Influence of the Heating Rate on the Quality of Metallurgical Coke

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ABSTRACT: Four bituminous coals of different origins and ranks and one industrial coal blend were carbonized at a semi-pilot scale at various temperatures to study the effect of heat treatment (i.e., different heating rates) on the structural evolution and hence the subsequent reactivity of the resulting cokes and their mechanical strength. The development of the coke microstructural order under different thermal treatments during carbonization was assessed by means of Raman spectroscopy. The results indicated an improvement in the structural order with increased operating temperatures and hence increased heating rates and a decrease in the active sites. The quality of the cokes was determined by means of the Japanese Industrial Standard (JIS) and the Nippon Steel Corporation (NSC) tests. In addition, the apparent reaction rate of cokes was measured using a fixed bed reactor. The increase in the heating rate during carbonization led to cokes with a lower mechanical strength and apparent reaction rate. Good correlation was found between the apparent reactivity of cokes and the coke strength after reaction.

1. INTRODUCTION

The economic and environmental constraints associated with the use of coal, together with the fact that the blast furnace (BF) route is the most commonly used method for steel production, underlines the importance of making significant efforts to improve the efficiency of the cokemaking process.1 High-strength coke is necessary to support the charge and minimize coke fine generation in order to maintain a porous structure that allows for the reducing gases to pass upward into the stack, and slag and iron droplets to pass downward to the hearth of the BF.2,3 Thus, enhancing the quality of coke improves BF performance, which results in higher productivity and lower costs.

The main criteria for measuring coke quality are the coke reactivity index (CRI) and the hot mechanical strength or coke strength after reaction (CSR).4 The CSR index was developed to serve as an indicator of coke degradation inside the BF. The lower the CRI and the higher the CSR, the better the coke quality. The CSR depends to a large extent on the degree of gasification of coke, as denoted by the CSR’s linear dependence on CRI.5,6 The main factors controlling coke reactivity are coke structure, porosity, and the ash chemistry. The properties of coke are influenced by coal characteristics (rank, petrographic, chemical, and rheological characteristics of coal) but they also depend to a large extent on oven operating variables (particle size, moisture content, bulk density, coking final temperature, coking rate, soaking time, quenching practice, and coke handling).7−11 Thus, by modifying the coking conditions, it is possible to control the structural properties of the coke. For instance, Amamoto12 found that the mechanical strength of coke decreases significantly and the CSR increases with increased heating rates during carbonization. More recently, Nyathi et al.13 studied the effect of the heating rate and bulk density on coke properties, coke pore structure, and carbon matrix development along the oven width, and found an improvement in CSR with the increase of both parameters. Most of the studies examining the effect of heating rate on coke reactivity were carried out with samples prepared at a laboratory scale, which underlines the importance of the present study with carbonizations carried out in a 17 kg movable wall oven. This oven has a configuration similar to industrial ovens with heating from the walls to the center of the oven and the existence of two coal layers in the plastic stage advancing toward the center. Wu et al. and Luo et al.13,14 reported that the gasification reactivity of cokes obtained at higher heating rate was higher than that of cokes prepared at slow heating rates. Jayaraman et al.15 noticed that the kinetic behavior of chars derived from various heating rates of high ash Indian coal with different sizes showed that the reactivity of char increased with the heating rate. However, other results about the carbonization heating rate effect on char reactivity seem to be contradictory. Gale et al.16 found that the intrinsic O₂ reactivity of a lignite and two bituminous coal chars decreased with an increase in the heating rate during pyrolysis. They attributed the decrease of reactivity in part to an increase in coal aromatics accompanied by ordering and smoothing of layered carbon planes (elimination of carbon active sites) as a consequence of increased mass release.

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The main objective of this work was to study the effect of the heating rate during pre-plastic, plastic, and post-plastic stages on the mechanical strength and reactivity to CO₂ of cokes prepared in a 17 kg capacity movable wall oven.

2. RESULTS AND DISCUSSION

2.1. Coal Properties. The coals selected for the study covered a wide range of volatile matter content (20.4–33.4 wt % db) and presented low ash and sulfur contents (Table 1).

Table 1. Main Characteristics of Coals and Coal Blend Used in This Study

| origin | LV | MV | HV1 | HV2 | B |
|--------|----|----|-----|-----|---|
| ash (wt % db) | 9.8 | 11.0 | 7.3 | 7.2 | 10.0 |
| VM (wt % db) | 20.4 | 23.5 | 30.9 | 33.4 | 23.4 |
| C (wt % db) | 80.7 | 79.3 | 81.8 | 80.1 | 79.4 |
| H (wt % db) | 4.5 | 4.6 | 4.9 | 5.1 | 4.6 |
| N (wt % db) | 2.0 | 2.0 | 1.7 | 1.7 | 1.7 |
| S (wt % db) | 0.57 | 0.85 | 0.82 | 0.93 | 0.66 |
| O (wt % db) | 3.4 | 3.7 | 4.4 | 5.3 | 3.8 |
| MF (ddpm⁻¹) | 192 | 354 | 11,047 | 25,418 | 658 |
| FSI | 8 | 8 1/2 | 6 1/2 | 6 | 8 |
| AI | 0.29 | 1.17 | 1.36 | 0.97 | 1.12 |

*Dry basis. †Volatile matter. ‡Maximum fluidity expressed in dial divisions per minute (ddpm). ††Free swelling index. ‡‡Alkalinity index.

The oxygen content was slightly higher in the case of high volatile coals. The Gieseler maximum fluidity varied from 192 to 25,418 ddpm and was lower for high rank coals. The FSI ranged between 6 and 8 1/2.

2.2. Coking Tests. Carbonization tests of single coals and coal blend were carried out at three wall temperatures, that is, 1020, 1100, and 1200 °C. Once the oven is charged, the coal is gradually heated from the walls to the center. Thus, a temperature gradient is established within the chamber that decreases during the carbonization.

Figure 1 shows the evolution of the temperature in the center of the charge of the single coals and the industrial coal blend with coking time at the three wall temperatures tested.

The coking time is the time from charging the coal to pushing of coke out of the oven. Coking rate, expressed in mm/h, was determined considering the width of the oven and the coking time. The heating rate was calculated from the slope of the curves of the temperature in the center of the charge in three temperature ranges, that is, 300–400, 400–500, and 500–750 °C, which coincide with the pre-plastic, plastic, and post-plastic stages during the coking process (Table 2).

As Table 2 shows, the coking pressure increased slightly for LV and MV single coals. If the coking pressure measured in the MWO17 is higher than 15 kPa, the coals are considered to be dangerous; consequently, even at 1200 °C, the coals in this study remained safe during coking. It is obvious that the rate of a reaction depends on the reaction temperature that is, the higher the temperature, the higher the reaction rate. A higher wall temperature means a higher gradient in the horizontal direction in the oven which will affect the coking rate that is usually expressed in mm/h and depends on the width of the oven and the coking time. The results shown in Table 2 indicate an increase in this parameter with oven wall temperature for all coals although to a greater extent in the case of the high volatile coal (HV2) from 15 to 25 mm/h and for the coal blend (B) from 15 to 24 mm/h.

2.3. Influence of Heating Rate on Coke Quality. The coke quality of the cokes in this study was assessed in terms of cold mechanical strength (JIS indices), reactivity to CO₂ (CRI), and mechanical strength after reaction (CSR) (Table 3).

Except for MV-1200 coke, there was an impairment in the cold mechanical strength in the cokes produced at higher heating rates (wall temperature 1200 °C), as indicated by the decrease in the DI15⁰F index. This is in agreement with Amamoto, who also reported an impairment of coke mechanical strength as a result of increased heating rates during carbonization. One of the main factors influencing coke strength is the development of fissures. Fissures are formed due to the different contraction rates of the coal layers caused by the temperature gradient present in the coke oven. A previous work has demonstrated that rapid heating during the post-plastic stage tends to lead to a strong contraction of the material, causing fissures that would be one of the possible causes of the lower mechanical strength of the coke. It is worth noting that the DI15⁰F index of MV cokes remained unchanged. For this coal, the heating rate between 500 and 750 °C decreased during carbonization at 1200 °C (Table 2), which may contribute to maintain the value of the cold mechanical strength of MV-1200 coke. Besides, the coking time of this coal with wall temperature 1200 °C was higher (4 h) in comparison with those of the other samples (around 3 h 30') (Figure 1, Table 2). According to the results from other authors, lengthening the residence time allows for the mechanical strength of cokes to improve because it allows more time for structure development, better wetting, and bonding between particles.

LV and MV cokes had lower CRI and higher CSR values than high volatile coals (HV1, HV2). Coke produced from coal blend B, had a similar CSR index to MV coal. In general, the increase in the heating rate produced a decrease of the CRI index, although there were only significant changes for HV2 and B cokes, with a 3-point decrease in the CRI value. With respect to the hot mechanical strength, the increase in heating rate resulted in an increase of CSR index values. Carbonization of HV2 and B at 1100 °C caused a 4 and 5.5-point increase in the CSR index. Although the effect was greater for HV2-1200 (+5.5 points) and B-1200 (+6 points) cokes. These results are consistent with work by other authors. During the plastic stage, an increase in the heating rate enhances the plasticity of coals, which improves the adhesion of coal particles and allows for the growth of textural domains, forming less-reactive carbon forms which leads to cokes with higher CSR.
Figure 1. Evolution of the charge center temperature with the coking time for cokes obtained at different heating rate.

Table 2. Heating Rate Calculated in Different Range of Temperature, Coking Rate, Coking Time, and Coking Pressure of Cokes Obtained at Different Temperatures

| heating rate (°C/min) | 300–400 °C | 400–500 °C | 500–750 °C | coking rate (mm/h) | coking time (h:min) | $P^{\text{a}}$ (kPa) |
|----------------------|------------|------------|------------|-------------------|-------------------|----------------|
| LV-1020              | 5.95       | 8.17       | 10.51      | 20                | 4:18              | 6 |
| LV-1100              | 7.77       | 9.84       | 11.25      | 24                | 3:36              | 11 |
| LV-1200              | 6.72       | 10.8       | 13.02      | 25                | 3:28              | 7  |
| MV-1020              | 6.60       | 9.91       | 12.02      | 18                | 4:40              | 9  |
| MV-1100              | 5.92       | 9.44       | 19.95      | 20                | 4:09              | 8  |
| MV-1200              | 7.61       | 12.29      | 14.59      | 22                | 3:58              | 11 |
| HV1-1020             | 7.68       | 9.99       | 11.79      | 19                | 4:23              | 4  |
| HV1-1100             | 12.18      | 13.06      | 18.11      | 22                | 3:52              | 4  |
| HV1-1200             | 12.93      | 16.17      | 18.26      | 24                | 3:31              | 4  |
| HV2-1020             | 4.82       | 6.11       | 10.02      | 15                | 5:39              | 3  |
| HV2-1100             | 12.15      | 19.29      | 10.81      | 22                | 3:59              | 4  |
| HV2-1200             | 14.42      | 19.51      | 10.10      | 25                | 3:24              | 5  |
| B-1020               | 6.15       | 6.35       | 7.11       | 15                | 5:41              | 4  |
| B-1100               | 8.77       | 9.91       | 7.10       | 20                | 4:37              | 4  |
| B-1200               | 7.25       | 9.46       | 10.12      | 24                | 3:31              | 8  |

$^{a}$Maximum coking pressure.
2.4. Effect of Heating Rate on Coke Microstructure.

The carbonaceous structure of cokes prepared at different coking rates was assessed by means of the Raman spectroscopy. This technique has been widely applied to analyze the microstructure of carbonaceous materials because it provides information for evaluating their degree of ordering and crystallinity.\textsuperscript{21–26} Coke structure is one of the key factors determining coke reactivity. Therefore, the Raman analysis of cokes prepared at different temperatures can provide information about the effect of the heating rate on coke structure development and hence on coke reactivity. As an example, the first-order Raman spectra (800–2000 cm\textsuperscript{-1}) of HV1-1020 and HV1-1200 cokes are shown in Figure 2.

The spectra of the other samples are included in the Supporting Information (Figure S1). The spectra of all samples showed two broad overlapping peaks ca. 1600 (G-band) and 1350 cm\textsuperscript{-1} (D-band).

These bands are typical for carbonaceous materials and correspond to the stretching vibration mode with a E\textsubscript{2g} symmetry in the aromatic layers of the crystalline graphite and the vibration mode with a A\textsubscript{1g} symmetry of the disordered graphitic lattices, respectively.\textsuperscript{21,22,27} Qualitatively, HV1 coke produced at 1200 °C had slightly better developed G bands than coke produced at 1020 °C (Figure 2).

The assignment of the additional bands that appeared in the deconvoluted spectra was performed in accordance with the literature.\textsuperscript{21,22,28–30} The D\textsubscript{2} band, ca. 1620 cm\textsuperscript{-1}, is attributed to the vibration mode of disordered graphitic lattices, thus its intensity decreases with increasing degree of organization. The D\textsubscript{1} band, ca. 1500 cm\textsuperscript{-1}, indicates amorphous forms of carbon (sp\textsuperscript{2} bonded forms) and the D\textsubscript{G} band, ca. 1200 cm\textsuperscript{-1}, is a signal of very poorly organized materials (mixed sp\textsuperscript{2}–sp\textsuperscript{3} or sp\textsuperscript{3} bonded forms). Besides, D\textsubscript{1} and D\textsubscript{G} bands may be related to the reacting sites.\textsuperscript{27} In order to produce a semi-quantitative estimation of the degree of carbon structural order, two indices were calculated, the A\textsubscript{D1}/A\textsubscript{G} ratio, which indicates improvement of the structural order as the ratio decreases\textsuperscript{21,22} and the A\textsubscript{D1+4}/A\textsubscript{G} ratio which represents the amorphous phase of carbon; a reduction of this index implies more organized structures in the coke sample and a reduction in the active sites and consequently in char reactivity.\textsuperscript{27} As Table 4 shows, the D\textsubscript{1}-fwhm (full width at half maximum) was lower for cokes prepared at higher temperatures, which suggests more ordered structures in these samples.

### Table 3. Quality Parameters of Cokes Produced from Coals and Coal Blend at Different Heating Rate

| coke       | D\textsubscript{1}/A\textsubscript{G} (%) | D\textsubscript{G}/A\textsubscript{G} (%) | CRI (%) | CSR (%) |
|------------|-----------------------------------------|-----------------------------------------|---------|---------|
| LV-1020    | 15.2                                    | 79.1                                    | 16.5    | 72.5    |
| LV-1100    | 10.4                                    | 80.4                                    | 16.5    | 72.5    |
| LV-1200    | 15.0                                    | 76.5                                    | 15.5    | 73.5    |
| MV-1020    | 16.1                                    | 78.8                                    | 14.5    | 68.0    |
| MV-1100    | 15.8                                    | 80.1                                    | 15.5    | 67.5    |
| MV-1200    | 14.3                                    | 81.4                                    | 16.0    | 71.5    |
| HV1-1020   | 16.0                                    | 77.4                                    | 25.5    | 53.5    |
| HV1-1100   | 15.9                                    | 77.3                                    | 25.0    | 54.5    |
| HV1-1200   | 18.1                                    | 73.9                                    | 24.0    | 55.0    |
| HV2-1020   | 20.1                                    | 74.9                                    | 32.5    | 43.0    |
| HV2-1100   | 19.9                                    | 73.8                                    | 30.0    | 47.0    |
| HV2-1200   | 19.5                                    | 71.1                                    | 29.5    | 48.5    |
| B-1020     | 15.4                                    | 79.3                                    | 26.0    | 58.5    |
| B-1100     | 15.3                                    | 79.4                                    | 23.5    | 64.0    |
| B-1200     | 20.4                                    | 72.6                                    | 23.0    | 64.5    |

### Table 4. Carbon Microstructure Parameters of Cokes Obtained at Different Heating Rate

| coke       | A\textsubscript{D1}/A\textsubscript{G} | A\textsubscript{D1+4}/A\textsubscript{G} | D\textsubscript{1}-fwhm (cm) |
|------------|---------------------------------------|----------------------------------------|----------------------------|
| LV-1020    | 6.12                                  | 2.37                                   | 186                        |
| LV-1200    | 4.88                                  | 2.25                                   | 164                        |
| MV-1020    | 6.40                                  | 1.62                                   | 188                        |
| MV-1200    | 5.37                                  | 1.94                                   | 183                        |
| HV1-1020   | 6.05                                  | 2.22                                   | 187                        |
| HV1-1100   | 4.23                                  | 1.16                                   | 117                        |
| HV1-1200   | 6.72                                  | 2.35                                   | 186                        |
| HV2-1020   | 4.33                                  | 2.27                                   | 172                        |
| HV2-1100   | 6.56                                  | 2.59                                   | 194                        |
| HV2-1200   | 5.37                                  | 2.02                                   | 186                        |

The A\textsubscript{D1}/A\textsubscript{G} ratio calculated for cokes obtained at 1020 and 1200 °C was in the range of 6.72–6.05 and 4.23–5.37 cm\textsuperscript{-1}, respectively. These values are similar to those obtained by Sheng\textsuperscript{27} for coal chars generated in a horizontal tube furnace. The higher A\textsubscript{D1}/A\textsubscript{G} ratio of cokes prepared at 1020 °C reflects the lower degree of ordering of the carbon microcrystalline structure in these samples. With the increase in the carbonization temperature, this ratio is reduced. The highest reduction was observed for cokes produced from low rank coals (HV1 and HV2). A good correlation was found between the A\textsubscript{D1}/A\textsubscript{G} index and the heating rate during the plastic stage. This stage is considered the most important phase during coke formation with the processes occurring between 400 and 500 °C, and is responsible for the development of the coke microstructure\textsuperscript{31} (Figure 3a). The A\textsubscript{D1+4}/A\textsubscript{G} index decreased with increases in the heating rate, which suggests that the...
The main process that occurs over 700 °C is the elimination of condensation, resulting in the formation of a more ordered structure. The contribution of well-ordered structures is higher in cokes prepared at 1200 °C. There was also a relationship between the $A_{D3+4}/A_G$ ratio and the heating rate calculated between 500 and 750 °C (Figure 3b).

During the post-plastic stage (500–750 °C), hydrogen is eliminated by condensation, resulting in the formation of a more ordered structure. The main process that occurs over 700 °C is the elimination of interlayer defects, which is reflected in this correlation.32 Even though the relationship between the heating rate and the Raman indices is clear, this parameter may not be the sole cause for the changes observed in the structural order of coke samples.13,27,33

2.5. Influence of Heating Rate in the Apparent Reactivity of Cokes. The apparent reaction rate of cokes was measured using a fixed bed reactor. Tests were carried out under chemically controlled conditions where the reaction is not limited by either gas pore diffusion or mass transfer. In addition, reaction inhibition by the reaction gas product is not limited by either gas pore diffusion or mass transfer. The ash chemical composition is maximized by maintaining the CO concentration below 1%. Experiments were performed up to 10% carbon conversion. This conversion represents the initial coke properties in the early stages of gasification and is useful for comparing the reactivity of cokes obtained at different heating rates.34 The activation energy ($E_a$), frequency factor ($A$), and apparent rate ($\rho$) of coke gasification reaction are listed in Table 5. The activation energy values were between 189 and 294 kJ/mol, with the higher values (253–294 kJ/mol) corresponding to cokes produced from higher rank coals that is, LV and MV. The magnitude of these numbers is consistent with the data found in the literature for chemically controlled reaction of metallurgical coke with CO$_2$.35,36 In general, the activation energy increased for cokes prepared at higher heating rates that is, higher energy is needed to overcome the barrier of the gasification reaction resulting in lower reaction rates for these cokes. Although as noted above, the carbonization temperature also influences the kinetic parameters of the gasification reactivity. Seneca and Salatino37 reported an increase in the activation energy of cokes with increasing carbonization temperature.

The apparent reaction rate of cokes prepared from higher rank coals (LV, MV) is approximately constant with carbon conversion (Figure 4a,b), whereas, for cokes prepared from lower rank coals and the coal blend (HV1, HV2, B), the apparent reaction rate increases uniformly with increasing carbon conversion except at the initial stages (Figure 4c–e). There was a decrease in the reactivity for cokes prepared at higher wall temperatures (i.e., heating rate) and this effect was more noticeable for lower rank coals HV1 and HV2.

A relationship was observed between the apparent reaction rate and the heating rate in the plastic stage ca. 400–500 °C (Figure 5).

To explain the difference in the reactivity values of coals, it is also necessary to consider the coal rank. It is known that the coke reactivity increases with the decreasing of coal rank.38,39 Another factor to consider is the alkalinity index (AI) of the ashes. This was calculated from the ash chemical composition using the ratio of the total content of the basic oxides (Fe$_2$O$_3$, CaO, MgO, Na$_2$O, and K$_2$O) to the total content of acidic oxides (Al$_2$O$_3$ and SiO$_2$) according to X-ray fluorescence (XRF) analysis (Table 1). The ash chemical composition is one of the key factors influencing coke reactivity due to the catalytic effects on the gasification reaction.1 In the present case, the highest rank coal (LV) had the lowest AI (0.29) compared to the lower rank coals (0.97–1.36).

The apparent reaction rate can also be influenced by other factors such as the increase in coal carbon aromaticity and a more ordered structure (elimination of carbon active sites), which causes decreased coke reactivity.10 As explained in Section 2.4, more drastic carbonization conditions led to cokes with more ordered structures and less structural defects responsible for the active reaction sites which was reflected in the reduction of $A_{D3+4}/A_G$ and $A_{D3+4}/A_C$ indices, respectively. Nevertheless, no direct relationships were found between these indices and coke reactivity.

The micropore surface area of cokes prepared from MV coal was lower in comparison with values obtained for LV cokes.

| coke    | $A$ (g/g/s) | $E_a$ (kJ/mol) | $\rho \times 10^{-6}$ (g/g/s) | $S_{mic}$ (m$^2$/g) |
|---------|-------------|----------------|-------------------------------|---------------------|
| LV-1020 | 2,499,379   | 257            | 8.7                           | 24                  |
| LV-1100 | 1,600,523   | 253            | 8.3                           | 25                  |
| LV-1200 | 1,802,713   | 255            | 8.3                           | 17                  |
| MV-1020 | 20,640,694  | 279            | 7.9                           | 15                  |
| MV-1100 | 3,328,353   | 261            | 7.9                           | 10                  |
| MV-1200 | 54,736,198  | 294            | 4.3                           | 12                  |
| HV1-1020| 189,531     | 223            | 21.8                          | 21                  |
| HV1-1100| 1,303,068   | 244            | 17.9                          | 10                  |
| HV1-1200| 1,195,086   | 245            | 14.2                          | 12                  |
| HV2-1020| 106,83      | 197            | 18.6                          | 24                  |
| HV2-1100| 481,638     | 233            | 16.0                          | 16                  |
| HV2-1200| 648,214     | 241            | 11.5                          | 3                   |
| B-1020  | 3358        | 189            | 13.3                          | 34                  |
| B-1100  | 10,982      | 200            | 14.4                          | 34                  |
| B-1200  | 2,288,650   | 254            | 11.6                          | 14                  |
This fact may partly explain the lower reactivity of MV cokes (Table 5). The micropore surface area of cokes prepared from higher rank coals (LV and MV) was not significantly affected by the heating rate. However, a slight decrease of the micropore area of HV1 and HV2 cokes with the increase of heating rate was observed (Table 5). Nyathi et al. suggested that a faster coking rate enhances the adhesion of coal particles and diminishes the coking time, which may result in limited pore structural development and hence a less porous coke. Although the variations in the microporosity observed in this work was not so significant as to consider this factor decisive in the reactivity of HV2 cokes.

The apparent reaction rate of cokes correlated with CSR (Figure 6). It was observed that the decrease in the apparent rate of cokes was related to an increase in hot mechanical strength.

3. CONCLUSIONS

The main objective of this work was to clarify the effect of heating rate during carbonization on the mechanical strength and reactivity of the cokes and hence on their mechanical strength after reaction. The increase in heating rate led to cokes with higher CSR. Raman analysis demonstrated that the increase in the heating rate during the plastic and post-plastic stages of coal carbonization enhanced the degree of ordering in the resulting cokes. The apparent reaction rate was found to decrease with an increased heating rate during the plastic stage.
of coal during carbonization. This resulted in coals with higher CSR.

4. MATERIALS AND METHODS

4.1. Materials. Four coals of different rank and geographical origin were selected for the study, a low-volatile bituminous coal (LV), a medium-volatile bituminous coal (MV), and two high-volatile bituminous coals (HV1, HV2). In addition, an industrial coal blend (B) was selected. The main characteristics of the coals are shown in Table 1.

Proximate analyses were performed following the ISO562 and ISO1171 standard procedures for volatile matter and ash content, respectively. The elemental analysis was determined by means of a LECO CHN-2000 for C, H, and N (ASTM D5373), a LECO S-144DR (ASTM D5016) for sulfur and a LECO VTF-900 for direct oxygen determination. The coking properties of the individual coals and blend were assessed by means of the free-swelling index (ISO 501:2012) and the Gieseler fluidity tests (ASTM D2639-08).

4.2. Carbonization Test. Carbonization tests were carried out in a movable wall oven of approximately 17 kg capacity (MWO17). The dimensions of the oven are 275 mm × 170 mm × 860 mm H. A programmable controller was used to control the oven temperature. The temperature at the center of the coal charge was monitored by means of a thermocouple connected to a computer. The coking tests were carried out under similar conditions while varying the coking rate. Carbonization at an industrial scale is carried out at a constant wall temperature which is fixed in order to control other variables such as coking rate or coking time. Similarly, in the present research work, the heating rate was controlled by regulating the temperature of the oven walls to obtain three heating programmes, the initial wall temperature being set at 1020, 1100, and 1200 °C. The temperature of the walls was kept constant throughout the test. As the bulk density varies as a function of grain size and moisture content, both parameters were kept as close as possible in each series of carbonizations to give mean values of 782 kg/m³ ± 4. The moisture of the charge was fixed at 5 wt % and ca. 80 wt % of the grain size of the coal blends was smaller than 3 mm. The coke was pushed out of the oven 30 min after the center of the charge had reached 950 °C. The average of the final coke temperature of all test was calculated for each coal individually with the following results: 1070 ± 33, 1062 ± 25, 1046 ± 57, 1031 ± 88, 1042 ± 58 °C, for LV, MV, HV1, HV2, and B, respectively.

4.3. Coke Quality. The cold mechanical strength of the cookes produced was assessed by applying the JIS test (JIS K2151 standard procedure). After the test the coke was sieved and the Di15% and Di35% indices were calculated from the amount of coke with a particle size smaller than 5 mm and larger than 15 mm respectively. Coke reactivity (CRI) and mechanical strength after reaction (CSR) were assessed by means of the NSC test (ASTM D5341 standard procedure). The tests were carried out at least twice and the repeatability errors of the CRI and CSR were ±1.6 and ±1.8% respectively.

4.4. Reactivity Tests. A laboratory-scale fixed-bed reactor was used to measure the rate of coke reaction with CO2 under conditions of chemical control. Coke samples were dried at 200 °C overnight before the analysis. Coke samples (0.35 g) were supported over a porous quartz plate sintered in a quartz reaction tube. The reactor was placed in a vertical electrically-heated furnace. The reaction temperature was selected to achieve a CO concentration less than 1%. A mass-flow controller was used to pass 100% CO2 from the bottom to the top flowing at a rate of 250 mL/min. The temperature of the center of the sample was measured with a thermocouple and monitored during the test. The concentration of CO in the exhaust gas was measured continuously by means of a gas chromatograph. The apparent reaction rate (ρ) and activation energy were calculated as reported in previous papers. Following the procedure from Stoeckli, Ea was related to the average width of the micropores (Lb) and the characteristic adsorption energy (E0) by means of the following empirical equations:

\[ L_b (\text{nm}) = \frac{10.8}{E_0 (\text{kJ/mol}) - 11.4} \]  
\[ S_{\text{mic}} (m^2/g) = \frac{2000W_0 (cm^3/g)}{L_b (\text{nm})} \]

The inorganic matter composition of each sample was analyzed by XRF using a SRS 3000 Bruker spectrometer in accordance with the ASTM D4326-04 standard procedure. The presence of minerals in the samples is typically characterized by means of the AI. The AI measures the ratio of basic to acidic oxides in the ashes

\[ AI (\%) = \frac{[\text{Fe}_2\text{O}_3] + [\text{CaO}] + [\text{MgO}] + [\text{K}_2\text{O}] + [\text{Na}_2\text{O}]}{[\text{SiO}_2] + [\text{Al}_2\text{O}_3]} \times \text{ash} (\%) \]

The basic oxides (CaO, K2O, Na2O, MgO and Fe2O3) generally act as a catalyst, while acidic oxides (SiO2 and Al2O3) act as an inhibitor.

4.6. Raman Spectroscopy. Raman spectroscopy was conducted in a LabRAM HR 800 (HORIBA Jobin Yvon).
spectrometer equipped with a CCD detector. A 100× objective lens of an Olympus M Plan optical microscope was used both to focus the excitation laser beam (532 nm exciting line of a green DPSS laser) at a power of ~25 mW and collect the scattered radiation. Extended scans from 800 to 2000 cm⁻¹ were carried out to obtain the Raman spectra of the samples, with typical exposure times of 30 s. In order to obtain the spectral parameters that is, peak position, fwhm, intensity (I), and integrated area of each band (A) the Raman spectra were satisfactorily resolved into five different bands, four Lorentzian bands (G, D₁, D₂, D₃), and one Gaussian band (D₄) with Origin Pro 2019 software. This curve-fitting method refers to the studies by various researchers.²¹,²⁷,⁴⁴ At least four spectra were recorded from each sample, each being taken from a different coke particle and the results averaged. To provide information about the structural order of the coals produced at different coking rates, the A₃/₄, A₁/₄, and A₄/₃₄₅ band area ratios were calculated from the peak areas dividing the D₁ band area by the sum of the D₃ and D₄ band areas respectively by the G band area.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05007.

Curve fit Raman spectra of coals obtained from LV, MV, and HV2 coals at different temperature [PDF]

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Díez, M. A.; Alvarez, R.; Barrio Canal, C. Coal for Metallurgical Coke Production: Predictions of Coke Quality and Future Requirements for Cokemaking. Int. J. Coal. Geol. 2002, 50, 389-412.
(2) Li, K.; Khanna, R.; Zhang, J.; Liu, Z.; Sahajwalla, V.; Yang, T.; Kong, D. The Evolution of Structural Order, Microstructure and Mineral Matter of Metallurgical Coke in a Blast Furnace: A Review. Fuel 2014, 133, 194-215.
(3) Loison, R.; Foch, P.; Boyer, A. Coke: Quality and Production; Elsevier: London, 1989.
(4) ASTM. Standard Test Method for Measuring Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR); ASTM International, 2019.
(5) Koszorek, A.; Krzesińska, M.; Pusz, S.; Pilawa, B.; Kwiecińska, B. Relationship between the Technical Parameters of Cokes Produced from Blends of Three Polish Coals of Different Coking Ability. Int. J. Coal. Geol. 2009, 77, 363-371.
(6) Cheng, H.; Liang, Y.; Guo, R.; Sun, Z.; Wang, Q.; Xie, Q.-a.; Wang, J. Effects of Solution Loss Degree, Reaction Temperature, and High Temperature Heating on the Thermal Properties of Metallurgical Cokes. Fuel 2021, 283, 118936.
(7) Nyathi, M. S.; Kruse, R.; Mastalerz, M.; Bish, D. L. Impact of Oven Bulk Density and Coking Rate on Stamp-Charged Metallurgical Coke Structural Properties. Energy Fuels 2013, 27, 7876-7884.
(8) Gajic, D. Influences on Bulk Density and Its Effect on Coke Quality and Internal Gas Pressure. AISTech-Iron and Steel Technology Conference Proceedings, 2013; Vol. J, pp 307-319.
(9) Nomura, S. Effect of Coal Briquette Size on Coke Quality and Coal Bulk Density in Coke Oven. ISIJ Int. 2019, 59, 1512-1518.
(10) Wenger, R. O.; Neubaum, V. A. The Effect of Coke Plant Operating Variables on the Quality of Metallurgical Coke. JOM 1970, 22, 55-60.
(11) Yadav, U. S.; Sharma, R.; Dash, P. S.; Guha, M.; Deshpande, D. P. Effect of Carbonisation Time at Stamp Charged Battery on Properties of Blast Furnace Coke. Ironmaking Steelmaking 2004, 31, 15-22.
(12) Amamoto, K. Coke Strength Development in the Coke Oven: 1. Influence of Maximum Temperature and Heating Rate. Fuel 1997, 76, 17-21.
(13) Wu, S.; Gu, J.; Zhang, X.; Wu, Y.; Gao, J. Variation of Carbon Crystalline Structures and CO₂ Gasification Reactivity of Shenhui Coal Char at Elevated Temperatures. Energy Fuels 2008, 22, 199-206.
(14) Luo, C.; Watanabe, T.; Nakamura, M.; Uemiya, S.; Kojima, T. Gasification Kinetics of Coal Char Carbonized Under Rapid and Slow Heating Conditions at Elevated Temperatures. J. Energy Resour. Technol. 2000, 123, 21-26.
(15) Jayaraman, K.; Gokalp, I.; Bonifaci, E.; Merlo, N. Kinetics of Steam and CO₂ Gasification of High Ash Coal—Char Produced under Various Heating Rates. Fuel 2015, 154, 370-379.
(16) Gale, T. K.; Bartholomew, C. H.; Fletcher, T. H. Effects of Pyrolysis Heating Rate on Intrinsic Reactivities of Coal Chars. Energy Fuels 1996, 10, 766-775.
(17) Tian, B.; Qiao, Y.-y.; Tian, Y.-y.; Liu, Q. Investigation on the Effect of Particle Size and Heating Rate on Pyrolysis Characteristics of a Bituminous Coal by TG–FTIR. J. Anal. Appl. Pyrolysis 2016, 121, 376-386.
(18) Casal, M. D.; Barrio Canal, C.; Díez, M. A.; Alvarez, R. Influence of Porosity and Fissuring on Coking Pressure Generation. Fuel 2008, 87, 2437-2443.
(19) Díaz-Faes, E. Study at Different Scales of Coking Pressure and Coke Quality of Coking Coals; Universidad de Oviedo: Oviedo, 2010.
(20) Amamoto, K. Coke Strength Development in the Coke Oven. 2. Homogenizing the Strength of Coke throughout the Coke Oven Chamber. Fuel 1997, 76, 133-136.
(21) Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niesser, R.; Pöschl, U. Raman Microspectroscopy of Soot and Related Carbonaceous Materials: Spectral Analysis and Structural Information. Carbon 2005, 43, 1731-1742.
(22) Cuesta, A.; Dhamelincourt, P.; Laureyns, J.; Martinez-Alonso, A.; Tascón, J. M. D. Raman Microprobe Studies on Carbon Materials. Carbon 1994, 32, 1523-1532.
(23) Kawakami, M.; Karato, T.; Takenaka, T.; Yokoyama, S. Structure Analysis of Coke, Wood Charcoal and Bamboo Charcoal by Raman Spectroscopy and Their Reaction Rate with CO₂. ISIJ Int. 2005, 45, 1027-1034.
(24) Rantitsch, G.; Bhattacharyya, A.; Schenk, J.; Linsdoff, N. K. Assessing the Quality of Metallurgical Coke by Raman Spectroscopy. Int. J. Coal. Geol. 2014, 130, 1-7.
(25) Xing, X. Effects of Coal Interactions during Cokemaking on Coke Properties under Simulated Blast Furnace Conditions. Fuel Process. Technol. 2020, 199, 106274.

(26) Rantitsch, G.; Bhattacharyya, A.; Günbatı, A.; Schulten, M.-A.; Schenk, J.; Letofsky-Papst, I.; Albering, J. Microstructural Evolution of Metallurgical Coke: Evidence from Raman Spectroscopy. Int. J. Coal Geol. 2020, 227, 103546.

(27) Sheng, C. Char Structure Characterised by Raman Spectroscopy and Its Correlations with Combustion Reactivity. Fuel 2007, 86, 2316–2324.

(28) Beyssac, O.; Goffé, B.; Petitet, J.-P.; Froigneux, E.; Moreau, M.; Rouzaud, J.-N. On the Characterization of Disordered and Heterogeneous Carbonaceous Materials by Raman Spectroscopy. Spectrochim. Acta, Part A 2003, 59, 2267–2276.

(29) Smdowski, Ł.; Krzesinska, M.; Kwasny, W.; Kozancki, M. Development of Ordered Structures in the High-Temperature (HT) Cokes from Binary and Ternary Coal Blends Studied by Means of X-Ray Diffraction and Raman Spectroscopy. Energy Fuels 2011, 25, 3142–3149.

(30) Rouzaud, J. N.; Oberlin, A. Structure, Microtexture, and Optical Properties of Anthracene and Saccharose-Based Carbons. Carbon 1989, 27, 517–529.

(31) Radovic, L. R.; Walker, P. L.; Jenkins, R. G. Importance of Carbon Active Sites in the Gasification of Coal Chars. Fuel 1983, 62, 849–856.

(32) Xu, J.; Zuo, H.; Wang, G.; Zhang, J.; Guo, K.; Liang, W. Gasification Mechanism and Kinetics Analysis of Coke Using Distributed Activation Energy Model (DAEM). Appl. Therm. Eng. 2019, 152, 605–614.

(33) Wei, R.; Ren, L.; Geng, F. Gasification Reactivity and Characteristics of Coal Chars and Petcoke. J. Energy Inst. 2021, 96, 25–30.

(34) Yin, Z.; Xu, H.; Chen, Y.; Zhao, T. Coal Char Characteristics Variation in the Gasification Process and Its Influencing Factors. Energy Explor. Exploit. 2020, 38, 1559–1573.