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Relationships between Combustion Behavior in Air and the Chemical Structure of Bituminous Coal during Combustion Processes

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Abstract: The structural parameters of five bituminous coals were analyzed by using X-ray diffraction and attenuated total reflection–Fourier transform infrared spectroscopy. The combustion behavior of coal was investigated by using a thermogravimetric analyzer under air conditions. Furthermore, the relationships between combustion parameters and the coal structure were established. The results show that bituminous coals contain crystalline and amorphous carbon. The aromaticity, interlayer spacing, average stacking height, aliphatic chain length, and the hydrocarbon-generating potential varied with the different bituminous coals. The coal samples exhibited similar weight changes during the combustion process, and the combustion parameters increased with increments in heating rate. The maximum combustion rate and activation energy increased with declining interlayer spacing and hydrocarbon-generating potential and increasing aromaticity, average stacking height, and aliphatic chain length. The bituminous coal for the utilization of combustion should have high aromaticity, a degree of graphitization, crystalline, long aliphatic chain length, and weak hydrocarbon-generating potential.

Keywords: bituminous coals; combustion behavior; carbon structure; functional groups; activation energy

1. Introduction

The use of pulverized coal injection (PCI) has the potential to reduce fuel consumption and optimize blast furnace efficiency in the blast furnace ironmaking process [1]. Coal, used in the pulverized coal injection, usually contains anthracite, bituminous coal, and lignite, etc., and its combustion behavior has a strong relationship to pulverized coal injections. Furthermore, considering environmental concerns and economic efficiency, extensive attention has been paid to bituminous coals. As a result, the interest in bituminous coal combustion has been revived.

The combustion behavior of bituminous coal is different from that of other coals. The combustion of lignite and anthracite coals is considered as single-carbon combustion process due to their low volatility [2–5], while that of bituminous coal follows two steps because of high volatility [4]. Recently, several efforts focus on coal combustion behavior by analyzing combustion reactivity and kinetics analysis. Coal reactivity varies with the parent coal [6], and the combustion rate coefficient decreases in a range of eleven coals from low-rank to high-rank (anthracite) coal [7]. Additionally, the apparent combustion rate of lignite coal is significantly higher than that of bituminous coal [2]. In addition, the first-order reaction mechanism has been used to obtain the kinetic parameters of coal combustion [8]. The apparent reactivity of coal combustion declines with the increasing rank of coal from...
lignite to bituminous coals [9]. As mentioned, bituminous coal exhibits complex combustion behavior and preferable reactivity. Therefore, the analysis of bituminous coal combustion is still vitally needed for its better understanding and utilization.

The two-step combustion of bituminous coal involves volatile pyrolysis that occurs during the initial heating process, accompanied by complex chemical structure changes and the subsequent combustion of the resultant coal char. Furthermore, these two steps are strongly affected by the coal’s physical properties and chemical structure. Several studies have focused on the relationships between the coal combustion behavior and physical properties, and the results conclude that the smaller particle and large pore structure leads to a better combustion rate [10–13]. However, rare works have focused on the relationships between coal combustion behavior and chemical structure. Currently, coal chemical structure has been analyzed using several modern techniques such as X-ray diffraction (XRD), attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), nuclear magnetic resonance (NMR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM) [14–16]. This work will initially view the coal chemical structure and then provide a greater understanding of relationships between the coal combustion and chemical structure.

In this work, five bituminous coal samples were studied by using XRD and ATR-FTIR. The structural parameters, including aromaticity, average stacking height, aliphatic chain length, and hydrocarbon-generating potential, were deduced from XRD and ATR-FTIR spectra, respectively. The coal combustion behavior was undertaken by using a thermogravimetric analyzer (TGA). The kinetic parameters, including apparent activation energy ($E$) and frequency factor ($A$) during coal combustion, were obtained from Distributed Activation Energy Model (DAEM) methods. Finally, the relationships between the combustion behavior and chemical structure were constructed.

2. Experimental
2.1. Sample Preparation

Five bituminous coal samples, Illinois coal from America (marked as coal1), Guizhou coal from China (marked as coal2), Shanxi coal from China (marked as coal3), Queensland coal from Australia (marked as coal4), and New South Wales coal from Australia (marked as coal5), were used in this work. Table 1 shows the proximate analysis of bituminous coal, which is characterized by the American Society for Testing and Materials (ASTM) as D3172-13. The coal samples were crushed to a particle size of under 74 µm and dried in a heating oven at a temperature of 110 °C for six hours. The five bituminous coal samples are assigned the notations of coal1, coal2, coal3, coal4, and coal5.

| Sample   | Moisture, air dry (%) | volatile, dry (%) | Ash, dry (%) | Fixed Carbon, dry (%) |
|----------|-----------------------|-------------------|--------------|-----------------------|
| coal1    | 3.05                  | 24.39             | 8.54         | 67.07                 |
| coal2    | 4.07                  | 26.06             | 6.36         | 67.58                 |
| coal3    | 3.58                  | 27.15             | 4.32         | 68.53                 |
| coal4    | 4.12                  | 25.01             | 7.78         | 67.21                 |
| coal5    | 3.36                  | 25.31             | 8.02         | 66.67                 |

2.2. Coal Chemical Structure Characterization

The carbon structure of the bituminous coal samples was analyzed by an XRD analyzer (PANalytical, Netherlands) with a monochromator and a copper Kα X-ray source ($\lambda = 0.154$ nm). The accelerating voltage and current were 40 kV and 150 mA, respectively. The samples were scanned at 4° min⁻¹ over an angular range of 10°–90° with a scanning interval of 0.02° per step. The broad peak of 2θ ranging from 15° to 30° was fitted by two Gaussian peaks around 21° and 26°, which represents the $\gamma$-band and $\pi$-band (002-band), respectively [15,17]. From these XRD peaks, the contents of aliphatic carbon ($C_{al}$) and
aromatic carbon (C_ar) were calculated using the areas of the γ-band and π band (002-band), respectively. Then, aromaticity (f_a) is obtained from the following equation [15,17,18]:

\[ f_a = \frac{IA_\pi}{(IA_\pi + IA_\gamma)} \]  

(1)

where IA represents the area of band.

The interlayer spacing (d_{002}) and the average stacking height (L_c) of the crystallite were calculated using the classical Scherrer equations [19–21]:

\[ d_{002} = \frac{\lambda}{2\sin \theta_{002}} \]  

(2)

\[ L_c = 0.97\frac{\lambda}{\beta_{002} \cos \theta_{002}} \]  

(3)

where \( \lambda \) is the wavelength of the X-ray (0.154 nm), \( \beta \) is the full width at half maximum of 002-band, and \( \theta \) is the 002-band scattering angle.

The organic functional group structure of bituminous coal samples was carried out by ATR-FTIR (PerkinElmer, Waltham, MA, USA). The coal samples were analyzed at room temperature, from a collection of 32 scans per spectrum measured at a resolution of 4 cm\(^{-1}\) with wavenumbers from 4000 to 650 cm\(^{-1}\). The structural parameters, A-factor and CH\(_2\)/CH\(_3\), were calculated by curve-fitting two regions at 3000–2800 cm\(^{-1}\) and 1800–1520 cm\(^{-1}\) [22,23]. The detailed equations are as follows:

\[ \frac{CH_2}{CH_3} = \frac{(IA_{2920 \, \text{cm}^{-1}} + IA_{2860 \, \text{cm}^{-1}})}{(IA_{2950 \, \text{cm}^{-1}} + IA_{2890 \, \text{cm}^{-1}})} \]  

(4)

\[ A - \text{factor} = \frac{(IA_{3000} - 2800 \, \text{cm}^{-1})}{(IA_{3000} - 2800 \, \text{cm}^{-1} + IA_{1600} - 1520 \, \text{cm}^{-1})} \]  

(5)

where CH\(_2\)/CH\(_3\) ratio represents the chain length of the aliphatic side functional groups within the macromolecular structure of coal, A – factor stands for the hydrocarbon-generating potential of coal, and IA is the area of band.

2.3. TGA Experiment

The combustion behaviors of bituminous coal samples were studied by TGA (PerkinElmer, Waltham, MA, America). Approximately 30 mg of coal samples was placed into the ceramic crucible and heated from room temperature to 1050 °C with five different heating rates, containing 5, 10, 15, 20, and 25 °C min\(^{-1}\), under the air condition of 20 mL min\(^{-1}\). Then, the weight of each sample can be determined and recorded simultaneously. To reduce the experimental error and achieve the required precision, the TGA experiments of five coal samples were repeated at least three times. Furthermore, the derivative of thermogravimetric (DTG) was calculated from the TG curve. Then, relative pyrolysis characteristic parameters including \( T_{\text{in}}, T_i, T_{\text{max}}, \) and \( \left(\frac{dw}{dt}\right)_{\text{max}} \) can be obtained. According to the American Society for Testing and Materials (ASTM), the value of \( T_{\text{in}} \) is defined as the ignition temperature, which is the temperature relative to the 5% weight loss of the total weight loss, \( T_i \) is the burnout temperature that is related to the temperature relative to the 95% weight loss of the total weight loss, \( T_{\text{max}} \) is the temperature to the maximum combustion rate, and \( \left(\frac{dw}{dt}\right)_{\text{max}} \) is the maximum combustion rate that is connected with the maximum weight loss rate. \( w \) and \( t \) refer to the weight loss and time of the coal samples, respectively. Furthermore, all the parameters above were obtained when the temperature is over 150 °C.

2.4. Kinetics Analysis

This work used the DAEM method rather than simple kinetic models to describe coal combustion due to bituminous coal experiencing complex reactions during the coal combustion process. The Miura integral method was used in DAEM without assuming the forms of the activation-energy (E) distribution function and the fixed-frequency factor.
(A) values in advance [24]. The detailed theoretical basis and derivation processes can be obtained from previous works [24–26], and the final equation can be expressed as follows:

\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{E} \right) + 0.6075 - \frac{E}{RT}
\]

(6)

where \( \beta \) is the heating rate (K s\(^{-1} \)), \( T \) is the temperature (K), \( A \) is the frequency factor (1 s\(^{-1} \)), \( R \) is the universal gas constant (8.314 J mol\(^{-1} \) K\(^{-1} \)), and the \( E \) is the activation energy (J mol\(^{-1} \)).

3. Results and Discussion

3.1. Phase Composition of Bituminous Coal

Figure 1 shows the XRD patterns of five bituminous coal samples. The high background exists in all the samples due to the presence of amorphous carbon. Nevertheless, XRD patterns of all the coal samples exhibit a prominent diffraction peak near 26\(^{\circ} \), which is characteristic of the \( \pi \)-band (002-band) of graphite. These results imply that the carbon structure in coal samples is an intermediate between the graphite and the amorphous state, which can be described as the class structure of graphitization. Furthermore, coal samples consist of several kinds of minerals such as kaolinite, quartz, and calcite. Although the calcite and pyrite may have the catalytic effect on coal combustion [27,28], this work has not been considered for catalysis due to the low content of these minerals in bituminous coal.

Figure 1. XRD patterns of different bituminous coal samples.

Figure 2 depicts several prominent peaks fitted by Gaussian functions. The peaks of minerals (kaolinite and quartz) are also considered in this work to ensure accurate fitting of the data. The characteristic parameters (\( f_a, d_{002}, L_c \)) obtained from the curve-fitting of the \( \gamma \) and 002 bands are plotted in Figure 3. According to Figure 3a, the aromaticity (\( f_a \)) values from the different bituminous coal samples varied from 0.653 to 0.723, which are
consistent with the literature [14,15]. From Figure 3b, the interlayer spacing ($d_{002}$) values of bituminous coal samples are in the range of 0.352–0.359 nm. Remarkably, those values are higher than that of graphite (0.335 nm) and smaller than the asphaltene (0.370 nm) [29,30], indicating that the coal samples own the class structure of graphitization. Furthermore, the more the $d_{002}$ values were closer to 0.335 nm, the higher the graphitization degree of coal [29,30]. Therefore, coal3 has the highest degree of graphitization, while coal5 has the smallest. The average stacking heights ($L_c$) values range from 1.771 to 2.043 nm. Coal3 has the largest $L_c$ value among five coal samples, implying that these types of coal have the largest crystalline structure in the five bituminous coal samples.

Figure 2. Gaussian curve-fitting of peaks for coal2 in the 2 Theta range of 15–32°.

Figure 3. Structural parameters obtained from the curve-fitting of XRD spectra: (a) $f_a$ and (b) $d_{002}$ and $L_c$. 
Figure 4 shows the ATR-FTIR spectra of five bituminous coal samples. A broad and low-intensity transmittance band between 3700 cm$^{-1}$ to 3100 cm$^{-1}$ is related to the vibration of O–H in all coal samples. Two distinct bands located at 2920 and 2850 cm$^{-1}$ in the coal samples correspond to the aliphatic $–\text{CH}_2$ and $–\text{CH}_3$ stretching vibrations [22]. The transmittance peak at 1800–1500 cm$^{-1}$ is attributed to the C=O and C=C aromatic-ring stretching vibrations. The band located at 1035 and 1009 cm$^{-1}$ is related to the C-O-R stretching vibration. The region from 900 cm$^{-1}$ to 700 cm$^{-1}$ is attributed to the vibration of substituted aromatic rings with one, two or three, and four adjacent C-H groups [22,26].

![Figure 4. ATR-FTIR spectra of bituminous coal samples.](image)

Two regions (3000–2800 cm$^{-1}$ and 1800–1520 cm$^{-1}$) are focused upon in order to evaluate the chain length of the aliphatic side functional groups and hydrocarbon-generating potential of bituminous coal. Then, the structural parameters, CH$_2$/CH$_3$ ratio and $A$-factor, can be obtained from the curve-fitting of these two regions, and the details are shown in Figure 5. The values of CH$_2$/CH$_3$ ratio ranges from 2.31 to 2.43. Furthermore, it should be observed that coal3 has the most extended aliphatic chain length, while coal5 has the shortest. The $A$-factor values of coal samples are in the range of 1.47–1.65. Combined with the proximate analysis of coal samples in Table 1, the higher the $A$-factor value, the higher the amount of volatile matter in coal samples. Furthermore, the higher value of the $A$-factor indicates that improved hydrocarbon-generating potential takes place in the coal.
Figure 5. Structure parameters of bituminous coal samples obtained from the curve-fitting of ATR-FTIR spectra.

3.2. Combustion Behavior of Bituminous Coal

Figure 6 shows the TG and DTG curves of bituminous coal combustion under different heating rates. For coal1 combusted at the heating rate of 5 °C min⁻¹, its weight was reduced due to the crystal water evaporation before 200 °C. With the increase in combustion temperature, the coal’s weight slightly increased, and this mainly resulted from oxygen absorptions under an air atmosphere [31]. After that, the coal’s weight decreased noticeably because the coal started to experience volatile pyrolysis, which is the first step in bituminous coal combustion. During this step, oxygen-containing functional groups, alkyl side chains, or bridge bonds would break and release small molecular gas compounds, and some of them formed a fluid phase or tar [22,26,32]. When the combustion temperature reaches up to ignition temperature, these substances and char will combust. Finally, it can be seen that about 11% of coal weight remains in the samples, and this includes mainly minerals that resulted from the transformation of kaolinite, quartz, or others. Furthermore, the weight loss and weight loss rate decreased with an increase in heating rate. Interestingly, this bituminous coal cannot burn completely in the entire heating range (room temperature—1050 °C) when the heating rate reaches up to 20 and 25 °C min⁻¹. It should be observed that the other four coal samples had the same weight change with coal1 except for the maximum weight loss rate.

The corresponding combustion characteristic parameters of coal samples are listed in Table 2. For coal1, with the increase in heating rate, the ignition temperature ($T_i$), burnout temperature ($T_f$), and temperature relative to the maximum combustion rate ($T_{max}$) increased, while the maximum combustion rate ($d_w/d_t|_{max}$) decreased. Furthermore, the combustion characteristic parameters vary with the different bituminous coal samples. Coal3 has the largest maximum combustion rate, while coal1 has the smallest rate.
Figure 6. TG and DTG curves of bituminous coal samples.
Table 2. Combustion parameters of bituminous coal samples.

| Samples | Heating Rate \((^\circ \text{C} \text{ min}^{-1})\) | \(T_i\) (°C) | \(T_f\) (°C) | \(T_{\text{max}}\) (°C) | \((\text{d}_w/\text{d}_t)_{\text{max}}\) (% min\(^{-1}\)) |
|---------|---------------------------------|----------------|----------------|-----------------|------------------------|
| Coal1   | 5                               | 489            | 687            | 589             | 0.492                  |
|         | 10                              | 507            | 834            | 615             | 0.317                  |
|         | 15                              | 533            | 972            | 634             | 0.260                  |
|         | 20                              | 547            | -              | 637             | 0.194                  |
|         | 25                              | 553            | -              | 642             | 0.172                  |
| Coal2   | 5                               | 537            | 724            | 630             | 0.538                  |
|         | 10                              | 552            | 847            | 643             | 0.355                  |
|         | 15                              | 557            | 991            | 650             | 0.256                  |
|         | 20                              | 591            | -              | 685             | 0.219                  |
|         | 25                              | 597            | -              | 700             | 0.167                  |
| Coal3   | 5                               | 497            | 674            | 587             | 0.585                  |
|         | 10                              | 500            | 820            | 598             | 0.316                  |
|         | 15                              | 507            | 972            | 603             | 0.248                  |
|         | 20                              | 543            | -              | 632             | 0.202                  |
|         | 25                              | 554            | -              | 656             | 0.182                  |
| Coal4   | 5                               | 534            | 753            | 550             | 0.499                  |
|         | 10                              | 574            | 875            | 569             | 0.338                  |
|         | 15                              | 600            | 1044           | 593             | 0.248                  |
|         | 20                              | 608            | -              | 602             | 0.188                  |
|         | 25                              | 616            | -              | 613             | 0.151                  |
| Coal5   | 5                               | 442            | 642            | 548             | 0.519                  |
|         | 10                              | 464            | 798            | 564             | 0.324                  |
|         | 15                              | 484            | 1044           | 581             | 0.243                  |
|         | 20                              | 602            | -              | 594             | 0.184                  |
|         | 25                              | 610            | -              | 606             | 0.158                  |

3.3. Kinetics Analysis

Combustion behavior occurs in the range from \(T_i\) to \(T_f\), and the corresponding reaction conversions \(\alpha (\alpha = \frac{W_i - W_t}{W_i - W_f})\). \(W_i\) is the weight of coal samples at the ignition temperature of \(T_i\), \(W_t\) stands for the weight of coal samples at time \(t\), and \(W_f\) is the weight of coal samples at the burnout temperature of \(T_f\) range from 0.1 to 0.9. The kinetics parameters, including \(E\) and \(A\) at different conversions, can be obtained using the DAEM method. The large values of \(E\) and \(A\) indicate that the reaction proceeds with greater difficulty and is more complex during coal combustion process. Figure 7 shows the Arrhenius plots of bituminous coal samples at various conversions from \(\alpha = 0.1\) to \(\alpha = 0.9\) during combustion processes. Table 3 lists the \(E\) and \(A\) values of bituminous coal samples calculated using Equation (6). The high correlation coefficients \((R^2 > 0.940)\) obtained indicate that a high level of confidence can be given to the determined \(E\) and \(A\) values. On the other side, the apparent activation energy and frequency factor of coal samples vary with the different reaction conversions, indicating that more than one single mechanism exists during the bituminous coal combustion process. For the five coal samples, a linear relationship between \(E\) and \(\ln A\) \((R^2 \geq 0.998)\) shows that the perfect kinetic compensation effect occurred. In addition, previous studies confirmed that the values of \(E\) in solid-state reactions are in the range of 50–350 kJ mol\(^{-1}\), implying that \(E\) values obtained in this work are also comparable [33,34]. In addition, the \(E\) and \(\ln A\) values vary with different bituminous coal samples, and the rank of these two values are followed as coal3 > coal2 > coal5 > coal4 > coal1.
Figure 7. Arrhenius plots of bituminous coal samples at various conversion from $\alpha = 0.1$ to $\alpha = 0.9$.

Table 3. Kinetic parameters of bituminous coal samples.

| Samples | $E$ (kJ mol$^{-1}$) | ln$A$ (s$^{-1}$) | $r^2$ | $E$ (kJ mol$^{-1}$) | ln$A$ (s$^{-1}$) | $r^2$ | $E$ (kJ mol$^{-1}$) | ln$A$ (s$^{-1}$) | $r^2$ | $E$ (kJ mol$^{-1}$) | ln$A$ (s$^{-1}$) | $r^2$ | $E$ (kJ mol$^{-1}$) | ln$A$ (s$^{-1}$) | $r^2$ | Average | Relationship of $E$ and ln$A$ |
|---------|-------------------|-----------------|-------|-------------------|-----------------|-------|-------------------|-----------------|-------|-------------------|-----------------|-------|-------------------|-----------------|-------|----------|--------------------------|
| Coal1   | 96.266            | 4.984           | 0.913 | 98.205            | 4.631           | 0.981 | 77.639            | 1.023           | 0.985 | 65.360            | 1.161           | 0.993 | 54.526            | 3.077           | 0.999 | 45.455            | 4.681           | 0.991 | 34.917            | 6.498           | 0.993 | 27.971            | 7.781           | 0.953 | 22.200            | 8.880           | 0.947 |
| Coal2   | 223.483           | 23.219          | 0.8019| 175.832           | 15.186          | 0.961 | 136.48            | 8.956           | 0.999 | 100.045           | 3.385           | 0.999 | 79.065            | 0.101           | 0.999 | 58.850            | 4.855           | 0.979 | 47.636            | 6.837           | 0.974 | 35.306            | 8.175           | 0.918 |
| Coal3   | 393.433           | 51.289          | 0.905 | 219.187           | 23.184          | 0.966 | 142.400           | 10.934          | 0.999 | 90.295            | 2.742           | 0.978 | 65.421            | 1.313           | 0.978 | 50.972            | 3.753           | 0.974 | 36.206            | 6.229           | 0.973 |
| Coal4   | 104.343           | 5.007           | 0.97 | 98.644            | 3.533           | 0.977 | 82.584            | 0.867           | 0.999 | 71.141            | 1.088           | 0.993 | 57.465            | 3.27            | 0.992 | 47.051            | 4.966           | 0.992 | 40.298            | 6.476           | 0.999 |
| Coal5   | 88.279            | 4.581           | 0.962 | 73.396            | 1.414           | 0.976 | 65.233            | 0.333           | 0.986 | 53.789            | 2.491           | 0.981 | 42.908            | 2.491           | 0.981 | 35.211            | 5.98            | 0.982 | 27.976            | 7.376           | 0.949 |
|         |                   |                 |       |                   |                 |       |                   |                 |       |                   |                 |       |                   |                 |       |                   |                 |       |                   |                 |       |                   |                 |       |                   |                 |       |

Coal1: $\ln A = 0.181E - 12.902, R^2 = 0.998$
Coal2: $\ln A = 0.159E - 12.476, R^2 = 0.999$
Coal3: $\ln A = 0.163E - 12.069, R^2 = 0.997$
Coal4: $\ln A = 0.169E - 12.975, R^2 = 0.998$
Coal5: $\ln A = 0.196E - 12.924, R^2 = 0.999$
3.4. Relationships between Coal Combustion Parameters and Coal Structure

Coal is treated as a mixture of organic coal matrix and inorganic minerals. Furthermore, the coal matrix can be regarded as large molecular units with intertwining and interlinking C–C, –CH₂–, –CH–, –O–, –S– and –N– inside. The units are linked by weak bridges with some low weight molecules attached. However, the heterogeneous coal structure makes coal parameters different in this work. During coal combustion processes, the different coal parameters will result in different combustion behavior.

Figure 8 shows the relationships between the maximum combustion rate and coal structure from XRD analysis. From Figure 8a, the maximum combustion rate has a slight increase when the aromaticity of bituminous coal increases, implying that the bigger the ratio of aromatic carbon atoms to total carbon atoms in the coal molecular structural unit, the more significant the maximum combustion rate, and the better coal combustion behavior. As shown in Figure 8b, the maximum combustion rate decreases slightly with increasing interlayer spacing. It indicates that the high degree of graphitization would be beneficial for coal combustion. It can also be found that the maximum combustion rate increases with an increasing average stacking height from Figure 8c, suggesting that the larger crystalline structure would be better for coal combustion behavior. Moreover, the relationships between the maximum combustion rate and coal structure from ATR-FTIR analysis can be shown in Figure 9. As described in Figure 9a, the maximum combustion rate increases with increasing CH₂/CH₃. However, it declines with the increase in A-factor, which is shown in Figure 9b.

Figure 10 shows the relationships between activation energy and coal structure from XRD analysis. It can be seen that the values of activation energy increase with decreasing interlayer spacing, increasing aromaticity, and increasing average stacking height. This indicates that lower interlayer spacing, larger aromaticity, and higher average stacking height produce larger activation energies in bituminous coal. Furthermore, the relationships between activation energy and coal structure from ATR-FTIR analysis is shown in Figure 11. The activation energy of bituminous coal has an increasing trend when the A-factor decreases and CH₂/CH₃ ratio increases. This means that the weaker hydrocarbon-generating potential and longer aliphatic chain length of coal contribute to the larger activation energy of coal. When coal is heated initially during coal combustion processes, depolymerization reactions causes the rupture of weaker branched-chain bridges in the coal macromolecule, and this releases low hydrocarbon gases such as the methane, ethane, ethylene, and acetylene, and heavier molecules, such as fluid phase and coal tar [22,26,32]. Furthermore, these molecules can significantly affect coal combustion. The longer the aliphatic chain length and the weaker hydrocarbon-generating potential, the more these molecules would be produced, and the better the coal combustion behavior would be. Combined with the relationships between coal combustion behavior and carbon structure, the bituminous coal for the utilization of combustion should have low interlayer spacing, large aromaticity, big average stacking height, long aliphatic chain length, and weak hydrocarbon-generating potential.
3.4. Relationships between Coal Combustion Parameters and Coal Structure

Coal is treated as a mixture of organic coal matrix and inorganic minerals. Furthermore, the coal matrix can be regarded as large molecular units with intertwining and interlinking C–C, –CH2–, –CH–, –O–, –S– and –N– inside. The units are linked by weak bridges with some low weight molecules attached. However, the heterogeneous coal structure makes coal parameters different in this work. During coal combustion processes, the different coal parameters will result in different combustion behavior.

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Figure 8. Relationship between maximum combustion rate and coal structure from XRD analysis: (a) fa, (b) d002, and (c) Lc.

Figure 9. Relationship between maximum combustion rate and coal structure from ATR-FTIR analysis: (a) CH2/CH3 and (b) A-factor.
4. Conclusions

(1) Crystalline and amorphous carbon exist in bituminous coals. The structural parameters, including aromaticity, interlayer spacing, average stacking height, aliphatic chain length, and hydrocarbon-generating potential, vary with the different bituminous coals.

(2) The same weight changes were observed, and the maximum combustion rate decreased with increasing heating rate during the combustion process of bituminous coals. The maximum combustion rate and activation energy reflected an increasing trend when the interlayer spacing and hydrocarbon-generating potential decreased and aromaticity, average stacking height, and aliphatic chain length increased.

(3) Bituminous coal possesses high aromaticity, degree of graphitization, crystalline, long the aliphatic chain length, and weak hydrocarbon-generating potential, which are all valuable for combustion in blast-furnace ironmaking processes.
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