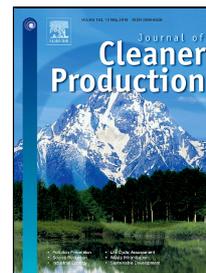


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CO₂ capture in existing power plants using second generation Ca-Looping systems firing biomass in the calciner

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Abstract

Calcium looping (CaL) is an emerging CO₂ capture technology that uses high temperature circulating fluidized beds, CFB, using CaO particles as functional material and can be retrofitted to existing power plants and. Its similarity to existing CFB combustion technology has made it possible to demonstrate its feasibility at MW scale and to obtain an accurate estimation of its energy efficiency and cost. This work analyzes a novel CaL system that incorporates recent developments tested at large pilot scale, where the calciner operates under an oxygen-rich atmosphere and the sorbent is reactivated by recarbonation allowing a reduction in the thermal input needed in the calciner. It has been shown that, when this 2nd generation CaL system is coupled to existing large sources of flue gases and biomass is used as fuel in the calciner, the full system becomes carbon-negative, with CO₂ emissions falling to as low as -245.3 kg_{CO2}/MWh since the biomass source is carbon-neutral. The net electric efficiencies achieved for the entire system including capture are more than 33%. Moreover, the total investment required for this CaL system can be reduced by more than 30% compared to conventional CaL systems due to the reduced footprint of the calciner-related equipment when the calciner is fired with pure oxygen.

Keywords

CO₂ capture, Calcium looping, biomass, sorbent recarbonation, second generation

Nomenclature

a_1	Sorbent deactivation constant
a_2	Sorbent deactivation constant
b	Sorbent deactivation constant
F_0	Limestone make-up flow into the Ca-Looping system [kmol/s]
f_a	Fraction of CaO particles in the carbonator that are reacting in the first chemically controlled stage [-]
f_1	Sorbent deactivation constant
f_2	Sorbent deactivation constant
F_{Ca}	Molar flow of Ca (i.e. as CaO, CaCO ₃ and CaSO ₄) flowing between carbonator and calciner [kmol/s]
f_{calc}	CaCO ₃ molar content of particles at calciner outlet [-]
f_{carb}	CaCO ₃ molar content of particles at calciner inlet [-]
F_S	Molar flow of SO ₂ reacting with CaO in the Ca-Looping system [kmol/s]
r_0	Fraction of particles circulating in the Ca-Looping system that have not been calcined [-]
W_{CB}	Inventory of solids in the carbonator [kg/m ²]
W_{CC}	Inventory of solids in the calciner [kg/m ²]
W_{RC}	Inventory of solids in the recarbonator [kg/m ²]
T_{CB}	Operation temperature in the carbonator [°C]
T_{CC}	Operation temperature in the calciner [°C]
X_{ave}	Average maximum CO ₂ carrying capacity of CaO particles [-]
X_{carb}	Average CaCO ₃ content of CaO particles at calciner inlet [-]
X_{calc}	Average CaCO ₃ content of CaO particles at calciner outlet [-]
X_N	Maximum CO ₂ carrying capacity of CaO during cycle N [-]

Greek letters

η	efficiency
ΔX_R	Sorbent conversion beyond X_{ave} in the recarbonator reactor
ΔX_{Rmax}	Maximum sorbent conversion beyond X_{ave} under recarbonation conditions

Acronyms

AC	Avoided Cost
ASU	Air Separation Unit
CFB	Circulating Fluidized Bed
COE	Cost of Electricity
CPU	Compression and Purification Unit
FC	Fuel Cost
FCF	Fixed Charge Factor
FOM	Fixed Operating and Maintenance cost
TCR	Total Capital Required
TRL	Technical Readiness Level
VOM	Variable Operating and Maintenance cost

1. Introduction

Carbon capture and storage (CCS) and bio-CCS technologies are recognized as key climate mitigation approaches for achieving the objective of limiting the increase in global mean temperature to 2°C (Edenhofer et al., 2014) and lower temperatures, as negative emissions systems may be essential to reach the 1.5°C long-term target agreed upon in COP21 (Fuss et al., 2014). However, the power generation capacity of existing and expected coal-fired power plants represents a serious threat to the realization of these ambitious GHG reduction goals. Therefore, the retrofitting of existing power plants (or other large-scale emitters) with post-combustion CO₂ capture equipment has been recognized as essential in order to achieve a steep reduction in global CO₂ emissions in the coming decades (Finkenrath et al., 2012; IEA, 2013).

Among the post-combustion CO₂ capture alternatives, Calcium looping (CaL) is an emerging technology that uses CaO as sorbent (Shimizu et al., 1999) and has been demonstrated to be highly effective in recent years under realistic environments at large pilot scale (Alonso et al., 2014; Arias et al., 2013; Diego et al., 2016b; Dieter et al., 2014; Hiltz et al., 2017; Kremer et al., 2013). The CO₂ is captured by CaO particles in a carbonator reactor operating at temperatures of around 650 °C in the form of CaCO₃. From this reactor, a lean CO₂ flue gas is released while a stream of partially carbonated particles is sent to the calciner in order to decompose the CaCO₃. Coal is burnt under oxy-fuel conditions at temperatures above 900 °C in this second reactor in order to supply the thermal power needed to drive the calcination reaction and to heat up the streams of gas and solids entering the calciner. As a result, the CO₂ is obtained in a highly concentrated stream, ready for purification and compression. The loop is closed by sending back the regenerated CaO to the carbonator reactor. Compared with other CO₂ capture technologies, CaL requires a large thermal energy input into the system and higher upfront investment costs. However, the high operation temperature in the reactors makes it possible to efficiently recover a large fraction of the energy input and to produce additional power. Consequently, the retrofitted CaL system can be seen as a new oxy-fired power plant that repowers the existing plant, while capturing the CO₂ produced in the existing plant. Several works have reported overall energy penalties of around 7-9 net points with respect to power plants without CO₂ capture (Hawthorne et al., 2009; Martínez et al., 2016, 2011; Romeo et al., 2008; Ströhle et al., 2009; Yang et al., 2010).

Several optimized process schemes considered as 2nd generation CaL technology have been proposed and are being tested at different experimental scales. These are mostly improved versions of first-generation existing capture technologies (ZEP, 2017). The common aim of most of these processes is to reduce the energy requirements in the oxy-fired calciner as this is the most capital intensive part of the full CaL system. Reduction of the calciner footprint can be achieved by minimizing the circulation of solids between reactors, which is done by increasing the activity

of the sorbent (Arias et al., 2012, 2010; Blamey et al., 2010; Broda et al., 2015; Curran and Gorin, 1970; Duan et al., 2016; Hughes et al., 2004; Manovic et al., 2008; Martínez et al., 2011; Valverde et al., 2014b, 2014a; Yu et al., 2017)), by reducing the difference in temperature between the carbonator and calciner (through intermediate gas-solid (Abanades et al., 2013; Diego et al., 2016a) or solid-solid (Epple, 2009) heat exchange steps), or by using pure oxygen in the calciner (Arias et al., 2017).

The aim of the present work is to analyze the performance of a specific configuration of a post-combustion CaL system that involves the oxy-firing of biomass in the calciner. This system retains the advantages of 2nd generation capture systems in that it is made up of proven reactors (tested at least individually at large pilot scale or, TRL 6) and it can be retrofitted into existing power plants. The possibility of retrofitting may prove crucial for the deployment of CO₂ capture technologies, as it is becoming increasingly clear that the priority for CCS systems is to tackle the problems of emission of the vast fleet of relatively modern, existing power plants and industrial fossil infrastructures. The CaL system proposed in this work does not require any modification in the existing power plant and is able to transform the existing sources of CO₂ into negative CO₂ emitters. To the author's knowledge, the potential benefits of using biomass in the calciner of a CaL system have not been assessed in the literature, and the performance benefits associated to its use should be therefore addressed. In addition to carrying out process simulations to illustrate how the system operates, a basic economic analysis is made to show the conditions under which a CaL configuration of this type may be competitive.

2. Process description and modelling assumptions

The basic process scheme considered for this study is represented in Figure 1. It consists of an existing air-fired power plant integrated within a 2nd generation post-combustion CaL system. The CaL configuration is still based on two interconnected circulating fluidized bed (CFB) reactors (Abanades et al., 2015) which have served as the basis for the rapid progress, scaling up and demonstration of CaL technology in the last few years (Alonso et al., 2014; Arias et al., 2013; Chang et al., 2014; Dieter et al., 2014; Kremer et al., 2013), by exploiting its obvious similarities with commercial CFB combustors.

[FIGURE 1, double column width]

A special characteristic of the CaL system depicted in Figure 1 is that the solids exiting the carbonator are sent to an intermediate recarbonator reactor before being sent to the calciner. In the recarbonator, the carbonated solids meet a concentrated stream of CO₂ where they are

subjected to intense carbonation conditions that are known to increase the CO_2 carrying capacity, X_N , in the subsequent calcination/carbonation cycle (Barker, 1973). The idea behind the recarbonation process of Figure 1 is to compensate for the decay in sorbent activity during cycling by increasing the carbonate content of the sorbent to above the maximum CO_2 carrying capacity in each carbonation/calcination cycle (Grasa et al., 2014; Valverde et al., 2014a, 2014c). In order for the necessary amount of sorbent to be converted in short reaction times (below 3 min), it has been demonstrated that the recarbonator has to operate at a temperature above $750\text{ }^\circ\text{C}$ under high concentrations of CO_2 ($>60\%$) (Grasa et al., 2014). This procedure has been recently put into practice in a $1.7\text{ MW}_{\text{th}}$ pilot plant facility where the positive effect of recarbonation on sorbent activity has been demonstrated by increases in the CO_2 carrying capacity of up to 8-10 percentage points (Diego et al., 2016b).

Moreover, in the 2nd CaL scheme assessed in this work, the calciner is operated with a pure oxygen stream as oxidant (i.e. without the rich- CO_2 gas recycle characteristic of other O_2 -fired combustion systems). This reduces the thermal requirements demanded by the calciner because, in a standard CaL scheme, a large fraction of the thermal input into the calciner (about 20%) is used to increase the temperature of the O_2/CO_2 oxidant. Therefore, in the 2nd CaL scheme assessed in this work, this fraction of heat devoted to heat up the recycled CO_2 is saved. Operation under conditions of an extremely high oxygen concentrations is feasible in the oxy-CFB calciner of a CaL system because of the thermal ballast effect of the large circulation of solids from the carbonator and the “heat sink” character of each carbonated particle while the CaCO_3 is being calcined. State-of-the-art simulations of the temperature profiles in the combustion chamber have indicated that this operational approach is valid with moderate temperature profiles in the combustor (Parkkinen et al., 2017). Furthermore, operating without the CO_2 recycle allows for more compact calciner reactors with a much reduced footprint. Experimental proof of the concept of a rich concentration of oxygen in the calciner has been confirmed by a EU project (“CaO2”) in a $1.7\text{ MW}_{\text{th}}$ pilot plant (Arias et al., 2017) using coal as fuel in the calciner.

The firing of biomass in the calciner is a very attractive option in the process of Figure 1 because, if the biomass is considered as carbon-neutral fuel, the negative emission factor when CCS is applied to the biomass-fired calciner could lead to negative emission values for the entire system of Figure 1 (i.e. including the existing coal power plant retrofitted with the CaL capture system). The use of CFB combustors for biomass and waste derived fuels has already achieved commercial status (Jäntti, 2012), although intense research and development work is still ongoing to tackle other biomass-related problems (fire side corrosion, emissions of chlorine, N_2O , slagging and fouling on the furnace walls and convection surfaces, etc.) (Khan et al., 2009).

Concerning the use of pure oxygen in a CFB biomass boiler, problems associated to the higher reactivity of biomass than coal that could reach to extremely high temperatures close to the oxidant injection ports could not be disregarded. These high temperatures may derive to melting/vaporization issues of the biomass ashes, which can lead to agglomeration problems. The oxyfired calciner of a CaL system could help to reduce some of these problems because the absence of heat transfer surfaces within the calciner will avoid the problem of corrosion in the boiler heat exchanger tubes, which are generally built with high-resistant expensive alloys (Khan et al., 2009). Moreover, the large circulation of CaO within the reactor would greatly reduce the problems of agglomeration typically related with the alkali content of biomass ashes and would have positive effects for the reduction of organic gas emissions, due to the well-known catalytic effect of CaO on the cracking of volatiles reported in the biomass gasification literature (Sutton et al., 2001).

Figure 2 shows a more detailed scheme of the reactor used in the 2nd generation CaL process analyzed in this work, incorporating the notation and key variables assumed in the simulations.

[FIGURE 2, single column width]

The flue gas is assumed to come from an amortized air-fired pulverized coal subcritical power plant with a production capacity of 365 MW_e. A reasonable composition and flow rate for the flue gas has been calculated based on the assumptions shown in Table 1 and Table 2, resulting in a desulfurized flue gas flow rate of 337 Nm³/s with 13 % of CO₂ entering the carbonator. Before this flow enters the carbonator reactor, a draft-forced fan increases the flue gas pressure to compensate for the pressure loss in the carbonator and in the flue gas coolers.

Table 1 Specifications of the coal used in the existing power plant and of the coal and biomass used in the calciner of the CaL system for the cases analyzed

Composition [%wt.]	Power plant coal	Calciner coal	Calciner biomass
C	63.75	78.85	43.51
H	4.50	4.68	5.17
N	1.54	1.17	0.02
O	6.88	5.75	35.11
S	2.51	0.68	0.02
Ash	9.70	6.24	0.99
Moisture	11.12	2.63	15.00
LHV [MJ/kg]	27.5	33.0	19.1

Table 2 Main assumptions used for the calculations

<i>Existing subcritical power plant</i> Coal thermal input [MW _{th} , referred to the LHV of the coal]	1013.7
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Air excess in the boiler [%]	30.0
Net electric efficiency of the plant [%]	36.0
Desulfurization efficiency in the existing plant [%]	95.0
Flue gas flow rate [Nm ³ /s]	337
Flue gas composition [%vol.]	13.0% CO ₂ , 75.4% N ₂ , 7.0% H ₂ O, 4.6% O ₂ (100 ppm SO ₂)
<i>CaL system</i>	
<u>Carbonator reactor</u>	
Operating temperature [°C]	650.0
CO ₂ capture efficiency [%]	90/80*
Pressure losses in the nozzles and cyclone [kPa]	1.9
Pressure losses in the gas cooling section [% inlet pressure]	6
Desulfurization efficiency [%]	99.0
<u>Calciner reactor</u>	
Operating temperature [°C]	910 / 890*
Coal combustion efficiency [%]	99.6
Calcination efficiency [%]	95.0
Desulfurization efficiency [%]	99.0
Pressure losses in the nozzles and cyclone [kPa]	1.9
Pressure losses in the gas cooling section [% inlet pressure]	7
Temperature of the recycled flue gas [°C]	350.0
Oxidant concentration in the oxidant stream [%vol.]	40**/95
Oxygen concentration in the flue gas [%]	4.0
Calcined limestone lost by attrition [% of make-up flow]	5.0
Coal ashes lost as fly ashes [%]	60.0
<u>Recarbonator reactor</u>	
Pressure losses in the nozzles [kPa]	1.0
Excess of CO ₂ [%]	50
Fluidization gas velocity [m/s]	0.4
$\Delta X_{R, \max}$ [-]	0.03
Fans isentropic efficiency [%]	80.0
Fans mechanical-electrical efficiency [%]	94.0
<i>Air Separation Unit (ASU)</i>	
Oxygen purity [%vol.]	95.0
Electric consumption [kWh/t _{O₂}]	200
<i>CO₂ compression and purification unit</i>	
Number of LP/HP intercooled compression stages	3+2
Minimum ΔT in the surface heat exchanger [°C]	2
Compressor isentropic efficiency [%]	82.0
Compressor mechanical efficiency [%]	94.0
CO ₂ discharge pressure in the last intercooled compressor stage [bar]	89.1
Pump hydraulic efficiency [%]	75.0
Pump mechanical efficiency [%]	90.0
CO ₂ delivery pressure [bar]	150.0

*Considered for the BioCaL case

**Oxidant concentration in the oxidant stream for the reference case

As discussed below, the interconnected fluidized bed reactors involved in the CaL process of Figure 2 have been modeled on the basis of simple fluid-dynamic assumptions in order to facilitate their integration into the process model. Therefore, an instantaneous and perfect mixing of the solids and a plug flow for the gas phase have been assumed for the three reactors.

A key parameter in CaL systems is the average maximum CO₂ carrying capacity of the CaO particles (X_{ave}). This parameter has been calculated by assuming that the inventory of solids in the CaL system is composed of CaO particles that have undergone a different number of

calcination/carbonation cycles (N). They therefore have different maximum CO₂ carrying capacities (X_N) (Abanades, 2002). Since CaO particles do not usually achieve their maximum conversion either in the carbonator or in the calciner reactor, the average maximum CO₂ carrying capacity of the CaO particles in a CaL system has been calculated using Eq. (1) according to the methodology proposed by Rodríguez et al. (2010). The term F_S/F₀ included in this expression takes into account the deactivation of the CaO as a results of its reaction with the sulfur coming into the CaL (i.e. the coal burnt in the calciner and the flue gas fed into the carbonator) (Abanades et al., 2005), it being assumed that the SO₂ reacts exclusively with the active CaO.

$$X_{ave} = (F_0 + F_{Ca}r_0)f_{calc} \left(\frac{a_1f_1^2}{F_0 + F_{Ca}f_{carb}f_{calc}(1-f_1)} + \frac{a_2f_2^2}{F_0 + F_{Ca}f_{carb}f_{calc}(1-f_2)} + \frac{b}{F_0} \right) - \frac{F_S}{F_0} \quad (1)$$

In this expression, F₀ is the molar flow of fresh limestone introduced into the calciner, F_{Ca} is the molar flow of Ca (i.e. in the form of CaO, CaCO₃ and CaSO₄) between the reactors and F_S is the molar flow of sulfur that reacts with the CaO within the CaL system. The coefficients a₁, a₂, f₁, f₂ and b are the sorbent deactivation constants of the equation proposed by Li et al. (2008) for the evolution of X_N with the number of cycles. Values of a₁=0.1045, a₂=0.7786, f₁=0.9822, f₂=0.7905 and b=0.07709 which have been demonstrated to fit the evolution of X_N with N for a large number of limestones up to 500 cycles (Rodríguez et al., 2010) have been used for the reference CaL case. The parameters f_{carb} and f_{calc} correspond to the extent of carbonation and calcination reactions, and are calculated as a function of the variation in the CaCO₃ content of the CaO particles in the corresponding reactor with respect to the maximum feasible variation. A definition of these parameters can be found in the work of Rodríguez et al. (2010). For the CaL system without recarbonation, the f_{carb} needed in Eq (1) is calculated through an iterative process within the carbonator model once the maximum average conversion of CaO particles in this reactor has been solved (Alonso et al., 2009).

Regarding the fate of the sulfur entering the system, the large circulation of CaO between the reactors typically used in a CaL system results in Ca/S ratios several orders of magnitude larger than those typically used for in-furnace desulfurization in CFB boilers. As a result, large SO₂ removal efficiencies can be expected in both of the CFB reactors of the CaL system. On the basis of the experimental data available, a 95% desulfurization efficiency has been assumed for each reactor (Arias et al., 2013).

The carbonator reactor is considered to be a CFB reactor that operates at 650°C, which corresponds to an equilibrium CO₂ partial pressure for the carbonation reaction of 0.012 bar (Barker, 1973). Due to the neutral CO₂ emissions assumed from the combustion of biomass in the calciner, it is feasible to achieve higher overall capture efficiencies in the full CaL system with reduced CO₂ capture efficiency in the carbonator. This lower efficiency in the carbonator would

translate into a benefit on the calciner heat demand, which would be also reduced. Therefore, a value of 80% has been established as the target for the case where biomass is used in the calciner, while a CO₂ capture efficiency of 90% has been assumed for the other cases using coal in the calciner. The reactor model follows the assumptions and structure of the fluidized bed carbonator model proposed by Alonso et al. (2009). In the case of the kinetic model for the carbonation reaction of the CaO particles, the Random Pore Model (RPM) adapted to highly cycled particles has been implemented (Grasa et al., 2009). This model is based on the well-known two-stage reaction process for the carbonation reaction of CaO (i.e. an initial fast reaction stage controlled exclusively by the chemical reaction, which is followed by a second stage controlled by the CO₂ diffusional resistance to the unreacted core of CaO) (Barker, 1973; Bhatia and Perlmutter, 1983; Mess et al., 1999; Shimizu et al., 1999; Silaban and Harrison, 1995). The solid residence time distribution of the CaO particles in the carbonator is used to determine the fraction of particles that are reacting at each reaction stage and to calculate the sorbent conversion at the exit of the reactor (X_{carb}).

In the process model developed in this work, the recarbonator has been assumed to be an adiabatic bubbling fluidized bed whose operation temperature is determined by the heat released from the carbonation reaction. As shown below, reactor temperatures for the recarbonation process of around 750-800°C can be achieved, ensuring a rapid recarbonation (Grasa et al., 2014). A basic recarbonator model adapted from that proposed by Diego et al. (2014) has been integrated into the process model. This includes a simplified particle reaction model which assumes the instant conversion from X_{carb} to X_{ave} at recarbonation conditions. From this point onwards, a constant reaction rate between X_{ave} and maximum conversion under recarbonation conditions ($X_{\text{ave}} + \Delta X_{\text{R,max}}$) is assumed. In this work, a conservative $\Delta X_{\text{R,max}}$ value of 0.03 has been chosen from data reported elsewhere (Grasa et al., 2014). Experimental studies at TG have shown that increments of 0.02 above the maximum CO₂ carrying capacity in the carbonator (ΔX_{R}) are sufficient to maintain the residual activity of natural CaO sorbents above 0.16. Therefore, the recarbonation model has been used to estimate the inventory of solids needed in the reactor to achieve an increment in conversion of 0.02. In addition, representative values of $a_1 = 0.22$, $a_2 = 0.67$, $f_1 = 0.955$, $f_2 = 0.75$ and $b = 0.173$ have been chosen from data reported in the literature obtained from experiments carried out at laboratory scale (Arias et al., 2012; Grasa et al., 2014). To integrate the recarbonation system in these cases, f_{carb} is assumed to be 1 in Eq. (1), as CaO particles are forced to achieve their maximum average CO₂ carrying capacity (X_{ave}). The amount of CO₂ reacted in the recarbonator is the sum of that needed to carbonate the CaO particles entering the reactor from X_{carb} up to $X_{\text{ave}} + \Delta X_{\text{R}}$. The amount of rich-CO₂ gas at the calciner exit which is recirculated to the recarbonator needs to be calculated to ensure that the amount of CO₂ fed in is enough to sustain the carbonation reaction and that the bed of solids is properly fluidized.

For this purpose, a CO₂ excess of 50% with respect to that consumed by carbonation is fed into the recarbonator. The cross-section of the recarbonator has been calculated so as to ensure a fluidization gas velocity of 0.4 m/s at the exit of the reactor.

The calciner reactor of the CaL system is assumed to be an adiabatic reactor operating at temperatures slightly above (i.e. around 15-20°C) equilibrium so as to guarantee fast calcination reaction rates with limited solids inventories (Martínez et al., 2013). The thermal energy needed in the calciner to reach such a high temperature is provided by the oxy-combustion of a high-rank coal or woody biomass, whose characteristics are given in Table 1 **Table 1**. The high purity oxygen (i.e. 95% O₂, the rest being Ar and N₂) used in the calciner is produced in a cryogenic ASU that consumes 200 kW_{he} per ton of oxygen produced (IEA GHG, 2005). In the calciner of the standard CaL system, oxygen preheated to 200°C is mixed with a fraction of the rich-CO₂ gas coming from the calciner outlet. This gas is recirculated to the calciner after being cooled down to 350°C. The flow rate of recirculated rich-CO₂ gas is calculated to have an O₂ content of 40 %v. in the oxidant stream fed to the calciner. In the 2nd generation CaL case, high purity oxygen preheated to 200°C is directly fed into the calciner.

The calciner has been modeled on the reactor model scheme proposed by Martínez et al. (2013). This includes a calcination rate based on a grain model that is consistent with calcination kinetic studies on cycled CaO sorbents in TGA (Martínez et al., 2012). According to this particle model, there is a characteristic time at which full calcination of the sorbent is achieved. This value and the particle solid residence time in the reactor are used to calculate the fraction of particles that has not reached full conversion in the calciner bed. The calciner model is used to estimate the inventory of solids needed to achieve a calcination efficiency of 95%. The amount of oxygen fed to the calciner is adjusted so that it has an O₂ content of 4 % (wet basis) at the calciner outlet. Moreover, a draft-forced fan is introduced into the rich-CO₂ recycle to compensate for the pressure losses caused either by the calciner or by the recarbonator. The pressure drops introduced by these reactors and the efficiency of the fans are indicated in Table 2. Solids losses in the calciner cyclones associated with limestone attrition and fly ashes have also been taken into account in the calculations and are included in the table. Sorbent lost by attrition has been estimated as a fraction of the limestone make-up flow, considering that attrition mainly takes place in the first calcination of the material (Coppola et al., 2012; González et al., 2010; Jia et al., 2007).

The CO₂ compression and purification unit (CPU) considered in this work is based on a single flash auto-refrigerated process described in detail elsewhere (Romano, 2013; Shah, 2011). In this process, the rich-CO₂ gas coming from the CaL process is first compressed to around 20 bar in a three-stage inter-refrigerated compressor before being dried and cooled down to around -50°C for

it to condense into a high-purity CO₂ liquid fraction. This liquid fraction has a CO₂ purity higher than 96%vol. and it is separated in a knock-out drum from the non-condensable gas phase containing the main impurities (i.e. O₂, Ar and N₂). The separated liquid CO₂ is then expanded in a throttle valve to reduce its temperature and is then used in the regenerative heat exchanger to cool the main rich-CO₂ stream down to -50°C. After being re-evaporated and heated up to almost 23°C in the heat exchanger, the CO₂ is compressed to 90 bar in a two-stage inter-cooled compressor, after which it is pumped until it reaches 150 bar. The vented gas separated in the knock-out drum is expanded to almost ambient pressure and then introduced into the regenerative heat exchanger to be heated up before being emitted to the atmosphere, thereby contributing to the cooling duty in the heat exchanger. This vented gas has a CO₂ purity of around 40-42% and contains 2-3.5% of the CO₂ that enters the CPU.

2.1. Secondary heat recovery steam cycle

As indicated in the conceptual scheme shown in Figure 2, the high temperature heat sources available in the CaL process can be found in: (i) the carbonator, where the energy from the exothermic carbonation reaction and from the sensible heat contained in the circulating solids arriving from the calciner can be recovered at a constant temperature of 650°C; (ii) the flue gas from the carbonator, which exits the carbonator cyclone at 650°C and needs to be cooled down to 100°C before being emitted to the atmosphere through the stack; (iii) the rich-CO₂ gas from the calciner, which is cooled down from the calciner temperature of 910°C to 60°C before being sent to the cooler prior to the CPU; and (iv) the solids purged from the calciner at 910°C, which are cooled down to nearly ambient temperature before being put to use (i.e. as raw material for cement production or for desulfurization purposes in a nearby power plant) or disposed of.

To cool the rich-CO₂ gas leaving the calciner, the cooling system has been divided into two separate convective sections. The rich-CO₂ gas is first cooled down to 350°C before being split into two streams. One stream is recirculated either to the calciner or to the recarbonation reactor, while the other is further cooled down to 60°C before being sent to the CPU. From the second heat recovery section, a fraction of the heat recovered is used to heat the oxygen stream arriving from the ASU at 25°C up to 200°C. The oxygen is then fed into the calciner reactor of the CaL process.

In view of the amount of energy available at high temperature from the CaL system, an ultra-supercritical (USC) steam cycle with reheat has been considered, whose parameters and configuration have been taken from the published literature (Romano, 2013). Figure 3 shows the layout of the 2nd generation CaL process integrated with the USC steam cycle just mentioned.

[FIGURE 3, double-column width]

Waste energy from the intercooled air compressors in the ASU and the CPU has not been considered for recovery within the heat recovery steam cycle, as this only receives energy from the CaL heat sources listed above. Due to the large amount of high temperature heat (i.e. above 350°C) available in the CaL process, mainly destined for steam evaporation, superheating and reheating, several regenerative feedwater heaters are needed in the steam cycle. A total of four feedwater heaters (including the deaerator) are needed in the steam cycle, where steam bled from the steam turbine at different pressures is used for heating the water. The rich-CO₂ stream that is not recirculated to the CaL system (i.e. to the calciner or the recarbonator) is used in the high and low pressure feedwater heaters and also to heat up the oxygen stream coming from the ASU. Table 3 summarises the main assumptions used to calculate the heat recovery steam cycle for the cases analysed.

Table 3 Main assumptions used to calculate the heat recovery steam cycle

<i>Steam cycle</i>	
Boiler feedwater temperature [°C]	307.5
Boiler feedwater pressure [bar]	320
Temperature of steam at SH/RH outlet [°C]	600/620
Pressure of steam at SH/RH outlet [bar]	270/60
SH/RH piping thermal losses [°C]	2
SH/RH pressure losses at turbine inlet valve [% of inlet pressure]	2
Steam pressure loss in RH [bar]	4
Condenser pressure [bar]	0.048
Pinch-point ΔT in surface feedwater heaters [°C]	5
<i>Steam turbine</i>	
Steam turbine mechanical efficiency [%]	99.6
Electric generator efficiency [%]	98.5
Hydraulic efficiency of feedwater and condenser pumps [%]	85.0
Mechanical/electric efficiency of feedwater and condenser pumps [%]	98.5/95.0
Auxiliaries for condenser heat rejection [% of heat transferred]	0.8

3. Simulation results and discussion

Mass and energy balances for the CaL system, the heat recovery steam cycle and the CPU have been calculated using Aspen Hysys. For the CaL system and the CPU, the thermodynamic properties of the fluids have been estimated using the Peng Robinson equation of state. The NBS Steam package has been used to calculate the heat recovery steam cycle. The thermodynamic properties of the solids have been implemented in Aspen Hysys from Perry's Chemical Engineers' Handbook (Perry et al., 1997).

Mass and energy balances for a standard post-combustion CaL process scheme, in which the CaL is operated without any recarbonation, employing a recycled CO₂ in the calciner to dilute the

oxygen that is used as oxidant, have been solved to serve as a basis for comparison. This configuration is an example of a 'standard CaL' system. The main results of the balances solved for this standard case are summarized in Table 4 together with those corresponding to the 2nd generation cases explained below. Representative operating conditions for this standard CaL system have been chosen on the basis of the data available in the literature (Martínez et al., 2016). Thus, a moderate limestone consumption corresponding to a F_0/F_{CO_2} ratio of 0.12 has been fixed (defined as moles of fresh $CaCO_3$ fed into the calciner per moles of CO_2 fed to the carbonator in the flue gas from the existing plant) aiming to minimize the heat demand in the calciner. This results in a maximum average CO_2 carrying capacity of the CaO particles of almost 0.125. For this reference case, an inventory of solids in the carbonator of 1500 kg/m² has been considered in order to increase the residence time of the particles in this reactor and to maximize the sorbent carbonation conversion. Under these conditions, X_{carb} is 0.092 and the circulation of solids through the carbonator is 6.4 kg/m²s. As indicated above, the calciner is assumed to operate with a calcination efficiency of 0.95. To achieve this objective, an inventory of 240 kg/m² of solids is needed in this reactor. For this reference case, a thermal input in the calciner of 989 MW_{th} has been calculated which is supplied by burning 30 kg/s of coal. The oxidant fed into the calciner is a mixture of 84 kg/s of oxygen from the ASU and a recycled flow of rich- CO_2 gas of 158 kg/s. As a result, the fraction of thermal input fed into the calciner with respect to the total thermal input into the whole process (H_{calc}/H_{tot}) is 0.49, which is in agreement with the data reported in the literature for conventional CaL systems (Martínez et al., 2016).

Table 4 Detailed results for the CaL process integrated with the existing power plant for the different cases analyzed

	Standard CaL	Second generation CaL		
		BioCaL	HighF0	LowF0
Temperature of the solids at the recarbonator outlet [°C]	--	817	800	748
Specific limestone make-up flow, F_0/F_{CO_2} [-]	0.12	0.05	0.12	0.06
Carbonator CO_2 capture efficiency [%]	90.0	80.0	90.0	90.0
Specific Ca circulation, F_{Ca}/F_{CO_2} [-]	10.38	5.73	5.74	9.75
Maximum average CO_2 carrying capacity, X_{ave} [-]	0.125	0.199	0.239	0.143
$CaCO_3$ content at the carbonator outlet, X_{carb} [-]	0.092	0.151	0.170	0.100
$CaSO_4$ content of CaO particles at the calciner outlet [%]	3.35	2.29	2.66	6.02
Ash content in the solids at the calciner outlet [%wt.]	5.26	2.53	4.00	8.50
Kg fresh limestone /kg total fuel [-]	0.35	0.143	0.40	0.18
Calciner cross-section [m ²]*	175.6	113.4	106.6	119.0
Carbonator cross-section [m ²]*	196.7	196.7	196.7	196.7
Recarbonator cross-section [m ²]**	--	128	78	105
Solids circulation at the carbonator inlet [kg/m ² ·s]	6.4	3.4	3.5	6.5
Solids circulation at the calciner inlet [kg/m ² ·s]	7.6	6.8	7.5	11.7
Fuel input into the calciner [kg/s]	30.0	37.6	21.7	26.9
Fuel thermal input into the calciner [MW _{LHV}]	989.5	609.7	716.7	886.4
Oxygen introduced into the calciner [kg/s]	83.6	54.5	61.3	75.0
CO_2 -rich gas recycle in the recarbonator [kg/s]***	157.7	49.4	50.8	59.9
H_{calc}/H_{tot} [%]	49.4	37.9	41.4	46.7

*Calculated assuming a superficial gas velocity of 5 m/s at the reactor outlet

**Calculated assuming a superficial gas velocity of 0.4 m/s at the reactor outlet

***In the standard CaL, this corresponds to the CO₂-rich gas recycled back to the calciner

The results for the balances of the 2nd generation CaL using biomass as fuel in the calciner are summarized in Table 4. This is referred to as the ‘*BioCaL* case’. As indicated above, a CO₂ capture efficiency of 80% has been set as a target for this specific case. Due to the characteristics of the biomass (low sulphur and ash content), a reduced flow of fresh limestone with a F₀/F_{CO₂} ratio of 0.05 has been adopted which is enough to sustain an average sorbent CO₂ carrying capacity (X_{ave}) of around 0.20 thanks to the recarbonator reactor. As can be appreciated from the results in Table 4, even for this low make-up flow, the reduced ashes and sulphur content in the biomass yields the lowest amount of inerts buildup for CaL and the lowest circulation of solids of all the cases analyzed. As a result, the circulation of solids at the carbonator inlet is greatly reduced from 6.4 kg/m²·s of the standard CaL case to 3.4 kg/m²·s.

As indicated above, an increment of 0.02 above X_{ave} in the carbonate conversion has been set as the objective in the recarbonator reactor. Therefore, a gas flow of 49 kg/s is recycled from the rich-CO₂ flue gas leaving the calciner in order to fulfill the CO₂ requirements and to fluidize the bed. Due to reduced flow of solids entering the recarbonator, an operation temperature of 817 °C can be sustained in this reactor by the exothermic carbonation reaction. In order to maintain a gas velocity at the exit of the recarbonator of 0.4 m/s, a cross-sectional area of 128 m² has been estimated for this reactor. According to the recarbonator model, an inventory of 2470 kg/m² is therefore needed in the reactor to obtain a sorbent conversion at the reactor exit of 0.22.

The relatively large content of moisture and hydrogen in the biomass results in a higher steam content in the flue gas exiting the calciner. This allows the operating temperature to be reduced to 890°C necessary to reach the 95% calcination efficiency target. The lower operating temperature and smaller amount of CaCO₃ to be calcined in the calciner, as well as the reduced circulation of solids, translates into a thermal input into the calciner of almost 610 MW_{th} which represents a reduction of 38% with respect to the standard case. Such a large reduction in the calciner fuel input with respect to the ‘standard CaL’ case results from the reduced circulation of solids needed between the reactors (3.4 kg/m²·s), the low calciner operating temperature and the reduced heat demand for calcination (due to the lower CO₂ capture efficiency and make-up flow consumption). The absence of a CO₂-recycle and the reduced heat demand allows for a more compact calciner reactor design with a cross-sectional area of 113 m² in comparison with the reference case that has a cross-section area of 176 m². As a result, the inventory of solids needed in the calciner increases to 1150 kg/m². Temperature, pressure, flow rate and composition of the different process streams in Figure 3 for the ‘*BioCaL* case’ are indicated in Table 5.

Table 5 Temperature, pressure, flow rate and composition of the process streams shown in Figure 3 for 'BioCaL' case

Stream	T [°C]	P [bar]	G [kg/s]	Q [kmol/s]	<i>Molar composition of gas streams [%]</i>						<i>Mass composition of solid streams [%]</i>			
					Ar	N ₂	O ₂	CO ₂	H ₂ O	SO ₂	CaO	CaCO ₃	Ash	CaSO ₄
1	171.0	1.20	422.8	14.24	0.88	73.79	4.58	13.74	6.99	0.01				
2	275.0	0.99	353.8	12.67	0.99	82.92	5.14	3.09	83.91	--				
3	185.5	0.98	353.8	12.67	0.99	82.92	5.14	3.09	83.91	--				
4	105.6	1.01	353.8	12.67	0.99	82.92	5.14	3.09	83.91	--				
5	200.0	1.25	54.5	1.69	3.02	1.98	95.0	--	--	--				
6	350.0	1.00	214.4	5.94	1.12	0.78	4.0	66.24	27.85	--				
7	350.0	1.00	165.0	4.57	1.12	0.78	4.0	66.24	27.85	--				
8	275.0	0.99	165.0	4.57	1.12	0.78	4.0	66.24	27.85	--				
9	182.3	0.97	165.0	4.57	1.12	0.78	4.0	66.24	27.85	--				
10	35.0	1.01	145.6	3.49	1.46	1.02	5.25	86.67	5.59	--				
11	890.0	1.03	6.07	0.10							90.36	1.91	2.53	5.20
12	20.0	1.11	37.56								<i>Biomass composition in Tab.1</i>			
13	20.0	1.11	10.66	0.11							--	100	--	--
14	600.0	270.0	172.6	9.58	--	--	--	--	100.0	--				
15	368.0	64.0	172.2	9.56	--	--	--	--	100.0	--				
16	620.0	60.0	172.2	9.56	--	--	--	--	100.0	--				
17	32.2	0.048	152.6	8.47	--	--	--	--	100.0	--				
18	35.7	150.0	132.7	3.05	0.80	0.23	2.97	96.0	--	--				
19	600.0	270.0	98.3	5.45	--	--	--	--	100.0	--				

Two additional cases have been solved for the 2nd generation CaL process scheme using coal as fuel in the calciner. The first case (referred to as '*HighF0*') operates with the same level of limestone consumption as in the reference case ($F_0/F_{CO_2} = 0.12$). When the recarbonator process is integrated within the CaL process, the activity of the CaO particles increases notably to 0.24, which is almost double that of the standard CaL. This increase in activity has a pronounced effect on the solids circulation at the carbonator inlet, which decreases to 3.5 kg/m²·s. Due to the high activity of the particles in the CaL system and the lower solids circulation, a reduced inventory of solids in the carbonator is needed to achieve the CO₂ carbonator efficiency target. Therefore, an acceptable solids inventory in the carbonator for this specific case is assumed to be 750 kg/m².

In the case of the recarbonator reactor, a gas flow of 51 kg/s is recycled from the rich-CO₂ flue gas leaving the calciner in order to meet the CO₂ requirements and to fluidize the bed. In this case, an operation temperature of 800 °C can be maintained in this reactor due to the exothermic carbonation reaction. A cross-sectional area of 105 m² is estimated for this reactor which, according to the recarbonator model, translates into an inventory of 1725 kg/m² allowing a sorbent conversion of 0.26 to be achieved.

In this case, a thermal input of 717 MW_{th} is needed in the calciner, which represents a reduction of almost 28% compared to the calciner thermal input of the standard case. In addition, the calciner cross-sectional area is 107 m² which results in an inventory of 660 kg/m². In terms of the buildup of inerts, the reduction in the amount of sulphur and ashes fed in with the coal into the CaL in the *HighF0* case responsible for the lower CaSO₄ content of the CaO particles compared to that of the standard CaL, as can be seen in Table 4.

When the spent sorbent from the CaL process cannot be used elsewhere (e.g. as feedstock for flue gas desulphurization or for cement production), it may be preferable to operate the system with a reduced limestone make-up flow. Therefore, another 2nd generation case (referred to as '*LowF0*') using coal as fuel has been solved with the aim of operating at a reduced F_0/F_{CO_2} ratio of 0.06. Despite a 50% reduction in limestone consumption with respect to the reference case, a slightly higher maximum average CO₂ carrying capacity is achieved due to the recarbonation step, as is shown in Table 4 (0.143 vs 0.125). However, the amount of solids to be circulated through the carbonator in the *LowF0* case is almost the same (6.5 kg/m²·s) because of the increase in inerts (CaSO₄ and ashes) in the system. As the operation conditions are similar, the same solids inventory is assumed for the carbonator as in the standard case (1500 kg/m²).

However, the recarbonator operation conditions in the *LowF0* case differ from those of other 2nd generation cases analyzed. A larger CO₂ recycle is needed in this case despite the smaller increase in the carbonate of the sorbent due to the large amount of CaO flowing between the CaL reactors.

This results in an operation temperature of 748 °C which is still favorable for maintaining fast reaction kinetics under high CO₂ partial pressures (Grasa et al., 2014).

In the case of the calciner, the heat requirements for the *LowFO* case are reduced by 10% with respect to the standard case because of the absence of the CO₂-recycle and the reduced make up flow of fresh limestone. This results in a slightly larger calciner cross-sectional area compared to the *HighFO* case (119 m² vs 107 m²) and a lower solids inventory in this reactor (i.e. 525 kg/m²).

Table 6 shows the performance results obtained for the full process consisting of the existing power plant and the 2nd generation CaL system integrated with the USC heat recovery steam cycle. For the *HighFO* and *LowFO* cases, a slightly different integration scheme to that depicted in Figure 3 is used to maximize the heat transferred to the steam cycle. In these cases, the reduced amount of heat introduced into the calciner results in the recovery of less energy from the rich CO₂ gas compared to the standard CaL case. As a result, the evaporation section introduced into the convective pass of the calciner in the standard CaL case (shown in Figure 3) is no longer possible, and it has been transferred to the convective heat recovery pass located in the carbonator (i.e. between the superheater and economizer sections). Moreover, in the *LowFO* case the energy recovered within the waterwall tubes of the carbonator is no longer dedicated exclusively for producing superheated steam since the amount of steam produced would be excessively high for being reheated within the CaL (i.e. the solid circulation is almost the same as in the standard CaL and the energy recovered within the carbonator barely changes), but it is also dedicated for reheating.

Table 6 Energy balance and main performance results obtained for the different cases analyzed

	<i>Standard CaL</i>	Second generation CaL		
		<i>BioCaL</i>	<i>HighFO</i>	<i>LowFO</i>
<i>Electric power balance [MW]</i>				
From the existing power plant	364.9	364.9	364.9	364.9
Steam turbine integrated with the CaL	461.7	285.6	326.0	423.1
Steam cycle pumps	-13.37	-7.85	-9.13	-12.05
Condenser heat rejection auxiliaries	-4.11	-2.65	-3.01	-3.81
Carbonator fans	-15.82	-14.83	-11.68	-15.70
Calciner fan/recarbonator fan	-3.13	-2.29	-1.98	-2.47
ASU	-60.22	-39.2	-44.14	-54.0
CO ₂ compression	-72.75	-55.5	-62.24	-66.43
Auxiliaries for heat rejection (other than. cond)	-1.16	-1.15	-0.96	-1.06
Net electric plant output [MW]	656.1	527.1	557.8	632.7
Net electric efficiency* [% _{LHV}]	33.45	32.85	33.03	33.67
CO ₂ from coal combustion in the existing power plant [kg/s]	86.09	86.09	86.09	86.09
CO ₂ from limestone calcination[kg/s]	10.33	4.69	10.33	5.16
CO ₂ emitted with the carbonator flue gas [kg/s]	8.61	17.22	8.61	8.61
CO ₂ emitted in the CPU [kg/s]	6.23	4.68	4.40	5.61

Carbon Capture Ratio (E_{CO_2}) [%]	91.88	85.4	91.81	91.57
CO ₂ emission factor [$kg_{CO_2}/MWhe$]	81.4	-245.3	84.0	80.9

*Calculated discounting from the total fuel thermal input the energy required to calcine the fresh limestone

Regarding the power balance, the power output of the new USC steam cycle is lower in the 2nd generation CaL cases due to the reduction in energy introduced into the calciner of this kind of systems. However, this will have a major positive impact on capital requirements, as will be discussed below. There is also a positive effect on the electric consumption associated with the ASU and CPU auxiliaries.

Similar net electric efficiency values affecting the whole process have been calculated for all the cases analyzed. Of the 2nd generation cases, *LowF0* shows the highest electric efficiency, i.e. 33.7 %. In this case, the larger circulation of solids between the reactors increases the fuel input to the calciner, thereby maximizing the amount of heat transferred to the steam cycle with respect to the other 2nd generation cases. Compared to the standard CaL, a slight improvement in electric efficiency can be appreciated in the *LowF0* case due to a reduction in consumption in the ASU and CPU units.

The main differences between the cases analyzed are to be found in the CO₂ balance and the CO₂ emission factor of the full process analyzed in this work (Figure 1). The CO₂ emissions result from the CO₂ emitted with the clean flue gas from the carbonator and the gas vented in the CPU. Except in the case of *BioCaL*, where carbonator efficiency has been kept at 80%, the amount of CO₂ in the clean flue gas remains constant in the *standard CaL*, *HighF0* and *LowF0* cases and equal to 8.6 kg/s, as can be appreciated from the results in Table 6. The amount of CO₂ lost in the CPU (which is proportional to the amount of CO₂ sent to this unit) represents the main difference between these cases. However, in terms of overall CO₂ capture efficiency, a global capture efficiency of 91.6-91.8% has been calculated for the *standard CaL*, *HighF0* and *LowF0* cases.

Table 6 shows the CO₂ emission factor calculated as net direct specific CO₂ emissions emitted. For the *BioCaL*, the biomass used in the calciner has been considered strictly as a carbon-neutral fuel. Therefore, the CO₂ derived from the biomass combustion in this reactor is considered as a negative emission. As a result, the full process including the existing coal power plant and the 2nd generation CaL system with biomass fuel presents a CO₂ emission factor of -245.3 $kg_{CO_2}/MWhe$. This is a remarkable carbon balance for an existing air-fired coal power plant in which the fuel and operating conditions are left unchanged. The retrofitted CaL system in Figure 1 is not only able to decarbonize the flue gases from the power plant but it also generates a large credit of negative emissions from the use of biomass in its calciner. Other capture technologies cannot so easily achieve negative emission factors for the overall system after capture unless substantial modifications are introduced into the existing power plant; for example, by transforming the power plant into an oxygen-fired combustion system. Since this would not be possible for a

substantial number of the existing fleet of coal power plants, it seems that CaL offers a strategic opportunity for reducing the emissions factor from coal power generation systems to zero and or below zero.

4. Cost analysis

A basic economic analysis has been carried out in order to illustrate the cost structure associated with the different CaL systems analyzed in this work. It has been assumed that the existing power plant is already amortized and no modifications or renovations are needed in the power plant when integrating the post-combustion CO₂ capture system. Therefore, the total capital requirements necessary to achieve the full process scheme of Figure 1 only involve the CaL system. Two parameters have been used to compare the costs of different technologies, the cost of electricity (COE) and CO₂ avoided costs (AC), which can be calculated as follows:

$$COE = \frac{TCR \cdot FCF + FOM}{CF \cdot 8760} + VOM + \frac{FC}{\eta_{plant}} \quad (2)$$

$$AC = \frac{COE_{capture} - COE_{reference}}{\left(CO_2/kWh_e\right)_{reference} - \left(CO_2/kWh_e\right)_{capture}} \quad (3)$$

In these expressions, TCR refers to the total capital required, FCF to the fixed charge factor, FOM to the fixed operating cost, VOM to the variable operating cost, FC to the fuel cost and η_{plant} to the net electric efficiency of the whole system including the CaL system while CO₂/kWh_e is the CO₂ emission factor. For comparison purposes, the same variable, fixed, limestone and fuel costs have been assumed for the different CaL systems based on the data available in the literature (DOE/NETL, 2015), as shown in Table 7. For the biomass, the same fuel costs as coal have been assumed taking into account that the higher cost associated with this kind of fuel may be compensated for by green certificates. In order to estimate the avoided costs, the cost of electricity in the existing amortized power plant has been used as reference (i.e. assuming that only the operating cost and fuel cost contribute to the COE of the reference plant).

To facilitate discussion about the estimation of TCR, the total capital requirement of the different elements depicted in Figure 1 has been expressed per unit of thermal power as in other similar works on CaL systems (Abanades et al., 2015). The main cost of the CaL system is associated

with the handling of the solids equipment (i.e. coal and ash), the air separation unit, the carbonator reactor (which is the boiler that produces the steam in the CaL system), the flue gas cleaning system, the equipment needed for heat recovery and the steam turbine and a fraction of the CPU associated with the coal burned in the Ca-Looping system. The cost associated with these elements has been assumed to be the same as that of an oxy-fired CFBC system: 1225\$/kWth (DOE/NETL, 2010; ZEP, 2011). In the second generation cases, the cost associated with the recarbonator reactor is also included in this sub-system as it can be considered as a modified loop seal. The equipment needed for the recycling of CO₂ has already been included in the oxy-fired CFBC. A fraction of the CPU is associated with the CO₂ captured from the existing power plant. The TCR of this part of CPU has been assumed to be 80 \$/kWth (NETL, 2012). Finally, the TCR associated with the refractory calciner has been assumed to be 125 \$/kWth on the basis of the data available for precalciners in cement plants due to their similarities (IEA, 2008). Once the cost associated with the different components has been defined, the TCR of the whole system can be calculated per unit of electric power by simply using the net electric efficiency calculated for each system:

$$TCR = \left(TCR_{CPU} \right) \left(1 - \frac{H_{CaL}}{H_{tot}} \right) + \left(TCR_{Oxy-CFB} + TCR_{CC} \right) \frac{H_{CaL}}{H_{tot}} \left(\frac{1}{\eta} \right) \quad (4)$$

Table 7 Summary of main assumptions used for the economic analysis and cost results

	Existing power plant	Standard CaL system	Second generation CaL		
			<i>BioCaL</i>	<i>HighF₀</i>	<i>LowF₀</i>
TCR [\$/kWe]	---	2115	1710	1835	2000
FOM [\$/kWe]	40	40	40	40	40
FCF [-]	---	0.1	0.1	0.1	0.1
VOM [\$/kWe]	0.007	0.007	0.007	0.007	0.007
Fuel cost [\$/GJ]	2	2	2	2	2
Total investment costs (M\$)	---	1390	900	1020	1265
Limestone cost [\$/ton]	----	20	20	20	20
COE [\$/kWe]***	0.030	0.064	0.058	0.060	0.061
CO ₂ emission factor (kg _{CO2} /MWh _e)	879.0	81.4	-245.3	84.0	80.9
AC [\$/t _{CO2} avoided]	---	42.0	24.8	37.8	39.0

According to the assumptions shown in Table 7, the cost of the electricity produced in the existing coal power plant calculated by means Eq. 2 is 0.030 \$/kWh_e which is in agreement with the data available in the literature for this kind of amortized power generation systems (Zhai et al., 2015). When this power plant is retrofitted with a standard CaL system, the COE increases to a value of 0.064 \$/kWh_e. Lower values between 0.058 and 0.061 \$/kWh_e are obtained in the 2nd generation cases. However, greater differences are observed when the avoided costs of the different CaL systems are compared. The calculated AC of a standard CaL system is 42.0 \$/t_{CO2} avoided. However,

when biomass is used in the calciner, a CO₂ avoided cost of 24.8 \$/t_{CO₂ avoided} is estimated which represents a reduction of 41% compared to the CaL system. This reduction is the result of the negative emission factor of this system as indicated in Table 7 and represents a major incentive for the development of biomass-based CaL systems, as shown in the scheme of Figure 1

Another approach for comparing the different CaL systems is to take into account the total investment needed for retrofitting the existing power plant with a CO₂ capture system. For this purpose, the total investment costs for the different systems have been estimated from the TCR and total electric power produced in each case. In this case, a clear advantage in favour of the 2nd generation process schemes is observed. For the power plant considered in this work, the capital expenditure of integrating a standard CaL will be around 1390 M\$. For the 2nd generation *HighFO* case, the reduced thermal capacity of the CaL system results in a total investment cost of 1020 M\$ which is 25% lower than that of the standard case. The total investment costs of the *LowFO*, which is aimed only at reducing limestone consumption, is still favorable and a value of 1265 M\$ is estimated. The most favorable case is that of *BioCaL* which reduces the total capital expenditure to 900 M€ (34% less than that of the reference system).

The use of the 2nd generation CaL proposed in this study is clearly an attractive option for retrofitting installed coal-fired power plants. The installation of such high temperature CO₂ capture processes allows the repowering of existing power plants thanks to the high-valuable energy sources available in the CaL process, which are able to almost double the power production capacity. The reduced size of the calciner and the ASU components of the CaL system is an important additional advantage in terms of both capital expenditure and energy fuel consumption. Finally, and most important of all, the use of biomass in the calciner makes the entire system a negative CO₂ emitter and therefore a valuable contributor to the climate change mitigation scheme.

Conclusions

The performance of a second generation CaL scheme integrated into an existing coal-fired power plant has been analyzed. This system offers the option of using biomass in the calciner as well as improvements in the form of recarbonation and oxy-fuel combustion with pure oxygen in the calciner. As shown in this study, the implementation of this kind of 2nd generation CaL system provides a solution for decarbonizing the vast fleet of already installed coal-fired power plants. The integration of the CaL allows the repowering of existing power plants thanks to the integration of high-valuable energy sources available in the CaL process for a new steam cycle. The CO₂ capture system shows an overall energy efficiency of 32.9-33.6% (LHV-based) with

modest energy penalties. In addition, by using biomass in the calciner, existing energy-consuming sources of CO₂ can be transformed into negative CO₂ emitters. In this study, a negative CO₂ emission factor of -245.3 kg_{CO2}/MWh_e has been achieved for the 2nd generation case using biomass while the total investment cost of this 2nd generation CaL scheme has been proven to be 30% lower than that of a conventional CaL system.

ACCEPTED MANUSCRIPT

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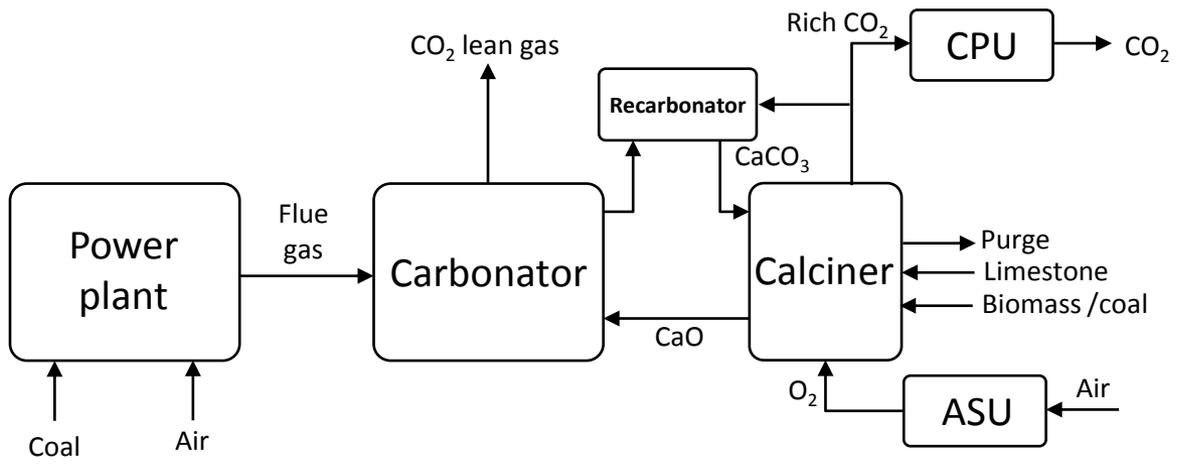
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Figure captions

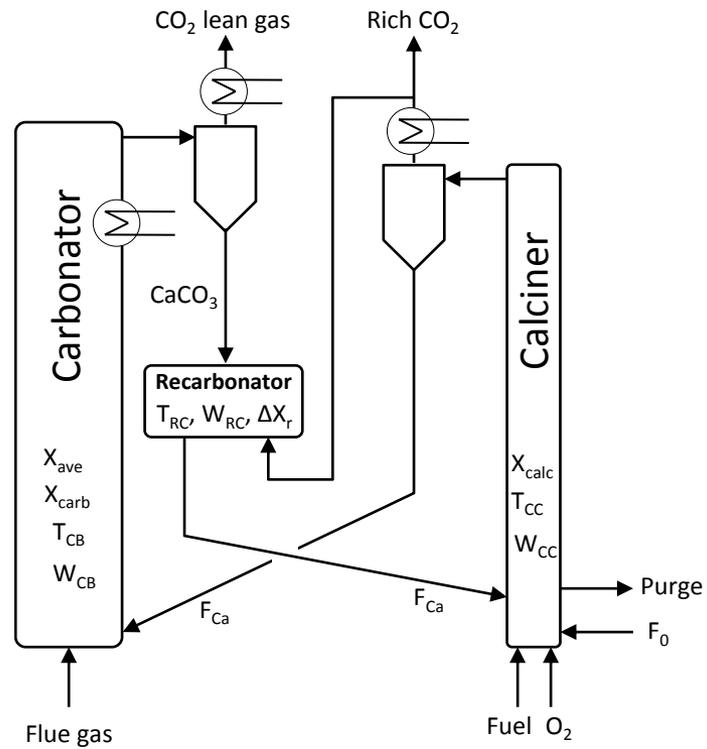
Figure 1. Schematic diagram of the 2nd generation CaL system used in this work, retrofitted to an existing power plant.

Figure 2. Scheme and main variables of the second generation CaL system assessed in this work.

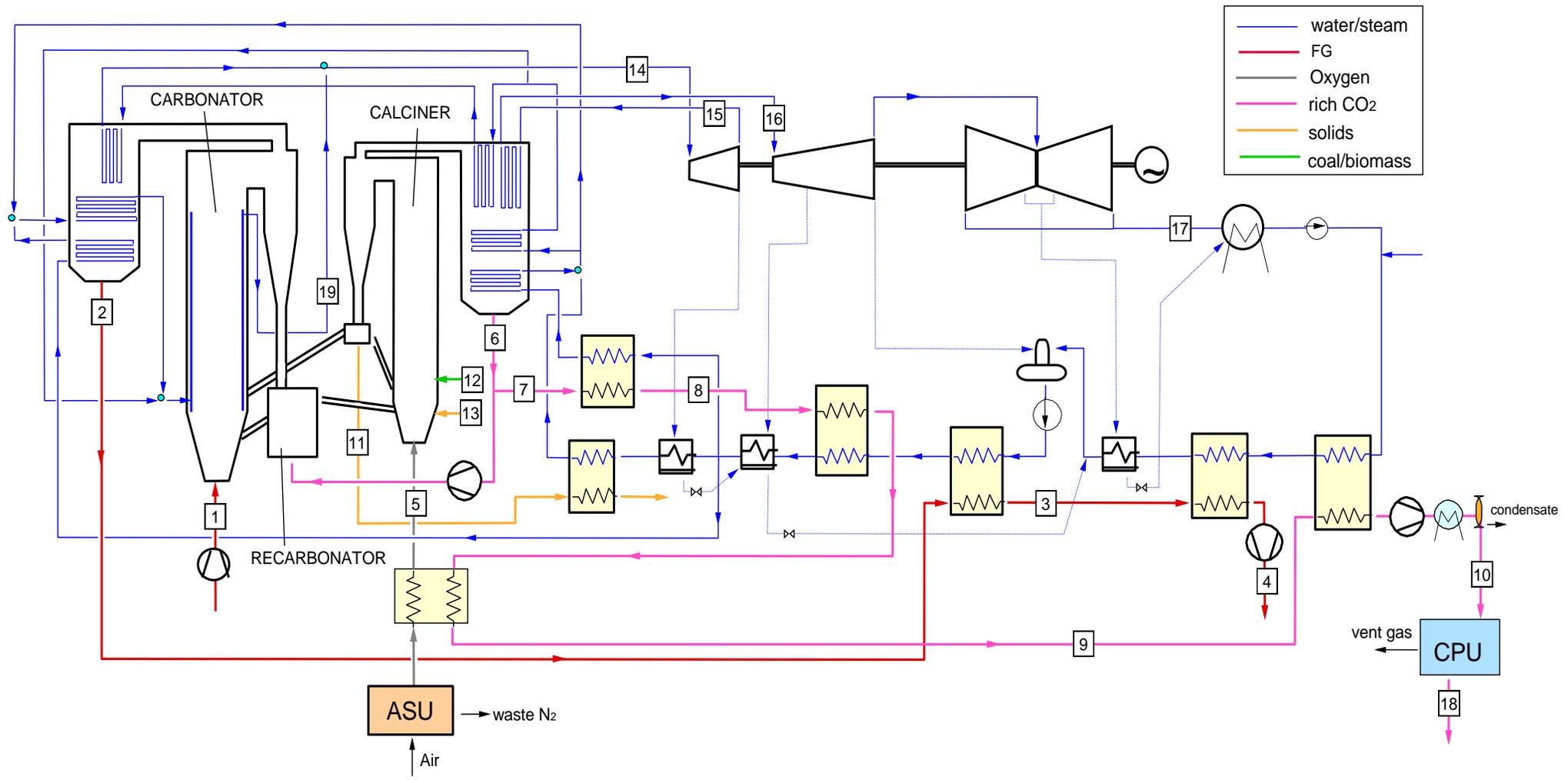
Figure 3 Flowsheet of the 2nd generation CaL system integrated with the heat recovery steam cycle. *The position of the different heat exchangers in this layout corresponds to the BioCaL and to the standard CaL cases analyzed in this work*



Black and White, double column width



Black and White, single column width



Color, Double column width

Highlights

- A second generation Calcium Looping technology using biomass is assessed
- Operation with a highly stable sorbent and pure oxygen combustion is considered
- Negative overall system emissions while keeping untouched the existing power plant
- Capital investment cost reduced by 30% compared to conventional Calcium Looping