Effect of temperature and stress on molecular structure and carbon monoxide generation of lignite from Kailuan mining area

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Abstract: In order to analyze the origin of carbon monoxide (CO) in coal seams, stress-strain experiments under temperature of 50, 150 and 250 °C were conducted using lignite from Kailuan mining area. Fourier transform infrared spectroscopy and elemental analysis were carried out before and after deformation of the samples. The results indicated that CO generated at 150 and 250 °C; the gas component was mostly oxygen (O₂), with small amount of carbon dioxide (CO₂), methane (CH₄) and hydrogen (H₂). At 50 °C, O₂ and a little CO₂ were observed and no CO was found. The carbon content of the coal samples increased slightly after deformation, and the oxygen content, H/C ratio, and O/C ratio decreased. The molecular structure of coal displayed different evolution characteristics at various temperatures. At 50 and 150 °C, the falling off of side chains, broken of ether bond and directional realignment of the aliphatic chains resulting in the formation of long chains were the main performance of coal molecular structure evolution. While at 250 °C, the side chains fell off and short chains formed. Furthermore, at both 150 and 250 °C, condensed degree of aromatic ring increased. Under the action of temperature and pressure, CO forms in two ways. The first is that ether bond breaks, oxygen and carbon atoms combine together and forms CO, or O₂ forming in the broken of ether-oxygen bond leads to the oxidation of free radicals and resulting in the formation of CO. And the second is that CO derives from falling off of C=O group.

Keywords: Lignite; Molecular structure; Carbon monoxide generation; Deformation; Temperature

1. Introduction

Coal, one kind of organic rock, is very sensitive to temperature and pressure. In the process of the geological evolution, various tectonic-thermal events inevitably lead to a series of physical and chemical changes of coal. Aromatic structure, aliphatic structures, as well as oxygen containing functional groups in coal molecular structure perform different evolution characteristics, along with the generation of some kind gases. By employing fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) methods to study the molecular structure of tectonic deformation coal, some researchers considered that tectonic deformation coal and primary structure coal with the same metamorphic degree are different in their chemical structure [1-10].

In recent years, carbon monoxide (CO) over safety standard has been detected from an increasing number of coal mines in China. Research shows that the origin of CO is not only due to the oxidation of coal in the open air, but also due to the primary deposition of CO in the coal seam [10,11]. Coal pyrolysis experiments show that CO is produced when the pyrolysis temperature reaches 300-800 °C [11]. CO is also produced in deformation experiments at temperature of 200 °C [12]. However, it is still not clear whether the original occurrence of CO in coalbed is caused by the side chain rupture of molecular structure at certain temperature at present.

In the past, deformation experiments at high temperatures and pressures usually concentrated on temperature, pressure, and strain rate. However, the chemical changes in the molecular structure has not been systematically studied in those experiments, and whether or not CO has been generated during the process of deformation have been received little attention in those experiments. In this study, coal samples were collected from the Cuijiazhai Coal Mine of the Kailuan Mining Group, where CO concentration has once exceeded the safety limitation during the year of 2012. The deformation experiments were performed at temperatures 50, 150, and 250 °C. The evolution of coal molecular structure and the CO generation mechanism has been studied. And the purpose of this is to find the origin of CO and provide a theoretical basis for the coal mining safety.

2. Experimental

2.1 Sample collection and preparation

Samples in the study were obtained from E11510 working face of the Cuijiazhai Coal Mine, at depth of 835 m. Three columns with 40 mm length and 20 mm diameter were prepared. Then, following the national standard "GB474-2000", the remained samples were crushed and split for elemental, macerals component and industrial analysis, and for the measurement of vitrinite reflectance.

2.2 Stress-strain experiment

Experiments were conducted by using a high temperature and high pressure apparatus, which belongs to the institute of geology, China Earthquake Administration. The temperature was controlled by a set of device, which was used to adjust the power of the heating furnace. To ensure uniform pressure and safe heating of the samples, argon gas was used to apply the confining pressure. And the axial load was controlled with a digital hydraulic servo.

Firstly, 30 min of vacuating was conducted, and then 20 MPa confining pressure was applied. The

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airtightness was detected. If the entire system was completely sealed, another 15 min of vacuating was applied. Secondly, let the system heating be the experiment temperature. The heating rate was set at 5 °C per minute. After the temperature reached the desired value, the experimental confining pressure was set to 30 MPa. Thirdly, the axial pressure was added. The axial deformation rate was set to 0.001 mm per second until the deformation displacement reached 3-3.5 mm, then kept the temperature at 50, 150 and 250 °C, deformation and axial pressure were stable for 7 h and ended the experiment. During the experiment, the temperature was strictly controlled to ensure the accuracy of the experimental results. Meanwhile, a vacuum bag was used to collect the gas generated in the process of deformation. The deformed samples were broken and ground to 200 mesh for infrared spectroscopy and elemental analysis. The detection of gas composition was performed in the Beijing Coal Chemical Research Branch of the China Coal Science and Technology Research Institute, using an Agilent 7890 meteorological chromatograph.

2.3 Fourier transform infrared spectroscopy

A Vertex 70 Fourier transform infrared spectrometer of Bruker Dalton was used in the infrared spectrum analysis. Each sample was cut into thin slices with a diameter of about 13 mm. For the test sample, KBr ratio was 1:160, in the range of 400-4000 cm^{-1} for collecting spectral information, and the resolution was 4 cm^{-1} . FTIR spectrum was obtained after 32 cumulative scans. In addition, the above experiment was conducted for both samples before and after stress-strain experiments.

3. Results analysis

3.1 Coal quality

The values listed in Table 1 show that the sample represents a low-degree metamorphism of lignite.

Table 1 Coal quality data

Sample	Industrial analysis (% by weight)			Elemental analysis (% by weight)					Maceral composition (% by weight)				R_0 (%)
	M_{ad}	A_d	V_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}	V	I	E	M	
CJZ	18.36	5.54	55.58	73.14	4.38	21.31	0.86	0.31	47.37	38.21	0.78	13.64	0.41

3.2 Deformation feature and gas composition

In order to analyze the molecular structure changes of the sample under different temperatures, the deformation experiments were performed at 50, 150, and 250 °C. Fig. 1 shows the results of the experiments.

Fig. 1. Strain curves of the deformation experiments at different temperatures

To ensure purity of the collected gas, the impact of the air and gas adsorbed in coal were minimized. Before the experiment, the air collecting-bag was connected directly to the experimental equipment. And it was vacuumed through the vacuum system together with the whole system simultaneously. Coal samples were kept under vacuum state and significant amount of adsorbed gas was desorbed, and only little part of the adsorbed gas in the confined pores was difficult to expel. This little amount of adsorbed gas had insignificant effect on the experimental results, thus the collected gas mostly came from the deformation experiment. The gases detected in the experiment are listed in Table 2.

Table 2 Composition of gases generated in the deformation experiment (% by volume)

Sample number	H ₂	CO ₂	C ₃ H ₈	C ₃ H ₆	C ₂ H ₄	C ₂ H ₆	O ₂	CH ₄	CO
50 °C	0	4.6499	0	0	0	0	95.3501	0	0
150 °C	0.0052	17.4538	0.0428	0.0013	0.0311	0.0907	81.4745	0.311	0.5896
250 °C	0.0952	97.5516	0.0732	0.0084	0.0387	0.0774	0.7630	1.2816	0.1109

Note: N₂ and O₂ have been deduced according to the proportion of N₂ and O₂ in the air.

The values listed in Table 2 indicate that CO is not collected at 50 °C; and CO is collected at both 150 and 250 °C. Similar performance is observed for other gases, such as H₂ and CH₄. Other observations show that the concentration of O₂ content is the highest at 50 and 150 °C, while the CO₂ concentration is the highest at 250 °C.

3.3 Elemental analysis

Coal is mainly composed of five elements: carbon, hydrogen, oxygen, nitrogen and sulfur. Carbon is of the highest concentration of all elements in coal. Carbon is mainly present as aromatic nucleus and aliphatic side chains, such as C-C, C-O, and C-H bonds. Hydrogen is also present in coal mainly as C-H bonds. Oxygen in coal is represented by molecular bridge bonds and functional groups, mainly in the form of C-O, COO, and C=O bonds. In order to analyze the effect of deformation on the coal macromolecular composition, elemental analysis of the deformed samples was performed.

Elemental analysis before and after deformation was performed using an Elementar Vario MACRO Cube test at the Chemical Engineering Department of the China University of Mining and Technology (Table 3).

Table 3 Analysis of the elements in coal before and after deformation (% by weight)

Sample	C _{daf}	H _{daf}	O _{daf}	O/C	H/C
Undeformed coal	73.14	4.38	21.31	0.29	0.06
50 °C	75.28	4.33	19.45	0.26	0.06
150 °C	75.84	3.97	19.24	0.25	0.05
250 °C	76.96	3.98	18.12	0.24	0.05

Deformation led to the increase in the carbon content of all three samples; however, the oxygen content decreased. The percentage of O reduces, which leads to a material basis for the collection of CO and O₂ during the experiment. This indicated the formation of the oxygen gas as a result of the deformation.

The C/H atom ratio in coal is 3:2 (Table 1), which is greater than the ratio 1:1 in the benzene ring. This value of ratio indicates that the aromatic structure, with at least two substituents on the benzene ring, represents the main part of the coal molecular structure. Moreover, the aliphatic structure, with the average of three substituents, is relatively less, indicating the presence of many aliphatic side chains in coal macromolecular structure.

Compared to undeformed coal, the O/C ratios decreased at 50 °C while H/C ratio kept stable. O₂ and a small amount of CO₂ were collected, which might be attributed to that after the falling off of the oxygen atom from oxygen containing functional groups, carbon atoms combined directly with each other to form C-C bonds, resulting in O/C decrease. And only small amount aliphatic side chains -CH₃ and -CH₂ were broken, which resulted in the stable of H/C ratio.

At 150 and 250 °C, the O/C and H/C ratios decreased, and H₂ was collected, which might be caused by the dehydrogenation of aromatic structure. Hydrocarbon gases such as CH₄ were probably produced as a result of the partly falling off of aliphatic side chains. At these two temperatures, the contents of CO₂ and CO were different, a consequence caused by different amounts of C-O, C=O, and COOH functional groups in coal.

3.4 Fourier transform infrared

3.4.1 Fourier transform infrared spectrum

Fig. 2 shows the FTIR spectra of the samples before and after the deformation. The absorption peak at 3212 cm⁻¹ is the stretching vibration of the aliphatic hydrogen-bonded association and aromatic OH. Peak at 2906 cm⁻¹ is attributed to the stretching vibration of aliphatic CH and CH₃. The peak at 2831 cm⁻¹ corresponds to the stretching vibration of CH₂. Peak observed at 1690 cm⁻¹ is the C=O stretching vibration of unsaturated carboxylic acid, and at 1579 cm⁻¹ is the stretching vibration peak of hydrogen bond associated with C=O or aromatic skeleton C=C. Peak at 1330-1110 cm⁻¹ corresponds to the stretching vibration of phenol, ether, and alcohol. Peaks at 870, 815, and 750 cm⁻¹ are attributed to 2, 3, and 4 hydrogen deformation vibration of the same aromatic nucleus of aromatics [13].

Fig. 2. Infrared spectra of the samples at different temperatures

Compared to undeformed coal, no variation takes place for the peak numbers and peak shape of the FTIR spectra, indicating that the kind of functional group in coal molecular structure keeps stable. And the intensity

changes at different temperatures reflect that the deformation causes changes in the content or number of them.

3.4.2 Qualitative and semi-quantitative analysis

Different concentration of sample may lead to different peak intensities. To reduce this error, base-line correction and normalization processing of the spectrum were performed in this study [14]. The FTIR peaks locating at 3000-3600 cm^{-1} correspond to the hydroxyl group, and those at 2800-3000 cm^{-1} attribute to aliphatic hydrocarbon, those at 1000-1800 cm^{-1} are ascribed to oxygen containing functional groups, and those at 700-900 cm^{-1} correspond to the aromatic CH outside surface deformation and vibration. In order to analyze the origin of CO and the changes in aliphatic structure during the experiment, only oxygen containing functional groups and aliphatic hydrocarbons were analyzed here. Fig. 3 shows the proceeding FTIR spectrum.

Fig. 3. Process of FTIR spectrum

Fig. 3 shows that after deformation, the aliphatic hydrocarbons and the oxygen containing functional groups are characterized by different peak intensities and shapes at various temperatures. The highest peak intensity of the aliphatic hydrocarbons is observed at 250 °C. The intensity decreases in the order of undeformed coal, 150 and 50 °C. The peaks for the oxygen functional groups perform a reverse order, and the highest intensity is observed at 50 °C. And the intensity decreases from 150 °C to undeformed coal then to 250 °C.

In this study, the software origin was used to perform peak fitting (using Gaussian distribution) [14]. The contents of the functional groups before and after deformation at three temperatures are listed in Table 4.

Table 4 Content functional groups (cm^{-1})

Peak	1579	2944	2906	2831	1703	1330-1110
Undeformed coal	29.831	0.017	0.059	0.080	2.021	33.00299
50 °C	32.539	0.012	0.057	0.042	2.203	35.27863
150 °C	33.631	0.013	0.063	0.063	2.198	34.06171
250 °C	14.369	0.030	0.066	0.811	1.925	10.40158

The molecular structures of the samples are different at three temperatures. At 250 °C, the intensity of peak at 1579 cm^{-1} decreases and the same results have also been reported [15]. This means that C=O of hydrogen bonds content decreases [13]. While at 50 and 150 °C, the intensity of the same peak increases slightly compared to undeformed coal, similar phenomenon was reported [3]. At 50 and 150 °C, the impact of the temperature and pressure to C=O of hydrogen bonds is small, alone with the broken of aliphatic side trains, will lead to relative increase of C=O of hydrogen bonds content after deformation, and the increasing of peak intensity [13].

3.4.3. Infrared structure parameter

During the infrared analysis of coal, the sample thickness and experimental temperature will affect the intensity of the infrared spectrum. In order to eliminate the influence of these two factors, peak intensity ratios (peak ratios or peak height ratios) is adopted to illustrate the characteristics and changes of various coal structures. The reason of doing this is that the peak areas of the FTIR spectrum are affected less by sample and instrument than peak height [14]. In this study, the peak area ratio (I_1 - I_5 in Table 5) were used for quantitative analysis of the microstructure of coal [14,16, 17]. In Table 5, $I_1=A_{2944}/A_{1579}$ (where A represents the area of certain peak, the number after it represents the wavenumber of the peak, same as below) represents the degree of the falling off of CH_3 ; $I_2=A_{2831}/A_{1579}$ represents the degree of the falling off of CH_2 ; $I_3=A_{2924}/A_{2964}$ characterizes aliphatic chain length and branched degree, the larger the I_3 , the longer the aliphatic chain and the less the branched degree is; $I_4=(A_{1703}+A_{1745})/A_{1579}$ characterizes of the relative content of oxygen containing functional groups C=O and aromatic hydrocarbons; and $I_5=(A_{1330}+A_{1110})/A_{1579}$ characterizes the relative content of C-O and the aromatic

hydrocarbons.

The results of the quantitative peak area analysis are listed in Table 5.

Table 5 Infrared structure parameters

Sample	I_1	I_2	I_3	I_4	I_5
Undeformed coal	0.0006	0.0027	3.4706	0.0678	1.1063
50 °C	0.0004	0.0013	4.7500	0.0677	1.0842
150 °C	0.0004	0.0019	4.8462	0.0653	1.0128
250 °C	0.0021	0.0564	2.2000	0.1340	0.7239

Note: the peaks at 1703 and 1745 cm^{-1} are too close and is taken as one in the calculations.

Table 5 shows that I_1 and I_2 are lower at 50 and 150 °C compared to the undeformed coal, indicating that the aliphatic side chains are broken off. The lack of hydrocarbon gases, such as CH_4 , which were not collected at 50 °C, indicates that the aliphatic side chains may exist in the form of free radicals. The values of I_1 and I_2 increase at 250 °C, which may be attributed to the formation of the short chains by the broken of the aliphatic side chains due to the action high temperature.

At 50 and 150 °C, I_3 increases relative to undeformed coal, which may be due to the broken of the C-O bond, resulting in the falling off of oxygen atom and leading to the formation of some small molecules, such as O_2 , CO, and CO_2 . Moreover, C-C bond is also formed at the same time. At 250 °C, decrease of I_3 demonstrates the shortening aliphatic side chains, and the increase in the content of side chains.

I_4 refers to the process of falling off of the carboxyl and carbonyl of the coal macromolecular structure [18]. At 50 °C, almost no change is observed; this means that the temperature and pressure have less impact on it. At 150 °C, I_4 decreases slightly, which means that carboxyl and carbonyl begin to fall off. At 250 °C, it increases relative to undeformed coal and accompanying with relatively large amount of CO_2 and H_2 generation, because of stronger condensation of aromatic ring, and significantly influences of C=O on the spectral peak. Another possibility is that O_2 generated during the deformation can not be released timely and combines with carbon atoms to form carboxyl groups, leading to the increase of the C=O group content [15].

Under the three temperature conditions, I_5 is lower than that of undeformed coal, indicating that the effect of temperature and pressure on C-O of phenol, alcohol, and ether is significant, thus, the oxygen atoms of the oxygen-containing gas may partly come from the breaking of C-O bond.

The analysis mentioned above shows that the molecular structure evolution of coal is different under different temperature conditions. The C-O bond breaks to different degrees while the temperature is 50, 150 and 250 °C, respectively. At 50 and 150 °C, aliphatic side chains fall off and rearrangement occurs, leading to the formation of a directional long chain. While at 250 °C, aliphatic side chains fall off, and a short-chain structure is formed. And at 150 and 250 °C conditions, the degree of condensation of aromatic ring increases.

4. Generation of CO

Molecular structure of coal is extremely sensitive to stress. Under the influence of temperature and pressure, bridge bond, aliphatic side chains connected to the coal molecular skeleton, and oxygen containing functional groups may break off easily in the process of deformation. And a certain amount of hydrocarbons will be generated and released in the process [5].

In the process of deformation, the differential stress will acts on the coal molecular structure in the form of mechanical force or kinetic energy. The C-O bond is easy to be broken, the oxygen content is reduced compared to undeformed coal, and I_5 is also reduced. This indicates that the oxygen in the gas generated may be derived from the broken of C-O bond. At 150 and 250 °C, there exists CO in the gas generated and it is absent at 50 °C, these indicates that CO may originate from oxygen atoms in C-O combining with the carbon atoms of the aliphatic hydrocarbon radicals. However, at low temperature, i.e., 50 °C, sufficient energy required for the formation of CO is not present.

At 50 °C, I_4 decreases a little, and the gas contains a small amount of CO_2 , which may originate from COOH. While at 150 °C, further decrease of I_4 takes place, which indicates the broken of C=O and the formation of CO. And at 250 °C, I_4 relatively increases, and the CO content in the gas generated is 0.1109%, lower than that at 150 °C (0.5896%). As the influence of C=O on the intensity of peak at 1579 cm^{-1} is significant, it is considered that less decrease of C=O, resulting in the lower content of CO at 250 °C.

The analysis mentioned above shows that CO forms in two ways during the deformation. The first is that ether bond breaks, oxygen and carbon atoms combine together and forms CO, or O_2 forming in the broken of aether-oxygen bond leads to the oxidation of free radicals, resulting in the formation of CO. And the second is that CO derives from falling off of C=O group.

The process of CO generation is shown in Fig. 4.

Fig. 4. Process of CO generation

5. Conclusions

From the analysis mentioned above, following conclusions are obtained.

(1) The lignite sample was collected from Cuijiazhai Coal Mine. Deformation causes an increase in the relative content of carbon, and a decrease of oxygen, and H/C and O/C ratios. O_2 and CO_2 are formed at three temperature conditions (50, 150, and 250 °C), CO is produced at 150 and 250 °C, along with CH_4 , C_2H_4 , H_2 , and other hydrocarbon gases.

(2) The characteristics of the coal molecular structure evolution process vary under different temperature conditions. At 50 and 150 °C, the molecular structure of the aliphatic side chains and the ether bonds break, and the molecular structure rearrange to form a long directional chain. At 250 °C, the aliphatic side chains break off and form a short-chain structure. At 150 and 250 °C, aromatic rings are formed.

(3) CO is produced forms in two ways during the deformation. The first is that ether bond breaks, oxygen and carbon atoms combine together and forms CO, or O_2 forming in the broken of ether-oxygen bond leads to the oxidation of free radicals and resulting in the formation of CO. And the second is that CO derives from falling off of C=O group.

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