Comparison of Bimetallic Fe-Cu and Fe-Ca Oxygen Carriers for Biomass Gasification

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Abstract: Two bimetallic Fe-Cu and Fe-Ca oxygen carriers were studied for chemical looping gasification (CLG) of biomass. The SEM results indicated that there was no obvious agglomeration on the bimetallic Fe-Cu oxygen carrier supported on Al₂O₃ and Fe-Ca oxygen carrier after five redox cycles while agglomeration occurred on CuO supported on Al₂O₃ due to the low melting point of CuO. The XRD results indicated the presence of copper-ferrite and calcium-ferrite phases in the bimetallic materials. The two bimetallic oxygen carriers can be re-oxidized with air to form a crystalline that is similar to the fresh materials. The Fe-Ca oxide became active at 360 °C which was lower than 380 °C for the Fe-Cu oxygen carrier. The high thermal stability and redox reactivity of bimetallic Fe-Cu and Fe-Ca oxygen carriers make the bimetallic oxygen carriers more suitable for recycling during CLG. The method for preparing Fe-Cu oxygen carriers had no significant impact on biomass conversion efficiency but had significant effect on the quality of syngas. Proper control of the biomass/oxygen carrier mass ratio is critical to achieve high selectivity towards gasification instead of combustion. The Fe-Ca oxygen carrier could achieve higher selectivity towards gasification than the Fe-Cu oxygen carrier.

Keywords: chemical looping; gasification; bimetallic oxygen carrier; biomass; metal oxide

1. Introduction

Biomass can be partially oxidized in a gasification process to produce syngas that mainly consists of H₂, CO, CO₂ and CH₄. The syngas can be further used to synthesize liquid hydrocarbons via a Fischer–Tropsch process [1,2]. Conventional gasification technologies use steam, air and pure oxygen as gasifying agents. However, the use of air introduces a large amount of nitrogen into the syngas; the supply of oxygen increases the production cost; and the use of steam causes high energy consumption and high tar content in the syngas, and needs external heat supply [3]. The lattice oxygen of metal oxides has been studied as an alternative oxygen source for the combustion and gasification of fuels in a chemical looping process [4–6].

A typical chemical looping gasification (CLG) process takes place in two interconnected reactors including a fuel reactor where a fuel such as biomass and coal is partially oxidized by a metal oxide as an oxygen source and an air reactor where the reduced metal oxide is re-oxidized with air for recycling. The recycling of an oxygen carrier through a redox cycle of two reactors during the CLG can provide a continuous oxygen supply for biomass gasification, and the hot metal oxides can be used as a heat carrier for endothermic gasification reactions during the CLG. Furthermore, an oxygen carrier can also serve as a catalyst to enhance tar cracking [4].

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Single metal oxides and their mixtures have been studied as oxygen carriers in a chemical looping process. Although chemical looping has been well established for clean combustion of gaseous fuels, more research is highly needed to develop oxygen carriers with high activity for the combustion and gasification of abundant solid fuels such as coal and biomass [7–9]. An iron oxide has been considered as a promising oxygen carrier due to its good stability at high temperatures, affordability, non-toxicity and environmental friendliness. However, an iron oxide has low reactivity and oxygen carrying capacity [10,11]. Copper-based oxygen carriers have high oxygen carrying and releasing capacity, high reactivity and oxygen uncoupling properties, which are useful in solid fuel conversion [12,13]. However, copper-based oxygen carriers have a low melting point, which causes agglomeration at a typical chemical looping temperature [13]. Mixing oxides of Cu and Fe have been reported to have a positive synergetic effect during chemical looping combustion of coal and methane due to their complementing properties [14].

In addition to poor solid–solid interaction during CLG of solid fuels, it is also difficult to control the oxidation reactions toward the production of syngas instead of complete combustion because an oxygen carrier can further oxidize the syngas to CO₂ and H₂O. Therefore, it is necessary to develop an oxygen carrier which has high reactivity with char and tar but low reactivity with syngas. Research showed that a calcium ferrite had a high reactivity with coal but low reactivity with syngas, which makes it attractive for gasifying a solid fuel to achieve high syngas selectivity [15]. This study was to analyze the technical feasibility and compare the performance of bimetallic Fe-Cu, and Fe-Ca oxides as oxygen carriers for biomass gasification.

2. Materials and Methods

2.1. Materials

Woody biomass dried at 105 °C for 24 h was used as an example solid fuel. Proximate analysis carried out by a thermogravimetric analyzer (TGA) (SDT Q600, TA Instrument, New Castle, DE, USA) showed that the woody biomass contained 2.34% moisture, 84.17% volatile matter, 11.79% fixed carbon and 1.70% ash by mass (as received basis). The elemental composition analysis that was carried out on an elemental analyzer (Perkin Elmer 2400 series II) showed that the biomass contained 45.45% C, 5.06% H, 47.73% O, 1.15 % N and 0.61% S by mass (dry and ash free bases). The chemical formula of the biomass can be expressed as: \( \text{CH}_{1.336}\text{O}_{0.788}\text{N}_{0.0217}\text{S}_{0.00503} \). Table 1 gives the theoretical mass ratios of biomass to the oxygen carriers of Fe₂O₃, CuO and CaO for complete oxidation and ideal gasification when all lattice oxygen in the oxides can be used.

**Table 1.** Theoretical mass ratios of biomass to the oxygen carriers of Fe₂O₃, CuO and CaO for complete oxidation and ideal gasification.

| Oxygen Carrier | Type of Oxidation | Reaction Formula (Ignore N and S in Biomass) | Mass Ratio of Biomass to Oxide |
|----------------|-------------------|---------------------------------------------|-------------------------------|
| Fe₂O₃          | Gasification      | \( \text{CH}_1.336\text{O}_{0.788} + 0.074\text{Fe}_2\text{O}_3 \rightarrow \text{CO} + 0.668\text{H}_2 + 0.148\text{Fe} \) | 2.19:1                        |
|                | Combustion        | \( \text{CH}_1.336\text{O}_{0.788} + 0.627\text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + 0.668\text{H}_2\text{O} + 1.253\text{Fe} \) | 0.26:1                        |
| CuO            | Gasification      | \( \text{CH}_1.336\text{O}_{0.788} + 0.212\text{CuO} \rightarrow \text{CO} + 0.668\text{H}_2 + 0.212\text{Cu} \) | 1.54:1                        |
|                | Combustion        | \( \text{CH}_1.336\text{O}_{0.788} + 1.88\text{CuO} \rightarrow \text{CO}_2 + 0.668\text{H}_2\text{O} + 1.88\text{Cu} \) | 0.17:1                        |
| CaO            | Gasification      | \( \text{CH}_1.336\text{O}_{0.788} + 0.212\text{CaO} \rightarrow \text{CO} + 0.668\text{H}_2 + 0.212\text{Ca} \) | 2.19:1                        |
|                | Combustion        | \( \text{CH}_1.336\text{O}_{0.788} + 1.88\text{CaO} \rightarrow \text{CO}_2 + 0.668\text{H}_2\text{O} + 1.88\text{Ca} \) | 0.25:1                        |

2.2. Preparation of Fe-Cu and Fe-Ca Bimetallic Oxygen Carriers

The Fe-Cu bimetallic oxygen carrier supported on Al₂O₃ was synthesized via four different methods: (1) direct mixing—the precursors of the oxides of aluminum, iron and copper were mixed thoroughly after deionized water was added to the mixture to form a paste. The paste was dried at a room temperature and then calcined in air at 800 °C for 8 h; (2) direct decomposition—the precursors of the nitrates of Cu, Fe and Al were well mixed and heated under a fume hood at a temperature of 250 °C
for 4 h and then calcined in air at 800 °C for 8 h; (3) dry impregnation—copper nitrate and iron nitrate were mixed and dissolving in deionized water. The solution was then added to alumina powder while stirring. The resulting paste was dried at a room temperature for 24 h. The dried sample was calcined in air at 800 °C for 8 h; (4) a combination of coprecipitation and dry impregnation. The Fe-Ca bimetallic oxygen carrier was synthesized by the sol gel method. Nitrates of iron and calcium were mixed and dissolved in 100 ml distilled water with 2 M citric acid. The solution was mixed at 80 °C for 4 h. A total of 6 ml ethylene glycol was then added to the solution. The solution was heated at 80 °C while stirring magnetically. After most of the water had evaporated, a viscous brown gel was formed. The gel was further dried at the same temperature to form a brown powder. The powder was washed with ethanol, dried and calcined in air at 800 °C for 8 h.

Direct mixing was the simplest method to prepare the Fe-Cu oxygen carrier with different metal loadings supported on the Al₂O₃. The mass of the support of Al₂O₃ was kept at 30 wt.%. The mass of Fe₂O₃ in the bimetallic oxygen carriers varied from 60% to 40% while the mass of CuO was from 30% to 10%. The composition of the Fe-Ca oxygen carrier was 80% Fe₂O₃ and 20% CaO. Table 2 gives the compositions of various oxygen carriers used in this study.

### Table 2. Chemical compositions of the oxygen carriers.

| Oxygen Carrier          | Fe₂O₃ | CuO | Al₂O₃ | CaO |
|-------------------------|-------|-----|-------|-----|
| 70Fe₂O₃/30Al₂O₃         | 70    | 0   | 30    | -   |
| 60Fe₂O₃:10CuO/30Al₂O₃   | 60    | 10  | 30    | -   |
| 50Fe₂O₃:20CuO/30Al₂O₃   | 50    | 20  | 30    | -   |
| 40Fe₂O₃:30CuO/30Al₂O₃   | 40    | 30  | 30    | -   |
| 70CuO/30Al₂O₃           | 0     | 70  | 30    | -   |
| 80Fe₂O₃:20CaO           | 80    | -   | -     | 20  |

2.3. Characterization of the Oxygen Carriers

The oxygen carriers before and after use were analyzed. Temperature programmed reduction and oxidation (TPR & TPO) were carried out in a chemisorption unit (Autochem II Chemisorption analyzer 2920, Micrometrics Inc., Norcross, GA, USA) to determine the redox properties of the oxygen carriers. A gas mixture with 10% H₂ in argon was used as a reducing gas during TPR, while air was used as the oxidant during TPO. During both TPR and TPO, the temperature was ramped from 25 °C to 1000 °C at a heating rate of 10 °C/min.

An X-ray diffractometer equipped with a monochromated CuKα radiation generated at 40 mA and 40 kV was used to determine the crystalline phases of fresh and regenerated oxygen carriers (Agilent Technologies, Santa Clara, CA, USA). The measurement was conducted at room temperature with 2θ range of 20–80° using a step counting time of 2 s and step size of 0.02°.

Surface morphology and sample transformation after five redox cycles were analyzed using a scanning electron microscope (SEM) (Zeiss EVO LS10, Zeiss, San Diego, CA, USA). The element distribution on the surface of the sample was analyzed using an energy-dispersive spectroscope equipped with the SEM system. The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution of the oxygen carrier were determined by a N₂ physical adsorption apparatus (ASAP 2020, Micrometrics Inc., Norcross, GA, USA).

2.4. TGA Analysis of Thermal Degradation Characteristics of Biomass with Oxygen Carriers

The degradation characteristics of biomass with the oxygen carriers for biomass oxidation were investigated on a TGA (SDT Q600, TA Instrument, New Castle, DE, USA). About 10 mg of biomass-oxygen carrier mixture at a mass ratio of 0.4:1 was loaded in an aluminum pan and placed in a TGA furnace. A mass ratio of biomass to oxygen carriers at 0.4:1 provides almost half theoretical amount of available lattice oxygen required for the complete combustion according to the data given
Table 1. Both experiments were conducted from an ambient temperature to 800 °C at a heating rate of 10 °C/min purging with nitrogen gas at 60 ml/min. Sand was used in the place of an oxygen carrier as a control. One set of experiments was used to compare the performance of the Fe-Cu oxygen carriers prepared by different methods. The second set of experiments was conducted to compare the oxidation characteristics of the two oxygen carriers of Fe-Cu and Fe-Ca for the oxidation of biomass.

2.5. Biomass Gasification with the Oxygen Carriers in a Bench-Scale Fixed Bed Reactor

A bench-scale fixed-bed reactor with 7 mm inner diameter and 400 mm length was used to evaluate the biomass gasification using the two oxygen carriers. A total of 1.0 g sample containing an oxygen carrier and biomass at two mass ratios of biomass to the oxide of 0.2:1 and 0.4:1 was loaded into the reactor. The compositions of the outlet gases of CO₂, H₂, and CO from the reactor were analyzed using a gas chromatograph (SRI multiple gas analyzer, Torrance, CA, USA) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). The sample was heated in nitrogen at a flow rate of 100 cm³/min from an ambient temperature to 800 °C for 60 min. After the gasification step, the sample was exposed to air at 800 °C for 60 min. Nitrogen gas was allowed to flow in between reduction and oxidation steps to avoid back mixing. Baseline experiments were carried out using quartz sand and biomass at the same mass ratios of the oxygen carriers and biomass mixture. Multicycle oxidation-reduction (redox) reactions were conducted using 10% ethylene in N₂ as a fuel instead of biomass in order to recover the oxygen carriers for the analysis of their agglomeration after multiple redox cycles at high temperatures.

3. Results and Discussion

3.1. The Phase and Morphologic Properties of the Oxygen Carriers

Agglomeration is one of the major challenges associated with copper-based oxygen carriers. Figure 1a–f shows the SEM images of the fresh and regenerated Cu- and Fe-Cu based oxygen carrier samples after five redox cycles in a fixed bed reactor with 10% ethylene in N₂ as a fuel.

There was a significant difference in the morphology of fresh and used Fe-Cu oxygen carriers containing various amounts of Cu. As the amount of CuO in the Cu-Fe oxides increased, particle agglomeration and pore blockage became worse, which could be attributed to the low melting point of CuO. Therefore, Fe₂O₃ should be used as the primary oxygen carrier and CuO can only be used as a promoter to improve reactivity and meanwhile minimize the agglomeration issue. Unlike the copper-containing oxygen carriers, there was no significant change in the SEM images for the Fe-Ca oxygen carriers after five redox cycles as shown in Figure 1f.

Figure 2a,b shows the Energy Dispersive X-ray (EDX) results for the elemental map of both Cu and Ca based oxygen carriers. The Cu and Ca elements were well distributed in the oxygen carriers.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Cont.
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When a mixture of Fe

As shown in Figure 3, there were three or four major reduction peaks for the Fe-Cu oxygen carriers. When a mixture of Fe
When a mixture of Fe

3.2. Reduction Characteristics of Oxygen Carriers

Figure 3 shows the TPR profiles of the Fe-Cu oxygen carriers prepared by various methods. As shown in Figure 3, there were three or four major reduction peaks for the Fe-Cu oxygen carriers. When a mixture of Fe$_2$O$_3$ and CuO with a high concentration of Fe$_2$O$_3$ was calcined at a temperature higher than 488 °C, two solid phases of Fe$_2$O$_3$-CuO and Fe$_2$O$_3$ possibly formed [14]. The observed three peaks therefore indicated the reduction of Fe$_2$O$_3$-CuO to Cu and Fe$_3$O$_4$, and further reduction of Fe$_3$O$_4$ to FeO. The fourth peak observed in one of the oxygen carriers might be caused by the further reduction of FeO to elemental Fe. The first reduction peak of the bimetallic Fe$_2$O$_3$-CuO oxygen carrier was observed at about 200 °C and the last peak was observed at a temperature of about 800 °C, which were much lower than first reduction peak at 400 °C and the last one at 950 °C for the reduction of an Fe$_2$O$_3$ oxygen carrier without a Cu promoter. Therefore, the addition of CuO as a promoter helped in lowering the reaction temperature of an Fe-based oxygen carrier. The Fe$_2$O$_3$-CaO oxygen carrier had much higher temperature at 600 °C for the first reduction peak and the reduction proceeded beyond 1000 °C.
Figure 3. $\text{H}_2$-TPR of oxygen carriers prepared by different methods.

Figure 4a,b shows the XRD spectra of fresh and regenerated oxygen carriers after five redox cycles. Crystalline phases of $\text{Fe}_2\text{O}_3$-$\text{CaO}$ and $\text{Fe}_2\text{O}_3$ were detected in the fresh samples of the bimetallic Fe-Ca oxide and the $\text{Fe}_2\text{O}_3$-$\text{CuO}$ and $\text{Fe}_2\text{O}_3$ phases were detected in the fresh samples of the Fe-Cu oxide. However, the CaO and CuO phases were not detected possibly because small amounts of CaO and CuO were used as a promoter and hence all the available CuO and CaO might have been used to form $\text{Fe}_2\text{O}_3$-$\text{CaO}$ and $\text{Fe}_2\text{O}_3$-$\text{CuO}$, respectively. The XRD patterns of the regenerated samples were in agreement with those of the fresh samples, which indicates that the lattice oxygen of the oxygen carriers can be recovered after gasification by re-oxidized with air.

Figure 4. XRD patterns of fresh and regenerated oxygen carriers; (a) Fe-Cu oxide and (b) Fe-Ca oxide.

3.3. Thermal Degradation Characteristics of Biomass with Various Oxygen Carriers in a TGA

Figure 5 shows the TGA profiles of the biomass conversion using the Fe-Cu oxygen carriers with 60% $\text{Fe}_2\text{O}_3$-10% CuO supported on 30% $\text{Al}_2\text{O}_3$ prepared by different methods at a mass ratio of biomass to the oxide of 0.4:1. There was no significant difference in biomass conversion efficiency.
using the Fe-Cu oxygen carriers prepared by different methods. The total mass losses for all three samples at 800 °C were about 33.5% to 34.5% of the original mass of the samples. The original mass of the samples was 28.6% biomass, which was lower than the mass losses. That means that the oxygen carrier lost oxygen too during TGA analysis.

Figure 5. Thermogravimetric (TGA) profiles for the oxidation of biomass using the Fe-Cu oxide with 60% Fe$_2$O$_3$/10% CuO/30% Al$_2$O$_3$ prepared by various methods at a 0.4:1 mass ratio of biomass to oxide.

Figure 6 shows the TGA profiles for the biomass conversion using the bimetallic Fe-Cu oxygen carrier (60% Fe$_2$O$_3$/10% CuO/30% Al$_2$O$_3$) prepared by direct mixing and Fe-Ca oxygen carrier (80%Fe$_2$O$_3$/20%CaO) prepared by the sol gel method at a mass ratio of biomass to the oxide of 0.4:1. As shown in Figure 6, the mass loss for the first heating stage at a temperature up to 250 °C was mainly caused by drying. The slight difference among three curves at this stage might be caused by the variation of the moisture contents of the samples. The active conversion that occurred at the second stage was mainly caused by the devitalization of hemicellulose and cellulose in the biomass. There was no significant difference in mass loss rates at the second stage for the Fe-Cu oxygen carriers that occurred in the temperature range approximately from 250 °C to 380 °C, but the second stage of the biomass sample with the Fe-Ca oxygen carrier occurred in the temperature range approximately from 250 °C to 400 °C. Lignin devitalization occurred at the third stage with a temperature higher than 380 °C, according to the curve for the sample with sand as shown in Figure 6. Figure 6 showed both Fe-Cu and Fe-Ca oxygen carriers could significantly enhance the biochar gasification at the third stage, compared to sand. However, the Fe-Ca showed high activity at the temperature from 360 °C to 400 °C while the Fe-Cu oxygen carrier showed activity over a large temperature range from 380 °C to 800 °C. As the reduction temperature of Fe-Ca started at 600 °C, as shown in Figure 3, the enhancement of the biomass gasification with the Fe-Ca at a temperature from 360 °C to 400 °C might be caused by the catalytic tar decomposition over CaO to enhance the pyrolysis at a relatively low temperature [16]. The CaO can also adsorb CO$_2$ at a relatively low temperature and release CO$_2$ at higher temperature to enhance the char gasification [16]. The total mass losses for samples with Fe-Cu, Fe-Ca and sand at 800 °C were about 32%, 31% and 27.3%, respectively, compared to 28.6% of biomass in the samples.
Figure 5. Thermogravimetric (TGA) profiles for the oxidation of biomass using the Fe-Cu oxide with 60% Fe$_2$O$_3$/10% CuO/30% Al$_2$O$_3$ prepared by various methods at a 0.4:1 mass ratio of biomass to oxide.

Figure 6. TGA profiles for the oxidation of biomass using Fe-Cu and Fe-Ca oxides at a 0.4:1 mass ratio of biomass to oxide.

3.4. Biomass Gasification with the Oxygen Carriers in a Tubular Fixed Bed Reactor

Figure 7a,b and Figure 8 show the compositions of CO, CO$_2$ and H$_2$ in the syngas produced during the gasification of biomass with Fe-Cu oxide (60Fe$_2$O$_3$-10CuO/30Al$_2$O$_3$) and Fe-Ca oxide (80Fe$_2$O$_3$-20CaO) oxygen carriers in a fixed bed reactor. As seen in Figure 7a, when the mass ratio of the mixture of biomass and Fe-Cu oxide was 0.2:1, the dominant gas generated was CO$_2$ for the oxides prepared by different methods. This is because an excess amount of Fe-Cu oxide resulted in the further oxidation of CO. When the mass ratio of biomass to the Fe-Cu oxide was increased from 0.2:1 to 0.4:1, the CO and H$_2$ contents in the syngas increased while CO$_2$ content decreased as shown in Figure 7. For the Fe-Cu oxide with the composition of 60% Fe$_2$O$_3$-10% CuO/30% Al$_2$O$_3$ prepared by the direct mixing, the CO and H$_2$ contents in the syngas increased from 34.97% to 40.62%, and 19.81% to 20.35%, respectively, and the CO$_2$ content decreased from 42.63% to 36.24% when the mass ratio of biomass to the oxide increased from 0.2:1 to 0.4:1. At a high biomass to oxygen carrier ratio, the partial oxidation of biomass might contribute to higher CO, H$_2$ and liquid content that could not react completely with the lattice oxygen from oxygen carrier. In addition, the Boudouard reaction is enhanced with increasing residual carbon when biomass to oxygen carrier ratio is increased, which produces more CO production by the consumption of CO$_2$. However, a very high biomass to the oxygen carrier would lead to a very low biomass conversion efficiency. Therefore, it is necessary to find the optimum biomass to oxygen carrier ratio to ensure both good selectivity and conversion.

The method for the preparation of the oxygen carriers had significant impact on the quality of syngas produced. However, the TGA results given in Figure 5 showed that the method used in synthesizing Fe-Cu oxygen carriers did not have noticeable impact on biomass conversion efficiency with the carriers. At the mass ratio of biomass to oxide of 0.2:1, the lowest CO$_2$ content in the syngas was 42.63% using the Fe-Cu oxide prepared by the direct mixing and the highest CO$_2$ content was 59.76% using the Fe-Cu oxide prepared by the direct decomposition.
Figures 7a,b and 8 show the compositions of CO, CO$_2$ and H$_2$ in the syngas produced during the gasification of biomass with Fe-Cu oxide (60Fe$_2$O$_3$-10CuO/30Al$_2$O$_3$) and Fe-Ca oxide (80Fe$_2$O$_3$-20CaO) oxygen carriers in a fixed bed reactor.

(a) Biomass to oxygen carrier mass ratio of 0.2:1

(b) Biomass to oxygen carrier mass ratio of 0.4:1

**Figure 7.** The compositions of syngas produced by the gasification of biomass with Fe-Cu and Fe-Ca oxides at various biomass to oxygen carrier mass ratios at 800 °C, (a,b). (DIMP: Dry impregnation, DM: Direct mixing, DD: Direct decomposition, CO+IMP: Coprecipitation + Impregnation).

At the mass ratio of biomass to oxide of 0.4:1, the lowest CO$_2$ content in the syngas was 35.56% using the Fe-Cu oxide prepared by dry impregnation and the highest CO$_2$ content was 44.37% using the Fe-Cu oxide prepared by coprecipitation and impregnation.

As seen in Figure 7, there was no significant difference in CO and H$_2$ yield when the mass ratio of biomass to Fe-Ca oxide was increased 0.2:1 to 0.4:1. In both cases, CO was the major gaseous product for the oxidation of biomass using the Fe-Ca oxide. At the mass ratio of biomass to oxide of 0.2:1, the CO and H$_2$ contents in the syngas obtained by the Fe-Ca oxide were 42.33% and 23.81% for the Fe-Ca oxide, compared to 26.22% to 34.97% and 9.18% to 20.91% for the Fe-Cu oxide prepared by different methods. When the mass ratio of biomass to oxide of 0.4:1, the CO and H$_2$ contents were 39.39% and 24.72% for the Fe-Ca oxide, compared to 33.83% to 40.62% and 18.63% to 25.93% for the Fe-Cu oxides. The reaction of CO and H$_2$ with Fe-Ca oxide is not thermodynamically feasible at a typical CLG temperature. Therefore, the Fe-Ca oxide is a more suitable oxygen carrier for biomass gasification. The Fe$_2$O$_3$-CaO is not an active oxygen carrier at a low temperature (i.e., 600 °C, as shown in Figure 3) but it can catalyze tar cracking and adsorb CO$_2$ at a low temperature and release CO$_2$ at a higher temperature to enhance biochar gasification [16].
When the loading of CuO in the Cu-Fe oxygen carrier was increased, the combustion reaction was dominant as CO\textsubscript{2} was the main carbon product as shown in Figure 8. At the higher mass ratio of biomass to the oxide of 0.4:1, when the CuO content was increased from 10% to 30%, the CO\textsubscript{2} content in the syngas increased from 35.56% to 70.71%, while the CO and H\textsubscript{2} contents decreased from 36.91% to 13.54% and 25.92% to 15.74%, respectively. As CuO is known to have a high oxygen carrying and releasing capacity, it would be unfavorable for a CLG process if the CuO is the primary carrier instead of a promoter in the bimetallic Fe-Cu oxygen carrier.

![Syngas composition](image)

**Figure 8.** Gasification of biomass with the bimetallic Fe-Cu oxygen carrier with various Cu loadings at a 0.4:1 mass ratio of biomass to oxygen carrier at 800 °C.

4. Conclusions

Both Fe-Cu and Fe-Ca bimetallic oxides are promising oxygen carriers for biomass gasification. A CuO promoter lowers the reduction temperature of a Fe-based oxygen carrier. Both Fe-Cu and Fe-Ca oxygen carriers had higher biomass conversion efficiency. As the Fe-Cu oxide has high reactivity with the syngas toward the complete combustion, it is critical to optimize the amount of CuO in the bimetallic Fe-Cu oxide and the ratio of biomass to the oxygen carrier for their application during CLG of biomass. The bimetallic Fe-Cu with a high content of CuO also had high tendency of agglomeration after five redox cycles. Therefore, less than 10% CuO should be used as a promoter in the bimetallic Fe-Cu oxygen carrier to improve its lifetime and the quality of syngas for CLG of biomass. The method for preparing Fe-Cu oxygen carriers had no significant impact on biomass conversion efficiency but had significant effect on the quality of synthesis gas. At the mass ratio of biomass to the Fe-Cu oxide of 0.4:1, the lowest CO\textsubscript{2} content in the syngas was 35.56% using the Fe-Cu oxide prepared by the dry impregnation and the highest CO\textsubscript{2} content was 44.37% using the Fe-Cu oxide prepared by the coprecipitation and impregnation. Therefore, the bimetallic Fe-Cu oxide prepared by the combination of coprecipitation and impregnation method is not suitable for CLG of biomass. The bimetallic Fe-Ca oxide had low reactivity with syngas at a temperature lower than 1000 °C, which makes it to be a promising oxygen carrier for gasification. A bimetallic Fe-Ca oxygen carrier also had no significant agglomeration after five redox cycles. Although an iron-based oxygen carrier is a low-cost and earth-abundant option, porous supports and promoters should be studied to improve its reactivity and stability. The bimetallic oxygen carriers such Fe-Cu and Fe-Ca should be designed to maximize the conversion efficiency and selectivity of carbon and hydrogen to carbon monoxide and hydrogen gas, and minimize the tar formation during CLG.
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