Primary fragmentation of Biomass-Cement-CaO pellets for Calcium Looping

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Abstract
This work explores the effect of biomass templating on fragmentation of calcium-aluminate based pellets. Three different types of pellets have been tested: one with calcium aluminate cement (LC), another with flour (LF) and one with both cement and flour (LCF). Fragmentation has been investigated by two different techniques, namely with a pressurized heated strip reactor (PHSR) and a bubbling fluidized bed (BFB), under different conditions. Both sets of experiments showed that that the addition of biomass enhances the propensity to undergo fragmentation. The addition of cement partially counteracts this effect.

Introduction
Calcium looping (CaL) for CO_2 capture is based on the reversible exothermic calcium oxide carbonation reaction and is typically carried out in two interconnected fluidized bed reactors: in the first reactor (the carbonator) the CaO-based sorbent captures CO_2 from power plant flue gas at temperatures of 650-700°C [1-3]. The carbonated sorbent is then transferred to the other reactor (calciner) where CO_2 is released at high temperatures of 850-950°C. The regenerated material is returned to the carbonator for the subsequent cycles.
Limestone and dolomite are natural sorbents of low cost and availability. Complex production procedures have been proposed to modify limestone or to create new synthetic sorbents in order to increase the CO_2 uptake capacity. Pellets of limestone and biomass such as powdered leaves or flour have been recently suggested as a much cheaper alternative [4, 5].
Previous results have shown the beneficial effect of biomass addition in terms of CO_2 uptake and increase of porosity. However, some discrepancies have been observed between TGA and BFB results; these sorbents had a dramatic decline in apparent capacity when compared to calcium-aluminate

pellets. These differences are believed to be due to attrition and fragmentation [6-10].

Primary fragmentation occurs when the sorbent is injected into the reactor as a consequence of thermal stresses and of the overpressures caused by CO_2 release upon calcination. Secondary fragmentation occurs due to mechanical stresses from collisions between particle and bed internals; finally attrition by abrasion is also caused by mechanical stresses but generates finer particles with respect to secondary fragmentation [6-10]. It is typically reported that the attrition rate is higher during the initial cycles and progressively decreased afterword [11,12].

This work explores the effect of biomass templating on primary fragmentation of three different types of calcium aluminate-based pellets.

Experimental

Three materials were produced: (i) 10% calcium aluminate cement and 90% calcined limestone (LC); (ii) 10% flour and 90% calcined limestone (LF); and (iii) 10% flour, 10% calcium aluminate cement and 80% calcined limestone (LCF). Longcal limestone from the UK was used as lime precursor.Commercial calcium aluminate cement, CA-14, manufactured by Almantis, was used as binder in the pelletisation process and as a source of Al_2O_3. Commercial flour was used as biomass templating material.

The particles were prepared introducing the desired proportional quantities in 1 kg batches into a pelletizer vessel (4 L). Mixing was accomplished inside the vessel by means of a chopper and agitator under a continuous water spray. A more detailed explanation of this procedure can be found elsewhere [13]. After pelletization of the samples, the particles were sieved to different particle sizes. The material was air dried for 24 h before storage. The particle size cut 500-710 μm was used in the present work.

For the fragmentation experiments two experimental apparatus have been used: a pressurized heated strip reactor and a bubbling fluidized bed.

The PHSR, described in detail in other work [13], was used to perform primary fragmentation tests in pure N_2. Batches of approximately 100 mg were evenly spread on the strip and heated to 950°C at a rate of 4000°C/s. The final temperature was held for 30 s. After the test, particles were recovered. Experiments were repeated several times in order to collect enough material for particle size analyses. PSD was obtained by laser granulometry using a Malvern Sizer granulometer.

The lab-scale BFB, used to reproduce conditions typical of the first calcination step, was 40 mm ID and was operated at atmospheric pressure and heated at 900°C by an external electric furnace. Calcination was performed either with 100% vol air and with a mixture of 70% vol CO_2/30% vol air. For the BFB tests, 20 g of sorbent were diluted in 150 g of silica sand (particle size distribution of 850-100 μm) to avoid excessive decrease of temperature in the bed during calcination. After each tests the reactor bed was recovered and sand was removed by sieving. Then the particle size distribution of sorbents was assessed by sieving.

Results

Figures 1-3 report the results of the PHST tests on LC, LF and LCF respectively. The particle size distributions of the samples before and after the heat treatment are compared. The particle size distributions of LC before and after the PHSR tests are quite similar, suggesting negligible fragmentation. On the contrary for LF the particle size distribution changes drastically with a decrease of the mean particle diameter from 520 μm to 116 μm. For LCF the change is less pronounced, although significant fragmentation is still occurring with the average diameter decreasing from 524 μm to 290 μm.

Figure 4 reports the results of the FBR tests in air. The weight distribution of the recovered sample in different size cuts is shown. Notably LC undergoes less fragmentation then the other samples; in fact 82% of the sample still falls in the original size range. Instead only 33% of the sample retains its initial size in the case of LF and 47% in the case of LCF. Fig.5 reports the weight distribution of the material recovered after calcination in 70% CO_2/30% air. It can be seen again that LF particles fragment the most with only 30% of the sample remaining in the initial size range, followed by LCF with 43% and LC with 90%. As already noted in the PHSR experiments, biomass addition increases the propensity to fragmentation, but the presence of cement partly counteracts this effect.

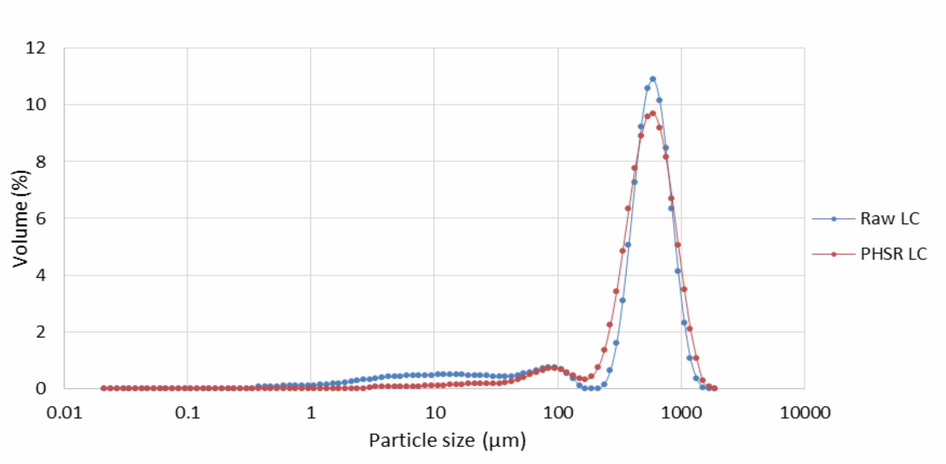

Figure 1: Particle size distribution of LC before and after the PHSR tests

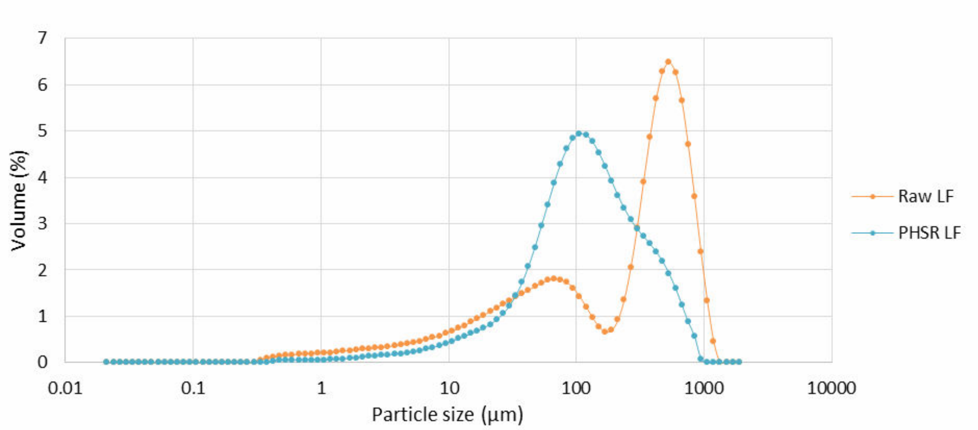

Figure 2: Particle size distribution of LF before and after the PHSR tests

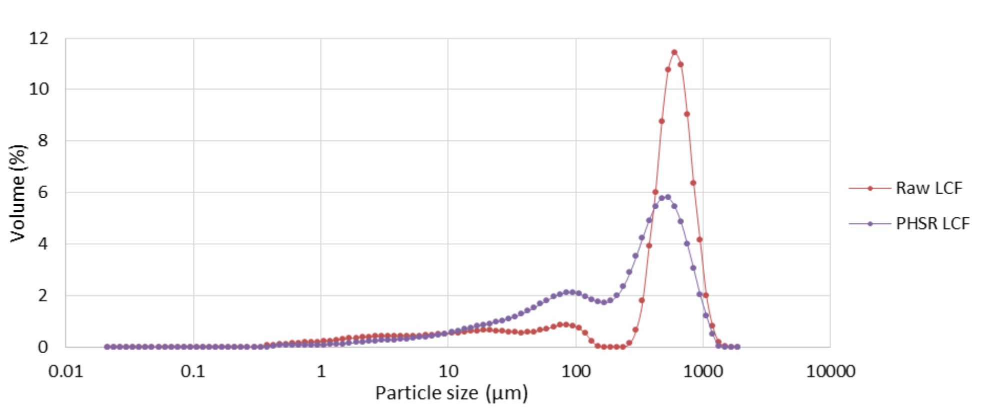

Figure 1: Particle size distribution of LCF before and after the PHSR tests

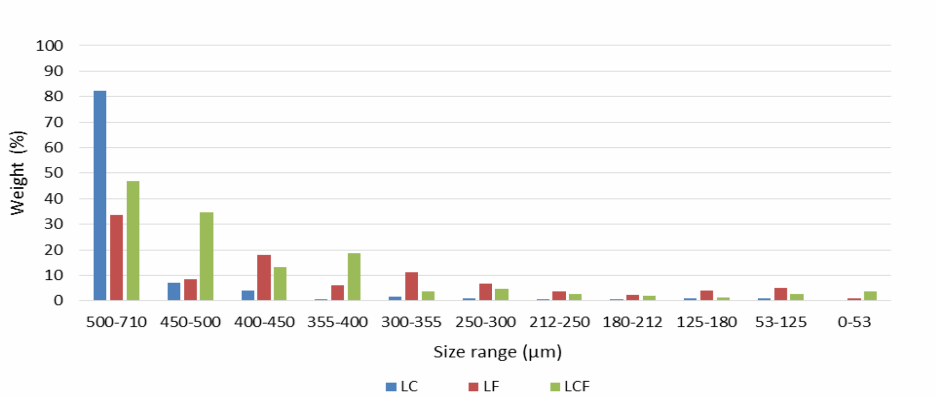

Figure 2: Weight distribution percentage of recovered material in air

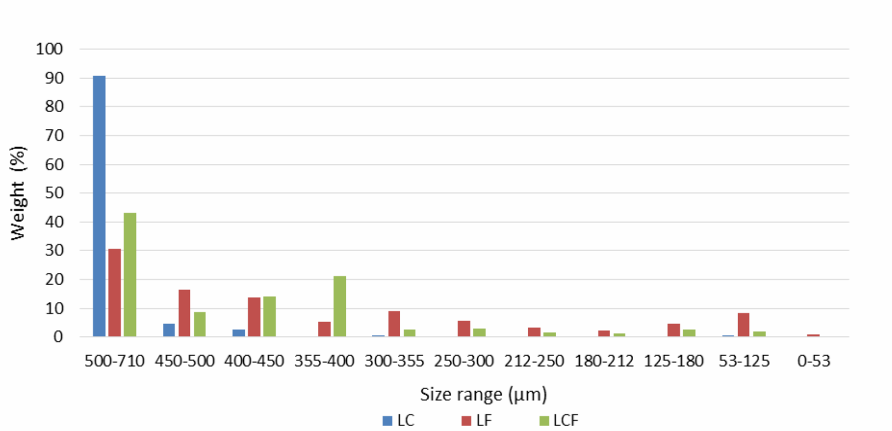

Figure 5: Weight distribution percentage of recovered material with 70% CO_2

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