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# Fluidized Bed Combustion Systems Integrating CO<sub>2</sub> Capture with CaO

J. CARLOS ABANADES,<sup>\*,†</sup>  
EDWARD J. ANTHONY,<sup>‡</sup>  
JINSHENG WANG,<sup>‡</sup> AND JOHN E. OAKEY<sup>§</sup>

*Instituto Nacional del Carbón (CSIC),  
C/Francisco Pintado Fe no. 26, 33011, Oviedo, Spain,  
CANMET Energy Technology Centre, Natural Resources  
Canada, 1 Haanel Drive, Ottawa, Ontario, K1A 1M1 Canada,  
and Power Generation Technology Centre,  
Cranfield University, Cranfield MK430AL, U.K.*

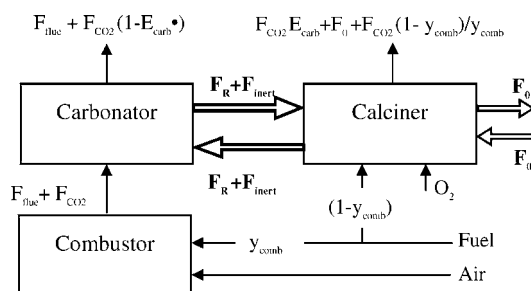
Capturing CO<sub>2</sub> from large-scale power generation combustion systems such as fluidized bed combustors (FBCs) may become important in a CO<sub>2</sub>-constrained world. Using previous experience in capturing pollutants such as SO<sub>2</sub> in these systems, we discuss a range of options that incorporate capture of CO<sub>2</sub> with CaO in FBC systems. Natural limestones emerge from this study as suitable high-temperature sorbents for these systems because of their low price and availability. This is despite their limited performance as regenerable sorbents. We have found a range of process options that allow the sorbent utilization to maintain a given level of CO<sub>2</sub> separation efficiency, appropriate operating conditions, and sufficiently high power generation efficiencies. A set of reference case examples has been chosen to discuss the critical scientific and technical issues of sorbent performance and reactor design for these novel CO<sub>2</sub> capture concepts.

## Introduction

Power generation combustion systems are responsible for about one-third of the anthropogenic CO<sub>2</sub> emissions. Among them, the use of fluidized bed combustors (FBCs) are increasing because the technology offers fuel flexibility, competitive cost, environmental performance, high reliability, and efficiency in terms of energy conversion. However, the rising concentration of CO<sub>2</sub> in the atmosphere and its effect on climate is forcing humanity to reconsider the role of combustion systems in the generation of energy for the medium to long term.

CO<sub>2</sub> can be captured from combustion flue gases and stored in a range of geological formations (1). Application of these storage options to existing and future combustion systems requires separation of CO<sub>2</sub> from the flue gas, where volume fractions are typically below 15%. The huge volume throughput of flue gas from a combustion power plant gives this separation step the highest economic and efficiency penalties in the process, if current separation techniques are applied (1). Advanced combustion cycles are needed to integrate the CO<sub>2</sub> separation step more efficiently.

The use of CaO-based solids to capture CO<sub>2</sub> at high temperatures and/or pressures has been placed at the core



**FIGURE 1. General scheme and main mass flows in the CO<sub>2</sub> capture system using a carbonation–calcination cycle.**

of several CO<sub>2</sub> capture and zero-emission power plant concepts (2–8). These processes make use of the following carbonation–calcination equilibrium:



There are intrinsic benefits in utilizing this carbonation–calcination cycle to separate CO<sub>2</sub>. As a high-temperature CO<sub>2</sub> separation process, there will be modest efficiency penalties and opportunities for a high degree of integration in the combustion plant (for example, at atmospheric pressure the heat required for calcination at temperatures over 900 °C is recovered in the carbonation step at 650 °C). It is also clear that there are plentiful sources of cheap, widely available sorbent (limestone). Furthermore, there is a strong background of knowledge for the required reactions in this separation process that dates back to 1867, when DuMotay and Marechal first patented the use of lime to aid the gasification of carbon by steam (9). The separation of CO<sub>2</sub> using the carbonation reaction of CaO was demonstrated in a 40 t/d fluidized bed pilot plant during the development of the Acceptor Gasification Process in the United States (10) designed to produce “pipeline” quality gas from coal during the 1960s and 1970s. The performance of the sorbent reported in the previous tests, in terms of decay of carbonation conversion with the number of cycles, was recently found to be comparable with those found for combustion systems by a range of authors and experimental techniques reviewed in ref 12. Using this background on sorbent performance studies, we discuss in this paper a range of environmental technologies that tackle the effective separation of CO<sub>2</sub> (together with the SO<sub>2</sub> in some options) with CaO, in processes highly integrated into a FBC power plant.

## Discussion

Figure 1 summarizes the general scheme of a CO<sub>2</sub> carbonation–calcination cycle valid for all the options considered in this work. In the unit where the carbonation reaction takes place, a large molar flow of CO<sub>2</sub> (in the flue gas of a power plant), designated as  $F_{\text{CO}_2}$ , must contact a large molar flow of sorbent ( $F_R$ ) to allow sufficiently high CO<sub>2</sub> capture. The remaining components of the carbonation–calcination loop, designated as  $F_{\text{flue}}$  and  $F_{\text{inert}}$ , will only be relevant to cycle heat balances, described later. The fuel split ( $y_{\text{comb}}$ ) between the main combustor, where the fuel is fired with air, and the calciner, where the fuel may be fired with O<sub>2</sub>, will also be discussed below for each process case.

A first advantage of CaO as a regenerable sorbent with respect to other high-temperature sorbents (13) is the relatively high “mass capture capacity” of a molecule of CaO (at full conversion 1 kg of CaO can capture 0.786 kg of CO<sub>2</sub>). Furthermore, it is well-known that the carbonation reaction

of CaO can progress in a fast reaction regime at temperatures above 600 °C (14, 15), allowing for compact reactor designs for the CO<sub>2</sub> absorbers (16). Therefore, with sufficient amount of fast-reacting CaO in the carbonator, the concentration of CO<sub>2</sub> at the exit of the carbonator will be close to the equilibrium value and allow very high CO<sub>2</sub> capture efficiencies (16). However, there is a rapid end to the fast reaction period, well before the full conversion of the particles, as noted by many authors referred elsewhere (12). This maximum carbonation–calcination cycles following the empirical equation:

$$X_N = f_m^N(1 - f_w) + f_w \text{ with } f_m = 0.77 \text{ and } f_w = 0.17 \text{ for natural limestones (2)}$$

that represents well a wide range of data from different sources (12) for a number of cycles lower than 50. Under these conditions, a continuous supply of fresh limestone ( $F_0$ ) to the system described in Figure 1 is necessary to keep the overall capture capacity of the absorber at an “acceptable level”. Hence, a mass balance in Figure 1 provides a definition of the CO<sub>2</sub> capture efficiency in the carbonator as a function of the molar flows of CO<sub>2</sub> and sorbent entering the carbonator:

$$E_{\text{carb}} = \min\left(\frac{F_R X_{\text{ave}}}{F_{\text{CO}_2}}, E_{\text{equil}}\right) \quad (3)$$

For sufficiently large flows of sorbent, this capture efficiency is only limited by the maximum attainable recovery of CO<sub>2</sub>, given by the equilibrium of CO<sub>2</sub> on CaO. As detailed elsewhere (11), for a slightly different definition of eq 2, for fluidized bed calciners (perfectly stirred reactors) the fraction of active CaO ( $X_{\text{ave}}$ ) entering the carbonator to form CaCO<sub>3</sub> can be estimated from:

$$X_{\text{ave}} = \frac{f_m(1 - f_w)F_0}{F_0 + F_R(1 - f_m)} + f_w \quad (4)$$

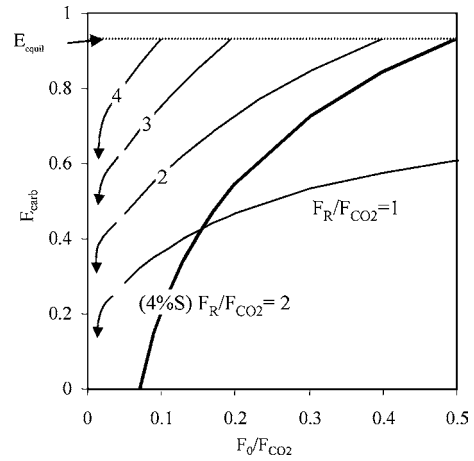
For the case of sorbent deactivation by CaSO<sub>4</sub> formation, a conservative assumption can be adopted, assuming that all sulfur present in the fuel reacts quantitatively with the active fraction of CaO:

$$X_{\text{ave}} = \frac{f_m(1 - f_w)F_0}{F_0 + F_R(1 - f_m)} + f_w - \frac{F_{\text{CO}_2}}{F_0 r_{\text{C/S}} y_{\text{comb}}} \quad (5)$$

where  $r_{\text{C/S}}$  is the C/S mole ratio in the fuel. This equation considers the capture of all the sulfur contained in the fuel that is fed to the combustor and the calciner of Figure 1. If the fuel fed to the calciner for sorbent regeneration does not contain sulfur, the equation will have to be corrected by deleting the term  $y_{\text{comb}}$ .

Equation 4 or eq 5 can be combined with eq 3 to estimate the attainable CO<sub>2</sub> capture efficiency in the carbonator for any given combination of critical sorbent flow ratios,  $F_{\text{CO}_2}/F_R$  and  $F_0/F_R$ . The critical assumption to carry out this exercise in the absence of detailed reactor models of the individual units is to assume that the typical conversions of all the particles leaving the carbonator after a few minutes (1–5 min) of residence time will be around the value given by eq 2. Despite the large solid circulation rates, fluidized beds can provide this order of residence time. As an example, we note that the sorbent data available from the continuous pilot experiments carried out for the acceptor process (10) were also well fitted with eq 2 (see ref 12).

Figure 2 illustrates the dependency of capture efficiency in the carbonator on the sorbent flow ratios. The left-hand side of the figure has been left undefined since, at values of



**FIGURE 2.** Required flow ratios of sorbent ( $F_R$  and  $F_0$ ) with respect to the flow of CO<sub>2</sub> ( $F_{\text{CO}_2}$ ) to achieve a given CO<sub>2</sub> capture efficiency in the carbonator. Arrows indicate a region of uncertainty in sorbent performance ( $N$  beyond 50 cycles). The thin lines are valid for any fuel without sulfur, and the thick solid line is for the case of the pet coke of Table 1 (4% sulfur). Dotted line is the limit imposed by equilibrium at 650 °C.

$F_0/F_{\text{CO}_2} < 0.05$ , most sorbent particles in the system have experienced a number of cycles much higher than 50 and eq 2 is only valid to describe sorbent performance for  $N < 50$ . As seen in Figure 2, the capture efficiency can be kept high (limited only by the equilibrium) despite the decay in sorbent activity, by increasing the fresh feed ratio ( $F_0/F_{\text{CO}_2}$ ) and/or the sorbent/carbon ratio ( $F_R/F_{\text{CO}_2}$ ). The problem is that these large ratios can become unacceptable in practice. This is because both  $F_0/F_{\text{CO}_2}$  and  $F_R/F_{\text{CO}_2}$  are referred to a large number ( $F_{\text{CO}_2}$  from a power plant is necessarily a very large number). Therefore,  $F_R/F_{\text{CO}_2}$  must be as close as possible to unity to minimize solid flows between units and maximize solid residence time in carbonators and calciners of any given size. The second ratio ( $F_0/F_{\text{CO}_2}$ ) is the makeup flow of limestone, and this has to be maintained as low as possible to minimize the operating costs associated with fresh sorbent addition to the plant and the energy requirements for its calcination. There is much scope to improve sorbent performance through reactivation, pretreatment, or the manufacture of completely synthetic CaO-based sorbents (18–22). This is an obvious subject for research in the future if these systems are to become of practical interest. However, since natural limestones are very cheap sorbents and their deactivated residue can find markets in the cement industry, higher values of  $F_0/F_{\text{CO}_2}$  may be economically feasible (17). Also, as will be discussed later, the deactivated CaO contains an important energy credit if used in cement manufacture.

Further restrictions on sorbent flow ratios appear when the total heat requirements in the calciner are taken into account. To calcine the CaCO<sub>3</sub> contained in the solid stream ( $F_R + F_{\text{inert}} + F_0$ ) of Figure 2, we need to supply heat to bring to the calcination temperature all the solids circulating between both reactors as well as to drive the endothermic calcination of CaCO<sub>3</sub>. The ratio of the necessary heat to calcine 1 mol of CaCO<sub>3</sub> sorbent in the stream ( $F_R + F_{\text{inert}}$ ) and the heat input to the plant (heat generated in the combustion of 1 mol of CO<sub>2</sub>) needs to be as low as possible. With highly deactivated sorbent (low  $X_{\text{ave}}$ ) and/or working sorbents with high proportion of inert material, the heat requirements to bring these solids to the calcination temperature can become very important and even make the separation of CO<sub>2</sub> unfeasible with this approach.

Despite the previous limitations, we have identified a range of technology options using natural limestones as such (as represented by eq 2) to achieve the desired CO<sub>2</sub> separation

**TABLE 1. Fuel Properties Used in the Calculations**

	fuel analysis (as received, in wt %)		
	biomass	coal	pet coke
C	31	65	83
H	4	3	5
S	0	0	4
O	24	8	3
H <sub>2</sub> O	40	8	5
Ash	1	16	0
Total	100	100	100
$\Delta H_{\text{comb}}$ (MJ/kg)	11.2	25	32

with the chemical loop of Figure 1, choosing values of  $F_0/F_{\text{CO}_2}$  and  $F_R/F_{\text{CO}_2}$  (see Table 2) that allow good capture efficiency in the carbonator, maintaining under control the heat requirements in the calciner, as well as reasonable sorbent makeup flows.

Furthermore, any system following the scheme of Figure 1 is capturing CO<sub>2</sub> not only in the carbonator but also in the calciner. Assuming 100% capture efficiency for the portion of the fuel burned with O<sub>2</sub> in the calciner and full calcination of the sorbent, we can define an overall CO<sub>2</sub> capture efficiency as

$$E_0 = \frac{y_{\text{comb}}E_{\text{carb}} + (1 - y_{\text{comb}}) + \frac{F_0}{F_{\text{CO}_2}}y_{\text{comb}}}{1 + \frac{F_0}{F_{\text{CO}_2}}y_{\text{comb}}} \quad (6)$$

In addition, the spent sorbent leaving the calciner ( $F_0$ ) qualifies directly for a CO<sub>2</sub> credit as a substitute of CaCO<sub>3</sub> in the cement industry. If released, it eventually reacts with CO<sub>2</sub> in air to form CaCO<sub>3</sub>. Therefore, higher capture efficiency can be claimed for these overall calcination–combustion systems as

$$E_{\text{sys}} = y_{\text{comb}}E_{\text{carb}} + (1 - y_{\text{comb}}) + \frac{F_0}{F_{\text{CO}_2}}y_{\text{comb}} \quad (7)$$

A range of process options is described below using all of these CO<sub>2</sub> capture efficiencies as well as the power generation efficiencies. All simulations have been performed for a 100 MW thermal power plant delivering the CO<sub>2</sub> compressed at 10 MPa (suitable for storage in geological formations). The composition of the fuels considered in this study is given in Table 1. An overall CO<sub>2</sub> capture efficiency ( $E_0$ ) of 90% of the carbon contained in the fuel has been assumed for all fossil fuel options. The reference combustion power plant without CO<sub>2</sub> capture is assumed to have 46% LHV power generation efficiency. Power losses for CO<sub>2</sub> compression and, where relevant, vacuum, air separation, and steam generation have been estimated with ASPEN Plus ( $\eta_{1-4}$ ). Table 2 also includes the calcination heat ( $\eta_5$ ) of the make up flow of fresh sorbent. A fraction of this heat is a power loss in estimating power generation efficiencies ( $\eta_{\text{pow}}$ ). However, this heat could be claimed as an energy credit if the sorbent was used in a cement plant as a feedstock substitute for CaCO<sub>3</sub>. Although this number cannot be added directly to the power generation efficiency, it is obviously an added source of efficiency for the overall power/cement production plant emerging in some of the following discussions. The energy penalty for a combined system power–cement plant is therefore very low and unaffected by moderately large values of  $F_0/F_{\text{CO}_2}$ . Table 2 also includes in the right-hand column a case where all coal is burned in a FBC with O<sub>2</sub> that qualitatively agrees with the study by Shimizu et al. (2).

**Case A.** A coal-based power plant of any type incorporating a CaO-based CO<sub>2</sub> absorber in the form of a circulating fluidized bed carbonator (Figure 3). Regeneration of CaCO<sub>3</sub> with O<sub>2</sub>/CO<sub>2</sub> mixture occurs in a fluidized bed. Shimizu et al. (2) described in detail this option and simulated overall system performance. However, these authors overestimated sorbent performance by ignoring the decay in sorbent activity after only four carbonation–calcination cycles. We have, therefore, run a simulation of the process with makeup flow of fresh limestone of 0.542 kg/kg of coal (see Table 2). The generation efficiency is predicted to be 38.8%. The main sources of efficiency penalty are compression of CO<sub>2</sub>, and the necessary power for O<sub>2</sub> generation (about one-third of the fuel is burned with O<sub>2</sub> in the calciner).

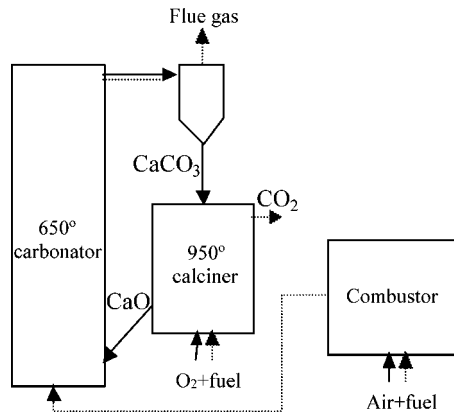
**Case B.** Fluidized bed coal-based power plant following the scheme of Figure 4, with a high-temperature circulating fluidized bed combustor ( $T = 1050$  °C) transferring heat through metallic walls to a fluidized bed calciner ( $T = 850$  °C) operating at a CO<sub>2</sub> partial pressure of 0.4 bar obtained in the calciner by injecting steam (5.28 kg/s). Solids in the calciner are fluidized with a mixture of steam and the CO<sub>2</sub> generated during calcination. The carbonator operates at 650 °C after cooling the gases coming from the combustor. Heat requirements in the calciner are estimated to be around 48% of the energy input to the plant. Assuming an overall heat transfer coefficient between the two beds of 300 W/m<sup>2</sup> K, an area of approximately 800 m<sup>2</sup> of metallic wall needs to be provided for transfer of the necessary heat between combustor and calciner. This area will require a special configuration of combustor and calciner cross-sections to closely integrate both units (typically 20–40 m high and almost 30 m<sup>2</sup> cross section for the 100 MW<sub>t</sub> base case, when assuming a gas velocity of around 5 m/s). These configurations require special metallic materials that have not yet been tested in practice for similar applications. It is therefore not clear if these systems will be more feasible than the system of case A despite their higher efficiency and the lack of air separation unit. However, it should always be possible to take advantage, at least to some extent, of the potential for direct heat transfer from combustor to calciner as outlined in Figure 4.

**Case C.** This is a system (Figure 5) with identical process conditions to case B except in two variations: heat transfer is attempted using a solid heat carrier and the low CO<sub>2</sub> partial pressure of 0.4 atm, required for lower calcination temperature in the calciner, is attempted through application of vacuum (alternatively, this could be done with steam as in case B). For the case studied, a heat carrier flow of 226 kg/s is required to transfer the heat required for calcination from the combustor to the calciner. This large circulation rate of hot solids from the combustor is still reasonable (below 10 kg/m<sup>2</sup> s) as compared to standard practice in circulating fluidized bed combustors. Calcination of the sorbent will take place in contact with this hot solid stream. The heat carrier can be CaO (calcined sorbent) identical to the sorbent circulating in the carbonation–calcination loop, although its activity might tend to deteriorate in the high-temperature conditions in the CFBC. However, we can also use highly sintered and dense CaO particles in the combustor–calciner loop or a completely different dense solid heat carrier (for instance Al<sub>2</sub>O<sub>3</sub>). In this case, the intention is to make use of the different particle density of the active sorbent particles (approximately 1500 kg/m<sup>3</sup>) and of the heat carrier (higher than 3000 kg/m<sup>3</sup>). Continuous segregation of the solids should be possible to achieve partial separation in a continuous mode. A similar segregation mechanism was used successfully to separate heavy ashes from the sorbent in the pilot plant used for the development of the Acceptor Gasification Process (10). However, it has never been tested at the scale required for this application. Therefore, as in case B, it is not yet clear

**TABLE 2. Mass and Heat Flows for the Different Options<sup>a</sup>**

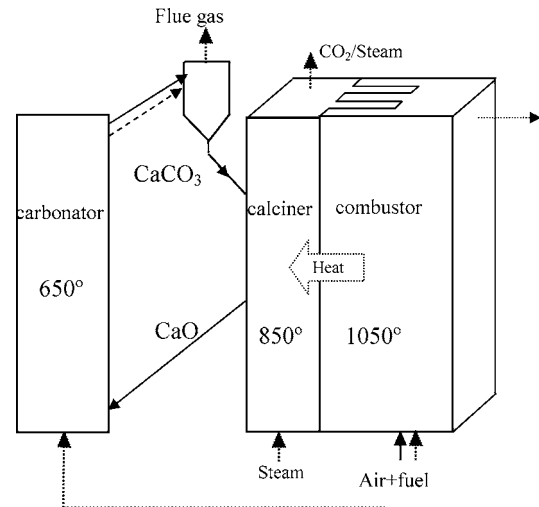
	A	B	C	D	E	O <sub>2</sub> /CO <sub>2</sub>
fuel	coal	coal	coal	biomass	pet coke	coal
fuel feed (kg/s)	4.0	4.0	4.0	8.93	3.12	4.0
$Y_{\text{comb}}$	0.67	1	1	0.682	0.66	
air in (N·m <sup>3</sup> /s)	20.3	30.3	30.3	22	21.6	
O <sub>2</sub> in (N·m <sup>3</sup> /s)	1.81	0	0	1.7	2.02	5.3
$T_{\text{combustion}}$ (°C)	850	1050	1050	700	850	850
$P_{\text{combustion}}$ (bar)	1	1	1	1	10	1
$F_{\text{CO}_2}$ (kmol/s)	0.145	0.216	0.216	0.157	0.143	0.216
$F_{\text{CO}_2}/F_R$	1/3	1/4	1/4	1/3	1/4	—
$F_0/F_{\text{CO}_2}$	0.1	0.15	0.15	0.1	0.3	0
make up flow (kg of limestone/kg of fuel)	0.541	0.813	0.813	0.176	1.37	0
$T_{\text{carbonation}}$ (°C)	650	650	650	700	850	
$P_{\text{carbonation}}$ (bar)	1	1	1	1	10	
$T_{\text{calcination}}$ (°C)	950	850	850	950	1080	
$P_{\text{calciner}}$ (bar)	1	1 (60% steam)	0.4 (vacuum)	1	10	
$X_{\text{ave}}$	0.251	0.188	0.188	0.202	0.137	0
$X_{\text{sulf}}$	0	0	0	0	0.091	
$E_{\text{carb}}$	0.753	0.752	0.752	0.607 <sup>b</sup>	0.549	—
$E_{\text{CO}_2}$	0.845	0.784	0.784	0.749	0.752	—
$E_0$	0.9	0.9	0.9	0.8*	0.9	—
$H_{\text{cal}}$ (MW)	33	48.2	48.2	28.8	34	0
calciner penalty, $\eta_1$	0.0317			0.0208	0.0353	0.0928
calciner penalty, $\eta_2$		0.0113				
calciner penalty, $\eta_3$			0.0055			
compress. penalty, $\eta_4$	0.0285	0.028	0.028	0.0267	0.0125	0.0312
makeup calcination, $\eta_5$	0.0258	0.0579	0.0579	0.028	0.0762	0
power generation efficiency, $\eta_{\text{pow}}^c$	0.388	0.394	0.400	0.400	0.377	0.336

<sup>a</sup> Base case of 100 MW using calcined limestone as CO<sub>2</sub> sorbent that decays in activity following eq 2. Electricity generation efficiency is  $\eta_{\text{ref}} = 0.46$  LHV (also for heat outputs at  $T \geq 650$  °C). Combustion is carried out with 20% excess air O<sub>2</sub> over the stoichiometric. <sup>b</sup> This is captured from the biomass plant (CO<sub>2</sub> neutral) and is therefore associated with a “negative CO<sub>2</sub>” emission. <sup>c</sup> This is calculated as  $\eta_{\text{pow}} = 0.46(1 - \eta_5) - \eta_1 - \eta_2 - \eta_3 - \eta_4$ .


**FIGURE 3. Process scheme of case A, with the carbonation–calcination cycle separated from the combustor chamber.**

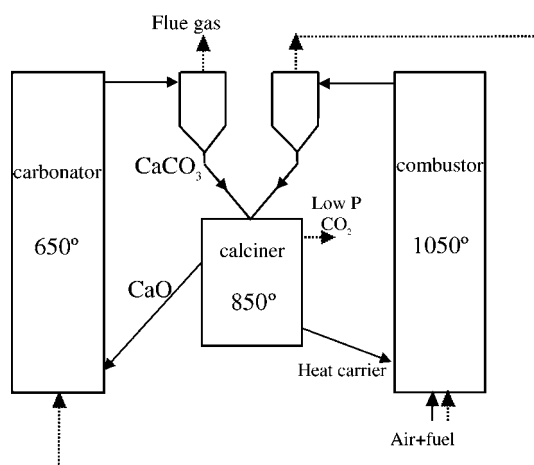
if the complexities associated with the operation of the calciner of Figure 5 will compensate for the savings arising from the lack of O<sub>2</sub> separation plant and the improved values of generation efficiencies (see Table 2).

**Case D.** In situ capture of CO<sub>2</sub> with CaO in a low-temperature fluidized bed combustor (Figure 6). According to the CaO/CaCO<sub>3</sub> equilibrium, if a fuel could be burned at sufficiently low temperature (about 700 °C) it would be possible to capture, in situ, the CO<sub>2</sub> generated in the combustion (8). Biomass is a potentially attractive fuel for this application. Furthermore, the idea of capturing CO<sub>2</sub> from biomass-fired systems is receiving increasing attention (23) since it can offer a route to power plants with negative emission factors (i.e., a net CO<sub>2</sub> sink). This is because the burning of biomass without CO<sub>2</sub> capture is considered CO<sub>2</sub>-neutral; therefore, any capture and storage of CO<sub>2</sub> from biomass will translate into a net sink of CO<sub>2</sub> from the atmosphere (24). The scale of biomass power plants is,

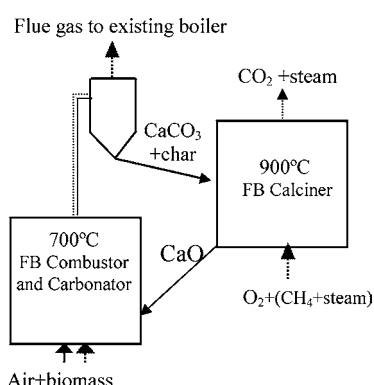

**FIGURE 4. Process scheme of case B, with direct heat transfer from the combustor to the calciner.**

however, always limited, and we have assumed that the plant of reference in Table 2 is close to an existing power plant based on fossil fuel. In the selected case, approximately 68% of the C content of the biomass is fed to a fluidized bed combustor operating at 700 °C where a capture of around 60% of the CO<sub>2</sub> generated in the FBC is achieved. The unburned C is burned in the calciner. Flue gas, with a reduced amount of CO<sub>2</sub>, and which might also contain CO, tar, and unburned C, is fed to the existing power plant in such a manner that these compounds are fully oxidized and the heat is recovered in the equipment of the existing boiler. As a result, the heat required for regeneration in the calciner, which accounts for 28.8% of the total heat, comes from the unburned char accompanying the carbonated sorbent leaving the carbonator. More fuel (coal, gas, oil) from the main





**FIGURE 5. Process scheme of case C, with indirect heat transfer from the combustor to the calciner by means of a dense solid heat carrier (for example, sintered CaO or  $\text{Al}_2\text{O}_3$ ).**



**FIGURE 6. Process scheme of case D, with biomass burned in a low-T fluidized bed combustor and  $\text{CO}_2$  generated from residual char combustion (and natural gas if needed) with oxygen in the calciner. The scheme is identical for option E (high pressure), changing the fuels and the temperatures as indicated in Table 2.**

combustor might also be used to supply heat to the calciner. An interesting point of this case is that it can be used as a retrofitting option to existing plants to reduce  $\text{CO}_2$  emissions while increasing the energy output of the plant. Therefore, it can also facilitate a strategic move from large emission factors in an existing combustion plant to negative emission factors in the future when/if the plant can be fully sustained by biomass.

**Case E.** In situ capture of  $\text{CO}_2$  at high pressures and temperatures. This is a similar scheme to case D but is applied to a high-pressure (10 bar) and high-temperature (850 °C) fluidized bed combustor and calciner. The simulation has been run for pet coke with no ashes but high sulfur content. The details of this system have been described elsewhere (8) including the full ASPEN simulation sheet (25) incorporating the expansion of the flue gases in gas turbines. As in case D, the key benefit is high levels of system integration since combustion,  $\text{CO}_2$  capture, and  $\text{SO}_2$  capture are all achieved in a single pressurized fluidized bed reactor. The high sulfur content in the fuel makes necessary a large supply of fresh sorbent to maintain the activity of the  $\text{CO}_2$  capture loop, in accordance with eq 5. This has reduced the power generation efficiency with respect to other cases (37.7% LHV), but the energy and carbon credits associated with the large flow of deactivated sorbent leaving the plant (mainly CaO) should also be considered.

From the results of Table 2, we can conclude that  $\text{CO}_2$  capture concepts based on the carbonation–calcination cycles of CaO described above have inherent advantages

because the efficiency penalties associated with separation of  $\text{CO}_2$  are intrinsically low. The system uses a low-cost, widely available  $\text{CO}_2$  sorbent to compensate for its activity decay. In some cases (A and D) the individual units are commercially proven and/or there exist similar large-scale commercial processes operating in similar conditions. In the remaining cases (B, C, and E) the challenge is to demonstrate novel reactor concepts that offer substantial gains in efficiency and/or avoid the air separation unit. No hazardous materials are involved in the new processes. The concepts can, in principle, be applied to  $\text{CO}_2$  capture from the combustion of several fuel types, from fossil fuels and petroleum residues to biomass and waste. Sulfur capture is expected to be very effective in the system because the very high Ca/S ratios. However, a successful  $\text{CO}_2$  capture system is that which can deliver  $\text{CO}_2$  at the lowest possible cost, when all factors are properly considered in the definition of that cost. Clearly, for some of the process alternatives outlined in this work, several uncertainties need to be addressed before carrying out an economic comparison with existing  $\text{CO}_2$  capture processes or other novel concepts currently under development.

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## Nomenclature

$E_{\text{carb}}$	fraction of $\text{CO}_2$ entering the carbonator that is captured as $\text{CaCO}_3$
$E_{\text{equil}}$	fraction of $\text{CO}_2$ entering the carbonator that can be captured if achieving equilibrium conditions between CaO and $\text{CO}_2$
$E_o$	overall capture efficiency of the system or ratio between $\text{CO}_2$ captured in the calciner and amount of $\text{CO}_2$ that would be released in a plant without $\text{CO}_2$ capture
$E_{\text{sys}}$	system capture efficiency or fraction of $\text{CO}_2$ leaving the calciner with respect to total C (as fuel and as $\text{CaCO}_3$ ) entering the plant
$y_{\text{comb}}$	mass ratio between fuel going to the main combustor and total fuel into the plant
$F_{\text{CO}_2}$	flow rate of $\text{CO}_2$ produced by combustion (kmol/s) in the combustion chamber only (excluding $\text{CO}_2$ generated by combustion in the calciner)
$F_{\text{flue}}$	flow rate of all other gases, except $\text{CO}_2$ , from the combustor (kmol/s)
$F_{\text{inert}}$	flow rate of inert solids cycling in the carbonation calcination loop of Figure 1 (kg/s)
$f_{m,w}$	fitting constants in eq 2
$F_o$	makeup flow rate of fresh limestone. It is also the $\text{CO}_2$ produced from this limestone on calcination (kmol/s)
$F_R$	flow rate of recycled sorbent (kmol/s), excluding fresh makeup
$H_{\text{cal}}$	heat required in the calciner (MW)
$N$	number of carbonation–calcination cycles
$r_{c/s}$	molar C/S ratio in the fuel
$w_C$	carbon weight fraction in the fuel

$X_{ave}$	average carbonation conversion of the sorbent that leaves the carbonator of Figure 1
$X_N$	carbonation conversion achieved after $N$ cycles of carbonation–calcination
$X_{sulf}$	average conversion of CaO to CaSO <sub>4</sub>
$\Delta H_{comb}$	heat of combustion (LHV) of the fuel (kJ/kg)
$\eta_1$	net penalty in power generation efficiency due to O <sub>2</sub> separation from air
$\eta_2$	net penalty in power generation efficiency due to the steam requirements in the calciner
$\eta_3$	net penalty in power generation to achieve the low pressure (0.4 atm) in the calciner
$\eta_4$	net penalty in power generation efficiency of the CO <sub>2</sub> compression to 100 atm
$\eta_5$	heat requirements for the calcination of the CaCO <sub>3</sub> used as sorbent makeup. This is also an energy credit when CaO is used in a cement plant instead of CaCO <sub>3</sub>
$\eta_{pow}$	power generation efficiency (LHV basis)
$\eta_{ref}$	power generation efficiency of the reference plant without CO <sub>2</sub> capture = 46% LHV in this work

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