Combined calcium looping and chemical looping combustion process simulation applied to CO_2 capture

By
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Statement of contribution of Collaborators

I am the sole author of all the chapters of this thesis. My supervisors, Dr. Arturo Macchi, Dr. Poupak Mehrani of the Department of Chemical and Biochemical engineering, University of Ottawa and Dr. Edward J. Anthony of Cranfield University supervised my work during the M.A.Sc. program and provided editorial corrections.

Signature: ___________________________ Date: ___________________________

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Abstract

The new Canadian laws on CO_2 emissions aim to lower the emissions of coal-fired power plants down to those of natural gas combined cycle units: 420 kg CO_2/MW_eh. In order to meet these requirements, calcium looping and two process variants are investigated through process simulations using Aspen Plus V8.2. The combination of calcium looping and chemical looping combustion, replacing the required air separation unit, is a way to reduce the energy penalty of the capture process. The addition of copper as an oxygen carrier in two different process configurations is compared to calcium looping and shown to reduce the efficiency penalty from 7.8% to 4.5% points but at the price of circulations rates up to about 3800 kg/s. The other improvement path studied is the implementation of calcium looping to a pressurized fluidized bed combustion unit. The pressurized carbonator acts as a reheater for the gas turbine and operating the carbonator at temperatures up to 798°C results in a reduction of the energy penalty from 5.1% to 3.1% points.

Sommaire

Les nouvelles lois Canadiennes limitant les émissions de CO_2 ont pour but de réduire les émissions des centrales thermiques au charbon jusqu'au niveau de centrales à cycles combinés au gaz naturel : 420kg CO_2/MW_eh. Pour satisfaire ces limites, le procédé au calcium et deux variations sont étudiées à l'aide de simulations sous Aspen Plus V8.2. La combinaison du procédé au calcium avec la combustion en boucle chimique, remplaçant l'unité de séparation de l'air, permet de plus hautes efficacités énergétiques. L'addition de cuivre comme transporteur d'oxygène dans deux configurations du procédé réduit la pénalité énergétique de 7.8% à 4.5% points mais au prix d'une une augmentation de la circulation de solides jusqu'à 3800 kg/s. La deuxième option opère la capture à la suite d'une unité de combustion fluidisée sous pression. L'opération du réacteur de carbonatation sous pression permet l'augmentation jusqu'à 798°C de la température du réacteur et réchauffe les gaz de combustion pour la turbine, entrainant une réduction de la pénalité énergétique de 5.1% à 3.1% points.

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Acronyms

ASU: Air separation unit

CaL: Calcium looping

CCS: Carbon capture and storage

CLC: Chemical looping combustion

CPU: Compression and purification unit

DoE: Department of energy

GHG: Greenhouse gas

HHV: Higher heating value

IPCC: Intergovernmental panel on climate change

kWe: kilowatt electrical. Unit of electrical power

kW_{th}: kilowatt thermal. Unit of thermal power, based on a fuel HHV

MW_e: megawatt electrical. Unit of electrical power

MW_{th}:megawatt thermal. Unit of thermal power, based on a fuel HHV

OECD: Organization for economic cooperation and development

PC: Pulverized coal

PCaL: Pressurized calcium looping

PFBC: Pressurized fluidized bed combustion

Chapter 1 - Introduction

The global production of electricity is strongly dependent on the use of fossil fuels. In 2012, 68% of the world power originated from coal, natural gas and oil combined, and over 40% from coal alone as shown on Figure 1.1 [1]. The share of natural gas is predicted to increase in the future as it is a cleaner fuel and due to the higher efficiency of natural gas fired power plants [1,2], but the overall share of fossil fuels is expected to remain important.

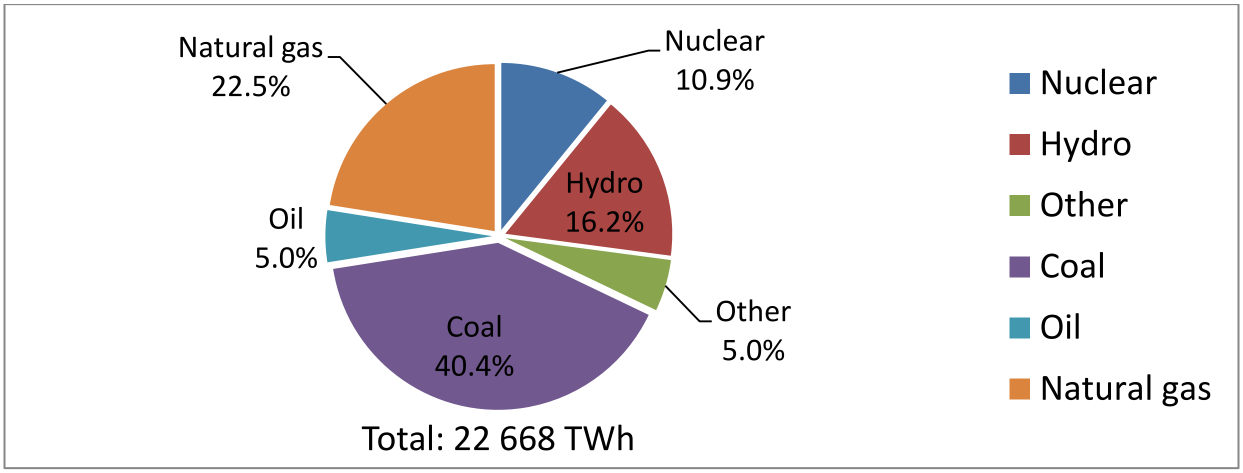

Figure 1.1: World electricity production in 2012 [1]**.**

The combustion of fossil fuels is a major source of greenhouse gases (GHG) with the electricity and heat production sector responsible for about 31% of the total GHG released to the atmosphere [3]. The anthropogenic release of GHG and the increase of their concentration in the atmosphere have been associated with climate change [4] and in order to limit the impact of such gases on the global climate, governments started taking action. Carbon dioxide accounting for 76% of the global GHG emissions, it is an important target of such regulations [5–7].

The recent regulation work done in Canada and the United States targets the coal sourced power in particular [6,7] as it is the most CO_2 intensive power. The CO_2 or carbon intensity of a power producing process is defined as the emission of CO_2 per unit of power:

$$CO_2\ intensity = \frac{CO_2\ emissions\ [kg/h]}{Power\ output\ [MW]} \tag{1.1}$$

On average, coal produces about 900 kg CO_2/MW_eh while oil and natural gas respectively produce 670 and 400 kg CO_2/MW_eh[1] [8]. Canada recently adopted a target of 420 kg CO_2/MW_eh

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[1] Based on data on electricity production from OECD member countries between 2009 and 2011.

for both new and old coal fired power plant [6]. This means that their CO_2 emissions have to be reduced by more than half and that process efficiency improvements would not be sufficient to reach the set target. Consequently, in addition to those efficient improvements, coal power plants will have to implement carbon capture systems.

1.1 Carbon capture and storage

Several options are possible to mitigate carbon dioxide emissions [9]. Incremental improvements of technology, materials and process design have already contributed to an increase of energy conversion efficiency over long periods of time. However, such improvements are not sufficient on their own to achieve deep reductions in GHG emissions. Switching to less carbon-intensive fuels is also a solution where substantial CO_2 reductions can be achieved, as was shown previously comparing coal with oil or natural gas emissions, but this change is not easily applied to existing plants burning more carbon intensive fuels. In addition, availability or economic reasons might be a hurdle for this switch to occur. Energy sources that do not rely on fossil fuels are also available including nuclear, wind, solar, hydro, and geothermal which some are already in use. However, they account for a smaller share of the global energy production compared to fossil fuels and it will take time before this trend can be reversed. The last solution presented in the Intergovernmental Panel on Climate Change (IPCC) report [9] is the capture and storage (CCS) of CO_2 to prevent its release to the atmosphere. This approach has the advantage that it offers “end-of-pipe” solutions that avoid major modifications to the base process.

Carbon capture processes all have one objective which is to produce a concentrated stream of CO_2. The transportation to a storage site is then operated under supercritical conditions [10,11]. The supercritical state results in higher densities, allowing the transport of CO_2 with a reduced pressure drop per unit of mass [10]. The purification of the CO_2 stream in capture processes avoids the presence of a residual gas phase at the pipeline conditions and the formation of acids or hydrates due to the presence of impurities and free water [10].

The technologies available to design a post-combustion capture process are varied and include absorption, adsorption, membrane process and solid sorbents [9,12,13]. Amine scrubbing processes in particular are the most mature processes and are already available at a certain scale [9]. However, the regeneration of the amine sorbent consumes steam that would be extracted from the power plant main steam cycle. This represents the main drawback of this type of technology as it reduces the plant power output and efficiency [13]. The net efficiency reduction, also called energy penalty, is expected to be around 10.5 points [13–15], meaning that a base power plant with a net efficiency of 40.5% would have a net efficiency of 30% once the carbon capture process is implemented.

The conversion of a burner to oxy-combustion is also a well-regarded option. The operation of a burner in oxygen-fired mode consists of using high purity oxygen to burn a fuel instead of air. The resulting flue gas of such a combustion is then mainly composed of water vapor and CO_2, reducing the purification requirement for transport. While this technology does not require withdrawing steam from the main cycle, it is necessary to produce a nearly pure oxygen stream. The operation of an air separation unit (ASU) is energy intensive and the energy penalty associated with oxy-combustion compared to a conventional air-fired burner is expected to be similar to that of amine scrubbing processes [9,15,16].

The power production efficiency directly impacts the cost of electricity, making low penalty capture process particularly attractive. A carbon capture option expected to have a lower penalty than previously mentioned processes is solid sorbents or carbonate looping. Based on the successive carbonation and calcination of a solid sorbent, this type of process has the particularity to operate at high temperature, allowing energy recovery and additional power production. This unique feature reduces the energy penalty compared to other capture processes, making solid sorbent processes competitive [9,12,17].

The goal of this thesis is to focus on a sorbent based CO_2 capture process. Using calcium oxide as a sorbent, the calcium looping process (CaL) is at the base of this thesis. The state of the technology and its principles are described next, along with two variations of the process.

1.2 Calcium looping for post-combustion carbon capture

The capture of CO_2 in a CaL process is based on the reversible carbonation reaction of CaO:

$$CaO_{(s)} + CO_{2\,(g)} \rightleftharpoons CaCO_{3\,(s)} \quad \Delta H_{650°C} = -172.4\ kJ/mol \tag{1.2}$$

The extent of the reaction is limited by equilibrium. An empirical relation between CO_2 partial pressure and temperature was established by Baker [18] as follow :

$$\log P[atm] = 7.079 - \frac{38000}{4.574 * T[K]} \tag{1.3}$$

The principle of this process is to remove CO_2 from a flue gas by using the sorbent at a relatively low temperature and then operate a regeneration step at a higher temperature. Using equation (1.3), it can be calculated that at equilibrium and atmospheric pressure, the CO_2 concentration can be reduced to 1% at 642°C. The regeneration of the sorbent can be achieved even in a pure CO_2 atmosphere at atmospheric pressure and temperatures greater than 900°C. With a typical coal power plant flue gas containing 13% CO_2, a temperature below 770°C would activate the carbonation reaction.

The process could be carried out in both fixed bed and fluidized bed reactors. However, this thesis focuses on fluidized bed operation. This choice is attributed to the continuous mode of fluidized bed reactors, producing a constant flow rate CO_2 stream required for the compression and purification unit (CPU) downstream without the multiplication of unit operations. In addition, it has been found that calcium oxide sorbents suffer from a fast decay of their conversion as the particles undergo carbonation-calcination cycles [19,20]. The purge of spent sorbent and make-up of fresh particles that are thus required are easier to implement with the facilitated transfer of solids that fluidized bed reactors allow.

The regeneration of the sorbent in the calciner is achieved by the combustion of a fuel such as coal or natural gas. To avoid the dilution of CO_2 by nitrogen, the calciner has to operate in oxy-combustion mode. The presence of excess nitrogen would require additional purification of the stream and increase the energy penalty. Thus in addition to the two reactors (carbonator and calciner), the operation of CaL process also requires an air separation unit.

The typical decay of conversion of the sorbent at high cycle numbers has been attributed to the sintering of the sorbent [21,22]. The process of sintering causes a decrease of the small pores volume and an increase of the large pores volume, contributing to a reduction of the specific surface area and a reduction of the CO_2 carrying capacity [21]. It was also observed that this loss of conversion was dependent on the source of the limestone [20] or nature of synthetic Ca-based pellets [23,24]. Natural limestones have been observed to have a very similar type of decay but Grasa and Abanades highlighted that differences between limestones will matter for system design purposes, especially when operating with low purge rate of the solids [20]. For synthetic sorbents, it has been found that the inert support material can stabilize the structure of the sorbent and provide sintering-resistant properties depending on its proportion and the manufacturing mixing method [23,24]. Additionally, the temperature and gas environment in which both the carbonation and calcination take place affect the sorbent conversion [20,25,26]. High temperatures cause stronger sintering of the sorbent and accelerate the conversion decay [20] while the presence of steam during carbonation is believed to enhance the solid-state diffusion of carbonates, resulting in better conversion [26,27].

The investigation of sorbent performance is where much research effort is focused. While natural limestone is used in many studies [20,26,28], Ca-based synthetic sorbents manufactured from powdered limestone as well as calcium hydroxides and an inert support [29,30] or calcium salts [23,24] have also been tested. Improvements of conversion through doping [31,32], pelletization with a support [29,33,34] or reactivation by steam [26,35,36] are methods that have been experimented with and discussed by various research teams. In addition to conversion improvements, the pelletization of calcium oxide or synthetic sorbents was also found to result in improved resistance to attrition compared to natural limestone and to reduce the loss of sorbent due to elutriation during fluidized bed operation [29,37]. Steam can have various positive influences on the process. Spent sorbent can be reactivated using steam, which increases the specific surface area of the particles [35]. This reactivation potential lead to the design of a CaL process with the addition of a hydrator reactor and has been studied by Wang et al. [36]. The presence of steam during carbonation was mentioned above to have a positive effect on conversion while during calcination, it dilutes the CO_2 and allows lower calcination temperatures (see equation 1.3). Despite the benefits of steam, the hydration of the sorbent (not to be confused with the addition of steam in the carbonator/calciner) also has a negative effect in that it reduces the particles mechanical strength [38]. This would increase the attrition rate of the sorbent and cause problems regarding the loss of particles due to elutriation.

Steam is not the only species which presence affects the sorbent performance. If the flue gas to be treated includes SO_2, the carbonation reaction then competes with the sulphation of the sorbent:

$$CaO_{(s)} + SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow\ CaSO_{4\,(s)} \tag{1.4}$$

$$CaCO_{3\,(s)} + SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow\ CaSO_{4\,(s)} + CO_{2\,(g)} \tag{1.5}$$

The irreversibility of the $CaSO_4$ formation at operating temperatures reduces the availability of CaO for CO_2 capture and hence SO_2 accelerates the decay of the sorbent conversion with particles cycling [27,28,39]. CaL has the potential to remove sulfur in addition to CO_2 but the simultaneous removal of both species negatively affects the CO_2 carrying capacity of the sorbent. Desulfurization of the flue gas before the carbon capture is still desirable.

The CaL process has been brought to the pilot scale in unit sizes ranging from 75 kW_{th} to 1.7 MW_{th} [40–44]. These pilot plants were operating fluidized bed reactors with fluidizations regimes varying from circulating [43,44] to bubbling or moving beds [40,41]. Results from all these works pointed to high CO_2 capture levels (above 90%) and high sulfur capture when present in the flue gas [43]. Problems regarding high sorbent loss due to attrition was mentioned by Lu et al. [40] and the negative influence of SO_2 was highlighted by Symonds et al. [27]. Nevertheless, the operation of the pilot units was deemed successful by the operators.

Process simulations of post-combustion CaL have also been published and report the estimated energy efficiency penalty of the process to be between 6 and 11%, generally lower than amine scrubbing or oxy-combustion (both around 10.5%) [15,45–48]. The simulations mostly focus on the integration of the heat from the capture process and estimate the energy consumption of the ASU and the CPU [46,47]. Recent work added the complete simulation of a dedicated steam cycle to recover the capture process heat [45] and coupled the simulation with reactor modeling [15]. It was observed that the compression work represents the major contribution to the energy penalty, followed by the ASU [15,45–47].

While the compression of the CO_2 is inherent to CCS, there is an alternative to oxy-fired burners that could significantly reduce the impact of CaL which is chemical looping combustion (CLC).

This solid looping technology replaces the ASU by using a solid oxygen carrier. The combination of CaL and CLC process is explained in the next section and detailed in Chapter 2.

A significant part of the energy requirement in the calciner (about 20%) comes from heating the solids from the carbonator to the operating temperature of the calciner. The reduction of the temperature difference between the two reactors is beneficial but also limited by the reaction equilibrium or the energy balance. A particular application of the CaL process which allows higher operating temperatures of the carbonator is pressurized calcium looping (PCaL). This modification of the process is detailed in section 1.4. and explored in Chapter 3.

1.3 Chemical looping combustion and combined CaL-CLC

Chemical looping combustion (CLC) offers an alternative to oxy-combustion process while keeping the advantage of avoiding CO_2 dilution by nitrogen in the combustion flue gas. Instead of gaseous oxygen, a solid oxygen carrier (e.g., CuO, Fe_2O_3, Mn_3O_4, and NiO) is used for the combustion in a fuel reactor. The exothermic reduction of the oxygen carrier (the copper case is illustrated on equation 1.6) provides the required heat for the calcination of $CaCO_3$.The reduced solids are then transferred to a second reactor where they are brought back to their oxidized state (see equation 1.7 for the copper case) using air [49,50].

$$CuO_{(s)} + 0.25\ CH_{4\ (g)} \rightarrow\ Cu_{(s)} + 0.25\ CO_{2\ (g)} + 0.5\ H_2O_{(g)} \quad \Delta H_{900°C} = -50.4\ kJ/mol \tag{1.6}$$

$$Cu_{(s)} + \frac{1}{2} O_{2\ (g)} \rightarrow\ CuO_{(s)}\ \ \Delta H_{950°C} = -149.7\ kJ/mol \tag{1.7}$$

The combination of CaL and CLC thus avoids the ASU requirement and an energy efficiency gain can be expected. The new process operates three reactors: the carbonator, the calciner/fuel reactor and an air reactor. The sequencing of the reactors and the looping configuration is particularly important in the operation of the overall process. Indeed, depending on the operating conditions and gas environment within the reactors, some configurations may result in CO_2 loss or inefficient energy use. This is discussed in further details and configurations are compared in Chapter 2.

1.4 Pressurized calcium looping

To avoid the equilibrium temperature limitation on the carbonator, an option would be to increase the operating pressure of the reactor. It was presented in section 1.2. that at atmospheric pressure for a 13% CO_2 flue gas, the equilibrium temperature is 770°C. An increase of the total pressure to 2 atmosphere would double the partial pressure of CO_2 and result in a temperature limitation of 811°C. This represents a 30% reduction of the temperature difference between calciner and carbonator and thus a similar reduction of the energy required to heat the carbonated solids in the calciner.

While an improvement of the calciner fuel consumption does not require very high pressures, the compression of a combustion flue gas would consume excessive amounts of energy due to the important volumetric flow rate and the temperature of such a stream. However, if the combustor was already operating under pressure, additional compression would not be required and thus the process could benefit from a higher temperature in the carbonator.

An emerging combustion technology that fits this description is pressurized fluidized bed combustion (PFBC). The combustion of coal at elevated pressure (up to about 10 bar [51]) allows the production of power from the hot flue gas at high temperature using a gas turbine [51,52]. The use of a combined cycle makes PFBC units a high efficiency direct coal combustion process and a good candidate for the implementation of a CaL process.

When combined with CaL, a PFBC process would expand the flue gas to the desired carbonator operating pressure. After the removal of CO_2 in the carbonator, the flue gas is further expanded to atmospheric pressure to recover extra power. The carbonator would also reheat the flue gas before the expander, increasing the energy recovered compared to the gas turbine alone.

The idea of operating the carbonator and the calciner at a different pressure has been investigated before in an isothermal pressure swing setup by Butler et al. [53]. They concluded that a pressure differential between carbonation and calcination could indeed allow carbon capture. In the process simulated in this thesis, both pressure and temperature swings are used to allow high temperature carbonation and low temperature calcination of the solids. This is described in further details in Chapter 3.

1.5 Thesis objectives

CaL is a promising developing carbon capture technology. It offers the possibility to capture CO_2 with a relatively low energy efficiency penalty and is based on a widely available material. Natural limestone can be used directly, is relatively inexpensive and already used in some combustion processes as a way to control SO_x emissions.

Improvements to CaL have been studied, notably by manufacturing pellets to obtain better resistance to sintering and refining the integration of the energy released in the capture process with the power plant. It has been highlighted that the production of oxygen for the calciner accounts for a significant part of the energy penalty. In addition, an important part of the fuel requirement in the calciner is due to the heating of the carbonated solids to the calciner temperature. The current state of the combined CaL-CLC technology is not as advanced as CaL. Research has been focusing on proof of concept work by manufacturing and testing pellets [54–58] as well as some process simulations [15,59–61], not always in a post-combustion context. Only one published paper thus far has compared CaL to CaL-CLC [15]; and thus, the information on the process performance is limited and no results showing the impact of reactors operating conditions is available. In addition, only one looping configuration was studied (composite Ca-Cu pellets circulating in a carbonator-calciner-air reactor loop [15]) and the solids flow rate required to operate the process were not reported. Solids flow rate is an important parameter for consideration in the operation of such process and it is expected that switching from CaL to CaL-CLC process would results in a significant increase of solids flow rates. Thus the first objective of this thesis is to study different looping configurations.

Pressurized CaL is only an option to consider when working with combined cycles due to the energy that would be required to compress a combustion flue gas stream. PFBC units are currently the most energy efficient processes burning coal directly. Studies implementing PCaL with combined cycles power plant exist but only focus on coal gasification which already has lower carbon intensity levels [62] or reforming units [63]. The combination of CaL and PFBC has not yet been researched and thus is the second objective of this thesis.

The overall goal of this thesis is to explore two CaL upgraded pathways of combined CaL-CLC and pressurized CaL. This thesis presents the process simulation of two systems using Aspen

Plus V8.2: (a) a PC power plant with CO_2 capture using CaL-CLC (2 looping variations of it); and (b) a PFBC power plant with pressurized CaL. In each case, the proposed modification of CaL is compared to the base CO_2 capture process in terms of energy efficiency, solids circulation rates and power output.

1.6 Thesis outline

This thesis is divided into four chapters. Chapter 1 introduces the CaL and two potential applications (CaL-CLC and pressurized CaL) that could lead to an improvement of the energy efficiency of the base process. References are provided to explain the state of the technology and illustrate the principles of the process and its performance compared to other carbon capture processes.

Chapter 2 is a manuscript prepared for a journal submission. It presents the results of Aspen Plus simulations of CaL and CaL-CLC processes. The simulation details are described and the different implementations of the processes are compared against each other based on the solids circulation rates and energy efficiency. The results of a sensitivity analysis on the operating conditions of the process are also presented.

Chapter 3 covers the simulations investigating the application of CaL to capture CO_2 from a PFBC unit. A sensitivity analysis on the operating conditions of the process and a rough optimization is proposed. Based on the results, guidelines for a new experimental campaign on the sorbent performance are proposed in order to improve the confidence in the simulation results.

Chapter 4 concludes the thesis and summarizes the results of the work presented in Chapter 2 and Chapter 3. General recommendations for future work are also made.

Chapter 2 - Combined calcium looping and chemical looping combustion for post-combustion CO_2 capture: process simulation and sensitivity analysis

Manuscript prepared for publication in an academic journal.

2.1 Abstract

The calcium looping (CaL) process is an intensively researched post-combustion CO_2 capture technology that uses the reversible carbonation reaction of the calcium oxide. Compared to other carbon capture processes, CaL produces extra power and is estimated to have a reduced energy penalty. Part of the penalty comes from the air separation unit (ASU) required to produce the oxygen used to operate the oxy-combustion calciner. An alternative has been previously proposed that replaces the ASU with chemical looping combustion (CLC) in a combined process [64]. In this work, this CaL-CLC technology is simulated at thermodynamic equilibrium conditions and the results in terms of efficiency, power production and solids circulation rates are compared to the case using CaL alone. In addition, a new solids looping configuration of the CaL-CLC process is proposed with the purpose of mitigating the loss of calcium oxide conversion after high cycle numbers. Simulations show an improved process efficiency of the CaL-CLC compared to CaL alone (34.2 HHV% against 31.2 HHV%) and an increased power output (136 MW_e against 110MW_e additional power) due to the higher energy requirement to preheat the reactants. The simulations of the newly proposed solids looping configuration also provides higher efficiency (34.7 HHV%) with a 22% reduction of the solids flow rate compared to the original CaL-CLC. A sensitivity analysis of the process operating parameters is performed and highlights the particular importance of the reactors temperature difference, which has a strong impact on the required mass of solids circulating in the loops. Finally, partial CO_2 capture (down to 50%) scenarios are considered and indicate that lower capture levels are suitable to match regulations targets.

2.2 Introduction

The combustion of fossil fuels represents the major source of energy for electricity production in the world. In 2012, approximatively 68% of the world production relied on fossil fuel with coal alone accounting for 40% of the global power output [1]. Whilst energy production predictions foresee a shift towards renewable sources of energy (e.g., solar, hydro, wind, etc.), fossil fuels and coal in particular will still constitute an important source of energy [1].

Compared to coal, natural gas represents a cleaner source of energy as it is less carbon intensive. Coal also contains more sulfur and generates ashes and a range of micro-pollutants. Coal and oil-fired power plants, with respectively CO_2 intensities of ~900 and ~600 kg CO_2/MW_eh, appear to be the first stationary carbon sources where carbon capture and sequestration (CCS) should be employed [8]. Indeed, recent regulations in Canada and in the USA could push carbon emission from coal power plants to natural gas fired combined cycle level (~400 kg CO_2/MW_eh) [6–8]. Based on this data, lowering coal based power plants CO_2 emissions to such levels is not feasible without the implementation of a carbon capture process.

Post-combustion CO_2 capture technologies are the only "end-of-pipe" solutions that would allow the mitigation of carbon emissions from stationary sources without the need for major modifications to the power plant itself. The most mature capture technology is the absorption of CO_2 by amine solutions but this process requires a significant amount of power, reducing the output of the power plant and its efficiency [13,65]. Reactive solids processes however make use of high temperature reactions and allow the recovery of high quality heat to produce more electricity [12,13,17].

Calcium looping is a specific implementation of a reactive solids process. It uses the reversible carbonation reaction by circulating calcium oxide based solids between two reactors operating at different temperatures. The lower temperature in the carbonation reactor causes the formation of calcium carbonate (reaction 2.1), reducing the amount of CO_2 released by the plant while the higher temperature of the calciner regenerates the sorbent and releases the CO_2 (reaction 2.2).

$$CaO_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)} \quad \Delta H_{650°C} = -172.4\ kJ/mol \tag{2.1}$$

$$CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)} \quad \Delta H_{900°C} = 166.2\ kJ/mol \tag{2.2}$$

This technology has been intensively investigated where laboratory experiments first provided proof-of-concept results, understanding of reaction mechanism, and investigation of sorbent performances [19–23,25,33,35,66]. Process simulation [45–47,67,68], reactor modelling [69–74], and economic analysis [67,75] helped to show the potential of the process and its feasibility. Several pilot plants have been constructed with capacity ranging from 75 kW_{th} up to 1.7 MW_{th} , the later treating a fraction of the flue gas from an existing 50 MW_e CFBC power plant [40,42–44,76]. The results of the operation of these systems showed that the process was able to reach capture efficiencies above 90% [40,43,44]. The deactivation of the sorbent [43,44] and particles loss due to attrition [40] caused the capture efficiency to decline but it remained at an acceptable level (above 75% in [40]). In addition, the adaptation of the bed inventory can compensate for the sorbent capacity drop [43]. Calcium oxide also reacts with SO_2 and could serve as a sulphur removal method. However, the irreversibility of the sulphation of calcium oxide at operating conditions significantly affects the extent of the carbonation reaction [27,40,43].

In order to improve the conversion of sorbent particles, calcium oxide can be pelletized with a cement support. It has been shown that pelletized sorbents are less susceptible to attrition [37] and that the use of calcium aluminate cement as a binder can increase the conversion of calcium oxide [29,34]. This is especially true at high cycle numbers where the formation of $CaO\text{-}Al_2O_3$ compounds stabilizes the structure of the sorbent, making it more resistant to sintering [29,34,77].

The CaL calciner is operated in oxy-combustion conditions to avoid the dilution of CO_2 by nitrogen and thus requires the implementation of an air separation unit (ASU). Along with the CO_2 compression train, the ASU is another significant contributor to the energy penalty of the capture process [45,46]. An alternative to the operation of the calciner in oxy-fuel conditions is chemical looping combustion (CLC) which uses a solid oxygen carrier to avoid direct contact between air and the fuel (Figure 2.1) [50]. A metal oxide carries oxygen in a solid form to the fuel reactor where it is reduced by reacting with the fuel (reaction 2.3 for copper), methane in this case. The reduced solids are then transferred to an air reactor where air is used to re-oxidize the metal back to its original higher oxidation state (reaction 2.4 for copper). While a fluidized bed reactors system is discussed here, the process can also be achieved in a fixed bed configuration [50].

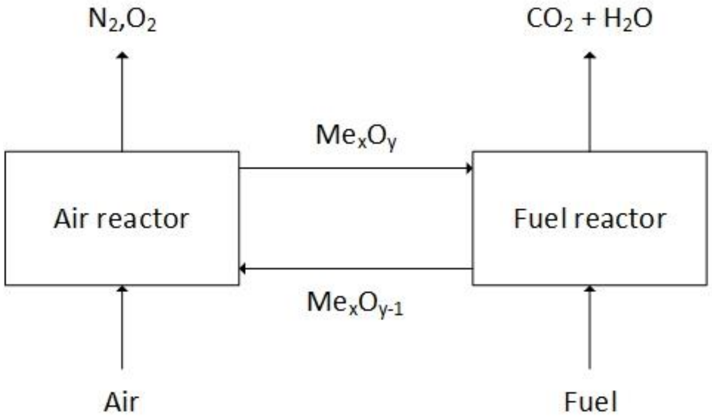

Figure 2.1: General scheme of a CLC process

$$4\,CuO + CH_4 \rightarrow 4\,Cu + CO_2 + H_2O \quad \Delta H_{900°C} = -201.5\ kJ/mol \tag{2.3}$$

$$Cu + 0.5\,O_2 \rightarrow CuO \quad \Delta H_{950°C} = -149.7\ kJ/mol \tag{2.4}$$

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \quad \Delta H_{900°C} = -802.3\ kJ/mol \tag{2.5}$$

The energy released in the two reactors system is equivalent to the direct combustion of the fuel (reaction 5) but the distribution of that energy between the air and fuel reactors depends on the chosen fuel and oxygen carrier [12,50]. The choice of the solid carrier depends on multiple factors: the reactivity with the fuel, its oxygen carrying capacity, its resistance to attrition, its tendency to agglomerate, its toxicity and price. Commonly used carriers include copper, nickel, cobalt, manganese and iron oxides [12,50,54].

When CaL and CLC are coupled, the resulting process consists of three reactors (Figure 2.2) and the solids circulating between them are a composite of CaO, the oxygen carrier and a binder. In the calciner, the CaO is regenerated using the energy produced by the reaction between the metal oxide and the fuel. This can only be achieved in a case where the reduction of the oxygen carrier by the fuel is an exothermic reaction, which constitutes another important parameter to consider when choosing the right sorbent formulation. Manovic and Anthony [54] performed a screening of potential oxygen carrier suitable for a combined CaL-CLC process. Multiple metals and fuels were included in their analysis and the Cu/CuO system was chosen as an ideal candidate, mostly due to its fast reaction kinetics and the high ratio of energy produced by unit of mass of carrier when reduced by methane which was the fuel most likely to be used. Despite its advantages, the choice of copper as an oxygen carrier also raises concern about particle agglomeration due to the low melting point of metallic copper at 1085°C. However, studies have shown that by changing the loading of copper in the solid particles or the pellets manufacturing method, this problem could be avoided, and agglomeration of the particles could be avoided up to 950°C [58,78].

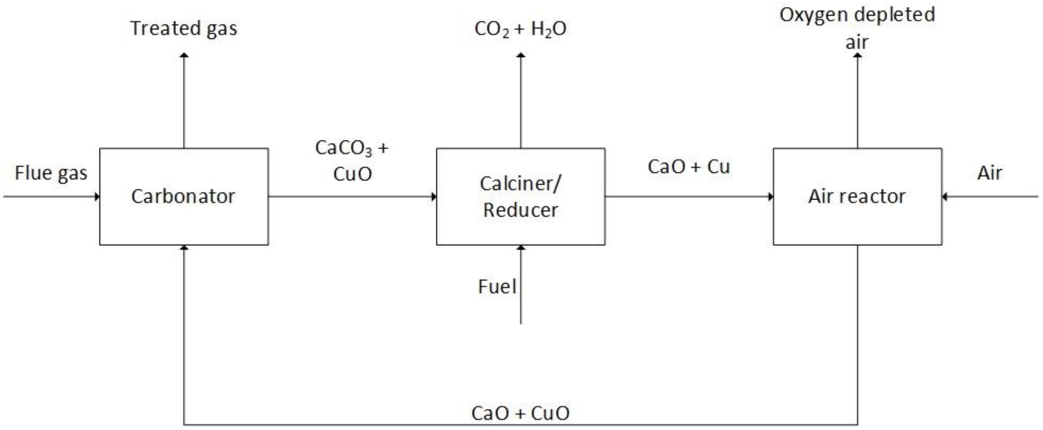

Figure 2.2: General scheme of a combined CaL-CLC process.

In this work the combined CaL-CLC process conducted in fluidized bed reactors was simulated in Aspen Plus V8.2. The combined CaL-CLC process has previously been simulated for steam-methane reforming in a fixed bed configuration [63,79]. Although fixed beds are easier to operate, fluidized bed reactors were chosen in this work due to the mitigated risk of hot spots [59] and the continuous need for fresh sorbent addition. Moreover, the operation of fluidized beds generates a continuous feed of CO_2 to the compression train whereas fixed bed would require the installation of multiple units to achieve such operation. Ozcan et al. [15] conducted the preliminary process simulation on a combined CaL-CLC in fluidized bed reactors using CaO-CuO-Al_2O_3 composite pellets and compared this capture process to oxy-combustion, CaL and amine scrubbing. The combined CaL-CLC process consistently showed to have 2 to 5% points higher efficiencies than the other technologies. The present study expands on this first work by providing a more detailed sensitivity analysis in addition to proposing a new configuration of the solids looping process.

When operating the CaL-CLC process, most of the energy from the fuel is released in the air reactor (see reactions 3 and 4). The implemented solution in that work was then to operate the air reactor at higher temperature and circulate hot solids back to the calciner in order to transfer additional energy through the sensible heat of the solids. While effective, this modification significantly increases the solids circulation rate and the sorbent particles are exposed to high temperatures in the air reactor. To limit sorbent sintering due to temperature effects and reduce solids flow rate, a new configuration of the process is presented in this work where the calcium and copper species are separated into two distinct particles and circulated in two loops. The CaL and the two configurations of CaL-CLC are studied through a sensitivity analysis on parameters including reactors temperature, sorbent performance and overall CO_2 capture target.

2.3 Simulation description

2.3.1 Base power plant and flue gas properties

The CO_2 capture process is based on the flue gas of a supercritical pulverized coal power plant burning Illinois #6 coal and generating 550 MWe of net power (case 11 in [14]). The flue gas is treated for NO_x with selective catalytic reduction and for SO_x with wet limestone forced oxidation scrubbing. Final flue gas conditions used in the simulations are listed in Table 2.1. The SO_x levels are reduced below 20 ppm in the flue gas desulfurization unit and its effect on the CaO sorbent is considered negligible in this study.

Table 2.1: Flue gas conditions [14]**.**

Properties	**Value**
Temperature (°C)	57
Flow rate (kmol/h)	74091
N_2 mole fraction	0.683
H_2O mole fraction	0.152
CO_2 mole fraction	0.135
O_2 mole fraction	0.024
Ar mole fraction	0.006

The steam cycle conditions and the efficiency of the power production are indicated in Table 2.2.

Table 2.2: Steam cycle conditions and efficiencies [14]**.**

Properties	**Value**
Steam conditions	
Main steam	593°C – 24.1 MPa
Reheat steam	593°C
Boiler efficiency	88%
Net plant efficiency	39.3 HHV%

2.3.2 Capture process configurations

2.3.2.1 Calcium looping

Calcium looping serves here as the basis of comparison. Calcium oxide based sorbents are circulated between the carbonator where they react with the CO_2 and the calciner where the sorbent is regenerated by the combustion of methane (Figure 2.3). Methane is chosen here instead of coal to compare the different processes on the same fuel basis. Previous work from various authors has shown that the cycling of calcium oxide at high temperatures causes sintering which degrades the sorbent structure and reduces its capture capacity [19–22]. To maintain a sufficiently high conversion in the carbonator, deactivated sorbent has to be purged and fresh solids are added to the process.

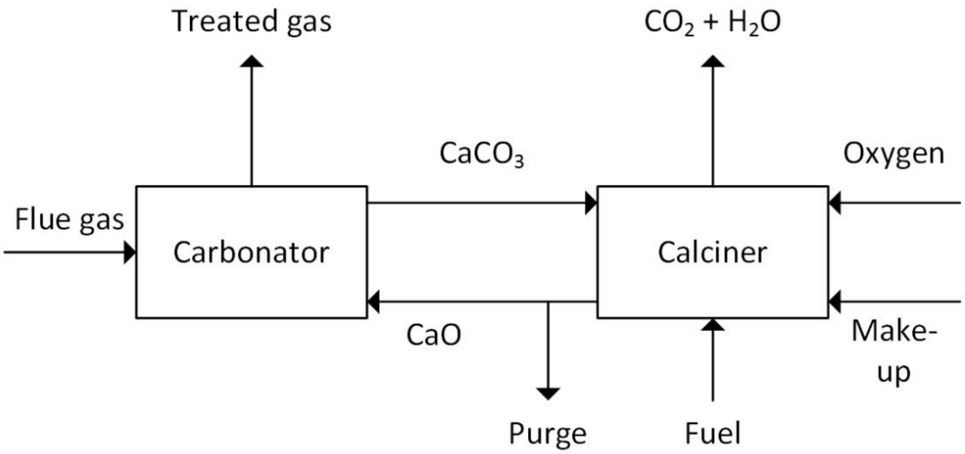

Figure 2.3: General schematic of the calcium looping process.

2.3.2.2 CaL-CLC single loop

The addition of copper to the circulated pellets requires the addition of a third reactor, where the reduced copper will react with air to return to its oxidized state. Multiple sequencings of the reactors are possible.

It has been shown that the carbonation and the oxidation reactions could be carried in the same reactor [80]. The fixed bed experiments demonstrated that the oxidation of copper was feasible using the residual oxygen typically present in a combustion flue gas and at a temperature that also allows the carbonation to happen. However, the low quantity of oxygen present in the flue gas would not be sufficient to oxidize the calculated amount of copper circulating in the process and a dedicated air reactor is required.

In order to minimize the fuel consumption, a different sequencing of three reactors (carbonator -> air reactor -> calciner) could operate the air reactor at a higher temperature than the calciner. This would naturally transfer heat from the oxidation reaction to the calciner through the sensible heat of the solids. However, this configuration would cause the calcination of the calcium carbonate in the air reactor, leading to a lower net CO_2 capture efficiency. The rate of this undesired decomposition could be controlled by increasing the pressure of this reactor but it would complicate the overall process and calcination would always happen if the temperature is high enough [53].

The choice has been made to operate the calciner before the air reactor to avoid the loss of CO_2 during the oxidation of copper (Figure 2.4). To recover the heat from the air reactor in the calciner, a recycle loop is implemented between the air reactor and the calciner (dashed arrow on Figure 2.4) as was done by Ozcan et al. [15]. The former will operate at a higher temperature and the oxidized and calcined solids will be returned to the calciner in order to release sensible heat and contribute to the calcination of the sorbent from the carbonator.

Part of the calciner gas outlet is recycled to dilute the fuel feed stream before entering the reactor. It is also assumed that there is no leakage of gas between the air reactor and the calciner, as was proven possible by Adánez et al. [81].

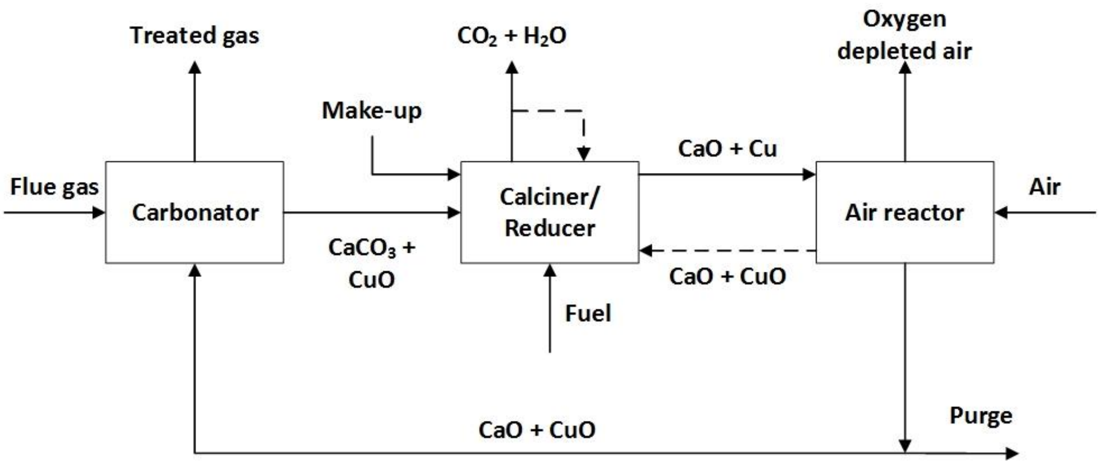

Figure 2.4 : General schematic of the combined CaL-CLC single loop process.

2.3.2.3 CaL-CLC dual loop

The CaL-CLC process presented in Figure 2.4 circulates CaO-CuO-Al_2O_3 composite pellets between the three reactors. As such, the sintering of the sorbent is accelerated as calcium oxide is exposed to higher temperatures than in the CaL process alone. In consequence, a higher make-up flow would be required to maintain the desired carbonation reaction conversion level.

To avoid the transfer of calcium oxide to the air reactor, a new process configuration is proposed as illustrated on Figure 2.5. This new configuration combines CaL and CLC in two separate loops, with the calciner as a crossing point between them. The CaL side of the process would work in the same manner shown in Figure 2.3 while the CLC side would circulate alumina-supported copper between the air reactor and the calciner as a typical CLC process shown in Figure 2.1.

While offering benefits over the previous looping configuration, this process also comes with the challenge of continuous solid-solid separation. A first solution would involve introducing differences in size and/or densities of the 2 particles during manufacturing. This would create different fluidization conditions for each particle and allow their classification during the operation of the reactor. Unit operations dedicated to this type of separation also already exist in the form of air classifiers. However, the high solid load and temperature are not the typical operating conditions of such units.

Another solution would involve indirect heat transfer for the calcination of the calcium carbonates. The calciner would consist of two distinct chambers and the solids would not be mixed. The use of cyclonic preheaters [82] and integrated reactors [48] could achieve such a process. The implementation of indirect heating for a CaL process was investigated by Reitz et al. [83] in a 300kW$_{th}$ unit with an air fired combustor coupled to the calciner. The use of indirect heating with CLC has not been demonstrated yet. In this simulation, it is assumed that either one of these options is implemented, that the solids remain in their own loop and that the energy released by the copper oxide reduction is fully used to heat and calcine the solids from the carbonator. Similarly to the single loop configuration, no gas leakage between the air reactor and the calciner is assumed.

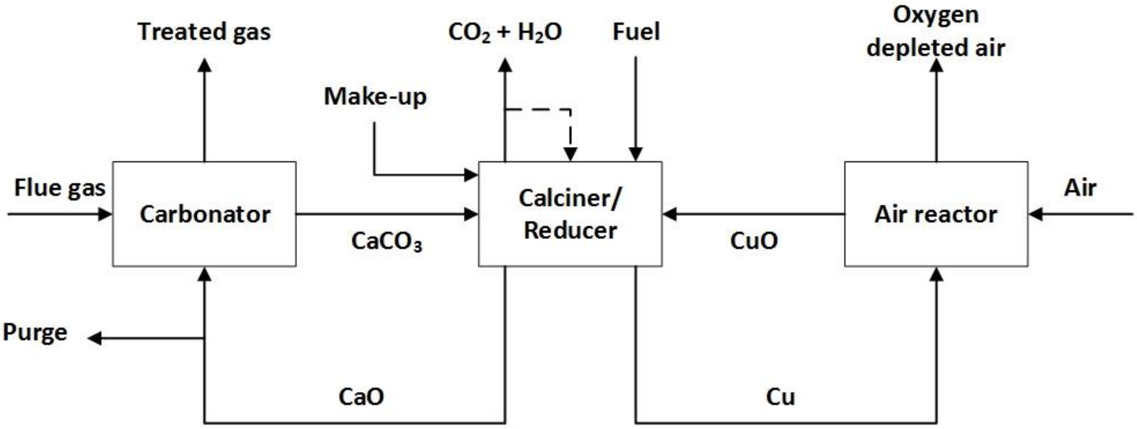

Figure 2.5 : General schematic of the combined CaL-CLC dual loop process.

2.3.3 Sorbent formulation

Each configuration of the capture process (explained in section 2.2) uses a different solids composition as presented in Table 2.3. In the CaL case, calcium oxide is pelletized with alumina as a support. The mass fraction of support is set to 10%, based on the work of Manovic and Anthony [34]. In the CaL-CLC single loop process, copper oxide is added to the pellets. The proportion of copper is adjusted so that the energy produced by the copper oxide reduction matches the energy required to calcine the calcium carbonate in the calciner and maintain the temperature of the reactor. In the CaL-CLC dual loop case, the CaL side circulates the same solids as in the CaL case while the CLC loop contains alumina supported copper oxide. The composition of the latter is again adjusted to have a neutral calciner heat duty.

It has been found [78] that in a CLC setup, pellets with a copper content above 15 wt% could lead to agglomeration and defluidization depending on the operating temperature of the reactors. In the present case, the calculated copper content of the pellets is always below that limit. In addition, the works of García-Lario et al. [84] and Abdul Rahman et al. [58] show that higher copper content can be used if a different pellet manufacturing technique is used.

Table 2.3: Sorbent formulation

Solid compounds	CaL	CaL-CLC single loop	CaL-CLC dual loop	
			CaL side	CLC side
CaO	90 wt%	Depends on energy balance (86.2 to 89.2 wt%)	90 wt%	0 wt%
CuO	0 wt%	Depends on energy balance (0.8 to 3.8 wt%)	0 wt%	Depends on energy balance (1.0 to 5.0 wt%)
Al_2O_3	10 wt%	10 wt%	10 wt%	Depends on energy balance (95 to 99.0 wt%)

2.3.4 Capture process

2.3.4.1 Carbonator

There has been much work concerning the carbonation reaction [19–23,25,26,35] and carbonator modelling [70,71,73,74] since it is the core of the CO_2 capture process. It is well know that both the carbonation and calcination conditions (temperature, CO_2 and water vapor concentrations) have an effect on the sorbent cyclic CO_2 uptake capacity [25,26] and different limestones show different resistance to sintering [20]. A complete approach of the reactor simulation would require calcium oxide sorbent performance data on its capacity decay for every combination of reactor temperatures in the overall process in order to calculate an average conversion in the carbonator. Because such data is not available, the choice has been made to set the conversion of the CaO in the carbonator. Set at 20% in the base case simulation, it is also varied between 10 and 40%. While the conversion of the sorbent observed during pilot operation [27,43,44] is in the lower end of the investigated range, studies on CaL-CLC composite pellets have shown that high conversion are achievable [85,86]. In addition, sorbent conversion calculations based on TGA data showed that such conversion are possible [15].

The carbonator is operated at 650°C. Many thermal gravimetric analyser (TGA) studies perform the carbonation at this temperature [20,23,25,30,87,88] since the reaction equilibrium favours the formation of calcium carbonate and allows carbonation efficiencies above 90%. Higher temperatures cause an increase in the equilibrium CO_2 concentration (equation 2.6 from [18]) and limit the carbon removal potential. However, if only partial carbon capture is considered, increasing the carbonator temperature could be beneficial to the process as it reduces the fuel requirement in the calciner due to lower temperature difference between reactors. In addition, it also leads to accelerated reaction kinetics. Temperatures up to 700°C are also tested in a sensitivity analysis.

$$\log P[atm] = 7.079 - \frac{38000}{4.574 * T[K]} \tag{2.6}$$

2.3.4.2 Calciner

Most previous simulation work on the calcination reactor assumed complete calcination [45–47,67,68]. Recent work on the calcination kinetics of carbonated particles [66] and the development of calciner reactor models [69,72] show that calcination efficiencies above 95% can be obtained. Full calcination will be assumed in all cases presented in this work.

Natural gas is employed as the fuel for the calciner. The combustion of a solid fuel in a chemical looping combustion scenario is possible [50,89,90] but natural gas has been chosen to avoid the presence of sulfur and ash, since both affect the sorbent performance negatively [28,39,71,91]. The reduction of copper oxide by methane in composite CaL-CLC pellets has also been investigated by multiple authors and fast reaction kinetics were observed [56,59,84], which is also positive for the process as it favours the complete reduction of copper and thus the complete release of the required heat for the calcination.

The calciner is operated at 900°C, a temperature sufficiently high to calcine calcium carbonate in an atmosphere containing 99% CO_2 at equilibrium. While lower temperatures reduce the CO_2 partial pressure at equilibrium, it also reduces the energy required to heat the solids transferred from the carbonator to the calciner. The extent of that fuel consumption reduction is investigated in a sensitivity analysis by lowering the calciner temperature to 863°C.

The simulation of the calciner (like the other reactors) is based on material and energy balance only. As no reactor model is applied here, the effect of the configuration or geometry of the reactor cannot be assessed directly. The simulation of the calciner also accounts for an air infiltration of 2% (based on flue gas flowrate). For CaL cases, the oxygen is fed to the calciner in excess to reach a 2.7% (dry basis) residual O_2 concentration in the flue gas [92]. A flue gas recycle is also implemented to dilute the oxygen feed concentration to 30% [93]. For CaL-CLC cases, the flue gas recycle loop aims to dilute the methane feed to avoid possible carbon deposition or safety issues and provide appropriate fluidization conditions. A ratio of $(CO_2+H_2O)/CH_4$ of 1 is used in the base case. As the hydrodynamics of the reactor are not modeled here, the effects of higher ratios on the process are also discussed in the case where higher gas velocities would be required.

2.3.4.3 Air reactor

The operation of the air reactor as a fluidized bed reactor for CaO-CuO composite pellets has not been explored experimentally yet. However, reactor modelling and process simulation have been carried out on a reforming process in a fixed bed configuration [60,61,63]. The oxidation reaction of copper in a CaO-CuO composite pellet has been studied in TGA experiments before [54–56,85,86] and literature on chemical looping combustion using copper is also available [78,94–97]. All investigations show that the use of copper as the oxygen carrier results in fast reaction kinetics, complete or very high conversion (above 90%) and long reliability of the carrier performance over cycles number up to 70 [55]. For these reasons, complete and stable oxidation is assumed for the air reactor.

In order to transfer the heat of the oxidation to the calciner, the air reactor has to operate at a higher temperature. Base case simulations set the air reactor temperature to 950°C and values down to 910°C are tested in a sensitivity analysis.

2.3.4.4 CO_2 compression and purification

After the calcination of the carbonate in the calciner, the produced gas is enriched in CO_2 but also contains a significant amount of water vapour that needs to be condensed along with residual oxygen and nitrogen from either the oxygen feed or the infiltrated air. Depending on the dry basis purity of the CO_2 stream, two different compression and purification process are used. Following the recommendations of the CAESAR project [98], water vapor content is kept below 50 ppm and the sum of non-condensable gases below 4%. Depending on the application considered, additional oxygen removal might be required as the limit of 100 ppm for enhanced oil recovery is not met in the simulated cases.

In the CaL cases, purification is required due to excessive nitrogen content (about 7% on a dry basis). The cryogenic process proposed by Xu et al. [99] is used. The flue gas is compressed to 2.1 MPa in a multi-stage compression before being cooled to -35°C. The CO_2 is condensed and separated from the other gases to meet the desired specifications. The cooling cycle operates with a COP of 1.36 and CO_2 recovery above 95% is achieved.

In the CaL-CLC cases, there is only a need for water vapor removal due to the low concentration of nitrogen and oxygen. This is carried out by implementing a refrigeration and compression process using the Joule-Thomson effect, as chosen by Abbas et al. [100,101]. The flue gas is compressed to about 4.0 MPa and throttled to 1.0 MPa in a Joule-Thomson valve. The resulting temperature drop causes the condensation of the water vapor in order to meet the specification.

In both processes, the final product is compressed to 15.0 MPa. The compressors are simulated with an efficiency of 80% and pumps have an efficiency of 75%.

2.3.4.5 Air separation unit

The cryogenic distillation unit producing concentrated oxygen is not part of the presented simulation. The energy consumption of the ASU is determined based on the oxygen requirements of the calciner and available data on air separation. According to Darde et al. [102], air separation plants require a specific energy of separation of around 200$kW_eh/t\ O_2$. New designs, optimized for lower purity (95%) oxygen production, could decrease this energy of separation to 160 $kW_eh/t\ O_2$. However, the specific energy of separation does not consider compressor motor efficiencies, heat of regeneration of driers and cooling system power consumption. Because such information was not provided, the value of 200 kW_eh/t O_2 was assumed in this work. This value is similar to energy consumption used in previous works [45,46]. The oxygen stream fed to the process has a purity of 95%, the balance being nitrogen.

2.3.5 Steam cycle and power production

High quality heat is available in several locations within the capture process. The implemented heat integration is illustrated in Figure 2.6 and uses a temperature approach of 20°C. The recovered energy is then integrated in a dedicated supercritical steam cycle with reheat to produce power ([14], case 11).

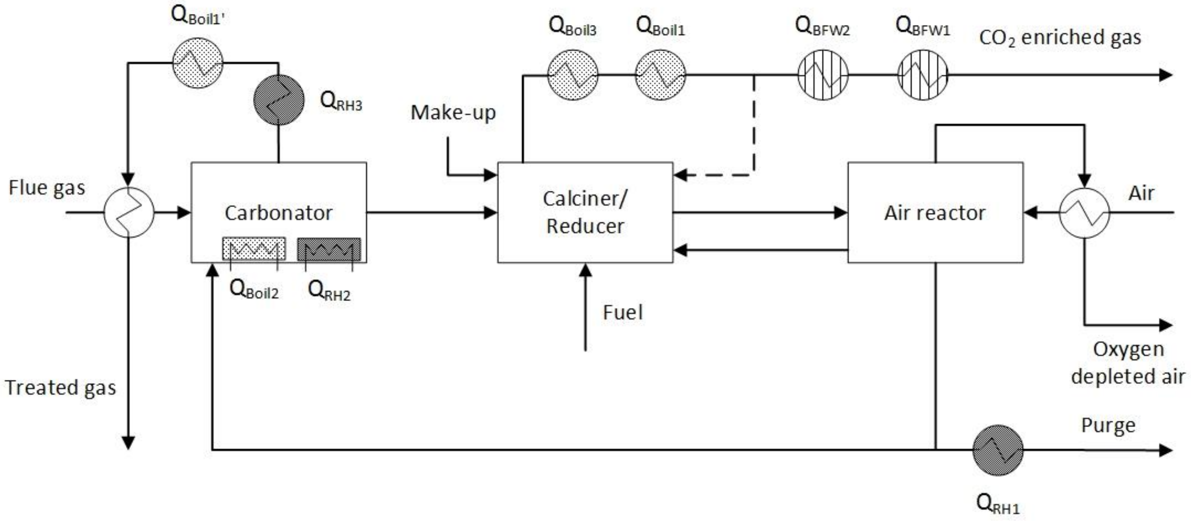

Figure 2.6: Heat exchanger network for CaL-CLC single loop process.

The boiler is replaced by 4 heat exchangers in series: the CO_2 enriched gas and the treated flue gas first generate vapor at 383°C (Q_{Boil1} and $Q_{Boil1'}$). Half of the carbonator heat duty (Q_{Boil2}) followed by the calciner gas outlet (Q_{Boil3}) then heat the vapor to 593°C at 24.2 MPa. The reheat of the steam between the high pressure and the intermediate pressure turbines is carried out by three heat exchangers. The solids purge along with the other half of the carbonator duty and the carbonator gas outlet stream contain enough energy to raise the temperature of the returning steam back to 593°C at 4.5 MPa.

Before being compressed and purified, the CO_2 stream is further cooled using the boiled feed water (Q_{BFW1} and Q_{BFW2}) of the steam cycle. This allows the reduction of the steam extraction in the turbines and increases the power output. The heat exchanger network (HEN) implementation is evaluated based on the proportion of energy transferred to the steam cycle, compared to the fuel energy value (HHV) fed to the calciner:

$$\eta_{HEN} = \frac{Q_{SC}}{q_{fuel} \ * HHV_{fuel}} \tag{2.7}$$

With η_{HEN} the efficiency of the HEN, Q_{SC} the rate of thermal energy transferred to the steam cycle (MW_{th}), q_{fuel} the mass flow rate of fuel fed to the calciner (kg/s) and HHV_{fuel} the higher heating value of the fuel fed to the calciner (MJ/kg).

The heat exchanger network has an efficiency of 78% for CaL, whereas the boiler efficiency of the base power plant is 88%. The difference with the power plant can be attributed to an increased number of process outlet streams, increasing the energy loss. For the same reason, the CaL-CLC configurations heat exchange network efficiencies are slightly lower with 73% for the single loop and 76% for the CaL-CLC dual loop. The dual loop configuration results in a greater efficiency due to the reduced energy required to heat solids to the reactors operating temperature.

The simulated steam cycle converts thermal energy to electrical energy with an efficiency of 45.6%. The net electrical power production efficiency (see equation 2.8) is calculated based on the fuel energy input rate, the heat transfer efficiency in the HEN (assumed to be 100%), the HEN efficiency, the efficiency of the steam cycle and the power consumed by the capture process. The auxiliaries contributing to this power consumption are composed of the fans used to maintain the fluidized conditions in the reactors and overcome their 10 kPa pressure drop; the ASU used to produce the required oxygen for the calciner operation (CaL cases only) and the CO_2 purification and compression system. In addition, an additional 5% power is deduced from the gross power output of the capture process to account for various auxiliaries not simulated in this work such as sorbent handling, fines removal and cooling tower fans. The following formula illustrates the efficiency calculation:

$$\eta_{net\ tot} = \frac{q_{fuel} * HHV_{fuel} * \eta_{HEN} * \eta_{SC} * 0.95 - P_{Fans} - P_{ASU} - P_{CPU}}{q_{fuel} * HHV_{fuel}} \tag{2.8}$$

With $\eta_{net\ tot}$ the total net energy conversion efficiency, η_{SC} the efficiency of the steam cycle, P_{Fans} the power used by the reactors fans (MW_e), P_{ASU} the power consumed by the ASU (MW_e) and P_{CPU} the power consumed by the CPU (MW_e).

The power consumed by the reactors fans as well as the compressors and pumps in the CPU is calculated under Aspen Plus with a compression efficiency of 75%, 80% and 75% respectively. The mechanical efficiency of the units is set at 98%.

2.4 Results

2.4.1 Base case conditions

The simulation base case parameters are listed in Table 2.4. These parameters are chosen to obtain favourable conditions in the reactors for the capture and release of the CO_2, with a low carbonator temperature and a high calciner temperature. The solid make-up ratio is defined as follow:

$$\text{Make-up ratio} = \frac{F_0}{F_{CO_2}} = \frac{\text{Molar flowrate of CaCO}_3\text{ in make-up stream}}{\text{Molar flowrate of CO}_2\text{ in flue gas in carbonator}} \tag{2.9}$$

Both F_0 and F_R(the molar flow rate of CaO entering the carbonator) affect the conversion that the sorbent reaches in the carbonator because they determine the number of cycles the sorbent particles will go through [19]. The adjustment of the make-up ratio and the solids circulation flow rate depending on the sorbent conversion decay allow a desired average conversion to be obtained. As there is no reactor modeling in the simulation, the make-up ratio is fixed to 0.1 to match the work by Ozcan et al. [15] and represent an average from a previous simulation study by Alonso et al. [70]. A partial capture scenario was chosen for the base case as it would be sufficient to meet current emissions regulations [6,7]. The flue gas composition and flow rate has been described in Table 2.1.

Table 2.4: Base case simulation parameters

Carbonator Temperature	Calciner Temperature	Air reactor Temperature	Carbonator CaO conversion	Make-up ratio	Global CO_2 capture	Reactors pressure drop
650°C	900°C	950°C	20%	0.1	60%	10 kPa

2.4.2 Base case simulation

The base case results provide a first comparison between CaL and both configurations of the combined CaL-CLC. Table 2.5 and Table 2.6 present key results from the three capture process configurations. Note that all the reported solids flow rates correspond to the highest flowrate observed in the process. This corresponds to the outlet of the carbonator for the CaL, the outlet of the air reactor for the CaL-CLC single loop and the outlet of the calciner for the CaL-CLC dual loop.

CO_2 capture processes based on calcium looping are able to generate a significant amount of additional power. Compared to the base power plant output of 550 MWe, the implementation of the capture process yields a 20 to 25% increase in power production depending on the configuration used. While this extra power allows for a reduced size of the main boiler for new power plants, existing plants must be able to handle this additional power to implement a CaL based solution for carbon capture.

The calculated penalties of the three simulated processes are in accordance to other works [15,67] and generally lower than other capture technologies such as conventional amine absorption having penalties of about 10% points [14,15]. The combined CaL-CLC processes result in efficiencies 3 to 3.5% points higher than the CaL case. Such an improvement is due to the absence of both the ASU and purification step in the compression of the CO_2 stream. The combined processes also require less fuel as the energy required to heat the reactants in the calciner is reduced with the absence of oxygen feed to the reactor. Note that if higher flue gas recycle ratios are required to maintain fluidization conditions in the CaL-CLC cases, the increased air infiltration requires the purification step in the CO_2 compression section. This change occurs around a $(CO_2+H_2O)/CH_4$ ratio of 1.5, causing the efficiency difference between CaL and CaL-CLC to fall to about 1.5% points (not shown).

Table 2.5: Key results for base case simulations.

	CaL	**CaL-CLC single loop**	**CaL-CLC dual loop**
Thermal input (HHV, MW_{th})	716.5	604.5	574.3
Extra Gross power (MW_e)	256.0	202.0	199.5
ASU consumption (MW_e)	38.1	-	-
Process fans (MW_e)	17.1	17.5	17.3
CPU (MW_e)	78.1	38.2	37.7
Process auxiliaries (MW_e)	12.8	10.1	10.0
Extra Net power (MW_e)	109.9	136.2	134.6
Global net power (MW_e)	659.9	686.2	684.6
Global net efficiency (HHV%)	31.2	34.2	34.7
Energy penalty (HHV%)	8.1	5.1	4.6

As explained in section 2.2, the two CaL-CLC configurations require the transfer of the energy released in the air reactor to the calciner and this is achieved by using the solids sensible heat. The required solids circulation rates are also shown in Table 2.6. The oxidation of copper generates about 75% of the total heat from the carbon capture process, thus relatively high circulation rates are necessary to transfer the energy to the calciner. Both combined CaL-CLC looping processes require solids flow rate an order of magnitude above the CaL case. The CaL-CLC dual loop does not require energy to heat the copper pellets as they are fed directly from the air reactor at a higher temperature, explaining the difference between the two configurations.

The CaL process also appears to have a higher CO_2 intensity, defined as:

$$CO_2\ intensity = \frac{q_{CO_2\ tot}}{P_{net\ tot}} \tag{2.10}$$

With $q_{CO_2\ tot}$ the total CO_2 remaining in the flue gas after the capture process (kg CO_2/h) and $P_{net\ tot}$ the total net power produced by both the base power plant and the capture process (MW_e).

The difference in CO_2 intensity is due to greater power output from the combined CaL-CLC processes. The slight difference between the two CaL-CLC configurations is observed because the dual loop process captures more CO_2 in the carbonator, reducing the emissions level while having a similar power output, as shown in Table 2.6.

Note that the differences in solids flow rate should also impact the auxiliaries due to the solid transfer between reactors. In the pilot work mentioned in section 2.2, this was achieved either by fluidized bed loop seals [43], an air conveying line [40] or a screw conveyor [44]. Given the high solids circulation rates expected in the process, the design of a loop seal using Basu's method [103] has been estimated. The results showed that the power duties required to operate the loop seals were negligible compared to the power consumed by the reactors fans. Consequently, the exact design of the loop seals and the power associated with their operation are not part of this work.

Table 2.6: Key results for base case simulations – continued.

	CaL	**CaL-CLC single loop**	**CaL-CLC dual loop**	
Solids flow rate (kg/s)	476	7314	CaL side	463
			CLC side	5333
Cu content (wt%)	-	3.8	5.0	
CO_2 intensity (kg CO_2/MW_eh)	371	347	343	

2.4.3 Sensitivity analysis

The effect of the carbonator temperature on the three process configurations can be seen in Table 2.7. The CaL case reaches equilibrium conditions at 707°C while the CaL-CLC are limited to 700°C due to a lower required carbon capture in the carbonator. Operating the carbonator at a temperature closer to that of the calciner reduces the energy required for reactants heating, reducing the fuel consumption. With a reduced methane feed rate, the flue gas flow rate is also reduced and consequently, the power produced by the capture process goes down.

The energy penalty is not affected by this change. The power production efficiency associated with the capture process (not shown) decreases slightly due to the reduction of the power output while having very similar auxiliaries power consumption. However, the reduction of the proportion of low efficiency power (from the capture process) in the overall process increases the overall efficiency, balancing the negative effect.

The solids flow rate increases slightly in the CaL case as it is required to capture more carbon in the carbonator to maintain the global capture level. The opposite trend is observed in the CaL-CLC cases as the circulation of solids is mostly related to the energy balance in the calciner.

Table 2.7: Parameter analysis results - Impact of carbonator temperature. (Calciner temperature = 900°C; air reactor temperature = 950°C)

	Configuration		Carbonator T = 650°C	Carbonator T = 675°C	Carbonator T = 700°C	Carbonator T = 707°C
Thermal input (MW_{th})	CaL		716.5	698.1	679.9	674.6
	CaL-CLC single loop		604.5	589.8	575.0	-
	CaL-CLC dual loop		574.3	559.7	545.0	-
Extra net power (MW_e)	CaL		109.9	104.4	99.0	97.4
	CaL-CLC single loop		136.2	130.9	125.3	-
	CaL-CLC dual loop		134.6	129.2	123.8	-
Penalty (HHV%)	CaL		8.1	8.1	8.1	8.1
	CaL-CLC single loop		5.1	5.1	5.1	-
	CaL-CLC dual loop		4.6	4.6	4.6	-
Solids flow rate (kg/s)	CaL		476	478	480	481
	CaL-CLC single loop		7315	7138	6958	-
	CaL-CLC dual loop	CaL side	463	465	467	-
		CLC side	5333	5198	5061	-
CO_2 intensity (kg CO_2/MW_eh)	CaL		371	373	374	374
	CaL-CLC single loop		346	347	348	-
	CaL-CLC dual loop		343	344	346	-

In order to observe the effect of the calciner temperature independently from the air reactor temperature, both temperatures are varied to maintain a temperature difference of 50°C. The results of this analysis are summarized in Table 2.8. Decreasing the calciner temperature has a similar influence as an increase of the carbonator temperature but with a stronger effect. It causes a reduction of the energy required to heat the solids transferred from the carbonator but also the make-up stream, fuel feed and flue gas recycle stream. The same interpretation can thus be applied here.

A minimum operating temperature of the calciner is reached when the gas composition in the reactor reaches the equilibrium CO_2 concentration at that temperature. This temperature varies depending on the process: 863°C for CaL, 867°C for CaL-CLC single loop and 868°C for CaL-CLC dual loop. A difference is observed because higher methane feed flow rate also produces more water diluting the gas environment.

Table 2.8: Parameter analysis results - Impact of calciner temperature. (Carbonator temperature = 650°C; air reactor temperature = 50°C above calciner temperature)

	Configuration		**Calciner Min. T (°C)**	**Calciner T = 880°C**	**Calciner T = 900°C**
Thermal input (MW_{th})	CaL		672.2	692.4	716.5
	CaL-CLC single loop		579.1	589.1	604.5
	CaL-CLC dual loop		550.2	559.2	574.3
Extra net power (MW_e)	CaL		96.68	102.71	109.93
	CaL-CLC single loop		126.9	130.6	136.2
	CaL-CLC dual loop		125.7	129.1	134.6
Penalty (HHV%)	CaL		8.1	8.1	8.1
	CaL-CLC single loop		5.1	5.1	5.1
	CaL-CLC dual loop		4.6	4.6	4.6
Solids flow rate (kg/s)	CaL		481	479	476
	CaL-CLC single loop		7085	7176	7315
	CaL-CLC dual loop	CaL side	467	465	463
		CLC side	5190	5244	5333
CO_2 intensity (kg CO_2/MW_eh)	CaL		374	373	371
	CaL-CLC single loop		348	347	346
	CaL-CLC dual loop		345	344	343

Table 2.9 presents the influence of the air reactor temperature on the overall process. Changes in energy production depend on the temperature difference between the calciner and the air reactor

and two different trends can be observed depending on the process configuration. In the CaL-CLC single loop process, the copper content of the composite pellet is adjusted along with the recycle rate to obtain a thermally neutral calciner and air reactor. With an increase in air reactor temperature, the copper fractional content becomes higher to maintain the same mass of circulating copper with a reduced global solids flow rate. The total mass of solids transferred from the carbonator to the calciner is thus higher at higher air reactor temperatures, causing an increase in the fuel consumption and energy output.

The change in air reactor temperature in the CaL-CLC dual loop case only affects the amount of support material circulated in the CLC loop. The amount of solids from the carbonator is not affected by this change and the energy production in this case is not changed either. Consequently, the only observable change in the simulation is the solids flow rate. The covered range of temperature causes a modification of the solids circulation by an order of magnitude. The reason for such an important change is that 75% of the energy contained in the fuel is released in the air reactor and that it is transferred to the calciner through the solids sensible heat.

Table 2.10 summarizes the influence of the CaO conversion on the overall process. At higher conversion, the amount of inert solids circulating in the process loops is reduced which decreases the energy required in the calciner, leading to lower energy input and power output. The CO_2 intensity of the processes at higher sorbent conversion increases due to the reduced power output.

The impact of the solids conversion on the energy penalty varies depending on the process configuration. For both CaL and CaL-CLC single loop processes, a decrease of the penalty is observed although the efficiency of the power produced from the capture process decreases (not shown). This is due to the increase of the high efficiency power proportion (from the base power plant) in the overall process, balancing the negative effect. The trend is reversed for the CaL-CLC dual loop configuration. In this case, the overall process is less affected by changes on the CaL-side loop and results in higher energy loss through the process outlets at high solids conversion. The balancing effect mentioned for the two other configuration is then not great enough here and the energy penalty is increased.

Table 2.9: Parameter analysis results – Impact of air reactor temperature. (Carbonator temperature = 650°C; calciner temperature = 900°C)

	Configuration		AR T = 910°C	AR T = 920°C	AR T = 930°C	AR T = 940°C	AR T = 950°C
Thermal input (MW_{th})	CaL-CLC single loop		580.2	586.1	592.2	598.3	604.5
	CaL-CLC dual loop		574.2	574.2	574.2	574.2	574.2
Extra net Power (MW_e)	CaL-CLC single loop		134.9	135.3	135.6	136.0	136.2
	CaL-CLC dual loop		134.6	134.6	134.6	134.6	134.6
Penalty (HHV%)	CaL-CLC single loop		4.7	4.8	4.9	5.0	5.1
	CaL-CLC dual loop		4.6	4.6	4.6	4.6	4.6
Solids flow rate (kg/s)	CaL-CLC single loop		34920	17663	11912	9038	7315
	CaL-CLC dual loop	CaL side	463	463	463	463	463
		CLC side	26330	13206	8832	6645	5333
Copper content (wt%)	CaL-CLC single loop		0.8	1.5	2.3	3.1	3.8
	CaL-CLC dual loop		1.0	2.0	3.0	4.0	5.0
CO_2 intensity (kg CO_2/MW_eh)	CaL-CLC single loop		344	344	345	345	346
	CaL-CLC dual loop		343	343	343	343	343

Table 2.10: Parameter analysis results – Impact of CaO conversion. (Carbonator temperature = 650°C; calciner temperature = 900°C; air reactor temperature = 950°C)

	Configuration		CaO Conversion 10%	CaO Conversion 20%	CaO Conversion 30%	CaO Conversion 40%
Thermal input (MW_{th})	CaL		858.6	716.5	667.3	641.5
	CaL-CLC single loop		741.4	604.5	555.7	530.7
	CaL-CLC dual loop		687.5	574.2	534.4	514.1
Extra net power (MW_e)	CaL		152.7	109.9	95.2	87.5
	CaL-CLC single loop		178.4	136.2	121.2	113.6
	CaL-CLC dual loop		176.5	134.6	119.9	112.4
Penalty (HHV%)	CaL		8.2%	8.1%	8.1%	8.1%
	CaL-CLC single loop		5.3%	5.1%	5.0%	4.9%
	CaL-CLC dual loop		4.5%	4.6%	4.7%	4.7%
Solids flow rate (kg/s)	CaL		863	476	341	272
	CaL-CLC single loop		8971	7315	6725	6422
	CaL-CLC dual loop	CaL side	834	463	332	265
		CLC side	6385	5333	4963	4774
CO_2 intensity (kg CO_2/MW_eh)	CaL		363	371	374	376
	CaL-CLC single loop		339	346	348	349
	CaL-CLC dual loop		335	343	347	348

Increasing the targeted CO_2 capture level causes greater requirements of sorbent and fuel in order to increase the CO_2 capture in the carbonator as well as provide the energy for calcination and reactants heating in the calciner (see Table 2.11). The power production from the capture process becomes more efficient at higher capture level. This is due to a higher proportion of energy recovered from the carbonator duty which does not contribute to energy loss as opposed to material streams when they leave the process. However, the extra power obtained from the capture process is produced with a lower efficiency than that of the base power plant. At higher CO_2 capture levels, the contribution to the overall power output of this low efficiency part increases, resulting in a reduction of the overall efficiency.

Capture levels below 60% were also investigated with the goal to reach the Canadian regulations of 420 kg CO_2/MW_eh. This could be achieved for the CaL process with a capture level of 54.9%. The two other process configurations could not reach the target as the carbonator temperature of 650°C could not be maintained at low capture level. The CaL-CLC single loop capture level was lowered to 52.5% resulting in a carbon intensity of 416 while the dual loop was limited to 414 kg CO_2/MW_eh at 52.4% capture.

Cases where multiple operating parameters were changed are also simulated, providing a preliminary rough optimization of the different processes. The calciner temperature is set 20°C above the minimum found in the previous parametric study. The carbonator is operated at the highest possible temperature, but not lower than the base case temperature of 650°C. The air reactor in the CaL-CLC processes is fixed at 950°C. The CO_2 capture level is reduced to achieve a carbon intensity of 420 kg CO_2/MW_eh or to maintain the carbonator temperature, whichever is reached first. The results of this analysis are presented in Table 2.12. Compared to the base case results, fuel consumption is reduced by about 15% in all cases while the solids circulation rate are decreased by 11% for CaL and 30% for the two CaL-CLC configurations.

Table 2.11: Parameter analysis results – Impact of CO_2 capture level. (Carbonator temperature = 650°C; calciner temperature = 900°C; air reactor temperature = 950°C)

	Configuration		**Capture 60%**	**Capture 70%**	**Capture 80%**	**Capture 90%**
Thermal input (MW_{th})	CaL		716.5	873.1	1044.7	1233.4
	CaL-CLC single loop		604.5	732.4	870.7	1020.4
	CaL-CLC dual loop		574.2	693.5	821.8	960.0
Extra net power (MW_e)	CaL		109.9	143.8	180.9	221.7
	CaL-CLC single loop		136.2	174.4	215.5	260.0
	CaL-CLC dual loop		134.6	171.9	212.0	255.3
Penalty (HHV%)	CaL		8.1	8.8	9.4	10.0
	CaL-CLC single loop		5.1	5.3	5.6	5.8
	CaL-CLC dual loop		4.6	4.8	5.0	5.2
Solids flow rate (kg/s)	CaL		476	603	741	894
	CaL-CLC single loop		7315	8863	10536	12348
	CaL-CLC dual loop	CaL side	463	580	707	843
		CLC side	5333	6441	7632	8916
CO_2 intensity (kg CO_2/MW_eh)	CaL		371	277	184	91
	CaL-CLC single loop		346	255	167	82
	CaL-CLC dual loop		343	253	166	81

Table 2.12: Parameter analysis results – Multiple parameters optimization.

Configuration	CaL	CaL-CLC Single loop	CaL-CLC Dual loop	
Energy input (MW_{th})	614.5	518.1	486.1	
Extra power (MW_e)	85.3	108.3	106.5	
Penalty (HHV%)	7.8%	5.0%	4.5%	
Solids flow rate (kg/s)	422.3	5005.9	CaL side	385
			CLC side	3676
CO_2 intensity (kg CO_2/MW_eh)	420.0	412.7	411.0	

2.5 Conclusion

Process simulations were performed using Aspen Plus for multiple carbon capture process configurations including calcium looping, and combined calcium looping and chemical looping combustion.

The comparison of CaL and the combined CaL-CLC showed that using the combined processes result in a more efficient process, with an energy penalty reduced by up to 40%. However, such results were at the cost of greater solids circulation rates and process complexity, both increasing the capital and operating costs of the process. The alternative CaL-CLC dual loop configuration managed to reduce the solids mass flow rate by about 10 to 20% and produced less power while maintaining very similar energy efficiency. The solids circulation could also be reduced by considering partial CO_2 capture level as the analysis showed that only lower capture levels are required to meet the current regulations in Canada.

The influence of key process operating parameters was also investigated. The air reactor temperature showed to have a strong influence on the mass of solids circulating in the process. Indeed, the temperature difference has a direct effect on the amount of energy transferred to the calciner per unit of solids mass. Results indicated that increasing the ΔT between the air reactor and the calciner from 10 to 50°C changes the solid circulation by an order of magnitude.

To assess the importance of reactors temperatures on both the process operation and sorbent performance degradation, reactor modeling could be implemented in the process simulation but would also require extensive experimental data. This would also provide details on the hydrodynamics of the reactors and allow sizing and costing of the process unit operations.

Chapter 3 - PFBC-CaL system simulation and case analysis

3.1 Introduction

Recently, new regulations in north America have set stringent limits on CO_2 emissions from coal-fired power plants [6,7]. Coal based energy is targeted due to its higher carbon intensity of about 900 kg CO_2/MW_eh, compared to natural gas units emissions of around 400 kg CO_2/MW_eh [8]. While the proportion of natural gas based energy or the use of non-fossil fuels sources is predicted to increase, coal will still account for a significant share of the global power production [1].

Due to the deep reduction required to achieve the imposed levels of emissions, improvements of the process efficiency are not sufficient on their own and carbon capture processes have to be implemented. Amongst the available technologies for CO_2 capture, calcium looping (CaL) offers a relatively low energy efficiency penalty, resulting in a reduced impact on the base power plant compared to other technologies such as amine scrubbing [13,15]. The CaL process is based on the reversible CaO carbonation reaction. The process circulates calcium oxide based solids between two reactors: the carbonator where CO_2 reacts with the solids (equation 3.1); and the calciner where the combustion of a fuel generates energy to calcine the calcium carbonate (equation 3.2). This process is illustrated on Figure 3.1.

$$CaO_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)} \quad \Delta H_{650°C} = -173.3\ kJ/mol \tag{3.1}$$

$$CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)} \quad \Delta H_{890°C} = 169.5\ kJ/mol \tag{3.2}$$

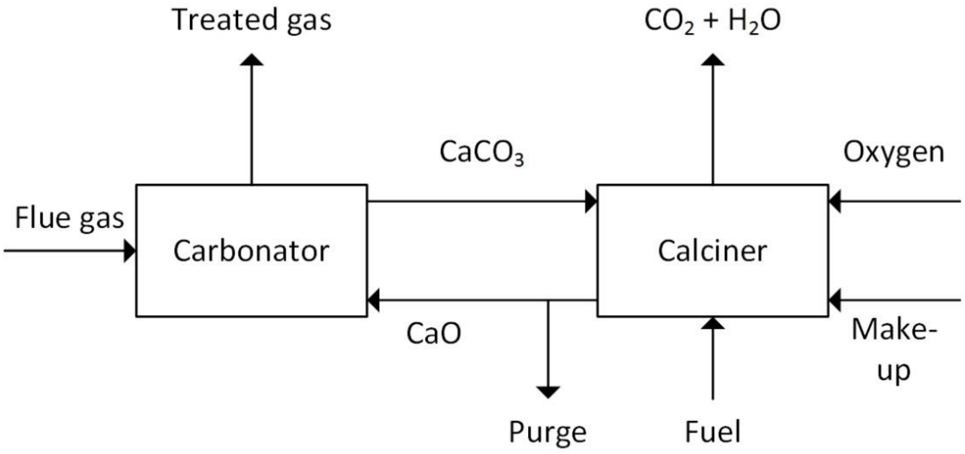

Figure 3.1: Calcium looping process schematic.

Due to the sorbent sintering and/or reaction with other species (e.g., SO_2), the conversion of calcium oxide in the carbonator decreases as the sorbent is cycled in the process [28,39]. To maintain the conversion at a desired level, a make-up of fresh limestone and a purge to remove spent sorbent are implemented. The calciner operates in oxy-combustion mode to avoid the dilution of CO_2 in nitrogen and to reduce the energy required for the compression of the calciner gas outlet.

Carbon emission regulations also push new coal power plants to build high efficiency processes in order to reduce carbon intensity. Pressurized fluidized bed combustion (PFBC) is a particular implementation of fluidized bed combustion where the boiler is operating under pressure [52,104]. Such a process can then recover energy from the hot flue gas using a gas turbine, in addition to the steam cycle used in all power plants. This combined cycle allow efficiencies above 40 HHV% and is the most efficient direct coal combustion power generation technology [52,105].

The work presented here focuses on the simulation of a CaL process to capture CO_2 from the flue gas of a PFBC power plant. Mass and energy balances are performed to investigate the effect of various reactors operating parameters on stream characteristics in a case analysis. Estimations of the energy penalty of CaL on a base power plant are also provided as an additional comparison criterion.

3.2 PFBC Process simulation

3.2.1 PFBC Model Unit

The PFBC is modeled based on the available information on the Japanese unit, Karita P800. This unit produces 360 MW_e with a net efficiency of 41.8 HHV% [105,106]. The power output is split between a steam turbine (290 MW_e) and a gas turbine (70 MW_e).

The main specifications of this unit are summarized in Table 3.1. The fuel fed to the boiler is a paste containing coal, a sorbent for in-situ desulfurization and water. The water content of the paste is approximatively 25 wt% [105]. The combustion takes places at 1.3 MPa and 850°C. A two-stage cyclone is used to reduce the particle concentration before sending the flue gas to the gas turbine. After the turbine, the gas is treated for NO_X and passes through the steam cycle economizer to preheat the boiler feedwater. A last particle removal step is carried by an electrostatic precipitator (EP) before sending the flue gas to the stack.

Table 3.1: Main specifications of Karita P800 [106]

Boiler type	Pressurized bubbling fluidized bed
Total output	360 MW_e
Gas turbine output	70 MW_e
Steam turbine output	290 MW_e
Net efficiency	41.8 HHV%
Gross efficiency	42.8 HHV%
Steam conditions (supercritical)	
Pressure	24.1 MPa
Temperature	566/593°C (Main/reheat)
Gas conditions	
Pressure	Approx. 1.3 MPa
Temperature	Approx. 850°C
De-SOx system	In-situ with limestone
De-NOx system	PFBC combustion + SCR
Dust collector	2 stage cyclones + EP

Fuel analysis of the coal burnt in the Karita PFBC could not be found, thus the unit was simulated burning Highvale coal. Proximate and ultimate analysis of this coal is presented in Table 3.2. The coal feeding rate was adjusted to match the desired power output of 360 MW_e. Note that the power production of the PFBC unit is directly calculated from the fuel HHV and the net efficiency of the PFBC:

$$Coal\ feedrate\ [kg/s] = \frac{Karita\ P800\ net\ output\ [MWe]}{Coal\ HHV\ [MJ/kg] * Net\ efficiency\ [HHV\%]} = \frac{360}{19.03 * 0.418} = 45.26\ kg/s \tag{3.3}$$

The sorbent feed rate was based on results from the operation of the Tidd demonstration project [107] where a calcium-to-sulfur ratio (Ca/S) of 1.5 was sufficient to achieve 95% sulfur capture level.

Table 3.2: As received Highvale coal proximate and ultimate analysis

Proximate analysis		
Moisture	wt%	5.43
Volatile matter	wt%	28.21
Fixed carbon	wt%	40.28
Ash	wt%	26.08
Total	wt%	100
Ultimate analysis		
Moisture	wt%	5.43
Carbon	wt%	49.80
Hydrogen	wt%	2.86
Nitrogen	wt%	0.60
Chlorine	wt%	-
Sulfur	wt%	0.28
Ash	wt%	26.08
Oxygen	wt%	14.95
Total	wt%	100
Calorific analysis (HHV)	MJ/kg	19.03

The hypothetical location of the simulated PFBC unit is in the Keephills (AB) generation station site. The location has an elevation of 671 m (2,201 ft.) above sea level. The barometric pressure is calculated using the following equation [92]:

$$P\,[psia] = 14.696 * \left(1 - (6.8753 * 10^{-6} * Z[ft])\right)^{5.2559} = 13.56\,psia = 93.5\,kPa \tag{3.4}$$

The combustion air was compressed from atmospheric pressure to 1.3 MPa. The composition was assumed to be 79 mol% nitrogen and 21 mol% oxygen. Following the simulation guidelines from the NETL [92], the stage pressure ratio was limited to 2.5, meaning that a triple stage compression was required. Inter stage cooling was implemented so that the gas temperature did not exceed 167°C [108]. Each cooler caused the pressure to drop by 2% of the inlet pressure [92].

The boiler was simulated by a Gibbs reactor. The combustion efficiency was set to 99.5% based on the operation of the Tidd unit [107]. The operating conditions of the boiler were 850°C and 1.3 MPa.

The isentropic efficiency of the turbine was calculated by reproducing the Karita unit performance. The efficiency was adjusted until the power output from the gas turbine was 70 MW_e, resulting in an efficiency of 82.3%.

For the present work, the efficiency calculated above was adopted. The discharge pressure was set to 103.5 kPa, to account for an assumed pressure drop of 10 kPa in the calcium looping carbonator. The mechanical efficiency of the turbine was set to 98.5% [92].

3.2.2 PFBC Simulation

3.2.2.1 Difference with Karita P800

The PFBC unit used in the CaL simulations is based on the Japanese P800 unit but uses a dry fuel feeding system instead. Without water fed with the fuel, the flue gas flow rate is reduced and so is the power output of the gas turbine. On the other hand, the absence of water should increase the output of the steam cycle as the energy from the sensible heat and vaporization of water is now available. However, as the flue gas of the PFBC is also used to pre-heat the boiler feed water of the steam cycle and this cycle is not simulated, the impact on the performance cannot be observed easily.

In this simulation, it is assumed that the steam cycle output is maintained constant at 290 MW_e and the gas turbine output is reduced. All parameters and material feed rate are kept similar to the Karita unit, with the exception of the feeding system type.

3.2.2.2 PFBC simulation results

The simulation of the PFBC unit serves two purposes. Firstly, it generates the flue gas that will be sent to the calcium looping process. Secondly, the power output of the PFBC serves as basis to estimate the impact of CaL on the overall system efficiency. The flue gas temperature, pressure and composition are listed in Table 3.3. The simulation predicted a complete removal of the SO_X , thus it will be assumed for the capture process that there is no sulfur entering the carbonator.

Table 3.3 : PFBC flue gas conditions.

Pressure (kPa)	103.65
Temperature (°C)	442.1
Flow rate (kmol/h)	41358
Composition (mole fraction)	
N_2	0.745
CO_2	0.163
H_2O	0.067
O_2	0.025
$Total\ NO_X$	40.2 ppm

Table 3.4 shows the energy output and net efficiency of the modified PFBC. As explained before, only the reduction of the gas turbine output has been considered.

Table 3.4: Simulated PFBC energy output and efficiency

Parameter	
Fuel energy input (MW_{th})	861.3
Steam cycle output (MW_e)	290
Gas turbine output (MW_e)	55.5
Net efficiency (HHV%)	40.1

3.3 Carbon Capture Process Simulation

3.3.1 Base case simulations

3.3.1.1 Base case parameters

The base case simulations (illustrated in Figure 3.2) include the use of both coal and natural gas as fuels for the calciner. Between these two simulations, all the operating conditions are identical, with the exception of the fuel nature and the presence of sulfur for coal cases. The sulfur causes a slight increase in the CaO circulation rate and the presence of $CaSO_4$ circulating in the loop as well.

Note that the influence of ashes on both the CaO conversion and the energy balance is not considered here. The quantity of ashes introduced in the system depends on the ash content of the coal used in the calciner. Compared to the amount of circulating solids, the fuel feed rate is an order of magnitude lower, with the ash feed rate being only a fraction of this. Regarding the energy requirement in the calciner, heating the coal represent about 10% of the total energy demand, heating the ashes thus represents a few percent, depending on the ash content and composition of the ashes.

Base case simulations parameters are presented in Table 3.5. The reactors operate at atmospheric pressure and at a temperature within the range of published experiments and pilot units operation [20,40,43]. The conversion of the CaO in the carbonator is tied to the solids circulation rate, the make-up rate and the sorbent properties. The calcium oxide conversion comes from thermogravimetric analyzer (TGA) experiments [16] showing the sorbent conversion decay with increasing the number of process cycles (Figure 3.3).

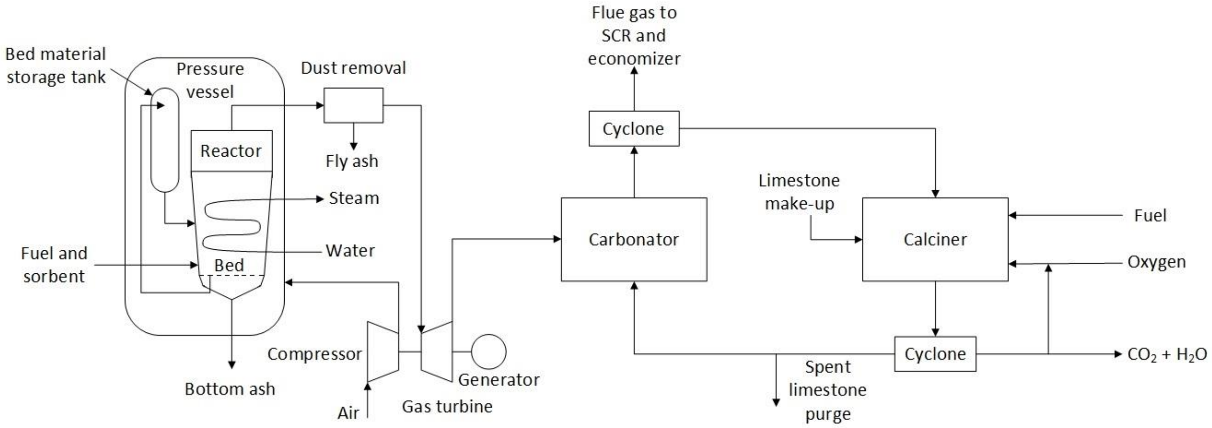

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Figure 3.2: PFBC-CaL system schematic

Table 3.5: Base case simulation parameters.

Parameter	Value
Carbonator Temperature (°C)	650
Calciner Temperature (°C)	900
Reactors pressure drop (kPa)	10
Calcium oxide conversion (%)	21.9 – 26.3
Make-up (F_0/F_{CO2})	0.05
Carbon intensity (kg CO_2/MW_eh)	420

Due to the sorbent conversion decline as the particles are cycled, it is required to estimate the residence time of the particles in the process. In addition, a model is also required to predict the conversion of particles that have a cycle number not covered by the TGA results. The conversion of the particles that went over N process cycles X_N is calculated from the following equation [20]:

$$X_N = \frac{1}{\frac{1}{1 - X_r} + kN} + X_r \tag{3.5}$$

Where k is a decay parameter and X_r is the residual conversion at high cycle numbers.

The average conversion of all the solids in the carbonator, X_{ave}, is a weighted average over the cycle numbers [19] :

$$X_{ave} = \sum_N r_N X_N \tag{3.6}$$

$$r_N = \frac{F_0 F_R^{N-1}}{(F_0 + F_R)^N} \tag{3.7}$$

Where r_N represents the fraction of particles of cycle number N, F_R is the molar flow rate of CaO fed to the carbonator and F_0 is the molar flow of $CaCO_3$ in the make-up stream. The sum in equation 3.6 is an infinite sum. During this project, enough cycles have been considered to account for over 95% of the solids.

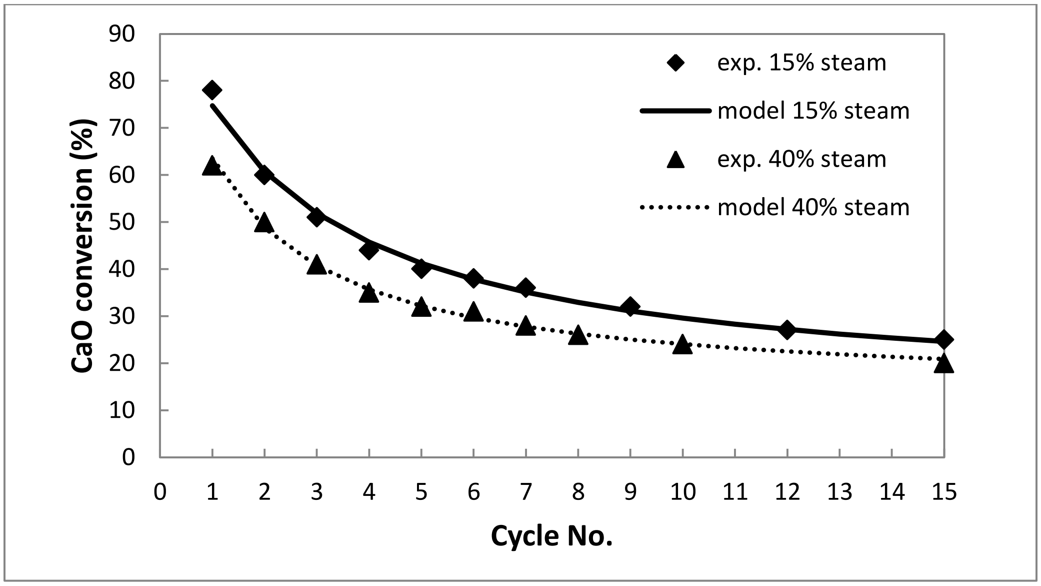

Figure 3.3: CaO sorbent conversion decay curve, experimental [16] and model results.

The two chosen decay curves are shown in Figure 3.3 and the fitted parameters for the conversion model are presented in Table 3.6. The experimental data was taken from published

Cadomin tests over multiple cycles [16]. The curve for the 15% steam condition is used for coal case simulations and the 40% steam is used for natural gas case simulations.

Note that the direct effect of the presence of sulfur or ashes on the sorbent conversion is not included in the experimental data. In the simulations, additional circulating CaO is added to account for the sulfur.

Although the 15% steam case provides higher conversion below 15 cycles, the model predicts lower conversions than the 40% case at higher cycle numbers (X_r is lower). The predictions show that above 63 cycles, the CaO sorbent shows better conversions in a 40% steam atmosphere. If a significant fraction of the solids remain in the process for more than 63 cycles, it can be expected that the coal cases will require more solids.

Table 3.6: CaO sorbent conversion model parameters.

	Natural gas cases	**Coal cases**
k	0.8480	0.4603
X_r	0.1366	0.1216

The make-up rate of limestone and the circulation of calcium oxide are both defined by ratios based on the amount of CO_2 in the flue gas to be treated:

$$Make-up\ ratio = \frac{F_0}{F_{CO_2}} \tag{3.8}$$

$$Circulation\ ratio = \frac{F_R}{F_{CO_2}} \tag{3.9}$$

Where F_{CO_2} is the molar flow rate of CO_2 in the flue gas from the power plant.

The amount of circulating CaO and the fuel feed rate are calculated so that the calciner neither produces nor consumes energy and to meet the Canadian carbon intensity (420 kg CO_2/kW_eh) emissions regulation [6].

The production of oxygen is not simulated and the air separation unit (ASU) energy consumption is calculated from a specific energy consumption of 231 $kW_eh/ton\ O_2$ [93]. The oxygen is fed in excess to have a remaining 2.7 mol% (dry basis) in the gas outlet of the calciner [92].

The recycling of the calciner flue gas is implemented as it is commonly required to maintain fluidization conditions and reduce the oxygen concentration in the fluidization gas. While the process simulation does not include a hydrodynamic model or sizing of the reactor, the recycle ratio is calculated to limit the oxygen concentration to 30 mol% at the reactor inlet, in agreement with the base case of experiments conducted by the DoE [93]. The recycled flue gas stream is cooled to limit the booster temperature to 190°C. The booster compensates for the calciner pressure drop and increases the gas stream pressure by 10 kPa.

The energy required to compress the concentrated CO_2 is calculated from a compression process with inter-stage cooling simulation illustrated in Figure 3.4. Depending on the operating pressure of the calciner, 4 or 5 compression stages are required. The condensate after each cooling step, mainly composed of water, is separated before sending the gas phase to the next compression stage. The CO_2 stream is compressed this way until it can be condensed at 20°C, after which it is pumped to the final pressure of 15 MPa.

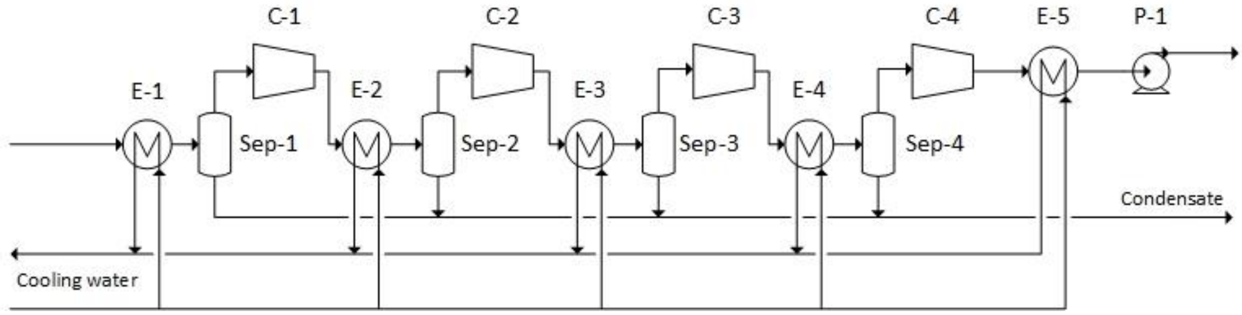

Figure 3.4: CO_2 compression train schematic.

3.3.1.2 Base case results

The impact of the calcium looping process on the PFBC energy efficiency is calculated by taking into account the PFBC unit performance, the fuel feed rate to the calciner, the recycle booster energy consumption, the ASU and the compression train for the CO_2 stream. It is assumed that extra power can be generated from the CaL process. The heat integration with a steam cycle is not simulated but the gross efficiency associated with that power generation is estimated to be 35.4 HHV%, based on the work presented in Chapter II.

Table 3.7 shows the impact that the calcium looping process has on the PFBC energy efficiency. It can be seen that the energy penalty comes mostly from the ASU and the CO_2 compression and that they have similar contributions. The energy input of the calciner is mostly consumed to heat the solids from the carbonator and the make-up stream (around 20%) as well as for the calcination of $CaCO_3$ (approximatively 42%). Heating the recycle stream is another significant part of the energy requirement (around 21%), the rest being sensible heat to raise the temperature of the fuel and the oxygen.

Relative to natural gas, using coal as a fuel results in lower solids circulations. Due to the high carbon content of coal, lower carbonator CO_2 capture is required to meet the regulations as the carbon introduced in the fuel is captured directly. Over 83% of the sorbent is cycled less than 63 times, explaining the higher average sorbent conversion for the coal case: 26.3% against 21.9% for natural gas. Only 37% of the sorbent is cycled 15 times or less, indicating that further testing might be required to increase the confidence of conversion predictions at high cycle numbers.

However, coal is also associated with a higher energy penalty. Higher overall capture level is required to meet the capture target: 52.9% for natural gas and 59.4% for coal. Consequently, more CO_2 is captured in the coal cases, explaining the higher compression duty and the lower overall efficiency (see Table 3.7).

Table 3.7: Calcium looping and overall process efficiency.

	Natural gas case	Coal case
PFBC net power output (MW_e)	345.5	345.5
PFBC net efficiency (HHV%)	40.1%	40.1%
Estimated CaL gross efficiency (HHV%)	35.4%	35.4%
Fuel energy input (MW_{th})	351.9	349.4
ASU (MW_e)	23.3	22.7
CO_2 compression (MW_e)	21.5	27.7
Recycle booster (MW_e)	1.4	1.4
Overall net output (MW_e)	423.9	417.5
Overall net efficiency (HHV%)	34.9%	34.5%

The flow rate of different reactants is listed in Table 3.8. As explained previously, less CaO is required in the coal case but the difference in total solid circulation is reduced due to the additional $CaSO_4$ present in the coal case.

Table 3.8: Calcium looping key reactants flow rates.

	Natural gas case	Coal case
Fuel feed rate (t/h)	24.3	66.1
Oxygen feed rate (t/h)	100.8	98.3
CaO to carbonator (t/h)	690.1	586.4
Make-up flow rate (t/h)	33.7	33.7
Max. solids flow rate (t/h)	808.5	732.6

3.3.2 Sensitivity analysis

Multiple parameters have been modified during a sensitivity analysis to evaluate their influence on the process performance. Most of the results here are only shown with natural gas fed to the calciner as the trends are identical for both fuels. Coal cases are shown when additional information can be obtained from the results.

If the temperature difference between the reactors is lowered, the energy required to heat the reactants to the calciner temperature can be reduced. It was shown earlier that the material streams sensible heat accounts for a significant part of the energy requirement in the calciner. The carbonator temperature is increased until the carbonation equilibrium does not yield the required carbon capture in the carbonator. Similarly, the calciner temperature is decreased until the calcination reaction is not possible given the CO_2 partial pressure in the reactor.

Lower temperatures in the reactors also limit the sorbent sintering and higher conversion should be observed. Due to limited conversion data, the same TGA results are used between the different cases. At lower temperatures, the calculated amount of sorbent required for the capture should then be a conservative estimate.

The carbonator temperature could be further increased if the total pressure in the reactor is increased. The equilibrium temperature can be calculated based on the CO_2 partial pressure using the following relationship [18]:

$$\log P[atm] = 7.079 - \frac{38000}{4.574 * T[K]} \tag{3.10}$$

While compressing the flue gas would require excessive amounts of energy, the discharge pressure of the gas turbine can be modified. Considering the challenges to transfer solids between reactors operating at different pressures, pressurized cases will be limited to 200 kPa. In those cases, the carbonator temperature is set at its maximum and the calciner temperature at its minimum based on thermodynamic equilibrium. When the carbonator pressure is increased, the treated flue gas is then expanded to atmospheric pressure, also acting as a reheater for the gas turbine. The pressurization of the whole system is also tested.

The make-up rate F_0 is varied from 0.01 to 0.05. Due to the specification of the carbon intensity of the process, F_0 and F_R cannot be varied independently (they would provide the exact same information). Both values will be reported together.

3.3.2.1 Sensitivity analysis results

a. Carbonator temperature

The maximum operating temperature possible for the carbonator was found to be 751°C for the natural gas cases and 752°C for the coal cases.

An increased carbonator temperature reduces the energy required to heat the solids to the calciner temperature hence reducing the fuel and oxygen consumption (Table 3.9). The extra power generated from the capture process is also reduced and in order to maintain the targeted carbon intensity, the CaO circulation rate is increased. This is the consequence of a reduction of the fuel feed rate, leading to higher carbonation efficiency requirement to maintain the desired carbon intensity.

The decrease of the energy penalty can be attributed to two factors. Firstly, at higher carbonation temperatures, the net efficiency of the power generation from the CaL increases due to the fixed estimated gross efficiency and the reduction of power consumption for the ASU, the recycle booster and the CO_2 compression. Secondly, as the power output of the CaL is reduced, the proportion of high efficiency power (from the PFBC) in the total power output increases thus reducing the impact of the lower efficiency power from the CaL.

Table 3.9: Case analysis – Natural gas – Effect of carbonator temperature (Calciner temperature = 900°C).

Carbonator temperature (°C)	**650**	**700**	**751**
Energy penalty (HHV%)	5.2	5.1	5.0
Fuel feed rate (t/h)	24.3	23.2	22.0
Oxygen feed rate (t/h)	100.8	96.6	92.0
CaO to carbonator (t/h)	690.1	709.9	719.0
Make-up flow rate (t/h)	33.7	33.7	33.7
Max. solids flow rate (t/h)	808.46	824.1	841.2

b. Calciner temperature

The lowest calciner temperature was calculated to be 860°C for the natural gas cases and 880°C for the coal cases (see Table 3.10 for natural gas results). The difference in temperature is due to the composition of the two fuels used. The flue gas resulting from the combustion of natural gas contains significantly more water vapour, decreasing the CO_2 partial pressure and allowing calcination at lower temperatures.

The effect of the calciner temperature is similar to that of the carbonator temperature. As the reactors temperatures are brought close to each other, it reduces the fuel and oxygen consumption, along with the energy penalty. The solid circulation rate also increases to maintain the 420 kg CO_2/MW$_e$h carbon intensity.

Table 3.10: Case analysis – Natural gas – Effect of calciner temperature (Carbonator temperature = 650°C).

Calciner temperature (°C)	**860**	**880**	**900**
Energy penalty (HHV%)	5.0	5.1	5.2
Fuel feed rate (t/h)	22.8	23.5	24.3
Oxygen feed rate (t/h)	95.1	97.9	100.8
CaO **to carbonator (t/h)**	708.8	699.4	690.1
Make-up flow rate (t/h)	33.7	33.7	33.7
Max. solids flow rate (t/h)	829.6	819.0	808.5

c. Sorbent make-up rate

As the sorbent make-up rate is increased, the circulation rate of CaO has to be reduced in order to maintain the required capture rate and the carbon intensity of the process (Table 3.11) because the make-up stream is fed as limestone ($CaCO_3$). As a consequence, there is a higher proportion of solids with a low cycle number and the CaO conversion increases.

Table 3.11 shows that the fuel consumption reaches a minimum at a make-up ratio between 0.025 and 0.0375. This can be explained by the effect that the make-up rate has on the required circulation rate. At low make-up rate, a large quantity of solids is circulated to reach the desired capture level. The energy required to heat these solids and calcine the $CaCO_3$ in that stream is then high and makes the total energy consumption high as well.

When increasing the make-up-rate, the energy requirement for the circulating solids decreases and that of the make-up stream increases. The total energy consumption (directly related to the fuel feed rate) decreases at first but start increasing once the make-up stream becomes more important. A similar observation can be made for coal for which the optimum make-up ratio is between 0.0375 and 0.05. This optimum value depends on the sorbent conversion and might be biased due to a lack of data available above 15 process cycles.

Table 3.11: Case analysis – Natural gas – Effect of sorbent make-up rate.

F_0/F_{CO_2}	**0.010**	**0.0250**	**0.0375**	**0.05**
F_R/F_{CO_2}	2.54	2.20	2.00	1.83
Energy penalty (HHV%)	5.05	5.08	5.12	5.17
CaO **conversion (%)**	15.7	18.1	20.0	21.9
Fuel feed rate (t/h)	24.2	24.0	24.1	24.3
Oxygen feed rate (t/h)	100.3	99.8	100.1	100.8
CaO **to carbonator (t/h)**	958.1	831.9	753.4	690.1
Make-up flow rate (t/h)	6.7	16.9	25.3	33.7
Max. solids flow rate (t/h)	1076.0	950.3	871.9	808.5

d. Reactors pressure

Changing both the carbonator and calciner temperatures in a same case allows further reduction of the energy allocated for the sensible heat of the reactants. This explains lower energy penalty than cases where only the carbonator or calciner temperature were modified (minimum penalty of 5.0 HHV% for natural gas cases). When operating the carbonator under pressure, the increased CO_2 partial pressure allows a higher operating temperature before reaching equilibrium conditions (see Table 3.12 and Table 3.13). The carbonator also acts as a reheater for the expander located after the reactor, recovering more total energy on the flue gas when compared to the gas turbine alone in the atmospheric pressure case (55.5 MW_e versus 72.0 MW_e). It should be noted that depending on the case, the carbonator gas outlet or the expander outlet do not have the same temperature (751°C in the atmospheric case and 659°C in the pressurized carbonator case) and that an eventual effect on the steam cycle is not accounted for.

The operation of both the carbonator and the calciner under pressure requires a higher calciner temperature due to a higher CO_2 partial pressure. However, the efficiency reduction due to that higher temperature is compensated for by the reduction of the CO_2 compression, resulting in a penalty lower than the pressurized carbonator case. It is also important to consider that higher temperatures should have an impact on the CaO conversion as it increases the sintering of the sorbent. This effect is not considered in the simulation, meaning that either the solids circulation rate or the make-up flow should be higher in reality to maintain the same conversion level when the calciner temperature is increased, leading to a higher energy penalty.

Table 3.12: Case analysis - Natural gas – Effect of reactors pressure.

Case name	Modified base case	Press. carb.	Press. system
Carbonator temperature (°C)	751	798	799
Calciner temperature (°C)	862	863	913
Energy penalty (HHV%)	4.8	3.1	2.9
Fuel feed rate (t/h)	20.6	18.7	20.3
Oxygen feed rate (t/h)	86.4	78.5	84.7
CaO to carbonator (t/h)	737.5	706.4	672.1
Make-up flow rate (t/h)	33.7	33.7	33.7
Max. solids flow rate (t/h)	862.0	826.9	788.2

Table 3.13: Case analysis - Coal – Effect of reactors pressure.

Case name	Modified base case	Press. carb.	Press. system
Carbonator temperature (°C)	750	798	799
Calciner temperature (°C)	882	882	935
Energy penalty (HHV%)	5.4	3.6	3.4
Fuel feed rate (t/h)	58.6	53.3	57.6
Oxygen feed rate (t/h)	87.6	79.8	85.9
CaO to carbonator (t/h)	617.6	587.5	553.9
Make-up flow rate (t/h)	33.7	33.7	33.7
Max. solids flow rate (t/h)	766.5	729.0	691.1

3.3.3 Steam injection

In order to reduce the CO_2 partial pressure in the calciner, the use of steam injection is considered. The goal of this analysis is to dilute the calciner atmosphere in order to allow lower calciner temperature and potentially reduce the energy penalty. The steam is assumed to be saturated steam at a pressure equal to the calciner operating pressure plus the reactor pressure drop (i.e., 103.5 kPa).

As mentioned earlier, the available TGA data for the sorbent conversion is limited and steam concentration above 40% could not be found. The presented results only show natural gas cases and use the same sorbent conversion decay curve that was presented before.

Steam injection has multiple effects on the overall process. It reduces the CO_2 partial pressure in the calciner and allows lower operating temperatures in that reactor, both effects should improve sorbent conversion. However, as the identical TGA data is used for the steam injection simulation, that positive effect cannot be observed. In addition, the steam is assumed to be generated from the cooling of the flue gas and the flue gas recycle. This would reduce the energy recovered from the CaL process to generate power and thus reduce the efficiency; but this cannot be observed either as the integration in a steam cycle was not performed. The sorbent performance improvement and the energy efficiency reduction are counteracting each other and at this point, and it cannot be concluded which effect dominates. The results of this section should then only be used as a general guideline before detailed data can be used in the simulation.

The cases explored here correspond to a dilution sufficient to reduce the temperature of the calciner by 10, 20 and 40°C compared to the modified base case from Table 3.12.

3.3.3.1 Steam injection results

The results (see Table 3.14) show that the injection of steam does not improve the efficiency despite reducing the calciner temperature. This is due to the energy required to heat the steam to the reactor temperature compensating for the gain obtained through the temperature reduction.

Unlike when the calciner temperature was changed in the earlier case analysis, the reduction of temperature here causes a decrease of the solids circulation rate between the reactors. This can again be attributed to the sensible heat of steam. This extra energy requirement compared to a case without steam injection increases the fuel consumption which then increases the carbon capture level. To maintain the same carbon intensity, the extent of the carbonation reaction in the carbonator has to be reduced with a lower solids flow rate.

Table 3.14: Steam injection - Natural gas - Results

Calciner temperature (°C)	862	852	842	822
Carbonator temperature (°C)	751	750	750	750
Steam flow rate (t/h)	0	19.6	43.6	106.1
Energy penalty (HHV%)	4.8	4.9	5.0	5.1
Fuel feed rate (t/h)	20.6	20.9	21.3	22.5
Oxygen feed rate (t/h)	86.4	87.5	89.0	94.0
CaO to carbonator (t/h)	737.5	735.9	730.9	714.5
Make-up flow rate (t/h)	33.7	33.7	33.7	33.7
Max solids flow rate (t/h)	862.0	860.22	854.5	836.0

3.4 Conclusion and Recommendations

In this work, carbon capture from a PFBC unit flue gas using a CaL process was investigated. The Aspen Plus simulation of both the combustion unit and the carbon capture process led to the estimation of energy efficiency penalty that CaL would have on the base process. The comparison of natural gas and coal as fuels for the calciner was performed as well as a sensitivity analysis on the operating conditions of the process.

The fuel comparison showed natural gas to be a better choice as the presence of sulfur and reduced water vapor content in coal combustion gases resulted in higher required solid circulations and lower efficiencies. Under identical conditions, CaL using coal had an overall net efficiency of 34.1 HHV% while the natural gas based process led to a value of 34.9 HHV%.

The sensitivity analysis highlighted the importance of the temperature difference between the reactors and how it affected the process performance. Heating the carbonated solids to the calciner conditions used about 22% of the energy released in the calciner, showing that high temperature carbonation and low temperature calcination could significantly reduce the fuel consumption.

An optimal sorbent make-up flow rate leading to minimum fuel consumption was identified. The calculation of the minimum depends on the sorbent performance and operating conditions of the process.

The operation of the capture process at higher pressures was considered as PFBC units are the only direct combustion power plants offering this possibility without having to compress the flue gas. Significant improvements of the process efficiency were obtained as the higher pressure allowed higher carbonator temperatures and the reheating of the gas turbine discharge gas.

Steam injection was also considered but did not show promising results. The simulations showed that the sensible heat of the steam was more important than the benefit obtained from the calciner temperature reduction.

While the use of sorbent conversion experimental data and a predictive model allow for more accurate simulations, it was pointed that the sorbent conversion decay is affected by the reactors temperature and their gas environment. It is particularly important to use conversion data of highly cycled particles due to the importance of the residual conversion in the calculation of the average carbonation of the particles in the process. It is recommended that future studies involving CaL use experimental data obtained in the same conditions as the simulation.

Specific recommendations can be made based on the results presented in this chapter. The criterion of including 95% of the solids was reached after a prediction of about 120 while 80 cycles were enough to include 90% of the solids. This could be a target for a new experimental campaign. If such high number of process cycles cannot be practically obtained, a new limit could be decided on by determining an approach criterion to the plateau of the sorbent conversion. A small conversion increment threshold would be an example of an approach function.

The investigated reactor conditions should include low temperatures for the calciner and high temperatures for the carbonator. The results from section 3.3.2.1.d could be used but are calculated at thermodynamic equilibrium and would require the addition of a temperature driving force. For process operating at atmospheric pressure and with a driving force of 20°C, this would result in 731°C carbonation and 882°C calcination.

The gas composition during the calcination step should be based on the fuel used. Matching coal cases would typically result in higher CO_2 content (matching the modified base case explained in 3.3.2.1.d: 82.3% CO_2, 14.8% H_2O, 2.3% O_2, 0.6% N_2) compared to natural gas cases (62.0% CO_2, 35.9% H_2O, 1.7% O_2, 0.4% N_2).

Chapter 4 - Conclusions and recommendations

The objective of this thesis was to simulate and compare carbon capture processes based on the use of calcium oxide as a solid sorbent. While being a competitive capture process with a relatively low energy penalty, two potential points of improvement have been highlighted. The production of oxygen necessary to operate the calciner is energy intensive and is the second most important contributor to the penalty of CaL. Replacing the ASU by CLC was proposed and two solid looping configurations were explored. The second improvement studied was the operation of the carbonator under pressure, allowing higher operating temperature. Reducing the temperature difference between carbonator and calciner reduces the fuel consumption as heating the carbonated solids is a significant part of the calciner energy balance.

The combination of CLC with CaL was implemented using copper as an oxygen carrier. The first configuration investigated was circulating CaO-CuO-Support composite pellets between three reactors. The use of CLC indeed resulted in the increase of net energy efficiency from 31.2 HHV% for CaL to 34.2 HHV%, representing a 37% reduction of CaL penalty. CaL based capture processes also produce extra power: a 19% output increase was observed for CaL and 27% for CaL-CLC. The efficiency improvement was at the cost of higher solids flow rate and process complexity due to the use of an additional reactor and solids sensible heat to transfer energy to the calciner. The separation of copper and calcium based solids in two separate loops showed reduced solids flow rate, although still significantly higher than for CaL. The efficiency was also improved to 34.7 HHV%, but this configuration was based on the assumption that the two solids could by separated continuously or that the calciner could be heated indirectly. A sensitivity analysis was also performed, highlighting that capture levels between 50 and 55% are sufficient to meet the current regulations. In addition, the temperature difference between calciner and air reactor was shown to strongly influence the required solids circulation.

The implementation of CaL to a PFBC unit was explored for its potential to operate the carbonation at higher pressures without having to compress the flue gas. Both natural gas and coal were used to fire the calciner. The fuel effect on the sorbent was assumed to be related to the gas environment in the calciner. Natural gas showed better results, mainly due to its lower carbon content. The operation of the carbonator at a pressure of 2 atmosphere and the optimization of the operating temperature of the reactors based on equilibrium decreased the penalty from 4.8 HHV% (atmospheric case) to 3.1 HHV% (pressurized case). Operating both the carbonator and the calciner at 2 atmosphere further reduced the penalty to 2.9 HHV%. However, the pressurized calciner required higher temperatures and the impact of this temperature increase on the sorbent conversion could not be estimated due to a lack of data. A reduction of the conversion, causing an increase of the energy penalty is however expected. Further reduction of the calciner temperature could be achieved by using steam injection with the aim to reduce the fuel consumption even lower. While the complete effect of steam on the sorbent conversion could not be assessed in this work, the preliminary calculations showed that the energy required to heat the steam to the reactor temperature causes a reduction of the process energy efficiency.

Both options considered in this thesis lead to reduction of the energy penalty associated with the capture of CO_2. However, several assumptions have been made and the simulations would benefit from additional information:

- The CaL-CLC simulations estimated the conversion of calcium oxide and performed a sensitivity analysis. However, conversion should be calculated from experimental data on sorbent conversion decay with cycle number. An experimental campaign using the composite pellets under different reaction conditions would result in a more accurate simulation.
- It was mentioned that although CaL-CLC improves the process energy efficiency, it also require a high solids circulation. The transfer of solids between reactors is performed using loop seals, similar to a small fluidized bed. The energy consumption of such seals was not accounted for and would require the sizing of the reactors to calculate the actual pressure drop through the bed of solids. This addition would then account for the drawback of the combined process in the energy efficiency calculations as well.
- In the PCaL analysis, sorbent conversion data was used but was limited to 2 concentrations of steam and temperatures. Similarly to the CaL-CLC recommendations, further testing of limestones in varying conditions would make the results more accurate. In addition, it was observed that the residual conversion of the sorbent has an important effect on its performance. Testing of the sorbent at cycle numbers greater than 15 would make the results more reliable.

- The heat integration in the PCaL process was assumed based on the gross efficiency of previous CaL work. The addition of the steam cycle and the energy recovery in the simulation would make the efficiency calculations more reliable.

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