Thermodynamic Analysis and Synthesis Gas Generation by Chemical-Looping Gasification of Biomass with Nature Hematite as Oxygen Carriers*

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ABSTRACT

Thermodynamic parameters of chemical reactions in the system were carried out through thermodynamic analysis. According to the Gibbs free energy minimization principle of the system, equilibrium composition of the reactions of chemical-looping gasification (CLG) of biomass with natural hematite (Fe₂O₃) as oxygen carrier were analyzed using commercial software of HSC Chemistry 5.1. The feasibility of the CLG of biomass with hematite was experimental verified in a lab-scale bubbling fluidized bed reactor using argon as fluidizing gas. It was indicated the experimental results were consistent with the theoretical analysis. The presence of oxygen carrier gave a significant effect on the biomass conversion and improved the synthesis gas yield obviously. It was observed that the gas content of CO and H₂ was over 70% in CLG of biomass. The reduced hematite particles mainly existed in form of FeO. It was showed that the reduction of natural hematite with biomass proceeds in a stepwise manner from Fe₂O₃ → Fe₃O₄ → FeO. Reduction product of natural hematite can be restored the lattice oxygen by oxidation with air.

Keywords: Thermodynamics; Synthesis Gas; Natural Hematite; Oxygen Carriers; Biomass Chemical Looping Gasification

1. Introduction

Chemical-looping gasification (CLG) is a novel gasification technique that involves the use of oxygen carrier, which transfers oxygen from air to the fuel, which is partially oxidized into H₂ and CO, avoiding the direct contact between them. Therefore, the air to fuel ratio is kept low to prevent the fuel from becoming fully oxidized to CO₂ and H₂O. [1]. A basic chemical-looping gasification system has two reactors, one for air and one for fuel, as is illustrated in Figure 1. On the contrast of traditional gasification technologies, CLG has several potential benefits as follows [2]. Firstly, the recycling of oxygen carrier can provide the oxygen needed for gasification, thus, it can save the cost for making pure oxygen. Secondly, the oxidation reaction of the metal oxide is very exothermic; however, the reduction reactions are endothermic. So, the heat for the endothermic reduction reactions is given by the circulating solids coming from the air reactor at higher temperature. And the same time, the oxygen carrier also can catalyze tar cracking, which reduced the content of tar in biomass gasification [3-5].

There are some works studying chemical looping gasification of solid fuels. He et al. [6] investigated the CLG of biomass with natural hematite as oxygen carriers in a bubbling fluidized bed reactor. It was found that the gasification efficiency and carbon conversion reached up to 75.8% and 94%, respectively. Cao et al. [7] tested in circulating fluidized bed reactor different oxygen carriers, which can capture that the concentration of CO₂ enriched to 99%. B. Acharya et al. [8] put forward a set of system which produced hydrogen through biomass chemical-looping gasification. Efficiency of the system was as high as 87.49%, and the hydrogen concentration was found to be 71%, in addition, zero discharge of CO₂ can realize.

The objective of this investigation was to explore the possibility of using natural hematite (Fe₂O₃) as the oxygen carrier in CLG of biomass. In the present work, the thermodynamics of biomass chemical looping gasification was analyzed, and the same time, CLG of biomass with natural hematite as oxygen carrier was experimen-
tally investigated in a lab-scale bubbling fluidized bed reactor using argon as fluidizing gas.

2. Thermodynamic Analysis of Chemical-Looping Gasification

2.1. Chemical Reactions

Fe$_2$O$_3$ as oxygen carriers in the air reactor, the main reactions at 750°C probably are:

$$\begin{align*}
4\text{Fe}_2\text{O}_3 + \text{O}_2 & \rightarrow 6\text{Fe}_3\text{O}_4 \\
\Delta H &= -483.07 \text{ kJ/mol} \\
4\text{FeO} + \text{O}_2 & \rightarrow 2\text{Fe}_2\text{O}_3 \\
\Delta H &= -554.68 \text{ kJ/mol}
\end{align*}$$

In the fuel reactor, the main reactions probably are: pyrolysis of biomass:

$$\begin{align*}
\text{C}_n\text{H}_{2m}\text{O}_x & \rightarrow \text{char} + \text{tar} + \text{syngas} \\
& (\text{CO}, \text{H}_2, \text{CO}_2, \text{CH}_4)
\end{align*}$$

The reduction reactions of oxygen carrier particle with pyrolytic products of biomass at 650°C [9]

$$\begin{align*}
\text{CO} + 3\text{Fe}_2\text{O}_3 & \rightarrow \text{CO}_2 + 2\text{Fe}_2\text{O}_4 \\
\Delta H &= -37.67 \text{ kJ/mol}
\end{align*}$$

$$\begin{align*}
\text{CO} + \text{Fe}_2\text{O}_3 & \rightarrow \text{CO}_2 + 2\text{FeO} \\
\Delta H &= -3.22 \text{ kJ/mol}
\end{align*}$$

$$\begin{align*}
\text{H}_2 + 3\text{Fe}_2\text{O}_3 & \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}_2\text{O}_4 \\
\Delta H &= -2.01 \text{ kJ/mol}
\end{align*}$$

$$\begin{align*}
\text{H}_2 + \text{Fe}_2\text{O}_3 & \rightarrow \text{H}_2\text{O} + 2\text{FeO} \\
\Delta H &= 32.44 \text{ kJ/mol}
\end{align*}$$

$$\begin{align*}
\text{CH}_4 + 3\text{Fe}_2\text{O}_3 & \rightarrow 2\text{H}_2 + \text{CO} + 2\text{Fe}_2\text{O}_4 \\
\Delta H &= 221.76 \text{ kJ/mol}
\end{align*}$$

$$\begin{align*}
\text{CH}_4 + 4\text{Fe}_2\text{O}_3 & \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 8\text{FeO} \\
\Delta H &= 317.87 \text{ kJ/mol}
\end{align*}$$

$$\begin{align*}
\text{C} + 3\text{Fe}_2\text{O}_3 & \rightarrow \text{CO} + 2\text{Fe}_2\text{O}_4 \\
\Delta H &= 133.65 \text{ kJ/mol}
\end{align*}$$

Therefore, in the presence of oxygen carriers, these reactions occur sequentially and simultaneously during biomass pyrolysis and gasification. The final products of biomass gasification are determined by the interaction of a couple of above mentioned reactions.

2.2. Thermodynamic Analysis of Gasification Process

Effect of the temperature on the Gibbs free energy ($\Delta rG$) and chemical equilibrium constant ($\text{Log}K$) of reactions (4)-(11) was shown in Figure 2. In Figure 2, it found that the $\Delta rG$ is less than zero and the $\text{Log}K$ is more than zero, which means that the reactions (4)-(11) can react in the thermodynamics. If dividing the reactions (4)-(11) into four groups, that is (4)-(5); (6)-(7); (8)-(9); (10)-(11), it can be seen that the former is less than the later for $\Delta rG$, but the trend of $\text{Log}K$ is opposite from the Figure 2, further, the trends of change increased with the increase of temperature. As we known, if the smaller $\Delta rG$ and the greater $\text{Log}K$, the reaction will be easier to occur. So, it can conclude that oxygen carriers were reduced gradually in the atmosphere of biomass pyrolysis. It meant the oxygen carriers changed as follows: Fe$_2$O$_3$ $\rightarrow$ Fe$_3$O$_4$ $\rightarrow$ FeO.

2.3. Chemical Equilibrium of Biomass Gasification Process

There were a number of reactions in the CLG according to the theory analysis. However, some reactions were predominant and the other reactions were secondary in the actual process. If the secondary reactions were ignored, it can help us a better understanding of the CLG. According to the principle of Gibbs free energy minimization, equilibrium components of biomass with Fe$_2$O$_3$,

$$\begin{align*}
\text{C} + 2\text{Fe}_2\text{O}_3 & \rightarrow \text{CO}_2 + 4\text{FeO} \\
\Delta H &= 164.88 \text{ kJ/mol}
\end{align*}$$

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were investigated through HSC Chemistry 5.1 software, which is a produced by Outokumpu company in Finland. The approximate formula of biomass is CH$_{1.34}$O$_{0.65}$, regardless the S and N.

In order to illustrate the influence of the biomass to Fe$_2$O$_3$ ratio on equilibrium composition, the equilibrium composition was calculated by changing Fe$_2$O$_3$ content at the same temperature. The result was shown in Figure 3. The temperature is set at 750°C and the initial value of CH$_{1.34}$O$_{0.65}$ is 1kmol in the process. In Figure 3(a), the Fe$_2$O$_3$ content was gradually increased from 0.02 kmol to 6 kmol. As seen in figure, the content of incomplete oxidation products (CO + H$_2$) gradually decreased and the content of complete oxidation products (CO$_2$ + H$_2$) gradually increased with the amount of Fe$_2$O$_3$ gradually increased, respectively. As the amount of Fe$_2$O$_3$ is nearly 5 kmol, the amount of H$_2$ + CO is almost zero, and the content of H$_2$O + CO$_2$ is almost constantly. At the same time, the amount of carbon which produced by carbon deposit reaction decreased with increase the amount of Fe$_2$O$_3$, the carbon is almost disappeared as the Fe$_2$O$_3$ content near 1kmol. It can be observed the reduction products of Fe$_2$O$_3$ are mainly FeO and Fe$_3$O$_4$. As the amount of Fe$_2$O$_3$ is less than 3.5 kmol, the main reduction product is FeO, however, the main reduction product is Fe$_3$O$_4$ when the amount of Fe$_2$O$_3$ is more than 3.5 kmol. In this paper, it concerned to produce syngas which is mainly composed of H$_2$ and CO. Thus, in order to obtain syngas instead of CO$_2$ and water, it is necessary to keep the ratio of lattice oxygen to fuel as low as to prevent the fuel from being fully oxidized to CO$_2$ and H$_2$O. The effect of the amount of Fe$_2$O$_3$ from 0.02 to 1.2 kmol on the equilibrium composition is shown in detail in Figure 3(b). As shown in the figure, the amount of CO reaches maximum when the Fe$_2$O$_3$ content is about 0.2 kmol, and then which is declined gradually with the amount of Fe$_2$O$_3$ increasing. It is worth to note that the amount of CO$_2$ is more than CO as the Fe$_2$O$_3$ content is more than 0.7 kmol, which means that biomass is completely oxidized due to the lattice oxygen increasing. So, it can produce more CO$_2$ rather than CO. Therefore, the amount of Fe$_2$O$_3$ must be kept between 0.2 kmol and 0.7 kmol to obtain the syngas. The reduction product of Fe$_2$O$_3$ is mainly FeO, and almost nonexistent Fe$_3$O$_4$. At the same time, it can infer that carbon deposition was caused by material excessive from the Figure 3.

According to the analysis of the thermodynamic theories, it can obtain the synthesis gas which the main component is CO and H$_2$ through the ratio of fuel to lattice oxygen is kept low level. Meanwhile, the main reduction product of Fe$_2$O$_3$ is FeO.

In the next work, CLG of biomass with natural hematite as oxygen carrier was experimentally studied in a lab-scale bubbling fluidized bed reactor using argon as fluidized gas.

3. Experimental

3.1. Raw Materials

The sawdust of pine with particle sizes between 250 - 425 μm was dried in the oven which kept 105°C. The dry-basis proximate analysis and ultimate analysis of the sawdust are showed in Table 1. The hematite with particle sizes between 180 - 250 μm which was supplied by Guangdong Iron & Steel Group Co. Ltd. The elements composition analysis of the hematite is presented in Table 2. According to the Fe$^{3+}$ fraction, it is calculated that the Fe$_2$O$_3$ content is about 81.66% in the hematite.

3.2. Laboratory Setup

The experiments were conducted with a bubbling fluidized bed reactor of quartz placed in a transparent furnace, as is illustrated in Figure 4. The reactor is in length of 1000 mm and an inner diameter of 60 mm. The bed tem-
Table 1. Proximate and ultimate analysis of pine.

<table>
<thead>
<tr>
<th></th>
<th>Proximate analysis wad %</th>
<th>Ultimate analysis wad %</th>
<th>Q&lt;sub&gt;av&lt;/sub&gt; KJ/kg</th>
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<tr>
<td></td>
<td>M V FC A C H O N S</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>49.66 5.55 43.33 0.021</td>
<td>1.44</td>
<td>18506</td>
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*: by difference.

Table 2. Elements composition analysis of iron ore (%).

<table>
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<tr>
<th>Item</th>
<th>S</th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Fe&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
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<td>0.41</td>
<td>5.64</td>
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<table>
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<th>Item</th>
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<th>MgO</th>
<th>Na&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>K&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>P</th>
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<tbody>
<tr>
<td>Content</td>
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<td>0.035</td>
<td>0.10</td>
<td>0.048</td>
<td>0.017</td>
</tr>
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</table>

Figure 4. Schematic layout of the laboratory setup.

Temperature was measured 5 mm above the porous quartz plate using a K-type thermocouple. Oxygen carrier particles were placed on the porous plate and were then heated in air flow to set temperature. During the reducing period, the fluidizing gas was argon (800 L/hr), which was introduced from the bottom of the reactor. When the temperature comes to the set value, biomass was continuously fed (by a screw feeder) in a hopper at the top of the reactor. At the same time, argon (200 L/hr) was introduced from the top of the hopper. Therefore, the biomass sample was pushed by argon flow into the fluidized bed through a drop tube. The flue gases are passed through the cold trap to collect solid particles, water, and tar then introduced into the sampling bag. The composition of the gas products is measured using a gas chromatograph (SHIMADZUA Gas Chromatograph, GC-20B). All the oxygen carrier samples were performed with an X-Ray Diffraction (X’Pert PRO XRD).

4. Results and Discussion

4.1. Effect of the Presence of Hematite Particles on the Biomass Gasification

Based on the thermodynamic analysis, the mass of oxygen carriers and biomass material were set to 150 g and 44 g in a single test, respectively. The ratio of lattice oxygen to fuel is 0.42.

The effect of the presence of hematite particles on the CLG of biomass was investigated at temperatures of 750°C. Figure 5 shows the comparison of the gas yields
of each gaseous component and the sum of the yields of H₂, CH₄, CO and CO₂ in the process of biomass CLG with those of blank tests during testing period of 30 min. In the blank tests, the hematite particles were replaced by silica sand. Therefore, the process taking place in the blank tests is only pyrolysis rather than CLG of biomass. As shown in Figure 5, the volume yields of each gaseous constituent were obviously enlarged in the presence of hematite particles. The total gas yields were increased from 25.17 L up to 42.39 L at 750°C. The yields of the generated gases (H₂, CH₄, CO, and CO₂) obtained with hematite particles were apparently larger than with silica sand, which suggest that the lattice oxygen in the hematite particles was used as the gasifying agent during biomass gasification. The main components of gaseous product are CO and H₂ which reached about 70% amount of the total volume of the gaseous product. The promoter action of lattice oxygen to carbon conversion was more obvious than to hydrogen conversion. So, the carbon can convert into carbon dioxide and carbon monoxide more completely, it can cause the volume of gaseous product which contained carbon element going up obviously, especially the volume of carbon dioxide. Figure 5 also illustrates gas concentrations (on the basis of argon free) of biomass gasification with oxygen carrier and pyrolysis with silica sand during 30 min at 750°C. Clearly, it was found that the concentrations of H₂, CH₄, CO and CO₂ were kept stable when biomass was pyrolyzed with inert silica sand. Whereas, there were significant changes for the gaseous concentration of biomass with hematite particles as reaction time increasing, especially the concentration of CO₂ and H₂. The CO and CH₄ concentrations of biomass with hematite particles were both lower than those of biomass with silica sand. H₂ concentration increased with the reaction time going on in the CLG of biomass probably owing to a part of biomass was totally oxidized into CO₂ and H₂O which subsequently accelerated the hydrogen generation reactions taking place rightward. In addition, in the initial stage of biomass gasification with hematite particles, the CO₂ fraction was more than 30% in the generated gas due to the easily availability of active lattice oxygen in the oxygen carrier particles. As the reactions proceeded, the concentration of CO₂ decreased gradually to 10% approximately. These results may be contributed to the amount of valid hematite particles decreasing with the reactions proceeding. So, portion of biomass taken out by fluidized gas after only pyrolytic reaction, which can cause the proportion of pyrolysis gas increasing in the gaseous products. Through the contrast test, it experimental verified the feasibility of biomass chemical-looping gasification with hematite particles as oxygen carriers.

4.2. XRD Analysis of Oxygen Carriers

Figure 6 shows the XRD patterns of fresh oxygen carrier, the oxidized oxygen carrier with the air, and the reduced oxygen carrier of the fuel reactor under different temperature, respectively. In Figure 6(b), it can be seen that the mainly existed in form of Fe₂O₃ and SiO₂ for fresh oxygen carrier. Comparison to fresh oxygen carrier, there was no chemical changes occurred in the regeneration of reacted oxygen carrier, and Fe₂O₃ was found the major phase with minor amounts of Fe₃O₄. The forms of oxygen carriers after the reduction reaction changed as temperature rising, as seen in Figure 6(a), at lower temperature (650°C), the variation of oxygen carriers was from Fe₂O₃ to Fe₃O₄, the main existence form of reduced oxygen carriers was FeO at higher temperature (≥750°C).

However, the variation of hematite particles as oxygen carriers was from Fe₂O₃ to Fe₃O₄ in the CLC of biomass [10-12].

The elements content of Fe in hematite particles was analyzed as shown in Figure 7, it found that the ferric
iron was reduced to ferrous iron in the CLG of biomass. The tendency of conversion was more and more obviously with increase of temperature. The capacity of lattice oxygen in oxygen carriers was recovered by air oxidization, which was affected slightly on the reduction temperature. So, it is feasible that the hematite particles can be used circularly as oxygen carriers in the CLG of biomass, which have higher oxygen transfer ability.

According to the analysis of existence form of reduced oxygen carriers, it found that hematite particles undergone the process of biomass gasification as oxygen carriers, and the mainly existence form of hematite particles were FeO after reduction as the temperature higher than 750°C. Further, the reduction of hematite particles with biomass proceeded in a stepwise manner from Fe2O3 \( \rightarrow \) Fe3O4 \( \rightarrow \) FeO. So, the main reactions were (2), (5), (7), (9), and (11) in the CLG of biomass with the hematite particles as oxygen carriers.

5. Conclusion

The process in CLG of biomass mixed with natural hematite as oxygen carriers was analyzed using the theory of thermodynamics, and then, the verification test was studied in a bubbling fluidized bed reactor with argon as fluidizing gas. It was found that the theory analysis was coincidence with the results of experiment. Consequently, it is feasibility natural hematite as oxygen carriers in CLG of biomass. It can obtain synthesis gas which mainly included CO and H2 by limiting the ratio of lattice oxygen to fuel between 0.2 and 0.7. The presence of oxygen carriers could obviously affect the process of biomass thermal conversion, which can significantly increase gas yield and carbon conversion rate. The main components of gaseous product were CO and H2 which reached about 70% amount of the total volume of the gaseous product. The concentration of CO was the highest and the concentration of CH4 was the lowest during the biomass gasification. In addition, the concentrations of H2, CO, and CH4 in the product gas slowly increased with the reaction proceeding, and the CO2 concentration showed an opposite trend. XRD analysis showed that the iron element in the reduced hematite particles mainly existed in form of FeO, with minor formation of Fe3O4. Further, the lattice oxygen released, corresponding to the transformation Fe2O3 \( \rightarrow \) Fe3O4 \( \rightarrow \) FeO, provided the oxygen element needed in biomass gasification. The capacity of lattice oxygen in reduced oxygen carriers can be recovered through air oxidization.

6. Acknowledgements

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