

Adaptability of Coal Gasification in Molten Blast Furnace Slag on Coal Samples and Granularities

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ABSTRACT: In this work, coal gasification in molten blast furnace (BF) slag was performed at atmospheric pressure in a molten bath reactor in the temperature range from 1573 to 1773 K. The effects of coal samples and coal granularities on the gasification reaction rate, carbon conversion, and gas composition were studied, and the kinetic mechanism function was calculated. The results show that the method using coal gasification to recover sensible heat of molten BF slag is possible and effective. The coal gasification using molten BF slag as a carrier has wide adaptability on coal granularities and coal samples. It is effective to gasify lean coal. In this study, the gasification reaction rate of Shennan (SN) coal that represents lean coals is high and almost equal to that of Datong (DT) and Fuxin (FX) coals. The carbon conversion of all types of coal can become 0.99. Under the action of molten slag, the tar and hydrocarbon decompose fully; the content of other hydrocarbons in synthesis gas is almost zero. The reaction rates using different coal granularities increase in the order of $0.177 < 0.125 < 0.147$ mm, but the difference is little. The calorific capacity of synthesis gas under different conditions is almost equal and can become $10\,000$ kJ/m³. The mechanism functions are different before and after the carbon conversion rate of 0.5. The mechanism function is shown as follows:

$$f(a) = \begin{cases} 3(1-a)[- \ln(1-a)]^{2/3} & a \leq 0.5 \\ 2(1-a)[- \ln(1-a)]^{1/2} & a > 0.5 \end{cases}$$

1. INTRODUCTION

Molten blast furnace (BF) slag is the byproduct of iron-making at the high-temperature range from 1723 to 1923 K, and a large amount of sensible heat remains. BF slag mainly consists of SiO₂, Al₂O₃, CaO, FeO, and MgO. The energy of molten BF slag is about 2–3% of comprehensive energy consumption per ton of steel, and the sensible heat is currently emitted into the atmosphere without any recovery. Many researchers^{1–10} studied this problem and proposed several methods to recover the energy of molten BF slag. The energy of slag when it becomes solid can be recovered by most methods, but the sensible heat of slag when it is liquid cannot be recovered efficiently. For this problem, Yu and Li¹¹ proposed a new method to recover the sensible heat of liquid slag. This method is coal gasification using molten BF slag as a heat carrier.

The conventional gas–solid coal gasification has a series of drawbacks for both the plant and the environment. Of major concern for the plant operation is ash generation and its disposal, fouling by unburned coal. Environmental problems arise from gaseous polluting emissions containing gaseous sulfurous compounds, heavy hydrocarbons, and particulate. The molten bath gasification processes have been proposed for their potential to overcome these disadvantages.¹² Otherwise, the composition of BF slag can catalyze coal gasification, which can increase the gasification reaction rate. CaO in slag can absorb the sulfide and carbon dioxide. The liquid slag provides heat for coal gasification, which makes the calorific value of syngas higher. It is an environmentally friendly and high-energy-efficient technology.

Accordingly, the purpose of this work is to study the adaptability of coal gasification in molten BF slag on coal samples and granularity and investigate the composition of generated combustion gas and the effects of coal samples and granularity on the carbon conversion and reaction rate.

2. EXPERIMENTAL SECTION

2.1. Raw Materials. In the present series of experiments, four different types of coal, Datong (DT) coal, Fuxin (FX) coal, Shennan (SN) coal, and coke and a BF slag sample, were used. The proximate analyses of the coal samples in the gasification are summarized in Table 1. The granularities of coal samples are 0.177, 0.147, and 0.125 mm. The chemical compositions of BF slag are 41.21 mass % CaO, 34.38 mass % SiO₂, 11.05 mass % Al₂O₃, 8.22 mass % MgO, 0.35 mass % TiO₂, and some minor constituents of iron.

2.2. Apparatus and Procedure. The experiments were conducted in a tube-type setup. Figure 1 shows the schematic diagram of the experimental apparatus of coal gasification in molten BF slag. The reactor was made of a high-purity alumina tube, whose bottom was closed. The inner diameter of the reactor was 30 mm. The reactor was vertically placed in an electric furnace (about 12 kW), whose temperature could be measured by a S-type thermocouple. About 10 kg of BF slag was set at the bottom of the reactor. Another alumina tube, whose inner diameter was 5 mm, was inserted into the slag; it coal particles and gasification agent can be introduced into the molten slag pool. The gasification agent

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Table 1. Proximate Analysis of the Raw Coal and Char

	proximate analysis (%)				fusion point (K)		
	moisture	ash	volatile matter	fixed carbon	T_{def}	T_{hem}	T_{flow}
coke	0.07	12.5	1.59	85.84	>1773	>1773	>1773
DT coal	9.05	14.15	38.38	38.42	1498	1578	1653
FX coal	6.59	34.41	26.05	32.95	1673	1723	1773
SN coal	2.30	58.47	26.38	12.85			

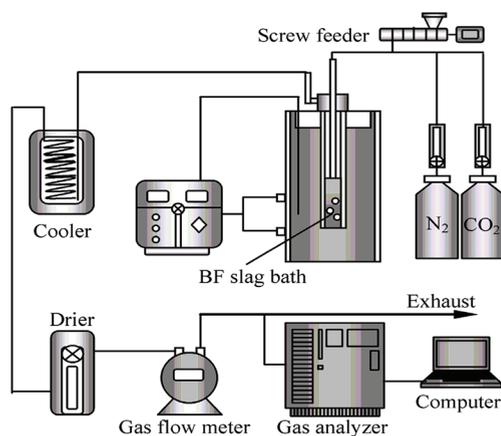


Fig. 1. Schematic diagram of experiment apparatus

Figure 1. Schematic diagram of the experimental apparatus.

came from the gas cylinder, and it was the carrier gas of coal particles from the screw feeder. The screw feeder can be controlled by the controller, which can change the feeding rate from 2 to 15 g/s. First, the slag was heated to the desired temperature. After holding for 40 min and the temperature of the reactor reaching a constant, the coal particles and gasification agent were introduced into the molten slag pool at constant conditions of the ratio of CO_2/coal and atmosphere pressure. Then, the gasification of coal immediately took place.

For each experiment, the synthesis gas was analyzed by a gas analyzer and was measured by a gas flow meter. The gas analyses were conducted for the gas species of H_2 , CO , CO_2 , and CH_4 . The carbon conversion rate is calculated by the following equation:

$$\eta_c = \frac{V_1 f_1 + V_2 f_2 + \dots + V_i f_i + \dots + V_n f_n}{C_m} \quad (1)$$

where V_i is the volume of the content i , f_i is the carbon in the content i , and C_m is the carbon in the coal sample.

3. RESULTS AND DISCUSSION

3.1. Effect of Coal Samples on Coal Gasification in Molten BF Slag. As mentioned earlier, four types of coal were used in the present investigation to study the effect of different types of coal on coal gasification in molten BF slag. Figure 2 presents the change of carbon conversion rates with time at the same gasification condition.

Panels a and b of Figure 2 show the changed carbon conversion with time for all four types of coal particles, whose diameters are 0.125 and 0.147 mm, respectively. It may be noted from Figure 2 that the carbon conversion rate increases with increasing time; the carbon conversion rate of DT coal is highest, whereas that of coke is at a minimum. For Figure 2a, in which the coal particle diameter is 0.125 mm, the time needed for 100% carbon

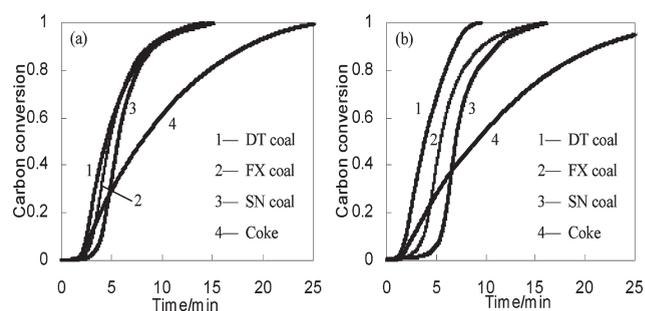


Figure 2. Carbon conversion changed with time for different types of coal: (a) 0.125 mm and (b) 0.147 mm.

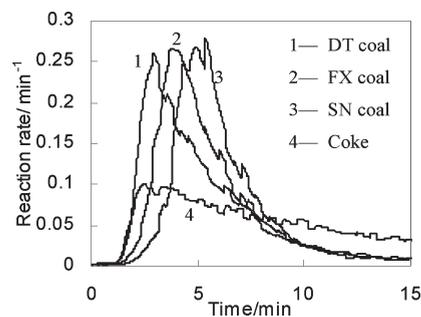


Figure 3. Coal gasification reaction rate changed with time for different types of coal.

conversion of DT coal, FX coal, and SN coal is the same and shorter than that of coke. When the carbon conversion rate is below 0.8, the carbon conversion rate for different coal samples increases in the order of SN coal < FX coal < DT coal. However, when the carbon conversion rate is higher than 0.8, the carbon conversion rates of the three types of coal are same. For Figure 2b, in which the coal particle diameter is 0.147 mm, the times needed for 100% carbon conversion of four types of coal char are all different. There are many reasons for this phenomenon. From Table 1, we know that DT coal represented high-quality coal, FX coal represented medium-rank coals, and SN coal represented lean coals. We can see that the time needed for 100% carbon conversion increases with an increasing ash content. We inferred that the diffusion is the main bottleneck for the coal gasification in molten BF slag. Besides, the reason that the carbon conversion rate of coke is at a minimum is that the pyrolysis condition reduces its activity. The detailed description of the effect of the pyrolysis condition on gasification was studied by Liu et al.¹³ and Chen et al.¹⁴

Figure 3 presents the change of the coal gasification reaction rate with time. It may be noted from Figure 3 that the coal gasification reaction rate increases first and then decreases with time. The peak value of the reaction rate of coke is lowest, and those of other types of coal are almost equal. The reason that the reaction rate of coke is at a minimum is as mentioned earlier. The time reaction rate of SN coal reaching a peak value is longest, and the time reaction rate of coke reaching a peak value is shortest. The time reaction rate of FX coal reaching a peak value is longer than that of DT coal. This is because the more the ash content, the more difficult the diffusion. The reason that the peak value of the reaction rate of SN coal is highest is that the ash fusion of SN coal is low and the diffusion is easier than others.

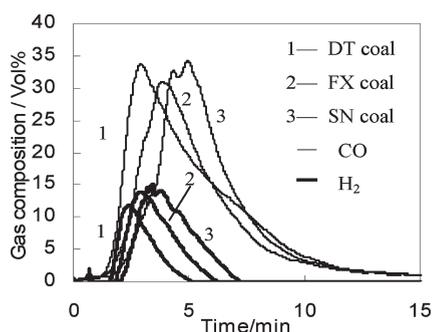


Figure 4. Gas composition changed with time for different types of coal.

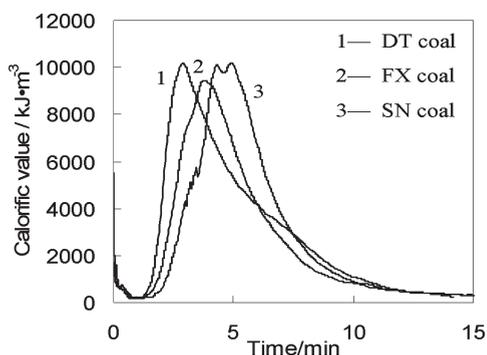


Figure 5. Calorific value of gas changed with time for different types of coal.

Figure 4 presents the change of synthesis gas composition with time for different types of coal. It is found that the H_2 content in synthesis gas using different types of coal increases in the order of DT coal < FX coal < SN coal and that the CO content in synthesis gas using different types of coal increases in the order of DT coal \approx SN coal < FX coal. This is because the ratio of volatile matter/fixed carbon of SN coal is highest. In the gasification process, molten BF slag is the heat resource of coal gasification as the heat carrier; the volatile matter does not need combustion to provide the heat of gasification.

Figure 5 presents the change of the calorific value of synthesis gas with time for different types of coal. It is found that the calorific value of synthesis gas of DT coal and SN coal are almost equal and that of FX coal is lower. However, for all of them, the difference of the calorific value of gases is little.

From that, it is found that the gasification character of lean coals is good. The adaptability of coal gasification in molten BF slag on coal samples is wide.

3.2. Effect of the Coal Granularity on Coal Gasification in Molten BF Slag. The effect of coal granularity on the carbon conversion rate is shown in Figure 6. It is seen that there is little difference in the carbon conversion rate for different granularities. The time that the gasification reaction started for different granularities increases in the order of $0.125 < 0.147 \approx 0.177$ mm. However, the time needed for 100% carbon conversion increases in the order of $0.177 < 0.125 < 0.147$ mm. Figure 7 shows the change of the coal gasification reaction rate with time for different granularities. It is noted from Figure 3 that the coal gasification reaction rate increases first and then decreases with time. It is found that the peak value of the reaction rate using different coal granularities increase in the order of $0.177 < 0.125 < 0.147$ mm.

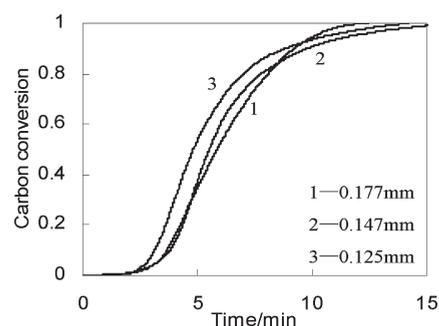


Figure 6. Carbon conversion changed with time for different granularities.

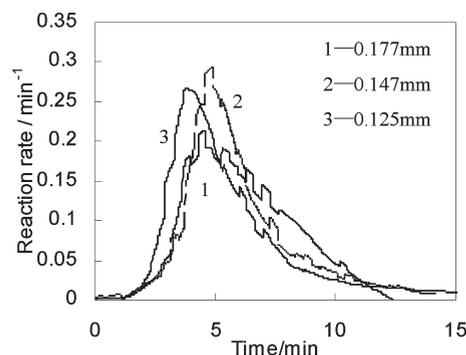


Figure 7. Coal gasification reaction rate changed with time for different granularities.

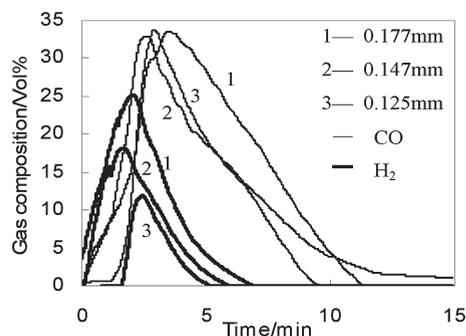


Figure 8. Gas composition changed with time for different granularities.

There are several reasons. First, in the process, the diffusion is the main bottleneck of gasification. The diffusion of large coal granularity is more difficult than that when the diameter is small. Therefore, when the coal granularity diameter is 0.177 mm, the gasification reaction rate is the lowest. Second, the longer the resident time in the molten bath, the higher the gasification reaction rate. For the two reasons, the gasification reaction rate of the coal particle whose diameter is 0.147 mm is the highest.

Figure 8 shows the change of the gas composition with time. It is found that the H_2 content in synthesis gas using different coal granularities increases in the order of $0.125 < 0.147 < 0.177$ mm and that the CO content in synthesis gas using different coal granularities is almost the same. This is because the resident time of large coal granularity in the molten bath is longer and their

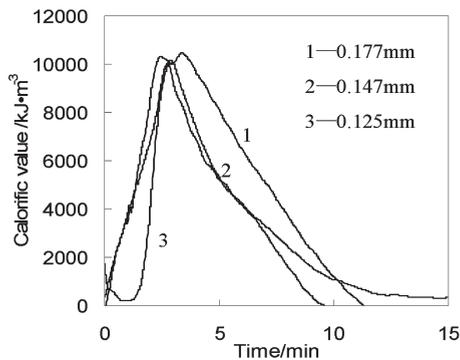


Figure 9. Calorific value changed with time for different granularities.

Table 2. Common Kinetic Mechanism Function

function	$f(a)$	$G(a)$
$D_1(a)$	$1/2a^{-1}$	a^2
$D_2(a)$	$[-\ln(1-a)]^{-1}$	$(1-a)\ln(1-a) + a$
$D_3(a)$	$3/2(1-a)^{2/3}[1-(1-a)^{1/3}]^{-1}$	$[1-(1-a)^{1/3}]^2$
$D_4(a)$	$3/2[(1-a)^{-1/3} - 1]^{-1}$	$(1-2/3a) - (1-a)^{2/3}$
$F_1(a)$	$1-a$	$-\ln(1-a)$
$R_2(a)$	$2(1-a)^{1/2}$	$1-(1-a)^{1/2}$
$R_3(a)$	$3(1-a)^{2/3}$	$1-(1-a)^{1/3}$
$A_2(a)$	$2(1-a)[-\ln(1-a)]^{1/2}$	$[-\ln(1-a)]^{1/2}$
$A_3(a)$	$3(1-a)[-\ln(1-a)]^{2/3}$	$[-\ln(1-a)]^{1/3}$

pyrolysis is enough and concentrated. The change of the calorific value with time for different granularities is shown in Figure 9. It is found that the calorific values of synthesis gas with different granularities are almost equal. Therefore, the effect of coal granularities on the gasification reaction in molten BF slag is little. This gasification method has a strong adaptability to the coal granularities.

4. REACTION MECHANISM FUNCTION

The kinetic equation in the heterogeneous phase system is shown as eq 2.

$$\frac{da}{dt} = A \exp(-E/RT)f(a) \tag{2}$$

Sharp define that

$$G(a) = \int_0^a da/f(a) = \int_0^t A \exp(-E/RT)dt = kt$$

$$= \frac{G(a)_{a=0.5}}{G(a)_{a=1.0}} \left(\frac{t}{t_{0.5}} \right) \tag{3}$$

where A is the pre-exponential factor, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), E is the activation energy, and a is the carbon conversion rate.

From the comparison of the experimental and theoretical values, the reaction mechanism function will be found. Many researchers^{15,16} use this method to obtain the reaction mechanism and proof that the method is correct. The solid–gas reaction equations are shown in Table 2.

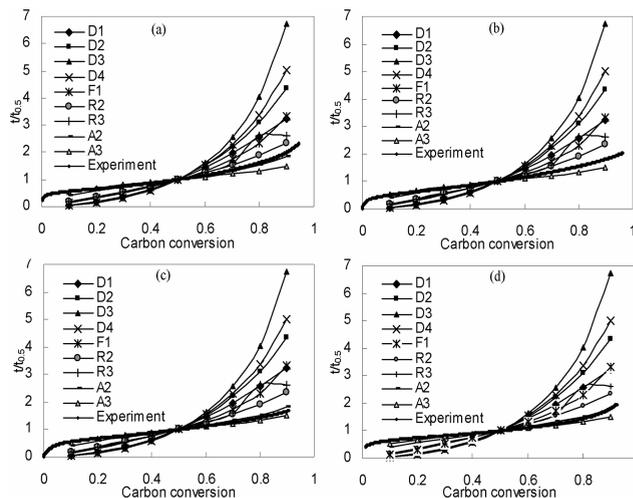


Figure 10. Comparison of the experimental and theoretical values of different kinetic mechanism functions for different coal samples and coal granularities: (a) DT coal, 0.125 mm; (b) DT coal, 0.147 mm; (c) DT coal, 0.177 mm; and (d) FX coal, 0.125 mm.

Figure 10 shows the comparison of the experimental and theoretical values of different kinetic mechanism functions for different coal samples and coal granularities. It is found that, when the carbon conversion rate is lower than 0.5, the experimental values almost equal the theoretical values of A_3 , and when the carbon conversion rate is higher than 0.5, the experiment values almost equal the theoretical values of A_2 . Therefore, it can be obtained that the kinetic mechanism function of coal gasification in molten BF slag is shown as follows:

$$f(a) = \begin{cases} 3(1-a)[-\ln(1-a)]^{2/3} & a \leq 0.5 \\ 2(1-a)[-\ln(1-a)]^{1/2} & a > 0.5 \end{cases} \tag{4}$$

5. CONCLUSION

Coal gasification in molten BF slag was performed at atmospheric pressure in a molten bath reactor at the temperature from 1573 to 1773 K. The effect of coal samples and coal granularities on the gasification reaction rate, carbon conversion, and gas composition was studied. The results are summarized as follows: (1) The reaction rate of SN coal that represented clunker coals was high and almost equal to the reaction rates of DT and FX coals. The H_2 content in synthesis gas using different types of coal increases in the order of DT coal < FX coal < SN coal, and the CO content in synthesis gas using different types of coal increases in the order of DT coal \approx SN coal < FX coal. The gasification with time increases with increasing the ash content. For this method, coal gasification in molten BF slag has wide adaptability on coal samples. It is especially good for clunker coals. (2) The peak value of reaction rates using different coal granularities increases in the order of $0.177 < 0.125 < 0.147 \text{ mm}$. The H_2 content of synthesis gas using different coal granularities increases in the order of $0.125 < 0.147 < 0.177 \text{ mm}$, and the CO content in synthesis gas using different coal granularities increases in the order of $0.125 \approx 0.147 \approx 0.177 \text{ mm}$. However, the difference is little, and all of their calorific values are almost equal. Therefore, this method has wide adaptability on coal granularities. (3) The kinetic mechanism

function was calculated. The mechanism function was shown as follows:

$$f(a) = \begin{cases} 3(1-a)[- \ln(1-a)]^{2/3} & a \leq 0.5 \\ 2(1-a)[- \ln(1-a)]^{1/2} & a > 0.5 \end{cases}$$

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■ REFERENCES

- (1) Akiyama, T.; Oikawa, K.; Shimada, T.; Kasai, E.; Yagi, J. *ISIJ Int.* **2000**, *40* (3), 286–291.
- (2) Purwanto, H.; Akiyama, T. *Curr. Adv. Mater. Processes* **2005**, *18*, 241–244.
- (3) Maruoka, N.; Akiyama, T. *Energy* **2006**, *31*, 1632–1642.
- (4) Kasai, E.; Kitajima, T.; Akiyama, T.; Yagi, J.; Saito, F. *ISIJ Int.* **1997**, *37* (10), 1031–1036.
- (5) Shimada, T.; Tominaga, H. *Fuel* **2006**, *85*, 170–178.
- (6) Shimada, T.; Kochura, V.; Akiyama, T.; Kasai, E.; Yagi, J. *ISIJ Int.* **2001**, *41* (2), 111–115.
- (7) Maruoka, N.; Mizuochi, T.; Purwanto, H.; Akiyama, T. *ISIJ Int.* **2004**, *44* (2), 257–262.
- (8) Purmanto, H.; Akiyama, T. *Int. J. Hydrogen Energy* **2006**, *31*, 491–495.
- (9) Shimizu, T.; Tominaga, H. *Fuel* **2006**, *85*, 170–178.
- (10) Bandyopadhyay, D.; Singh, S. D.; Sanyal, D.; Singh, K. K.; Singh, K. N. *Chem. Eng. J.* **2003**, *94*, 79–92.
- (11) Li, P.; Qin, Q.; Yu, Q.; Du, W. *Adv. Mater. Res.* **2010**, *97–101*, 2347–2351.
- (12) Elliott, M. A. *Chemistry of Coal Utilization*; Wiley: New York, 1981; Vol. 2.
- (13) Liu, H.; Kaneko, M.; Luo, C.; Kato, S.; Kojima, T. *Fuel* **2004**, *83*, 1055–1061.
- (14) Chen, H.; Luo, Z.; Yang, H.; Ju, F.; Zhang, S. *Energy Fuels* **2008**, *22*, 1136–1141.
- (15) Sun, Z.; Wu, J.; Zhang, D. *Energy Fuels* **2008**, *22*, 2160–2165.
- (16) Liu, H.; Luo, C.; Toyota, M.; Uemiya, S.; Kojima, T. *Fuel Process. Technol.* **2006**, *87*, 769–774.