Improvement of Iron Coke Strength by Adding Coal Tar During Coking

Chen Yin, Mingxuan Song, and Shengfu Zhang

Abstract This paper aims to provide useful knowledge on the use of coal tar as binder for the production of iron coke. The components of coal tar were investigated by gas chromatography-mass spectrometer (GC–MS); consequently, the effects of coal tar on strength and structure of iron coke were analyzed. The results show that the main components of coal tar are benzene and aliphatic compounds, and its pyrolysis resultants are similar to the metaplast (fluid phase) components, which is helpful to improve the strength of iron coke. The addition of coal tar increases the degree of graphitization, aromaticity, and crystallite size of iron coke and reduces the specific surface area and reactivity of iron coke, thereby increasing the mechanical strength and the index of coke strength after reaction (CSR) of iron coke. 3% coal tar addition amount was determined as the optimal binder for strength optimization, and the iron coke with 40.21% CRI and 55.86% CSR was prepared.

Keywords Iron coke · Strength improvement · Coal tar · GC–MS · Metaplast

Introduction

As the current main ironmaking process, blast furnace with high energy consumption and carbon dioxide emissions is difficult to fulfil ever stricter environmental regulations [1, 2]. According to the Rist line and many previous studies [3], iron coke, as a new type of burden, is considered to have the effect of reducing the fuel ratio and CO_2 emissions of blast furnace ironmaking.

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Iron coke is produced by co-pyrolysis of iron-containing minerals and coal at high temperature and has higher index of reactivity [4–6]. However, compared with the ordinary coke used in blast furnace, the iron coke has lower index of CSR, which is unfavorable to the blast furnace [7–9]. Therefore, the strength of iron coke should be optimized to realize the industrial application of iron coke. As we known, the coke strength is closely related to the thermoplasticity of coal during coking process. Generally, the larger the fluidity and the thermoplastic range, the higher the coke strength after reaction. At present, according to the thermoplasticity change of coal in coking process, the method of coal blending or adding binder to improve coke strength has been studied. Chang et al. [10] studied the effect of the addition of phenolic oil extract of weakly-bonded coal during coking and found that the thermoplasticity of coal was improved during coking, and the strength of obtained coke increases, indicating that coal extract is an effective binder in coal coking. Tsubouchi et al. [11] have co-coked the pyridine extract of HPC (hyper-coal) with low-quality coal in thermoplastic stage and found that coal samples containing HPC pyridine extract component are more capable of producing high-strength coke than raw coal or coal samples containing extract component. Coal extracts are converted into gaseous and liquid products during coal pyrolysis, thereby stabilizing free radical fragments and forming coke in the pore structure of the coal matrix. Collin et al. [12] have added tar and pitch as a binder to coal for coking and found that the cohesiveness of coal and the index of CSR have been greatly improved. Polycyclic aromatic hydrocarbons (PAHs) is the main component of pitch. Hayashizaki et al. [13] added PAHs to coal and found that when PAHs with molecular weight between 178.23 and 378.47 Da are added to the coal, the maximum expansion of coal and the strength of the resulting coke increases significantly. Although many researchers have done some research on the enhancement of iron coke strength, and some results have been achieved, none of the above studies gives the mechanism of the binder in the coking process. Therefore, there are certain limitations on the choice and use of the binder, which leads to defects in the optimization of the iron coke strength.

Our previous research [14, 15] has confirmed that the main reason for the strength decrease of iron coke is that the addition of Fe_2O_3 reduces the formation of liquid phase in the coking process, resulting in the reduction of the aromaticity and the average accumulation height of iron coke. As a by-product of coal coking, the composition of coal tar is very similar to that of the fluid phase produced during coking. In this study, it was selected as a binder to optimize the strength of iron coke, and the influence of coal tar on the properties and structure of iron coke were obtained by analyzing the thermoplastic changes before and after the addition of coal tar.

Table 1 Proximate and ultimate analyses of the coals (wt%)

Samples	Proximate analyses (wt%)				Ultimate analyses (wt%)					R_0 (%)	H/C
	M_{ad}	V_{daf}	FC_d	A_d	C_{daf}	H_{daf}	O_{daf}	N_d	S_d		
Coal-A	2.30	22.25	71.90	7.52	87.97	4.95	5.11	1.45	0.37	1.228	0.056
Coal-B	1.74	31.72	61.72	9.61	85.49	5.10	6.28	1.36	1.47	1.008	0.060
Coal-C	2.34	34.40	60.94	7.12	84.30	5.66	8.87	0.94	0.15	0.85	0.067
Coal-D	1.70	18.34	70.30	13.92	88.80	4.51	5.23	1.25	1.06	1.713	0.051

M moisture, *V* volatile matter, *FC* fixed carbon, *A* ash, *ad* air dry, *d* dry, *daf* dry and ash-free, R_0 the maximum reflectance of vitrinite, *H/C* the ratio of element H to C

Experiment

Sample Preparation

Four coals, Coal-A, Coal-B, Coal-C, and Coal-D from a steel corporation located in Northeast of China, with 1–3 mm particle size distribution were used in this work and the basic properties of the coals were described in Table 1. A standard mixed coal is composed of Coal-A (30 wt%), Coal-B (20 wt%), Coal-C (40 wt%), and Coal-D (10 wt%), and Fe_2O_3 (Purity > 99.9%, particle size < 50 nm) was used as the iron-containing mineral. The coals and Fe_2O_3 were dried under vacuum at 100 °C for 12 h before used.

Coal Tar Collection and Analyses

A sample of 2 kg of standard mixed coal was loaded into a laboratory coke oven that was fitted with a condenser at gas outlet. Thermal extraction was performed under nitrogen atmosphere and extracting at temperatures of 1050 °C for 2 h. The coal tar obtained is used as binder [16].

The chemical composition of the tar was identified by GC–MS system (QP 2010 Ultra, Shimadzu). 1 mL tar (with butyl acetate as solvent) was injected into the inlet in split injection mode at a split ratio of 30: 1 under a voltage of 70 eV. The temperature in the oven was maintained at 80 °C for 3 min, then raised to 300 °C at a heating rate of 10 °C/min, and held at this temperature for 5 min. Helium (purity > 99.999%) was used as a carrier gas at a current speed of 1 mL/min in the experiment. The chemical composition of the tar was identified using NIST 11 library data, and their quantitative analyses were conducted using the area normalization method in GC–MS solution 4.11 (software developed by Shimadzu). Further, the peak of butyl acetate was removed after treatment.

Iron Coke Preparation

Coking experiments were carried in a 2 kg laboratory coke oven. Approximately, 2 kg of standard mixed coal, 200 g distilled water, 600 g Fe_2O_3, and a certain amount of coal tar (1 wt%, 3 wt%, 5 wt%, 7 wt% of coal mass respectively) were mixed homogeneously. Then they were loaded into a coking tank with an inner diameter of 100 mm and a height of 500 mm with the bulk density of 0.85 t/m^3. The coking tank was quickly placed into the coke oven with preheating temperature of 800 °C. After the temperature of the coal cake center was raised to 800 °C, rising the temperature of the coal cake center to 1050 °C at a heating rate of 10 °C/min, and then keeping the coke temperature constant for 6 h. Finally, stopped heating, so that the coal sample was cooled to room temperature with the furnace under a nitrogen atmosphere to obtain the iron coke sample we excepted.

Coke Characterization

The cold mechanical strength of the resultant cokes was assessed by the Chinese Industrial Standard method (GB/T 2006–2008), while the reactivity towards carbon dioxide at 1100 °C (CRI) and the index of coke strength after reaction (CSR) were recorded using the SAC method (GB/T 4000–2017).

The carbon structure of iron coke was analyzed by an X-ray diffractometer (MAX2500PC X, Nippon koji co. LTD). All samples were pulverized in the laboratory and screened to below 0.074 mm. The X-ray source was generated by a copper $K\alpha$ radiation (40 kV, 150 mA). The scanning angular started from 15° to 90° at a rate of 4°/min, 0.02°/step. The broad peak of 2θ ranging from 15° to 32° was fitted by two Gaussian peaks around 21° and 26°, representing the γ-band, π-band (002), respectively. In this work, f_a was obtained from the following equation [17].

$$f_a = A_{C_{ar}} / \left(A_{C_{al}} + A_{C_{ar}} \right) = A_{\pi} / \left(A_{\pi} + A_{\gamma} \right) \quad (1)$$

where A is the diffraction peak area, Cal is aliphatic carbon, and Car is aromatic carbon.

Furthermore, d_{002}, L_c, and L_a were calculated using the classical Scherrer equations [18, 19].

The specific surface area (S_g) of iron coke is obtained through an automatic multi-station ratio surface and aperture analyzer (Max-II, McGee bayer, Japan). Samples with particle size of 3–5 mm were selected for isothermal nitrogen adsorption/ desorption at 77 K, and calculate the specific surface area of the sample by the BET adsorption isotherm equation and specific surface area calculation formula [20].

$$S_g = A_m \times N_A \times \frac{V_m}{22414} \times 10^{-18} \tag{2}$$

where A_m is the average cross-sectional area of the nitrogen molecule (nm^2), N_A is 6.02×10^{23}, and V_m is the single-layer saturated nitrogen adsorption.

Results and Discussion

Compositional Analyses of Coal Tar

Figure 1 is the GC–MS chromatogram of the tar of the standard mixed coal. It can be seen that coal tar contains a variety of substances, and the molecular weight of the compounds detected in coal tar increases gradually with the extension of residence time. As shown in Table 2, there are 38 kinds of compounds with a relative content of more than 1% in coal tar, mainly complex polycyclic compounds, such as naphthene, and some aliphatic compounds and phenolic substances. In fact, after treatment by GCMS solution 4.11, it was found that coal tar contained about 200 kinds of organic compounds, indicating the complexity of coal tar composition. At the same time, it should be noted that the relative content of sulfur and nitrogen compounds in coal tar is generally low, so it is not shown in Table 2.

The 38 compounds in coal tar are divided into three categories: (1) benzene compounds, including monocyclic benzene compounds and complex polycyclic compounds, such as o-xylene, naphthalene, anthracene, and phenanthrene; (2) aliphatic compounds such as n-butyl ester, Butyl butyrate, tridecane, tetradecane, undecane, and docosane. It is worth noting that the presence of alcohols and acids

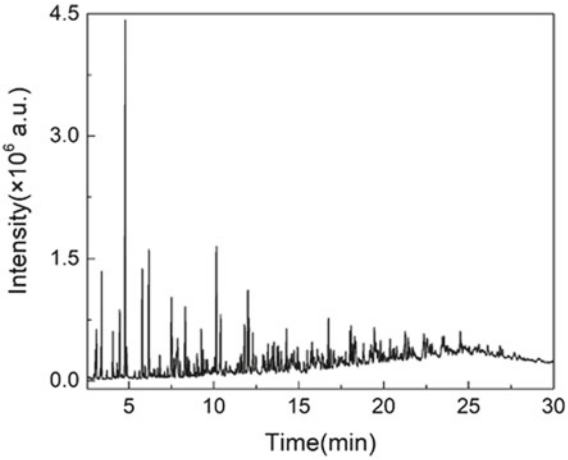


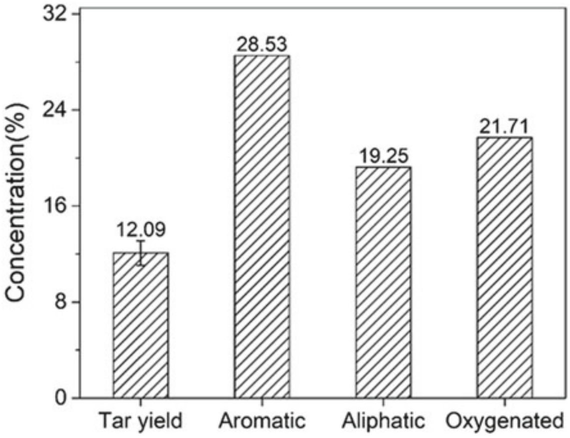
Fig. 1 GC–MS chromatogram of standard mixed coal tar

Table 2 Chemical compounds in coal tar (%)

Time (min)	Components	Relative amount (%)	Time (min)	Components	Relative amount (%)
3.03	o-Xylene	1.04	13.19	1,4,6-trimethylnaphthalene	1.17
3.10	N-butyl ester	1.08	13.67	Pentadecane	1.29
3.39	Butyl propionate	2.76	14.28	Fluorene	1.71
4.05	2-methyl propionate	2.28	14.37	Nonadecane	1.14
4.47	phenol	1.17	16.67	Tricosane	1.08
4.78	Butyl Butyrate	3.22	16.75	Anthracene	1.77
4.87	1,2,4-trimethylbenzene	7.58	18.01	Tetracosane	1.19
5.79	2-methylphenol	2.59	18.08	1-methylanthracene	1.62
6.18	3-methylphenol	1.28	18.28	5-methylanthracene	1.43
7.50	2,4-dimethylphenol	2.74	18.81	2-methylanthracene	1.47
7.87	3,5-dimethylphenol	1.17	19.45	2,5-dimethylphenanthrene	2.21
8.32	2,3-dimethylhydroquinone	1.25	20.37	Pyrene	1.21
9.27	2-ethyl-5-methylphenol	3.93	20.79	Pentacosane	1.34
9.35	Tridecane	1.36	21.27	benzofluorene	1.12
10.15	Naphthalene	2.24	22.38	O-terphenyl	1.63
10.39	2-methylnaphthalene	1.81	23.55	chrysene	1.39
11.56	Tetradecane	1.42	24.24	Hexacosane	1.09
11.80	1,2-dimethylnaphthalene	1.45	24.51	1-methylchrysene	1.08
11.99	1,7-dimethylnaphthalene	2.76	Others [a]	–	30.51
12.29	1,3-dimethylnaphthalene	1.42			

[a] Component content < 1.00%

Fig. 2 Classification and amount of coal tar



can greatly promote the fluidity of metaplast in the thermoplastic stage [14]. Therefore, in this section, esters are classified as aliphatic substances; (3) oxygenated compounds, mainly phenolic substances.

It is well known that the strength of coke is closely related to the metaplast (fluid phase) in coal coking [21, 22]. Qiu et al. [14] found that the composition of metaplast is mainly monocyclic benzene compounds, such as methylbenzene, ethylbenzene and o-xylene, and long-chain unbranched alkanes with 19 to 26 carbon atoms. The addition of Fe_2O_3 inhibits the formation of ethylbenzene, o-xylene, and long-chain unbranched alkanes with 24–26 carbon atoms in the thermoplastic stage of coal, which reduces the amount of metaplast produced, which in turn leads to a decrease in iron coke strength.

It can be seen from Fig. 2 that the proportion of benzene compounds in the tar of mixed coal is as high as 28.53%, and the content of aliphatic compounds mainly composed of alkanes is as high as 19.25%. These substances all contribute to the formation of metaplast in the thermoplastic stage of the coal coking process. Therefore, coal tar can be used as a binder to optimize the strength of iron coke.

Effects of Coal Tar on the Properties of Iron Coke

Figure 3 shows the mechanical properties of iron coke obtained by adding coal tar with different amounts. With the increase of coal tar content (0 wt%, 1 wt%, 3 wt%, 5 wt%, and 7 wt%), the crushing strength of iron coke increases by 0.78%, 1.19%, 1.14%, and 1.09%, respectively, while the wear resistance index decreases by 0.42%, 1.70%, 1.64%, and 1.66%, respectively. From the perspective of the overall trend, the cold performance of iron coke is enhanced with the increase of the amount of coal tar. When the amount of coal tar is increased from 1 to 3%, the strength indexes of iron coke increase more obviously. When the added amount is increased to 5%

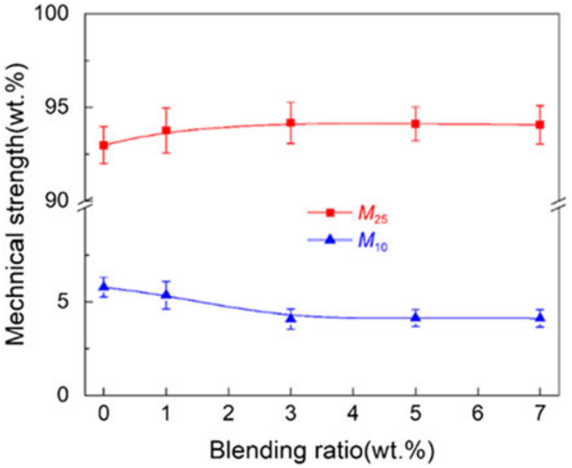


Fig. 3 Mechanical strength of iron coke with different blending ratio of coal tar

and 7%, the intensity change is not obvious, but there is a slight downward trend. It shows that reasonable addition of coal tar is beneficial to improve the cold strength of iron coke.

Figure 4 shows the thermal property and the particle size distribution of iron coke obtained by adding coal tar with different contents. When coal tar is not added, the iron coke has a CRI of 41.57% due to the addition of 3% Fe_2O_3 during the previous preparation. As the amount of coal tar added increases, the CRI of iron coke gradually decreases, but when the amount of coal tar reaches 3%, the CRI of iron coke is still above 40%. When the amount of coal tar is within 3%, the index of CSR of iron coke gradually increases as the amount of tar added increases, and when the addition of coal tar is 3%, the index of CSR reaches a maximum of 55.86% which meets

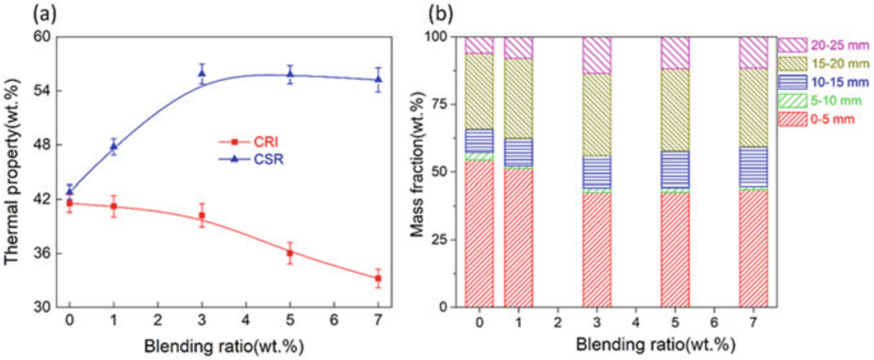


Fig. 4 Thermal property and particle size distribution after of iron coke with different blending ratio of coal tar: **a** thermal property and **b** particle size distribution

the national secondary coke strength standard. However, there was a slight decrease when tar was added at 5% and 7%. With the increase of the addition of coal tar, the content of iron coke with particle sizes in the range of 15 ~ 20 mm and 20 ~ 25 mm first increased and then decreased, and the pulverization rate decreased first and then increased slightly.

Effect of Coal Tar on the Structure of Iron Coke

Figure 5 shows the XRD spectrum of iron coke after adding coal tar with different contents (10–50°). It can be seen that XRD patterns of samples have strong diffraction peaks around the diffraction angle 26. This diffraction peak is a mixture of γ and π peaks, indicating that iron coke is between graphite and amorphous carbon after adding coal tar [23]. However, after adding coal tar, the peak intensity of the diffraction peak increases, indicating that adding coal tar can increase the degree of graphitization of iron coke. Further, the diffraction pattern is subjected to Gaussian peak processing to obtain the carbon structure characteristics of iron coke after adding coal tar with different contents.

When the amount of coal tar is added within 3%, the aromaticity of iron coke gradually increases, and the interlayer spacing of the carbon microcrystalline structure gradually decreases, indicating that the degree of graphitization of coke at this time gradually increases with the increase of the amount of coal tar added. The average stacking height and lateral size also gradually increase with the increase of the addition of coal tar, indicating that the crystallite size of the coke gradually increases at this time. However, when the addition of coal tar is 5 and 7%, the aromaticity, average stacking height, and lateral size of coke are reduced to a certain extent, and the interlayer distance is slightly increased. Combining the influence of coal tar addition on the mechanical strength and thermal properties of iron coke, (Figs. 3 and 4), it can be found that coal tar can gradually increase the graphitization degree

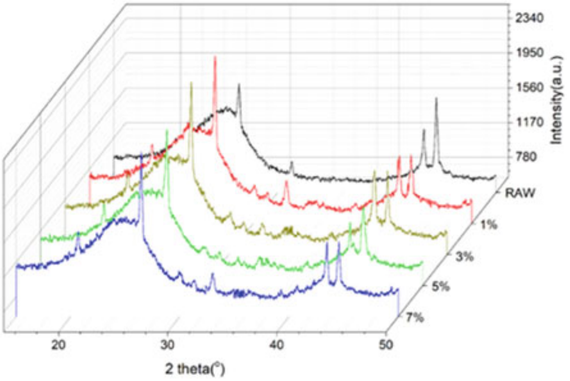
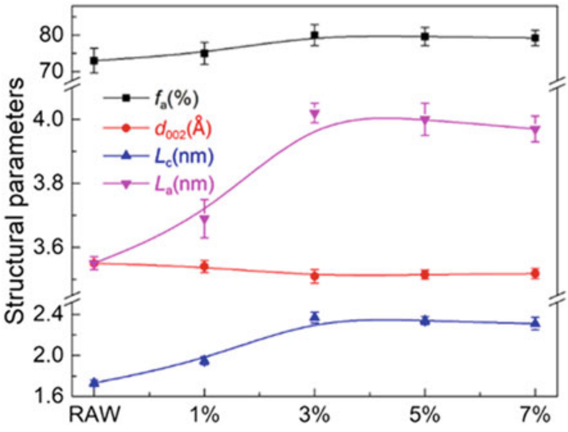


Fig. 5 XRD spectra of iron coke with different blending ratio of coal tar

Fig. 6 Carbon structural parameters of iron coke with different addition of coal tar

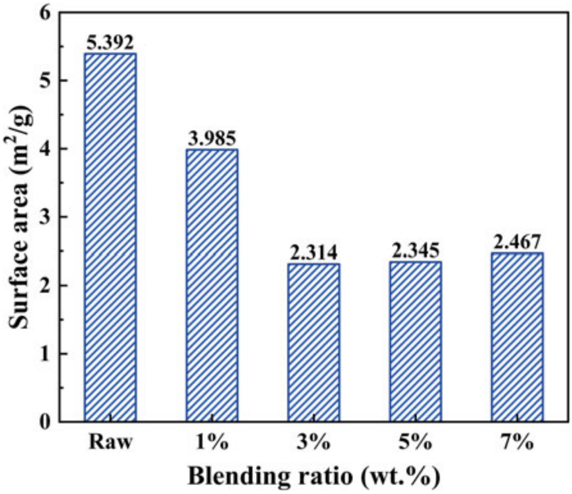


and grain size of iron coke within 3%, thereby gradually increasing the mechanical strength and CSR index of iron coke. However, when the addition amount is 5 and 7%, due to the limited effect of coal tar on the structure and properties of iron coke, the microcrystalline structure parameters of iron coke slightly decrease, which in turn leads to a slight decrease in coke strength (Fig. 6).

Effects of Coal Tar on Specific Surface Area of Iron Coke

The specific surface area of iron coke after adding different amounts of coal tar is displayed in Fig. 7. It can be seen that the specific surface area of the raw iron

Fig. 7 Surface area of iron coke with different addition content of coal tar



coke is 5.392 m^2/g. With the addition of coal tar, the specific surface area of iron coke decreases and reaches a minimum value of 2.314 m^2/g when the amount of coal tar is 3%. It shows that the addition of coal tar can reduce the specific surface area of iron coke and then reduce the amount of contact between the surface of the iron coke and CO_2, which is conducive to improving the strength of the iron coke. Considering the influence characteristics of coal tar on the reactivity, strength, and structure (microcrystalline structure and specific surface area) of iron coke, the coal tar content of 3% was selected to optimize the strength of iron coke, and the iron coke with a reactivity of 40.21% and a strength of 55.86% after the reaction was prepared.

Conclusion

In this study, the composition of coal tar was analyzed using GC–MS, and compared with the composition of metaplast, coal tar was determined as an additive to optimize the strength of iron coke. Then the influence of coal tar on the properties and structure of iron coke was analyzed by XRD and BET. The components of coal tar are mainly complex polycyclic compounds, aliphatic compounds, and phenolic substances. The pyrolysis products of complex polycyclic compounds and aliphatic compounds are similar to the components of metaplast, so coal tar can be selected as the strength optimization additive of iron coke. The addition of coal tar can increase the cold performance and post-reaction strength of iron coke and reach the optimal value when the addition amount is 3%, but the reactivity of iron coke decreases slightly after the addition of coal tar. It is due to the fact that the added coal tar can increase graphitization degree, aromatic degree, and microcrystalline size of coke and reduce specific surface area of coke. After comprehensively considering the influence characteristics of coal tar on the mechanical strength, CRI, CSR, the carbon structure, and the specific surface area of iron coke, the 3% (based on coal mass) coal tar addition amount was selected as the optimal binder addition amount to prepare iron coke with 40.21% CRI and 55.86% CSR.

References

1. Srishilan C, Shukla AK (2017) Static thermochemical model of COREX melter gasifier. Metall Mater Trans B 49:388–398
2. Zhang X, Yee SA, Yee ZL (2019) Three-terminal heterojunction bipolar transistor solar cells with non-ideal effects: efficiency limit and parametric optimum selection. Energy Convers Manage 188:112–119
3. Nomura S, Terashima H, Sato E (2007) Some fundamental aspects of highly reactive iron coke production. ISIJ Int 47(6):823–830
4. Price JD, Mador ME (1958) Coal carbonization research—a world-wide problem. Indus Eng Chem 50(1):17–20
5. Nok PS (1959) Production of pig iron with the use of coke iron. Metallurgist 3(6):237–239

6. Michitaka S, Hidetoshi M, Kunihiko I (2015) Recent development of mid-and long-term CO_2 mitigation technology at JFE Steel. In: Paper presented at Asia steel international conference, Yokohama, Japan
7. Nomura S, Naito M, Yamaguchi K (2007) Post-reaction strength of catalyst-added highly reactive coke. ISIJ Int 47(6):831–839
8. Xu RS, Dai BW, Wang W (2018) Effect of iron ore type on the thermal behavior and kinetics of coal-iron ore briquettes during coking. Fuel Process Technol 173:11–20
9. Xu RS, Zheng H, Wang W (2018) Influence of iron minerals on the volume, strength, and CO_2 gasification of ferro-coke. Energy Fuel 32(12):12118–12127
10. Chang CM, Whang TJ, Huang DS (2014) Thermoplasticity and strength improvement of coking coal by addition of coal extracts. Fuel 117:364–371
11. Tsubouchi N, Naganuma R, Mochizuki Y (2019) Production of high-strength coke from low-quality coals chemically modified with thermoplastic components. ISIJ Int 59(8):1396–1403
12. Collin G, Bujnowska B (1994) Co-carbonization of pitches with coal mixtures for the production of metallurgical cokes. Carbon 32(4):547–552
13. Hayashizaki H, Kanehashi K, Uebo K (2019) Effects of hydrocarbon addition on increase in dilatation of coal. Isij Int 59(8):1404–1412
14. Qiu S, Zhang S, Sou G (2020) Effecvts of Fe_2O_3 addition on the thermoplasticity and structure of coking coal matrix during thermoplastic stage of pyrolysis. Fuel 260:374–383
15. Zhou H, Wu CF, Onwudili JA (2015) Effect of interactions of PVC and biomass components on the formation of polycyclic aromatic hydrocarbons (PAH) during fast co-pyrolysis. RSC Adv 5(15):11371–11377
16. Qiu S, Zhang S, Fang Y (2019) Effects of poplar addition on tar formation during the co-pyrolysis of fat coal and poplar at high temperature. RSC Adv 9:28053–28060
17. Qiu S, Zhang S, Zhu R (2018) Influence of TiO_2 addition on the structure and metallurgical properties of coke. Int J Coal Prep Util. https://doi.org/10.1080/19392699.2018.1496913
18. Gupta S, French D, Sakurovs R (2008) Minerals and ironmaking reactions in blast furnaces. Prog Energy Combust 34:155–197
19. Gupta S, Sahajwalla V, Burgo J (2005) Carbon structure of coke at high temperatures and its influence on coke fines in blast furnace dust. Metall Mater Trans B 36(3):385–394
20. Barrett EP, Joyner LG, Halenda PP (1951) The Determination of pore volume and area distributions in porous substances. Computations from nitrogen isotherms. J Am Chem Soc 73(1):373–380
21. Alvarez R, Diez MA, Barriocanal C (2017) An approach to blast furnace coke quality prediction. Fuel 86(14):2159–2166
22. Gayo F, Garcia R, Diez MA (2016) Modelling the Gieseler fluidity of coking coals modified by multicomponent plastic wastes. Fuel 165:134–144
23. Sonibare O, Haeger T, Foley SF (2010) Structural characterization of Nigerian coals by X-ray diffraction Raman and FTIR spectroscopy. Energy 35(12):5347–5353