

## Production of syngas from dry reforming of bio-oil model compound in granulated blast furnace slag

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**Abstract**—The characterization of dry (CO<sub>2</sub>) reforming of bio-oil model compound (BMC) in granulated BF (blast furnace) slag for syngas production is presented in this study. The effects of temperature, CO<sub>2</sub>/C (the molar ratio of CO<sub>2</sub> to C in the BMC), liquid hourly space velocity (LHSV) and granulated BF slag on the coke yield, combustible gas yield, syngas composition and lower heating value of the dry reforming process were investigated by fixed-bed experiments. The results indicated that using granulated BF slag as the heat carrier, temperature reaching 750 °C, CO<sub>2</sub>/C of 0.75 and LHSV of 0.45 h<sup>-1</sup> could be the optimal condition for the dry reforming process, where the combustible gas yield and lower heating value were up to 1.85 L/g and 23.00 kJ/g, respectively. Granulated BF slag showed positive effects on the dry reforming process, promoting the combustible gas yield and lower heating value and increasing the compositions of H<sub>2</sub> and CO. Granulated BF slag could be used as a superior heat carrier for the dry reforming of BMC.

Keywords: Syngas, Dry Reforming, Bio-oil Model Compound, Granulated Blast Furnace Slag, Heat Recovery

### INTRODUCTION

Currently, due to the shortage of fossil resources and environmental degradation, more attention is being paid to utilizing renewable and environmentally friendly energy resources. Biomass containing low nitrogen and sulfur, as a renewable and neutral CO<sub>2</sub> energy, has been regarded as one of the potential resources to replace fossil fuels [1-3]. Fast pyrolysis of biomass to produce bio-oil can overcome its disadvantages of low density and difficulties in storage and transportation; then, reforming of the obtained bio-oil is a potential method to utilize biomass [4]. The technology of biomass pyrolysis is fairly mature, and the obtained bio-oil yield is up to 70 wt% [5-7]. Thus, reforming of bio-oil to obtain syngas has been researched in recent years [8-12]. Compared to steam reforming, dry reforming can absorb a gasification agent (CO<sub>2</sub>) and produce syngas containing H<sub>2</sub> and CO, reducing the net greenhouse gas emissions, which has attracted attention [13-16]. Fu et al. [12] investigated the dry reforming of bio-oil model compound (BMC) using Ni/Al<sub>2</sub>O<sub>3</sub> as the catalyst, reporting that the conversion of BMC was 96.87% at 700 °C, CO<sub>2</sub>/bio-oil of 0.75 and weight hourly space velocity of 0.9 h<sup>-1</sup>. The dry reforming of bio-oil is an endothermic process in which temperature is higher than 700 °C. Thus, using an appropriate heat carrier to replace fossil fuels and electric energy to provide the heat for dry reforming of bio-oil is also a critical factor for its industrial production.

At present, the iron and steel industry is an energy-intensive and CO<sub>2</sub>-intensive industry that accounts for approximately 5% of

the world's energy consumption [17]. Energy conservation and emission reductions in the iron and steel industry will play a significant role in achieving sustainable development [18]. Blast furnace (BF) slag, as the by-product of smelting pig iron, is discharged at 1,550 °C, and its energy is approximately 1,700 MJ/t<sub>slag</sub> [19]. Because of its low thermal conductivity and easy crystallization behavior, molten BF slag is currently disposed of by a water quenching method to obtain a hard glassy slag, which is used as an industrial cement material. However, this process wastes the high calorific energy in the molten BF slag. It has been proven that the utilization of chemical reactions can efficiently recover the waste heat of molten BF slag [18, 20-24]. Molten BF slag disposed of by a rotary cup atomizer (RCA) to obtain granulated BF slag with a high glassy content is also regarded as one of the best methods to deal with molten slag, and it has been researched in recent years [25-29]. Due to the temperature of granulated BF slag obtained by the RCA reaching 1,100 °C, numerous chemical methods have been implemented to recover the heat of granulated BF slag [30-39]. Luo et al. [30] conducted an experiment of biomass steam gasification using granulated BF slag as the heat carrier, determining that granulated BF slag could improve the hydrogen yield and hydrogen composition in the syngas. Li et al. [31] applied coal gasification to recover the waste heat of granulated BF slag and showed that granulated BF slag could improve the coal char gasification reactivity index. Yao et al. [32-34] investigated the characterizations of biomass CO<sub>2</sub> gasification in granulated BF slag. Their results showed that granulated BF slag could decrease the activation energy of biomass char-CO<sub>2</sub> gasification and improve the gas yield and the lower heating value of biomass CO<sub>2</sub> gasification. Additionally, sludge gasification [35,36], pyrolysis of sludge [37] and biomass [38] and tire pyrolysis [39] for recovering the heat from granulated BF slag were investigated, demonstrating that granulated BF slag could weaken the C-H and C-C bonds and be beneficial to these endothermic chemical reac-

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**Table 1. The composition of BF slag**

BF slag	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Trace component
Mass%	34.38	41.21	8.22	11.05	2.78	0.35	2.01

tions.

After examining the characterizations of chemical reactions in granulated BF slag, utilizing chemical reaction of dry reforming of bio-oil to recover the waste heat of granulated BF slag was feasible, but it had not been previously researched. Before reforming of true bio-oil, reforming of BMC was necessary to master the fundamental reaction performance [9,12,40,41]. The characterizations of dry reforming of BMC in granulated BF slag were interesting and are presented in this study. The optimal condition was obtained to guide latter experiments of dry reforming of true bio-oil and identify the industrial application.

## EXPERIMENT

### 1. Materials

The bio-oil was a dark brown liquid whose composition was limited due to the biomass type and production process, but the primary components of the bio-oil were alcohols, acids, ketones and phenols [9]. Besides, a mixture of ethanol, acetic acid, acetone and phenol with the equal mass ratio could be regarded as the BMC [9,12,41], and it was used in this study. The chemical formula of the BMC was calculated as CH<sub>1.89</sub>O<sub>0.43</sub>. BF slag was supplied from an iron & steel company, and its composition is shown in Table 1. Granulated BF slag was obtained from molten slag by an RCA with the screened diameter lower than 2 mm. The mineral phase of granulated BF slag analyzed by X-ray diffractometry (XRD, Shimadzu XRD-7000) using Cu K<sub>α</sub> radiation is shown in Fig. 1.

### 2. Experimental Methods

A schematic diagram of the laboratory-scale apparatus is shown in Fig. 2. The experiments of dry reforming of BMC were carried

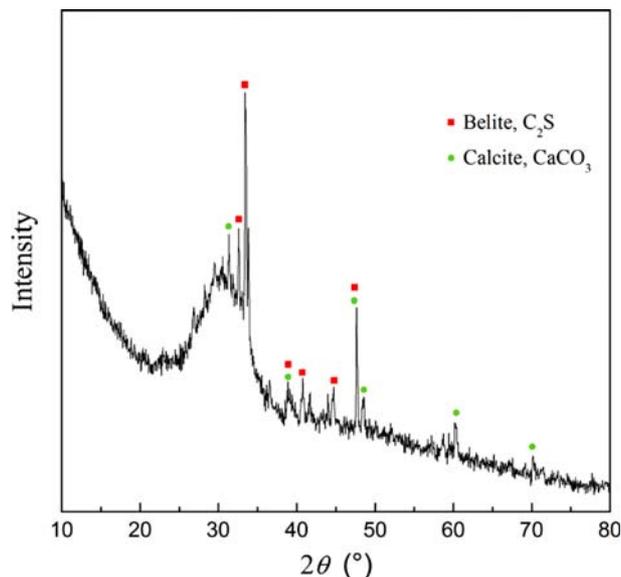


Fig. 1. The results of XRD spectrogram of granulated BF slag.

out in a fixed-bed reactor (height of 900 mm, inside diameter of 30 mm), to investigate the effects of the reaction temperature, molar ratio of CO<sub>2</sub> to C in the BMC (CO<sub>2</sub>/C), liquid hourly space velocity (LHSV) and granulated BF slag on the product distributions. The dry reforming reaction system contained a reaction system, a cooling system and an analysis system. The ceramic ball had no effects on the gasification and reforming reactions [30,42]. To investigate the effects of granulated BF slag on the dry reforming process, ceramic ball with a similar diameter was used as the blank heat carrier in our study. The detailed parameters of the apparatuses such as the electric furnace, gas meter and gas analyzer and the properties as densities and size distributions of the ceramic ball were provided in our previous studies [33,38]. To keep reaction temperature stabilization and balance, a heat carrier (granulated BF slag or ceramic ball) was placed in the middle tube with the height of 15 cm, and it was regarded as the packing bed height. After

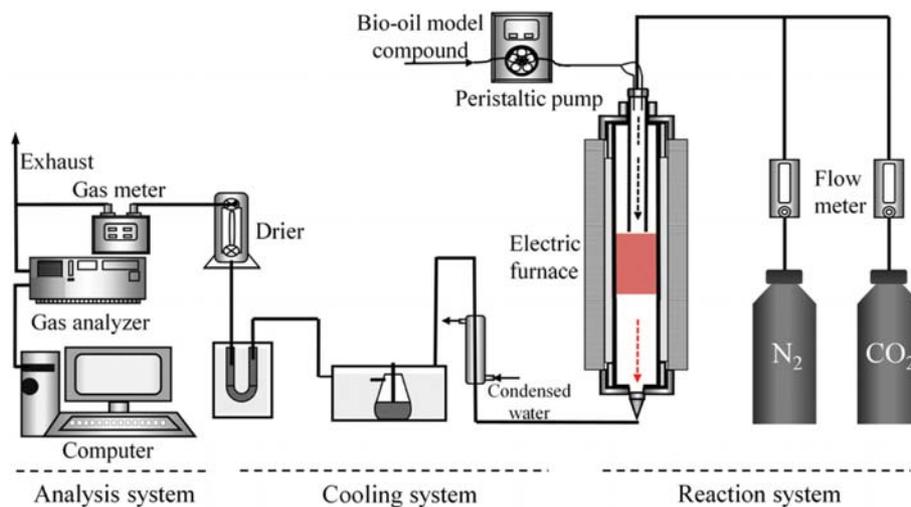


Fig. 2. A schematic diagram of experimental apparatus.

that, the packing bed was heated from room temperature to the desired temperature (600 °C, 650 °C, 700 °C, 750 °C, 800 °C) at a heating rate of 10 °C/min by the electric furnace. The desired temperature was held for 10 min. Then, the BMC and CO<sub>2</sub> whose volume was, respectively, controlled by a peristaltic pump and a flow meter were fed into the packing bed for 20 min. The LHSV and CO<sub>2</sub>/C varied with the BMC and CO<sub>2</sub> volume flow rates. The coke was calculated by the weight differentiation of heat carriers before and after the reaction. The syngas was cooled in the cooling system and analyzed in the analysis system. The syngas volume and composition were detected by a gas meter and a gas analyzer, respectively. The experimental data were gathered on-line by a computer until the syngas composition was equal to zero.

### 3. Data Analysis

The primary compositions of syngas from the dry reforming of BMC were H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> and the purpose of the research was to obtain high calorific value syngas. Thus, the coke yield, combustible gas yield, syngas composition and lower heating value were evaluated to obtain the optimal condition, and they were defined as follows.

The coke yield ( $Y_{Coke}$ , mg/g) was defined as the mass of coke produced by per gram of BMC and calculated by Eq. (1) as follows:

$$Y_{Coke} = \frac{\text{Mass of coke}}{\text{Mass of bio-oil model compound}} \quad (1)$$

The combustible gas yield ( $Y_{Combustible\ gas}$ , L/g) was defined as the total volumes of H<sub>2</sub>, CO and CO<sub>2</sub> produced by per gram of BMC and calculated by Eq. (2) as follows:

$$Y_{Combustible\ gas} = \frac{\text{Combustible syngas volume (H}_2 + \text{CO} + \text{CH}_4)}{\text{Mass of bio-oil model compound}} \quad (2)$$

The corresponding syngas composition ( $P_{H_2(CO, CO_2, CH_4)}$ , %) was defined as follows:

$$P_{H_2(CO, CO_2, CH_4)} = \frac{n_{H_2(CO, CO_2, CH_4)}}{n_{H_2} + n_{CO} + n_{CO_2} + n_{CH_4}} \times 100\% \quad (3)$$

where  $n_{H_2(CO, CO_2, CH_4)}$  is the whole mole of H<sub>2</sub>(CO, CO<sub>2</sub>, CH<sub>4</sub>) during the dry reforming process.

The lower heating value (LHV, kJ/g) was calculated by Eq. (3) as follows:

$$LHV = \left( 108.0 \frac{P_{H_2}}{P_{H_2} + P_{CO} + P_{CH_4}} + 126.4 \frac{P_{CO}}{P_{H_2} + P_{CO} + P_{CH_4}} + 358.2 \frac{P_{CH_4}}{P_{H_2} + P_{CO} + P_{CH_4}} \right) Y_{Combustible\ yield} \times 10^{-3} \quad (4)$$

The LHSV (h<sup>-1</sup>) of dry reforming of BMC was defined as follows:

$$LHSV = \frac{\text{Volumetric flow rate of bio-oil model compound}}{\text{Volume of heat carrier}} \quad (5)$$

## RESULTS AND DISCUSSION

### 1. Effects of Temperature

The endothermic process of dry reforming of BMC was seriously affected by temperature. Fig. 3 shows the effects of temperature on the coke and combustible gas yields with granulated BF

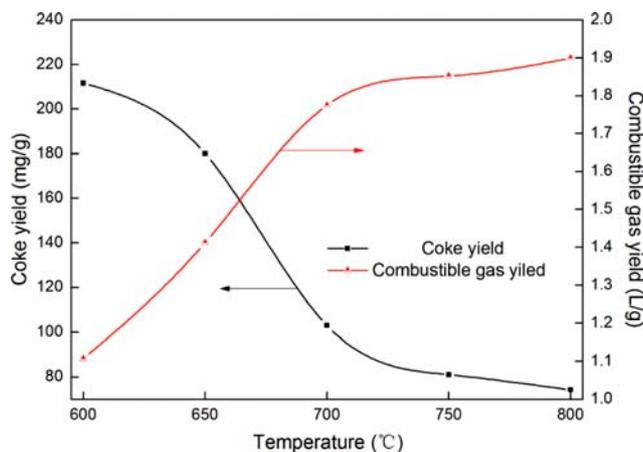


Fig. 3. The effects of temperature on the coke yield and combustible gas yield with granulated BF slag, a CO<sub>2</sub>/C of 0.75 and an LHSV of 0.45 h<sup>-1</sup>.

slag, a CO<sub>2</sub>/C of 0.75 and an LHSV of 0.45 h<sup>-1</sup>. As presented in Fig. 3, the higher temperature, the lower coke yield and the higher combustible gas yield were obtained. With the temperature increasing from 600 °C to 750 °C, the coke yield decreased rapidly from 211.70 mg/g to 81.02 mg/g, while the combustible gas yield increased rapidly from 1.11 L/g to 1.85 L/g. The increasing temperature could improve the endothermic decomposition reaction of BMC (Eq. (6)), the dry reforming reactions of BMC (Eqs. (7), (9), (10)) and the Boudouard reaction (Eq. (11)), decreasing the coke yield and increasing the combustible gas yield. When the temperature was higher than 750 °C, the variations in coke yield and combustible gas yield were not obvious, indicating that the endothermic process of dry reforming of BMC was almost complete at 750 °C.

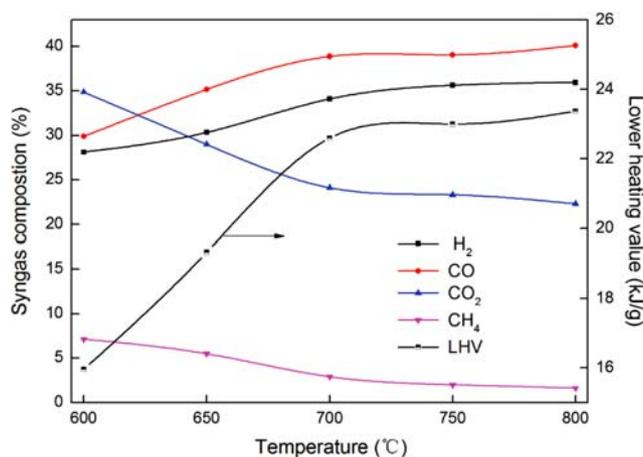
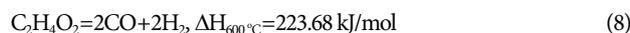
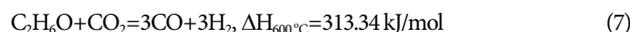


Fig. 4. The syngas composition and lower heating value under different temperature with granulated BF slag, a CO<sub>2</sub>/C of 0.75 and an LHSV of 0.45 h<sup>-1</sup>.

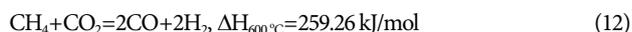
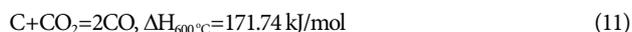
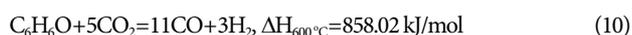
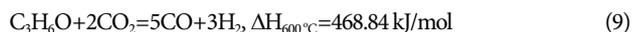


Fig. 4 shows the variations of syngas composition and LHV of dry reforming of BMC under different temperature with granulated BF slag, a  $\text{CO}_2/\text{C}$  of 0.75 and an LHSV of  $0.45 \text{ h}^{-1}$ . As presented in Fig. 4, the compositions of  $\text{H}_2$  and  $\text{CO}$  in the syngas increased from  $600^\circ\text{C}$  to  $750^\circ\text{C}$ , from 28.13% and 29.88% to 35.63% and 39.06%, respectively; then, there were no evident changes as the temperature increased from  $750^\circ\text{C}$  to  $800^\circ\text{C}$ , only up to 35.95% and 40.11%, respectively, when the temperature was  $800^\circ\text{C}$ . The compositions of  $\text{CO}_2$  and  $\text{CH}_4$  showed opposite trends compared to that of  $\text{H}_2$  and  $\text{CO}$ , and they were 23.31% and 2.01% respectively, when the temperature was  $750^\circ\text{C}$ . The increasing temperature was beneficial for the endothermic reactions (Eqs. (6)-(12)), increasing  $\text{H}_2$  and  $\text{CO}$  in the syngas. The Boudouard reaction (Eq. (11)) and the methane dry reforming reaction (Eq. (12)) were also promoted by the increasing temperature, which resulted in decreases in  $\text{CH}_4$  and  $\text{CO}_2$  in the syngas. Also shown in Fig. 4, the LHV increased rapidly from 15.96 kJ/g to 23.00 kJ/g as the temperature increased from  $600^\circ\text{C}$  to  $750^\circ\text{C}$ . The higher LHV was attributed to the increasing combustible gas and the compositions of  $\text{H}_2$  and  $\text{CO}$ . The change in LHV was not obvious as the temperature increased from  $750^\circ\text{C}$  to  $800^\circ\text{C}$ .

As a higher temperature, a higher combustible gas yield and

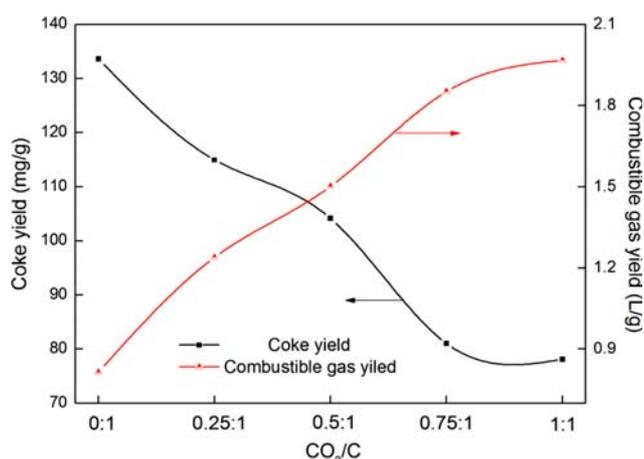


Fig. 5. The effects of  $\text{CO}_2/\text{C}$  on the coke yield and combustible gas yield with granulated BF slag and an LHSV of  $0.45 \text{ h}^{-1}$  at  $750^\circ\text{C}$ .

LHV were obtained. The combustible gas yield and LHV were approximated to maximum values at a temperature of  $750^\circ\text{C}$ . In addition, at a higher reaction temperature, there are stricter requirements for the equipment to be used in the industrial application. Considering all of these factors, the optimal temperature should be  $750^\circ\text{C}$ .

## 2. Effects of $\text{CO}_2/\text{C}$

It is well known that the gasification agent has significant effects on the dry reforming performance. Fig. 5 shows the effects of  $\text{CO}_2/\text{C}$  on the coke and combustible gas yields with granulated BF slag and an LHSV of  $0.45 \text{ h}^{-1}$  at  $750^\circ\text{C}$ . As presented in Fig. 5, the coke yield was lower but the combustible gas yield was higher with the gasification agent. With the  $\text{CO}_2/\text{C}$  increasing from 0 to 1, the coke yield decreased from 133.65 mg/g to 78.11 mg/g, while the combustible gas yield increased from 0.81 L/g to 1.97 L/g, respectively. When the  $\text{CO}_2/\text{C}$  was 0, decomposition reaction of BMC (Eq. (6)) could take place, obtaining a certain amount of coke. With a reforming agent ( $\text{CO}_2$ ), the coke yield was lower than that without a reforming agent. The higher the  $\text{CO}_2/\text{C}$ , the lower the coke yield obtained. These variations were mainly due to the Boudouard reaction (Eq. (11)). With reforming agent, the Boudouard reaction could take place, decreasing coke formation. Besides, according to the Le Chatelier's principle, the Boudouard reaction would shift to the right side with the increasing  $\text{CO}_2/\text{C}$ . Meanwhile, these reactions (Eqs. (7), (9)-(11)) would be accelerated by the increase in  $\text{CO}_2/\text{C}$ , increasing the combustible gas yield.

Fig. 6 shows the variations of syngas composition and LHV of dry reforming of BMC under different  $\text{CO}_2/\text{C}$  with granulated BF

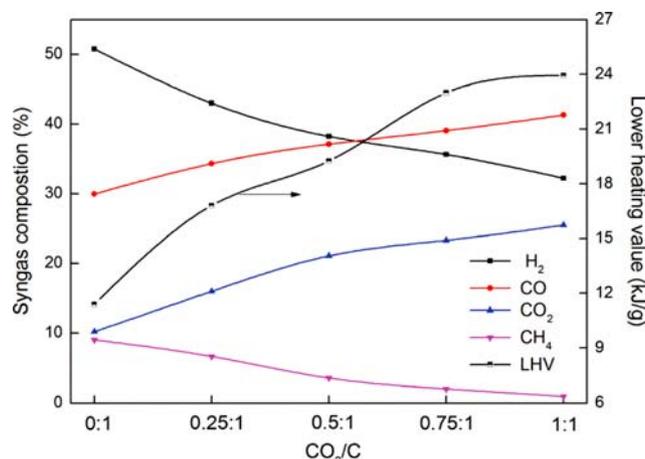


Fig. 6. The syngas composition and lower heating value under different  $\text{CO}_2/\text{C}$  with granulated BF slag and an LHSV of  $0.45 \text{ h}^{-1}$  at  $750^\circ\text{C}$ .

Table 2. The  $\text{H}_2$  yield,  $\text{CO}$  yield,  $\text{CH}_4$  yield and  $\text{CO}_2$  surplus under different  $\text{CO}_2/\text{C}$  with granulated BF slag and an LHSV of  $0.45 \text{ h}^{-1}$  at  $750^\circ\text{C}$

Syngas (g/L)	$\text{CO}_2/\text{C}=0$	$\text{CO}_2/\text{C}=0.25$	$\text{CO}_2/\text{C}=0.5$	$\text{CO}_2/\text{C}=0.75$	$\text{CO}_2/\text{C}=1$
$\text{H}_2$ yield	0.46	0.63	0.73	0.86	0.85
$\text{CO}$ yield	0.27	0.51	0.71	0.94	1.09
$\text{CH}_4$ yield	0.08	0.10	0.07	0.05	0.03
$\text{CO}_2$ surplus	0.09	0.24	0.40	0.56	0.67

slag and an LHSV of  $0.45 \text{ h}^{-1}$  at  $750^\circ\text{C}$ . As presented in Fig. 6, the compositions of CO and  $\text{CO}_2$  increased from 29.96% and 10.21% to 41.32% and 25.50% respectively, while these of  $\text{H}_2$  and  $\text{CH}_4$  decreased from 50.80% and 9.03% to 32.29% and 0.96% as the  $\text{CO}_2/\text{C}$  increased from 0 to 1. The  $\text{H}_2$  yield, CO yield,  $\text{CH}_4$  yield and  $\text{CO}_2$  surplus under different  $\text{CO}_2/\text{C}$  condition with granulated BF slag and an LHSV of  $0.45 \text{ h}^{-1}$  at  $750^\circ\text{C}$  is presented in Table 2. From Table 2, the  $\text{H}_2$  yield increased with the  $\text{CO}_2/\text{C}$  increasing from 0 to 0.75, then it was stable with the  $\text{CO}_2/\text{C}$  ranging from 0.75 to 1. When the  $\text{CO}_2/\text{C}$  increased from 0 to 0.75, dry reforming reactions (Eqs. (7), (9), (10), (12)) would shift to the right sides, increasing the  $\text{H}_2$  yield. When the  $\text{CO}_2/\text{C}$  reached 0.75, these dry reforming reactions were almost saturated, resulting in the increasing  $\text{CO}_2/\text{C}$  having little effects on the  $\text{H}_2$  yield. The increasing  $\text{CO}_2/\text{C}$  could be beneficial to the dry reforming reactions (Eqs. (7), (9), (10), (12)) and the Boudouard reaction (Eq. (11)), increasing the CO yield. Also from Table 2, the  $\text{CO}_2$  surplus increased with the increasing  $\text{CO}_2/\text{C}$  and the  $\text{CH}_4$  yield increased first then decreased with the increasing  $\text{CO}_2/\text{C}$ . As the  $\text{CO}_2/\text{C}$  increased, Boudouard reaction (Eqs. (11)) would be shifted to the right side, decreasing coke yield. The decreasing coke yield could be beneficial for the decomposition reaction (Eq. (6)), increasing the  $\text{CH}_4$  yield. Meanwhile, the increasing  $\text{CO}_2/\text{C}$  could be beneficial to the dry reforming reaction of  $\text{CH}_4$  (Eq. (12)), decreasing the  $\text{CH}_4$  yield. Though the  $\text{H}_2$  yield increased, then it was stable and the  $\text{CH}_4$  yield first increased then decreased with the increasing  $\text{CO}_2/\text{C}$ ; the CO yield and  $\text{CO}_2$  surplus had a large increase when the  $\text{CO}_2/\text{C}$  increased from 0 to 1. Thus, the compositions of  $\text{H}_2$  and  $\text{CH}_4$  decreased with the  $\text{CO}_2/\text{C}$ . As shown in Fig. 6, when the  $\text{CO}_2/\text{C}$  was below 0.75, the LHV of dry reforming of BMC increased obviously, but when the  $\text{CO}_2/\text{C}$  was at 0.75, the growth of LHV slowed with an increase in  $\text{CO}_2/\text{C}$ . These results were attributed to the increasing combustible gas yield and CO composition and decreasing  $\text{H}_2$  composition and  $\text{CH}_4$  composition in response to the increasing  $\text{CO}_2/\text{C}$ .

The higher the  $\text{CO}_2/\text{C}$ , the higher the combustible gas yield and LHV obtained, which was beneficial for industrial application. An increasing  $\text{CO}_2$  composition was obtained in response to the increase in  $\text{CO}_2/\text{C}$ , which might decrease the quality of the syngas. In addition, the higher is the  $\text{CO}_2/\text{C}$ , the more heat of granulated BF slag carried off during the practical production. When the  $\text{CO}_2/\text{C}$  was 0.75, the LHV was approximated to its maximum value. Considering all of the factors, the optimal  $\text{CO}_2/\text{C}$  for dry reforming of BMC was 0.75.

### 3. Effects of LHSV

It is well known that the LHSV has significant effects on the dry reforming performance. Fig. 7 shows the effects of LHSV on the coke and combustible gas yields with granulated BF slag and a  $\text{CO}_2/\text{C}$  of 0.75 at  $750^\circ\text{C}$ . As presented in Fig. 7, when the LHSV was lower than  $0.45 \text{ h}^{-1}$ , the variation of coke yield was not obvious in response to the increase in LHSV, and it only increased from 76.80 mg/g to 81.02 mg/g when the LHSV increased from  $0.15 \text{ h}^{-1}$  to  $0.45 \text{ h}^{-1}$ . When the LHSV was increased to  $0.6 \text{ h}^{-1}$ , the coke yield increased quickly up to 144.20 mg/g. The combustible gas yield showed an opposite trend compared to the coke yield, and it decreased to 1.69 L/g with an LHSV of  $0.6 \text{ h}^{-1}$ . The higher the LHSV, the more insufficient was the reaction, resulting in a higher

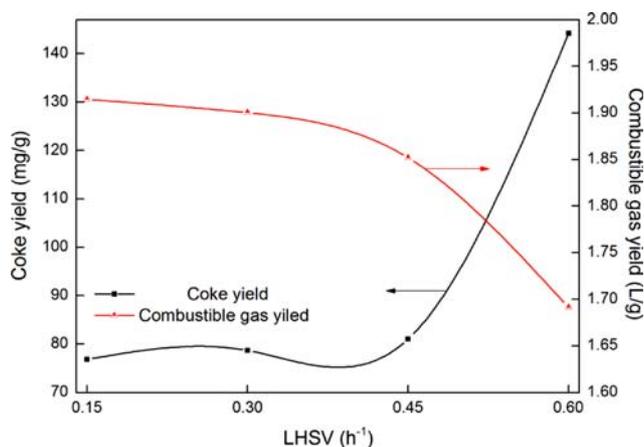


Fig. 7. The effects of LHSV on the coke yield and combustible gas yield with granulated BF slag and a  $\text{CO}_2/\text{C}$  of 0.75 at  $750^\circ\text{C}$ .

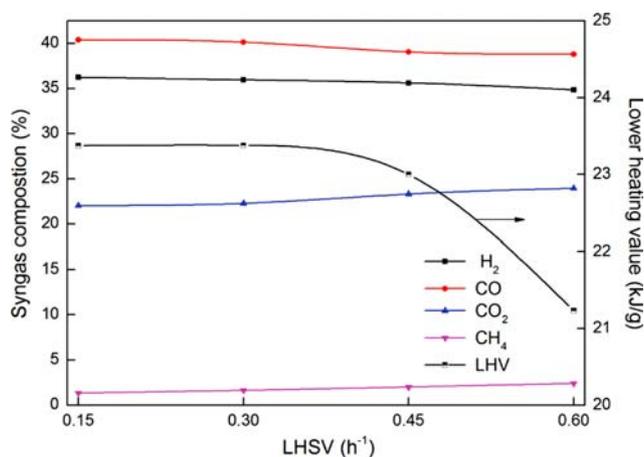


Fig. 8. The syngas composition and lower heating value under different LHSV with granulated BF slag and a  $\text{CO}_2/\text{C}$  of 0.75 at  $750^\circ\text{C}$ .

coke yield and lower combustible gas yield.

Fig. 8 shows the variations of syngas composition and LHV of dry reforming of BMC under different LHSV with granulated BF slag and a  $\text{CO}_2/\text{C}$  of  $0.45 \text{ h}^{-1}$  at  $750^\circ\text{C}$ . As presented in Fig. 8, the compositions of  $\text{H}_2$  and CO decreased, but the compositions of  $\text{CO}_2$  and  $\text{CH}_4$  increased with an increase in LHSV. The main reasons were as follows: the higher LHSV corresponding to the shorter reaction time for the dry reforming process (Eqs. (6)–(12)), caused the BMC to be converted incompletely, obtaining lower compositions of  $\text{H}_2$  and CO and higher compositions of  $\text{CO}_2$  and  $\text{CH}_4$ . Also shown in Fig. 8, when the LHSV was lower than  $0.45 \text{ h}^{-1}$ , the variation of LHV was not obvious with the increase in LHSV, but it decreased from 23.00 kJ/g to 21.23 kJ/g when the LHSV increased from  $0.45 \text{ h}^{-1}$  to  $0.6 \text{ h}^{-1}$ . The LHV defined in Eq. (4) depended on the syngas composition and combustible gas yield. Also from Fig. 8, the variation of syngas composition was not obvious compared to that of combustible gas yield. Thus, the variation of LHV was attributed to the variation of combustible gas yield.

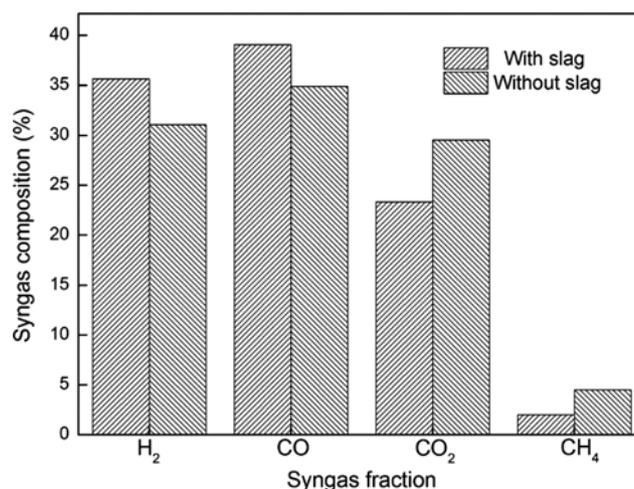
**Table 3. The effects of granulated BF slag on the coke yield, combustible gas yield and lower heating value with a  $\text{CO}_2/\text{C}$  of 0.75 and an LHSV of  $0.45 \text{ h}^{-1}$** 

Conditions		$Y_{\text{Coke}}$ (mg/g)	$Y_{\text{Combustible gas}}$ (L/g)	LHV (kJ/g)
750 °C	With BF slag	81.02	1.85	23.00
	Without BF slag	134.64	1.53	20.45

The higher the LHSV, the lower the combustible gas yield and LHV, but the higher handling capacity was obtained in the industrial production. Meanwhile, the combustible gas yield and LHV were approximated to their maximum values with an LHSV of  $0.45 \text{ h}^{-1}$ . Considering all of the factors, the optimal LHSV for dry reforming of BMC was  $0.45 \text{ h}^{-1}$ .

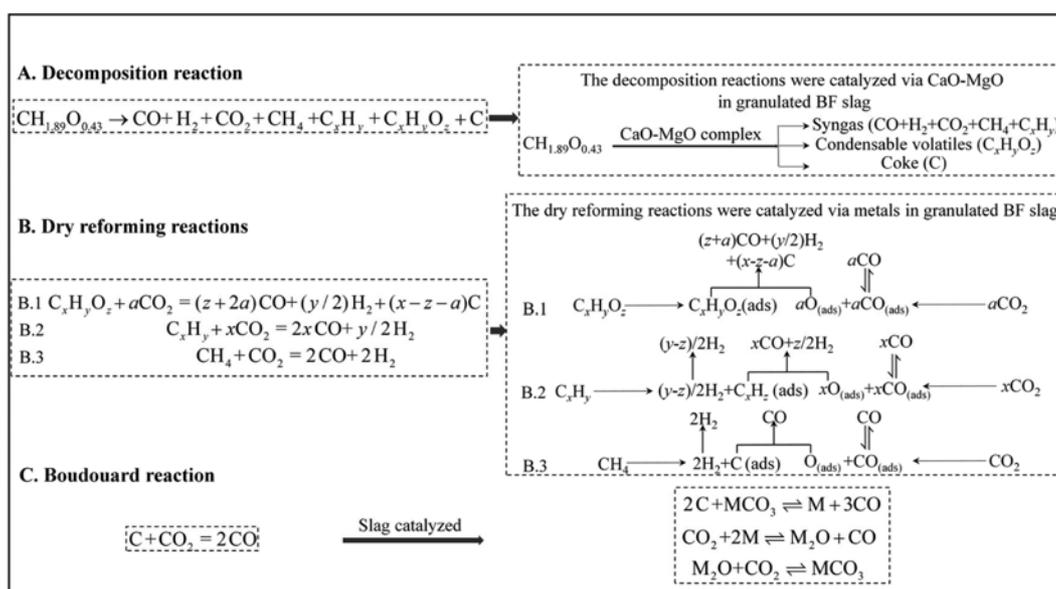
#### 4. Effects of Granulated BF Slag

To investigate the effects of granulated BF slag on the dry reforming reaction, a ceramic ball having little effect on the reforming reaction was used as the comparison heat carrier [30,33,38]. Meanwhile, using the ceramic ball as heat carrier was regarded as “without BF slag” in this paper. The coke yield, combustible gas yield and LHV at a  $\text{CO}_2/\text{C}$  of 0.75 and an LHSV of  $0.45 \text{ h}^{-1}$  with or without granulated BF slag at 750 °C are shown in Table 2. As presented in Table 3, granulated BF slag could promote the combustible gas yield, and LHV and decrease the coke yield to some degree. Fig. 9 shows the effects of granulated BF slag on the syngas composition of dry reforming of BMC with a  $\text{CO}_2/\text{C}$  of 0.75 and an LHSV of  $0.45 \text{ h}^{-1}$  at 750 °C. As presented in Fig 9, granulated BF slag could promote the compositions of  $\text{H}_2$  and CO and decrease the compositions of  $\text{CO}_2$  and  $\text{CH}_4$ . Thus, granulated BF slag could not only be used as a thermal medium but also as a catalyst for the reactions of dry reforming of BMC. During the dry reforming of BMC process, the primary reactions contained decomposition reaction, dry reforming reactions and Boudouard reaction. Granulated BF slag was composed of CaO-MgO complex, which


**Fig. 9. The effects of granulated BF slag on the syngas composition with a  $\text{CO}_2/\text{C}$  of 0.75 and an LHSV of  $0.45 \text{ h}^{-1}$  at 750 °C.**

could weaken C-C bond and speed up the hydrocarbon transformation into  $\text{H}_2$ , CO,  $\text{CO}_2$  and  $\text{CH}_4$  by some catalytic reactions [39]. Meanwhile, metals as Ca, Fe in granulated BF slag could catalyze the dry reforming reactions and Boudouard reaction [21,43–45]. Combining literature and experimental results, the mechanism of dry reforming of bio-oil model compound in granulated BF slag was established and presented in Fig. 10.

The characterizations of biomass steam gasification in BF slag indicated that BF slag could improve tar cracking and enhance char gasification [30]. The experiments of biomass pyrolysis within granulated BF slag demonstrated that granulated BF slag could decrease the bio-oil yield and promote the  $\text{H}_2$  concentration [38]. It was also proven that BF slag could catalyze the Boudouard reaction (Eq. (11)) [32,34] and dry reforming reaction of methane (Eq. (12)) [46] by kinetic mechanisms, decreasing the corresponding reaction activation energies. These results are consistent with our researches.


**Fig. 10. The integrated catalytic mechanism of dry reforming of bio-oil model compound in granulated BF slag.**

## CONCLUSION

Syngas production from dry reforming of BMC in granulated BF slag was investigated. The primary findings are as follows.

(1) With an increase in temperature, the coke yield decreased, but the gas yield and LHV increased. Above 750 °C, these increases were not obvious. The LHV was approximated to the maximum value with a CO<sub>2</sub>/C of 0.75. When the LHSV was higher than 0.45 h<sup>-1</sup>, the combustible gas yield and lower heating value decreased quickly with an increase in LHSV. The optimal condition of dry reforming of BMC in granulated BF slag is thus a temperature reaching 750 °C, CO<sub>2</sub>/C of 0.75 and LHSV of 0.45 h<sup>-1</sup>.

(2) Compared with ceramic ball as the blank heat carrier, granulated BF slag could decrease the coke yield and improve the combustible gas yield and LHV of the dry reforming process. Meanwhile, the compositions of H<sub>2</sub> and CO were higher using granulated BF slag than that using ceramic ball as heat carrier. Granulated BF slag could therefore be used not only as a heat carrier and a medium, but also as a catalyst for the dry reforming process.

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