Design, Process Simulation, and Construction of an Atmospheric Dual Fluidized Bed Combustion System for *In Situ* CO_2 Capture Using High-temperature Sorbents

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Introduction

The need to reduce CO_2 emissions along with pollutants such as SO_2 and NO_X is now generally accepted[1]. At the same time, there is a growing need for increased electrical power generation. If both sets of requirements are to be met without excessive economic disadvantage to the world economy, then new electrical generation methods with low or zero CO_2 emissions must be developed.

The use of the carbonation reaction in a combustion system could potentially meet the needs of a modern, high-volume, CO_2 capture system. The process outlined below operates continuously, producing a flue gas containing less than 3% CO_2 and a marketable CO_2 product stream with a purity exceeding 85%.

The carbonation reaction can remove carbon dioxide from combustion systems at elevated temperatures (~650°C-760°C) and atmospheric pressure *via*:

$$CaO + CO_2 \Leftrightarrow CaCO_3 \qquad (1)$$

The efficiency of systems using dual fluid beds for carbonation and sorbent regeneration have been shown to be comparable to current combustion systems without CO_2 segregation[2,3]. Sulphur dioxide emissions will be on the order of a few parts per million since the calcium required for CO_2 removal will be equivalent to a Ca:S molar ratio on the order of 20-30. Circulating fluidized bed combustors (CFBCs) are intrinsically low producers of NO and are amenable to NH_3 injection if very low emissions of NO are desired[4]. N_2O emissions can be minimized by operating at temperatures around 900ºC or by producing high-temperature windows in the cyclone[5].

The dual fluid bed carbonation process can be applied to stationary emitters of carbon dioxide including coal-fired generating stations and cement kilns. Limestone, the main feedstock, is inexpensive and readily available throughout most of the world allowing this process to have a global impact on greenhouse gases.

Information needed for scale-up to an industrial process using dual fluid bed technology for carbon dioxide capture is not currently available in the literature. To obtain some of the required information, a mini-pilot plant has been constructed. The design and process simulation of this system are presented here.

Experimental

Dual Fluid Bed Design Figure 1 shows a process flow diagram for the twin fluid bed combustion system with CO_2 capture operating at atmospheric pressure. Solid fuel combustion, with air, occurs in the first stage of the carbonating combustor at an optimum temperature for combustion (850ºC-950ºC) while carbonation occurs in the second stage at an optimum temperature for CO_2 capture (650ºC-750ºC for reaction (1)).

The combustion section will operate in the bubbling bed regime with allowance for both primary and secondary combustion air. Heat can be removed from the combustion stage of the Carbonating Combustor to allow high steam cycle efficiency. Sulphur removal is possible using spent sorbent through the reaction:

$$CaO + ½O_2 + SO_2 \Leftrightarrow CaSO_4 \qquad (2)$$

The carbonation section will operate in the bubbling bed regime. Heat removal is possible in the Carbonating stage to control the reaction temperature for reaction (1). A distribution plate separates the combustion stage from the carbonating stage.

The Carbonating Combustor is designed such that it can operate as a single stage circulating fluidized bed combustor with CO_2 removal. This mode of operation is not expected to result in optimum long-term cyclic conversion of the sorbent, however, it may be of interest for commercial retrofit. The sorbent is transported to the regenerator using calciner product gas, composed primarily of CO_2, or by steam. The carbon dioxide or steam is later used as a temperature mediator in the regenerator.

Sorbent regeneration occurs in the second fluid bed; the Oxygen Combustor & Calciner. Heat is supplied in the calciner by burning a low ash fuel such as petroleum coke with oxygen, to supply the heat necessary to drive reaction (1) to the left, releasing carbon dioxide. The Oxygen Combustor/Calciner can be operated as either a bubbling fluidized bed, or a circulating fluidized bed.

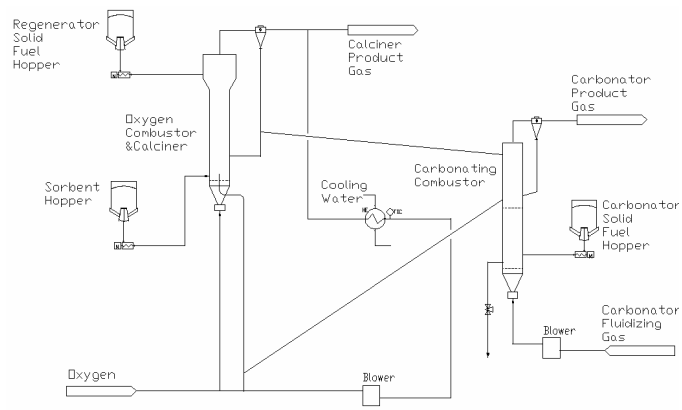

Figure 1. Atmospheric Dual Fluidized Bed Combustion System with CO_2 Capture.

Procedure

Process simulation using ASPEN Plus been used to establish the mass and energy balances of interest for equipment selection and design. A high-level view of the simulation can be seen in Figure 2. Combustion, carbonation, calcination and sulphation are simulated using combinations of the RYIELD, RSTOIC, RCSTR, and REQUIL reactor blocks. Fluidized bed combustion simulation for this system is described by Sotudeh-Gharabaagh *et al.*[6] Sorbent degradation and fluidization requirements are calculated using an Excel calculation block within ASPEN.

Model verification for bubbling fluidized bed combustion and circulating fluidized bed combustion has been verified using an existing 0.1-metre inner diameter CETC-O mini-circulating fluidized bed combustor. Results of mini-pilot plant studies will be used to fine tune process simulations for both atmospheric carbonation as described here, and pressurized carbonation as described by Wang[7].

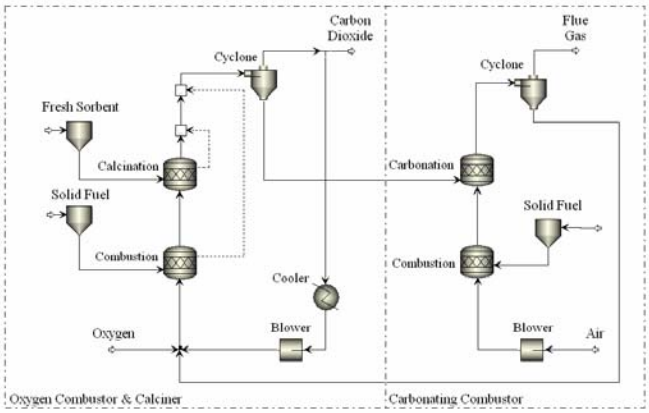

Figure 2. ASPEN Plus Simulation of Fluidized Bed Combustion System with CO_2 Capture.

Results and Discussion

Preliminary investigations using the existing CETC-O mini-fluidized bed combustor indicate that varying operating conditions and limestone sorbents can result in a range of sorbent conversions. In general, the sorbent conversion can be estimated using the model proposed by Abanades[8]:

$$X_N = f_m^N (1 - f_W) + f_W \qquad (3)$$

where X_N is the maximum carbonation conversion obtained after N cycles for a predetermined carbonation time (often reported at 20 minutes). Parameter values of $f_m = 0.77$ and $f_W = 0.17$ for this model have been shown to fit data for unmodified limestone sorbents quite well. This model indicates that conversion is reduced to ~0.17 after 20 carbonation-calcination cycles. Batch studies in the bubbling fluidized bed regime show that the mini-fluidized bed combustor results in conversions similar to those reported for thermogravimetric analysis under most conditions[9]. Limestone type, CO_2 concentration, and operating temperature can affect conversion to a small extent. Sorbent losses through attrition have been found to be low.

Recent pore modification studies[10] at CETC-O indicate that conversion can be greatly increased by a simple treatment step prior to sorbent injection into the carbonator. Conversion as high as 52% after 20 cycles (20-minute carbonation) can be obtained in a thermogravimetric analyzer. Conversions as high as 59% after 20 cycles (20-minute carbonation) are predicted through extrapolation of tests with the number of cycles limited to four. Operating at conditions resulting in these high conversions could result in a combustion process with less than 3% CO_2 in the flue gas, and a separate concentrated CO_2 stream (>85% CO_2). However, the pore modification step increases the friability of the sorbent, which will lead to increased sorbent losses due to attrition. The mini-pilot plant will be used to examine sorbent losses due to elutriation and to study conversion in a continuous process.

Conclusions

A flexible atmospheric dual fluidized bed combustion system using high temperature sorbents for *in situ* CO_2 capture has been designed and constructed. The process simulations developed for the design of the mini-pilot plant will be used for scale-up studies and process verification of commercial scale simulations based on the results of pilot plant operation. The pilot plant is expected to combust coal and petroleum coke in a clean and efficient manner, emitting a flue gas containing less than 3% CO_2, while producing a relatively pure carbon dioxide stream ready for compression. SO_2 emissions are expected to be in the parts per million range.

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