

**Optimal Strategic Deployment and Novel Biomass Fly-ash Derived Solid Adsorbent
Modelling for Carbon Capture Applications**

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

This thesis aims to advance the fight against global warming by developing modelling tools aimed to determine the optimal location of capture plants, and through the development of new process flowsheets that make use of biomass waste as sorbents for CO₂ capture and utilization. The first approach explores different strategies of decarbonization through optimal deployment planning and development of alternative carbon capture technologies. Initially a new framework for national optimal deployment of strategic carbon capture implementation is presented. This framework considers external environmental and social considerations often missing from implementation frameworks, which will aid policy makers in more well-rounded deployment decisions. The Canadian case study utilizing the proposed optimal planning strategy shows that implementation of 58 post-combustion carbon capture (PCC) plants located in seven provinces (Alberta, British Columbia, New Brunswick, Nova Scotia, Ontario, Quebec, and Saskatchewan) would result in Canada meeting the national targets. Through a sensitivity analysis on these targets, it was determined that plant distribution is heavily dependent on provincial energy and CO₂ transport prices. Additionally, if Alberta were to reduce their GHG emissions by 50% through alternative sustainable methods, only 35 PCC plants would be required to meet national targets.

In the second approach, a new modelled system of a biomass-based lithium orthosilicate solid adsorbent derived from industrial biomass fly-ash used to capture CO₂ from power plant flue gas emissions is presented. The model includes pre-treatment of biomass fly-ash, the synthesis of adsorbent which utilizes fly-ash as the silicone source and a laboratory produced lithium source, the adsorption of CO₂ from flue gas, and regeneration of adsorbent. The study compares the model results from pre-treated and non-pre-treated biomass fly-ash, with

benchmark CO₂ capture rates of 87% and 89.7%, respectively. Results display a maximum CO₂ capture rate of 93.23%. Key insights show an increased CO₂ flue gas composition requires a higher adsorbent mass and the most effective flue gas volume to adsorbent mass ratio exists between 3.7 – 4.1. Additionally, higher regeneration temperatures result in improved CO₂ capture while pre-treatment of fly-ash does not impact the kinetics of regeneration. Energy analysis show that the pre-treated fly-ash adsorbent is more efficient than the non-pretreated adsorbent, and both could be an improvement over amine-based post-combustion carbon capture with the incorporation of heat integration. However, the cost and water consumption of the pre-treatment process were high compared to that of the industry standard. As such, this model was improved and further examined by incorporating additional wastewater treatment units to recycle used water back to the pre-treatment water washing step and elemental extraction as a waste management tactic for the water treatment waste stream. The enhanced system recycles 85% of the used water and the benchmark results show a 4.2% cost reduction compared to the original process. Additionally, results determine that the cost of resource consumption (CRC) can be reduced by 14.5 % compared to the existing benchmark system. The key insights show that the amount of DI water and acid have the largest impact on process cost and CRC and that both straw and grass show potential as a silicone source for Li₄SiO₄ synthesis. Furthermore, an analysis on further utilization of CO₂ and waste streams through elemental extraction of iron (III) hydroxide and calcium carbonate extraction were considered using different flowsheet configurations. Results from these tests showed that selling captured CO₂ and waste streams to cement production is a suitable and sustainable alternative. A cost analysis from this strategy resulted in a 1.35% decrease in process costs from the baseline results and a 1.61% decrease in the CRC from the benchmark results thus promoting a circular carbon economy.

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List of Abbreviations

ACTL	Alberta carbon trunk line
	carbon capture process using biomass fly-ash derived adsorbents which have not been
BCCS	pre-treated
	carbon capture process using biomass fly-ash derived adsorbents which have been
BCCS – P	pre-treated using the original pre-treatment model
	carbon capture process using biomass fly-ash derived adsorbents which have been
BCCS – P(R)	pre-treated using the modified/advanced pre-treatment model
CAAF	climate action awareness fund
CAD	Canadian
CaCO ₃	calcium carbonate
CCS	Carbon capture and storage
CCUS	carbon capture utilization and storage
CKD	cement kiln dust
CLC	chemical looping combustion
CO ₂	carbon dioxide
CO ₂ e	carbon dioxide equivalent
DAC	Direct air capture
DI	Deionized
DIP	decarbonization incentive program
EOR	enhanced oil recovery
	biomass fly-ash which has been pre-treated using the process described in
FA - P	chapter 4

	biomass fly-ash which has been pre-treated using the advanced process
FA - P(R)	presented in chapter 5
FeCO ₃	iron (III) carbonate
g	gram
GDP	Gross Domestic Product
GHG	Greenhouse gas
GWh	gigawatt hour
kW	kilowatt
L	liter
LCA	Life Cycle Assessment
MgCO ₃	magnesium carbonate
MHI	Mitsubishi Heavy Industry
MINLP	mixed integer non-linear problem
Mt	Mega-tonne
MWh	megawatt hour
NDC	Nationally determined contributions
PCC	Post-combustion carbon capture
RHS	right hand side
s	second
t	tonnes
TWh	Terawatt hour

List of Symbols

<i>i</i>	index for total number of new carbon capture plants that can be installed
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j	index for each region
k	index for each sector
P	index for each type of carbon capture technology
CCA	Cost of CO ₂ avoided
SPC	Social Perspective Cost
ω	scaling factor
$z_{P,i,j,k}$	binary decision variable for whether or not a plant of P, of number I, exists in province j, removing from sector k
$\phi_{economics}$	economics term
$\phi_{emissions}$	emissions term
e_j	electricity price in province j
Y_P	years of operation for technology type P
$E_{j,k}^*$	emissions levels of province j in sector k for the year 2020
Σ	summation
O_P	operating cost of technology type P
S	social cost of carbon
x	CO ₂ captured by each facility
C_P	capacity for capture in technology P
B_P	Annualized energy cost for technology P
R_P	retrofitting cost for technology P
T_j	Transportation cost in province j
$targets_k$	removal targets in sector k
P_u	plant constraint upper limit

P_l	plant constraint lower limit
L	land constraint level
UL	upper limit of CCA
$\$$	dollars
$\%$	percent
P_j^{road}	provincial price of road transportation
P_j^{rail}	provincial price of rail transportation
P_j^{CT}	provincial price of transportation
$B_{CO_2}^{CT}$	baseline cost of CO2 transport in Canada
X_P	cost to build a new plant of technology P
Li_4SiO_4	lithium orthosilicate
CO_2	carbon dioxide
Li_2CO_3	lithium carbonate
Li_2SiO_3	lithium silicate
$\hat{k}$	reaction rate constant for the adsorption
t	time
Z	proportion of carbonated in the product layer
α	adsorbent conversion rate
m_1	initial mass of adsorbent
m_2	final mass of solid after adsorption
m_0	theoretical adsorption capacity
$m_{Li_2SiO_3}$	mass of lithium silicate
$m_{Li_2CO_3}$	mass of lithium carbonate

$M_{Li_2SiO_3}$	molar mass of lithium silicate
$M_{Li_2CO_3}$	molar mass of lithium carbonate
m_{CO_2}	mass of carbon dioxide
η_{CO_2}	moles of carbon dioxide
$m_{Li_4SiO_4}$	mass of lithium orthosilicate
$\eta_{Li_4SiO_4}$	moles of lithium orthosilicate
$M_{Li_4SiO_4}$	molar mass of lithium orthosilicate
M_{CO_2}	molar mass of carbon dioxide
ξ	extent of reaction
α_{des}	desorption conversion rate
$\hat{k}_r$	reaction rate constant for the regeneration
$C_{Li_4SiO_4-CO_2}$	adsorption capacity of adsorbent
$m_{Li_4SiO_4RR}$	mass of solid post regeneration
BCCS	carbon capture process using fly-ash derived lithium orthosilicate
BCCS – P	carbon capture process using pre-treated fly-ash derived lithium orthosilicate
$\%CO_2$	percent of carbon dioxide captured
$\%Li_4SiO_4RA$	percent of adsorbent remaining after adsorption
$\%Li_4SiO_4RR$	percent of adsorbent remaining after regeneration
Q_T	overall energy requirement of a process on a mass of co2 captured basis
m_{CO_2,CO_2}	mass of co2 in the CO2 stream
$m_{CO_2,RICH1}$	mass of co2 in the RICH1 stream
$m_{CO_2,FLUEGAS}$	mass of co2 in the FLUEGAS stream
$m_{Li_4SiO_4,RICH1}$	mass of li4sio4 in the RICH1 stream
$m_{Li_4SiO_4,ADSORBENT}$	mass of li4sio4 in the ADSORBENT stream
$m_{Li_4SiO_4,RECYCLE}$	mass of li4sio4 in the RECYCLE stream

Q_i	Energy requirement of each process unit
i	subset including each energy consuming process unit
$m_{CO_2 \text{ captured}}$	mass of total co2 captured by a process
T_{ADS}	adsorption temperature
F_{ads}	Fly-ash flowrate
F_{ADS}	adsorbent flow rate
F_{CO_2}	flue gas flow rate
x_{CO_2}	co2 composition in the flue gas
R'	adsorbent mass to flue gas flow ratio
T_{REGEN}	regeneration temperature
$P_{capture}$	carbon capture systems operating pressure
Al_2O_3	aluminum oxide
HCl	hydrochloric acid
$AlCl_3$	aluminum chloride
H_2O	water
MgO	magnesium oxide
$MgCl_2$	magnesium chloride
CaO	calcium oxide
$CaCl_2$	calcium chloride
K_2O	potassium oxide
KCl	potassium chloride
SO_3	sulphur trioxide
H_2SO_4	sulphuric acid
Fe_2O_3	iron (III) oxide

$FeCl_3$	iron (III) chloride
P_2O_5	phosphorus pentoxide
H_3PO_4	phosphoric acid
Cl_2	chlorine gas
C	carbon
CCl_4	tetrachloromethane
H_2	hydrogen gas
$NaOH$	sodium hydroxide
Na_2O	sodium oxide
$NaCl$	sodium chloride
$Fe(OH)_3$	iron (III) hydroxide
Al^{3+}	aluminum ion
Cl^-	chloride ion
Mg^{2+}	magnesium ion
Ca^{2+}	calcium ion
K^+	potassium ion
Fe^{3+}	iron ion
H^+	hydrogen ion
HSO_4^-	hydrogen sulphate ion
SO_4^{2-}	sulphate ion
$H_2PO_4^-$	dihydrogen phosphate ion
HPO_4^{2-}	hydrogen phosphate ion
PO_4^{3-}	phosphate ion

Na^+	sodium ion
OH^-	hydroxide ion
X_r	conversion of reaction r
i	each compound/element
r	reaction number (39-46)
$m_{i,T-FA}$	mass of component i in the treated fly-ash
$m_{i,R-FA}$	mass of component i in the raw fly-ash
pH^{PERM}	pH of the permeate
EC	electrical conductivity
ER	electrical resistivity
TDS	total dissolved solids
$TH - CaCO_3$	total hardness as $CaCO_3$
$[Ca]$	calcium
$[Mg]$	magnesium
$[Fe]$	iron
$[Cu]$	copper
$[Si]$	silica or SiO_2
$[Cl]$	chloride
$[S]$	sulphate
F_{FA}	raw fly-ash flow rate
$R_{A:FA}$	acid to fly-ash ratio
$\%H_2O_R$	percentage of water recycled
$V_{NaOH,N}$	volume of NaOH used for neutralization (7 M)

$Z_{i,R-FA}$	raw fly-ash composition of component i
T_{pre}	system operating temperature
P_{pre}	system operating pressure
CRC	cost of resource consumption

Chapter 1 Introduction

Over the last few decades, the task of finding ways to reduce the carbon footprint has been a global concern and point of focus [1][2][3][4]. Tactics include a transition from coal/gas-fueled energy to “green” energy such as wind/solar/nuclear, alternative modes of transportation from gasoline fired motors, and the capture of carbon dioxide (CO₂) from heavily emitting stationary sources [4]. After the Paris agreement in 2016, involved countries released their plans for emission reduction tactics to comply with the 2050 net-zero goals. Countries proposed different interim goals for GHG emissions levels; in Canada, a 40% reduction in the nations emissions by the year 2030 is meant to act as a steppingstone for GHG emissions levels to reach net-zero in 2050 [5]. Many countries proposed plans include carbon capture storage and utilization (CCSU) implementation but lack strategic methods to deploy their carbon capture technologies. The main deterrent of implementing carbon capture technology for many years has been the high cost and low efficiency associated with installation and operation [2]. While simulated and pilot scale [6][7][8] testing of carbon capture processes occurred implementation of commercial operations has not made the same progress [9]. Carbon capture and storage (CCS) is a broad field and while new developments are vital, the need for technological research to be utilized in existing industries to achieve true environmental impacts is key. This work aims to provide an optimal deployment framework which can fill the gap of strategic carbon capture implementation tools needed for countries large scale decarbonization.

Currently, the most mature technology in CCS is amine-solvent based post combustion carbon capture (PCC) [9][10]. This process includes the separation of CO₂ from carbon heavy sources (often flue gas) with an amine-based solvent (ex. monoethanolamine (MEA)) and solvent regeneration. The regeneration produces highly pure CO₂ and recovery of the expensive

solvent which is recycled to the feed stream. Although effective and highly applicability in retrofitting applications, there are ample projects investigating how to further improve and optimize this process [11][12][13][14][15][16][17]. Due to the properties of amine solvents such as MEA, the temperature required in the regeneration section of the process is high (800 – 1200 °C) [18][19]. This high energy consumption is the main drawback of amine solvent PCC, along with the high cost of acquiring these solvents [19][9]. As such, further research on alternative PCC sorbent materials and techniques are needed to develop feasible large-scale carbon capture methods. This thesis aims to investigate novel or emerging methods and techniques that can partially fill-in this gap.

As the climate change and the need for decarbonization develops, the incorporation of CCS in renewable energy to promote net-negative emissions processes becomes more attractive. Power plants which have adopted biomass utilization as part of energy production can include the addition of carbon capture; energy production which utilizes waste as a feed source, while simultaneously capturing CO₂, results in net negative emissions thus promoting decarbonization and lower dependence of fossil-fired power plants. Studies in Sweden have shown bioenergy with carbon capture and storage (BECCS) as a promising large-scale operation to integrate into their energy generation infrastructure [20]. Carbon capture integration into processes using bioenergy promotes the adoption of environmentally sustainable processes. Additional tactics to increase the environmental and economic sustainability of a process is achieved through waste management and utilization.

Carbon capture utilization promotes industrial processes with high emissions to find ways to capture produced CO₂ and reintegrate it into the process for alternative use [21]. The cement industry is known to have a high rate of CO₂ emissions, and as such there has been studies on

approaches that can be implemented to capture, integrate, and utilize this CO₂ [22][23][24]. One area which has recently gained attention in CCUS studies in cement production is carbonate formation from cement kiln dust (CKD) waste [25]. By combining CKD with captured CO₂, carbonate compounds such as calcium carbonate (CaCO₃), magnesium carbonate (MgCO₃), and iron carbonate (FeCO₃) are formed and can be further utilized. Specifically, the capture of CO₂ and use in CaCO₃ production has shown many benefits [22]. CaCO₃ is used as an additive in cement production to improve the physical properties of the produced cement. There is a lack of computational models for processes which incorporate CO₂ reintegration in the form of waste management; these are needed to develop large scale implementations, control schemes, and identifying the system's operability region such that they can be used to demonstrate the potential of such processes. One of the main challenges with CCSU aside from choosing the type of carbon capture to implement (i.e., post-combustion, pre-combustion, oxy-fuel combustion, chemical-looping combustion), is finding the optimal path for captured CO₂; meaning, once the CO₂ is captured, should it be sequestered, used in enhanced oil recovery, stored in the form of a salt and further utilized in other industries, etc. There are many routes to follow with captured CO₂ and aspects such as CO₂ purity, volume, temperature, plant location, operational costs, all impact the decision for the resulting optimal path. Different CO₂ capture technologies are reviewed and utilization/management techniques are explored further in this thesis by comparing results from presented models, along with technoeconomic analyses on the individual systems.

1.1. Research Objectives

The aim of this thesis is to first provide a strategic deployment framework for optimal implementation of carbon capture technologies to aid in the pursuit of net-zero emissions by 2050. Previous models have lacked the incorporation of key decisions variables such as

environmental and social considerations, which can derail the implementation of capture projects in the later stages. This framework aims to avoid these issues by including all necessary factors at the onset. As advancements in alternative capture techniques which incorporate a circular carbon economy are needed for many countries to reach their 2050 emissions goals, an alternative carbon capture method which employs waste utilization as the adsorption technique is developed and investigated. This CO₂ capture model is further developed by incorporating water treatment, recycle, and elemental extraction to increase the sustainability of the total process. The specific objectives for this MASc thesis are as follows:

- Develop a new optimization model for strategic deployment of carbon capture technologies. The proposed model includes economic, social, socioeconomic, and environmental factors in optimal decision making.
- Develop a rigorous model of the Li₄SiO₄-CO₂ adsorption process for CO₂ capture. The proposed model includes the pre-treatment of fly-ash feedstock, followed by CO₂ adsorption and regeneration with Li₄SiO₄ solid adsorbent.
- Develop a model for treating used water from fly-ash pre-treatment to meet deionized (DI) water standards and include a recycle stream into the water-washing step of pre-treatment process. The extended model includes pre-treatment and water-treatment waste utilization through elemental extraction and carbonate precipitation and is integrated with the CO₂ capture model.

The contributions of this work extend into many different areas of the CCUS field. First, the optimal deployment model can aid in policy making as it can be adapted to accommodate small regions deployment as well as leveraged for national implementation. Through the model's use, countries can develop a planning strategy for the deployment and implementation of various

carbon capture technologies, which will improve decarbonization tactics in various regions. By developing the first pilot-scale model of biomass-based Li_4SiO_4 sorbent CO_2 capture and incorporating water treatment, recycle, and waste utilization, this carbon capture technology is one step closer to industrial-scale modelling thus promoting the technical viability of this technology. With the ability to simulate a pilot-scale operation of this system, appropriate testing, control schemes, and optimal operating conditions can be explored, which will allow for further development and eventually commercial implementation; the presented model improves process scale-up feasibility.

1.2. Outline of Thesis

This thesis is structured as follows:

Chapter 2: This chapter presents an overview of the literature available on the current outlook for carbon capture projects in Canada and a summary of relevant studies proposing deployment models. Background on biomass and bioenergy including the involvement in the carbon capture field, models which explore biomass-based sorbent carbon capture, and literature pertaining to the utilization of waste products and waste management in carbon capture processes follows. The gaps in this literature which motivate this thesis are discussed further in this chapter.

Chapter 3: This chapter introduces a model used to optimally deploy carbon capture technologies utilizing novel socioeconomic and environmental features. The model capabilities and applications are further explored through a Canadian case study. This study examines the resulting impact when under baseline conditions and sensitivity analyses on national targets and Alberta's emissions are investigated. The outcomes of this chapter have been published in *The Canadian Journal of Chemical Engineering* [4].

Chapter 4: This chapter introduces and describes a rigorous process model that simulates the pre-treatment of biomass fly-ash that is then used for capturing CO₂ from coal-fired flue-gas. The model validation, energy and cost comparison to amine-based PCC, and model case studies are presented in this chapter. The outcomes of this study have been submitted for publication to *Chemical Engineering Research and Design* [26].

Chapter 5: This chapter describes the changes made to the pre-treatment process of biomass fly-ash presented in Chapter 4 to include DI water treatment and recycle to the water-washing step of pre-treatment. The model is evaluated by case study outcomes and outlines the additional steps necessary when including CO₂ utilization to recover CaCO₃ precipitate. The outcomes of this chapter will be submitted for publication to *Chemical Engineering Research and Design* [27].

Chapter 6: This chapter presents the conclusions from this work along with potential areas of development and proposed future work.

Chapter 2 Background and Literature Review

This chapter provides an in-depth review of the current state of carbon capture in Canada including the country's existing and upcoming projects, complemented with an overview of current and emerging carbon capture technologies globally in Section 2.1. This chapter further discuss biomass and its vital integration into carbon capture technologies in Section 2.2. Section 2.3 covers the importance of waste management and integration for sustainable processes. The end of each section highlights the current gaps in modelled systems of optimal deployment, biomass carbon capture applications, and waste utilization in carbon capture respectively.

2.1. Canadian Decarbonization Through CCS

A detailed overview of different carbon capture techniques and review of the current global advancements for each method (pre-combustion, post-combustion, oxy-fuel combustion, direct air capture, and alternatives) are discussed in appendix A. This section describes Canada's emissions profile, followed by the ongoing and proposed Canadian industrial-scale CCS projects. Monetary amounts are reported in 2023 Canadian dollars.

Globally, Canada has a reputation as being a leader in sustainability and carbon capture [28]. Even with growing research and expansion of technologies, Canada's CO₂ emissions are high in comparison to countries with similar technological advancements. Figure 1 outlines six countries that are publicly perceived to have a similar status of technological advancement, comparing each countries total CO₂ emissions, and CO₂ emissions per millions of dollars of gross domestic product (GDP). This figure shows that although Canada has an average total emission, the country's emissions per GDP is the highest. Comparing Canada's economic contribution to the other countries against the total population shows it is one of the highest CO₂ emitters.

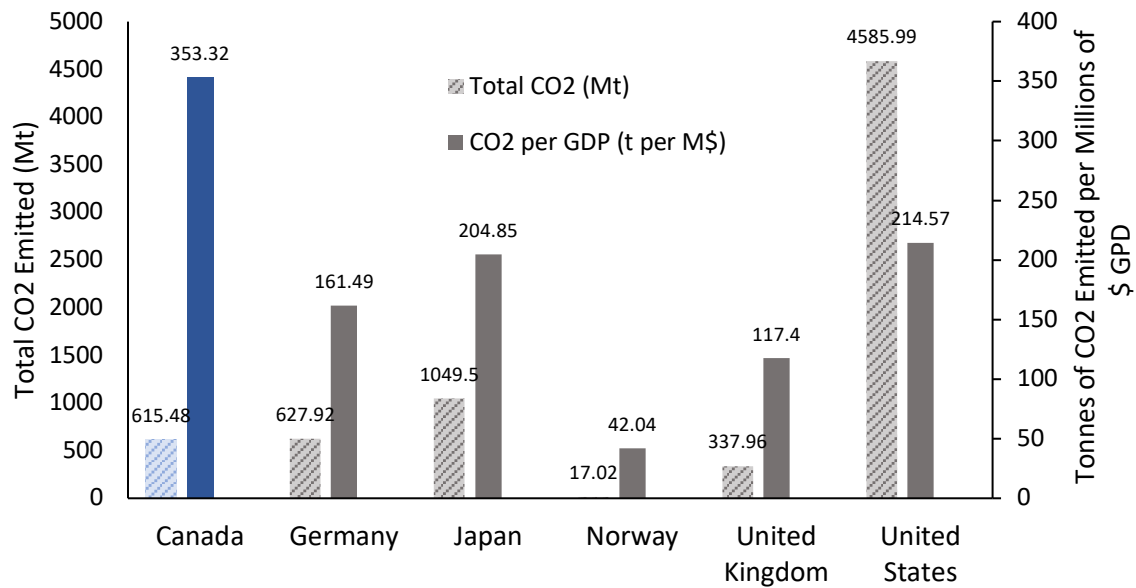


Figure 1. Total tonnes of CO₂ emitted by each country compared to the tonnes of CO₂ emitted per millions of dollars GDP [29].

Since 2005, emissions have decreased in all provinces except for Alberta and the Northwest Territories; the top five provinces contributing to GHG emissions being Alberta, Ontario, Quebec, Saskatchewan, and British Columbia. Figure 2 and 3, respectively, show the emissions from each economic sector and the different types of energy sources used to produce electricity in each province.

The first bar in Figure 3 (Province: Alberta) shows the two main sources used to produce electricity in Alberta are natural gas and coal. Alberta has the largest oil and gas reserve in Canada stored in the province's oil sands. Moreover, Alberta's highest emitting sector is oil and gas, which accounts for over 52% of the province's GHG output, as shown in Figure 2. A reliance on high carbon emitting sources is the main factor resulting in Alberta's high GHG emissions.

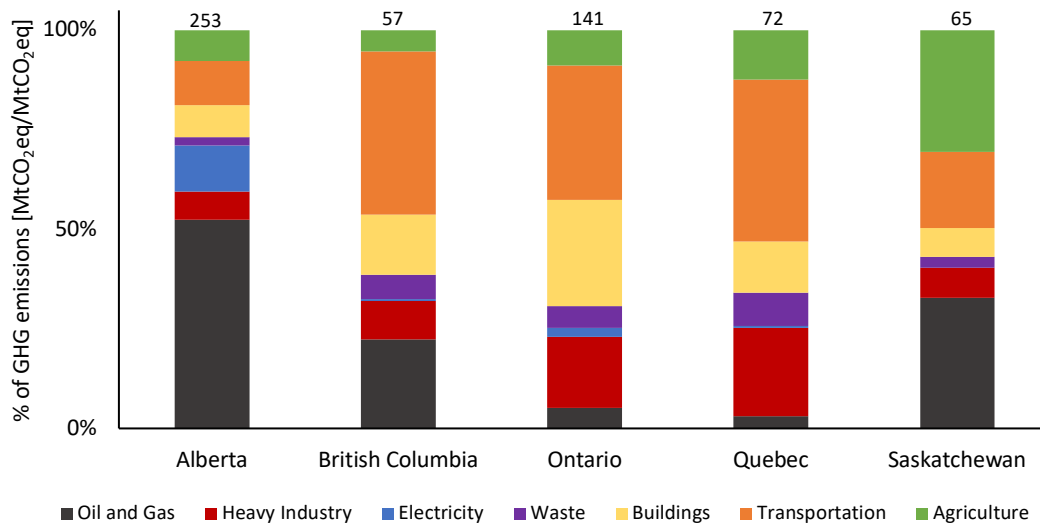


Figure 2. Greenhouse gas emissions emitted by each province broken down by sector. The numbers at the top of each bar represent the total amount emitted per province in 2020 in Mt of CO₂ [30].

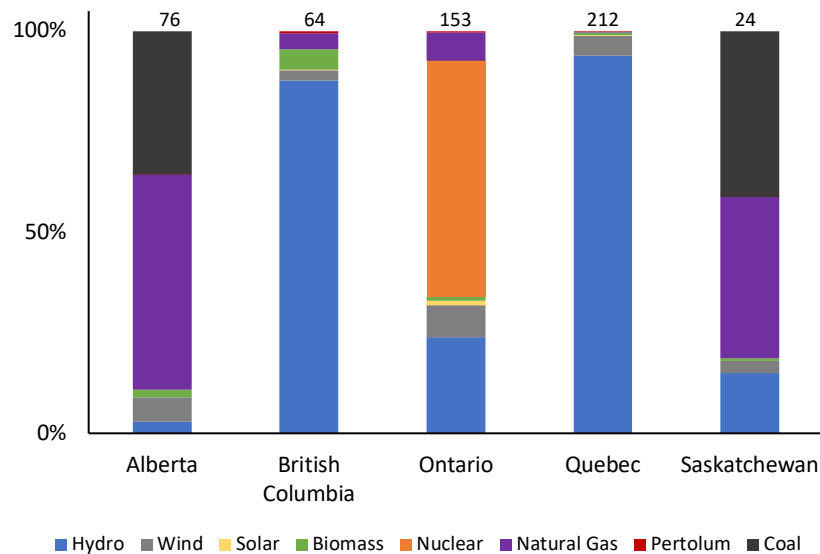


Figure 3. Sources of electricity generation in different provinces in 2020. The numbers at the top of each bar represent the total amount of energy used per province in 2020 in TWh. Data collected from [31][32][33][34][35] and graph adapted from [36].

Ontario is the second highest GHG emitter [5]; however, their GHG profile is different from Alberta's. Due to a high percentage of Ontario's electricity being produced from nuclear

and hydroelectric energy, adding carbon capture technology to power plants is less tactical. As Niagara Falls (one of the world's largest waterfalls) is located in Ontario, the province can access this energy source for electrical power generation. As shown in Figure 2, the sectors that have the biggest impact on emissions in Ontario are Transportation, Buildings, and Heavy Industry making up 33.8%, 26.7%, and 17.9%, respectively [5]. Similar trends were found in British Columbia and Quebec, where the highest emitting sectors were not closely related to electricity generation, but transport, central and water heating for buildings, and construction. However, the integration of CCS systems for transport and building emissions are difficult since they are not produced by large stationary sources. Instead, the uptake of electric vehicles powered by clean energy sources, and the use of geothermal heating and cooling systems [37] for housing is more practical. Hence, alternative methods will need to be further developed and deployed to reach net-zero emissions in Canada.

An important aspect to note when examining the emissions distribution relates to the distribution of product and resources produced from fossil fuels in Canada. Although the emissions by sector and energy distribution show a significant portion of stationary GHG emissions come from Alberta, the products which are produced and result in the promotion of increased GHG levels are used nation-wide. Indeed, it is necessary to identify where and how emissions are produced to understand the best tools and strategies necessary for mitigating those gases, i.e., carbon capture application can be deployed where stationary emissions sources are highest or replace those power plants with more advanced, sustainable, and cleaner energy technologies [38][39]. However, the implementation of mitigation is not necessarily the sole responsibility of the region producing the GHG emissions as other regions may play a large role in the demand promoting them.

Although Canada promotes clean energy and research of CCS technologies, there are few large-scale implementations that aid in reducing the country's GHG emissions. As leaders in CCS, it is necessary that larger economies (including Canada) develop strategic policies and plans to reduce emissions. Part of this plan should consider the deployment of full-scale carbon capture technologies, which will also help accomplish long-term sustainability.

2.1.1. Current Carbon Capture Projects

2.1.1.1. Boundary Dam CCS (2014 – present)

The world's only commercial-scale fully operational coal-fired power plant with retrofitted carbon capture is in Saskatchewan, Canada and operated by SaskPower [40]. The carbon capture unit was added to the power plant in 2014 [41]. Boundary Dam uses solvent based post-combustion capture technology and, as of January 23rd, 2023, the facility had captured over 5 million tonnes of CO₂ which is equivalent to over 50% of Newfoundland and Labrador's total GHG emissions in 2020 [42][43]. The CO₂ captured from this facility is partially used for Enhanced Oil Recovery (EOR) in Weyburn-Midale North Dakota while the rest is sequestered underground [42][43].

The project's initial investment was set at \$1.3 *billion* with \$800 *million* being allocated to the carbon capture and sequestration process and \$500 *million* for retrofitting costs [44]. Due to the projects inability to initially meet the capture requirements, fines increased the projects price increased to \$1.5 *billion* [44]. While the federal government has imposed a carbon tax, they have also implemented a carbon tax threshold. Anything above this predetermined value (the carbon tax threshold) is subject to said carbon tax which is currently 549 *tonnes of CO₂/MWh* . In the last update from SaskPower on the CO₂ capture unit, they

reported an average emissions rate of 383.2 *tonnes of CO₂/GWh*, well below the federal limit [45].

2.1.1.2. Quest (2015 – present)

This project aimed to capture over one million tonnes of CO₂ per year using a pipeline to transport the captured CO₂ from ore mines in Alberta's Athabasca Oil Sands and then store it in deep rock formations located in the Basal Cambrian Sands, Alberta [46][47]. The project started in 2009 and commercial operation began in 2015 [47]. The main investors are Shell, the Government of Canada and Alberta, and the Athabasca Oil sands [46]. The project is for hydrogen production by upgrading bitumen whereby CO₂ is generated as a by-product. The CO₂ is captured using an amine solvent and is then compressed into liquid form and transported underground into well storage, which is covered by deep rock formations [48].

The final capital cost of the project reached \$790,000 in 2017, while the operational costs and revenue for the project in 2021 were reported to be \$56,000 and \$85,000, respectively [49]. By the end of 2021 Quest reached a total of 6.8 *Mt* of injected CO₂ since the project began in 2015 while maintaining an average yearly safe injection of 1.055 *Mt of CO₂* in 2021 [49]. This carbon capture project continues to operate at a net profit; it is expected that between 2022-2025 the yearly revenue for the Quest project will reach \$270,000 [49].

2.1.1.3. Alberta Carbon Trunk Line (ACTL) (2020 – present)

The Alberta Carbon Trunk Line (ACTL) is a capture, transport, and utilization system that can move up to 14.6 *Mt* of CO₂ per year when running at full capacity (since 2022) and is used for Enhanced Oil Recovery (EOR) in Alberta's oil sands [50]. The capacity of this system accounts for 20% of all the current emissions produced by the oil sands in Alberta. North West Redwater Sturgeon Refinery and Nutrien Redwater Fertilizer Facility capture CO₂ (3.5 *MtCO₂*

as of 2022) from their gasification processes and feed it to the ACLT, which are the two main suppliers to the line [46][50].

Enhance Energy, the main developers, were awarded government funding to help complete the \$1.2 *billion* project, which includes the ACTL capturing, transporting, and sequestering up to 1.8 *Mt* of CO₂ per year. Furthermore, ACTL is expected to supply 30,000 more jobs in Canada, increase the country's GDP by \$6 *billion*, and generate \$15 *billion* for the province during the first phase of this project [51].

2.1.1.4. Weyburn-Midale Project (2000 – present)

This initiative started as a research project to monitor the sequestration and storage of CO₂ along with investigating the feasibility of EOR in Saskatchewan [46]. CO₂ emissions are captured from a facility in North Dakota and transported to Saskatchewan via pipeline. Since launching in 2000, the research aspect of the project was completed in 2012, and now the oil fields continue to use the captured CO₂ from North Dakota as well as Boundary Dam for EOR utilization [52].

The total cost of the project is about \$40.9 *million* with funding being allocated by the Government of Canada, Provincial governments, United States government, and Petroleum Technology Research Centre industry partners [53]. The injecting of CO₂ started in 2005; over 18 *Mt* of CO₂ have been injected at the Weyburn site, and 3 *Mt* of CO₂ has been injected at the Midale site, with an expected 30 and 10 *Mt* of CO₂ to be injected and stored in total at the respective sites over the lifespan of the project [53].

A cumulative effort from all the existing CCS projects in Canada has resulted in \$2,741,690,000 spent to capture 36.3 *Mt CO₂*, which is over \$75.5 *million/Mt CO₂ captured*. The existence of these projects has helped industries recognize the importance of CCS and the

impact they have on GHG emissions. While these projects promote decarbonization efforts in Canada, they alone will not reduce CO₂ emissions enough to meet the proposed emission targets. The expected emissions profile in 2030 is further explored in section 2.3.3.

2.1.2. Upcoming Carbon Capture Projects

2.1.2.1. Svante

Svante's new carbon capture adsorbent is one of the main projects and technologies the government is funding with the goal of reaching the emissions target [5]. Svante has been working on the development, manufacturing, and commercialization of a low-cost carbon capture system that uses a novel solid filter in large industrial applications [5]. The product is an engineered adsorbent made of nanomaterials loaded into a packed bed, which can catch and release CO₂ within a sixty second cyclic timeframe [54]. The manufacturing plant for this material (located in Burnaby, British Columbia) is designed to run twenty-four hours a day, seven days a week, and is to be fully operational by the end of 2023 [5][54]. This adsorbent technology will be used in a new DAC facility being built in the United States [55].

Ground broke in 2022 on the proposed \$97 *million* project in Burnaby [56]. Pilot and industrial scale tests have been performed in Richmond, British Columbia on a 1 *t* of CO₂ per day plant; as well as in Lloydminster, Saskatchewan, on a 30 *t* of CO₂ per day plant [57]. When construction is complete, the manufacturing plant is expected to produce filter modules that in total have the capacity to remove 3 *Mt* of CO₂ per year [57].

2.1.2.2. Pathways Alliance

Canada's six largest oil sands companies (Cenovus, Canadian Natural, ConocoPhillips Canada, Imperial, MEG Energy, and Suncor) have partnered to form the Pathways Alliance with the collective goal of advancing decarbonization of the oil sands to help achieve the national

2050 net-zero emissions goal [58]. This project is still in its early stages and the method of capture has not yet been decided; however, the company has multiple feasibility studies underway to determine the best locations and approaches for the capture and storage network [59]. The project will consist of three phases which include construction, use of carbon capture units with a transport system to reduce emissions by up to 12 *Mt* of CO₂ by 2030, and continued innovation as new technologies emerge [59].

In phase one, which is scheduled from 2020-2030, Pathways alliance will invest \$24.1 *billion*; \$16.5 *billion* has been allocated to the CCS network in Alberta and \$7.6 *billion* invested in major emission reduction projects and technologies [57]. Funding for phase two has not yet been announced.

2.1.2.3. Genesee

Capital Power, a power generation company based in Edmonton, Alberta, has been implementing post-combustion carbon capture (PCC) systems on their two natural gas units located at the Genesee Generating Station [60]. They have partnered with Mitsubishi Heavy Industries Group (MHI Group) and Kiewit Energy Group for a front-end engineering and design study to determine feasibility of the project, which is expected to be completed in 2023 [60]. MHI Group's KS-21 solvent is being used in this amine-based PCC process and is expected to be used in the full-scale implementation. Industry tests report that when running the process with the KS-21 solvent, lower regeneration energy is required [60]. A final investment decision will be made mid-2023 by Capital Power based on the study's outcome and if approved, they are expecting to start with the capture of CO₂ by 2027 [60]. The project is expected to capture 3 *Mt* of CO₂ per year [61]. An additional project called the Grande Prairie Project run by Naticol

Energy was in planning stages up until February 2023 but was cancelled; this is further discussed in appendix A.

A study that considered economic and environmental factors to determine an optimal deployment of a CCS supply chain for Northeast China was reported [62]. While this model considered key economic components, e.g., capture, transport, storage, and utilization cost, key environmental considerations and terms are missing, e.g., land constraints, public perception, and socioeconomic deterrents. In general, existing carbon capture deployment models lack these types of social and environmental impacts that contribute to policy making [63][64][65]. The proposed model in chapter 3 of this thesis aims to maintain the key economic features, while including social and additional environmental factors to fill that existing gap in the literature.

2.2.Biomass

In recent years there has been extensive growth in investigating biomass integration into energy production as a sustainable energy alternative [66][67][68]. Biomass sources are often waste products from large industrial or agricultural processes. The benefit of a biomass feedstock is that by including biomass in the production of energy, industry is taking a material that would otherwise become waste and reusing it in a new way that may be beneficial for the environment thus improving the carbon cycle. One of the main challenges with biomass utilization is product variability [69][70]. Although biomass can be abundant and inexpensive, if the waste products meet guidelines to ensure safe disposal, composition requires vary widely. Therefore, it can be difficult to have a product with similar properties and characteristics unless efficient operating strategies are deployed [71][72][11]. This lack of consistency also means that the energy density of the biomass fuel source could vary; if biomass is the only fuel source, this will change the amount required to power production [66]. Therefore, when incorporating biomass into a

process, pre-treatment is key to reducing product (biomass) variability and allow a smoother operation of the downstream process. Depending on the process and application of the biomass, aspects such as chemical composition, melting point, and activation energy need to be considered [73]. Utilization of biomass as an energy source has been a very popular area of research for the past several years which has helped motivated the investigation of biomass applications in carbon capture [73][66].

The use of different biomass sources including algae, hydrocarbon waste products, and metal doped compounds is a growing area of interest [73]. The main reason for the utilization of biomass adsorbents over conventional amine-based solvent technology is because of the lower cost and energy requirements [74]. However, due to the variation in biomass sources, application methods, and evaluation metrics on performance, the comparison of these methods and concluding which is the most effective is difficult to assess [66][74]. Many lab-scale and pilot scale experiments have been conducted to determine the adsorption potential of different biomass materials for carbon capture [75][74][76][77][78]; however, there are a limited number of models or simulations to complement those studies. There have been studies which examine the modelling of various biomass waste materials such as Tequila Vinasses, corn husk, activated carbon waste, etc. [79][80][81]. However, as the focus of this thesis is on biomass waste utilization as a carbon capture method, a detailed review on biomass waste materials is outside the scope of this work. Studies that simulate the adsorption of CO₂ using a biomass-based adsorbent on a molecular level have been conducted [72][82][83]. Inayat et al. [84] provided a MATLAB model for hydrogen production from biomass using calcium oxide (CaO) as a CO₂ adsorbent; although there are biomass sources for CaO, this was not included in the model. Biomass adsorbents for CO₂ capture literature lacks studies which model the entire carbon

capture process. That is, the existing models that simulate the integration of biomass as an energy source and molecular interactions between biomass adsorbents and CO₂ do not provide a holistic view which allow for comparison between total process effectiveness and efficiency.

There have been recent studies which experimentally investigate the CO₂ adsorption capacity and reaction kinetics of biomass derived lithium orthosilicate (Li₄SiO₄) [85][86][87]. Utilizing this waste product as the biomass base for a solid adsorbent in the carbon capture process has been tested in lab-scale application but has yet to be modelled. One of the main motivations for fly-ash derived lithium orthosilicate is due to the high silicon composition in fly-ash. As a waste product, fly-ash is an untapped source of valuable material which can be reused to help reduce emissions from many fossil-fired processes. Without the system model, it is challenging to predict production requirements, efficiency, and cost of scaled up systems. The Aspen Plus model presented in chapter 4 of this work rigorously simulates the Li₄SiO₄ – CO₂ capture system, providing validated results of an alternative pilot-scale modelled carbon capture method.

2.3.Waste-management and Recycling

Waste management is an essential aspect of process design, planning, and sustainability as the by-products of a process often need special handling and treatment. For example, the CO₂ capture process is a form of waste management, as the flue gas produced through the burning of fossil fuel needs to be stripped of CO₂ to avoid the increase in GHG emissions. Additionally, waste management plays a key role in addressing the overall sustainability of a process. One of the 12 principles of Green Chemistry addresses the need to prevent waste where possible [88]. If a waste product can be reused or recycled into the system, the entire process becomes more sustainable.

Studies in the field of waste management have investigated the removal of heavy metals and other compounds from solid waste. Mining and incineration processes have been found beneficial areas for waste recovery and elemental extraction [89]. Previous works have focused on additional process steps and treatment methods to aid in the extraction of different desired elements/compounds (e.g., iron, magnesium, zinc, copper, tin, phosphorous) such as bioleaching and water-washing [90][91][92][25]. For fly-ash waste specifically, there has been studies performed on how acid and water washing can help increase these elemental removal rates [91][93]. Originally this treatment has been considered to retrieve valuable compounds from the waste products, such as zinc, magnesium, iron, copper, and other widely used elements. This process includes an acid washing and water washing step which are both steps in the pre-treatment of biomass-based fly-ash Li_4SiO_4 production [90][93][85]. By integrating the optimal conditions found in previous studies on fly-ash elemental extraction with the necessary pre-treatment for Li_4SiO_4 preparation, not only could the adsorption pre-treatment costs be partially negated, but additional compounds that are key for different industries could be retrieved/re-used.

On the other hand, additional studies have been performed on the utilization of CO_2 in carbonate compound production such as CaCO_3 , MgCO_3 , and FeCO_3 [24][89]. CaCO_3 , also known as limestone, is a highly used component in industry, specifically in the cement industry [23]. Limestone is used to improve the mechanical properties of cement such as decreased setting times and increased compressive strength [94]. One technique to synthesis/produce limestone is through the following reaction series:





where CO₂ gas is dissolved in water forming carbonic acid (H₂CO₃) which dissociates into carbonate ions (CO₃²⁻) and hydronium ions (H⁺) [95]. The full dissociation of CO₂ gas to carbonate ions is favourable in solutions with higher pH values (roughly 10); otherwise, the reverse reaction is more prominent in the equilibrium and bicarbonate ions (HCO₃⁻) remain in solution [95]. This is then followed by a reaction with calcium ions (Ca²⁺), which results in the formation of calcium carbonate (CaCO₃). One of the common compounds found in biomass fly-ash is calcium oxide (CaO), which when treated with acid washing and water washing, is converted into calcium ions that can be further utilized in salt precipitates depending on the final concentration in waste streams.

In the field of CCUS and waste management, there are studies which focus on the utilization of waste products and studies where minimizing waste and process optimization is the end goal [96][92][97][98][99][100]. However, there are few studies in the literature which present a model where both waste utilization and optimization are prioritized. In particular, studies in CaCO₃ production utilizing CO₂ have focused on optimal operating conditions for maximum CaCO₃ output and CO₂ utilization, thereby promoting the decrease of the carbon footprint in a process such as cement production [23][24]. The focus of studies in this area which include both optimal plant operation and waste management are often Life Cycle Assessments (LCAs); which may not involve detailed modelling of each process, e.g., modelling of energy and mass balances. A few studies have considered detailed modelling of process optimization and waste utilization and management; however, they often analyse the effects of integrating the carbon capture process on waste treatment systems, and less on using waste materials as a sorbent to

capture CO₂ [97][101][102][16]. Ramos et al. and Kaur et al. performed studies which assessed the functionality of waste silicon/aluminum and plastic waste as activated carbon as sorbent materials for carbon capture, respectively. The works inspect aspects of the physical system such as reaction kinetics and carbon capture efficiency of the different adsorbent materials. However, both studies lack computational models which can simulate the system [103][104]. A study by Peres et al. proposed a predictive machine learning model for biomass waste (passion fruit peel) utilization for CO₂ capture. In that work, the biomass source modelled was an activated carbon adsorbent and as such the kinetic model varies significantly from Li₄SiO₄ adsorbents [105]. The work focuses more heavily on the ways a machine learning model benefits the modelling of passion fruit peel biomass waste as a CO₂ capture agent. Additionally, that study did not consider the integration of management strategies for the waste produced by the process. A pilot scale system of CO₂ capture utilizing industrial biomass derived Li₄SiO₄ adsorbent is presented in chapter 4 of this thesis as the literature has yet to explore the modelling of this system in detail. An extension of this process which includes the integration of resource waste reduction and fly-ash elemental extraction modelling has the potential to promote a circular carbon economy by closing the loop of solid waste, wastewater, and CO₂ capture modelling. To the author's knowledge, the studies presented in the literature have not considered a model that connects all these aspects. Chapter 5 of this thesis provides a model for a carbon capture system which transforms and utilizes biomass waste material into an adsorbent for CO₂ capture; the model then incorporates waste from the adsorbent's pre-treatment into a utilization process for the captured CO₂ by selling both streams to the cement industry, where they could be further utilized in dust suppression and carbonate formation. Developing models such as that proposed in this thesis aims to promote the importance and value of a circular carbon economy.

2.4.Summary

This literature review revealed that there exist few carbon capture deployment models to aid in optimal decarbonization planning, and those that do are missing key environmental and socioeconomic factors which impact deployment decision making. Additionally, biomass-derived sorbent materials have shown promise in experimental applications, but there has been no model provided for the biomass-based industrial fly-ash derived Li_4SiO_4 – CO_2 capture system. To allow large scale implementations of this system, process modelling is necessary to test the full capability of the system; this literature review found gaps in this area for many biomass-derived adsorbents, but specifically for Li_4SiO_4 . Furthermore, waste utilization and management in carbon capture systems was investigated and found that the use of biomass sorbent for CO_2 capture models do not consider waste stream utilization. In the interest of prioritizing fully sustainable processes, modelling studies that consider full utilization of product and waste materials are essential to promote net-zero emissions and a circular carbon economy.

Chapter 3 An Optimal Sustainable Planning Strategy for National Carbon Capture

Development

This chapter presents an optimal framework for the strategic deployment of carbon capture plants in a specific region. This framework considers external environmental and social considerations often missing from implementation frameworks, which can aid policy makers in more well-rounded deployment decisions. The proposed framework was implemented in Canada with the aim to provide insights on the potential number, type, and locations of carbon capture plants that may be needed to meet specific emission targets.

The ongoing and proposed carbon capture projects in Canada are outlined in section 2.1. For the three projects on track for deployment, it is expected that they will reduce the total CO₂ emissions by 48 *MtCO₂* as of 2030, given the following assumptions: the first Svante unit will begin capture in 2025, and one additional unit will be added each year starting in 2027 capturing 3 *MtCO₂ per year per unit* while the emissions are being removed equally from each sector; the Pathways Alliance project will reduce emissions by 12 *MtCO₂* total in 2030 removing only from the oil and gas sector, Genesee will capture 3 *MtCO₂ per year* starting in 2027 removing only from the electric sector. This is also assuming that the projects become operational by the dates previously outlined. As outlined in Table 1, even with these added projects, Canada will only be able to reach the reduction targets in one of the three main energy sectors. This further motivates the need for an optimal deployment plan for countries with similar initiatives.

Section 3.1 introduces the general framework for mathematical modelling and information needed to implement this strategy. Section 3.2 describes a case study done on Canada and the parameters used in the model for this study, followed by base case results, a sensitivity analysis on the national emissions targets, and an analysis on variation in Alberta's

emissions levels in Sections 3.2.1, 3.2.2, and 3.2.3, respectively. The outcomes of this chapter have been published in The Canadian Journal of Chemical Engineering [4].

Table 1. Proposed CO₂ emissions [Mt] if the upcoming projects in Canada become operational.

Sector	2020 Emissions [31]	Predicted 2030 Emissions without upcoming projects	Predicted 2030 Emissions with upcoming projects	2030 Emissions Target [5]
Oil & Gas	183.4	327.2	299.2	110
Heavy Industry	73.6	65.9	49.9	52
Electricity	53.7	46.8	18.8	14

3.1. Mathematical framework for national optimal carbon capture deployment

As outlined above, there are many countries developing sustainable carbon capture technologies; however, there is no plan for how the technologies will be used and their impact in global decarbonization. To address this issue, a model was developed to aid in strategic and optimal placement and choice for different carbon capture technologies.

The model formulation was developed for a national framework; however, this can be adapted for other regions with minimal adaptation. The problem statement is described next.

Given: 1) the types of carbon capture plants available for implementation, 2) the emissions from each region in different industrial sectors, 3) total emission targets for each industrial sector, 4) the price of energy in each region, 5) the size, capacity, retrofitting cost, transportation cost, and operating cost of the different capture technologies, 6) the social cost of carbon, 7) the lifetime of each carbon capture technology, and 8) additional environmental and land constraints, determine an optimal allocation of various carbon capture technologies in a given region that meets the CO₂ emission targets and constraints outlined above.

For this work, only emission from stationary sources were considered (carbon capture plants used in commercial implementation are not currently equipped to handle emissions from other sources such as residential and automotive emissions). Therefore, only emission from Electricity, Heavy Industry, and Oil and Gas sectors are considered since those come from stationary sources. Moreover, emissions data from each individual location (i.e., power plants, steel factories, oil refineries) would not be collected because of lack of availability; hence, to accurately represent the capture, transport, and storage process, the cost of CO₂ transport and storage are combined and vary depending on region. In this model, emissions levels are assigned for every region and sector. A more detailed explanation on the limits and boundaries of this model is given in appendix B section B1.

The following notation is introduced: for every plant $P \in PL$ (i.e., the set PL contains the different possible plant types), a possible plant installation $i \in PN$ (i.e., the set PN contains the total number of new carbon capture plants that can be installed), in region $j \in PT$, reducing emissions from sector $k \in SE$. The optimal configuration of carbon capture plants in a specified region is as follows:

$$\min_{Z_{P,i,j,k}} CCA + \omega SPC \quad (1)$$

s. t.

$$CCA = \frac{\phi_{economic}}{Y_{min} \sum_j \sum_k E_{j,k}^* - \phi_{emissions}} \quad (2)$$

$$SPC = \sum_j \sum_k \frac{\sum_P \sum_i (Y_P O_P Z_{P,i,j,k}) + S(E_{j,k}^* - \sum_i \sum_P x C_P Z_{P,i,j,k})}{\sum_i \sum_P x C_P Z_{P,i,j,k}} \quad (3)$$

$$\phi_{emissions} = \sum_j \sum_k (E_{j,k}^* - \sum_i \sum_P x C_P Z_{P,i,j,k}) \quad (4)$$

$$\phi_{economic} = \sum_i \sum_j \sum_k \sum_P (e_j B_P + R_P + T_j x C_P) Z_{P,i,j,k} \quad (5)$$

$$\sum_P Z_{P,i,j,k} \leq 1 \quad \forall i \in PN \quad \forall j \in PT \quad \forall k \in SE \quad (6)$$

$$\sum_j (E_{j,k}^* - \sum_i \sum_P x C_P Z_{P,i,j,k}) \leq targets_k \quad \forall k \in SE \quad (7)$$

$$\sum_i \sum_j \sum_k \sum_P Z_{P,i,j,k} \leq Pu \quad (8)$$

$$\sum_i \sum_j \sum_k \sum_P Z_{P,i,j,k} \geq Pl \quad (9)$$

$$\sum_i \sum_k \sum_P Z_{P,i,j,k} \leq L \quad \forall j \in PT \quad (10)$$

$$CCA \leq Ul \quad (11)$$

$$Z_{PCC,i,j,k}, Z_{PRE,i,j,k}, Z_{OXY,i,j,k} \in \{0,1\} \quad \forall i \in PN \quad \forall j \in PT \quad \forall k \in SE \quad (12)$$

where CCA and SPC represent the cost of CO₂ avoided and social perspective cost, respectively. CCA is defined as the cost to remove one tonne of CO₂e, while SPC is the monetary value allocated to major social factors that will impact the type and number of carbon capture plants to be installed, e.g., social perception, carbon tax. SPC is minimized by adding more carbon capture plants to the proposed deployment plans, which will contribute to improve the social perception of capturing CO₂ emissions. This term incorporates a combination of variables that assign a monetary value to social considerations including the public's perspective on incorporating carbon capture plants into infrastructure, how long different types of carbon capture technologies are operation for, and societal views on the vitality of reducing GHG emissions. Both SPC and CCA can be scaled to determine their significance using a scaling factor (ω). This factor (ω) can be determined from heuristics, historical data, and model calibration. A suitable weight will be dependent on the region under consideration, the model's end goal and the application under analysis. Thus, ω is a tuning parameter that needs to be adjusted such that it reflects realistic results for each user's application. $Z_{P,i,j,k}$ is an optimization variable that represents whether or not a P^{th} type of technology (e.g., post-combustion, pre-combustion, or oxy-fuel combustion plant) can be utilized for plant installation i for removal of CO₂ emissions in sector k in location j . Moreover, $\phi_{emission}$ and $\phi_{economic}$ are the new (i.e., with removal deployed) emission levels and their cost of implementation, respectively. Y_{min} is the minimum number of years the plant is expected to be in operation for which is included in

order to allocate the cost per year. $E_{j,k}^*$ is the initial emission levels (i.e., without removal) from a sector k in location j . This information can be collected from historical data. C_p is the CO₂ removal capacity of each type of plant; x is the amount of CO₂ captured by each facility; e_j is the price of energy in each location j ; T_j is the cost of transporting CO₂ in each province j , B_p is the annualized energy requirement for each plant type; S is the social cost of carbon which considers factors such as health, environmental effects, as well as the country/region's imposed carbon tax. This term is able to monetize the cost associated with the societal and environmental impacts that GHG emissions have. A more in-depth explanation on how this value is determined can be found elsewhere [106]. Y_p are the years each type of plant is expected to remain operational for after implementation.

Equations (6) – (12) represent the constraints needed for decision making in this type of networking scheme. Equation (6) ensures that for every installed carbon capture plant, province, and sector scenario, only one type of capture plant is being selected. Equation (7) requires the new (i.e., with removal) emission values $E_{j,k}^*$ in each region j to be below the pre-defined targets in sector k , i.e., $targets_k$. These targets are set by governing bodies of countries or regions and should be considered in a measurement of CO₂e emissions. Equations (8) and (9) enforce the limits on the number of plants installed, respectively, implementing upper Pu and lower bounds Pl on the total plant number. Equation (10) is assigned to land constraints which can be imposed if there are specific locations j that have a maximum/minimum number of plants required which will affect the deployment plan. In practice, Equation (10) could be expressed as a combination of specific land constraints for different j locations. Including land constraints allows for more specific allocation of carbon capture technology that can be adjusted according to the region's requirements. Examples of this are discussed further in the case study found in section B4 of

appendix B. Equation (9) is the upper bound Ul for CCA to account for the project's feasibility reduction if the cost of CO_2 avoided surpasses a particular threshold.

The optimization problem presented above utilizes the integer variable $z_{P,i,j,k}$, and because this allows for multiple types of carbon capture technologies and plants to be considered, this problem is posed as a Mixed-Integer Non-Linear Problem (MINLP). To the authors' knowledge, this is the first study that presents a formulation to determine the optimal location of CO_2 capture plants in a region; hence, the novelty of this work.

3.2. Optimal carbon capture implementation in Canada

The optimization framework presented in the previous section has been used to illustrate the optimal distribution of CO_2 capture plants that may be required to reduce CO_2 emissions in Canada by year 2030. To better understand the impact on Canada if no new CO_2 capture plants are installed and none of the future projects proposed in section 2.1 are implemented, prediction of emission levels in 2030 were conducted. Under the assumption that emissions in each province follow a linear trend based on previously reported emission from the last 15 years [31], Canada's emissions in each sector would be above the national targets (shown in Table 2) by 217 Mt, 14 Mt, and 33 Mt of CO_2 from Oil and Gas, Heavy Industry, and Electricity, respectively. To evaluate the viability of Canada's plan to reduce emissions by 2030 outlined in Table 2, the MINLP optimization problem presented above was adapted to determine the cost associated with meeting these targets and estimate the number of carbon capture plants that may need to be installed in Canada to reach the target of 40% reduction by 2030. The model parameters PL , PN , PT , and SE are defined in section B1 of appendix B. B1 also lists the values assigned for $E_{j,k}^*$, C_P , S , e_j , T_j , B_P , R_P , Y_P , O_P , $targets_k$, and Ul , which were taken from provincial and federal government reports.

For this study, only pre-combustion (PRE), post-combustion (PCC), and oxy-fuel combustion (OXY) technologies were considered, i.e., $P = \{PCC, PRE, OXY\}$. The level of development for other carbon capture technologies (e.g., DAC, CLC) is not advanced enough to handle the scale of emissions needed to process [107]. For these reasons, the industry standards of the chosen technologies were used. The sectors previously mentioned (i.e., Electricity, Heavy Industry, and Oil & Gas) are used as inputs to the optimization and are highlighted in Table 2. The targets reported therein (14 Mt, 52 Mt, and 110 Mt) correspond to national emissions. The last column in Table 2 (% Reduction) shows the distribution of the overall 40% reduction in emissions per sector, as per Canada's goal.

Table 2. Canada's Federal government's breakdown for emission reductions taken [5]. Highlighted sectors are those used as targets in this case study.

<i>Sector</i>	<i>2005 (Mt)</i>	<i>2019 (Mt)</i>	<i>Projected Targets 2030 (Mt)</i>	<i>% Reduction</i>
<i>Buildings</i>	84	91	53	-37%
<i>Electricity</i>	118	61	14	-88%
<i>Heavy Industry</i>	87	77	52	-39%
<i>Oil and Gas</i>	160	191	110	-31%
<i>Transportation</i>	160	186	146	-11%
<i>Agriculture</i>	72	73	71	-1%
<i>Waste and Others</i>	57	51	29	-49%
<i>Natural Climate Solutions</i>			-30	
<i>TOTAL</i>	739	730	443	-40%

Preliminary tests found in section B2 of appendix B were performed to determine a suitable scaling factor (ω) for the present case study. A wide range of ω values were tested, i.e., between 0.0001 to 1000. After narrowing this search and conducting a sensitivity analysis between 0.001 and 0.1, it was determined that when ω was set to a value below 0.0075, the solutions were

heavily influenced by CCA to only minimizing plant costs while still meeting the required targets. Values of ω ranging between 1 to 10 put more emphasis on minimizing SPC, which deployed a large number of plants, and therefore lowered emissions. In the appendix B section B4, Tables B4.10-B4.17, we present an example of the solutions found when using ω value of 1, outlining the difference in shifting the optimizer's objective to minimizing emissions despite increased costs. Based on this analysis, an ω of 0.005 was chosen for the present case study since it provides a compromise between minimizing costs and CO₂ emissions.

To determine the cost of CO₂ transport and storage in each province, a value of \$20.24 per tonne of CO₂ was used as Canada's baseline [108]. The cost of both road (P_j^{Road}) and rail (P_j^{Rail}) transportation in each province was found [108] and the average of the two values was defined as the province's cost of transportation; this is referred from heretofore to as P_j^{CT} . The average of the P_j^{CT} values were taken and used as the cost of transportation in Canada ($avg(P_j^{CT})$). As shown in Equations (13)-(14), each P_j^{CT} was compared to Canada's transportation cost and the percent difference above or below Canada's transportation cost was calculated. This percent difference was then multiplied by the baseline cost of CO₂ transport and storage in Canada ($B_{CO_2}^{CT}$); these final values were taken as the provincial costs of CO₂ transport and storage (T_j). A table of T_j values can be found in the appendix B.

$$\frac{P_j^{Road} + P_j^{Rail}}{2} = P_j^{CT} \quad (13)$$

$$\left(\frac{P_j^{CT}}{avg(P_j^{CT})} \right) B_{CO_2}^{CT} = T_j \quad (14)$$

Assumptions were made to specify the values to use for retrofitting and operating costs represented as R_P [million \$CAD] (Equation (5)) and O_P [million \$CAD] (Equation (3)), respectively, while the capacities of the plants (C_P) were found in literature as reported in

appendix B section B1. The cost of building a new power plant with and without post-combustion, pre-combustion, and oxy-fuel combustion capture were found. On the other hand, retrofitting costs were not available in the open literature. To accommodate this, the cost associated with retrofitting a post-combustion capture plant (PCC) was defined as the difference in cost of a plant with CO₂ capture and without CO₂ capture:

$$R_{PCC} = Co_{WCC} - Co_{NCC} \quad (15)$$

where Co_{WCC} represents the cost associated with building a power plant with post-combustion carbon capture and Co_{NCC} represents the cost associated with building a power plant without post-combustion capture technology. Pre-combustion and oxy-fuel combustion were defined as 90% of cost reported for plants with carbon capture:

$$R_{PRE} = 0.9X_{PRE} \quad (16)$$

$$R_{OXY} = 0.9X_{OXY} \quad (17)$$

where X_{PRE} and X_{OXY} represent the cost to build a pre-combustion and oxy-fuel combustion power plant that includes CO₂ capture, respectively. The process of retrofitting pre-combustion and oxy-fuel combustion is much more complicated than PCC which often requires extreme process flow changes [109]. O_p was assumed to be 15% of the total investment as previously reported [109]. Variables associated with cost (S, e_j, T_j, R_p, O_p) were converted into \$CAD 2030 using Taylor scoring index since these emission targets need to be met by the year 2030. S and e_j were taken from a report by Nordhaus [105] describing the social cost of carbon and its predicted value in 2030 which includes the associated carbon tax and government reports on provincial electricity prices, respectively.

An initial upper limit on the number of plants installed Pu of 1000 was chosen. This was done to ensure that the target constraints, equation (3), would be met while ensuring the available

number of plants would not restrict the solution. The lower limit Pl was chosen as 0. Constraint (10) was considered to impose land restrictions in Canada for the provinces of Prince Edward Island, Ontario, and Alberta. These land constraints are as follows:

$$\sum_i \sum_k \sum_P Z_{P,i,PE,k} \leq L^{PE} \quad (18)$$

$$\sum_i \sum_k \sum_P Z_{P,i,ON,k} \leq L^{ON} \quad (19)$$

$$\sum_i \sum_k \sum_P Z_{P,i,AB,k} \leq L^{AB} \quad (20)$$

This specifies that in PEI the maximum number of plants L^{PE} was assumed to be 1 due to limited space in the province. Ontario must have less than L^{ON} set to 15 plants due to the greenbelt limiting industrial construction locations [110][111]; Alberta should not have more than L^{AB} plants which was defined as 50 because of the indigenous land that surrounds oil sands [112][113]. The MINLP problem was solved in GAMS using DICOPT. The basic problem formulation includes 3,383 constraint equations, 10,007 total variables, 9,945 of which are discrete.

3.2.1. Base Case Results

This scenario can be defined as the previously described optimization problem with no additional constraints or considerations, solved to determine the best location and plant type for carbon capture installation. The formulation presented in equation (1) under the conditions stated in section 4 found that the installation of 58 PCC plants was the optimal policy; results from this case can be found in Table 3. The plant distribution per province for the base case scenario is depicted in Figure 4. With these capture units in place, the 2030 emissions targets (constraint (7) set to values as listed in Table 2) are met while the estimated cost of CO₂ avoided and social perspective cost were calculated as \$27.54/*tCO₂* and \$648.44/*tCO₂*. Currently the average cost of CO₂ avoided for most carbon capture projects ranges from \$40 – \$60 per tCO₂ [114].

This comparison shows a minimum \$12.46 decrease in the cost needed to remove CO₂ if the suggested 58 PCC plants were to be installed. Note however that social cost of carbon includes costs such as the carbon tax, which is typically incorporated into CCA. This reallocation is likely the source of the decreased CCA. Due to the high cost of retrofitting and operating PRE and OXY plants, it is reasonable to expect the deployment of PCC plants. Although PRE and OXY plants are more efficient and decrease emissions more, resulting in a lower SPC than that of PCC, the increased cost in CO₂ avoided due to retrofitting for these technologies of nearly 3.5 and 2 times larger, respectively, is considerable. When looking at the placement of each suggested CO₂ plant (Figure 4), the results are concurrent with expectations, i.e., provinces with the highest emission levels in the proposed sectors are those suggested for plants installation.

With the current outlook on Canada's emissions, if there are no new decarbonization tactics put in place in a short-term, the 2030 targets are highly unlikely to be met. However, if the proposed optimal policy obtained from the base case scenario were to be implemented, Canada would not only meet the targeted CO₂ emissions in each evaluated sector but would surpass the reduction targets by 15.6 %, 46.9%, and 2.7% in the electricity, heavy industry, and oil and gas sector, respectively.

To further evaluate the capabilities of the present planning model, and in addition to the base case as described above, cases under changes in the emission targets and a sensitivity analysis on Alberta's emissions levels were also performed. These are discussed in the next sections.

Table 3. Base case scenario: carbon capture plant distribution and emissions levels per province; all numbers represent PCC plants.

<u>Sector</u>	Province							Plants per Sector	National Targets [MtCO ₂]	GHG emitted [MtCO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	10		1	2	1		2	16	14.00	11.82

Heavy Industry		2			9	5		16	52.00	27.63
Oil & Gas	19	4	1		2			26	110.00	107.01
<u>Plants per province</u>	29	6	2	2	12	5	2	58	176.000	146.46
CCA [$\frac{\$}{tCO_2}$]	27.543									
SPC [$\frac{\$}{tCO_2}$]	648.439									
Economics [M\$CAD 2030]	66135.934									

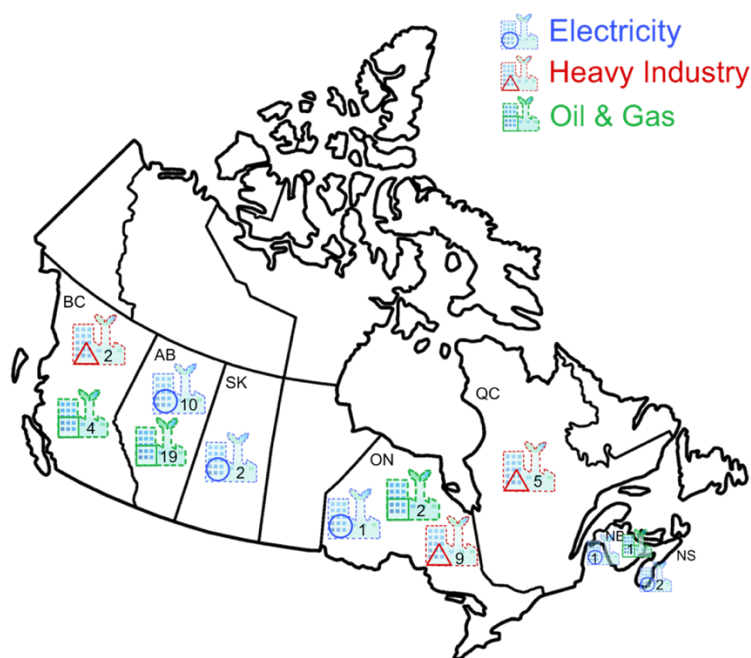


Figure 4. Plant placement of the base case deployment plan. The plants with the blue outline and circle represent the electricity sector, red outline and triangle represent the heavy industry sector, and green outline and square represent the oil and gas sector. The number inside each plant represents the number of plants to be deployed in each province.

3.2.2. Changing the 2030 target levels

To gain further insights on the aspects of the model that influence plant deployment, a sensitivity analysis was conducted on Canada's target emission constraints. The aim was to understand which provinces and sectors had the most variation as the target constraints fluctuated.

The formulation in described in section 4 was executed between $\pm 15\%$ of the nominal targets (14, 52, and 110 $Mt CO_2$), in increasing/decreasing steps of 5%. Results from this analysis can be found in Tables 4-5, Tables B4.1-B4.4 in appendix B, and Figures 5 and 6. In the interest of comparing the results from each target adjustment directly against one another and the base case, Table 6 has been included and shows the changes in resulting emissions levels.

When relaxing the target (i.e., increasing the RHS of constraint (3)) there were minor changes from the base case results. When the targets were adjusted by +5%, one plant was removed from the electricity sector in Saskatchewan, three were removed from the oil and gas sector in Alberta, and two were added to the heavy industry sector in Alberta. These changes can be attributed to the relaxation of the oil and gas and electricity sector targets. As shown in Table 4, these two sectors are driving the changes since their emissions levels are very close to the targets. With the acceptance of higher emissions in these sectors, two plants can be removed allowing for an increase in emissions. However, when these plants are no longer included, the overall emissions levels of the country increase, which in turn increases SPC. To counteract this, two additional plants are added to a province where costs will be minimized, while ensuring the emissions in each province and sector remain positive. Therefore, the addition of two heavy industry plants in Alberta occurs. The only difference in plant distribution between the +5%, +10% and +15% results, is two fewer plants in Alberta's oil and gas sector from +5% to +10%, and four fewer plants from +5% to +15%. CCA for each 5%, 10%, and 15% relaxation decreases minorly by 0.3%, 0.7%, and 1.3%, and SPC increases by 3.1%, 6.4%, and 11.9%, respectively. The plant distribution for the +15% relaxation can be found in Figure 5.

When tightening the target constraints (-5% , -10% , -15%), a similarly inverse relationship to that of relaxing the targets was observed in Alberta's oil and gas sector. Results for the

–5%, –10% and –15% scenarios can be found in Tables B4.3, B4.4, and 5, respectively. Since the distribution from the base case resulted in emissions for the electricity and heavy industry sectors being more than 15% below the targets, there were very few changes in these sectors, with zero changes to electricity. However, Alberta’s oil and gas plants increased from 19 in the base case to 20 for the –5% scenario, then 24 for both the –10% and –15% scenarios as seen in Tables B4.3, B4.4, and 5. Similar to the results observed when relaxing the constraints, the oil and gas emissions as the active constraint was the driving force for these changes. An addition of one heavy industry plant in Alberta for the –5% scenario was added to improve the SPC, while two were added for the –15% scenario for similar reasons. Expected trends of increased CCA and decreased SPC were observed as the targets were further tightened. Through this analysis, the balance between meeting target constraints and implementing capture in provinces with lower energy and transport prices, while ensuring a province’s emissions never reach values below zero is examined. In each scenario where plants were removed, it was found to be beneficial for SPC to allocate a plant to a province with lower energy and transport prices so long as the emissions could be minimized and that the targets were still met (e.g., Table 4 results compared to Table B4.1 results). There exists a trade-off between emissions reduction and CCA as evident through the sensitivity analysis; more stringent targets require removal in more emissive provinces while heavily relaxed targets would eventually enable plants to be installed in provinces where the removal incentives are better (e.g., lower energy prices in Manitoba, or lower transport prices in Newfoundland). In the Canadian context, provinces with low energy and transportation prices are relatively small in industry and population size, thus not very emissive; accordingly, CCS deployment in these provinces is only appropriate with relaxed targets.

Table 4. Results of the 5% relaxation of the target constraints and the proposed carbon capture placement plan.

Sector	Province							Plants per Sector	Adjusted Targets [MtCO ₂]	GHG emitted [MtCO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	10		1	2	1		1	15	14.70	14.58
Heavy Industry	2	2			9	5		18	54.60	22.11
Oil & Gas	16	4	1		2			23	115.50	115.29
Plants per province	28	6	2	2	12	5	1	56	184.800	151.98
CCA [$\frac{\$}{tCO_2}$]	27.444									
SPC [$\frac{\$}{tCO_2}$]	668.546									
Economics [M\$CAD 2030]	63625.082									

Table 5. Results of the 15% tightening of the target constraints and the proposed carbon capture placement plan.

Sector	Province							Plants per Sector	Adjusted Targets [MtCO ₂]	GHG emitted [MtCO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	10		1	2	1		2	16	11.90	11.82
Heavy Industry	2	2			9	5		18	44.20	22.11
Oil & Gas	24	4	1		2			31	93.50	93.21
Plants per province	36	6	2	2	12	5	2	65	149.600	127.14
CCA [$\frac{\$}{tCO_2}$]	27.804									
SPC [$\frac{\$}{tCO_2}$]	587.81									
Economics [M\$CAD 2030]	74820.231									

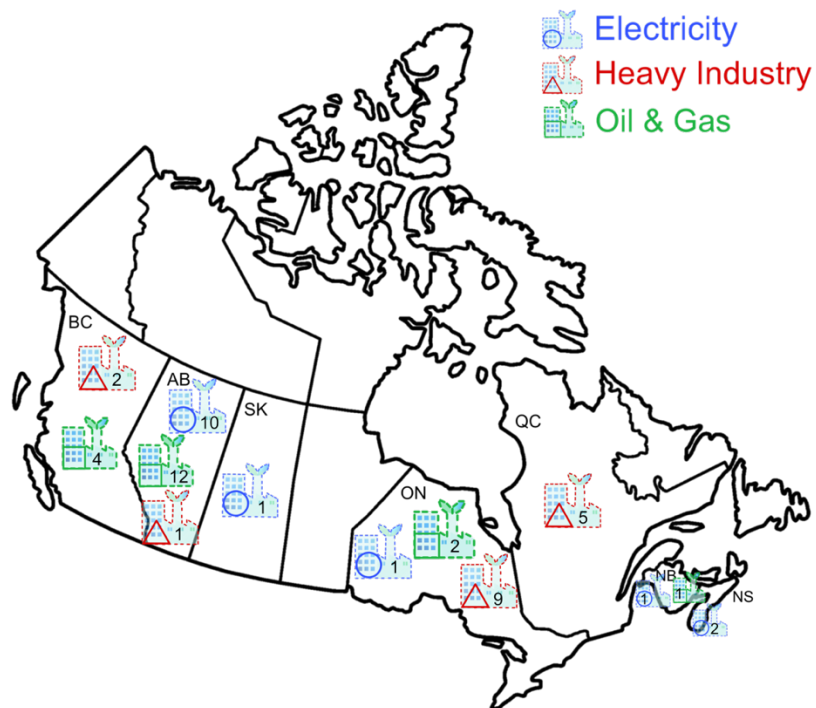


Figure 5. Plant distribution for the 15% relaxation of the target emission constraints from the base case scenario.

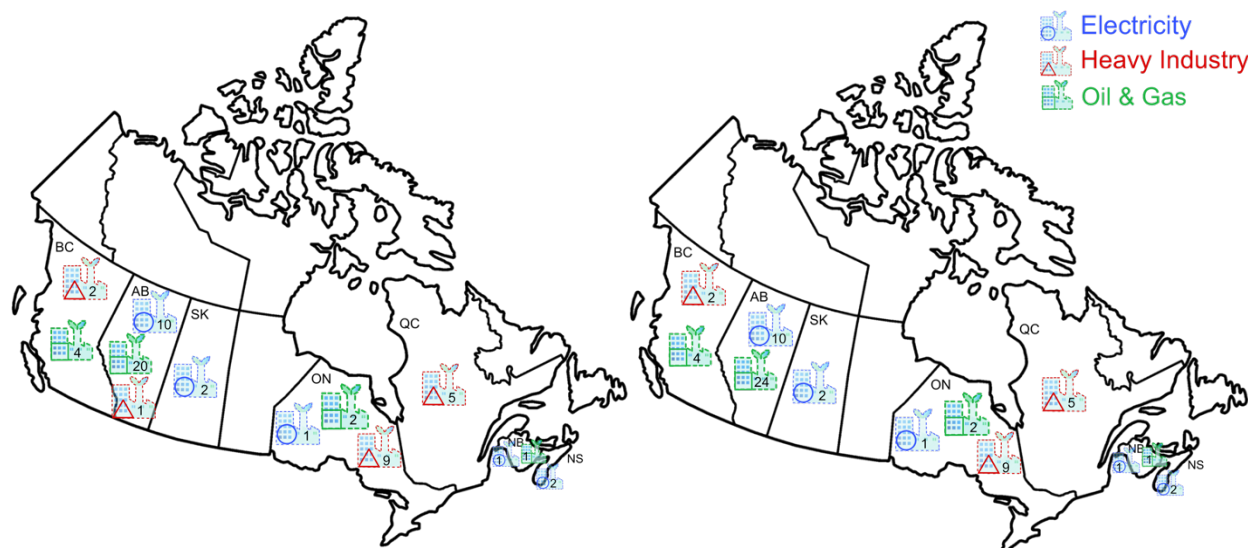


Figure 6. The distribution of plants for 5% (left) and 10% (right) tightening from the base case emission targets.

Table 6. Summary of the resulting emissions levels from each variation in the target constraints.

Sector	Each scenario and the GHG emitted by Canada [$MtCO_2$]	
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	National Targets [MtCO ₂]	Base Case	Targets: -15%	Targets: -10%	Targets: -5%	Targets: +5%	Targets: +10%	Targets: +15%
Electricity	14.00	11.82	11.82	11.82	11.82	14.58	14.58	14.58
Heavy Industry	52.00	27.63	22.11	27.63	24.87	22.11	22.11	24.87
Oil & Gas	110.00	107.01	93.21	93.21	104.25	115.29	120.81	126.33
Total	176.000	146.46	127.14	132.66	140.94	151.98	157.5	165.78
	CCA [$\frac{\$}{tCO_2}$]	27.543	27.804	27.735	27.624	27.444	27.35	27.196
	SPC [$\frac{\$}{tCO_2}$]	648.439	587.81	603.758	629.673	668.546	690.142	725.712
	Economics [M\$CAD 2030]	66135.93	74820.23	72339.00	68617.16	63625.08	61143.85	57422.01

3.2.3. Analysis when changing Alberta's emissions

As shown in Figure 1 of [5], Alberta is the most emissive province in Canada, thus it entails the largest emission reduction opportunity. This could occur if the province were to introduce alternative renewable energy sources to replace part of their coal energy production [115]. This case will thus model the possible outcomes if Alberta's emissions were to decrease by up to 25% in all sectors. It was assumed that Alberta's current emissions would decrease by a specific amount ($x\%$), where x is between 5% to 25%, through alternative sources which would be included in the reduction targets. To perform this analysis, the difference between Alberta's contribution to Canada's total emissions with and without the reduction were subtracted from the 2030 targets shown in Table 2. Appendix B3 describes the calculations performed for 20% reduction. Similar to section 3.2.2, two summary tables have been included to compare the scenario's results to the base case. This comparison of national emissions levels can be seen in Table 10 and the variation in provincial and sector plant distribution can be found in Table 11.

When decreasing the emissions from 5% to 25% in Alberta, there is consistent changes in the plant distribution of this province, as well as in Saskatchewan. When emissions are decreased

5%, there are two fewer plants required in Alberta in the oil and gas sector. Due to the decrease in overall emissions, there is also one less plant required in the electricity sector, resulting in the removal of a plant from the province with the most expensive energy and second highest transport price, i.e., Saskatchewan. These changes result in both the electricity and oil and gas sectors to be very close to the emissions targets making them active constraints; to balance the increase in overall emissions levels, the results show that adding two plants to Alberta's oil and gas sector decreases SPC. The CCA and SPC for the 5% decrease in Alberta's emissions are \$27.49/ tCO_2 and \$641.59/ tCO_2 as seen in Table 7. For the 10%, 15% and 20% decreases, Alberta's plant distribution decreased by one in electricity and two in oil and gas, one in electricity and three in oil and gas, and then two in electricity and 4 in oil and gas, respectively. The results for these scenarios can be seen in appendix B Tables B4.5-B4.7. Tables 7 and B4.5-B4.7 show the CCA decreasing slightly the more Alberta's emissions are decreased while the SPC remained mostly constant with a very minor overall decrease. These observations are expected since the decrease in Alberta's emissions through alternative sources results in fewer plants needed to reach the same emissions levels. The remaining plants distribution found from decreasing Alberta's emission by 25% resulted in three fewer plants in Alberta's electricity sector, one more plant in Saskatchewan's electricity sector, and five fewer plants in Alberta's oil and gas sector relative to the base case results. The reason for the reallocation of the electricity plant from Alberta to Saskatchewan, is because if Alberta had 8 plants in the electricity sector the emissions would be negative, but without an additional plant to capture CO_2 , Canada's target constraints would not be met. Therefore, the results show the least expensive province that still has emissions which can be capture, hence the new plant in Saskatchewan. This distribution also

resulted in the lowest CCA and SPC with values of \$27.22/ tCO_2 and \$631.89/ tCO_2 . A visual representation of the 25% scenario results can be seen in Figure 7.

Due to Alberta being the highest GHG emitter in Canada, it would be beneficial for the province to utilize multiple methods of decarbonization to ensure CO_2 capture becomes less expensive. Based off these results it can be observed that if Alberta were to reduce CO_2 emissions by up to 25%, there would be a 1.2% and 2.6% decrease in CCA and SPC, respectively as seen in Table 8. To further understand how Alberta's decreasing emissions could impact the deployment of CO_2 capture, a 50% decrease in Alberta's emissions were found and are shown in Table 9 and Figure 8. If the province were to cut their emissions in half through alternative sources to carbon capture, there the CCA would be \$26.32/ tCO_2 , a 4.4% decrease from the base case found in section 4.1. Although this results in a 14.9% increase in SPC, it is a result of the emissions reductions from alternative sources not being included in the calculation. This is likely the cause for the resulting value of \$744.85/ tCO_2 being higher than expected.

From a policy perspective, it is evident that Alberta's decarbonization provides the largest opportunity of the deployment of CCS because of the high emissions from each sector in this province. In particular, the province's high reliance on fossil fuels is unlikely to change in the coming years. Nevertheless, it is important to understand the trade-off between CCS efficiency and alternative decarbonization sources found herein as it can inform the choice of strategy used when a planning national carbon capture strategy is deployed; this is evident by the additional plants necessary to meet emission reduction targets.

Table 7. Results for plant location and new emissions levels from reducing Alberta's emissions 5%. All plant numbers represent PCC plants.

Sector	Province			
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	AB	BC	NB	NS	ON	QC	SK	AB's Emissions Levels [MtCO ₂]	Adjusted National Targets [MtCO ₂]	GHG emitted by Canada [MtCO ₂]
Electricity	10		1	2	1		1	27.84	13.62	13.12
Heavy Industry	2	2			9	5		16.82	51.37	21.23
Oil & Gas	17	4	1		2			126.19	106.02	105.92
Plants per province	29	6	2	2	12	5	1	170.839	171.009	140.27
CCA [$\frac{\$}{tCO_2}$]	27.488									
SPC [$\frac{\$}{tCO_2}$]	641.591									
Economics [M\$CAD 2030]	64865.695									

Table 8. Results for plant location and new emissions levels from reducing Alberta's emissions 25%.

Sector	Province							AB's Emissions Levels [MtCO ₂]	Adjusted National Targets [MtCO ₂]	GHG emitted by Canada [MtCO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	7		1	2	1		3	21.98	12.09	10.02
Heavy Industry		2			9	5		13.28	48.87	23.21
Oil & Gas	14	4	1		2			99.62	90.08	87.63
Plants per province	21	6	2	2	12	5	3	134.873	151.047	120.86
CCA [$\frac{\$}{tCO_2}$]	27.224									
SPC [$\frac{\$}{tCO_2}$]	631.889									
Economics [M\$CAD 2030]	57481.263									

Table 9. Results for plant location and new emissions levels from reducing Alberta's emissions 50%.

Sector	Province							AB's Emissions Levels [MtCO ₂]	Adjusted National Targets [MtCO ₂]	GHG emitted by Canada [MtCO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	5		1	2	1		3	14.65	10.18	8.21
Heavy Industry		2				5		8.85	45.75	43.62
Oil & Gas	9	4	1		2			66.42	70.17	68.23

Plants per province	14	6	2	2	3	5	3	89.915	126.093	120.06
CCA [$\frac{\$}{tCO_2}$]	26.321									
SPC [$\frac{\$}{tCO_2}$]	744.854									
Economics [M\$CAD 2030]	38139.101									

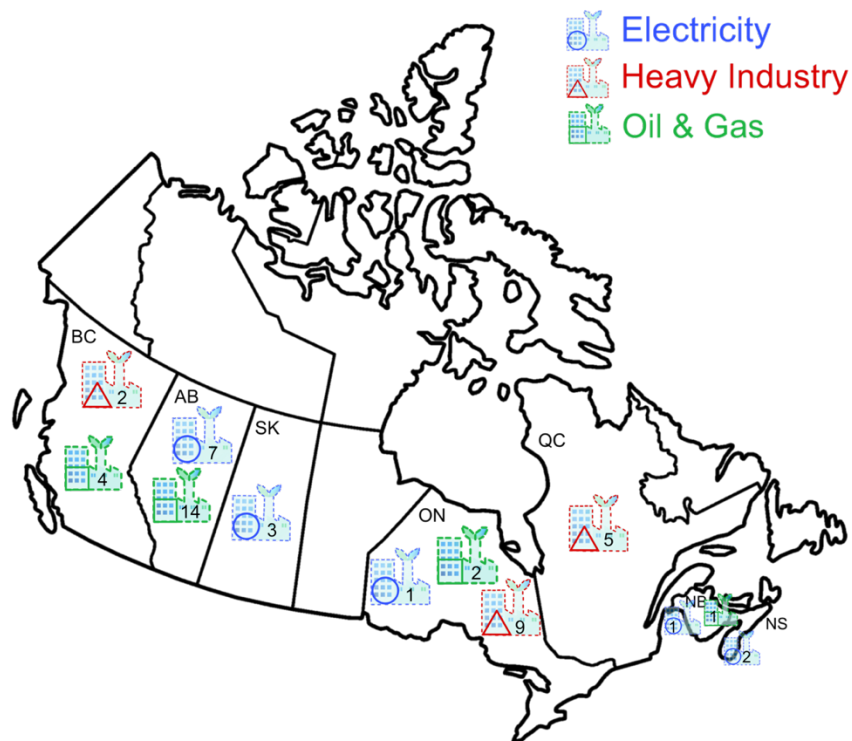


Figure 7. Plant distribution when Alberta's emissions are decreased by 25% through alternative sources.

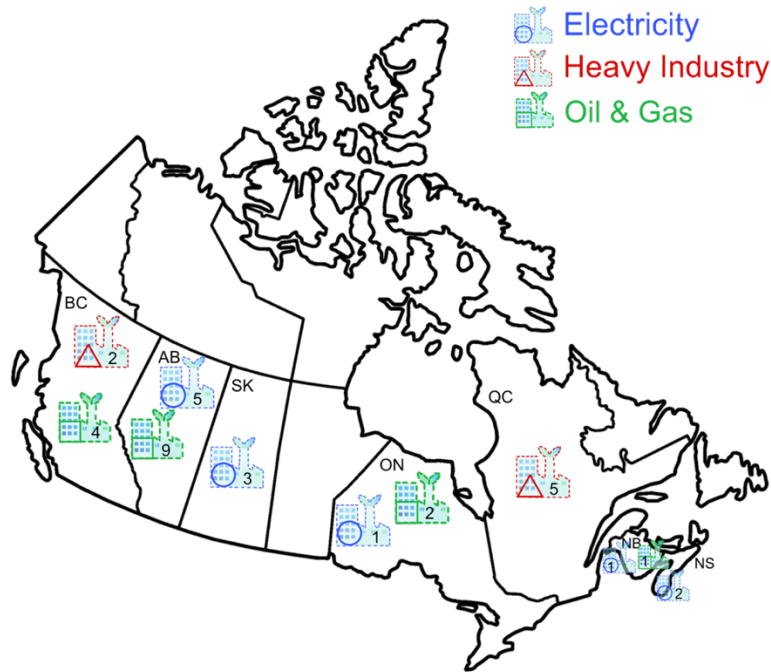


Figure 8. Plant distribution for the scenario when Alberta's emissions are reduced by 50%.

Table 10. Summary of the results from the base case and each scenario in Alberta's emission reduction case study.

Sector	National Targets [$MtCO_2$]	Each scenario and the GHG emitted by Canada [$MtCO_2$]						
		Base Case	Alberta: 5%	Alberta: 10%	Alberta: 15%	Alberta: 20%	Alberta: 25%	Alberta: 50%
Electricity	14.00	11.82	13.12	11.65	10.19	11.48	10.02	8.21
Heavy Industry	52.00	27.63	21.23	25.86	24.98	24.09	23.21	43.62
Oil & Gas	110.00	107.01	105.92	99.28	95.4	91.51	87.63	68.23
Total	176.000	146.46	140.27	136.79	130.57	127.08	120.86	120.06
	CCA [$\frac{\$}{tCO_2}$]	27.543	27.488	27.411	27.363	27.263	27.224	26.321
	SPC [$\frac{\$}{tCO_2}$]	648.439	641.591	644.383	637.029	639.776	631.889	744.854
	Economics [$M\$CAD$ 2030]	66135.93	64865.70	62414.09	61173.48	58692.25	57481.26	38139.10

Table 11. Summary of the provincial and sector plant distribution to compare the Alberta emissions reduction scenario results to those of the base case. Please note that only provinces whose results changed from the base case scenario were included in this summary.

Sector	Each scenario and the number of plants located in each sector for select provinces						
	Base Case	Alberta: 5%	Alberta: 10%	Alberta: 15%	Alberta: 20%	Alberta: 25%	Alberta: 50%

	AB	ON	SK	AB	SK	AB	AB	AB	AB	SK	AB	ON	SK
Electricity	10	1	2	10	1	9	9	8	7	3	5	1	3
Heavy Industry		9		2									
Oil & Gas	19	2		17		17	16	15	14		9	2	
Plants per province	29	12	2	29	1	26	25	23	21	3	14	3	3

Two additional cases involving an increase in the land restrictions (case 4) and changing the ω values (case 5) were also performed. The results from these cases are shown in appendix B (section B4). When performing case 4, it was assumed that land restrictions in different provinces would change the number of plants that could be placed in that province. It was found that restricting the number of plants in Alberta had the largest impact, while limiting Ontario's plants slightly change the outcome. The results for these scenarios can be found in Tables B4.8 & B4.9. For case 5, different ω values were evaluated to see if it would have a significant enough impact on the plant distribution and *SPC* to change the type of plant being installed. The results showed that changing ω did change the outcome of the type of plants, i.e., PCC and OXY plants were the best capture technology in the different cases evaluated. These scenarios are presented in appendix B Tables B4.10-B4.17.

Although PCC, pre-combustion, and oxy-fuel combustion were all included as possible plant options, PCC plants were chosen for every scenario considered in this study. It is important to note however that this is in part due to the weight ω chosen for the objective function. When a higher value is put on minimizing costs, PCC becomes the most beneficial choice. This aligns with the current state of development of PCC in comparison to pre and oxy-fuel combustion. The technology for the latter is not as developed which results in lower confidence from investors and higher process costs. As such, the need for further investigation into alternative carbon capture technologies to improve operation and cost effectiveness. The goal of the following

chapters is to provide a feasibly alternative system for carbon capture application which if used in this deployment framework, would decrease the CCA and increase SPC.

3.3. Summary

In this chapter, a model for optimal deployment of carbon capture technologies was presented. Factors such as land constraints, the social cost of carbon, and operational lifetime were incorporated into the SPC term of the model, while the CCA term maintained the economics needed to evaluate optimal deployment. A Canadian case study was executed to display the full capability of the model. The results from these tests showed that with the implementation of existing carbon capture technology, it could be feasible to meet the governments proposed emission targets in 2030. Scenarios varying the target levels and Alberta's emissions were also examined finding that removal from Alberta's electricity and oil and gas sectors are included in every proposed deployment plan.

Chapter 4 Modelling Biomass-based CO₂ Capture using Li₄SiO₄ Solid Adsorbent for Treatment of Power Plant Emissions

This chapter presents a carbon capture model which utilizes biomass fly-ash as feed for the synthesis of the solid adsorbent Li₄SiO₄. As a waste product, the utilization of biomass fly-ash in carbon capture applications provides net neutral, and in some cases, net negative GHG emissions processes. Computational modelling of the Li₄SiO₄ – CO₂ system has not yet been presented in the literature, but experimental testing shows that this adsorption process has high potential for flue-gas treatment. The pre-treatment and synthesis of biomass fly-ash derived Li₄SiO₄ has also been explored experimentally but there is a lack of models which can be used to examine and test this process. Since the experimental work done has shown potential to provide a carbon capture technology with energy requirements lower than the industry standard, modelling of the process is needed to evaluate its performance.

Section 4.1 outlines the details of the physical system and model assumptions while section 4.1.1 explores the implementation in Aspen Plus; this includes the kinetic model and equations for the system and their utilization in the Aspen model. Section 4.2 presents simulation results from the carbon capture model. Section 4.2.1 describes the model validation process and presents the validation results and section 4.2.2 details each case study examined the outcomes. Section 4.2.2.1, 4.2.2.2, 4.2.2.3, and 4.2.2.4, include the benchmark, variation on adsorbent mass and CO₂ flu gas composition, sensitivity of flue gas to adsorbent mass ratio, and heat of regeneration case study results and discussion. Section 4.3 examines the water and acid consumption of the process and includes a cost analysis and comparison between a standard MEA process and the two process variations presented for this model. The outcomes of this chapter have been submitted to Chemical Engineering Research and Design [27].

4.1. Process Description

Figure 9 outlines the process investigated in this thesis. Biomass is used as a feed source for energy production from a vibrating grate biomass boiler; the fly-ash waste from this process is taken and further utilized. The vibrating-grate system within the power plant unit helps ensure uniform distribution of biomass for sufficient combustion to take place [116]. The energy production unit also emits flue gas which contains 2% to 9% of CO₂ [118]. Figure 9 indicates that these flue gas emissions are a feed to the carbon capture section of the process; nevertheless, the flue gas stream could come from non-biomass energy sources such as natural gas/coal-fired power plants (4% to 20% CO₂ content) [119]. As the biomass fly-ash is one of the main waste products produced by the combustion unit that can include complex and costly disposal, alternative use as a cement additive has shown promise to decrease its environmental impact [120][121]. In this work, the biomass fly-ash waste that comes from energy production is then further treated through acid washing and water washing before it is reacted with a lithium (Li) source to synthesis Li₄SiO₄. Although there are avenues to retrieve Li from biomass and waste sources such as free-floating aquatic plants and brine extraction [122][123], we assume that the Li source is chemically/lab produced [85]. This is because the focus of this work is on the modelling of fly-ash treatment and carbon capture utilizing the synthesised adsorbent. Lithium has many applications in today's economy for different technologies (e.g., batteries). However, because this adsorbent can be regenerated and possibly repurposed after the sorbent's adsorption capacity is depleted, it is essential to investigate the viability of this process on a larger scale to address the need for global decarbonization. The Li₄SiO₄ is further processed to generate a solid powdered Li₄SiO₄ that can act as an adsorbent for CO₂ capture. As shown in Figure 9, the adsorbent is utilized in a post-combustion carbon capture process (adsorption and regeneration

cycle) that treats the emissions/flue gas stream from biomass and non-biomass stationary power plants. To account for changes in CO₂ content in the flue gas stream, the proposed model was developed and tested under varying compositions of CO₂ in the flue gas which included levels found in biomass, coal, and natural gas emissions. One of the main motivations for using fly-ash derived lithium orthosilicate is due to the high silicon composition in fly-ash (some sources containing over 90 wt.% depending on incineration temperatures) [124][121]. The main benefit of utilizing this material as the basis for the silicon contribution to the adsorbent is that it allows for continued use of a waste product that can be complicated to dispose of. As a waste product, fly-ash is an untapped source of valuable material which can be reused to help reduce emissions from many fossil-fired processes. Without a system model for the process depicted in Figure 9, it is challenging to predict process requirements, efficiency, and cost of scaled up systems. The goal of this work is to fill this gap by providing a rigorous process model that simulates the pre-treatment of an adsorbent partially synthesised from biomass fly-ash which is then used to capture CO₂ from coal-fired flue gas.

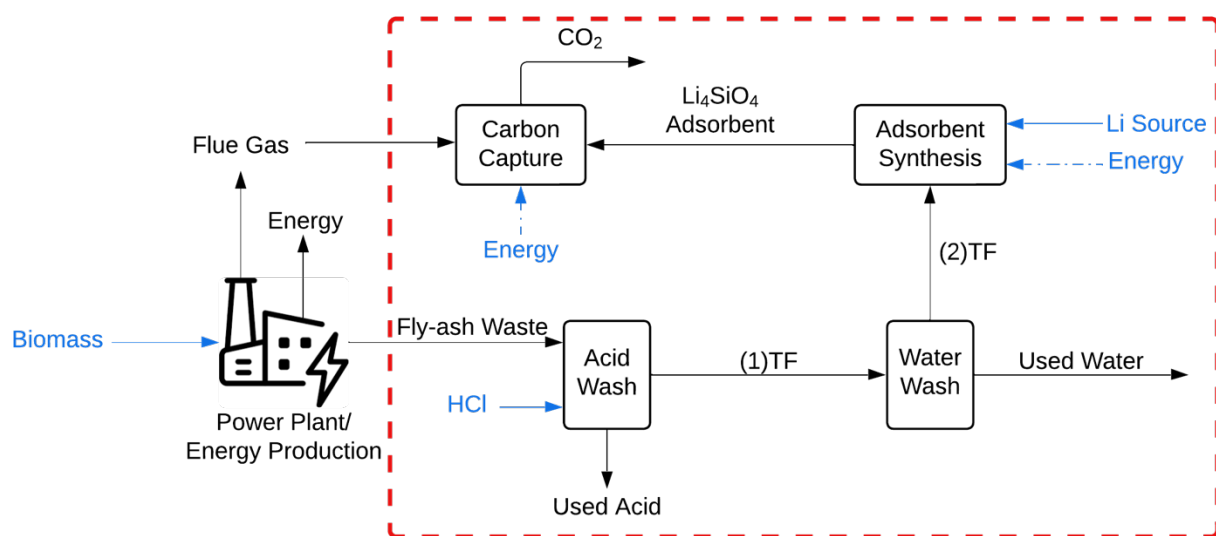
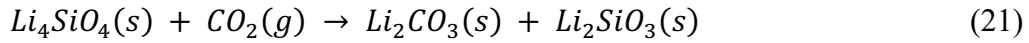
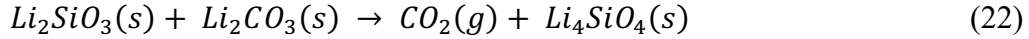


Figure 9. This process flowsheet is an overview of the system being proposed in this work. The basis for the adsorbent which captures CO₂ comes from biomass fly-ash, the waste product of energy production that uses biomass as the feed. The red dashed line shows the boundary for the model presented herein.

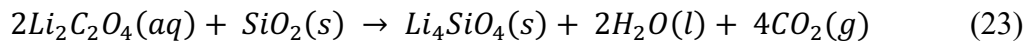
The system considered in this work is a solid adsorbent partially derived from biomass fly-ash (waste) being used to capture CO₂. The solid adsorbent material Li₄SiO₄ reacts with CO₂ to create a new solid layer on the adsorbent which is comprised of lithium carbonate (Li₂CO₃) and lithium silicate (Li₂SiO₃). In literature this is referred to as the “Core-shell model”. The reaction occurs as follows:



The regeneration of the lithium orthosilicate adsorbent from the new solids is also possible and favourable at higher temperatures. This reaction is as follows:



Previous experimental work has provided kinetic behaviour and parameters of this system, as well as the fly-ash pre-treatment process followed to adjust the adsorption capacity of the adsorbent [85]. Figure 10 a) shows the details of the pre-treatment process including the acid washing, water washing, drying, synthesising (combining), and grinding and sifting steps. The synthesis of Li₄SiO₄ occurs as specified in the experimental procedure provided by Yang et al. [85] via a wet-mixing method. The reaction that takes place during this process is dependent on the Li source that is used. In this study lithium oxalate (Li₂C₂O₄) was chosen since it was the source used in the experimental work the present model was derived from. The synthesis reaction is summarized as follows:



where $Li_2C_2O_4(aq)$ is aqueous lithium oxalate, $SiO_2(s)$ is solid silicon dioxide, $Li_4SiO_4(s)$ is solid lithium orthosilicate, $H_2O(l)$ is liquid water, and $CO_2(g)$ is gaseous carbon dioxide. Note

that the solution is heated throughout the reaction process to promote the evaporation of solution in its ion counter parts post solid formation and prior to liquid and gas formation. This heating minimizes the amount of CO₂ produced during this process [125][86][85].

The calculator block C1 in Figure 10 is equivalent to a controller which sets the flowrate of the lithium source. This is then followed by Figure 10 b) which depicts the physical pilot scale set up of the system. The nature of this capture process is semi-batch, and the details on the experimental setup and operating conditions this work can be found elsewhere [85][86]. Figure 10 b) shows the column under (1) the adsorption conditions, as well as (2) the regeneration conditions. As this is a semi-batch process, the solid adsorbent is exposed to a volume of flue gas under continuous mixing for a 30-minute interval and certain conditions for the adsorption to take place, after which the remaining gas is vented. The system operating conditions are then changed to initiate regeneration which takes place over a 10-minute interval. This results in regenerated sorbent and pure CO₂ gas which can be removed and stored/utilized alternatively. This cycle is then repeated until the loading capacity of the adsorbent reaches below the minimum threshold, after which the adsorbent is replaced with fresh supply.

This process was modeled using Aspen Plus with the ELECNRTL and added UNIFAC property package and method as it uses thermodynamic equations such as the Arrhenius equation, which experimental results found to fit the data appropriately [85]. As previously stated, the physical nature of this capture process is semi-batch; however, ASPEN plus is not capable of incorporating both continuous and batch process units into the same process. Therefore, the model has been approximated using a continuous system. More details on how this aspect of the model was handled is addressed in section 4.2.1 when describing the model validation. Modelling of this system was attempted in Aspen Adsorption; however, the system

kinetics were not compatible with the reaction integration and resulted in an error stating that the equation variables were proprietary.

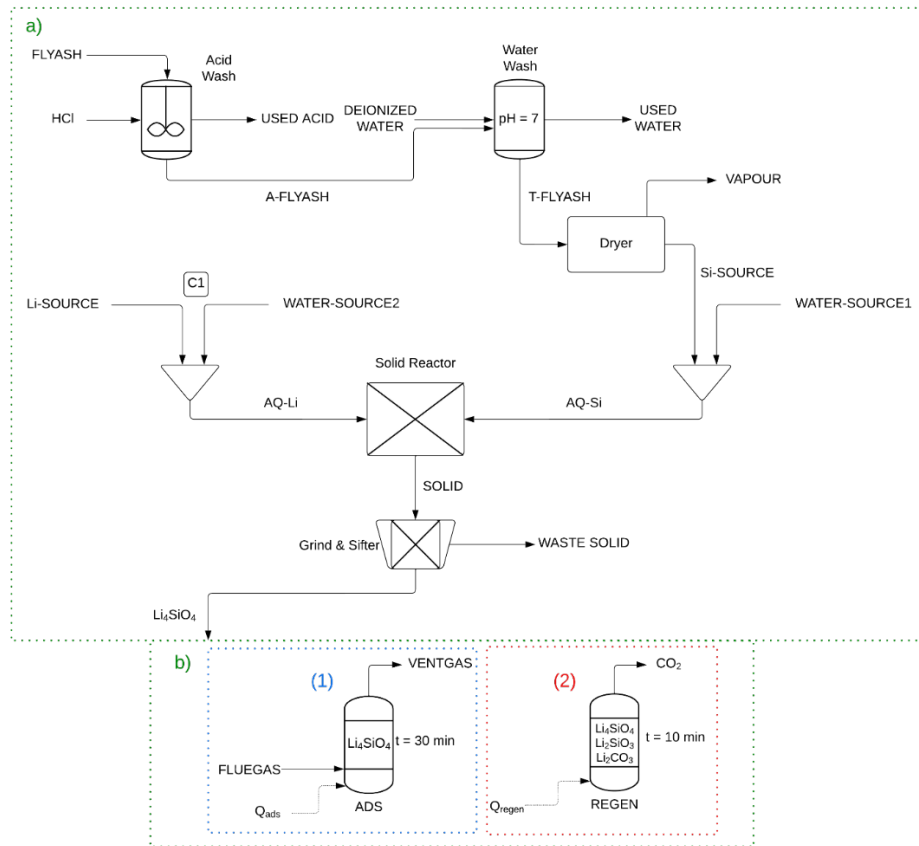


Figure 10. Process Flow Diagram of the biomass-based capture process in which Li_4SiO_4 is used to capture CO_2 : a) pre-treatment of Si-sourced fly-ash; b) CO_2 capture process.

Since the model is a continuous approximation of the semi-batch process, an additional flowsheet is presented in Figure 11 to show the simulation setup. Note that the pre-treatment presented in Figure 10 is consistent with the modelled pre-treatment; hence, this section was not included in Figure 11. The model is split into two main sections which is further separated into subsections: Figure 10 (a) pre-treatment section and the Figure 11 capture section. The capture section is then further split into the (1) adsorption and (2) regeneration subsections where the CO_2 capture and adsorbent regeneration takes place, respectively.

In Figure 11, the adsorption subsection has 2 main blocks, the stream split unit (ADS) and reactor unit (ADSRXN), which is complimented by a calculator (C2) to incorporate the reaction kinetics described by [85]. A similar set up is followed in the regeneration section, with the reactor unit (REGENRXN) being executed prior to the stream split (REGEN). The stream split units mimic the gas removal/venting post adsorption and regeneration, while the reactors integrate the reaction process and associated heat duty. For more details on the block types chosen for each unit outlined in Figure 11, please see the appendix C section C2. The reason for incorporating calculator blocks in this model is because of the unique reaction kinetics this system experiences; the Aspen Plus data base does not include the type of reaction kinetics experience by this reaction. The calculator block in the adsorption section implements equations 24 through 29 with the overall purpose of recalculating the mass balance of the system while including this system's kinetic equations. More detail about these blocks is discussed in section 4.1.1.

The goal in this work is to simulate the adsorption of CO_2 onto Li_4SiO_4 from flue gas and the regeneration of the sorbent, modeling the entire pre-treatment and CO_2 capture process. The model developed to achieve this goal can thus be used to gain insight on the systems performance under different operating conditions, which is vital for developing and scaling up this process. Note that for the purpose of this study and with the aim to simplify the analysis, the physical nature of this process is semi-batch but has been modelled as a continuous process. The assumptions made for this model are as follows:

1. The semi-batch process is approximated by the continuous system where time is manually incorporated into calculator blocks C2 and C3. This is explained in further detail in section 4.1.1.

2. Thermodynamic properties throughout the process behave as decided by the chosen property package unless otherwise stated.
3. Reactions are assumed to reach completion within the experimentally determined time frame (30 minutes for adsorption, 10 minutes for regeneration) [85].
4. The adsorption capacity of the solid is assumed to remain the same until a predetermined number of 36 cycles is reached, after which the sorbent must be replaced [126].
5. The scale of this model is that of a pilot scale plant, with the assumption that flue gas flow corresponds to a 0.15 MW coal fired power plant. This assumption was made based off comparison to similarly scaled pilot scale systems [127][128][1].

Figure 11. PFD of the modelled system as produced in ASPEN Plus. 1) adsorption process; 2) regeneration section.

To simulate this adsorption process, adjustments were made to the default modelling parameters. This includes the calculator blocks C2 and C3 in Figure 11 in the adsorption and regeneration sections of the model and a $k_r(T)$ function which was introduced to the regeneration section. Both calculator blocks utilize Aspen's Excel tab function to incorporate a detailed mass balance adjustment. Since this type of solid-gas reaction is not included in the

Aspen database, the calculator blocks are necessary to estimate the kinetics of the reaction, and final mass of solid and CO₂ present in the system. As described in section 4.1, the reaction that takes place when the adsorbent is exposed to CO₂ creates a new solid which forms an outer layer on each adsorbent pellet. In the literature, the kinetic model that this reaction is assumed to follow is referred to as the Jander-Zhang model [77][126], i.e.,

$$\hat{k}t = (1 - (1 - Z\alpha)^{1/3})^3 \quad (24)$$

where $\hat{k}$ (s⁻¹) represents the reaction rate constant, t (s) is the time the reaction takes place for, Z is the proportion of carbonates in the product layer which for Li₄SiO₄ reacting with CO₂ is equal to 0.5, and α (%) is the adsorbent conversion rate, which can be estimated as follows:

$$\alpha = \frac{m_2 - m_1}{m_1 m_0} \times 100\% \quad (25)$$

where m_1 (g) represents the initial mass of adsorbent, m_2 (g) represents the final mass of solid in the system after the total reaction time has elapsed (i.e., 30 minutes), and m_0 is the theoretical adsorption capacity of the adsorbent. Combining equations 3 and 4 yields the following expression, which was utilized in calculator block C2:

$$m_2 = m_1 \left(1 + m_0 \left[\frac{1 - (1 - (\hat{k}t)^{1/3})^3}{Z} \right] \right) \quad (26)$$

when examining this equation in the context of Li₄SiO₄ – CO₂ adsorption, m_2 represents the new solid adsorbent weight, which is comprised of Li₂SiO₃ and Li₂CO₃. Utilizing the stoichiometric ratios, it is assumed that m_2 is made of equal molar parts Li₂SiO₃ and Li₂CO₃. The mass of each component present post adsorption can be computed as follows:

$$m_{Li_2SiO_3} = \frac{m_2}{1 + \frac{M_{Li_2CO_3}}{M_{Li_2SiO_3}}}; \quad m_{Li_2CO_3} = m_{Li_2SiO_3} \left(\frac{M_{Li_2CO_3}}{M_{Li_2SiO_3}} \right) \quad (27)$$

where $M_{Li_2CO_3}$ and $M_{Li_2SiO_3}$ are the molar mass of Li_2CO_3 and Li_2SiO_3 , respectively. To complete the mass balance for the remaining compounds in the system (CO_2 and Li_4SiO_4), equation 28 and 29 are incorporated, i.e.,

$$m_{CO_2} = (\xi + \eta_{i,CO_2})M_{CO_2} \quad (28)$$

$$m_{Li_4SiO_4} = (\xi + \eta_{i,Li_4SiO_4})M_{Li_4SiO_4} \quad (29)$$

where ξ represents the extent of reaction which is dependent on if there is excess adsorbent or excess flue gas, η_{i,CO_2} and η_{i,Li_4SiO_4} represent the initial moles of CO_2 and Li_4SiO_4 in the feed, whereas M_{CO_2} and $M_{Li_4SiO_4}$ represent the molar mass of CO_2 and Li_4SiO_4 , respectively.

The reaction in the regeneration section is presented in equation 23. The kinetic model for the regeneration section of the process is displayed in equation 30, which can be reformulated as shown in equation 31.

$$\alpha_{des} = -\hat{k}_r t \quad (30)$$

$$(m_{i,Li_2SiO_3} + m_{i,Li_2CO_3})(1 + \hat{k}_r t) = m_{t,Li_4SiO_4} \quad (31)$$

From the above equations, α_{des} is the desorption conversion rate, $\hat{k}_r$ (s^{-1}) is the kinetic constant of the desorption/regeneration reaction, t (s) is the time of the reaction, m_{i,Li_2SiO_3} (g) and m_{i,Li_2CO_3} (g) are the mass of Li_2SiO_3 and Li_2CO_3 at the beginning of the reaction, and m_{t,Li_4SiO_4} (g) is the mass of Li_4SiO_4 at time t . The kinetic constant ($\hat{k}_r$) was obtained through a linear regression of the experimental data reported in Yang et al. [85]. Each temperature that regeneration takes place at, has a corresponding $\hat{k}_r$ value, which in the case of Yang et al. was performed at 750 °C; meaning that if the regeneration temperature were to be changed, the $\hat{k}_r$ value would need to manually be changed in the C3 calculator block. However, the data collected in Yang et al. does not include regeneration kinetic constants at multiple temperatures.

To accommodate for the possibility of regeneration temperatures to be adjusted, a temperature dependant regeneration kinetic constant function $\hat{k}_r(T)$ was developed.

The $\hat{k}_r(T)$ function was introduced into the regeneration calculator block C3 (Figure 11) and was incorporated so that when changing the temperature of the regeneration block, the reaction kinetics ($\hat{k}_r$) would adjust accordingly. As the experiments done in Yang et al. only covered regeneration at a temperature of 750 °C, additional data was used and adjusted to fit the conditions of the previously described fly-ash and experiment [87]. This model was found through regression and data fitting and can be seen in equation (32). More details on the experimental process, fly-ash conditions, and the fitting of this model can be found in appendix C section C1.

$$\hat{k}_r(T) = \delta(4.192 \times 10^{-8}T^2 - 5.512 \times 10^{-5}T + 0.0183187) \quad (32)$$

After these changes were made the model was overshooting the amount of desorption, so an additional condition was added into the calculator block C3. The maximum desorption found from Yang et al. was 93.26%; hence, the model was simulated at conditions that will not surpass this limit. Moreover, the calculator block C3 was implemented to consider this condition. Details on the ASPEN Plus variable implementation for the C2 and C3 blocks can be found in appendix C (section C2) Tables C2.2 and C2.3.

4.2. Results

4.2.1. Model Validation

To validate the rigorous Aspen Plus model presented in the previous section, the experimental results reported by Yang et al. [85] were used as a reference. The three main metrics used for evaluating the validity of the model were the mass of solid present post adsorption (m_2), adsorption capacity of the sorbent ($C_{Li_4SiO_4-CO_2}$), and the mass of solid present

post regeneration ($m_{Li_4SiO_4,RR}$). The experimental procedure described in Yang et al. states that the pellets are weighed, exposed to 15% CO₂ gas for 30 minutes, and then weighed again to record the weight gain to determine how much CO₂ has been adsorbed [85]. This procedure takes place at two different temperatures to obtain two different k values (defined in equation 24). The $\hat{k}$ values reported in Yang et al. were used as the reaction kinetics introduced into this model, the value for which can be found in appendix C section C2 Table C2.4, along with the remaining design parameters.

Figure 12 outlines experimental results found at each temperature and the corresponding metrics, compared to the simulation results found when running the model described in section 4.1. Due to the process being semi-batch and the capabilities of the ASPEN Plus model, the process is modelled as a continuous system at steady state. The time t (i.e., time introduced in equation 24) was set as 30 minutes to emulate the completion of the reaction and thus returning the steady state value. To confirm that the kinetics reflect the experimental work, the model was run starting at $t = 0$ followed by 5-minute intervals until reaching 30. After running the model, the mass of solid post adsorption and post regeneration, was found by checking the results from Stream: RICH 2 and RICH 3 (Figure 11), respectively. In Figure 12 the modelled results are shown as square points, while the experimental results are displayed as the solid curve which were taken from Yang et al [85]. The validation was performed for 600 °C and 650 °C, and $\hat{k}$ values both with and without pre-treatment. Experimental work has found that at temperatures of 700 °C and above, the forward and backwards reaction may take place (i.e., equations 21 and 22). For this reason, the model was not tested at 700 °C as it does not incorporate the dual reaction mechanisms or kinetics. A similar procedure was followed to validate the model during regeneration. Weight change measurements were taken in 10 second intervals from the

RECYCLE stream (Figure 11) at 750 °C for the first 2 minutes, after which measurements were taken every 1 minute until reaching 10. Figure 13 compares the data found in Yang et al. to the model executed during regeneration.

From the results presented in Figure 12 the model fits the experimental data. Although the model deviates slightly from the experimental data it is not significant enough to cause concern as the variation is likely noise due to experimental sources of error. The trend of the data and model agree, all points being within $\pm 3\%$. From this analysis, it was determined that the model is able to predict the extent of adsorption and properly preforms the necessary kinetic changes to the mass balance. The regeneration overall shows agreement with the experimental results as displayed in Figure 13. As previously stated, the linear trend in the data was fit to the first 120 seconds of the model, after which the maximum regeneration was assumed as this was the most linear timeframe during regeneration. The largest discrepancy between model and experimental results is at 2 minutes being 14.7% lower than experimental, but this quickly decreases to 7.89% below at 3 minutes. Most importantly, the steady state value of 93.26% regeneration is observed from this model at 10 minutes.

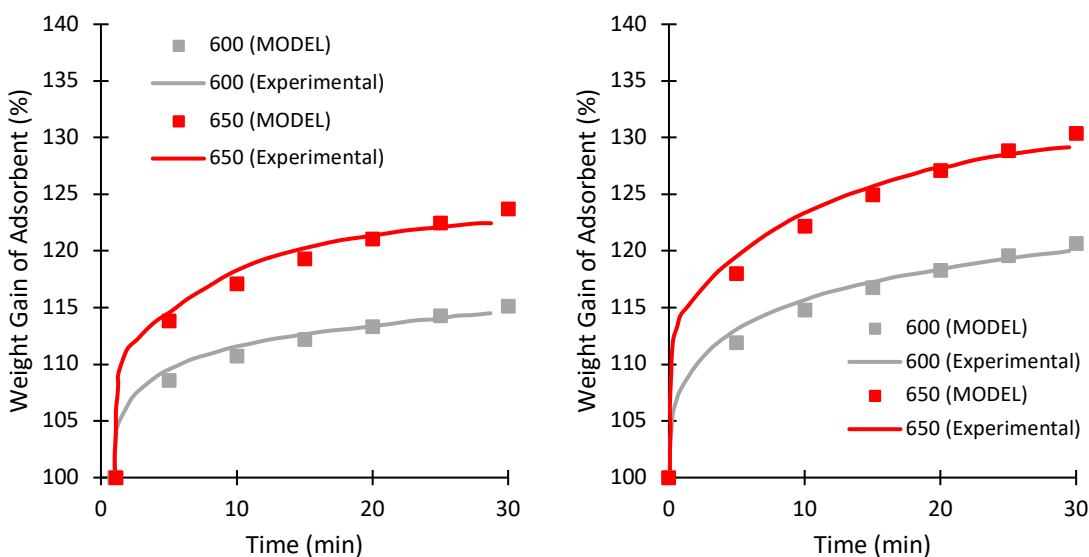


Figure 12. Comparison of experimental results from Yang et. al [85] to model interval and steady state results where (left) is the adsorbent that has not be pre-treated and (right) is the adsorbent that was put through pre-treatment. The grey is for 600 °C, red is for 650 °C, squares represent the corresponding model value at each time interval, while the last point represents the steady state value (30 minutes).

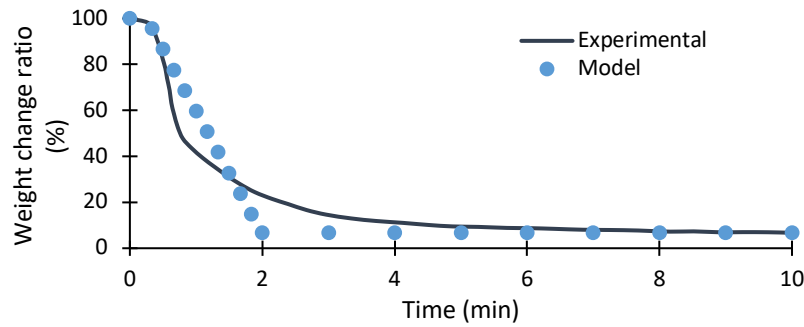


Figure 13. Comparison of experimental results from Yang et al. to model interval results which are used for both pre-treated and non-pre-treated fly-ash. The experimental results are shown by the solid grey line while the experimental results are the blue circles.

4.2.2. Results & Discussion

4.2.2.1. Benchmark Scenario

To determine a benchmark scenario and performance for this model, it was simulated at conditions which were scaled up from Yang et al. to emulate a pilot-scale sized plant. These conditions will further be referred to as the nominal conditions indicated in Table 12. Note that the mass of adsorbent to flue gas ratio was initially 10 mg to 100 mL and has been scaled up to 100 g of adsorbent [85][129]. The pre-treatment and CO₂ capture process were incorporated into the same flowsheet and modelled together by using a transfer block T1; however, these two processes can be readily decoupled and executed independent of one another under the assumption that enough adsorbent is being supplied by the pre-treatment process. The results from this process model under continuous or decoupled operation are unchanged for a single CO₂ capture cycle as it was performed in this work. Note that 24 hours of continuous operation

of the post-combustion CO₂ capture plant would be equivalent to 36 adsorbent and regeneration cycles. During this cycle, approximately 93% of the adsorbent is regenerated each time, meaning additional adsorbent is required to replenish the capture process. To account for this, additional and similar pre-treatment processes may be installed and run in parallel to supply the make-up adsorbent in the post-combustion system. Nevertheless, batch and process scheduling is required for a fully continuous operation of this system over multiple cycles. This aspect is outside of the scope of this work. Additionally, previous experimental studies have indicated that the best temperature for Li₄SiO₄ regeneration is near 750 °C [85][87]. Above this temperature the possibility for lithium degradation increases significantly, and below this value the kinetics of the reaction perform more slowly. From these findings, the nominal temperature of regeneration is set to 750 °C. This benchmark also includes an energy and cost analysis, which is compared against two amine-based PCC systems to evaluate system performance. This analysis helps gauge the efficiency and applicability of the biomass-based system both with and without pre-treatment. The biomass-based Li₄SiO₄ adsorbent capture process without pre-treatment and with pre-treatment will be referred to herein as BCCS and BCCS – P, respectively. The main metrics that were monitored to evaluate the efficiency of the model are the percent of CO₂ captured (%CO₂), the percent of adsorbent remaining after adsorption (%Li₄SiO₄RA), the percent of adsorbent recovered post regeneration (%Li₄SiO₄RR), and the overall energy requirement of the process (Q_T). The equation for calculating the percent of CO₂ captured is as follows:

$$\%CO_2 = \frac{m_{CO_2,CO_2} - m_{CO_2,RICH1}}{m_{CO_2,FLUEGAS}} \times 100\% \quad (33)$$

where m_{CO_2,CO_2} represents the mass of CO₂ present in the pure CO₂ stream (Figures 10 and 11), $m_{CO_2,RICH1}$ is the mass of CO₂ present in the RICH1 stream which would be any excess CO₂ that was not captured by the adsorbent, and $m_{CO_2,FLUEGAS}$ is the mass of CO₂ initially present in the

FLUEGAS stream presented in Figure 11. As shown in Eq (33), the excess CO₂ that is not captured by the adsorbent is subtracted. This is because in the physical system, this CO₂ would be vented with the remaining components of the flue gas after the initial 30-minute adsorption period. However, because the system is approximated as a continuous process, the excess CO₂ needs to be accounted for at the end of the process (30 minutes) when calculating %CO₂. The percentage of adsorbent (Li₄SiO₄) remaining post adsorption and the percentage of adsorbent regenerated post regeneration are defined as follows:

$$\%Li_4SiO_4RA = \frac{m_{Li_4SiO_4,RICH1}}{m_{Li_4SiO_4,ADSORBENT}} \times 100\% \quad (34)$$

$$\%Li_4SiO_4RR = \frac{m_{Li_4SiO_4,RECYCLE}}{m_{Li_4SiO_4,ADSORBENT}} \times 100\% \quad (35)$$

where $m_{Li_4SiO_4,RICH1}$, $m_{Li_4SiO_4,ADSORBENT}$, and $m_{Li_4SiO_4,RECYCLE}$ represents the mass of Li₄SiO₄ in streams RICH1 (after the adsorption process), ADSORBENT (before the adsorption process/present in the adsorber), and RECYCLE (post regeneration before being returned to the adsorber) streams as defined in Figure 11, respectively. These metrics aid in understanding the efficiency of both the adsorber and the regeneration. The total energy required by a process on a kilogram of CO₂ capture basis (Q_T) is defined as follows:

$$Q_T = \frac{\sum_i Q_i}{m_{CO_2,captured}} \quad (36)$$

where Q_i represents the energy requirements of different process units i . Note that $i = \{DRYER, GRIND\&SIFT, HEATY DUTY, COOLING DUTY, ELECTRIC\}$ stands for each unit considered in the process. The energy requirements (i subsets) of each capture process can be found in appendix C section C3. This was defined on a mass of CO₂ captured basis to more accurately compare the processes. Note that the energy requirements reported in the proceeding case studies described in sections 4.2.2.2 through 4.2.2.4 are for specific batches and are reported

in kW . This is different than the Q_T metric in $\frac{MJ}{kg \text{ of } CO_2 \text{ captured}}$ reported in this section of the study.

As previously mentioned, the adsorption reaction of this process is an exothermic reaction and requires cooling; however, there is a heat duty associated with the regeneration to maintain the system at 750 °C. This combination allows for the possibility to utilize the released heat from the exothermic reaction and using the energy towards the regeneration heating requirement. The incorporation of heat integration is outside of the scope of this work; nevertheless, an additional metric was included to determine if the addition of heat integration would significantly impact the energy consumption of the system. To simplify the analysis, it was assumed that all the energy needed to maintain a temperature at 650 °C during adsorption (cooling duty) could be used towards the heating requirement during regeneration. Thus, an updated energy requirement for the process on a kilogram of CO_2 capture basis (ΔQ_T) can be defined as follows:

$$\Delta Q_T = \frac{Q_{regeneration} - Q_{adsorption}}{m_{CO_2, captured}} \quad (37)$$

where $Q_{regeneration}$ represents the heat duty required during regeneration (REGENRXN unit in Figure 11) whereas $Q_{adsorption}$ is the cooling duty required during adsorption (ADSRXN in Figure 11) which is assumed to be equivalent to the exothermic energy produced by the adsorption. Results from these benchmark scenarios can be found in Table 13.

Table 12. Variable definitions and nominal values for model parameters.

Variable Name	Variable	BCCS	BCCS – P
Adsorption Temperature [°C]	T_{ADS}	650	650
Fly-ash flow rate [mol/s]	F_{FA}	1.306	1.278
Adsorbent flow rate [g/s]	F_{ads}	100	97.798

Flue gas flow rate [L/s]	F_{CO_2}	410	410
CO ₂ composition in flue gas [mol. %]	x_{CO_2}	0.15	0.15
Adsorbent mass to flue gas flow ratio $[\frac{L \text{ of flue gas}}{g \text{ of } Li_4SiO_4}]$	R'	4.1	4.19
Regeneration temperature [°C]	T_{REGEN}	750	750
System operating pressure [bar]	$P_{capture}$	1.01	1.01

Table 13. Resulting metrics found when the model was run at nominal values.

Metric	BCCS	BCCS – P
%CO ₂ [%]	87.00	89.66
%Li ₄ SiO ₄ RA [%]	9.51	4.65
%Li ₄ SiO ₄ RR [%]	93.87	93.54
$Q_T [\frac{MJ}{kg \text{ of } CO_2 \text{ captured}}]$	25.26	20.17
$\Delta Q_T [\frac{MJ}{kg \text{ of } CO_2 \text{ captured}}]$	1.522	4.745

To gain insights on how this process compares to the current state of the art, an energy analysis was performed to compare two similarly sized MEA-based pilot scale plants against the BCCS and BCCS – P processes. A full breakdown of this comparison can be found in Tables C3.1 and C3.2 in appendix C, including each plants operating temperatures, pressures, flowrates, and capture rates. This was compared against two MEA PCC systems both being pilot scale of similar but not identical design, denotes as MEA1 and MEA2, with MEA2 having a larger process flow capacity to ensure there is a variation and range for the benchmark comparisons.

The Q_T values from the amine-based PCC systems are found to be $10.163 \frac{MJ}{kg \text{ CO}_2 \text{ captured}}$

(MEA1) [127] and $19.9 \frac{MJ}{kg \text{ CO}_2 \text{ captured}}$ (MEA2) [128] while BCCS and BCCS – P require

25.264 $\frac{MJ}{kg\ CO_2\ captured}$ (MEA1) and 20.170 $\frac{MJ}{kg\ CO_2\ captured}$ (MEA2), respectively. This analysis shows that both the BCCS and BCCS – P systems have a higher total energy consumption than the two amine-based PCC plants. However, when comparing the MEA PCC systems energy requirements to the BCCS and BCCS – P systems energy requirement when considering heat integration (ΔQ_T), the proposed systems can reduce energy consumption by 85% (MEA1) and 92% (MEA2) for BCCS while BCCS – P reduces energy by 53% (MEA1) and 76% (MEA2), respectively. The results of this analysis show that with further incorporation of heat integration this process (BCCS and BCCS – P) has the potential to significantly improve the energy requirements of CO₂ capture when compared to standard MEA PCC pilot-scale plants. To make a fair comparison, the energy consumption of the solvent/sorbent synthesis was not included in the energy analysis discussed above. This is because the MEA for the amine-based PCC processes was purchased, and its synthesis was not incorporated into the pilot plant systems; hence, including the energy consumption of Li₄SiO₄ synthesis would have resulted in an unfair comparison.

Like amine-based PCC, the majority of the energy required for BCCS and BCCS – P occurs during regeneration. However, as this system is proposed for high temperature CO₂ capture (as defined in Yang et al.'s experimental work) the heat duty, which comes from introducing a fired heat utility (e.g., furnace), requires a maximum temperature increase of 100 °C. The amount of cooling required by the BCCS – P system is lower than that of the MEA-PCC process but not for BCCS. As previously mentioned, the adsorption process is an exothermic reaction so the adsorption unit in the BCCS and BCCS – P processes require cooling to be maintained at 650 °C. This is the main reason BCCS has a higher energy requirement during adsorption than MEA PCC. Results showing this comparison can be found in appendix C

(Table C3.2). The reason BCCS – P requires less energy during adsorption is due to the increased efficiency of the adsorbent resulting from the pre-treatment process. With the adsorbent able to capture more CO₂ in a shorter amount of time, the cooling duty on a kilogram of CO₂ basis is for pre-treated adsorbent is lower than for adsorbent which has not been pre-treated (BCCS). While MEA feed must be maintained at roughly 40 °C and must be cooled post regeneration and being recycled into the absorber, the only cooling required in the BCCS and BCCS – P systems is to maintain isothermal conditions during adsorption; meaning the recycled adsorbent does not need to undergo as intensive of a cooling process. The percentage of CO₂ captured is similar for each process, all within 10% of one another. The MEA PCC processes ranging from 85% [128] to 95% [127] and the BCCS and BCCS – P process benchmark is 87% and 89.6%, respectively.

To gain further insights on the behaviour of this system, five scenarios were investigated and compared to the benchmark analysis, i.e., (1) a variation in the initial mass and flue gas CO₂ composition, (2) a sensitivity analysis of flue gas flow to mass of adsorbent (R'), (3) a sensitivity analysis on heat of regeneration, (4) a sensitivity on initial mass of adsorbent, and (5) a sensitivity on CO₂ composition in the flue gas. For the sake of brevity, the first three cases (1-3) are discussed next, while results from the remaining two cases (4 and 5) can be found in Figures C4.3-C4.10 in appendix C.

4.2.2.2. Variation on adsorbent mass and composition of CO₂ in flue gas

Since the CO₂ capture rate and conversion of Li₄SiO₄ after adsorption and regeneration are dependent on both the initial mass of adsorbent and the flue gas' CO₂ composition, a case study was conducted on the effects of changing both parameters. The mass was varied $\pm 20\%$ of the nominal value with a step size of 5% whereas the composition was varied between 0.08 – 0.20

mol.% (-47% to $+33\%$ of the nominal value $0.15 \text{ mol. \%}$) in steps of $0.02 (\pm 13\%)$, as this is the most common CO_2 composition range for power plant flue gas emissions. For the BCCS – P process, the mass of fly-ash fed to the pre-treatment process was varied which resulted in the change of adsorbent mass. These variations were done as previously stated, to ensure that the mass of adsorbent was within $\pm 20\%$ of the nominal value. While the benchmark remains at 87.00% and $89.66\% \text{ \%CO}_2$ for BCCS and BCCS – P, in both Figure 14 and Figure 15 it is clear that increasing the composition of CO_2 in flue gas and decreasing the initial mass of adsorbent both decreases the amount of CO_2 captured. Therefore, for the BCCS process, to achieve the highest capture of CO_2 , if there is 120 g of adsorbent available, a flue gas composition no higher than $15 \text{ mol. \%}$ of CO_2 should be used for this pilot scale model. Note that if there is less adsorbent available (e.g., 80 g), then a lower CO_2 composition flue gas should be sourced for adequate CO_2 capture rates as shown in Figure 14 and 15. For flue gas streams with higher levels of CO_2 , it would be recommended that a larger amount of adsorbent be initially introduced into the system otherwise there will be excess flue gas compared to adsorbent and there will be an increase in the percentage of CO_2 vented/not captured. When comparing the BCCS (Figure 14) and BCCS – P (Figure 15) process, the trends for more effective performance are similar. The key difference between the two is that a smaller amount of adsorbent is required to capture the same amount of CO_2 (due to the higher $\hat{k}$ value, i.e., faster reaction kinetics) for the BCCS – P process. This means that the highest $\text{\%CO}_2$ can be reached with less adsorbent and a higher composition of CO_2 in the flue gas stream, making it more appealing if the adsorbent is limited and the flue gas contains high levels of CO_2 . Overall, increasing the mass of adsorbent and decreasing the CO_2 flue gas composition will increase the total amount of CO_2 captured. However, the system does reach a maximum $\text{\%CO}_2$ for both BCCS and BCCS – P of 93.23% ,

meaning there is 6.77% of CO_2 not captured and remaining in the form of unregenerated solids at the most effective conditions.

The results for $\% \text{Li}_4\text{SiO}_4\text{RA}$ and $\% \text{Li}_4\text{SiO}_4\text{RR}$ coincide with the results found for $\% \text{CO}_2$. As the $\% \text{CO}_2$ reaches its maximum, there become excess adsorbent present in the system. In turn, the $\% \text{Li}_4\text{SiO}_4\text{RA}$ and $\% \text{Li}_4\text{SiO}_4\text{RR}$ both increase as the initial mass of adsorbent increases and CO_2 composition in the flue gas decrease. The values range between 56.91% – 9.51% and 97.08% – 93.87% for $\% \text{Li}_4\text{SiO}_4\text{RA}$ and $\% \text{Li}_4\text{SiO}_4\text{RR}$, respectively. Results are displayed in appendix C (section C4) Tables C4.1-C4.4.

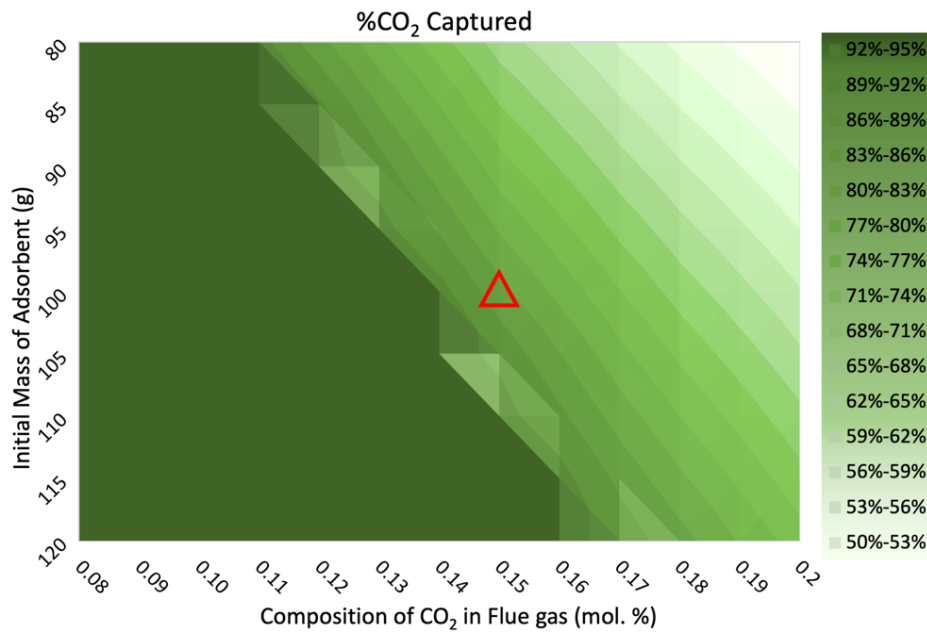


Figure 14. Results of BCCS process for the $\% \text{CO}_2$ captured when varying mass of adsorbent and flue gas CO_2 composition. Dark green represents a higher capture while the lighter green is a lower capture, and the red triangle represents the benchmark value.

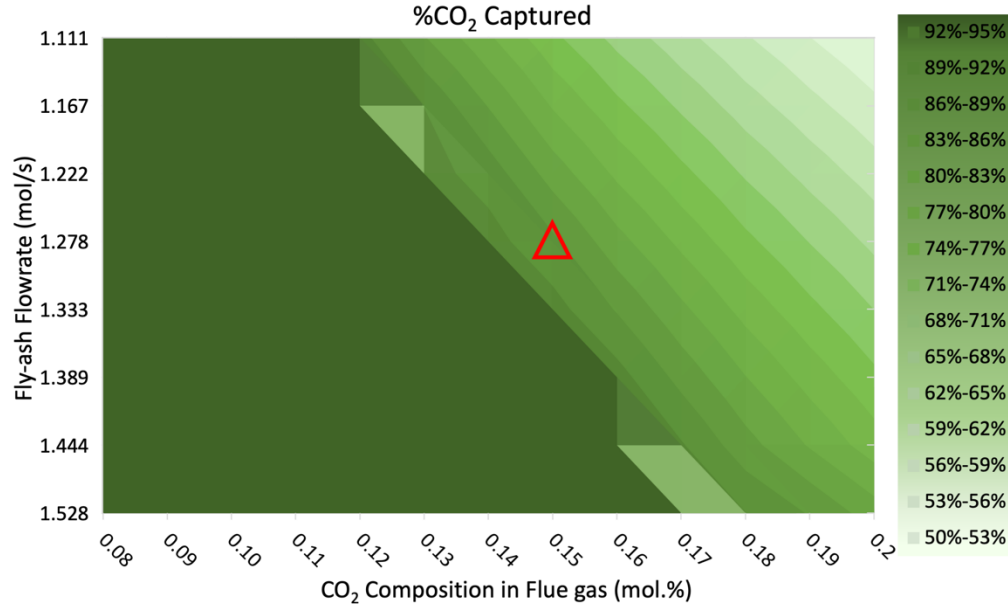


Figure 15. Results of BCCS – P process for the %CO₂ capture when varying the fly-ash flow rate (which dictates the mass of adsorbent) and flue gas CO₂ composition. Dark green represents higher capture while lighter green is a lower capture amount. The red triangle represents the benchmark.

The energy requirements in different sections of the process are discussed next. The two units that are examined for the BCCS process are the adsorption and regeneration sections, while the BCCS – P also includes the dryer. As shown in appendix C Tables C4.5 and C4.6 during adsorption and regeneration, as the mass of adsorbent and flue gas CO₂ composition are increased, the energy required in the column increases for both BCCS and BCCS – P. This is concurrent with theoretical predictions as increasing the amount of adsorbent and CO₂ present in the system would increase the mass reacting which in turn needs a higher cooling/heat duty. The largest discrepancy between the two processes lies in the cooling duty for the adsorber. The pre-treatment allows for a much more energy efficient adsorption, meaning there is between 27.2% - 65.2% less cooling required for every variation. The heat duty of the regeneration is nearly equal for both processes. Although the adsorption requires less energy for the pre-treated fly-ash, the

pre-treatment does require additional energy in the form of an electric dryer. These results can be found in Table C4.7, where the energy requirement ranges between 3.7 – 5.6 *kW*.

The main insights that can be drawn from this analysis is the trade-off between CO₂ capture efficiency and the energy required. Although the BCCS – P does require additional energy during pre-treatment and has a slightly higher heat duty during regeneration, the improvement to the adsorbents capacity for CO₂ capture reduces the energy required for adsorption up to 65% and returns a 4.7% higher %CO₂ on average.

4.2.2.3. Sensitivity analysis on the ratio of flue gas flowrate to adsorbent mass

A sensitivity analysis on the flue gas flow ratio to initial mass of adsorbent (R') was performed. This ratio is computed as follows:

$$R' = \frac{F_{CO_2}}{m_{Li_4SiO_4, ADSORBENT}} \quad (38)$$

where F_{CO_2} is the flowrate of flue gas (*L/s*) and $m_{Li_4SiO_4, ADSORBENT}$ as previously defined is the mass of adsorbent present in the system before adsorption. Therefore, as this ratio increases, the amount of CO₂ introduced into the adsorber increases, and/or the mass of Li₄SiO₄ introduced decreases.

This sensitivity analysis was done by changing the $R' \pm 20\%$ of the nominal value (i.e., 4.1) in step sizes of 5%. To understand the outcome of this analysis, the %CO₂ and associated percentage of CO₂ vented for BCCS and BCCS – P are plotted in Figure 16. Similar to the case study performed and discussed in section 4.2.2.2, it is evident that the increase in flue gas flow or a decrease in adsorbent will result in a lower %CO₂ and in turn, higher percentage of CO₂ included in the vented gas. In addition to this, the R' value which returns the highest %CO₂ for both processes are clearly identifiable in Figure 16. BCCS's best R' value is between 3.7 and 3.9

while BCCS – P's is between 3.9 and 4.1; the R' value of the pre-treated fly-ash being 5.4% higher than non-pre-treated adsorbent.

As found in the scenario presented in section 4.2.2.2, the $\%Li_4SiO_4RA$ and $\%Li_4SiO_4RR$ followed the same trends. When there was an excess of adsorbent in the system, $\%CO_2$ reached the maximum; hence, both $\%Li_4SiO_4RA$ and $\%Li_4SiO_4RR$ increased. These results can be found in Figures C4.1 and C4.2 of appendix C.

The energy requirement for the adsorber, regeneration, and dryer unit were also examined during this sensitivity analysis and these results are depicted in Figure 17. The heat and cooling duty for both processes followed the same trend as found in the previous scenario. The decrease in R' (decrease in CO_2 present/increase in adsorbent mass) requires less energy. However, once the ratio is below a level which results in the maximum $\%CO_2$, the energy requirement levels out; meaning that although excess CO_2 exists in the system which would be vented, it does not require additional heating/cooling duties. Figure 17 shows this leveling off for both BCCS and BCCS – P. Since there was no variation in the pre-treatment section for this analysis, the energy requirement for the dryer remains constant at 4.48 kW.

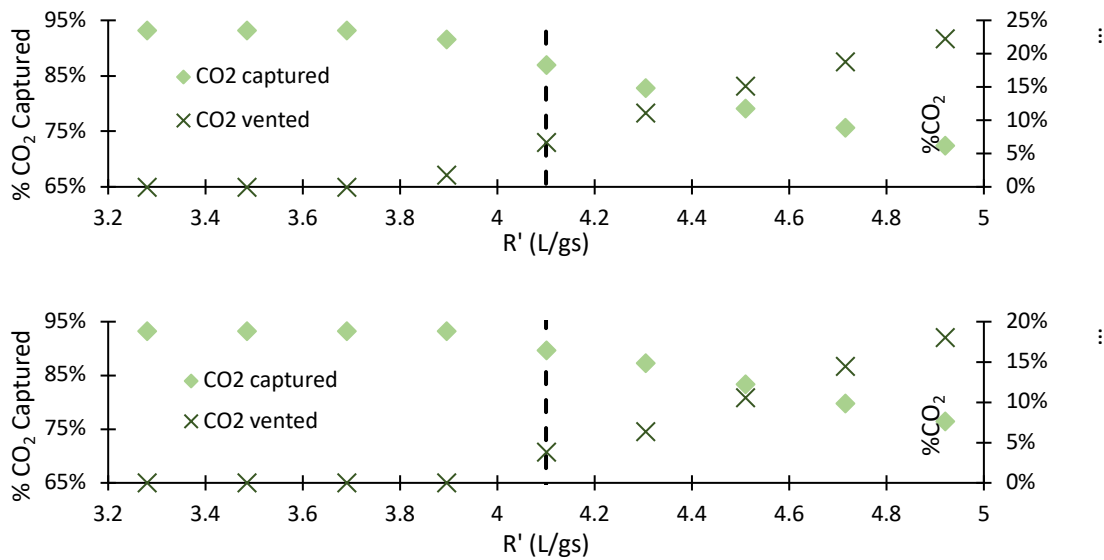


Figure 16. %CO₂ capture results from the sensitivity analysis on varying R' for (top) BCCS and (bottom) BCCS – P processes. The black dotted line represents the benchmark case.

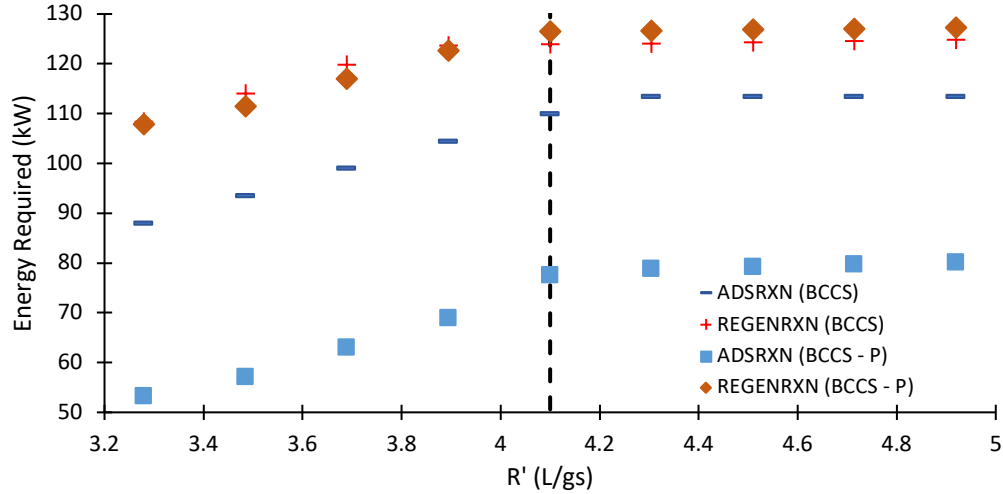


Figure 17. Heating and cooling requirements for the adsorption and regeneration units for the BCCS (crosses and horizontal dashes) and BCCS – P (diamonds and squares) processes. The red icons represent the regeneration reaction while the blue represent the adsorption. The black dashed line represents the benchmark.

4.2.2.4. Sensitivity analysis on heat of regeneration

To gain further insights on this process, a sensitivity analysis on the heat of regeneration was performed. Due to the increased probability of lithium degradation and compromising the integrity of the adsorbent at temperatures above 750 °C, the likelihood of regeneration operating temperatures being set above 750 °C is unlikely; the maximum temperature chosen for this sensitivity analysis was 755 °C to avoid this issue. The remaining values were chosen in –5°C intervals until reaching a minimum value of 700 °C. This was chosen as the minimum value because it is the minimum temperature required for the regeneration reaction to take place [85][87]. All other operating conditions were kept consistent with the nominal values presented in the benchmark scenario in section 4.2.2.1.

Figure 18 shows the %CO₂ and the %Li₄SiO₄RR for BCCS and BCCS – P from this sensitivity analysis. For both processes, the amount of CO₂ captured and Li₄SiO₄ regenerated decrease with the reduction in temperature. At the minimum required temperature, %CO₂ is 42.78% and 45.24% and %Li₄SiO₄RR is 50.99% and 48.35% for BCCS and BCCS – P, respectively. This indicates that, if regeneration is occurring, at least 50% or 48% (depending on the process) of the adsorbent will be regenerated. Experimental results concluded that the pre-treatment process has very little effect on the regeneration process, which seems to agree with the model results shown in Figure 18. Although the BCCS – P has a slightly higher %CO₂ and lower %Li₄SiO₄RR, there is not a significant difference between the values of these two processes. To achieve a minimum CO₂ capture rate of 80%, a regeneration temperature between 740 – 745 °C is needed for both processes.

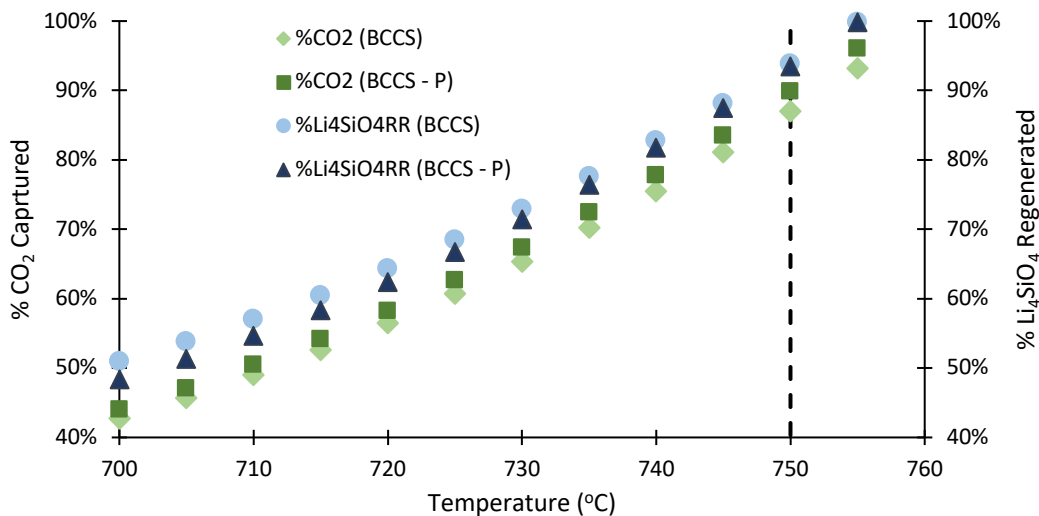


Figure 18. %CO₂ capture and %Li₄SiO₄ recovered results for the BCCS and BCCS – P processes during a sensitivity analysis on the heat of regeneration. The green diamonds and squares represent %CO₂C for BCCS and BCCS – P, while the blue circles and triangles represent the %Li₄SiO₄ for BCCS and BCCS – P, respectively. The black dashed line represents the benchmark.

When examining the energy requirements for both processes during this sensitivity analysis, the same trend was observed, i.e., increasing the regeneration temperature required a higher heating duty in the regeneration section, while the adsorption cooling duty remained constant. Although the heat duty of the BCCS – P process was slightly higher during regeneration due to the higher amount of adsorbed CO₂, the cooling duty of the adsorption was significantly lower than the BCCS process; similar to the energy requirement trends seen in section 4.2.2.3. This energy analysis is depicted in Figure 19. As in the previous scenario, since no changes were made to the pre-treatment section, the duty of the dryer remained constant at 4.48 kW. Process conditions and requirements will likely determine the temperature range, and in turn, the energy requirement of the system. If the minimum amount of CO₂ captured is required to be 80% or above, this would result in a T_{REGEN} between 740 – 745 °C which means the heat duty of the regeneration would lie between 121.8 – 122.9 kW or 124.4 – 125.5 kW for BCCS and BCCS – P, respectively. When compared to the regeneration energy requirement of standard MEA processes, both BCCS and BCCS – P display on average a 20% higher heat duty thus making the latter processes less energy efficient. This further drives the motivation for considering heat integration for these processes.

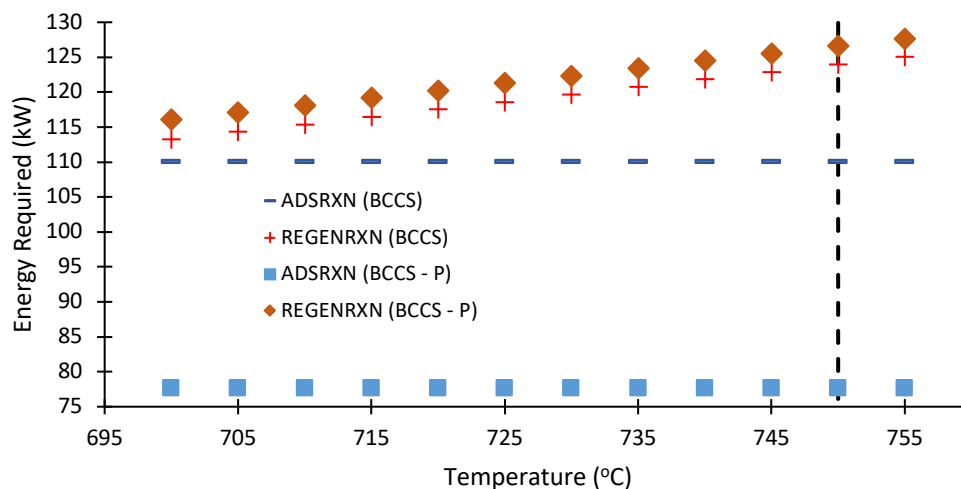


Figure 19. Energy requirements of the adsorption and regeneration sections of the BCCS (crosses and horizontal dashes) and BCCS – P (diamonds and squares) process when executing a sensitivity analysis on the heat of regeneration. The red icons represent the regeneration reaction while the blue represent the adsorption. The black dashed line represents the benchmark.

4.2.3. Water Consumption, Acid Consumption, & Cost Analysis

One major factor that impacts the feasibility of this process is the use of water. During pre-treatment, there is an acid-wash and a water-wash step. These are the Acid Wash and the Water Wash units depicted in Figure 10. The conditions for acid washing are for the fly-ash to be immersed in 0.5 M hydrochloric acid (HCl) at a 40:1 liquid to solid ratio, and continuously stirred for 24 h. The solid is then removed and repeatedly washed with deionized (DI) water until the pH reaches seven as the specified stop condition in Yang et al [85]. While for a lab scale process this is not a major factor, when increased to a pilot scale implementation the amount of water required becomes significant. As this is a batch process, 1.5×10^7 L of DI water is required for each pre-treatment batch. As described previously, the calculator blocks require a manual input of time which is on a per second basis. In the pre-treatment section, all flowrates must also be on a per second basis. However, the acid wash and water wash processes are also both batch processes; hence, the assumption that the semi-batch process is continuous, requires each second of the pre-treatment to be equal to one batch. A more detailed explanation on how water consumption was determined can be found in section C5 of appendix C. In the semi-batch process, the washer washing step varies slightly from the modelled unit. The solid fly-ash is completely submerged in the DI water and stirred to enhance exposure, and then drained. This process is repeated until the pH reaches an acceptable level (7 ± 0.2) [85]. However, when modelled, the solid is continuously rinsed with water until the outlet stream's pH reached hydrogen ion concentrations of 1.0×10^{-7} (pH = 7) or below. Since this process is not

continuous, it can be assumed that this value is higher than the true water requirement for the process. Using 1.5×10^7 L of fresh DI water for every batch of pre-treatment is not sustainable while considering implementing this process. To address this, a treatment process and recycle for the USED WATER stream depicted in Figure 10 is being considered and integrated.

Table 14 shows a simple breakdown of the cost of a standard MEA capture process (Nittaya et al. [127]), compared to both the BCCS and BCCS – P processes including BCCS – P under alternative operating conditions. The only costs that are considered were purchasing cost of raw materials and energy costs; capital costs were not considered. This results in a lower cost of CO₂ capture for the MEA PCC than typically found in literature. To compare the processes, the total cost is calculated based on the resource (material or energy) requirement for 24 hours of operation. The price of the DI water assumes that the water will be treated on site using deionization filtering system [130]. Prices are reported in Canadian dollars (\$CAD) from literary sources such as government or industry sites. More details on exact calculations performed can be found in section C6 of appendix C.

As previously mentioned in section 4.2.2.1, the energy analysis of this process did not include the energy requirements of the solvent and sorbent synthesis. However, the present cost analysis considers a cost to purchasing MEA. To make a fair comparison, a cost to Li₄SiO₄ synthesis was also considered in the present cost analysis for both BCCS and BCCS - P. This cost was assigned based on the operational (energy) costs associated with running the synthesis reactor. Details on how this value was determined can be found in section C6 of appendix C.

From the analysis depicted in Table 14, the most economically suitable process is BCCS. Due to the adsorbent source for silicon being a waste product and only raw material cost being the lithium contribution, the price associated with this process is significantly lower than the

others. Although the BCCS – P performs more efficiently than BCCS in terms of capture and energy consumption, because of the high levels of HCl and DI water needed, it is 1 order of magnitude more expensive than the MEA PCC process, and 2 orders of magnitude more expensive than the BCCS process. The largest contribution to the cost of BCCS – P is from the necessary water and acid consumption.

To obtain a better understanding of the acid washing and water washing impact on process cost, two alterations were made in the pre-treatment process (BCCS – P): 1) variation on the acid to solid ratio and 2) incorporating a used water recycle stream. The cost of HCl accounts for nearly 85% of the BCCS – P process, hence the need for testing its impact on the process economics and operation. Additionally, the DI water consumption of this process is high and represents the second highest contributor to cost. Since there have not been reported experimental studies done using different acid to fly-ash ratios for industrial fly-ash derived Li_4SiO_4 , the impact on the reaction kinetics cannot be modelled. Hence, this cost analysis assumes that reaction kinetics are valid within 25% of the acid to solid ratio.

The acid to solid ratio was decreased from 40:1 by 12.5% (35:1) and 25% (30:1), and the percentage of water recycled was varied from 20% to 80% in 20% step increments, as well as at 90%. It was assumed that although treating the used water would add an additional cost, the profit that would be made from the metal and compound extraction during treatment may balance this cost [93][90]. Therefore, the overall recycle cost was assumed to be 0 and no profit will be made. The results of this analysis are shown in columns under the “Recycled Water” and “Acid: Fly-ash” labels of Table 14. By recycling 90% of the water used in the water washing process, the consumption of fresh DI water is reduced by an order of magnitude from the BCCS – P process ($1.5 \times 10^6 \text{ L}$ vs. $1.5 \times 10^7 \text{ L}$) which significantly impacts the overall sustainability

of this process. Additionally, reducing the acid to fly-ash ratio from 40:1 to 35:1 decreases acid consumption by over 350L of HCl which reduces the need for a corrosive and acutely toxic material, following one of the 12 Principles of Green Chemistry [88].

Table 14. Cost analysis performed on the benchmark results.

Resource	PRICE		MATERIAL AND ENERGY SPECIFICATIONS				BCCS-P: RECYCLED WATER					BCCS-P: ACID: FLY-ASH	
	UNITS	Value	UNITS	PCC	BCCS	BCCS - P	20%	40%	60%	80%	90%	35:1	30:1
MEA	$\frac{\$}{kg}$	1.95	kg	17362.35									
Synthesis	$\frac{\$}{kg\ FA}$	500	kg FA		3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
Li source	$\frac{\$}{kg}$	20	kg		4.892	4.558	4.558	4.558	4.558	4.558	4.558	4.558	4.558
HCl	$\frac{\$}{L}$	50	L			4000	4000	4000	4000	4000	4000	3500	3000
DI water (fresh)	$\frac{\$}{kg}$	0.00177	kg			1.50E+07	1.20E+07	9.00E+06	6.00E+06	3.00E+06	1.50E+06	1.50E+07	1.50E+07
DI water (recycled)	$\frac{\$}{kg}$		kg				3.00E+06	6.00E+06	9.00E+06	1.20E+07	1.35E+07		
Steam heat	$\frac{\$}{kWh}$	0.19	kW	3686.4									
Fired Heat	$\frac{\$}{kWh}$	0.323	kW		4461.768	4433.76	4433.76	4433.76	4433.76	4433.76	4433.76	4433.76	4433.76
Cooling water	$\frac{\$}{kWh}$	0.00104	kW	4149.6	3959.82	2751.0228	2751.023	2751.023	2751.023	2751.023	2751.023	2751.023	2751.0228
Electric	$\frac{\$}{kWh}$	0.103	kW		5.6	9.95	9.95	9.95	9.95	9.95	9.95	9.95	9.95
Total Cost*			\$	34561.31	3343.68	229918.9	224601.9	219284.9	213967.9	208650.8	205992.3	204918.9	179918.9
CO ₂ captured*			kg	2775.792	1200.83	1284.1524	1284.152	1284.152	1284.152	1284.152	1284.152	1284.152	1284.1524
Normalized value			$\frac{\$}{kg\ CO_2/day}$	12.451	2.784	179.043	174.903	170.762	166.622	162.481	160.411	159.575	140.107
% change from BCCS - P						0.00%	-2.31%	-4.63%	-6.94%	-9.25%	-10.41%	-10.87%	-21.75%

*data estimated per day (24 hours) of operation

After comparing the cost of each process variation, it is clear that implementing the changes in the acid wash and water washing steps of the pre-treatment will significantly reduce the cost of the BCCS – P. Reducing the acid consumption by 25% (30:1) resulted in a 21% cost reduction from the 40:1 process. Although the inclusion of used water recycling did not decrease costs as significantly, recycling 60% of the used water resulted in a 6.94% cost reduction from the original BCCS – P and drastically effects resource consumption from an environmental and sustainability viewpoint. Although the BCCS – P process is still 1 and 2 orders of magnitude and more expensive than the MEA and BCCS processes with the proposed changes, it is significantly closer to being a viable comparable option for CO₂ capture. Additionally, there are some factors that have not been considered in the present analysis. When comparing MEA to the biomass adsorbents, it is not a full life cycle that is being analysed. MEA production needs a high pressure and temperature while consuming ammonia, water, and ethylene oxide [131]. The use of these raw materials and their production results in emitting CO₂, which were not factors included in the cost analysis. Alternatively, the biomass processes are using a waste product which otherwise would go unused, as opposed to a separately sourced and synthesised product. Although this does not explicitly receive a cost in the analysis done herein, it does have a positive environmental and socioeconomic value/impact. However, more research is needed to better understand the full extent of this integration, which will be explored in future work.

4.3. Summary

In this chapter a model for waste derived biomass solid adsorbent utilized for carbon capture was developed. The proposed model was validated using experimental data; operating conditions/system bounds were investigated both with and without pre-treating the fly-ash and compared to standard MEA PCC. The benchmark CO₂ capture rates were determined to be 87%

and 89.7% for adsorbent synthesised from non-pretreated and pre-treated fly-ash respectively, while the maximum CO₂ capture capacity was 93.23%. Case studies determined the following key insights: i) increased CO₂ flue gas compositions requires higher adsorbent mass, ii) the most effective flue gas volume to adsorbent mass ratio exists between 3.7-4.1, iii) higher regeneration temperatures improve CO₂ capture, and iv) pre-treatment does not impact the regeneration kinetics. Energy analysis showed that capture using pre-treated adsorbent is more efficient than capture using non-pretreated adsorbent. This analysis also showed that MEA PCC is more energy efficient than both proposed processes (BCCS and BCCS – P) although they could be improved to outperform MEA PCC by 85% and 54% if 100% efficient heat integration were to be considered, respectively; however, the pre-treatment process as presented was determined to increase the process costs by 2 orders of magnitude if no water recycle or acid ratio decreases are incorporated. BCCS showed over a 77% decrease in cost when compared to MEA PCC. The next chapter investigates alternative process flowsheets aimed to reduce costs and promote circular carbon economy thorough the utilization of metals from wastewater and CO₂ capture.

Chapter 5 Waste Management and Utilization Integration for Biomass Fly-ash Derived Li_4SiO_4 Solid Adsorbent Pre-treatment Model for CO_2 Capture: A Circular Carbon Economy

The results from the process presented in chapter 4 found that the pre-treatment section of the BCCS – P process required large amounts of DI water, which significantly increases process costs. The treatment and recycling of used water can decrease the fresh DI water requirement which in turn should improve costs. Additionally, there are valuable compounds from the treated fly-ash that remain in the used water from the water-washing unit. If they are removed and collected, these compounds could be further processed to produce new materials; alternatively, they can also be sold elsewhere. To consider these aspects, new systems, processing units, and streams were added to the flowsheet presented in chapter 4 to make their operation more economically attractive and sustainable. The section outlined by the purple box in Figure 20 highlights these enhancements; wastewater treatment, recycle to the water washing unit, and elemental extraction/precipitate formation. The integration of resource waste reduction and fly-ash elemental extraction during pre-treatment has the potential to promote a circular carbon economy by closing the loop of solid waste, wastewater, and CO_2 capture thereby improving the sustainability of this process.

Section 5.1 outlines the details of the enhanced process and the differences between the process previously presented in chapter 4. Section 5.1.1 describes the Aspen plus implementation which includes an additional reactor, mixer, pump, and separation while and section 5.1.2 explores the flowsheets for the elemental extraction investigation and how they are implemented in Aspen plus. Section 5.2 presented the simulation results of the enhanced pre-treatment and carbon capture model. Section 5.2.1 outlines the model validation and results while sections

for CO₂ capture (Carbon Capture block in Figure 20). A more detailed description and analysis of this process can be found elsewhere [26]. The major innovations that are made to the process and presented in this study occur in the pre-treatment section of the flowsheet and enclosed in the purple dashed line in Figure 20. The new processes added aim to decrease the systems waste production and reintegrating waste products thereby improving process sustainability. The previous study [26] showed that the main factors impacting the cost of the carbon capture process with pre-treated adsorbent material were the amount of acid and fresh DI water used in the pre-treatment of industrial biomass fly-ash. The process considered in [26] includes the pre-treatment of the fly-ash, synthesis of Li₄SiO₄, and capture of CO₂ using the Li₄SiO₄ adsorbent. This process is referred from heretofore as BCCS – P. The amount of DI water needed for one batch of pre-treated fly-ash in this process is 1.5×10^7 L. The high cost and resource consumption required by BCCS – P motivates the need to incorporate a recycle stream for the used water during pre-treatment.

The two key steps considered in the process proposed herein are the Acid Wash and Water Wash units shown Figures 20 and 21. Figure 21 depicts the flowsheet for the Aspen plus implementation of the improved pre-treatment process and is a more detailed version of the “Acid Wash”, “Water Wash” and “Water Treatment” blocks shown in Figure 20. Within the acid and water washing steps, a number of chemical reactions take place which result in changes to the fly-ash composition and surface morphology. These reactions contribute to what makes the treated fly-ash a more suitable adsorbent for CO₂ capture. The experimental results reported in Yang et al. [85] do not describe the kinetics associated with the acid and water washing processes, i.e., only the raw fly-ash composition and resulting composition of the treated fly-ash stream were reported (FLYASH and Si Source streams in Figure 21). To account for this, the

reaction conversion for the acid washing reactions is assumed to be equal to the solid removal rate determined from the difference in elemental compositions. More details on this assumption and the specific reactions and removal rate calculation are further described in section 5.1.1.

The next stage of fly-ash pre-treatment is the water-wash where the solids are rinsed with DI water until the pH of the USED WATER stream (Figure 21) reaches 7 ± 0.2 as specified in the experimental work [85]. The solid material, stream TF-2 in Figure 21, is then sent to a dryer and further used for the synthesis of Li_4SiO_4 adsorbent. The additional process units that were incorporated into the enhanced system are the neutralization mixer, water pump, and reverse osmosis (RO) membrane. The pump and RO membrane act together as an RO system, where the solid particulates, ions, and organic materials present in the recycled water are removed. These three steps ensure that the recycled water meets the necessary requirements for DI water listed in Table 15. The treated water referred to as PERMEATE in Figure 21 is then recycled to the water washing step, and the amount of pure DI water (DI H₂O in Figure 21) is decreased to match the required total input ($\sim 1.5 \times 10^7 \text{ L}$) [26]. The concentrate stream that leaves the RO unit (CONC in Figure 21) contains small amounts of precipitated iron (III) oxide-hydroxide ($\text{Fe}(\text{OH})_3$) and varying levels of dissolved calcium (Ca^{2+}), magnesium (Mg^{2+}), chlorine (Cl^-), potassium (K^+), aluminum (Al^{3+}), and sodium (Na^+). This concentrate stream could then be further processed to produce new materials/products such as valuable salts; potential processing options to recover these materials from this stream are discussed further in the section 5.1.2.

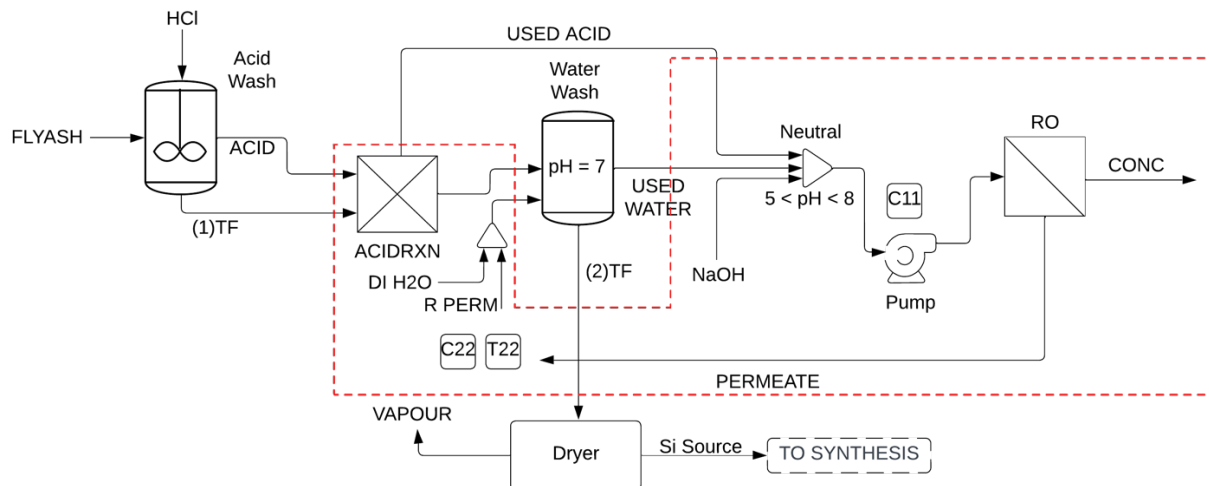


Figure 21. PFD of the pre-treatment model implemented in Aspen Plus, where the red dashed line shows the section of model that was added from the model presented in [26].

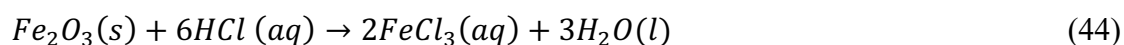
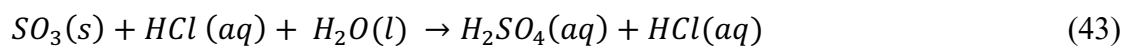
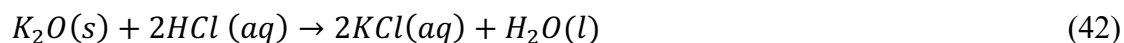
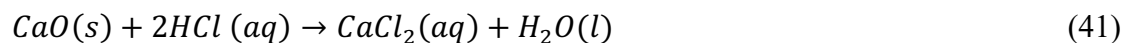
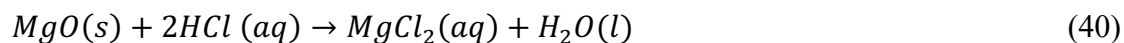
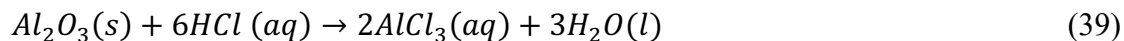
Table 15. DI water specification [132].

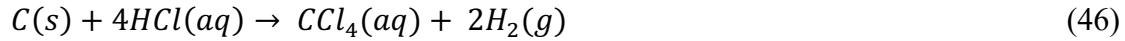
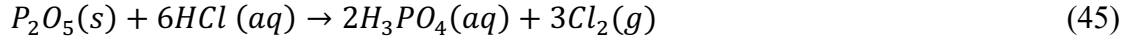
SPECIFICATIONS	Units	Requirement
pH		5.0-8.0
Electrical Conductivity	$\mu S/cm$	< 1
Electrical Resistivity	M Ω -cm	> 1
Total Dissolved Solids	ppm	< 100
Total Hardness as CaCO ₃	ppm	< 50
Calcium	ppm	< 25
Magnesium	ppm	< 25
Iron	ppm	< 1
Copper	ppm	< 1
Silica, SiO ₂	ppm	Not Detected
Chloride	ppm	< 2
Sulphate	ppm	< 25

5.1.1. Modelling details for Aspen plus implementation

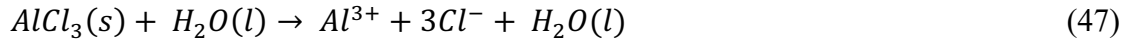
A schematic of the wastewater treatment model shown in Figure 21 was implemented in Aspen plus. The model consists of a solid wash unit (Acid Wash) followed by a reactor (ACIDRXN) which implements the reactions for the acid washing process. This is followed by another solid wash block (Water Wash) which splits the solid product to a dryer block (Dryer) and sends the used water to a mixer (Neutral), then a pump (Pump), and stream split unit (RO). Compared with the BCCS – P process modelled in chapter 4 [26], the enhanced model presented herein integrates the synthesis of adsorbent and capture of CO₂ with the water recycle system shown in Figure 21. The enhanced process will be referred to as BCCS – P(R). Moreover, we denote FA – P and FA – P(R) to refer to the fly-ash that has been pre-treated using BCCS – P and to fly-ash which has been treated using BCCS – P(R), respectively. The red dashed line in Figure 21 outlines the additional Aspen plus units included to model the physical system for the enhanced pre-treatment process presented in Figure 20; this includes the ACIDRXN reactor block, the two calculator blocks C11 and C22, and the transfer block T22.

During the acid washing process, the solid compounds in the fly-ash are exposed to 0.5 M hydrochloric in a 40:1 acid volume to solid mass ratio. The following reactions occur in this process:





where $Al_2O_3(s)$, $MgO(s)$, $CaO(s)$, $K_2O(s)$, $SO_3(s)$, $Fe_2O_3(s)$, $P_2O_5(s)$, and $C(s)$ represents solid aluminum oxide, magnesium oxide, calcium oxide, potassium oxide, sulphur trioxide, iron (III) oxide, phosphorus pentoxide, and carbon, respectively. $AlCl_3(aq)$, $MgCl_2(aq)$, $CaCl_2(aq)$, $KCl(aq)$, and $FeCl_3(aq)$, represents aqueous aluminum chloride, magnesium dichloride, calcium chloride, potassium chloride, and iron (III) chloride salts, respectively. $HCl(aq)$ represents aqueous hydrochloric acid, $H_2O(l)$ is liquid water, $H_2SO_4(aq)$ is aqueous sulphuric acid, $H_3PO_4(aq)$ represents aqueous phosphoric acid, $CCl_4(aq)$ represents aqueous tetrachloromethane, $Cl_2(g)$ represents chloride gas, and $H_2(g)$ represents gaseous hydrogen. As these reactions take place, each of the products in reactions 39-46 further dissociate into their ion counter parts as follows:



where Al^{3+} and Cl^- represent aluminum and chloride ions, respectively. For the sake of brevity, we will drop the notation in the remaining dissociation reactions on liquid water from the reaction and instead represent each salt in the aqueous phase. The remaining dissociation reactions that take place are:





where Mg^{2+} , Ca^{2+} , K^+ , Fe^{3+} , HSO_4^- , SO_4^{2-} , $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , and H^+ , represent magnesium, calcium, potassium, iron (III), hydrogen sulphate, sulphate, dihydrogen phosphate, hydrogen phosphate, phosphate, and hydrogen ions, respectively. Reactions 39 – 46 are specified explicitly in the ACIDRXN block (Figure 21), while reactions 47 – 56 are incorporated into the global chemistry of the model and determined using the electrolyte wizard built into Aspen Plus. All equilibrium constants for these reactions are calculated internally using the ENRTL-RK method. By coupling the ACIDRXN reactions (39-46) with the complete dissociation of the salts formed, the assumption stated in the previous section that the solid removal rate is equal to conversion of each reaction (X_r defined in eq. 59) ensures that the treated fly-ash reaches the appropriate compositions specified by experimental results. Additional reactions that occur downstream in the process (NEUTRAL mixer in Figure 21) but are also included in the global chemistry of the model are:



where $NaOH(aq)$ represents aqueous sodium hydroxide, Na^+ represents a sodium ion, and OH^- represents a hydroxide ion. The ACIDRXN reactor block was chosen as a STOICH reactor block in Aspen Plus, meaning that either the reaction conversion, or extent of reaction needs to be specified. As stated previously, X_r was assumed to be equal to the solid removal rate and is determined as follows:

$$X_r = \left(1 - \frac{m_{i,T-FA}}{m_{i,R-FA}}\right) \times 100\% \quad (59)$$

where r represents each reaction number, X_r is the conversion of reaction r , $\hat{i}$ represents each compound/element, $m_{i,T-FA}$ is the mass of element $\hat{i}$ present in the pre-treated fly-ash, and $m_{i,R-FA}$ is the mass of element $\hat{i}$ in the raw fly-ash. A list of each calculated reaction conversions (X_r) determined at nominal conditions (see section 5.2.2) can be found in Table 16. To ensure that all the appropriate reactions took place, some of the reactor blocks required modified chemistry ID's. For example, to define reactions 39 – 46 in the ACIDRXN block, the dissociation of HCl into H^+ and Cl^- must be postponed; otherwise, there is not enough HCl available for the reactions. As such, in the Acid Wash unit (Figure 21) a separate chemistry ID is specified to ensure that the dissociation does not immediately take place. The details of each unit operation block are defined in Table D1.1 of the appendix D.

Two calculator blocks and one transfer block are introduced into the model to ensure sufficient pressure and energy is supplied to the pump for the RO membrane (C11 in Figure 21) and simplify the connection of the recycled water. Transfer block T22 supplies stream R PERM with the conditions calculated by model for the PERMEATE stream but allows for decoupling of the system to avoid internal model errors such as inaccurate mass balances or incorrect sequencing orders. Calculator block C22 re-calculates the flow of stream DI H2O, after the treated water has been recycled acting as a flow controller for the DI H2O stream. The details for implementing each calculator block in Aspen Plus are included in Table D1.2 of appendix D. Additional details are included in appendix D on the Aspen plus implementation of the RO block, with the separation ratios based on RO membrane removal rates.

Table 16. Conversion values for each reaction [85].

Reaction	Key Component	X
1	Al	47.95%

2	Mg	71.02%
3	Ca	91.02%
4	K	66.30%
5	S	96.64%
6	Fe	56.66%
7	P	97.71%
8	C	39.11%

5.1.2. Integration of wastewater and CO₂ utilization

Another new aspect of this process included in the Aspen plus model is the utilization of the water treatment waste and the captured CO₂. To complete the loop of waste and CO₂ utilization shown in Figure 20 and promote a circular carbon economy, captured CO₂ from the adsorption process is incorporated with the water treatment waste stream (CONC in Figure 21) to produce valuable precipitates such as CaCO₃ and MgCO₃. Both CaCO₃ and MgCO₃ are used in cement production as fillers to improve cement properties; hence, the production of these compounds with captured CO₂ and wastewater containing Ca²⁺ and Mg²⁺ ions is attractive since it may help to reduce waste and has the potential to decrease cost through the sale of carbonate products [22][94][133]. Two different flowsheets for possible system configurations are considered in this work.

The first flowsheet (Figure 22) considers the BCCS – P(R) process presented in the previous section, with additional process units which are required to utilize the captured CO₂ and wastewater. The first addition is the introduction of a centrifugal separator (CENTRIFUGE block in Aspen Plus) to remove any precipitated Fe(OH)₃. This can be collected from the Fe(OH)₃ Solid stream and sold. The liquid stream CONC 2 (wastewater) is further processed by

combining with the captured CO₂ CO₂USE from the capture process. The CO₂ is then dissolved by introducing 7 M NaOH (the volume of base added is ~97% the volume of CO₂ added) with the wastewater stream using a mixer as these conditions favour CaCO₃ formation (pH = ~10). The sections of this flowsheet that vary from the proposed BCCS – P(R) process shown in Figure 21 are enclosed in a red box.

Next depicted in Figure 23 is the BCCS – P(R) with a second RO system and CaCO₃ extraction. The sections and units in this flowsheet which were added to the previously proposed BCCS – P(R) process (section 5.1.1) are highlighted by the red box. As shown in this Figure, a double RO filter is introduced to determine if recycling more water and increasing the concentration of Ca²⁺ in the waste stream promotes increased precipitate formation. After incorporating the centrifuge as described for the flowsheet presented in Figure 22, an additional pump and split stream block (Pump and RO 2 in Figure 23) are introduced to the Aspen Plus model. The same conditions as the previous RO membrane in BCCS – P(R) are used for the pump and RO 2 to recycle more of the used water. These conditions are stated in Table D1.1 of appendix D. Details of the Aspen Plus block implementation is included in the appendix D. These flowsheet options are further tested and their results discussed in section 5.2.6.

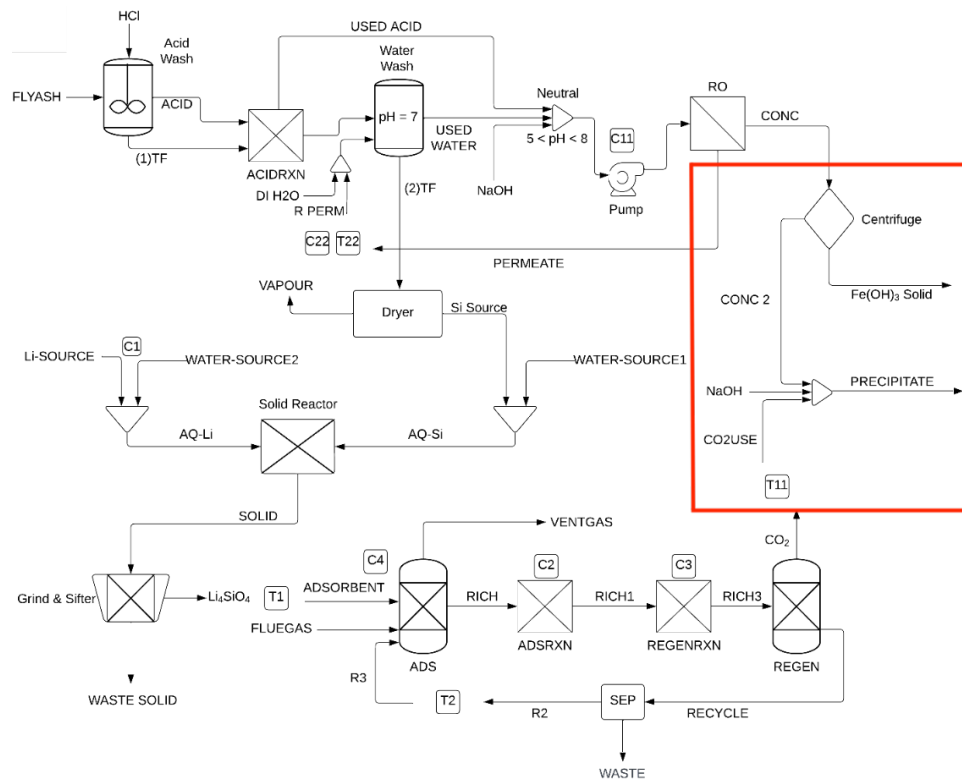


Figure 22. Flowsheet for an Aspen Plus model when incorporating elemental extraction and precipitation.

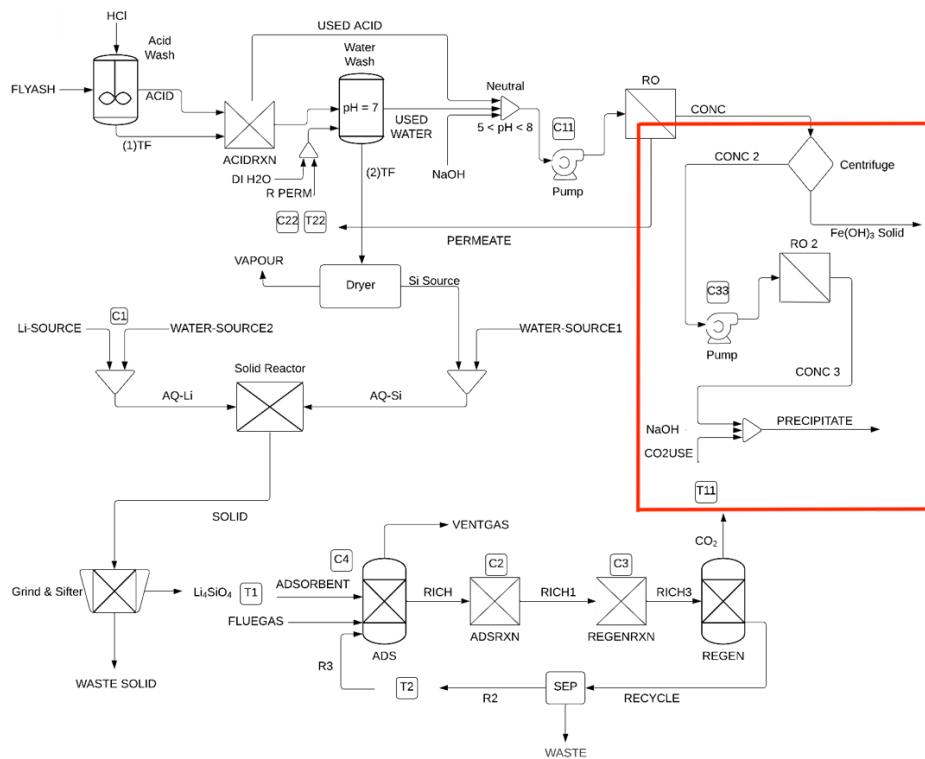


Figure 23. Flowsheet for an Aspen Plus model when incorporating the double RO system and elemental extraction and precipitation.

5.2. Results

5.2.1. Model Validation

This section describes the validation for the sections of the process flowsheet that were integrated to the pre-treatment and CO₂ capture systems shown in Figure 21, i.e., ACIDRXN, Neutral, Pump, and RO. Validation of the pre-treatment and post-combustion capture sections of the model are presented in chapter 4 [26]. The simulation results were compared to the experimental results reported in Yang et al. [85]. The experimental compositions that were reported in that previous study include a composition for trace elements classified as “Other”. The raw fly-ash composition in the present model was specified to match that reported in Yang et al. [85]. Moreover, as the composition of the “other” components only consisted of 0.16 wt% in Yang et al., this aspect was not included when defining the composition of the fly-ash stream in Aspen plus. To compare the experimental result of the acid washing, the mass fraction of each component in the TF-2 stream (Figure 21 post acid and water washing) was recorded. A comparison of the treated fly-ash compositions from experimental work and the modelled process after incorporating the water treatment and recycle are shown in Table 17.

Table 17. Validation of treated fly-ash mass fraction of each compound for the model results compared to the experimental results reported in Yang et al. [85]. R – FA and T – FA represent the distinction between raw and treated fly-ash, respectively. FA – P and FA – P(R) denote fly-ash pre-treated from the BCCS – P process and BCCS – P(R) processes, respectively.

Compound	R - FA composition [wt. %]		T - FA composition [wt. %]	
	Yang et al. [85]	Current Model	FA - P, Yang et al. [85]	FA - P(R), Current Model
SiO ₂	52.53	52.61	75.08	75.02
Al ₂ O ₃	12.89	12.91	9.59	9.58

MgO	6.35	6.36	2.63	2.63
CaO	6.08	6.09	0.78	0.78
K ₂ O	4.9	4.91	2.36	2.36
Cl	2.85	2.85	0	0
SO ₃	2.29	2.29	0.11	0.11
Fe ₂ O ₃	2.26	2.26	1.4	1.4
P ₂ O ₅	0.61	0.61	0.02	0.02
TiO	0.37	0.37	0.37	0.53
Other	0.16	0	0.08	0
LOI	8.71	8.72	7.58	7.57

The results presented in Table 17 outline that the process implemented in this work captures the experimental process after incorporating water treatment and recycle since there is less than a 0.3% difference between any of the compound compositions in both the raw fly-ash (R – FA) and pre-treated fly-ash (T – FA). Moreover, to ensure that the treatment of the recycled water is effective and that the treated water meets the required DI specifications, the stream parameters were recorded before (USED WATER in Figure 21) and after (PERMEATE in Figure 21) implementing the water treatment steps. The full stream details are presented in the appendix D (section D2), while a summary of both streams is depicted in Table 18.

Table 18. Details on DI water specifications and the used water streams before and after incorporating water treatment and recycle.

SPECS	Variable	Units	Requirement [132]	FA – P	FA – P(R)
pH	pH^{PERM}		5.0-8.0	4.0154	6.7137
Electrical Conductivity	EC	$\mu S/cm$	< 1	1.055E-05	9.191E-07
Electrical Resistivity	ER	M Ω -cm	> 1	94766.073	1088033.66
Total Dissolved Solids	TDS	ppm	< 100	3.43447	0.45623
Total Hardness as CaCO ₃	$TH - CaCO_3$	ppm	< 50	0	0
Calcium	[Ca]	ppm	< 25	0.0002648	1.558E-05
Magnesium	[Mg]	ppm	< 25	0.0001821	0.0001071

Iron	[Fe]	ppm	< 1	8.085E-05	1.133E-06
Copper	[Cu]	ppm	< 1	0	0
Silica, SiO ₂	[Si]	ppm	ND	0	0
Chloride	[Cl]	ppm	< 2	3.43362	0.27862
Sulphate	[S]	ppm	< 25	0.0001778	0.0001046

Most of the DI water specification for the water used to treat FA – P were met when comparing columns “Requirement” and “FA – P” in Table 18. Note the pH and chloride levels obtained with the used water from FA – P do not align with the requirements. Without proper treatment, the water used to treat FA – P is too acidic (pH of roughly 4) and contains too much dissolved chlorine (3.4 ppm) to be recycled back into the system. Hence, the water treatment process described in section 5.1 was introduced to address these issues. As shown in column FA – P(R) of Table 18, once treated, the water meets all the specifications for DI protocol and can be recycled back to the water washing step of the BCCS – P(R) process.

5.2.2. Benchmark Scenario

To determine a benchmark level of operation for the system proposed in Figure 21 and further evaluate its performance, the model was run under similar conditions to the nominal values defined in chapter 4 [26]. These conditions will further be referred to as the nominal conditions, and the simulated results at these conditions will be referred to as the benchmark scenario/results, i.e., BENCH. The nominal conditions for this system are stated in Table 19 whereas the results for the benchmark scenario, BENCH, is presented in Table 20. As discussed in our previous study, this process is a semi-batch system being modelled in Aspen Plus as a continuous system. As such, the volumes and flows of streams are defined in Aspen Plus as $\frac{volume}{time}$, however in the physical system the process streams would be on a volume basis and be processed in multiple batches. Although the pre-treatment and CO₂ capture process are combined

into the same flowsheet, because of the use of a transfer block T1 they can be decouple and executed independently. This is under the assumption that ample adsorbent is supplied to the carbon capture process by the pre-treatment process. The results from this process model remain unchanged for one CO₂ capture cycle (as was performed in this work) for both continuous and decoupled operation. Throughout the adsorption and regeneration cycle, approximately 93% of the adsorbent is regenerated each time. This results in additional adsorbent required to replenish the capture process. To account for this adjustment, additional pre-treatment units like those previously presented may be installed and run in parallel to supply the required make-up adsorbent. Note that batch and process scheduling is required for a fully continuous operation of this system for multiple cycles which is outside of the scope of this work.

The main metrics that were monitored to determine the efficiency of the model were each of the DI water specifications defined in Table 18, the composition of compound i in the treated fly-ash prior to adsorbent synthesis ($Z_{i,T-FA}$), the pH of the USED WATER stream (Figure 21) ($pH^{USED\ WATER}$), and the amount of fresh DI water needed (DI H₂O in Figure 21) (V^{DIH_2O}). The pH of a stream is determined as follows:

$$pH^s = -\log [H_3O^{+,s}] \quad (60)$$

where pH^s is the pH of stream s (i.e., $pH^{PERMEATE}$ or $pH^{USED\ WATER}$ are the pH values of stream PERMEATE and USED WATER, respectively), and $[H_3O^{+,s}]$ represents the concentration of H₃O⁺ ions in the same streams. The electrical conductivity (EC) and electrical resistivity (ER) of the PERMEATE stream (Figure 21) were determined as follows:

$$EC = \frac{TDS^{mg}}{0.5 \times 100\ 000} \quad (61)$$

$$ER = \frac{1}{EC} \quad (62)$$

where TDS^{mg} is the total dissolved solids present in the permeate stream in $\frac{mg}{L}$. Each of the remaining metrics ($Z_{i,T-FA}$, V^{DIH_2O} , $TH - CaCO_3$, $[Ca]$, $[Mg]$, $[Fe]$, $[Cu]$, $[Si]$, $[Cl]$, $[S]$) are values which can be found in the Aspen plus results. The BENCH results are displayed in Table 20.

This work assumes that if the water-washing step meets the same considerations specified in Yang et al. [85] (acid wash is at a 40: 1 $\pm$ 25% ratio and solid is rinsed until the used water reaches a pH of 7 $\pm$ 0.2,) and washing water is classified as DI, the surface morphology and in turn adsorbent characteristics remain unchanged for capturing CO₂. With this consideration in mind, the BCCS – P(R) capture and regeneration rates did not change compared to BCCS – P.

Table 19. Variable definitions and nominal values for model parameters [26][85].

Variable Name		Variable	Value
Raw fly-ash flow rate [g/s]		F_{FA}	1000
Acid: fly-ash ratio [L/g]		$R_{A:FA}$	40
Percentage of water recycled [%]		$\%H_2O_R$	85
Volume of 7 M NaOH used for neutralization [mol/s]		$V_{NaOH,N}$	17260
Raw fly-ash composition [wt. %]	Compound		
	SiO ₂	$Z_{SiO_2,R-FA}$	52.61
	Al ₂ O ₃	$Z_{Al_2O_3,R-FA}$	12.91
	MgO	$Z_{MgO,R-FA}$	6.36
	CaO	$Z_{CaO,R-FA}$	6.09
	K ₂ O	$Z_{K_2O,R-FA}$	4.91
	Cl	$Z_{Cl,R-FA}$	2.85
	SO ₃	$Z_{SO_3,R-FA}$	2.29
	Fe ₂ O ₃	$Z_{Fe_2O_3,R-FA}$	2.26
	P ₂ O ₅	$Z_{P_2O_5,R-FA}$	0.61
	TiO	$Z_{TiO,R-FA}$	0.37
	LOI/C	$Z_{C,R-FA}$	8.72
System operating temperature [°C]		T_{pre}	25
System operating pressure [bar]		P_{pre}	1.01

Table 20. Benchmark scenario results at nominal conditions (BENCH).

DI Water Specification			
Metric	Units	Requirement	Measured
pH^{PERM}		5.0-8.0	6.7137
EC	$\mu S/cm$	< 1	9.191E-07
ER	M Ω -cm	> 1	1088033.67
TDS	ppm	< 100	0.45623
$TH - CaCO_3$	ppm	< 50	0
$[Ca]$	ppm	< 25	1.558E-05
$[Mg]$	ppm	< 25	0.00010709
$[Fe]$	ppm	< 1	1.133E-06
$[Cu]$	ppm	< 1	0
$[Si]$	ppm	ND	0
$[Cl]$	ppm	< 2	0.27862
$[S]$	ppm	< 25	0.00010456
Fly-ash Compositions			
Metric	Units	Value	
$Z_{SiO_2,T-FA}$	wt. %	75.02%	
$Z_{Al_2O_3,T-FA}$	wt. %	9.58%	
$Z_{MgO,T-FA}$	wt. %	2.63%	
$Z_{CaO,T-FA}$	wt. %	0.78%	
$Z_{K_2O,T-FA}$	wt. %	2.36%	
$Z_{Cl,T-FA}$	wt. %	0.00%	
$Z_{SO_3,T-FA}$	wt. %	0.11%	
$Z_{Fe_2O_3,T-FA}$	wt. %	1.40%	
$Z_{P_2O_5,T-FA}$	wt. %	0.02%	
$Z_{TiO,T-FA}$	wt. %	0.53%	
$Z_{C,T-FA}$	wt. %	7.57%	
Recycle Streams			
Metric	Units	Value	
$pH^{USED\ WATER}$		6.9986	
V^{DIH_2O}	L/s	2246406	

To further understand how the integrated pre-treatment model BCCS – P(R) compares to the original pre-treatment (BCCS – P), a cost and resource consumption analysis was performed. A complete cost breakdown between the BCCS – P and BCCS – P(R) processes can be found in the appendix D (section D3). Results from this comparison showed that including the water

treatment and recycle process reduced the cost by nearly 5% under nominal conditions for BCCS – P(R) compared to BCCS – P. The main changes that impact the cost under nominal conditions and result in the cost reduction are the amount of fresh DI water which needs to be purchased for each pre-treatment batch (V^{DIH2O}), and the electric energy required. Although the pump needed for the RO system requires energy and increases the electric energy requirement from 9.95 kW to 24.41 kW, the V^{DIH2O} value decreases by 1 order of magnitude ($1.5 \times 10^7 L$ to $2.25 \times 10^6 L$) resulting in an 4.2% decrease in process cost. The energy consumption for the BCCS – P(R) process was determined to be 0.2% higher than that of the BCCS – P process. This increase was due to the energy required by the pump. However, as mass of raw fly-ash processed and amount of adsorbent produced are the same for both processes, the resulting energy required by the dryer, adsorption, and regeneration units remained the same. Due to this, the energy comparison between processes is not discussed further in the following section.

To gain further insights on the systems behaviour, four scenarios were investigated and compared against BENCH; (1) a sensitivity analysis on the percentage of water recycled, (2) a sensitivity analysis on the acid volume to solid fly-ash ratio, (3) a variation of the raw fly-ash source, and (4) a sensitivity analysis on the reaction conversions (X_r). The first three case studies are discussed in the following sections while results from the fourth case can be found in appendix D (section D4). Note that when investigating the system in the following scenarios, the $Z_{i,T-FA}$ values should not change significantly unless the raw fly-ash compositions $Z_{i,R-FA}$ or the reaction conversions X_r change. This metric will not be discussed in case studies that do not meet either of the conditions specified, and it is to be known that the treated fly-ash compositions $Z_{i,T-FA}$ are unchanged from those reported in BENCH (Table 20).

5.2.3. Sensitivity analysis on the percentage of recycled water

To determine the impact of volume of used water to recycle, which can also minimize both cost and fresh resource consumption, a sensitivity analysis on the percentage of recycled water was conducted. The percentage of recycled water was specified in the RO block (Figure 21) and varied from 50% to 85% with a step size of +5% as these are the lower and upper bounds of water retention for an RO system [134]. The resulting treated fly-ash composition is impacted only by the initial fly-ash composition and the reaction conversions that are defined in the ACIDWASH reactor; as such, this sensitivity analysis did not result in any changes to the nominal $Z_{i,T-FA}$ (see table D4.2 in appendix D). Each of the DI water specifications were within the boundaries, as depicted in table D4.1 in appendix D section D4. The $pH^{USED\ WATER}$ for each recycle percentage remained unchanged at a value of 6.999 as its recycled portion was treated the same each time, and the fraction not recycled was made up by fresh DI water. Both the volume of fresh DI water (V^{DIH2O}) and level of total dissolved solids (TDS) in the recycled water stream (PERMEATE in Figure 21) were recorded. Figure 24 shows that as the percentage of recycled water increases, the amount of fresh water needed in the water washing unit, V^{DIH2O} , decreases. This relationship follows a linear trend and is proportional to the level of recycle, which is expected as these are the only two water sources being used in the water-washing process. As one decreases, the other must increase to maintain the balance of water needed to produce a used water stream with a pH of 7. Likewise, the TSD level also decreases as the percentage of water recycled increases and this trend also follows a linear correlation. The amount of water recycled is not the only factor that influences the TDS level in the permeate stream; however, they are highly related and likely proportional.

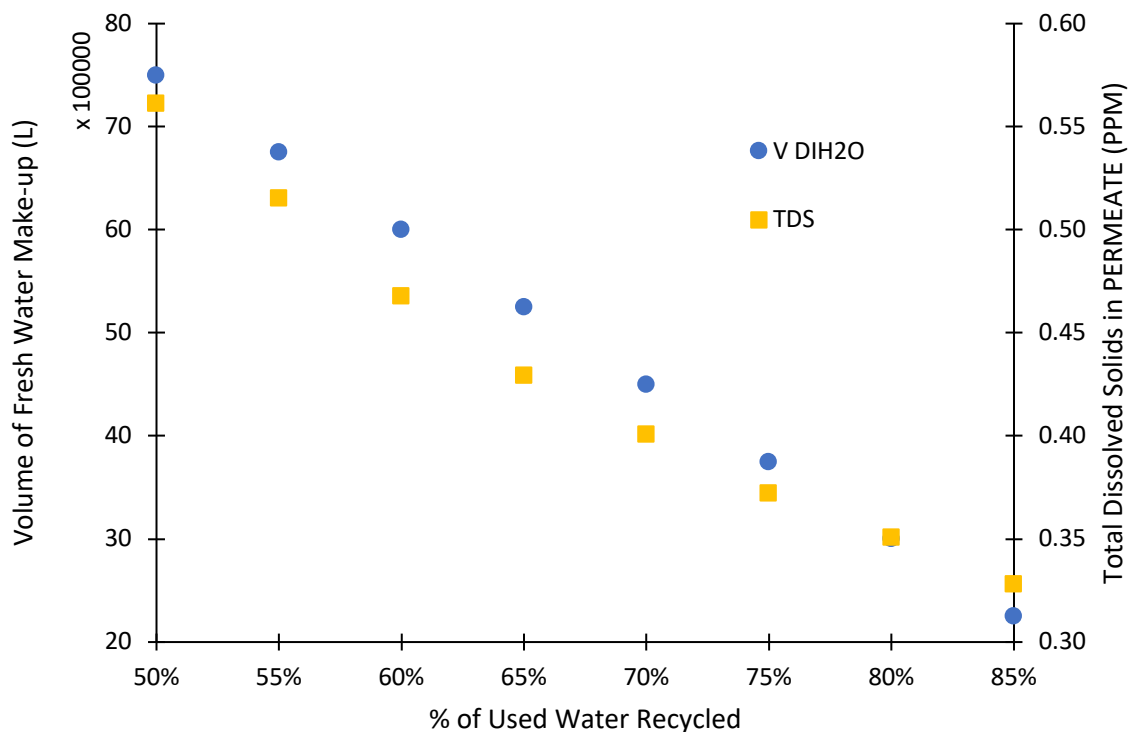


Figure 24. Results from the sensitivity analysis executed on percentage of used water recycled. The yellow squares represent the level of TDS in the recycled stream while the blue circles represent the amount of fresh DI water fed into the water-wash.

A cost analysis was performed as it was previously found that incorporating water recycle may help to reduce process costs [26]. The results of the cost analysis are depicted in Table 21. Results show a breakdown of the BCCS – P and the BCCS – P(R) under each tested water recycle rate; to execute the cost analysis the amount of material/energy needed to run one pre-treatment batch (which supplies enough adsorbent for 36 adsorption/regeneration cycles) is multiplied by the material cost and summed for each process. This total cost is then normalized on a per kilograms of CO₂ captured in 36 cycles (i.e., 24 hours) basis so that each process can be compared using the same basis. More details and example calculations on how this analysis was executed are described in [26]. The *CRC* is a term introduced in this study to account for consumed resources, which aids in evaluating the sustainability of the different changes made to the BCCS – P(R) process. The consumed resources in the *CRC* term are positive terms which

add to the cost while recycled or reused resources are considered negative terms that reduce the cost. The equation which defines the *CRC* is as follows:

$$CRC = \sum_{in} S_{in} C_S - \sum_{reuse} S_{reuse} C_S$$

$$in = \{HCl, DI \text{ water}, NaOH\}; reuse = \{DI \text{ water recycled}, Fe(OH)_3, CaCO_3\}. \quad (63)$$

where *in* and *reuse* are sets which include the streams/resources which are only consumed (*in*) and recycled (*reuse*) in the BCCS – P(R) process, respectively. S_{in} and S_{reuse} are the amount of a resource needed for one pre-treatment batch of S streams resources *in* and *reuse*, respectively, and C_S is the cost of stream S . More details and an example calculation on this term can be found in appendix D (section D5).

The results in Table 21 determine that the most economically feasible version of this process has a maximum recycle of 85%. This results in a 4.16% decrease in process costs from the BCCS – P process, and a 14.5% decrease in *CRC* shown in row “% change from BCCS – P” and row “CRC % change from BCCS – P” in Table 21. The expressions used to estimate these metrics are shown in equations 64-66. Although the 85% recycle rate shows the largest cost reduction, under the minimum recycle conditions with the RO membrane only retaining 50% of the used water, there is still a 2.19% decrease in cost compared to the original BCCS – P process. The resource consumption cost with minimum recycle is also reduced significantly as the *CRC* decreases by 8.3%. As shown in Table 21, the components which contribute the most significantly to the process costs and *CRC* are the fresh DI water as it is needed in very large volumes and the HCl as it is expensive and requires a 40:1 ratio at nominal conditions. Recycling the used water and decreasing the cost for fresh DI water as the recycle level increases improves both process costs as well as *CRC*. As more water is recycled and the amount of fresh DI water decreases the cost of resource consumption (*CRC*) decreases. Overall, these results indicate that

including the added cost of the water treatment equipment and operation does not outweigh the resource reintegration as recycling the water increases the cost efficiency and sustainability of the BCCS – P(R) process.

Table 21. Cost analysis performed on the benchmark, water recycle, and acid to fly-ash ratio cases.

Resource	PRICE		MATERIAL AND ENERGY REQUIREMENTS		BCCS – P(R): RECYCLED WATER					ACID: FLY-ASH	
	UNITS	Value	UNITS	BCCS - P	50%	60%	70%	80%	85%	35:1	30:1
Li source	$\frac{\$}{kg}$	20	kg	4.8916	4.8916	4.8916	4.8916	4.8916	4.8916	4.8916	4.8916
Synthesis	$\frac{\$}{kg}$	500	kg	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
HCl	$\frac{\$}{L}$	50	L	4000	4000	4000	4000	4000	4000	3500	3000
DI water (fresh)	$\frac{\$}{L}$	0.00177	kg	1.50E+07	7.50E+06	6.00E+06	4.50E+06	3.00E+06	2.25E+06	2.25E+06	2.25E+06
DI water (recycled)	$\frac{\$}{L}$	0.00091	kg	0.00E+00	7.50E+06	9.00E+06	1.05E+07	1.20E+07	1.28E+07	1.28E+07	1.28E+07
NaOH (total)	$\frac{\$}{L}$	5	L	0.00E+00	2.85E+02	2.85E+02	2.85E+02	2.85E+02	2.85E+02	2.49E+02	2.14E+02
Fired heat	$\frac{\$}{kWh}$	0.323	kW	4433.76	4433.76	4433.76	4433.76	4433.76	4433.76	4433.76	4433.76
Cooling water	$\frac{\$}{kWh}$	0.00104	kW	2751.0228	2751.0228	2751.0228	2751.0228	2751.0228	2751.0228	2751.0228	2751.0228
Electric	$\frac{\$}{kWh}$	0.103	kW	9.95	24.4144	24.4144	24.4144	24.4144	24.4144	24.4144	24.4144
Total Cost*			\$	229905.66	224874.16	223582.57	222290.97	220999.38	220352.79	195173.18	169998.57
CO ₂ captured*			kg	1284.1524	1284.1524	1284.1524	1284.1524	1284.1524	1284.1524	1284.1524	1284.1524
Normalized value			$\frac{\$}{kgCO_2/day}$	179.03	175.12	174.11	173.10	172.10	171.59	151.99	132.38
% change from BCCS – P				0.00%	-2.19%	-2.75%	-3.31%	-3.87%	-4.16%	-15.11%	-26.06%
CRC			$\frac{\$}{kg/day}$	226585.14	207877.36	203850.81	199824.27	195797.73	193782.00	168603.21	143429.41
CRC % change from BCCS–P					-8.26%	-10.03%	-11.81%	-13.59%	-14.48%	-25.59%	-36.70%

*data estimated per day (24 hours) of operation

$$\text{Normalized Value} = \frac{\text{Total Cost}}{\text{CO}_2 \text{ Captured}} [=] \frac{\$}{kgCO_2/day} \quad (64)$$

$$\% \text{ change from BCCS} - P = \frac{\text{Normalized value}_{BCCS-P(R), \% \text{ recycle}} - \text{Normalized value}_{BCCS-P}}{\text{Normalized value}_{BCCS-P}} \quad (65)$$

$$\text{CRC \% change from BCCS} - P = \frac{\text{CRC}_{BCCS-P, \% \text{ recycle}} - \text{CRC}_{BCCS-P}}{\text{CRC}_{BCCS-P}} \quad (66)$$

5.2.4. Variation of acid to fly-ash ratio

As mentioned in section 5.2.2 when introducing the benchmark results, one of the assumptions made while developing the model presented herein is that the kinetics of the produced adsorbent remain unchanged if the pre-treatment conditions in Yang et al. [85] remain unchanged. However, one of the main costs associated with the BCCS – P process was the acid washing step in the pre-treatment (as seen in Figure D3.2 of appendix D). The 40:1 HCl: fly-ash ratio accounted for nearly 85% of the process costs. Accordingly, the ratio was evaluated at 40:1 (benchmark), 35:1, and 30:1 to gain insights on the effect of this ratio to the entire system. It was assumed that the hydrochloric acid remained in excess for each of these ratios and did not exceed a 25% decrease from the nominal value. Also, we assumed that the kinetics of the synthesized adsorbent (Li_4SiO_4) remain unchanged. The BCCS – P(R) process was simulated with all other parameters under nominal conditions (shown in Table 19) while the acid volume was adjusted to the 35:1 and 30:1 ratio.

The results of this case study are presented in Figure 25 and the cost analysis can be seen in the “ACID: FLY-ASH” columns of Table 21. When simulated at nominal conditions with the tested HCl: fly-ash ratios, the pH^{PERMEATE} was above the upper bound for both the 35:1 and 30:1 ratios. As the amount of acid decreased but the volume of NaOH used to neutralize the used water remained unchanged, the pH of the PERMEATE stream continued to rise to 9.2 and 9.5 for 35:1 and 30:1 (shown by the data points circled in blue), respectively; these are depicted as the orange square and green triangle outside of the two read dashed lines in Figure 25. To accommodate this, the volume of NaOH for the 35:1 and 30:1 ratio scenarios were decreased by 12.7% and 25.1% from the nominal value, respectively. These percent decrease values were determined by systematically decreasing the NaOH volume until the pH^{PERMEATE} level was

within 5% of the benchmark value. As shown in Figure 25, this resulted in the $pH^{PERMEATE}$ level adjusting to within the appropriate bounds ($5.0 < pH^{PERMEATE} < 8.0$). The remaining DI water metrics can be found in Table D4.3 of appendix D.

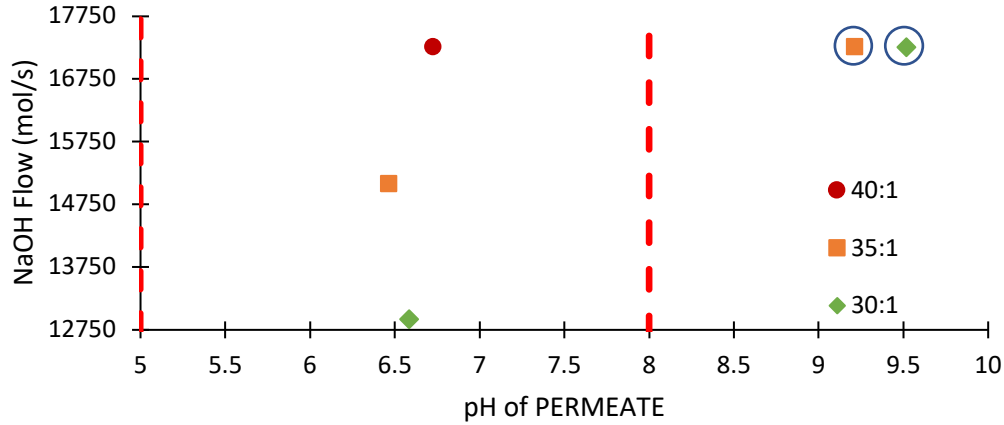


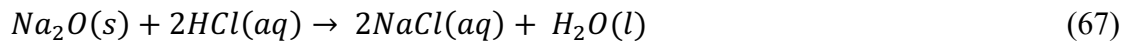
Figure 25. Results of the $pH^{PERMEATE}$ level when utilizing different NaOH volumes to neutralize the recycled water. The red dashed lines represent the boundary conditions for the acceptable $pH^{PERMEATE}$ levels, while the red dot, orange square, and green triangle represent the 40:1, 35:1, and 30:1 acid: fly-ash ratio scenarios evaluated.

As shown in Table 21, the cost analysis showed that by reducing the acid consumption by only 12.5% (35:1 ratio), the cost of the process decreased by 15.1% compared to BCCS – P and 11.4% from BCCS – P(R) under nominal conditions. This change also resulted in a 25.6% and 13.0% decrease in CRC from the BCCS – P and BCCS – P(R) processes, as show in Table 21. When the acid was decreased further (25% at the 30:1 ratio), there was a larger reduction of 26.1% and 22.9% in process cost from BCCS – P and BCCS – P(R). CRC for this ratio were reduced 36.7% and 26.0% for BCCS – P and the benchmark BCCS – P(R), respectively. These results suggest that as the ratio continues to decrease, the process cost and resource consumption will also tend to decrease; however, when the ratio reaches a critical point in which the adsorbent kinetics are impacted, the amount of CO_2 captured per kilogram of adsorbent would also begin to decrease which would compete with the cost reduction. Further experimental work on the acid:

fly-ash ratio for industrial biomass-based Li_4SiO_4 needs to be explored to better understand the fly-ash's (and in turn Li_4SiO_4 adsorbent's) kinetic response to explore possible cost reduction further.

5.2.5. Variation of fly-ash source

The main reason that the industrial biomass fly-ash source utilized for this study (chosen by Yang et al. [85]) is an appropriate feed for Li_4SiO_4 production/synthesis is because it contains a high fraction of SiO_2 and is a waste product produced in large quantities. To understand the applicability and robustness of this pre-treatment process, three additional biomass fly-ash sources were tested. Wood, grass, and straw biomass sources were examined in this study since they are some of the most common biomass sources used that produce significant amounts of fly-ash [121]. However, as the adsorption capacity of Li_4SiO_4 derived from these various biomass fly-ash sources has not been tested or experimentally determined, the results from the capture section of the BCCS – P(R) process were not considered. As the reaction kinetics and adsorption capacity cannot be estimated using the available information in the literature, the results of the CO_2 capture process (adsorption and regeneration) are not validated and therefore these aspects are not included in the present scenario. A step that is required to include these alternative fly-ash sources in the pre-treatment process is the addition of a reaction in the ACIDRXN block (Figure 21). All the new biomass sources used in this scenario contain sodium oxide (Na_2O), so the following reaction is included:



where $\text{Na}_2\text{O}(s)$ is solid sodium oxide and $\text{NaCl}(aq)$ is aqueous sodium chloride salt. The conversion of this reaction (X_r) was chosen as 98%, as it is a strong condensation reaction and highly forward favoured [135]. The dissociation of NaCl salt in water is included in the global

chemistry, so after this addition to the ACIDRXN block the model is adjusted appropriately for the fly-ash variation investigation. The wood, grass, and straw fly-ash compositions that were used for this case study are listed in Table D6.1 of appendix D.

Utilizing each biomass as a raw fly-ash source resulted in very minimal changes to the PERMEATE stream as it was still within the appropriate boundaries and met all DI water specifications. These results are presented in appendix D (Table D4.4). The final composition of the treated fly-ash (FA – P(R)) however, did vary significantly and are compared to the benchmark results and shown in Figure 26. Additionally, Figure 27 shows a comparison between the mass of Li_4SiO_4 adsorbent produced and the composition of SiO_2 in the treated fly-ash.

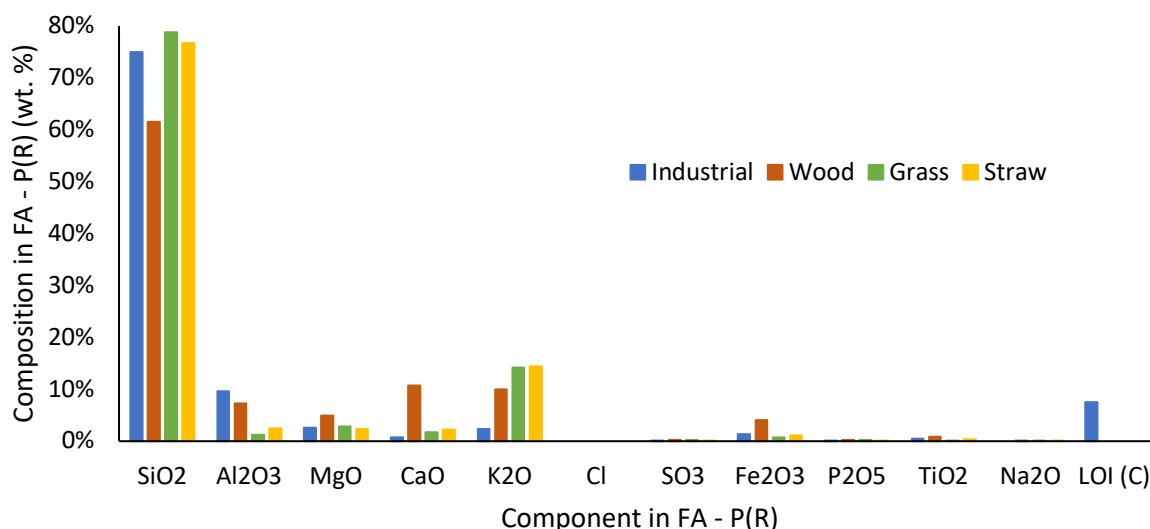


Figure 26. Compositions of the treated fly-ash using different biomass sources for the raw fly-ash feed. The blue, orange, green, and yellow bars represent the fly-ash sources from industrial (FA – P), wood, grass, and straw biomass, respectively.

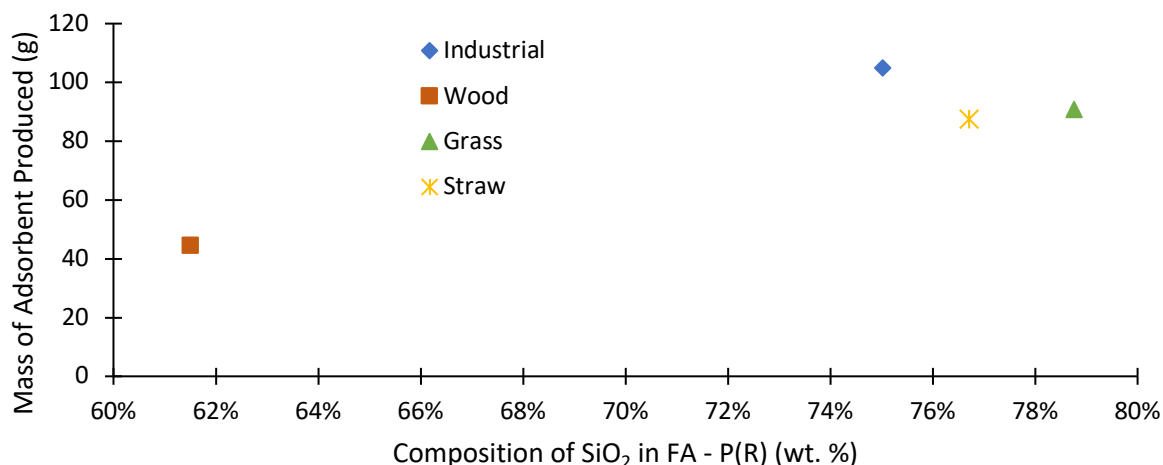


Figure 27. Relationship between the mass of adsorbent produced for each biomass source and the percentage of SiO₂ present in the treated fly-ash. The blue diamond, orange square, green triangle, and yellow cross represents the biomass sources from industrial (FA – P), wood, grass, and straw, respectively.

The results presented in Figure 27 show that both grass and straw derived biomass fly-ash could be suitable to produce Li₄SiO₄ as they have a significant SiO₂ composition available; the wood biomass fly-ash has a much lower initial SiO₂ composition which reduces the amount available for adsorbent production making it a less suitable option. The industrial biomass fly-ash used in the study performed by Yang et al. [85] was comprised of cotton stalk, corn stalk, wheat straw, bark, woodblock, and sawdust, confirming that grass and straw biomass is appropriate for Li₄SiO₄ synthesis. Although the mass fraction of SiO₂ in the treated fly-ash ($Z_{SiO_2,T-FA}$) for grass and straw fly-ash was 3.74% and 1.68% higher than industrial fly-ash respectively, because the raw fly-ash composition ($Z_{SiO_2,R-FA}$) for grass and straw is lower, the total mass of SiO₂ in the treated fly-ash is lower. This results in a lower amount of adsorbent produced from the grass and straw over industrial fly-ash, even with a higher composition after the pre-treatment process. As such it was determined that the industrial biomass currently is an

attractive option for Li_4SiO_4 production to capture CO_2 , but it would be beneficial to investigate grass and straw fly-ash further in this area.

Although the wood biomass fly-ash did not provide high levels of SiO_2 and would not be beneficial for adsorbent production, it had much higher compositions of calcium, magnesium, and iron compared to the grass, straw, and industrial fly-ashes. This opens possibilities for different elemental extraction when utilizing wood biomass fly-ash. Due to these higher compositions, the water treatment and wastewater stream contain higher levels of Ca^{2+} , Mg^{2+} , and Fe^{3+} ions. As there was a higher concentration of Fe^{3+} ions, there was also more $\text{Fe}(\text{OH})_3$ precipitate produced. Tables with the stream compositions from this scenario can be found in appendix D (section D7). Further details and cost analysis on precipitate removal is discussed next.

5.2.6. Precipitation Evaluation

Figure 20 outlines a process that promotes a circular carbon economy through means of elemental extraction and precipitate formation. For example, under nominal conditions there is a solid precipitate $\text{Fe}(\text{OH})_3$ that forms in the RO waste stream, and as discussed in section 5.2.5, the mass of this precipitate can be increased by varying different parameters such as the raw fly-ash source. The aim of this section is thus to investigate the economic viability of three different flowsheet variations to promote circular carbon economy: (A) BCCS – P(R) (Figure 21) with the addition of a centrifuge after the CONC stream, (B) BCCS – P(R) with calcium carbonate production (Figure 22), and (C) BCCS – P(R) with a double RO and calcium carbonate production (Figure 23). These scenarios will furthermore be referred to as BCCS – P(R): $\text{Fe}(\text{OH})_3$, BCCS – P(R): CaCO_3 , and BCCS – P(R): 2RO as defined above. The conditions used

to model these flowsheets were the nominal conditions specified in Table 19 unless otherwise specified.

To determine the viability of each flowsheet, an economic analysis similar to that performed for the analyses shown in sections 5.2.3 and 5.2.4 was performed. The additional units that were added to the cost analysis for each scenario was dependant on the processing steps required by each flowsheet. For flowsheet BCCS – P(R): $\text{Fe}(\text{OH})_3$ the centrifuge energy requirement and amount of $\text{Fe}(\text{OH})_3$ recovered were included. Flowsheet BCCS – P(R): CaCO_3 included the centrifuge energy requirement, amount of $\text{Fe}(\text{OH})_3$ recovered, the additional NaOH needed for dissolving CO_2 , and the amount of CaCO_3 recovered. Flowsheet BCCS – P(R): 2RO which had the most additional units included the centrifuge energy requirement, amount of $\text{Fe}(\text{OH})_3$ recovered, the second RO system (pump and membrane) and its energy requirements, additional NaOH needed for dissolving CO_2 , and the amount of CaCO_3 recovered.

Column “BCCS – P(R): $\text{Fe}(\text{OH})_3$ ” of Table 22 shows that although $\text{Fe}(\text{OH})_3$ can be sold for a profit, the amount recovered and sold is not enough to compensate for the associated energy costs. However, if it is not properly considered and disposed of, this compound can be harmful if released into bodies of water and impact the aquatic environment [136]. Row “% change from BCCS – P(R)” in Table 22 showed this process cost increased 1.08% from that of BCCS – P(R) without the centrifuge, determining that the addition may not be competitive. Additionally, Table 22 shows that the mass of CaCO_3 recovered for flowsheets BCCS – P(R): CaCO_3 and BCCS – P(R): 2RO was zero. This is mostly because calcium and magnesium ions are not in high enough concentration to form any precipitates (i.e., they were too diluted in the waste stream).

Flowsheet BCCS – P(R): CaCO_3 was first examined by directly combining the waste stream with dissolved CO_2 in a solution with pH of 10. However, this resulted in a low carbonate ion

concentration ($\sim 1 \times 10^{-10} M$). To increase the ion concentration and promote calcium carbonate formation, the amount of CO_2 introduced was increased. It was assumed that the carbon capture process was run 10000 times, and the CO_2 captured from all of these processes was dissolved in solution to be combined with one batch of the pre-treatment's waste stream. Despite this change, it did not result in the formation of $CaCO_3$ as the concentration of Ca^{2+} and CO_3^{2-} ions were again not concentrated enough to elicit precipitation. This change resulted in a significant increased process cost and *CRC*. The results in Table 22 column "BCCS – P(R): $CaCO_3$ " are for the single batch of CO_2 capture where the process cost and *CRC* increased by 3.75% and 2.84%, making flowsheet BCCS – P(R): $CaCO_3$ an unsustainable option.

The double RO filter was introduced to determine if recycling more water and increasing the concentration of Ca^{2+} in the waste stream would allow for precipitate formation (Flowsheet BCCS – P(R): 2RO). As shown in Figure 23, an additional pump and split stream block were introduced to the Aspen Plus model with the same conditions as the previous RO membrane to recycle more of the used water. Flowsheet BCCS – P(R): 2RO was tested with one and 10000 batches of capture CO_2 (same as flowsheet BCCS – P(R): $CaCO_3$); however, both did not produce $CaCO_3$ as the concentration of calcium and carbonate ions were still too low to promote a precipitate formation. The stream results from the 10000-batch test of flowsheets BCCS – P(R): $CaCO_3$ and BCCS – P(R): 2RO can be found in the appendix D (section D7). Table 22 column "BCCS – P(R): 2RO" shows the results of the economic analysis done for 10000 batches of CO_2 captured. Without the profit from $CaCO_3$ sales there is nothing to counter the expenses for the extra RO system or additional NaOH; compared to BCCS – P(R) process costs were 12 times larger and *CRC* was over 13 times larger.

One additional scenario investigated the use of wood fly-ash as it has a higher initial composition of calcium oxide present than that of the other biomass fly-ashes and the industrial fly-ash. Increasing the initial composition of CaO from 6.08 wt.% in the industrial fly-ash to 43.03 wt.% in the wood fly-ash may increase the concentration of calcium in the water treatment waste stream. Flowsheet BCCS – P(R): CaCO₃ (Figure 22) was utilized under nominal conditions except the fly-ash source (i.e., $Z_{i,R-FA}$) was chosen for this additional scenario as wood biomass fly-ash [121]. The flowsheet and cost analysis were first executed using 1 batch of captured CO₂ and then 10000 batches of CO₂. The results of the cost analysis shown in column “BCCS – P(R): CaCO₃ FA” of Table 22 are for the model using 10000 batches of CO₂. Results from these tests showed that the concentrations for calcium and carbonate ions were still insufficient to result in CaCO₃ precipitate formation. Results of the stream concentrations and output can be found in Table D7.1 of appendix D. The process cost and *CRC* were significantly lower than that of the double RO membrane as there were fewer additional costs for flowsheet BCCS – P(R): CaCO₃ than flowsheet BCCS – P(R): Fe(OH)₃, however they were still 3.7 and 4.1 time larger in cost and *CRC* compared to BCCS – P(R).

Table 22. Cost analysis results from various flowsheet options for elemental extraction and precipitate formation investigation.

Resource	PRICE		Process Flowsheet Configuration					
	UNITS	Value	UNITS	BENCH	BCCS - P(R): Fe(OH) ₃	BCCS - P(R): CaCO ₃	BCCS - P(R): 2RO	BCCS - P(R): CaCO ₃ FA
Li source	$\frac{\$}{kg}$	20	kg	4.891644	4.891644	4.891644	4.891644	4.891644
Synthesis	$\frac{\$}{kg}$	500	kg	3.6	3.6	3.6	3.6	3.6
HCl	$\frac{\$}{L}$	50	L	4000	4000	4000	4000	4000
DI water (fresh)	$\frac{\$}{L}$	0.00177	kg	2246405.8	2246405.787	2.25E+06	3.34E+05	2.25E+06
DI water (recycled)	$\frac{\$}{L}$	0.00091	kg	12753619	12753619.21	1.28E+07	1.47E+07	1.28E+07

NaOH (total)	$\frac{\$}{L}$	5	L	285	285	1.39E+03	4.85E+05	1.24E+05
Fe(OH) ₃ cost	$\frac{\$}{g}$	0.7	g	0	1.58E-02	1.58E-02	1.69E-02	2.41E-02
Centrifuge	$\frac{\$}{kWh}$	0.103	kW	0	5.50E+01	5.50E+01	5.50E+01	5.50E+01
CaCO ₃ cost	$\frac{\$}{g}$	0.45	g	0	0	0.00E+00	0.00E+00	0.00E+00
Fired heat	$\frac{\$}{kWh}$	0.323	kW	4433.76	4433.76	4433.76	4433.76	4433.76
Cooling water	$\frac{\$}{kWh}$	0.00104	kW	2751.0228	2751.0228	2751.0228	2751.0228	2751.023
Electric	$\frac{\$}{kWh}$	0.103	kW	24.414395	24.4143946	24.4144	28.0305	24.4144
Total			\$	220352.79	222729.66	228229.66	2646363.83	844847.08
CO ₂ Captured			kg	1284.1524	1284.1524	1284.1524	1284.1524	1284.1524
Normalized value			$\frac{\$}{kgCO_2/day}$	171.59	173.445	177.728	2060.786	657.903
% change from BCCS – P(R)					1.08%	3.57%	1100.97%	283.41%
CRC			$\frac{\$}{kg/day}$	193782.00	193781.99	199281.99	2613763.80	814657.98
CRC % change from BCCS – P(R)					0.00%	2.84%	1248.82%	320.40%

Although the previous process flowsheet configurations showed that internally incorporating CO₂ utilization with the water treatment waste stream was not sustainable or competitive, water and CO₂ use in cement production were further investigated to understand if there were plausible application for both streams in the process/industry. It was determined that the main uses for water in the cement manufacturing process involves dust suppression technologies, while CO₂ is best utilized as a reactant in CaCO₃ synthesis [137][22][25]. Since feasible applications for the waste and CO₂ streams in cement manufacturing were determined, a cost analysis on the BCCS – P(R) process was conducted to include the profit of selling these streams to a cement facility. The results of this analysis are shown in Table 23. The transport costs are assumed to be in Canada to a cement facility that is within a 100 km radius [138][108], the price which CO₂ is sold at is assumed to be an average within Canada [108], and the price water is sold at is assumed to be the same for that of cooling water. The conditions the captured CO₂ and waste

streams are produced at (temperature, pressure, purity, etc.) are suitable for the conditions at which they are also sold so no further processing is required.

Table 23. Results from the cost analysis done when selling the captured CO₂ and water treatment waste streams to the cement industry.

Resource	PRICE		Cases		
	UNITS	Value	UNITS	Baseline	Cement
Li source	$\frac{\$}{kg}$	20	kg	4.8916	4.8916
Synthesis	$\frac{\$}{kg}$	500	kg	3.6	3.6
HCl	$\frac{\$}{L}$	50	L	4000	4000
DI water (fresh)	$\frac{\$}{L}$	0.00177234	L	2.246E+06	2.246E+06
DI water (recycled)	$\frac{\$}{L}$	0.00091146	L	1.28E+07	1.28E+07
NaOH (total)	$\frac{\$}{L}$	5	L	285	285
Fe(OH) ₃ cost	$\frac{\$}{g}$	0.7	g	1.69	1.69
Centrifuge	$\frac{\$}{kW}$	0.103	kW	55.00	55.00
Transport Water	$\frac{\$}{L}$	0.00005	L	0.00	2.251E+06
Transport CO ₂	$\frac{\$}{tCO_2}$	20.24	t	0.00	2.881632
Sold Water	$\frac{\$}{L}$	0.00132926	L	0.00	2250639.8
Sold CO ₂	$\frac{\$}{tCO_2}$	95.5704	t	0.00	2.881632
Fired heat	$\frac{\$}{kW}$	0.19	kW	4433.76	4433.76
Cooling water	$\frac{\$}{kW}$	0.00103795	kW	2751.0228	2751.0228
Electric	$\frac{\$}{kW}$	0.103	kW	24.4144	24.4144
Total			\$	220357.27	217381.40
CO ₂ Captured			kg	1284.1524	1284.1524
Normalized value			$\frac{\$}{kgCO_2/day}$	171.597	169.280

% change from BCCS – P(R)			-1.35%
CRC	$\frac{\$}{kg/day}$	193782.00	190666.42
CRC % change from BCCS – P(R)			-1.608%

From this analysis, it is evident that although small, there is a decrease in cost when selling the CO₂ and waste streams to a cement production facility. The process costs for this waste management and CO₂ utilization tactic is reduced to \$169.28 *per kgCO₂ a day*, which is 1.35% lower than BCCS – P(R) and 4.33% lower than BCCS – P. When including the benefit of reintegrating waste streams as process feed stream, the CRC of the process decreases by over 1.61% and 16.93% compared to the benchmark BCCS – P(R) and BCCS – P, respectively. Although it was not economically viable to reintegrate the waste stream and captured CO₂ for the presented BCCS – P(R) process, the strategy of repurposing both streams in cement manufacturing may be an economically sustainable alternative route to promote circular carbon economy.

5.3.Summary

In this chapter, the pre-treatment section of the process described in chapter 4 was further developed to incorporate water treatment and recycle. A model for the advanced pre-treatment process was developed and investigated. Cost reduction capability was examined, and it was determined that maximizing the level of recycled water (85%) results in over 4.1% lower process costs. Additional case studies investigated the impact of changing the acid to fly-ash ratio in the acid washing step and varying the source of biomass fly-ash. Different units and operating conditions were added to the model to promote CaCO₃ precipitation and determine the most economically feasible process flowsheet presented. Results showed that selling both the captured CO₂ and water treatment waste streams to a cement production facility was economically

feasible and satisfies the goal of promoting a circular carbon economy and sustainable strategy for this process.

Chapter 6 Conclusions and Recommendations

6.1. Conclusions

The objective of this thesis is to provide helpful modelling tools and alternative technology to advance the field of decarbonization. Two major objectives were pursued in this thesis. In the first objective, an optimal deployment framework which incorporates socioeconomic and environmental constraints was developed to provide tools for regions to strategically implement different carbon capture technologies to reduce GHG emissions. This thesis also developed a novel model for CO₂ adsorption using Li₄SiO₄ synthesized partially from industrial biomass fly-ash. With the incorporation of waste management and utilization, this process model can be used to gain insights on the system performance under varying operating conditions which is vital to study the technical feasibility and viability of this technology at a larger (industrial) scale. Conclusions drawn from each of the studies conducted are presented next.

6.1.1. Conclusions for the optimal deployment framework

The optimal deployment framework provides a modelling tool for others to forecast possible carbon capture implementation. It allows different target levels to be tested to determine the feasibility of carbon capture implementation and flexibility for carbon capture technologies and methods to progress. The model that incorporates economic, social, environmental considerations in decision making was tested and evaluated using various case studies involving the provinces in Canada. The main outcomes drawn from this study are as follows:

- With the implementation of commercially developed carbon capture technology (PCC, pre-combustion, and oxy-fuel combustion), it could be feasible for Canada to meet the government's proposed emission targets in 2030, reducing emissions levels to 11.82

$MtCO_2$, 27.63 $MtCO_2$, and 107.01 $MtCO_2$ in the electricity, heavy industry, and oil and gas sectors, respectively. This installation consists of 58 PCC plants located in 7 provinces (Alberta, British Columbia, New Brunswick, Nova Scotia, Ontario, Quebec, and Saskatchewan).

- The results consistently determine that optimal plant location exists in provinces with higher emissions values and lower energy costs. The balance between these factors is also dependant on the target levels and meeting the required emissions. Often Alberta, Ontario, Quebec, and Saskatchewan are presented as ideal locations for the reasons listed above.
- Although post-combustion (PCC), pre-combustion, and oxy-fuel combustion carbon capture technology were all included as possible plant options, PCC plants were chosen for every scenario as they are the most developed and least expensive choice for implementation currently.
- Removal of GHG emissions from Alberta's electricity and oil and gas sector is an essential aspect of Canadian decarbonization as it is a part of the proposed deployment planning in every scenario examined.
- The GHG emissions that are produced in Alberta play a large role in Canada's decarbonization. A significant reduction of the cost of CO_2 avoided (*CCA*) was seen when Alberta's emissions were reduced through alternative sources by at least 25%. If the province could reduce GHG emissions by 50% through alternative sources, the number of carbon capture plants required by the country could also be reduced from 58 to 35 thus leading to significant savings.

6.1.2. Conclusions for the biomass fly-ash adsorbent carbon capture model

As alternative carbon capture technologies need to be developed to aid in lowering the costs associated with decarbonization, a novel carbon capture model which utilizes a biomass fly-ash derived solid adsorbent (Li_4SiO_4) was presented. The model was validated by comparing it against experimental data from a lab-scale version of the process for both the adsorption and regeneration sections of the CO_2 capture process. This process was further examined by comparing the Li_4SiO_4 adsorbent performance with and without pre-treatment and compared both against a standard MEA PCC pilot scale process. The main findings from this study are as follows:

- Both non-pretreated adsorbent capture process (BCCS) and pre-treated adsorbent capture process (BCCS – P) show promising result as alternative carbon capture techniques. The energy analysis shows that the benchmark MEA PCC outperforms both the BCCS and BCCS – P processes but incorporating heat integration could significantly reduce both the latter processes energy requirements (~85% and 54%, respectively) to make them the more efficient technology.
- There is a trade-off between CO_2 capture efficiency and energy required by the system. BCCS – P requires additional energy during pre-treatment and regeneration; however, the process produces an adsorbent with a higher capacity to capture CO_2 which reduces the energy requirement during adsorption.
- Cost analysis shows that the BCCS process reduces cost by 78% compared to a standard MEA PCC process. With the appropriate implementation, BCCS has the potential to be a suitable sustainable large scale carbon capture technology.

- BCCS – P has a higher Li_4SiO_4 - CO_2 adsorption capacity, resulting in a reduced adsorption cooling requirement. However, the pre-treatment process proposed in this model results in a cost 2 orders of magnitude larger than that of MEA PCC.

To gain further insights into the present process flowsheet configuration, enhancements were made to the BCCS – P to include water treatment, recycle, and waste utilization strategies. The enhanced process (BCCS – P(R)) was validated through comparison to experimental data and proves to be a suitable representation of the actual system. Additional scenarios and sensitivity analyses were performed to determine and quantify the improvements made from the BCCS – P to the BCCS – P(R) process. A cost and resource analysis were executed to understand the most economically beneficial process and waste utilization tactic. The main findings from this part of the study are as follows:

- The benchmark results for the BCCS – P(R) process show a reduction in process costs and *CRC* when compared to the BCCS – P process concluding that the enhancements made to the process are beneficial and should be included in further studies.
- A maximum recycle level of 85% resulted in the lowest process cost and *CRC*. The major factors which contributed to reducing the *CRC* were the amount of DI water recycled and the volume of HCl used in the acid washing step. Higher amounts of recycled water and less HCl showed the largest improvement in both process cost and *CRC*.
- The system is capable of processing fly-ash from various biomass sources with minor modifications to the NaOH neutralization volume, i.e., this pre-treatment process model can be utilized in various applications which do not require the use of the carbon capture

aspect of the model. With small alterations, the pre-treatment model could be used to analyse systems for specific elemental extraction applications.

- Carbonate precipitation under the nominal conditions and flowsheet options presented in this work was determined not to be economically viable. However, alternative waste utilization techniques that were employed through waste stream sale to the cement industry were found to improve costs (i.e., economically viable method). This technique promotes a circular carbon economy and could be implemented in pilot scale testing of this technology.

6.2. Recommendations

The work presented in this thesis can be extended to further improve the models developed in this work and the insights gained from these studies. These extensions would provide more rigorous models that will aid in decarbonization from a policy making perspective, as well as technological feasibility. The models presented in this work provide system testing of alternative carbon capture techniques that utilize biomass waste and a circular carbon economy. These models are needed for further scale up the processes presented to implement feasible large scale alternative carbon capture technologies. Recommendations for future work that can be pursued in this area are as follows:

6.2.1. Recommendations for work relating to the optimal deployment framework

- Model adaptations which increase the level of complexity for data handling and parameter uncertainty is recommended. With large data bases available, parameters such as location grids for CO₂ sinks and sources, transportation networks, and specific locations for power plants and their emissions can be incorporated which will address aspects of uncertainty thus providing more realistic scenarios.

- A detailed uncertainty analysis is recommended as specific parameters (e.g., retrofitting cost R_P , provincial transportation cost T_j , and Social Perspective Cost SPC) are likely to be highly uncertain and may impact the current CO₂ capture deployment decisions.
- There will likely be a trade-off between locating capture plants close to emissions sources and storage locations; thus, further investigation in this area is recommended since it will improve the deployment strategy. That is, investigation into the role of CO₂ utilization and storage location while expanding into different sectors will increase the accuracy of specific plant location.
- Additional consideration of extending the framework to incorporate points of consumption for products produced by stationary emissions should be explored. Understanding the economic/fiscal responsibility of regions could impact the final deployment strategy.
- Investigation on the impact of water use and pollution in CO₂ capture processes could impact factors included in the social perspective cost (SPC). Therefore, more research into these aspects is recommended since the number of plants implemented and their location could vary depending on these factors.
- Key recommendation is the inclusion of alternative decarbonization methods such as renewable energy and other sustainable process methods (e.g., wetland conservation and tree planting) since they would allow more specific locations for optimal plant deployment to be explored.

6.2.2. Recommendations for work relating to the biomass fly-ash derived adsorbent based carbon capture process

- Preliminary investigation of pre-treatment process alterations (reducing the acid to fly-ash ratio and water recycle) in section 4.2.3 resulted in cost reductions for the BCCS – P process. Further discussed in section 5.2.4, a key factor that impacts the process costs and *CRC* is the acid: fly-ash ratio in the acid washing step. Increased access to data which describes the adsorbents CO₂ capture kinetics for different biomass fly-ash sources is recommended since it would allow for more accurate reaction conversion results. Therefore, experiments that examine the impact of varying the acid to solid ratio on the produced adsorbents CO₂ capture kinetics for multiple biomass fly-ashes are necessary to validate model results and bring new insights to this model.
- As discussed in section 5.2.5, the kinetic model for Li₄SiO₄ may vary depending on pre-treatment conditions and the fly-ash sources used to synthesis this material. Testing of different biomass fly-ash sources is recommended since it may be useful for examining if there are other waste Si source that can be used for adsorbent production.
- Experimentation that investigates data on kinetic models for varying sources of industrial biomass fly-ash under different pre-treatment conditions need to be investigated and developed to further expand this model.
- Sections 4.1 and 4.2.2.1 discusses the assumptions made about the continuous approximation for the semi-batch system. This limits the expansion of this model when considering the dynamic aspects of the system. Development of models that account for more accurate sizing and dynamic conditions should be explored in the future as this will

allow for control implementation and introducing heat integration as discussed in these sections.

- The process flowsheets presented in this work were obtained from preliminary analysis, process heuristics, and similar plant designs reported in the literature. Process flowsheet optimization can be crucial to further improve the design and operation of these systems. While attempting the optimization of flowsheets using chemical engineering software such as Aspen Plus is time consuming and challenging, recent works in the literature have considered the generation of optimal process flowsheets like those discussed in this work using advanced hybrid optimization algorithms [139] and machine learning frameworks [140]. Hence, the application of those methodologies to explore novel and optimized process flowsheets for this emerging system is recommended.
- A life cycle analysis (LCA) is recommended for this system since they further support the potential sustainability of the process flowsheets presented in this work.

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Appendices

Appendix A – Review of the existing and emerging carbon capture technologies globally

The objective of carbon capture technologies is to prevent the release of CO₂ emitted from anthropological activities to the atmosphere by separating CO₂ or other carbon-containing molecules from the bulk stream in a process. Coal-based fuel and feed streams are often high in hydrocarbons because they have a high energy density; however, when they combust and release that energy, the reaction generates high amounts of CO₂ in the off gas. Since this is typically vented to the atmosphere, processes have been adapted to remove the carbon before the combustion has taken place in the feed stream, after combustion from the flue gas, or directly from the atmosphere. The following sections provide an overview of the main types of carbon capture technologies and the most recent advancements made in this field.

Pre-Combustion Capture

In pre-combustion carbon capture the CO₂ is separated from the initial fuel creating a product called synthesis gas, and the reformed fuel is utilized further for combustion while the separated CO₂ is collected [141]. One of the main applications of pre-combustion capture is in integrated gasification combined cycle (IGCC) power plants. There are still many countries (e.g., China and India) that rely on coal for the majority of their power generation; by incorporating pre-combustion carbon capture into the IGCC system, the high CO₂ emissions that result from burning coal can be further reduced [142][18]. One of the major challenges faced when attempting to implement pre-combustion capture is the system's poor ability to be retrofitted. The order of operations for pre-combustion capture requires fuel processing prior to combustion, which interrupts the process flow in existing infrastructure. This eliminates feasible retrofitting applications on processes that have high capital and operational costs [143].

More recently, there have been studies on incorporating pressure swing adsorption (PSA) units with pre-combustion capture. The positive attention for PSA is due to its low energy requirement resulting in highly desirable pre-combustion CO₂ capture conditions, as well as the ability to obtain high purity H₂, which increases profitability [144]. For instance, Moon et al [145] investigated the combination of PSA for hydrogen recovery in an IGCC pre-combustion plant, which resulted in the increase of hydrogen purity, recovery, and productivity; as a result, the process was far more profitable while maintaining a reduced level of CO₂ emissions [145]. Moreover, there has been continued investigation on the most effective solvents for removal through absorption and adsorption [146], with metal-organic frameworks (MOFs) gaining traction over recent decades as an adsorption technique. Since this technique (MOF adsorption) generally requires less energy, it has been an attractive area of investigation [125][147][148]. MOFs experience a decrease in their adsorption capacities at high temperatures. However, Hu et al. [125] showed that MOFs doped with nitrogen at lower temperatures (i.e., 25 °C), experience their highest adsorption capacity due to the high surface area and thermal stability [147]. The study was performed to improve the adsorption capacity for CO₂ in a post-combustion setting; however, adsorption separation techniques are very common in pre-combustion systems and could be applied in similar systems [147]. Cryogenic separation is an alternative separation technique that has been found suitable for gases containing more than 50% carbon, typical in pre-combustion carbon capture. This method involves a physical separation that depends on the boiling points and desublimation properties of the gases [147]. This process includes cooling the flue gas to −100 °C then −135 °C where the solid CO₂ is then removed and compressed, resulting in 90 – 95% recovery of CO₂ [147]. The energy required for this cryogenic technique

was reported to be 0.74 MJ/kgCO_2 , which is lower than the energy requirement for some absorption and standard oxy-fuel combustion technologies in carbon capture applications [9].

Post-Combustion Capture (PCC)

Post combustion carbon capture entails the removal of CO_2 from flue gas after the burning of fuels such as coal, oil, and natural gas. The three main forms of post combustion capture are solvent, sorbent, and membrane removal, with solvent based post combustion carbon capture currently being the most established and mature technology in the industry [19][11][9]. The regeneration process requires significant amounts of energy to power the reboiler resulting in a high operating cost as the main deterring factor for large scale implementation. However, the ability to retrofit PCC into existing plants and infrastructure makes the technology attractive to industrial emitters. The cost avoided with a retrofit design as opposed to a new build is extensive; thus, many companies investigate PCC options before considering alternative technologies [9].

There are consistent efforts to reduce energy consumption in the post-combustion process [11][9] and optimize the process through methods of process intensification [149]. There has been a continued focus on optimizing which solvent to use in PCC and investigation into a variety of different amine, eutectic, and ionic liquid solvents [150][151][68][152]. General consensus is that using MEA is standard practice; however, Sachde and Rochelle [153] found that aqueous piperazine provides the system with more optimal conditions such as lower energy consumption [153]. There have also been experimental and modelling results showing that certain eutectic and ionic liquids can highly outperform amine solvents [68][151]. In 2021, Li et al. reported protic ionic liquids with decreased viscosity during carbon capture resulted in faster adsorption rates than typical ionic liquids [154][147]. It has also been concluded that mixing MEA with ionic

liquids reduces the regeneration energy demand by at least 7% [155]. Along with solvent research, there has been increased interest in hybrid column membrane models in post-combustion applications. Atlaskin et al. [156] and Scholes et al. [157] found advantageous results when incorporating a hybrid membrane into a post-combustion capture system; this resulted in increased efficiency of ~8%, decreased energy consumption of $\sim 0.6 \frac{MJ}{kg \text{ of } CO_2}$, decreased cost, or a combination of these benefits.

A recent development for PCC is emerging in Norway involving the Klemetsrud waste-to-energy plant. In early 2022, the plant was granted additional funding that will allow them to add a solvent based post-combustion system to their process [158]. This new installation will make Klemetsrud the first net-negative incineration plant in the world, thereby demonstrating increased commercial-scale viability by having net negative impact instead of the typical goal of net-neutral CO₂ emissions [159].

In Canada there has been a surge in projects on simulating and testing different types of membranes and operating conditions to optimize the carbon capture process [143][18][11]. The Clean Energy Technologies Research Institute (CETRI) located at the University of Regina, previously known as the International Test Centre for CO₂ Capture is one of the main hubs for clean energy research in Canada [160]. CERTI's focus includes low-carbon and near-carbon-free research as well as zero-emission hydrogen [160]. One of the most recent advances made at the institute uses a patented catalysts-aided amine capture process with hot water instead of steam; this was found to drastically lower PCC costs [161][160].

Oxy-fuel Combustion

Oxy-fuel combustion is the process where fuel is combusted using a pure oxygen stream instead of an air stream. This results in a product gas that consists almost entirely of CO₂ and

water, from which a pure CO₂ stream can be obtained by dehydrating the gas mixture [162]. The typical high-energy complex process needed to separate the CO₂ from the other flue gas components is no longer a factor with this method; however, there is a high amount of energy ($\sim 180 \text{ kJ/kg}$) needed to produce the pure O₂ used as a reactant stream, which can be a deterrent [162]. The air separation unit (ASU) that separates the pure oxygen is the most energy intensive unit in this process and often the focus when investigating design improvements.

Modifications to this process are being implemented with the intention to improve efficiency and reduce costs. Pressurized oxy-fuel combustion analyzed by Soundararajan and Gundersen [163], Hong et al. [164], and Gopan et al [165] all showed an increase in power output and a reduction in auxiliary power consumption, concluding that this process offers an overall increase in efficiency between 2-3%. Chemical looping combustion (CLC) has also shown promise as an alternative decarbonization method. By using an oxygen carrier, the NO_x emissions are inherently reduced since the nitrogen from the air does not come in contact with the fuel during combustion, making separation of CO₂ far less energy intensive. Further investigation of CLC under varying operating conditions and using other oxygen carriers to determine if this results in better separation is also being done [166][167][148]. There has been development in the co-firing and gasification of coal and biomass in oxy-fuel fluidized bed reactors as an option for carbon capture applications [168]. Sher et al. [169] and Varol et al. [170] studied the co-firing of biomass blends in an oxy-fuel combustion plant using circulating fluidized bed (CFB) combustion to determine CO₂ composition in the flue gas. Similar studies have concluded that using this method can provide a possible alternative avenue to carbon capture, however the cost of these projects were not discussed and it is unclear if upscaling would be economically viable [168].

Direct Air Capture (DAC)

The main driving factor behind DAC is the removal of CO₂ that has already been emitted to the atmosphere; thus, there is a reversal of carbon pollution [171]. Air from the atmosphere can be collected often through the use of fans and processed through a variety of methods including: physical and chemical sorbents [172][173][174], membranes [173][175], alternatives such as electrolysis, calcium looping, and MOFs [173]. Through one of these separation techniques, the CO₂ is then isolated, compressed, and stored or utilized accordingly.

DAC is one of the most expensive capture techniques currently on the market due to the high energy demand required along with high capital costs. However, owing to its flexibility and ability to be used in virtually any location, there has been a surge of support for pilot-scale studies [55] and industrial implementation [176][173]. Both absorption and adsorption-based DAC for CO₂ are being examined, with both showing positive outlooks [177]. While absorption techniques often require high amounts of energy for heating during the regeneration stage, Zhu et al. [175] has proposed an absorption-based DAC cycle using organic salts and amino acids with regeneration temperatures significantly lower than the typical 800 °C [177][175]. By reducing the temperature needed to regenerate the solvent, the energy consumption is lowered, reducing the associated operating cost. DAC adsorption techniques require significantly lower regeneration temperatures compared to absorption, ranging from 80 – 120 °C [175]. However, the overall energy consumption required is still roughly three times higher than capturing directly from flue gas which allows for continued enhancement [175]. Other studies have focused on the use of membranes and electrochemical regeneration [173]; however, a significant amount of testing and development is needed to evaluate the technical feasibility of these technologies [175].

Additional CO₂ Capture Emerging Technologies

In addition to the most common carbon capture methods discussed above, there are many alternative methods that are being developed to advance decarbonization efforts. A recent review by Lefvert et al. [20] states that bioenergy with carbon capture and storage (BECCS) has led to a new framing of carbon capture in Sweden. BECCS uses biomass as a feedstock to produce energy, while also incorporating a mode of carbon capture into the process. Along with the need to reduce emissions from fossil fuels overall, the use of BECCS has the ability to produce negative CO₂ emissions and make more significant steps in reaching emission reduction goals [20]. Since the fuel source (biomass) is a previously existing carbon sink, using it to produce energy and capture the produced CO₂ results in net negative emissions. The integration of biomass into the carbon capture process through alternative forms is also being investigated. Through modification such as water and acid washing, biomass sources are being developed as adsorbents [178]. This has shown promising preliminary results as a possible alternative method due to the biomass' high adsorption capacity for CO₂ in lab scale testing; however, further investigation needs to be conducted on its scalability and ability to adapt to different feed stream conditions that may include varying impurities [178][85].

International Collaborations

Collective efforts have been initiated worldwide to reduce CO₂ emissions at a major scale. This can be seen through the support for projects such as the Northern Lights Project, an initiative that will occur across much of Europe led by Equinor, Total, and Shell. As the first ever cross-border CO₂ transport and storage network, this project involves the capture of CO₂ in several European countries and the transport of this CO₂ by ship to the coast of Norway. From Norway, it will be transported via pipeline to a platform in the North Sea, which will sequester the CO₂ over 100 kilometers down into saline aquifers [159][179]. The countries that are

involved in the project proposals as of 2022 are the United Kingdom, Norway, Netherlands, Northern France, Belgium, Denmark, and Sweden [159]. By fostering collaboration, the expectation is that more carbon capture projects will follow through to completion; while some countries lack storage locations, others are able to provide a viable solution whereby all parties are accountable for their own NDCs.

Norway also has an additional project named the Longship CCS Project [180], adjacent to Northern Lights. Using emissions captured from the Norcem cement factory [137] and Fortum Oslo Varme waste-to energy plant [181], they will have a capacity of 0.8 million tonnes of CO₂ per year allocated from the Northern Lights project for sequestration [137]. The types of technologies used to capture CO₂ for this project are not yet specified and will vary depending on company and country; however, Norway has stated that they have begun to investigate the use of DAC as one of many possible application [159].

There is a North American collaboration taking place with Svante and Carbon Engineering that will be further discussed in Chapter 3. To the authors' knowledge, the collaborations discussed above are the current major international collaborations; hence, there is a strong motivation to develop such collaborations to collectively reduce CO₂ emissions.

Appendix B – Supplemental information on the optimal deployment framework

B1. Model Parameters for Canada case studies

This model can be used to strategically allocate different carbon capture technologies to be implemented in different regions and sectors while minimizing the economic and social perspective costs. The following section includes the data used for the Canada case studies investigated for the carbon capture deployment optimization model. The tables list the index/parameter, and relevant units, the numerical values assigned in the model, and any of the associated sources. The complexity of the application is dependent on the size of the data initially input into the model. For example, the more technology types, regions, plant locations, and sectors, the larger the problem becomes and therefore the longer the model may take to converge.

It was determined that for the Canadian case studies, the plant location index i , had the largest impact on the problems complexity. Note that if this value is too small, the model may reach this boundary and it can limit the results (i.e., if i was chosen as 20, PCC plants in Alberta's oil and gas sector would have been restricted to only 20).

Table B1.1. The sets included in the optimization formulation.

P	PL	{PCC, PRE, OXY}
j	PT	{AB, BC, MB, NB, NL, NT, NS, NU, ON, PE, QC, SK, YT}
i	PN	{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47,

		48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80}
k	SE	{Electricity, Heavy Industry, Oil & Gas}

Table B1.2. The parameters included in the optimization formulation including parameter name, units, numerical value, and source for each value.

Parameter	Units	Value				Source
$E_{j,k}^*$	Mt CO ₂		<u>Electricity</u>	<u>Heavy Industry</u>	<u>Oil & Gas</u>	[31]
		<u>AB</u>	29.3	17.7	132.83	
		<u>BC</u>	0.25	5.53	12.77	
		<u>MB</u>	0.04	1.25	0.89	
		<u>NB</u>	2.91	0.55	3.36	
		<u>NL</u>	0.96	0.74	2.09	
		<u>NT</u>	0.00	0.28	0.06	
		<u>NS</u>	6.34	0.31	0.02	
		<u>NU</u>	0.00	0.03	0.00	
		<u>ON</u>	3.16	25.4	7.19	
		<u>PE</u>	0.00	0.01	0.00	
		<u>QC</u>	0.36	15.98	2.27	
		<u>SK</u>	12.61	3.98	17.32	
		<u>YT</u>	0.05	0.03	0.00	
C_p		{0.92, 0.94, 0.99}				[182] [183]

S	$\frac{\$CAD\ 2030}{tCO_2}$	294			[106] [184]
e_j	$\frac{M\$CAD\ 2030}{MW}$	<u>AB</u>	14.8204		[184]
		<u>BC</u>	11.2492		
		<u>MB</u>	8.8387		
		<u>NB</u>	11.3385		
		<u>NL</u>	12.3205		
		<u>NT</u>	34.1047		
		<u>NS</u>	15.2668		
		<u>NU</u>	33.4797		
		<u>ON</u>	11.6063		
		<u>PE</u>	15.5346		
		<u>QC</u>	6.5174		
		<u>SK</u>	16.1596		
		<u>YT</u>	16.6952		
T_j	[\$CAD 2030/tCO2]	<u>AB</u>	38.42		
		<u>BC</u>	30.81		
		<u>MB</u>	10.87		
		<u>NB</u>	6.42		
		<u>NL</u>	3.90		
		<u>NT</u>	0.79		
		<u>NS</u>	7.39		

		<u>NU</u>	0.79		
		<u>ON</u>	99.73		
		<u>PE</u>	1.03		
		<u>QC</u>	47.16		
		<u>SK</u>	15.02		
		<u>YT</u>	0.79		
B_p	MW	{70.30, 170.81, 228.58}			[181] [11] [182]
R_p	M\$CAD 2030	{92.81, 336.34, 210.62}			[109]
Y_p	yr	{15, 30, 25}			[185][186][109]
O_p	M\$CAD 2030	{69.82, 72.44, 45.43}			[109]
$targets_k$	Mt CO ₂	{14, 52, 110}			[6]
Ul	\$CAD 2030	100			[114]
x	Mt CO ₂				

B2: Analysis of Scaling Factor ω

Table B2.1. Initial sweep to find appropriate range for ω value.

ω	CCA	SPC	OBJ	Plant type
0.0001	27.563	751.91	27.638191	PCC
0.001	27.563	751.91	28.31491	PCC
0.01	28.658	448.302	33.14102	PCC

0.1	28.652	405.614	69.2134	PCC
1	28.652	405.614	434.266	PCC
10	47.706	397.734	4025.046	PCC, OXY
100	47.706	397.734	39821.106	PCC, OXY
1000	47.706	397.734	397781.706	PCC, OXY

Table B2.2. Narrowed search for specific ω value for Canadian case study applications.

ω	CCA	SPC	OBJ	Plant type
0.001	27.563	751.91	28.31491	PCC
0.005	27.657	725.775	31.286	PCC
0.0075	28.658	448.302	32.020	PCC
0.01	28.658	448.302	33.14102	PCC
0.05	28.651	405.614	48.932	PCC
0.1	28.652	405.614	69.2134	PCC
1	28.652	405.614	434.266	PCC
1.5	29.913	404.578	636.78	PCC, OXY
2	34.24	402.53	839.3	PCC, OXY

2.5	41.501	399.712	1040.781	PCC, OXY
2.75	46.706	397.734	1140.4745	PCC, OXY
5	46.706	397.734	2035.376	PCC, OXY
7.5	46.706	397.734	3029.711	PCC, OXY
10	47.706	397.734	4025.046	PCC, OXY
100	47.706	397.734	39821.106	PCC, OXY

B3: Example calculation for Alberta emissions reduction case study

Table B3.1. Example of newly calculated values for sensitivity analysis on reduction of Alberta's emissions.

Sector	Alberta 2020	Ratio of Canada's total emissions	Alberta's reduced emissions	Ratio of Canada's total emissions with reduction	Difference between the ratio's	New Target
Electricity	29.3	54.56%	14.65	43.65%	10.91%	12.47
Heavy industry	17.7	24.05%	8.85	19.24%	4.81%	49.50

Oil & Gas	132.83	72.43%	66.415	57.94%	14.49%	94.07
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Example Calculations for the Electricity Row

Ratio of Canada's total emissions:

$$\frac{\text{Alberta's Emissions 2020}}{\text{Canada's Total Emissions 2020}} = \frac{29.3 \text{ MtCO}_2}{53.7 \text{ MtCO}_2} \times 100\% = 54.56\%$$

Alberta's reduced emissions:

$$\text{Alberta's Emissions 2020} \times (1 - x\%) = 29.3 \text{ MtCO}_2 \times (1 - 0.2) = 14.65 \text{ MtCO}_2$$

Ratio of Canada's total emissions with reduction:

$$\frac{\text{Alberta's Emissions after reduction}}{\text{Canada's Total Emissions 2020}} = \frac{14.65 \text{ MtCO}_2}{53.7 \text{ MtCO}_2} \times 100\% = 43.65\%$$

Difference between the ratios:

$$\text{Ratio of total} - \text{Ratio of total with reduction} = 54.56\% - 43.65\% = 10.91\%$$

New target value:

$$\text{Basis target value} \times (1 - \text{difference}) = 14 \text{ MtCO}_2 - (1 - 0.1091) = 12.47 \text{ MtCO}_2$$

B4: Additional Results on the Sensitivity Analysis

Target Analysis

Table B4.1. Results of the 10% relaxation of the target constraints and the proposed carbon capture placement plan.

<u>Sector</u>	Province							Plants per Sector	Adjusted Targets [MtCO ₂]	GHG emitted [MtCO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	10		1	2	1		1	15	15.40	14.58
Heavy Industry	2	2			9	5		18	57.20	22.11
Oil & Gas	14	4	1		2			21	121.00	120.81
Plants per province	26	6	2	2	12	5	1	54	193.600	157.5
CCA[$\frac{\$}{tCO_2}$]	27.35									
SPC [$\frac{\$}{tCO_2}$]	690.142									
Economics [M\$CAD 2030]	61143.854									

Table B4.2. Results of the 15% relaxation of the target constraints and the proposed carbon capture placement plan.

<u>Sector</u>	Province							Plants per Sector	Adjusted Targets [MtCO ₂]	GHG emitted [MtCO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	10		1	2	1		1	15	16.10	14.58
Heavy Industry	1	2			9	5		17	59.80	24.87
Oil & Gas	12	4	1		2			19	126.50	126.33
Plants per province	23	6	2	2	12	5	1	51	202.400	165.78
CCA[$\frac{\$}{tCO_2}$]	27.196									
SPC [$\frac{\$}{tCO_2}$]	725.712									
Economics	57422.013									

Table B4.3. Results of the 10% tightening of the target constraints and the proposed carbon capture placement plan.

<u>Sector</u>	Province									
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	AB	BC	NB	NS	ON	QC	SK	Plants per Sector	Adjusted Targets [MtCO ₂]	GHG emitted [MtCO ₂]
Electricity	10		1	2	1		2	16	12.60	11.82
Heavy Industry		2			9	5		16	46.80	27.63
Oil & Gas	24	4	1		2			31	99.00	93.21
Plants per province	34	6	2	2	12	5	2	63	158.400	132.66
CCA [$\frac{\$}{tCO_2}$]	27.735									
SPC [$\frac{\$}{tCO_2}$]	603.758									
Economics [M\$CAD 2030]	72339.003									

Table B4.4. Results of the 5% tightening of the target constraints and the proposed carbon capture placement plan.

<u>Sector</u>	Province			
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	AB	BC	NB	NS	ON	QC	SK	Plants per Sector	Adjusted Targets [MtCO ₂]	GHG emitted [MtCO ₂]
Electricity	10		1	2	1		2	16	13.30	11.82
Heavy Industry	1	2			9	5		17	49.40	24.87
Oil & Gas	20	4	1		2			27	104.50	104.25
Plants per province	31	6	2	2	12	5	2	60	167.200	140.94
CCA [$\frac{\$}{tCO_2}$]	27.624									
SPC [$\frac{\$}{tCO_2}$]	629.673									
Economics [M\$CAD 2030]	68617.162									

Alberta's Emissions Analysis

Table B4.5. Results for plant location and new emissions levels from reducing Alberta's emissions 10%.

<u>Sector</u>	Province							AB's	Adjusted	GHG
	AB	BC	NB	NS	ON	QC	SK	Emissions Levels [MtCO ₂]	National Targets [MtCO ₂]	emitted by Canada [MtCO ₂]
Electricity	9		1	2	1		2	26.37	13.24	11.65
Heavy Industry		2			9	5		15.93	50.75	25.86
Oil & Gas	17	4	1		2			119.547	102.03	99.28
Plants per province	26	6	2	2	12	5	2	161.847	166.019	136.79
CCA [$\frac{\$}{tCO_2}$]	27.411									
SPC [$\frac{\$}{tCO_2}$]	644.383									
Economics [M\$CAD 2030]	62414.093									

Table B4.6. Results for plant location and new emissions levels from reducing Alberta's emissions 15%.

<u>Sector</u>	Province			
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	AB	BC	NB	NS	ON	QC	SK	AB's Emissions Levels [MtCO ₂]	Adjusted National Targets [MtCO ₂]	GHG emitted by Canada [MtCO ₂]
Electricity	9		1	2	1		2	24.91	12.85	10.19
Heavy Industry		2			9	5		15.05	50.12	24.98
Oil & Gas	16	4	1		2			112.91	98.05	95.4
Plants per province	25	6	2	2	12	5	2	152.856	161.028	130.57
CCA [$\frac{\$}{tCO_2}$]	27.363									
SPC [$\frac{\$}{tCO_2}$]	637.029									
Economics [M\$CAD 2030]	61173.479									

Table B4.7. Results for plant location and new emissions levels from reducing Alberta's emissions 20%.

Sector	Province			
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	AB	BC	NB	NS	ON	QC	SK	AB's Emissions Levels [MtCO ₂]	Adjusted National Targets [MtCO ₂]	GHG emitted by Canada [MtCO ₂]
Electricity	8		1	2	1		2	23.44	12.47	11.48
Heavy Industry		2			9	5		14.16	49.50	24.09
Oil & Gas	15	4	1		2			106.26	94.07	91.51
Plants per province	23	6	2	2	12	5	2	143.864	156.037	127.08
CCA [$\frac{\$}{tCO_2}$]	27.263									
SPC [$\frac{\$}{tCO_2}$]	639.776									
Economics [M\$CAD 2030]	58692.252									

CASE 4 – Land Restrictions

Table B4.8. Results when $L2$ is set to 18 ($j = AB$) which was the minimum number of plants required in Alberta to return a feasible solution.

<u>Sector</u>	Province															Plants per Sector	National Targets [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB			BC		NB		NS		ON		QC		SK				
	PCC	PRE	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY			
Electricity	5		2			1		2			1			4		15	14	13.95
Heavy Industry				2						9		5		1		17	52	24.87
Oil & Gas	5	1	5		4		1				2			6		24	110	109.95
<u>Plants per province</u>	18			6		2		2		12		5		11		56	176	148.77
CCA [$\frac{\$}{tCO_2}$]	41.589																	
SPC [$\frac{\$}{tCO_2}$]	664.501																	
Economics	98421.867																	

[M\$CAD 2030]	
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Table B4.9. Results when $L3$ is set to 0 ($j = ON$) showing there are no mandatory plants required in Ontario to meet the national emissions targets.

<u>Sector</u>	Province							Plants per Sector	National Targets [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	10		1	2			3	16	14	11.82
Heavy Industry	1	2				5		8	52	49.71
Oil & Gas	20	4	1					25	110	109.77
<u>Plants per province</u>	31	6	2	2	0	5	3	49	176.000	171.3
CCA [$\frac{\$}{tCO_2}$]	27.446									
SPC [$\frac{\$}{tCO_2}$]	751.845									
Economics [M\$CAD 2030]	55676.914									

CASE 5 – Sensitivity analysis on ω

Table B4.10. Results when ω is set to 1.

<u>Sector</u>	Province							Plants per Sector	Target [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB	BC	NB	NS	ON	QC	SK			
Electricity	10		1	2	1		4	18	14	6.3
Heavy Industry	6	2			9	5	1	23	52	8.31
Oil & Gas	48	4	1		2		6	61	110	10.44
<u>Total Count</u>	64	6	2	2	12	5	11	102	176	25.05
CCA [$\frac{\$}{tCO_2}$]	28.652									
SPC [$\frac{\$}{tCO_2}$]	405.614									
Economics [M\$CAD 2030]	126465.1287									

Table B4.11. Result when ω is set to 1.5.

	<u>Sector</u>	Province							Sector Totals	Target [Mt CO ₂]	GHG emitted [Mt CO ₂]
		AB	BC	NB	NS	ON	QC	SK			
PCC	Electricity	10		1	2	1		4	Electricity	14	6.3
	Heavy Industry	6	2			9		1			
	Oil & Gas	48	4	1		2		6	Heavy Industry	52	7.26
OXY	Electricity								Industry		
	Heavy Industry						5		Oil & Gas		
	Oil & Gas										
<u>Total Count</u>		64	6	2	2	12	5	11	102	176	24
CCA [$\frac{\$}{tCO_2}$]		29.913									
SPC [$\frac{\$}{tCO_2}$]		404.578									

Economics	126788.2618
[M\$CAD 2030]	

Table B4.12. Results when ω is set to 1 and Pu is set to 54 for the -15% targets scenario.

Sector	Province												Adjusted Targets [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB		BC		NB		NS	ON		QC	SK			
	PCC	OXY	PCC	OXY	PCC	OXY	OXY	PCC	OXY	OXY	PCC	OXY		
Electricity		9			1		2		1		1	1	11.90	11.85
Heavy Industry			2					3		5			44.20	43.14
Oil & Gas	3	19		4		1			2				93.50	93.3
Plants per province	31		6		2		2	6		5	2		149.600	148.3
CCA [$\frac{\$}{tCO_2}$]	67.278													
SPC [$\frac{\$}{tCO_2}$]	657.316													
Economics [M\$CAD 2030]	159732.342													

Table B4.13. Results when ω is set to 1 and Pu is set to 54 for the -10% targets scenario.

Sector	Province														Adjusted Targets [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB		BC		NB		NS		ON		QC		SK			
	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y		
Electricity	10				1		2		1				2		12.60	11.82
Heavy Industry			2						2			5			46.80	45.9
Oil & Gas	22		4		1				2						99.00	98.76
Total Count	32		6		2		2		5		5		2		158.400	156.5
CCA [$\frac{\$}{tCO_2}$]	29.923															
SPC [$\frac{\$}{tCO_2}$]	686.26															
Economics [M\$CAD 2030]	67366.98															

Table B4.14. Results when ω is set to 1 and Pu is set to 54 for the -5% targets scenario.

Sector	Province														Adjusted Targets [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB		BC		NB		NS		ON		QC		SK			
	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y	PC C	OX Y		
Electricity	10				1		2		1				2		13.30	11.82
Heavy Industry			2						4			5			49.40	40.38
Oil & Gas	20		4		1				2						104.50	104.28
Total Count	30		6		2		2		7		5		2		167.200	156.48
CCA [$\frac{\$}{tCO_2}$]	29.873															
SPC [$\frac{\$}{tCO_2}$]	686.26															
Economics [M\$CAD 2030]	67254.167															

Table B4.15. Results when ω is set to 1 and Pu is set to 54 for the 5% targets scenario.

<u>Sector</u>	Province							Adjusted	GHG
	AB	BC	NB	NS	ON	QC	SK	Targets	emitted

	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	[Mt CO ₂]	[Mt CO ₂]
Electricity	10				1		2		1				1		14.70	14.58
Heavy Industry			2						9				5		54.60	26.58
Oil & Gas	16		4		1				2						115.50	115.3
<u>Total Count</u>	26		6		2		2		12		5		1		184.800	156.5
CCA [$\frac{\$}{tCO_2}$]	29.734															
SPC [$\frac{\$}{tCO_2}$]	686.26															
Economics [M\$CAD 2030]	66942.509															

Table B4.16. Results when ω is set to 1 and Pu is set to 54 for the 10% targets scenario.

<u>Sector</u>	Province														Adjusted Targets [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB		BC		NB		NS		ON		QC		SK			
	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY		
Electricity	10				1		2		1				1		15.40	14.58

Heavy Industry	2		2						9			5			57.20	21.06
Oil & Gas	14		4		1				2						121.00	120.8
Total Count	26		6		2		2		12		5		1		193.600	156.5
CCA [$\frac{\$}{tCO_2}$]	29.734															
SPC [$\frac{\$}{tCO_2}$]	686.26															
Economics [M\$CAD 2030]	66942.509															

Table B4.17. Results when ω is set to 1 and Pu is set to 54 for the 15% targets scenario.

<u>Sector</u>	Province														Adjusted Targets [Mt CO ₂]	GHG emitted [Mt CO ₂]
	AB		BC		NB		NS		ON		QC		SK			
	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY	PCC	OXY		
Electricity	10				1		2		1				1		16.10	14.58
Heavy Industry	4		2						9			5			59.80	15.54
Oil & Gas	12		4		1				2						126.50	126.4

<u>Total Count</u>	26	6	2	2	12	5	1	202.400	156.5
CCA [$\frac{\$}{tCO_2}$]	29.734								
SPC [$\frac{\$}{tCO_2}$]	686.26								
Economics [M\$CAD 2030]	66942.509								

B5: Cancelled Canadian CCS project

Nauticol Energy began a project to produce net zero methanol, which included a carbon capture facility in the process design. Unlike the previous projects, Grande Prairie's goal was to have a pre-combustion carbon capture system [187]. The Grande Prairie Project was to be located in Grande Prairie, Alberta, which is an attractive location because of the existing infrastructure and proximity to the natural gas supply [187]. It is also located close to nearby underground water reservoirs, which will be used as the sequestration sites of the captured CO₂ [187].

The project was estimated to cost \$4 *billion* and produce 3.4 *Mt* of blue methanol. Due to previous parties withdrawing funding, the project was cancelled in February of 2023 [127]. A final report on the reasons for cancelling the project has not yet been released; however, there was an ongoing feasibility study taking place, and it is likely that the cost of the project was valued as overly expensive.

Appendix C – Supplemental information on the biomass fly-ash adsorbent based CO₂ capture model

C1: Modelling details for $k_r(T)$ function

Experimental results for regeneration from Yang et al. [84] were only found at one temperature, so to further understand the behaviour of the kinetics relationship to temperature, other studies need to be examined. Hernández et al. [86] performed a study examining the desorption behaviour of the Li₄SiO₄ – CO₂ reaction. This study as well as other experimental work, have found that this reaction can be described as a linear reaction, and the reaction kinetic constant can be found from results displayed in Figure C1.1 by finding the slope each line. Model fitting was used to define the relationship between each of the $\hat{k}_r$ values from Hernández et al.'s work (column 4 of Table C1.1). However, because this model was developed from results which used a different fly-ash source and did not undergo the same pre-treatment or synthesis process, it did not accurately represent the regeneration kinetics found in Yang et al. [84]. Therefore, this relationship was multiplied by a scaling factor of δ (16.0947) to account for this difference. The scaling factor was determined by comparing the $\hat{k}$ at 750 °C from Hernández et al. [86] and Yang et al. [84]. The resulting model is displayed in equation 31 of the main text. The $\hat{k}$ values determined by each model iteration are compared to the experimental results and are shown in Table C1.1.

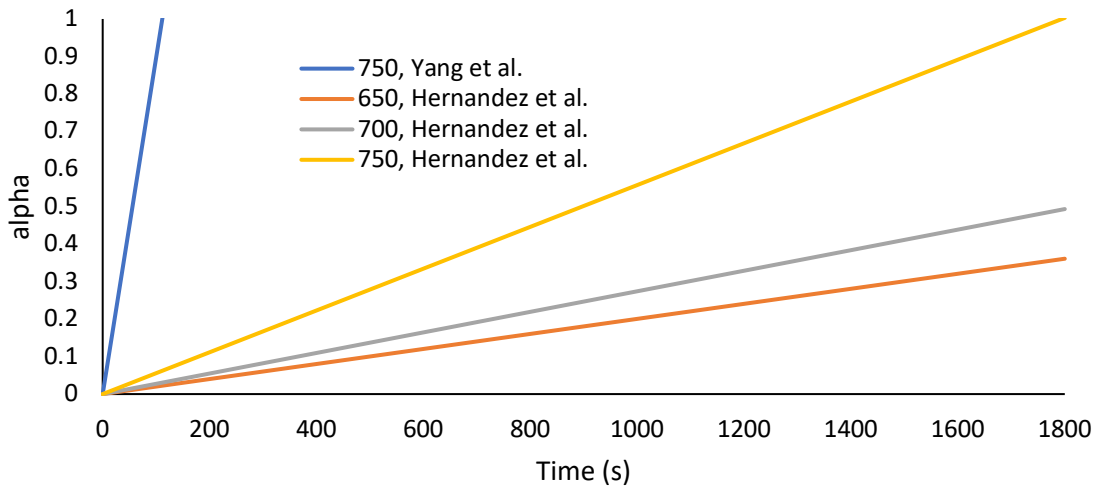


Figure C1.1: Desorption of CO₂ from Li₄SiO₄ from two different fly-ash sources [84][86].

Table C1.1: Experimental k values found and compared to model predicted k values found through systemic trial and error fitting of a quadratic $k_r(T)$ model.

Temperature [°C]	k (Hernandez et al.) [s^{-1}]	k (Yang et al.) [s^{-1}]	k_r model predicted value ($\delta = 1$)	k_r model predicted value ($\delta = 16.0947$)
650	0.00020049		0.000200318	0.00322406
700	0.00027403		0.000273834	0.00440728
750	0.00055718	0.0089667	0.000556955	0.00896402

C2: ASPEN Plus implementation- variable values and details

A description of how each of the blocks in Aspen Plus were implemented is included in Table C2.1. The unit shown in Figure 11 along with its Aspen Plus block type and any specific details necessary are outlined here.

The kinetic equations were incorporated into calculator blocks C2 (adsorption equations, 23-28) and C3 (regeneration equations, 29-31) so the mass balance can be recalculated appropriately. For the calculator blocks, the masses of each component were defined as import or export variables if it was an inlet or outlet stream of the adsorption/regeneration, respectively. Tables C2.2 and C2.3 outlines the variables, stream, component, and variable type used in C2 or C3. Aspen Plus's default settings allow for calculator blocks to be executed in unison; however, this results in incorrect mass balances since the outlet to the adsorber changes prior to the regeneration happening. To avoid this, a sequencing order was implemented so each block would begin once the previous had been completed. The sequence is as follows: T1, C4, ADS, ADSRXN, C2, REGENRXN, C3, REGEN, SEP, T2, C4. Each unit is as labeled in Figure 11. Table C2.4 shows the design parameters reported in Yang et al. [84] and have been used in ASPEN Plus to execute the validation of this model.

Table C2.1. Unit operation block implementations in Aspen Plus model.

Label	Aspen Plus Block Type	Details
Acid Wash	SWash	40:1 liquid to solid ratio
Water Wash	SWash	40:1 liquid to solid ratio

Dryer	Dryer	80 °C
Solid Reactor	RStoich	Synthesis reaction (23) specified with conversion of 100% SiO ₂ Temperature of 95 °C Calcification (baking) assumed to elapse for 4 hours post synthesis reaction completion
Grind & Sifter	Sep	Assume electric utility (discussed in section 4.2.2) Stream split specification (100% Li ₄ SiO ₄ goes to capture process, remaining goes to WASTE SOLID)
ADS	Sep	100% CO ₂ and Li ₄ SiO ₄ split to RICH Remaining components to VENTGAS
ADSRXN	RStoich	Reaction 1 specified and results overwritten by C2 calculator Temperature of 650 °C and pressure of 1.01 bar
REGENRXN	RStoich	Reaction 2 specified and results overwritten by C3 calculator Temperature of 750 °C and pressure of 1.01 bar
REGEN	Sep	100% CO ₂ sent to CO ₂ stream Remaining solids sent to RECYCLE
SEP	Split	Separates unregenerated sorbent with regenerated 100% Li ₄ SiO ₄ goes to R2

Table C2.2 Details on calculator block C2 variable implementation

C2			
Variable	Stream	Component	Type
m_1	RICH	Li ₄ SiO ₄	Import
$\eta_{i,CO_2} \cdot M_{CO_2}$	FLUEGAS	CO ₂	import
$m_{Li_2SiO_3}$	RICH1	Li ₂ SiO ₃	export
$m_{Li_2CO_3}$	RICH1	Li ₂ CO ₃	export
m_{CO_2}	RICH1	CO ₂	export

$m_{Li_4SiO_4}$	RICH1	Li_4SiO_4	export
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Table C2.3. Details on calculator block C3 variable implementation

C3			
Variable	Stream	Component	Type
m_{i,Li_2SiO_3}	RICH1	Li_2SiO_3	import
m_{i,Li_2CO_3}	RICH1	Li_2CO_3	import
m_{CO_2}	RICH1	CO_2	import
$m_{Li_4SiO_4}$	RICH1	Li_4SiO_4	import
m_{t,Li_4SiO_4}	RICH3	Li_4SiO_4	export
m_{t,CO_2}	RICH3	CO_2	export
$m_{Li_2SiO_3}$	RICH3	Li_2SiO_3	export
$m_{Li_2CO_3}$	RICH3	Li_2CO_3	export
T	REGENRXN		import

Table C2.4. Design parameters determined through experimental work in Yang et. al and used in the Aspen Plus model.

Parameter	Value
Temperature [°C]	650
Pressure [atm]	1
Mass of Li_4SiO_4 [g]	0.01
Volume of gas [L]	0.1
% CO_2 [mol. %]	0.15
k [s^{-1}]	1.01×10^{-6}
Reaction time [s]	1800
m_o [g/g]	0.367
Z [g/g]	0.5

C3: Energy analysis and comparison breakdown

This section includes a detailed breakdown of the energy analysis and comparison done between two MEA PCC processes and the BCCS and BCCS – P processes. Table C3.1 outlines the different flowrates, operating conditions, and other relevant plant details for each of the processes. Table C3.2 shows the detailed energy requirements of each section in the processes, how much CO₂ was captured by each process, the Q_T value for each process, and how much the BCCS and BCCS – P processes reduce energy consumption.

Table C3.1. Process specifications for compared MEA PCC and biomass adsorbent processes. The amine-based (MEA) PCC process details are enclosed in Nittaya et al. [126] and Montanes et al. [188].

Parameter	(Nittaya et al.)	(Montanes et al.)	Biomass Based Energy Consumption	
	PCC	PCC	BCCS	BCCS - P
Column size [m ³]	3.54	42.47	0.79	0.79
Flue gas composition [mol. %]	0.18	0.12	0.15	0.15
Flue gas flowrate [kmol/hr]	4.1	714	5.4	5.4
Flue gas temperature [°C]	46.5	-	650	650
Flue gas pressure [bar]	1.01	-	1.01	1.01

Table C3.2. Energy analysis and comparison between two different amine-based (MEA) PCC pilot plant processes (Nittaya et al. [126] and Montanes et al. [188]) and the biomass-based models with and without pre-treatment presented in chapter 4 section 4.2.

Process Unit	(Nittaya at al.) [kW]	(Montanes et al.) [kW]	Biomass Based Energy Consumption [kW]	
	PCC	PCC	BCCS	BCCS – P
Regeneration (reboiler / steam heat)	3686.4	80760	4461.768	4433.76
Condenser (regen)	206.4			

Buffer tank (absorber)	3943.2	124368		
Heat exchanger		248592		
Adsorber Cooling			3959.82	2751.0228
Dryer (pre-treatment)				4.35
Grind & Sifter (pre)			5.6	5.6
TOTAL	7836	453720	8427.188	7194.7328
Delta Q [kW]			507.548	1692.6872
CO2 captured [kg/h]	2775.792	82080	1200.8304	1284.1524
Energy Usage [kWh/kgCO2]	2.823	5.528	7.018	5.603
Energy Usage [MJ/kgCO2]	10.163	19.900	25.264	20.170
ΔQ_T [MJ/kg]			1.522	4.745
Reboiler [MJ/kgCO2]	4.781	3.542	13.376	12.430
% change from PCC	0.00%	0.00%	Nittaya	Nord
			-85.03%	-92.35%
			Nittaya	Nord
			-53.31%	-76.15%

The equations used to determine the above values and example calculations can be found in equations C3.1 – C3.3. The total energy (row TOTAL in Table C3.2) in kW is found by added the energy requirements from each of the process units whereas the amount of CO₂ captured was taken directly from the Nittaya et al. and Montanes et al. The energy usage was determined by dividing these two values as seen in the following example which shows the calculation for the PCC example from Nittaya et al. [126]. The ΔQ_T is the estimated energy required by the system if 100% heat integration were to be introduced.

$$Total = \sum_i Q_i = 153.6 \text{ kW} + 8.6 \text{ kW} + 164.3 \text{ kW} = 326.5 \quad (\text{C3.1})$$

$$Energy \text{ Usage} = \frac{\sum_i Q_i}{m_{CO_2, captured}} = \frac{24 \text{ hours of operation (326.5 kW)}}{24 \text{ hours (115.658 } \frac{kgCO_2}{hour})} = 2.823 \frac{kWh}{kgCO_2} \quad (\text{C3.2})$$

$$\Delta Q_T = \frac{Q_{regeneration} - Q_{adsorption}}{m_{CO_2, captured}} = \frac{4461.768 \text{ kW} - 3959.82 \text{ kW}}{1200.83 \text{ kgCO}_2 \text{ in 24 hours}} \times 3.6 \frac{\text{MJ}}{\text{kW}} = 1.522 \frac{\text{MJ}}{\text{kgCO}_2} \quad (\text{C3.3})$$

C4: Case study results

Case 1: Variation on adsorbent mass and composition of CO₂ in flue gas

The tables below (C4.1-C4.4) outline the resulting changes in the amount of adsorbent present post adsorption and regeneration when varying both the initial mass of adsorbent and composition of CO₂ in the flue gas. Tables C4.5-C4.7 show the variation in energy consumption from the ADSRXN, REGENRXN, and DRYER units of the model.

Table C4.1: Results from BCCS of adsorbent remaining post regeneration (%Li₄SiO₄RR) when varying the mass of adsorbent and CO₂ composition in the flue gas.

% Li ₄ SiO ₄ regenerated		% CO ₂ in flue gas [mol. %]					
		0.08	0.1	0.125	0.15	0.175	0.2
Mass of adsorbent [g]	120	97.08%	96.35%	95.44%	94.53%	93.87%	93.87%
	110	96.82%	96.02%	95.02%	94.03%	93.87%	93.87%
	105	96.66%	95.83%	94.79%	93.87%	93.87%	93.87%
	100	96.50%	95.62%	94.53%	93.87%	93.87%	93.87%
	95	96.31%	95.39%	94.24%	93.87%	93.87%	93.87%
	90	96.11%	95.13%	93.92%	93.87%	93.87%	93.87%
	80	95.62%	94.53%	93.87%	93.87%	93.87%	93.87%

Table C4.2: Results from BCCS of adsorbent remaining post adsorption (%Li₄SiO₄RA) when varying the mass of adsorbent and CO₂ composition in the flue gas.

% Li ₄ SiO ₄ converted		% CO ₂ in flue gas [mol. %]					
		0.08	0.1	0.125	0.15	0.175	0.2
Mass of adsorbent	120	56.91%	46.13%	32.67%	19.20%	9.51%	9.51%
	110	52.99%	41.24%	26.55%	11.85%	9.51%	9.51%

[g]	105	50.75%	38.44%	23.05%	9.51%	9.51%	9.51%
	100	48.29%	35.36%	19.20%	9.51%	9.51%	9.51%
	95	45.57%	31.96%	14.95%	9.51%	9.51%	9.51%
	90	42.54%	28.18%	10.22%	9.51%	9.51%	9.51%
	80	35.36%	19.20%	9.51%	9.51%	9.51%	9.51%

Table C4.3: Results from BCCS – P of adsorbent remaining post regeneration (% Li_4SiO_4RR) when varying the mass of adsorbent and CO₂ composition in the flue gas.

% Li_4SiO_4 regenerated		% CO ₂ in flue gas [mol. %]							
		0.08	0.1	0.125	0.15	0.16	0.175	0.185	0.2
Mass of adsorbent [g]	122.25	97.13%	96.42%	95.52%	94.63%	94.27%	93.73%	93.54%	93.54%
	108.67	96.78%	95.97%	94.96%	93.95%	93.55%	93.54%	93.54%	93.54%
	103.23	96.61%	95.76%	94.70%	93.64%	93.54%	93.54%	93.54%	93.54%
	97.80	93.23%	93.23%	93.23%	89.66%	84.05%	76.85%	72.70%	67.24%
	92.37	96.21%	95.26%	93.86%	93.54%	93.54%	93.54%	93.54%	93.54%
	86.93	95.97%	94.96%	93.70%	93.54%	93.54%	93.54%	93.54%	93.54%
	81.50	95.70%	94.63%	93.54%	93.54%	93.54%	93.54%	93.54%	93.54%

Table C4.4: Results from BCCS – P of adsorbent remaining post adsorption (% Li_4SiO_4RA) when varying the mass of adsorbent and CO₂ composition in the flue gas.

% Li_4SiO_4 converted		% CO ₂ in flue gas [mol. %]							
		0.08	0.1	0.125	0.15	0.16	0.175	0.185	0.2
Mass of adsorbent [g]	122.25	57.70%	47.12%	33.91%	20.69%	15.40%	7.47%	4.65%	4.65%
	108.67	52.41%	40.51%	25.64%	10.77%	4.82%	4.65%	4.65%	4.65%
	103.23	49.91%	37.38%	21.73%	6.08%	4.65%	4.65%	4.65%	4.65%
	97.80	47.12%	33.91%	17.38%	4.65%	4.65%	4.65%	4.65%	4.65%

	92.37	44.01%	30.02%	12.52%	4.65%	4.65%	4.65%	4.65%	4.65%
	86.93	40.52%	25.64%	7.05%	4.65%	4.65%	4.65%	4.65%	4.65%
	81.50	36.55%	20.69%	4.65%	4.65%	4.65%	4.65%	4.65%	4.65%

Table C4.5: Cooling and heat duty required for the adsorption and regeneration of the BCCS process respectively.

Energy consumption [kW]			Mass of adsorbent [g]						
			120	110	105	100	95	90	80
% CO ₂ in flue gas [mol. %]	ADS	0.08	58.6636	58.6636	58.6636	58.6636	58.6636	58.6636	58.6636
		0.1	73.3297	73.3297	73.3297	73.3297	73.3297	73.3297	73.3297
		0.125	91.6625	91.6625	91.6625	91.6625	91.6625	91.6625	90.7496
		0.15	109.995	109.995	109.995	109.995	107.765	102.093	90.7496
		0.175	128.329	124.781	119.109	113.437	107.765	102.093	90.7496
		0.2	136.124	124.781	119.109	113.437	107.765	102.093	90.7496
	REGEN	0.08	81.2958	79.6038	78.7578	77.9118	77.0658	76.2197	74.5276
		0.1	96.544	94.8519	94.0058	93.1598	92.3137	91.4677	89.7755
		0.125	115.604	113.912	113.066	112.22	111.374	110.528	99.2953
		0.15	134.664	132.972	129.917	123.938	117.958	111.979	100.02
		0.175	148.581	136.622	130.642	124.663	118.683	112.704	100.745
		0.2	149.305	137.347	131.367	125.388	119.409	113.429	101.47

Table C4.6: Cooling and heat duty required for the adsorption and regeneration of the BCCS – P process, respectively.

Energy consumption [kW]			Fly-ash flow rate [mol/s]						
			1.528	1.289	1.333	1.278	1.222	1.167	1.111
	ADS	0.08	20.4218	25.027	26.9184	28.8332	30.7676	32.7173	34.6773

%CO ₂ in flue gas [mol. %]		0.1	34.3147	38.9283	40.8252	42.7469	44.6898	46.6496	48.6218
		0.125	51.6931	56.3178	58.2218	60.1524	62.106	64.0787	66.0662
		0.15	69.085	73.7214	75.6327	77.5723	74.3254	70.1572	66.0061
		0.16	76.0454	80.6867	82.3754	78.1246	73.9796	69.8167	65.6717
		0.175	86.49	86.0838	81.8486	77.6435	72.4652	69.3102	65.1746
		0.185	93.4557	85.7323	81.5002	77.2988	73.125	68.9754	64.846
		0.2	95.9324	85.2089	80.9815	76.7858	72.6188	68.4772	64.3573
	REGEN	0.08	81.5962	79.2979	78.3786	77.4593	76.5399	75.6206	74.7012
		0.1	96.8243	94.526	93.6066	92.6873	91.7679	90.8485	89.9291
		0.125	115.859	113.561	112.642	111.722	110.803	0	105.462
		0.15	119.77	132.59	131.677	126.554	119.77	112.98	106.189
		0.16	142.509	140.21	133.633	126.845	120.057	113.269	106.48
		0.175	153.93	140.858	134.07	127.282	120.493	113.705	106.917
		0.185	158.12	141.149	134.361	127.573	120.784	113.996	107.208
		0.2	158.556	141.586	124.797	128.009	121.221	0	107.644

Table C4.7: Energy requirement of the dryer in the pre-treatment section of the BCCS – P process.

Fly-ash Flow Rate [$\frac{mol}{s}$]	Energy Consumption [kW]
1.528	5.60072
1.289	4.97842
1.333	4.7295
1.278	4.48058
1.222	4.23166

1.167	3.98274
1.111	3.73381

Case 2: Sensitivity analysis on R'

The results below outline the changes seen in adsorbent remaining post adsorption and regeneration when a sensitivity analysis was performed on R' . The figures show % Li_4SiO_4RA and % Li_4SiO_4RR when varying the flue gas to adsorbent ratio.

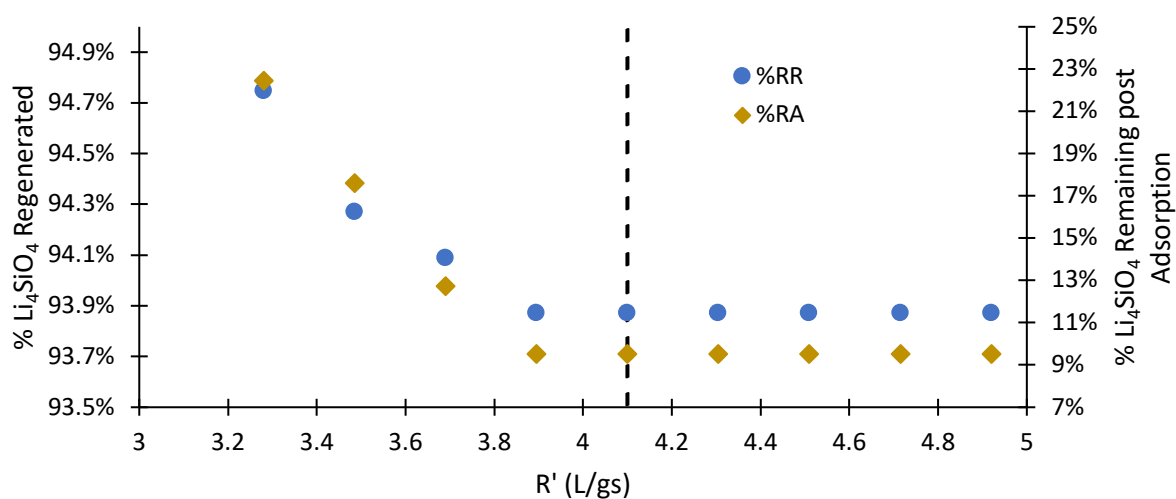


Figure C4.1: Results from BCCS of adsorbent remaining post adsorption (% Li_4SiO_4RA) and adsorbent remaining post regeneration (% Li_4SiO_4RR) when varying the flue gas to mass of adsorbent ratio.

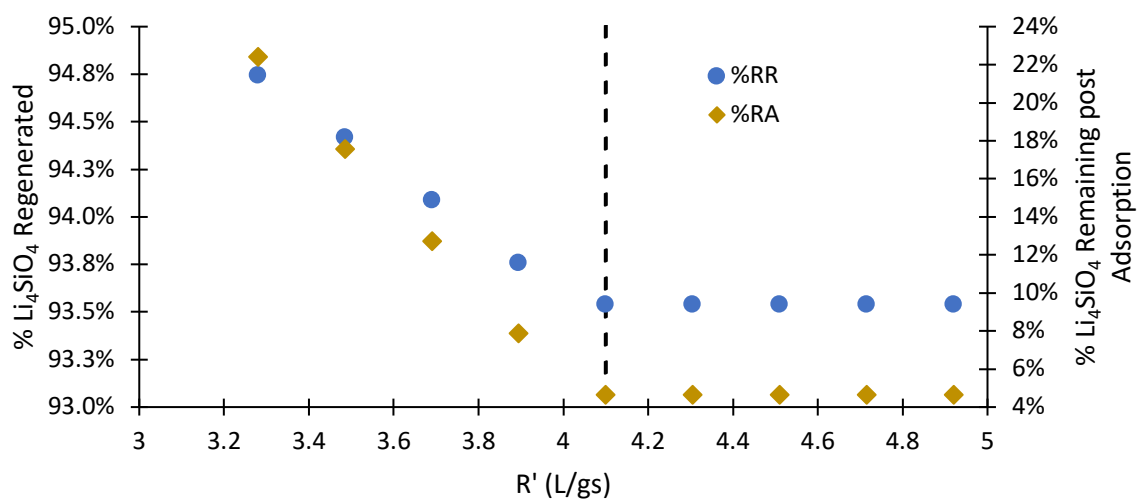


Figure C4.2: Results from BCCS – P of adsorbent remaining post adsorption ($\%Li_4SiO_4RA$) and adsorbent remaining post regeneration ($\%Li_4SiO_4RR$) when varying the flue gas to mass of adsorbent ratio.

Case 4: Sensitivity on initial mass of adsorbent

The results below show the outcome of running a sensitivity analysis on the initial mass of adsorbent introduced into the system. The figures below show the percentage of CO_2 captured, as well as the adsorbent conversion and regeneration in the adsorption and regeneration sections.

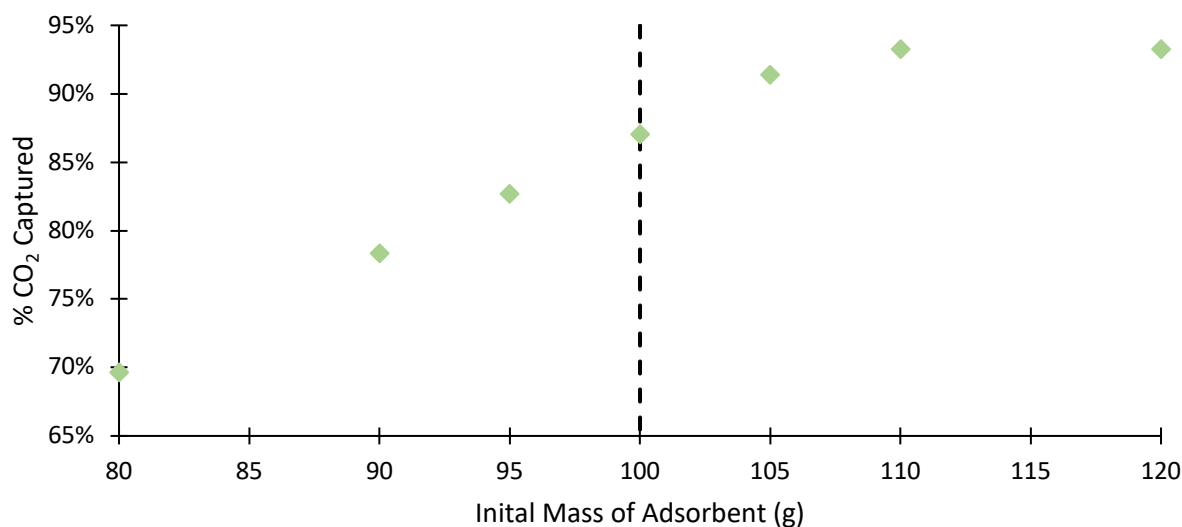


Figure C4.3: Results of BCCS when varying initial mass of adsorbent and the resulting $\%CO_2$.

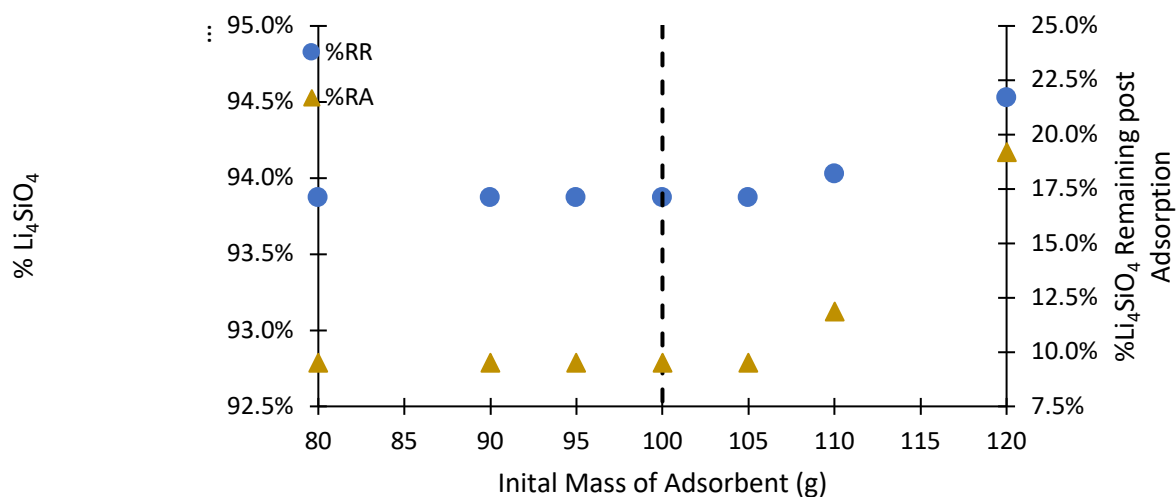


Figure C4.4. Results from BCCS of adsorbent remaining post adsorption ($\%Li_4SiO_4RA$) and adsorbent remaining post regeneration ($\%Li_4SiO_4RR$) when varying the mass of adsorbent.

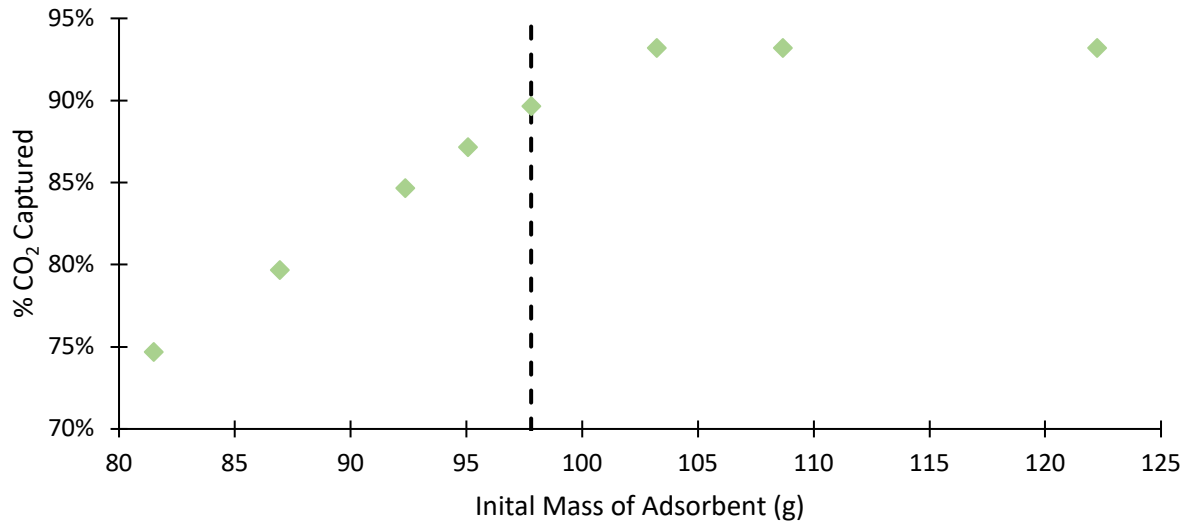


Figure C4.5. Results of BCCS – P when varying initial mass of adsorbent and the resulting $\%CO_2$.

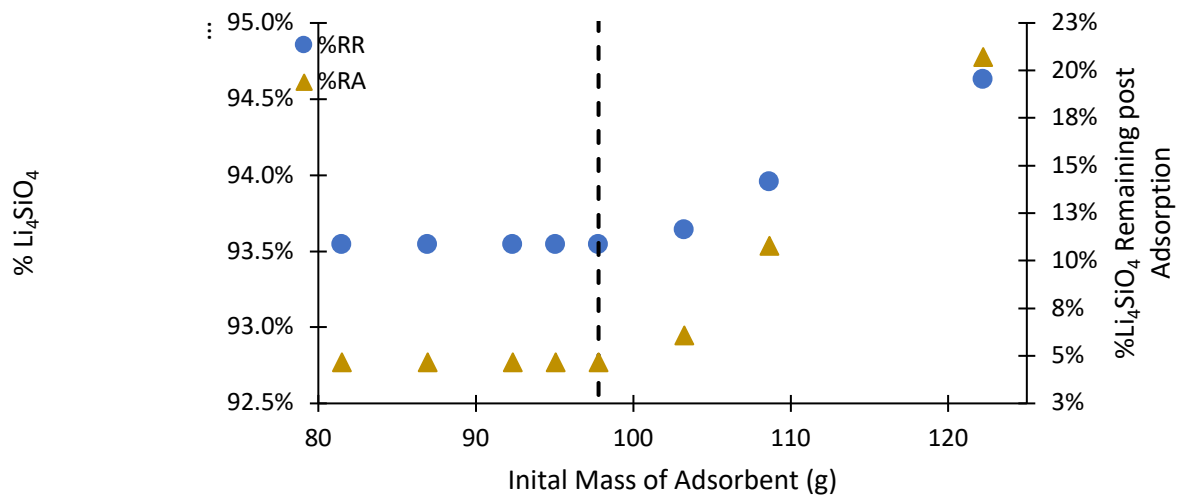


Figure C4.6: Results from BCCS – P of adsorbent remaining post adsorption ($\%Li_4SiO_4RA$) and adsorbent remaining post regeneration ($\%Li_4SiO_4RR$) when varying the mass of adsorbent.

Case 5: Sensitivity on CO₂ composition in flue gas

This section presents the results collected when executing a sensitivity analysis on the composition of CO_2 in the flue gas. Included are the results for CO_2 captured ($\%\text{CO}_2$), adsorbent post adsorption ($\%\text{Li}_4\text{SiO}_4\text{RA}$), and adsorbent post regeneration ($\%\text{Li}_4\text{SiO}_4\text{RR}$).

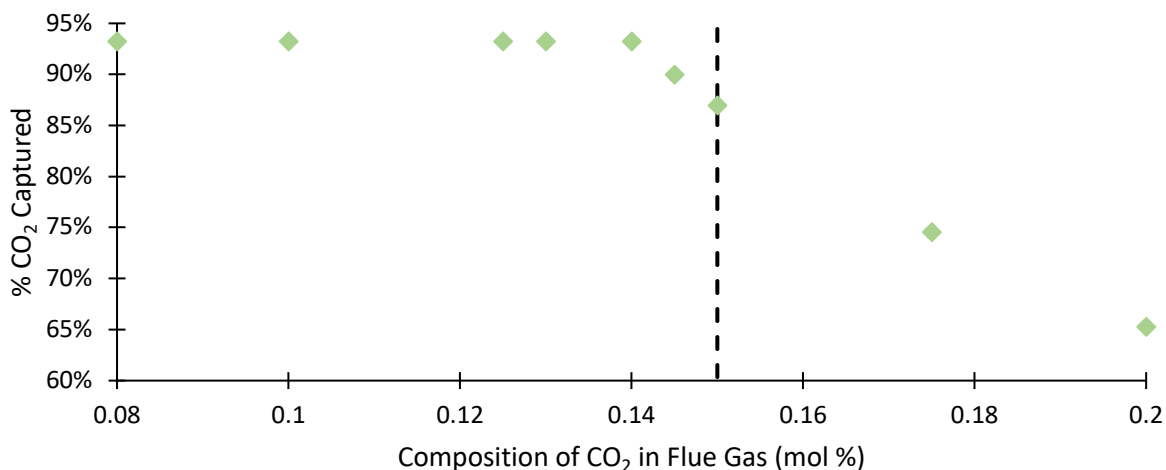


Figure C4.7: Results of BCCS when varying the composition of CO_2 in the flue gas, and the resulting $\%\text{CO}_2\text{C}$.

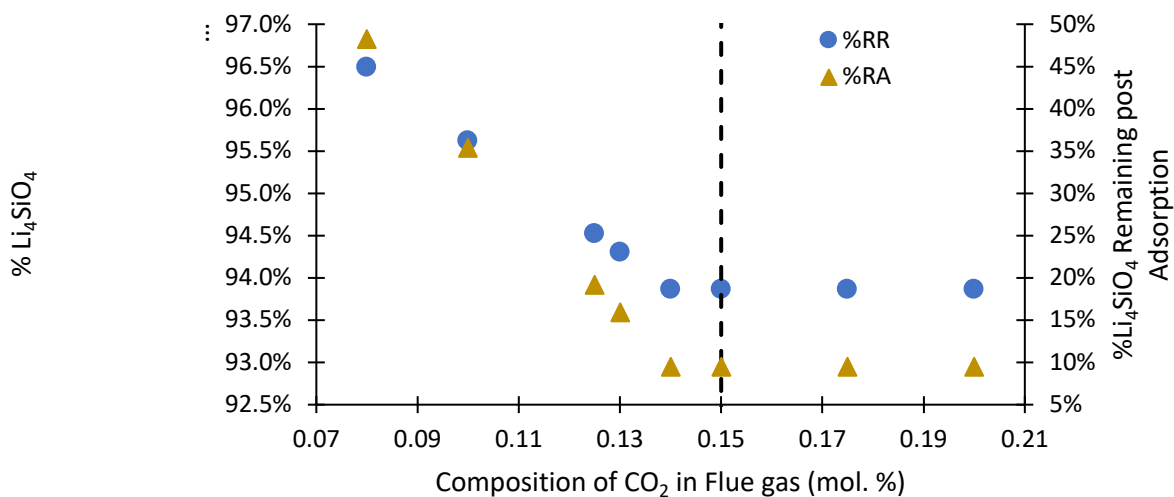


Figure C4.8: Results from BCCS of adsorbent remaining post adsorption ($\%\text{Li}_4\text{SiO}_4\text{RA}$) and adsorbent remaining post regeneration ($\%\text{Li}_4\text{SiO}_4\text{RR}$) when varying the CO_2 composition in the flue gas.

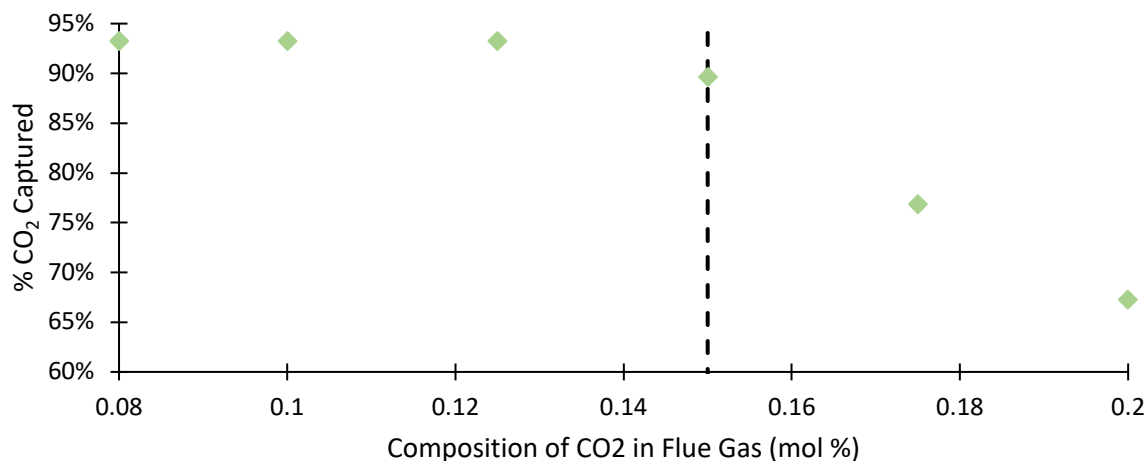


Figure C4.9: Results of BCCS – P when varying the composition of CO₂ in the flue gas, and the resulting %CO₂C.

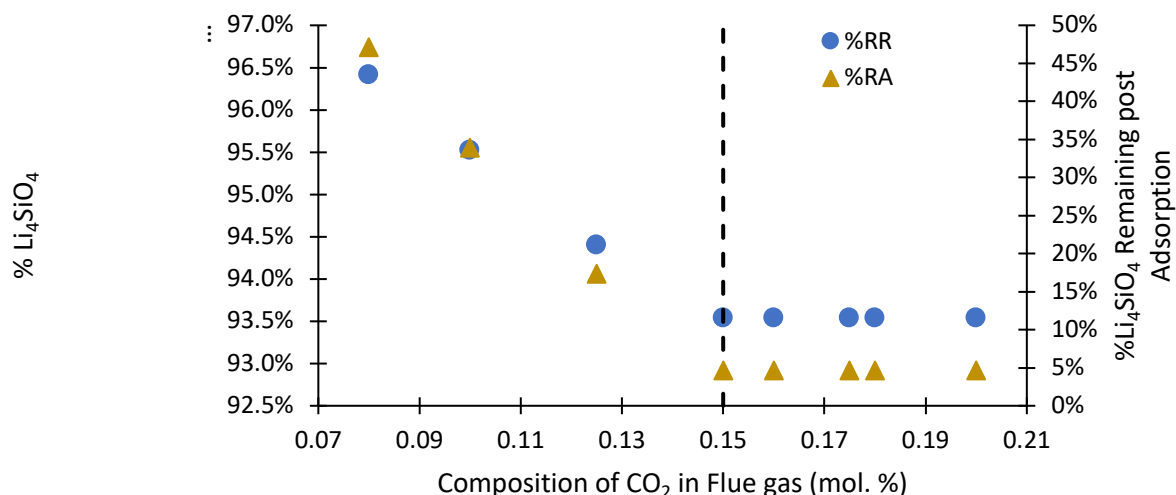


Figure C4.10: Results from BCCS – P of adsorbent remaining post adsorption (%Li₄SiO₄RA) and adsorbent remaining post regeneration (%Li₄SiO₄RR) when varying the CO₂ composition in the flue gas.

C5: Water Consumption Calculations

The amount of water required for this process is based off the pre-treatment process described in Yang et al. [84], where the water washing process is completed under the stop criteria of a pH equal to 7. In the experimental procedure, it is stated the treated fly-ash is to be rinsed with water until the pH reads 7, then the next step of pre-treatment can commence. Using this assumption in the designed model, the required amount of water into the system is such that the wastewater/wash water leaving the system has a pH of 7 or equivalently, a hydrogen ion (H₃O⁺) concentration of 1×10^{-7} . However, the pH was

assumed to be valid withing a certain range (± 0.2), therefore this was built into the calculation method. Equations C5.1 and C5.2 below are introduced to show the calculations done to find the volume of water required for this process.

$$[H_3O^+] = \frac{V_{H_2O}}{\eta_{H_3O^+}} \quad (C5.1)$$

$$pH = -\log_{10}[H_3O^+] \quad (C5.2)$$

where $[H_3O^+]$ is the concertation of H_3O^+ ($\frac{mol}{L}$), V_{H_2O} is the volume of water entering the water washing unit ($\frac{L}{s}$), and $\eta_{H_3O^+}$ is the moles of H_3O^+ in the stream leaving the water washing unit (Figure 10, USED WATER) ($\frac{mol}{s}$). To accurately determine the amount of water required by the system, a trial-and-error method was executed to determine the least amount of water required to reach the appropriate pH. An initial value of 2.5×10^{10} was used as V_{H_2O} , and after the process was run, the USED WATER stream (Figure 10) had 2499.22 mols per second of hydrogen ions; the resulting pH of the stream was 7.000135. Although this meets the necessary conditions of the system, the amount of water used is exceptionally high. Therefore, this process of changing the V_{H_2O} was done until a pH closer to the lower limit (6.8) was reached. These trials can be found in Table C5.1.

Table C5.1. Calculation of necessary water consumption for water washing pre-treatment of fly-ash.

$V_{H_2O} [\frac{L}{s}]$	$\eta_{H_3O^+} [\frac{mol}{s}]$	$[H_3O^+] [\frac{mol}{L}]$	pH
2.50E+10	2499.22	9.9969E-08	7.0001E+00
2.00E+10	1999.51	9.9976E-08	7.0001E+00
5.00E+04	1.33618	2.6724E-05	4.5731E+00
1.00E+05	1.33625	1.3363E-05	4.8741E+00
1.00E+06	1.34364	1.3436E-06	5.8717E+00
5.00E+06	1.50248	3.0050E-07	6.5222E+00
5.00E+07	5.70979	1.1420E-07	6.9423E+00
1.50E+07	2.30948	1.5397E-07	6.8126E+00

C6: Cost analysis calculations

The cost for each process was found by multiplying the cost of each product (raw material/energy) by the required amount required over a 24-hour period and summing all these costs. Since amine-based PCC (MEA) is a continuous process, this means that the process flowrates in $\frac{kg}{hr}$ are multiplied by 24 *hours*. For the semi-batch biomass processes however, this 24-hour period is assumed to be equal to 36 adsorption/regeneration cycles. Assuming there is no downtime between adsorption (30 minutes) and regeneration (10 minutes), the total process takes 40 minutes. This cost is then normalized over kilograms of CO₂ captured per day. As the maximum number of ad-desorption cycles before sorbent replacement is assumed to be 36, the pre-treatment section of this process only needs to be run once, i.e., one batch of fly-ash must be pre-treated for 24 hours of operation. Table C6.1 shows the costs of each product, while table C6.2 shows the required amounts from each process. An example calculation of how each cost is calculated is included below for the MEA process using the costs and amounts found in tables C6.1 and C6.2.

$$\begin{aligned} Total \$ &= (\$1.95 \times 17326.35 \text{ kg}) + (\$0.19 \times 3686.4 \text{ kW} + \$0.00103795 \times (206.4 + 3943.2)) \\ &= \$34\,561.31 \end{aligned}$$

The amount of CO₂ per hour or per batch was taken from simulation results and were multiplied by 24 hours (or 36 batches for BCCS and BCCS – P) to obtain the CO₂ in 24-hours.

$$\begin{aligned} \text{Normalized Value} &= \frac{\text{Total \$}}{\text{CO}_2 \text{ in } 24h} \\ &= \frac{\$34\,561.31}{2775.192 \text{ kg CO}_2 \text{ per day}} \\ &= \$12.45 \text{ per kg CO}_2 \text{ per day} \end{aligned}$$

Table C6.1. Prices of each material required by the different CCS processes. Units, values, and sources are specified in each column.

Resource	PRICE		Source
	UNITS	Value	
MEA	$\frac{\$}{kg}$	1.95	[189]

Li source	$\frac{\$}{kg}$	20	[190]
HCl	$\frac{\$}{L}$	50	[191]
DI water	$\frac{\$}{kg}$	0.00177234	[129]
Steam heat	$\frac{\$}{kWh}$	0.19	ASPEN Plus Database
Fired Heat	$\frac{\$}{kWh}$	0.323	ASPEN Plus Database
Cooling water	$\frac{\$}{kWh}$	0.00103795	ASPEN Plus Database
Electric	$\frac{\$}{kWh}$	0.103	[192]

Table C6.2. Amounts of each resource needed over a 24-hour period. Units and amounts specified in each column, while the values were taken from Nittaya [126] for the PCC process, and this work for both BCCS and BCCS – P.

Resource	UNITS	PCC	BCCS	BCCS – P
MEA	<i>kg</i>	17362.35		
Li source	<i>kg</i>		4.558	4.558
HCl	<i>L</i>			2884.3
DI water	<i>kg</i>			1.50E+07
Regeneration (reboiler / steam heat)	<i>kW</i>	3686.4	4461.768	4433.76

Condenser (regeneration)	<i>kW</i>	206.4		
Buffer tank (absorber)	<i>kW</i>	3943.2		
Adsorber Cooling	<i>kW</i>		3959.82	2751.023
Dryer (pre-treatment)	<i>kW</i>			4.35
Grind & Sifter (pre-treatment)	<i>kW</i>		5.6	5.6

Appendix D – Supplemental information on the enhanced biomass fly-ash derived adsorbent CO₂ capture model

D1: Modelling details for Aspen plus implementation

This section covers the details of how different unit operation blocks and calculators were implemented in the Aspen Plus model. Table D1.1 outlines each of the unit operation blocks and the chemistries chosen prior to running the model. Table D1.2 provides the details on the pump pressure calculator block C11 and Table D1.3 supplies the details for calculator block C22 which adjusts the flow of pure water post recycle.

The details of the “GLOBAL” chemistry model are discussed in the body of the paper, while the conditions for “ACIDWASH” and “SOLIDREM” vary slightly. For “ACIDWASH” the only compounds which were chosen in the electrolyte wizard were HCl and H₂O, and the reaction type chosen was dissociation only. The reaction produced was the same as eq. 19 in the body of this text, and the equilibrium constant Keq in Aspen was redefined so HCl would be present in the ACIDRXN block. Constants A, B, and C were chosen to be 10, 100, and 5. “SOLIDREM” was defined almost exactly as “GLOBAL”, however when using the electrolyte wizard, both dissociation and salt precipitate reaction were chosen as the reaction types. As this produces a much larger number of equations, it was only chosen for select unit operations because the computational time increases significantly, and only needs to be selected when the concentration of ions is high enough for precipitates to form.

Table D1.1. Block details including block type and chemistry chosen.

Label	Aspen Plus Block Type	Chemistry	Details
Acid Wash	SWash	ACIDWASH	40:1 liquid to solid ratio
ACIDRXN	RStoich	GLOBAL	Reactions 1-8 are implemented Temperature of 25 °C and P of 1.01 bar
Water Wash	SWash	GLOBAL	40:1 liquid to solid ratio
Neutral	Mixer	GLOBAL	Mixer, specify flash conditions as liquid only
Pump	Pump	GLOBAL	C11 recalculated pump pressure, can specify as atmospheric
RO	Sep	SOLIDREM	Stream split specifications specified in Table D1.4

Dryer	Dryer	GLOBAL	80 °C
Solid Reactor	RStoich	GLOBAL	Synthesis reaction (23) specified with conversion of 100% SiO ₂ Temperature of 95 °C Calcification (baking) assumed to elapse for 4 hours post synthesis reaction completion
Grind & Sifter	Sep	GLOBAL	Assume electric utility (discussed in section 4.2.2) Stream split specification (100% Li ₄ SiO ₄ goes to capture process, remaining goes to WASTE SOLID)
ADS	Sep	GLOBAL	100% CO ₂ and Li ₄ SiO ₄ split to RICH Remaining components to VENTGAS
ADSRXN	RStoich	GLOBAL	Reaction 1 specified and results overwritten by C2 calculator Temperature of 650 °C and pressure of 1.01 bar
REGENRXN	RStoich	GLOBAL	Reaction 2 specified and results overwritten by C3 calculator Temperature of 750 °C and pressure of 1.01 bar
REGEN	Sep	GLOBAL	100% CO ₂ sent to CO ₂ stream Remaining solids sent to RECYCLE
SEP	Split	GLOBAL	Separates unregenerated sorbent with regenerated 100% Li ₄ SiO ₄ goes to R2

The equations implemented in the pump pressure calculator block are as follows:

$$\pi = cRT \quad (D1.1)$$

where π is the osmotic pressure in Pa, c is the concentration of solute particles in $\frac{mol}{L}$, R is the universal gas constant equal to $0.08206 \frac{L atm}{mol K}$, and T is the temperature of the stream in K . This is how the pressure needed from the pump to adequately supply the stream to the RO membrane is determined. The pressure supplied to the pump (P) is defined as 25% more than the RO pressure. The concentration of the stream c , is defined by properties in Aspen as follows:

$$c = \frac{\rho_s(\eta_s - \eta_{H_2O})}{m_s} \quad (D1.2)$$

where ρ_s is the mass density of the stream in $\frac{g}{L}$, η_s and η_{H_2O} are the molar flows of the stream and solvent (water) in $\frac{mol}{s}$, and m_s is the mass flow of the stream in $\frac{g}{s}$.

Table D1.2. Calculator block C11 details for Aspen Plus implementation.

C11				
Variable	Variable Type	Stream/Block	Component	Info Flow
η_s	Stream-Var	S4	mole flow	Import
η_{H_2O}	mole flow	S4	H2O	Import
m_s	Stream-Var	S4	Mass Flow	Import
T	Stream-Var	S4	Temp	Import
P	Block-Var	Pump	DELP	Export
π	Stream-Var	S4	Mass-Density	Import

Calculator block C22 adjusts the flow of “pure” DI water fed to the water washing unit after the recycled water has been accounted for. This is a simple balance block that utilizes the following equations:

$$F_{TOTAL} = F_{RECYCLE} + F_{FRESH} \quad (D1.3)$$

where F_{TOTAL} is the total flow of DI water needed and equivalent to $1.5 \times 10^7 \frac{L}{s}$, $F_{RECYCLE}$ is the flow of the recycled stream in $\frac{L}{s}$, and F_{FRESH} is the flow of fresh DI water in $\frac{L}{s}$.

Table D1.3. Calculator block C22 details for Aspen Plus implementation.

C22				
Variable	Variable Type	Stream/Block	Component	Info Flow
$F_{RECYCLE}$	Stream-Var	PERMEATE	Mass Flow	Import
F_{FRESH}	Mass Flow	PUREH2O	H2O	Export

Table D1.4. RO Split stream ratios

Compound	Split Fraction
H ₂ O	0.85

H_3O^+	0.85
OH^-	0.85
Cl^-	0.05
K^+	0.7
Ca^{2+}	0.05
Al^{3+}	0.05
Mg^{2+}	0.5
Fe^{3+}	0.05
SO_4^{2-}	0.5
PO_4^{3-}	0.5
H_2PO_4^-	0.5
HPO_4^{2-}	0.5
FeOH_2^+	0.01
$\text{Fe}(\text{OH})_2^+$	0.01
CaOH^+	0.5
MgOH^+	0.5
HSO_4^+	0.5
Cl_2	0
ClO^-	0.05
H_2	0
Na^+	0.049091238

D2: Validation stream details

Table D2.1. Used water stream compositions before implementing water treatment and recycle.

Compound	Mole frac. [mol. %]	Mole flow [mol/s]	Conc. [mol/L]	Mass flow [g/s]	PPM
H2O	0.999997	830423801	55.3510408	1.496E+10	999994.721
HCl	4.3851E-24	3.6415E-15	2.4272E-22	1.3277E-13	8.8749E-18
H2SO4	4.3776E-26	3.6353E-17	2.4231E-24	3.5655E-15	2.3833E-19
H2PO4	9.6799E-14	8.0385E-05	5.3579E-12	0.0078773	5.2654E-07
HOCl	4.8466E-11	0.04024747	2.6827E-09	2.11138412	0.00014113
CCL4	3.4207E-10	0.28406795	1.8934E-08	43.6958428	0.00292077
H3O+	1.7438E-06	1448.08399	9.6521E-05	27546.4238	1.84128972
OH-	1.9115E-12	0.00158734	1.058E-10	0.02699739	1.8046E-06
CL-	1.7448E-06	1448.90399	9.6575E-05	51368.3553	3.43362264
K+	8.3196E-11	0.06908799	4.605E-09	2.70118504	0.00018056
Ca+2	1.1903E-10	0.09884347	6.5883E-09	3.96133972	0.00026479
Al+3	1.4623E-10	0.12143159	8.0939E-09	3.27621088	0.00021899
Mg+2	1.3496E-10	0.11207206	7.47E-09	2.72378807	0.00018207
Fe+3	9.9742E-13	0.00082828	5.5208E-11	0.04625582	3.0919E-06
SO4-2	3.3008E-11	0.02741081	1.827E-09	2.63321112	0.00017601
PO4-3	3.9168E-23	3.2526E-14	2.168E-21	3.0891E-12	2.0649E-16
H2PO4-	1.0026E-11	0.00832554	5.5493E-10	0.80747603	5.3974E-05
HPO4-2	6.7613E-15	5.6147E-06	3.7425E-13	0.00053891	3.6022E-08
Fe(OH)2	7.2464E-18	6.0176E-09	4.011E-16	8.768E-07	5.8608E-11
FeOH+2	1.4566E-11	0.01209576	8.0623E-10	0.88121556	5.8903E-05
Fe(OH)2+	3.7799E-12	0.00313894	2.0922E-10	0.28206895	1.8854E-05
CaOH+	2.5637E-19	2.129E-10	1.4191E-17	1.2153E-08	8.1236E-13
MgOH-	5.0558E-18	4.1985E-09	2.7984E-16	1.7345E-07	1.1594E-11

HSO4-	3.3056E-13	0.00027451	1.8297E-11	0.02664702	1.7812E-06
CL2(g)	9.4095E-16	7.8139E-07	5.2083E-14	5.5405E-05	3.7034E-09
CIO-	1.2714E-14	1.0558E-05	7.0374E-13	0.00054324	3.6312E-08
H2(g)	6.8415E-10	0.56813589	3.7869E-08	1.14529378	7.6555E-05

Table D2.2. Used water stream parameters before implementing water treatment and recycle.

Parameter	Value
vol. flow [L/s]	15002857.9
vol. flow [m ³ /s]	15002.8579
mass density [g/cc]	0.99717
mass density [g/m ³]	997170
mass flow [g/s]	1.496E+10

Table D2.3. Permeate stream compositions after implementing water treatment and recycle.

Compound	Mole flow [mol/s]	Conc. [mol/L]	Mass flow [g/s]	PPM
H2O	705926722	55.35	1.2717E+10	1.00E+06
HCl	5.11E-19	4.01E-26	1.80E-17	1.42E-21
H2SO4	7.82E-23	6.13E-30	7.07E-21	5.56E-25
H2PO4	6.31E-08	4.94E-15	5.85E-06	4.60E-10
HOCl	0.0002087	1.64E-11	0.01111584	8.74E-07
CCL4	0	0.00E+00	0	0.00E+00
H3O+	2.46584933	1.93E-07	45.2982104	3.56E-03
OH-	0.66281912	5.20E-08	11.6735236	9.18E-04
CL-	99.952025	7.84E-06	3543.38205	2.79E-01
K+	0.04891699	3.84E-09	1.89089778	1.49E-04

Ca+2	0.00499902	3.92E-10	0.19807783	1.56E-05
Al+3	0.00614065	4.81E-10	0.16379904	1.29E-05
Mg+2	0.0566782	4.44E-09	1.36190979	1.07E-04
Fe+3	1.63E-10	1.27E-17	8.37E-09	6.59E-13
SO4-2	0.01400072	1.10E-09	1.32975335	1.05E-04
PO4-3	2.88E-09	2.26E-16	2.87E-07	2.26E-11
H2PO4-	0.00320819	2.52E-10	0.30497161	2.40E-05
HPO4-2	0.00104543	8.20E-11	0.10183975	8.01E-06
Fe(OH)2	6.80E-17	5.33E-24	9.04E-15	7.11E-19
FeOH+2	1.22E-06	9.60E-14	8.52E-05	6.70E-09
Fe(OH)2+	0.00016124	1.26E-11	0.014329	1.13E-06
CaOH+	5.46E-09	4.28E-16	3.19E-07	2.51E-11
MgOH+	1.08E-06	8.45E-14	4.56E-05	3.58E-09
HSO4-	2.90E-07	2.28E-14	2.69E-05	2.11E-09
CL2(g)	6.70E-13	5.25E-20	4.65E-11	3.66E-15
ClO-	2.69E-05	2.11E-12	0.00145499	1.14E-07
H2(g)	0	0.00E+00	0	0.00E+00
Na+	98.0945637	7.69E-06	2255.11751	1.77E-01

Table D2.4. Permeate stream parameters after implementing water treatment and recycle.

Parameter	Value
vol. flow [L/s]	12753579.2
vol. flow [m ³ /s]	12753.5792
mass density [g/cc]	0.997171
mass density [g/m ³]	997171

mass flow [g/s]	1.2717E+10
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D3: Cost breakdown and comparison for BCCS, BCCS – P, and BCCS – P(R)

This section shows a breakdown of the proportional costs of the BCCS BCCS – P, and BCCS – P(R) processes. Included is a table of all the costs and required material/energy amounts as well as figures with show the fraction each resource contributes to the overall process cost.

Table D3.1: Cost breakdown comparison between BCCS, BCCS – P, and BCCS – P(R)

Resource	PRICE		AMOUNT REQUIRED			
	UNITS	Value	UNITS	BCCS	BCCS - P	BCCS - P(R)
Li source	$\frac{\$}{kg}$	20	<i>kg</i>	4.8916	4.8916	4.8916
Synthesis	$\frac{\$}{kg}$	500	<i>kg</i>	3.6	3.6	3.6
HCl	$\frac{\$}{L}$	50	<i>L</i>	0	4000	4000
DI water (fresh)	$\frac{\$}{L}$	0.00177	<i>kg</i>	0	1.50E+07	2.25E+06
DI water (recycled)	$\frac{\$}{L}$	0.00091	<i>kg</i>	0	0	1.28E+07
NaOH (total)	$\frac{\$}{L}$	5	<i>L</i>	0	0	285.00
Fired heat	$\frac{\$}{kWh}$	0.323	<i>kW</i>	4461.768	4433.76	4433.76
Cooling water	$\frac{\$}{kWh}$	0.00104	<i>kW</i>	3959.82	2751.023	2751.023
Electric	$\frac{\$}{kWh}$	0.103	<i>kW</i>	5.6	9.95	24.4144
Total Cost			\$	3343.68	229905.03	220353.79

CO2 captured	<i>kg</i>	1200.8304	1284.1524	1284.1524
Normalized value	$\frac{\$}{kgCO_2/day}$	2.78	179.03	171.59

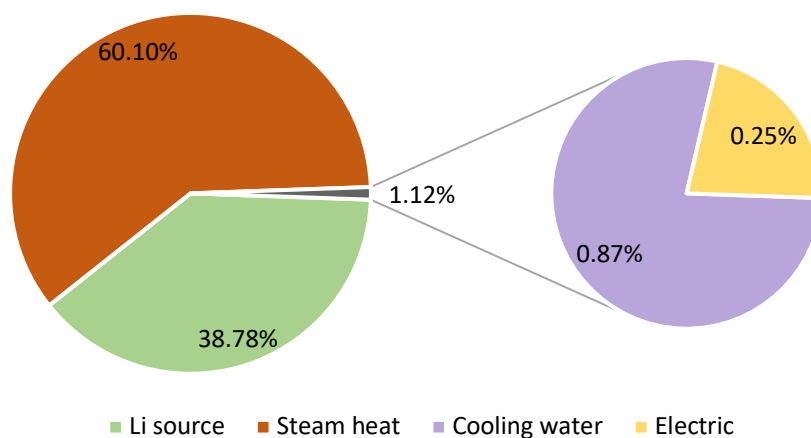


Figure D3.1. Fraction each resource contributes to the BCCS process

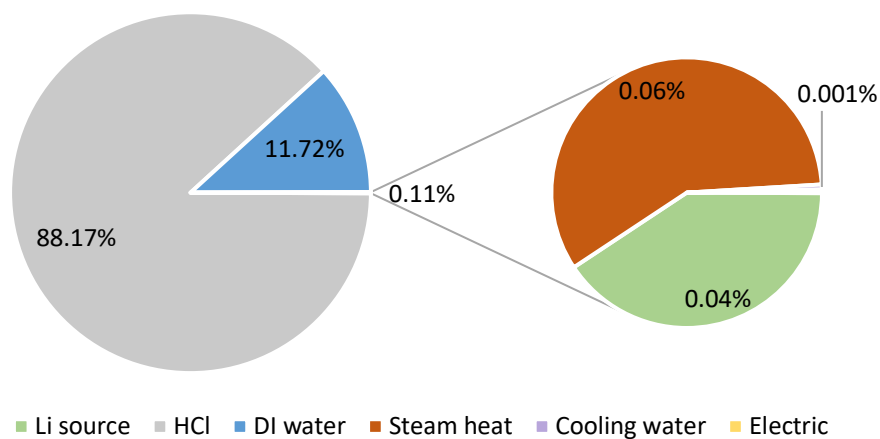


Figure D3.2. Fraction each resource contributes to the BCCS – P process

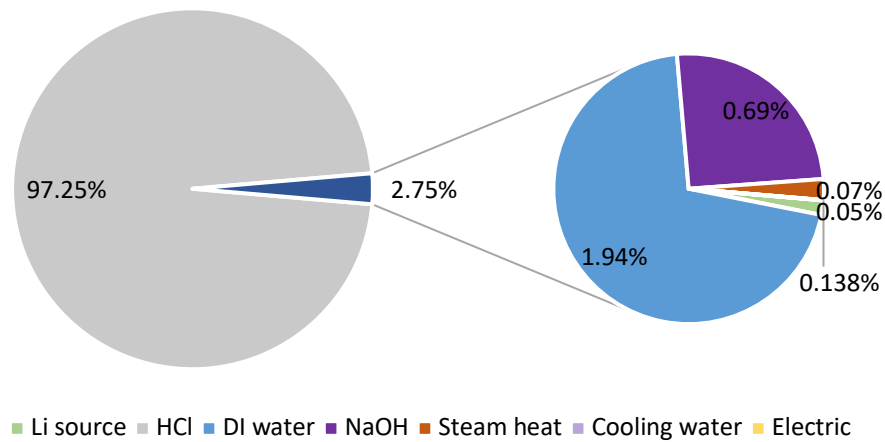


Figure D3.3. Fraction each resource contributes to the BCCS – P(R) process

D4: Case study results

This section shows the extra results from examined case studies. This includes all the DI water specification metrics evaluated for case studies 1-3 found in tables D4.1-D4.3, as well as the additional case study (4) on variation to the reaction conversion values. Results for case 4 can be found in Tables D4.4-D4.5 and Figure D4.1-D4.3.

Case 1: Sensitivity on level of water recycled.

Table D4.1. DI water specification metrics showing permeate stream conditions for each recycle rate.

SPECS	Units	Requirement	Recycle %						
			50	55	60	65	70	75	80
pH^{PERM}		5.0-8.0	6.7438	6.6019	6.7438	6.6019	6.7439	6.6019	6.7439
EC	$\mu S/cm$	< 1	1.1E-06	1.4E-06	9.4E-07	1.2E-06	8.1E-07	1.0E-06	7.1E-07
ER	M Ω -cm	> 1	8.9E+05	7.1E+05	1.1E+06	8.4E+05	1.2E+06	9.6E+05	1.4E+06
TDS	ppm	< 100	5.6E-01	7.0E-01	4.7E-01	5.9E-01	4.0E-01	5.2E-01	3.5E-01
TH – $CaCO_3$	ppm	< 50	0	0	0	0	0	0	0
[Ca]	ppm	< 25	3.7E-04	3.4E-04	3.1E-04	2.9E-04	2.7E-04	2.5E-04	2.3E-04

[Mg]	ppm	< 25	1.8E-04	1.7E-04	1.5E-04	1.4E-04	1.3E-04	1.2E-04	1.1E-04
[Fe]	ppm	< 1	1.9E-06	1.8E-06	1.6E-06	1.5E-06	1.4E-06	1.3E-06	1.2E-06
[Cu]	ppm	< 1	0	0	0	0	0	0	0
[Si]	ppm	ND	0	0	0	0	0	0	0
[Cl]	ppm	< 2	3.4E-01	4.3E-01	2.9E-01	3.6E-01	2.5E-01	3.2E-01	2.2E-01
[S]	ppm	< 25	1.8E-04	1.6E-04	1.5E-04	1.4E-04	1.3E-04	1.2E-04	1.1E-04

Table D4.2. $Z_{i,T-FA}$ values when varying the level of water recycled.

Zi	Level of water recycled						
	50	55	60	65	70	75	80
$Z_{SiO_2,T-FA}$	75.02%	75.02%	75.02%	75.02%	75.02%	75.02%	75.02%
$Z_{Al_2O_3,T-FA}$	9.58%	9.58%	9.58%	9.58%	9.58%	9.58%	9.58%
$Z_{MgO,T-FA}$	2.63%	2.63%	2.63%	2.63%	2.63%	2.63%	2.63%
$Z_{CaO,T-FA}$	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%
$Z_{K_2O,T-FA}$	2.36%	2.36%	2.36%	2.36%	2.36%	2.36%	2.36%
$Z_{Cl,T-FA}$	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
$Z_{SO_3,T-FA}$	0.11%	0.11%	0.11%	0.11%	0.11%	0.11%	0.11%
$Z_{Fe_2O_3,T-FA}$	1.40%	1.40%	1.40%	1.40%	1.40%	1.40%	1.40%
$Z_{P_2O_5,T-FA}$	0.02%	0.02%	0.02%	0.02%	0.02%	0.02%	0.02%
$Z_{TiO,T-FA}$	0.53%	0.53%	0.53%	0.53%	0.53%	0.53%	0.53%
$Z_{C,T-FA}$	7.57%	7.57%	7.57%	7.57%	7.57%	7.57%	7.57%

Case 2: Sensitivity on acid to fly-ash ratio.

Table D4.3. DI water specification metrics showing permeate stream conditions for each acid to fly-ash ratio. This includes both the nominal NaOH levels and scenarios once the NaOH levels were adjusted.

SPECS	Units	Requirement	Ratio & Nominal Conditions		Ratio & Adjusted NaOH	
			30:1	35:1	30:1	35:1
pH^{PERM}		5.0-8.0	9.5169	9.2150	6.5840	6.4664
EC	$\mu S/cm$	< 1	1.90E-06	1.40E-06	6.91E-07	8.07E-07
ER	$M\Omega\text{-cm}$	> 1	5.27E+05	7.15E+05	1.45E+06	1.24E+06
TDS	ppm	< 100	3.85E-01	4.20E-01	3.41E-01	3.97E-01
$TH - CaCO_3$	ppm	< 50				
[Ca]	ppm	< 25	2.18E-04	2.18E-04	2.18E-04	2.18E-04
[Mg]	ppm	< 25	1.08E-04	1.08E-04	1.07E-04	1.07E-04
[Fe]	ppm	< 1	1.13E-06	1.13E-06	1.13E-06	1.13E-06
[Cu]	ppm	< 1	0	0	0	0
[Si]	ppm	ND	0	0	0	0
[Cl]	ppm	< 2	2.09E-01	2.44E-01	2.09E-01	2.44E-01
[S]	ppm	< 25	1.04E-04	1.04E-04	1.05E-04	1.05E-04

Case 3: Variation of fly-ash source

Table D4.4. DI water specification metrics showing permeate stream conditions for different biomass fly-ash sources.

SPECS	Units	Requirement	FA source		
			Wood	Grass	Straw
pH^{PERM}		5.0-8.0	6.7284	6.6061	6.6231
EC	$\mu S/cm$	< 1	9.23E-07	9.23E-07	9.23E-07

<i>ER</i>	MΩ-cm	> 1	1.08E+06	1.08E+06	1.08E+06
<i>TDS</i>	ppm	< 100	4.58E-01	4.57E-01	4.57E-01
<i>TH – CaCO₃</i>	ppm	< 50	0	0	0
[<i>Ca</i>]	ppm	< 25	1.54E-03	3.96E-04	5.05E-04
[<i>Mg</i>]	ppm	< 25	1.02E-04	9.31E-05	7.83E-05
[<i>Fe</i>]	ppm	< 1	1.72E-06	4.83E-07	7.09E-07
[<i>Cu</i>]	ppm	< 1	0	0	0
[<i>Si</i>]	ppm	ND	0	0	0
[<i>Cl</i>]	ppm	< 2	2.79E-01	2.79E-01	2.79E-01
[<i>S</i>]	ppm	< 25	1.27E-04	1.64E-04	1.37E-04

Case 4: Sensitivity analysis on the reaction conversion (X_r) specified the ACIDRXN block.

To ensure that the assumptions made about the reaction conversion for this process and model implementation were valid and feasible, a sensitivity analysis was done on the reaction conversion. The conversion of each component was varied $\pm 15\%$ in 5% increments. Tables D4.5-D4.6 show the conversion value specified for each reaction and associated compound and the resulting composition in the treated fly-ash. Figures D4.1-D4.3 show the change in mass fraction of SiO₂ present in the fly-ash, mass flow of the treated fly-ash, and the pH of the permeate stream as these changes are made.

Table D4.5. Composition of the treated fly-ash stream ($Z_{i,T-FA}$) after adjusting the reaction conversion X_r –15%, –10%, and –5%.

Reaction Number	Compound	-15%		-10%		-5%	
		X_r	$Z_{i,T-FA}$	X_r	$Z_{i,T-FA}$	X_r	$Z_{i,T-FA}$
	SiO ₂		68.55%		70.58%		72.73%

1	Al ₂ O ₃	0.32947	11.28%	0.37947	10.75%	0.42947	10.18%
2	MgO	0.56022	3.64%	0.61022	3.33%	0.66022	2.99%
3	CaO	0.76024	1.90%	0.81024	1.55%	0.86024	1.18%
4	K ₂ O	0.51302	3.11%	0.56302	2.88%	0.61302	2.63%
	Cl		0.00%		0.00%		0.00%
5	SO ₃	0.81639	0.55%	0.86639	0.41%	0.91639	0.27%
6	Fe ₂ O ₃	0.41659	1.72%	0.46659	1.62%	0.51659	1.51%
7	P ₂ O ₅	0.82706	0.14%	0.87706	0.10%	0.92706	0.06%
	TiO		0.48%		0.50%		0.51%
8	C	0.24112	8.63%	0.29112	8.30%	0.34112	7.95%

Table D4.6. Composition of the treated fly-ash stream ($Z_{i,T-FA}$) after adjusting the reaction conversion X_r

15%, 10%, and 5%.

Reaction Number	Compound	5%		10%		15%	
		X_r	$Z_{i,T-FA}$	X_r	$Z_{i,T-FA}$	X_r	$Z_{i,T-FA}$
	SiO ₂		77.40%		79.74%		81.93%
1	Al ₂ O ₃	0.52947	8.94%	0.57947	8.23%	0.62947	7.45%
2	MgO	0.76022	2.24%	0.81022	1.83%	0.86022	1.38%
3	CaO	0.96024	0.36%	1.00000	0.00%	1.00000	0.00%
4	K ₂ O	0.71302	2.07%	0.76302	1.76%	0.81302	1.43%
	Cl		0.00%		0.00%		0.00%
5	SO ₃	1.00000	0.00%	1.00000	0.00%	1.00000	0.00%
6	Fe ₂ O ₃	0.61659	1.28%	0.66659	1.14%	0.71659	1.00%
7	P ₂ O ₅	1.00000	0.00%	1.00000	0.00%	1.00000	0.00%
	TiO		0.55%		0.56%		0.58%

8	C	0.44112	7.17%	0.49112	6.73%	0.54112	6.23%
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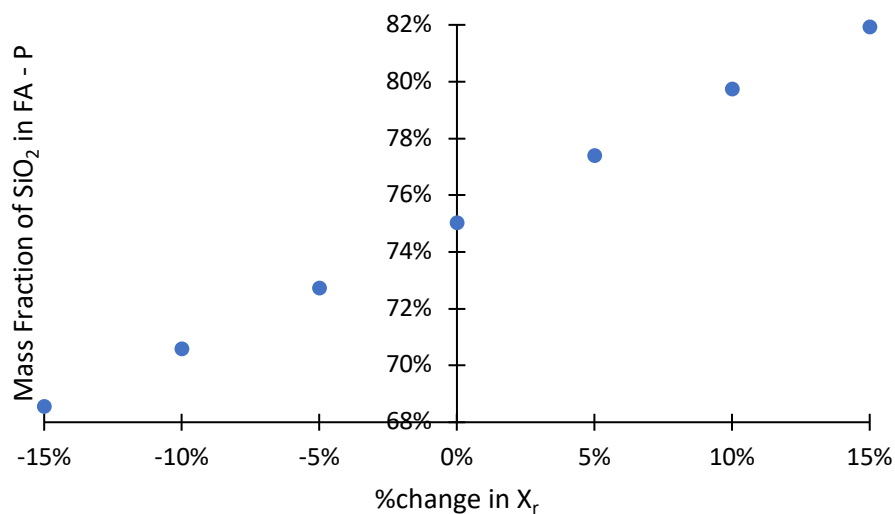


Figure D4.1. Mass fraction of SiO_2 present in the treated fly-ash as X_r is varied.

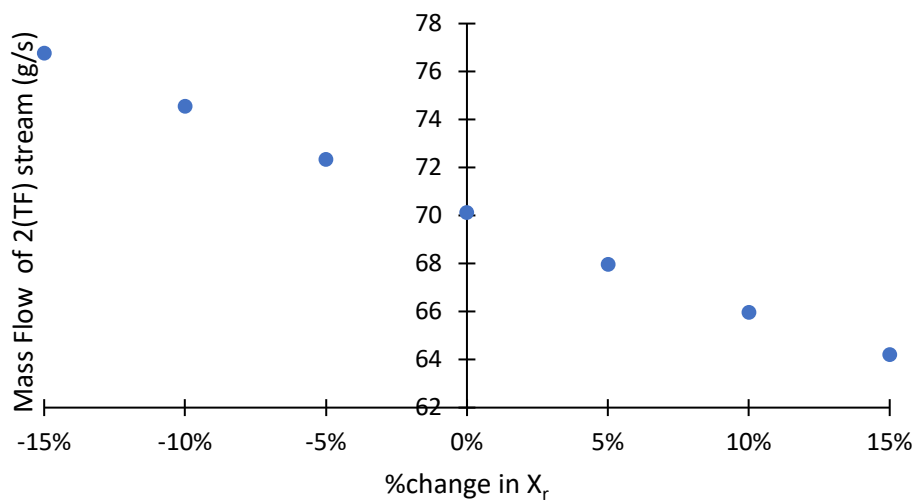


Figure D4.2. Mass flow of the treated fly-ash stream 2(TF) as X_r is varied.

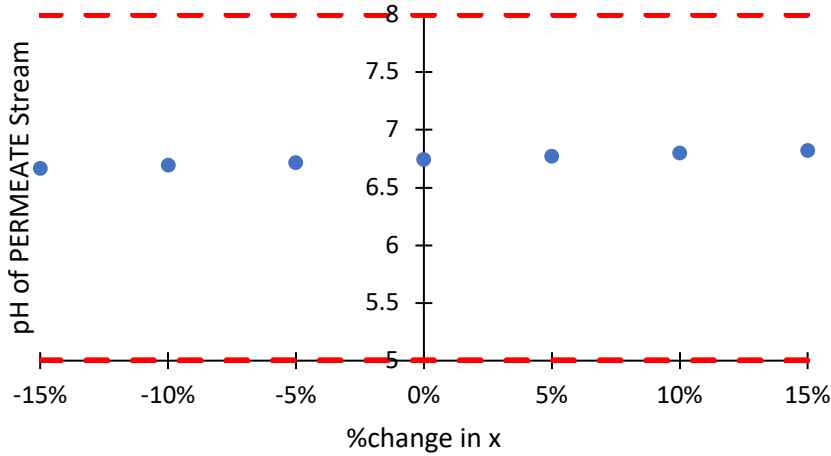


Figure D4.3. pH of the permeate stream ($pH^{PERMEATE}$ value) as X_r is varied.

Although there is variation in the treated fly-ash composition, it stays within approximately $\pm 6.5\%$. Additionally, as the $pH^{PERMEATE}$ level is well within the bounds for DI water with these fluctuations, therefore the assumption that the reaction conversions (X_r) for reactions 5.1-5.8 holds true, even if there is some slight variation in the true X_r value.

D5: CRC sample calculation

The *CRC* as defined in the main body of this work is a term introduced in this study that accounts for consumed resources which aids in evaluating the sustainability of the different changes made to the BCCS – P(R) process. Recall that the consumed resources indexed as *in* are positive terms which add to the cost while recycled or reused resources indexed as *reuse* are considered negative terms. An example calculation for this term when utilizing nominal conditions is shown below. For reference, the set for *in* and *reuse* are listed below.

$$in = \{HCl, DI\ water, NaOH\}$$

$$resue = \{DI\ water\ recycled, Fe(OH)_3, CaCO_3\}.$$

$$CRC = \sum_{in} S_{in} C_S - \sum_{reuse} S_{reuse} C_S$$

$$= S_{HCl} C_{HCl} + S_{DI\ water} C_{DI\ water} + S_{NaOH} C_{NaOH} - S_{DI\ water\ recycled} C_{DI\ water\ recycled} -$$

$$S_{Fe(OH)_3} C_{Fe(OH)_3} - S_{CaCO_3} C_{CaCO_3}$$

$$= 50 \frac{\$}{L} (4000\ L) + 0.00177 \frac{\$}{L} (2.25 \times 10^6\ L) + 5 \frac{\$}{L} (285.17\ L) - 0.00091 \frac{\$}{L} (1.28 \times 10^7\ L) -$$

$$0.7 \frac{\$}{g} (0\ g) - 0.45 \frac{\$}{g} (0\ g)$$

= \$193 782.00

D6: Fly-ash compositions for source variation

Table D6.1: Compositions of the raw biomass fly-ash used in the Aspen Plus simulation.

Compound	Composition [wt. %]			
	Wood [31]	Grass [31]	Straw [31]	Yang et al. [84]
SiO₂	22.22%	46.18%	43.94%	52.53%
Al₂O₃	5.09%	1.39%	2.71%	12.89%
MgO	6.07%	5.62%	4.66%	6.35%
CaO	43.03%	11.23%	14.13%	6.08%
K₂O	10.75%	24.59%	24.49%	4.90%
Cl	0.00%	0.00%	0.00%	2.85%
SO₃	2.78%	3.66%	3.01%	2.29%
Fe₂O₃	3.44%	0.98%	1.42%	2.26%
P₂O₅	3.48%	6.62%	4.31%	0.61%
TiO₂	0.29%	0.08%	0.22%	0.37%
Na₂O	2.85%	1.25%	1.35%	0.00%

D7: Precipitate trials and results

This section contains the results of the precipitate trials which are discussed in section 5.2.5 in the main body of this work. The results are separated based on the different cases/flowsheet configurations analysed.

BCCS – P(R): CaCO₃

Table D7.1. Concentrate stream results

Compound	Molar Flow [mol/s]	Concentration [mol/L]
----------	-----------------------	--------------------------

H ₂ O	124574058.1	55.35050979
HCl	9.24E-18	4.10387E-24
H ₂ SO ₄	6.58E-23	2.92348E-29
H ₃ PO ₄	5.76E-08	2.5594E-14
HOCl	0.035250725	1.56625E-08
CCl ₄	0.284077108	1.26221E-07
H ₃ O ⁺	0.43852929	1.94847E-07
OH ⁻	0.12321063	5.47447E-08
Cl ⁻	1898.939752	0.000843733
K ⁺	0.020726938	9.20935E-09
Ca ⁺²	0.093904521	4.17235E-08
Al ⁺³	0.115350754	5.12524E-08
Mg ⁺²	0.056036223	2.48979E-08
Fe ⁺³	9.79E-11	4.34891E-17
SO ₄ ⁻²	0.01384215	6.15032E-09
PO ₄ ⁻³	3.67E-09	1.63019E-15
H ₂ PO ₄ ⁻	0.003083059	1.36986E-09
HPO ₄ ⁻²	0.001122497	4.98746E-10
Fe ₂ (OH) ₂	1.37E-16	6.10751E-23
FeOH ⁺²	6.50E-07	2.8873E-13
Fe(OH) ₂ ⁺	8.00E-05	3.55582E-11
CaOH ⁺	9.60E-08	4.26707E-14
MgOH ⁺	9.96E-07	4.42679E-13

HSO4-	2.57E-07	1.14063E-13
Cl2(G)	1.15E-08	5.12297E-15
ClO-	0.004767507	2.11829E-09
H2	0.568154216	2.52441E-07
Na+	1897.99547	0.000843314
Fe(OH)3	1.28E-08	5.7038E-15

Table D7.2. Solids formed in concentrate stream

Compound	amount [g]
Fe(OH)3	0.015821292

Table D7.3. CO2USE stream results from Figure 22

Compound	Molar Flow [mol/s]	Concentration [mol/L]
CO2	357565.0382	0.039729449
H2O	343694.7398	0.038188304
H3O+	0.000192052	2.13391E-11
OH-	0.009136002	1.01511E-09
Na+	7737.63857	0.000859738
HCO3-	7486.303418	0.000831811
CO3-2	125.6631041	1.39626E-05

Table D7.4. Volume of streams examined

Vol. Flow CONC [L/s]	2250639.76
Vol. Flow CO2USE [L/s]	9000000

BCCS – P(R): 2RO

Table D7.5. Concentrate stream results

Compound	Molar Flow [mol/s]	Concentration [mol/L]
H ₂ O	18684426.94	8.301829227
HCl	8.27434E-18	3.67644E-24
H ₂ SO ₄	2.65054E-23	1.17768E-29
H ₃ PO ₄	2.59578E-08	1.15335E-14
HOCl	0.034837997	1.54792E-08
CCl ₄	0.284051541	1.26209E-07
H ₃ O ⁺	0.067610821	3.00407E-08
OH ⁻	0.019772999	8.7855E-09
Cl ⁻	1803.830404	0.000801475
K ⁺	0.006217522	2.76256E-09
Ca ⁺²	0.089201233	3.96337E-08
Al ⁺³	0.109573354	4.86854E-08
Mg ⁺²	0.028015645	1.24479E-08
Fe ⁺³	2.0971E-11	9.31777E-18
SO ₄ ⁻²	0.006920471	3.07489E-09
PO ₄ ⁻³	2.64736E-09	1.17627E-15
H ₂ PO ₄ ⁻	0.001474577	6.55181E-10
HPO ₄ ⁻²	0.000628043	2.79051E-10
Fe ₂ (OH) ₂	3.9789E-17	1.7679E-23
FeOH ⁺²	1.12875E-07	5.01526E-14
Fe(OH) ₂ ⁺	1.23436E-05	5.48451E-12
CaOH ⁺	8.1305E-08	3.61253E-14
MgOH ⁺	4.42819E-07	1.96753E-13
HSO ₄ ⁻	1.09675E-07	4.87306E-14

Cl ₂ (G)	6.66384E-08	2.96087E-14
ClO ⁻	0.004938226	2.19414E-09
H ₂	0.568103082	2.52418E-07
Na ⁺	1803.237639	0.000801211
Fe(OH) ₃	6.74162E-05	2.99543E-11

Table D7.6. Solids formed in concentrate stream

Compound	amount [g]
Fe(OH) ₃	0.016921297

Table D7.7. CO₂USE stream results from Figure 23

Compound	Molar Flow [mol/s]	Concentration [mol/L]
CO ₂	0.031499478	6.2999E-08
H ₂ O	27586565.22	55.17313044
H ₃ O ⁺	2.73839E-06	5.47677E-12
OH ⁻	5546.491753	0.011092984
Na ⁺	733759.1382	1.467518276
HCO ₃ ⁻	2370.276986	0.004740554
CO ₃ ⁻²	362921.1847	0.725842369

Table D7.8. Volume of streams examined

Vol. Flow CONC [L/s]	337589.058
Vol. Flow CO ₂ USE [L/s]	500000

Closed-loop BCCS – P(R) with Wood FA feed (BCCS – P(R): CaCO₃ FA)

Table D7.9. Concentrate stream results

Compound	Molar Flow [mol/s]	Concentration [mol/L]
----------	--------------------	-----------------------

H2O	124574058.7	55.35051007
HCl	9.38565E-18	4.17022E-24
H2SO4	8.22551E-23	3.65474E-29
H3PO4	3.34585E-07	1.48662E-13
HOCl	0	0
CCl4	0	0
H3O+	0.445383755	1.97892E-07
OH-	0.121315926	5.39029E-08
Cl-	1899.981	0.000844196
K+	0.045399609	2.01719E-08
Ca+2	0.663527378	2.94817E-07
Al+3	0.045476798	2.02062E-08
Mg+2	0.053479645	2.3762E-08
Fe+3	1.02548E-10	4.55638E-17
SO4-2	0.016777116	7.45438E-09
PO4-3	2.03452E-08	9.03973E-15
H2PO4-	0.01763267	7.83451E-09
HPO4-2	0.006321291	2.80866E-09
Fe2(OH)2	1.46277E-16	6.49937E-23
FeOH+2	6.70319E-07	2.97835E-13
Fe(OH)2+	8.12797E-05	3.6114E-11
CaOH+	6.68132E-07	2.96863E-13
MgOH+	9.362E-07	4.15971E-13
HSO4-	3.15995E-07	1.40402E-13
Cl2(G)	0	0

ClO-	0	0
H2	0	0
Na+	1898.081167	0.000843352
Fe(OH)3	1.57629E-08	7.00374E-15

Table D7.10. Solids formed in concentrate stream

Compound	amount [g]
Fe(OH)3	0.024084096

Table D7.11. CO2USE stream results

Compound	Molar Flow [mol/s]	Concentration [mol/L]
CO2	1.50523E-06	1.17387E-11
H2O	70348.93925	0.548623737
H3O+	1.20635E-09	9.40788E-15
OH-	307.492147	0.00239801
Na+	1875.000195	0.01462239
HCO3-	0.674549125	5.26054E-06
CO3-2	783.4167494	0.006109559

Table D7.12. Volume of streams examined

Vol. Flow CONC [L/s]	2250639.71
Vol. Flow CO2USE [L/s]	128228.027

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