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ORIGINAL RESEARCH ARTICLE

The influence of thermal modification on lignite structure by FT-IR

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ABSTRACT

The modification experiment of Inner Mongolia Baiyinhua lignite by hot air at 200 °C for 1 h was carried out. The structural changes of Baiyinhua lignite before and after thermal modification were analyzed by infrared spectrum. The results show that the moisture and oxygen content in lignite are greatly reduced by thermal modification, and the carbon content and calorific value are also increased to varying degrees. In the process of thermal modification, various oxygen-containing functional groups in lignite are reduced in different degrees due to thermal decomposition. Thermal modification also causes substitution reaction of aromatic hydrocarbons in lignite, CH_2 in aliphatic hydrocarbon structure breaks, but hydroxyl group in lignite does not change significantly before and after thermal modification.

Keywords: Lignite; Low Temperature Thermal Modification; Infrared Spectrum; Coal Structure

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1. Introduction

China is rich in coal resources, among which the reserves of low-grade lignite are huge. The proven reserves of lignite are 1,311.42 billion tons, accounting for about 13% of the total coal reserves, and its production has also grown at a fast rate in recent years[1]. Lignite generally has the characteristics of high water content, high volatile content, high ash content, low calorific value, porous and so on. China's "Clean Coal Technology Development" Twelfth Five-Year Plan proposes to make lignite quality improvement and conversion, gasification, dry distillation and other basic research as the key task of clean utilization of lignite. Therefore, it is very important to study the structural changes of lignite in the thermal modification process for later cleaning and utilization of lignite such as dry distillation and coal slurry gasification. Low temperature thermal modification is a simple and feasible method for lignite quality improvement. For example, Hao *et al.*[2] conducted low temperature heat treatment on coals of different metamorphic degrees, and modified the surface properties of coal. The results show that low temperature heat treatment can reduce the oxygen-containing functional groups on coal surface, reduce the binding capacity of water molecules and increase the slurry formation concentration for coal-water slurry preparation. Zhang *et al.*[3] investigated the liquid carbon dioxide slurry formation concentration of lignite and found that low-temperature thermal modification treatment could significantly increase the maximum liquid carbon dioxide slurry formation concentration of lignite. The improvement of slurry formation of both water coal slurry and liquid carbon dioxide coal slurry after thermal modification of lignite is closely related to the changes of structure and functional group distribution of lignite during the thermal modification process, especially the decomposition of active oxygen-containing functional groups can significantly reduce the water absorption of coal, and the change of carboxyl functional groups and coal water absorption are important factors affecting the slurry formation characteristics of low-rank coal[4]. It can be seen that studying the evolution of functional groups of lignite during low temperature thermal modification is of great significance to lignite processing and clean utilization.

In this study, lignite from Inner Mongolia, the main lignite producing area in China, was selected to analyze the structure of various surface functional groups of lignite before and after thermal modification by Fourier Transform Infrared Spectroscopy (FT-IR), and to study the structural changes of lignite in the process of thermal modification at low temperature.

2. Experimental methods

2.1 Experimental sample and thermal modification method

In this study, Inner Mongolia Baiyinhua lignite was selected as the sample, and the raw coal was crushed by a coal mill and sieved to 200 mesh (0.074 mm) with a screen and then sealed.

The low temperature thermal modification of lignite is done by hot air drying method. A coal sample of 15 g was placed in a 50 mL corundum crucible. The crucible was placed in a muffle furnace, and the drying temperature was set to 200 ℃ with a drying time of 1 h. After drying, the crucible was removed after the temperature of the muffle furnace was lowered to room temperature, and the modified lignite sample was sealed and set aside.

Table 1 shows the industrial analysis and element analysis of Baiyinhua lignite before and after thermal modification.

Table 1. Industrial analysis and elemental analysis of Baiyinhua lignite before and after thermal modification

Coal samples	**Industrial Analysis/%**			Q_{daf}/MJ·kg^{-1}	**Elemental Analysis/%**				
	M_{ar}	A_{ad}	V_{daf}		C_{daf}	H_{daf}	N_{daf}	$S_{t,daf}$	O_{daf}
Before modification	30.25	20.49	50.22	16.21	68.30	4.80	1.42	0.79	24.68
After modification	9.09	18.47	48.8	21.78	75.76	5.17	1.59	0.51	22.64

Industrial analysis and elemental analysis methods are carried out according to national standards GB/T476-2001, GB/T212-91 and GB/T213-2003, where oxygen content is derived by differential subtraction. As shown in **Table 1**, the moisture of the thermally modified lignite was reduced by 70%, the dry basis ash A_{ad} was reduced by 9.8%, the dry ash-free basis volatile matter was reduced by 2.8%, the C_{daf}, H_{daf} and calorific value were increased by 10.9%, 7.7% and 34.4%, respectively, and the O_{daf} was reduced by 8.3%.

2.2 Lignite FT-IR analysis method

FT-IR analysis of lignite was performed by Nicolet IS50 Fourier Transform Infrared Spectroscopy. The coal samples were processed by the KBr press method: 2 mg of coal samples were placed in a mortar, 200 mg of KBr powder was added and mixed well, and then the samples were made into transparent slices of 0.1–1.0 mm thickness and placed in a Fourier Transform Infrared Spectroscopy for detection. The resolution of the infrared spectrometer was set to 4 cm^{-1}, the scanning range was 400–4,000 cm^{-1}, and the number of scans was 32 times/min. The infrared spectra were obtained after three times of sample analysis.

2.3 Infrared spectral split-peak fitting method

In this study, Origin9.0 software was used to determine the approximate number and location of the initial fitted peaks based on the second-order derivatives of each spectral line using a linear-based or compensated baseline calibration method. The interactive function of the program is used to optimize the peak shape, while modifying and adjusting the detailed parameters of each simulated peak, including peak position, peak height, half-peak width and intensity, area, etc. The fitting criterion uses the sum of squared residuals between the original and fitted spectral lines as the minimum objective function, normalizes the final results obtained after segmented peak fitting, determines its functional group content, and finds its structural parameters characterizing coal macromolecules[5]. The whole spectrum was divided into four parts: aromatic structure (700–900 cm^{-1}), oxygenated functional group (1,000–1,800 cm^{-1}), aliphatic functional group (2,700–3,000 cm^{-1}) and hydroxyl functional group (3,000–3,600 cm^{-1}). The position, half-peak width and area parameters were taken, and each functional group was quantified separately by the change of the split-peak fitting area.

3. Results and discussion

3.1 Infrared spectral analysis of Baiyinhua lignite before and after thermal modification

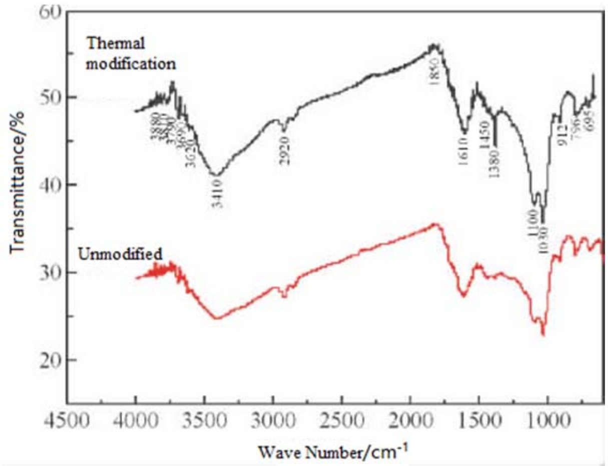

Figure 1. FT-IR spectrum of Baiyinhua lignite before and after thermal modification**.**

Figure 1 shows the comparison of FT-IR spectra of Baiyinhua lignite before and after thermal modification. It can be seen that after thermal modification, the absorption rate of surface functional groups of lignite in each band is significantly enhanced. The absorption peak is more obvious especially in the 500–600 cm^{-1}, 1,000–1,300 cm^{-1}, 1,800 cm^{-1}, 2,300 cm^{-1} and 3,800 cm^{-1}. Since the functional groups in the coal samples are prone to superposition of spectral peaks at certain positions in the spectra, the spectra need to be decomposed by the method of split-peak fitting, so that the changes of each functional group before and after thermal modification can be quantitatively analyzed.

3.2 Spectral fitting analysis of aromatic structure before and after thermal modification

The absorption peaks in the wave number of 700–900 cm^{-1} are mainly caused by the CH out-of-plane deformation vibrations in the aromatic structure. The fitted curves of the spectral peaks of lignite before and after thermal modification are shown in **Figure 2**, and the parameters of the split peak fitting of lignite before and after thermal modification are shown in **Table 2** and **Table 3** respectively.

According to the infrared spectrum and peak fitting parameters, there are five kinds of substitution methods for coal samples in this area. Number of 860–900 cm^{-1} is classified as penta-substituted benzene ring (1H), which is increased from 30.02% to 36.88% after thermal modification; between 810–860 cm^{-1} is classified as o-tetrasubstituted aromatics (2H), which is increased from 25.77% to 42.96% after thermal modification; between 750–810 cm^{-1} is o-trisubstituted aromatics (3H), which is reduced from 15.84% to 6.76% after thermal modification. The percentage of o-disubstituted aromatics (4H) between 720–750 cm^{-1} was also reduced from 25.88% to 13.40%; o-site monosubstituted aromatics (5H) between 700–720 cm^{-1}, which was 2.48% in the original coal, was not found after thermal modification.

From the analysis of the above split-peak fitting results, it can be seen that the proportion of penta-substituted benzene ring and tetra-substituted benzene ring functional groups in Baiyinhua lignite is larger, and the tetra-substituted benzene ring functional groups are greatly enhanced after thermal modification. This suggests that the aromatic structure may have undergone a substitution reaction during the thermal modification process, where the hydrogen atom on the benzene ring was replaced by other atoms or functional groups, resulting in a change in the functional group structure of the coal.

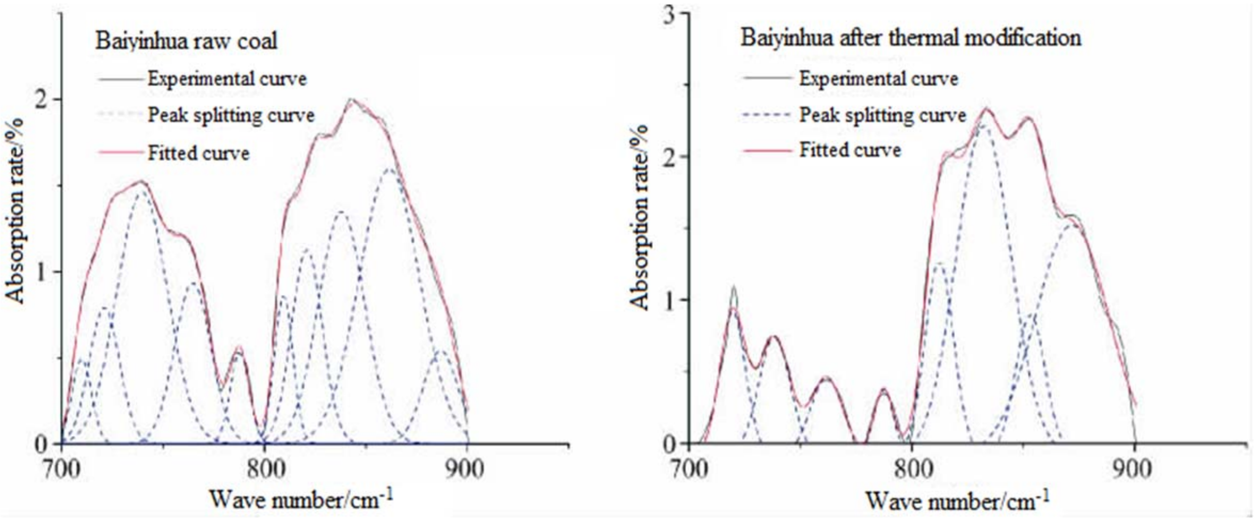

Figure 2. Results of spectral peak fitting of the aromatic structure of lignite before and after thermal modification.

Table 2. Parameters of each absorption peak in the simulation of infrared spectral splitting of aromatic structure of lignite before thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm^{-1}	Half-peak width
1	G	2.48	O-site monosubstituted aromatics (5H)	709.88	11.26
2	G	6.33	O-disubstituted aromatics (4H)	721.05	17.65
3	G	19.55	O-disubstituted aromatics (4H)	739.72	29.35
4	G	8.97	O-trisubstituted aromatics (3H)	764.58	21.03
5	G	2.65	O-trisubstituted aromatics (3H)	787.81	10.90
6	G	4.22	O-trisubstituted aromatics (3H)	809.43	10.73
7	G	9.24	O-tetrasubstituted aromatics (2H)	820.92	17.98
8	G	16.53	O-tetrasubstituted aromatics (2H)	838.00	26.84
9	G	25.28	Penta-substituted benzene ring (1H)	861.57	34.92
10	G	4.74	Penta-substituted benzene ring (1H)	886.84	20.29

Table 3. Parameters of each absorption peak in the simulation of infrared spectral splitting of aromatic structure of lignite after thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm^{-1}	Half-peak width
1	G	6.67	O-disubstituted aromatics (4H)	719.75	13.53
2	G	6.73	O-disubstituted aromatics (4H)	738.43	16.52
3	G	4.49	O-trisubstituted aromatics (3H)	761.83	16.74
4	G	2.27	O-trisubstituted aromatics (3H)	787.39	9.98
5	G	10.07	O-tetrasubstituted aromatics (2H)	812.35	15.10
6	G	32.89	O-tetrasubstituted aromatics (2H)	832.24	28.98
7	G	7.53	Penta-substituted benzene ring (1H)	863.22	15.64
8	G	29.35	Penta-substituted benzene ring (1H)	871.89	38.55

3.3 Spectral fitting analysis of oxygen-containing functional groups before and after thermal modification

The absorption peaks in the wave between 1,000 and 1,800 cm^{-1} can be classified to the absorption vibration region of oxygen-containing functional groups in coal. Oxygen-containing functional groups in coal mainly include hydroxyl group, carboxyl group, carbonyl group and ether oxygen. At the same time, C = C stretching vibration of aromatics, CH_2 and CH_3 deformation vibration are also included in the region. Therefore, the peak fitting in this wave region is complex. The spectral peak fitting is shown in **Figure 3**, and the peak fitting parameters before and after thermal modification are shown in **Table 4** and **Table 5**.

From the fitted parameters of the spectral peaks, it can be seen that the stretching vibration of phenolic hydroxyl C–O in lignite before thermal modification was mainly between 1,200 and 1,330 cm^{-1} with the proportion of 58.39%, while it decreased to 47.73% after thermal modification. The absorption peak near 1,700 cm^{-1} is attributed to the C=O stretching vibration of the carboxylic acid,

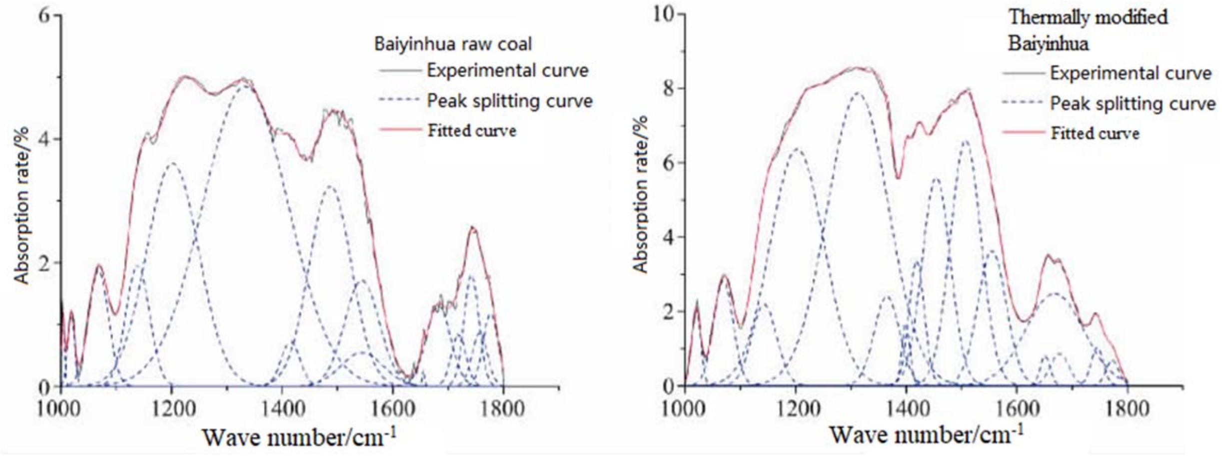

Figure 3. Results of fitting the spectral peaks of oxygen-containing functional groups of lignite before and after thermal modification**.**

Table 4. Parameters of each absorption peak in the simulation of infrared spectral splitting of oxygen-containing functional groups of lignite before thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm^{-1}	Half-peak width
1	G	0.31	Alkyl ether	1,003.74	6.52
2	G	0.76	Alkyl ether	1,018.45	14.07
3	G	3.60	Ar-O-C, C-O-C stretching vibration in Ar-O-Ar, C-O-C stretching vibration in Ar-O-Ar	1,068.06	42.15
4	G	4.47	Stretching vibration of the ether-oxygen bond	1,138.63	50.27
5	G	18.24	Stretching vibration of phenolic hydroxyl C-O	1,201.78	111.24
6	G	40.15	Stretching vibration of phenolic hydroxyl C-O	1,333.34	181.99
7	G	1.32	Symmetric bending vibration of CH_3	1,414.98	40.02
8	G	13.27	Asymmetric deformation vibration of CH_2 and CH_3	1,487.02	90.15
9	G	2.25	C=C vibration of aromatic hydrocarbons	1,544.22	90.38
10	G	5.76	C=C vibration of aromatic hydrocarbons	1,544.22	73.87
11	G	0.06	Conjugate C=O stretching vibration	1,655.08	5.11
12	G	3.09	Conjugate C=O stretching vibration	1,682.28	51.77
13	G	1.19	C=O stretching vibration of carboxylic acid	1,718.85	31.07
14	G	2.59	C=O stretching vibration of carboxylic acid	1,742.11	31.60
15	G	1.28	C=O stretching vibration of aliphatic carboxylic acids	1,757.04	32.61
16	G	1.64	C=O stretching vibration of aliphatic carboxylic acids	1,776.61	32.00

Table 5. Parameters of each absorption peak in the simulated infrared spectral splitting of oxygen-containing functional groups of lignite after thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm^{-1}	Half-peak width
1	G	1.06	Alkyl ether	1,020.14	19.32
2	G	3.18	Ar-O-C, C-O-C stretching vibration in Ar-O-Ar,	1,069.31	41.38
3	G	3.16	Stretching vibrations of C-O-C in the ether-oxygen bond Ar-O-Ar	1,143.04	53.30
4	G	19.69	Stretching vibration of phenolic hydroxyl C-O	1,202.54	113.91
5	G	28.04	Stretching vibration of phenolic hydroxyl C-O	1,312.71	131.34
6	G	3.54	Symmetric bending vibration of CH_3	1,364.84	54.25
7	G	0.78	Symmetric bending vibration of CH_3	1,399.42	17.09
8	G	2.96	Asymmetric deformation vibration of CH_2 and CH_3	1,418.67	32.63
9	G	9.10	Asymmetric deformation vibration of CH_2 and CH_3	1,454.29	59.93
10	G	11.64	C=C vibration of aromatic hydrocarbons	1,507.56	65.12
11	G	5.98	C=C vibration of aromatic hydrocarbons	1,555.01	60.66
12	G	0.46	Conjugate C=O stretching vibration	1,651.10	21.03
13	G	8.26	Conjugate C=O stretching vibration	1,668.19	123.33
14	G	0.92	C=O stretching vibration of carboxylic acid	1,677.37	38.99
15	G	0.74	C=O stretching vibration of carboxylic acid	1,745.23	26.42
16	G	0.50	C=O stretching vibration of aliphatic carboxylic acids	1,772.53	26.98

and the presence of carboxyl groups is the main characteristic of lignite. The percentage of C=O stretching vibration of carboxylic acid was 3.78%, which decreased after thermal modification, due to the fact that during the thermal modification of lignite, the coal started to decompose and depolymerize, and –OH and C=O were removed in the form of H_2O, CO, and CO_2[7]. It can be seen from the above analysis that in the process of thermal modification, the oxygen-containing functional groups in lignite are reduced to varying degrees due to thermal decomposition. The reduction of oxygen content can reduce the liquid reabsorption rate of the lignite after thermal modification, and the polarity of pulverized coal particles surface is weakened, which has a significant improvement effect on the increase of the maximum slurry concentration of CWS and liquid CO_2 coal slurry[2,3].

3.4 Spectral fitting analysis of fat functional groups before and after thermal modification

The absorption peaks between 2,800 and 3,000 cm^{-1} correspond to the absorption vibration region of aliphatic C–H in coal. The fitted curves of the spectral peaks before and after thermal modification of lignite are shown in **Figure 4**, and the parameters of the split peak fitting are shown in **Tables 6** and **7**.

It can be seen from **Figure 4** that there are two main peaks in the range of 2,800–3,000 cm^{-1}, which are the symmetric stretching vibration of $–CH_2–$ near 2,850 cm^{-1} and the antisymmetric stretching vibration of $–CH_2–$ near 2,925 cm^{-1} respectively[8]. After thermal modification, the proportion of the antisymmetric stretching vibration absorption peak of $–CH_2–$ decreases, while the symmetric stretching vibration absorption peak of $–CH_2–$ increases. These results indicate that $–CH_2–$ in the aliphatic structure may fracture during thermal modification, resulting in methane release. The absorption peaks near 2,870 cm^{-1} and 2,955 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of RCH_3, respectively, while the absorption peaks near 2,895 cm^{-1} are attributed to the stretching vibration of R_3CH. This suggests that the macromolecular backbone of lignite contains complex fatty-like structures and methyl structure.

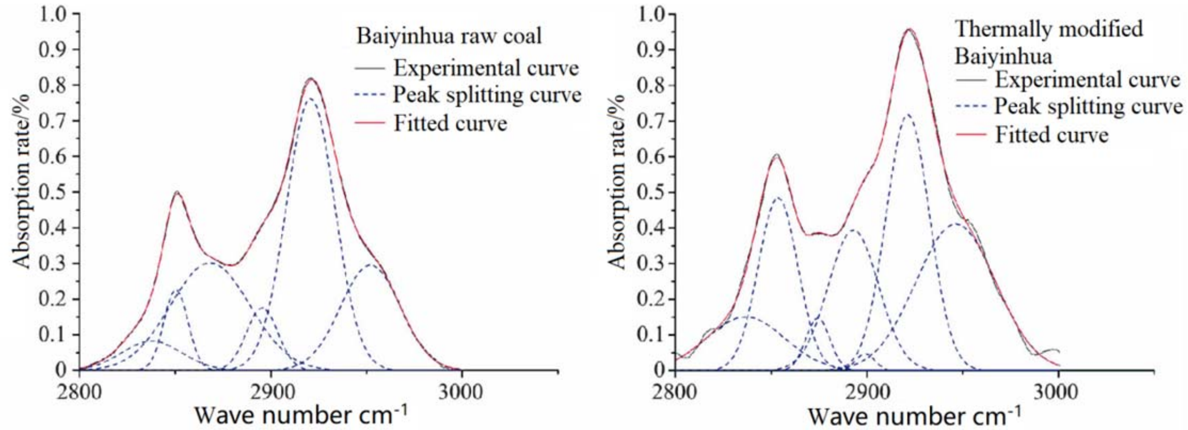

Figure 4. Results of fitting the spectral peaks of fatty substances in lignite before and after thermal modification.

Table 6. Parameters of each absorption peak of infrared spectral splitting simulation of fatty substances in lignite before thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm^{-1}	Half-peak width
1	G	5.19	$–CH_2–$ symmetric stretching vibration	2,837.67	36.92
2	G	5.78	$–CH_2–$ symmetric stretching vibration	2,850.34	14.88
3	G	25.27	Symmetric RCH_3 telescopic vibration	2,868.24	48.76
4	G	5.82	R_3CH telescopic vibration	2,895.37	19.34
5	G	39.30	Antisymmetric stretching vibration of $–CH_2–$	2,920.74	30.04
6	G	18.64	Asymmetric RCH_3 Stretching vibration	2,952.02	36.73

Table 7. Infrared spectral splitting simulation of each absorption peak parameters of fatty substances in lignite after thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm^{-1}	Half-peak width
1	G	9.51	$–CH_2–$ symmetric stretching vibration	2,836.61	47.78
2	G	16.19	$–CH_2–$ symmetric stretching vibration	2,853.59	24.39
3	G	2.97	Symmetric RCH_3 telescopic vibration	2,874.35	14.58
4	G	16.72	R_3CH telescopic vibration	2,892.95	30.93
5	G	0.75	R_3CH telescopic vibration	2,899.09	11.66
6	G	26.40	Antisymmetric stretching vibration of $–CH_2–$	2,921.35	26.86
7	G	27.47	Asymmetric RCH_3 Stretching vibration	2,946.42	49.02

3.5 Spectral fitting analysis of hydroxyl functional groups before and after thermal modification

The absorption peaks in the wavelength band between 3,000–3,600 cm^{-1} are attributed to the absorption vibration region of hydroxyl groups in coal. The hydroxyl group is the main functional group for the formation of hydrogen bonds in coal, and it forms different types of hydrogen bonds with different hydrogen bond acceptors. The fitted curves of the spectral peaks before and after thermal modification of lignite are shown in **Figure 5**, and the parameters of the split peak fitting are shown in **Tables 8** and **9** respectively.

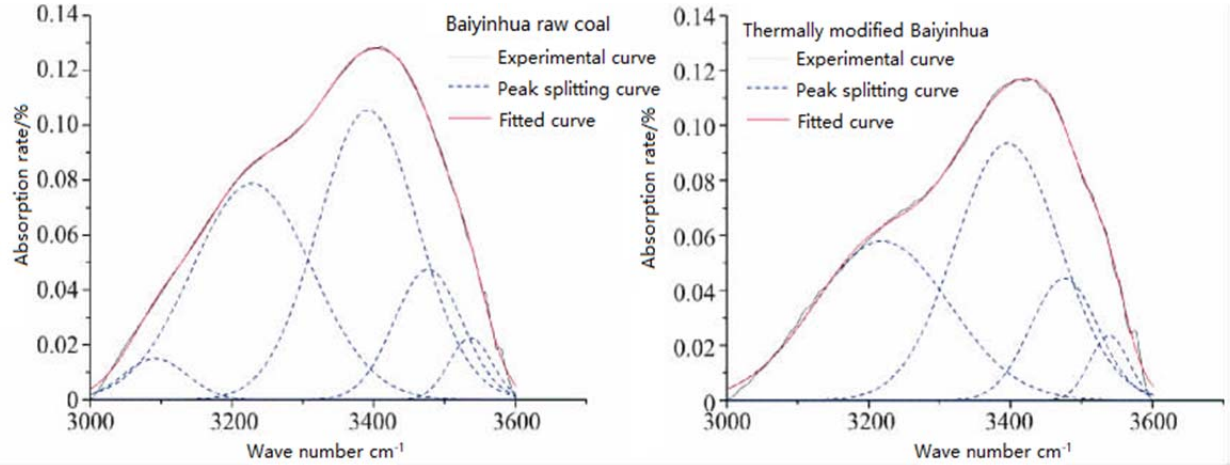

Figure 5. Results of fitting the spectral peaks of hydroxyl groups in lignite before and after thermal modification.

Table 8. Parameters of each absorption peak in the simulated infrared spectral splitting of hydroxyl groups in lignite before thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm-1	Half-peak width
1	G	3.74	OH–N	3,091.66	105.65
2	G	37.64	Cyclic hydrogen bond	3,228.42	198.86
3	G	42.03	OH–OH	3,391.87	165.54
4	G	12.80	OH–OH	3,476.48	112.23
5	G	3.79	OH–π	3,536.30	70.66

Table 9. Parameters of each absorption peak in the simulated infrared spectral splitting of hydroxyl groups in lignite after thermal modification

Peak number	Peak type	Area ratio	Attribution	Location/cm^{-1}	Half-peak width
1	G	36.07	Cyclic hydrogen bond	3,218.70	223.62
2	G	45.81	OH–OH	3,395.94	174.24
3	G	13.92	OH–OH	3,475.77	111.94
4	G	4.20	OH–π	3,539.01	63.91

According to data analysis, Baiyinhua lignite in this study mainly contains four hydrogen bonds: OH–N hydrogen bond, cyclic hydrogen bond, self-associating hydroxyl hydrogen bond and OH–π. The proportion of self-associating hydroxyl hydrogen bonds in Baiyinhua lignite is large, and its content does not change significantly after thermal modification, and the proportion is larger than other types of hydrogen bonds. The cyclic hydrogen bond was the second, and its proportion did not change significantly after thermal modification. The OH–π hydrogen bond in coal reflects the hydrogen bond formed by hydroxyl group and aromatic system in coal, and the ratio of this type of hydrogen bond is slightly increased after thermal modification.

4. Conclusion

After thermal modification, water content of Baiyinhua lignite decreases significantly. Calorific value increases correspondingly, and oxygen content decreases. It shows that complex reaction takes place between coal and oxygen during thermal modification.

Infrared spectrum analysis of Baiyinhua lignite before and after thermal modification shows that the thermal modification process has a complex effect on the structure of lignite. Aromatic hydrocarbons in the original coal have a large proportion of benzene ring penta-substituted and tetra-substituted structures. During the thermal modification process, aromatic hydrocarbons undergo substitution reactions in which the hydrogen atoms on the benzene ring are replaced by other atoms or functional groups and the structure is changed. After thermal modification, the content of oxygen-containing functional groups of lignite decreases due to thermal decomposition, and the contents of four oxygen-containing groups change in different degrees. The proportion of symmetric and antisymmetric stretching vibrations of $–CH_2–$ in the fatty substances in the raw coal is large, and the CH_2 in the lipid-hydrogen structure is broken after thermal modification, which results in the change of the ratio of these two $–CH_2–$. The content of self-associating hydroxyl hydrogen bond in raw coal hydroxyl group is the largest, followed by ring hydrogen bond. The thermal modification process has no significant effect on the hydroxyl structure in lignite.

Conflict of interest

The authors declared that they have no conflict of interest.

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