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# Thermodynamic analysis of hydrogen-rich gas generation from coal/steam gasification using blast furnace slag as heat carrier

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ABSTRACT

Thermodynamic analysis with Gibbs free energy minimization through Lagrange multiplier method was performed for coal gasification with steam using blast furnace (BF) slag as heat carrier and recycling its waste heat to produce hydrogen-rich gas (HRG). Simulations were carried out to study the operation temperature, pressure, S/C and BF slag basicity based on chemical equilibrium calculations. The optimal thermodynamic conditions were determined to improve hydrogen concentration and total syngas production as high as possible. The results suggested that the preferential conditions for HRG from Datong coal were achieved at 775 °C, atmospheric pressure and S/C of 2.0–3.0. Under these conditions, hydrogen concentration reached to 62.36% and the total gas production was 2.45 mol per mole of carbon in the coal. What's more, not only was the quality of HRG improved significantly, but also the BF slag waste heat was recycled effectively when using BF slag as heat carrier. The effect of BF slag basicity upon the gasification characteristics was also investigated, and the production of hydrogen increased significantly when basicity was 1.3.


## Introduction

Coal gasification is a clean and highly efficient way of utilizing coal, and it has attracted a lot of researchers' interest in recent years [1–3]. One of the major coal gasification products is $H_2$, and it is most widely used in industrial process, particularly in methanol, dimethyl ether synthesis and fuel cells, because of its economic feasibility [4–6].

Generally, hydrogen content elevation can be achieved by two methods: steam gasification [7–10] and catalytic gasification [4,11–13]. Galvita et al. [14] studied the coal gasification with steam and air atmosphere under arc plasma conditions and found the amount of produced syngas of steam gasification was 30–40% higher than that of in air gasification. Jin [15] studied the coal gasification to produce hydrogen with supercritical water gasification system in a fluidized bed reactor. A chemical equilibrium model was adopted to predict the yield of gaseous products and their fraction, and the hydrogen fraction reached to 69.78%. Zhang et al. [16] studied the hydrogen production at low temperature catalytic steam gasification of pig compost in a two-stage fixed bed reactor. Their research showed that the hydrogen yield could increase to 660.67 mL/g pig compost at the reaction temperature of

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600 °C with the presence of $Ni/Al_2O_3$ catalyst. Hanaoka et al. [17] reported the higher $H_2$ content could be obtained by steam gasification using CaO as $CO_2$ sorbent. The yield of $H_2$ and other gas products depended on the reaction pressure and molar ratio of CaO to carbon, and the maximum yield of $H_2$ was obtained when the reaction pressure was about 0.6 MPa and the molar ratio of [CaO]/[C] was 2.

On the other hand, the gasification is an endothermic process, and the heat has to be supplied continuously to this process to ensure the appropriate reaction temperature. Yu and Li [18–21] proposed a new system using the BF slag waste heat as heat source to ensure the heat required for coal gasification. Wang [22] studied the possibility of combustible production from municipal solid waste using BF slag waste heat. In his study, the effects of temperature, gasifying agent (air, $N_2$, steam) and BF slag on gas productions were investigated at 600–900 °C. Luo et al. [23–24] also investigated the reliability of HRG production by biomass gasification using hot BF slag as thermal media and catalyst, as well as identified the optimal operation parameters for obtaining the highest HRG yields.

Therefore, in the present study, an attempt was made to explore the potential of the BF slag waste heat applied into coal gasification process. Besides, the equilibrium calculations employing the Gibbs free energy were used to evaluate the influence of operation temperature, pressure, and mass ratio of steam to coal (S/C) on HRG production. Moreover, the effect of BF slag and its basicity on coal gasification were also analyzed.

## Methodology

### *Coal gasification mechanism*

Gasification is a thermal chemical process in which the solid fuels are converted to combustible gases by partial oxidization with steam or oxygen, and carbon dioxide. The coal gasification is a two-step process: pyrolysis/devolatilization and gasification. The first step mainly produces tars and non-condensable gases at 300–500 °C, and the gases include CO, $CO_2$, $H_2$, $CH_4$, and so on. The gasification process takes place at 500 °C–1800 °C. Although the devolatilization process takes place at the first stage, the volatile may not complete in the gasification environment if oxygen is limited. In the gasifier, the devolatilization and gasification take place simultaneously. The results are interpreted based on the following simplified reversible chemical reactions which occur in gasification.

Boudouard (BD):

$$C_S + CO_2 \rightleftharpoons 2CO \quad \Delta H_r = 162\ \text{kJ/kmol} \tag{1}$$

Oxidation (OD):

$$C_S + O_2 \rightleftharpoons CO_2 \quad \Delta H_r = -109\ \text{kJ/kmol} \tag{2}$$

Partial oxidation (POD):

$$C_S + 1/2O_2 \rightleftharpoons CO \quad \Delta H_r = -123\ \text{kJ/kmol} \tag{3}$$

Primary water gas (PWG):

$$C_S + H_2O \rightleftharpoons CO + H_2 \quad \Delta H_r = 131\ \text{kJ/kmol} \tag{4}$$

Methane formation (MF):

$$C_S + 2H_2 \rightleftharpoons CH_4 \quad \Delta H_r = -75\ \text{kJ/kmol} \tag{5}$$

Water gas shift (WGS):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H_r = -41\ \text{kJ/kmol} \tag{6}$$

Methane reforming (MR):

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H_r = 206\ \text{kJ/kmol} \tag{7}$$

In the above reactions, only WGS and MR are homogeneous reactions and the others are heterogeneous reactions. BD, PWG and MR are endothermic reactions, considered as the most important reactions in gasification process to recover the BF slag waste heat. OD and other exothermic reactions provide the energy promoting endothermic reactions.

### *Feedstock and production characterization*

The simulations were performed for gasification of China Datong bituminous coal using the BF slag as heat carrier under the adiabatic condition. The composition and properties of Datong coal were shown in Table 1.

Considering the diversity of compositions and the complex structure in the coal, it was necessary to simplify its compositions to analyze the results and make sure this did not affect the conclusions drawn in the present work using the HSC chemistry software. A thermodynamic research involved with the effect of temperature, pressure and feed $CO_2$ and steam ratios in gasification of lignite coal was carried out by Ganesh R. Kale [25]. The coal composition was simplified as carbon, oxygen and hydrogen in this article. The results and conclusions obtained when only these three elements were considered do not deviate much when other elements were also included [26]. This simplified method was used in this paper to advance the coal gasification. Based on the above detailed description, the molecular formula of coal was assumed to be $CH_{0.696}O_{0.082}$ according to the elemental analysis.

In the present study, the Gibbs free energy minimization approach through Lagrange multiplier for gasification process was used, and the model predicts 25 gas species in the production, shown in Table 2. The estimation result of the production species was widely accepted by many researchers. Li

**Table 1 – Properties of Datong bituminous coal.**

| Proximate analysis (wt%) | | Ultimate analysis (wt%) | | Fusion point (K) | |
|---|---|---|---|---|---|
| Item | Value | Item | Value | Item | Value |
| Moisture | 9.05 | Carbon | 64.53 | Deformation temperature | 1498 |
| Volatile matter | 38.38 | Hydrogen | 3.746 | Soften temperature | 1578 |
| Fixed carbon | 38.42 | Nitrogen | 0.956 | Fluid temperature | 1653 |
| Ash | 14.15 | Sulfur | 0.561 | | |
| | | Oxygen | 7.007 | | |