Comparison of energy penalty in post-combustion and pre-combustion calcium looping systems using aspen plus

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Abstract
Calcium looping (CaL) is a recent technology that utilizes calcium oxide (CaO) and the carbonation-calcination equilibrium reactions to capture carbon dioxide (CO_2) from the flue stream of fossil fueled power plants. In this paper, system level simulations are developed in Aspen Plus to calculate the energy penalty of introducing calcium looping in a coal fired power plant. Both post-combustion and pre-combustion capture scenarios are investigated. The relationship between various flow ratios, the conversion rate of CaO, and the carbon capture efficiency is used to validate the Aspen Plus model for the calcium looping process; it agrees well with the experimental data and simulation results available in the literature. The simulation shows an increasing marginal energy penalty associated with an increase in the carbon capture efficiency, which limits the maximum carbon capture efficiency in real-world applications of calcium looping to between 95% and 98% before the energy penalty becomes too large.
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Keywords: Calcium looping; Process simulation; Pre-combustion capture; Post-combustion capture; Computational fluid dynamics.

1. Introduction
New technologies for carbon capture, utilization and storage (CCUS) have become an active area of research in recent years to combat the "unequivocal" warming of the global climate system [1]. Various approaches have been proposed for the capture of carbon dioxide(CO_2) from power plants, for example the pre-combustion capture with integrated gasification combined cycle and post-combustion treatment with sorbent-based absorption, and oxy-combustion. The use of calcium oxide (CaO) as the sorbent to capture CO_2 from the flue stream of a power plant has been proposed in several studies [2-6]. This process, known as calcium looping, is a versatile process that can be implemented in both post-combustion and pre-combustion scenarios in a power plant; it can also be utilized for carbon capture from other sources of greenhouse gases such as steel mills and cement factories.

The calcium looping process consists of two interconnected reactors called the carbonator and the calciner in which the carbonation and calcination reactions respectively take place. The overall carbonation-calcination equilibrium reaction is given by

$$CaO_{(s)} + CO_{2(g)} \rightleftharpoons CaCO_{3(s)} \tag{1}$$

The carbonation reaction entraps the CO_2 from the flue gas stream using the calcium oxide sorbent to form calcium carbonate ($CaCO_3$).The flue stream exiting the carbonator is CO_2-lean and can be

exhausted into the atmosphere in the case of post-combustion CaL or can be used for clean combustion in the case of pre-combustion CaL. The solid $CaCO_3$ from the carbonator is transported to the calciner where it is heated to decompose into CaO and CO_2.

The calciner produces a stream of pure CO_2 that is sent for pressurized storage for subsequent sequestration or use. The CaO is transported back into the carbonator to complete the loop. The typical setup for CaL mirrors that of a chemical looping combustion (CLC) plant, with the carbonator and calciner analogous to the air and fuel reactor respectively in CLC, and the $CaO/CaCO_3$ equivalent to the oxidized/reduced metal oxide oxygen carrier in CLC. A schematic representation of the CaL process is shown in Figure 1. The make-up CaO flow and solids disposal are required to maintain reactivity of the sorbent; if the CaO was not replenished, the reaction rates would degenerate over time as the loop ran its course.
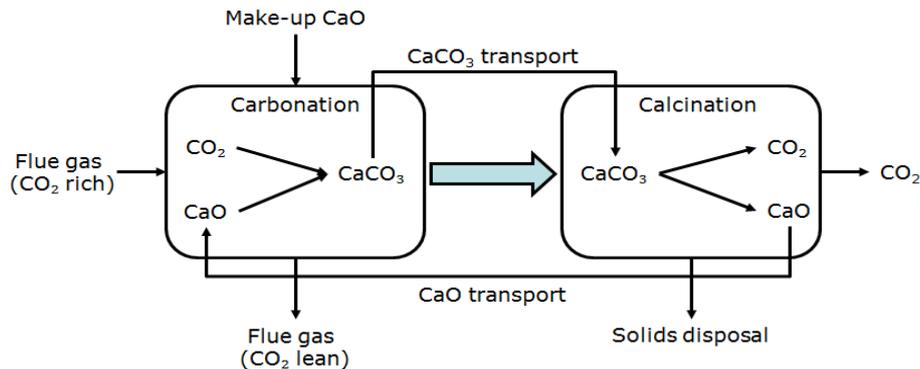

Figure 1. Schematic representation of a calcium looping system with interconnected reactors.

The energy penalty is often used to characterize the performance of a carbon capture system. In the context of CaL, the energy penalty is a measure of the portion of energy consumed by the carbonator and calciner and the transport of solids between the two reactors compared to the total energy released by the combustion process. The goal of a carbon capture process is to consume the least amount of energy while achieving a high CO_2 capture efficiency. Therefore, the estimation of the energy penalty in CaL is of great interest in the field of CCUS.

In this paper, process models of calcium looping are developed using Aspen Plus to determine the energy penalty in a CaL system. The two main types of calcium looping systems are studied-post-combustion capture and pre-combustion capture-and their performance in terms of the energy penalty is compared. It should be noted that only thermal energy analysis is performed; the turbines and generators in the power plant are not included. Since heat energy does not transform into other forms of energy such as mechanical or electrical energy, the term 'heat' is used interchangeably with 'energy' in this paper. Aspen Plus also does not provide any means of calculating the energy required to transport the solids between the carbonator and calciner and back. However, from the work of Lyngfelt et al. [7] on the solids transport in CLC, the energy penalty of the transport process is typically less than 1% of the energy released by combustion.

2. Calcium looping with post-combustion capture
In post-combustion capture, the carbonator and calciner are included downstream of the combustion process to capture the CO_2 from the flue gases generated by the combustion of coal. In order to investigate the energy penalty associated with a calcium looping system for post-combustion capture, the overall heat production from a power plant without and with calcium looping must be determined. In the simulation, all inlet materials are set at room temperature and the inlet coal properties are set as received rather than using those of dry coal.

2.1 Process simulation setup
The materials used in the simulation include conventional and non-conventional components. Pure materials, which include all possible simple substances and chemical compounds comprising the elements C, N, O, H, S, and Cl that might be produced during the chemical reactions, are designated as conventional. Properties for conventional materials are obtained from the Aspen Plus data bank. Mixtures such as coal and ash are designated as nonconventional solids.

2.1.1 Combustor

The doctoral dissertation of Sivalingam [8] is used as a basis for developing the process models of calcium looping in this paper. Therefore, Illinois #6 coal is used in the current simulation to match the work reported by Sivalingam [8] who also used Illinois #6 coal. Since coal is designated as a nonconventional solid in Aspen Plus, its attributes are defined based on the physical and chemical properties of the coal used. The RYIELD reactor block is employed in Aspen Plus to decompose the nonconventional material coal into its constituent conventional materials to be able to simulate their reactions. The products of decomposition are set as the simplest components-Ash, H_2O, C, H_2, N_2, Cl_2, S, and O_2. Mass percentages for the component yields are set based on the proximate and ultimate analysis of the Illinois #6 coal obtained from the work of Sivalingam [8] which is summarized in Table 1.

Table 1. Physical and chemical properties of Illinois #6 coal.

Proximate Analysis (wt. %)				Ultimate Analysis (wt. %)					
Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	Cl	S	O
11.12	34.99	44.19	9.70	80.51	5.68	1.58	0.37	3.17	8.69

The material stream from the RYIELD reactor goes into a burner which is modeled as a RGIBBS reactor along with air for combustion. The pressure and temperature are set at 1 bar and 1400ºC (1673 K) in accordance with the work of Sivalingam [8]. The RGIBBS reactor automatically calculates the combustion products at equilibrium such that the Gibbs free energy is minimized. The air flow rate into the RGIBBS reactor is set at the minimum value where the carbon is completely combusted. If it is less, energy will remain trapped in the coal; if it is more, energy will be wasted in heating the excess air to the reactor temperature. The calculation for the proper amount of air is discussed in section 2.2.1.After combustion, the materials are taken to a separator to isolate the ash from the other conventional materials. At this stage, the combustion process is considered complete; the CO_2-rich flue gas then undergoes the calcium looping process. The temperature of the flue stream is maintained at 150ºC in accordance with the lower limits on power plant flue gas temperatures provided by Feron [9].

2.1.2 Carbonator

The carbonator refers to the reactor where the carbonation reaction takes place. The RSTOIC reactor block is used in Aspen Plus to model the carbonator. The pressure is set at 1 bar and the temperature is set at 650°C. The RSTOIC is a reactor in which the user can define the specific reaction that occurs. The carbonation reaction is given by

$$CaO_{(s)}+CO_{2(g)} \rightarrow CaCO_{3(s)} \tag{2}$$

In real situations, CaO and CO_2 do not react completely with each other. The amount of CaO that can actually react is constrained by the surface area of CaO particles. Furthermore, the mixing between CO_2 and CaO is affected by how the fluidization develops in the reactor. These effects can be incorporated into Aspen Plus by defining the conversion fractionfor one of the reactants, i.e. CaO. The dependence of the CO_2 capture efficiency of the carbonator on the sorbent flow ratios is shown in Figure 2 [10]. Figure 2 has been translated into a table format by Sivalingam [8]; a part of the table used in this paper is shown in Table 2. In Figure 2 and Table 2, F_{CO_2} is the mole flow rate of CO_2, F_R is the mole flow rate of recycled (or looped) CaO, and F_0 refers to the make-up flow of CaO.

It is not possible to model the make-up flow of CaO in Aspen Plus. Hence, one value of $F_0/F_{CO_2}$is chosen to obtain one set of data for calculation. $F_0/F_{CO_2}= 0.1$ is chosen with three values of F_R/F_{CO_2} such that the three values of CO_2 capture efficiency are modeled in the range of 50% to 100%. For a certain flow ratio and CO_2 capture efficiency, there is certain associated CaO conversion fraction. Since the CO_2 capture efficiency cannot be directly controlled, multiple cases are run in Aspen Plus for a certain CaO conversion fraction until the correct CO_2 capture efficiency is obtained. As shown in Table 3Table, each specified CaO conversion fraction corresponds to a range of CO_2 capture efficiencies. The simulation results for various CaO conversion fractions are plotted in Figure 3. The small symbols (circles and triangles) in Figure 3 represent all the trial cases conducted in Aspen Plus; these are called

the results calculated from extrapolated data in future discussions in the paper. The large symbols refer to the cases whose results fit the data of Sivalingam [8]; these cases are called results obtained from experimental data in the future discussions in the paper.
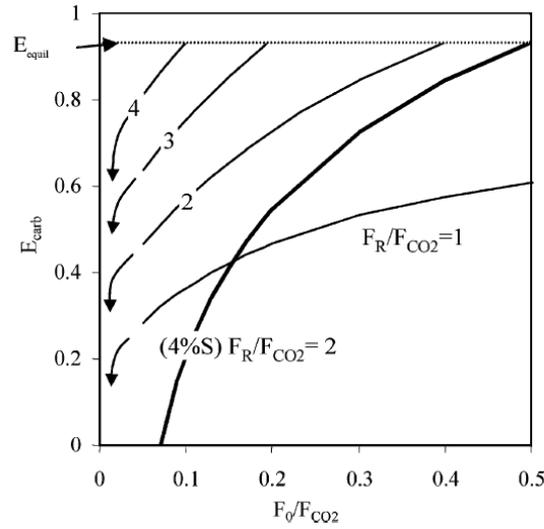
Figure 2. CO_2 capture efficiency for different flow ratios of CaO and CO_2 [10].

Table 2. CO_2 capture efficiency for different flow ratios of CaO and CO_2 [8].

F_0/F_{CO_2}	$F_R/F_{CO_2} = 3$	$F_R/F_{CO_2} = 4$	$F_R/F_{CO_2} = 5$
0.05	0.63	0.81	0.99
0.10	0.76	0.95	0.99

Table 3. Range of CO_2 capture efficiencies for each CaO conversion fraction.

F_R/F_{CO_2}	CaO conversion fraction	CO_2 capture efficiency
3	0.33	0.66–0.86
4	0.25	0.86–0.97
5	0.20	0.97–0.99
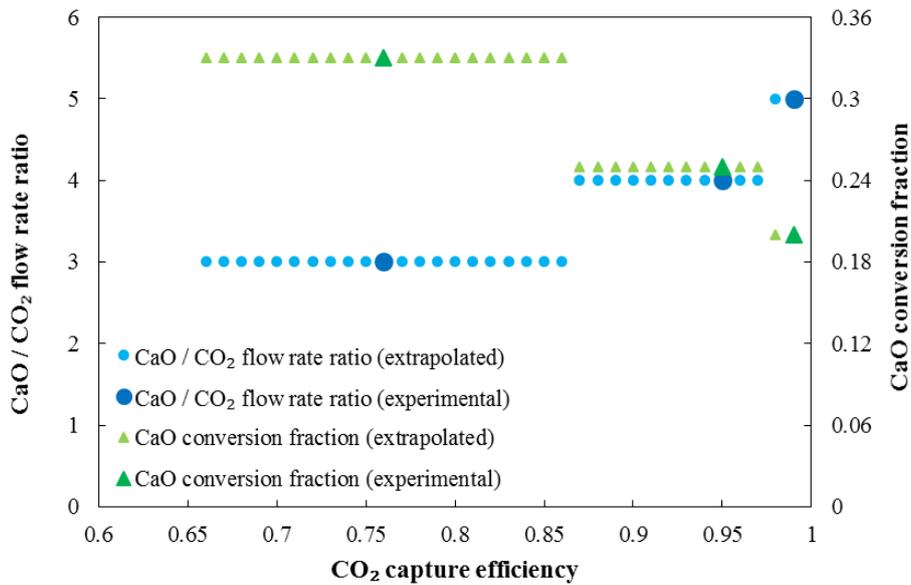
Figure 3. Range of CO_2 capture efficiencies for various CaO conversion fractions.

Down-stream of carbonator, the mixture of solids (primarily $CaCO_3$ with some CaO depending on the inlet flow rate of CaO) and the CO_2-lean flue gas is cooled back to 150°C by a heat exchanger and returns the heat released during the cooling-down process back to the carbonator. This step is necessary to account for the heat of the carbonator and the calciner separately. The stream then goes through a separator to separate the CO_2-lean flue gas from the solids, which are sent to the calciner to regenerate the CaO.

2.1.3 Calciner

Similar to the carbonator, the RSTOIC reactor block is employed for calciner in ASPEN Plus. The calcination reaction that takes place in the calciner is given by

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{3}$$

The temperature in this block is 900°C and the pressure is 1 bar in accordance with Sivalingam [8]. Unlike carbonation, the calcination reaction is a complete reaction, so all the $CaCO_3$ is decomposed. Therefore, the conversion fraction of $CaCO_3$ is set at 1. Post-stream of the calciner, the flow again passes through a heat exchanger and a separator like before. The heat absorbed from this heat exchanger is added to the heat of calciner.

3.1.4 Summary of the post-combustion setup

The reactor blocks used in Aspen Plus for CaL with post-combustion capture are listed in Table 4 along with their functions and reactions. For the heat stream, we add up the heat from decomposer, burner, heat exchanger for ash and heat exchanger for flue gas together to be the heat of the coal combustion process without CaL. The rest of the heat from the carbonator, post-carbonator heat exchanger, calciner, and post-calciner heat exchanger is the heat of the calcium looping process. It should be noted that these heat exchangers are not present in the real plant and are included in the process simulation only to isolate the heat gained and lost at each step. These values of heat, without and with CaL and the CO_2 fraction in the final outlet flow are indicative of the performance of the CaL system with post-combustion capture. The heat values of carbonation are also of interest in the evaluation of the performance of calcium looping with post combustion capture. Figure 4 shows the final flow sheet in Aspen Plus for CaL with post-combustion capture.

Table 4. Process models used for calcium looping with post-combustion capture setup in Aspen Plus.

Name	Reactor model	Function	Reaction formula
DECOMP	RYIELD	Converts non-conventional into conventional	Coal → char + simple substances
BURN	RGIBBS	Burns coal with air	Char + simple substances + O_2 → CO_2 + H_2O
CARBONAT	RSTOIC	Carbonation	$CaO + CO_2 \rightarrow CaCO_3$
CALCINER	RSTOIC	Calcination	$CaCO_3 \rightarrow CaO + CO_2$
SEP-ASH	SSPLIT	Flue gas and ash separation	-
SEP-CAR	SEP	Flue gas (CO_2-lean) and Ca-solids separation	-
SEP-CAL	SEP	CO_2 and Ca-solids separation	-
COOL-A	HEATER	Ash cooler	-
COOL-B	HEATER	Flue gas cooler	-
COOL-C	HEATER	Cooler downstream of carbonator	-
COOL-D	HEATER	Cooler downstream of calciner	-

Figure 4. Aspen Plus flow sheet for calcium looping with post-combustion capture.

2.2 Results and discussion
2.2.1 Calculation of the optimum of air flow

A typical coal-fired power plant employs10-15% excess air for combustion. Excess air was not considered in this paper to avoid the heat loss from heating the excess air to the combustor temperature so that only the heat produced by the coal could be compared against the net heat duty of the calcium looping process. In this paper, air is modeled in Aspen Plus as a mixture of around 21% O_2 and 79% N_2. The other components of air such as argon and CO2 are present in such small fractions that their effects on the results are negligible. The optimization module in Aspen Plus is employed to find the flow rates of the O_2 and N_2 such that the burner heat is maximized. The optimization setup and results are shown in Table 5 and Table 6 respectively. F_{CO}, F_{CO_2}, F_{O_2} and F_{N_2} refer to the mole flow rate of the various gases (CO and CO_2 downstream of the burner, O_2 and N_2 upstream of the burner). The basic idea behind the optimization is to change O_2 and N_2 flow rates separately within a small range in order to get the maximum CO_2 flow out of the burner. Constraints for this process cover the flow rate of CO out of the burner, and ratio between O_2 and N_2. This ensures that nearly all the combustion product is CO_2 (indicating complete combustion) with the smallest amount of O_2 and N_2 remaining with the ratio of O_2 and N_2 being the same as that in the air. The optimized flow rates of O_2 and N_2 are 4.20kmol/s and 15.76 kmol/s respectively for 50 kg/s of coal. The sum of these two flow rates of nearly 20 kmol/s is the total air flow in the burner. For scaled higher flow rates of coal, the O_2 and N_2 flow rates are changed proportionately.

Table 5. Optimization variables setup and results.

	O_2	N_2
Manipulation range (kmol/s)	3–5	12–16
Maximum step size (kmol/s)	0.5	0.5
Optimized result (kmol/s)	4.20	15.76

Table 6. Constraints and convergence results for optimization of amount of air.

Convergence criteria	Tolerance	Result
F_{CO} = 0.001 kmol/s	0.001 kmol/s	0.00059 kmol/s
F_{O_2}/F_{N_2} = 0.2658	0.01	0.2664
Maximize F_{CO_2}	-	2.653 kmol/s

2.2.2 Carbonation and calcination analysis

Since the main objective of CaL is to reduce the amount of CO_2 released into the atmosphere, the CO_2 capture efficiency is the most important metric in evaluating the performance of the process. Therefore, the CO_2 capture efficiency is employed as the independent variable on the x-axis, and all other quantities of interest are plotted on the y-axis to examine how the CO_2 capture efficiency affects the other quantities. Since there are no other energy losses that need to be considered, the energy penalty of CaL is the sum of the heat gain and loss from the carbonation and calcination.

For each CaO conversion fraction, there is a corresponding CO_2 capture efficiency from the experimental data [8]. Once the CaO conversion fraction is defined in Aspen Plus, the CO_2 capture efficiency is manipulated to be equal to the experimental result by changing the CaO inflow to the carbonator. With change in CaO inflow, the heat duty of the carbonator and calciner change. Therefore, for each set of experimental data, one can calculate one data point of heat duty for the carbonator and calciner. In order to obtain additional data points for the heat duty, the extrapolated data in Figure 3 are also considered, which correspond to a range of CO_2 capture efficiencies for each CaO conversion fraction due to varying CaO flow rates instead of just the one that matches the result of Sivalingam [8]. The heat duty of the carbonator and calciner obtained from for both the experimental data (non-extrapolated) and extrapolated data are shown in Figure 5.
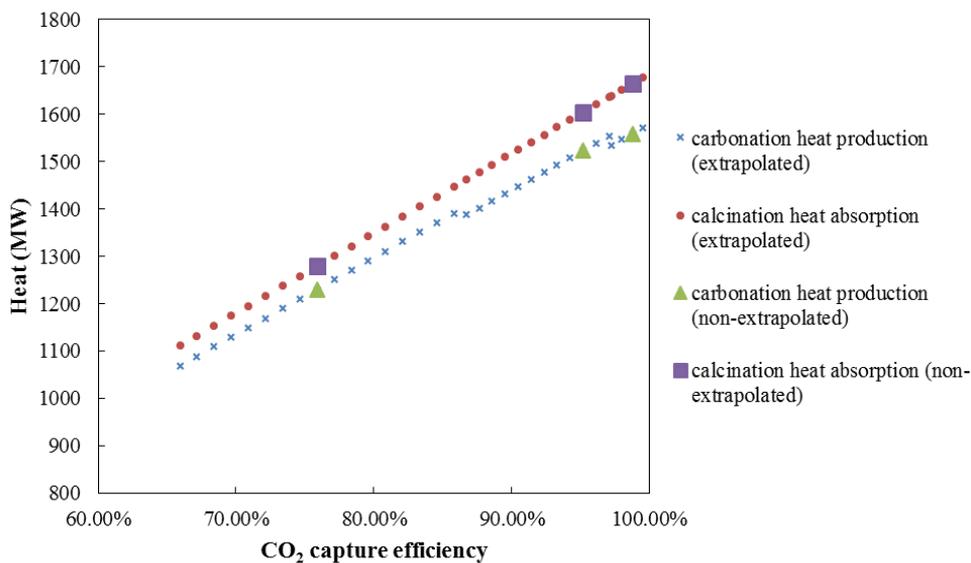

Figure 5. Heat duty of carbonator and calciner for original experimental data and extrapolated data

It should be noted that the calcination reaction is an endothermic reaction since heat must be added to precipitate the decomposition of $CaCO_3$. As such, the heat duty of the calciner from Aspen Plus is negative. However, the absolute value of the calciner heat is plotted in Figure 5 to compare it with the heat production in the carbonator. For each value of CO_2 capture efficiency, the heat absorbed by the calciner is greater than the heat produced in the carbonator, which confirms that there is a net energy penalty associated with the calcium looping process.

Extrapolating the data to account for additional CO_2 capture efficiencies is necessary because it is not possible to get an accurate representation of a trend from only three experimental data points available. It can be observed from Figure 5 that the calcination results form an almost perfect line, and the extrapolated and non-extrapolated data are coincident with the line. This linearity is expected since the calculation is based on a stoichiometric relation, thus resulting in the heat produced being also proportional to the inflow rate of the reactant, $CaCO_3$. The CaO conversion fraction does not affect the heat absorbed by the calciner. This is due to the fact that the calciner has the same temperature for both inlet and outlet flow (150 ºC). When there is an excess amount of CaO fed into the carbonator, the unreacted CaO will pass through the carbonator and enter the calciner; this unreacted part of CaO has no effect on thereaction within the calciner. Thus the heat duty of calciner remains unchanged by the excess amount of CaO.

For the carbonator, the extrapolated data around each of the three experimental data points are linear but these lines do not coincide. The linearity of each section can be explained the same way as for the calciner. However in this case, the CaO conversion fraction has some effect. Each straight line section corresponding to a range of extrapolated data has a reduced y-intercept compared to the previous section and has a more gradual slope compared to the calciner. From the modeling point of view, the only difference between these two reactors, beside the chemical reaction, is the inlet stream temperature. Since the CaO stream entering the carbonator is an external input, the inlet stream has a temperature of 25ºC compared to 150 ºC for the calciner (internal input from the carbonator outlet stream). Thus, some heat is consumed in the carbonator for heating up the inlet stream to the temperature of the outlet. The heat production of the carbonator decreases as the CO_2 capture efficiency is increased since more heat is consumed to heat the higher CaO flow that is required for the increased capture of CO_2. This is the main reason for the difference in behavior of the calciner and the carbonator described above.

2.2.3 Energy penalty analysis
For 50 kg/s of inlet coal flow, the heat of combustion is calculated to be 1168 MW (i.e., without calcium looping). When the net heat gained and lost in the carbonator and calciner respectively are added, the total heat of the power plant with calcium looping ranges from 1060 to 1130 MW, as shown in Figure 6. As expected based on the trends in calciner and carbonator heat discussed in section 2.2.2, the total heat output of the power plant decreases as more carbon is captured.
The energy penalty for CaL refers to the fraction of energy produced by a power station that must be dedicated to the carbonation and calcination process in order to capture CO_2. The energy penalty can be defined as

$$\text{Energy penalty} = \frac{\left|Q_{looping}\right|}{Q_{total} - \left|Q_{looping}\right|} \qquad (4)$$

where Q_{total} is the total heat produced by the power plant and $Q_{looping}$ is the net heat for the CaL process.
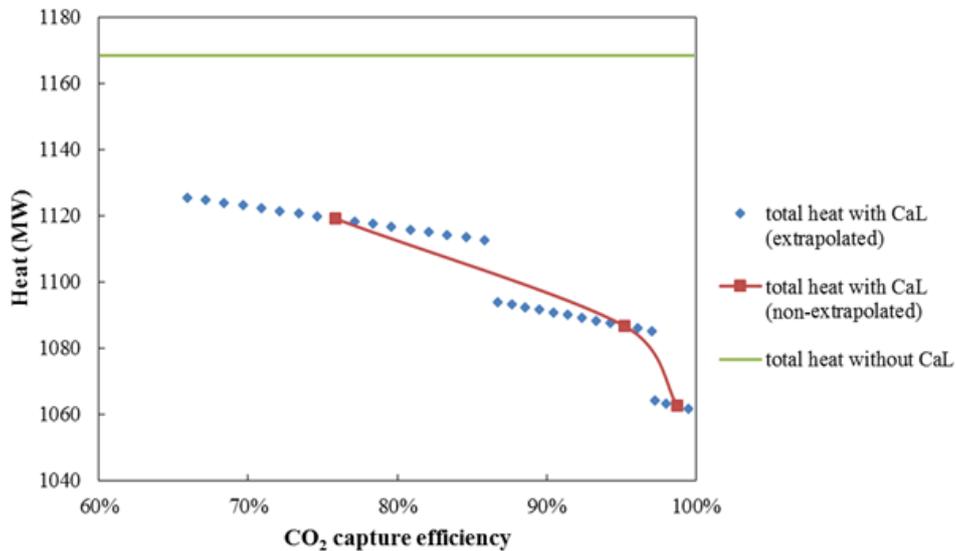

Figure 6. Plot of total energy (heat) output vs. CO_2 capture efficiency without CaL and with post-combustion CaL.

Figure 7 shows the energy penalty for CaL with post-combustion capture calculated using Eq. (4). From Figure 7, the energy penalty ranges from 3.5% to 9.0%over the corresponding range of CO_2 capture efficiencies from 65% to 99%. These results are in line with the work of Cormos and Petrescu [11] that found energy penalties ranging from 5% to 10% for capture efficiencies between 92% and 93% for various power plants. More recently, a study by BP Alternative Energy (BPAE) [12] showed that the marginal energy penalty associated with increasing carbon capture efficiency past 98% increases drastically, which further validates the results of the current work.
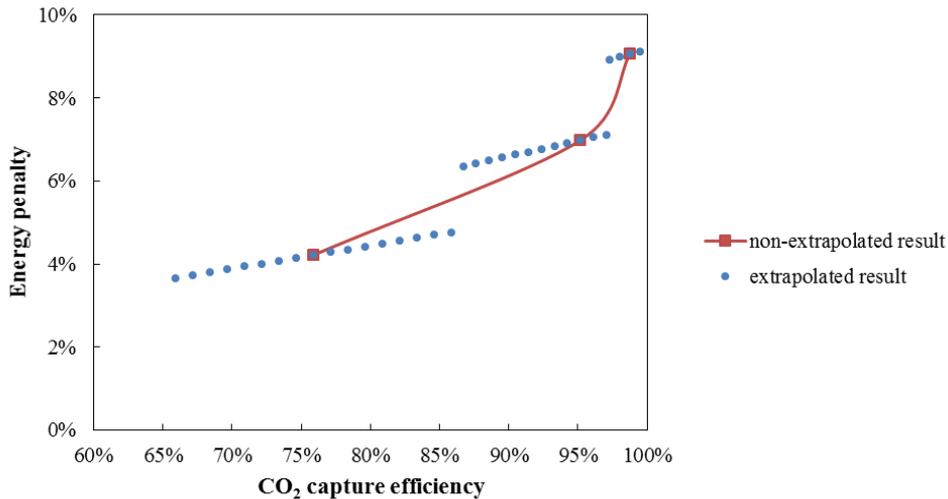
Figure7. Plot of energy penalty vs. CO_2 capture efficiency for CaL with post-combustion capture.

Figure 7 follows the curve for the total energy (heat) shown in Figure 6. From Figure 6 and Figure 7, it can be seen that the results obtained from the extrapolated data form three sections of straight lines with discontinuities. On the other hand, the curve fit for the non-extrapolated result connecting the three points from the experimental data also shows a gradually increasing slope. At first glance, the curve fit looks more reasonable and the extrapolated data seems notto be an accurate representative because of the discontinuities. For more accurate calculations to determine how the energy penalty varies with the CO_2 capture efficiency between the experimental data points, the combination of these two methods may be desirable. Since the blue dots show linear relation in certain range, it could be used to extrapolate between the blue dots for a given straight line. However, in the regions where there is jump between the two straight lines, it may be desirable to create an appropriate smooth curve.

It should be noted that the only heat output of the combustor and the CaL process is assessed in the results presented above. In a real plant, heat generated from coal combustion will heat up the steam to drive a steam turbine connected to an electric generator to generate electricity. Thus, it is the difference in temperatures that matters in the power plant.Even with some heat sources having the same amount of thermal energy, difference in temperatures can lead to different amounts of electricity generated by these sources. In many papers, the energy penalty is calculated based on the electric power generated by the whole power plant. However, since the steam cycle is not considered in this work, the energy penalty is calculated based only on the heat of coal combustion. Therefore the effect of high temperature is not reflected in the present model. It is assumed that all heat sources can contribute to energy until they reach a temperature as low as 150ºC. Furthermore, when considering the whole plant, transportation of the solid calcium will cost extra energy, although as discussed earlier, this amount is likely to be negligible [7]. In summary, this paper considers a simplified model of calcium looping, which only takes into account the heat of chemical reaction in a stoichiometric fashion. As a result of the various simplifications, the energy penalty calculated from this work should be considered as a lower bound for any investigation on calcium looping.

3. Calcium looping with pre-combustion capture
3.1 Process simulation setup
Calcium looping with pre-combustion capture is a technology that substantially alters the combustion process. Instead of burning the coal in a boiler, incomplete combustion takes place in a gasifier to convert the carbon into CO. Next, a water-gas-shift reaction occurs between the CO and injected steam (H_2O) to form H2 and CO_2, which enter the carbonator and calciner loop to capture the CO_2 prior to the final step of combusting H_2 for energy production.

3.1.1 Gasifier setup
In a typical integrated gasification combined cycle power plant, oxygen from an air separation unit (ASU) is used to gasify the coal to form CO and H_2 while avoiding production of CO_2 and H_2O. However, the air separation unit has a significant high energy penalty associated with it. From an energy

standpoint, as long as the initial reactants and the final products remain the same, the heat produced in the gasification process will remain the same. Thus, to simplify gasification and eliminate the energy penalty of ASU, steam gasification is considered in this work. Similar to the post-combustion setup described in section 2.1.1, the RYIELD and RGIBBS reactor blocks are used in the pre-combustion setup as well. The difference is that the coal in the gasifier reacts with steam instead of air, unlike in the burner in the post-combustion setup. The pressure of the gasifier unit is set at 1 bar and the temperature is set at 1400ºC as before.

3.1.2 Carbonator and calciner
The carbonator and calciner have the same setup as in the post-combustion capture since the calcium looping process runs independent of the combustion scenario. However, an additional RSTOIC reactor is added upstream of the carbonator to implement the water-gas-shift reaction. The stream of syngas out of the gasifier comprises CO and H_2. The purpose of the shift reaction is to react CO with steam to form CO_2 and H_2. These gases then undergo the CaL process to capture the CO_2 and isolate the H_2 for combustion to produce energy. The pressure and temperature in the shift reactor are set at 1 bar and 650ºC respectively.

3.1.3 Hydrogen burner
In the post-combustion capture setup, the burning of coal in the combustor produces energy, part of which is absorbed in the calcium looping process. In pre-combustion capture, energy is produced by burning the H_2 in the CO_2-lean flue gas that comes out of the carbonator; both gasification and calcium looping processes absorb a part of this energy. Thus, in the pre-combustion setup in Aspen Plus, an additional RSTOIC reactor is used to burn the H_2 produced in air. The inlet air temperature for the hydrogen burner is set at 150 ºC, which is the same as the final outlet temperature. This is done in order to eliminate the influence of the air flow rate in the calculations such that a steady excess air flow value can be maintained. Otherwise, if the inlet air was at 25 ºC and was in excess for the amount of H_2, some energy would be wasted in heating up the excess air to the outlet stream temperature of 150 ºC.

3.1.4 Summary of Pre-combustion model setup
The various reactor blocks used in ASPEN Plus and their specifications for pre-combustion capture are listed in Table 7. The flow sheet setup in ASPEN Plus is shown in Figure 8.

Table 7. Process models used for calcium looping with pre-combustion capture setup in Aspen Plus.

Name	Reactor model	Function	Reaction formula
DECOMP	RYIELD	Converts non-conventional into conventional	Coal → char + simple substances
GASIFIER	RGIBBS	Gasifies coal with steam	Char + simple substances + H_2O → CO + H_2 + volatile matter
CARBONAT1	RSTOIC	Water-gas-shift reaction	CO + volatile matter + H_2O → CO_2 + H_2
CARBONAT2	RSTOIC	Carbonation	CaO + CO_2 → $CaCO_3$
H2-BURN	RSTOIC	Burns H_2 in air	H_2 + O_2 → H_2O
CALCINER	RSTOIC	Calcination	$CaCO_3$ → CaO + CO_2
SEP-ASH	SSPLIT	Flue gas and ash separation	-
SEP-CAR	SEP	Flue gas (H_2) and Ca-solids separation	-
SEP-CAL	SEP	CO_2 and Ca-solids separation	-
COOL-A	HEATER	Ash cooler	-
COOL-B	HEATER	Flue gas cooler	-
COOL-C	HEATER	Cooler downstream of carbonator	-
COOL-D	HEATER	Cooler downstream of H_2 burner	-
COOL-E	HEATER	Cooler downstream of calciner	-
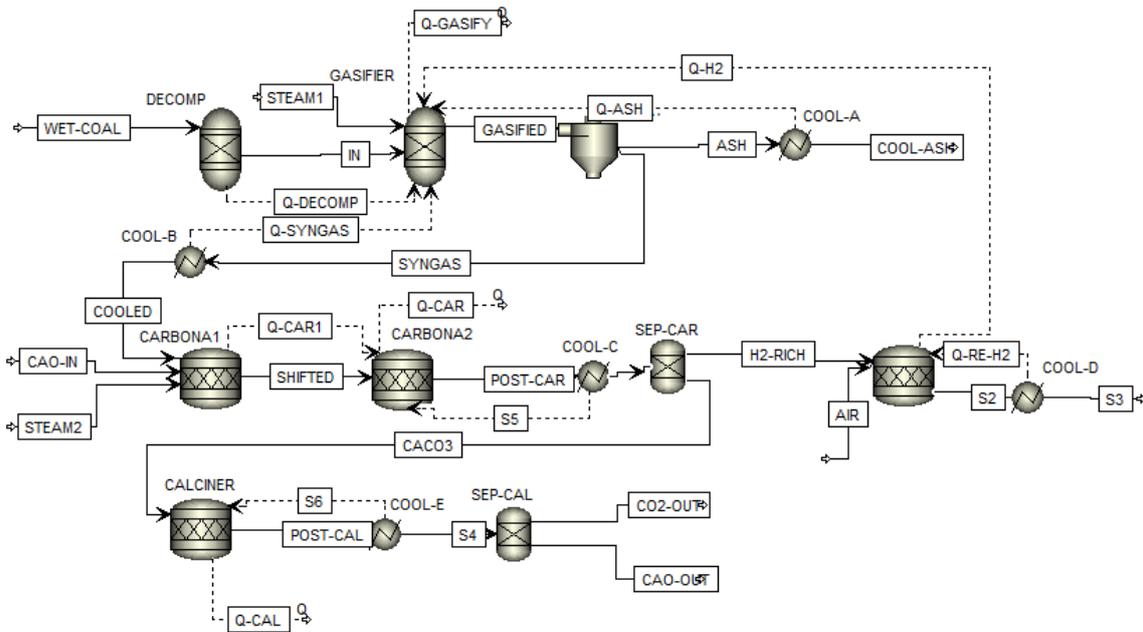
Figure 8. Aspen Plus flow sheet for calcium looping with pre-combustion capture.

3.2 Results and discussion
3.2.1 Calculation of the optimum steam flow rate for gasifier

In the coal gasification step, the carbon content in the coal is turned into CO. The goal in this step is to determine the H_2O flow rate to maximize the CO flow into the water-gas-shift reactor. A sensitivity analysis is employed to achieve this goal. The steam flow rate is incrementally increased to 3 kmol/s, and the C, CO, and CO_2 outflow rates are monitored as shown in Figure 9. It can be observed from Figure 9 that at a 2.1 kmol/sflow rate of H_2O, all the carbon content (C) in the coal is burnt and CO_2 starts to form, and the CO output begins to decrease. Thus, 2.1 kmol/s is the optimum H_2O flow rate for the gasifier.

3.2.2 Calculation of the optimum steam flow rate needed for shift reactor

The optimum steam flow rate for the water-gas-shift reactor is obtained in a similar manner. The outflow of CO, CO_2, and H_2 are monitored as the inlet flow rate of H_2O is increased to 3 kmol/s. The results, shown in Figure 10, indicate that the optimum steam flow in this case is 2.7 kmol/s when the entire CO is converted and the CO_2 and H_2 flow rates acquire their highest values.
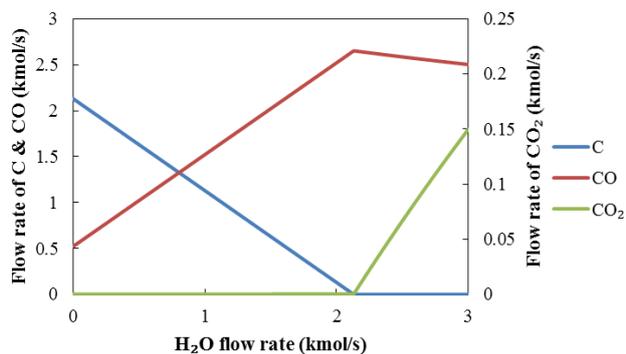
Figure 9. Variation in gasifier outflow components with steam flow rate.
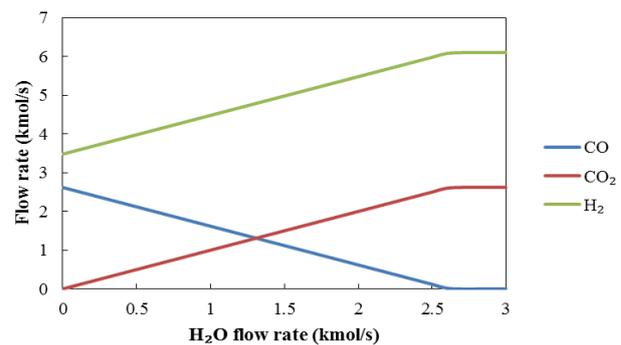
Figure 10. Variation in shift reactor outflow components with steam flow rate.

3.2.3 Energy penalty analysis

Without CaL for pre-combustion capture, the net heat from the coal gasification and H2 combustion combined is 1132 MW for a coal feeding rate of 50 kg/s. Taking into account the heat produced and absorbed in the carbonator and calciner respectively, the total heat with CaL ranges from 980 to 1060 MW as shown in Figure 11.

It should be noted that Figure 11 shows a slightly lower total heat output without CaL compared to the post-combustion case because more energy is lost in pre-combustion from heating both steam and air from the external input temperature of 25ºC to the stream temperature of 150ºC. The various trends observed in Figure 11 are similar to those observed in Figure 6 for the post-combustion capture case; explanations of these trends can be found in section 2.2.3.

Based on the results of Figure 11, Eq. (4) is used to compute the energy penalty for different values of the CO_2 capture efficiency. The energy penalty for pre-combustion is compared to that of the post-combustion case in Figure 12. It can be observed that the pre-combustion capture has a consistently higher energy penalty.
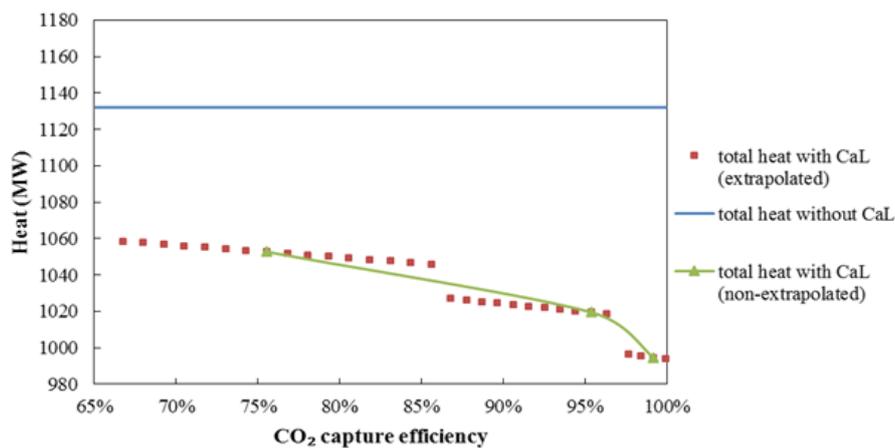
Figure 11. Plot of total energy (heat) output vs. CO_2 capture efficiency without CaL and with pre-combustion CaL.
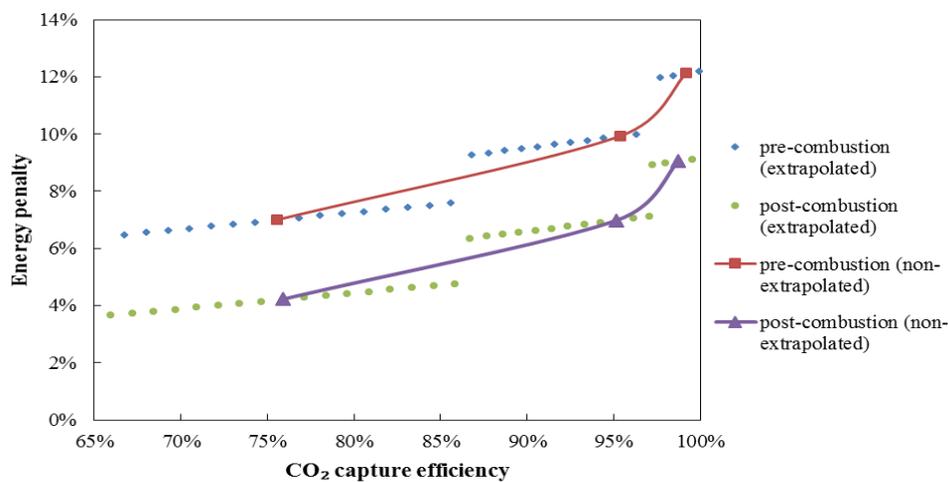
Figure 12. Comparison of energy penalty vs. CO_2 capture efficiency for CaL with post- and pre-combustion capture.

4. Scaling considerations

The coal feeding rate considered in the simulations thus far is 50 kg/s following the work of Sivalingam [8]. In order to investigate the effect of a change in scale, CaL process models are developed with a smaller coal feeding rate of 5 kg/s with both post- and pre-combustion capture. For the down-scaled case, the heat outputs for the post-combustion and pre-combustion cases are shown in Figure 13. The total heat output is reduced by approximately an order of magnitude, in line with the order of magnitude reduction in the coal feeding rate. Even in the down-scaled model, the total energy output in the pre-combustion case is smaller than that for the post-combustion case, as expected. Figure 14 shows the comparison between the energy penalty in pre-combustion and post-combustion case for the down-scaled coal feeding rates. By overlaying the data for the original model from Figure 12 onto Figure 14, it is clear that the energy penalty is unaffected by the change in scale.
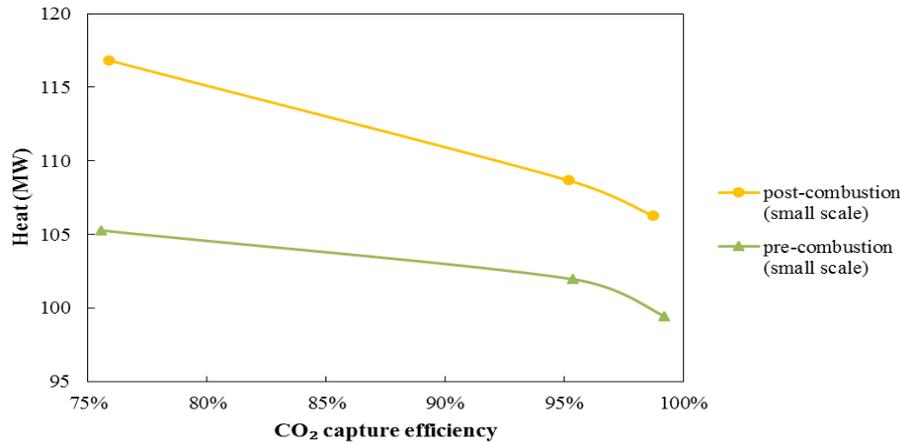
Figure 13. Comparison of total heat output vs. CO_2 capture efficiency for CaL with post- and pre-combustion capture for the down-scaled model with reduced coal feeding rate of 5 kg/s.
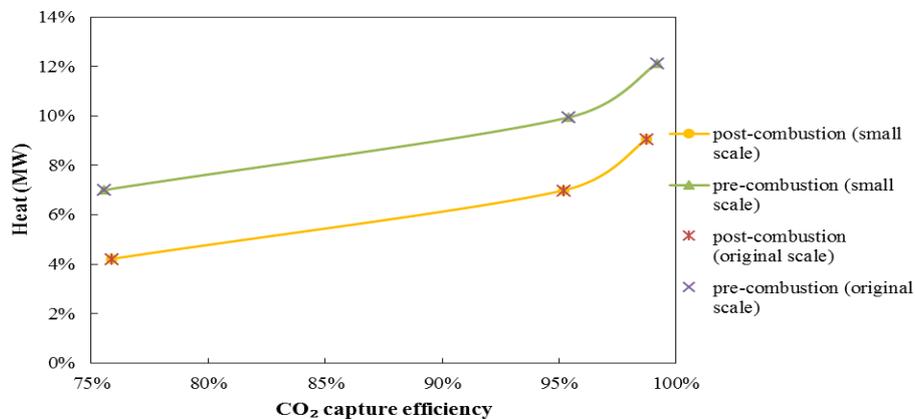

Figure 14. Comparison of energy penalty vs. CO_2 capture efficiency for CaL with post- and pre-combustion capturefor the original scale model and the down-scaled model.

5. Conclusions

The energy penalty associated with the calcium looping process for both post-combustion and pre-combustion capture of CO_2 is investigated using Aspen Plus. Flow sheets for post-combustion and pre-combustion CO_2 capture models are developed to accurately mirror the physical processes in each plant with the exclusion of the steam cycle. The results of this paper indicate that the energy penalty in both post-combustion and pre-combustion cases depends on the flow rate of CaO into the carbonator. It was found that post-combustion capture has a lower energy penalty compared to pre-combustion capture irrespective of the CO_2 capture efficiency. To achieve a capture efficiency of 50–99%, the energy penalty for post-combustion capture is in the range of 4–10%; for pre-combustion capture, it is in the range of 6–12%. An important result from this work is that for high CO_2 capture efficiencies (above 90%), the marginal energy penalty associated with increased capture efficiency increases dramatically. This is in line with similar observations in literature and suggests that calcium looping systems may be limited to around 95–98% CO_2 capture, beyond which the process becomes impractical due to the energy consumption. The models developed in this paper can be scaled for higher and lower flow rates of coal input without affecting the trends observed in the results.

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