The Effect of Hydrothermal Treatment on Structure and Flotation Characteristics of Lignite and a Mechanistic Analysis

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ABSTRACT: Lignite is difficult to obtain highly efficient indexes by conventional flotation due to its poor surface hydrophobicity. Although the modification of flotation reagents has made some progress in improving the flotation performance, they all remain at the stage in the laboratory. Here, we proposed to improve the flotation performance by hydrothermal treatment dewatering (HTD) for lignite. Combined with the $^{13}$C NMR and FT-IR analysis, the impact of the HTD process on lignite’s chemical structural evolution and flotation performance was investigated. The results showed that the HTD process is an effective means for dehydration and deoxygenation to increase lignite quality and the metamorphic degree of coal. The content of oxygen-containing functional groups generally decreases during the HTD process, especially carboxyl acid and ether groups. Therefore, surface properties and wettability of HTD coal samples were changed, and the contact angle gradually increases with the HTD temperature increased, which enhance the hydrophobicity and decrease hydrophilia of the lignite surface. The HTD process effectively improves the flotation performance of lignite during the conventional flotation operation condition, even if the coal pulp after HTD was directly used as a flotation feedstock. Specifically, the coal oil and capryl alcohol were used as collector and forming agents, respectively, and the pulp concentration was adjusted to 60 g/L. The yield of the cleaned coal increased from 12.14% of the raw coal to 55.58% of HTD310, and combustible matter recovery increased from 13.83% of the raw coal to 65.17% of HTD310 by raw coal basis.

1. INTRODUCTION

Lignite is rich in reserves, accounting for about 13% of total coal reserves in China. It is an indispensable potential resource to guarantee energy security, and it has low mining costs and high reactivity, which has many advantages used as a chemical feedstock. With the constant consumption of high-quality coal, the development and utilization of lignite resources are urgent. However, lignite quality is poor in China. In addition to its high moisture content, low heating value, and high oxygen content, lignite also has a high ash content in China. This would increase spontaneous combustible risk and transportation costs, and the application range is limited. For example, the high water content of lignite decreases energy use efficiency and results in higher greenhouse gas emissions per unit power conversion. The high ash content seriously restricts its performance as a carbonaceous material and metallurgical reducing agent. Therefore, dewatering and deashing have become the basis and premise of high value-added industrial application of lignite.

With the mine production mechanization degree unceasing enhancement and large-scale, the output of the coal was increased, but large quantities of a pulverized coal were also produced. Froth flotation is an effective method to realize coal separation for a <0.5 mm pulverized coal. Coal flotation takes advantage of the natural hydrophobicity of carbonaceous materials in a coal. The good flotation performance of a high-rank coal comes from its good natural hydrophobicity. However, the surface of the lignite contains a large number of polar groups with an oxygen atom, which increases the hydrophilic points on the surface of the coal sample. In the flotation system, the hydrogen bonding between those polar groups and polar water molecular is easy to form a stable hydration shell on the surface of a lignite, and the effective adhesion between coal particles and air bubbles is hampered due to the presence of a hydrated shell, which results in the poor performance of flotation. Therefore, the conventional collector (fuel oil) has a small amount of adherence amount to...
particles of a lignite, and a large amount of collector is needed to obtain a satisfactory flotation yield. Therefore, finding a way to remove oxygen-containing functional groups and changing the surface characteristics of a lignite may be feasible schemes to improve flotation efficiency.

At present, to improve the flotation recovery and the selectivity, the flotation of a lignite mainly focuses on the modification of flotation reagents and has made some achievements. Xia et al. used a mixture of dodecane and 4-dodecylphenol as a collector for lignite flotation, and the flotation performance of lignite was improved. Dodecane can cover the medium hydrophobic sites on the surface of a lignite, and the polar side of phenolic hydroxyl in 4-dodecylphenol can form hydrogen bonding with oxygen-containing functional groups on the surface of lignite, which covers hydrophilic sites on the lignite surface. Jia et al. used a tetrahydrofuran derivative as a lignite flotation collector, and combustible matter recovery increased. However, although some progress has been made in the pretreatment of lignite and modification of flotation reagents for many years, it is difficult to realize industrial applications on a large scale. At present, they are still all in the laboratory stage because of the high cost of the reagent.

Hydrothermal treatment dewatering is a nonevaporative dehydration technique in which the removal of water as liquid water is a more energy-efficient way. It has an important influence on the lignite structure and has the potential for large-scale practical applications. Yu et al. used two kinds of a lignite, Baotou and Ximeng, as raw coals, and the impact of the hydrothermal process on the coal water pulp was investigated. Results showed that the solid concentration of a coal pulp increased after hydrothermal treatment for two kinds of lignite, and both the point of zero charges and the contact angle increased, indicating that hydrothermal treatment promoted the improvement of hydrophobicity of a lignite. Wu et al. used Xinglongtan lignite as a raw coal, and the effect of hydrothermal treatment on pulp ability was studied. Results showed that the point of zero charges increased, indicating that hydrothermal treatment promoted the improvement of hydrophobicity of a lignite.

As can be seen from the above discussion, the hydrothermal treatment dewatering is an effective way to realize dehydration and oxidation of lignite and can change the surface characteristics of a lignite.

Hydrothermal treatment dewatering is an effective solution for removing water as liquid water, which is a more energy-efficient way. As can be seen from the above discussion, the hydrothermal treatment dewatering is an effective solution for removing water as liquid water, which is a more energy-efficient way.
and the temperature and pressure of the system were measured and recorded using temperature and pressure sensors. After the experiment, the reactor was cooled to room temperature, and the exhaust valve was opened. The solid—liquid product was separated by a qualitative paper. The solid product was placed in a vacuum drying oven at 50 °C for 8 h and was used to analyze properties and flotation feedstock as well as the calculation of yield for the HTD solid product. The yield of the solid product after the HTD process was calculated by formula 1:

\[ Y_i = \frac{m_{\text{HTD coal.d}}}{m_{\text{raw coal.d}}} \times 100\% \]  

where \( Y_i \) represents the yield of HTD coal samples for different treated temperatures in dry basis; \( m_{\text{HTD coal.d}} \) represents the weight of HTD coal samples for different treated temperatures in dry basis; and \( m_{\text{raw coal.d}} \) represents the weight of a raw coal in dry basis.

In addition, in consideration of the wastewater treatment produced by the HTD process, an another same set of HTD process was finished. The coal pulp included the water, and coal was directly used as the flotation feedstock.  

2.1.3. The Flotation Process. The flotation experiment was carried out in a laboratory-used single flotation groove of RK/ FD, and the volume of the groove is 1.5 L. The rotating speed of the vane was 1900 r/min, and aeration quantity was set as 0.25 m³/min. Capryl alcohol and coal oil were used as forming agents and collectors, respectively. According to the preliminary exploration experiment, the ratio of the collector to the forming agent was set as 3:1, and the total amount was 4000 g/t. The parameters of another flotation process are the same as the last group. In each run, 60 g of the HTD coal sample (the dry basis) was weighed and was wet by deionized water in advance. Then, the pulp was poured into the flotation cell, and the pulp concentration was adjusted to 60 g/L by adding deionized water. The coal oil was added into the flotation cell after pulp agitation for 3 min. The capryl alcohol was added below the pulp surface after 2 min, and the pulp was conditioned for 30 s. Flotation products were collected with an interval period of 3 min.

In another set of flotation experiments, the mixture of the water and coal generated by the HTD process was used as a flotation feedstock. The parameters and operating conditions were the same as the first flotation experiment. The difference was that the extra deionized water was calculated and added to adjust the pulp concentration to 60 g/L according to the solid yield \( Y_i \) for HTD coal samples, water was added during the HTD process, and the moisture was changed before and after the HTD process for the feedstock. In the HTD process, we presumed that the amount of water in the system was unchanged. The yields of the cleaned coal and tailing coal and combustible matter recovery are calculated by formulas 2–4:

\[ Y_c = \frac{m_{\text{cleaned coal.d}}}{m} \times 100\% \]  

\[ Y_t = \frac{m_{\text{tailing coal.d}}}{m} \times 100\% \]  

\[ R_c = \frac{Y_c(100 - A_1)}{100 - A_2} \times 100\% \]  

where \( Y_c \) and \( Y_t \) represent the yield of cleaned coal and tailing coal for the original sample and HTD coal samples in dry basis, respectively; \( m_{\text{cleaned coal.d}} \) represents the weight of a cleaned coal in the flotation process in dry basis; \( m_{\text{tailing coal.d}} \) represents the weight of a tailing coal in flotation in dry basis; the initial weight of HTD coal samples comes from the yield after the HTD process for the raw coal; \( R_c \) represents the combustible material recovery; \( A_1 \) represents the cleaned coal ash of the original sample and HTD samples in dry basis; and \( A_2 \) represents the tailing coal ash of original sample and HTD samples in dry basis.

To be more comparable, the yield of cleaned coal and combustible matter recovery by sample basis were converted into raw coal basis, and the transformation formula is as follows:

\[ Y_{cr} = Y_c \times Y_t \times 100\% \]  

\[ R_{cr} = R_c \times Y_t \times 100\% \]  

where \( Y_{cr} \) represents the yield of the cleaned coal for HTD coal samples by raw coal basis, and \( R_{cr} \) represents the combustible matter recovery for HTD coal samples by raw coal basis.

The particle analysis of raw coal was finished according to the GB/T 477-2008 and is shown in Table 1. The results showed that the yield of different fraction coals increases with the decrease in grain size, the dominant grain size is <0.045 mm, and the yield is 58.11% that is consistent with the typical characteristics of a lignite due to being fragile and slimy.

2.2. Analysis Methods. 2.2.1. \(^{13}C \) NMR. The \(^{13}C \) NMR tests of the original sample and HTD coal samples were operated by a Varian INOVA300 NMR spectrometer with a superconducting magnet. The solid dual resonance probe was adopted, with an external diameter of a ZrO₂ rotor and a magic angle rotation speed of 6–7 kHz. The resonance frequencies were set to be 75.43 MHz, and the sampling time was 0.05 s. The pulse width and the time of loop latency are 4.2 × 10⁻⁶ and 4 s, respectively. The scan times are 2000–4000. The cross-polarization technology was applied, and the Toffe sideband suppression technique was applied to suppress the sideband. The contacting time is 0.005 s, and the spectral width is 30 000 Hz. The structure assignment of the chemical shifts in \(^{13}C \) NMR according to the literature²⁹,³⁰ is shown in Table 2.
The overlapping peak was containing functional group according to the literature32,33 is assignment of the containing groups are found in the region of 1000 containing functional groups in the coal. The bonds of oxygen-Therefore, this paper focused on the content of oxygen-quantified absorption peak for every oxygen-containing functional group for every oxygen-containing functional group according to the literature32,33.

2.2.2. FT-IR Analysis. A Vector 22 infrared spectrometric analyzer manufactured by Bruker in Germany was employed to test the original sample and HTD samples. The test conditions were as follows. The luminous flux was 15,000, the spectral range was 400–4000 cm⁻¹, and the scan times are 32. The coal samples and dried KBr were put into an agate mortar with a mass ratio of 1:100, and ground well and mixed well. The sample was pressed into thin sheets of 0.1 mm thick by using a tableting mold and hydraulic press. Then, the slice was placed on the sample shelf of an infrared spectrometer test chamber.

The content of oxygen-containing functional groups in the coal has an important effect on the surface property of the coal. Therefore, this paper focused on the content of oxygen-containing functional groups in the coal. The bonds of oxygen-containing groups are found in the region of 1000–1800 cm⁻¹. The overlapping peak was finished by OriginPro2018. The assignment of the fitted absorption peak for every oxygen-containing functional group according to the literature32,33 is shown in Table 3.

Table 3. Assignment of Oxygen-Containing Functional Groups for 1000–1800 cm⁻¹

| Wavenumber (cm⁻¹) | Assignment  | Symbols |
|------------------|-------------|---------|
| 1710–1750        | aryl esters | S1      |
| 1685–1710        | carboxyl acids | S2   |
| 1600–1685        | conjugated C=O | S3   |
| 1440–1600        | aromatic C=C | S4      |
| 1370–1440        | CH₃, Ar, CH₃=, and CH₂= | S5   |
| 1110–1300        | C=O phenol   | S6      |
| 1000–1110        | allyl ethers and aryl ethers | S7   |

2.2.3. Hydrophilic Measurement of the Coal Sample Surface. The hydrophilia of the coal samples’ surface can be quantified by measuring contact angles. The pulverized coal sample was pressed for 30 min at a pressure of 10 MPa to form a cylindrical sheet with a diameter of 20 mm and a height of about 2 mm. The drooping droplet slowly hit on the surface of the coal sheet. The drooping process was continuously collected using the JC2000C system produced by Shanghai Zhongchen Co. In this paper, the contact angle between the sheet and droplet was calculated by choosing the photograph of the moment when the droplet just hit the surface of the coal sheet.

2.2.4. The Zeta Potential. The samples were mixed with deionized water to form a 0.08 wt % suspension for the raw coal and HTD coal samples. The other same concentration suspension was prepared by mixing the HTD coal samples and separating water from the solid–liquid product after HTD. The pH value was adjusted by using an acid or an alkali. Then, the suspension was stirred evenly by an oscillator and left it for 3 h. The supernatant of the diluted fine suspension was extracted for zeta potential measurement using a Zetasizer 3000.

2.2.5. Liquid Product Analysis. Metal cations were measured by inductively coupled plasma mass spectrometry manufactured by Jiangsu Skyray Instrument Co. Ltd. (ICP-MS 2000). Anions were analyzed by an ion chromatograph manufactured by Guangzhou Xiaofen Instrument Co. Ltd. (CIC-D160A). The total organic carbon was measured by a TOC-V CPN analyzer (Shimadzu, Japan).

3. RESULTS AND DISCUSSION

3.1. Change of Coal Characteristic Indexes. 3.1.1. The Ultimate Analysis and Proximate Analysis of the Raw Coal and Treated Coal. Table 4 shows the change of coal characteristic indexes of the raw coal and treated samples, indicating that HTD significantly reduced the content of moisture (air dry basis) for a lignite. The content of moisture continually decreased with the increase of HTD temperature. Specifically, the moisture content of the raw coal decreased from 28.25 to 6.37% of HTD310, resulting from the removal of oxygen functionalities and the collapse of pore structure during the HTD process, which give rise to the reduction of water-holding ability after the HTD process. The effective removal of moisture for a lignite can decrease the cost of long distance transportation. The volatile matter decreased, and the content of fixed carbon and calorific value increased, indicating that the HTD process can promote the improvement of energy density for a lignite. Researches showed that the HTD process offers an evolution condition of high-temperature and high-pressure for a lignite, which equates to the manual imitation of the natural coal-forming process. Therefore, the HTD process also presents the variation of the metamorphic degree of a coal in nature. From what has been discussed above

Table 4. Change of Coal Characteristic during the HTD Process

| Property                | Raw Coal | HTD150 | HTD200 | HTD250 | HTD310 |
|-------------------------|----------|--------|--------|--------|--------|
| Ultimate analysis (wt %, daf) |          |        |        |        |        |
| Carbon                  | 69.13    | 70.18  | 72.36  | 73.28  | 75.46  |
| Hydrogen                | 4.91     | 5.09   | 5.17   | 5.49   | 5.06   |
| Nitrogen                | 1.13     | 1.24   | 1.23   | 1.25   | 1.28   |
| Sulfur                  | 0.81     | 0.76   | 0.83   | 0.77   | 0.78   |
| Oxygen                  | 24.03    | 22.73  | 20.41  | 18.49  | 17.41  |
| Proximate analysis (wt %) |          |        |        |        |        |
| Moisture (ad)           | 28.25    | 9.27   | 8.34   | 7.81   | 6.37   |
| Ash (d)                 | 25.56    | 25.68  | 26.02  | 26.38  | 26.85  |
| Volatile matter (daf)   | 45.32    | 44.93  | 43.26  | 41.01  | 38.19  |
| O₄/C                    | 16.36    | 17.78  | 19.47  | 19.28  | 20.32  |
| R₁₁/C                   | 0.96     | 0.96   | 0.98   | 1.00   | 0.87   |
| R₁₂/C                   | 0.26     | 0.24   | 0.21   | 0.19   | 0.17   |

*O* by difference; ad: air-dry basis; d: dry basis; daf: dry ash-free basis.
clearly confirms that HTD is an effective means for dehydration and deoxygenation to increase lignite quality.

3.1.2. Structural Analysis of Different Carbon Types during the HTD Process. The structure of a lignite can be changed irreversibly at a high temperature and high pressure during the HTD process due to the cleavage of unstable chemical bonds and aliphatic side chains. The carbon structures of different types of the raw coal and HTD coal samples were measured by $^{13}$C NMR, and the spectra are shown in Figure 2a. As shown, it included two main peaks. The chemical shifts of $0−100$ and $100−170$ ppm are aliphatic carbon areas and the aromatic carbon peak areas, respectively. At the same time, it also contains a few of carbonyl units, and the chemical shift in the spectra is $170−220$ ppm. To quantitatively analyze the relative content of different carbon types from a single peak area to the total simulated area of $^{13}$C NMR spectra, the fitting curves of the original sample and HTD samples are shown in Figure 2b.

The effect of the HTD process on the chemical structure is shown in Figure 3 and indicates that the $F_{al}^1$ (alkyl carbon) value decreases and the $F_{ar}^1$ (aromatic carbon) value increases with the treatment temperature increased. This is mainly due to the cleavage of unstable chemical bonds and aliphatic side chains for a lignite during the HTD process (3). The $F_{ar}^2$ (an oxygen-containing aromatic carbon) value increases at a temperature below 250 °C and decreases subsequently. The $F_{al}^1$ value begins to decrease at a temperature above 250 °C. The $F_{ar}^2$ (an oxygen-containing aromatic carbon) value increases at a temperature below 250 °C and decreases subsequently. The $F_{CC}$ (carbonyl carbon units) value constantly decreases with the temperature increased and indicates that the carbonyl carbon units gradually decompose as upgraded temperature increased during the HTD process.

3.1.3. The Analysis of Oxygen-Containing Functional Groups during the HTD Process. Figure 4a shows the IR spectra of the original sample and HTD samples. To investigate semiquantitatively the evolution of oxygen-containing functional groups after the HTD process, the region of oxygen-containing functional groups at $1000−1800$ cm$^{-1}$ is fitted and shown in Figure 4b. The relative content of every group is calculated by their area to the total fitted peak area and is shown in Table 5 (sample basis). Besides, the change in oxygen-containing functional groups has the greatest influence on the surface wettability and flotation characteristics of a lignite. Therefore, to explain clearly the effect of the HTD process on the evolution of oxygen-containing functional groups, the sample coal basis was converted into raw coal basis for the relative content of each oxygen-containing functional group and is shown in Table 6.

From the data in Table 6, $S1$ (aryl esters) value, $S2$ (carboxyl acids) value, and $S7$ (alkyl ethers and aryl ethers)
value constantly decrease with the increasing temperature, indicating that HTD promotes the hydrolysis and cleavage of ester, carboxyl groups, and ether groups during the HTD process. Nao Kashimura et al. investigated that the effect of subcritical water and subcritical 1-methylnaphthalene on conversion behavior and found the total conversion of the lignite to the extract and gas products obtained over 70 wt %, which was higher than that of 1-methylnaphthalene solvent. This is due to the fact that hot water benefits from the hydrolysis and breakage of ester, carboxyl groups, and ether groups in the lignite. The S6 (C=O phenol) value did not change much. However, the S6 value increases slightly with the temperature increased because the hydrogen ions and hydroxide ions in the water are possibly transferred to the benzene or phenoxy to generate phenol by the electrophilic substitution reaction. Besides, the S3 (conjugated C=O) value constantly increases with increasing temperature, and this may be due to the fact that the quinonyl is generated and participated in the hydrogen transfer between water and lignite with the increase of phenolic groups during the HTD process, which results in an increment in the conjugated C–O content. The S4 value (aromatic C=C) and S5 value (CH3−Ar, CH3−, and CH2−) are slightly changed during the HTD process. Although the contents of conjugated C=O by raw coal basis increase during the HTD process, the total content of oxygen-containing functional groups decreases. Moreover, relevant researches showed that the carboxyl groups have the greatest influence on the wettability of a lignite. Compared with the carboxyl groups, the alkane (CH3−Ar, CH3−), and CH2−) aromatic C=C, and quinonyl groups are non-hydrophilic and have a little influence on the wettability. Thus, the polarity of the lignite surface is decreased, and the hydrogen bonds between those polar groups and polar water molecules are decreased, which increases the hydrophobic area for HTD coal samples. The effective adhesion between coal

Figure 4. Change of oxygen-containing functional groups during the HTD process. (a) FT-IR spectra of the original sample and HTD samples and (b) fitted FT-IR spectra of the original sample and HTD samples.

Table 5. Content of Oxygen-Containing Functional Groups of Original Samples and HTD Coal Samples by Sample Basis

| wavenumber (cm⁻¹) | samples     | S1 (1710–1750) | S2 (1685–1710) | S3 (1600–1685) | S4 (1440–1600) | S5 (1370–1440) | S6 (1110–1370) | S7 (1000–1110) | total (%) |
|------------------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------|
| raw coal         | 1.89        | 17.03          | 10.08          | 27.78          | 13.50          | 16.08          | 15.64          |               | 100      |
| HTD150           | 1.17        | 15.39          | 11.07          | 27.02          | 14.32          | 16.98          | 14.05          |               | 94.41    |
| HTD200           | 0.87        | 13.26          | 12.68          | 29.51          | 13.77          | 17.39          | 12.52          |               | 90.23    |
| HTD250           | 0.60        | 8.30           | 17.20          | 30.29          | 14.64          | 19.23          | 9.74           |               | 88.45    |
| HTD310           | 0.32        | 6.34           | 20.01          | 32.56          | 15.73          | 18.26          | 6.78           |               | 84.09    |

Table 6. Content of Oxygen-Containing Functional Groups of the Original Sample and HTD Samples by Raw Coal Basis

| wavenumber (cm⁻¹) | samples     | S1 (1710–1750) | S2 (1685–1710) | S3 (1600–1685) | S4 (1440–1600) | S5 (1370–1440) | S6 (1110–1370) | S7 (1000–1110) | total (%) |
|------------------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------|
| raw coal         | 1.89        | 17.03          | 10.08          | 27.78          | 13.50          | 16.08          | 15.64          |               | 100      |
| HTD150           | 1.10        | 14.53          | 10.45          | 25.51          | 13.52          | 16.03          | 13.26          |               | 94.41    |
| HTD200           | 0.79        | 11.96          | 11.44          | 26.63          | 12.42          | 15.69          | 11.30          |               | 90.23    |
| HTD250           | 0.53        | 7.34           | 15.21          | 26.79          | 12.95          | 17.01          | 8.62           |               | 88.45    |
| HTD310           | 0.27        | 5.33           | 16.83          | 27.38          | 14.07          | 15.35          | 4.86           |               | 84.09    |
particles and air bubbles is more likely to happen, which would result in the good performance of flotation.

3.2. The Flotation Experimental Analysis. 3.2.1. The Effect of the HTD Process on the Wettability and Floatability. The contact angle \( \theta \) is an important index to characterize the wettability of the coal surface. The \( \cos \theta \) can be used as an estimate of wettability, and the \( 1 - \cos \theta \) can be considered as an estimate of floatability.\(^7\) The effect of the HTD process on the wettability and floatability of a lignite is shown in Figure 5 and indicates that the wettability continually decreases and the floatability continually increases with the increasing HTD temperature. As discussed above, the decrease of wettability is mainly due to the fact that a large amount of strong polar oxygen-containing functional groups in the lignite are removed. More importantly, these oxygen-containing functional groups have a strong hydrophilicity. Therefore, the removal of these oxygen-containing functional groups can effectively decrease hydrophilicity and increase the hydrophobicity of the lignite surface. In addition, a relevant study showed\(^{14} \) that the thickness of the hydration shell was in proportion to the wettability of minerals. For purpose of the attachment of mineral particles to bubbles, the hydration shell of the mineral surface must be displaced. The decrease of the wettability of the lignite surface means the decrease of the thickness of the hydration shell. Therefore, the attachment between lignite particles and bubbles becomes a lot easier, and the floatability is improved.

3.2.2. The Flotation Process Used the Dried HTD Coal Sample as a Feedstock. The effect of the HTD process on the floatation characteristics is shown in Figure 6, indicating that the yield of the cleaned coal and combustible matter recovery significantly increased, and the yield of the tailing coal gradually decreased with the increasing HTD temperature even based on raw coal basis. Specifically, based on raw coal basic, the yield of the cleaned coal increased from 12.14% of the raw coal to 52.67% of HTD310, and combustible matter recovery increased from 13.83% of the raw coal to 58.70% of HTD310. In contrast, the yield of the tailing coal decreased from 87.86% of the raw coal to 31.42% of HTD310, and the ash content of the tailing coal significantly increased with the temperature increased. In addition, it is obvious that the floatation effect based on the sample basis is better than that of the one based on the raw coal basis, and it is mainly due to the decomposition of the lignite during the HTD process, which results in the decrease in solid product yield.

The improvement of the floatation effect is mainly due to the structural change during the HTD process, and many polar groups with oxygen atoms as the main body was removed for lignite, especially carboxyl acids and ether groups. Therefore, the surface properties of the lignite are changed during the HTD process. The hydrophilic area of the lignite surface decreases, and the hydrophobic area increases, which results in the improvement of the floatation performance. On the other hand, lignite has developed a pore structure and high adsorption ability\(^3,41\) and makes the coal particles have stronger adsorption for water and a reagent. Therefore, the mechanism of action is changed between coal particles and reagent and results in the poor index for floatation and lots of reagent dosages too.\(^{14} \) Lignite was slightly pyrolyzed during the HTD process due to the high-temperature and high-pressure reaction environment, and a small amount of pyrolysis tar was generated by the cleavage of unstable chemical bonds. This

![Figure 5](https://pubs.acs.org/doi/10.1021/acsomega.0c04713)

Figure 5. Effect of the HTD process on the wettability and floatability. (a) Wettability and (b) floatability.

![Figure 6](https://pubs.acs.org/doi/10.1021/acsomega.0c04713)

Figure 6. Effect of the HTD process on the floatation process that used dried HTD coal samples as a feedstock. (a) Yield and ash of the cleaned coal based on the raw coal basis and sample basis; (b) yield and ash of the tailing coal based on the raw coal basis and sample basis; and (c) combustible matter recovery based on the raw coal and simple basis.)
pyrolysis tar is trapped in the pore structure of the lignite, and some pore structures are blocked to a certain extent and decreased the reagent adsorption, which resulted in the improvement of flotation performance.

The ash content of the cleaned coal decreases slightly with the increasing HTD temperature, and this could be due to the fact that the finer particles of coal samples are a dominant fraction, which results in entrainment of fine slime during the flotation process. The grain compositions of a cleaned coal and its flotation feed are shown in Figure 7, indicating that the grain compositions of the cleaned coal and its flotation feed have the same changing trend. This is why the ash content of the cleaned coal has decreased slightly. The decrease in the particle size of the raw coal and HTD samples (the flotation feed) is likely due to the fact that the HTD process promotes fragmentation of coal particles under high-temperature and high-pressure reaction conditions.

3.2.3. The Flotation Process Used the HTD Coal Pulp as a Feedstock. In consideration of the wastewater treatment problem produced by the HTD process, it may be an obstacle for the industrial application of HTD because the wastewater contains lots of inorganic salts and organic compounds. Therefore, the HTD coal pulp was used directly as the flotation feedstock, and the flotation performance was investigated. The comparative analysis of flotation indexes for using the dried coal and coal pulp is shown in Figure 8, and the yield of a cleaned coal and combustible matter recovery was calculated based on the raw coal and is shown in Figure 8a and Figure 8b, respectively. From the data in Figure 8, it shows that the yield of a cleaned coal and combustible matter recovery still increases as the HTD temperature increases for using coal pulp as a flotation feedstock and does not worsen the flotation process and even increases a little than that of using a dried coal as a flotation feedstock. Specifically, when the temperature is at 310 °C, the yield of the cleaned coal increased from 12.14 to 55.58%, and combustible matter recovery increased from 13.83 to 65.17% by raw coal basis. Also, note that the main reason for the enhancement of flotation results from the change of structure brought by the HTD process. From what has been discussed, it can be confirmed that the combined process of HTD and flotation was an effective method for dewatering and deashing. In addition, the wastewater produced by the HTD process can be used as process water of flotation, and the filter pressing water after the flotation process is returned and used as process water of the HTD and flotation process. These results provide an important reference for the development of high value-added applications and industrial applications for lignite.

3.2.4. The Mechanism Analysis of Promotion by Using the Coal Pulp as a Flotation Feedstock. The isoelectric point of the raw coal and HTD samples is measured and shown in Table 7 when the potential value is zero, and the corresponding pH value is called the isoelectric point. As shown in Table 7, the pH value gradually increases with the increasing HTD temperature.

Table 7. Isoelectric Point of the Raw Coal and HTD Samples

| samples                  | raw coal | HTD200<sup>a</sup> | HTD310<sup>a</sup> | HTD200<sup>b</sup> | HTD310<sup>b</sup> |
|--------------------------|---------|--------------------|--------------------|--------------------|--------------------|
| isoelectric point        | 2.14    | 2.21               | 2.23               | 3.63               | 3.66               |

<sup>a</sup>Deionized water. <sup>b</sup>Separated water from the solid–liquid product after HTD.
increasing HTD temperature, and this is consistent with the removal of oxygen-containing functional groups. The increase in the pH value means a decrease in the zeta potential, which would improve effectively the flotation effect. In addition, the pH value that added the separated water from the solid—liquid product after HTD is higher than that of adding deionized water. This is likely due the fact that lots of inorganic salts were stripped in the wastewater during the HTD process. Therefore, the flotation characteristics got better. This is consistent with the research results of many scholars.42–44

The main cation and anion in wastewater after the HTD process are measured and shown in Table 8, indicating that lots of inorganic salts were stripped in the wastewater during the HTD process. Arnold et al.45 found that the flotation index was enhanced in tap water compared with the deionized water and believed that the presence of inorganic salts compresses the double electrical layer, and the wetting film at the surface of the coal particle became much thinner and more susceptible to breakdown. Therefore, the drainage of the water film is facilitated, and it is easier to form stable bubble—particle aggregates that are a very important step for flotation,46–47 which results in the improvement of the flotation effect.

4. CONCLUSIONS

The Baiyinhua No. 2 mine lignite was applied as the original sample. Combined with the FT-IR and 13C NMR test, the effect of hydrothermal treatment dewatering on the structure change and flotation behavior of the original sample and HTD samples were studied, and especially the solid—liquid product was directly used as feedstock flotation, and the flotation indexes were investigated. The main results are summarized here.

(1) The HTD is effective to improve low-rank coal quality for dewatering and deoxygenation. The moisture content decreases from 28.25% of the raw coal to 6.37% of the HTD310 coal sample, and the R0/1 value from 0.26% of the raw coal to 0.17% of the HTD310 coal sample.

(2) The HTD process facilitates the conversion of an aliphatic structure to the aromatic structural unit and aromatization of organic components in the lignite, which results in a decrease of aliphatic structural units and an increase in aromatic structural units, thus increasing the degree of coal metamorphism.

(3) The oxygen-containing functional groups generally decrease during the HTD process, especially carboxyl acid and ether groups. The carboxyl acid and ether groups decrease from 17.03 and 15.64 to 6.34 and 6.78%, respectively. The content of hydroxy groups increased slightly at a temperature below 250 °C and decreased subsequently, but, in general, it is not much of a change. Quinone groups increase during the HTD process, but it has little effect on the wettability of the coal.

(4) The HTD process changes surface properties and wettability of HTD coal samples, and the wettability continually decreases, and the floatability continually increases with the increasing HTD temperature. This is due to the removal of oxygen-containing functional groups and the increase in coal rank, which enhances the hydrophobicity and decreases hydrophilicity of the lignite surface. This would contribute for improving the flotation performance of HTD coal samples.

(5) The HTD process effectively improves the flotation performance of the lignite, even if the coal pulp was directly used as a flotation feedstock. Specifically, the yield of a cleaned coal increased from 12.14% of the raw coal to 55.58% of HTD310, and combustible matter recovery increased from 13.83% of the raw coal to 65.17% of HTD310 by raw coal basis.

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### Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (grant nos.: 51704016 and 51574252) and the State Key Program for Basic Research of Basic research on large-scale utilization of low-quality coal (grant no.: 2012CB214902).

NOMENCLATURE

HTD hydrothermal treatment dewatering
HTD150 The coal sample treated by HTD at 150 °C
HTD200 the coal sample treated by HTD at 200 °C
HTD250 the coal sample treated by HTD at 250 °C
HTD310 the coal sample treated by HTD at 310 °C
F1 the relative content of wavenumbers at 1710 cm−1 of FT-IR
F1,1 the relative content of wavenumbers at 1710−1750 cm−1 of FT-IR
F1,2 the relative content of wavenumbers at 1685−1710 cm−1 of FT-IR
F2 the relative content of wavenumbers at 1600−1685 cm−1 of FT-IR
F2,1 the relative content of wavenumbers at 1440−1600 cm−1 of FT-IR
F2,2 the relative content of wavenumbers at 1370−1440 cm−1 of FT-IR
F3 the relative content of wavenumbers at 1110−1300 cm−1 of FT-IR
F3,1 the relative content of wavenumbers at 1000−1110 cm−1 of FT-IR
F3,2 the relative content of wavenumbers at 0−65 ppm of 13C NMR
F3,3 the relative content of wavenumbers at 65−100 ppm of 13C NMR
F3,4 the relative content of wavenumbers at 150−220 ppm of 13C NMR
F3,5 the relative content of wavenumbers at 65−100 ppm of 13C NMR
F3,6 the relative content of wavenumbers at 150−170 ppm of 13C NMR
F3,7 the relative content of chemical shifts at 0−65 ppm of 13C NMR
FT-IR Fourier transform infrared spectroscopy
13C NMR solid-state 13C nuclear magnetic resonance

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