Research Article

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Combustion and gasification characteristics of low-temperature pyrolytic semi-coke prepared through atmosphere rich in CH_4 and H_2

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Abstract: Thermoanalysis was used in this research to produce a comparative study on the combustion and gasification characteristics of semi-coke prepared under pyrolytic atmospheres rich in CH_4 and H_2 at different proportions. Distinctions of different semi-coke in terms of carbon chemical structure, functional groups, and micropore structure were examined. The results indicated that adding some reducing gases during pyrolysis could inhibit semi-coke reactivity, the inhibitory effect of the composite gas of H_2 and CH_4 was the most observable, and the effect of H_2 was higher than that of CH_4; moreover, increasing the proportion of reducing gas increased its inhibitory effect. X-ray diffractometer and Fourier-transform infrared spectrometer results indicated that adding reducing gases in the atmosphere elevated the disordering degree of carbon microcrystalline structures, boosted the removal of hydroxyl- and oxygen-containing functional groups, decreased the unsaturated side chains, and improved condensation degree of macromolecular networks. The nitrogen adsorption experiment revealed that the types of pore structure of semi-coke are mainly micropore and mesopore, and the influence of pyrolytic atmosphere on micropores was not of strong regularity but could inhibit mesopore development. Aromatic lamellar stack height of semi-coke, specific surface area of mesopore, and pore volume had a favorable linear correlation with semi-coke reactivity indexes.

Keywords: coal pyrolysis, semi-coke, blast furnace injection, reactivity, pore structure

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1 Introduction

Low-temperature pyrolytic semi-coke is a solid product after removing a number of volatiles from low-rank coal under low-temperature pyrolysis (500–600°C) and tar is separated out [1,2]. Part of this product has been applied to fields like coal gasification, ferroalloy smelting, and calcium carbide production; however, there is still a large quantity of semi-coke resources that require market consumption. In the field of iron-making, pulverized coal injection (PCI) in blast furnace replaces expensive and highly deficient metallurgical coke with relatively low-priced coal to reduce the coke ratio in the blast furnace during iron-making process, and thereby reduce pig iron cost [3,4]. With the continuously increasing blast furnace injection ratio, iron and steel enterprises have an increasing demand for anthracite. Moreover, anthracite reserves only occupy 10.9% of coal reserves in China with unceasingly prominent scarcity, which is then accompanied by rising price. Therefore, under the background of an increase in PCI ratio in blast furnace, seeking for new low-cost and high-quality injecting fuels such as biochar [5] and waste plastics [6] has always been a research emphasis of metallurgists. Using low price semi-coke as PCI fuel to replace expensive anthracite has been an important research orientation for optimizing blast furnace fuel structures, and the reduced production cost has attracted attention from metallurgists [7–11]. Semi-coke

is a potential excellent blast furnace fuel by virtue of favorable transport performance, high calorific value, and no explosiveness [7,10]. However, compared with anthracite, the nature difference of semi-coke is considerable because of its instable quality; moreover, the fluctuation of its combustion performance is remarkable and hinders its application and promotion in blast furnace injection, because during semi-coke production, pyrolysis conditions will influence the semi-coke composition and structure and cause changes in its reactivity. Even if the same coal category is used as a pyrolytic raw material, the reactivity of prepared semi-coke will be critically different, and high pyrolysis degree is adverse to follow-up combustion of semi-coke [11,12]. Factors, such as devolatilization behavior, pore structure, specific surface area, and ordering degree of carbon lattice structure, will result in substantial loss of semi-coke reactivity [13–15]. Combustion reactivity in later phase of semi-coke under high temperature is closely related to semi-coke nature before combustion [16].

The present industrialized pyrolytic processes generally use internal heating-type gas-carrier pyrolysis reactors. In such pyrolysis environments, the raw coal exists not in a pure N_2 atmosphere but in mixed reducing gases such as CO, H_2, and CH_4. Moreover, pyrolysis atmosphere contents are different to a certain degree at various positions inside the furnace. The influences of pyrolysis conditions, such as pyrolysis temperature, heating rate, atmosphere pressure, and holding time, on semi-coke composition, structure, and reactivity [17–19] have been extensively studied; however, the effects of pyrolytic atmosphere on semi-coke reactivity remain controversial. Colette et al. [20,21] studied the influence of the coke-oven gas atmosphere on product distribution and semi-coke characteristics in fixed beds and found that semi-coke combustion characteristics were not eminently different under H_2 and inert atmospheres. Liao et al. [22] indicated that the combustion reactivity of coal–coke-oven gas co-pyrolytic semi-coke is related to pyrolysis pressure and heating rate, and that low pyrolysis pressure and high heating rate contribute to semi-coke combustion reactivity. Zhong et al. [23] found that hydrogen-free radicals generated by H_2 and CH_4 could permeate semi-coke and influence its oxidizing reactivity. Thus, the influence of mixed atmospheres containing reducing gases on semi-coke nature and its reactivity requires further research.

During iron-making technology in blast furnace, PCI fuels experience processes, such as volatile extrusion and combustion and gasification of fixed carbon, within confined spaces in the tuyere and raceway region. Compared with the process of release and combustion of volatiles, char combustion and gasification are relatively slow (20 ms vs 1–4 s), and the time needed for a complete reaction of coal is primarily and jointly determined by char combustion and gasification time [24]. Combustion and gasification properties are highly important for the utilization ratio of fuels inside the furnace and the stable operation of the blast furnace because the combustion of atmosphere inside the hearth is gradually variational. In the front of the tuyere, generated coal gas components are different because of different combustion conditions at different positions along the hearth radius in front of the tuyere. O_2 is sufficient in front of the tuyere and reacts with fuel combustion to generate a large quantity of CO_2, O_2 abruptly decreases and disappears, and CO_2 rapidly rises to its maximum value. Therefore, the injected fuel first experiences atmospheric combustion with sufficient O_2 and then experiences gasification under the atmosphere with a continuously rising CO_2. However, many research on reactivity of PCI fuels only focuses on combustion reactivity [3,25,26] and neglects the importance of gasification reactivity on the consumption of unburned char; moreover, comparative studies on the two above-mentioned subject matter are lacking.

In the present research, thermoanalysis was applied to comparatively study the combustion and gasification reactivity of semi-coke prepared under pyrolytic atmospheres containing different proportions of H_2- and CH_4-reducing gases. Moreover, the relationships between semi-coke composition/structure and combustion/gasification reactivity were obtained by analyzing the carbon chemical structures of different semi-coke, functional group analysis, and micropore structures to provide reference for further scientific and highly efficient application of semi-coke in PCI.

2 Experimental procedure

2.1 Experimental raw materials

Coal samples used in the experiment were typical low-rank coals from Sunjiacha coal mine in Shenmu region of Northern Shaanxi. Proximate analysis and element analysis of coals are illustrated in Table 1. Vertical-type pyrolyzing furnace was used to prepare semi-coke samples, and the pyrolysis system is shown in Figure 1. A total of 250 g samples with granularity within 20–40 mm was placed in a furnace and suspended on an electronic scale. A total of six pyrolytic atmospheres (respectively being (1) pure N_2; (2) 10% CH_4 in N_2; (3) 20% CH_4 in N_2; (4) 10%

Table 1: Proximate analysis and ultimate analysis of coal and chars

Samples	Proximate analysis (wt%, ad)				Ultimate analysis (wt%, ad)				
	M_{ad}	A_{ad}	V_{daf}	FC	C	H	N	O	S
Coal	3.83	7.53	37.06	55.97	71.97	4.08	0.93	10.21	0.20
char1	1.17	9.15	8.21	81.47	82.8	2.42	0.61	1.17	0.23
char2	1.38	9.99	8.04	80.59	83.71	2.02	0.38	1.38	0.20
char3	1.44	8.23	8.01	82.32	83.09	1.87	0.28	1.44	0.21
char4	1.40	9.01	8.49	81.10	82.81	2.24	0.55	1.34	0.16
char5	1.32	8.99	7.40	82.29	83.45	2.01	0.62	1.26	0.19
char6	1.23	8.40	7.11	83.26	83.02	1.95	0.51	1.31	0.17

H_2 in N_2; (5) 20% H_2 in N_2; and (6) 10% H_2, and 10% CH_4 in N_2) were pumped into the reaction jar at a 0.6 L/min flow rate. Samples were heated to 600°C at a rate of 5°C/min and heat was preserved for 30 min, then nitrogen was pumped in for cooling in room temperature. After pyrolysis, semi-coke samples were extracted, labeled char1–char6, and preserved in a drying vessel for further property analysis. The detailed properties of the samples are summarized in Table 1.

2.2 Representation of semi-coke properties

Combustion and gasification reactivity of semi-coke with an experimental weight of 10 ± 0.1 mg was tested using STA449C thermal analyzer from German NESZCH company. Under atmosphere of air (combustion)/CO_2 (gasification) and a flow rate of 50 mL/min, the temperature was elevated from room temperature to 1,000°C (combustion)/1,400°C (gasification) at a rate of 15°C/min, and weight change was synchronously recorded. For the quantitative comparison of semi-coke reactivity, the combustion reactivity index R_c and gasification reactivity index R_g were introduced [27,28]:

$$R_c = \frac{V_{rate}}{T_{ignition}}, \tag{1}$$

$$R_g = \frac{0.5}{t_{0.5}}, \tag{2}$$

where V_{rate} is the average reaction rate of semi-coke combustion, $T_{ignition}$ is the ignition point of semi-coke combustion determined through thermogravimetry-derivative thermogravimetry (TG–DTG) method [29], and $t_{0.5}$ is the time for carbon conversion rate α to reach 50%. α was determined using:

$$\alpha_i = \frac{w_0 - w_i}{w_0 - w_{ash}}, \tag{3}$$

where w_0 is the initial semi-coke mass, w_i is the semi-coke mass at any time, and w_{ash} is the ash content mass in the semi-coke.

Carbon chemical constitution of semi-coke was measured through X-ray diffractometer (XRD) (X'Pert PROMPD)

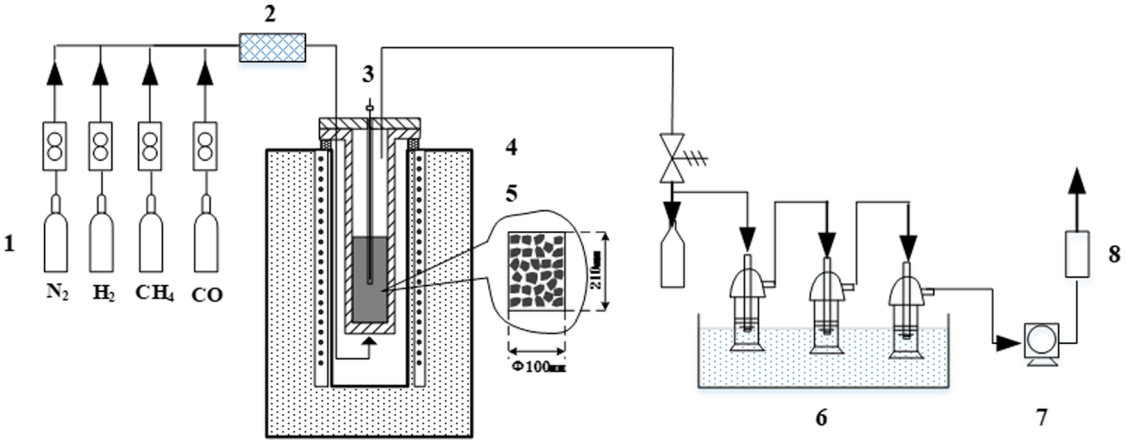

Figure 1: Pyrolysis device diagram. (1) Gas cylinder; (2) gas blending instrument; (3) sample temperature thermocouple; (4) temperature thermocouple inside furnace; (5) pyrolyzing furnace; (6) gas purification and tar collection; (7) pump; (8) gas analyzer.

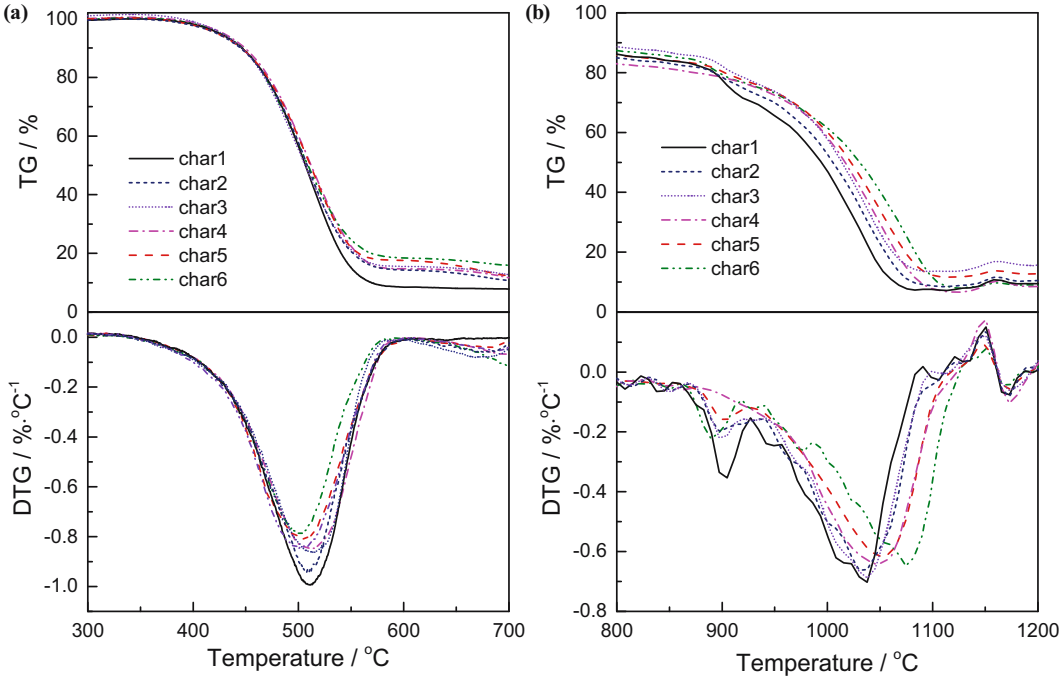

Figure 2: TG–DTG curves of combustion and gasification processes of semi-coke samples prepared under different pyrolytic atmospheres. (a) Air atmosphere; (b) CO_2 atmosphere.

using Cu-Kα target at a scanning rate of 4°/min. Feature sizes of the microcrystalline structure of the semi-coke are represented by d_{002}, L_a, and L_c and were solved according to the Scherrer formula and Bragg equation [30]:

$$d_{002} = \frac{\lambda}{2 \sin \theta_{002}}, \tag{4}$$

$$L_c = \frac{0.89\lambda}{\beta_{002} \cos \theta_{002}}, \tag{5}$$

where d_{002} is the distance between the single aromatic layers of the sample, L_c is the microcrystal stack height perpendicular to the aromatic lamellas, θ_{002} is the glancing angle, β_{002} is the full width at half maximum of the diffraction peak, and λ is the wavelength at 0.15406 nm of the incident X-ray.

Functional group of semi-coke was detected through Fourier-transform infrared spectrometer (FTIR) (German Bruker, Vector 22). Semi-coke samples were prepared using the KBr squashing technique, and test spectral range was 400–4,000 cm^{-1} with a resolution ratio of 4 cm^{-1}. The sample spectra were obtained through scanning after deducting the blank KBr background. Aromaticity was derived using the formulas by Brown and Ladller [31]:

$$f_a = 1 - C_{al}/C, \tag{6}$$

$$C_{al}/C = [(H_{al}/H)\cdot(H/C)]/(H_{al}/C_{al}), \tag{7}$$

where C_{al}/C is the content of aliphatic carbon, H/C is the ratio of hydrogen/carbon numbers, which can be solved through elemental analysis, H_{al}/H is the proportion occupied by aliphatic hydrogen in total hydrogen, H_{al}/C_{al} is the carbon/hydrogen ratio in lipid groups and is taken as 1.8 for coal [31], and H_{al} is the aliphatic hydrogen, which can be solved by dividing the integral area A_{al} inside the wave band by the extinction coefficient a_{al} (a_{al} is taken as 744 cm^{-1} for semi-coke), as shown in Eq. 8:

$$H_{al} = \frac{A_{al}}{a_{al}}. \tag{8}$$

Physicochemical absorber (US Micromeritics, ASAP 2020M+C) and N_2 adsorption method were used to test the specific surface area and micropore structure of semi-coke, with a degasification temperature during the test at 200°C.

3 Results and discussion

3.1 Combustion/gasification reactivity

TG–DTG curves of combustion and gasification of semi-coke samples prepared under different pyrolytic

atmospheres are shown in Figure 2, and semi-coke combustion and gasification characteristic parameters are presented in Table 2.

As shown in Figure 2a, under air atmosphere, six semi-coke samples started losing weight under 368°C or higher, which indicated that volatiles in semi-coke have started to decompose. Subsequently, weight loss rate increased, which suggested that the fixed carbon experienced a rapid combustion reaction. Weight loss basically ended under 570°C or so, which indicated semi-coke after-combustion. In the initial phase of rapid combustion of six semi-coke samples, differences between TG and DTG curves were not evident. In the phase of maximum weight loss rate, the maximum combustion rates of different semi-coke were distinctive, with the reaction rate of char1 being the fastest, followed by char2; moreover, minor differences existed in the reaction rates of char3–char6. In the late combustion phase, DTG curves of semi-coke no. 2–6 slightly advanced. The range of ignition temperature of the six semi-coke samples was from 447°C to 455°C, which indicated that the differences in ignition temperature in the various semi-coke samples were poor. To compare the semi-coke combustion reactivity values, the six curves were analyzed through combustion reactivity indexes in Eq. 1. After calculation, semi-coke combustion reactivity indexes were sorted in descending order: char6 > char5 > char4 > char3 > char2 > char1, which indicated that compared with the pyrolysis atmosphere of N_2, adding reducing gases CH_4 and H_2 in the pyrolysis process of raw coal will reduce the combustion reactivity and gasification reactivity of semi-coke.

Figure 2b indicates that under a CO_2 atmosphere, the six semi-coke samples experienced a volatile and slow gasification phase before 870°C or so, and a rapid gasification reaction happened under 870°C or so; moreover, the finishing temperature of gasification reaction was from 1,050°C to 1,100°C. The six semi-coke samples had noticeable differences in TG and DTG curves compared with char1 prepared under a nitrogen atmosphere; furthermore, the TG and DTG curves of char2–char6 prepared after adding reducing gases experienced retroposition, and the maximum reaction rate and reaction finishing temperature escalated. The semi-coke gasification reactivity indexes were arranged in descending order: char6 > char5 > char4 > char3 > char2 > char1. The results indicated that the addition of reducing gases in the pyrolysis phase of raw coal resulted in a clear degradation of gasification reactivity and inhibition of composite gas of H_2; in addition, CH_4 was the most recognizable, the influence of H_2 was stronger than that of CH_4, and the increased concentration of reducing gases increased its inhibitory effect.

To compare the combustion and gasification reactivity of different semi-coke, time-dependent changes in carbon conversion rates of different semi-coke are illustrated in Figure 3. At the same combustion reaction time, the difference in combustion conversion rates of the different semi-coke was minimal. From Figure 3b, at the same gasification reaction time, different semi-coke had observable differences in gasification reactivity. The time required by char1 to complete combustion and gasification was 700 s or so, and that of char2–char6 continuously increased; thus, this phenomenon became increasingly apparent during gasification. This indicated that the pyrolytic atmosphere conditions influenced the gasification reactivity at a higher degree than that of combustion reactivity. The semi-coke has favorable combustion reactivity; therefore, the after-combustion temperature was lower than 600°C, and the chemical reaction itself could be the restrictive link of combustion. The semi-coke gasification reaction temperature was higher than that of the combustion reaction; moreover, the chemical reaction itself proceeded rapidly and the diffusion of reactants and products should be the restrictive link of this gasification process. Emphasis will be placed on the factors influencing semi-coke chemical reactions, such as carbon chemical structure, functional group distribution, and micropore structural characteristics that influence diffusion.

Table 2: Characteristic parameters of semi-coke during combustion and gasification processes

Samples	T_{max} (°C)	V_{max} (°C min^{-1})	T_i (°C)	T_f (°C)	R_c (×10^3)	$T_{0.5}$ (°C)	R_g (s^{-1} [×10^4])
char1	510	0.9915	447	574	2.21812	1,007	11.65501
char2	509	0.9396	454	567	2.0696	1,016	10.77586
char3	512	0.8657	447	559	1.93669	1,020	10.5042
char4	515	0.8468	448	572	1.89018	1,028	9.80392
char5	505	0.8106	450	579	1.80133	1,034	9.27644
char6	501	0.7875	455	570	1.73077	1,048	8.47458

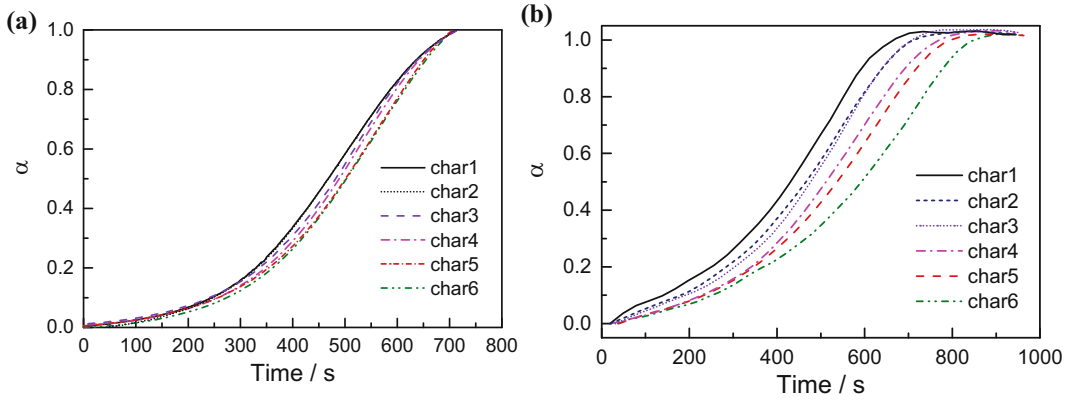

Figure 3: Time-dependent changes in carbon conversion rates of different semi-coke. (a) Air atmosphere; (b) CO_2 atmosphere.

3.2 XRD analysis of chars

Figure 4 shows the XRD spectrums of the six semi-coke samples. The C(002) peaks of samples char1–char6 sharpened, which indicated that the carbon microcrystalline structures of semi-coke prepared by adding reducing gases in the atmosphere were likely to be of the graphite state. X'Pert highscore analysis software, together with Eq. 4 and 5, was used to obtain the position of C(002) peak, lamellar spacing d_{002}, and aromatic lamella stack thickness L_c, and the results are listed in Table 3.

In Table 3, the differences in 2θ angle and d_{002} corresponding to the C(002) peaks of different semi-coke are unsatisfactory. However, the L_c values of char1–char6 gradually increased, thereby indicating that the aromatic lamella stack thickness of the semi-coke gradually expanded. The number of carbon stack lamellas increased, which indicated the enhancement of the pseudo-crystalline phase degree of semi-coke samples and further indicated the enhancement of the carbon ordering degree in the semi-coke. Adding the reducing gases in semi-coke pyrolysis probably promoted the enhancement of the semi-coke graphitization degree because the hydrogen-free radicals generated by H_2 and CH_4 could permeate the semi-coke surface and would enhance the condensation of aromatic rings, thereby decreasing the number of available active sites [20–22].

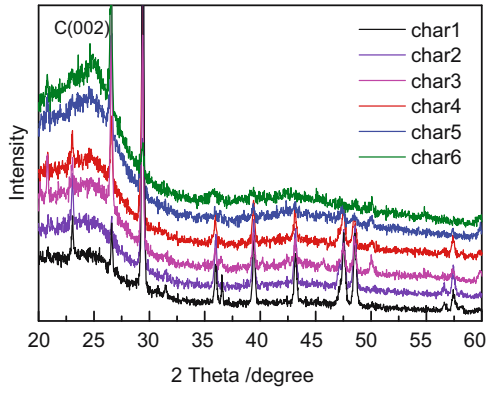

Figure 4: XRD spectrums of different semi-cokes.

Figure 5 shows the relationships of semi-coke L_c with the combustion and gasification reactivity indexes. As shown in Figure 5, semi-coke carbon microcrystalline structure has identical influence rules on combustion reactivity and gasification reactivity, namely, with the enhanced ordering degree of carbon microcrystalline structure, decreased semi-coke reactivity indexes, and the certain linear relation of the two. In a study on the influence of heat treatment temperature and heating rate on coke reactivity, Lu et al. found [24] that from amorphous carbon, the carbon structure described by the aromaticity and crystallite size became highly systematized with the rise in heat treatment temperature and decline in heating rate, thus, semi-coke reactivity was degraded. With the increased proportion of reducing gases in the nitrogen atmosphere, the semi-coke carbon structure became highly ordered, which degraded semi-coke reactivity because when the size of the aromatic lamella

Table 3: Characteristic parameters of microcrystalline structure of semi-coke

Samples	C(002) (°)	d_{002} (10^{-10} m)	L_c (10^{-10} m)	L_c (d_{002})
char1	24.83	3.58	12.09	2.26
char2	24.91	3.57	12.21	2.20
char3	25.01	3.56	12.26	2.32
char4	25.02	3.56	12.39	2.36
char5	25.03	3.56	12.50	2.39
char6	25.04	3.56	12.93	2.51

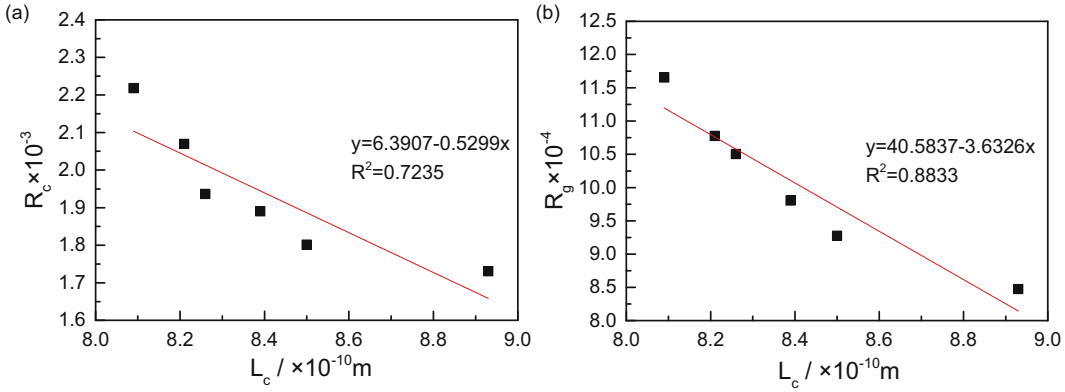

Figure 5: Relationships of semi-coke L_c with combustion and gasification reactivity indexes. (a) L_c vs R_c; (b) L_c vs R_g.

increased, the ratio of the active marginal carbon atoms to the non-active carbon atoms in the cardinal plane will be reduced [32]. Moreover, when the arrangement of the aromatic lamellas became organized, the active carbon atoms bonded with the defects and the hetero atoms were reduced [21]. Both could degrade semi-coke combustion and gasification reactivity.

3.3 FTIR analysis of chars

Figure 6 shows the FTIR spectra of different semi-coke. To carry out specific analysis on the wave number region of semi-coke 4,000–400 cm^{-1}, the entire infrared spectrum is divided into four parts [31] as follows: hydroxyl absorption peak (3,600–3,000 cm^{-1}), aliphatic hydrocarbon absorption peak (3,000–2,700 cm^{-1}), oxygen-containing functional group absorption peak (1,800–1,000 cm^{-1}), and aromatic hydrocarbon absorption peak (900–700 cm^{-1}). It can be seen from Figure 6 that the distribution of functional groups in different semi-coke samples is different. Compared with other semi-coke samples, there is an obvious hydroxyl absorption peak between char1 and char2, but char2 is mainly composed of free hydroxyl groups, char1 is mainly composed of phenol, alcohol, carboxylic acid, and hydroxyl in water, and there are obvious antisymmetric stretching vibrations of CH_3 and CH_2 in naphthenes or aliphatic groups. All the semi-coke samples had stretching vibration of S–H bond near 2,510 cm^{-1}, but the vibration peak shape of char1 was not obvious. CH_3 vibration peak exists in all samples near 1,440 cm^{-1}, but obvious vibration peak exists in char1 and char2 near 1,590 cm^{-1}. This is the vibration peak of aromatic C=C, and it is the skeleton vibration of benzene ring. char1–char6 have obvious characteristic peaks near 880 and 710 cm^{-1}, but the peak intensity of char1 is significantly lower than that of other semi-focal points. char1 has obvious vibration peaks at 1,058 and 1,183 cm^{-1}, which are stretching vibration peaks of Si–O–Si, Si=O, or Si–O–C. Oxygen-containing functional groups are obvious in char1. When the pyrolytic atmosphere contains H_2 or CH_4, removal of hydroxyls and oxygen-containing functional groups reduced content of

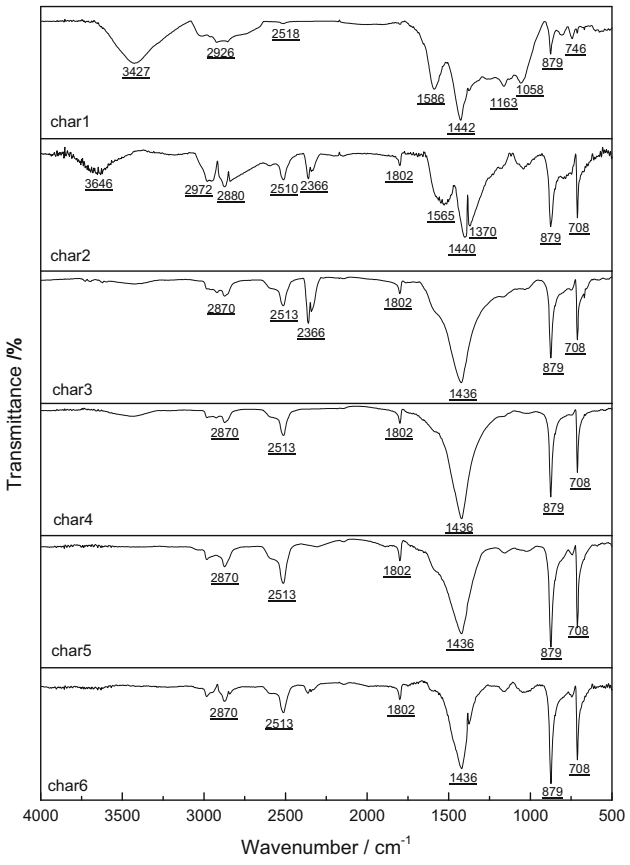

Figure 6: Semi-coke FTIR spectrums.

Table 4: Structure parameters deduced from FTIR for chars

Samples	H_{al} (%)	H_{al}/H	C_{al}/C	f_a
char1	0.789	0.326	0.05261	0.94739
char2	0.559	0.277	0.04344	0.95656
char3	0.497	0.266	0.04051	0.95949
char4	0.412	0.184	0.04869	0.95131
char5	0.37	0.184	0.04336	0.95664
char6	0.359	0.184	0.04228	0.95772

unsaturated side chains, and elevated condensation degree of macromolecular network will be facilitated.

To further describe the differences in various semi-coke samples in the macromolecular structure, Eq. 6–8 were used to calculate and compare the aromaticity of semi-coke. Table 4 presents the obtained IR structural parameters. It can be seen from the table that when CH_4 or H_2 is added in the pyrolysis atmosphere, aliphatic hydrocarbons and carbon groups in the raw coal are more easily decomposed and precipitated, which is specifically reflected in the significant decrease in the contents of H_{al} and H_{ar} and the significant increase in f_a of the samples. However, the influence of CH_4 atmosphere and H_2 atmosphere is different. Compared with H_2 atmosphere, CH_4 atmosphere has a more obvious effect on f_a promotion.

Relationships of semi-coke aromaticity with combustion and gasification reactions are shown in Figure 7. There is no obvious relationship between the aromaticity and combustion and gasification reaction index, but char1 gasification reactivity and combustion reactivity are best, its corresponding f_a also minimum, shows that N_2 pyrolysis atmosphere compared to add CH_4 and H_2, can maintain the sample in a certain amount of reactive strong aliphatic group, inhibit samples influence the reactivity of the increase of aromatic carbon.

In summary, when CH_4 or H_2 is added in the pyrolysis atmosphere, aliphatic hydrocarbons and carbon groups in raw coal are more easily decomposed and precipitated, so as to improve the f_a of semi-coke and reduce the reactivity of semi-coke. The influence of its functional groups is manifested in the fact that hydroxyl group, C═C, and oxygen-containing functional groups have a promoting effect on the improvement of reactivity, whereas the increase in S–H and aromatic hydrocarbon contributes to the improvement of aromaticity, thus reducing the reactivity of semi-coke.

3.4 Effects of pore structure of chars on reactivity

Figure 8 shows the pore structural distribution of the six semi-coke samples. Figure 8a shows that micropores below 2 nm and mesopores at 2–50 nm contributes to the main specific surface area. Independent addition of H_2 or CH_4 to the pyrolytic atmosphere increased the specific surface area of semi-coke micropores, and the micropore-specific surface areas of char2 and char3 added with CH_4 gas were significantly enlarged. Differences in specific surface area between semi-coke mesopores were visible, and the independent addition of H_2 or CH_4 in pyrolytic atmosphere reduced the specific surface area of the semi-coke mesopores. Mesopore-specific surface areas of char3 and char4 added with H_2 gas decreased more evidently than those of char2 and char3 added with CH_4 gas, and the specific surface areas of mesopores added with both H_2 and CH_4 were mostly reduced. Mesopores contributed to the main pore volume and the order of pore volumes of the different semi-coke was consistent with rule of specific surface area. The difference between

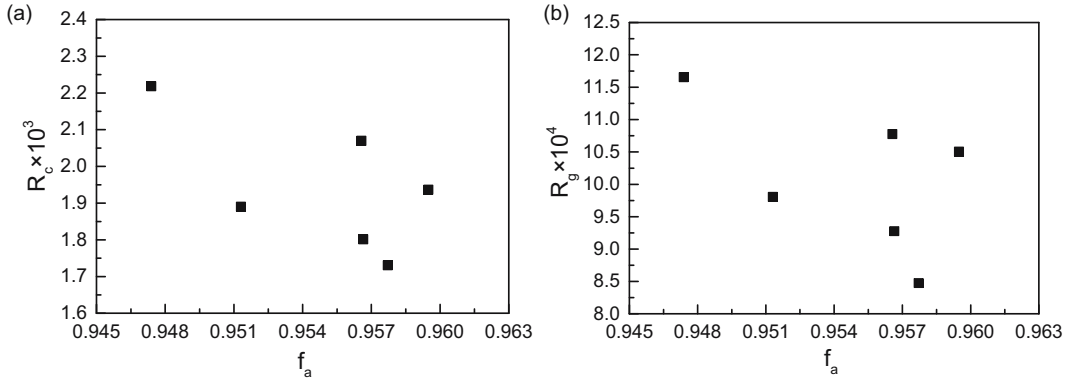

Figure 7: Relationships of semi-coke f_a with combustion and gasification reactivity indexes. (a) f_a vs R_c; (b) f_a vs R_g.

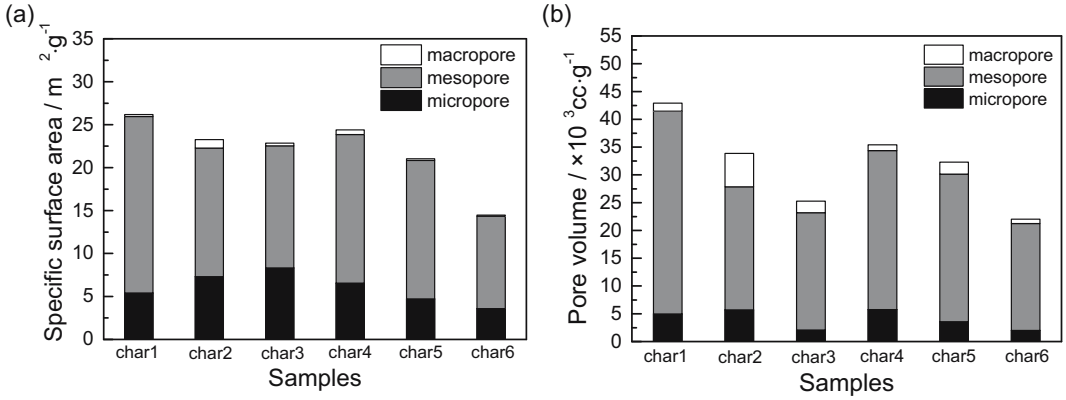

Figure 8: Specific surface area and pore volume of semi-coke.

micropores in terms of pore volume was not obvious, and pore volumes 50 nm above pores were small. The above results showed that the main pore structural types of semi-coke were micropores and mesopores; moreover, the influence of the regularity of the pyrolytic atmosphere on micropores was not strong, but the pyrolytic atmosphere could reduce the quantity of mesopores. This is because, with an elevated pyrolysis degree, the generation of micropores, which dominated the semi-coke-specific surface area, was reduced. Moreover, the CH_4 and H_2 in the pyrolytic atmosphere reacted with macromolecular side chains in the coal during pyrolysis to improve the yield and precipitation rate of pyrolytic gases [33], which then further boosted the development and growth of micropores toward mesopores, as well as the cross-linking and combination of mesopores. As a result, the pore-specific surface area and pore volume were reduced.

Figures 9 and 10 show the relationships between semi-coke-specific surface area and combustion and gasification reactivity indexes. Combustion and gasification reactivity indexes presented weak linear correlations with micropore-specific surface area and pore volume. However, they have a favorable linear correlation with mesopore volume (i.e., as mesopore-specific surface area and pore volume increased, the combustion and gasification reactivity were improved) because compared with homogeneous reaction, as heterogeneous reaction processes, the semi-coke combustion and gasification

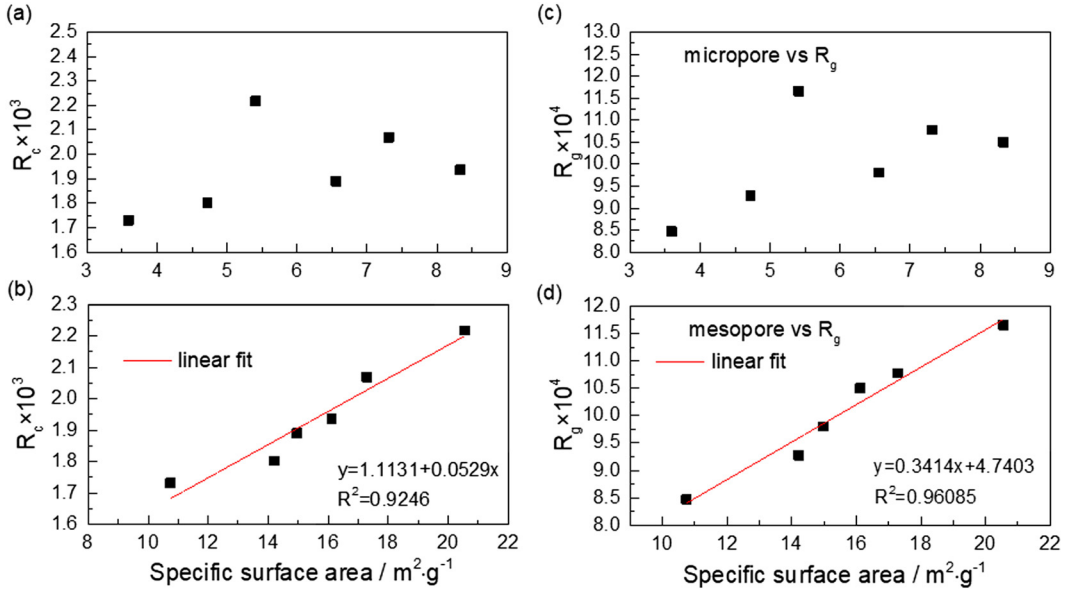

Figure 9: Relationships between semi-coke-specific surface area and reactivity indexes. (a) Micropore vs R_c; (b) mesopore vs R_c; (c) micropore vs R_g; (d) mesopore vs R_g.

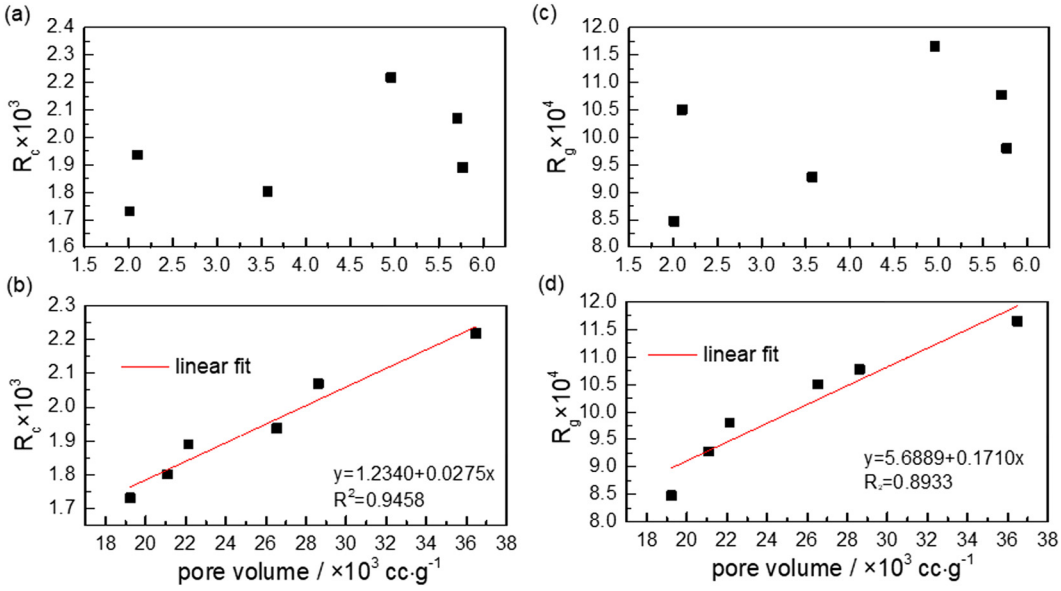

Figure 10: Relationships between semi-coke pore volume and reactivity indexes. (a) Micropore vs R_c; (b) mesopore vs R_c; (c) micropore vs R_g; (d) mesopore vs R_g.

contained two important features, namely diffusion of reactant molecules and reaction interface conditions. Semi-coke pore structure not only provided a diffusion channel for oxygen/carbon dioxide molecules that is required by combustion and gasification but also provided a large specific surface area for gas analysis and solid contact during gas–solid heterogeneous reaction [28]. Therefore, the developed pore structure of semi-coke improved their combustion and gasification reactivity.

Semi-coke combustion and gasification reactivity were closely related to the ordering degree of carbon chemical structure and micropore structure; moreover, they had a certain relationship with the distribution of functional groups. For the convenience of semi-coke application in iron-making, the pyrolysis temperature, holding time, heating rate, and other conditional parameters during pyrolysis should be reasonably regulated to counterbalance the adverse effects of reducing gases in the pyrolytic atmosphere on the semi-coke reactivity, so that they meet blast furnace PCI requirements.

4 Conclusions

In this research, the combustion and gasification characteristics of semi-coke prepared under pyrolytic atmospheres rich in CH_4 and H_2 at different proportions were investigated, and the effect of carbon chemical structure, functional groups, and micropore structure of char on reactivity was also analyzed. The results showed that CH_4 and H_2 exhibited inhibiting effect on semi-coke reactivity. This inhibiting effect on gasification reactivity was stronger than that of combustion reactivity, and the influence of H_2 was stronger than that of CH_4. The reducing gases in the atmosphere enhanced the disordering degree of the carbon crystalline structure, boosted removal of hydroxyl and oxygen-containing functional groups, reduced content of unsaturated side chains, and elevated the condensation degree of the macromolecular network. The main semi-coke pore structural types were micropores and mesopores. Influence on the regularity of the pyrolytic atmosphere on micropores was not strong, but the pyrolytic atmosphere could inhibit mesopore development. Aromatic lamella stack height of the semi-coke, specific surface area of mesopore, and pore volume had favorable linear correlations with semi-coke reactivity indexes.

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