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Thermodynamics of Hydrogen Production from Steam Reforming of Tar Model Compound with Blast Furnace Slag

Xin Yao[1], Qingbo Yu[1*], Guowei Xu[1], Huaqing Xie[1] and Qin Qin[1]

[1] School of Metallurgy, Northeastern University, Shenyang, Liaoning 110819, China

[*]Corresponding author's e-mail: yuqb@smm.neu.edu.cn

Abstract. A novel method combining steam reforming of tar for hydrogen production and recovery waste heat of BF (blast furnace) slag was proposed. The thermodynamic characterizations of steam reforming of tar model compound with BF slag were obtained via Gibbs minimization approach. The effects of temperature, S/C (the mole ratio of steam to carbon in the tar model compound) and BF slag on the process of steam reforming were illuminated. With BF slag, the hydrogen yield first increased then decreased with the increasing temperature and it reached the maximum value with the temperature of 590℃. The hydrogen yield increased with the increasing S/C and the optimal S/C was 7 for industry application. At the optimal condition, the hydrogen yield reached 25.98 moles per mole of tar model compound. BF slag could promote the hydrogen yield at the optimal condition, which was regarded as a promising heat carrier for the steam reforming process.

1. Introduction

Coal gasification and pyrolysis to produce syngas are regarded as a promoting method to promote the cold-gas efficiency and save the maintenance cost [1]. While, coal tar will be generated from the gasification and pyrolysis process, which may block and corrode pipeline in the industry production. The coal tar containing carbon and hydrogen elements, is gathered and disposed via steam reforming to produce hydrogen [2]. In recent years, some researchers have investigated the catalysts on the tar steam reforming to promote hydrogen yield and hydrogen composition [2, 3]. However, it is uneconomical using fossil fuel to provide heat for the steam reforming process.

On the other side, BF (blast furnace) slag as a byproduct of ironmaking process is discharged at 1550℃ [4]. The molten BF slag is disposed via water quenching method in the industry application to overcome its characterizations of low thermal conductivity and crystallization behavior. The cooling BF slag is used as the raw material of cement industry, but this process wastes the high grade energy of BF slag. Kasai et al. [5] proved that it was feasible using chemical methods to recover the waste heat of BF slag. Luo et al. [6] used biomass steam gasification recovering the waste heat of BF slag to produce syngas. Li [7, 8] and Duan [9-11] researched the characteristics of coal gasification in BF slag. Besides, municipal solid waste gasification [12], sludge gasification [13, 14] and tire pyrolysis [15] using BF slag as heat carrier had been investigated. The results implied that these chemical methods could efficiently utilize the high grade waste heat of BF slag.

Therefore, tar steam reforming recovering waste heat of BF slag was feasible and was proposed in this study. Besides, the composition of tar from coal gasification and pyrolysis was so complex, thus a tar model compound was used in the calculation process. The equilibrium productions were obtained via minimum Gibbs free energy approach to evaluate the effects of temperature, S/C (the mole ratio of steam to carbon in the tar model compound) and BF slag on the process of steam reforming for hydrogen

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production.

2. Methodology

2.1. Materials

BF slag from an iron and steel company containing 42.11% CaO, 8.22% MgO, 34.38% SiO_2, 11.05% Al_2O_3, 2.78% Fe_2O_3 and other minor oxides was used as the slag material. Besides, 1-methylnaphthalene ($C_{11}H_{10}$) could decompose naphthalene and benzene at high temperature, which was used as the tar model compound in this numerical calculation [16]. The mass ratio of BF slag to $C_{11}H_{10}$ was 10.

2.2. Thermodynamic analysis

The equilibrium production of steam reforming of tar model compound with or without BF slag was obtained via Gibbs minimization approach using HSC 6.0 software and its principle was shown as follows [17]:

The total of Gibbs free energy (G) of steam reforming process could be obtained as follow.

$$G=\sum_{\mathrm{i}=1}^{N} n_{\mathrm{i}}\mu_{\mathrm{i}}\text{, i=1, 2, 3, ……, } N \tag{1}$$

Where, n_i was the amount of substance of i_{th} matter specie and μ_i was the corresponding chemical potential.

The minimum Gibbs free energy was obtained with the reactions reaching balance. Then, an appropriate n_i was obtained via the Lagrange multiplier [18].

$$\sum_{\mathrm{i}=1}^{N} a_{\mathrm{ij}}n_{\mathrm{i}}=A_{\mathrm{j}}\text{, j=1, 2, 3, ……, } M \tag{2}$$

Where, a_{ij}, A_j and M were the number of j_{th} element in i_{th} matter specie, the number of j_{th} element during the process and the number of atom specie present during the process, respectively.

Meanwhile, the principle of Lagrange multiplier was shown as follow.

$$L=\sum_{\mathrm{i}=1}^{N} n_{\mathrm{i}}\mu_{\mathrm{i}}-\sum_{\mathrm{j}=\mathrm{i}}^{M}\lambda_{\mathrm{j}}\left(\sum_{\mathrm{i}=1}^{N}(a_{\mathrm{ij}}n_{\mathrm{i}}-A_{\mathrm{j}})\right) \tag{3}$$

Where, λ_j represented the Lagrange multiplier of j_{th} element during the process. To obtain equilibrium production, the Eq. (3) could be translated into Eq. (4) as follow.

$$\frac{\partial \mathrm{L}}{\partial n_{\mathrm{i}}}=\mu_{\mathrm{i}}-\sum_{\mathrm{j}=1}^{M}\lambda_{\mathrm{j}}a_{\mathrm{ji}}=0 \tag{4}$$

2.3. Process of steam reforming and evaluation

During the process of steam reforming of tar model compound with BF slag, the following reactions might occur and its characterizations were shown as follows:

Thermal cracking reaction

$$\mathrm{C_{11}H_{10}\rightarrow C_{\mathit{x}}H_{\mathit{y}}+\mathit{o}H_2+\mathit{p}CO+\mathit{q}CO_2+\mathit{r}CH_4+\mathit{s}C},\ \Delta\mathrm{H}^{\theta}_{800℃}>0 \tag{5}$$

Hydrodealkylation

$$\mathrm{C_{11}H_{10}+H_2\rightarrow C_{10}O_8+CH_4},\ \Delta\mathrm{H}^{\theta}_{800℃}=-53.89\ \mathrm{kJ/mol} \tag{6}$$

Steam reforming reactions

$$\mathrm{C_{\mathit{x}}H_y+2\mathit{x}H_2O\rightarrow \mathit{x}CO_2+(2\mathit{x}+\mathit{y}/2)H_2},\ \Delta\mathrm{H}^{\theta}_{800℃}>0 \tag{7}$$

$$\mathrm{C_{10}H_8+4H_2O\rightarrow C_6H_6+4CO+5H_2},\ \Delta\mathrm{H}^{\theta}_{800℃}=478.64\ \mathrm{kJ/mol} \tag{8}$$

$$\mathrm{C_6H_6+6H_2O\rightarrow 6CO+9H_2},\ \Delta\mathrm{H}^{\theta}_{800℃}=751.58\ \mathrm{kJ/mol} \tag{9}$$

$$\mathrm{CH_4+2H_2O\rightarrow CO_2+4H_2},\ \Delta\mathrm{H}^{\theta}_{800℃}=191.10\ \mathrm{kJ/mol} \tag{10}$$

Water gas reaction

$$\mathrm{C+H_2O\rightarrow CO+H_2},\ \Delta\mathrm{H}^{\theta}_{800℃}=135.77\ \mathrm{kJ/mol} \tag{11}$$

Water gas shift reaction

$$CO + H_2O \rightarrow H_2 + CO_2,\ \Delta H^{\theta}_{800℃} = -34.12\ \text{kJ/mol} \tag{12}$$

Reactions of CaO with CO_2

$$CaO + CO_2 \rightarrow CaCO_3,\ \Delta H^{\theta}_{800℃} = -167.62\ \text{kJ/mol} \tag{13}$$

The gas concentration ($P_{H_2(CO,CO_2,CH_4)}$, %) was obtained via Eq. (14).

$$P_{H_2(CO,CO_2,CH_4)} = \frac{n_{H_2}(n_{CO}, n_{CO_2}, n_{CH_4})}{n_{H_2} + n_{CO} + n_{CO_2} + n_{CH_4}} \times 100\% \tag{14}$$

Where, $n_{H_2}(n_{CO}, n_{CO_2}, n_{CH_4})$ was the mole of H_2 (CO, CO_2, CH_4) in the syngas.

3. Results and discussions

3.1. Effects of temperature

Figure 1 shows the effects of temperature on the production yield and syngas composition during the steam reforming of tar model compound with BF slag from 400℃ to 1000℃ at the S/C of 7. From Figure 1(a), the yields of H_2 and CO_2 increased first then decreased with the increasing temperature. The CO yield increased but the CH_4 yield decreased with the increasing temperature. As the temperature increased, the endothermic reactions (Eqs. (5, 7-10, 11)) would shift to the right side, increasing the yields of H_2, CO and CO_2. While, the exothermic reaction (Eq. (12)) would shift to the left side, decreasing the yields of H_2 and CO_2. The decreasing CH_4 yield was mainly due to the methane steam reforming reaction (Eq. (10)) shifting to the right side with the increasing temperature. From Figure 1(b), the trend of syngas composition was similar to that of corresponding yield. It could also be obtained from Figure 1(a) that the maximum H_2 yield was obtained with the temperature of 590℃, which reached 25.98 mole per mole of $C_{11}H_{10}$. Meanwhile, it was obtained from Figure 1(b) that the H_2 composition reached 93.54% when the temperature was 590℃, which was closed to its maximum value. Thus, 590℃ was regarded as the optimal temperature when steam reforming of tar model compound with BF slag.

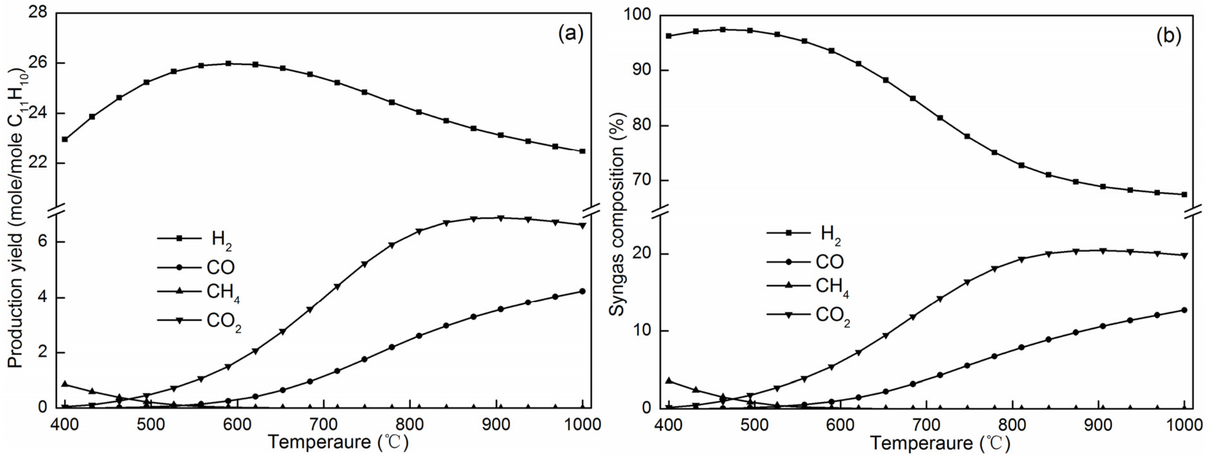

Figure 1. The effects of temperature on the production yield and syngas composition during the steam reforming of tar model compound with BF slag at the S/C of 7

3.2. Effects of S/C

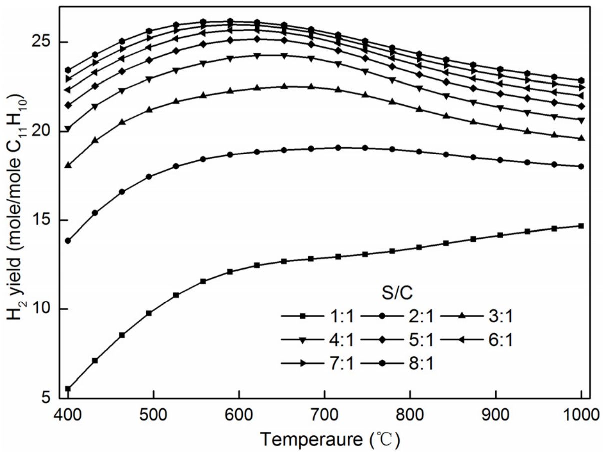

Figure 2. The effects of S/C on the H_2 yield during the steam reforming of tar model compound with BF slag

Figure 2 shows the effects of S/C on the H_2 yield during the steam reforming of tar model compound with BF slag. From Figure 2, with the temperature ranging from 400°C to 1000°C, the H_2 yield increased with the increasing S/C. As the S/C increased, the steam reforming reactions (Eqs. (7-10)) would shift to the right side, increasing the H_2 yield. While, when the S/C reached 7, the variation of H_2 yield was not obvious with the increasing S/C. Taking the temperature of 590°C for example, the H_2 yield was 25.98 mole per mole of $C_{11}H_{10}$ at S/C of 7, but it was only up to 26.17 mole per mole of $C_{11}H_{10}$ with the S/C reaching 8. Besides, the higher S/C, the more heat of BF slag would be carried out from the industrial application, which was adverse to the process of steam reforming of tar model compound. Considering all the factors, the S/C of 7 was regarded as the optimal condition for the process of tar steam reforming.

3.3. Effects of BF slag

The production yield during the steam reforming of tar model compound at the S/C of 7 with and without BF slag is shown in Figure 3. It could be obtained from Figure 3 that BF slag could promote the H_2 yield and decreased the yields of CO, CO_2 and CH_4 with the temperature lower than 840°C. For example, at temperature of 590°C and S/C of 7, BF slag could promote the H_2 yield from 24.97 mole per mole of $C_{11}H_{10}$ to 25.98 mole per mole of $C_{11}H_{10}$. It was because that BF slag containing 41.21% CaO, which absorbed CO_2 via Eq. (13), could promote the steam reforming reactions (Eqs. (7, 10)) and the water gas shift reaction (Eq. (12)), increasing the H_2 yield and decreasing the yields of CO and CH_4. Luo et al. [19] had proven that BF slag could improve tar cracking during the biomass pyrolysis process, whose results were similar with ours. Thus, BF slag not only provided heat but also was beneficial to the steam reforming of tar model compound, which was regarded as a promising heat carrier for the steam reforming process.

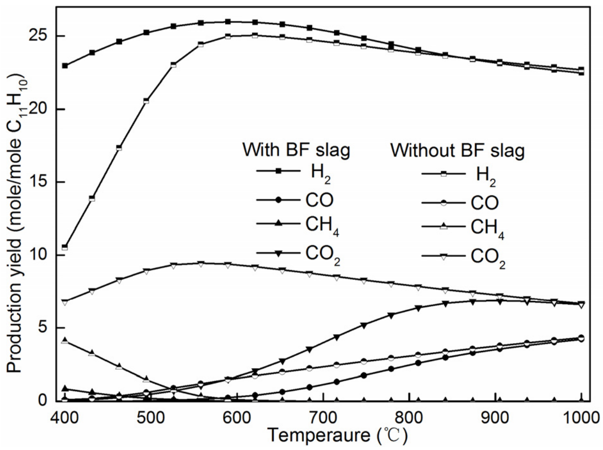

Figure 3. The effects of BF slag on the production yield during the steam reforming of tar model compound at the S/C of 7

4. Conclusion

In this paper, 1-methylnaphthalene ($C_{11}H_{10}$) was used as the tar model compound and the equilibrium production of steam reforming of tar model compound was calculated via Gibbs minimization approach to evaluate the effects of temperature, S/C and BF slag on the process of steam reforming for hydrogen production. The temperature of 590℃ and S/C of 7 was regarded as the optimal condition of steam reforming of tar model compound, where hydrogen yield reached 25.98 moles per mole of $C_{11}H_{10}$. With the temperature lower than 840℃, the hydrogen yield was higher with BF slag than that without BF slag, implying that BF slag not only provided heat but also was beneficial to the steam reforming process.

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