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# HYDROGEN GENERATION FROM COAL USING NOVEL CHEMICAL LOOPING PROCESS WITH CuO AND CaO AS SOLID CARRIER

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## ABSTRACT

A novel process for hydrogen generation from coal using two chemical-looping processes through three main reaction stages in a three-interconnected fluidization bed reactor was proposed in this paper. During three stages, steam gasification of coal producing the hydrogen, calcination of  $\text{CaCO}_3$  yielding  $\text{CO}_2$ , and regeneration of as-reduced oxygen carrier in the air were carried out respectively. Auto-thermal balance with  $\text{CO}_2$  capture can **achieve** by adjusting the ratio of solid carriers.

The feasibility of the novel process is verified by thermogravimetric experiments and it demonstrates that the solid carrier has a good reactivity during the above-mentioned three stages. The temperature has a **great** influence on the reaction rate and the purity of hydrogen in stage I. **However**, the existence of CuO **restrains** the  $\text{CO}_2$  capture capability of CaO. **Accordingly**, the preparation method of CuO-CaO solid carrier rather than their simple mixture should be further investigated for this proposed process.

## INTRODUCTION

Chemical looping process for combustion of gaseous and solid fuels, possessing the merit of high efficiency, inherent  $\text{CO}_2$  separation and low  $\text{NO}_x$  emission, has been investigated widely. Syngas/hydrogen generation from natural gas or solid fuels can be achieved using chemical looping process by supporting insufficient lattice oxygen from oxygen carrier(1). Syngas generation through the chemical looping process has been investigated by some researchers (2-5). Fan et al (2) developed three chemical looping processes to convert carbonaceous fuels into products (i.e. hydrogen, electricity, and synthetic fuels). Mattisson (6) proposed two chemical-looping reforming processes for syngas generation from hydrocarbon. Recently, He (7) and de Diego (8, 9) investigated the chemical looping reforming of methane to produce syngas using different metal oxides as oxygen carriers. However, they obtained syngas **either** from the steam or from dioxide carbon reforming using the reduced metal oxide (e.g. Fe) or chemical looping reforming of gaseous hydrocarbon, **rather than** from solid carbon fuel gasification using lattice oxygen of metal oxides directly.

Nevertheless, Andrus (10) developed a calcium-based hybrid combustion gasification chemical looping technology for electricity, syngas or hydrogen from coal based on three basic ways by controlling the air-to-coal ratio (i.e. oxygen carrier-to-coal ratio in the fuel reactor). If enough oxygen supported by  $\text{CaSO}_4$  oxygen carrier **reacts** with coal, the carbon and hydrogen in coal leaves the fuel

reaction as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Otherwise, the syngas  $\text{CO}/\text{H}_2$  can be generated, and hydrogen can be produced if coupling with water shift and  $\text{CO}_2$ -capture using  $\text{CaO}$ . Compared with  $\text{CaSO}_4$  oxygen carrier,  $\text{CuO}$  is characterized by low reaction temperature and exothermic characteristic in both reduction and oxidation reaction.

To date, the process using  $\text{CuO-CaO}$  as solid carrier has been investigated by previous researchers (11-13). However, they mainly integrated chemical looping combustion with calcium looping to supply the heat for post-combustion  $\text{CO}_2$  capture. Anthony (11, 12) designed a core-in-shell  $\text{CaO/CuO}$  composite to provide the heat for  $\text{CO}_2$  carrier regeneration ( $\text{CaCO}_3/\text{CaO}$ ). Qin (13) also examined the behavior of  $\text{CaO/CuO}$  based composite in a combined calcium and copper chemical looping process for the post-combustion  $\text{CO}_2$  capture via a thermogravimetric analyzer. For the pre-combustion  $\text{CO}_2$  capture systems, a preliminary design based on the principles of fixed bed operation has been completed by Fernández et.al.(14), and it was reported good potential for high efficiency. However, the high temperature PSA (pressure swing adsorption) was used in this process to inhibit calcination of  $\text{CaCO}_3$  during  $\text{CuO}$  oxygen carrier regeneration, which made the process complicated.

Considering the exothermic characteristic of redox reaction of  $\text{CuO}$  oxygen carrier and calcination temperature of  $\text{CaCO}_3$ , a novel process for hydrogen generation from coal using two chemical looping processes integrating three main reaction stages in a three-interconnected fluidization bed reactor, was proposed and evaluated in this paper.

## PROCESS DESCRIPTIONS

In this paper, the novel hydrogen generation process was performed through three reaction stages in a three-interconnected fluidization bed reactor. As shown in Figure 1, the schematic diagram included the following three reaction stages: a) The gasification of coal with steam was carried out in stage I. Simultaneously, carbonation of  $\text{CaO}$  with the  $\text{CO}_2$  and the reduction of  $\text{CuO}$  with generation syngas occurred, enhancing the hydrogen generation; b) the reacted solids including  $\text{Cu}$  and  $\text{CaCO}_3$  were calcined to product pure  $\text{CO}_2$  for capture-ready in stage II; c) The regeneration of as-reduced oxygen carrier in the air was performed in stage III.

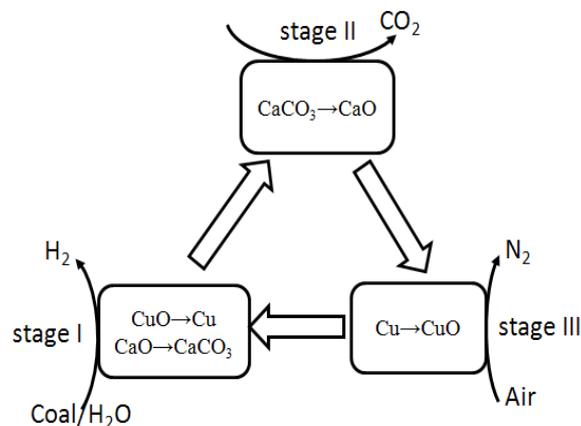


Figure 1. Schematic diagram of the novel process for hydrogen generation

In this process, the calcination of  $\text{CaCO}_3$  was designed to occur before the oxidation of as-reduced CuO oxygen carrier, which can prohibit the decomposition of  $\text{CaCO}_3$  during stage III, a strong exothermic process. Because the solid carrier particles, including CaO and CuO, went through three stages in turn, a three-interconnected fluidization bed reactor was the best candidate reactor. Each stage was carried out in the corresponding fluidization bed reactor sequentially. The main referred reactions in three stages were listed in Table 1. In the stage I, there exists the steam gasification, reforming of coal for hydrogen generation, together with inherent capture of  $\text{CO}_2$ . Further, the generation syngas will react with CuO oxygen carrier, integrating with oxidation exothermic reaction of as-reduced oxygen carrier in stage III, which supplies enough heat for calcination of  $\text{CaCO}_3$ . It can be found that stage II is endothermic while the other two stages are exothermic and the processes can achieve auto-thermal balance by adjusting the ratio of coal-CuO-CaO.

**Table 1. Main reactions occurred in each stage**

Main referred reactions		
stage I	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	$\Delta H_{273.15} = 130.88 \text{ kJ/mol}$
	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$\Delta H_{273.15} = -41.20 \text{ kJ/mol}$
	$\text{CO} + \text{CuO} \rightarrow \text{Cu} + \text{CO}_2$	$\Delta H_{273.15} = -126.92 \text{ kJ/mol}$
	$\text{H}_2 + \text{CuO} \rightarrow \text{Cu} + \text{H}_2\text{O}$	$\Delta H_{273.15} = -85.72 \text{ kJ/mol}$
	$\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$	$\Delta H_{273.15} = -178.25 \text{ kJ/mol}$
stage II	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	$\Delta H_{273.15} = 178.25 \text{ kJ/mol}$
stage III	$2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$	$\Delta H_{273.15} = -311.72 \text{ kJ/mol}$

## EXPERIMENTAL

### Materials

The solid carrier adopted herein was the mechanical mixture of analytical pure CuO and CaO, with whose size distribution 50~100  $\mu\text{m}$ . The Shenmu coal was used, whose proximate and ultimate analysis listed in Table 2.

**Table 2 Proximate and ultimate analysis of coal**

Proximate analysis, % (mass, ad)				Ultimate analysis, % (mass, ad)				Low heat value, $\text{MJ}\cdot\text{kg}^{-1}$
M	V	Ash	FC	C	H	N	O	
8.30	29.46	10.21	52.03	65.00	3.83	0.88	11.38	24.58

### Experiment Procedure

To evaluate the feasibility of the novel process, the experiment of the determined mass ratio of CuO-CaO solid carrier and coal was done in the thermal gravimetric analyzer (TGA, Netzsch STA 409 PC, Germany). In this test, the desired mass ratio mixture in TGA was heated from room temperature directly to 750 °C with the heating rate of 20 K/min in 20 mL/min argon, then stage I was conducted at this temperature for 20 min under 20 mL/min argon saturated with  $\text{H}_2\text{O}$ . After this

process, the temperature was raised to 850 °C. During stage II, the calcination of  $\text{CaCO}_3$  lasted for 20 min. Then, Cu was oxidized back to CuO in air for 10 min (stage III).

The similar experiment of the mass ratio of CuO-CaO solid carrier and coal was also performed in a fluidized bed, whose dimension is 55 mm in diameter and 1000 mm in height (see Figure 2). To simplify the process and evaluate the feasibility of each stage, three stages were carried out in one fluidized bed by switching the inlet gas and the temperature for each stage. When it raised to the desired temperature for stage I, the experiment was timed and the gas was collected for analysis. After 40 min, it increased to the desired temperature for stage II. Then, stage III was accomplished by alternating air and adjusting temperature. The collected gases were analyzed directly by the gas chromatograph analyzer (PE Clarus 500), using TDX-01 packed column/thermal conductivity detector. Five temperatures ranged from 700 to 800 °C in stage I was selected to investigate its effect on the  $\text{H}_2$  generation and  $\text{CO}_2$  capture.

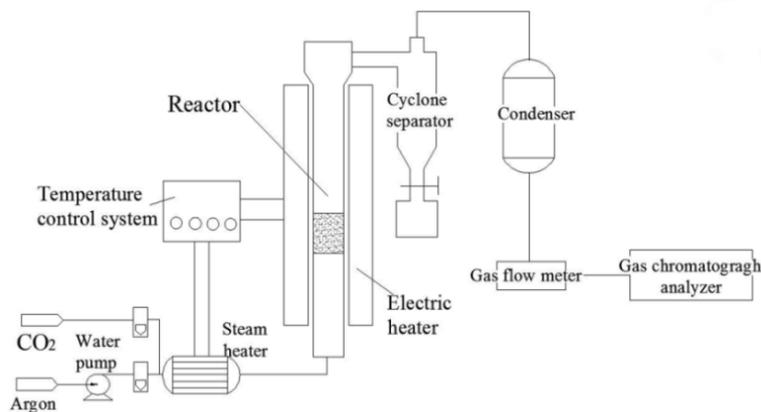


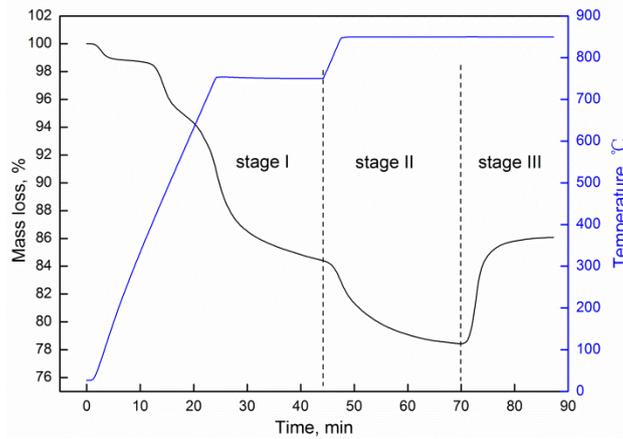
Figure 2 Schematic layout of the laboratory setup

## RESULTS AND DISCUSSION

### Thermogravimetric experiment

The feasibility of the novel process was verified by the thermogravimetric experiment, with stage I and the other two stages occurring at the temperatures 750 °C and 850 °C, respectively. The atmospheres of three stages were argon saturated with  $\text{H}_2\text{O}$ , pure argon and air, respectively. Mass loss of mixture sample with C/CuO/CaO mole ratio of 1:1:1 was described in Figure 3.

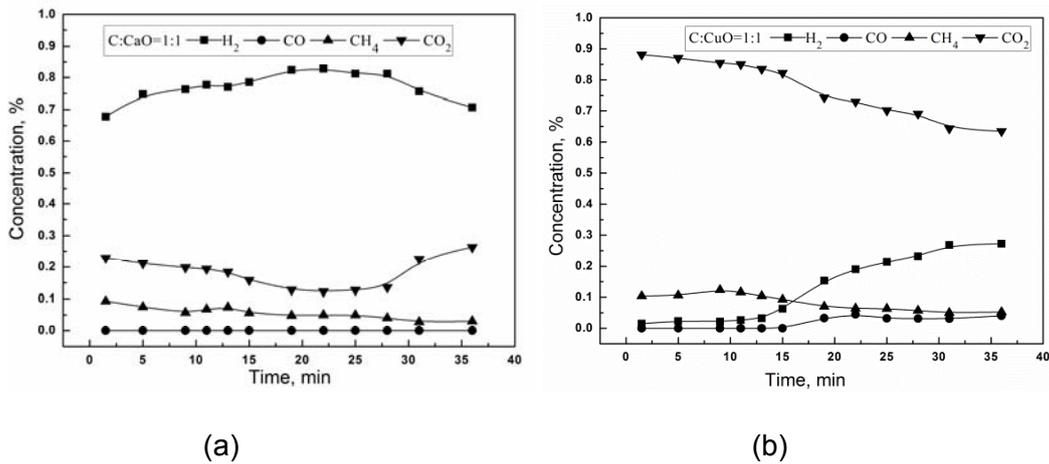
Mass loss before 750 °C was due to the drying of the mixture and pyrolysis of coal. During 25~45 min, it can be seen that a mass loss occurred, which was a result of hydrogen generation combining  $\text{CO}_2$  capture. During 48~70 min, the mass loss represents calcination of  $\text{CaCO}_3$ . The intensive mass loss in stage II reveals that the CaO possesses excellent capacity of  $\text{CO}_2$  capture during stage I. The mass rise during 70~90 min was due to the oxidation of Cu, which reveals that the CuO possesses excellent capacity of reduction-oxidation cycle. These correspond with three stages I-III, as illustrated in Figure 1.



**Figure 3. TG curve of reactivity of CuO-CaO in three stages**

**Effect of solid carrier on the gaseous product**

The concentration of gaseous product varying with the time using CaO, CuO as solid carrier individually, where the same mass of Al<sub>2</sub>O<sub>3</sub> was used instead of the other solid carrier, in the fluidized bed was illustrated in Figure 4. When CaO was used as solid carrier, the main gaseous product was H<sub>2</sub>. The concentration of H<sub>2</sub> increases firstly, and then decreases. The concentration of CO<sub>2</sub> has an opposite trend, which is explained by the reactions in stage I. Thus the carbonization reaction of CaO promoted the generation of hydrogen. When the coal has reacted completely, the decomposition of CaCO<sub>3</sub> took place. Accordingly, the concentration of H<sub>2</sub> began to reduce, while that of CO<sub>2</sub> increased after 25 min. Other gaseous production including CO and CH<sub>4</sub> was mainly due to the pyrolysis of coal.

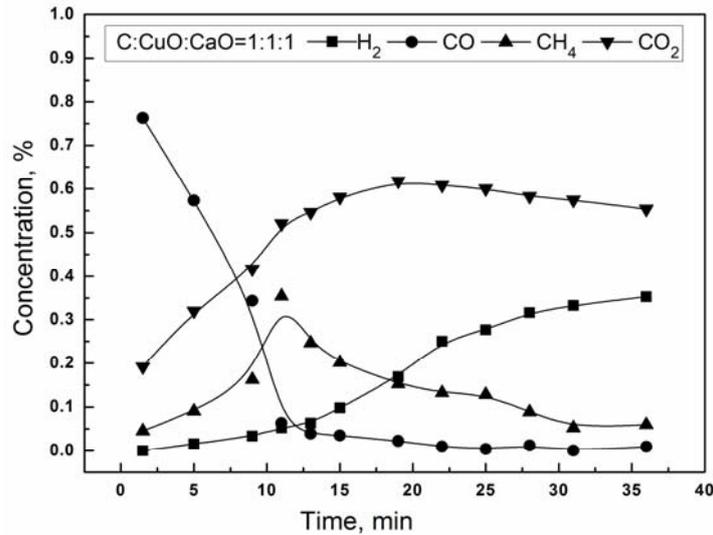


**Figure 4. Variation of concentration of gaseous product with time using the single solid carrier. (a) C/CaO/Al<sub>2</sub>O<sub>3</sub>; (b) C/CuO/Al<sub>2</sub>O<sub>3</sub>.**

When CuO was used as solid carrier, the concentration of CO<sub>2</sub> was higher than 85% at the first 15 min, while there existed hardly H<sub>2</sub>. At 15min, the concentration of H<sub>2</sub> began to increase, while that of CO<sub>2</sub> began to decrease. The reaction

between coal and CuO to produce CO<sub>2</sub> was the main reaction, which was so-called chemical looping combustion of solid fuel. With the consumption of CuO, the coal steam gasification generating syngas was the main reaction, and the concentration of H<sub>2</sub> began to increase.

The variation of concentration of the gaseous product with time using CuO-CaO mixtures as solid carrier was described in Figure 5. During the first 10 minutes, the concentration of CO was high while that of the other three gases was relatively low. The concentration of CH<sub>4</sub> reached its maximum value at 12 min. Similar to Figure 4(a), the concentration of CO<sub>2</sub> increased with time before 15 min, and then decreased slightly. The variation of concentration of H<sub>2</sub> is in good agreement with that in Figure 4(b). Due to the existence of CaO and CuO, the sorption of CO<sub>2</sub> using CaO enhanced the syngas generation, while CuO was inclined to react with H<sub>2</sub>. It can explain the variation trend of concentration of gaseous product in the first 15 min. Moreover, with the consumption of CuO, the coal steam gasification reaction generating syngas was changed into the main reaction. Thus, the concentration of H<sub>2</sub> intended to increase.



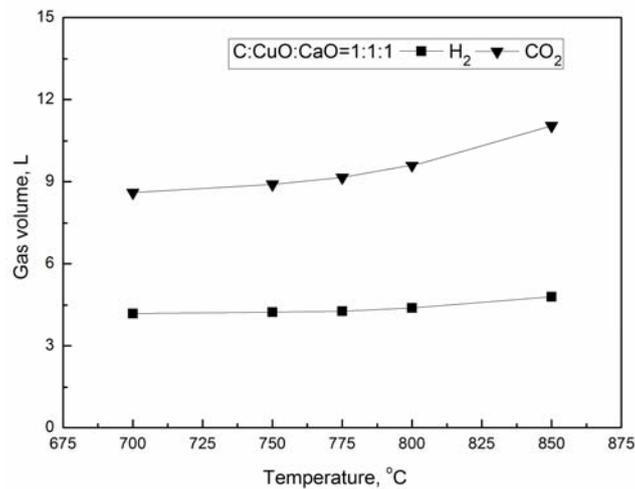
**Figure 5. Variation of concentration of gaseous product with the time using CuO-CaO as solid carrier**

It indicated that the existence of CuO restrained the CO<sub>2</sub> capture capability of CaO. Qin(13) also revealed this phenomenon through thermogravimetric experiment. He ascribed this negative effect to the “wrapping” of Cu/CuO on the outer surface of CaO. In particular, this effect might be enlarged when solid fuel such as coal was used as fuel. Additionally, the effect of coal ash on the CuO-CaO solid carrier should be considered. The preparation method of CuO-CaO solid carrier rather than their simple mixture should be further investigated for this proposed process.

### Effect of temperature on the H<sub>2</sub> generation and CO<sub>2</sub> capture

Temperature has an influence on the carbonization reaction of CaO and the reduction reaction of CuO. The variation of generation volume of H<sub>2</sub> and CO<sub>2</sub> with

temperature was illustrated in Figure 6. It revealed that the H<sub>2</sub> generation changed slightly with temperature, while the volume of CO<sub>2</sub> increased with temperature obviously. The variation is related to the calcination of CaCO<sub>3</sub> occurred in high temperature.



**Figure 6. Effect of temperature on the H<sub>2</sub> generation and CO<sub>2</sub> capture**

## CONCLUSIONS

The following conclusions can be obtained.

- 1) Thermogravimetric experiment indicated that the proposed process can be realized easily and is a potential process for hydrogen generation with inherent CO<sub>2</sub> capture.
- 2) The existence of CuO restrained the CO<sub>2</sub> capture capability of CaO, and the preparation method of CuO-CaO solid carrier with high reactivity was a key factor for the process.
- 3) Temperature influenced the CO<sub>2</sub> capture capacity highly, while affected the amount of H<sub>2</sub> generation slightly. The optimal temperature ranges for stage I ranged from 700 to 750 °C.

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