PROCESS INTEGRATION OF CALCIUM LOOPING TECHNOLOGY

A Thesis

by

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ABSTRACT

Around 36 gigatonnes of CO_2 are released into the atmosphere every year. Mitigation of CO_2 emissions is essential in reducing the rising level of greenhouse gas emissions and associated climate change. Calcium Looping Process (CLP) is one of the promising technologies developed as part of the continuous efforts for Carbon Capture and Utilization (CCU). It is essentially a CO_2 capture process that utilizes calcium oxide (CaO) as a sorbent for the removal of CO_2, producing a concentrated stream of CO_2 (~99%) that is suitable for storage and reuse is produced in this process. Although still in the pilot stage, CLP presents several advantages over conventional carbon capture systems like amine-scrubbing. These advantages include low cost of the sorbent and relative ease of bolt-on retrofitting of existing power plants and industrial processes. The objective of this work is to use mass and energy integration to couple CLP with industrial facilities and power plants in order to enhance industrial symbiosis and reduce cost. Special attention is given to plants that generate large amount of CO_2 and/or provide excess heat that can be used in driving CLP. A case study was solved to assess the integration of CLP with candidate processes including power plants, cement production, gas-to-liquid (GTL) facility, and ammonia synthesis. The captured CO_2 can be re-utilized in CO_2 sinks that utilize CO_2 as a raw material for making chemicals. This use of CO_2 as a chemical feedstock provides a suitable alternative to sequestration and storage. The CO_2 sinks considered in the case study include the production of: urea, polymer, methanol and acetic acid. The solution to the case study shows the merits for integration of a GTL plant with

CLP to supply CO_2 for the production of a polymer, methanol and acetic acid. Additionally, the captured CO_2 stream from the ammonia plant is integrated with urea production. Excess heat from the GTL facility and the power plant were also used. Cogeneration of power and heat improves the economic feasibility of the integrated system. The highlights of this symbiosis are the re-use of waste calcium oxide from the cement plant, utilization of waste heat and reduction of CO_2 emissions and raw-material usage due to utilization of the captured CO_2.

DEDICATION

To

My loving family and friends

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First and foremost, I would like to thank my advisor Dr. Mahmoud El-Halwagi for his invaluable support and patience. I consider myself truly blessed to have worked under Dr. El-Halwagi's guidance. Not only is he an excellent teacher but also an exemplary human being whom I will always look up to.

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CONTRIBUTORS AND FUNDING SOURCES

Contributors

NOMENCLATURE

CCUS	Carbon Capture, Utilization and Storage
CLP	Calcium Looping Process
GTL	Gas-to-Liquid
PC	Pulverized coal
NGCC	Natural Gas Combined Cycle
IGCC	Integrated Gasification Combined Cycle
MEA	Monoethanolamine
TCI	Total Capital Investment
AFC	Annualized Fixed Cost
AOC	Annual Operating Cost
TAC	Total Annualized Cost
ROI	Return on Investment
PBP	Payback Period

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

The massive contribution of CO_2 emissions from industrial fossil fuel conversions processes to climate change is a matter of growing concern. About 36 gigatonnes of CO_2 is emitted into the atmosphere every year (Fennell and Anthony, 2015). The impact of the of the increasing greenhouse gas emissions, with CO_2 being the largest contributor, is seen in the rise in average sea levels, atmospheric and ocean temperatures and irreversible melting of snow (Blamey et al., 2010). Through the world, governments have imposed targets to reduce these emissions and restrict the rise in temperature to a reasonable figure of 2ºC (Fennell and Anthony, 2015). For instance, the United Kingdom (UK) has set a target to reduce its greenhouse gas emissions by 80% by the year 2050. Likewise, the European Union (EU) has targeted reduction in emissions by 20% by the year 2020 (Fennell and Anthony, 2015).

Most of the current infrastructure is built around the use of fossil fuels as a source of supplying energy. Fossil fuels, although available in abundance and cheap, emit CO_2 in large amounts. These are used for power generation (40% of global CO_2 emissions), industrial processes (40% of global CO_2 emissions) and transportation (Fennell and Anthony, 2015). Figure 1 shows the approximate distribution of emissions from industrial processes.

Carbon Capture, Utilization and storage (CCUS) includes a suite of technologies being developed to reduce net CO_2 emissions to the atmosphere and their subsequent

effect on climate change (Dean et al., 2011). These technologies are crucial to meeting the targets set to reduce greenhouse gas emissions. Currently, there are two pathways for post-combustion CO_2 capture that are in the pilot stage and are expected to be commercialized in the near future.
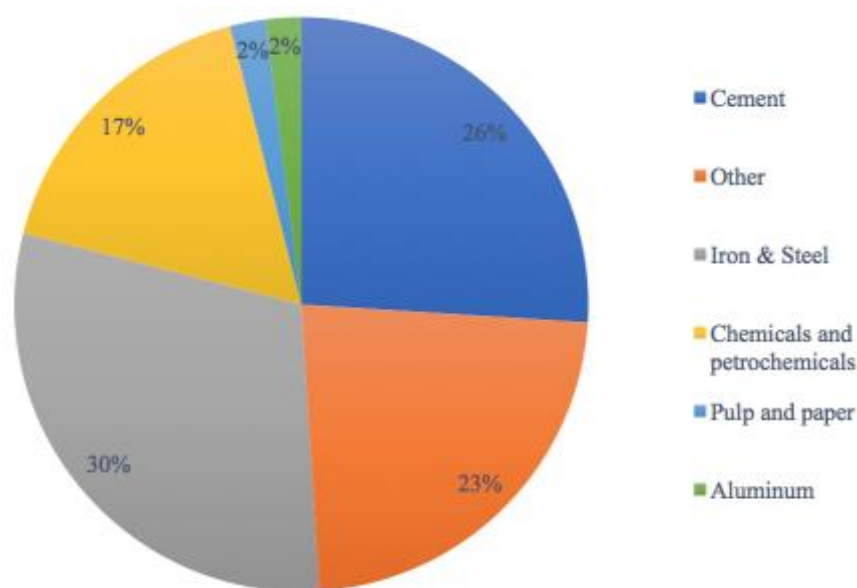
Figure 1: Distribution of CO₂ emissions from different industrial processes (Adapted from Fennell and Anthony, 2015)

The first method is amine absorption, with monoethanolamine (MEA) being the preferred choice of solvent. Although amine scrubbing is a relatively mature technology, there are a number of problems associated with it (Blamey et al., 2010):

i. High cost of solvent

ii. Sorbent degradation at elevated temperatures

iii.   Large amount of heat (3.0-5.0 GJ/ton CO_2) required for solvent regeneration (Fennell and Anthony, 2015)

iv.   Reaction of MEA with O_2 and SO_2 present in flue gas

Another technology that is close to market scale is oxyfuel combustion. Here, coal is burnt with a mixture of O_2 and recycled CO_2. The CO_2 dilutes the otherwise pure O_2 stream and thereby brings down the high flame temperature. However, oxyfuel combustion also poses a few problems that are yet to be addressed (Blamey et al., 2010):

i.   Requirement of expensive cryogenic separator

ii.   Stringent safety requirements

iii.   Fouling and leaks affecting CO_2 purity

In case of power plants, it has been reported that MEA scrubbing and oxyfuel combustion pose an energy efficiency penalty of ~12% and ~10% respectively. This observation combined with the disadvantages listed above, has necessitated investigation to develop other CCUS techniques. Calcium Looping process (CLP) is one such technology that utilizes solid Calcium Oxide (CaO) as a CO_2 sorbent. It employs a set of twin fluidized bed reactors. In the first reactor, CO_2 from the flue gas stream is adsorbed onto CaO. In the subsequent reactor, the $CaCO_3$ formed in the first reactor is calcined i.e. broken down into CaO and a pure stream of CO_2. A flowsheet of the CLP is seen in Figure 2. This process offers a number of advantages such as:

i.   High-temperature process creating possibility of power generation

ii.   Use of cheap sorbent, limestone

iii.   Partial desulphurization of flue gas

iv.   Use of fluidized beds, a mature process technology

Calcium Looping can be employed for both pre-combustion and post-combustion CO_2 capture. The approach towards integration of Calcium Looping with gasification processes, power plants and cement plants has been reviewed in literature (Blamey et al., 2010). A number of CLP pilot plants have been constructed across the world. So far, no major issues with this process have come to light. Hence, CLP is a promising technology that is moving towards the demonstration scale (Blamey et al., 2010).
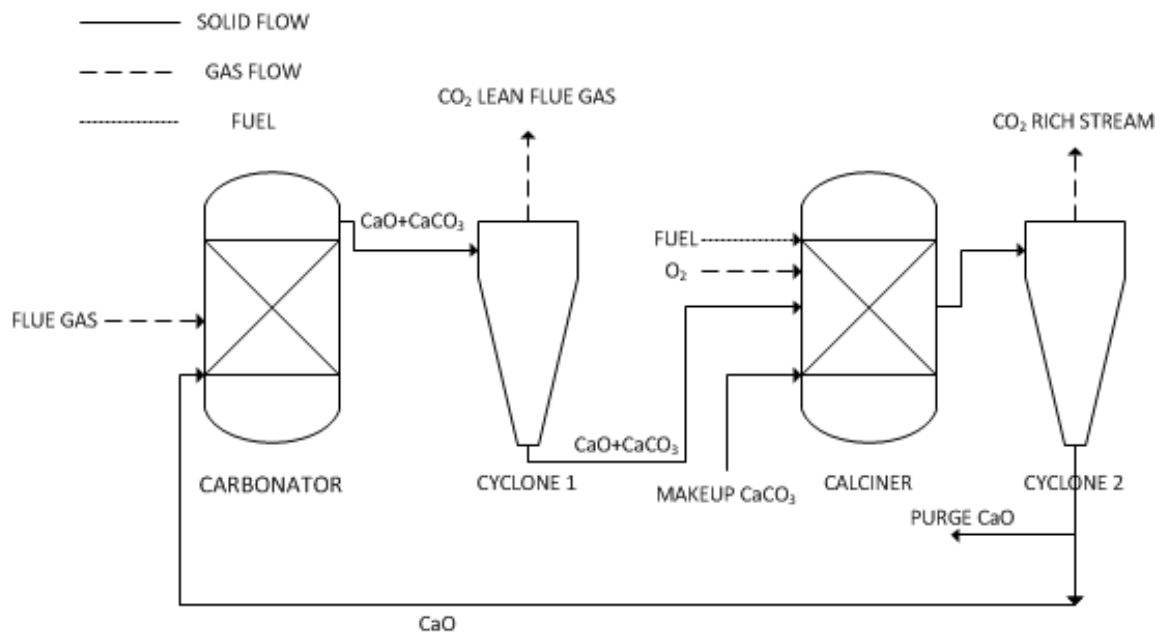
Figure 2: Schematic of Calcium Looping Process (Adapted from Zhao et al., 2013)

This thesis presents a techno-economic assessment of integration of Calcium Looping Process (CLP) with industrial processes that emit CO_2 in sizeable amounts. For this, the CLP was reviewed in-depth. Several processes were examined and shortlisted to meet the required criteria for integration with the CLP. Simulations of this integration was performed in ASPEN Plus. The energy consumption and reduction in CO_2 emissions achieved from the coupling of each process with CLP were determined from this simulation. Further, processes that utilize CO_2 as a raw material were examined for downstream integration with CLP. The CO_2 capture efficiency and purity of CO_2 captured was also examined. An economic analysis was performed to determine the ROI (return on investment) for incorporation of CLP in an existing process plant. The cost saved by this integration indicates the practical feasibility of this approach.

CHAPTER II

LITERATURE REVIEW

This chapter presents the literature reviewed for this thesis. First, the current literature available on Calcium Looping is presented, that examines the salient features and explains the vital parameters involved in this process. Next, the current applications of CLP are studied, followed by a review of the CLP pilot plants being operated all over the world. Last, the tools used for economic assessment of the CLP integration have been presented.

II.1 Background on Calcium Looping

The Calcium Looping Process (CLP) exploits the reversible reaction of CO_2 with Calcium Oxide (CaO) to produce a highly pure stream of CO_2 (~95%) that can be compressed and sent for storage. The CO_2 capture efficiency of this process is in the excess of 90% and varies as per sorbent flowrate. The use of Calcium Looping for CO_2 capture was first suggested in 1999 (Shimizu et al., 1999). This process employs a twin fluidized bed reactors where the following reversible reaction takes place:

$$CaO + CO_2 \Leftrightarrow CaCO_3$$
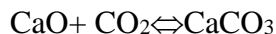
The forward reaction is called carbonation and is exothermic (ΔH=-178 kJ/mol) in nature, where CO_2 is captured onto the sorbent and the solid is transported to the second reactor. Endothermic calcination (ΔH=+178 kJ/mol) takes place in the second reactor and a pure stream of CO_2 is generated that is compressed and sent for storage. The twin fluidized bed reactors are coupled for transport of solids.

Figure 3 is a flow diagram of the Calcium Looping Process. Both the reactors operate at atmospheric pressure, one of the prime advantages of this process. The carbonator operates at a temperature around 600-700ºC. The total molar flowrate of flue gas entering the carbonator (also referred to as capture reactor or absorber) is F_{flue} (kmol/s). F_{flue} is the sum of the flowrate of CO_2 in the flue gas stream F_{CO2} (kmol/s) and flowrate of all other gaseous components in the flue gas stream combined as F_{gas} (kmol/s). The molar flowrate of the solid stream between the carbonator and the calciner is F_R(kmol/s). F_0(kmol/s) is the flowrate of the makeup limestone. The efficiency of CO_2 capture in the carbonator is E_{CO2}. The solids from the carbonator, consisting of unreacted CaO and formed $CaCO_3$ are transported to the calciner (also referred to as regenerator), operating at a higher temperature in the range of 850-900 ºC. Since the reverse reaction is exothermic, energy is supplied by means of oxyfuel combustion, using pure O_2. The flowrate of fuel injected in the calciner is F_{fuel} and that of the CO_2 generated by combustion in the calciner is $F_{CO2,fuel}$. Additional CO_2 is generated in the calciner, that can be practically completely captured. This produces a stream consisting of ~95% CO_2, that is suitable for sequestration or further utilization. The regenerated sorbent is cycled back to the capture reactor.

$$F_{gas}+F_{CO_2}(1-E_{CO_2})$$ $$F_{CO_2}E_{CO_2}+F_{CO_2,fuel}$$

$$F_R$$

Carbonator   Calciner

$$F_0$$ $$F_0$$

$$F_0+F_R$$

$$F_{flue}=F_{gas}+F_{CO_2}$$ $$F_{fuel}$$
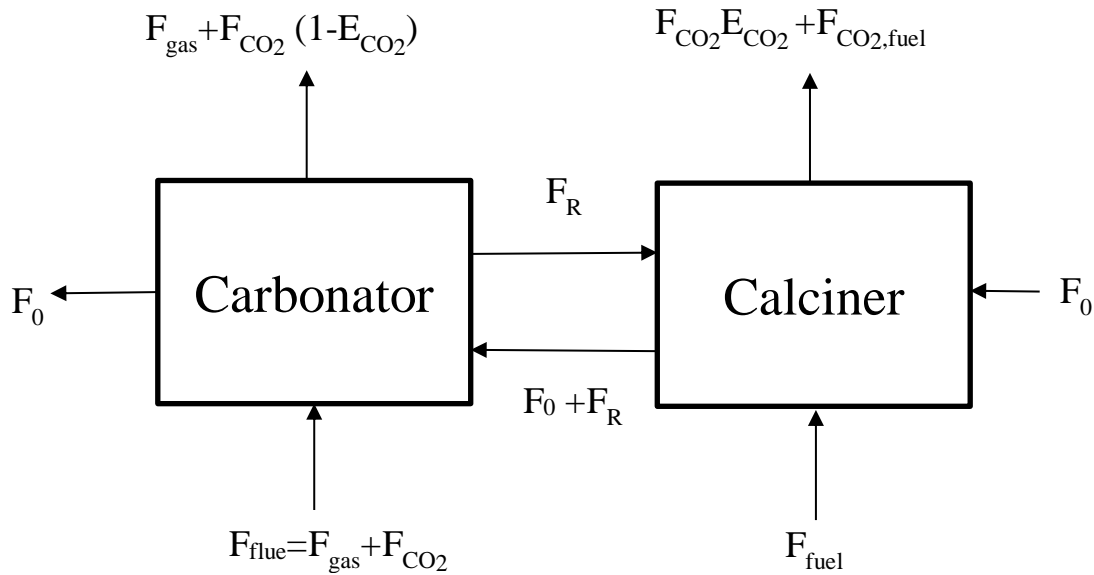
Figure 3: Flow diagram of Calcium Looping Process

The incoming flue gas stream is likely to contain a small percentage of water vapor. $Ca(OH)_2$ formation in the carbonator is avoided since the equilibrium pressure of H_2O for $Ca(OH)_2$ formation is higher than 1 atm at carbonation temperature (Shimizu et al., 1999). This can be also seen from Figure 4 (Blamey et al., 2010).

$$CaO+H_2O \rightarrow Ca(OH)_2$$
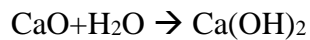
The equilibrium vapor pressure of gaseous CO_2 and H_2O above CaO as a function of temperature is plotted in Figure 4. An important observation from this plot is that carbonation is favored at partial pressure of CO_2 greater than the equilibrium partial pressure, at a particular temperature. Conversely, calcination is favored at a pressure greater than the equilibrium partial pressure (Dean et al., 2011). Thus, cyclic transport of

8

CaO at suitable temperatures will prompt carbonation in the absorber and calcination in

the regenerator.
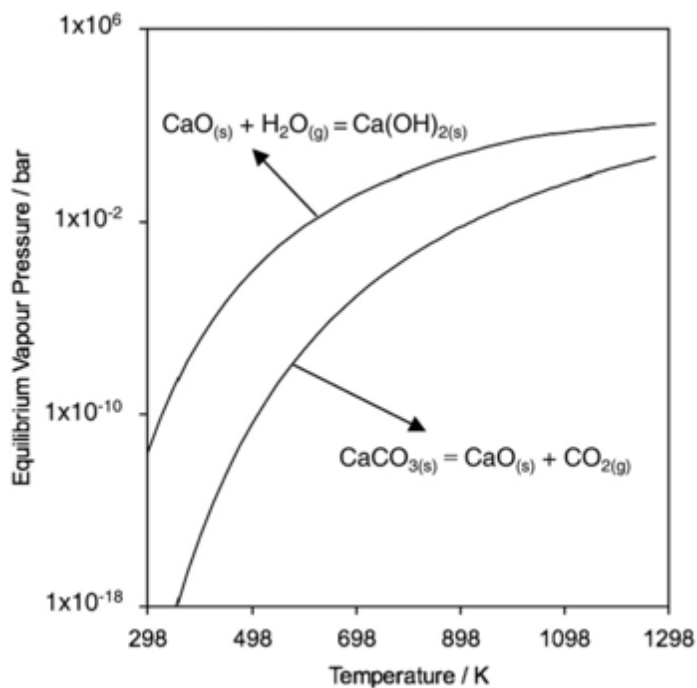
**Figure 4: The equilibrium vapor pressure of gaseous CO_2 and H_2O above CaO vs
temperature (Reprinted from Blamey et al., 2010)[1]**

[1] Reprinted from Progress in Energy and Combustion Science, 36, Blamey, J., Anthony, E., Wang,
J., Fennell, P., 2010, The calcium looping cycle for large-scale CO_2 capture, 260-279, Copyright
(2010), with permission from Elsevier.

The sorbent activity is an important factor affecting the overall CO_2 capture efficiency of the process. Ideally, one mole of CaO would cyclically react with CO_2 and produce 1 mol of CO_2 per cycle. However, the activity of CaO decreases with time i.e. with increasing number of cycles. The rate of carbonation transforms from a fast to a very slow diffusion-controlled rate, thereby restricting complete conversion of CaO to $CaCO_3$. Hence, high capture efficiencies can be obtained by using a suitable amount of fast-reacting CaO (Abanades et al., 2005). However, the fast-reaction period is short-lived and full conversion of the particles is not practically possible. The decay trend of the CO_2 capture capacity of limestone has been fitted experimentally (Abanades and Alvarez, 2003), as follows:

$$X_N = f_m^N(1-f_w) + f_w$$

X_N expresses the carbonation conversion achieved after N cycles, with $f_m = 0.77$ and $f_w = 0.17$ for natural limestone. The average carbonation conversion in the carbonator (X_{ave}) can be given as:

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

X_{ave} is one of the vital parameters in CLP. For lower values of X_{ave}, F_0 is small but then F_R takes a higher value. This also increases fuel consumption in the calciner since the high F_R would require large amount of heat for calcination.

The overall CO_2 capture efficiency (E_{CO_2}) of the system is given as CO_2 emitted from the calciner divided by total CO_2 generated in the system. It is assumed that 100%

of the CO_2 generated in the calciner is captured. For the carbonator, the capture efficiency (E_{carb}) is dependent on the ratio F_0/F_{CO_2} and F_R/F_{CO_2}.

It is desirable to maintain the ratio F_0/F_{CO_2} as low as possible to reduce the costs associated with addition of fresh sorbent to the system. This will also help minimize the fuel consumption required for calcination. Another requirement is that the ratio F_R/F_{CO_2} should be as close to unity as possible to minimize the solid transport between the two connected reactors. With this view in mind, optimum values for F_0/F_{CO_2} and F_R/F_{CO_2} are 0.1 and 4 respectively to achieve a carbonator capture efficiency of 0.95 (Abanades et al., 2005). The experimental values of carbonator capture efficiency with variation in F_0/F_{CO_2} and F_R/F_{CO_2}, reported by these authors, have been summarized in Table 1.

Table 1: Carbonator efficiency vs F_0/F_{CO_2} for different values of F_R/F_{CO_2} (Adapted from Abanades et al., 2005)

F_0/F_{CO_2}	E_{carb}			
	$F_R/F_{CO_2}=1$	$F_R/F_{CO_2}=2$	$F_R/F_{CO_2}=3$	$F_R/F_{CO_2}=4$
0.1	0.36	0.57	0.76	0.95
0.2	0.45	0.70	0.95	0.95
0.3	0.50	0.83	0.95	0.95
0.4	0.57	0.92	0.95	0.95
0.5	0.60	0.95	0.95	0.95

II.2 Applications of Calcium Looping Process (CLP)

II.2.1 Power generation

Calcium Looping Process was originally proposed for CO_2 capture from a 1000 MW coal-fired power plant (Shimizu et al., 1999). It was claimed that the efficiency of such a power plant was higher than that of an oxyfuel combustion process. A life-cycle assessment of this process was presented (Hurst et al., 2012). Further work suggested that the efficiency penalty for a coal-fired power station integrated with CLP is between 6 to 8% (Abanades et al., 2005). Efforts have been made in order to optimize this process by reduction in addition of external fuel to the calciner and internal heat integration (Abanades et al., 2005). The use of a cyclonic preheater for internal heat integration between the captured CO_2 stream and the solids entering the calciner has also been proposed in literature (Martínez et al., 2013). This work indicated a ~11% decrease in the fuel requirements in the calciner, with a loss of ~3% of captured CO_2 (Martínez et al., 2013).

Calcium Looping can also be integrated with a NGCC power plant (Berstad et al., 2012). This poses an efficiency penalty of ~10% on the power plant (Berstad et al., 2014) as opposed to ~8% or an NGCC plant integrated with MEA. With exhaust gas recirculation (EGR), the efficiency penalty for CLP integration can be reduced to 9% (Hu and Ahn, 2017).

II.2.2 Cement production

Cement production alone is responsible for 26% of the total CO_2 emissions from industrial processes (Fennell and Anthony, 2015). It is a highly energy intensive process. The energy consumption per ton of cement produced ranges from 3.1 to 7.5 GJ. 1.67 tons of raw material are required for production of 1 ton of cement. Also, this process emits 0.6-1 ton of CO_2 per ton of cement produced. (Dean et al., 2011). The requirement of huge quantity of limestone and vast amount of CO_2 produced make cement production and excellent candidate for integration with Calcium Looping. A reduction of direct CO_2 emissions from the calcination of $CaCO_3$ for cement production is possible (Dean et al., 2011). This involves use of very hot CaO particles sent from a combustor, increasing the energy requirement by 0.8 GJ/ton cement but capturing around 60% of the CO_2 emissions. The purged material from the Calcium Looping system majorly consisting of CaO can be used in place of fresh limestone. Thus, integration of Calcium Looping with cement production also presents opportunities for mass integration. An economic analysis of integration of CLP with a cement plant that is capable of capturing 99% of the CO_2 emitted by the plant has been presented in literature (Rodríguez et al., 2012).

II.2.3 Pre-combustion carbon capture

CLP is capable of integration with coal gasification. This makes cogeneration of electricity and hydrogen possible, with simultaneous capture of a concentrated CO_2 stream that can be stored or used in other industrial processes. This process developed by Ohio

State University combines both the water-gas shift (WGS) reaction and acid gas removal in the carbonator itself (Fan et al., 2008).

The reactions taking place in the carbonator are:

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CaO + CO_2 \rightarrow CaCO_3$$

$$CaO + H_2S \rightarrow CaS + H_2O$$

$$CaO + COS \rightarrow CaS + CO_2$$

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

$$C_xH_y + xH_2O \rightarrow xCO + (x+y/2) H_2$$
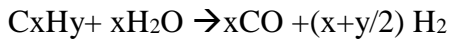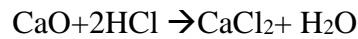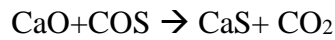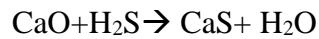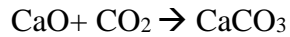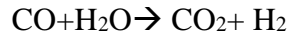
The calcium carbonate formed is sent to the calciner, where it decomposes to calcium oxide and carbon dioxide.

This integration presents three important advantages (Blamey et al., 2010):

i. CO_2 removal in the carbonator accelerates the WGS reaction rate and eliminates the need for a catalyst

ii.   The exothermic carbonation reaction reduces the overall energy consumption of the process

iii. CaO and $CaCO_3$ aid in tar elimination, making the production of fuel-cell grade H_2 possible.

CLP can be applied to syngas derived from coal, natural gas or other fuels for H_2 and electricity production (Connell et al., 2013). The efficiency of this integration for production of fuel-cell grade H_2 from coal is 63% as against 57% for conventional

processes. Hence, this process provides a path to increase process efficiency with a reduction in the carbon footprint.

II.3 Calcium Looping pilot plants

Since its inception (Shimizu et al., 1999) in the year 1999 till now, CLP has moved from the experimental stage to pilot plant scale. Table 2 lists the lab-scale and pilot plant scale CLP facilities built around the world (Fennell and Anthony, 2015).

Results based on studies from these plants indicate good levels of CO_2 capture efficiency (~80-90%). Current research is focused on improving this efficiency and on producing a CO_2 stream suitable for sequestration.

Table 2: List of lab and pilot-scale CLP plants across the world

	Location	Size	Scale
1	University of Stuttgart	10 kWth	Lab-scale
2	INCAR-CSIC, Oviedo, Spain	30 kWth	Lab-scale
3	CANMET, Ottawa, Canada	75 kWth	Lab-scale
4	Ohio State University, USA	120 kWth	Lab-scale
5	ITRI, Hsinchu, Taiwan	3 kWth	Lab-scale
6	La Pereda, Spain	1.7 MWth	Pilot scale
7	TU Darmstadt, Germany	1 MWth	Pilot scale
8	University of Stuttgart, Germany	200 kWth	Pilot scale

II.4 Economics of Calcium Looping

The economics of Calcium Looping are vital to its implementation. The economic benefits of CLP are still somewhat marginal in the EU (Fennell and Anthony, 2015). A cost assessment of CLP integration with coal-fired power plant was presented (Abanades et al., 2007). The system under consideration included the full power plant and the CLP system consisting of the calciner and carbonator. The capture cost of this system was indicated to be 15\$/ton of CO_2 avoided. Use of Calcium Looping for other post-combustion application indicates a higher cost in the range of 17-35 \$/ton CO_2 avoided (Fennell and Anthony, 2015). This makes the performance of a basic cost analysis essential for evaluation of any CLP system. One of the key drawbacks faced by this system is that reaction equilibrium limits the achievement of 100% CO_2 capture efficiency. Also, CO_2 capture efficiencies of less than 90% are most effective. However, the state-of-art technology of amine scrubbing has a capture efficiency of 95%, making it essential that the capture efficiency of CLP must be able to compete with this technology.

The process simulation and economic analysis for integration of CLP with hydrogen and electricity production has been presented in previous literature (Connell et al., 2013). The components of the CLP unit included in the reference plant are summarized as follows (Connell et al., 2013):

i.   Carbonator

The carbonator is a fluidized bed reactor with internal heat transfer surface in order to enable heat recovery from exothermicity of the reaction. This is a commercially proven technology.

ii. Calciner

The calciner is an entrained flow reactor i.e. a flash calciner, since it does not need to have a provision for internal heat recovery. Like the carbonator, the flash calciner is commercially proven technology. However, the use of oxyfuel combustion has not been demonstrated for this type of technology. This is modeled similar to the oxy-firing system design used in PC power plant applications.

iii. Calciner ASU

A cryogenic ASU is used to generate O_2 required for oxyfuel combustion to provide energy to the calciner.

iv. Carbonator Product Lock hoppers

Lock hoppers are feeding devices used for depressurizing the solids that are circulating between the carbonator and calciner.

v. Cyclones

A cyclonic preheater that enables heat exchange between the captured hot CO_2 stream and the solid stream from the carbonator. Although this provides a marginal temperature rise, it can significantly help reduce the calciner fuel consumption because of the large volume of solids entering the calciner.

vi. Calciner off-gas HRSG

The gaseous stream exiting the cyclone is then sent to a Heat Recovery Steam Generator(HRSG) to produce steam.

vii. CO_2 stream condenser

    The water content of the CO_2 stream exiting the calciner is removed using a condenser

viii. Solids Purge Fabric Filter

    Fabric filters are necessary to separate the captured CO_2 stream from the solids. The purge stream is also taken from here to prevent buildup of inert materials in the calcium looping cycle.

ix. Other equipment includes calciner off-gas ID fan, limestone storage and make-up and solid byproduct handling system.

    A breakdown of the equipment costs and fixed and variable operating costs for this process has also been provided. This can be used to determine the costs of the new CLP system. When the capacities of the reference plant (Capacity A) and the new plant (Capacity B) are both known, it is possible to determine the fixed capital investment (FCI) of the new plant using the following correlation called the six-tenths-factors rule (El-Halwagi, 2011):

$$FCI_B = FCI_A \left(\frac{Capacity_B}{Capacity_A}\right)^x$$

where the exponent 'x' generally takes the value 0.6.

    Operating cost or working capital investment (WCI) constitutes of cost of energy, raw materials, labor and maintenance (El-Halwagi, 2011) Utility cost includes cost of steam, electricity and fuel (El-Halwagi, 2011). WCI and FCI sum up the total capital investment that indicates the total project cost. The Chemical Engineering Plant Cost

Index (CEPCI) is used to update the FCI from a past date to the current time, to better reflect the economics of the process.

The evaluation of processes that utilize the captured CO_2 i.e. CO_2 sinks is carried out on the basis of a stoicho-nomic indicator called 'Metric for Inspecting Sales and Reactants' abbreviated as MISR. It is given as follows (El-Halwagi, 2011):

$$\text{MISR} = \frac{\sum_{p=1}^{N_{products}} \text{Annual production rate of product p*Selling price of product p}}{\sum_{r=1}^{N_{reactants}} \text{Annual feed rate of reactant r*Purchase price of reactant r}}$$

Higher values of MISR are certainly more desirable, with a value of '1' being the minimum requirement. If MISR>1, the process can be considered for a further detailed analysis. If MISR<1, the process is certainly not desirable from an economic perspective. It is important to select 'winning processes' for downstream integration of CLP on the basis of MISR, since this gives a broad understanding of the feasibility of the process, by eliminating the requirement for a detailed analysis.

CHAPTER III

PROBLEM STATEMENT AND SOLUTION APPROACH

III.1 Problem Statement

Carbon Capture and Utilization (CCU) is a promising option for reducing emissions of CO_2 to the atmosphere from power plants and industrial processes. As such, this work aims to determine the techno-economic feasibility of integration of Calcium Looping with processes emitting CO_2. The captured CO_2 is utilized in chemical syntheses that utilize CO_2 as feedstock.

The questions to be addressed by this integration are:

i.   What is the concentration of CO_2 in the captured stream?

ii.   How much CO_2 can be sequestered in the processes downstream of the CLP?

iii. How much net reduction in CO_2 emissions can be achieved because of this integration?

iv.   What is the net energy consumption of this integration?

To answer these questions, following tasks are to be undertaken:

i.   Heat and Mass integration of said process with CLP

ii.   Economic Assessment of the integration

The schematic representation of the problem is shown in Figure 5.
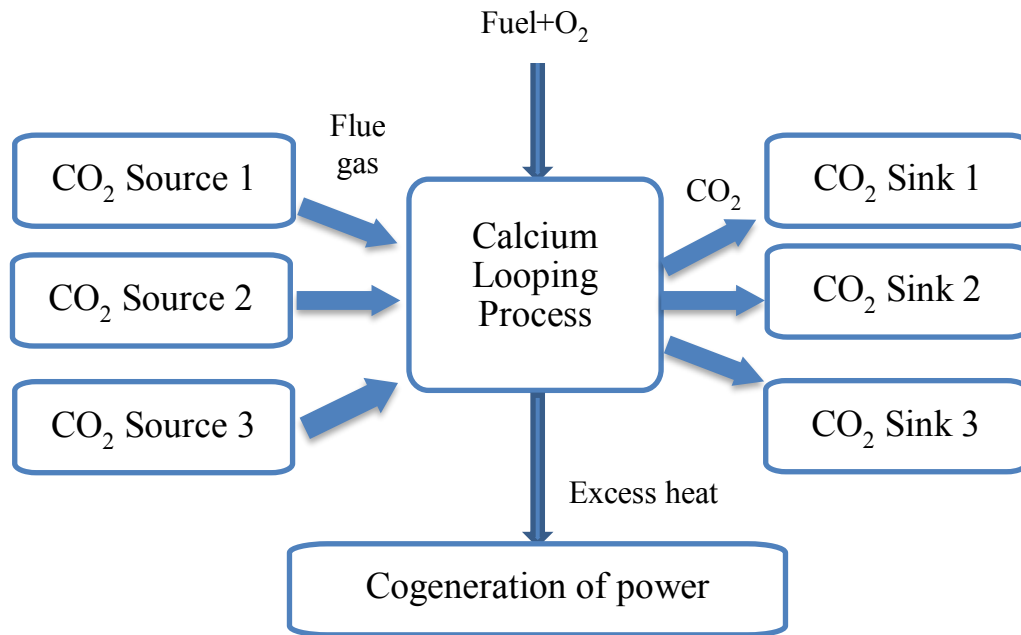
Figure 5: Schematic of the problem statement

III.2 Methodology and Approach

Carbon Capture, Utilization and Storage (CCUS) is a promising option for reducing CO_2 emissions from industrial processes. By far, the three most widely researched application of Calcium Looping Process (CLP) are:

1. Power Plants

2. Cement Production

3. H_2 and electricity production

The aim of this research is to go beyond these conventional applications and explore the application of CLP as an alternate to MEA scrubbing. The CLP system is to be treated as a separate unit, that is capable of taking in flue gas from a source and

producing a highly concentrated stream of CO_2, by minimal utilization of energy and resources. This captured stream can be used as a CO_2 feedstock for chemical syntheses. This generates an eco-industrial park (EIP) configuration, wherein heat and mass integration can take place. This approach would make economic sense only when the cost saved by substituting the feedstocks in the downstream process enables a reasonable value of the ROI (return on investment) for the project. A reasonable value of ROI is 10-15% for the project to generate an economic benefit. The systematic approach followed is shown in Figure 6.
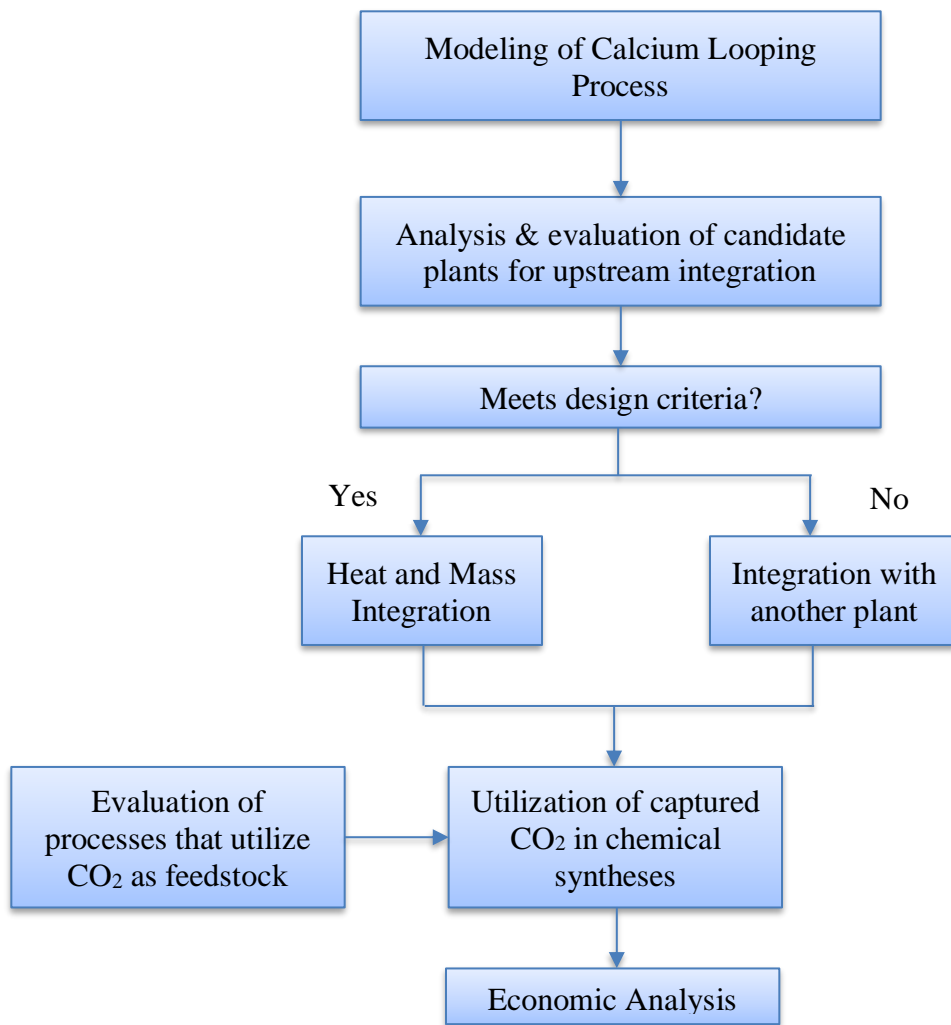
Figure 6: Approach methodology of techno-economic analysis

III.2.1 CO$_2$ sources

For integration with Calcium Looping, it is necessary to identify processes that are major emitters of CO$_2$. The composition of flue gas entering the carbonator largely determines the energy consumption of the system. Hence, to avoid large parasitic energy consumption, a practical constraint of 15 vol% CO$_2$ is placed on the carbonator inlet (Valverde et al., 2014). The potential CO$_2$ sources are evaluated according to the following criteria:

i.   Source of feed flue gas with acceptable CO$_2$ percentage

ii.   Possibility of mass integration with CLP

iii.   Possibility of heat integration with CLP

Processes that meet one or more criteria of the following have been considered in this thesis. These are discussed further next.

III.2.1.1 PC power plant

As discussed in Chapter II, Section II.2.1, PC power plants are major emitters of CO$_2$.The flue gas from the combustor of a PC power plant contains 13-14 vol% CO$_2$. This makes it an excellent candidate for integration with CLP. The integration of CLP with a PC power plant has been presented earlier in literature (Abanades et al., 2005; Hurst et al., 2012; Zhen-shan et al., 2008). However, it is critical to perform a simulation of integration of CLP with a PC power plant to view it from the perspective of an EIP.

III.2.1.2 NGCC power plant

The CO_2 emission factor of an NGCC power plant (364 kg CO_2/MWh) is 50% lesser than that for a PC power plant (800 kg CO_2/MWh) (Hu and Ahn, 2017). However, the flue gas stream contains only 4 vol% CO_2 as against 15 vol% for a coal fired plant. This makes carbon capture much more difficult than for a PC power plant. The parasitic energy consumption in this case increases and can lead to an energy efficiency penalty as high as 10%. Hence, an NGCC power plant has been coupled with CLP in order to perform an equivalent comparison with a PC power plant.

III.2.1.3 Cement plant

Due to the excellent synergy between CLP and cement manufacture, there is tremendous potential for integration between the two processes. Calcination of $CaCO_3$ is responsible for approximately 80% of CO_2 emissions in cement manufacture (Dean et al., 2011). The added advantage is the superior quality of sorbent generated in this process that has greater sorbent capacity and undergoes slower deactivation.

It has previously been established in literature that the purged CaO from the Calcium Looping unit of a power plant can be used to substitute limestone in cement manufacture (Dean et al., 2011). An industrial symbiosis of a cement plant, a coal-fired power plant and Calcium Looping unit has been demonstrated in literature (Romeo et al., 2011).

For this thesis, a cement plant of capacity 3000 TPD has been integrated with a Calcium Looping process to perform an analysis that indicates a saving in the cost of fresh limestone. The purged CaO from the CLP unit can be utilized as feedstock in the cement

plant. The goal of this simulation is targeting the reduction in limestone requirements and also determining the composition of the capture CO_2 stream.

III.2.1.4 GTL plant

A techno-economic assessment of a GTL plant that has been presented in literature was considered for this integration (Bao et al., 2010). This process uses natural gas as feedstock in the Fischer-Tropsch process to produce different liquid hydrocarbon fractions. Complete heat integration of the plant has been carried out. The tail gas stream is burnt in order to generate additional heat. This heat can be used for cogeneration. The pure CO_2 stream so generated can be used in any of the downstream processes. Given the high capacity of the GTL process, the amount of captured CO_2 would also be high. The electricity generation can help to offset some of the costs of Calcium Looping by internal utilization.

III.2.1.5 Ammonia synthesis plant

Majority of the ammonia synthesis is for fertilizer production. Ammonia is produced by the Haber process. The ammonia formation reaction is:

$$N_2 + 3H_2 \rightarrow 2NH_3$$
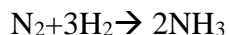
The hydrogen required is produced by stream reforming of natural gas. Syngas formation takes place and air is added to meet the required ratio of nitrogen to hydrogen. It is important to remove CO_2 from the syngas since it can damage the ammonia synthesis catalyst. Currently, MEA absorption is used for CO_2 removal. However, due to the disadvantages of this method discussed in Chapter I, it is worthwhile to perform a

comparative assessment of these processes for CO_2 removal. The captured CO_2 can be used in the downstream process of urea synthesis.

III.2.2 CO_2 sinks

The use of CO_2 as chemical feedstock is a suitable option for the capture CO_2 to be utilized. This would mean utilization of some alternate pathways for chemical syntheses. There are however some constraints on this kind of CO_2 reuse (Aresta, 2010):

i.   The net CO_2 emissions should be reduced as result of this integration

ii.   The integration must be economically feasible

iii.   The new process must be less material and energy intensive than the conventional approach

iv.   The new process should not pose any compromise on safety

The chemical syntheses considered as CO_2 sinks are discussed further next.

III.2.2.1 Urea synthesis

Urea synthesis is carried out on a large industrial scale for fertilizer production. Urea is produced industrially by the Haber-Bosch process, using NH_3 and CO_2 as raw materials (Ullmann et al., 1985).

$$2NH_3 + CO_2 \Leftrightarrow NH_2COONH_4$$

$$NH_2COONH_4 \Leftrightarrow CO(NH_2)_2 + H_2O$$
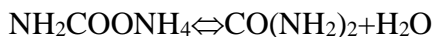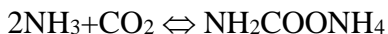
A major part of the ammonia produced in a plant is sent for urea production. Hence, the integration of CLP in this scheme offers great incentive for urea yield boosting. When natural gas is used as the feedstock for urea production, surplus ammonia is usually produced. A typical surplus of ammonia may be 5 per cent to 10 per cent of total ammonia

27

production. If additional CO_2 can be obtained, this can be compressed and combined with the surplus ammonia to produce additional urea (Brinckerhoff, 2011). Alternatively, it can be used as a direct input to the process instead of natural gas, while maintaining the same product yield. The CO_2 captured from the ammonia plant discussed in Section III.2.1.2 can be sent directly to the urea process. This integration scheme is described in Figure 7.
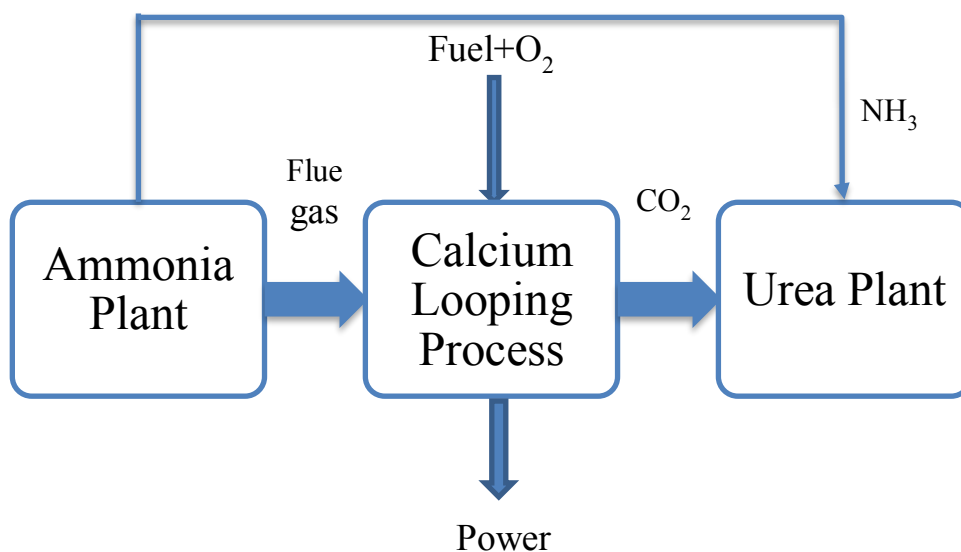
Figure 7: Integration of CLP with ammonia and urea production

III.2.2.2 Polymer synthesis

Polymers consist of large number of repeating structural units called monomers. The use of CO_2 as raw material is part of a new approach to polymer production. The state-of-the art for production of industrially important polycarbonates utilizes bisphenol A and diphenyl carbonate as raw materials. Both being toxic in nature, it is important to move to a safer and sustainable pathway for polycarbonate production. The production of Polypropylene Carbonate using CO_2 and Propylene Oxide presents a sustainable and economic approach to this synthesis. A sustainability and economic analysis of this production process has been presented in literature (Demirel, 2015). The reaction for this synthesis is:

$$nCH_3CHCH_2O + nCO_2 \rightarrow CH_3C_2H_3O_2CO + [CH(CH_3)CH_2OCO_2]_n$$
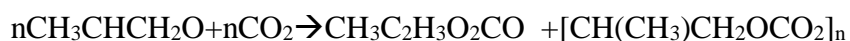
III.2.2.3 Methanol production

Conventional methanol production takes place via Fischer-Tropsch synthesis, where the syngas is obtained from natural gas. The captured CO_2 can be used as a raw material since this process already requires CO_2. Use of dry reforming for methanol production is not suitable due to extensive coke formation (Cañete et al., 2014). Use of combined forming or bi reforming, that combines dry reforming and steam reforming, is more suitable to produce methanol. The overall reaction is given as:

$$3CH_4 + 2H_2O + CO_2 \rightarrow 4CH_3OH$$

Theoretical studies indicate that combined reforming has lower operating costs and capital costs in comparison with steam reforming (Cañete et al., 2014). This makes it competitive with conventional methanol production processes.

III.2.2.4 Acetic Acid production

Conventional production of acetic acid is carried out by carbonylation of methyl alcohol, also called the Monsanto process. However, CO_2 fixation is possible by reaction of methane and CO_2 in the presence of Vanadium-based catalysts (Taniguchi et al., 1998). $VO(acac)_2$ (acac: acetylacetonate) was used as a catalyst. The overall reaction is given as:

$$CH_4 + CO_2 \rightarrow CH_3COOH$$

The conventional process operates at 450 K and 30 bar whereas the proposed process operates at 350 K and 25 bar. This process operates at a lower pressure and temperature than the conventional process. The conversion obtained in this process is 97%, comparable to 100% for the conventional process. Also, the conventional process utilizes carbon monoxide which is toxic in nature. This is replaced by CO_2 and CH_4, that are both greenhouse gases.

CHAPTER IV

PROCESS ANALYSIS

In this chapter, the integration of Calcium Looping Process (CLP) with CO_2 sinks and sources is presented. This chapter has been divided into 3 parts. The simulation of CLP using ASPEN Plus has been described in detail in the first part. The second part of the chapter presents the results of the individual integration of the CO_2 sources with the CLP unit. The purity of the captured CO_2-rich stream is the most essential parameter that is calculated herein. The CO_2 capture efficiency for each of the integrated processes and the energy consumption per ton of captured CO_2 have also been determined by this simulation. The third and last part of this chapter presents the pathways that utilize the CO_2 captured and determine the specific raw material requirements that would help determine the MISR for each path.

IV.1 Calcium Looping Process

The simulation of the CLP is discussed in this section. This simulation has been performed in ASPEN Plus. The carbonator and calciner are modeled along with the accompanying heat exchangers. The objective is to determine the following:

i.   Energy consumption for CLP

ii.   Net CO_2 emissions

iii.   Concentration of CO_2 in the captured stream

The simulation is based on thermodynamic equilibrium. The Redlich-Kwong-Soave equation is used to calculate thermodynamic phase equilibrium. The property

method RK-SOAVE in ASPEN Plus is used for this purpose. The chemical and phase equilibriums are based on a Gibbs free energy minimization model. Maximum internal heat integration is carried out, to minimize the energy consumption of the process.

IV.1.1 Inlet Setup

ASPEN Plus cannot model a looping process; hence a serial process is modeled in this simulation. The ambient pressure and temperature are 1 atm and 25 ℃ respectively. The temperature of the incoming materials is set at 25 ℃ i.e. room temperature. In case of the PC power plant and cement plant, the choice of fuel is coal since these plants already utilize CO_2 and would have required coal handling facilities, making integration with CLP easier. Likewise, for the NGGC power plant, GTL plant and ammonia synthesis plant, use of natural gas as a fuel is a more viable option.

The important assumptions and inputs are as follows:

i. Coal utilized is Illinois #6 coal (Fan, 2011). HHV (Higher Heating Value) of this coal is 27.5 MJ/kg. Coal is defined as a 'Nonconventional' component in ASPEN Plus. The coal input data includes the proximate, ultimate and sulfate analysis of coal. This is given in Tables 3 and 4.

Table 3: Proximate and Ultimate Analysis of Illinois #6 coal

	%wt., As received	%wt., Dry
Proximate Analysis		
Moisture	11.12	-
Fixed Carbon	44.19	49.72
Volatile Matter	34.99	39.37
Ash	9.7	10.91
Ultimate Analysis		
Moisture	11.12	-
Ash	9.7	10.91
Carbon	63.75	71.72
Hydrogen	4.5	5.06
Nitrogen	1.25	1.41
Chlorine	0.29	0.33
Sulfur	2.51	2.82
Oxygen	6.88	7.75

Table 4: Sulfate Analysis of Illinois #6 coal

Constituents	Wt.%
Pyritic	1
Sulfate	1
Organic	0.82

ii.   Air consists of 79 vol% N_2 and 21 vol% O_2.

iii.   The inlet temperature and pressure of the natural gas stream are 26°C and 26 bar respectively. The LHV of natural gas is 47.13 MJ/kg. The composition of natural gas is given in Table 5.

Table 5: Natural gas feed composition

Component	Composition (mol %)
Methane	95.39
Ethane	3.91
Propane	0.03
CO_2	0.59
N_2	0.08

iv.   Power requirement for Air Separation Unit (ASU) is 26 MJ/kmol O_2 and CO_2 compression is 24.5 MJ/kmol CO_2.

v.   The CaO disposal ratio F_0/F_{CO_2} is set to 0.1 (Abanades et al., 2005).

vi.   The average carbonation conversion of CaO in the absorber is set to 0.251 (Hurst et al., 2012).

IV.1.2 Carbonator setup

The reaction taking place in the carbonator is as follows:

$$CaO + CO_2 \rightarrow CaCO_3 \quad \Delta H = -178 \text{ kJ/mol}$$
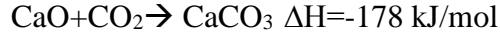
The carbonator is modeled as a RSTOIC reactor, operating at a pressure of 1 atm and temperature 650 °C. In an RSTOIC reactor, it is necessary to define the reaction and the extent of conversion of the reaction. The CO_2 capture efficiency of the carbonator is set to 95%. The carbonator exit stream then goes through a carb

The stream exiting the carbonator consists of the solids and the CO_2-lean flue gas stream. This is separated by means of an SSPLIT reactor to simulate the cyclone separator. The solid stream is sent ahead to the calciner and the CO_2-lean flue gas stream is cooled down to 150 °C to extract heat.

IV.1.3 Calciner setup

The reaction taking place in the calciner is as follows:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 178 \text{ kJ/mol}$$

Similar to the carbonator, the calciner is modeled as a RSTOIC reactor, operating at a pressure of 1 atm and temperature 900 °C. This reaction attains complete conversion, Hence, the conversion fraction of $CaCO_3$ is set to 1.

Since the calcination reaction is endothermic, additional heat is to be provided by means of oxyfuel combustion of the fuel considered for the particular process. Since the solids entering the calciner are at 650 °C, a large amount of sensible heat is also employed in raising their temperature to 900 °C. The fuel consumption required for this can be reduced by internal heat exchange in the system.

IV.1.4 Heat exchanger setup

The CLP system has the following heat exchangers:

i.   Cooler for CO_2-lean flue gas stream

This stream is at 650 ℃. It can be let down to 150 ℃ to extract useful heat. The temperature of 150 ℃ is set to make it suitable for power generation in the power plant steam cycles.

ii.   Cyclonic preheater for heat exchange between captured CO_2 stream and solids inlet to calciner

The solids exiting the calciner are at 650 ℃. The calciner temperature is 900 ℃. Hence, preheating of the solids prior to entering the calciner is important to reduce the fuel required in the calciner. Hence, a cyclonic preheater is employed to carry out heat exchange between the two streams. The solids are preheated from 650 ℃ to 715 ℃ and the CO_2 stream is let down to 700 ℃ from 900℃. This has simulated by means of different heat exchangers for both the streams such that the heat duty of both the exchangers is the same. This 'traps' about 3% of the CO_2 leaving the calciner as part of the solid sorbent, thereby decreasing the overall capture efficiency.

iii.   Cooler for captured CO_2 stream

This follows the cyclonic preheater. The temperature of the captured CO_2 stream is let down to 150 ℃.

iv.   Condenser for water removal

The captured stream is let down to 25ºC in a flash column to remove the water

from this stream. This produces the desired highly concentrated stream of CO_2.

IV.2 CO_2 sources

IV.2.1 PC power plant

Fossil fuel combustion in power plants is a major source of CO_2 emissions. The

amount of CO_2 generated by coal-fired power plants is much greater than that released

during power generation using oil and natural gas. Hence, a coal-fired power plant has

huge potential for CO_2 removal and incorporation into an eco-industrial park type

configuration.

Amine absorption is the most mature technology for CO_2 capture for current

consideration for CO_2 removal from power plant flue gas. This process requires a large

amount of low-temperature heat for solvent regeneration. A major drawback of this

process is the low-temperature level of the waste heat that renders it difficult to be utilized

in the steam cycle (Fennell and Anthony, 2015). In contrast, the carbonator in the Calcium

Looping releases heat at 600-700 °C. This energy can be integrated in a power cycle to

generate additional amount of electricity, thereby improving the energy efficiency of the

power plant (Romano et al., 2012).

For the purpose of this thesis, a pulverized coal power plant coupled with Calcium

Looping was simulated using Aspen Plus. The simulation considered the equipment

associated with CLP only. The turbines and generators required for power generation were

not simulated. Instead, the power plant efficiency for a PC power plant was obtained from

literature (Abanades et al., 2007; Hurst et al., 2012). Similarly, for the PC plant integrated with CLP, the primary and secondary turbine efficiencies were taken from literature (Shimizu et al., 1999).

For the PC power plant, it is necessary to model the Fluidized Bed Combustor (FBC) as well. Since coal must be defined as a non-conventional component in ASPEN Plus, it cannot be directly modeled. It must be first decomposed into its constituent elements using a RYIELD reactor model. The mass percentages of the component yields are set according to the Ultimate Analysis of coal.

The exit stream of the RYIELD reactor is sent to a RGIBBS reactor model that simulates the coal combustion process. The air flowrate is set such that the entire amount of carbon is converted to CO_2 and that no CO (Carbon Monoxide) remains in the system. Post-burner, the stream is sent to a SSPLIT separator for separation of ash from the flue gas stream. The flue gas stream is cooled down to 650 ℃ i.e. the carbonator inlet temperature.

In practice, the oxyfuel combustion is carried out in the calciner itself. However, for the sake of simplicity in modeling, the oxyfuel combustion process is simulated separately in a decomposer (RYield) followed by a combustor (RGibbs) reactor. The following assumptions were made for the simulation:

i.   A feed rate of 50 kg/s of Illinois #6 coal is used.

ii.   The combustor temperature was set to 1400 ℃.

iii.   For the primary steam cycle, heat was extracted from the combustor bed, combustor flue gas and the CO_2-lean flue gas streams. This cycle has an efficiency of 46.6%.

iv.   For the secondary steam cycle, heat is recovered from the heat of reaction in the carbonator and the sensible heat of the captured CO_2 stream. This cycle has an efficiency of 46.6%.

v.   The efficiency of a PC power plant without CO_2 capture is set to 43% (Abanades et al., 2007)

IV.2.1.1 Simulation Results

The simulation results of this analysis seem to be in agreement with literature (Hurst et al., 2012; Shimizu et al., 1999). The fraction of coal sent to the combustor is y_{comb}. It is necessary to maximize this value to reduce the energy efficiency penalty of the system. At the same time, the fuel requirement of the calciner must be satisfied. Hence, y_{comb} is an important parameter to be optimized in this simulation. this value is obtained to be 0.63 from the simulation. The flow rates of recovered heat as primary and secondary steam are 712 MW and 655 MW respectively. The flowsheet of the simulation is attached in the Appendix as Figure 9. The simulation results are summarized in Table 6.

Table 6: Simulation results of PC+CLP system

Parameter	Value	UOM
Flowrate of captured CO_2	122.76	kg/s
Percentage mass of CO_2	98.22	%
F_R	7.12	kmol/s
F_0	0.17	kmol/s
Primary cycle power	331.88	MW
Secondary cycle power	279.01	MW
ASU power requirement	30.82	MW
CO_2 compression power	67.13	MW
Other losses	12.94	MW
Total power generated	500	MW
CLP energy consumption	1718	MJ/ton CO_2
Overall CO_2 capture efficiency	94.09	%

The efficiency of the power plant is 36.5% on HHV basis. This gives an energy efficiency penalty of 6.5%. This value is acceptable since it is in agreement with literature (Abanades et al., 2005; Abanades et al., 2007). Hence, the net energy needed to drive the looping is 741 MJ/ton CO_2 captured.

The composition of the CO_2 stream produced is summarized in Table 7.

Table 7: Composition of captured CO_2 stream from PC+CLP system

Component	Mol%
CO_2	96.57
N_2	0.29
O_2	0.86
H_2O	2.28

IV.2.2 NGCC power plant

NGCC power plants account for 21% of electricity production around the world. Natural gas is a relatively clean fuel and NGCC power plants are capable of achieving efficiencies as high as 60% (Erans et al., 2016). The modeling and simulation of the NGCC+CLP setup is carried out in a fashion similar to the PC+CLP system.

In practice, the oxyfuel combustion is carried out in the calciner itself. However, for the sake of simplicity in modeling, the oxyfuel combustion process is simulated separately in a combustor (RGibbs reactor). The salient features of this simulation are:

i.   The natural gas flowrate to the combustor is 3500 kmol/hr and to the calciner is 1400 kmol/hr.

ii.   The combustor is modeled as an RGibbs reactor, operating at a temperature of 1200 ºC.

iii.   For the primary steam cycle, heat was extracted from the combustor bed, combustor flue gas and the CO_2-lean flue gas streams. The gas turbine efficiency

and primary steam turbine efficiency are set at 37.7% and 16.7% respectively on gas cycle fuel basis (Hu and Ahn, 2017).

iv. For the secondary steam cycle, heat is recovered from the sensible heat of the captured CO_2 stream. The secondary steam turbine efficiency is assumed to be 52.9% on calciner fuel basis (Hu and Ahn, 2017).

IV.2.2.1 Simulation Results

The capacity of the NGCC power plant is also 500 MW. The flowrates of natural gas to the combustor and calciner are 3500 kmol/hr and 1400 kmol/hr respectively. The flowsheet of the simulation is attached in the Appendix as Figure 10. The simulation results for this power plant are summarized in Table 8.

The energy efficiency for the NGCC+CLP system is 47.2%. The energy efficiency penalty is 10% compared to a standalone NGCC plant. Hence, the net consumption for the CLP system can be determined to be 1614 MJ/ton CO_2. This value is more than twice that for capture of CO_2 from the PC power plant. This is expected because of the low concentration of CO_2 in the flue gas stream of an NGCC plant. The composition of the CO_2 stream produced is summarized in Table 9.

Table 8: Simulation results of NGCC+CLP system

Parameter	Value	UOM
Flowrate of captured CO_2	66.54	kg/s
Percentage mass of CO_2	96.86	%
F_R	4.04	kmol/s
F_0	0.101	kmol/s
Primary steam turbine power	128.29	MW
Secondary steam turbine power	161.81	MW
Gas turbine power	289.62	MW
Auxiliary consumption in primary cycle	4.23	MW
Auxiliary consumption in secondary cycle	0.49	MW
Auxiliary power in capture unit	3.24	MW
Other losses	1.44	MW
ASU power requirement	42.88	MW
CO_2 compression power	27.44	MW
Total power generated	500	MW
CLP energy consumption	2408	MJ/ton CO_2
Overall CO_2 capture efficiency	93.78	%

Table 9: Composition of captured CO_2 stream from NGCC+CLP system

Component	Mol%
CO_2	94.79
N_2	0.06
O_2	2.9
H_2O	2.25

IV.2.3 Cement plant

The cement plant capacity is set to 3000 TPD. For the integration of cement plant with CLP, the purged CaO from the calciner will be used to subsidize the fresh limestone to the process. The input to the cement plant is 1.667 kg raw materials/kg clinker (Engin and Ari, 2005). This constitutes around 75% limestone and 25% clays (Romeo et al., 2011). The preheater exhaust gas from the cement plant is 2.094 kg/kg clinker. This gas is sent as flue gas to the CLP unit. The pre-heater exhaust gas consists of 1.8% O_2, 27.4% CO_2 and 70.8% N_2 (Engin and Ari, 2005).

Mass balance computations are performed to evaluate the reduction in fresh limestone feed. This will offset the CO_2 emissions from the process as well. The excess heat from the process: heat of reaction from the carbonator and heat from CO_2-rich and lean streams can be used for power generation to further reduce the energy consumption of the process.

IV.2.3.1 Simulation Results

A basic mass balance indicates that the purge stream of CaO exiting the calciner can reduce the fresh limestone requirement to the cement plant by 40%. This will significantly reduce the operating cost of the cement plant as well as eliminate the problem of purge disposal to an extent. This also implies a significant decrease in the CO_2 emissions of the cement production process since much of the CO_2 emissions emerge from calcination of the limestone itself. The coal input to the cement plant is 345 TPD. However, 60% of the emissions arise from decarbonisation of limestone (Dean et al., 2011). Since the limestone requirements go down by 40%, we can assume that the CO_2

emissions are also reduced by 40%. Equivalently, the coal use for the cement plant also goes down by approximately 40% to 207 TPD. The flowrate of coal to the CLP system is 3.3 kg/s, this corresponds to a value of 285 TPD. Hence, the resulting increase in coal consumption is 147 TPD. The CLP energy consumption can be determined by the net increase in coal consumption. The flowsheet of the simulation is attached in the Appendix Figure 11. The simulation results are summarized in Table 10. The composition of the captured stream is summarized in Table 11.

Table 10: Simulation results of Cement plant+CLP system

Parameter	Value	UOM
Flowrate of captured CO_2	20.56	kg/s
F_R	1.08	kmol/s
F_0	0.027	kmol/s
Percentage mass of CO_2	98.49	%
CLP energy consumption	2246	MJ/ton CO_2
Overall CO_2 capture efficiency	94.22	%

Table 11: Composition of captured CO_2 stream from Cement plant+CLP system

Component	Mol%
CO_2	96.92
N_2	0.31
O_2	0.49
H_2O	2.28

IV.2.4 Gas-to-liquid (GTL) process

GTL process has been previously optimized and analyzed in literature (Bao et al., 2010). The tail gas stream from this process can be combusted to generate additional heat. The composition of the tail gas stream is given in Table 12. The combustion of hydrocarbons from this stream can be used for cogeneration. This burner is simulated by means of an adiabatic RGibbs reactor in ASPEN Plus.

Table 12: Composition of tail gas stream

Component	Mole %
CO_2	24.15
H_2	64.51
CO	7.70
N_2	0.06
C_2	2.13
C_3	1.45

Since the tail-gas has a high inert (carbon dioxide and nitrogen) concentration and is at a low pressure (3 psig), there are likely to be flame-stability problems related with its combustion. Hence, some percentage of natural gas is added to it. Since it is recommended that the proportion of tail-gas should not be greater than 85 vol%, this value of tail-gas is supplemented by natural gas. The furnace temperature is set to 1200°C. The heat from this stream can be used to reduce the fuel consumption in the calciner, thereby reducing the overall energy of the CLP. The remaining heat from this combustion as well as the reaction

46

heat coming from the absorber are used for cogeneration. This is modeled as a heat exchanger followed by a turbine. The isentropic efficiency of the turbine is set to 80%. This will help reduce the electricity consumption cost of the GTL plant and reduce costs.

IV.2.4.1 Simulation Results

The GTL plant capacity as presented by the authors is 118,000 BPD. Naturally, the flowrates of the flue gas stream and captured CO_2 stream would be much higher than the cases considered earlier. Hence, it could be prudent to perform integration with a plant of smaller capacity such that most of the captured CO_2 can be reutilized for chemical syntheses. Shell has developed its own commercial GTL technology in Malaysia, operating at 14,700 BPD (Bao et al., 2010). Hence, for the simulation, the flowrate of the tail gas is accordingly scaled down to capacity. The fuel requirement in the oxyfuel calciner is 7.18 kg/s of natural gas at STP. The flowsheet of the simulation is attached in the Appendix as Figure 12. The simulation results are summarized in Table 13. The composition of the CO_2 stream produced is summarized in Table 14.

Table 13: Simulation results of GTL+CLP system

Parameter	Value	UOM
Flowrate of captured CO_2	81.12	kg/s
F_R	5.2	kmol/s
F_0	0.13	kmol/s
Percentage mass of CO_2	99.02	%
Power generated by cogeneration	237	MW
CLP energy consumption	4171	MJ/ton CO_2
Overall CO_2 capture efficiency	93.63	%

Table 14: Composition of captured CO_2 stream from GTL+CLP system

Component	Mol%
CO_2	97.56
N_2	0.02
O_2	0.14
H_2O	2.28

IV.2.5 Ammonia synthesis

For the integration of ammonia plant with CLP, the ammonia synthesis plant was first simulated in Aspen Plus followed by a coupling with the CLP system. The heat surplus from the ammonia plant units can be utilized to reduce the energy consumption of the CLP. A capacity of 2000 TPD of NH_3 was assumed for the ammonia plant.

The Kellogg process for ammonia synthesis is used for this simulation (Ullmann et al., 1985). The process along with the CLP system is briefly described below:

i.   Catalytic reforming of natural gas

Desulfurized natural gas is sent to the primary reformer, where almost 70% of the hydrocarbon feed is converted to syngas. The molar flowrate of inlet steam to natural gas is set to 6:1 to satisfy the primary reformer. The primary reformer operates at a temperature and pressure of 700ºC and 20 bar respectively. Air is added to the secondary reformer to supply the required nitrogen. The secondary reformer operates at a temperature of 900ºC and pressure of 20 bar. Air flow rate is controlled such that the ratio of H_2:N_2 is 3:1. The reformers are modeled as RGIBBS reactors in ASPEN Plus.

48

ii. Shift and methanation

The shift reaction is carried out in two stages: HT (high temperature) and LT (low temperature) shift. The HT shift reactor operates at a temperature of 400ºC and pressure of 20 bar. The LT shift reactor operates at a temperature of 210ºC and pressure 20 bar. These are modeled as RSTOIC reactors in ASPEN Plus. The carbon monoxide and water are converted to carbon dioxide and hydrogen. Following this, the remaining water is separated out. After that, CO_2 removal is carried out. Conventionally, this is done by amine scrubbing. However, in this integration, the CLP system is used. It is imperative to compare the capture efficiencies and costs of these two processes to establish the benefits of using CLP. After purification, the syngas is sent to the methanator to convert the remaining traces of carbon monoxide and carbon dioxide to methane. The methanator is modeled as a RGIBBS reactor. The methanator reactor operates at a temperature of 325 ºC and pressure of 20 bar.

iii. Calcium Looping unit

The Calcium Looping is modeled as previously explained for the NGCC power plant. Additional internal heat integration is possible due to the high temperature streams present in the ammonia synthesis plant. This will help to further reduce the energy consumption of the CLP.

iv.   Compression and cooling

The purified syngas is cooled and compressed in a three-stage unit. The multiple stages help in complete elimination of water. The pressures of these three compressors are set at 50, 130 and 330 bar.

v.   Ammonia synthesis stage

The syngas, along with a recycle loop, is sent to the ammonia formation reactor, operating at a pressure of 330 bar and temperature of 400ºC. Here, about 26% conversion is obtained. The outlet from the reactor, modeled as a RSTOIC reactor in ASPEN Plus, is cooled to -30 ºC. This condenses more than half the ammonia formed in the conversion reactor. The rest is recycled back to the conversion reactor. A portion of this stream is purged to prevent build-up of impurities in the loop. The purge flowrate is adjusted such that the concentration of inerts to the synthesis reactor inlet is maintained at not more than 12%.

vi.   CLP system

The CLP systems is modeled similar to those done previously. Natural gas is used as fuel for oxyfuel combustion in the calciner. For the sake of simplicity in simulation, natural gas combustion is carried out in an RGibbs reactor in ASPEN Plus and the resulting heat and material streams are directed to the calciner.

IV.2.5.1 Simulation results

The NH_3 plant production capacity is 2000 TPD. This plant requires 1440 TPD of natural gas, 9333 TPD steam and 3421 TPD of air as raw materials. The stream from which CO_2 is to be separated consists of 62.15% H_2, 18.3% CO_2, 19.3% N_2 and 0.25% of other gases. This 'flue gas' stream is sent to the CLP system. The simulation results of this integration have been summarized in Table 15. The composition of the captured CO_2 stream is given in Table 16. The flowsheets for the ammonia synthesis and integration with CLP have been attached in the Appendix as Figures 13 and 14 respectively.

Table 15: Simulation results of NH₃+CLP system

Parameter	Value	UOM
Flowrate of captured CO_2	64.4	kg/s
Percentage mass of CO_2	97.39	%
F_R	3.08	kmol/s
F_0	0.077	kmol/s
Power generated by cogeneration	55	MW
CLP energy consumption	4073	MJ/ton CO_2
Overall CO_2 capture efficiency	93.63	%

Table 16: Composition of captured CO₂ stream from NH₃+CLP system

Component	Mol%
CO_2	95.5
N_2	0.01
O_2	2.21
H_2O	2.28

Currently, MEA scrubbing is the technology used for CO_2 capture from ammonia plants. It is essential to assess how CLP measures against MEA to establish the usefulness of this process.

IV.3 CO_2 Sinks

The downstream integration of CLP is carried out in order to evaluate if the captured CO_2 can be reutilized in an effective manner. It is important to ascertain that these processes are economically viable and that integration of the looping with them will be profitable from both an economic and environmental perspective. The environmental benefits are evaluated by complete integration of the CO_2 source(s), CLP unit and sinks. These are presented further on in Chapter V.

Since a detailed process analysis of the CO_2 sinks is not required, we need to only determine the capacity of CO_2 sequestration of each of these sinks. The CO_2 requirements for an average sized production plant of each product are first determined.

i. Urea:

    Since a one-on-one integration with the ammonia plant has been performed, the ammonia flowrate to the urea synthesis plant is 2000 TPD. The amount of CO_2 required for this plant is 2589 TPD. The plant produces 3530 TPD urea.

ii. Polymer:

    The production capacity of the reference plant is 330 TPD of polypropylene carbonate, with 19 TPD of propylene carbonate as a byproduct. The raw material requirements are 158 TPD CO_2 and 208 TPD propylene oxide (Demirel, 2015).

iii.   Methanol:

The methanol plant capacity is 1300 TPD(Pérez-Fortes et al., 2014). Stoichiometric calculations indicate that the production requirements are 447 TPD CO_2, 366 TPD H_2O and 488 TPD CH_4.

iv.   Acetic Acid:

The production capacity of the acetic acid plant is set to 8000 TPD. Stoichiometric calculations indicate that the production requirements are 5867 TPD CO_2 and 2133 TPD CH_4.

CHAPTER V

ECONOMIC ANALYSIS

In this chapter, a high level economic analysis is performed to determine the cost of integration of Calcium Looping Process (CLP) with the CO_2 source and sink plants. The fixed and operating costs of each CLP unit is determined on the basis of its capacity, energy consumption and costs of raw material and utilities required. The operating costs also include the cost of additional maintenance and labor for each unit. Raw materials costs are taken from relevant literature sources (Connell et al., 2013; El-Halwagi, 2011). The costs of the raw materials for both sources and sinks are taken from energy information administration (EIA) and ICIS website.

The requirement of CO_2 is the limiting factor for the economics of the integration process. Since there are multiple sources of captured CO_2, the CO_2 stream with the highest purity is first considered for reutilization. Once that stream is utilized, the stream with second-highest purity is considered for integration and so on. Hence, we first discuss the economics of the CO_2 sinks and determine the requirement of CO_2 for reutilization. Following this, the economics of the CLP capture units has been considered.

V.1 CO_2 sinks

The downstream integration of CLP is carried out in order to evaluate whether the captured CO_2 can be reutilized in an effective manner. It is important to ascertain that these processes are economically viable and that integration of the looping with them will be profitable from both an economic and environmental perspective. If MISR<1 or slightly

greater than 1, it will be a struggle to make that process profitable if integrated with looping. Hence, it is important to integrate looping with processes where MISR>1.

For the computation of MISR, the raw material requirements for an average sized production plant of each product as determined in Section III.3 are utilized. The prices of the raw materials have been taken from ICIS website. The raw material costs and product selling prices are summarized in Table 17.

It is essential to establish that use of CO_2 as feedstock poses a significant advantage over the conventional pathways for chemical synthesis of these compounds. Industrially, CO_2 required for this pathway is obtained by combustion of natural gas. Thus, production of one mole of CO_2 would require combustion of one mole of natural gas. At standard conditions, 4\$/1000 scf is equivalent to 200\$/kg, a value much greater than the selling price of 30\$/ton CO_2 assumed for the sake of economic analysis in this thesis.

Table 17: Raw material and product costs

Species	Cost (\$/kg)
Carbon Dioxide	0.03
Ammonia	0.4
Urea	0.6
Propylene Oxide	2.2
Polypropylene Carbonate	3.8
Propylene Carbonate	1.58
Water	0.001
Methanol	0.5
Methane	0.18
Acetic Acid	1.5

The values of MISR for each of the compounds discussed above is summarized in Table 18.

Table 18: MISR of CO_2 sinks

Product species	Value of MISR
Urea	2.31
Polymer	1.58
Methanol	6.33
Acetic Acid	20.56

Since the value of MISR for each of these processes is greater than 1, it is practical to consider them for downstream integration with CLP. The total requirement of CO_2 for the polymer, methanol and acetic acid processes combined is 6472 TPD. This translates to an annual requirement of 2.29 MMTPA. The annual requirement of CO_2 for urea synthesis is 0.92 MMTPA.

V.2 CO_2 sources

V.2.1 Fixed Capital Investment (FCI) & Annualized Fixed Cost (AFC)

The economic analysis of the CLP unit for an IGCC power plant has been presented in literature (Connell et al., 2013). The total plant costs of an IGCC power plant (base case) and IGCC power plant integrated with a CLP unit have been presented. Hence, the cost of the CLP unit alone has been determined by the difference between the two.

The components of the CLP unit included in the reference plant are summarized as follows (Connell et al., 2013):

i. Carbonator

ii. Calciner

iii. Calciner ASU

iv. Carbonator Product Lock hoppers

v. Cyclones

vi. Calciner off-gas HRSG

vii. CO_2 stream condenser

viii. Solids Purge Fabric Filter

ix. Other equipment: Calciner off-gas ID fan, limestone storage and make-up and solid byproduct handling system.

Detailed sizing and design are not a part of this analysis. The cost of each of the integrated CLP units is calculate using a capacity factor. The flowrate of the captured CO_2 is used as the scaling factor. The costs are escalated from 2007 USD to 2017 USD using the Chemical Engineering Plant Cost Index (CEPCI). The value of CEPCI for 2007 was 525.4 and the value as of March 2017 is 558.46.

The annualized fixed cost (AFC) is calculated by the linear depreciation method. The salvage value of the plant (FCI_s) is assumed to be 0\$ after a period (N) of 10 years. The formula for calculation of AFC is given as follows (El-Halwagi, 2011):

$$AFC = \frac{FCI_0 - FCI_s}{N}$$

The FCI and AFC for each unit are summarized in Table 19.

V.2.2 Annual Operating Cost (AOC)

The annual operating cost consist of the costs of raw materials, material and energy utilities, labor and maintenance (El-Halwagi, 2011). The annual variable operating cost of the reference CLP unit (not including fuel costs) is 16.75 MM$. The variable operating cost includes the cost of raw materials, energy and limestone required. The following assumptions have been made for calculation of AOC for each of the plants:

i.   The variable operating costs change linearly as per the CO_2 capture rate.

ii.   Since the CLP unit is retrofitted to the base plant, it has been assumed that the increase in maintenance costs, including labor and materials, is 10% of the FCI (El-Halwagi, 2011). No other additions to the fixed operating cost have been considered.

iii.   The costs of natural gas and coal are assumed to be 4$/1000 scf and 42$/ton. The fuel costs are accounted for in the variable operating costs.

The annual operating costs for each of the units is summarized in Table 19.

V.2.3 Total Annualized Cost (TAC)

The total annualized (TAC) is the sum of the annualized fixed costs(AFC) and the annual operating cost (AOC).

$$TAC=AFC+AOC$$

The total annualized cost (TAC) for each of the units is given in Table 19.

Table 19: Costs of CLP unit addition to each system

CO_2 source plant	FCI (MM$)	AFC (MM$/year)	AOC (MM$/year)	TAC (MM$/year)
PC power plant	234.50	23.45	26.94	50.39
NGCC power plant	162.39	16.24	18.13	34.37
Cement production	80.27	8.03	10.80	18.83
GTL	182.89	18.29	66.65	84.94
Ammonia synthesis	159.23	15.92	44.47	60.39

V.2.4 Annual income

The annual income is determined assuming that there is a market availability of the entire amount of CO_2 being produced. The selling price of CO_2 was set to 30$/ton CO_2.

For the power plants, an efficiency penalty of 6.5% and 10% is determined for the PC and NGCC power plants respectively. This loss in revenue from electricity production is deducted from the CO_2 sale revenue.

For the CLP unit coupled with the ammonia synthesis plant, the reutilization of captured CO_2 is limited by CO_2 requirement for urea synthesis, provided that entire ammonia from the source plant is utilized for ammonia synthesis. For the cement plant, the reduction in cost due to lesser requirement of limestone is a part of savings and hence is included in annual revenue.

For the GTL and ammonia synthesis plant, the TAC exceeds the annual revenue obtained by sale of CO_2. Hence, cogeneration of power and heat is considered to improve the economics of the process. The power generated by cogeneration can be used to generate revenue. Since the economics of only the CLP unit have been discussed here, the power generation has been included in the annual sales, with electricity priced at 64\$/MWh. Table 20 summarizes the revenue obtained by sale of CO_2 and electricity from each plant.

Table 20: Annual income obtained from each CO_2 source plant

CO_2 source plant	CO_2 sale revenue (MM\$/year)	Electricity sale revenue (MM\$/year)
PC power plant	95.02	-
NGCC power plant	33.88	-
Cement production	28.98	-
GTL	75.46	128.93
Ammonia synthesis	4.49	39.89

V.2.5 Return on investment (ROI)

The ROI indicates the profitability of a certain project. A hurdle rate of 10 to 15% is required for undertaking many projects(El-Halwagi, 2011). The ROI is given by the following formula:

$$\text{ROI} = \frac{\text{Annual Net (After-Tax) Profit}}{\text{TCI}} \times 100$$

The annual net (after-tax) profit is calculated as follows:

Annual net (after-tax) profit = (Annual income - Annual operating cost - Depreciation) *

(1-Tax rate) +Depreciation

A tax rate of 30% has been assumed for this project. The selling price of CO_2 was assumed to be 30\$/ton CO_2. Under these conditions, the ROI for each of the plants is summarized in Table 21.

V.2.6 Payback period (PBP)

The payback period is an indicator of the time required to recover the depreciable FCI (El-Halwagi, 2011). A smaller payback period is deemed desirable. For most projects, a payback period of five to ten years is acceptable, and maybe as less as 6 months to a year for more risky projects (El-Halwagi, 2011). The payback period (PBP) for each of the integration paths is tabulated in Table 21, using the following formula:

$$\text{Payback period} = \frac{\text{Depreciable FCI}}{\text{Annual net (after-tax)profit}}$$

Table 21: ROI and PBP for each CLP unit

CO$_2$ source plant	ROI (%)	PBP (years)
PC power plant	23.32	4.29
NGCC power plant	9.70	10.31
Cement production	18.86	5.30
GTL	4.27	23.39
GTL (with cogeneration)	55.34	1.81
Ammonia synthesis	9.20	10.87
Ammonia synthesis (with cogeneration)	26.98	3.71

V.2.7 Cost of CO$_2$ capture

The cost of CO$_2$ capture is given in terms of \$/ton of CO$_2$ captured. This metric quantifies the average cost of producing a ton of CO$_2$ using CLP. Assuming that the CO$_2$ sinks are in close vicinity of the sources, the costs of transport and storage have been neglected. This cost is calculated for each unit of CO$_2$ captured, without accounting for benefits of cogeneration. The costs of CO$_2$ capture for each CO$_2$ source are tabulated in Table 22.

Table 22: Costs of CO$_2$ capture

CO$_2$ source plant	Cost of CO$_2$ capture (\$/ton CO$_2$)
PC power plant	13.42
NGCC power plant	16.88
Cement production	29.92
GTL	34.22
Ammonia synthesis	30.65

CHAPTER VI

RESULTS & DISCUSSION

In the previous chapters, a techno-economic assessment of the integration of Calcium Looping with industrial processes that generate CO_2 (CO_2 sources) and those that utilize CO_2 (CO_2 sinks) has been performed. In this chapter, some of the salient features of this integration are discussed in greater detail. The results obtained are also examined qualitatively herein.

VI.1 Selection of optimum process configuration

The environmental benefit is achieved only if there is a net reduction in CO_2 emissions on coupling the process with CLP. The purity and the quantity of captured CO_2 will vary depending on the source of CO_2. The sources of CO_2 are compared according to their purities and energy consumption per ton CO_2 produced, as collated in Table 23, to determine the stream most suitable for integration with downstream processes.

Table 23: Comparison of CLP units

CO_2 source plant	Mass percentage of CO_2 in captured stream	Net energy consumption (MJ/ton CO_2)
PC power plant	98.22	1718
NGCC power plant	96.86	2408
Cement production	98.49	2246
GTL	99.02	4171
Ammonia synthesis	97.39	4073

The captured CO_2 stream from the GTL plant has been chosen for integration with the CLP unit. Additionally, integration of ammonia plant with CLP followed by urea production is deemed to be a good fit. Some aspects of this solution are discussed below:

i. From the above table, it is evident that the captured CO_2 stream from the GTL plant has the highest purity.

ii. As seen in Table 21 from the previous chapter, it has the highest ROI when coupled with cogeneration. Cogeneration will also significantly reduce the operating costs of the base GTL plant if utilized therein or can be sold.

iii. The flow rate of captured CO_2 from this stream is capable of meeting the CO_2 demands of the methanol, acetic acid and polymer syntheses. Hence, this can be viewed to be an eco-industrial park (EIP) type of configuration.

iv. The energy consumption per ton CO_2 can be seen in Table 23. The values for the power plants is lower than others because of the utilization of excess heat in secondary steam cycles. For the cement plant, this value is lesser because of the decrease in limestone requirements due to utilization of purged CaO as a raw material. This translates into a reduced coal requirement for cement production itself, although the calciner would still consume energy.

v. The PC and NGCC power plants both produce 500 MW. However, since the percentage of CO_2 in the flue gas streams is higher for the PC power plant, the parasitic energy consumption goes down. This results in a lower value of energy consumption per ton of captured CO_2.

vi. The efficiency penalty of the CLP for the NGCC power plant is 10%. This significantly reduces the sales revenue of the power plant itself. Also, since the incoming flue gas stream consists of a lower percentage of CO_2 as compared to the other processes, the total revenue obtained by CO_2 sale is also lesser. These two factors render the process uneconomical.

vii. The ammonia synthesis plant can capture adequate CO_2 to meet the demands of the urea synthesis process. Since almost all the ammonia is utilized to produce urea, the captured CO_2 can be used to reduce the demand of fresh CO_2 required. Alternatively, it can be combined with the excess ammonia from the urea production process to increase the yield of the urea plant. The former approach has been chosen for this integration because of its simplicity.

viii. Also, the one-on-one integration of ammonia synthesis with urea synthesis is deemed more practical over a 'big picture approach. Since most of the ammonia is sent for urea production, this integration approach works best due to on-site production of CO_2. This eliminates the cost of transport and storage of CO_2.

The solution can be represented schematically as shown in Figure 8.

ix. The use of coal as fuel for the oxyfuel combustion also introduces the issue of ash removal. Electrostatic precipitators (ESPs) are required to additionally separate ash from other components. Proper disposal of ash is necessary since it can pose health problems to humans. In case of facilities that do not currently handle coal, ash handling systems would also not be present. This would lead to a further addition in the capital cost.
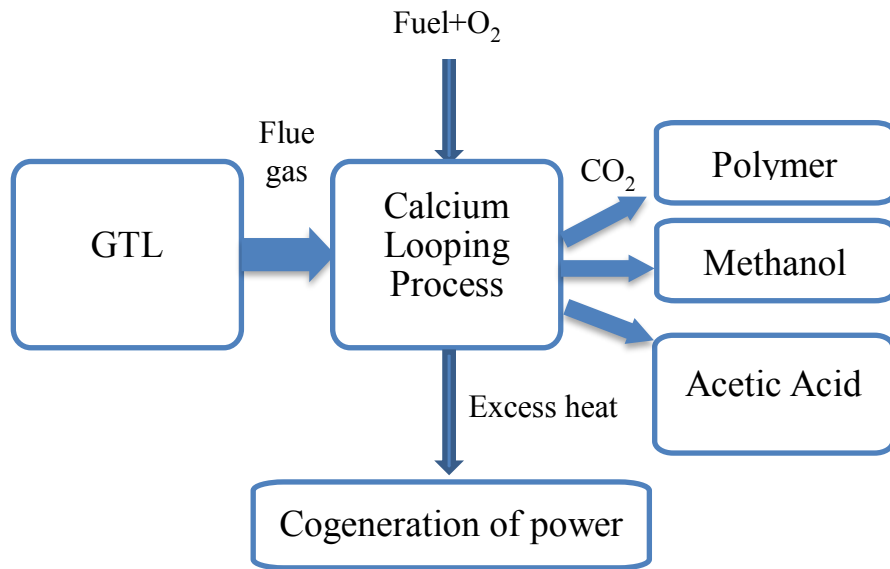
Figure 8: Schematic of solution

VI.2 Simulation of CLP unit

The simulation of the CLP unit consisting of the carbonator, calciner and the heat exchangers is common to all the CO_2 sources. Some of the important features of the simulation are discussed below:

i.   Depending on the plant, the fuel for oxyfuel combustion in the calciner has been varied. The PC power plant and cement production process use coal for providing heat, hence coal is chosen for oxyfuel combustion. For GTL and ammonia synthesis, the choice of fuel is natural gas over coal since the base processes already utilize natural gas.

ii.   A major advantage of the CLP process is that since it employs oxyfuel combustion within the calciner, the entire amount of CO_2 generated by oxyfuel combustion can

be captured in the calciner. Thus, introduction of fuel does not result in a net increase in the CO_2 emissions to the atmosphere.

iii.   Oxyfuel combustion has been simulated in a separate reactor to exactly and easily determine the amount of CO_2 generated.

iv.   Internal heat integration has been maximized by means of a cyclonic preheater to enable heat exchange between the captured CO_2 stream and the solids entering the calciner. However, this leads to about 3% of the captured CO_2 being 'trapped' in the cycle (Martínez et al., 2013). Hence, the overall CO_2 capture efficiency goes down marginally. This establishes a tradeoff between the cost of additional fuel consumption in the calciner and loss in CO_2 capture efficiency of the process.

VI.3 Economics of integration of CLP

Eventually, the feasibility of the integration is largely controlled by its economics. A high level economic analysis has been presented in this thesis. The main observations from this economic analysis are:

i.   The capital cost of the equipment has been estimated using capacity factor with exponent (value of exponent is 0.6). This gives rise to economies of scale. Here, the flowrate of CO_2 has been used to determine the capacity factor. Hence, for cement and ammonia synthesis plants that have a much lower rate of captured CO_2, the TCI does not decrease at an equivalent rate. For instance, the CLP unit of PC power plant produces 6 times as much CO_2 as that of the cement plant. But, the TCI is only 3 times higher.

ii.   The current state-of-art technology for CO_2 capture used for PC and NGCC power plants and in ammonia synthesis is MEA scrubbing. The capture cost per ton of CO_2 for PC and NGCC power plants is 32 $/ton CO_2 and 41 $/ton CO_2 (David and Herzog, 2000). The equivalent costs using CLP for PC power plants is 13.42 $/ton CO_2 and for NGCC power plants is 16.88 $/ton CO_2. Thus, CLP does pose a significant advantage over MEA absorption.

iii. The chosen solution utilizes GTL as the source of CO_2. The GTL production rate of the Bintulu plant of Malaysia under consideration is 14,700 BPD. The capacity presented in the original GTL plant that has been taken as reference for composition of tail gas stream is 118,000 BPD. The capture cost for the 118,000 BPD capacity plant is 9 $/ton CO_2 as against 34.22 $/ton CO_2 for a plant of capacity 14,700 BPD. If the entirety of this the CO_2 produced from this plant can be reutilized, it is possible to obtain a 54.48% ROI with a payback period of 1.84 years without cogeneration at a selling price of 30 $/ton CO_2. However, since this value of CO_2 produced (0.56 MMTPD) is much higher than the collective requirement of the CO_2 sinks, it is more prudent to consider the plant of lower capacity since the ROI would be limited by the annual sales of CO_2, reiterating the fact that the market demand of a commodity holds far more importance than the supply capabilities.

iv.   The ROI of the GTL plant is 55.34%, a value much higher than the other processes. This has been solely achieved due to cogeneration in this process. The annual sales of electricity produced are high enough to make CO_2 available for free and still

achieve an ROI of 18%. In absence of cogeneration, the ROI would be merely

6%, thus rendering the process incapable of further consideration.

CHAPTER VII

CONCLUSIONS & RECOMMENDATIONS

This thesis provides a framework for upstream and downstream integration of Calcium Looping Process (CLP). The tasks performed here are as follows:

i. A basic CLP unit has been and designed.

ii. The integration of CLP with CO_2 sources has been optimized in terms of the sorbent flow rates and fuel requirements.

iii. CO_2 sinks are identified and evaluated for downstream integration with CLP.

iv. The optimum configuration of integration has been proposed by assuming precedence of CO_2 stream of highest purity.

v. A high level economic analysis has been performed to indicate the economic feasibility and practicality of this approach.

vi. The importance of economies of scale has been examined.

The important results can be summarized as:

i. The captured CO_2 stream from the GTL plant has the highest purity and is capable of meeting the feedstock requirements of Polymer, Methanol and Acetic Acid syntheses combined. Cogeneration of electricity is also carried out by means of the excess heat from this process to improve the economics of this process. For a selling price of 30 $/ton CO_2 and electricity price of 64 $/MWh, an ROI of 55.34% can be achieved.

ii.   The captured CO_2 stream from the Ammonia plant is used as feedstock for Urea synthesis. When coupled with cogeneration, the ROI of this process is 26.98% for a selling price of 30 \$/ton CO_2. This can be improved for an Ammonia plant of higher capacity.

The following recommendations are suggested for further work:

i.   Use of modified limestones having greater sorbent capacity over natural limestones

ii.   Further reduction of calciner energy consumption

iii.   Effect of presence of sulfur in the flue gas stream

iv.   Detailed design and economic analyses of the CLP units

v.   Consideration of more downstream chemical pathways

vi.   Safety considerations in application of CLP to H_2 production

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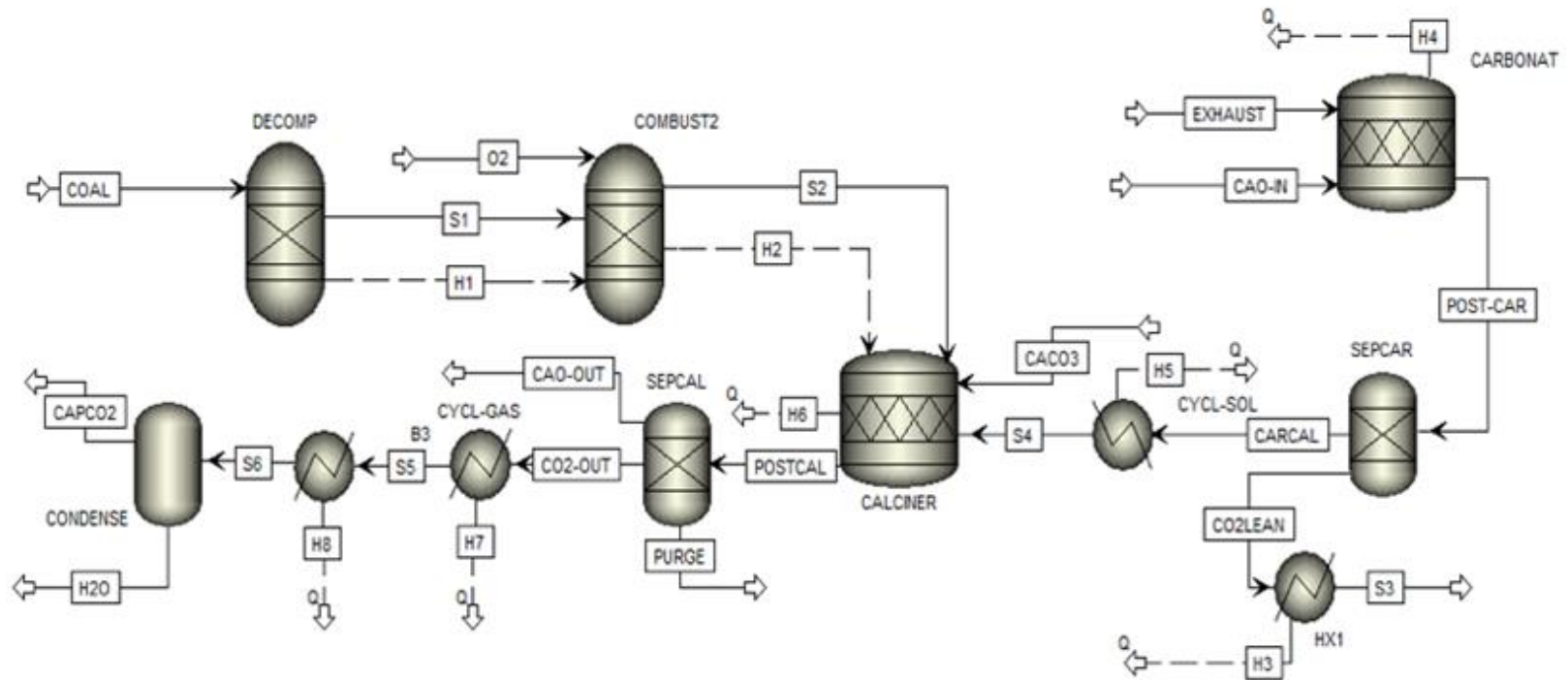
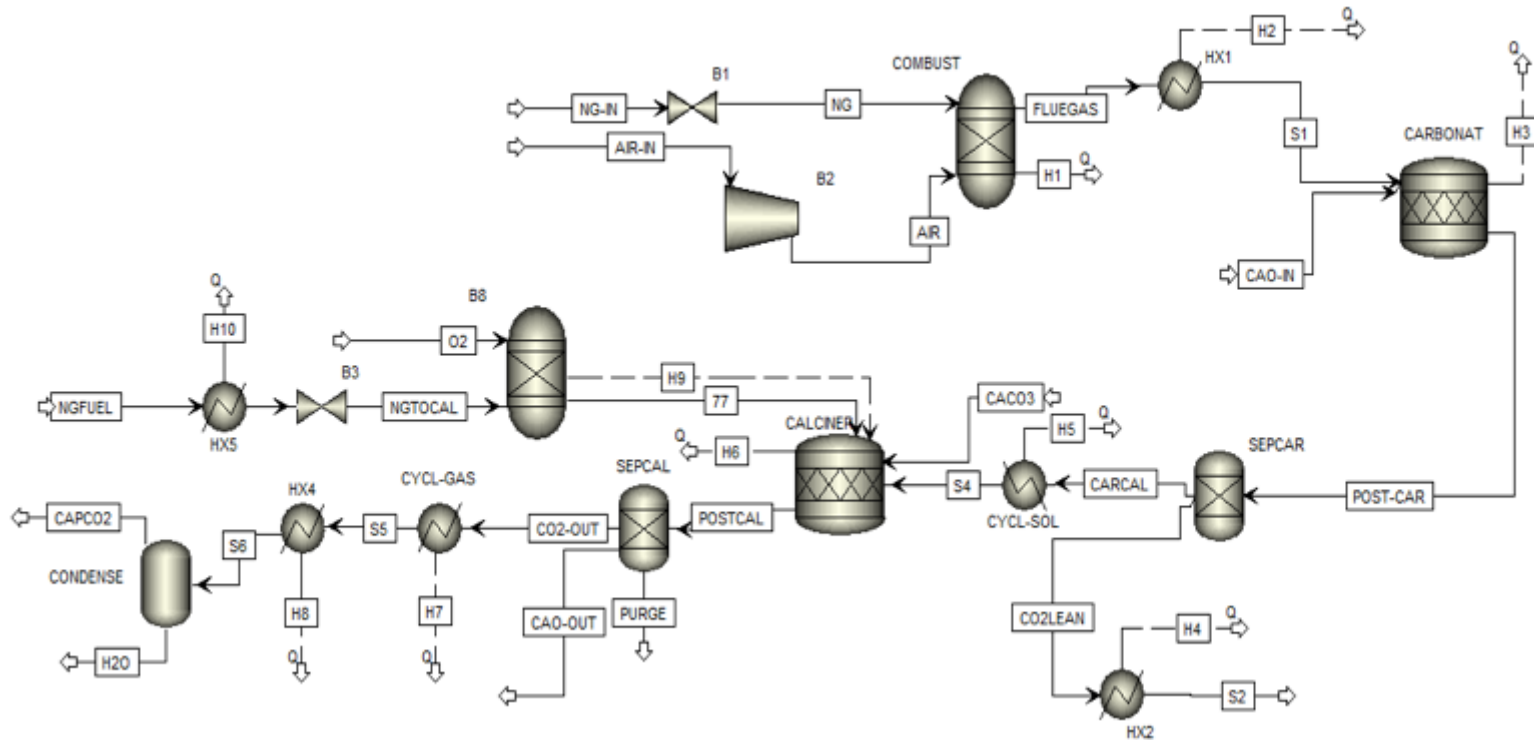**Figure 9: ASPEN Plus flowsheet - Integration of PC power plant with CLP**

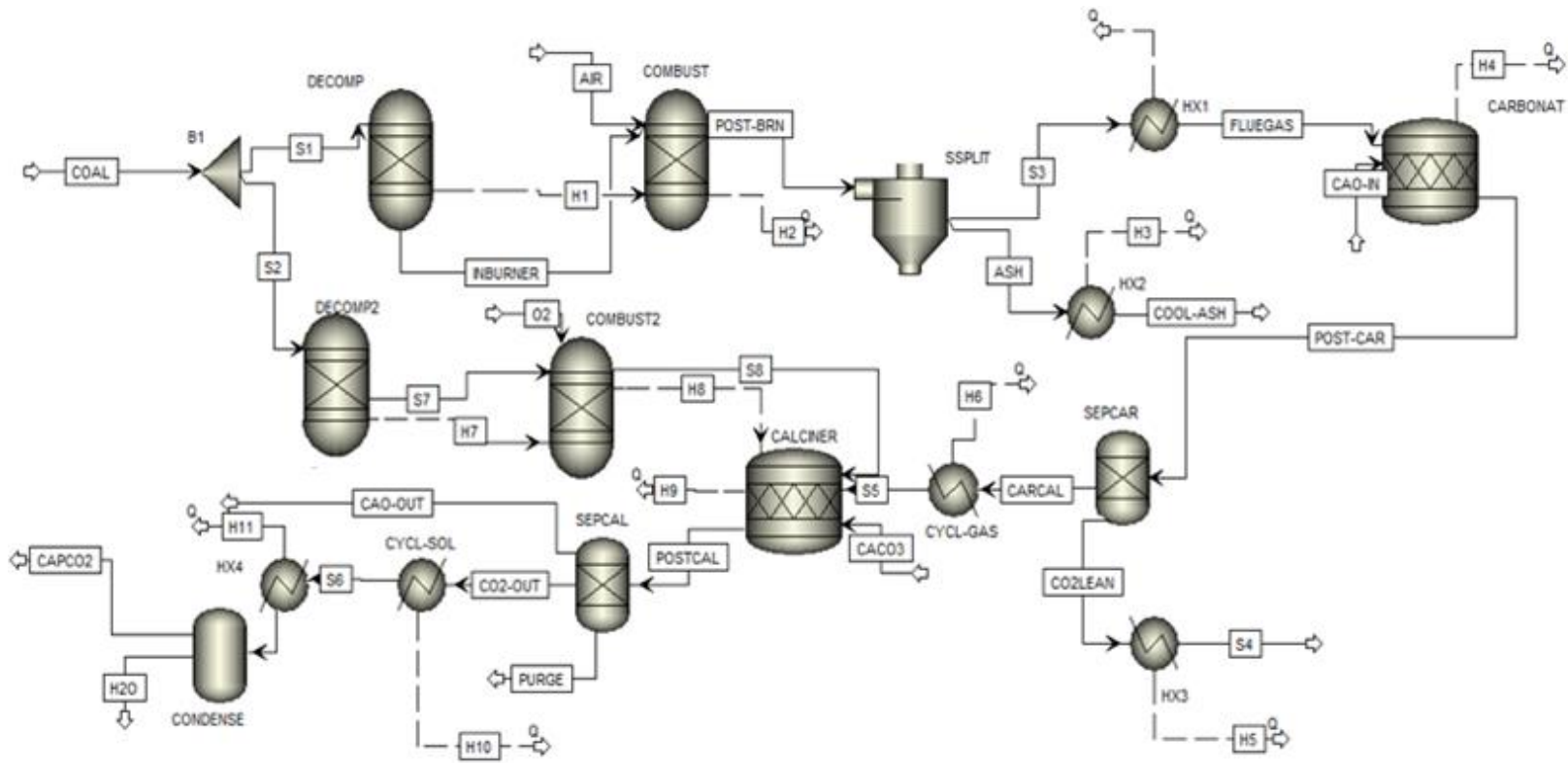**Figure 10: ASPEN Plus flowsheet - Integration of NGCC power plant with CLP**

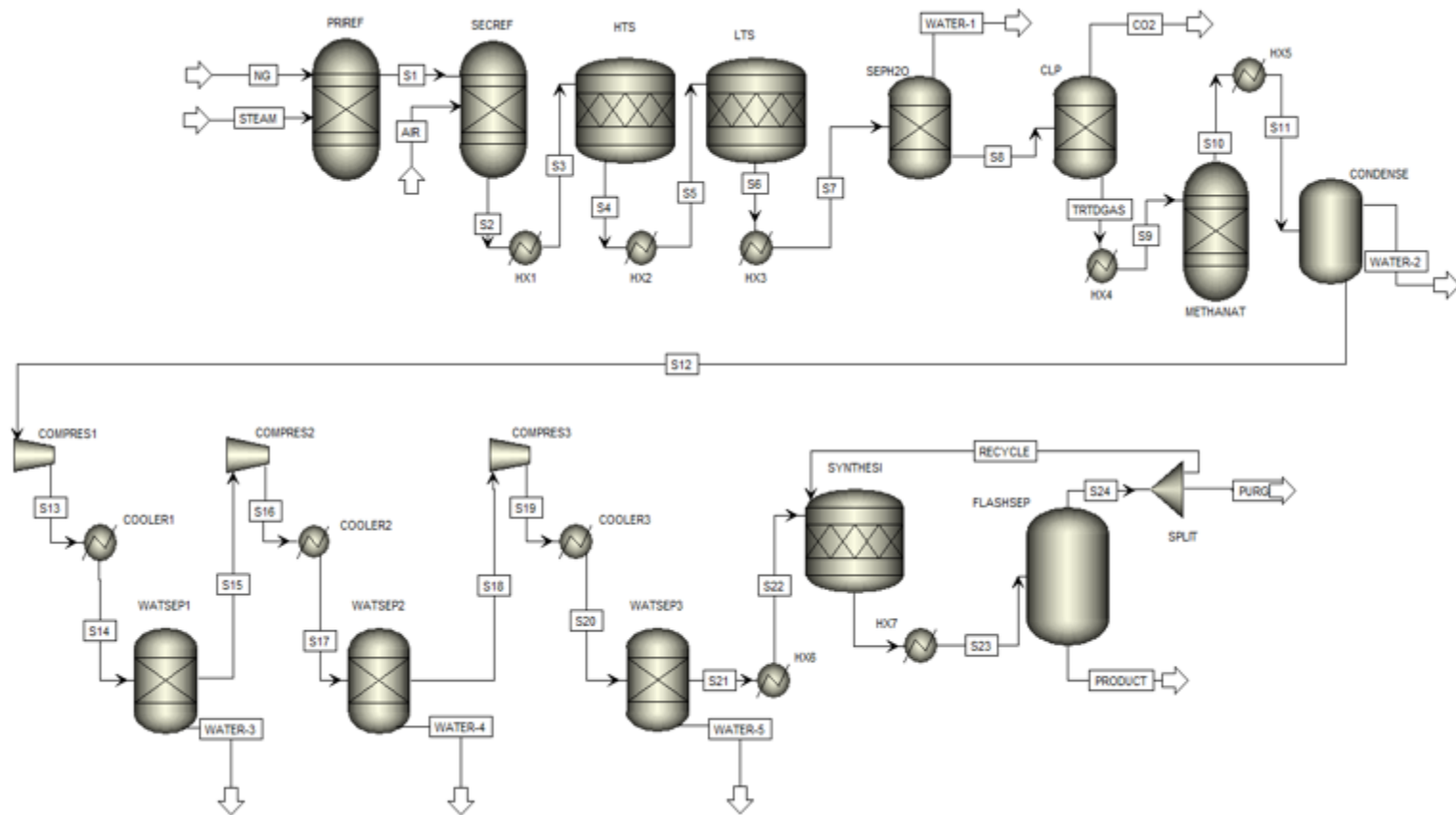**Figure 11: ASPEN Plus flowsheet - Integration of cement plant with CLP**

Figure 12: ASPEN Plus flowsheet - Integration of GTL plant with CLP

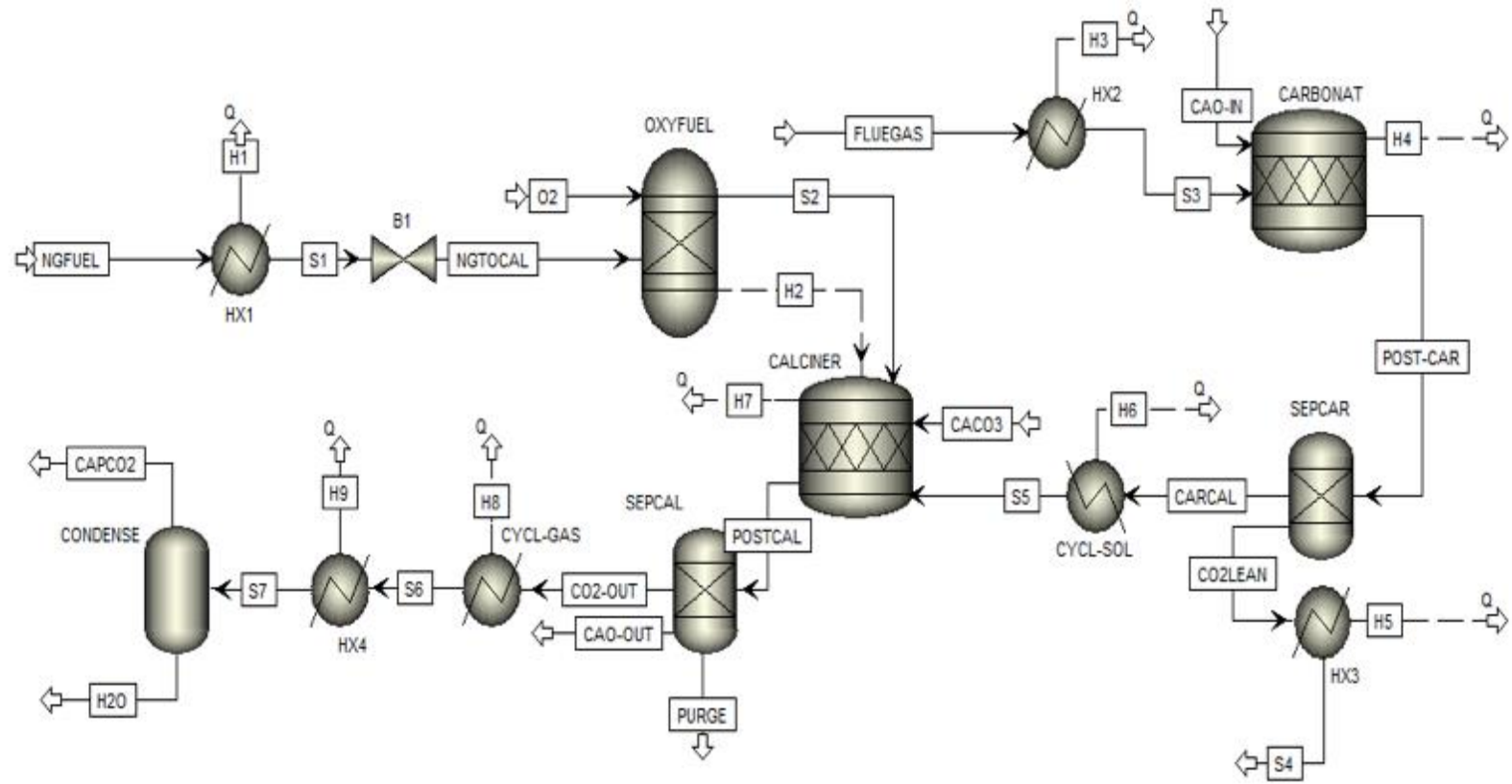**Figure 13: ASPEN Plus flowsheet - Ammonia synthesis plant**

Figure 14: ASPEN Plus flowsheet - Integration of NH₃ synthesis plant with CLP