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Thermodynamic Analysis of Hydrogen Production via Steam Reforming of Bio-oil with Blast Furnace Slag

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Thermodynamic Analysis of Hydrogen Production via Steam Reforming of Bio-oil with Blast Furnace Slag

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Abstract. Steam reforming (SR) of bio-oil with blast furnace (BF) slag was investigated via thermodynamic analysis in this paper. As the temperature and S/C ratio (the mole ratio of steam to carbon in the bio-oil) rose, the hydrogen yield first increased rapidly and then flattened out, and under the temperature of 700℃ and S/C of 6:1, the hydrogen yield can reach 86%. Under the above conditions, the slag and its amount hardly have any effect on the products of bio-oil SR, but it can provide the heat that the strongly endothermic SR process need. To ensure the SR reaction under the above condition, the B/S ratio (the mass ratio of bio-oil to BF slag) should be controlled at 1:5.27.

1. Introduction

Hydrogen is a clean and green energy, and also an important raw material widely used in the production of chemicals and power generation [1]. Hydrogen production from renewable bio-based feedstock is recognized as one of the ideal environmentally options to replace non-renewable fossil fuel, according to its abundant reserves and neutral CO_2 emissions [2]. Various technical pathways can be applied for hydrogen production from biomass, i.e. pyrolysis, gasification, fermentation, high-pressure supercritical conversion, anaerobic digestion, metabolic processing [3]. Steam reforming (SR) of bio-oil from the fairly mature pyrolysis with the bio-oil yield of 70-80%, is known as one of the most promising and economically viable methods for hydrogen production [1, 4]. Steam reforming of bio-oil is beneficial to both hydrogen yield and bio-oil conversion, and thus has widely been investigated in the past few years [5-10]. These investigations mainly focused on the developments of high-performance reforming catalysts to improve the hydrogen yield, but few concerned on the heat demand of the SR process, which was a highly endothermic reaction.

Blast furnace (BF) slag as a byproduct of ironmaking process, is discharged at 1450-1550 ℃ [11]. In 2017, China charged about 2.13 million tons of BF slags. However, the molten BF slag currently is mainly disposed via water quenching, causing the huge amount of sensible heat wasted. Kasai et al. [12] proved firstly that it was feasible to recover the waste heat of BF slag using chemical methods. Li [13-14] and Duan [15-16] performed the coal gasification within BF slag, and found that the slag not only provide heat for the gasification but also on some case had a catalytic effect on this reaction. Besides, municipal solid waste gasification [17], sludge gasification [18] and tire pyrolysis [19], with BF slag as heat carrier, had also been investigated, and all the results implied that these chemical methods could efficiently utilize the waste heat of BF slag.

Therefore, steam reforming of bio-oil for hydrogen production with BF slag as heat carrier was proposed and investigated via thermodynamic analysis in this paper. The effects of temperature, S/C ratio (the mole ratio of steam to carbon in the bio-oil) and B/S ratio (the mass ratio of bio-oil to BF slag) on the process of steam reforming for hydrogen production were performed. And, the energy
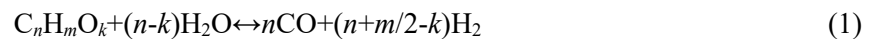
balance question also was involved.

2. Methodology

2.1. Materials
BF slag from an iron and steel company, containing 42.73 wt% CaO, 8.34 wt% MgO, 34.89 wt% SiO_2, 11.21 wt% Al_2O_3, 2.82 wt% Fe_2O_3 with other minor oxides neglected, was used in this paper. Besides, the bio-oil was represented by a mixture of typical compounds (15 mol% acetic acid, acetone, 15 mol% acetaldehyde, 15 mol% glycol, 15 mol% formic acid, 10 mol% methanol, 10 mol% formaldehyde, 5 mol% ethanol), according to the literature [1]. Their SR reactions can be expressed using Eq. (1) (bio-oil components represented as $C_nH_mO_k$), following the water gas shift reaction (WGS, Eq. (2)).

$$C_nH_mO_k+(n-k)H_2O\leftrightarrow nCO+(n+m/2-k)H_2 \tag{1}$$

$$CO+H_2O\leftrightarrow CO_2+H_2 \tag{2}$$

2.2. Process evaluation
The equilibrium production of steam reforming of bio-oil model compound with or without BF slag was obtained via Gibbs minimization approach using HSC software. Then, the energy balance calculations were carried out, with given mass-balances as the boundary conditions. In order to study the SR process, the following parameters (hydrogen yield, Y_{H2} and yields of the carbonaceous products) were discussed.

$$Y_{H2} = \frac{\text{moles of } H_2 \text{ in the reformed gas}}{\text{moles of theoretical obtained } H_2}\times 100\% \tag{3}$$

where the moles of theoretical obtained H_2 was the moles of H_2 obtained when all the compositions of bio-oil were reformed completely.

$$Y_i = \frac{\text{moles of } i \text{ in the reformed products}}{\text{moles of C in bio-oil}}\times 100\% \tag{4}$$

where i represented CO, CH_4, CO_2 and coke in the reformed products, respectively.

3. Results and discussions

3.1. Effects of temperature
Figure 1 shows the effect of temperature on the SR of bio-oil. Low temperature was not favorable to the endothermic SR reactions, but conversely accelerated some side reactions, such as decomposition reactions, causing the higher yields of coke and CH_4, among which especially the coke yield can reach 70% around. As the temperature and S/C ratio rose, the SR reactions was gradually to be initiative, resulting in H_2 yield improved rapidly, while the yield of coke and CH_4 were gradually decreased. CH_4 was almost not produced any more when the temperature was higher than about 600 ℃, and the coke yield was decreased to below 7% when the temperature was higher than about 700 ℃. However, H_2 yield reached 86% around and flattened out after 700 ℃, and even decreased slightly with the further increase of temperature, mainly attributed to the exothermic WGS reaction inhibited. This also can explain the decrease of CO_2 and the increase of CO with almost the same rate at higher temperature.

$$CaO+CO_2\leftrightarrow CaCO_3 \tag{5}$$

From Figure 1, the addition of BF slag had an enhancement for the SR process under low temperature range, with the increases of H_2 yield and CO_2 yield, the decreases of coke yield and CH_4

yield compared to the case without slag. It was because that CaO in BF slag adsorbed CO_2 from the WGS reaction via the carbonation reaction (Eq. (5)), and then the equilibriums of the WGS and SR reactions were displaced to higher H_2 production. But the enhancement was very slight. Under high temperature range, due to exothermic carbonation reaction, $CaCO_3$ was not formed any more, and thus the addition of BF slag has almost no effect on the yield of the products from the SR process of bio-oil, with the product curves almost coincided for both of the cases without and with BF slag.
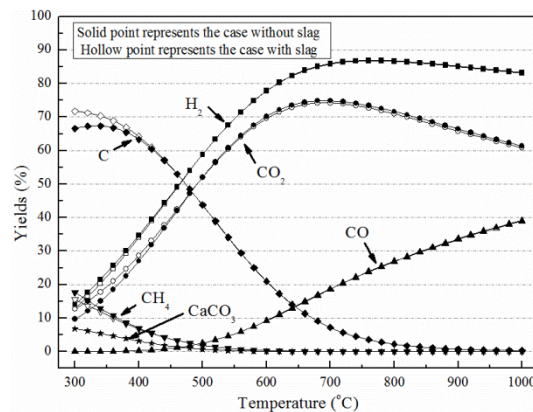

Figure 1. The effect of temperature on the SR of bio-oil without and with BF slag at the S/C ratio of 6:1 and B/S ratio of 1:1

3.2. Effects of S/C ratio

Figure 2 shows the effect of S/C ratio on the SR of bio-oil. As the S/C ratio increased, the SR reactions and WGS reaction were accelerated, resulting in the improvement of H_2 yield and the decreases of CO, coke and CH_4. What's more, as the S/C ratio increased, the temperature corresponding to the maximum H_2 yield and the temperatures at which coke and CH_4 just vanished moved to low temperature. However, after the S/C ratio reached 6:1, the above changes were tiny, indicating that increasing blindly steam amount for hydrogen production is economically inadvisable.
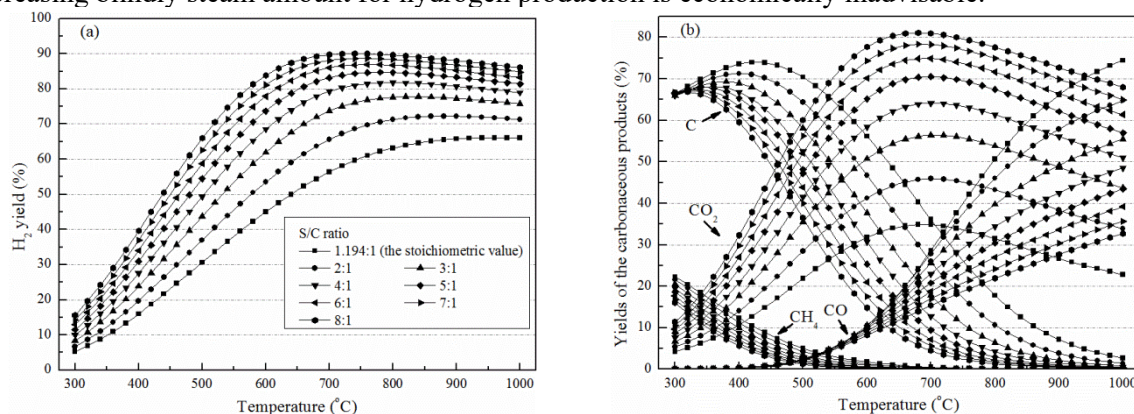

Figure 2. The effect of S/C ratio on the SR of bio-oil at B/S ratio of 1:1
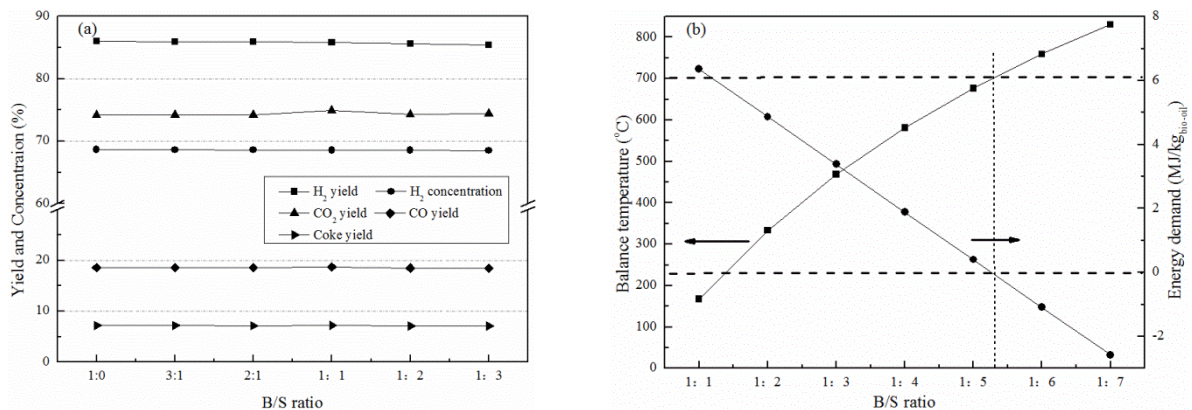
3.3. Effects of B/S ratio

Figure 3. The effect of B/S ratio on the SR of bio-oil at S/C ratio of 6:1 and 700 °C

From above, the optimum reaction conditions for SR of bio-oil were the temperature of 700 °C and the S/C ratio of 6:1. Under the condition, the effect of B/S ratio on the SR of bio-oil was conducted, and the results were shown in Figure 3. From Figure 3(a), the BF slag amount had almost no effect on the SR products. However, the result was just based on thermodynamics, and in the practical trial, certain compounds in the slag, such as Fe and Mg, maybe have catalytic effects on the SR reaction.

Although the BF slag had hardly any enhancement on the hydrogen production from steam reforming of bio-oil, it can provide the heat that the SR process need. In this part, the heat balance of the reaction system with BF slag was calculated, and the initial temperatures of BF slag, steam and bio-oil were set as 1450 °C, 200 °C and 25 °C. When the added slag amount was inadequate, extra energy was demanded into the reaction system and the balance temperature was lower than 700 °C (seen in Figure 3(b)). To control the SR reaction temperature at 700 °C, the B/S ratio should be set as 1:5.27, which was calculated via the following linear equation (Eq. (6)) with the correlation coefficient of 1.

$$T = -0.0112x^5 + 0.1436x^4 + 0.4593x^3 - 20.496x^2 + 222.47x - 35.371 \qquad (6)$$

where, T and x were represented as the balance temperature and the reciprocal of the B/S ratio, respectively.

4. Conclusion

In this paper, steam reforming of bio-oil with BF slag as heat carrier was investigated via thermodynamic analysis. The BF slag had some enhancement for the hydrogen production from SR of bio-oil at low temperature, yet the H_2 yield was obviously lower than that at high temperature, and had almost no effect for the SR reaction at high temperature. The temperature of 700 °C and the S/C of 6:1 were regarded as the optimal condition for steam reforming of bio-oil, where hydrogen yield reached 86%. Although the slag and its amount hardly have any effect on the products of bio-oil SR, it can provide the heat to the SR process. To ensure the SR reaction under the optimal condition, the B/S ratio should be controlled at 1:5.27 at least.

References

[1] Xie, H., Yu, Q., Lu, H., Zhang, Y., Zhang, J., Qin, Q. (2017) Thermodynamic study for hydrogen production from bio-oil via sorption-enhanced steam reforming: Comparison with conventional steam reforming. Int. J. Hydrogen Energy, 42: 28718-28731.

[2] Xie, H., Yu, Q., Zuo, Z., Han, Z., Yao, X., Qin, Q. (2016) Hydrogen production via sorption-enhanced catalytic steam reforming of bio-oil. Int. J. Hydrogen Energy, 41(4):2345-2353.

[3] Ni, M., Leung, D., Leung, M., Sumathy, K. (2006) An overview of hydrogen production from biomass. Fuel Process. Technol., 87(5): 461-472.

[4] Authayanun, S., Saebea, D., Patcharavorachot, Y., Assabumrungrat, S., Arpornwichanop, A. (2017) Optimal design of different reforming processes of the actual composition of bio-oil for high-temperature PEMFC systems. Int. J. Hydrogen Energy, 42: 1977-1988.

[5] Yao, J., Liu, J., Hofbauer, H., Chen, G., Yan, B., Li, W. (2016) Biomass to hydrogen-rich syngas via gasification of bio-oil/biochar slurry over $LaCo_{1-x}Cu_xO_3$ perovsikite-type catalysts. Energy Convers. Manage., 117: 343-350.

[6] Xie, H., Yu, Q., Yao, X., Duan, W., Zuo, Z., Qin Q. (2015) Hydrogen production via steam reforming of bio-oil model compounds over supported nickel catalysts. J. Energy Chem., 24: 299-308.

[7] Yan, C., Cheng, F., Hu, R. (2010) Hydrogen production from catalytic steam reforming of bio-oil aqueous fraction over Ni/CeO_2-ZrO_2 catalysts. Int. J. Hydrogen Energy, 35(21): 11693-11699.

[8] Authaynun, S., Wiyaratn, W., Assabumrungrat, S., Amornchai, A. (2013) Theoretical analysis of a glycerol reforming and high-temperature PEMFC integrated system: Hydrogen production and system efficiency. Fuel, 105: 345-352.

[9] Tian, X., Wang, S., Zhou, J., Xiang, Y., Zhang, F., Lin, B., Liu, S., Luo, Z. (2016) Simulation and exergetic evaluation of hydrogen production from sorption enhanced and conventional steam reforming of acetic acid. Int. J. Hydrogen Energy,41: 21099-21108.

[10] Dang, C., Wang, H., Yu, H., Peng, F. (2017) Co-Cu-CaO catalysts for high-pruity hydrogen from sorption-enhanced steam reforming of glycerol. Appl. Catal., A, 533: 9-16.

[11] Yao, X., Yu, Q., Wang, K., Xie, H., Qin, Q. (2017) Kinetic characterizations of biomass char CO_2-gasification reaction within granulated blast furnace slag. Int. J. Hydrogen Energy, 42: 20520-20528.

[12] Kasai, E., Kitajima, T., Akiyama, T., Yagi, J., Saito, F. (1997) Rate of methane-steam reforming reaction on the surface of molten BF slag-for heat recovery from molten slag by using a chemical reaction. ISIJ Int., 37: 1031-1036.

[13] Li, P., Lei, W., Wu, B., Yu, Q. (2015) CO_2 gasification rate analysis of coal in molten blast furnace slag-For heat recovery from molten slag by using a chemical reaction. Int. J. Hydrogen Energy, 40: 1607-1615.

[14] Li, P., Yu, Q., Qin, Q., Lei, W. (2012) Kinetics of CO_2/coal gasification in molten blast furnace slag. Ind. Eng. Chem. Res., 51: 15872-15883.

[15] Duan, W., Yu, Q., Wu, T., Yang, F., Qin, Q. (2016) Experimental study on steam gasification of coal using molten blast furnace slag as heat carrier for producing hydrogen-enriched syngas. Energy Convers. Manage., 117: 513-519.

[16] Duan, W., Yu, Q., Liu, J., Wu, T., Yang, F., Qin, Q. (2016) Experimental and kinetic study of steam gasification of low-rank coal in molten blast furnace slag. Energy, 111: 859-868.

[17] Zhao, L., Wang, H., Qing, S., Liu, H. (2010) Characteristics of gaseous product from municipal solid waste gasification with hot blast furnace slag. J. Nat. Gas Chem., 19: 403-408.

[18] Sun, Y., Zhang, Z., Liu, L., Wang, X. (2015) Integrated carbon dioxide/sludge gasification using waste heat from hot slags: syngas production and sulfur dioxide fixation. Bioresour. Technol., 181: 174-182.

[19] Luo, S., Feng, Y. (2017) The production of fuel oil and combustible gas by catalytic pyrolysis of waste tire using waste heat of blast-furnace slag. Energy Convers. Manage., 136: 27-35.