Thermodynamic Analysis of Iron Ore Sintering Process Based on Biomass Carbon

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Abstract: The sinter process of iron ore with biomass carbon instead of coke breeze as fuel was investigated via thermodynamic analysis in this paper through a comparison of sinter composition indexes, metallurgical properties, and pollutant emissions. Straw charcoal was used in this paper, and its replacement does not adversely affect the composition index of iron ore, namely Fe, FeO, basicity, S, nor the metallurgical properties, namely reduction degradation index and reduction index. However, the replacement has a great effect on the emissions of pollutant gases, including SO2, NOx, CO, and CO2. The thermodynamic analysis result shows that emissions of pollutant gases produced in the sinter process significantly decrease by using straw charcoal instead of coke breeze in sinter. The sintering maximum temperature has a great influence on sintering technical indicators. The best sintering maximum temperature is between 1300 and 1400 °C, where sinter ore with high quality can be obtained.

Keywords: biomass carbon; iron ore sintering; pollutant emissions; thermodynamic analysis

1. Introduction

Sinter is the first process in the whole ironmaking industry, which plays an important role in the iron and steel production process [1], and its energy consumption accounts for a large proportion of the entire ironmaking industry, reaching about 10%, which is the second largest energy-consuming process in the entire steel industry. The main energy consumption comes from the combustion of coke breeze, which supplies about 78% of the energy consumption in the sinter process [2,3]. Ironmaking enterprises’ dependence on fossil energy will cause an average of 1.65–1.8 tons of carbon dioxide per ton of liquid steel produced, and the total release of carbon dioxide in the sinter process accounts for over 10% of the total steel industry [4,5]. The combustion of coke breeze in the sinter process is also the main source of pollutants such as NOx and SOx [6]. The emission of NOx in the sinter process accounts for 48% of the entire ironmaking industry’s emission and SOX accounts for 70% [4,6].

As the main fuel used in the traditional sinter process, coke breeze (from the coke-making process) with the granulation less than 3 mm is a non-renewable fossil resource, with high S and N contents, which is one of the important reasons leading to the problem that the ironmaking industry’s energy consumption and air pollutants are both high. Biomass energy is first considered to replace the coke breeze in sinter because of its renewability and lower S and N [7–9]. Therefore, biomass is being used more often as an energy source for thermal processes, and it is currently the third largest natural and renewable energy in the world [10]. It is not necessary to change the equipment already
invested and the mature processes to achieve an alternative of the coke breeze in sinter process through biomass molding technology by which biomass is made into biomass carbon with similar structure and composition to coke breeze.

At home and abroad, experimental research on the quality of sinter ore and pollutant emissions has been carried out on the sinter of biomass charcoal instead of coke breeze. The results show that using biomass charcoal instead of coke breeze for the sinter process does not significantly affect the sintering characteristics of the sintering process and the quality of sintered ore; besides, the emission of pollutant gases produced in the sinter process decreases [11–14]. However, under different substitution ratios of biomass charcoal, the sinter ore’s quality and pollutant emissions from the sinter process are not the same. The sintering maximum temperature also has influence on the sinter process. In order to analyze the effects of different substitution ratios and the sintering maximum temperature on the quality of sinter ore and pollutant emissions, thermodynamic calculation is carried out in this paper. Compared with direct testing, the use of thermodynamic calculation has the advantages of simple operation, low cost, short cycle, and it is not affected by irrelevant factors.

2. Methodology

HSC Chemistry software is used to perform thermodynamic calculations, the calculation principle of which is to fit the thermodynamic property expression of each phase in the system and make the Gibbs free energy of the system the least with constant temperature and constant pressure under the premise of satisfying the material balance equation, through which the balanced phases of the system can be obtained.

2.1. Raw Materials

2.1.1. Solid Fuel

Solid fuels include coke breeze and straw charcoal, and their compositions are shown in Table 1 [15].

| Table 1. Composition of solid fuel (dry basis, %). |
|-----------------|-------|-------|-------|-------|-------|
|                | C     | H     | O     | S     | N     |
| Coke breeze    | 81.84 | 2.46  | 1.03  | 0.5   | 0.72  |
| Straw charcoal | 71.60 | 4.76  | 6.88  | 0.083 | 0.32  |

2.1.2. Iron Ore

The composition of the iron ore used in this paper is listed in Table 2.

| Table 2. Composition of iron ore (mass, %). |
|-----------------|-------|-------|-------|-------|-------|
| Iron Ore        | Fe₂O₃ | Fe₂O₃·H₂O | FeO  | SiO₂ | CaO  | Al₂O₃ | MgO | S |
| Composition     | 49.79 | 37.21 | 5.73 | 3.86 | 0.39 | 2.62  | 0.17 | 0.11 |

2.1.3. Other Materials

In addition to solid fuel and iron ore, other materials in the sinter process include flux, return mine, and converter slag, as shown in Table 3. The flux consists of dolomite, limestone, quicklime, etc. It can produce slags that can adsorb harmful impurities such as S and high-basicity sinter ores having a good self-fluxing property. The return mine refers to the undersize product produced during the sintering process, which consists of small particles of sinter ore and unsintered raw material with a loose porous structure and it can increase the gas permeability, the productivity, and the strength of the sinter. The converter slag is a waste produced by steelmaking, and it contains Fe, CaO, MnO, S, etc. The recycle of converter slag can reuse the Fe and CaO resources [16,17].
| Table 3. Composition of flux, return mine, and converter slag [16]. |
|---------------------------------------------------------------|
|                  | TFe   | FeO   | SiO₂  | CaO   | Al₂O₃ | MgO   | S    |
| Limestone        | 1.58  | 0     | 1.42  | 48.85 | 0.76  | 3.62  | 0.04 |
| Dolomite         | 0.18  | 0     | 1.19  | 33.15 | 0.68  | 18.25 | 0.024|
| Quicklime        | 0.37  | 0     | 3.08  | 67.88 | 0.96  | 1.41  | 0.13 |
| Return mine      | 56.13 | 7.35  | 5.22  | 9.22  | 2.88  | 2.15  | 0.024|
| Converter slag   | 17.89 | 13.24 | 10.78 | 45.62 | 3.15  | 8.02  | 0.14 |

2.1.4. Distribution Ratio

Table 4 shows the distribution of solid fuels, iron ore, various fluxes, and return mine required for sintering.

| Table 4. Ratios of sintering raw materials [16]. |
|-----------------------------------------------|
| Fuel                  | Mixed Iron Ore | Limestone | Dolomite | Quicklime | Return Mine | Converter Slag |
| Proportion/\%         | 4              | 53.97     | 4.56     | 2.85      | 2.92        | 27.2           | 3.28           |

2.1.5. Air

The introduction of air is required in the sintering process to provide the oxygen for solid fuel’s combustion. In order to ensure the full combustion of the solid fuel to provide the high temperature required for the sintering process, a higher air excess coefficient is often taken. The air excess coefficient is chosen as 1.5 in calculation.

2.2. Products

2.2.1. Sinter Ore

According to the main composition systems of different sinters and the test result obtained by Mežibrický et al. replacing some coke with charcoal and walnut shells [16,18], the main systems of sinter ores are shown in Table 5.

| Table 5. Main minerals of sinter ore [18]. |
|--------------------------------------------|
| System              | Mineral                  | Formula                        |
| Ferrite system      | Hematite                 | Fe₂O₃                          |
|                     | Magnetite                | Fe₃O₄                          |
| Iron silicate system| Fayatite                 | 2FeO·SiO₂                      |
| Calcium silicate system| Wollastonite               | CaO·SiO₂                       |
|                     | Calcium orthosilicate    | 2CaO·SiO₂                      |
|                     |                          | 3CaO·SiO₂                      |
| Calcium ferrite system| -                        | CaO·Fe₂O₃                      |
|                     |                          | 2CaO·Fe₂O₃                     |
|                     |                          | CaO·2Fe₂O₃                     |
| Calcium iron olivine system| Calcium iron olivine     | CaO·Fe₂O₃·SiO₂                 |
|                     | Hedenbergite             | CaO·Fe₂O₃·2SiO₂                |
|                     | Iron yellow feldspar     | CaO·Fe₂O₃·SiO₂                 |
| Calcium magnesium silicate system| Forsterite               | 2MgO·SiO₂                     |
|                     | Magnesium metasilicate   | MgO·SiO₂                      |
|                     | Calcium magnesium silicate| Diopside                   | CaO·MgO·SiO₂               |
|                     |                          | CaO·MgO·2SiO₂                  |
|                     | Merwinite                | 3CaO·MgO·2SiO₂                 |
|                     | Akermanite               | 2CaO·MgO·2SiO₂                 |
|                     | Calcium magnes           | 5CaO·2MgO·6SiO₂                |
2.2.2. Sinter Gases

The gases generated during the sintering process mainly include H$_2$O, CO$_2$, CO, SO$_2$, NOx, and H$_2$S. According to China’s current standards for sinter gas emissions, the pollutant gases CO, SO$_2$, NO$_x$, and the green-house gas CO$_2$ are taken into account [19].

2.3. Indexes

The effects of substitution ratio and sintering maximum temperature on sintering products are mainly reflected in the sintering technical indicators and air pollutants. The sintering technical indicators generally include chemical compositions, physical properties, and metallurgical properties. The chemical compositions include Fe content, basicity, FeO content, and S content. Physical properties include the drum index, screening index, and abrasion resistance index. Metallurgical properties include the reduction degradation index (RDI $+$ 3.15 mm) and reduction index (RI). In terms of sinter pollutant gases, the investigated objects include the emission concentrations of SO$_2$, NO$_x$, CO, and CO$_2$.

The gas $x$ concentration in the emission gases is defined as follows:

$$C_x\% = \frac{V_x}{V_a}$$

(1)

where $C_x$ is the concentration of gas $x$; $V_x$ is the volume of gas $x$, m$^3$; $V_a$ is the volume of total emission gases, m$^3$. According to the technical standard, the high-quality iron sinter technical indicators are shown in Table 6.

| Chemical Composition (Mass Fraction) | Metallurgical Performance |
|-------------------------------------|---------------------------|
| TFe/\%                             | CaO/SiO$_2$               | FeO/\% | S/\% | Reduction Degradation Index (RDI $+$ 3.15 mm)/\% | Degree of Reduction (RI)/\% |
| Allowable range of fluctuation      | $\pm0.40$                 | $\pm0.05$ | $\pm0.50$ | $\leq9.00$ | $\leq0.030$ | $\geq72.00$ | $\geq78.00$ |
| Index                              | $\geq57$                  | $\geq1.70$ | $\leq9.00$ | $\leq0.030$ | $\geq72.00$ | $\geq78.00$ |

3. Effect of Biomass Charcoal Substitution on Sintering Technical Indicators

3.1. Chemical Composition

3.1.1. Fe

Figure 1 shows the change of Fe content with straw charcoal substitution. As shown in the figure, the chemical composition of sinter almost does not change with the change of the substitution ratios. As the substitution ratio increases, the Fe content, as well as the other chemical compositions mentioned below, slightly decreases, which is attributed to the increase of volatile content in solid fuel. The Fe content increases with the temperature increasing between 1000 and 1500 °C, showing a linear relationship. When the sintering maximum temperature reaches 1200 °C, the Fe content of the sinter ore reaches the standard of high-qualitied sinter ore. From this analysis, when the straw charcoal is used instead of the coke breeze for sintering, the Fe content of the sinter is not affected obviously. However, the elevated temperature helps to increase the Fe content in sinter ore. The main reason is that with the increase of temperature, the reactions that S and N in iron ore and solid fuel generate SO$_2$, NOx, and other gases go more violent. The degree of these reactions increases with the increase of sintering maximum temperature, which would reduce the mass of the final sinter solid products, causing a slight increase of Fe content.
Figure 1. Change of Fe content with straw charcoal substitution.

3.1.2. Basicity

The basicity refers to the mass ratio of CaO to SiO$_2$ in the sinter ore. When the basicity of sinter ore is lower than 1.0, it has a good strength but a poor reducibility. However, it is opposite when the basicity is 1.0–1.5. When the basicity is 1.5–2.5, both good strength and reducibility sinter ore can be obtained [20].

As shown in Figure 2, the basicity first rises and then decreases with the increase of the maximum temperature in the sinter process. At the sintering maximum temperature of 1200 °C, the basicity is the largest, up to 3.7. When the sintering maximum temperature is about 1440 °C, the sinter basicity drops to 1.7, which is commonly the bottom line of the high-quality sinter’s basicity standard.

Figure 2. Change of basicity in the case of straw charcoal substitution.

The reactions related to CaO in the sintering process include the decomposition of CaCO$_3$ and the mineralization of CaO. During the actual sintering process, the decomposition temperature of CaCO$_3$ is low, beginning at around 750 °C. When the temperature rises, the decomposition degree of CaCO$_3$ also increases. Mineralization refers to the reaction of CaO with other compounds to form new compounds, which can reduce the decomposition temperature of CaCO$_3$. The degree of mineralization increases with the temperature increasing. Therefore, when the sintering maximum temperature is low, the CaO content increases with the increase of temperature and thus the basicity is high, as shown in Figure 2. However, as the sintering maximum temperature goes on increasing, the basicity will decrease. SiO$_2$ will participate in different solid phase reactions during the sintering process, such as reactions with CaO and FeO. When the sintering maximum temperature is low, the SiO$_2$ content increases at a low rate as the temperature increases, and when the sintering maximum temperature is
high (over 1200 °C), the SiO₂ content increases at a high rate. That is why the basicity decreases at higher temperature.

3.1.3. FeO

FeO in the sinter is converted from Fe²⁺, and it plays an important role in controlling the quality of sinter ore. When the FeO content in the sinter is low, the sinter strength, utilization factor, solid fuel consumption, and finished product yield are all low. When the content is high, it has a bad influence on the vertical sintering speed, reducibility, and reduction degradation index [21].

As shown in Figure 3, at the sintering maximum temperature of 1000 °C, the FeO content in the sinter ore is very low, about 2.2%, far lower than the limit of standard, at about 9%. However, with the increase of the sintering maximum temperature, the FeO content increases. At the sintering maximum temperature of 1300 °C, the content can reach 9%.

![Figure 3. Change of FeO content in the case of straw charcoal substitution.](image)

3.1.4. S

The lower the sulfur content, the better quality of sinter ore. As shown in Figure 4, the S content of the sinter increases as the sintering maximum temperature increases. As the substitution ratio of the straw charcoal increases, the S content decreases. When the sintering maximum temperature is 1500 °C and the solid fuel used is 100% coke breeze, the content of S in the sinter ore is 1.6 × 10⁻⁹%, which is much lower than that of the high-qualified sinter ore’s limit. Although the content of S rises rapidly with the increase of the sintering maximum temperature, its influence can be neglected in view of the fact that the amount of change is extremely small.

![Figure 4. Change of S content in the case of straw charcoal substitution.](image)
According to the above, when the sintering maximum temperature is between 1200 and 1400 °C, the Fe content, FeO content, basicity, and S content can reach the standard of high-quality sinter ore.

3.2. Metallurgical Performance

3.2.1. Reduction Degradation Index

The reduction degradation index of sinter [16] refers to the degree of pulverization when the ore enters the blast furnace. Increasing the sinter pulverization rate will reduce the blast furnace’s output, so it is necessary to control the low-temperature reduction pulverization rate of the sinter.

Sinter pulverization means that the sinter ore is broken for crystal transformation in the reducing atmosphere in blast furnace. The main reaction is that the reducing gas reacts with hematite to form magnetite. The reaction is as shown in Equation (2):

\[
3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + 0.5\text{O}_2. \quad (2)
\]

The skeleton crystal rhombohedral hematite is reduced to a cubic magnetite, and the internal stress is generated when the transformation occurs. When the internal stress generated by the reduction of \( \text{Fe}_2\text{O}_3 \) is greater than the consolidation strength of the sinter ore, sintering occurs in the sinter ore. Pimenta [22] believed that the reason of the reduction and pulverization of sinter was only the crushing and pulverization of the crystalline rhombohedral hematite. The research by Lei Chao [23] reported that it was also related to the carbon evolution reaction, and the pulverization was the result of mutual promotion of the carbon evolution reaction and the reduction reaction. The carbon precipitation reaction is as shown in Equation (3):

\[
2\text{CO} \rightarrow \text{CO}_2 + \text{C}. \quad (3)
\]

From the point of the mechanical strength of the sinter composition as shown in Table 7, those of hematite, magnetite, ferric acid–calcium, and fayalite are higher, while those of ferric acid–dicalcium, glass phase, wollastonite, and diopside are poor, and the compressive strength of the glass phase is the worst.

### Table 7. Compressive strength and reduction of main components of sinter ore [16].

| Mineral                | Formula                | Compressive Temperature (°C) | Reduction Rate (%) |
|------------------------|------------------------|-----------------------------|--------------------|
| Hematite               | \( \text{Fe}_2\text{O}_3 \) | 2670                        | 49.9               |
| Magnetite              | \( \text{Fe}_3\text{O}_4 \) | 3690                        | 26.7               |
| Fayalite               | \( 2\text{FeO}\cdot\text{SiO}_2 \) | 2000                        | 1.0                |
| Wollastonite           | \( \text{CaO}\cdot\text{SiO}_2 \) | 672.8                       | -                  |
| Ferric acid–calcium    | \( \text{CaO}\cdot\text{Fe}_2\text{O}_3 \) | 3700                        | 40.1               |
| Ferric acid–dicalcium  | \( 2\text{CaO}\cdot\text{Fe}_2\text{O}_3 \) | 1420                        | 28.5               |
| Calcium iron olivine (glass phase) | \( \text{CaO}\cdot\text{FeO}\cdot\text{SiO}_2 \) | 460                          | 3.1                |
| Diopside               | \( \text{CaO}\cdot\text{MgO} \cdot 2\text{SiO}_2 \) | 580.2                       | -                  |

3.2.2. Reduction Index

The reduction ratio of each component of the sinter ore is shown in Table 7. Among the main components, the reduction rates of hematite and ferric acid–calcium are high, while that of magnetite and ferric acid–dicalcium is low, and the reduction rates of fayalite and glass phase are the lowest.

In view of the reduction degradation index and reduction performance of the sinter ore, the strength and reduction of ferric acid–calcium are optimal. The hematite except for the skeleton crystal rhombohedral hematite has good strength and general reducibility. The ferric acid–dicalcium, the fayalite, and the glass phase's strength and the reducing property are very poor. To obtain sinter ore with good metallurgical properties, more ferrite–calcium content is needed. Hematite with good reducibility
and magnetite with good strength is needed to maintain balance. Minimizing the content of ferric acid–dicalcium, fayalite and the glass phase is also necessary.

The compositions of the metallurgical properties with the sintering maximum temperature are shown in Figures 5–7. According to the analysis of the graphs, although the content of fayalite increases, a higher content of ferric acid–calcium, lower content of ferric acid–dicalcium, and suitable content of hematite and magnetite can be obtained when the maximum temperature of sintering increases. For the glass phase having the worst strength, its reducibility is also minimized.

Therefore, a sinter ore with better metallurgical properties can be obtained at such a high sintering temperature between 1300 and 1400 °C.

**Figure 5.** Change of hematite, magnetite, ferric acid monocalcium, and ferric acid dicalcium.

**Figure 6.** Change of fayalite content in sinter ore in case of straw charcoal substitution.
4. Effect of Straw Charcoal Substitution on Sintering Pollutant Gases Emissions

4.1. SO$_2$

The straw charcoal is used instead of the coke breeze for sinter, and the obtained SO$_2$ concentration changes with the substitution ratio and the sintering maximum temperature are shown in Figure 8. The concentration of SO$_2$ is related to the sintering maximum temperature and the substitution ratio. It decreases with the increase of the substitution ratios of straw charcoal and remains almost unchanged with the increase of the sintering maximum temperature.

The concentration of SO$_2$ in the sinter gas produced in sinter with coke breeze as a solid fuel is about 1750 mg/m$^3$, which is consistent with the status of the sinter industry’s SO$_2$ emissions (originally, without any desulfurization process). The lowest SO$_2$ concentration in sinter gas is 1480 mg/m$^3$ when replacing with straw charcoal, decreasing by about 18%. The effect of the substitution on reducing SO$_2$ concentration is significant. With the desulfurization efficiency generally reaching 90% today, after desulfurization, the concentration of SO$_2$ can conform to China standard of 200 mg/m$^3$.
solid fuel generally forms the intermediate product H$_2$S, which will then react with H$_2$S and O$_2$ to form SO$_2$. The temperature has different effects on S in iron ore and organic S in solid fuel. The activation energy of sulfur in pyrite is higher than that of organic sulfur. The change of temperature has a greater influence on the reaction of pyrite. The organic sulfur in the solid fuel will be the first to form SO$_2$. The pyrite starts to lose sulfur at 300 °C and decomposes fiercely when the temperature reaches over 650 °C. Below 1200 °C, the SO$_2$ content increases with the increase of temperature, as shown in Figure 8. As the temperature continues to rise, the liquid phase will be generated during the sintering process, and the CaO content will also increases. Both of them will absorb SO$_2$, so the SO$_2$ concentration remains substantially unchanged when the temperature is above 1200 °C.

\[
\begin{align*}
2\text{FeS}_2 + 5/2\text{O}_2 & \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2 \\
3\text{FeS}_2 + 8\text{O}_2 & \rightarrow \text{Fe}_3\text{O}_4 + 6\text{SO}_2 \\
2\text{FeS} + 7/2\text{O}_2 & \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2 \\
& \quad \text{when the temperature is below 1250–1300 °C} \\
3\text{FeS} + 5\text{O}_2 & \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2 \\
& \quad \text{when the temperature is over 1300 °C} \\
\text{CaSO}_4 + \text{Fe}_2\text{O}_3 & \rightarrow \text{CaO}\cdot\text{Fe}_2\text{O}_3 + \text{SO}_2 + 1/2\text{O}_2 \\
\text{Sulfur in organic matter} & \rightarrow \text{H}_2\text{S} \\
2\text{H}_2\text{S} + 3\text{O}_2 & \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O} \\
\text{H}_2\text{S} + \text{CO} & \rightarrow \text{H}_2 + \text{COS} \\
\text{H}_2\text{S} + \text{CO}_2 & \rightarrow \text{H}_2\text{O} + \text{COS} \\
2\text{COS} + 3\text{O}_2 & \rightarrow 2\text{CO}_2 + 2\text{SO}_2
\end{align*}
\]

4.2. NOx

Since the emission concentration of NO$_x$ in 2012 has been included in the emission standard for sinter pollutant emissions, steel companies have begun to pay attention to the reduction of NO$_x$. China’s NO$_x$ emission reduction work is just in its infancy, and the denitrification rate can only reach about 50%. How to complete the NO$_x$ emission standard has become a severe problem for steel companies. As shown in Figure 9, the concentration of NO$_x$ in the sinter gas after straw charcoal substitution is independent of the maximum sinter temperature. However, the concentration decreases significantly with the increase of the substitution ratios of straw charcoal. According to the Zeldovich theory, there are three types of NO$_x$: fuel NO$_x$, thermal NO$_x$, and prompt NO$_x$. Among them, thermal NO$_x$ is just produced in minute quantities when the temperature is below 1500 °C, and the prompt NO$_x$ related to the air excess coefficient is also produced in minute quantities at almost any temperature [24]. So, the majority of NO$_x$ produced in the sintering process is fuel NO$_x$. When the substitution ratio of the biomass charcoal increases, the N content in the whole fuel feedstock decreases, and thus the generation of NO$_x$ also decreases.

When no straw charcoal is used, the concentration of NO$_x$ in the sinter gas is about 1150 mg/m$^3$. When the coke breeze is replaced by a high proportion of straw charcoal, the concentration of NO$_x$ in the sinter gas is 625 mg/m$^3$, indicating a decrease by 46%. The emission standard of 50 mg/m$^3$ can be fully achieved after the subsequent treatment of which the denitrification efficiency can be over 90%.
4.3. CO

CO has not been included in the sinter pollutant’s emission standard, but CO is toxic and endangers human’s health. As China furtherly advocates the energy conservation and emission reduction of steel companies, CO will gradually enter people’s vision.

Figure 10 shows the CO concentration changes with the increase of the sintering maximum temperature under the different substitution ratios of straw charcoal. At a low sintering maximum temperature, the CO concentration is basically unchanged with the different substitution ratios of the straw charcoal, with a very small CO amount. As the temperature rises, the CO concentration increases rapidly, and it can reach about 40 mg/m³ at 1500 °C. At the higher sintering maximum temperature, the increase of the substitution ratios can reduce the CO concentration, but just lightly.

4.4. CO₂

During the sintering process, C has two directions: CO and CO₂. The air excess coefficient of the sintering process is large, reaching 1.4–1.5. Most of the C in the fuel becomes CO₂, and CO only occupies a small part. Although CO₂ is not poisonous, it is the main greenhouse gas leading to global warming. The ironmaking industry’s CO₂ emission accounts for a considerable percentage of the world’s total CO₂ emission [25,26]. Therefore, limiting CO₂ emissions is also an important goal of energy saving for ironmaking companies.
As shown in Figure 11, from the perspective of the sintering maximum temperature, the CO\textsubscript{2} concentration increases with the increase of the sintering maximum temperature. From the perspective of the substitution ratio, CO\textsubscript{2} concentration in the sintering gas decreases as the substitution ratio of straw charcoal increases. The reason is that the C content of straw charcoal is lower than that of coke breeze. The concentration of CO\textsubscript{2} with no substitution is about 220 g/m\textsuperscript{3}. When straw charcoal is used instead, the concentration of CO\textsubscript{2} can be reduced by about 30 g/m\textsuperscript{3}, and the decrease rate is about 14%.

**Figure 11.** Change of CO\textsubscript{2} emission concentration in the case of straw charcoal substitution.

Combined with the change of CO concentration, as the sintering maximum temperature increases, the CO concentration will increase and the CO\textsubscript{2} emission concentration will decrease slightly. Equations associated with CO, CO\textsubscript{2} during the combustion process consist of the following components:

\[
2C + O\textsubscript{2} \rightarrow 2CO \tag{14}
\]
\[
C + O\textsubscript{2} \rightarrow CO\textsubscript{2} \tag{15}
\]
\[
2CO + O\textsubscript{2} \rightarrow 2CO\textsubscript{2} \tag{16}
\]
\[
CO\textsubscript{2} + C \rightarrow 2CO. \tag{17}
\]

As the reaction temperature increases, the degree of progress of Equations (14) and (17) increases. The degree of progress of Equation (15) has little relationship with temperature. The degree of progress of Equation (16) decreases with temperature increasing. As the sintering maximum temperature increases, the concentration of CO will increase, while the concentration of CO\textsubscript{2} will decrease.

### 5. Conclusions

(1) Through the thermodynamics analysis by using straw charcoal instead of coke breeze in the sinter process, the result shows that the sintering technical indicators of sinter ore, including chemical compositions and metallurgical properties, will not be affected with the substitution of straw charcoal. Meanwhile, the sintering technical indicators will get changed with the change of sintering maximum temperature. When the sintering maximum temperature is about 1300 to 1400 °C, sinter ore with high quality can be produced.

(2) The sintering maximum temperature has a slight effect on pollutant emissions, which can be ignored. Biomass replacement has a significant effect on the reduction in pollutant gases emissions. When using straw charcoal for sinter at the substitution ratio of 80%, SO\textsubscript{2} concentration decreases by about 18% compared to that with no substitution, and that of NO\textsubscript{x} and CO\textsubscript{2} is about 46% and 14%, respectively. CO concentration also decreases, but the degree is slight.
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