

Research article

Volatile matter capture by calcined limestone under Calcium-Looping process conditions

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ABSTRACT

This work proposes an approach to avoid hot-spot formation in the regenerator of Calcium-Looping CO₂ capture process. The basic principle is to capture volatile matter evolved from the fuel by porous sorbent (CaO) particles followed by the formation of solid carbon deposit within the particles. By reducing the amount of volatile matter, rapid combustion of volatile matter in the regenerator can be suppressed. Experimental work was carried out to assess the volatile matter capture by CaO particles in a fixed bed. Higher temperature was found to be favorable to capture volatile matter. Also combustion rate of carbon deposit was measured. The combustion rate of carbon deposit was found to be sufficiently lower than the rate of volatile matter combustion. The influences of temperature and oxygen concentration on deposit combustion rate were not remarkable. Several designs for fuel feed modification that enable volatile matter capture are proposed.

1. Introduction

Carbon capture and storage (CCS) technologies have been investigated extensively to suppress CO₂ emissions to the atmosphere. Calcium-Looping (CaL) CO₂ capture process, a dry absorption-desorption process using dual-fluidized bed solid circulation system, is a post-combustion CO₂ capture process. Carbon dioxide in flue gas from an air-blown combustor is captured by CaO to form CaCO₃ in a carbonator at about 873–923 K (600–650 °C) and decomposition of CaCO₃ to CaO and CO₂ is conducted in a regenerator at about 1173–1223 K (900–950 °C), as portrayed in Fig. 1 [1]. The heat to decompose CaCO₃ in the regenerator is supplied by burning fuel such as coal using pure O₂ so that the flue gas consists ideally only of CO₂ and H₂O. The CaL process is regarded as an energy-efficient and low-cost post-combustion CO₂ capture process [2–6]. Therefore, this process has been extensively investigated using dual-fluidized bed systems. Numerous reports have described CO₂ capture by CaO-based sorbents [7–20].

In practice, pure O₂ fed to the regenerator must be diluted by recycled CO₂ to avoid hot-spot formation due to rapid combustion of fuel in high O₂ concentration atmosphere. Especially, care must be given when high-volatile fuels are burned because volatile matter is rapidly oxidized in gas phase and char from such fuels is reactive; both volatile matter combustion and rapid char combustion are anticipated to cause hot-spot formation. However, dilution of O₂ by CO₂ increases the heat loss from the regenerator in the form of sensible heat of CO₂, thus it increases energy penalty [21]. In addition, dilution of O₂ by CO₂ are

anticipated to increase regenerator volume to attain a certain gas residence time, thus it increases external surface area of the regenerator and increases the heat loss through the reactor wall. Therefore, operation with less dilution by CO₂, *i.e.* with higher O₂ concentration, is favorable to reduce the energy penalty.

One of the approaches to suppress the rapid combustion of volatile matter is the use of “capacitance effect” of porous solids, *i.e.*, capture of gaseous hydrocarbons such as tar or volatile matter in the pores followed by carbon deposition, as illustrated in Fig. 2 [22–27]. Capacitance effect of porous bed materials such as alumina has been proven to be effective to capture volatile matter, to suppress rapid combustion of volatile matter, and to enhance horizontal carbon dispersion under fluidized bed combustion conditions [23–25]. However, previous works on capacitance effect were carried out by using mainly alumina and silica. It is not yet clear whether porous sorbent particles can capture volatile matter under conditions of CaL process.

The objective of this work is to assess the volatile matter capture by the sorbent particles under CaL conditions. As the first step of the assessment, volatile matter capture by CaO was evaluated. The sorbent drained from the carbonator is basically a mixture of CaO and CaCO₃. The conversion of CaO to CaCO₃ of the sorbent should be relatively low so that sufficient CO₂ capture efficiency can be attained; the present authors revealed that the CO₂ capture efficiency dramatically decreased when the average conversion of solids exceeded a certain value (about 10%) [20]. Such low conversion is explained by an experimental finding that only thin layer (about 50 nm) from pore surface is

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Nomenclature

$C_{IN,i}$	concentration at inlet of i -th stage of complete mixing vessels connected in series, %
$C_{OUT,i}$	concentration at outlet of i -th stage of complete mixing vessels connected in series, %
k	apparent first-order reaction rate constant, 1/s
t	time, s
X	solid carbon conversion, –
τ_i	residence time of i -th stage of complete mixing vessels connected in series, s

accessible to CO₂ [28]. It should be noted that the conversion of the sorbent is considered to have wide distribution because of nearly complete mixing of sorbent particles in the fluidized bed carbonator. The residence time distribution of solids in a complete mixing vessel with average residence time of τ is given as:

$$f(t) = \exp(-t/\tau)/\tau \quad (1)$$

where $f(t)$ gives the residence time distribution function for residence time of t . This function gives the highest value when $t = 0$, i.e., considerable portion of the particles drained from the carbonator resided there for only short time and the conversion to CaO to CaCO₃ of such sorbent particles is very low. For this reason, this work assesses the volatile matter capture by CaO particles as the first step to clarify the phenomena of capacitance effect. Experiments of feeding volatile matter to a fixed bed of CaO were carried out and the ratio of captured carbon in the volatile matter was determined. Also combustion rate of carbon deposit was measured. The effect of temperature on volatile matter capture and combustion rate of carbon deposit was investigated. Based on the experimental results, modifications of fuel feed system that enable volatile matter capture are proposed.

2. Experimental

Volatile matter capture by calcined limestone was evaluated by use of a fixed bed reactor system schematically shown in Fig. 3. The reactor system consisted of three parts, namely reactor A, B and C. They were all made of quartz glass. The whole reactor system was heated by an electric heater. The gas was fed from the top of the reactor downward through the reactors. The total gas flow rate was fixed at 1.64 mmol/s (2.2 L/min at 273 K, 1 atm). Reactor B was the main body of the system and its size was 27 mm in inner diameter and 1 m in length. In the reactor B, limestone of 28 cm³ in bulk volume (equivalent to mass of 53 g) was packed on a quartz sintered plate which located at the middle part of the tube. The reactor A, a quartz tube with a sintered plate at the bottom, was inserted in the reactor B above the packed bed. Fuel particles were fed into the reactor A onto the sintered plate and

devolatilization occurred there. Only the evolved volatile matter passed through the sintered plate and fed into the reactor B, conveyed by nitrogen stream. Part of the volatile matter was captured by the packed bed of CaO, whereas the rest of volatile matter reached reactor C which located below the packed bed. In reactor C, Pt/Al₂O₃ catalyst pellets were packed so that the unreacted volatile matter was oxidized to form CO₂ and CO by feeding O₂ through valve V₁. The produced CO₂ and CO were measured by non-dispersive infrared absorption analyzers. By converting the volatile matter to CO₂ and CO, the establishment of carbon balance became easier. After devolatilization, valve V₁ was closed and valve V₂ was opened to feed oxygen to reactor B, still feeding N₂ to reactor A. The carbon captured by the solid sample was burned in downward flow of O₂-N₂ mixture to form CO₂ and CO. Oxygen concentrations from 7 to 21% were employed for deposit combustion in the present work. Although the O₂ concentration in the fed gas to the regenerator of CaL process is higher than these values, the representative value of O₂ concentration in the regenerator is considered to be in the present range (between the inlet concentration and outlet concentration of only few %). Finally, oxygen was fed to the reactor A through valve V₃ and the char in the reactor A was converted to CO₂ and CO.

Chichibu limestone from Japan was employed as sample. The composition (wt%) of raw limestone included CaCO₃ 96.9, MgCO₃ 1.4, SiO₂ 0.6, Al₂O₃ 0.8, and Fe₂O₃ 0.3. The particle size was 0.35–0.42 mm. The raw limestone was packed in reactor B, then it was calcined at 1153 K feeding O₂-N₂ mixture. After calcination, the temperature was fixed at experimental temperature. Polyethylene (PE) pellets were employed as volatile matter source because PE is known to form only negligible amount of char [24].

3. Results and discussion

3.1. Experimental results

A typical result of CO₂ formation after feeding PE pellets to the reactor system is shown in Fig. 4. The first peak (0–120 s) corresponds to the combustion of volatile matter which was not captured by the calcined limestone bed. The second peak (120–240 s) corresponds to the combustion of carbon deposited on the calcined limestone bed. After 240 s oxygen was fed to the reactor A to burn residual char, but only slight formation of CO₂ was observed. The result shown in Fig. 4 indicates that a considerable amount of volatile matter was captured by calcined limestone. Fig. 5 shows typical results of material balance of carbon. The content of carbon in the fuel (polyethylene pellet) was assumed to be 12/14 [g-C/g-Pellet] (assumed molecular formula of C₂H₄). The total amount of carbon in the produced gas (as CO₂ and CO) was nearly equal to the carbon in the fed fuel. Thus the carbon in fed fuel was completely converted to gaseous products during the experiment.

Fig. 6 shows the effect of temperature on carbon retention by the CaO particles. Carbon retention was calculated from the total formation of CO₂ and CO during deposit combustion. Carbon retention increased with increasing temperature. These results imply that higher temperature is favorable for volatile matter capture. The amount of fed fuel had only little influence on the carbon retention.

Fig. 7 shows (a) the impulse response of CO₂ analyzer and (b) estimation of true CO₂ formation profile from the CO₂ analyzer output signal. As shown in Fig. 7(a), the half-height width of the impulse response of CO₂ analyzer was about 10 s. This value was not negligible to determine the combustion rate of carbon deposit. Thus the influence of analyzer's response on output signal was eliminated to estimate true CO₂ formation profile. First, the impulse response was approximated by a three-stage complete mixing vessels. The input ($C_{IN,i}$)–output ($C_{OUT,i}$) relationship of i -th vessel is given by a differential equation as:

$$dC_{OUT,i}/dt = (C_{IN,i} - C_{OUT,i})/\tau_i \quad (i = 1, 2, 3) \quad (2)$$

where τ_i refers to the average residence time in i -th vessel. As shown in

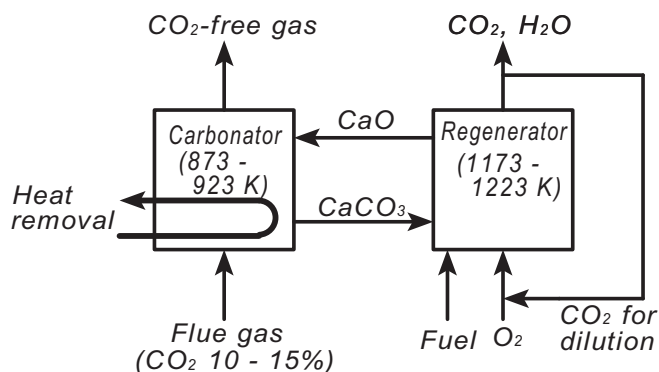


Fig. 1. Concept of Calcium Looping (CaL) process.

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