30ml min⁻¹, 60 ml min⁻¹, 90 ml min⁻¹ and 120 ml min⁻¹.

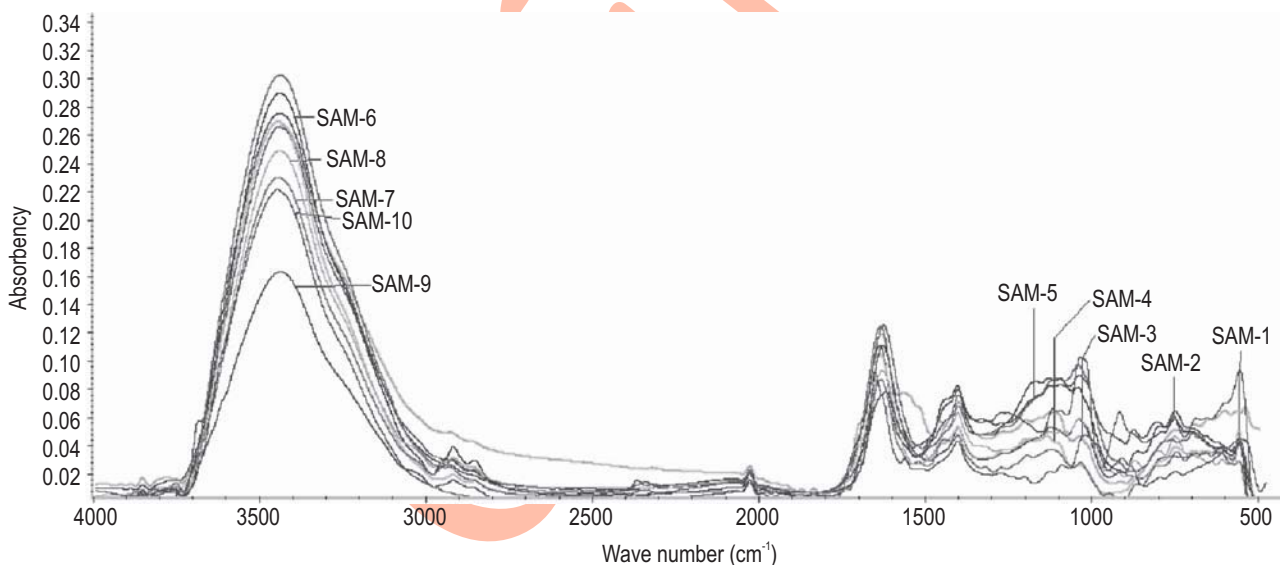


Fig. 1 : Primary infrared transmission spectra of infrared spectroscopy of coal

Results and Discussion

Based on the infrared transmission primary spectrogram of infrared spectroscopy (Fig.1), after background light spectrum noise reduction and baseline correction, second derivative of primary spectrogram was applied to get accurate positioning of spectrum absorption peak and shoulder peak and used Fourier deconvolution data processing technology to strengthen separation of serious overlap of spectral bands. After that, peak fitting method was adopted to fit each overlapping peak by computer fitting. The settled bands were broken up into peaks of Lorentzian function distribution or Gaussian function distribution. The peak shape of Lorentz function distribution was broad, but the peak shape of Gaussian function distribution was tall and narrow (Weng, 2010). Here combined the two function distributions to make good fitting of the original curves. All primary spectrograms were dealt with peak fitting in accordance with $4000\text{-}2000\text{cm}^{-1}$ and $2000\text{-}600\text{cm}^{-1}$ two segments. After fitting by significance test, R^2 was above 0.9999.

The main functional groups of coal are -OH , >C=O , -COOH , -O- , -CH_3 , $\text{-CH}_2\text{-}$, $\text{-}\dot{\text{C}}$ and -C=C- . According to infrared spectroscopy affiliation (Carpenter *et al.*, 1964) of different functional group, each peak of overlapping peak fitting was contrasted and then microstructure of different coal samples was achieved. Absorption peak affiliation of functional group and the functional group area percentage of each coal sample area is shown in Table 2. Table 2 shows that -C=C- content increased with addition of coalification degree. Meanwhile, total oxygenic functional group decreased. Hydroxy content decreased first, and then increased at the point of weakly caking coal, gas coal and fat coal, then decreased again, and finally increased at the

point of anthracite coal. Carbonyl decreased first, slightly rose in coking coal, then decreased. Carboxyl content decreased continuously while anthracite was slightly elevated. Through correlation analysis on total containing oxygen functional group, aliphatic hydrocarbons and aromatic hydrocarbon with C content and O content (level of significance is 0.01), it was obtained that oxygen containing functional groups content was positively related to O element content, with a correlation coefficient of 0.767, and the total carbon group amount was positively related to C element content, with a correlation coefficient of 0.868. These met the general change law of coal quality, which in turn proved reliability of infrared functional group analysis results.

The mean release rate of CO_2 emitted by ten Chinese typical coals during spontaneous combustion at different air supplies is shown in Fig. 3. CO_2 was released under room temperature. At low temperature oxidation stage, CO_2 release amount was small and increased slowly, but the overall growth was not obvious. After coal temperature exceeded a certain degree, CO_2 release rate presented a fast growth and rose with increase of air supply. At high temperature, CO_2 release rate was stable and did not increase rapidly any longer, some samples' CO_2 release even declined. The influence of air supply on CO_2 release was not obvious at low temperature, but at middle and high temperature, CO_2 release quantity rose with increase of oxygen supply significantly.

CO_2 release law of spontaneous combustion at low temperature had been researched a lot, but there were few researches of CO_2 release on the middle and high temperature stage of spontaneous combustion. Even in regular researches on CO_2 at low temperature, they were mainly about the change on

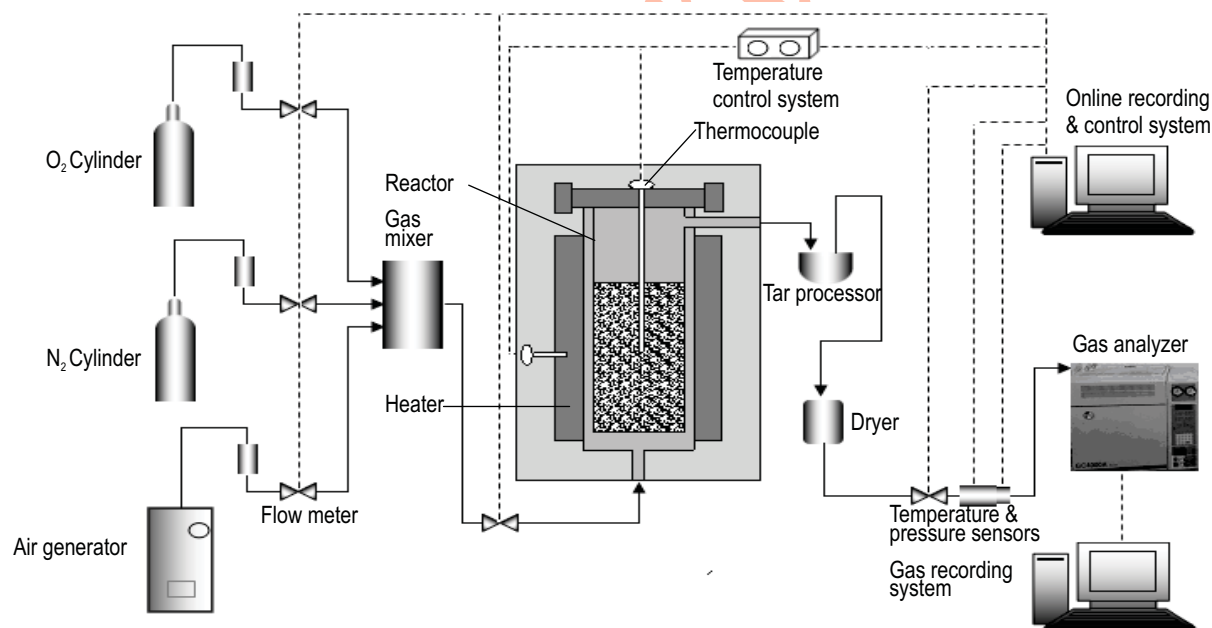
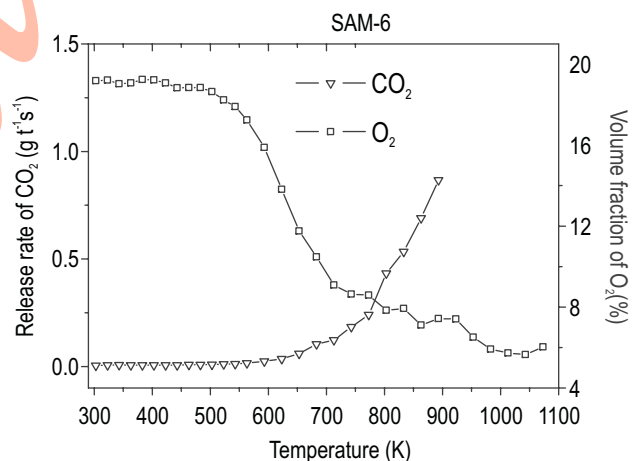
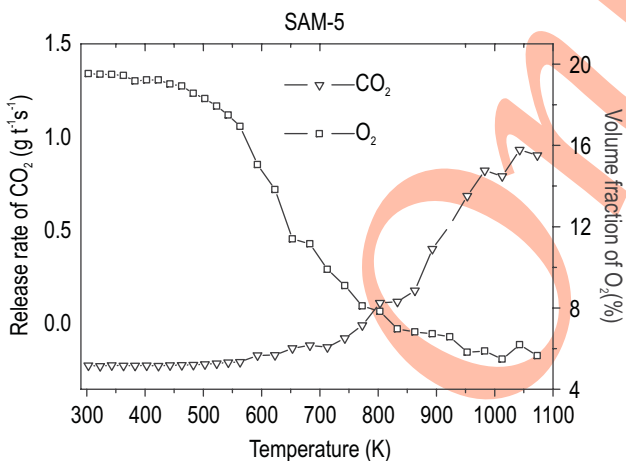
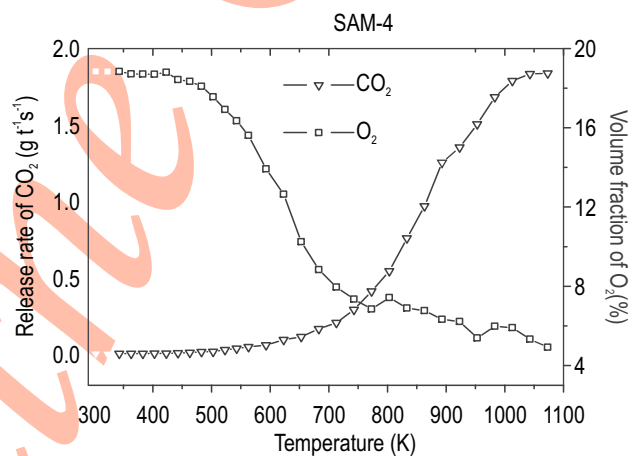
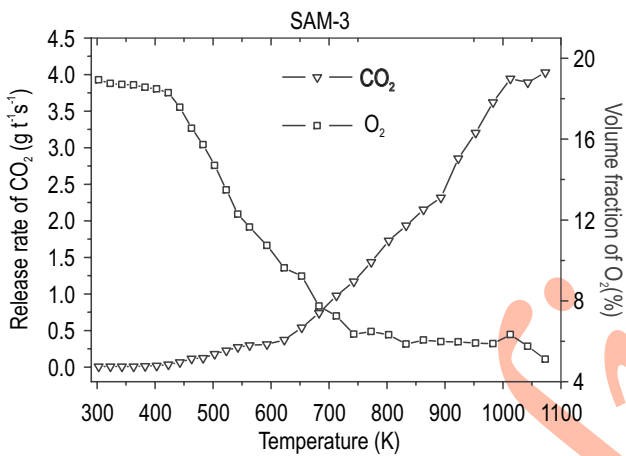
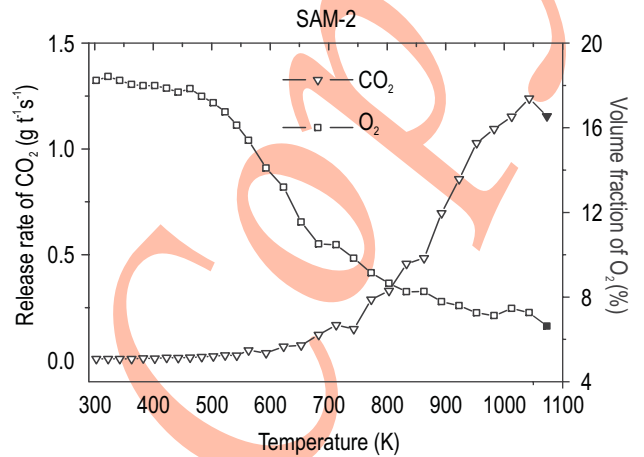
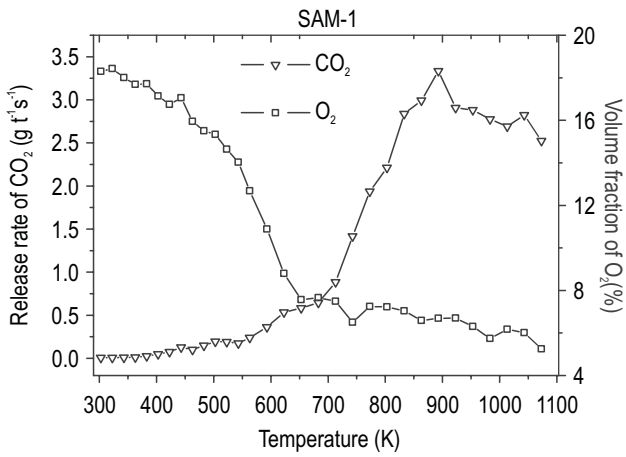


Fig. 2 : Experiment process of greenhouse gas released by coal spontaneous combustion

volume concentration. Fig.3 shows that CO_2 mass change rate of coal spontaneous combustion was smaller before 473K, similar to the experiment results of Wang (1999). After 473K, the quantity of CO_2 release was obviously and closely related with the process of coal molecular structure combining with oxygen. Except anthracite, the oxygen consumption of coal spontaneous combustion was very small before 473K; at about 473-673K, the oxygen consumption increased sharply, but later, the oxygen concentration was smaller due to deficiency of oxygen.

Correspondingly, when the coal temperature was higher than 673K, CO_2 release quantity rose sharply. But after that, due to lack of oxygen supply, CO_2 changed smoothly, and even decreased slightly. At higher temperature, oxygen concentration remained at around 6%, lower than 7% (Voracek, 1997), the minimum oxygen concentration standard to maintain the coal spontaneous combustion. According to Voracek (1997), at this kind of state, if there was no other way of supplying oxygen, the spontaneous combustion oxidation process would not last for a longer time, and



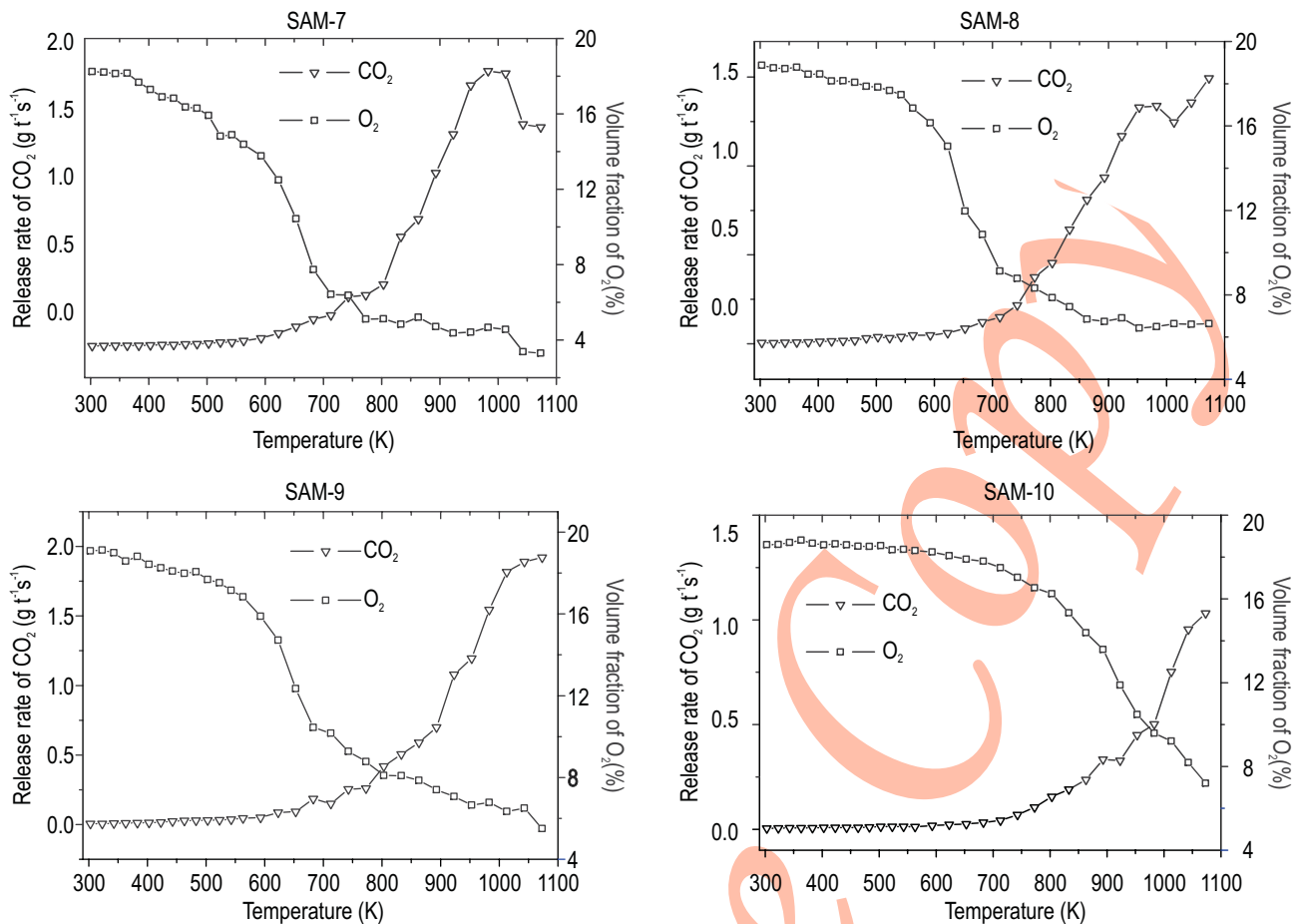


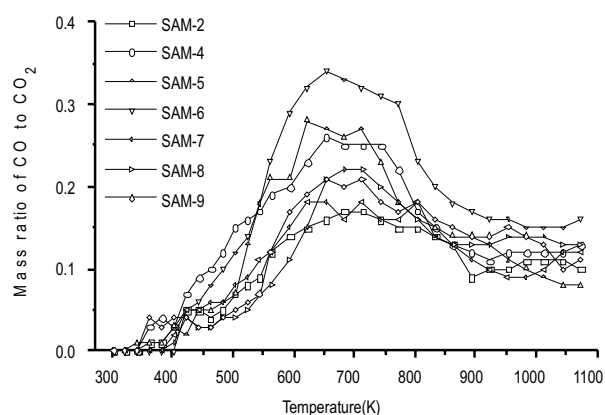
Fig. 3 : Mean release rate of CO₂ and the mean volume fraction of O₂ at different coal temperatures

Table 2 : Percentage of infrared spectroscopy absorption peak area of main functional groups

	Aliphatic hydrocarbons (%)	Aromatic hydrocarbons (%)	Oxygenic functional group (%)				Sum of oxygenic functional group
			-CH ₃ / -CH ₂ - / -Ċ	-C=C-	-OH	-Ċ=O	
SAM-1	9.58	9.50	56.12	12.30	6.41	6.09	80.93
SAM-2	9.89	12.60	52.35	11.26	7.19	6.71	77.51
SAM-3	10.62	12.21	51.87	11.49	7.55	6.25	77.17
SAM-4	8.04	18.17	53.41	9.04	5.75	5.58	73.78
SAM-5	9.14	15.99	56.11	7.43	7.18	4.15	74.86
SAM-6	8.94	19.96	54.19	6.36	6.45	4.10	71.10
SAM-7	8.17	23.50	49.72	7.17	8.06	3.38	68.33
SAM-8	7.82	25.66	47.23	5.57	8.29	5.43	66.52
SAM-9	8.88	29.48	43.87	5.13	8.75	3.87	61.63
SAM-10	6.68	31.12	47.09	3.99	7.77	3.35	62.20

the spontaneous combustion would gradually go out after a while. The experimental results also validated 7% of the minimum oxygen concentration (Voracek, 1997). CO is another kind of oxidation product during coal spontaneous combustion. The mass ratio of CO to CO₂ (CO/CO₂) of 10 typical coal samples is shown in Fig.4. Fig.4 revealed that the value of CO/CO₂ presented four-

stage feature for most coal types during the oxidation process of spontaneous combustion. Namely, CO/CO₂ was smaller than 0.10 before 473K. At about 473-673K, this value increased rapidly and reached top at about 673 K. And at 673-873K, the ratio decreased till the decrease was not so evident at about 873K. After 873K, CO/CO₂ was maintained at a relatively steady state, with an

Fig. 4 : Mass ratio of CO to CO₂Table 3: Accumulative mean value of CO/CO₂ at different temperature sections

Temperature	SAM-2	SAM-4	SAM-5	SAM-6	SAM-7	SAM-8	SAM-9
[373K,473K)	0.02	0.04	0.02	0.02	0.02	0.01	0.03
[473K,673K)	0.12	0.20	0.22	0.26	0.14	0.10	0.13
[673K,873K)	0.15	0.18	0.18	0.24	0.16	0.16	0.17
[873K,1073K)	0.11	0.12	0.11	0.16	0.10	0.13	0.13

Table 4 : Accumulated mean release rate of CO₂ at different temperature sections (g t⁻¹ s⁻¹)

Number	[303K,473K)	[473K,673K)	[673K,873K)	[873K,1073K)
SAM-1	0.04632	0.72345	1.82459	2.87626
SAM-2	0.01017	0.03742	0.27197	0.98828
SAM-3	0.02498	0.24818	1.37513	3.28012
SAM-4	0.00729	0.05162	0.42989	1.54277
SAM-5	0.00954	0.03551	0.20042	0.78988
SAM-6	0.00628	0.02046	0.29293	0.97386
SAM-7	0.00963	0.04712	0.38301	1.47494
SAM-8	0.00970	0.04548	0.35449	1.21632
SAM-9	0.01226	0.04781	0.31531	1.36117
SAM-10	0.00645	0.01530	0.10464	0.56097

Table 5 : Pearson relative coefficient of release rate of CO₂ with functional group quantity at different temperature sections

Temperature	$-\text{CH}_3$ / $-\text{CH}_2$ / $-\dot{\text{C}}$	$-\text{C}=\text{C}-$	$-\text{OH}$	$-\text{C}=\text{O}$	$-\text{O}-$	$-\text{COOH}$
[303K,473K)	0.519	-0.603	0.367	0.680*	-0.208	0.490
[473K,673K)	0.426	-0.593	0.424	0.656*	-0.314	0.461
[673K,873K)	0.576	-0.654*	0.396	0.741*	-0.277	0.559
[873K,1073K)	0.625	-0.589	0.257	0.716*	-0.161	0.556

*Significantly correlation as $\alpha=0.05$; **significantly correlation as $\alpha=0.01$

average value of 0.13. On the basis of three temperature points of 473K, 673K and 873K, the whole experiment temperature range was divided into four sections: [303K, 473K), [473K, 673K), [673K, 873K), [873K, 1073 K). And the accumulated mean values of CO/CO₂ at four temperature sections were calculated as in shown

in Table 3. Fig.4 and Table 3 reflects the release rate of CO₂ was always higher than that of CO during the whole process of coal spontaneous combustion. In the present study, the change law of CO/CO₂ at low temperature was same with that of Wang (2002). The accumulative mean values of CO/CO₂ four temperature stages were not higher than 0.26, and under most conditions, lower than 0.2. The quantity of heat released by carbon generating CO₂ reaction was almost 3 times as the generating CO reaction (Fu, 2003). Therefore, the results indicated that coal oxidation reaction, which was dominated by generating CO₂, could release more heat quantity and made the temperature rising rapidly. Moreover, it also influenced self heat process of coal inevitably, and accelerated coal spontaneous combustion.

The accumulated mean release rate of CO₂ at different temperature sections is list in Table 4. On the basis of Table 4 and Table 2, the relation of CO₂ quantity with functional group content in raw material at different temperature sections was analyzed and listed in Table 5. The results showed that CO₂ quantity was always positively related with carbonyl content of raw coal during the whole process of coal spontaneous combustion.

Qi (2014) and Wang (2010) proposed that primary and secondary carboxyl $-\text{COOH}$ and carbonyl $-\text{C}=\text{O}$ were the main material basis for generating CO₂ and CO during coal spontaneous combustion at low temperature stage. But the results indicated that the content of primary carboxyl of raw coal had important influence on CO₂ released by coal spontaneous combustion. Xin (2014) put forward that the main generating ways of CO₂ when coal spontaneous combustion included: direct burning reaction, unsteady chemisorptions, decomposition of steady oxygen-containing functional group $-\text{COOH}$. The generating ways of CO included two reactions: direct burning reaction; decomposition of steady oxygen-containing functional group. It should be mentioned that the CO₂ quantity that were tested in the present study was quantitative at reactor's outlet, therefore, the quantity of CO₂ should include the part generated by CO combined with O₂. At the same time, carbonyl (mainly is aldehyde group) could be easily oxidized by air. After air oxidation, the primary product of aldehyde group was peracid, namely creating carboxyl. This reaction process is free radical reaction, and is called autooxidation (Zhang, 2011). Therefore, the generating ways of CO₂ during coal spontaneous combustion also include decomposition of carbonyl to generate CO and then get oxidized to CO₂, and carbonyl auto-oxidatized to carboxyl and then decomposed to CO₂. It also indicated that carbonyl was not only the material basis of CO in the process of coal spontaneous combustion, but also the material basis of CO₂.

Combining Fig. 3 with Fig. 4, it can be judged that the main source of CO₂ was dissociation of CO₂ absorbed in coal under 473K, of course, there also may be some CO₂ generated by small amount of functional group. Between 473K and 673K, CO/CO₂ increased evidently, while the growth range of CO₂ was relatively small, which indicated that the change rate of CO was

higher than that of CO_2 . At this temperature, oxygen consumption also rose rapidly, which was related to breakage of functional group during pyrolysis of coal, i.e., the oxidation pyrolytic reactivity of coal was high and chemical links were easily broken. During coal spontaneous combustion, oxygen was deficient. But oxidation of functional group including carbonyl may consume large number of oxygen. Therefore, before 673K, CO was mainly obtained from dissociation of C-O and other functional groups (in general condition, C-O was the weak linkage in coal, and it would be released in the form of CO and CO_2 before 873K (Xie, 2002)). Beyond 673K, the decomposition of carboxyl and oxidation of CO increased CO_2 rapidly, but oxygen consumption was smaller than before, and decreased the process of CO/ CO_2 . Beyond 873K, oxygen concentration was lower than the lowest value for spontaneous combustion, the quantities of CO and CO_2 were in a state of generation balance.

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