Thermodynamic analysis of synergistic coal gasification using blast furnace slag as heat carrier

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Abstract

In this paper, a thermodynamic analysis of the synergistic coal/CO₂/H₂O gasification process with BFS (blast furnace slag) as heat carrier was performed using the Gibbs free energy minimization approach through Lagrange multiplier method. The effect of temperature, pressure and C/CO₂/H₂O were investigated. Carbon, CO₂ and H₂O conversion, H₂ and CO yield, and H₂/CO ratio were used to characterize the synergistic gasification performance. The results showed that the atmospheric pressure was preferable for coal gasification and the increasing of temperature caused the increase in carbon conversion and syngas production. The optimal temperature of the synergistic gasification was 800-900 °C. Not only did it ensure the coal gasification reaction completely, but also it recovered the BFS waste heat effectively. The results clearly showed that the addition of H₂O and CO₂ could lead to the reduction of the carbon residue and increase of the production of H₂ and CO, respectively. Meanwhile, it was beneficial to reduce the waste heat using to heating extra steam and enhance the coal/CO₂ gasification reaction rate by controlling the addition of CO₂ and H₂O reasonably. Moreover, the production syngas application was also investigated by changing the relative CO₂/C ratio and H₂O/C ratio in the feed to modify the H₂/CO ratio.

Keywords:

Blast furnace slag; Heat carrier; Thermodynamic analysis; Synergistic coal gasification; Syngas

1. Introduction

Coal was the most abundant natural energy resource available all over the world [1]. An interesting way, more efficiently and cleanly, was intensely focusing. Gasification technology was a clean and highly efficient way of utilizing coal, and it had attracted a lot of researcher's interest in recent years [2-4].

Traditionally, coal gasification reaction was performed using H_2O or CO_2 as agent. The situation of energy consumption in the steam gasification of coal was studied by Kale et al [5-7]. Although a large amount of the hydrogen could be produced, a great deal of energy was needed in gasification process. Meanwhile, an inevitable drawback of this process was the H_2/CO ratio higher than 3.0, which was higher than the needed ratio of the Fischer-Tropsch process [8-9]. Many researchers had performed numerous investigations on gasification reaction with CO_2 [10-13]. Although a large amount of CO_2 could be absorbed in the gasification process, the gasification reactivity was found to depend on reaction temperature strongly. Therefore, focusing on the coal gasification in mixture of CO_2 and H_2O was necessary to improve the coal reactivity and decrease the energy consumption.

Kale et al [5] found that the synergistic gasification was an important process to enhance reactivity and reduce energy consumption. Roberts [14] presented the data of coal char gasification with mixture of CO_2 and H_2O at high pressure. The results showed that the reaction rate was not the sum of the two pure gas reaction rates. It was a complex combination of the two, which appears to be dependent on the relative of slow C/CO_2 reaction. The same conclusion was also obtained by Scala [15]. Wang

[16] found that the reactivity of the CO₂ and H₂O gasification was better than that of any single agent and the synergistic effect was related to inherent minerals. Chen et al [17] found that the char gasification in mixture of CO₂ and H₂O was obviously lower than the sum of two rates of char independently reacting but higher than rate of each independent reaction. Guizani et al [18] indicated that CO₂ and H₂O reacted on the separate active sites when mixed atmospheres were used. CO₂ did not favor or inhibit the coal/H₂O gasification reaction as it did not affect the coal structure. However, Bai et al [19] found that coal/H₂O gasification occurred the most rapidly at high temperature and its rate decreased with the volume fraction of CO₂ increasing. Mostafavi [20] used the catalyst to enhance the gasification and water gas shift reaction rates and found that CO₂ shifted the water gas shift reaction equilibrium forward, to increase H₂ production. The same conclusion was also obtained by Sedghkarder [21]. The gasification characteristics of coal with H₂O and CO₂ were also investigated at different pressures by Li [22]. The results showed that coal gasification mechanism in mixture of CO₂ and H₂O was connected with relative partial pressures of two reactant gases.

As is known to all, the gasification was an intense endothermic reaction. The large amount of syngas must be burned to generate heat for gasification reaction. Therefore, obtaining an appropriate heat source was necessary to guarantee the successful reaction and reduce the syngas consumption. BFS as a kind of by-product during ironmaking process, was exhausted at extremely high temperature and the energy carried by BFS was about 1700 MJ/t_{slag} [23, 24]. Luo [25-26] and Sun [27] used the

biomass catalytic gasification reaction to recover the BFS waste heat and product syngas successfully. Meanwhile, Sun et al [28-29] also investigated the sewage sludge gasification using slags. Li [30-35] carried on the thorough research of utilizing coal gasification to produce the syngas with the proposed coal/CO₂/slag system. About 0.044 Mt/Mt_{slag} of CO was generated and the thermal-to-chemical conversion efficiency reached 35%. On the basis of Li's study, Duan [36-39] investigated the coal/H₂O gasification process and analyzed conditions of syngas production and the BFS waste heat utilization of the integrated system.

It could be seen from above studies mentioned that the coal gasification could proceed smoothly in the presence of BFS, and the slag waste heat could be recovered effectively. However, the conditions of energy conversion and syngas production in the process of synergistic coal gasification with CO₂ and H₂O using BFS as heat carrier had not been fully studied. Therefore, the effect of temperature, pressure and inlet C/CO₂/H₂O were fully investigated by thermodynamic analysis. The energy consumption and syngas production with various changes of CO₂/C and H₂O/C were also studied. Moreover, the production syngas application was also investigated to make it more extensive in industry.

2. Methodology

2.1 Equilibrium Modeling-Minimization of Gibbs free energy

For a system in which many simultaneous reactions took place, the equilibrium calculations were performed through the Gibbs free energy minimization method

[40-43]. The total Gibbs free energy of the system was defined as:

$$G_{T,P}^t = \sum_{i=1}^N n_i \mu_i \quad (1)$$

where $G_{T,P}^t$ was the total Gibbs free energy and n_i was referred to each species. μ_i was the chemical potential of species i that could be presented by:

$$\mu_i = G_{f,i}^0 + RT \ln (y_i) \quad (2)$$

where, $G_{f,i}^0$ was the standard Gibbs free energy of formation species; T was the temperature, K; y_i was the mole fraction of gas species.

Finding an appropriate value of n_i to make sure the total Gibbs free energy $G_{T,P}^t$ to reach minimum was a problem. In face of this problem, the method of the Lagrange multipliers was used to deal with this question by Koukkari P [44].

$$\sum_{i=1}^N a_{ij} n_i = A_j, j=1, 2, 3, \dots, k \quad (3)$$

where a_{ij} was the number of atoms of the j th element in each mole of the i th species. A_j was the total number of atoms of the j th element in the system and k was the total number of atoms. Next, the Lagrange multipliers (λ_k) was introduced in Eq. (4).

$$\sum_k \lambda_k \left(\sum_{i=1}^N a_{ij} n_i - A_j \right) = 0 \quad (4)$$

The Eq. (5) could be formed by Eq. (1) and (4).

$$L = G_{T,P}^t - \sum_{j=1}^k \lambda_k \left(\sum_{i=1}^N a_{ij} n_i - A_j \right) \quad (5)$$

In order to find the value of the equilibrium composition, the Eq. (5) could be processed into Eq. (6).

$$\left(\frac{\partial L}{\partial n_i} \right) = 0 \quad (6)$$

Consequently, the value of each species present could be obtained by this method and the mass and energy keep balance when reaching the state of $dG_{T,p}^t$.

2.2 Thermodynamic properties

In order to ensure the value of the $\bar{G}_{f,i}^0$, the values of the standard enthalpy of formation ($\Delta \bar{H}_{f,i}^0$) and standard entropy of formation ($\Delta \bar{S}_{f,i}^0$) at temperature T were needed.

$$\Delta \bar{G}_{f,i}^0 = \Delta \bar{H}_{f,i}^0 - T \Delta \bar{S}_{f,i}^0 \quad (7)$$

The heat capacity, enthalpy and entropy at constant pressure for the standard state were formulated in terms of the polynomial equations as follows, and the all parameters needed in the process of calculations were provided by NASA technical memorandum 4513 [45].

$$\frac{\bar{C}_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad (8)$$

$$\frac{\bar{H}_f^0(T_0)}{RT_0} = a_1 + \frac{a_2 T_0}{2} + \frac{a_3 T_0^2}{3} + \frac{a_4 T_0^3}{4} + \frac{a_5 T_0^4}{5} \quad (9)$$

$$\frac{\bar{S}_f^0(T_0)}{R} = a_1 \ln(T) + a_2 T_0 + \frac{a_3 T_0^2}{2} + \frac{a_4 T_0^3}{3} + \frac{a_5 T_0^4}{4} + b_2 \quad (10)$$

2.3 Feedstock characterization and conversion process

The simulations were performed for gasification of China DT (Datong) bituminous coal using BFS as heat carrier, and compositions and properties of DT coal were shown in Table 1. In order to develop the model, under the premise of calculation results were not affected, the simplification of DT coal compositions was necessary [5, 46]. Based on Li et al [47] and Shabbar et al [41] results, 25 gas species in the production were considered, and it could be seen from previous study [36].

Table 1 The properties of DT bituminous coal

The properties of DT bituminous coal			
Proximate Analysis (wt %)		Ultimate Analysis (wt %)	
Moisture	9.05	Carbon	64.53
Volatile matter	38.38	Hydrogen	3.746
Fixed carbon	38.42	Nitrogen	0.956
Ash	14.15	Sulfur	0.561
		Oxygen	7.007

Table 2 The list of BFS solid phase species

The BFS solid phase species				
C	Al_2O_3	$\text{CaO} \cdot \text{MgO}$	$\cdot 2\text{CaO} \cdot \text{Al}_2\text{O}_3$	$\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$
CaO	$\text{Al}(\text{OH})_3$	$\text{CaO} \cdot \text{Al}_2\text{O}_3$	$2\text{CaO} \cdot \text{SiO}_2$	$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$
CaO_2	Fe_2O_3	$\text{CaO} \cdot 2\text{Al}_2\text{O}_3$	$\cdot 2\text{FeO} \cdot \text{SiO}_2$	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
$\text{Ca}(\text{OH})_2$	FeO	$\text{CaO} \cdot \text{Fe}_2\text{O}_3$	$3\text{CaO} \cdot \text{SiO}_2$	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
CaC_2	Fe_3O_4	$\text{CaO} \cdot 6\text{Al}_2\text{O}_3$	$3\text{CaO} \cdot 2\text{SiO}_2$	$2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$
CaCO_3	$\text{Fe}_{0.947}\text{O}$	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	$\cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
MgO	Fe	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$\cdot 3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$
MgCO_3	SiO_2	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$\cdot 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$	$\cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$

Meanwhile, the BFS, from an iron and steel company was used in this numerical simulation as heat carrier, with the chemical compositions of 44.6% CaO, 38.5% SiO_2 , 8.1% Al_2O_3 , 5.4% MgO, 1.0% Fe_2O_3 and some minor constituents of titanium, sulfur and phosphor oxides. The effect of chemical compositions in BFS was considered in the process of thermodynamic calculation, and the species of slag solid phase were shown in Table 2. The existence of BFS would have a significant impact on coal gasification, and compositions of syngas would be different from the coal gasification

reaction without BFS [36].

The coal gasification reaction was a thermal-chemical process in which the solid fuels were converted to combustible gases by partial oxidization with $\text{H}_2\text{O}(\text{g})$ and/or CO_2 . The results were interpreted based on the following reversible chemical reactions simplified which occurred in the coal gasification reaction.

Boudouard reaction (BD)

Methane formation reaction (MF)

Primary water gas reaction (PWG)

Methane reforming reaction (MR)

Water gas shift reaction (WGS)

Meanwhile, there were some specific reactions occurred when the BFS existed in the process of coal gasification. It would have a significant impact on the gasification reaction rate and the composition of syngas.

The parametric analysis of coal gasification was based on the pressure, temperature, CD/C ratio (CO_2/C ratio) and S/C ratio ($\text{H}_2\text{O}/\text{C}$ ratio) in carbon conversion, CO_2 conversion, H_2O conversion, H_2 yield and CO yield [48, 49].

$$\text{Carbon conversion} = \frac{n_{\text{C},in} - n_{\text{C},out}}{n_{\text{C},in}} \times 100\% \quad (11)$$

$$\text{CO}_2 \text{ conversion} = \frac{n_{\text{CO}_2,in} - n_{\text{CO}_2,out}}{n_{\text{CO}_2,in}} \times 100\% \quad (12)$$

$$\text{H}_2\text{O conversion} = \frac{n_{\text{H}_2\text{O}(g),in} - n_{\text{H}_2\text{O}(g),out}}{n_{\text{H}_2\text{O}(g),in}} \times 100\% \quad (13)$$

$$\text{H}_2 \text{ Yield} = \frac{n_{\text{H}_2,out}}{n_{\text{H}_2,stoic}} \times 100\% \quad (14)$$

$$\text{CO Yield} = \frac{n_{\text{CO},out}}{n_{\text{CO},stoic}} \times 100\% \quad (15)$$

3. Results and discussions

In this section, we first shall present the thermodynamic analysis results of synergistic coal gasification with CO_2 and H_2O using BFS as heat carrier. The steady state simulation developed was tested by simulating variation of carbon conversion, CO_2 conversion and H_2O conversion, H_2 yield and CO yield with the changing of pressure, temperature, CD/C ratio and S/C ratio. Finally, the production syngas applications were also investigated by changing the relative CD/C ratio and S/C ratio modify the H_2/CO ratio.

3.1 Effect of pressure on coal gasification reaction

Fig. 1 showed the effect of various operation pressures on the performance of carbon conversion, CO_2 conversion, H_2 yield and CO yield from 0.1 MPa to 10 MPa

at 800 °C and CD/C of 1.0. It was observed that the conversion of carbon and the yield of H₂ and CO were significantly suppressed by the increasing pressure. It was because that the volume contracted with the pressure increasing based on the Le Chatelier's principle. Both BD reaction and PWG reaction shifted to the left and CO and H₂ were largely consumed, and carbon and CO₂ were generated. That was to say, the increasing pressure did not play a good role in promoting coal gasification with CO₂ using BFS as heat carrier. Therefore, the atmospheric pressure was preferable pressure for coal gasification. The atmospheric pressure was also very beneficial to solve the problem at high pressure (greater than 1 MPa) of the most Fischer-Tropsch synthesis industrial production process [50, 51].

Fig. 1 Effect of pressure on the equilibrium of the Carbon, CO₂ conversions and H₂, CO yield for the coal/CO₂ gasification reaction at 800 °C

3.2 Effect of steam addition on coal gasification reaction

Fig. 2 showed the effect of steam addition on the equilibrium of carbon, CO₂ and H₂O conversions for the C/CO₂/H₂O gasification reaction at different temperatures with C/CO₂=1.0 and atmospheric pressure. It could be seen from Fig. 2(a), steam addition had a significant effect on the carbon conversion in the process of coal

gasification. The carbon conversion increased steadily with increasing of steam addition when the temperature was lower than 800 °C. This result was consistent with the work of Jayaraman [52] and Roberts [14]. The reactivity of coal in CO₂ ambience was much lower than that in steam. Meanwhile, the coal gasification rate strongly depended on the mass of steam, the more steam addition was in the gasification process, the stronger reactivity was. However, the carbon conversion was ignored with steam addition when the gasification temperature was above 800 °C. It was because that the carbon conversion reached 100 % with the reaction of BD and PWG, which was limited by the mass of gasification agent [48].

Compared with the transformation of carbon conversion with steam addition, the CO₂ had its unique change rule. With increasing temperature, CO₂ conversion decreased firstly and then increased, and its value reached to the minimum at about 650 °C, as shown in Fig. 2(b). This result was due to the effect of BFS in the gasification with BFS as heat carrier. With the presence of CaO in BFS, CO₂ was absorbed and converted to CaCO₃, so CO₂ conversion was very high when the temperature was lower than 650 °C. With increasing temperature, CO₂ was released from CaCO₃ and reacted with carbon to produce CO [33, 36, 53]. CO₂ conversion increased with the increasing of temperature. Meanwhile, the reactivity of coal also increased significantly with the existence of CaO in BFS [33]. However, steam addition decreased CO₂ conversion and its effect was very remarkable. For example, CO₂ conversion was 86.3% when the S/C=0 at 1000 °C, but it decreased to 28.7% when the S/C=3.0. It was because that both CO₂ and steam acted as the co-agent in

process of gasification. The carbon reacted with steam, instead of CO_2 with the steam addition increasing. It was because that H_2O and CO_2 would be scrambling for some active sites on coal char and H_2O was more competitive than CO_2 [14, 19, 22]. Then from the thermodynamic, PWG and WGS reaction were promoted by adding steam, and a certain amount of CO_2 was generated, so CO_2 conversion decreased significantly even to be the negative when the S/C ratio was above 2.0.

Fig. 2 Effect of steam addition on the equilibrium of the Carbon, CO_2 and H_2O conversions for the combined C/ CO_2 / H_2O gasification reaction at different temperatures with $\text{C}/\text{CO}_2 = 1.0$ and atmospheric pressure

Although it was benefited to the carbon conversion in process of coal gasification using BFS as heat carrier, the extra steam was not favored for H_2O conversion and the gasification reaction. It could be seen from Fig. 2(c), H_2O conversion decreased with

the increasing of the S/C ratio at the higher temperature. Based on the Shabbar [41] and Duan [36] results, the extra steam was introduced than necessary for gasification, which caused a large amount of energy consumption and decreased the gasification efficiency. Therefore, it was necessary to manage the amount of addition steam appropriately in process of gasification.

The effect of steam addition on the equilibrium of H_2 yield (%), and CO yield (%) for the $C/CO_2/H_2O$ gasification reaction at different temperatures and atmospheric pressure with $CD/C=1.0$ were presented in Fig. 3. It was observed from the figure, the effect of steam had slight influence on both H_2 and CO yields at 700 °C. On the contrast, there was a significant reduction of H_2 and CO yields with steam addition when the temperature was higher than 700 °C. However, the change trend of H_2 yield was different from with/without steam addition. At S/C ratio of 0, H_2 yield reached the maximum and remained the same with the temperature higher than 900 °C. With increasing temperature, H_2 yield increased firstly and then decreased, and its yield reached to the maximum at 700-900 °C, which was varied from S/C ratios. It was because that PWG and MR reaction resulted favorably in the higher production of H_2 with the increasing temperature. But H_2 yield decreased when the temperature reached to a value, it was due to the rWGS reaction was promoted and the net effect was on the higher H_2 yield at lower temperature followed by a gradual decrease. Meanwhile, CO yield also reached to a relatively high value at 800-1000 °C and kept stable with the increasing temperature. Therefore, by analysis above, it was necessary to control the S/C ratio reasonably, so as to increase H_2 yield and change H_2/CO (in the range of

1-3 was desired for use in petrochemical manufacture). The temperature should be controlled at 700-1000 °C to get the maximum output of H₂ and CO. Meanwhile, it was beneficial to recover the waste heat of BFS when gasification reaction proceeding with slag as heat carrier.

Fig. 3 Effect of steam addition on the equilibrium of the H₂ yield (%), and CO yield (%) for the combined C/CO₂/H₂O gasification reaction at different temperatures with C/CO₂=1.0 and atmospheric pressure

3.3 Effect of gasification agent feed ratio on coal gasification reaction

According to obtained results from above, the thermodynamic analysis was performed at different feed ratio (CD/S/C=0-2/0-2/1) and different temperatures of 700-1000 °C to achieve the change of carbon, CO₂ and H₂O conversion, H₂ and CO yield in the process of synergistic coal gasification reaction using BFS as heat carrier. In Fig. 4, it was observed that increasing the feed ratio of CD/C and S/C were benefited for carbon conversion at 700 °C or 1000 °C. The carbon conversion increased significantly at lower CD/C and S/C ratios under 700-1000 °C. However, the change of carbon conversion was stable and near to 100% when CD/C and S/C ratios were higher. Under these conditions, the effect of temperature on carbon

conversion was negligible, especially at 900 °C and 1000 °C. That was to say, in the process of coal gasification using BFS as heat carrier, it was reasonable to control the temperature at 800-900 °C so as to guarantee the coal gasification completely and recover the waste heat of BFS as much as possible.

(a) Carbon conversion at different temperatures

(b) CO₂ conversion at different temperatures

(c) H₂O conversion at different temperatures

Fig. 4 The equilibrium of the (a) Carbon conversion (%), (b) CO₂ conversion (%) and (c) H₂O conversion (%) for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at different temperatures and atmospheric pressure

CO₂ conversion increased with the increasing of temperature for all feed ratios. It was because that the endothermic BD reaction was accelerated by the higher

temperature. Whereas, it was negative for CO_2 conversion when the low CD/C ratio and high S/C ratio were added in the system of coal gasification, even released more CO_2 than added. The existence of the large amount of steam caused the domination of PWG reaction and WGS reaction and produced a large amount of CO_2 . That was to say, it was a disadvantage to the utilization of CO_2 in the process of coal gasification when exceed steam was added in the gasification system. As for steam conversion, it was consisted with the change of CO_2 conversion at different temperatures, CD/C ratios and S/C ratios. Therefore, considering the above analysis, CO_2 and H_2O were obviously competitive and mutual inhibition in the process of synergistic coal gasification using BFS as heat carrier.

The effect of the equilibrium of H_2 yield and CO yield for $\text{C}/\text{CO}_2/\text{H}_2\text{O}$ gasification reaction for various CD/C ratios and S/C ratios at different temperatures and atmospheric pressure were shown in Fig. 5. It could be seen from Fig. 5, H_2 yield and CO yield increased high temperature at a certain CD/C ratio and S/C ratio. At 700-1000 °C, it was beneficial to produce H_2 and CO in synergistic coal gasification reaction. It was because that BD reaction and PWG reaction promoted producing H_2 and CO when the temperature increased. But with the higher temperature, the effect began to wane and nearly no effect on product yields after a certain stage of temperature, which resulted in the 100% carbon conversion. The difference was that, H_2 yield decreased with the increasing of CD/C and S/C ratios. As discussed in the previous section, both CO_2 and H_2O acted as co-agent in the process of gasification, and the larger of CD/C ratio inhibited the PWG reaction and decreased the utilization

efficiency of steam. However, with increasing of CD/C and S/C ratios, CO yield increased firstly and then decreased. That was to say, it was necessary to reasonably control CD/C and S/C ratios in synergistic coal gasification using BFS as heat carrier so as to obtain the more production.

(a) H₂ yield at different temperatures

(b) CO yield at different temperatures

Fig. 5 The equilibrium of the (a) H₂ yield (%), and (b) CO yield (%) for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at different temperatures and atmospheric pressure

3.4 The controlling of the CO₂/C ratios and H₂O/C ratios for the syngas applications

The coal gasification reaction was a thermal-chemical process aiming at the production of high heating value synthesis gas, a mixture of H₂ and CO, which was further utilized in a variety of downstream processes for production of liquid hydrocarbons, carbonylation and hydrogenation or reduction processes [8, 48, 54, 55]. Therefore, it was necessary to investigate the effect of CO₂ and H₂O addition (i.e. CD/C ratio and S/C ratio) in the process of coal gasification.

Fig. 6 showed the equilibrium of H₂/CO ratio for C/CO₂/H₂O gasification reaction for various CD/C and S/C at 800 °C and atmospheric pressure. The desirable synthesis gas ratio for used in the manufacture was easily obtained from Fig. 6. The long-chain hydrocarbon synthesis, dimethyl ether synthesis and acetic acid production usually required the synthesis gas with a H₂/CO ratio close to 1.0 [48, 56-58]. As can be seen from Fig. 6, CD/C ratio should be controlled lower than 2.5 in the range of S/C =

0~3.0. Meanwhile, CD/C ratio should be lower than S/C ratio of 0.5 in the process of synergistic coal gasification reaction using BFS as heat carrier.

Fig. 6 The equilibrium of the H₂/CO ratio for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at 800 °C and atmospheric pressure

Based on the above sections analysis, the total amount of H₂O and CO₂ addition also should reach to a certain amount to make sure the complete carbon conversion. The synthesis gas with a H₂/CO ratio of 2.0 was desired feedstock for Fischer-Tropsch and methanol syntheses [59, 60]. In order to obtain the desired syngas, CD/C ratio should be lower than 0.75 and S/C ratio was higher than 1.5. At this condition, PWG and WGS reactions were promoted and BD reaction was inhibited, and production of H₂ was improved significantly. The carbon could react completely with H₂O and CO₂ to produce H₂ and CO. The syngas with H₂/CO of 3.0 or more could be used for manufacture of synthetic natural gas as heat production of the SNG (synthetic natural gas) via a thermal-chemical process [61]. For the coal gasification using BFS as heat carrier, it was very hard to obtain the syngas with H₂/CO of 3.0 in synergistic gasification reaction with CO₂ and H₂O. To satisfy the condition of syngas used in the SNG production, CO₂ could not be added into the gasification system and S/C ratio

should be higher than 2.7. However, extra steam addition than necessary for gasification would decrease the gasification efficiency and took away a lot of waste heat of BFS, the same result was obtained by Wang [62] and Duan [36]. So, it was necessary to control the S/C ratio in the range of 2.7~3.0 in process of coal gasification.

The production syngas could be used for the power generation in turbines, heating and metallurgic enterprises production and so on. In such conditions, the superior LHV (lower heating value) of the production syngas was expected. Fig. 7 showed the LHV of production syngas for C/CO₂/H₂O gasification reaction for various CD/C and S/C at 800 °C and atmospheric pressure.

Fig. 7 The LHV of the production syngas for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at 800 °C and atmospheric pressure

As could be seen from the Fig. 7, the LHV of the production syngas increased with S/C increasing at a certain CD/C ratio. It was because that PWG reaction and WGS reaction were promoted with the increasing of S/C ratio, and the more H₂ was produced. It was beneficial to increase the LHV of the syngas when steam was added into the system as the gasification agent. However, the effect of CO₂ on the LHV of

the syngas was different from that of steam. The LHV of the syngas increased firstly and then was steady with the increasing of CD/C ratio at S/C ratios lower than 1.5. On the contrary, the LHV of the syngas decreased with the increasing of CD/C at the S/C ratios higher than 1.5. That was to say, the CD/C ratio of 2.5~3.0 was suitable for the gasification to produce syngas with higher LHV at S/C ratio of 0.5~1.0. The CD/C ratio at 0.5 was suitable when the S/C ratio was higher than 1.5. In addition to using the syngas in the petrochemical manufacture, it could be used as fuel in fuel cells (eg. SOFC (solid oxide fuel cells) and PEMFC (polymer electrolyte membrane fuel cells)) [5, 63, 64]. However, the content of CO and $\text{H}_2\text{O}/\text{CO}$ in the syngas should be strictly restricted. The syngas need to be processed through WGS reactor to reduce CO content by converting it to H_2 and further CO reduction was achieved by preferential oxidation reactors.

4. Conclusions

Thermodynamic analysis of the coal gasification using BFS as heat carrier was conducted by the method of Gibbs free energy minimization. The calculation was carried out at 0.1 MPa and 10 MPa, 400 °C-1400 °C, CD/C ratios and S/C ratios of 0.1-3.0 and 0.1-3.0, respectively. The results showed that the atmospheric pressure was preferable for the synergistic coal gasification reaction. The high temperature was benefited to conduct the coal gasification reaction, but excessively high temperature inhibited the production of syngas and decreased the utilization efficiency of waste heat. The optimal temperature of synergistic coal gasification should be controlled at

800-900 °C. With the addition of steam, the carbon conversion and H₂/CO increased considerably whereas CO₂ and H₂O conversions, H₂ yield and CO yield decreased. The addition of H₂O and CO₂ to the feed mixture could lead to a reduction of carbon residue and increase of the production of H₂ and CO, respectively. In addition, the production syngas could be used for many industrial manufactures. The needed H₂/CO ratio in the syngas could be modified effectively by changing the relative CD/C ratio and S/C ratio.

Nomenclature

$n_{i,in}$ = The mole of the i in the coal gasification reaction system, mol;

$n_{i,out}$ = The mole of the i out of the coal gasification reaction system, mol;

$n_{i,stoic}$ = The mole of stoichiometric amount of produced i , mol;

$G_{T,P}^t$ = The total Gibbs free energy;

μ_i = The chemical potential of species i ;

$\bar{G}_{f,i}^0$ = The standard Gibbs free energy of formation of species;

R = The universal gas constant, 8.314 kJ/kmol·K;

y_i = The mole fraction of gas species;

a_{ij} = The number of atoms of the j th element in each mole of the i th species;

A_j = The total number of atoms of the j th element in the system;

k = The total number of atoms;

$\bar{\Delta H}_{f,i}^0$ = The values of the standard enthalpy of formation at temperature T , kJ/kmol;

$\bar{\Delta S}_{f,i}^0$ = The standard entropy of formation at temperature T , kJ/kmol·K;

$\bar{C}_p$ = The heat capacity at constant pressure for the standard state, kJ/kmol·K;

T_o = The inlet temperature of the reactants, K.

Abbreviations

BFS = Blast furnace slag

DT coal = Datong coal

S/C = Steam to carbon ratio

CD/C = Carbon dioxide to carbon ratio

BD = Boudouard reaction

MF = Methane formation reaction

PWG = Primary water gas reaction

MR = Methane reforming reaction

WGS = Water gas shift reaction

SNG = Synthetic natural gas

LHV = Lower heating value

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TABLE CAPTION

Table 1 The properties of DT bituminous coal

Table 2 The list of BFS solid phase species

FIGURE CAPTION

Fig. 1 Effect of pressure on the equilibrium of the Carbon, CO₂ conversions and H₂, CO yield for the coal/CO₂ gasification reaction at 800 °C

Fig. 2 Effect of steam addition on the equilibrium of the Carbon, CO₂ and H₂O conversions for the combined C/CO₂/H₂O gasification reaction at different temperatures with C/CO₂=1.0 and atmospheric pressure

Fig. 3 Effect of steam addition on the equilibrium of the H₂ yield (%), and CO yield (%) for the combined C/CO₂/H₂O gasification reaction at different temperatures with C/CO₂=1.0 and atmospheric pressure

Fig. 4 The equilibrium of the (a) Carbon conversion (%), (b) CO₂ conversion (%) and (c) H₂O conversion (%) for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at different temperatures and atmospheric pressure

Fig. 5 The equilibrium of the (a) H₂ yield (%), and (b) CO yield (%) for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at different temperatures and atmospheric pressure

Fig. 6 The equilibrium of the H₂/CO ratio for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at 800 °C and atmospheric pressure

Fig. 7 The LHV of the production syngas for the combined C/CO₂/H₂O gasification reaction for various CO₂/C and H₂O/C at 800 °C and atmospheric pressure