

Thermodynamic study on Chemical Looping Gasification of Biomass with the CuMn_2O_4 and CaO dual-effect oxygen carrier

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Abstract: CuMn_2O_4 and CaO were mixed in a certain proportion to prepare dual-effect oxygen carriers. A model of biomass chemical looping gasification with corn cob as biomass, CuMn_2O_4 and CaO as the active ingredient of dual-effect oxygen carriers was performed, and the thermodynamic analysis of the reaction was performed. The appropriate reaction conditions and the appropriate proportion of reactants were obtained by taking the yield of syngas component, the carbon conversion rate and the removal capacity of CO_2 as the main evaluation indicators. The optimal value of $n(\text{CuMn}_2\text{O}_4)/n(\text{B})$ is 0.09, the optimal reaction temperature is 800°C , the optimal reaction pressure is standard atmospheric pressure, the optimal value of $n(\text{CaO})/n(\text{B})$ is 1.5, the optimal value of $n(\text{H}_2\text{O})/n(\text{B})$ is 1. In this reaction system, the yield of H_2 can reach 1.1857 mol/mol, the yield of CO can reach 0.33224 mol/mol, the carbon conversion rate can reach 50.70%, and the adsorption rate of CO_2 by CaO can reach 58.08%.

Key words: Biomass; chemical looping gasification; dual-effect oxygen carrier; CuMn_2O_4 ; CaO ; thermodynamic study; CLC number: TQ Document identification code: A

1. Introduction

Biomass is a kind of renewable energy with huge output. Biomass gasification has the most industrial application prospects among many biomass utilization methods. By using different gasification agents (oxygen, air, water vapor or carbon dioxide), biomass has a series of reactions such as pyrolysis, inadequate combustion and gasification and, are finally converted into gaseous products with CO_2 , CO , H_2 and CH_4 as the main components [1-4]. At present, among the gasification agents used in biomass gasification, the syngas produced by oxygen gasification has a high concentration of combustible gas and a high calorific value of the produced gas. However, the high costs of oxygen preparation lead to a great increase in oxygen gasification costs. Based on this, German scientist Richter et al. proposed a chemical looping gasification (CLG) [5] process based on lattice oxygen. The principle is to use lattice oxygen in oxygen carrier to react with fuel in gasification reactor, and by controlling the ratio of oxygen carrier to fuel, a synthesis gas with CO and H_2 as the main components is obtained; the oxygen carrier after the release of oxygen absorbs oxygen in the air in the air reactor to be oxidized and regenerated.

At present, the solid-solid reaction of solid oxygen carrier and solid carbon gasification in the chemical looping gasification process has problems such as high reaction temperature and slow reaction speed. Therefore, people drew on the idea of Chemical Looping with Oxygen Uncoupling (CLOU) [6] that the solid oxygen carrier first

undergoes oxygen decoupling reaction to generate gaseous oxygen, and proposed an oxygen decoupling chemical looping gasification method. The solid-solid reaction between the biomass coke and the oxygen carrier is transformed into a gas-solid reaction between the biomass coke and the oxygen carrier releasing oxygen. Thereby enhancing the gasification reactivity and increasing the gasification reaction rate. At this time, it is very important to choose an oxygen carrier with excellent oxygen decoupling performance and good economy.

In the current research field of oxygen carriers, CaSO_4 , perovskite and oxides of metals such as Mn , Ni , Cu , Co and Fe can be used as active components of oxygen carriers [7-10]. Among them, Mn is considered to be an excellent oxygen carrier material due to its high economy, good reactivity and high solid-phase circulation rate. At the same time, to reduce the thermodynamic limit of the re-oxidation of Mn single metal oxide oxygen carriers at low oxygen concentration levels, taking into account the advantages of various single metal oxide oxygen carriers, and enhancing structural stability and thermodynamic properties, composite oxygen carriers was an effective solution [11]. Chen Zhihao [12] et al. experimentally prepared and verified that two manganese-based composite oxygen carriers, MnFeO_3 and MnFe_2O_4 , have an effective catalytic effect on the pyrolysis of biomass and contribute to the yield of CO and H_2 in syngas improvement. Alexander Shulman [13] et al. studied the Mn/Fe , Mn/Si , Mn/Ni oxygen carriers in CLOU and showed that the three composite oxygen carriers have

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oxygen release and high reactivity with methane, and at the same time at 1100°C the methane conversion of the Mn/Fe oxygen carrier reaction group synthesized at also showed a long-term increasing trend. Li Fengcui [14] et al. measured the active components of Cu-Mn composite oxygen carrier CuO and Mn₂O₃ by the thermogravimetric analyzer and did not react with the inert carrier MgO, which effectively solves the problem that Mn single metal oxide oxygen carrier reacts with inert carrier MgO and fails.

At the same time, CO₂ must exist in the synthesis gas in the biomass gasification process. In order to further improve the quality and calorific value of the synthesis gas, CO₂ should be removed. If it is removed after gasification, an additional device for adsorbing CO₂ is required, and in-situ adsorption of CO₂ in the gasification process can save the adsorption device and facilitate the process of gasification reaction. Based on this, the concept of “in situ adsorption” is proposed in this paper. At this time, the selection of high-temperature CO₂ adsorbent has become one of the key links of “in-situ adsorption”. At present, lithium-based adsorbents and calcium-based adsorbents are the focus of high-temperature CO₂ adsorbent research. Lithium-based adsorbents are mainly represented by Li₂ZrO₃ and LiSiO₄ [15-17], which can absorb CO₂ chemically in the temperature range of 400 ~ 700°C, but Li₂ZrO₃ and LiSiO₄ have lower CO₂ adsorption capacities, and the saturated adsorption capacities are 0.287 g/g and 0.367 g/g, and have the disadvantages of low adsorption rate, long adsorption time, and Li volatilization at high temperature. While the calcium-based adsorbent is mainly CaO, which can absorb CO₂ in the temperature range of 500 ~ 800°C, its saturated adsorption capacity is 0.786 g/g, and it has excellent CO₂ adsorption performance and adsorption cycle stability, making it an ideal high-temperature CO₂ adsorbent [18]. Therefore, in this paper, CaO with excellent performance was selected as the in-situ adsorbent, and a dual-effect oxygen carrier composite material was fabricated to make the oxygen decoupling reaction and carbon dioxide adsorption occur simultaneously, so as to reduce the use of industrial equipment.

In this paper, thermodynamic analysis was carried out to study the chemical looping gasification process of biomass represented by corn cob (B) with CuMn₂O₄ and CaO compound as the active component. The results of the Ultimate analysis and Proximate analysis of corn cob are shown in Table 1. The main elements in corn cob are C, H, O, and the contents of other elements (N, S) can be ignored. The simplified formula of CH_{1.56}O_{0.79} represents the biomass composition. The whole gasification process is based on the carbon conversion rate (x_c , %), the amount of each generated gas and t and the adsorption rate of CO₂ by CaO as the main reference, the ratio of the oxygen carrier, biomass and CaO and the optimum conditions of chemical looping gasification reaction was filtered to achieve CO₂ emission reduction, promote the reaction process and reduce the use of instruments and equipment, so as to respond to China's policies such as carbon peaking, carbon neutrality, energy saving and emission reduction.

Table 1. Elemental analysis and industrial analysis of corn cob

Ultimate analysis, ω ad %					Proximate analysis, ω ad %		
C	H	O	N	S	Volatile	Fixed Carbon	Ash
45.25	5.89	47.79	0.83	0.21	79.68	17.78	2.54

2. Thermodynamic analysis methods

The thermodynamics software called “HSC Chemistry” is a thermodynamic calculation software based on the Gibbs free energy minimization principle, which is used to study the influence of different variables on the equilibrium of chemical systems. It is a very handy and useful tool that can help us find the optimal reaction conditions for experiments without expensive trial and error [19]. In this paper, the “Reaction Equation” and “Equilibrium Compositions” modules in “HSC Chemistry 5.0” software are used to calculate the thermodynamics of the gasification reaction characteristics of the chemical looping and analyze the results respectively, to determine the optimal reaction environment and material ratio of the reaction.

The main chemical equations involved in this chemical looping gasification reaction are as follows:

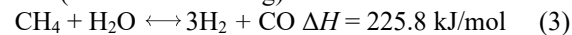
PWG (Primary water gas):



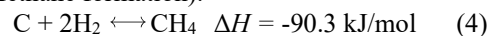
BD (Boudouard):



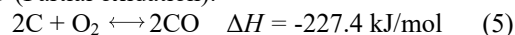
MR (Methane reforming):



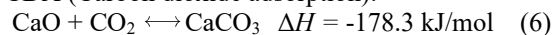
MF (Methane formation):



POD (Partial oxidation):



CDA (Carbon dioxide adsorption):



3. Determining optimal ratios and reaction parameters

3.1 Effects of n(CuMn₂O₄)/n(B) on chemical looping gasification

The gasification temperature was set to 1000°C, the gasification pressure was normal, and the amount of biomass was fixed to 1 kmol. Fig.1 shows the gas production rate and carbon conversion when the oxygen carrier CuMn₂O₄ and biomass are in different molar ratios (0.05-0.15). The analysis shows that with the increase of the molar ratio of CuMn₂O₄ to biomass, the content of CO increases first and then stabilizes. When the molar ratio of CuMn₂O₄ to biomass is less than 0.09, the H₂ content remained unchanged. When the molar ratio of CuMn₂O₄ to biomass is greater than 0.09, the H₂ content begins to increase with the molar ratio of CuMn₂O₄ to biomass and decreases. Due to the high gasification temperature, CH₄ is converted into CO and H₂, and the content of CH₄ is always small under different conditions of CuMn₂O₄ to biomass molar ratio. When the molar ratio of CuMn₂O₄ to

biomass is equal to 0.09, the total amount of CO, H₂, and CH₄ are the largest, and their total proportion is 98.5%. With the increase of the molar ratio of CuMn₂O₄ to biomass, the total dry concentrations of CO, H₂ and CH₄ start to decrease. The lattice oxygen provided by CuMn₂O₄ increases with the molar ratio of CuMn₂O₄ to biomass, and the biomass can be completely converted into CO₂ and CH₄. The generation of CO₂ and H₂O increased with the increase of the mole ratio of CuMn₂O₄ to biomass. Although the carbon conversion rate increases with the molar ratio of CuMn₂O₄ to biomass, the biomass needs to be partially oxidized to combustible syngas, not to CO₂ and H₂O in CLG, so the optimum molar ratio of CuMn₂O₄ to biomass is 0.09.

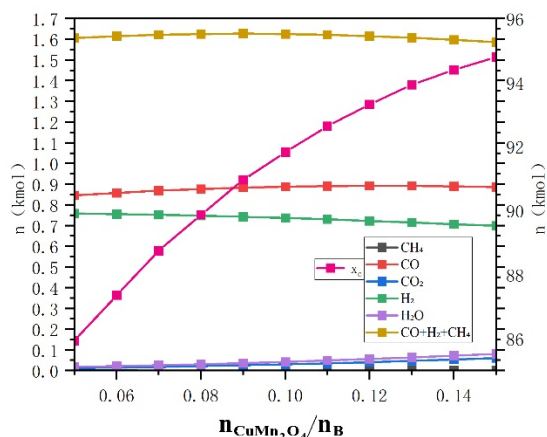


Figure 1. Effects of $n(\text{CuMn}_2\text{O}_4)/n(\text{B})$ on chemical looping gasification

3.2 Effects of reaction temperature on chemical looping gasification

Assuming the biomass is 1 kmol, CuMn₂O₄ is 0.09 kmol, adding an appropriate amount of CaO and at atmospheric pressure, the effect of temperature on gasification characteristics is shown in Fig.2. From Fig. 2(a), it can be seen that temperature has a significant effect on biomass gasification in CLG. When the temperature is less than 1000 °C, the H₂ content all increased greatly with the increase of temperature, reaching 0.743 kmol at 1000°C, and then increased slowly. At about 400°C, CO is produced and increases greatly with increasing temperature. At about 1000 °C, the amount of CO is 0.884 kmol. The content of CH₄ decreased with increasing temperature and dropped to zero after 800 °C. The changing trend of H₂O with temperature is the same as that of CH₄. At about 1000°C, the amount of H₂O decreases to zero. With the increase of temperature, the content of CO₂ increased first and then decreased, and its yield reached the maximum value of 0.241 kmol at about 600°C, and the content of CO₂ gradually decreased with the increase of temperature after 600°C. (1), (2), (3) are all endothermic reactions. According to Le Chatelier's principle, high temperatures favor the products of endothermic reactions, and elevated temperatures favor the formation of CO and H₂. With the continuous increase of temperature, the carbon conversion rate increases slowly, and the high temperature also inhibits the

formation of carbon deposits on the surface of CuMn₂O₄. However, CaCO₃ produced by CaO adsorption of CO₂ will be thermally decomposed at high temperatures, so CaO will fail at high temperatures. Fig.2 (b) and Fig.2 (c) show that when the temperature is greater than or equal to 825°C, the adsorption of CaO on CO₂ will be invalid, so the optimal reaction temperature can be determined to be 800°C based on the yield of each syngas and the adsorption of CO₂.

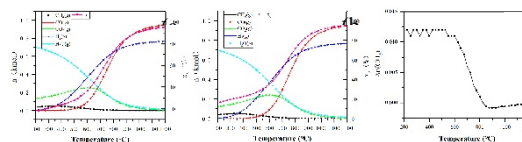


Figure 2. Effects of reaction temperature on chemical looping gasification

3.3 Effects of reaction pressure on chemical looping gasification

Assuming that the biomass is 1 kmol, CuMn₂O₄ is 0.09 kmol, an appropriate amount of CaO is added and the temperature is 800°C, Fig.3 shows the effects of pressure on gasification characteristics. With the increase of pressure, the production and proportion of CO and H₂ decreased, and the production and proportion of CO₂ and H₂ increased. The carbon conversion rate decreased and the carbon deposition amount on the surface of CuMn₂O₄ increased. According to Le Chatelier's principle, (1), (2), (3) and (5) all consume H₂ and CO by shifting to the left, (4) moves to the right. With the increase of pressure, the production and proportion of CH₄ increased slightly and high pressure is not conducive to the progress of CLG reaction of biomass. On the contrary, it is obvious that if the reduction process is under negative pressure, the yield of CO and H₂ can be improved, but the negative pressure also brings about the safety problem of the equipment, so the optimal pressure for this reaction is atmospheric pressure.

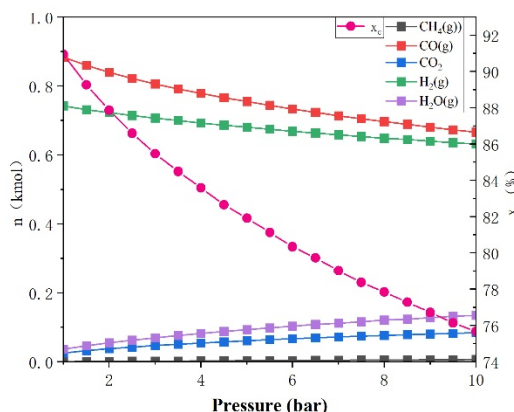


Figure 3. Effects of reaction pressure on chemical looping gasification reaction

3.4 Effects of $n(\text{CaO})/n(\text{B})$ on chemical looping gasification

When the molar ratio of CuMn_2O_4 to biomass was 0.09 and in the environment of 800°C and one-atmosphere pressure, the change of the remaining amount of CO_2 was observed by changing the mass ratio of CaO to biomass. As shown in Fig.4, as the value of $n(\text{CaO})/n(\text{B})$ increases, there is a significant reduction in the material amount of CO_2 . When the ratio of $n(\text{CaO})/n(\text{B})$ increases after 1.5, the rate of CO_2 absorption and CaCO_3 decomposition is gradually equal, (6) reaches equilibrium, the adsorbent CaO is gradually saturated, and the remaining amount of CO_2 tends to be stable gradually. So, the optimum molar ratio can be taken as 1.5. At this time, the absorption rate of CO_2 can reach 58.08%.

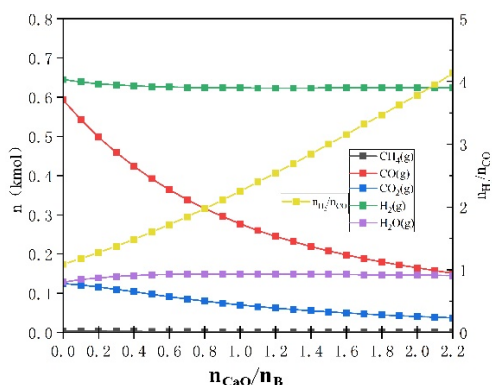


Figure 4. Effects of $n(\text{CaO})/n(\text{B})$ on chemical looping gasification

3.5 Effects of $n(\text{H}_2\text{O})/n(\text{B})$ on chemical looping gasification

Water vapor is not only the product of the gasification reaction, but the addition of water vapor during the reaction can change the molar ratio of H_2 and CO to optimize the syngas. When the molar ratios of CuMn_2O_4 and CaO to biomass are 0.09 and 1.5 and under the environment of 800°C and one-atmosphere pressure, the effect of $n(\text{H}_2\text{O})/n(\text{B})$ on gasification characteristics is as follows shown in Fig.5. With the increase of $n(\text{H}_2\text{O})/n(\text{B})$, the molar ratio of H_2 and CO , the amount of H_2 generated and the total amount of synthesis gas all increased significantly. When the value of $n(\text{H}_2\text{O})/n(\text{B})$ is less than 1, the CO production increases with the increase of the ratio; when the value of $n(\text{H}_2\text{O})/n(\text{B})$ is greater than 1, the CO production begins to decrease, and the synthesis gas changes the change of the total substance quantity also tends to be stable gradually. At the same time, with the increasing of water vapor, the pressure of the reaction environment will also increase accordingly, and the conclusion drawn from 2.3 can prove that the increase of pressure will inhibit the formation of syngas. Therefore, the optimum $n(\text{H}_2\text{O})/n(\text{B})$ value is determined to be 1.0 after synthesizing various factors. At this time, the yield of H_2 is 1.1857 mol/mol, the yield of CO is 0.33224 mol/mol, and the carbon conversion rate can reach 50.70%.

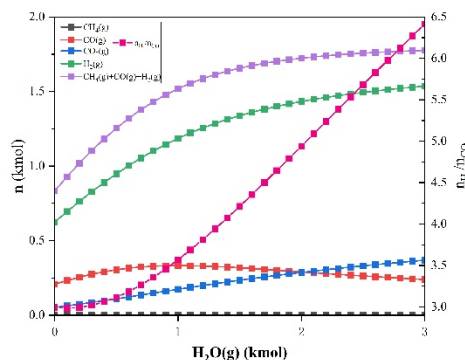


Figure 5. Effects of $n(\text{H}_2\text{O})/n(\text{B})$ on chemical looping gasification reaction

4. Conclusion

By establishing a chemical looping gasification reaction model with corn cob as biomass, CuMn_2O_4 and CaO as composite oxygen carriers, the reaction was thermodynamically analyzed using HSC and other software, and the total amount of syngas, relative proportion of syngas, the carbon conversion rate and CO_2 removal capacity are the main indicators to obtain the appropriate reaction environment conditions and the appropriate ratio relationship between the reactants:

- (1) The optimum molar ratio of CuMn_2O_4 to biomass is 0.09.
- (2) The optimum temperature for the reaction is 800°C .
- (3) The optimum pressure for the reaction is standard atmospheric pressure.
- (4) The optimum value of $n(\text{CaO})/n(\text{B})$ is 1.5, and the adsorption rate of CaO to CO_2 can reach 58.08%.
- (5) The optimum value of $n(\text{H}_2\text{O})/n(\text{B})$ is 1, the carbon conversion rate of the reaction reaches 50.70%, the H_2 yield can reach 1.1857 mol/mol, and the CO yield can reach 0.33224 mol/mol.

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