Effects of Parent Coal Properties on the Pyrolytic Char Chemical Structure: Insights from Micro-Raman Spectroscopy Based on 32 Kinds of Chinese Coals

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Abstract: The chemical structures of pyrolytic chars prepared from 32 kinds of Chinese coals were investigated with micro-Raman spectroscopy in this study. Both first-order and second-order Raman spectra of the chars were curve-fitted and analyzed. The effects of the parent coal properties, including coal rank, volatile, fixed carbon, and ash content, on the pyrolytic char chemical structures were detailed discussed and the correlations between these coal properties and pyrolytic char chemical structures were set up. Multiple-factor analysis was done to propose a comprehensive coal property index that relates well to the pyrolytic char chemical structure. The results indicate that the aromatization degree is the key distinguishable structure of pyrolytic chars prepared from coals with various rank, and the alkyl C−H and aryl C−H structures have no significant difference. The aromatization degree of pyrolytic char decreases with the increase of coal rank, while it increases with the increase of the fixed carbon content in parent coals. The high content of moisture in parent coal can induce condensation of the pyrolytic char, but the inorganic composition probably prevents the condensation of the char. Limited correlations between the coal rank, fixed carbon, moisture and ash content, and the aromatization degree of pyrolytic chars were found. A comprehensive coal property index: (fixed carbon content + moisture content)/(volatile content + ash content) (in air dry basis) combining the fixed carbon content in parent coals. The high content of moisture in parent coal can induce condensation of the pyrolytic char, but the inorganic composition probably prevents the condensation of the char. Limited correlations between the coal rank, fixed carbon, moisture and ash content, and the aromatization degree of pyrolytic chars were found. A comprehensive coal property index: (fixed carbon content + moisture content)/(volatile content + ash content) (in air dry basis) combining the coal properties together relates well to the aromatization degree of pyrolytic char and can act as a good indicator for the pyrolytic char chemical structure. This study reveals the effects of the parent coal properties, including coal rank, fixed carbon, moisture, and ash content, on the pyrolytic char chemical structure, and provides a new comprehensive coal property index to predict the pyrolytic char chemical structure.

Keywords: Raman spectroscopy; coal property; pyrolysis; char; chemical structure

1. Introduction

It is widely accepted that coal will still play a crucial role in the world’s energy mix in the near future, especially in developing countries, such as China, India, and South Africa [1–3]. Nowadays, pyrolysis, gasification, and combustion are the main ways for coal utilization [2,3]. In all these processes, coal pyrolysis is the first step, releasing volatiles and forming pyrolytic char, and then the pyrolytic char undergoes further conversion reactions [3–6]. Because the rate of char conversion reaction is significantly slower than that of devolatilization, the char conversion process is the rate-limited step during coal
conversion [3–6]. Thus, the char reactivity can directly determine the whole process of coal conversion [3,6]. Many studies have been conducted to clarify the factors affecting char reactivity to achieve a precise understanding and prediction of char reactivity [1,3–7]. In addition to the catalysis of inorganic minerals and reaction channels supplied by pores, the char chemical structure, including the carbon matrix and functional groups, also significantly influences the char reactivity [1,2,4–6,8–10].

The investigation of char chemical structures has attracted wide interest over the last decades [1–8]. Yu et al. (2007) and Borah et al. (2011) respectively reviewed the formation of char structures during devolatilization of pulverized coal in a pulverized furnace and large coal particles in a fluidized bed. The results indicate that char chemical structures are not only determined by the heating condition, including the heating rate, temperature, and time, but are also strongly dependent on the parent coal property [3,8]. Yi et al. (2016) studied the structures of pyrolytic chars from coals of three ranks in a drop tube furnace at 1000 °C in an N₂ atmosphere. Their results indicate that the char structures of these coals have significant differences [11]. The lean coal char has the highest order degree of the carbon structure, and the bituminous coal char not the lignite char has the lowest order degree of the carbon structure. Wang et al. (2012) studied the chemical structures of pyrolytic char from coals of four different ranks in an N₂ atmosphere and their results indicate that a higher-rank coal generally has a higher order degree of the carbon structure [12]. Nevertheless, the lignite char is contrary to the rule, and it has a relatively higher order degree of the carbon structure than bituminous coal. Lu et al. (2000) studied the characteristics of chars prepared from five Australian black coals at different temperatures in a drop tube furnace. Their results indicate that the atomic structure of pyrolytic char is dependent on the parent coal property [13], but the strong dependence on volatile matter observed for raw coals diminished for pyrolytic chars. Tomaszewicz et al. (2017) investigated the char chemical structures from 11 kinds of coals by X-ray diffraction (XRD) and Raman spectroscopy, and tried to establish a relationship between coal rank and pyrolytic char structures. The results indicate that the char aromaticity and order degree of the carbon structure increase with the increase of the parent coal rank (volatile content in dry ash free basis) [1], but there are obvious fluctuations for some coals and the relationship is limited. Morga et al. (2015) studied the relationships between the properties of 20 kinds of coking coals and the pyrolytic char structures with Raman spectroscopy. The results indicate that the order degree of the char structure generally increased with the increase of the coal rank [4], but the relationship between the coal rank and the order degree of the carbon structure is still limited.

From the above literature review, it is known that coal rank has an influence on the pyrolytic char chemical structures, but it is not the only factor. One special phenomenon that needs to be clarified is whether lignite chars have a higher order degree of the carbon structure than bituminous or even lean coals, which is contrary to the conventional wisdom that a lower rank coal results in a char with a lower order degree of carbon structures. In view of the coal property, except for a high volatile content, lignite generally has a high moisture content [14]. Some researchers have clarified that steam can take part in the early stage of the coal pyrolysis process, and influence the pyrolytic char structures significantly [6,9,11]. Some other researchers have also revealed that the inorganic component, such as alkali metal and iron particles, can inhibit the aromatization or graphitization of char during coal pyrolysis, while silicon, aluminum, etc. can crosslink with carbon and affect the carbon matrix structure [15–18]. Therefore, whether the moisture and ash in the parent coal influence the chemical structures of pyrolytic char, resulting in the higher order degree of the carbon structure, of lignite pyrolytic chars or not needs to be further studied. In addition, the heating condition or the heat treatment history of coal in a stable industrial process is relatively constant, but the coal properties sometimes cannot be controlled, especially in China, where a variety of coals with a wide-ranging rank can be used in a power plant or gasification boiler simultaneously [3,19]. Besides, the coal property parameters, such as coal rank, volatile content, and fixed carbon content, are macroscopic expressions of
the chemical structures of raw coal. They can be obtained with a standardized quantitative process, and are suitable as indicators to forecast the pyrolytic char chemical structure. Therefore, establishing effective quantitative relationships between coal properties and pyrolytic char chemical structures is very meaningful. It requires a comprehensive study about the effects of coal properties on the pyrolytic char chemical structures and a combination of coal properties to predict the char structures based on a certain amount of coal. Unfortunately, most of the previous studies have only focused on the influence of coal rank, ignoring the influences of other coal properties, such as moisture, fixed carbon, or ash content, and no comprehensive coal property index that relates well to the pyrolytic char chemical structures has been proposed [1,4].

In the past decades, many useful techniques, including Fourier transform infrared spectrometry (FT-IR), XRD, nuclear magnetic resonance (NMR), and Raman spectroscopy, have been developed to characterize coal/char chemical structures [1,5,6,9,11,20,21]. Among these technologies, Raman spectroscopy is being increasingly widely used to study the char structures due to its high sensitivity to not only well-ordered carbon structures but also amorphous carbon structures [2,5,22]. Besides, the detection of coal or chars by micro-Raman spectroscopy is very fast, which is beneficial for the application of Raman spectroscopy in on-line coal/char analysis. Our recent studies indicated that the Raman spectrum in the first-order range could be validly interpreted to clarify the aromatic ring structures of coals and chars, and the Raman spectrum in the second-order range could also be interpreted to reveal useful structure information about aryl C−H and C−H of methyl or methylene [23]. Further investigation of the pyrolytic char chemical structures using Raman spectroscopy and clarification of the roles coal properties play during coal pyrolysis are not only meaningful for revealing the fundamental formation mechanism of pyrolytic char structures, but also for rapid assessment of the pyrolytic char structures in industrial processes.

In this study, chars were prepared from 32 kinds of Chinese coals. The micro-Raman spectrometer was used to characterize the pyrolytic char chemical structures. Both first-order and second-order Raman spectrum of chars were interpreted to reveal the detailed chemical structures. The property parameters of parent coals, including moisture, volatiles, fixed carbon, and ash content, were related to the char structures to reveal the effects of the raw coal properties on the pyrolytic char chemical structures and to propose a comprehensive coal property parameter for the prediction of pyrolytic char chemical structures.

2. Experiments and Methods

In total, 32 kinds of Chinese coals with a volatile content in an air-dried basis (V<sub>ad</sub>) of about 5% to 35%, moisture content (M<sub>ad</sub>) of about 1% to 25%, fixed carbon content (FC<sub>ad</sub>) of about 30% to 70%, and ash content (A<sub>ad</sub>) of about 4% to 55% were selected as the raw coals. The properties of these coals are shown in Table S1 in the Supplementary Materials, and were also described in detail in our previous study [2].

The pyrolytic chars were prepared in a fixed-bed reaction system, described in our previous study [17]. Before an experiment, the temperature and gas flow rate in the reactor was respectively calibrated by a K-type thermocouple (Ω Company, American) and a digital bubble flow meter (Agilent Optiflow 650, American). During an experiment, the furnace temperature was first heated to 1173 K. N<sub>2</sub> with a flow rate of 2.00 L/min was then sent into the quartz tube reactor, removing the air to maintain a non-oxygen atmosphere. For each run, 1.0 ± 0.1 g of raw coal loaded by an alumina sample holder was sent to the constant temperature zone of the reactor rapidly and held for 7 min. After, the char was pushed to the end of the reactor and cooled down in an N<sub>2</sub> atmosphere. In order to study the effects of moisture in the parent coal on the pyrolytic char structures, five coals with a high moisture content were selected and dried in a furnace at 378 K for 24 h. The chars of dried coals were prepared in the same condition as those of raw coals. It must be pointed out that the chars were prepared in this condition mainly because the volatiles in coal were almost released and the pyrolysis process had occurred to a large extent [5], which is
beneficial for studying the effects of coal properties on pyrolytic char structures. Besides, it is similar to the test condition for the volatile content according to Chinese National Standard GB2132-2001, facilitating the set up of universality laws for the industry.

The Raman spectra of pyrolytic chars were tested in a micro-Raman spectrometer (Jobin Yvon Lab RAM HR800, Horiba Jobin Yvon Company, Paris, France) following the process described in our previous studies [2,6,23]. The laser was an Nd-YAG laser and the wavenumber was 532 nm. An Olympus BX41 optical microscope (50× objective lens, Olympus Company, Tokyo, Japanese) was employed to focus the laser on the sample surface. The beam diameter focusing on the sample surface was about 2 μm. The laser power was filtered and controlled at about 5 mW to reduce the thermal damage. All the Raman spectra were recorded in the range of 800 to 3400 cm⁻¹ with an acquisition time of 10 s. In total, 10 to 15 particles were randomly selected and tested to improve the accuracy of the results as pyrolytic chars are heterogeneous [2,6,23].

The first-order Raman spectrum from 800 to 1800 cm⁻¹ and second-order Raman spectrum from 2200 to 3400 cm⁻¹ were curve-fitted. The first-order Raman spectra of the chars were curve-fitted by 10 Gaussian bands according to our previous studies [2,6] and Li et al. [20,22]. Among these 10 bands, only the main bands: G band, D band, and the three bands G_L, V_L, and V_R between G and D bands, are briefly described. The G band located at about 1590 cm⁻¹ is generally attributed to aromatic rings and E₂_G graphite vibration. In view of the limited degree of graphitization of coal char structures at 1173 K and the low Raman intensity of the limited graphitic structures, the G band is mainly attributed to the aromatic ring structures of pyrolytic chars in this study. The D band at about 1330 cm⁻¹ mainly represents the large aromatic rings (not less than 6 rings) in the chars [24], and the three bands G_R, V_L, and V_R together represent the small aromatic rings in the chars. The Raman spectral parameter (G_R+V_L+V_R)/A_D (the ratio of the (G_R+V_L+V_R) bands area to the D band area) represents the ratio of small aromatic rings to large ones in pyrolytic chars, reflecting the aromatization degree of chars [9]. The second-order Raman spectra of chars were curve-fitted by 8 Gaussian bands according to our previous study [23]. The 2G and 2D band at 3180 cm⁻¹ and 2670 cm⁻¹ are the overtone of the G and D band in the first-order Raman spectrum, respectively, and the D+G band at 2925 cm⁻¹ is the combination band of the D and G band [23]. They can mainly be attributed to the aromatic rings structure in the pyrolytic char. The (2D) R_L band at 2810 cm⁻¹ can mainly be attributed to the C−H stretch in methyl and methylene, and the (2G) R_L band at 3060 cm⁻¹ can mainly be attributed to the aryl C−H stretch vibration [23]. The Raman band area ratio A_2D/L/S_2 and A_2D/G/S_2 (the ratio of (2D) L band area (A_2D/L) and the (2G) R band area (A_2D/G)) to the total Raman band area of the second-order Raman spectrum (S_2) respectively reflects the relative amount of the alky C−H structure and aryl C−H structure in the pyrolytic chars [23,25,26]. A sample of the spectrum curve-fitting is shown in Figure 1, and the band attributions are listed in Table 1.

![Figure 1. A sample of the bands’ curve-fitting.](image-url)

Table 1. A summary of the bands’ assignment [2,4–6,9,20,22,23,25–28].

| Description | Wavenumber (cm⁻¹) | Band Type |
|-------------|------------------|-----------|
| G band      | 1590             | Aromatic rings |
| D band      | 1330             | Large aromatic rings |
| 2G band     | 3180             | Small aromatic rings |
| 2D band     | 2670             | Large aromatic rings |
| 2S band     | 2300             | C-C on alkanes and cyclic alkanes; C-H on aromatic rings |
| 2L band     | 3320             | Overtone of the peaks at 1670 cm⁻¹, Carbonyl group C = O |
| 2G_L band   | 3060             | Overtone of the G band at 1590 cm⁻¹, Carbonyl group C = O |
| 2D_L band   | 2810             | C-H stretch of methyl and methylene, amorphous carbon structures |
| GR band     | 1680             | Aryl C-H stretch vibration |
| VL band     | 1465             | Methylene or methyl; semi-circle breathing of aromatic rings |
| VR band     | 1380             | Methyl group; semi-circle breathing of aromatic rings |
| 2G_R band   | 2925             | Combination of D band and G band, large aromatic rings |

Figure 1. A sample of the bands’ curve-fitting.
| Band Name | Band Position, cm\(^{-1}\) | Description |
|-----------|-----------------------------|-------------|
| R         | 960-800                     | C-C on alkanes and cyclic alkanes; C-H on aromatic rings |
| S\(_R\)   | 1060                        | C-H on aromatic rings; benzene (ortho-di-substituted) ring |
| S         | 1185                        | Caromatic-Calkyl; aromatic (aliphatic) ethers; C-C on hydro-aromatic rings; hexagonal diamond carbon sp3; C-H on aromatic rings |
| S\(_L\)   | 1230                        | Aryl-alkyl ether; para-aromatics |
| D         | 1320                        | D band on highly ordered carbonaceous materials; C-C between aromatic rings and aromatics with not less than 6 rings |
| V\(_R\)   | 1380                        | Methyl group; semi-circle breathing of aromatic rings; amorphous carbon structures |
| V\(_L\)   | 1465                        | Methylene or methyl; semi-circle breathing of aromatic rings; amorphous carbon structures |
| G\(_R\)   | 1540                        | Aromatics with 3-5 rings; amorphous carbon structures |
| G         | 1590                        | Graphite \(E^2_s\); aromatic ring quadrant breathing; alkene C = C |
| G\(_L\)   | 1680                        | Carbonyl group C = O |
| 2S        | 2300                        | Overtone of the band at 1150 cm\(^{-1}\), Caromatic-Calkyl, C = O structures |
| (2D)\(_R\) | 2480                        | Large aromatic rings system |
| 2D        | 2670                        | Overtone of the D band, C-C between aromatic rings, large aromatic rings system |
| (2D)\(_L\) | 2810                        | C-H stretch of methyl and methylene, amorphous carbon structures |
| D+G       | 2925                        | Combination of D band and G band, large aromatic rings system |
| (2G)\(_R\) | 3060                        | Aryl C-H stretch vibration |
| 2G        | 3180                        | Overtone of the G band at 1590 cm\(^{-1}\), aromatic rings |
| (2G)\(_L\) | 3320                        | Overtone of the peaks at 1670 cm\(^{-1}\), Carbonyl group C = O |

### 3. Results and Discussion

#### 3.1. The C-H Structures in Pyrolytic Chars

It is known that coal rank is the most important coal property index [1–4,8,11]. Many studies have reported that parent coal rank can affect the pyrolytic char structures [1,4]. Generally, the volatile content in dry-ash-free basis (V\(_{daf}\)) in raw coal can be used to reflect the coal rank [4,5]. Therefore, the correlations between the coal rank represented by V\(_{daf}\) and the pyrolytic char chemical structures are firstly discussed. Figure 2 shows the change trend of A\(_{2G}R/S_2\) and A\(_{2D}L/S_2\) of pyrolytic chars with V\(_{daf}\) in raw coals. It can be seen that both A\(_{2G}R/S_2\) and A\(_{2D}L/S_2\) just slightly increase with the increase of V\(_{daf}\) and there is a great fluctuation. When linearly curve-fitting the points, R\(^2\) is 0.05 and 0.3 for the relations between A\(_{2G}R/S_2\) and A\(_{2D}L/S_2\) and V\(_{daf}\), respectively. It indicates that there are no reasonable correlations between A\(_{2G}R/S_2\) and A\(_{2D}L/S_2\) of pyrolytic char and V\(_{daf}\) of the parent coal. It is known that A\(_{2D}L/S_2\) and A\(_{2G}R/S_2\) can respectively reflect the relative amount of alkyl C−H and aryl C−H structures in pyrolytic chars [23]. Thus, the results reveal that there is no significant relationship between the amount of alkyl C−H and aryl C−H structures in pyrolytic chars and the parent coal rank. Besides, from Figure 2, it can be seen that A\(_{2G}R/S_2\) changes from about 0.09 to 0.105, and A\(_{2D}L/S_2\) changes from about 0.13 to 0.145. The relative change percentage of A\(_{2G}R/S_2\) and A\(_{2D}L/S_2\) is about 15% and 10%, respectively, which is obviously lower than that of raw coals, with a value of about 50% and 17% shown in our previous study [23]. It reveals that the relative amount of alkyl C−H and aryl C−H structures in pyrolytic chars has no significant difference for the
3.1. The C-H Structures in Pyrolytic Chars

It is known that coal rank is the most important coal property index [1–4,8,11]. Many properties have a more significant difference than the C-H structures for wide rank coals investigated in this study. It is different from the results of raw coals, where it was found that the relative amount of alkyl C—H and aryl C—H structures relates well to the coal rank. This is mainly because the alkyl C—H and aryl C—H structures in raw coal are significantly released along with the release of volatiles during coal pyrolysis [29]. Thus, the amount of alkyl C—H and aryl C—H structures is very limited and has no obvious difference for the pyrolytic chars from coals with different ranks when the volatiles are almost released after pyrolysis [6,29].

![Figure 2](image_url)

Figure 2. The correlation between V\textsubscript{daf} in parent coal and A\textsubscript{(2D)L}/S\textsubscript{2} and A\textsubscript{(2G)R}/S\textsubscript{2} of its pyrolytic char.

3.2. The Aromatic Rings in Pyrolytic Chars

Figure 3 shows the correlation between A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} (the ratio of (G\textsubscript{R}+V\textsubscript{L}+V\textsubscript{R}) bands area to the D band area) and V\textsubscript{daf} in parent coals. From Figure 3, it can be seen that A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} of the pyrolytic char changes from about 0.8 to 1.15. The calculated relative change percentage of A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} for all the chars is about 30%, which is obviously larger than that of A\textsubscript{(2G)R}/S\textsubscript{2} and A\textsubscript{(2D)L}/S\textsubscript{2}. It is known that the Raman spectral parameter A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} mainly represents the relative ratio of small aromatic rings to large ones in char, reflecting the char aromatization degree [2,6,20]. Therefore, the aromatic ring structures have a more significant difference than the C-H structures for pyrolytic chars prepared from coals with various ranks. It means that the aromatic rings’ rearrangement and the aromatization degree is the key difference for pyrolytic chars from coals with various ranks. Besides, it can be seen that A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} of pyrolytic char increases with the increase of V\textsubscript{daf} in the parent coals on the whole. It indicates that a coal with a lower rank generally results in a char with a lower aromatization degree, which is in accordance with the literature [1,4]. However, when fitting the correlation between A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} and V\textsubscript{daf} with a linear equation, R\textsuperscript{2} is just about 0.4, which is not high due to the significant fluctuations of some chars. From the distribution of data points, it can be seen that A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} fluctuates significantly with V\textsubscript{daf}, especially for the chars from the parent coals with V\textsubscript{daf} larger than 25%. It indicates that the aromatization degree of pyrolytic chars is not just related to the parent coal rank. Only using the coal rank or V\textsubscript{daf} to predict the characteristic of the aromatization degree of pyrolytic chars has limited accuracy.

In order to clarify the reasons for the fluctuation of A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} with V\textsubscript{daf}, the distribution of data points was further analyzed by combining the detailed parent coal properties. It was found that the chars can mainly be divided into three types (type A, B, and C), as shown in Figure 3. It is interesting to point out that when fitting the correlations between A\textsubscript{(GR+VL+VR)}/A\textsubscript{D} and V\textsubscript{daf} for chars of type A, B, and C with a quadratic equation, R\textsuperscript{2} can be as high as 0.90, 0.81, and 0.82, respectively. This indicates that strong correlations exist between the aromatization degree of pyrolytic chars and V\textsubscript{daf} of parent coals for these three types of coal. From Table S1, it is known that relative to chars of type A, chars of type B are mainly from the parent coals of HSQ, SF, WCW, XLT, and HLH, all of which have common characteristics with a low ash content (A\textsubscript{ad} < 10%) and relatively high moisture.
The chars of type C are mainly from the parent coals of LY, ZC, XM, XWJ, and SX, all of which mainly have a high ash content ($A_{ad} > 30\%$). It reveals that apart from the influence of moisture and ash in the parent coal, the aromatization degree of pyrolytic char can be related to the parent coal rank better. It further indicates that the moisture and ash components in parent coals may have an influence on the aromatic ring structures in pyrolytic char, which deserves further deep investigation.

Figure 3. The correlation between $V_{daf}$ in parent coal and $A_{(GR+VL+VR)}/AD$ of its pyrolytic char. The chars of type A, B, and C were from coals with $10\% < A_{ad} < 30\%$, $A_{ad} < 10\%$, and $A_{ad} > 30\%$, respectively.

3.2.1. Effects of Moisture in Parent Coal on the Aromatic Rings’ Structure

Figure 4 shows the correlation between $M_{ad}$ in parent coal and $A_{(GR+VL+VR)}/AD$ of its pyrolytic char. It can be seen that there is no obvious relationship between $M_{ad}$ and the aromatic ring structures in its pyrolytic char overall. When dividing the chars into three types (type D, E, and F), it seems that a coal with higher $M_{ad}$ can result in a more condensed char. Among them, chars of type D were mainly from the coals with a moisture content lower than 5%. Chars of type E were mainly from the coals with a relatively high moisture content (>5%) and relatively low ash content (<10%). Chars of type F were mainly from the coals with a relatively high moisture content (≥5%) and relatively high ash content (≥10%). In this division, both the effects of the moisture content and the ash content were considered. In order to confirm the detailed effects of moisture in parent coal on the pyrolytic char structures, the structures of chars obtained from the dried coals were further analyzed. Figure 5 shows $A_{(GR+VL+VR)}/AD$ of pyrolytic chars from selected raw coals with a high moisture content and their dried coals. It can be seen that $A_{(GR+VL+VR)}/AD$ of pyrolytic chars from dried coals is slightly larger than the value from raw coals. It indicates that there are more small aromatic rings and less large aromatic rings for the chars prepared from dried coals than the chars from raw coals. In this study, the moisture in raw coals was dried at 105 °C for 24 h, which has very limited effects on the chemical structures of coals [14]. Therefore, the difference is mainly due to the effects of moisture in the parent coal during the coal pyrolysis process. Thus, it directly confirms that the moisture in parent coals can increase the aromatization degree of pyrolytic chars. It is known that the moisture in raw coal is mainly released in the early stage of coal pyrolysis [14]. When the heating rate is a medium to high heating rate, the volatiles in coal can also release along with the release of moisture. The temperature of char also increases rapidly and reaches a high temperature, in which the steam gasification reaction between the steam and char can take place [6,14]. Besides, the steam in the atmospheres can react with the active components in the gaseous phase, forming some free H radicals, which can induce the condensation of aromatic rings in char [6,30,31]. Therefore, during the pyrolysis process, the moisture in parent coals may participate in the following two processes. One is that the steam generated form moisture in the parent coal can react with the volatiles releasing from coals in the early stage, forming some free H radicals, which can induce the condensation of aromatic rings in char or
secondary condensation polymerization between the small aromatic rings or aliphatic hydrocarbon in gas and the aromatic rings in char [6]. Another one is that the steam gasification reaction can take place between the steam and the pyrolytic chars. The small aromatic rings can be selectively consumed during the steam gasification reaction, resulting in a more condensed char [5,30,31]. Both processes can result in more condensed pyrolytic chars, but these two processes have an opposite influence on the char weight change.

![Figure 4. The correlation between M_ad in parent coal and A_{(GR+VL+VR)}/A_D of its pyrolytic char. The chars of type D, E, and F were from coals with Mad < 5%, Mad > 5% and Aad < 10%, and Mad > 5% and Aad > 10%, respectively.](image)

![Figure 5. A comparison of A_{(GR+VL+VR)}/A_D of pyrolytic char from raw coal and dried coal.](image)

After accurate calculation and repeated experiments, the pyrolytic char yields of the raw coals and dried coals (in a dry basis) were obtained and are shown in Figure 6. It can be seen that the char yield of dried coals is 1% to 2% lower than that of raw coals. It means that the moisture in the parent coal results in char with greater mass. Therefore, the moisture in raw coal probably transforms into steam and then induces secondary polycondensation between the light component of volatiles released from the coal and the aromatic rings in pyrolytic char, resulting in an increase of the yield and aromatization degree of pyrolytic char. It also demonstrates that the effects of a high moisture content in parent coals on the chemical structures of pyrolytic char during coal pyrolysis cannot be ignored.

3.2.2. Effects of Ash in Parent Coal on the Aromatic Rings’ Structure

The correlation between A_ad and A_{(GR+VL+VR)}/A_D of pyrolytic char was set up and is shown in Figure 7.
3.2.2. Effects of Ash in Parent Coal on the Aromatic Rings’ Structure

When using the quadratic equation to curve-fit the points, $R^2$ of the correlations for chars of type M was as high as 0.82. It indicates that except for the influence of $V_{daf}$, there is also a reasonable correlation between the ash content in parent coals and the aromatization degree of their pyrolytic chars, revealing that the ash content in the parent coal can also affect the pyrolytic char structures. A coal with a greater ash content results in a less condensed char. Our previous study indicated that the inorganic components in these series coals are mainly silicium and aluminum, which mainly exist as aluminosilicate in raw coals [32]. During coal pyrolysis, the aluminosilicate, on the one hand, can reduce the heat transfer in the char and thus reduce the thermal deactivation of the pyrolytic char. On the other hand, it can encase the catalytic components, such as K and Na, in coal, inhibiting their catalysis during pyrolysis and reducing the condensation of pyrolytic chars [6]. Therefore, a coal with a higher ash content probably results in a less condensed char.

3.2.3. Effects of the Fixed Carbon Content in Parent Coal on the Aromatic Rings’ Structure

It is known that the volatiles and moisture in raw coal are released during coal pyrolysis, forming char containing a fixed carbon and ash content. The fixed carbon content is one parameter directly reflecting the organic content in pyrolytic chars. Therefore, it is
also very important to study the effects of fixed carbon on the pyrolytic char structures. The correlation between FC\text{ad} and \( A_{(GR+VL+VR)}/A_D \) was set up and is shown in Figure 8.

![Figure 8](image)

**Figure 8.** The correlation between FC\text{ad} in parent coal and \( A_{(GR+VL+VR)}/A_D \) of its pyrolytic char.

It can be seen that \( A_{(GR+VL+VR)}/A_D \) generally decreases with the increase of FC\text{ad}. It indicates that the aromatization degree of the chars increases with the increase of FC\text{ad} in the parent coal, which means a coal with higher FC\text{ad} results in a char with a higher aromatization degree. In order to evaluate the correlation between \( A_{(GR+VL+VR)}/A_D \) and FC\text{ad}, a quadratic equation was used to curve-fit the points. The result is:

\[
A_{(GR+VL+VR)}/A_D = 9.375 \times 10^{-1} + 9.500 \times 10^{-2} \times FC_{\text{ad}} - 1.438 \times 10^{-4} \times FC_{\text{ad}}^2
\]  

\( R^2 \) is about 0.67. The results in our previous study showed that the volatiles content in raw coals relates well to the C-H structures and aromatization degree of raw coals and the fixed carbon in raw coals is more related to the ordered structures, such as large aromatic rings [2,23]. During pyrolysis, the volatiles in coal are nearly all released, and the relatively stable structure leaves and undergoes a subsequent series pyrolysis reaction, forming the pyrolytic char finally. So, the fixed carbon content in the parent coal relates to the aromatization degree of pyrolytic char better. The results also reveals that a coal with a higher fixed carbon content results in a more condensed pyrolytic char.

### 3.3. Relationship between the Comprehensive Coal Property Index and Pyrolytic Char Structures

From the above discussion, it is known that the coal properties are all related to the aromatic structure of pyrolytic chars, but the correlations between the coal property parameters and the aromatic rings structure parameter are not good enough. Multiple-factor analysis was further done to search for a comprehensive coal property index, combining them together to reflect the pyrolytic char structures better [33]. \( A_{(GR+VL+VR)}/A_D \) of the pyrolytic chars was set as the dependent variable, and the moisture, volatile, fixed carbon, and ash content were set as the independent variables. Multiple linear regression was applied. The results indicate that the comprehensive coal property parameter \((-0.001 \times M_{\text{ad}} + 0.008 \times V_{\text{ad}} + 0.007 \times A_{\text{ad}})\) is related to \( A_{(GR+VL+VR)}/A_D \) best, and \( R^2 \) is 0.83. The results further demonstrate that the moisture, volatile, and ash content in parent coal all influence the pyrolytic char structures, and using only one of them to reflect the pyrolytic char structures is limited. It needs to be pointed out that, as there is a quantitative correlation between the four coal property parameters: \( M_{\text{ad}}, V_{\text{ad}}, FC_{\text{ad}}, \) and \( A_{\text{ad}} \), during the multiple-factor analysis, one of them would be eliminated in the comprehensive coal property index. In view of the fact that FC\text{ad} was obtained indirectly during proximate analysis, the comprehensive coal property index \((-0.001 \times M_{\text{ad}} + 0.008 \times V_{\text{ad}} + 0.007 \times A_{\text{ad}})\) without FC\text{ad} is shown and discussed above.

In order to optimize the results to obtain an easy-to-use index, the comprehensive coal property index was further simplified as \((FC_{\text{ad}} + M_{\text{ad}})/(V_{\text{ad}} + A_{\text{ad}}))\). The correlation between \((FC_{\text{ad}} + M_{\text{ad}})/(V_{\text{ad}} + A_{\text{ad}})\) and \( A_{(GR+VL+VR)}/A_D \) was set up and is shown in
Figure 9. It can be seen that $A_{(GR+VL+VR)}/A_D$ nearly linearly decreases with the increase of $(FC_{ad} + M_{ad})/(V_{ad} + A_{ad})$. The correlation is:

$$A_{(GR+VL+VR)}/A_D = 1.204 - 0.127 \times (FC_{ad} + M_{ad})/(V_{ad} + A_{ad})$$

$R^2$ is about 0.89, indicating a high relationship between $A_{(GR+VL+VR)}/A_D$ and $(FC_{ad} + M_{ad})/(V_{ad} + A_{ad})$. In fact, in the above analysis, it is known that coal with a higher fixed carbon and moisture content will result in a pyrolytic char with a higher aromatization degree, while coal with a higher ash and volatile content will result in a pyrolytic char with a lower aromatization degree. The comprehensive coal property index $(FC_{ad} + M_{ad})/(V_{ad} + A_{ad})$ combines these four parameters together, and thus it relates well to the aromatization degree of the pyrolytic chars. The comprehensive coal property index $(FC_{ad} + M_{ad})/(V_{ad} + A_{ad})$ can act as a good indicator of the aromatization degree of pyrolytic char from coals with various ranks.

4. Conclusions

The chemical structures of pyrolytic chars prepared from 32 kinds of Chinese coals were investigated by micro-Raman spectroscopy in this study. The effects of the parent coal properties on the pyrolytic char chemical structure were discussed in detail. Multiple-factor analysis was performed, and a novel comprehensive coal property index that reflects the pyrolytic char chemical structure was proposed. The following conclusions can be drawn:

1) The change of the chemical structure of pyrolytic chars with a coal rank is smaller than that of raw coals. For the pyrolytic chars from coals with various ranks, the alkyl C$\text{−}$H and aryl C$\text{−}$H structures have no significant diversity, and the aromatization degree is the key difference.

2) The high moisture content in parent coal can induce condensation of pyrolytic char, but the ash components probably inhibit the condensation of pyrolytic char.

3) The correlation between the volatile, fixed carbon, moisture, and ash content and the aromatization degree of pyrolytic chars is limited. Not only the coal rank but also the fixed carbon, moisture, and ash components can influence the pyrolytic char chemical structures.

4) The comprehensive coal property index $(FC_{ad} + M_{ad})/(V_{ad} + A_{ad})$ combining the coal properties together relates well to the aromatization degree of pyrolytic chars and can act as a good indicator for the aromatization degree of pyrolytic chars from coals with various ranks.

5) More factors that affect the chemical structure of the pyrolysis chars can be considered and stronger correlations can be further set up in future research. Besides, the influence mechanism of the detailed mineral components in the raw coal on the chemical structures of pyrolysis chars should be further clarified.
Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/pr9091575/s1. Table S1. Properties of Coal Samples.

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