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Enhanced CO_2 capture by biomass-templated $Ca(OH)_2$-based pellets

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HIGHLIGHTS

- Addition of biomass to CaO-based pellets increased the porosity of the pellets.
- Pellets doped with leaves performed better than those with cardboard, seeds and wood.
- A CO_2 capture capacity of 0.53 g CO_2/g was obtained with the modified pellets.
- Naturally occurring biomass materials are promising agents for modifying CaO-based sorbents.

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ABSTRACT

Biomass-templated $Ca(OH)_2$-based pellets were synthesized for high-temperature post-combustion CO_2 capture. Four types of biomass-derived materials were used for sorbent templating: cardboard, maple leaves, date seeds, and white soft wood. After calcination at 850 °C in air, composite pellets with leaves exhibited a high pore volume of 0.11 cm^3/g, compared to that of 0.07 cm^3/g for pellets without biomass addition. The alteration in porosity was attributed to the release of combustion gases during the combustion of biomass. After 20 capture cycles with no steam, these pellets captured 0.24 g CO_2/g calcined pellets, compared to 0.18 g/g for biomass-free pellets. The highest CO_2 uptake was achieved with pellets containing 10% leaves. This enhancement in CO_2 uptake allowed the possibility of doubling the binder content, thus improving the mechanical strength of the pellets. The introduction of steam to the carbonation environment resulted in relatively high uptakes of 0.53 and 0.41 g/g for the first and 20th cycles, respectively. In general, all composite pellets modified with biomass displayed better performance than their counterpart pellets, indicating the benefits of biomass addition. The dispersed biomass ash also appears to have helped stabilize the morphology of these pellets as well as acting as a doping agent assisting CO_2 capture via enhanced diffusion. Considering the fact that such biomass materials are readily available and cheaper than synthetic organic materials by at least an order of magnitude, their utilization should not significantly increase the cost of the templated sorbent.

1. Introduction

It has been widely acknowledged that the increasing concentration of CO_2 in the atmosphere is a major contributor to greenhouse gas effect and climate change. The World Energy Outlook (WEO) projects that CO_2 emissions from fossil fuel combustion will grow, to 40.2 Gt CO_2 by 2030. It was also reported that 43% of CO_2 emissions from fossil fuel combustion in 2008 were produced from coal-fired plants [1]. Carbon capture and storage (CCS) is one approach that has been proposed for CO_2 mitigation from stationary sources [2,3]. This approach consists of three stages: CO_2 capture/separation, transportation, and sequestration. The first step is a particularly critical step with respect to the technical feasibility and cost of CCS processes. Currently, the commercially-available technique for CO_2 capture is based on amine scrubbers [4,5]. However, this technology is energy-intensive and imposes various economic and environmental penalties including those due to the degradation of the expensive amine-based solvents [6,7].

Calcium looping technology is a promising process for capturing CO_2 [8]. The calcium looping cycle is carried out in a dual fluidized-bed combustion system where CO_2 is captured by a CaO-based sorbent (such as limestone) at 600–700 °C and released by subsequent calcination at 850–950 °C to produce a high-purity CO_2 stream ready for storage. However, two major problems are encountered

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in this process: (1) the decline in CO_2 capture capacity of the sorbent due to sintering; and (2) the attrition and fragmentation of limestone due to mechanical and thermal stress [9]. The severity of these two effects has been found to increase with increasing number of reaction cycles [10,11]. Maintaining a high make-up flow to replace the spent sorbents and elutriated materials has been found to negatively influence the economics of the process [12]. As a result, there have been extensive research efforts to improve the reactivity of the sorbent by chemical doping [10,13–15], organic acid treatment [16–19], and hydration [20]. In some cases of doping CaO-based material with metals, doped sorbents exhibited low performance, even inferior to that of the undoped material, such as in the case of doping CaO with the alkali metal lithium [13]. On the other hand, doping limestone with mineral acids, such as HBr, was found to result in a pronounced improvement in the CO_2 uptake of the doped sorbent [21]. However, these modification techniques risk being cost-ineffective due to the relatively high cost of chemicals and treatment procedures and require further development [22,23]. Pelletization still allows the possibility of sorbent doping but has also been proposed to improve the mechanical strength of the sorbent using different binders, such as bentonites [24], kaolin [25], alumina [25], and calcium aluminate cement [19,26].

In this work, a simple and cost-effective procedure for synthesizing CaO-based composite pellets containing biomass-based organic additives is presented. Burning the biomass template material in these pellets releases gases that alter the porosity of the sorbent, and subsequently enhance CO_2 capture. However, it is unclear at this stage whether the ash from the combustion of biomass also affects the performance of the pellets. Different commonly available biomass materials were therefore used to investigate their impact on the CO_2 capture performance of the pellets. In addition, the sorbents were pelletized with different ratios of binder and biomass. CO_2 capture cycles were performed with and without steam to investigate its impact and interaction effects on sorbent performance.

2. Experimental

2.1. Sorbent preparation

A batch of powdered Cadomin limestone was used as the source of the CaO in all biomass-templated sorbents in this work. Table 1 shows the elemental composition of the limestone obtained using an X-ray fluorescence XRF (Primus II Wavelength Dispersive XRF) spectrometer. The analysis was performed at ~40 °C under helium. Four biomass materials were used: cardboard, maple leaves, date seeds, and white soft wood. The samples were ground using a Planetary Mono Mill (Pulverizette 6) and sieved to <30 μm in diameter.

The composite sorbents were then prepared using a weighed quantity of CaO (~210–270 g obtained from the calcination of limestone at 850 °C in air for 2 h) with deionized water in a ceramic crucible. Excess deionized water was used to ensure a complete conversion of CaO to $Ca(OH)_2$. The $Ca(OH)_2$ mortar was then left to cool for few minutes and then weighed quantities of biomass and calcium aluminate cement (CA-14 with composition of 72.7% Al_2O_3, 27.2% CaO, and 0.1% impurities) were added. The contents of the crucible were then vigorously mixed and left for 3–5 min. It should be noted here that from the point of view of safety the sequence of these steps is important; for instance, the addition of biomass to CaO followed by hydration may result in devolatilization or even combustion of the biomass due to the exothermic nature of the hydration reaction (our preliminary experiments with cardboard have demonstrated such an effect.) The final mortar was then extruded through a 1.0 mm sieve to produce pellets with uniform diameters. The resulting pellets were air dried for 24 h. Different pellet samples were prepared with different biomass types and quantities (5, 10, and 20 wt%), and different cement content (10, 15, and 20 wt%). The pellets were designated using the first letter of the biomass used in their preparation. For instance, CaO-based pellets with cardboard were designated as Ca–C. Biomass-free pellets were also prepared for comparison purposes, and designated as Ca–P.

Table 1
XRF elemental analysis of limestone.

Component	wt%
SiO_2	1.14
Al_2O_3	1.12
Fe_2O_3	0.38
CaO	51.96
MgO	0.47
K_2O	0.25
LOF*	41.50
Sum	96.82

* LOF: Loss on Fusion.

2.2. Sorbent characterization

Biomass-templated composite pellets were characterized using a Cahn TherMax 700 thermogravimetric analyzer (TGA). Prior to N_2 isotherm measurement, sorbents were calcined in a muffle furnace at 850 °C (at a heating rate of ~10 °C/min) for 20 min in air which also allowed biomass combustion, then left at 250 °C overnight under a blanket of N_2. Brunauer–Emmett–Teller (BET) surface area and pore volume, and Barrett–Joyner–Halenda (BJH) pore size distribution were derived from N_2 adsorption isotherms obtained at −196 °C using a Micromeritics TriStar II-3020. BJH surface area distribution was derived from adsorption data, while BJH pore volume distribution was derived from the corresponding desorption data. The surface morphology of selected calcined sorbents was examined by scanning electron microscopy (SEM, Hitachi S-3400N).

2.3. CO_2 capture cycles

Capture cycles were performed by TGA. Although there are clear shortcomings in testing new sorbents in the TGA apparatus since the conditions are somewhat different than those in real CO_2 capture systems [27], this is still the most reasonable option taking into account the cost of large-scale tests. The mass sensitivity of the balance was 10^{-3} mg, and the mass change during cycles was continuously recorded. The initial mass of sorbent in all experiments was maintained at ~10 mg, and reactive gas flow rate was 40 mL/min. Capture cycles were commenced by heating the sample from ambient temperature to 850 °C at a heating rate of 20 °C/min in air required for burning biomass present in pellets. Calcination conditions were maintained at 850 °C for 5 min, followed by cooling down to 650 °C where the carbonation reaction was allowed to proceed in an atmosphere of 15 vol% CO_2 (N_2 balance) for 20 min. Cycles with steam were performed by introducing 15 vol% steam to the carbonation environment while maintaining CO_2 concentration of 15% [28].

3. Results and discussion

3.1. Characterization

The thermal decomposition profiles of the current biomass samples are shown in Fig. 1. From 50 °C to 150 °C the curves