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Chemical-looping auto-thermal reforming of biomass using Cu-based oxygen carrier

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HIGHLIGHTS

• Using Cu-based OC (oxygen carrier) in CLR of biomass is feasible, with heat balance in fuel reactor.

• The presence of Cu-based OC can evidently promote the biomass conversion.

• The presence of Cu-based OC is beneficial to tar removal and C₂H_m decrease.

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ABSTRACT

Chemical-looping reforming (CLR) of biomass, which utilizes active lattice oxygen from oxygen carrier (OC), provides a novel route to convert biomass into synthesis gas. This research utilized Cu-based OC rather than commonly-used Fe- or Ni-based OC in the process. The possible advantage is the exothermic reactions between CuO and gasification products are beneficial to auto-thermal reforming of biomass in fuel reactor. Batch fluidized bed experiments with different carriers (silica sand, Fe-based or Cu-based OCs) were conducted at different temperatures. It was found that when using Cu-based OCs, the gas yield and carbon conversion efficiency increased significantly, but the gasification group the carbon conversion and also consume more reducible gases. The presence of Cu-based OCs help reduce C₂Hm and tar in syngas. Additionally, the tar content decreased with temperature increase, while C₂H_m content first increased then decreased.

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1. Introduction

Chemical-looping reforming (CLR) provides a novel route to generate synthesis gas (H_2 and CO) from hydrocarbon fuels like coal and biomass. It has the similar basic principles as chemical-looping combustion (CLC) [1,2]. A CLR system mainly consists of two interconnected reactors (an air reactor and a fuel reactor) with oxygen carrier (OC) circulating between them. Fig. 1 shows the schematic conceptual design of the process. The OC particles are reduced in the fuel reactor and then they are transported to the air reactor. The reduced OC is oxidized by air in the air reactor. After that, the regenerated OC is circulated back to the fuel reactor. The CLR process has several advantages compared to conventional gasification technologies [3,4]. Firstly, the generated syngas is not diluted by nitrogen. Secondly, the reaction is mild and an explosive mixture/hot spot is prevented. Thirdly, the regenerable OC materials used in CLR are cheaper than metal

catalysts used in traditional reforming process. At last, the fluidized bed reactor system has better heat-mass transfer than fixed-bed reactor, which also takes care of coking issues and provide better throughput.

The concept of auto-thermal CLR (a-CLR) was initially proposed by Mattisson and Lyngfelt in 2001 [5]. Rydén and Mattisson et al. [4,6] carried out a comprehensive system analysis for H₂ generation using a-CLR. They found that the atmospheric a-CLR processes have high H₂ yield but the power needed is considerable. The heat balance is an important issue which should be taken into consideration in the a-CLR system. The heat for the endothermic reduction reactions is mainly supplied by the circulating solids coming from the air reactor at higher temperature. In order to achieve the heat balance in the system without requirement of any external energy source, the heat generated in the air reactor must be high enough. Mattisson et al. [6] studied the heat balance of the CLR systems using Cu-based and Ni-based OCs. They claimed that the fraction of oxygen supplied by the steam should not exceed 0.3 of the total oxygen added to the fuel reactor in order to maintain a high CH₄ conversion and temperature. Detailed heat and mass balance were







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Fig. 1. Schematic of chemical-looping reforming.

carried out by Ortiz et al. [7]. They focused on the operating conditions that can maximize H_2 generation in the a-CLR process of methane using Ni-based OC.

Biomass is a renewable and carbon-neutral resource [8]. It has been recognized that the utilization of biomass rather than fossil fuels can effectively address the problem of greenhouse gas emission [3,9]. A dual fluidized bed (DFB) technology has been developed by Hofbauer et al. [10] in Austria using steam as the gasification agent and providing the heat for the gasification reactor by circulating bed material. Later, Pröll et al. [11] developed the simulation model of the entire process in parallel and validated using the equation oriented software IPSEpro. Koppatz et al. [12] investigated the behavior of olivine compared to silica sand as bed material in a dual fluidised bed reactor system (DFB) for steam gasification of biomass. Kirnbauer et al. [13] studied the mechanism of bed material coating in dual fluidized bed biomass steam gasification plants and its impact on plant optimization where woody biomass was used as fuel. Additionally, it is expected that biomass with an inherent high content of volatiles can reach a higher conversion rate than other solid fuels like coal and petcoke, suiting well for chemical-looping utilization. In recent years, biomass has attracted increasing interests as the fuel or material of chemical-looping system. Thunman et al. [14] operated an 8-12 MWth circulating fluidized bed boiler for 60 h with wood pellets and wood chips. First analysis of the producer gas composition shows high contents of methane, making the installation a good match for substitute natural gas (SNG) production. Shen et al. [15] investigated chemical-looping combustion of biomass in a 10 kWth reactor. Dutta et al. [16] conducted chemical-looping gasification of biomass experiments in a batch fluidized bed steam gasifier. Using CaO as sorbent and sawdust as feedstock, they attained nearly 0% concentration of CO2 and 71% concentration of H_2 in the gas product.

A key issue for the CLR technology development is the selection of OC. The desired OC should have these suitable properties [17]: high reactivity to reduce solids inventory; good selectivity to CO and H₂; high resistance to attrition and agglomeration/sintering; negligible carbon deposition; low costs and environmental friendly. Fe-, Ni-, Cu-, and Mn-based OCs supported on different inert materials and prepared by different methods have been investigated in chemical-looping system [1,18,19]. Using a Ni-based OC as bed material, Tobias et al. [20] operated a dual circulating fluidized bed pilot plant in chemical looping reforming conditions at a scale of 140 kW fuel power with natural gas as fuel. Being expensive and easily deactivated by sulfur, Ni-based OC is less suitable for solid fuels [21]. Iron and manganese oxides are cheap, usually available in the form of waste materials and ores. Huang et al. [22] investigated natural hematite as OC of the biomass CLR processes in a bubbling fluidized-bed reactor. It was found that the presence of hematite particles can evidently promote the biomass conversion compared to inert particles like silica sand. However, the low reactivity of Fe-based OC limits its CLR application. The same investigators [23] then decorated iron ore via NiO to improve the reactivity of OC due to the formation of spinel-type nickel iron oxide NiFe₂O₄. With respect to tar reforming, Larsson et al. [24] used ilmenite as the catalytic material in the Chalmers 2–4 MWth dual fluidized bed gasifier to decrease the yield of tar. It was found that the impact of adding ilmenite depends upon the operational conditions of the gasifier.

Cu-based carriers have the advantage of cycle stability at suitable temperatures (e.g., ≤ 900 °C), high reactivity, high oxygen transport capacity, mechanical stability and capacity of satisfying the working conditions of the fluidized bed [25,26]. The reactions between CuO and the gasification products is exothermic, which is beneficial to auto-thermal biomass reforming. However, it should be noted that full conversion to CO₂ and H₂O is not achieved and the decomposition of fuel to CO and H₂ is always strongly endothermic in a reformer. Generally, the heat balance becomes more favorable for the fuel reactor if copper-oxides are decomposed instead of other oxides (Fe or Ni), but still heat will need to be transferred from the air reactor to the fuel reactor in such a configuration. Besides, Cu-based OC has higher reactivity than Fe-based OC and is cheaper than Ni-based OC. It is also environmental friendly and available in the form of ores. Therefore, this research proposed to utilize Cu-based OC rather than commonly-used Fe- or Ni-based OC in the CLR of biomass. The objective of this study is to evaluate the feasibility of CLR of biomass using Cu-based OC (CuO/CuAl₂O₄ and copper ore).

2. Experimental section

2.1. Materials

The experiments used sawdust of pine selected from Hebei province (China) as fuel. The sample was first rolled and crushed, and then sieved into particles of 0.3–0.6 mm, finally dried at 105 °C overnight in a drying oven before tests. The ultimate analysis of the pine sawdust with the air-dry basis was 44.25 wt.% carbon, 6.36 wt.% hydrogen, 0.48 wt.% nitrogen, 0.06 wt.% sulfur and 37.68 wt.% oxygen (by difference). It has a lower heating value (Q_b) of 17.14 MJ/kg. Its proximate analysis with the air-dry basis consisted of 10.09 wt.% moisture, 80.3 wt.% volatile, 14.68 wt.% fixed carbon and 1.08 wt.% ash.

The CuO/CuAl₂O₄ OC was prepared by sol–gel process with the advantage of controllable microstructure, good homogeneity, high purity and accurate stoichiometry. The detailed information of the sol–gel process could be found in our previous work [27]. The designed weight ratio in the OC is 60 wt.% CuO and 40 wt.% CuAl₂O₄. The Fe₂O₃/Al₂O₃ (60 wt.%:40 wt.%) particle was prepared by freeze granulation method due to its comprehensive performance of reactivity and durability [28,29]. Refined copper ore (CuO 21.04 wt.% and CuFe₂O₄ 70.05 wt.%, the rests are SiO₂, CaSO₄ and Al₂O₃) with the advantages of low cost and environmental friendliness [30] was also selected as OC in this study. The original refined ore was calcined for 5 h at 500 °C and then 10 h at 1000 °C in an air-atmosphere muffle oven. The target OC particles were with a size range of 0.2–0.3 mm.

2.2. Process simulation by Aspen Plus

To verify the feasibility of the a-CLR system using Cu-based OC, a simplified steady-state model was developed by Aspen Plus (version 8.0). It consisted of two heat exchangers, one air reactor, two cyclone separators, and one fuel reactor, as shown in Fig. 2. The fuel reactor module was composed of a Ryield block and a RGibbs block, and the air reactor was a RGibbs block. The temperature of fuel reactor was set to 800 °C and that of air reactor was 900 °C. The modules of fuel reactor and air reactor were based on the principle of minimization of Gibbs free energy. N₂ was selected as fluidizing agent in the fuel reactor which was 25 °C before being sent into the fuel reactor. The OC was circulated between the air reactor and the fuel reactor. The design spec option block was applied to set the heat needed for reduction reactor to zero by controlling the flow of CuO/CuAl₂O₄ (60 wt.%:40 wt.%), which indicated that the Cu-based OC/biomass mass ratio achieving heat balance was about 8.8, as shown in Fig. 3. Therefore, biomass gasification and reforming experiments with 1.7 g sawdust and 15 g carriers (silica sand, Fe-based or Cu-based OCs) for each run were conducted in a batch fluidized bed reactor.

2.3. Fluidized-bed setup and procedure

The biomass CLR experiments were carried out in a batch-operated fluidized bed reactor. It was made by stainless steel and placed in an electric furnace. The experimental system was illustrated in Fig. 4. The reactor length was 892 mm and its inner diameter was 26 mm. 15 g OC particles with a size range of 0.2–0.3 mm were placed on the porous plate and was then heated in air to the set-point temperature. A type K thermocouple at about 10 mm above the porous plate was used to measure the reactor temperature. During the reduction period, the fluidizing gas of 600 mL/min was introduced from the bottom of the reactor. When the temperature reached the prespecified value, 1.7 g biomass was fed into the reactor from a hopper at the top of the reactor. The flue gases passed through the filter and cold trap to collect solid particles, water, and tar, then introduced into the sampling bag. The composition of the gas products was measured using a gas chromatograph (Agilent 3000A micro-GC). The content of produced gas was attained according to nitrogen balance during the whole process. It was considered that the amount of other



Fig. 3. The effect of mass ratio to energy needed in fuel reactor.

products, such as light hydrocarbons (C_xH_y ($x \ge 3$)), was very small, and the effective syngas mainly consists of H₂, CH₄, CO, CO₂ and C₂H_m. During the oxidation period, the fluidization gas was switched from N₂ to air. The reduced OCs were re-oxidized by absorbing O₂ from air. And the regenerated OCs were recycled for next CLR experiment. The reforming process was considered to be completed in 10 min after the materials were added since little combustible gas was detected. The oxidation process was supposed to be completed when the oxygen concentration reached 20.95%.

The tar produced during the CLR process was collected in three tar traps using a mixture of HPLC grade methanol and dichloromethane (1:4, vol). The first trap with 50 ml solvent was placed in an ice-water bath (0 °C), which condensed the steam in the exhaust gas and avoided the blockage by ice of the inlet pipe in the gas bottle, and the other two traps were placed in a dry ice bath (-78 °C) [31]. The tar was captured efficiently by the second trap placed in the dry ice bath. It was found that the amount of heavy



Fig. 2. Schematic diagram of biomass a-CLR system.



Fig. 4. An overview of the fluidized bed reaction system.

tar in the third trap was negligible since there was no color in the solvent of the third trap. After each experiment, the well-mixed solvents from all three traps were evaporated at 35 °C for 12 h to remove all solvents, then the residues were accurately weighed to determine the tar yield.

2.4. Data evaluation

The gas yield, G_v (Nm³/kg) is calculated as the total volume (V_g) of gas products under standard state divided by biomass mass (m_b):

$$G_{\rm v} = V_{\rm g}/m_{\rm b} \tag{1}$$

Carbon conversion efficiency (η_c), which was usually used to measure the biomass gasification degree, was calculated as the ratio of the carbon converted into gaseous products to the total carbon in the biomass:

$$\eta_{c} = \frac{12 \times (V_{CO_{2}} + V_{CO} + V_{CH_{4}} + 2V_{C_{2}H_{m}}) \times G_{v}}{22.4 \times C\%}$$
(2)

where C_{∞}^{*} represents the carbon content of biomass; V_i is the volume fractions of gas *i* in the synthesis gas (here *i* = CO₂, CO, CH₄ and C₂H_m).

The lower heating value (*LHV*, kJ/Nm³) of the gas products was calculated as the sum of LHVs of all combustible gases. Here it is given by:

$$\begin{split} LHV &= 108.2V_{H_2} + 126.4V_{C0} + 358.8V_{CH_4} + 643.5V_{C_2H_6} \\ &\quad + 594.4V_{C_2H_4} + 564.9V_{C_2H_2} \end{split} \tag{3}$$



Fig. 5. Syngas volumes in the biomass CLR or pyrolysis processes at 800 °C.

Gasification efficiency (η) was calculated as the ratio of the calorific value of all combustible gas to the total calorific value of biomass:

$$\eta = \frac{LHV \times G_{v}}{Q_{b}} \tag{4}$$

here $Q_b = 17140 \text{ kJ/kg}$.

3. Results and discussion

3.1. Effect of OCs

To examine the effect of OCs, biomass CLR experiments with different OC particles were first carried out at 800 °C. The gas yields of each gaseous component (H_2 , CH_4 , C_2H_m , CO and CO_2) and all combustible gases were shown in Fig. 5. In the biomass pyrolysis experiment, the bed particles were silica sand of the same weight and size as OC particles. The total gas volume in the pyrolysis process was 1102 N mL, then 1345 N mL in the CLR with copper ore and 1529 N mL in the CLR with CuO/CuAl₂O₄ particles. Obviously Cu-based particles enhanced the conversion of biomass to gases. However the CO₂ yield using Cu-based OCs were much larger than using silica sand, but the other gas yields using Cu-based OCs were lower. It is ascribed to the reactions between CuO and synthesis gas, by which the required heat for reforming reactions can be supplied rather than additional heat, at the cost of the assumption of a part of synthesis gas by Cu-based OC.

The results of biomass pyrolysis with silica sand and CLR with OC particles was shown in Table 1. Generally, the gas yield and carbon conversion increased in the CLR processes using Cu-based OC particles. However, the gasification efficiency and gas LHV were lower than these in the pyrolysis process. Similarly, it is because that the reduction reactions of CuO consumed parts of H_2 , CO,

Table 1

The gas yield, LHV, carbon conversion efficiency, gasification efficiency and tar content using different bed particles.

	Silica sand	Fe_2O_3/Al_2O_3	CuO/CuAl ₂ O ₄	Copper ore
Temperature (°C)	800	800	800	800
Gas yield (Nm ³ /kg)	0.65	0.82	0.90	0.79
Gas LHV (MJ/Nm ³)	15.64	12.63	5.88	5.76
Carbon conversion	62.30	81.74	95.61	83.22
efficiency (%)				
Gasification efficiency (%)	59.15	60.07	30.84	26.62
Tar content (g/Nm ³)	22.15	10.03	7.29	10.18

CH₄ and C_2H_m to generate heat for auto-thermal CLR. The good things are the higher carbon conversion efficiency and lower tar content in the CLR. As shown, the tar contents were only 7.29 g/Nm³ and 10.18 g/Nm³ when using CuO/CuAl₂O₄ and copper ore OCs, respectively. On the one hand, the high-reactivity Cu-based OCs may react with tar directly. On the other hand, the Cu-based OC may act as a catalyst like Ni-, Fe-based OCs, prompting the secondary decomposition of tar [17].

3.2. Effect of reactor temperature

Some previous literature [32,33] have reported that the coal gasification is the rate-limiting step in the CLC of coal. Similarly, it can be inferred that reaction rate of CLR is determined by biomass gasification. A reasonable reaction temperature is very

Table 2

Effect of temperature on gas yield, LHV, carbon conversion efficiency, gasification efficiency and tar content in biomass CLR using CuO/CuAl₂O₄.

	Reactor temperature (°C)			
	600	700	800	850
Gas yield (Nm ³ /kg)	0.58	0.92	0.90	1.08
Gas LHV (MJ/Nm ³)	7.48	7.96	5.88	7.41
Carbon conversion efficiency (%)	59.20	89.67	95.61	98.91
Gasification efficiency (%)	25.39	42.50	30.84	46.67
Tar content (g/Nm ³)	22.24	12.21	7.28	4.09



Fig. 6. Effect of temperature on syngas volumes of biomass reforming using CuO/ ${\rm CuAl_2O_4}$ as OC.



Fig. 8. Tar content and C_2H_m concentration for different carriers at different temperature.

important for enhancing the biomass conversion efficiency. The effect of reactor temperature on the CLR process was investigated. The temperature varied from 600 to 850 °C. Although the optimal OC/biomass ratios which ensure the thermoneutrality of the fuel reactor under different temperatures are different, the heat for the laboratory scale CLR experiment was indeed supplied by the electric heating furnace. Here the mass ratio of OC and biomass at different temperatures was still kept constant at 15/1.7. Fig. 6



Fig. 7. Gas yield and carbon conversion efficiency of biomass CLR with different carriers at different temperature.

Table 3The physical properties of fresh and used OC particles.

	BET area (m²/kg)	Pore volume (cm ³ /kg)	Pore size (nm)	Crushing strength (N)
Fresh CuO/ CuAl ₂ O ₄	133.3	0.24	7.21	1.88 ± 0.12
Used CuO/ CuAl ₂ O ₄	46.1	0.08	7.04	1.73 ± 0.18
Fresh copper ore	216.9	0.46	8.68	1.71 ± 0.24
Used copper ore	122.0	0.24	7.86	1.63 ± 0.21

shows the gas volume at different temperature. Generally, the various gas volume and total gas volume increased with temperature. Some discrepant trends at 700 and 800 °C may be ascribed to gas measurement errors.

The further results under different temperature were concluded in Table 2. The gas *LHV* exhibited a downward trend with increase of temperature. The gas yield, carbon conversion efficiency and gasification efficiency increased with temperature. The results were explained by that a higher temperature is beneficial to more carbon being gasified in biomass gasification.

It was mentioned here that a high temperature may inactivate the OC particles. A high temperature can make the Cu-based OC particles more easily suffer form the risks of sintering/agglomeration because the elemental copper has a rather low melting point 1083 °C. As a result, the reactant gases would be difficult to diffuse into the core of the OC particles. Additionally, the sintering/agglomeration can also lead to defluidization of the bed materials. Thus, the reforming temperature should not be too high. On the other side, we also mentioned that some tailor-made Cu-based OC particles (including CuO/CuAl₂O₄, carefully selected copper ore in this study, and CuO/ZrO₂, CuO/MgAl₂O₄ reported in other references) can bear higher temperature of 950 °C without sintering and agglomeration in chemical looping with oxygen uncoupling of coal [27,34-36], and Fe-based OC performs good resistance to sintering and agglomeration at high temperatures. It is thus possible to carry out an experimental and thermodynamic study at higher temperature in the next phase of research.



Fig. 9. SEM images and EDX analysis of CuO/CuAl₂O₄ particles both fresh (left) and after used (right). General view of the particles (a) and image in high resolution (b). EDX profiles on particle surface (c).

3.3. Comparison of Cu-based OC and Fe-based OC

To compare the CLR performance using either Cu-based or Fe-based OCs, biomass CLR experiments with CuO/CuAl₂O₄ or Fe₂O₃/Al₂O₃ particles were conducted under different temperatures. Fig. 7 showed the gas yield and carbon conversion efficiency of biomass CLR with different carriers at temperatures between 600 and 850 °C. No matter what kind of bed material is used, the gas yield and carbon conversion efficiency increased significantly as the reforming temperature increased. Besides, it is not difficult to find that CLR with Cu-based OC attained higher gas yield and carbon conversion efficiency.

As shown in Fig. 8, the cumulative concentrations of C_2H_m and tar content were relatively low while using Cu-based OC. The tar content decreased with temperature increase, while C_2H_m concentration first increased then decreased. Taking the results of 800 °C as example, the tar content decreased from 22.15 g/Nm³ of biomass pyrolysis to 10.18 g/Nm³ of using copper ore, to 10.03 g/Nm³ of using Fe₂O₃/Al₂O₃ particles, to 7.29 g/Nm³ of using CuO/CuAl₂O₄ particles. It looks that the higher the OC reactivity is, the less the tar content is.

It is hard to give a conclusion that copper based oxygen carrier is better than or worse than iron based oxygen carrier for a biomass CLR at present. The disadvantage of using copper based OC is the decrease of gasification efficiency and LHV at the expense for maintaining heat balance in the CLR process. The disadvantage of using iron based OC is the low reactivity as well as the low carbon conversion efficiency. In addition, the selection of copper or iron based OC also depends on the purpose of the CLR and the downstream gas processing. If less tar and light hydrocarbon are expected for the downstream gas processing, copper based oxygen carrier may be a better choice.

3.4. Characterization of OC

The Cu-based OCs were characterized before and after tests in the batch fluidized bed reactor. The BET surface areas of the particles were evaluated by N₂-absorption method (Micromeritics, ASAP2020). The crushing strength was determined by a crushing strength apparatus (Shimpo FGJ-5) from 20 measurements. As shown in Table 3, the used OC had smaller BET areas and pore volumes, probably because of the blocking of fly ash generated in the biomass CLR process and a slight sintering in the OC particle. Although the OC had a relatively small BET area and pore volume, the reactivity was maintained well. The crushing strength decreased slightly after being used while it was still hard enough for chemical-looping utilization.

The surface texture and the solid structure of the OCs were analyzed by Environment Scanning Electron Microscope (ESEM, FEI Quanta 200). Fig. 9 shows the pictures of the CuO/CuAl₂O₄ particles, both fresh and continuously used samples in the biomass CLR processes. The used CuO/CuAl₂O₄ particles showed smaller grains on the surface (see Fig. 9b). However, the morphology of the used particles was similar to that of the fresh particles. The element distribution on the surface of the particles was analyzed by EDX (see Fig. 9c). It could be seen that the fresh CuO/CuAl₂O₄ particle was just composed of three kinds of elements: O, Cu, and Al (C is the conducting medium sprayed on the sample for detection). While there were some Si. K and Ca detected on the surface of the used particles, which indicated that some biomass ash was absorbed on the surface of the particles. SEM images of copper ore particles also showed similar surface texture and solid structure for the fresh and used ones. The OC particles never showed agglomeration or defluidization problems at these tested temperatures. In addition, chemical-looping with oxygen uncoupling (CLOU) of coal experiments using CuO/CuAl₂O₄ and copper ore as OCs were carried out at higher temperatures (such as $950 \,^{\circ}$ C) in the same batch-operated fluidized bed reactor [27,30]. It was found that Cu-based OC still performed good cycling stability. These results suggested that the Cu-based OC could have a good durability, being suitable for biomass CLR process.

4. Conclusions

The feasibility of biomass chemical looping reforming (a-CLR) using Cu-based oxygen carrier (OC) was investigated in a batch-operated fluidized bed reactor. By utilizing the exothermic nature of Cu-based OC reacted with oxidizable gases, an auto-thermal CLR operation is expected to be attained in the fuel reactor. The effects of OC and reactor temperature on the syngas composition distribution, gas yield, carbon conversion efficiency, lower heating value and gasification efficiency as well as tar content were examined. And the results of Cu-based OC were compared with these of Fe-based OC. While using Cu-based particles, the gas yield and carbon conversion were higher, the cumulative concentration of C_2H_m and tar content were less. As the temperature increased, the tar content decreased and the C2Hm concentration first increased then decreased. When the reactor temperature was set at 800 °C, the tar content decreased from 22.15 g/Nm³ of biomass pyrolysis to 10.18 g/Nm³ of using copper ore, to 10.03 g/Nm³ of using Fe₂O₃/Al₂O₃ particles, to 7.29 g/Nm³ of using CuO/CuAl₂O₄ particles, respectively.

In summary, the advantages of using copper based OC are the increase of carbon conversion efficiency as well as the decrease C_nH_m content and tar removal. The disadvantage is the decrease of gasification efficiency and LHV at the expense for maintaining heat balance in the CLR process. Moreover, it is difficult to control the residence time and reaction extent of OC particles and reduction products in the batch-operated fluidized bed reactor. For further study, the syngas quality can be improved by optimizing the operating conditions, such as the reaction temperature, steam to biomass ratio, oxygen to biomass ratio, and reaction time [37]. Higher syngas LHV and gasification efficiency are also expected to be achieved by limiting the oxygen availability (by the limited solid circulation rate and bed inventory, and/or the limited oxygen oxidation (air availability) in the air reactor) in the interconnected fluidized bed with continuous feeding system, which is the focus of our next research stage. However, the risk of sintering and agglomeration of Cu-based oxygen carrier if being deeply reduced should be always kept in mind. It is possible to improve the resistance of Cu-based particles to sintering and agglomeration by rational design and optimized preparation.

We also mentioned here, fully oxidized copper oxide was used in the batch tests, and high oxygen availability from the copper oxide (in contrast to other oxides) allows for effective oxidation of higher hydrocarbons, H_2 and CO, especially at the higher temperatures. However, the oxygen availability would be typically limited in a continuously operated a-CLR configuration. So, the effective oxidation of fuels cannot be expected due to a global lack of oxygen situation (otherwise the syngas may get fully oxidized to CO_2 and H_2O). This may limit the transferability of results from the batch testing to continuously operating units.

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