Evaluation of $CuO/MgAl_2O_4$ in Biomass Chemical Looping Gasification with Oxygen Uncoupling

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Chemical looping gasification (CLG) is a promising method for the utilization of biomass to produce syngas. However, its realization is largely dependent on the use of an oxygen carrier with a high and stable reactivity in cyclic reduction and oxidation. This work focused on the improvement of reactivity and stability of CuO in chemical looping gasification *via* the addition of $MgAl_2O_4$ as an inert material. First, the stability and reactivity of synthesized Cu-based oxygen carriers were studied in a thermogravimetric analyzer (TGA). Then, the characteristics of CLG of biomass and the oxygen carrier in syngas production were investigated by testing gas components, syngas production, and oxygen carrier sintering performance. The results show that CuO supported on $MgAl_2O_4$ has a better capacity for oxygen release than pure CuO and a superior stability and gasification activity in the cyclic chemical looping gasification with biomass. A higher operating temperature led to the production of more syngas from biomass gasification with $CuO/MgAl_2O_4$ as the oxygen carrier, particularly for CO and H_2. $CuO/MgAl_2O_4$ also demonstrated a much better effect on methane reforming in CLG. It is believed that $CuO/MgAl_2O_4$ is a suitable oxygen carrier for the chemical looping with oxygen uncoupling (CLOU) and CLG of biomass.

Keywords: Syngas; Oxygen carrier; $CuO/MgAl_2O_4$; Chemical looping gasification

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INTRODUCTION

Syngas is an important feedstock in the production of methanol, natural gas, and bio-oil, and it is primarily produced from biomass and coal (Mills 1994; Yaman 2004; Zhang *et al*. 2007; Ouyang *et al*. 2007), of which the technology has been studied across the world, especially for the conversion of biomass to syngas. However, traditional biomass gasification technology is complicated and has high costs, as oxygen-enriched gas or high-temperature steam needs to be provided as a gasifying agent (Mohammed *et al*. 2011). The process includes pyrolysis, a water-gas shift reaction, methane reforming, and carbon gasification (Wang and Kinoshita 1993; Sutton *et al*. 2011).

To reduce the costs related to the supply of the gasifying agent, some researchers have recently proposed a new method called chemical looping gasification (CLG) (Diego *et al*. 2007). CLG is a modification of the well-known technology called chemical looping combustion (CLC) (Hossain and de Lasa 2008; Zhao *et al*. 2012) that uses the lattice oxygen from metal oxide as the gasifying agent for fuel to obtain CO and H_2 syngas (Rydén *et al.* 2006; Hossain *et al.* 2008;

Diego *et al*. 2009; Zhao *et al*. 2012). Compared to CLG, CLOU is a process with two steps, by which the oxygen carrier releases gaseous oxygen and the fuel can be solid, liquid, or gaseous, which reacts with the gas-phase oxygen, as in normal combustion, to produce a stream of pure CO_2, H_2O, and so on (Mattisson *et al*. 2009). In the process of CLG of biomass, biomass reacts with gaseous oxygen in the fuel reactor, which is released from the metal oxide, and the metal oxide then absorbs oxygen to recover lattice oxygen from the air in the air reactor, as illustrated in Fig. 1.

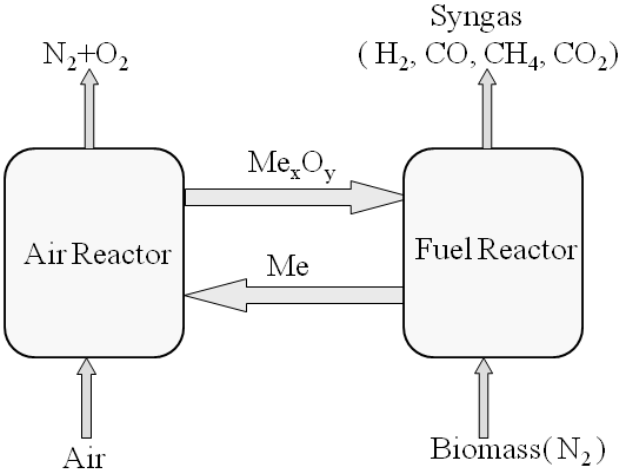

Fig. 1. Schematic diagram of the CLG process for biomass

Reactions in the CLG of biomass are complicated. It is well known that pyrolysis of biomass occurs first, with the production of char, tar, and a mixture of gases (CO, CO_2, H_2, CH_4), which would then react with CuO. The reactions that possibly exist in the fuel reactor are summarized in Table 1, according to previous works (Demirbas 2002; Chen *et al*. 2003; Haryanto *et al*. 2009; Abad *et al.* 2007; Kumar *et al*. 2009).

Table 1. Reactions of Biomass Pyrolysis Products with CuO

Main reaction	Δ*H* (kJ/mol)/923 °C	
$CuO + CO(g) \rightarrow Cu + CO_2(g)$	-128.65	(1)
$CuO + C \rightarrow Cu + CO(g)$	37.18	(2)
$CuO + C \rightarrow Cu + CO_2(g)$	-295.395	(3)
$CuO + H_2 \rightarrow Cu + H_2O(g)$	-131.829	(4)
$CuO + CH_4(g) \rightarrow Cu + H_2O(g) + CO(g)$	-470.935	(5)
$CO(g) + H_2O \rightarrow H_2(g) + CO_2(g)$	-35.656	(6)
$CH_4(g) + H_2O(g) \rightarrow H_2(g) + CO(g)$	223.73	(7)
$C + CO_2(g) \rightarrow CO(g)$	171.312	(8)
$C + H_2O(g) \rightarrow H_2(g) + CO_2(g)$	135.656	(9)

The continuous circulation of oxygen carriers between the air reactor and fuel reactor in CLG requires oxygen carriers to have good reaction characteristics, stable fluidization properties, acceptable attrition resistance, and low cost (Diego *et* *al*. 2009). Recently, Cu, Ni, Mn, Fe, and Ca have been among the most-studied metals in CLG (Gao and Shen 2009; He *et al*. 2009). Ni-based oxygen carriers have fine reactivity but high cost and possible environmental harm (Mattisson *et al*. 2001). Fe-based materials are very cheap, but they have less reactivity in cyclic oxidation and reduction (Wolf *et al*. 2005). Mn-based oxygen carriers have high sintering resistance but low oxygen-carrying capacity (Abad *et al*. 2006; Johansson *et al.* 2006). The oxygen-carrying capacity of Ca-based materials is high; however, they are easily decomposed to produce harmful gas components such as SO_2 at high temperatures (Shen *et al*. 2007). In contrast, CuO is non-poisonous and has a high oxygen-carrying capacity with good reactivity; thus, it has attracted increasing attention in recent years (Luis *et al*. 2007). Mattisson *et al*. (2009) reported that CuO/Cu_2O performed well in releasing oxygen after thermodynamic analysis. And it was observed that the surface of CuO became sintering at 750 °C with the gasification of biomass char, which could affect the release of oxygen (Ran *et al.* 2014). CuO needs to be supported on a suitable inert material because of the poor cyclic performance of pure CuO/Cu in repeated reduction and oxidation at high temperatures. Currently used inert supports include Al_2O_3, SiO_2, TiO_2, ZrO_2, MgO, kaolin, and bentonite (Liu *et al.* 2013). Investigations have been conducted on the feasibility of CuO supported on Al_2O_3 and $MgAl_2O_4$ for CLC and CLOU processes (Arjmand *et al.* 2011). Although partial Al_2O_3 and CuO was found to react with the generation of $CuAl_2O_4$, resulting in some loss of the active phase after several redox cycles, $MgAl_2O_4$-supported CuO appears to be a potential oxygen carrier for CLC and CLOU processes.

This study was done to analyze the use of $MgAl_2O_4$ as a support material on the oxygen-releasing characteristic of CuO and the gasification performance of biomass with $CuO/MgAl_2O_4$ in CLG. First, X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were used to test the existence of the phase of $CuO/MgAl_2O_4$ and to study the oxygen-releasing characteristic of CuO and $CuO/MgAl_2O_4$, respectively. Then, the production of syngas from biomass mixed with various oxygen carriers was investigated in a fixed bed reactor.

EXPERIMENTAL

Preparation of Materials

Biomass

The biomass used in the experiment was walnut shell. It was prepared by drying and grinding, finally obtaining a material with a particle size of approximately 150 mesh. The proximate analysis of the biomass was carried out according to ASTM E870-82 (Ran *et al.* 2014; Pu *et al.* 2015), and it is shown in Table 2.

Table 2. Proximate Analysis of the Biomass Used

Samples	Moisture $_{ad}$	Volatile $_{ad}$	Ash $_{ad}$	Fixed carbon $_{ad}$
Walnut shell	8.96	83.19	2.09	5.76

Ad: as determined basis

Oxygen carriers

To synthesize the oxygen carrier $Cu(NO_3)_2 \cdot 3H_2O/MgAl_2O_4$, with a mass ratio of 9:2 (Gayán *et al*. 2012; Arjmand *et al*. 2011), the support material, $MgAl_2O_4$, was first prepared. A predetermined amount of $Mg(NO_3)_2$ and Al_2O_3 was dissolved in a specified volume of deionized water, which was stirred strongly for 2 h on an electromagnetic stirrer, followed by 8 h of drying at 75 °C and a calcination lasting for 6 h at 1200 °C (Nordgreen *et al*. 2012). After $MgAl_2O_4$ was obtained, it was placed into a specific amount of $Cu(NO_3)_2 \cdot 3H_2O$ solution, followed by fully mixing for 2 h at a constant temperature of 75 °C. The oxygen carrier $CuO//MgAl_2O_4$ was finally obtained with a mass ratio of 3:2 after calcination for 2 h at 800 °C. For reference, CuO was prepared following the same procedure as mentioned above, but without the addition of $MgAl_2O_4$.

Thermodynamic Analysis Method

To reduce the workload, gasification conditions between biomass and the oxygen carrier were preliminarily determined through thermodynamic calculation using HSC Chemistry (UK, Chemistry Software Ltd. Gateways), which is common software used in the application of thermodynamic analysis. In the work, the Gibbs free energy minimization method was applied to calculate the gas composition produced in CLG after reaching the state of equilibrium. As we were more interested in carbon conversion and the production of CO, H_2, and syngas, only CuO, C, H, and O, were considered in the calculation by ignoring the effects of N, S, and other elements.

Test Procedure

X-ray diffraction (Japan, Shimadzu Corporation) was used to test for the content of different crystalline phases in the synthetic oxygen carrier prepared following the procedure of dissolution, stirring, and calcination from the precursors $Mg(NO_3)_2$ and Al_2O_3.

The performance of oxygen carriers in releasing oxygen and then being oxidized during the cyclic reactions of reduction and oxidation was studied using a thermogravimetric analyzer (TGA, STA-409, Germany, NETZSCH Ltd). During the test, oxygen carriers were dispersed on a crucible, which was suspended in a quartz tube and then exposed to preset testing conditions. First, the TGA reactor was heated from 0 to 1000 °C under a pure nitrogen atmosphere at a heating rate of 25 K/min, followed by retaining the conditions for 10 min. Then, it was cooled to 800 °C at a rate of 25 K/min under the same gas atmosphere. Once 800 °C was reached, the flow of nitrogen was switched to air for 5 min. For each sample, the cycle of reduction and oxidation described above was repeated 18 times.

Biomass gasification with the addition of oxygen carriers was carried out in a fixed-bed reactor. A quartz tube with a length of 1000 mm and diameter of 25 mm was placed in the fixed bed, where accurate temperature could be controlled and measured. In the test, the prepared oxygen carrier and biomass were loaded on a crucible slot, which was placed in the quartz tube at a constant temperature for 20 min under a nitrogen flow rate of 50 mL/min. At the end of the quartz tube, an air bag was used to collect the produced gas, which was analyzed by a gas chromatograph (GC 9700, China, Zhicheng Ltd.). Through the gasification process, the percentage of different gas products could be determined, and the volume of the gas production from biomass can be obtained by calculating the volume of nitrogen. The solid material left in the reactor was analyzed by scanning electron microscopy (VEGA 3 SBH SEM, Czech Republic, Tescan Ltd.).

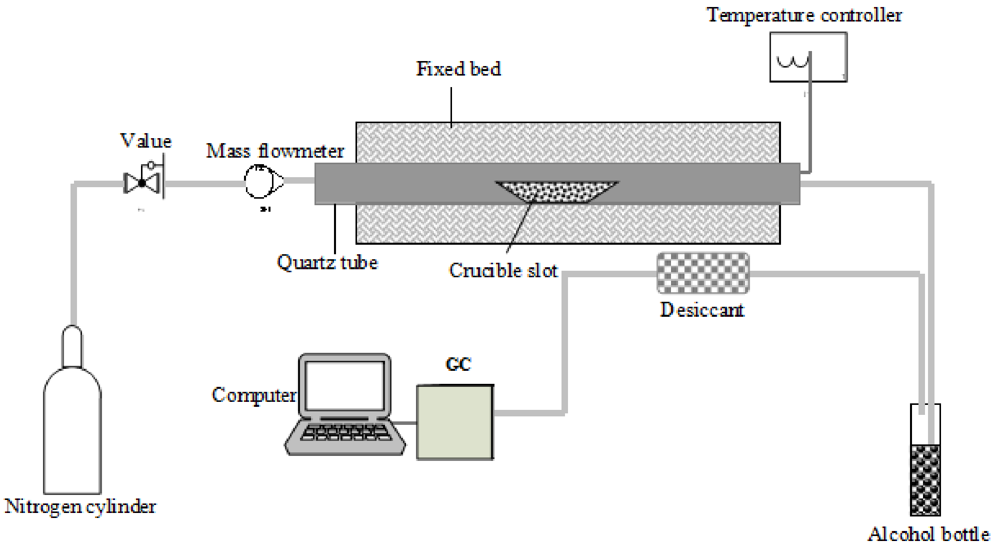

Fig. 2. Small tubular fixed bed reactor system

RESULTS AND DISCUSSION

XRD Results

The XRD results are shown in Fig. 3. The phase peaks of CuO and $MgAl_2O_4$ were very clear in the figure. The oxygen carriers were mainly CuO after calcination (containing a small bit of Cu_2O, and the gasification process was not affected), without any other materials, implying that there was no chemical reaction between CuO and $MgAl_2O_4$ during the sample preparation procedure. The results agree well with previous reports (Arjmand *et al*. 2011; Adánez *et al*. 2012).

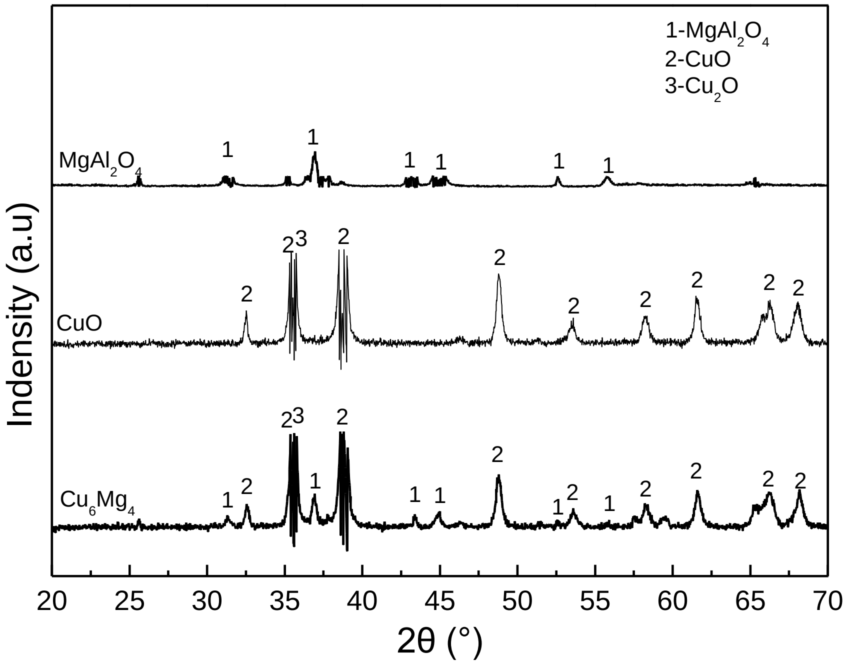

Fig. 3. XRD pattern for Cu-based oxygen carriers

Thermodynamic Analysis

Only CuO and $MgAl_2O_4$ were observed in the synthetic oxygen carrier, as discussed above. Additionally, it is well known that $MgAl_2O_4$ is very stable under biomass gasification conditions, meaning it would act only as a support material and would not react with other components in CLG (Gayán *et al.* 2012; Arjmand *et al*. 2011; Adánez *et al.* 2012). Therefore, the effects of $MgAl_2O_4$ could be ignored in the subsequent thermodynamic calculation and analysis.

Effect of CuO/C molar ratio

As the oxygen required in biomass gasification comes from oxygen carriers, which is CuO here, the molar ratio of CuO/C could greatly affect the production of syngas in CLG. This ratio was analyzed and is shown in Fig. 4. The calculation was achieved by the method of Gibbs free energy minimization with 1 mole of fixed carbon as the input at a constant temperature of 850 °C under atmospheric pressure.

In Fig. 4, the molar ratio of CuO/C gradually was increased from 0 to 1.0. It was clear that the production of fixed carbon and H_2 decreased with increasing CuO/C ratio, while the amount of CO first increased, followed by a reduction, with the gas yield peak appearing at the CuO/C molar ratio of 0.3 to 0.4. The reduction of CO yield at a higher CuO/C molar ratio is caused by the oxidation of CO into CO_2 with excess oxygen from CuO. From the calculation results, it was preliminarily concluded that the optimum molar ratio of CuO/C is 0.35, equal to a CuO/biomass mass ratio of 3:4.

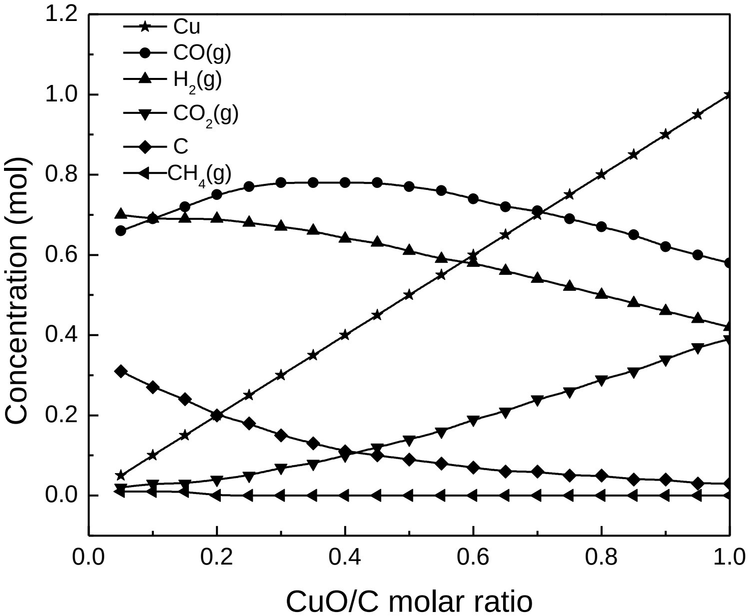

Fig. 4. Effects of CuO/C molar ratio on equilibrium composition at 850 °C

Effect of gasification temperature

It is well known that operating temperature plays an important role in biomass gasification reactions. Considering the potential application temperature in CLG using CuO as the oxygen carrier, the effect of temperature in the range of 600 to 1000 °C was calculated with the input molar ratio of CuO/C being fixed at 0.35 under atmospheric pressure. The results are summarized in Fig. 5.

As shown in Fig. 5, CuO released all of the oxygen and was changed into Cu after the full reaction under ideal conditions, similar to previous work (Wang and Kinoshita 1993) on the characteristics of CLG. With increasing reaction temperature, the contents of fixed carbon, CH_4, and CO_2 decreased gradually, while the gas yields of CO and H_2 increased. At 600 °C, the content of CO_2 was 0.54 mol, and that of CO was only 0.12 mol. When the temperature was over 660 °C, the production of CO surpassed that of CO_2. When the temperature was further increased to higher than 900 °C, the yield of H_2 became almost stable at 0.69 mol. More CO was produced because reactions between the remaining carbon and CO_2 would occur with increasing temperature. The content of CH_4, however, was almost 0 mol because methane reforming is an endothermic reaction, which would be restrained at higher temperatures.

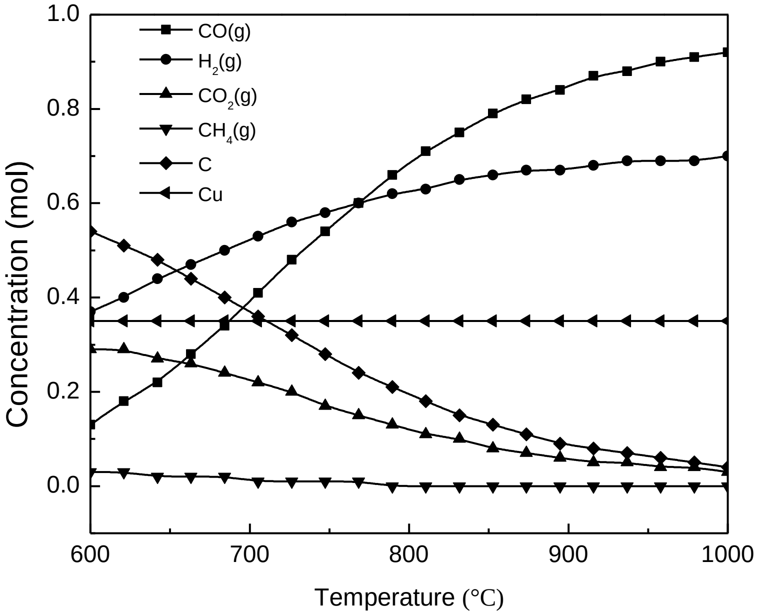

Fig. 5. The influence of varying temperature on the production of syngas

Reactivity in TGA

Cyclic stability of oxygen carriers

In practical industrial applications, oxygen carriers not only need to have a good capacity for oxygen transportation, but they also must be stable during a large number of CLG cycles. This study first tested the stability of pure CuO for 18 cycles of reduction (at 1000 °C under pure N_2 for 10 min) and oxidation (at 800 °C in air for 5 min), and then the mixture of $CuO/MgAl_2O_4$ was investigated under the same conditions. Comparison of experimental results is shown in Fig. 6.

As shown in Fig. 6(a), when pure CuO was tested, the same mass was left after each reduction, but its weight after 5 min of oxidation decreased gradually with increasing cycle number. In the first calcination, a mass loss of approximately 10% was observed because of the release of oxygen. In the following oxidation, there was a mass addition of 9.6% because of the absorption of oxygen. After the 18th cycle, the mass loss was 3.53%. By contrast, when the $CuO/MgAl_2O_4$ was tested using the same procedure, its reduction and oxidation rates were stable at 12.1% (regardless of the mass of $MgAl_2O_4$) from the first cycle to the 18th cycle, and the mass yield went beyond 100% in the first several cycles. This was attributed to the fact that the fresh oxygen carriers would containing a few Cu_2O sites, and the content of Cu_2O has little effect on circulation and gasification. Therefore, CuO is a suitable oxygen carrier in chemical looping with oxygen uncoupling (CLOU) after $MgAl_2O_4$ is added as a support.

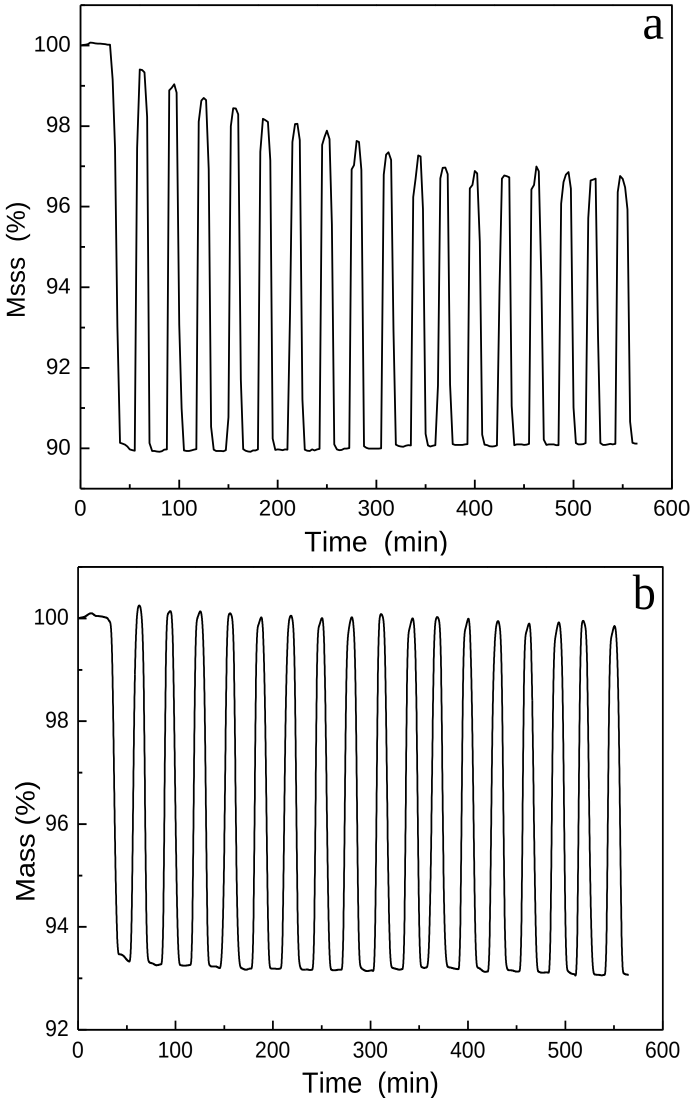

Fig. 6. TGA of (a) pure CuO and (b) CuO/$MgAl_2O_4$ in 18 successive cycles of reduction and oxidation

Gasification reactivity in TGA

Based on the thermodynamic analysis results, the mass ratio of CuO/biomass was 3/4, and the mass ratio of CuO/$MgAl_2O_4$ (at the mass ratio of 3:2) and biomass was 5/4, with the same mass (about 10 mg) of mixture that was prepared and tested in TGA. Figure 7 shows the gasification process of the mixtures from 50 to 950 °C at a constant heating rate of 25 °C/min in pure nitrogen. For the sake of contrastive analysis, when the data were processed, $MgAl_2O_4$ was not changed, because the inert carrier does not participate in the reaction for the preliminary experiment, which was in agreement with the work of Adánez-Rubio *et al.* (2012), Arjmand *et al.* (2011), and Gayán *et al.* (2012).

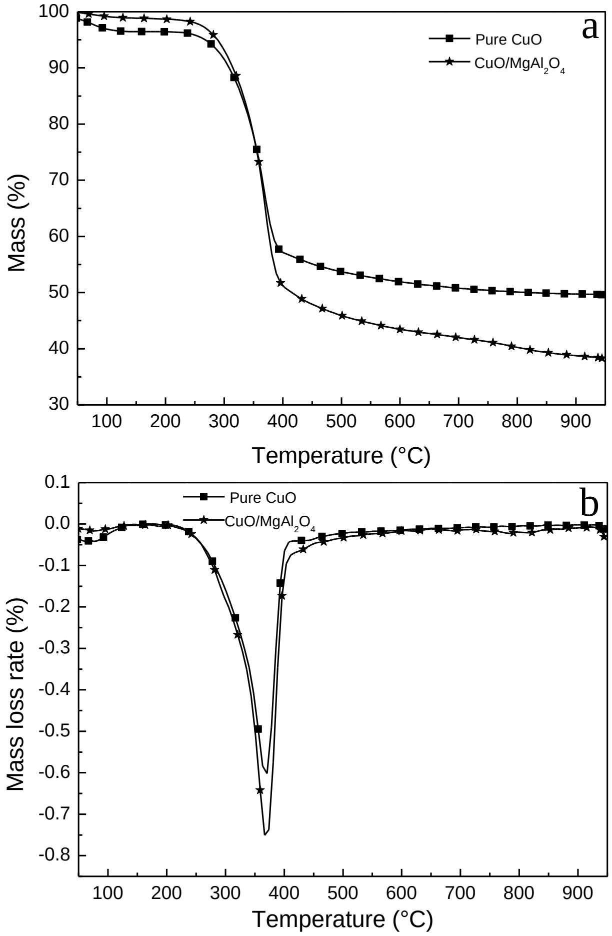

Fig. 7. TGA of the reactions between oxygen carriers and biomass

Figure 7(a) shows the variation of mass in TGA. The residue of CuO and biomass was 49.59%, and it was 38.27% for CuO/$MgAl_2O_4$. Figure 7(b) shows the mass loss rate of oxygen carrier and biomass in the gasification reaction. The gasification curve between pure CuO and the biomass showed two obvious weight loss peaks. The first peak appeared at 100 °C because of the evaporation of the moisture from the biomass, and the maximum mass loss rate was 0.042%. The second peak was due to the escape of volatiles from 250 to 450 °C, and the maximum mass loss rate was 0.61%. By contrast, CuO/$MgAl_2O_4$ demonstrated two weight loss peaks, at the same mixing ratio, the maximum mass loss rate of the second peak from 250 to 450 °C was about 0.75%. This may relate to the enhancement of the gasification reaction between CuO and biomass after the addition of $MgAl_2O_4$. Based on these analyses, it is believed that $MgAl_2O_4$ can promote the reactions between CuO and the biomass in the CLG process.

Chemical Looping Gasification in a Fixed Bed Reactor

To achieve a better understanding of the syngas production from the CLG of biomass with oxygen carriers, mixtures with the same biomass/oxygen carrier mass ratios mentioned above were tested in the fixed bed reactor; the amounts of biomass, CuO, and CuO/$MgAl_2O_4$ were set to 0.6, 0.45, and 0.75 g (including 0.45 g of CuO and 0.3 g of $MgAl_2O_4$). Also, the gases produced were analyzed using gas chromatography (GC). The syngas from the biomass gasification primarily includes CO, H_2, CO_2, and CH_4 (Zhao *et al*. 2013); other impurity gases were ignored.

Influence of $MgAl_2O_4$ on the gasification of biomass and CuO

The influence of $MgAl_2O_4$ on the generation of syngas from biomass and its composition was investigated at 800 and 900 °C, and the results are summarized in Fig. 8. The total gas yield increased from 628 to 648 mL when $MgAl_2O_4$ was added to the oxygen carrier as a support at 800 °C; the yield increased from 646 to 687 mL at 900 °C. The syngas yield obtained in biomass CLG with $CuO/MgAl_2O_4$ was larger than that with pure CuO, suggesting that the activity of CuO improved with the addition of $MgAl_2O_4$. Figure 8 also shows that $MgAl_2O_4$ plays a different role at 900 °C compared with 800 °C because of the occurrence of the transformation of CO_2 into CO and the reforming reaction of CH_4. The yield of CO was almost the same at 800 °C, whereas it increased from 50% at 800 °C to 52.5% at 900 °C. In contrast, the content of CH_4 decreased from 10.6% to 9.05% at 900 °C, which suggests that $MgAl_2O_4$ could promote the conversion of CH_4. These results agree well with the observation in the work of Adánez *et al*. (2012).

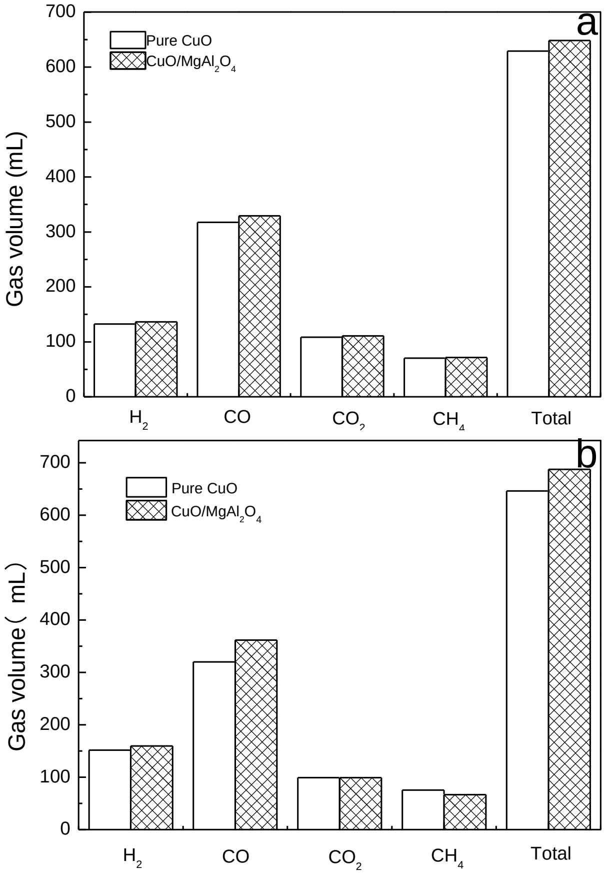

Fig. 8. Gas production from biomass with various oxygen carriers at (a) 800 °C and (b) 900 °C

The influence of temperature on gasification

Operating temperature plays an important role in the CLG of biomass. First, the main reactions in biomass gasification are endothermic. Second, the oxygen carrier can promote the cracking of hydrocarbons at high temperatures (Gayán *et al*. 2008; Arjmand *et al*. 2011). In this section, the effect of gasification temperature ranging from 700 to

950 °C on syngas production was studied in a fixed bed with the mass ratio of oxygen carrier/ biomass fixed at 0.75 on the basis of thermodynamic analysis; the mass of $CuO/MgAl_2O_4$ and biomass were set to 0.75 g and 0.6 g, respectively, and the results are summarized in Fig. 9.

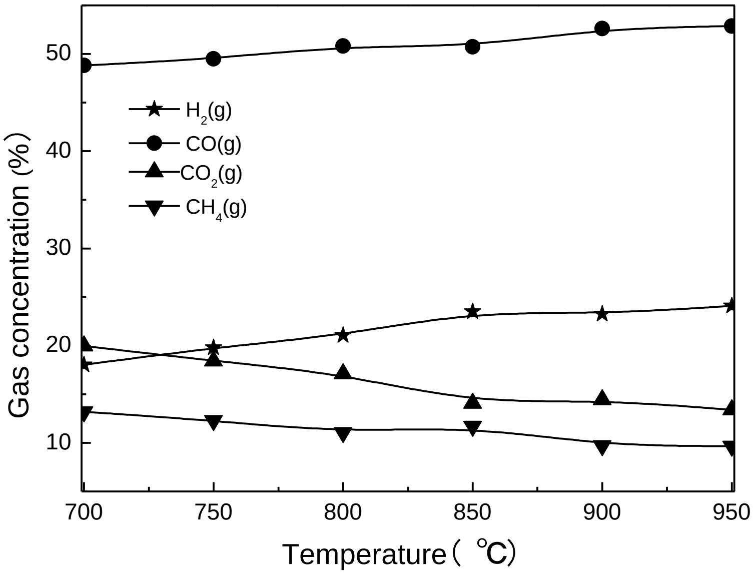

Fig. 9. The effects of temperature on the composition of syngas in biomass gasification

It is apparent in Fig. 9 that CO was the dominant component in the syngas, with a molar fraction of around one half. The concentrations of H_2 and CO increased with increasing gasification temperature. At 700 °C, the volume fraction of H_2 was 18.0%, increasing to 24.4% at 950 °C. Comparatively, the molar fraction of CO varied from 48.8% at 700 °C to 52.9% at 950 °C, as reaction 2 and the carbon gasification reaction were endothermic, meaning that a higher temperature was beneficial to the formation of H_2 and CO. At the same time, tar cracking occurred with the production of more H_2, CO, and other gases at high temperatures. By contrast, the contents of CH_4 and CO_2 decreased with increasing temperature. The concentration of CH_4 changed from 13.2% at 700 °C to 9.7% at 950 °C, while CO_2 concentration decreased from 20.0% at 700 °C to 13.1% at 950 °C. The main reason for this result was that CH_4 reforming is an endothermic reaction, so increasing temperature could promote its forward reaction, while the exothermic reaction of Table 1 (1), (3), and (6) toward the formation of CO_2 was prohibited to some extent. Additionally, the aforementioned tar cracking partially consumed CO_2, contributing to the reduction of CO_2 and CH_4 under higher temperatures. Anyway, the increase in temperature was advantageous for the production of syngas *via* biomass gasification with Cu-based oxygen carriers; however, sintering of the material would become more severe at higher temperatures, as discussed in the next section.

Morphological Analysis of Oxygen Carriers

To analyze the morphological features of oxygen carriers, SEM images of fresh and reacted oxygen carriers under various conditions are shown in Fig. 10 at magnifications of 1,000 times.

It can be seen that the fresh CuO contained needle-shape grains, and the fresh $CuO/MgAl_2O_4$ exhibits a porous structure, both of which are beneficial for reactions between biomass and oxygen carriers. After reaction at 800 °C, the needles of CuO grains began to disappear and sintered slightly, and this change would affect the oxygen release characteristics of CuO, while CuO/$MgAl_2O_4$ still demonstrated a porous surface. At 900 °C, the needles of pure CuO disappeared and serious thermal sintering occurred. By contrast, CuO/$MgAl_2O_4$ retained part of its porosity, and the thermal sintering was slighter. On the basis of this analysis, it can be concluded that the reactivity performance of CuO as an oxygen carrier could improve after adding $MgAl_2O_4$ as a support.

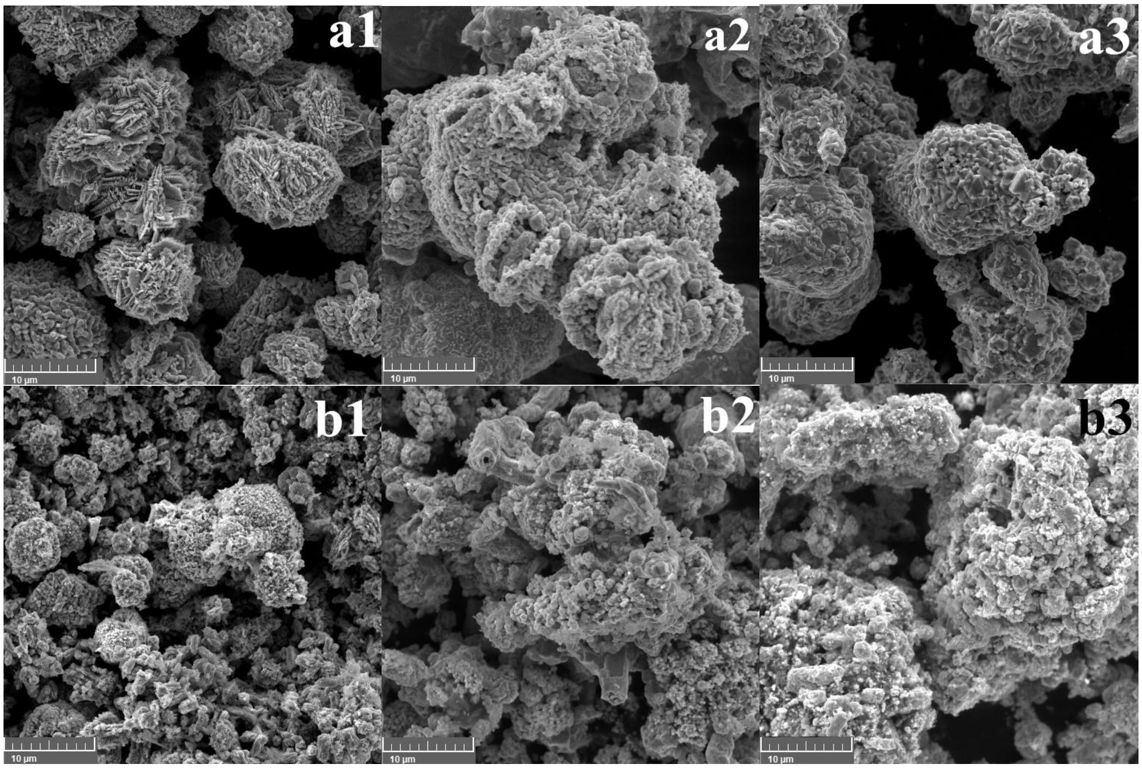

Fig. 10. SEM pictures of two oxygen carriers before and after reaction: (a1) fresh CuO; (a2) CuO used at 800 °C; (a3) CuO used at 900 °C; (b1) fresh CuO/$MgAl_2O_4$; (b2) CuO/$MgAl_2O_4$ used at 800 °C; (b3) CuO/$MgAl_2O_4$ used at 900 °C

CONCLUSIONS

In this work, the cyclic performance and gasification reactivity of oxygen carriers were tested by TGA and in a fixed-bed reactor, aiming to understand the influence of inert $MgAl_2O_4$ on the process of chemical looping gasification of biomass. Based on the thermodynamic analysis and experiments, the following conclusions were obtained:

1. The mass ratio of oxygen carrier to biomass has an important influence on biomass gasification and carbon conversion, and the optimal CuO/C molar ratio was determined to be 0.35 by thermodynamic analysis, equal to a CuO/biomass mass ratio of 0.75. In a certain range of temperature, the contents of H_2 and CO increased with increasing temperature, and the carbon conversion rate was also enhanced gradually with increasing reaction temperature.

2. Compared to pure CuO, the use of $MgAl_2O_4$ as a support for CuO improves reproducible and stable reactivity. After adding $MgAl_2O_4$, the syngas yield was improved, especially for CO and H_2. Thus, $CuO/MgAl_2O_4$ appears to be a suitable oxygen carrier for the CLOU and BCLG processes.
3. SEM images show that the $MgAl_2O_4$-supported CuO appears to be a suitable oxygen carrier for CLOU processes, and it is a favorable support to improve the sintering characteristics of CuO.

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