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Chemical looping conversion of coal with liquid oxygen carrier: thermodynamic research

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ABSTRACT

Liquid chemical looping technology is an innovation of chemical looping gasification technology. The use of liquid metal oxides as oxygen carriers in the gasification process could extend the service life of oxygen carriers and improve the gasification efficiency of carbon-based fuels. The combination of liquid chemical looping technology and bituminous coal traditional gasification technology can avoid the above problems, and can also improve the coal gasification efficiency and achieve almost zero greenhouse gas emissions. In this paper, based on the Gibbs minimum free energy principle, the computer simulation calculation of the chemical looping gasification technology of bituminous coal is carried out. The results indicated that increasing the temperature of the chemical looping gasification is conducive to the improvement of bituminous coal gasification efficiency. When the gasification temperature is 900~1000℃, the content of CO and H_2 is the highest. When the molar ratio of the oxygen carrier to the gasification raw material is 0.3, the CO output is the largest. The addition of water vapor is conducive to the increase of the H_2/CO molar ratio in the system.

Keywords: liquid chemical looping conversion, oxygen carrier, product distribution, thermodynamics analysis

1. INTRODUCTION

Energy shortage and environmental pollution have become global concerns. As a major energy country, the traditional use of coal in China is mainly combustion, so there will be problems such as low energy utilization efficiency and insufficient fuel combustion. The low efficiency of the intermediate links in the coal combustion process is the main reason for the low utilization rate of coal energy[1].

The chemical looping technology can avoid the environmental problems caused by the traditional combustion or gasification of coal. This technology is developed on the basis of chemical looping combustion. The process is carried out in two reactors (air reactor and fuel reactor, respectively). Gasification reaction provides oxygen supply to replace gasification medium[2],The basic principle of chemical looping gasification technology is shown in Figure 1. The process of oxidizing the reduced oxygen carrier by air occurs in the air reactor. The fuel in the fuel reactor is partially oxidized by the lattice oxygen provided by the oxygen carrier, which can produce hydrogen and carbon monoxide-based synthesis gas.

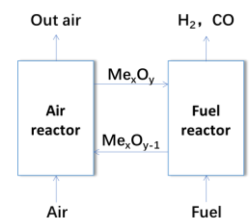

Figure 1 Schematic diagram of the chemical looping gasification process

In the application process, the oxygen carrier should meet the following performance requirements: 1) good oxidation-reduction performance; 2) higher oxygen-carrying capacity; 3) higher mechanical strength; 4) resistance to sintering and agglomeration[3, 4].At present, the research on oxygen carriers mainly focuses on oxides of transition metals such as Cu, Ni, Mn, Fe and a small amount of non-metallic oxygen carriers. There are many types of metal-oxygen carriers, iron-based, copper-based, and nickel-based are the most common, and sulfates represented by $CaSO_4$, $BaSO_4$, etc. are common non-metallic oxygen carriers[5].

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There are many studies on metal oxygen carriers. Li Min et al. [6] prepared upper Fe/CaO oxygen carriers with different Fe loadings and studied the role of the prepared oxygen carrier in the chemical looping gasification process. Wang et al. [7] prepared the CuFe2OATP oxygen carrier by sol-gel method, and studied the experimental research on the synthesis of synthetic gas by the chemical looping gasification of food waste in the fluidized bed reactor. Zeng et al. [8] studied the influence factors of natural iron ore as an oxygen carrier on the gasification of biomass chemical looping on a small atmospheric double fluidized bed developed by Zeng et al.

However, there are many disadvantages in the use of solid oxygen carriers. First, solid metal oxides are easy to coke and sinter in high-temperature environments. Secondly, the chemical looping gasification process the ash generated in the particles may be deposited on the surface of the particles[10]. These phenomena will affect the service life of the oxygen carrier. Jin et al[11] studied the effect of hematite on the chemical looping gasification of pine wood chips in a fluidized bed reactor. The XRD and SEM tests of the oxygen carrier found that after multiple chemical looping cycles, the specific surface area of hematite has decreased, and there are obvious sintering marks. Although solid metal-oxygen carriers are widely used, there are still certain defects in the chemical looping gasification process.

In recent years, Sarafraz[10] of the Energy Technology Center of the School of Mechanical Engineering at Adelaide University in Australia has proposed the concept of liquid chemical looping gasification. The liquid chemical looping gasification process is mainly improved in the two aspects. Firstly, use molten-metal oxide as an oxygen carrier for fuel gasification. And secondly, the system is composed of two interconnected bubble reactors. The material circulates continuously in the two reactors to provide heat and oxygen for the reaction[10]. Sarafraz[10] et al. used liquid CuO as the oxygen carrier and studied the chemical looping gasification characteristics of graphite based on thermodynamic analysis methods. Sarafraz[12] used thermochemical analysis methods to study the thermodynamics of chemical looping gasification of liquid bismuth oxide to syngas.

In this study, the chemical looping gasification process of bituminous coal and liquid oxygen carrier was simulated. The effects of temperature, molar ratio of oxygen carrier to bituminous coal, and steam on gasification equilibrium products were studied. Bismuth oxide has a relatively low melting point, about 850°C, and is suitable as an oxygen carrier for bituminous coal gasification.

2. MATERIAL AND METHODS

2.1 Material

In this paper, bituminous coal and bismuth oxide are used as raw materials to study the liquid chemical chain gasification process. The proximate analysis and ultimate analysis of bituminous coal are shown in Table 1.

Table 1 Analysis of BC

Proximate analysis /%				Ultimate analysis /%				
M Moisture	V Volatile	FC Fixed carbon	A Ash	C Carbon	H Hydrogen	O Oxygen	N Nitrogen	S Sulfur
4.18	30.56	49.88	15.38	79.31	4.72	13.38	1.03	1.3

2.2 Method

When bismuth oxide is used as the oxygen carrier, the oxidation process of the oxygen carrier occurs in the air reactor. In the fuel reactor, pyrolysis of fuel, pyrolysis products of biomass, gasification reaction of carbon, etc[14]. For such a complex system with multiple reactions, the final gasification product must be the result of comprehensive competition among multiple reactions.

Table 2 The mainly reactions in the liquid chemical looping gasification

Reactions	ΔH/kJ • mol^{-1} 900 ℃	
$Bi_2O_3(l)+3CO \rightarrow 2Bi(l)+3CO_2$	-317.08	(1)
$Bi_2O_3(l)+3H_2 \rightarrow 2Bi(l)+3H_2O$	-217.69	(2)
$Bi_2O_3(l)+3C \rightarrow 2Bi(l)+3CO$	+189.43	(3)

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$CO+H_2O(g)\rightarrow CO_2+H_2$	-33.13	(4)
$CH_4+H_2O(g)\rightarrow CO+3H_2$	+225.70	(5)
$C+H_2O(g)\rightarrow CO+H_2$	+135.71	(6)
$C+CO_2\rightarrow 2CO$	+168.84	(7)

One of the common methods of thermodynamic calculation is the Gibbs free energy minimization method[15]. In a system where the type of substance and the number of independent reactions are determined, under given conditions, Gibbs free energy is only related to the amount of component substance n_i[15], and the value of n_i corresponding to the smallest Gibbs free energy function is obtained It is a balanced composition. In addition, during the solution, the quantity n_i of the component substance is also limited by the conservation equation of the material (element).

Table 2 shows the reactions that are mainly considered in the liquid chemical looping gasification of bituminous coal. And suppose that Bi_2O_3 is all reduced to Bi during the simulation.

3. RESULTS AND DISCUSSION

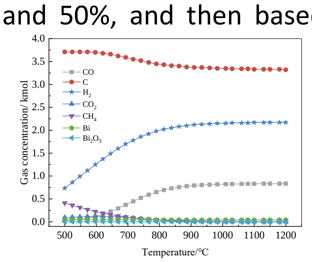
3.1 Effect of temperature

Temperature is an important factor affecting the gasification of coal liquid chemical looping[16].

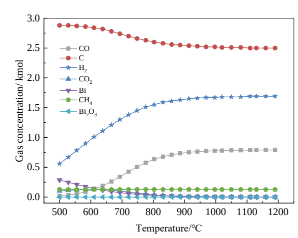
When study the effect of temperature on the equilibrium composition, the total feed mass is taken as 100 kg, where the mass fraction of the liquid oxygen carrier is 10%, 30% and 50%, and then based on the elemental analysis of bituminous coal , we can calculate the corresponding moles at different ratios. The effects of temperature on the gasification process of the bituminous coal/bismuth oxide chemical looping under the mass fractions of 10%, 30% and 50% of Bi_2O_3 can be obtained, as shown in Figure 2.

From the Figure 2 we can see that under different ratios of bismuth oxide and bituminous coal, the trend of equilibrium products was basically the same: the gasification products of bituminous coal are H_2 and CO Mainly, the content of the two gradually increases with the increase of temperature, but the content of CO_2 is very small, and gradually decreases with the increase of temperature.

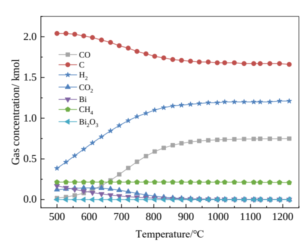
Taking Figure 2(a) as an example, with the increase of temperature, the growth rate of H_2 concentration gradually decreases. With the increase of temperature, the concentration of H_2 grows very slowly, so it can be considered that the optimal gasification temperature for producing H_2 is 900 ℃. The change trend of CO concentration is similar to H_2. For carbon, the residual fixed carbon content is 3.71 kmol at 500 ℃. When the temperature reaches 900 ℃, the remaining fixed carbon content is 3.37 kmol.



(a) Bi_2O_3 quality score is 10%



(b) Bi_2O_3 quality score is 30%



(c) Bi_2O_3 quality score is 50%

Fig. 2 Effect of temperature BC/Bi_2O_3 chemical looping gasification process at different mass fractions of Bi_2O_3

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3.2 Effect of blending ratio

Obviously, the oxygen carrier content will have a greater impact on the gasification equilibrium composition.

In order to investigate the effect of the mixing ratio of liquid oxygen carrier and bituminous coal on the equilibrium composition, in the simulated thermodynamic analysis process using bituminous coal and bismuth oxide as raw materials, the reaction temperature was set to 900 ℃, and given a bituminous coal molar amount of 1 kmol as a reference amount, then only by changing the feed molar amount of Bi_2O_3 can change the mixing molar ratio of the two. As shown in Figure 3, the mixing amount of Bi_2O_3 was increased from 0.001 kmol to 2.75 kmol, and the relationship between the equilibrium composition at 900 ℃ and the molar ratio of Bi_2O_3/BC was obtained. It can be seen from the simulation results that when the Bi_2O_3/BC molar ratio is 0.30, the mass ratio between the two is 9.48, and the CO concentration reaches the highest value. In the actual gasification system, the oxygen carrier cannot be fully reacted as in the simulated system[17], so the Bi_2O_3/BC molar ratio should be greater than 0.30 when actually performing gasification.

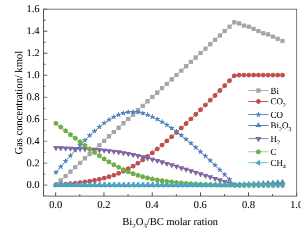


Fig 3 Variation of equilibrium composition at 900 ℃ with Bi_2O_3/BC molar ratio

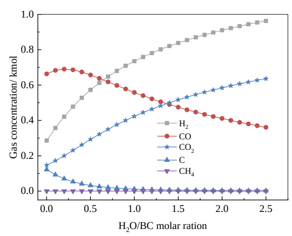
3.3 Effect of steam

The steam/bituminous coal ratio is an important parameter for low-order coal gasification to generate H_2. The addition of steam helps to increase the hydrogen content[12, 18, 19]. In other words, the addition of water vapor provides more hydrogen for the system, which is conducive to the positive reaction of H_2 generation (reactions 7, 8 and 9).

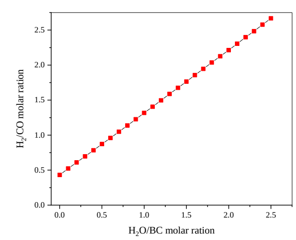
$$CO+H_2O(g)\rightarrow CO_2+H_2 \quad (7)$$

$$CH_4+H_2O(g)\rightarrow CO+3H_2 \quad (8)$$

$$C+H_2O(g)\rightarrow CO+H_2 \quad (9)$$



（a） Balance composition changes with H_2O/BC



（b）H_2/CO ratio changes with H_2O/BC

Fig 4 Variation of the BC/Bi_2O_3 chemical looping gasification equilibrium composition at 900 ℃ with the H_2O/BC molar ratio

Controlling the amount of water vapor added is particularly important for the system's gasification equilibrium composition. In order to study the effect of water vapor addition on liquid chemical looping gasification, in the simulation process of bituminous coal and bismuth oxide as raw materials, the reaction temperature was set to 900 ℃, the pressure was set to normal pressure, and Bi_2O_3/BC was given The molar ratio is 0.30, and then the feed molar ratio of water vapor to bituminous coal is changed from 0.001 to 2.50 gradually. The simulation results are shown in Figure 4.

Figure 4(a) shows the change of the equilibrium composition with the H_2O/BC molar ratio. As the water vapor content gradually increases, the H_2 and CO_2 content gradually increase, but the CO content gradually decreases. This is because With the addition, the oxygen content in the system also increases accordingly, and part of the CO reacts with H_2O to form CO_2 (reaction 7). Too much water vapor will increase the humidity of the generated gas, and a lot of energy will be wasted in the drying process, which will cause the efficiency of the entire gasification system to decrease. Figure 4(b) shows the trend that the H_2/CO molar ratio of the main component of syngas gradually increases with the increase of the H_2O/BC molar ratio. When the H_2/CO molar ratio reaches about 0.20, the hydrogen-carbon ratio can reach more than 2.20. In the liquid chemical looping gasification reaction system, the amount of water vapor needs to be reasonably controlled to ensure that low-order coal gasification can be effectively carried out.

CONCLUSIONS

According to the gasification simulation results of bituminous coal and bismuth oxide, the following main conclusions can be obtained. As the temperature in the

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fuel reactor increases, the efficiency of the bituminous coal chemical looping gasification increases, and the increase in temperature is beneficial to the bituminous coal Incomplete oxidation of coal produces more incomplete oxidation products CO and H_2. The optimum temperature for the gasification reaction between the oxygen carrier and the bituminous coal is in the range of 900~1000℃. Besides, when the content of the oxygen carrier gradually increases, the gasification system first undergoes incomplete oxidation and then gradually complete oxidation occurs. When Bi_2O_3 is used as an oxygen carrier for bituminous coal, the Bi_2O_3/BC molar ratio of 0.30 can be regarded as the turning point of the gasification process. When the Bi_2O_3/BC molar ratio is lower than 0.30, the main products are H_2 and CO; when Bi_2O_3/ When the BC molar ratio is higher than 0.30, the main products become H_2O and CO_2. (3) The addition of water vapor is conducive to the increase of H_2 content. With the increase of water vapor content, the H_2/CO molar ratio in the system will gradually increase.

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