

Techno-Economic Assessment of Carbon Capture for Integrated Steel Mills in Canada

by

Anne Adetola Titcombe

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2025

© Anne Adetola Titcombe 2025

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.

I understand that my thesis may be made electronically available to the public.

Abstract

Globally and within Canada, steel production accounts for 10% and 23% of total industrial CO₂-eq emissions, respectively. This is primarily owed to the prevalence of the traditional blast furnace-based integrated steel mill, responsible for 73% of steel production globally. This thesis investigates the techno-economic feasibility of carbon capture methods within a Canadian integrated steel mill, focusing on reducing the direct emission intensity of hot rolled steel slabs till non-emitting steel production methods can be employed.

The study emphasizes two post-combustion capture techniques: First, Monoethanolamine (MEA) absorption identified as the primary technology due to its maturity and cost efficiency. Second, hybrid methods combining vacuum pressure swing adsorption with low-temperature purification (VPSA-LTP) are explored for their commercial potential and lower thermal energy penalty relative to the chemical absorption base case.

A systematic framework involving performance modelling using Aspen Plus and Aspen Adsorption, and cost assessment evaluates energy consumption, cost implications, and environmental benefits of both carbon capture methods. The opportunity for waste heat recovery for the steel production process was also evaluated. A surrogate-based optimization framework was developed and proven to be a tool for conducting a less-computationally intensive techno-economic assessment of batch separation processes.

Key findings highlight that the lowest capture cost of \$75 per tonne of CO₂ captured (\$86 per tonne of CO₂ avoided) is achieved using a single-point of capture: the central power station, due to its volume and high CO₂ composition. To achieve this minimum cost alongside its' lowest achievable steel emission intensity, this carbon capture implementation includes MEA absorption with an oxy-combustion boiler and waste heat recovery from flared gas and flue gases to offset energy demand. In the case of natural gas supply constraints and overall reliance on electricity, using a hybrid VPSA-LTP process offers the lowest electricity consumption at a cost of \$120 per tonne of CO₂ avoided. Overall, carbon capture can be used to reduce the emission intensity to 0.76 tonnes of CO₂ per tonne of hot rolled steel slabs while increasing the production cost by 17% to \$741 per tonne of steel.

It is recommended that advanced solvents and sorbent be explored to further reduce the energy penalty and increase the productivity of their respective methods. There must also be evaluation of alternative decarbonization schemes for further emission reduction and the potential of heat integration with the existing power station to generate more steam in lieu of electricity. There must also be a multi-disciplinary assessment of the impact of policies on the viability of carbon capture as a decarbonization solution for the steel industry.

Acknowledgements

I offer the greatest thanks to God because He has never failed me yet.

I appreciate my family, whose physical, emotional and financial support made the completion of this work possible. To my dad, who always made me feel limitless and worked so hard to make sure I thrived here. To my mum, whose prayers never ceased and who started her master's degree at the same time and ensured we pushed each other right to the end. I thank my siblings for being my constant source of motivation and always being on the receiving end of many harrowing Facetime calls to give me solace and encouragement.

This journey would not have been quite the same without the family I have built here in Canada, who have been my sustenance. Simon-Peter, the very definition of dependability, who has been steadfast cheerleader and partner to me. To my friends, Ingowari, Belinda, Ophélie, Kara and Ekpereka who have taken turns in carrying me to the finish line. My research group members, who have been listening ears to tolerate my incessant yapping, and who have been so considerate despite my inconvenient takeover of computing resources.

I want to extend special thanks to Dennis Herman, who was crucial to the success of most of my ideas regarding the most efficient use of computing resources. To Judy Caron, Erene Georgiou and Sarah Fischer, our front desk gals, who did the invisible work that got me funding, feeding and fun throughout this journey. To Sarah Meunier, who encouraged me to start this journey, and who has never failed to check in since I started university till date.

I appreciate Professor Xianshe Feng and Professor Luis Ricardez-Sandoval who reviewed this work and offered much helpful feedback for improvement.

In all this, a lot of my drive would have come to nought without Professor Eric Croiset who has channelled this drive and given my interests, a strong focus over the last 5 years. I offer my sincere gratitude for his time, experience, advice, many calls and deadlines met with his support.

I'd like to acknowledge the NSERC Alliance Mission and the International Master Experience Program who provided the funding which made this work possible. I also want to thank the Kris Bajaj Foundation and the Inch Family whose scholarships offered me great support in completing this work.

Finally, I want to thank the team at STELCO, especially Chad Cathcart and Katie Chan, for their insight into the steel production process and their openness to possibilities and new ideas.

Table of Contents

Author's declaration.....	ii
Abstract	iii
Acknowledgements.....	iv
List of Figures	vii
List of Tables.....	ix
List of Abbreviations.....	xi
List of Symbols.....	xii
1 Introduction	13
1.1 Emissions Outlook.....	13
1.2 Case study overview	14
1.3 Decarbonization Measures.....	16
1.4 Objective of study	16
1.5 Structure of thesis	17
2 Background.....	18
2.1 Iron and Steel Industry Decarbonization	18
2.1.1 Iron and Steel Production Routes	18
2.1.2 Steel Plant Energy Consumption	22
2.2 Carbon Capture Technology	24
2.2.1 Carbon Capture Methods	24
2.2.2 Comparison of carbon capture methods	35
3 Methodology.....	44
3.1 Chemical Absorption Model Building.....	44
3.1.1 ASPEN Plus Simulation Development.....	45
3.1.2 Design Scale-up	54
3.1.3 Reboiler Duty Production	55
3.2 Hybrid VPSA-LTP Model Building.....	63
3.2.1 Rigorous Model Development.....	63
3.2.2 Surrogate Model Development.....	79
3.2.3 Genetic Algorithm Optimization.....	85
3.3 Economic Model Specification.....	88
3.3.1 Economic Assumptions.....	88

3.3.2	Surrogate Cost Model	94
3.3.3	Special Unit Costing	95
4	Results	96
4.1	CO ₂ capture using chemical absorption.....	96
4.1.1	Base Case - CO ₂ capture using MEA Absorption at different emission points	96
4.1.2	Reboiler Heat Substitution.....	102
4.2	CO ₂ Capture using a hybrid vacuum pressure swing adsorption.....	112
4.2.1	Surrogate Model Validation	112
4.2.2	Design Variable Analysis	118
4.2.3	Surrogate-Based Optimization Model Assessment.....	123
4.2.4	Optimal VPSA-LTP Process Configuration.....	128
5	Conclusions	132
6	Future Work	134
	References.....	136
	Appendices.....	152
	Appendix A: Coke and Slag Specification	152
	Appendix B: Software Interlinking	154
	B1. Excel-MATLAB.....	154
	B2. Excel-Aspen Plus	155
	B3. Excel-Aspen Adsorption	157
	Appendix C: Supplementary Information: Lessons Learned in Building VPSA and TSA Models	161
	C1. Setting User Subroutines for Custom Kinetic Models for RADFRAC	161
	C2. Convergence of Aspen Plus Model.....	166
	C3. Convergence of Aspen Adsorption Models	168

List of Figures

Figure 1: Canadian 2019 Heavy Industries Sector Emissions	13
Figure 2: Fuel and Flue gas flow schematic for an integrated steel mill. CO ₂ molar composition from [9]	14
Figure 3: Global Steel Production Routes [1]	18
Figure 4: Energy intensity of major steel production routes – Data from the Canadian Steel Producers Association [13]	23
Figure 5: Integrated Steel Mill showing the process streams, fuel streams and emissions[22],....	23
Figure 6: Published patents with active/pending status from 2003 - 2023	35
Figure 7: Techno-economic assessment modelling framework	44
Figure 8: Chemical Absorption Process Configuration	45
Figure 9: Experimental vs Simulation Data for a) CO ₂ Absorbed in Absorber b) Stripper CO ₂ Flow Rate	53
Figure 10: Production of steam through a) Gas-fired boiler b) Electric boiler	57
Figure 11: Heat Recovery Steam Generator Process Flow Diagram	58
Figure 12: Heat recovery from solid streams a) Coke Dry Quenching, b) Dry Slag Granulation	59
Figure 13: Integration of CO ₂ compression with Heat Recovery Steam Generator	62
Figure 14: Hybrid VPSA-LTP Process Flow Diagram	63
Figure 15: VPSA Cycle showing the 4 steps and the pressure swings	66
Figure 16: VPSA Simulation Development Framework	67
Figure 17: Breakthrough curves: a) Composition Profile b) Temperature Profile	73
Figure 18: TSA Dehydration Schematic	75
Figure 19: Low Temperature Purification Process Flow Diagram	77
Figure 20: Hybrid VPSA-LTP Model showing CPU times and unknown variables	79
Figure 21: Surrogate Model Development	80
Figure 22: Comparison of steel plant with and without CO ₂ capture	88
Figure 23: Capital cost levels and elements	92
Figure 24: Direct CO ₂ emission sources within the steel plant	96
Figure 25: MEA Absorption at different emission points in a steel plant showing the cost and emission reduction	100
Figure 26: Specific cost breakdown of MEA absorption cost at different emission locations ...	101
Figure 27: Impact of MEA absorption on the post-capture emission intensity of steel	102
Figure 28: Comparison of the impact of steam production from gas-fired boilers vs electric boiler on the capture costs and the post-capture emission intensity of hot metal	105
Figure 29: Comparing different combination of gas-fired boiler steam and waste heat utilization at 90% Capture of the Central Power Station, showing a breakdown of reboiler heat duty sources and the impact of the emission intensity	106
Figure 30: Impact of waste heat utilization supplemented with natural gas boilers on the capture costs	107
Figure 31: Comparing different combination of electric boiler steam and waste heat utilization at 90% Capture of the Central Power Station, showing a breakdown of reboiler heat duty sources and the impact of the emission intensity	107

Figure 32: Impact of waste heat utilization supplemented with electric boilers on the capture costs.....	108
Figure 33: Reboiler duty breakdown at varying capture levels contained by waste heat utilization	109
Figure 34: Capture cost at varying capture levels constrained by waste heat utilization	110
Figure 35: Comparing different combination of an oxy-combustion boiler and waste heat utilization at 90% Capture of the Central Power Station, showing a breakdown of reboiler heat duty sources and the impact of the emission intensity.....	111
Figure 36: Impact of waste heat utilization supplemented with electric boilers on the capture costs.....	111
Figure 37: Multimodal surrogate model approach.....	112
Figure 38: RMSE for different surrogate model type for different output variables a) Blowdown energy b) Desorption energy c) Blowdown time d) Desorption time e) CO ₂ Recovery f) CO ₂ Purity g) Total Product per Cycle	114
Figure 39: Surrogate Model Validation a) Specific Cost b) Specific Energy c) Overall Recovery d) Overall Purity	117
Figure 40: A) VPSA CO ₂ Purity vs VPSA CO ₂ Recovery B) Specific cost vs VPSA CO ₂ Purity for design points with recovery > 90%	119
Figure 41: Specific CO ₂ capture cost vs adsorption time	120
Figure 42: A) Specific CO ₂ capture cost vs blowdown time B) Specific CO ₂ capture cost vs evacuation time	120
Figure 43: A) Specific CO ₂ capture cost vs blowdown pressure B) Specific CO ₂ capture cost vs evacuation pressure C) Specific CO ₂ capture cost vs evacuation flowrate D) Specific CO ₂ capture cost vs LTP flash pressure.....	121
Figure 44: A) Specific CO ₂ capture cost vs column molar flowrate B) Specific CO ₂ capture cost vs H/D ratio C) Specific CO ₂ capture cost vs Height D) Specific CO ₂ capture cost vs Diameter	122
Figure 45: Impact of the sample size on the effect size for design variables	123
Figure 46: Impact of the sample size on the effect size for output variables.....	124
Figure 47: Overall Cost Breakdown of MEA Scrubbing and VPSA-LTP processes.....	130
Figure 49: Capital Cost Breakdown for the MEA Scrubbing and VPSA-LTP processes.....	130
Figure 50: Comparison of the Impact of the VPSA, VPSA-LTP and the MEA Scrubbing Base case on steel emission intensity and capture costs.....	131

List of Tables

Table 1: Characteristics of direct CO ₂ emission point sources. Data hidden for confidentiality..	14
Table 2: Direct emission reduction schemes in steelmaking	16
Table 3: Steel Production Routes by feedstock.....	18
Table 4: Raw material preparation for different steel production pathways.....	18
Table 5: Iron Ore Reduction Reactions.....	19
Table 6: Patent query	35
Table 7: Performance for reviewed Carbon Capture technologies	37
Table 8: Literature Overview of Post Combustion Capture Methods in Iron and Steel Plants	43
Table 9: Solution chemistry model	47
Table 10: Transport property models for the liquid and gas phases	48
Table 11: RATEFRAC Specifications.....	49
Table 12: MEA Zwitterion Mechanism Reactions.....	49
Table 13: Literature data on the reaction between CO ₂ and aqueous MEA	50
Table 14: Overall heat transfer coefficient.....	52
Table 15: Absolute error of different reaction kinetic models using NUST standalone column pilot data in [151], [152]	52
Table 16: Absolute percent error of different criteria in the coupled absorber and stripper model from MEA scrubbing plant [150].....	53
Table 17: Kinetic Rate Equations for different model units	54
Table 18: HRSG equipment specifications	58
Table 19: Literature Overview of VPSA Cycles.....	65
Table 20: VPSA Sorbent Properties	68
Table 21: Literature Overview of Equilibrium loading of pure CO ₂ on 13x Zeolite.....	69
Table 22: 13x Zeolite Langmuir Isotherm Constants	69
Table 23: Initial Bed Conditions	71
Table 24: VPSA step terminating conditions and bed profile conditions	71
Table 25: VPSA Evaluation Criteria	71
Table 26: Pilot Study Specifications	72
Table 27: Average absolute error for rigorous model	73
Table 28: TSA Bed Specifications [207].....	75
Table 29: TSA Sorbent Isotherm Specifications [207]	76
Table 30: TSA Dehydration specifications	76
Table 31: Phase-specific Overall Heat Transfer Coefficient.....	78
Table 32: Stage 1 Experiment Design Variables, Type and Range	81
Table 33: Stage 2 Experiment Design Variables, Type and Range	81
Table 34: Optimization Problem showing the objective, constraints and the decision variables .	86
Table 35: Feedstock and utility prices	92
Table 36: Surrogate Cost Model Equations and Validation Results	94
Table 37: Single point and combined points of capture and the % of the overall direct emissions	97
Table 38: Technical performance of the MEA Absorption Process designed to capture different emission points in the steel plant	97

Table 39: MEA Absorption Economic Performance at different emission points	99
Table 40: Marginal CO ₂ intensity reduction	102
Table 41: Waste heat streams in the existing steel plant, stream properties and heat recovery performance	103
Table 42: Exergy analysis of CCU modifications - Compressors vs Heat Pumps	104
Table 43: Description of different heat integration-constrained capture scenarios.....	109
Table 44: Multi-model Surrogate Models, Parameters and Validation Results	115
Table 45: Hypothesis test results for difference due to number of runs	124
Table 46: Surrogate-based GA optimization results	125
Table 47: Optimized design point validation for the VPSA-LTP process	126
Table 48: Optimization CPU times based on the rigorous model vs the surrogate model	127
Table 49: Minimum cost configuration for the VPSA-LTP process (Inlet CO ₂ 28 vol %).....	128

List of Abbreviations

- **BFS:** Blast Furnace Stoves
- **BOF:** Basic Oxygen Furnace
- **CCS:** Carbon Capture and Storage
- **CCU:** CO₂ Compression Unit
- **CDQ:** Coke Dry Quenching
- **CO:** Carbon Monoxide
- **CO₂:** Carbon Dioxide
- **COG:** Coke Oven Gas
- **CPS:** Central Power Station
- **DRI:** Direct Reduced Iron
- **DSG:** Dry Slag Granulation
- **EAF:** Electric Arc Furnace
- **GHG:** Greenhouse Gas
- **HRS:** Hot Rolled Steel
- **HSM:** Hot Strip Mill
- **LTP:** Low-Temperature Purification
- **MEA:** Monoethanolamine
- **Mt:** Metric tonne
- **MDEA:** Methyl diethanolamine
- **NO_x:** Nitrogen Oxides
- **PP:** Power Plant
- **SO_x:** Sulfur Oxides
- **TSA:** Temperature Swing Adsorption
- **VPSA:** Vacuum Pressure Swing Adsorption

List of Symbols

Symbol	Description
A	Cross-sectional area.
A_s	Surface area for heat exchange.
C_p	Specific heat capacity.
D	Diffusion coefficient.
f_i	Fugacity of species ii.
G_t	Total Gibbs energy.
C_p	Heat transfer coefficient.
H_{vap}	Heat of vaporization.
h	Enthalpy
K	Equilibrium constant.
k	Reaction rate constant or mass transfer coefficient (context-dependent).
L	Length of the column or system.
$\dot{m}$	Mass flow rate.
μ_i	Chemical potential of species i or Mean (depends on context)
P	Pressure.
$\dot{Q}$	Heat transfer rate.
R	Universal gas constant.
ρ	Density.
σ	Standard deviation
T	Temperature.
τ	Residence time.
U	Overall heat transfer coefficient.
v_i	Stoichiometric coefficient of species ii.
x_i	Mole fraction of species ii in the liquid phase.
y_i	Mole fraction of species ii in the gas phase.
z	Axial coordinate.
ϵ	Extent of reaction or void fraction in adsorption.
η	Efficiency factor.
γ_i	Activity coefficient of species ii.
ϕ	Fugacity coefficient.

1 Introduction

1.1 Emissions Outlook

Steel is a critical material that constitutes the backbone of construction of all forms of infrastructure, from buildings to automobiles, thus its production has a significant impact on the economy and the environment. According to the 2020 IEA estimations, iron and steel production accounts for 3.7 Gt of CO₂ eq emissions globally, corresponding to 10% of the direct and indirect CO₂ emissions attributed to industrial process globally [1]. In Canada – the base location for this study - based on 2019 estimates shown in Figure 1, steelmaking is the largest industrial energy user accounting for 23% of the industrial emissions and 3% of total CO₂ eq emissions [2].

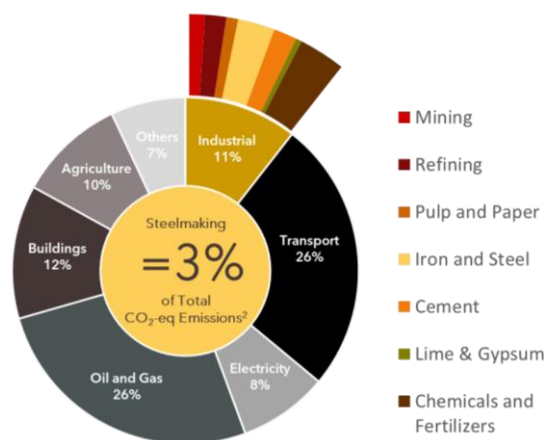


Figure 1: Canadian 2019 Heavy Industries Sector Emissions

Steel is produced at 13 plants in five Canadian provinces (Alberta, Saskatchewan, Manitoba, Ontario and Quebec). The industry is concentrated in Ontario, with six plants in operation, where this study is based.

So why is it critical to pursue the decarbonization of the existing steel production pathways in Canada?

One. To meet the 2050 net-zero targets needed to “avert the worst impacts of climate change” [3].

Two. To achieve environmentally sustainable economic growth. In 2021, this industry produced almost 13 million metric tons of crude steel [4]. Canadian steel industry on average yields an average emission intensity of 1.4 t CO₂ /t crude steel¹ [5]. For context, 1 light-built vehicle contains about 0.95 metric ton of crude steel, meaning each vehicle produced leads to a minimum of 1.3 t CO₂ released for steel supply. For economic growth, manufacturing of this kind is necessary [6]. With forecasted annual growth of 1.4 % in steel demands due to export and local industry needs (construction, transportation, manufacturing) [7], if steel production

¹ Crude steel” is the name given to steel in its first solid form, when it is cast after leaving the final furnace in a given production process.

emissions remains unabated, the national economic growth will remain inextricably linked with the increase in industrial emissions. Thus, meeting any net-zero targets while sustaining growth becomes challenging, if not impossible.

Without decarbonization, these two objectives become diametrically opposed.

1.2 Case study overview

As of 2023, globally and within Canada, 71% and 58% of steel respectively [8], were produced with an integrated steel mill, as shown in Figure 2. Thus, this means of production is the focus of this case study. The process consists of emission intensive units such as a coke oven, blast furnace, basic oxygen furnace, other reheating furnaces and an onsite power plant where the high calorific off-gases of the other units from these processes are combusted to improve energy efficiency.

This study focuses on the key processes of an integrated steel mill that generates █████ tonnes of hot rolled steel per day using pig iron and steel scrap in a █████ ratio. Figure 2 shows the flow of fossil and process fuels into multiple units of the steel plant, along with the flow of resulting emissions. Each solid line shown is proportional to the volume of emissions from the unit. This figure highlights how that the carbon capture design can be complex as it involves multiple emission sources of different volumes and compositions, all distances apart.

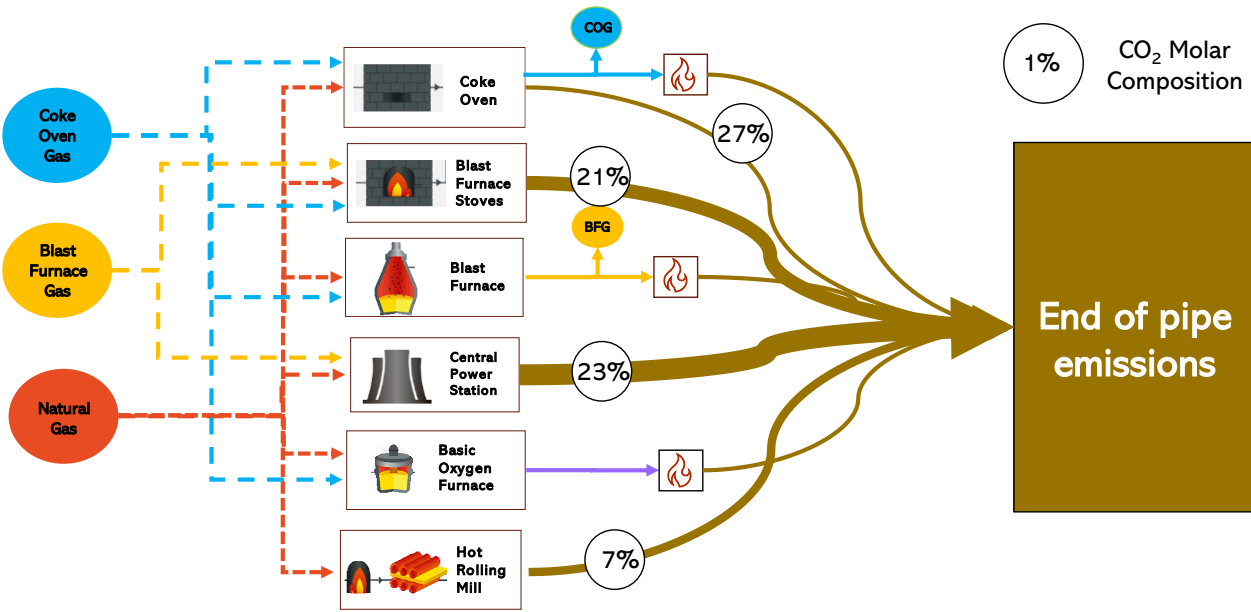


Figure 2: Fuel and Flue gas flow schematic for an integrated steel mill. CO₂ molar composition from [9]

The temperature, pressure and compositions of all the direct CO₂ emission point sources identified at a conventional integrated iron and steel mill are summarized in Table 1.

Table 1: Characteristics of direct CO₂ emission point sources. Data hidden for confidentiality.

					Flare Stack
--	--	--	--	--	-------------

Capture Location	Coke Oven	Hot Strip/Rolling Mill	Central Power Station	Blast Furnace Stoves	Coke Oven Gas	Blast Furnace	Basic Oxygen Furnace
Flue Gas ID	EG-1	EG-2	EG-3	EG-4	COG	BFG	BOFG
Flue Gas Description	Exhaust gas from coke oven	Exhaust gas from hot strip/rolling mill	Exhaust gas from power plant	Exhaust gas from blast furnace stoves	Coke Oven Gas to flare stack	Blast furnace gas to flare stack	Steelmaking process gas to the flare stack
Molar Composition							
CO							
CO ₂							
H ₂ O							
H ₂							
N ₂							
CH ₄							
C ₂ H ₄							
C ₂ H ₆							
C ₃ H ₈							
O ₂							
Flue gas design pressure [kPa]							
Flue gas design temperature [C]							

Beyond the emission stream properties, the selection of a decarbonization method must consider other factors peculiar to the case study. There may be a constraint of the natural gas supply available to the plant so considered methods cannot rely on an excessive expansion in fuel supply. We assume that there is no similar constraint on the electricity supply that can be bought from the grid. It is understood that the blast furnace and the coke oven have a lifetime of about 20 years so any emission reduction technology used must have reached commercial readiness to be implemented during its useful life. There is also opportunity for CO₂ storage at the location, CO₂ must be captured at a purity and pressure that is conducive for pipeline transport

1.3 Decarbonization Measures

Decarbonization measures can extend to a wide scope of direct or indirect emissions. The measures considered here only deal with “Scope 1” emissions of the plant. Scope 1 emissions refer to the direct greenhouse gas (GHG) emissions from sources that are owned or controlled by the steel companies such as fuel combustion, process and fugitive emissions. Thus, emission due to the grid’s electricity supply mix are not covered.

Ideally, a complete replacement of the existing manufacturing process with lower emission process can achieve reduction of the direct emissions. However, the typical lifetime of a steel making asset is 40 years [10]. This presents a challenge as the substantial capital investment for new processes gets delayed till the end of the asset’s useful life. Several innovative technologies need time to be economically feasible at the scale needed to replace existing ones. The decarbonization measures are subsequently categorized in Table 2, based on what is achievable in an existing integrated steel mill plant’s useful lifetime.

Table 2: Direct emission reduction schemes in steelmaking

Time scale	Decarbonization measures [11], [12], [13]
Short Term [0 – 5 years]	Energy efficiency schemes: - Reduction of air leakages - Furnace dehumidification - Improvement in cross cutting industrial systems: boilers, pumps and compressors
	Waste heat recovery
Mid term [5- 25 years]	Carbon capture, utilization and storage
	Renewable H ₂ as a fuel
	Blast furnace top gas recycling
	Electrification of heating via electric boiler, induction heating
Long term [25+ years]	Direct reduced iron ore using renewable H ₂
	Replacement of basic oxygen furnaces with electric arc furnaces

In this study, carbon capture and storage [CCS] is assessed as a midterm measure of curbing emissions in an integrated still mill. The national decarbonization strategy has emphasized the role of carbon capture, utilization and storage in reducing the emissions of the steel industry [14]. It has been estimated that for Canada to meet national emission target of 40% reduction by 2030 using post-combustion capture in an economically, socially and environmentally optimal manner, about 16 – 18 carbon capture plants would have to be implemented in the heavy industry sector [15]. In this thesis, one such scenario for the steel industry is explored in detail.

1.4 Objective of study

The objective of this thesis is to perform a techno-economic assessment of commercially viable carbon capture methods for an integrated steel mill – chemical absorption as the baseline and a

promising alternative, hybrid vacuum pressure swing adsorption. The potential of waste heat recovery to supplement the required energy for the capture process will also be evaluated.

The boundary of the existing process assessed in this study includes raw material preparation, all crude steel production units up until the production of [REDACTED] tonnes of hot rolled steel. It also covers the onsite co-generation power plant. Upstream and downstream emissions are not included in the context of this study.

The battery limit of the carbon capture process includes flue gas cooling and dehydration (if needed), CO₂ removal technology and compression of the CO₂ to 110 bars for transport. It excludes any flue gas treatment on the assumption that SO_x and NO_x impurities have been reduced to acceptable levels before carbon capture unit. The assessment also excludes any CO₂ transport and storage, and any considerations for onsite utilization.

The expected contribution of this thesis to the existing work is the quantification of the economic impact of carbon capture on the cost of “greener” integrated steel mill production in Canada. While several studies [13], [14], [16] highlight potential role in decarbonization of the steel industry in Canada, no comprehensive techno-economic study has been published to qualify its commercial feasibility.

1.5 Structure of thesis

The introduction outlines the current emissions outlook for the steel industry, decarbonization measures, and the specific case study of an integrated steel mill in Canada.

The background describes iron and steel production routes and carbon capture technologies. It contains a literature review of these capture technologies. It compares absorption, adsorption, and hybrid methods in terms of energy requirements, cost, and technical maturity.

The methodology details the development of performance and economic models for chemical absorption and hybrid vacuum pressure swing adsorption-low temperature purification (VPSA-LTP). It further details the literature reviewed and referenced in the development. It also describes work conducted within simulation tools such as Aspen Plus, Aspen Adsorption and the optimization framework employed.

Next the result section presents the outcomes of implementing the different carbon capture methods at various emission points within the steel mill. It analyses energy consumption, cost metrics, and the impact of heat integration strategies on feasibility.

Finally, the conclusion summarizes findings, emphasizing the viability of post-combustion MEA absorption and hybrid VPSA-LTP methods. Offers recommendations for future integration of capture technologies and policy implications for decarbonizing steel production.

The back matter includes supporting data, and supplementary information for replicating the study.

2 Background

2.1 Iron and Steel Industry Decarbonization

2.1.1 Iron and Steel Production Routes

Commercial grade steel is produced from iron ore - a compound of iron, oxygen and other minerals that occurs in nature, or from scrap steel. The processes shown in Table 3, categorised by feedstock, are primarily used to generate steel globally [17]:

Table 3: Steel Production Routes by feedstock

Feedstock	Iron Ore	Scrap Steel
Production Route	1. Blast-Furnace/Basic Oxygen Furnace process [BF - BOF] 2. Direct-reduction process/ Electric Furnace [DRI -EAF] 3. Direct-reduction process/ Basic Oxygen Furnace [DRI - BOF] 4. Smelting reduction process /Basic Oxygen Furnace process	1. Open-hearth furnace 2. Electric Furnace 3. Basic Oxygen Furnace
% of Global Production [1]	68	32

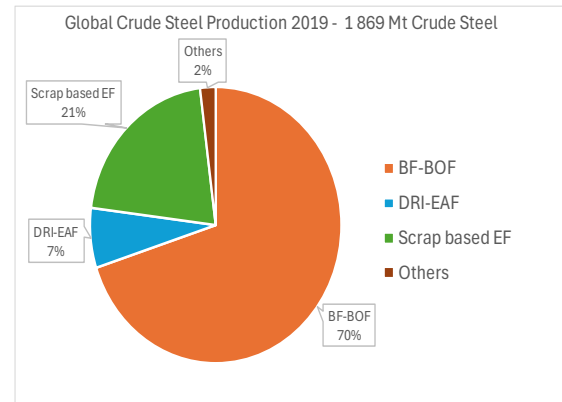


Figure 3: Global Steel Production Routes [1]

Regardless of the selected process, the commercial steel production pathway consists of 6 key steps.

- 1) Raw material preparation
- 2) Iron making (if iron ore is feedstock)
- 3) Steel making
- 4) Secondary Metallurgy
- 5) Casting and Rolling
- 6) Finishing

To identify opportunities to reduce steelmaking emissions, the steel production pathway, individual processes and their energy requirements, must be understood.

2.1.1.1 Raw Material Preparation

The raw material preparation differs drastically based on the production method. Table 4 shows the energy demands or raw material preparation for the main production pathways:

Table 4: Raw material preparation for different steel production pathways

	Blast-Furnace/Basic Oxygen Furnace process	Smelting	Direct Reduction	Scrap Steel Production
Raw material	Iron ore, Coal, Limestone	Iron Ore	Iron Ore	Scrap steel

Preparation method	Iron ore sintering + Coal gasification	Iron ore pelletisation	Iron ore sintering/pelletisation	Sorting, Decoating, Shearing/Grinding, Compacting
Fuel Energy Intensity (GJ/t-steel slab)	2.6	0.5	2.5	Preparation requirements reduce based on quality of the source [in order of increasing quality]: 1. Post-consumer products 2. Steel product manufacturing scrap 3. Steelmaking scrap
Electricity Energy intensity (GJ/t-steel slab)	0.3	0.1	0.3	
Source	[18]	[18]	[18]	

2.1.1.2 Iron Making

Steel is an alloy of Iron - Fe and Carbon - C. Iron ore, however, contains these 3 iron oxides relevant for metallic iron: hematite - Fe_2O_3 , Wustite - FeO , magnetite - Fe_3O_4 (in their molecular forms). Though Wustite is unstable at $> 570^\circ\text{C}$ and decomposes to Fe and Fe_3O_4 , the other oxides must be chemically reduced to Fe using agents, such as C, CO and H_2 , as shown in Table 5.

Table 5: Iron Ore Reduction Reactions

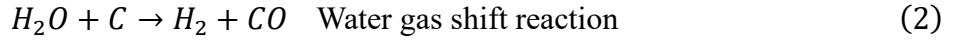
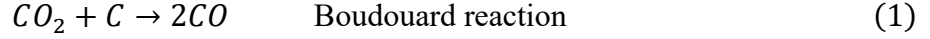
Reducing Agent	Reactions with standard heat of reaction per mol Fe at 25°C [19]	
C	$3 \text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2 \text{Fe}_3\text{O}_4 + \text{CO}$ $\text{Fe}_3\text{O}_4 + \text{C} \rightarrow 3\text{FeO} + \text{CO}$ $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}$	+22.1 kJ/mol Fe +30.5 kJ/mol Fe +163 kJ/mol Fe
H_2	$\text{Fe}_2\text{O}_3 + 3 \text{H}_2 \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O}$	+49.7 kJ/mol Fe
CO	$\text{Fe}_2\text{O}_3 + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{CO}_2$	-12.1 kJ/mol Fe

In the following sections, several iron-making process based on these reduction reactions are discussed.

2.1.1.2.1 Blast Furnace Process

In a blast furnace, the iron ore is converted to a molten state using a blast of preheated air at about 1300°C . The blasted air is preheated in the furnace ovens via combustion of coke or natural gas or other fuels, which generates CO_2 .

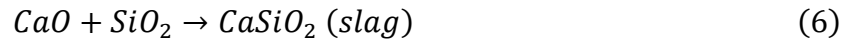
Although coke is the main reducing agent, exothermic side reactions of the coke with any present H_2O and CO_2 form auxiliary reductants such as H_2 and CO, known as the boudouard and water gas shift reactions, respectively:



The coke also undergoes partial and full combustion to generate heat for the highly endothermic reduction processes and more reducing gas and CO_2 .



With all 3 reducing agents present and the varying temperature and composition profile along the height of the furnace, different ratios of the reduction reactions occur to produce molten pig iron (Fe) and blast furnace gas - a CO , CO_2 and H_2 rich mixture. The limestone, fed into the furnace with iron ore, decomposes through a highly endothermic calcination reaction to generate even more CO_2 and CaO , which removes silica impurities to reacting to form slag:



The bevy of reactions highlighted show that CO_2 emissions from the blast furnace process is not merely a product of combustion to meet the thermal energy demands of the process, but also a major product of the reduction and purification reactions essential to creating highly pure and homogenous iron. The fuel consumption to meet this demand is estimated at 11.4 GJ/t steel [18]. Hence why this process' emissions is notoriously considered difficult to abate.

2.1.1.2.2 Smelting Reduction Process

This process cyclically pre-reduces the iron ore in a series of fluidized beds to partial direct reduced iron (DRI) and then further reduces iron ore in a melter gasifier which simultaneously smelts the ore, gasifies coal, and produces a stream of reducing gases for the fluidized bed. The fuel energy intensity for smelt reduction is estimated at 15.9 GJ/t steel [18]. As of 2020, it was only used at industrial scale in China, India and Korea [19].

2.1.1.2.3 Direct Reduction Process

This process was designed with intention to achieve reduction of iron ore in its solid-state form thus bypassing the high temperatures and consequently the high energy demands of melting. This process generates a hot briquetted or “sponge iron”.

The variation in commercially available DRI process depends on the type of reductant or the source of reducing gas which can be

1. Solid coal based – Some industrially adopted processes include: FASTMET, SL/RN, used primarily in Southeast Asia to process low grade ore with low-grade non-coking coal at smaller scale [20]. Coal is used directly as a reductant but can also undergo gasification. A rotary kiln is used for the reduction. Coal based DR processes are uncommon globally due to their low energy efficiency and high sulphur content from the coal used.

2. Gas based – Some industrially adapted process includes MIDREX, ENERGIRON. These processes require high quality iron-ore pellets and a reducing gas contacting at high temperatures. Gas-based direct reduction process commonly consists of 3 sections [17] :
- Shaft furnace or fluidized bed: the iron ore and hot reducing gas is fed for reduction in a shaft furnace if the ore is lumpy or a fluidized bed if the ore is fine. The energy needed for the reduction is directly related to the operating temperature. At higher operating temperatures, less energy is needed in the reduction reaction.
 - Gasification plant/ Reformer: here the reducing gas is generated via catalytic CO₂ or steam reforming of methane, partial oxidation of methane or coal gasification. This section can be altered, if hydrogen is partially or completely supplied through electrolysis.
 - Heat exchanger: For transfer of heat from the flue gas to the reformer feed.

Even though, the iron ore is not melted, the energy for the highly endothermic reductions must be supplied; the fuel consumption to meet these demands of the direct reduction process is estimated at 12.9 GJ/t steel [18]. However, lower emitting fuels can be used to meet this demand.

2.1.1.3 Steel Making

There are 2 main steel making processes, each with distinct energy demands: the electric furnace or the basic oxygen furnace processes.

2.1.1.3.1 The Electric Furnace processes

This includes the most common electric arc furnace and other processes used in production of ultra-pure or high quality alloys, such as induction furnaces, consumable electrode melting process and electro-slag remelting [17]. The main raw material for this process is usually solid scrap steel.

The electric arc furnace uses a high voltage electric current that arcs between 2 electrodes, typically graphite which directly melts the feedstock. Electricity equivalent to 1.7 GJ/t steel is needed for melting [18].

2.1.1.3.2 Basic Oxygen Furnace

This process involves blowing high-purity oxygen onto molten pig iron, direct reduced iron and steel scrap from above, promoting rapid oxidation of impurities and refining without an external heat source [17]. The process generates significant heat through the oxidation of silicon and carbon, alongside a CO rich exhaust gas that could be used as fuel. Slight variations in the process introduces oxygen and hydrocarbons from the bottom, utilizing the endothermic decomposition of hydrocarbons for cooling and delivering steel with very low carbon content and specific slag characteristics. Electricity consumption as high as 0.4 GJ/t steel is needed to produce oxygen through air separation [18].

2.1.1.4 Secondary Metallurgy/Refining

These are ladle treatments conducted to achieve specific steel quality (homogeneity) and compositions. They include desulphurization, dephosphorization, degassing treatment. The key energy requirement is heat needed to maintain the steel in its molten state supplied through chemical heating or an electric arc.

2.1.1.5 Casting and Rolling

Casting and Rolling are integral processes aimed at transforming liquid steel into semi-finished products such as blooms, slabs, or billets

According to Tupkary [21], the process of continuous casting involves several key components: a ladle holds the liquid steel, which is then transferred to a tundish that regulates the flow into a mold. The mold ensures adequate initial solidification of the steel, after which withdrawal rolls carefully remove the ingot from the mold. To ensure complete solidification, the ingot passes through cooling sprays. Energy is supplied to dry and preheat the ladles, heat the tundish, and for motors to drive the casting equipment. The primary energy consumed in continuous casting based on best practices is 0.1 GJ/t steel [18].

The continuous casting process produces steel with uniform properties, essential for further rolling and finishing processes. Because the steel has been solidified during casting, to become malleable for forming, significant thermal energy is supplied through furnaces to reheat the steel above recrystallization temperature. The fuel consumed in hot rolled products supplies about 1.3 – 1.9 GJ/t steel [13], [18]. This reheating energy demand is why this section is usually one of the largest emitters of this production following the steelmaking process.

2.1.1.6 Finishing

This includes bending and cutting to achieve adequate shapes and length, application of metallic or organic coating, rust protection treatments, electrocoating amongst other according to the consumers desired specification. The energy intensity depends on the types of finishing needed.

2.1.2 Steel Plant Energy Consumption

The processes described in section 2.1.1 are combined to produces steel in the two main methods in Canada:

Integrated Steel Mill	Scrap-Steel Mini-mills
• Coal Gasification • Blast Furnace Ironmaking • Basic Oxygen Furnace • Casting and Rolling • Finishing	• Steel collection and Recycling • Electric Arc Furnace • Casting and Rolling • Finishing

Figure 4 shows how the combination of the production methods shown can significantly alter the energy consumption. The energy intensity specified for each production route is based on a study published by the Canadian Steel Producers Association to reflect the different product mixes, local climate impact, production volumes, and grades of steel produced.

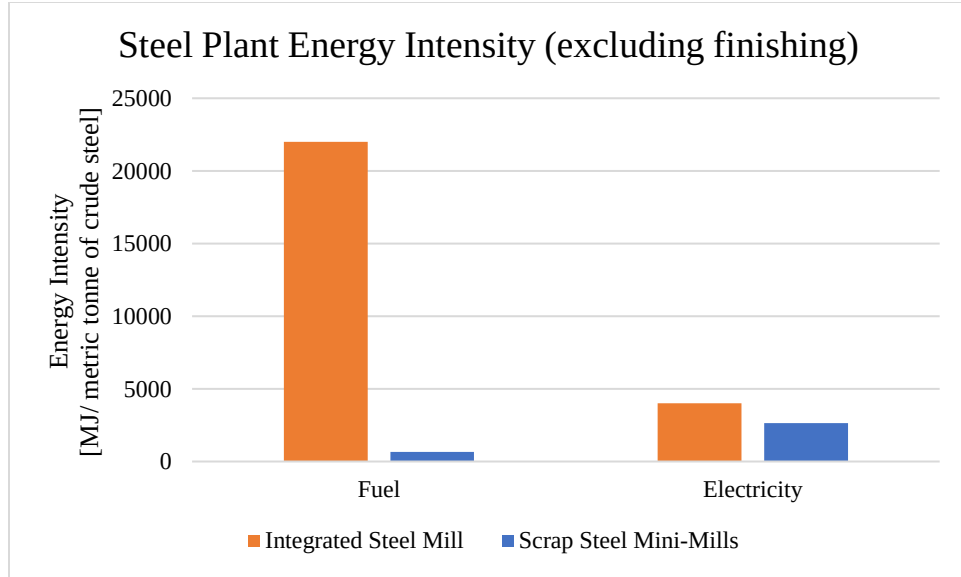


Figure 4: Energy intensity of major steel production routes – Data from the Canadian Steel Producers Association [13]

The **integrated steel mill**, which this study focuses on, accounts for 55% of steel produced in Canada in 2023 [8] and 91% of the steel industry's emissions [11].

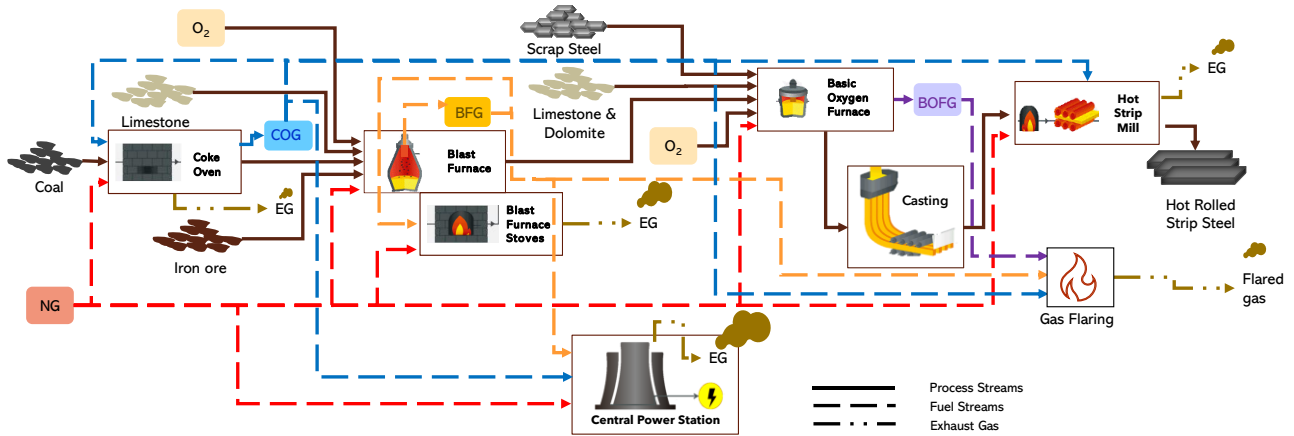


Figure 5: Integrated Steel Mill showing the process streams, fuel streams and emissions[22]

Illustrated in Figure 5 is the integrated steel mill process which shows the raw material preparation, the steel processing units and the flow of fuels to each of these units. Included in this process is an onsite power station where off-gases with high calorific value that are not used within the steel processing units, are sent to produce steam and electricity for the plant. As a result of the distribution of the off-gases across the plant, the large volume of CO₂ released at the blast furnace and coke oven due to natural gas combustion is released to the atmosphere at several point source across the mill: the coke oven stoves, the blast furnace stoves, the central power station, the hot strip mill and the flared gases. One of the challenges of reducing emission is that the locations where most emissions are first released is not the only location of capture and the composition and conditions of these emission streams vary. If there is greater reliance on

this pathway to create “fresh” steel, not made from scrap, the ensuing emissions of the steel production will continue to increase if its decarbonization and eventual phaseout is not pursued.

2.2 Carbon Capture Technology

Carbon Capture is considered in this study as a midterm measure of handling CO₂ emission from the integrated steel mill. This section will cover the different applications of this technology in the iron and steel industry with some reference to the expansive work that has been done in power plants.

Carbon capture covers methods of separating CO₂ streams from industrial processes and different stages of the combustion.

Post-combustion capture focuses on extracting CO₂ from flue gases after the fuel has been combusted with air, making it suitable for retrofitting existing plants like the one in this case study.

Oxy combustion, on the other hand, burns fuel in pure oxygen instead of air, resulting in a flue gas that is mostly CO₂ and water vapor, thus simplifying the capture process.

Pre-combustion capture involves removing CO₂, typically through gasification reactions that convert fuels into a synthesis gas mixture before complete combustion. The capture type could be suitable for CO-rich off gases generated in the steelmaking processes.

2.2.1 Carbon Capture Methods

2.2.1.1 Absorption

Absorption is a carbon capture method where carbon dioxide (CO₂) is removed based on Henry’s Law i.e. the gas solubility (physical solvent) or through the formation of weakly bonded intermediate compounds (chemical solvent). The absorption process consists of two main stages: the absorption stage, where CO₂ is captured by the solvent, and the regeneration stage, where the solvent is heated or depressurized to release the captured CO₂, allowing the solvent to be reused. Chemical solvent due to their chemical reaction are suitable for low CO₂ concentrations (< 30% volume) but need thermal energy for separation of the solvent. Physical solvent relies on a pressure difference for separation and suitable to high concentration (> 30% volume).

Technoeconomic studies of absorption can be largely classified based on the solvent type, as both types have been widely studied for application in the steel industry at different stages on combustion

A. Chemical Solvents

Chemical solvents are the most conventional carbon capture method used in industrial processes. The most widely used of them are the amine-based solvents. The first generation of these solvents adapted from gas treating processes since the 1970s are the alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA) amongst others.

One of the first technoeconomic studies on carbon capture for industrial processes conducted by Farla and Hendrix [23] assessed MDEA-based absorption process for blast furnace gas using

simplified costing methodology and concluded that the method primarily considered in thermal power plants could be adapted to the steel industry decarbonization at a lower cost. Several studies using MEA extended this assessment to all point sources within an integrated steel mill and found that it is more economically feasible to use chemical absorption to capture from few large volume sources like the power plant and blast furnace stoves than from all the point sources [9], [24], [25]. All these studies were in consensus on the substantial thermal energy consumption which ranged from 2 to 5 MJ/kg CO₂. Ho et al. [9] found that capturing from the reheat furnaces can cost 2.5 times more than capturing from the on-site plant or stoves. Integrated steel mills inherently have the advantage of producing off gases with high heating value or waste streams of high temperatures which could have an impact on reducing heat duty of regeneration.

Tsupari et al. [24] evaluated this impact by basing the capacity of the capture plant on the heat recoverable from the steel mill. They found that increasing the avoided emissions can be best achieved by diverting all the steam produced via off gases combustion from the power plant to the capture plant. The cost viability of this heat recovery carbon capture depended on the electricity prices since the electricity must now be bought, if the goal is avoiding more direct emissions.

In addition to the substantial energy consumption which accounts for 50 – 80% of the capture cost [9], other problems encountered in adsorption with these amines is the thermal degradation which limits the regeneration temperature and pressure, and oxidative degradation which leads to corrosion [26] and the environmental impacts of the solvent production process [27].

Much work has been dedicated to developing improved solvent that address some of these problems.

Sterically hindered solvents like aminomethylpropanol (AMP), additives such as piperazine (PZ) and mixed solutions of these solvents have been developed to reduce the regeneration duty and thermal degradation. Modelling their application in the steel plants in comparison to MEA, showed that AMP can reduce the energy penalty by 11 – 21%, while increasing the absorber size for the same level of recovery [28], [29]. The use of piperazine (a solvent which can cost up to 10 times that of MEA) while achieving up to 28% energy reduction, causes increase in the absorber size up to about 4 times due to its lower absorption capacity [28], [30]. Piperazine and other additives have reduced the rate of corrosion which allows the use of carbon steel over the stainless steel.

Non-amine based solvents like ammonia and potassium carbonate have been recommended for their thermal and chemical stability and about 27 – 32% reduction in the regeneration duty [31], [32]. The major constraint with ammonia is the cooling or high-pressure requirement needed to prevent vapor losses which can increase the electricity consumption significantly.

There's been much interest in ionic liquids as “green solvent” which does not need the ammonia production process, a major industrial emitter. Commercial production of these solvents can however cost 5-20 times the cost of conventional solvents [33]. Beyond this, there are challenges such as low CO₂ solubility, mass transfer limitations, high viscosity and insufficient

characterization of the thermodynamic and kinetic behaviour, necessary for large scale modelling [27], [34]. Recent study of ionic liquid/amine mixture solvents for large scale natural gas sweetening application with validated thermodynamic models showed that a 12 – 27% reduction in duty with an 11% reduction in overall capture cost [33]. More demonstration studies and experimental work to corroborate these findings and improve the understanding of ionic liquid behaviours is essential for commercial application to be viable.

Several studies have also considered process intensification to improve the thermal energy requirement such as multi-stage stripping at different pressures, lean vapor compression, rotating packed bed technology, solvent splits, absorber intercooling [25], [28], [35], [36], [37]. There is concern that this modification introduces additional capital cost that might not make any energy saving worth it. Mostafavi et al. showed that the extent of the impact on the capture cost depends on the solvent, with savings less evident on solvents of lower loading capacity [38].

“Superstructure configurations” that apply all forms of process intensification to a single plant, have become the target of optimization studies which have shown that the economic advantages are more evident when handling streams of higher CO₂ composition and volumes [25], [37]. Even with these cost assessments, there is more to be evaluated about the impact of the increased complexity on safe and reliable operation. Thus, any process intensification merits a case-by-case study to abide by the inherently safer design (ISD) principles.

Despite the drawbacks of amine-based absorption methods, they are the most utilized and can serve as a baseline for comparing methods which have not attained similar industrial prominence.

B. Physical Solvents

Physical solvent requires much higher CO₂ partial pressure and with the low composition of process streams, is generally considered for pre-combustion capture. This extends beyond a mere tail pipe addition to impacting the operation of the gas turbines and furnaces used in the steel plant.

Gielen [39] first assessed the use of physical solvents in a precombustion capture process considering that the CO-rich blast furnace gas (BFG) could undergo a water gas shift transformation from CO₂ volume composition of 20% to ~60%. He concluded that this process would incur half the cost of the amine scrubbing baseline. This study’s optimistic modelling did not account for the advanced water gas shift membrane needed for H₂ enrichment or the gas turbine modifications needed to accommodate the change in fuel quality. A more conservative study finds physical absorption of BFG more comparable to MEA capture cost [40]. The electrical energy consumption for this capture method has been estimated at 0.5 – 1.5 MJ/kg CO₂ owing mostly to the compression of the flue gas to 20 – 30 bars [39], [40], [41]. Onarheim [38] advocates for a stage-by-stage modification of a conventional blast furnace into an oxygen based blast furnace with a water gas shift reactor and capture unit, that could yield reduction in emissions with each implemented stage at lower immediate cost.

2.2.1.2 Adsorption

Adsorption carbon capture is a process that captures CO₂ using solid materials known as adsorbents, such as activated carbon, zeolites, and metal-organic frameworks (MOFs). The CO₂ molecules adhere to the surface of these adsorbents, which have high surface areas due to porous nature and specific chemical properties, making them effective at trapping varying levels of CO₂ at different temperatures and pressures. The captured CO₂ can then be released and the adsorbent regenerated through changes in pressure or temperature, allowing for repeated use.

Adsorption can be classified based on the mechanism for CO₂ attachment which can be through nonspecific dispersion and electrostatic interactions (physisorption) or specific and stronger chemical bonds (chemisorption).

The design of a sorbent must account for the sorbate and sorbents properties and the interaction between them [42]. The gas properties metrics considered are the molecule's kinetic diameter and the polarizability. Kinetic diameter is a measure of the molecules effective size when it interacts with other molecules. It impacts how the molecules diffuse through the sorbent pores, essentially making the sorbent a “molecular sieve”. Polarizability is the ability of a molecule to disperse its electron density unevenly in an electric field. Higher polarizability increases the strength of the electrostatic interaction between the sorbent and sorbate.

Activated carbon and zeolites, rely on physisorption, where CO₂ molecules adhere to the surface through weak Van der Waals forces, making it suitable for rapid adsorption and desorption cycles. Synthetic zeolites such as Zeolite 13X, the benchmark sorbent, are modified through an ion-exchange process to improve their basicity and tune the pore size for acidic gases like CO₂ which has a smaller kinetic diameter than N₂.

In contrast, amine-functionalized adsorbents use chemisorption, where CO₂ forms stronger chemical bonds with amine groups, resulting in higher selectivity and capacity for CO₂ but requiring more energy for regeneration [43].

Metal-organic frameworks (MOFs), can be designed for either physisorption or chemisorption depending on their functional groups and metal sites, offering a versatile approach for CO₂ capture with tunable properties.

Another common classification of adsorption methods is based on the method of regeneration: pressure swing adsorption (PSA), vacuum-pressure swing adsorption (VPSA), temperature swing adsorption (TSA) and electrical swing adsorption (ESA). Each method of regeneration has its specific advantages and applications, depending on the operational requirements and the properties of the gas mixture being processed.

PSA and VPSA are pressure-based methods for cases where rapid pressure changes are feasible and efficient. TSA relies on temperature changes, making it suitable for processes where thermal control is more practical. ESA, an emerging technology, uses electric fields for regeneration, promising precise control and potentially lower energy consumption [44]. The choice of method depends on factors such as the concentration of CO₂, the desired purity, energy efficiency, and the specific industrial application.

The basic swing adsorption cycle consists of 4 main steps:

1. Adsorption: During this step, the feed -as mixture is passed through an adsorbent material in a column or bed. The adsorbent selectively adsorbs one or more components from the feed gas based on differences in their adsorption affinities. The less strongly adsorbed component(s) pass through the column as the waste gas.
2. Desorption: For PSA, the pressure in the adsorption bed is reduced, causing the adsorbed components to desorb from the adsorbent. For TSA, the temperature is increased to desorb the adsorbed components. The desorbed gas, which contains the previously adsorbed components, is removed from the bed.
3. Purge: An inert or low-concentration gas (often a portion of the waste gas) is passed through the bed to purge remaining adsorbed species. This helps to clean the adsorbent and prepare it for the next cycle of adsorption.
4. Regeneration: For PSA, the bed is brought back to the higher operating pressure using the feed gas or a portion of the product gas. For TSA, the bed is cooled down to the operating temperature. This step ensures that the adsorbent is ready for the next adsorption cycle.

The published technoeconomic assessments of adsorption-based carbon capture in the steel industry primarily on pre-combustion carbon capture due the advantage of higher CO₂ composition. Thus, this section will cover steelmaking applications and those in other industries which could be extrapolated for steel industry.

A. Steel Industry Application

In a bid to reduce the blast furnace emissions, a process termed as “Top Gas Recycling” emerged which takes the off gas, extracts the reducing gases (CO and H₂) and feeds them back to blast furnace to reduce the reliance on coke as the main reducing agent [45]. The separation of CO₂ from the off gas is done with adsorption process. VPSA Demonstration tests conducted on the blast furnace gas shows that just increasing the CO₂ volume composition from 22% to 34% reduces the regeneration power consumption by 30% [46]. Quader [47] and Arasto [48] argued that relying on deep vacuum of VSA and VPSA processes instead of compression in PSA reduces the energy consumption. They showed that hybrid process with cryogenic purification have the potential to reduce the electricity consumption to make the equivalent energy requirements comparable to level of amine absorption.

B. Other Industrial Applications

In the earliest studies adsorption using Zeolite 13x on a dry flue gas stream from natural gas power plants (12 – 15 % CO₂), there was a consensus that lower adsorption pressures coupled with deeper vacuums can make adsorption economically viable. Zhang [49] showed that that using atmospheric adsorption pressures and lower feed temperatures (< 40°C) coupled with a deep vacuum (< 0.05 bars) for desorption, leads to lower energy penalty and cost for CO₂ avoided. Ho et al. compared different pressure swings methods using 4-step basic cycle to show that feed pressures above 2 bar do not enhance process economics [50]. Of all operating conditions using a basic 4-step cycle, the most critical factor for reaching high purity streams with over 70% recovery is the evacuation pressure of the desorption process which can consume more that 70% of the total power [49].

To tackle the purity limitations of vacuum-based desorption using 13X without very low vacuum pressure or reducing the recovery, the effectiveness of modifying the basic 4-step cycle has been evaluated. Webley and coworkers proposed multistep cycles including coupled pressure equalization steps, product rinses and refluxes which could permit relative higher vacuum pressure level (> 0.05 bars) [49], [51], [52]. Ho et al. showed that addition of a blow down step, pressure equalization and heavy product reflux can increase purity from 45% to 70% by reducing any N_2 during the evacuation [50]. Hagnapanah and coworkers [53],[54] showed that repressurizing the bed with the light product instead of the feed mixture can increase the product purity and confirmed with pilot studies that it could also extend the upper vacuum pressures limits for achieving over 95% purity to above 0.1 bar. However, these additional steps, even with productivity advantage, come with the penalty of higher capture cost [55].

Novel sorbents such as MOFs with better selectivity were also considered as a measure of meeting purity and recovery constraints at lower energy demands. These sorbents were designed with better thermal stability to take advantage of available heat sources. These improved properties and novelty mean higher price of sorbent. Several studies show that sorbents selection, must go beyond the CO_2 selectivity to consider the energy penalty and the process productivity. Danaci [56] accounted for all these factors in a method designed to screen sorbents based on the process economics and estimated a threshold cost above which the cost of the sorbent is relatively unimpactful. The UTSA-16 MOF has been extensively shown to deliver energy reduction benefits, with capture costs that are comparable to the benchmark 13x zeolite [55], [56], [57], [58], [59].

Rather than aiming for high adsorption purity, Fong et al. [60] investigated using a high recovery VSA process to concentrate the flue gas stream from 12% to $> 60\%$ volume CO_2 and then introducing a low temperature purification process. They found that when optimized for minimum energy consumption, this hybrid process can be comparable to the equivalent energy consumption of an MEA process at the same recovery rate.

Attempts to take advantage of heat sources in a temperature-based adsorption process have also been explored. One challenge for TSA application in post combustion capture is the high thermal energy requirement which can be significantly greater than the benchmark amine absorption for the large flue gas flow rates processes [61], [62], [63].

Direct heating with non-product streams (e.g. steam, inert gas, waste heat streams) would result in dilution of the CO_2 stream so this review focused on indirect means of heating. An earlier lab-scale study adopted indirect heating and found the cooling and heating steps to be significantly rate limiting [64]. Novel adsorption and heat exchanger structures which offer larger surface area have also been developed to improve the heat transfer rate [63], [65], [66].

Electrical swing adsorption, where electric current is used to heat up the sorbent by Joule effect [67], induction heating [68] or microwave process [69] have been considered as a means of speeding up the heating process at lab scale. A temperature-electric swing hybrid for power plant flue gas has been modelled which incurs an energy penalty on the plant that is 3 times that of benchmark amine process [44]. Due to scaleup challenges in achieving uniform heating and

novelty, this technology remains to be assessed rigorously based on process cost for industrial scale carbon capture.

A hybrid of vacuum and indirect temperature process, TVSA, has been suggested to allow more moderate vacuum pressure than VSAs and lower thermal energy consumption than TSA [61], [62], [70]. However, for large scale post combustion capture, more optimal configurations, heat exchange structures and vacuum systems that can handle the higher temperatures must be investigated.

2.2.1.3 Cryogenic Capture

Cryogenic Carbon Capture (CCC) is a technology that uses low temperatures to condense and separate CO₂ from gas streams. The main energy requirement of low-temperature capture processes is the compressor shaft work prior to chilling and the compression train of the refrigeration loop.

While there is sparse documentation of techno-economic assessments of cryogenic carbon capture as a standalone use in iron and steel industry, most of the findings on the power plant industry can be applied here. The high purity achieved in this separation is one of its greatest advantages. One of the earliest cryogenic separation technology is the Ryan Holmes distillation method which exploits the solubility of CO₂ in a certain hydrocarbon at low temperature for recovery [71]. The CO₂ is then stripped at high temperature from the hydrocarbon solvent. Herzog [72] modelled this technology for a coal power plant flue gas and found that compression to 30 bars makes it less economically favourable compared to the MEA scrubbing benchmark.

Subsequent cryogenic technologies aimed to remove the solvent and exploit the dew and de-sublimation point differences between CO₂ and N₂. Clodic and Younes [73], [74] proposed the first cryogenic process of frosting of CO₂ at atmospheric pressure on a heat exchanger surface which consumed less than 0.1 MJ/kg CO₂ at CO₂ composition above 8% [75]. Tuinier [76] proposed a dynamically cooled packed bed to depose gaseous CO₂ directly into dry ice onto the bed surface. Ali [77] argued that this packed bed technology could offer energy advantages over the conventional cryogenic distillation especially with increasing CO₂ composition. Song [78] proposed the idea of solid-vapor CO₂ separation using cooling by the Stirling Cycle instead of the widely used Vapor-Compression Refrigeration Cycle. Stirling coolers are theoretically more efficient than the regular refrigeration due to their closed system, regenerative heat exchange, isothermal compression and expansion and use of a gaseous working fluid (no phase changes). However, they are complex and costly to implement at large scale due to the required precision and high-quality materials. In fact, these technologies were limited to lab scale experiments, so their technical and economic feasibility at industrial scale is yet to be determined.

Baxter's group [79], [80] developed a cryogenic looping process (CCECLTM) where a heat-integrated cascade refrigeration cycle is used to freeze CO₂ into a slurry that can be pumped and sublimated separately at over >99% purity. This technology was demonstrated at several pilot programs, and predicted to achieve a 40% reduction in cost compared to amine scrubbing [81].

Belaissaoui et al. [82] modelled a hybrid of membrane and cryogenic flash which can yield high purity streams. They found that at 20% CO₂ volume, compared to the benchmark MEA

scrubbing process, cryogenic flashing will bring a 12% reduction in energy while a membrane-cryogenic hybrid can achieve up to 40% reduction.

Cryogenic capture is also an excellent candidate for precombustion capture since the higher concentration after the water gas shift reaction will make it more advantageous than other energy intensive capture methods. CCC may be favourable in hybrid conditions where the partial pressure of CO₂ can be raised with another capture technology suitable for lower partial pressure, making it potentially more economically feasible.

2.2.1.4 Membranes

Membrane based capture has a distinct advantage over the previously covered methods due to not requiring any form of regeneration or phase change. The process needs semi-permeable membrane that is selective for CO₂ and a sufficient driving force that exploits the difference in the physical, chemical and electronic properties of the species. This driving force is a chemical potential gradient, and the physical structure of the membrane determine the flux of the species.

Membrane's physical structure differs based on the material of construction [83]: Organic membranes refer to those made from polymers. Inorganic membranes are made of metals, ceramics, zeolites and various metallic oxides. They offer the advantages of better tunability, thermal and mechanical stability and less plasticization at lower cost. Mixed matrix membranes are a hybrid of both, having inorganic particles in polymer matrices. There are also carbon-based membranes such as carbon molecular sieve membrane, carbon nanotubes and graphene membranes. Based on their individual properties, molecular interactions, interlinking and layering, these materials could yield a porous or a non-porous membrane.

Depending on the membrane structure, separation can happen through porous or solution diffusion mechanisms. In porous membranes, gas separation can happen through Knudsen diffusion, surface diffusion, capillary condensation or molecular sieving [84]. In nonporous membrane, it happens through solution diffusion. Usually, nonporous polymeric membranes are used in gas separation. According to the solution diffusion model used to represent the behaviour of these membranes, the permeability is the product of diffusivity and solubility of a gas [84]. The selectivity is the ratio of permeabilities for a binary mixture. The productivity of a membrane is determined by these factors. High permeability, characterized by the permeance [GPU] metric, reduces the membrane area needed and high selectivity can improve product purity. Although high permeance and high selectivity for CO₂ over other species are desired, there can be trade-offs between them which can present an optimization challenge when designing a membrane separation unit.

Only a few studies have been dedicated to membrane application in the iron and steel industry, so several finding from power plant will be extrapolated here.

Membrane separation is strongly dependent of a partial pressure driving force which make it more suitable for high CO₂ concentration streams from pre-combustion. Low CO₂ concentration separation demands external energy input to create a pressure gradient. Merkel [85] emphasized that using a vacuum over compression to achieve this pressure gradient can reduce energy costs significantly up to a point and identified higher membrane permeance as another key factor for

cost reduction. Huang [86] found that a pressure ratio of 5 to 15 for feed pressure of 1 to 2 bar with moderate membrane selectivity is critical for membrane technology to become competitive with benchmark capture methods. This means the energy consumption required by compressor or vacuum could impair the commercial feasibility of this capture technology.

Polymeric membranes have shown great potential in gas separation for steelmaking flue gases due to their low production cost on a larger scale and cost reduction potential relative to benchmark amine process [87]. Baker's study [88] found that using the PolarisTM polymeric membrane technology, consumes 0.85 MJ/kg CO₂ at 80% capture, which shows promise for steel plants, particularly with improvements in membrane performance. Yun et al [25] reported that polyimide membrane separation becomes competitive with MEA scrubbing when the feed has a CO₂ mole concentration of 20 – 30 %.

Since the polymeric membrane can easily be poisoned by sulphuric components, Ramirez-Santos et al. [89], [90] investigated blast furnace gas, noting the impact of minor species on membrane permeance and selectivity under real conditions. The 50% decrease in overall membrane permeance and in CO₂ selectivity caused a 10% and 34% increase respectively.

Multi-stage membrane units have been recommended as a means of enhancing the driving force and purity. Zhai and Rubin [91] proposed the two stage system for a power plant as the only way of reaching higher purity than 95% at 90% recovery. Considering that there is a trade-off in permeance and selectivity, Roussanaly and Anantharaman [92] considered a two-stage process that exploited the strength of each factor at different feed concentration. They concluded that for a feed CO₂ of 20 – 30%, a process with a high permeance membrane stage followed with a high selective membrane stage, offers more cost savings over the single stage process. Jeon et al [93] used polysulfone membranes on the basic oxygen furnace gas and found that multistage process is necessary for over 80% recovery.

Multi-stage configurations incur high capital cost and make membrane process less competitive. Song [94] recommended using a hybrid sub-ambient membrane and cryogenic purification process instead of multiple stages, finding that a cooling step before the membrane could further reduce N₂ permeance and improve energy efficiency of the hybrid process. Lee [95] modelled this novel process for different flue gas streams in steel plant and found that it can be cost effective for higher CO₂ concentration streams (over 20%) but for low concentration stream, the capital cost is too prohibitive.

Another type of hybrid process which combine membrane and absorption has been pursued due to the higher CO₂ affinity of solvents and has been found to yield lower cost of CO₂ avoided than the individual methods [96]. This process suffers from the same energy duty requirements as the absorption process, albeit lower (2.9 vs 3.8 MJ/kg CO₂) since solvent is not vaporized for stripping but passed through a membrane for regeneration [97].

Ideally a highly selective and thermal and mechanically stable membrane would be favourable for post combustion so highly tunable, non-polymer membranes have also been considered. For steelmaking flue gas, Lie [98] found that amine-containing fixed site carrier (FSC) membranes have shown superior selectivity for CO₂ and high permeance, making them a favourable option

for CO₂ recovery from blast furnace effluents. Micari [99] explored single-layer graphene membranes with high CO₂ selectivity, which could reduce operational costs, that could make them competitive with benchmark amine systems. The high cost of these advanced membrane material is still a barrier to their adoption.

For industrial scale applications of membranes for gas separation, there are challenges in maintaining the membrane quality for large volume process and harsh operating conditions that must be addressed for membrane adoption to be commercially feasible [100].

2.2.1.5 Chemical Looping

Chemical looping utilizes the cyclic reaction of solid materials for CO₂ capture. The different types of chemical looping technologies can be classified by the type of solid material used [101].

There are “Type 1” materials which are oxygen carriers and cycle between oxidation and reduction reactors. These are commonly adopted in pre-combustion carbon capture for fossil fuel conversions, e.g. chemical looping combustion and chemical looping reforming. In the case of chemical looping combustion (CLC), they can transfer oxygen to from air to fuel creating separate streams of CO₂ and H₂O. Chemical looping reforming (CLR) uses metal oxides for partial oxidation of hydrocarbons to produce syngas or hydrogen with integrated CO₂ capture.

There are “Type 2” materials which are CO₂ carriers and cycle between carbonation and decarbonation reactors. These are commonly used in post combustion capture e.g. calcium looping, and in blue hydrogen production through sorbent-enhanced reforming. Calcium looping captures CO₂ using calcium oxide, forming calcium carbonate, which is then heated to release pure CO₂ and regenerate calcium oxide.

This section will cover application of O₂ Carriers (Type 1), CO₂ Carriers (Type 2) and mixed materials with both carriers in the iron and steel industry

A. O₂ Carriers

For the integrated power plant, Li [102] reviewed Ni-based O₂ carriers, finding that chemical looping combustion (CLC) was thermally and electrically comparable to conventional natural gas combined cycle but more cost-effective for CO₂ avoidance than an additional post capture process.

Several studies considered reducing the emissions of the natural gas fired furnaces through pre-combustion chemical looping methods. Spallina analysed H₂ production, showing CLC-SMR's cost-effectiveness (\$20 vs 85 per ton CO₂ avoided) compared to SMR with MDEA capture. Katayama's research [103] focused on CLC for water splitting to meet energy needs in sintering plants.

The choice of material is crucial for industrial feasibility. Materials that are low cost to produce, stable at the high pressure operation and can withstand the thousands of redox cycle are still largely underdeveloped [104].

B. CO₂ Carriers

Blamey [105] and Toledo [106] reviewed large-scale calcium looping applications, highlighting issues with spent sorbent such as competing reactions, attrition, thermal shock, and deactivation. Tian [107] reported that the incremental cost of steel due to calcium looping is comparable to membrane and solvent carbon capture, with 14-20 \$/t and more CO₂ avoided, while efficiency depends on increasing the fresh limestone feed percentage versus spent sorbent. Hashemi et al [108] experimented with modified natural and synthetic sorbents to overcome challenges of natural calcium oxide by improving the CO₂ capacity and the inert metal supports against attrition.

CO₂ carriers have been largely considered for reforming of the off gases into hydrogen. Xie [109] explored using CaO in pre-combustion as a looped sorbent in coke oven gas reforming and found the additional heat for desorption to be prohibitive. Xiang [110] discussed using a metal oxide mixture in steam-enhanced sorption reforming (SESR) of coke oven gas to reduce energy consumption compared to traditional steam methane reforming.

Several studies recognized the availability of CO₂ carriers in the steel production waste slag and attempted combining the capture and sequestration process into one. Mohammed [111] reviewed CO₂ capture using alkaline waste from steel slag, highlighting high CO₂ uptake capacity but slow kinetics of extracting Ca, Mg for carbonization. High pressures over 50 bars are needed to shorten the reaction time. Cormos [112] evaluated CaL using deactivated slag, finding a CO₂ avoidance cost of \$69 compared to \$73 for MDEA, but noted increased fuel and power consumption, leading to a 12-18% rise in steel production costs. The process relies on heat recovery to be economically feasible, and the study did not consider the impact of impurities on the activity of the sorbent. Tian [107] then modified sorbents from steel slag to create efficient CO₂ sorbents with a reduced cyclic decay rate of 12%. Stolaroff [113] and Huigen [114] examined slag CO₂ sequestration costs, with the former estimating the operating cost at \$8 per ton CO₂ and the latter assessing the total cost to be \$105 per ton CO₂ sequestered..

C. Mixed Carriers

Since the majority of emissions are owed to the blast furnace, several applications target the blast furnace gas by capturing CO₂ while still taking advantage of its heating value. To do this O₂ and CO₂ carriers were considered. Martinez [115] examined the use of Ca-Cu material for pre-combustion CO₂ removal from blast furnace gas (BFG), noting a higher CO₂ avoidance compared to MEA but without considering the cost impact of modifications needed for H₂ fuel reliance. Fernandez [116] explored Ca-Cu for steam reforming of BFG, achieving 31% CO₂ capture rate (CCR) and 27% decarbonization, with heat recovery opportunities. Fernandez et al. [117] introduced a novel CaCu packed bed configuration for converting BFG to H₂/N₂ and CO₂, achieving over 95% capture efficiency with moderate energy consumption. Tian's [118] study on Ca-Fe based oxides used raw materials from the steel plant for a looping process, leveraging BFG's heating value and metal oxide oxidation for heat, though it did not account for power losses from BFG diversion from the power plant.

2.2.2 Comparison of carbon capture methods

A review of globally published patents for carbon capture technologies was conducted on Lens [119] using the following queries:

Table 6: Patent query

Carbon capture method	Query	All published patents	Active and Pending patents
Absorption	((("carbon capture") OR ("CO2 capture") OR ("CO2 recovery")) AND (absorption OR absorber OR stripper OR desorption))	11757	9633
Adsorption	((("carbon capture") OR ("CO2 capture") OR ("CO2 recovery")) AND (adsorption OR "swing adsorption" OR sorbent OR PSA OR VSA OR PVSA OR VPSA OR TSA OR TVSA OR ESA))	8073	6683
Cryogenics	((("carbon capture") OR ("CO2 capture")) AND (cryogenic OR cryogenics OR "cryogenic separation" OR "liquefaction" OR sublimation OR desublimation) NOT "cryogenic drying" NOT "air separation")	2611	2151
Membrane	((("carbon capture") OR ("CO2 capture")) AND (membrane))	6986	5824
Looping	((("carbon capture") OR ("CO2 capture")) AND ("chemical looping" OR "calcium looping" OR "sorbent enhanced reforming"))	761	650
Sum		30188	24941

There are about 25000 active and pending patents filed globally since 1900 with 80% of them in the last 10 years, which is an indication of the rapid commercialization of this carbon capture in response to the net-zero goals. Figure 6 indicates a trend in commercial interests over the last 20 years.

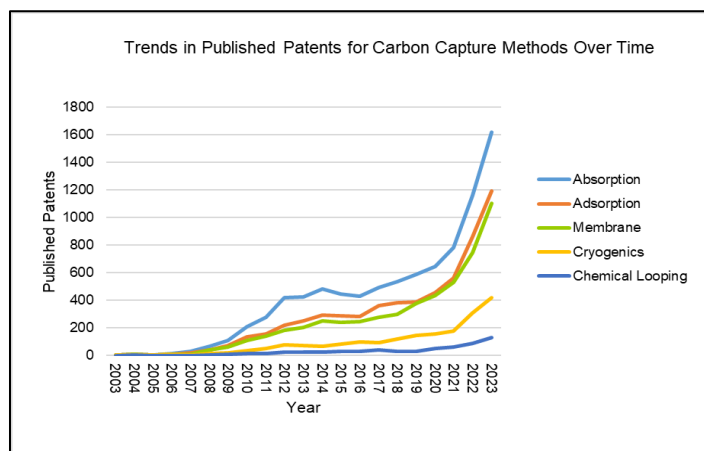


Figure 6: Published patents with active/pending status from 2003 – 2024

An increase in patents can be a sign that the technology is maturing. It indicates that various aspects and components of the technology are being refined, standardized, and protected, which is essential for moving from conceptual or experimental stages to practical applications. As more entities develop and protect their innovations, the technology becomes more robust, with

multiple players working to bring their versions to market. Of all carbon capture methods, absorption has garnered the highest commercial interest and the most explosive growth, even achieving large-scale operation in many industries. Cryogenics and chemical looping are beginning to pick up as more unconventional methods are being considered as alternatives to high-emitting capture technology.

While there is widespread application of absorption at industrial scale for power plants, for the steel industry, it is still in its early development. To date, there is only one large scale CCUS in operation. Sited at Emirate's Arkan DRI steel plant, the Al-Redayah CCUS facility has used an amine adsorption process to capture 0.8 Mt CO₂/yr for enhance oil recovery (EOR) since launching in 2016 [120]. In this case, carbon capture was able to handle up to 20% of the plant's reported emissions [121].

The 2023 grey paper by the Global CCS Institute gives a global stock take on commercial progress for each industry [122]. Axens Dreillard have a DMXTM process that they have demonstrated with capture rate of 0.5 Mt CO₂/hr at Arcellomittal's steel mill in Dunkirk since 2023. This process permits use of carbon steel due to less corrosive solvent. Huanneng, Sinopec's Nanjing Institute and Honeywell have all developed advance amine solvent blends currently in demonstration at steel plants with no published figures yet.

Sinopec has also demonstrated a 3-stage membrane process that can achieve over 80% recovery. Chart Industries has commenced commercial application of Baxter's CCECL, capturing 30 – 400 Mt CO₂/day [123].

There have been several applications of adsorption commonly in a hybrid solution with cryogenic purification units. Amongst them are the Honeywell PSA process used for pre-combustion capture with over 1150 units in operation and the Linde HISORP especially adapted for the blast furnace gas [122]. Air Liquide has a patented CryosteelTM process combining PSA with cryogenics, that handles flue gases with 20 – 50 mol% CO₂ at demonstration plants in France, Belgium and Korea. Hybrid membrane cryogenic process such as the Linde HISELT have also been found successful in handling gases with over 35% CO₂ feed concentration which is promising for pre-combustion applications.

Chemical looping process using O₂ carriers has been demonstrated primarily for power plants such as the 3 MWth CHEERS project in China [124]. Sumitomo has demonstrated a calcium looping process at a Swedish steel plant. The SCARLET project has been used to demonstrate calcium looping for 1 MWth pilot power plant with ongoing work to improve modelling tools for further scale up [125].

Beyond the discussed methods there are other methods such as electrochemical reduction which are still very early stage but have potential for efficiency gains and broader applications

A comparison of the techno-economic assessments conducted in the steel industry has been compiled in Table 7:

Table 7: Performance for reviewed Carbon Capture technologies

Reference	Capture method	Category	Technology	Source	Thermal energy [MJ-th/kg CO ₂]	Electrical Energy [MJ-e/kg CO ₂]	Cost per CO ₂ captured in 2024 USD [\$ / t CO ₂]	Purity
Farla (1995)	Absorption - Chemical	Post Combustion	MEA/MDEA	BFG	1.51		74	
Chisalita et al (2019)	Absorption - Chemical	Post Combustion	MEA	Stoves, PP, COG, Lime Kiln	3 - 6.2			> 95
Cheng et al (2010)	Absorption - Chemical	Post Combustion	MEA, PZ	Stoves	3.7			
Gazzani et al (2015)	Absorption - Chemical	Post Combustion	MEA	BFG	3.8 - 4.1			
Ho et al (2011)	Absorption - Chemical	Post Combustion	MEA	BFG, PP		1.5	107 - 117	
Chamchan et al (2017)	Absorption - Chemical	Post Combustion	MEA	BFG	4.5 - 6.5			
Goto et al (2011)	Absorption - Chemical	Post Combustion	MEA	BFG	4.2			
Goto et al (2011)	Absorption - Chemical	Post Combustion	RITE-A	BFG	3.3			
Goto et al (2011)	Absorption - Chemical	Post Combustion	RITE-B	BFG	3.1			
Sundqvist et al (2018)	Absorption - Chemical	Post Combustion	MEA	PP	3.1			
Cormos (2016)	Absorption - Chemical	Post Combustion	MDEA	Stoves, PP, COG, Lime Kiln	2.9		112 - 118	> 95
Biermann (2019)	Absorption - Chemical	Post Combustion	MEA	Stoves, PP, BFG	3.2		64	

Reference	Capture method	Category	Technology	Source	Thermal energy [MJ-th/kg CO ₂]	Electrical Energy [MJ-e/kg CO ₂]	Cost per CO ₂ captured in 2024 USD [\$ /t CO ₂]	Purity
Martinez (2018)	Absorption - Chemical	Post Combustion	MEA	PP	3			
Arasto et al (2013)	Absorption - Chemical	Post Combustion	MEA	Stove, PP	3.4	0.4	130 - 288	
Oko et al (2018)	Absorption - Chemical	Post Combustion	MEA	COG	4.1			
Cormos et al (2020)	Absorption - Chemical	Post Combustion	MDEA	Stoves, PP, COG, Lime Kiln	3.1		96	
Manzolini et al (2019)	Absorption - Chemical	Post Combustion	MEA	PP	4.8		79	100
Yun et al (2021)	Absorption - Chemical	Post Combustion	MEA	Sintering	3.5	0.28	82	
Yun et al (2021)	Absorption - Chemical	Post Combustion	MEA	COG	3.3	0.28	71	
Yun et al (2021)	Absorption - Chemical	Post Combustion	MEA	Lime Kiln	3.3	0.28	74	
Yun et al (2021)	Absorption - Chemical	Post Combustion	MEA	PP	2.9	0.28	61	
Yun et al (2021)	Absorption - Chemical	Post Combustion	MEA	Stoves	2.9	0.28	110	
Yang e tal (2021)	Absorption - Chemical	Post Combustion	MEA		4.4	0.78	96	
Yang et al (2021)	Absorption - Chemical	Post Combustion	MDEA/PZ	Stoves, PP, COG, Lime Kiln	2.3	0.6	79	
Ding et al (2023)	Absorption - Chemical	Post Combustion	MDEA/PZ, MEA/PZ,	BFG	4.4 - 5.6		41 - 45	

Reference	Capture method	Category	Technology	Source	Thermal energy [MJ-th/kg CO ₂]	Electrical Energy [MJ-e/kg CO ₂]	Cost per CO ₂ captured in 2024 USD [\$ /t CO ₂]	Purity
			MEA, MDEA/MEA					
Chung et al (2018)	Absorption - Chemical	Pre-Combustion	TGR-BF + PZ	BFG	2.4	0.2	54	95
Ujisawa et al (2016)	Absorption - Chemical	Pre-Combustion		BFG	2			90
Kim et al (2015)	Absorption - Chemical	Pre-Combustion	MEA	BFG, BOFG, COG	3.1	0.4	89	99
Han et al (2014)	Absorption - Chemical	Pre-Combustion	NH ₃	BFG	2.5			99
Ho et al (2013)	Absorption - Chemical	Pre-Combustion	TGR-BF + MEA	BFG		1.4 - 1.5	121 - 137	
Birat (2010)	Absorption - Chemical	Pre-Combustion	MDEA	BFG	3.2	0.61		
Sundqvist et al (2018)	Absorption - Chemical	Pre-Combustion	MEA	BFG	3	0.4		
Onoda et al (2016)	Absorption - Chemical	Pre-Combustion		BFG	2			
Onarheim (2016)	Absorption - Chemical	Pre-Combustion	MEA	BFG, BOFG	1.3	1.2		
Gazzani et al (2015)	Absorption - Chemical	Pre-Combustion	MDEA	BFG, BOFG, COG	2.9			98.6
Ho et al (2011)	Absorption - Chemical	Pre-Combustion	MEA	BFG	4.4		93	
Tobiesen (2007)	Absorption - Chemical	Pre-Combustion	MEA	BFG	3.7			90 -97

Reference	Capture method	Category	Technology	Source	Thermal energy [MJ-th/kg CO ₂]	Electrical Energy [MJ-e/kg CO ₂]	Cost per CO ₂ captured in 2024 USD [\$ /t CO ₂]	Purity
Tobiesen (2007)	Absorption - Chemical	Pre-Combustion	MDEA/PZ	BFG	2.92			90 -97
Tobiesen (2007)	Absorption - Chemical	Pre-Combustion	AMP	BFG	2.64			90 -97
Gielen (2003)	Absorption - Physical	Pre-Combustion	WGS + Selexol	BFG		0.62	35 - 37	
Ho et al (2011)	Absorption - Physical	Pre-Combustion	WGS + Selexol	BFG		1.08	82	
Onarheim (2016)	Absorption - Physical	Pre-Combustion	OBF + WGS + Selexol	BFG		1.7		
Susarla (2015)	Adsorption	Post Combustion	Zeolite 13X PVSA	15% CO ₂		1.0		
Nala (2020)	Adsorption	Post Combustion	Zeolite 13X VSA	20% CO ₂		0.594		
Akdag (2022)	Adsorption	Post Combustion	Biomass AC VSA	30% CO ₂		0.054		92
Subraveti (2023)	Adsorption	Post Combustion	Zeolite 13X VSA	20% CO ₂		0.722		
Peh (2023)	Adsorption	Post Combustion	UTSA-MOF TSA	15% CO ₂	3	0.89	96	97.7
Khurana & Farooq (2019)	Adsorption	Post Combustion	Zeolite 13X VSA	15% CO ₂		0.988	28	95
Baxter (2021)	Cryogenics	Post Combustion	CCECL	12% CO ₂		0.894	54	99.99
Belaissaoui (2012)	Cryogenics	Post Combustion	Cryogenic Flash	20% CO ₂		3.55		

Reference	Capture method	Category	Technology	Source	Thermal energy [MJ-th/kg CO ₂]	Electrical Energy [MJ-e/kg CO ₂]	Cost per CO ₂ captured in 2024 USD [\$ /t CO ₂]	Purity
Baker et al (2018)	Membrane	Post Combustion	Polaris	Stoves, PP		0.9 -1	48 – 62	99
Luca and Petrescu (2021)	Membrane	Post Combustion	PVAm	Stoves, PP		1.2		95.5
Yun et al (2021)	Membrane	Post Combustion	Polyimide	Sinter Plant		4.4	285	90
Yun et al (2021)	Membrane	Post Combustion	Polyimide	COG		1.7	103	90
Yun et al (2021)	Membrane	Post Combustion	Polyimide	Lime Kiln		1.4	94	90
Yun et al (2021)	Membrane	Pre-Combustion	Polyimide	Powerplant		1.2	61	90
Yun et al (2021)	Membrane	Pre-Combustion	Polyimide	Stoves		1.2	59	90
Chung et al (2018)	Membrane	Pre-Combustion	2 stage membrane	BFG		1	46	95
Lie et al (2007)	Membrane	Pre-Combustion	2 stage membrane	BFG		0.9	27	90
Belaissaoui et al (2012)	Membrane	Post combustion						
Li et al (2022)	Membrane	Pre-Combustion	Membrane + Cryogenics	BFG		1.6	28	97.1
Cormos (2016)	Chemical Looping	Post Combustion	CaO-CaCO ₃	Stoves, BFG, Lime kilns, COG, BOFG	2.9	0.5		95

Reference	Capture method	Category	Technology	Source	Thermal energy [MJ-th/kg CO ₂]	Electrical Energy [MJ-e/kg CO ₂]	Cost per CO ₂ captured in 2024 USD [\$ /t CO ₂]	Purity
Chisalita et al (2019)	Chemical Looping	Post Combustion	CaO-CaCO ₃	Stoves, BFG, Lime kilns, COG, BOFG	2.7	0.1		95
Xie et al (2017)	Chemical Looping	Post Combustion	CaO-CaCO ₃	COG	4.2 - 5.6			99
Tian (2018)	Chemical Looping	Post Combustion	CaO-CaCO ₃	BFG, COG	2.7	2.5		99

We will use carbon capture methods suited for post-combustion capture since the target streams in this case study are exhaust streams from high-temperature units and furnaces. Based on these studies and the commercialization status, the merits of each carbon capture technology were classified in Table 8, under these categories: energy consumption, technical maturity, capture cost, capture efficiency, concentration of emissions sources and the retrofit ability with existing post-combustion systems.

Table 8: Literature Overview of Post Combustion Capture Methods in Iron and Steel Plants

Capture Methods	Cost per t-CO₂ [2024 USD/Mt-CO₂]	Thermal Energy Penalty [MJ/kg-CO₂]	Electrical Energy Penalty [kWh/kg-CO₂]	Challenges	TRL [126]
Chemical Absorption	50 - 117	1.5 – 4.8	0.2 – 0.8	Energy intensive	TRL 9 Mature, Commercial Deployment
Adsorption	28 - 96	3.0	0.8 – 1.0	Energy intensive Less developed sorbents	TRL 7-9
Membrane Separation	26 - 285	N/A	0.9 – 4.4	Less developed membranes	TRL 6-7 Pilot Studies
Cryogenic Capture	N/A	N/A	0.9 – 3.55	Energy Intensive, Needs high CO ₂ concentration	TRL 9 Mature, Commercial Deployment
Chemical Looping	N/A	N/A	N/A	Under-developed	TRL 5-7 Feasibility Studies, Pilot Tests

Chemical absorption as the most mature technology. Monoethanolamine (MEA) absorption is chosen as the base case capture technology for this study. It is however notorious for its high thermal energy penalty.

Given its technical maturity, large-scale demonstration progress and reduced energy consumption, physical swing adsorption is a feasible alternative. Specifically, vacuum pressure swing adsorption and its hybrid with low-temperature technology will be considered commercially viable alternatives that rely solely on electrical energy input, which additional natural gas consumption.

3 Methodology

To conduct a techno-economic assessment, the two-model framework in Figure 7 was adopted. The first, is a performance model which uses design specifications such as the capture level and CO₂ purity to determine the equipment sizing and the energy consumption involved. The result of this model then feeds the second, a costing model that will allow estimation of the capital and operating cost, based on different assumptions and parameters.

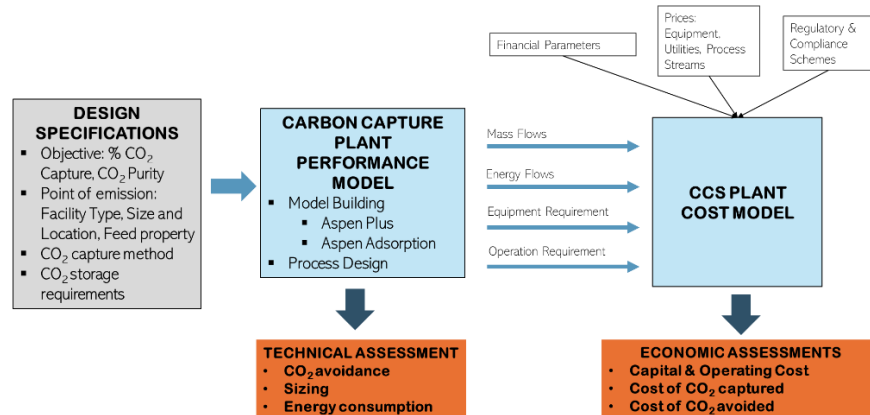


Figure 7: Techno-economic assessment modelling framework

The following sections describe the building of these individual models for the two carbon capture processes:

- 1) Chemical Absorption
- 2) Hybrid Vacuum Pressure Swing Adsorption + Low temperature Purification

3.1 Chemical Absorption Model Building

The base case carbon capture method, which is a conventional amine-based chemical absorption process, is modelled in Aspen Plus to predict and understand the energy and material flows within the chemical absorption process. Figure 8 summarizes the unit configuration/Aspen Plus flowsheet for this chemical absorption process.

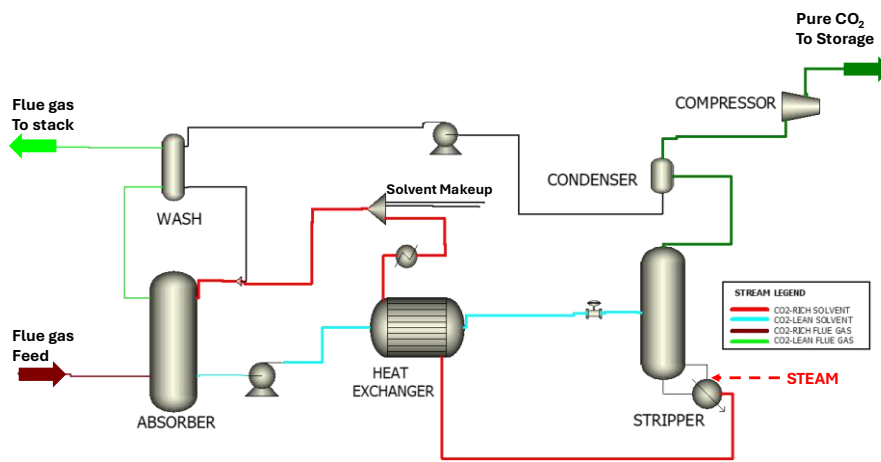


Figure 8: Chemical Absorption Process Configuration

There is an absorber where the flue gas is contacted with the solvent that chemically binds with the CO₂ from the feed gas stream. The treated flue gas is contacted with water in a smaller absorption column or a wash section to reduce solvent vapor loss.

The CO₂ - rich solvent from the bottom of the absorber column, after being heated in a heat exchanger, is delivered to the stripper where heat is delivered through a steam-supplied reboiler to generate a vapour for stripping and to provide the needed thermodynamic conditions to separate the CO₂, leaving a CO₂-lean solvent (the bottom product of the stripper column). The stripper vapour (the distillate product) is condensed to yield a pure CO₂ stream that can be compressed for storage and retrieve water-rich solvents that are recycled to the wash column.

To conserve the reboiler heat, a heat exchanger is used to transfer heat from the lean solvent to rich solvent. The recycled lean solvent is further cooled to 30°C, the temperature needed for absorption. Several pumps are introduced to overcome the pressure losses during fluid transport. Due to the inevitable loss of solvent, a solvent makeup stream is introduced to maintain the solvent flow rate

3.1.1 ASPEN Plus Simulation Development

Developing a reliable model to predict the performance of the chemical absorption is essential for sizing and costing. Two modelling approaches: equilibrium and rate-based models have been used to model the absorption and stripping process. The equilibrium stage (traditional) approach uses the concept of equilibrium or theoretical stages and that the gas and liquid contacted, reach equilibrium instantly. All deviation from equilibrium is accounted for by efficiency factors which can be difficult to accurately estimate. The rate-based model is recommended as a solution to this problem by accounting for mass and heat transfer limitation as well as the rate of the chemical reactions, resulting in a more accurate representation of the chemical absorption process [127], [128], [129]. Thus, the rate-based model is used in this study. Developing a rate-based model requires a comprehensive array of accurate input parameters to describe the physiochemical properties of both liquid and gas phases, reaction kinetics, mass and heat transfer, and hydrodynamics of the process.

3.1.1.1 Fluid Properties

The solvent used in the current base case is a 30 wt % Monoethanolamine (MEA) solvent due to prevent corrosion of higher amine compositions. The ideal property specification for a CO₂-MEA-H₂O system must accurately account for the liquid and gas phase equilibria, the chemical-reaction equilibrium in the liquid phase and their coupling.

The phase chemical equilibrium determines how the species are distributed to the gas and liquid phases. Gibbs [130] states that phase equilibrium is achieved when the chemical potential of a species is the same in each phase present under uniform temperature and pressure conditions as represented in Eq. 7

$$\mu_i^G = \mu_i^L \quad (7)$$

Where μ_i^G is the chemical potential of species i in the gas phase and μ_i^L is the chemical potential of species i in the liquid phase.

Due to the computational limitations of estimating the chemical potential in mixtures based on unknown absolute values of internal energy and entropy, the concept of fugacity as an easily estimable measure of chemical potential was developed by Lewis [131]. This relationship is expressed as shown Eq. 8

$$\mu_i - \mu_i^R = RT \ln \left(\frac{\hat{f}_i}{\hat{f}_i^R} \right) = RT \ln(a_i) \quad (8)$$

where μ_i^R and $\hat{f}_i^R$ are the chemical potential and fugacity of species i at a reference state, $\hat{f}_i$ is the fugacity of the species i in a mixture, a_i is the activity of the specie i . Lewis showed that at phase equilibrium, the fugacity of the species in each phase are also equal under isobaric and isothermal conditions.

$$\hat{f}_i^G = \hat{f}_i^L \quad (9)$$

Thus, to compute the species distribution at phase equilibrium based on Eq. 9, the fugacity or the activity can be estimated.

For the liquid phase, the fugacity is determined based on the activity of the species which can be expressed as a function of an activity coefficient:

$$a_i = x_i \gamma_i \quad (10)$$

where x_i is the mole fraction of the species i in the liquid phase and γ_i is the activity coefficient. The method for estimating the activity coefficient in this work is the Electrolyte NRTL activity coefficient model proposed by Chen and Evans [132]. This model is used to predict enthalpies and solution speciation.

For the gas phase, fugacity may be considered as a corrected partial pressure expressed as [131]:

$$\hat{f}_i^G = \hat{\phi}_i y_i P \quad (11)$$

where $\hat{f}_i^G$ is the fugacity of species i , $\hat{\phi}_i$ is the fugacity coefficient and y_i is the gas mole fraction, and P is the total pressure. In this work, the model used for the fugacity coefficient is the Soave Redlick Kwong Equation of State (EOS).

There is also the chemical reaction equilibrium in the liquid phase which is satisfied by the total minimum Gibbs energy:

$$\left[\frac{\partial(G^t)}{\partial \varepsilon} \right]_{T,P} = \sum_i v_i \mu_i = 0 \quad (12)$$

Where v_i is the stoichiometric number of species i in the chemical equilibrium reaction equations, G^t is the total Gibbs energy, ε is the extent of the reaction. Citing the same

computational limitations, the chemical potential is redefined in terms of the fugacity of the species in solution [133]:

$$\sum_i v_i * \left[G_i^o + RT \ln \left(\frac{\hat{f}_i}{\hat{f}_i^R} \right) \right] = 0 \quad (13)$$

Where G_i^o is the standard state Gibbs energy. Rearranging Eq. 13 yields the equilibrium constant K that must be estimated for each chemical reaction to determine the equilibrium state.

$$\prod_i \left(\frac{\hat{f}_i}{\hat{f}_i^R} \right)^{v_i} = \exp \left(- \frac{\sum_i v_i G_i^o}{RT} \right) = \exp \left(- \frac{\Delta G^o}{RT} \right) = K \quad (14)$$

K is estimated based on the activity coefficient using the equation:

$$K = \prod_i (x_i \gamma_i)^{v_i} \quad (15)$$

Thus, all that needed to be specified was the chemical reaction relevant to the system. Table 9 describes the solution chemistry of CO₂ absorption with MEA proposed by Hilliard [134]:

Table 9: Solution chemistry model

Amine protonation	$MEA H^+ + H_2O \leftrightarrow MEA + H_3O^+$
CO ₂ Hydrolysis	$CO_2 + 2 H_2O \leftrightarrow H_3O^+ + HCO_3^-$
Carbamate hydrolysis	$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^-$
Bicarbonate dissociation	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
Water dissociation	$2 H_2O \leftrightarrow H_3O^+ + OH^-$

Across Equations 7 – 15, is frequent mention of a reference state. In this model, two commonly used reference-state conditions for electrolyte systems are selected:

- Symmetric reference state: This assumes the activity coefficient of a pure component is unity at the system's temperature and pressure. This reference state is typically applied to solvents.
- Unsymmetric reference state: This assumes the activity coefficient of a component is unity when its concentration approached zero (infinite dilution) and is used for solutes and ionic species.

The reference states are retrieved from the Aspen data banks [135].

Henry's law is used to describe the physical solubility of gases, N₂, CO₂ and H₂O in solvents. The enthalpy of absorption process is derived based on an enthalpy balance proposed by Zhang et al [128]:

$$\Delta H_{abs} = \frac{n_{Final}H_{Final}^L - n_{Initial}H_{Initial}^L - n_{CO_2}H_{CO_2}^G}{n_{CO_2}} \quad (16)$$

where ΔH_{abs} is the enthalpy of absorption per unit mole of CO₂, H_{Final}^L is the molar enthalpy of the final solution, $H_{Initial}^L$ is the molar enthalpy of the initial solution, $n_{CO_2}H_{CO_2}^G$ is the molar enthalpy of gaseous CO₂ absorbed, n_{Final} is the number of moles of the final solution, $n_{Initial}$ is the number of moles of the initial solution, n_{CO_2} is the number of moles of CO₂ absorbed.

The adopted transport property models for the liquid and vapor phases tuned based on Aspen databanks [135] and validated by Zhang et al [128] are summarized in Table 10:

Table 10: Transport property models for the liquid and gas phases

Property	Liquid phase	Gas phase
Viscosity	Jones-Dole model	Chapman-Enskog-Brokaw model
Density	Clarke model	Redlich Kwong EOS
Surface tension	Hakim Steinberg model with Onsager-Samaras electrolyte correction	N/A
Thermal conductivity	Reidel electrolyte correction model	Polynomial
Binary diffusivity	Nernst- Hartley model	Chapman-Enskog-Wilke Lee model

3.1.1.2 Unit Design Specifications

3.1.1.2.1 Absorber and Stripper

The absorber and stripper stages were both modelled with RATEFRAC, a rate-based model which integrates heat transfer and mass transfer relationships into the equilibrium calculations to accurately represent the absorption process. The mass transfer of acidic gases from bulk liquid to bulk gas in the chemical absorption process involves the following steps:

1. Diffusion of gas from the bulk gas phase to the gas-liquid interface
2. Diffusion and convection from the interface to the bulk liquid phase
3. Reaction between the dissolved gas and the liquid components in the liquid phase
4. Diffusion of the products from the bulk liquid phase due to concentration gradients created by reaction

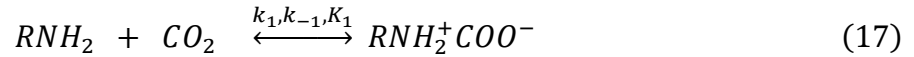
Several studies have assessed the impact of selecting different methods and correlations on rate-based model predictions [136], [137], [138]. Razi and coworkers assessed the hydrodynamic and mass transfer correlations used and made recommendation of suitable methods for different packing types and bed configurations [139], [140], [141]. Based on their findings, the mass transfer steps 1, 2 and 4 was modelled as shown in Table 11, using numerical discretization of the phases and sub-models for heat and mass transfer and hydrodynamics.

Table 11: RATEFRAC Specifications

Rate-based Model Specification	Value
Mass transfer coefficient method	Bravo and Fair (1992)
Heat transfer coefficient method	Chilton and Colburn
Interfacial area method	Bravo and Fair (1985)
Holdup method correlation	Bravo and Fair (1992)
Discretization type	Geometric
Vapor phase film discretization points	None
Liquid phase film discretization points	5
Flow model	Mixed - least computationally intensive model
Pressure drop	Stichlmair (1989)

For step 3, the reaction kinetics are defined for the rate determining step involving the formation of the carbamate where CO₂ reacts with MEA. There is some disagreement in literature on the intermediates formed in this process and the appropriate mechanism to represent this step. According to Aboundheir [142], this reaction is generally described by 2 mechanisms:

1. The zwitterion mechanism proposed by Dankwerts [143]. The zwitterion mechanism is a two-step process, the first of which involves the reaction of MEA (RNH₂) with CO₂ to form a zwitterion intermediate (RNH₂⁺COO⁻).



This intermediate gets deprotonated as shown in Table 12, by a base *B* (which could be amine, hydroxide or water) to form a carbamate, RNHCOO⁻.

Table 12: MEA Zwitterion Mechanism Reactions

Base	Reaction
Amine (RNH ₂)	$RNH_2^+ COO^- + RNH_2 \xrightleftharpoons{k_2, k_{-2}, K_2} RNH_3^+ + RNHCOO^-$
Water (H ₂ O)	$RNH_2^+ COO^- + H_2O \xrightleftharpoons{k_3, k_{-3}, K_3} H_3O^+ + RNHCOO^-$
Hydroxide (OH ⁻)	$RNH_2^+ COO^- + OH^- \xrightleftharpoons{k_4, k_{-4}, K_4} H_2O + RNHCOO^-$

The general rate of CO₂ with MEA via this reaction mechanism could then be described as

$$r_{CO_2-MEA} = \frac{[RNH_2][CO_2] - \frac{k_{-1}}{k_1} [RNHCOO^-] \left(\frac{\sum k_{-b}[BH^+]}{\sum k_b[B]} \right)}{\frac{1}{k_1} + \left(\frac{k_{-1}}{k_1 \sum k_b[B]} \right)} \quad (18)$$

If the reversibility is neglected due to fast deprotonation, the equation is reduced to:

$$r_{CO_2-MEA} = \frac{k_1 [RNH_2][CO_2]}{1 + \left(\frac{k_{-1}}{\sum k_b[B]} \right)} \quad (19)$$

$$r_{CO_2-MEA} = k_{app} [RNH_2][CO_2] \quad (20)$$

2. The termolecular mechanism by Crooks and Donnell [144] assumed that there is a single step reaction between the MEA and CO₂ which forms a loosely bound encounter complex. There exists no bond formation or charge separation. This intermediate complex can then break to give the initial reactants or reacts with amine or water to form ionic products. The forward reaction rate for this mechanism is presented as [144], [145]:

$$r_{CO_2-MEA} = -(k_{RNH_2} [RNH_2] + k_{H_2O} [H_2O]) [RNH_2][CO_2] \quad (21)$$

Upon identifying the limitation of this mechanism rate expression in handling highly loaded CO₂ in concentrated MEA solutions, the mechanism rate was modified by Aboudheir [142] to yield:

$$r_{CO_2-MEA} = -(k_{RNH_2} [RNH_2] + k_{H_2O} [H_2O]) [RNH_2] \times \left([RNH_2][CO_2] + \frac{1}{K_{RNH_2}} [RNHCOO^-][H_3O^+] \right) \quad (22)$$

Several rate constant expressions have been proposed for each type of mechanism based on experimental data using different techniques and spanning different operating temperatures and MEA concentrations. Table 13 outlines the list of mechanisms considered for the RATEFRAC model:

Table 13: Literature data on the reaction between CO₂ and aqueous MEA

Reference	Temperature Range [K]	MEA Concentration [mol/dm ³]	Model Mechanism k_{app} [m ³ mol ⁻¹ s ⁻¹]; k_i^T [m ⁶ mol ⁻¹ s ⁻¹]	Mechanism type
Hikita (1977) [146]	278.6 - 308	< 0.18	k_{app} $= 9.77 \times 10^7 \exp\left(-\frac{4955}{T}\right)$	Zwitterion mechanism
Versteeg (1996) [145]	< 313	< 3.2	k_{app} $= 4.4 \times 10^8 \exp\left(-\frac{5400}{T}\right)$	Zwitterion mechanism

Hong and Li (2002) [147]	303 - 313	0.1 – 0.5	k_{app} $= 3.014$ $\times 10^8 \exp\left(-\frac{5376.2}{T}\right)$	Zwitterion mechanism
Aboudheir (2003) [142]	293 - 333	0.2 – 5.5	$k_{RNH_2}^T$ $= 4.61 \times 10^9 \exp\left(-\frac{4412}{T}\right)$ $k_{H_2O}^T$ $= 4.55$ $\times 10^6 \exp\left(-\frac{3287}{T}\right)$	Termolecular mechanism
Aboudheir (2003) [142]	293 - 333	0.2 – 5.5	$k_{RNH_2}^T$ $= 4.61 \times 10^9 \exp\left(-\frac{4412}{T}\right)$ $k_{H_2O}^T$ $= 4.55$ $\times 10^6 \exp\left(-\frac{3287}{T}\right)$ K_{RNH_2} $= 10^{-10.41902 + \frac{1747.19}{T}}$	Termolecular mechanism – Modified for higher loadings
Luo (2015) [148]	297.1 – 338.4	1 - 5	$k_{RNH_2}^T = 2.003 \times$ $10^{10} \exp\left(-\frac{4742}{T}\right)$ $k_{H_2O}^T = 4.147 \times$ $10^6 \exp\left(-\frac{3110}{T}\right)$	Termolecular mechanism

Since there is no general agreement in the kinetic data adopted for this system, the most suitable mechanism and rate constant model is selected based on a sensitivity study, to be presented later.

Each packed tower was set up with stainless steel Mellapak 250.Y™ structured packing.

3.1.1.2.2 Heat Exchangers

The rigorous HEATX is used to model the cross-stream heat exchanger applying a LMTD approach. Phase-specific coefficients shown in Table 14 were used:

Table 14: Overall heat transfer coefficient

	U Value [W/m ² .K]
Liquid - Liquid	600
Liquid - Vapor	300
Vapor - Vapor	30

The design specification is 10°C outlet temperature approach to extract the maximum heat possible from the hot stream. The hot stream is further cooled with a cooling water.

3.1.1.3 Compressors and Pumps

An isentropic model using the GPSA method is adopted for the compressors with a motor efficiency of 0.96 and isentropic efficiency of 0.75 [149]. The pump model was specified with a pump efficiency of 0.75 and a driver efficiency of 0.98.

3.1.1.4 Model Validation

Pilot data obtained from the University of Kaiserslautern pilot MEA scrubbing plant [150] and the standalone absorbers and strippers at the Norwegian University of Science and Technology (NUST) [151], [152] were used in validating the model specifications. First, the different kinetic models were tested on the individual absorber and stripper. For the absorber, the CO₂ absorption rate was evaluated. For the stripper, the model was assessed based on the output streams: CO₂ distillate (top) flow rate and the CO₂ load of the lean solvent. Due to their low absolute error, as seen in Table 15, and good pilot data fit in Figure 9, two models were shortlisted: the Hikita model was selected as the representative zwitterion mechanism and the Luo model was selected for the termolecular mechanism.

Table 15: Absolute error of different reaction kinetic models using NUST standalone column pilot data in [151], [152]

Kinetics	Adsorber [%]	Stripper [%]
HIKITA – HIK [146]	37.51	22.50
VERSEEG – VER [145]	60.32	37.53
HONG & LI – HLI [147]	116.53	79.53
LUO [148]	34.30	14.74
ABHOUDEIR [ORIG] – ABO [142]	38.12	31.05
ABHOUDIER [ALT] – ABD [142]	45.16	100.00

a)

b)

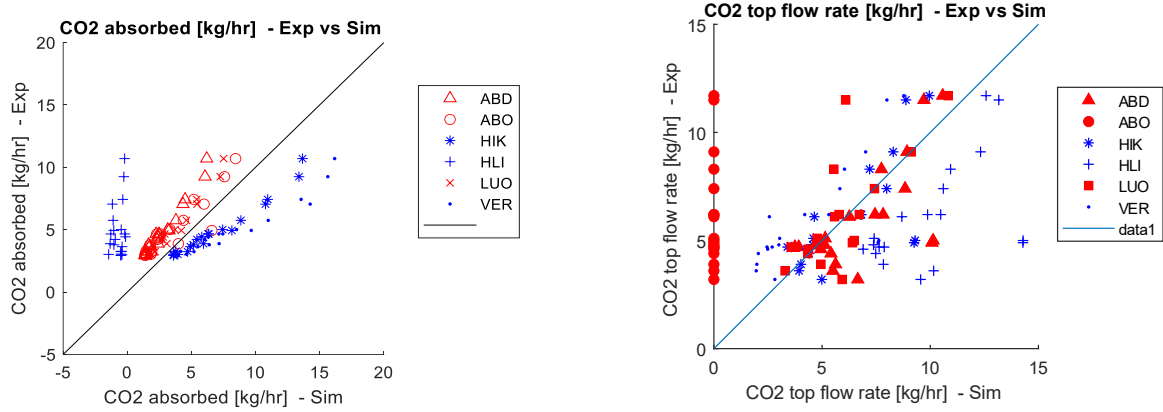


Figure 9: Experimental vs Simulation Data for a) CO₂ Absorbed in Absorber b) Stripper CO₂ Flow Rate

Next, the shortlisted kinetic mechanisms were tested on 42 cases of coupled absorber and stripper over a wide range of lean loadings, flue gas flowrates, CO₂ composition and the designed CO₂ removal rate. Considering the experimental uncertainty in the rate constant parameter estimations, a sensitivity study on the activation energy within 10% was done to achieve a better fit. Based on this, 10 combinations of reaction mechanisms (R1- R10) were tested on the pilot studies. The assessment criteria, collated in Table 16, was the absolute percent error for the CO₂ recovery, the CO₂ absorbed rate, the CO₂ purity and the regeneration energy. Convergence issues were encountered with certain models such as the Luo model for the absorber.

Table 16: Absolute percent error of different criteria in the coupled absorber and stripper model from MEA scrubbing plant [150]

Setup	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
Absorber	HIK	LUO	LUO	HIK	HIK [E _a +4%]	HIK [E _a +6%]	HIK [E _a +10%]	HIK [E _a +4%]	HIK [E _a +4%]	HIK [E _a + 8%]
Stripper	HIK	HIK	LUO	LUO	LUO	LUO	LUO	LUO	LUO [E _a +10% for k _{MEA} and k _{H₂O}]	LUO [E _a +10% for k _{MEA} and k _{H₂O}]
CO ₂ removal %	25.51	16.75	16.9 ₁	23.2 ₉	14.26	7.67	6.54	14.26	14.37	8.01
Pure CO ₂ mass	26.40	17.95	18.1 ₂	23.0 ₁	15.42	8.69	6.78	15.42	15.78	9.35
CO ₂ purity	0.05	0.05	0.04 ₈	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Reboiler duty per CO ₂	14.03	19.11	15.84	15.30	18.57	25.00	30.02	18.57	9.82	11.23
L/G ratio	8.75	1.74	1.89	2.28	1.74	1.74	1.73	1.74	1.74	1.75

The R10 combination of kinetic models in Table 16 is selected because it has the lowest errors. The final kinetic rate equations used for the model are described in Table 17:

Table 17: Kinetic Rate Equations for different model units

Model Name	Unit	Mechanism type	Model Mechanism k_{app} [m ³ mol ⁻¹ s ⁻¹]; k_i^T [m ⁶ mol ⁻¹ s ⁻¹]
Modified Hikita Model	Absorber	Zwitterion mechanism	$k_{app} = 9.77 \times 10^7 \exp\left(-\frac{5351}{T}\right)$
Modified Luo Model	Stripper	Termolecular mechanism	$k_{RNH_2}^T = 2.003 \times 10^{10} \exp\left(-\frac{5216}{T}\right)$ $k_{H_2O}^T = 4.147 \times 10^6 \exp\left(-\frac{3421}{T}\right)$

3.1.2 Design Scale-up

After model refinement and validation, it was necessary to scale up the model to handle the industrial scale flows. For the absorber and stripper sizing, the design methodology proposed by Madeddu and coworkers [153] was adopted.

To size the absorber, the following steps were followed:

1. For a desired CO₂ recovery and flue gas flow rate, estimate the minimum lean solvent. This is the flow rate at infinite height and yields the maximum diameter required. If the diameter needed exceeds the max allowable diameter, then the feed can split into two equal absorbers.
2. Estimate different effective flow rates as factor of the minimum flow rate by altering the packing height from infinity to a practical range.
3. Assess each scenario based on the following criteria
 - a. Maximum temperature bulge: review temperature profile to minimize isothermal zones that indicate low absorption activity.
 - b. Minimum bed height: review vapour composition profile for stagnant ranges to ensure maximum utilization of bed height.
 - c. Minimize the solvent usage: in terms of absorption level, this is usually inversely related to increasing bed height.

To size the stripper, the following steps were followed:

1. Select stripper pressure: increasing the stripper pressure raises the reboiler temperatures which can reduce the reboiler duty by improving heat transfer efficiency. However, there

is a limit on the temperature to avoid thermal degradation of the monoethanolamine solvent at 120°C.

2. Estimate the stripper feed temperature based on a 10 °C approach to the reboiler temperature.
3. Estimate the minimum distillate rate of the stripper based on the amount of CO₂ absorbed in the absorber column.
4. Select a desired lean loading and estimate the diameter needed to accommodate the rich solvent flow rate at infinite height without flooding using Aspen Plus in-built sizing tool.
5. Vary the height to minimize the reboiler duty.

Design specifications were introduced to alter the stripper distillate rate to achieve a CO₂ lean loading of 0.3. This loading was selected to simplify the design process based on extensive studies that find this to be optimum range for reboiler duty and the size of the capture columns.

Another design specification was set to change the lean solvent flowrate to the absorber to recover 90% of CO₂ in the flue gas.

3.1.3 Reboiler Duty Production

How the reboiler duty is produced is critical to the performance of the chemical absorption method. The duty could be supplied directly through fuel-fired heating or electricity or indirectly using steam.

Natural gas is a high-grade energy source and using it directly as an energy source for a reboiler would be wasteful. Fuel-fired reboilers also require regular maintenance, especially for burner efficiency, heat exchanger fouling, and emissions controls. For large-scale applications at temperatures below 200°C, direct electric heating through resistive heaters is considered impractical and still requires further development to prevent fouling and scaling of heater elements, uneven heat distribution and localized hotspots that could cause solvent degradation [154].

Even though energy losses occur in production and transport, indirect heating using steam is preferred in practice, due to the commercial maturity of steam reboilers for strippers. Better temperature control can also be achieved with steam at 130°C and 2.7 bar. The conventional method would be burning more fuel to generate steam. However, this could reduce the CO₂ avoided with this capture method. In a steel plant, in addition to alternate fuel sources, there may be opportunities for heat integration due to the high-temperature product and waste streams. Thus, the steam could be generated from the combustion of fresh fuel, such as natural gas or process fuel gas, such as coke oven gas, or heat recovery steam generators and electric boilers.

Heat integration of CO₂ capture has been widely studied and considered to reduce the energy penalty. In gas-fired power plants, heat recovery from high-grade products and waste streams has been proven [155], [156], [157], [158], [159] to even improve CCS efficiency and reduce the cost. The findings from these studies could be extrapolated to the iron and steel industry owing to the high flue gas temperatures. In the iron and steel industry [160], [161], [162], several studies have considered partial carbon capture primarily driven by the excess heat available for steam production. For large-scale capture where waste streams are insufficient to provide the

whole reboiler duty, others [163], [164], [165] have considered heat-pumping technologies that convert mechanical energy into thermal energy. These systems increase electricity consumption and limit extra natural gas consumption. Solar thermal plants have been considered for emission-free capture [166], [167] and have been found to reduce the thermo-economic cost depending on its integration and the cost of electricity. The adoption of solar heating for industrial processes still faces challenges due to space requirements, challenging integration and heat storage costs [168].

While heat integration is heavily regarded in process intensification studies, it is usually avoided in practice due to the capital cost, commission and maintenance complications [169]. Thus, while ideally advantageous for emission reduction, a thorough cost/benefit assessment is needed to ensure financial viability. One technical performance criterion used to evaluate the heat recovery is the recovery efficiency, which tells us how much of the available heating capacity of a waste heat stream is recovered to provide heat in the reboiler.

$$\text{Recovery efficiency} = \frac{\dot{Q}_{reb}}{\dot{H}_{max}} \quad (23)$$

Where $\dot{Q}_{reb}$ is the reboiler duty and $\dot{H}_{max}$ is the maximum recoverable enthalpy. The maximum recoverable enthalpy is evaluates based of the properties of the heating fluid at its the initial and final state:

$$\dot{H}_{max} = \dot{m}_{hs} * (H_{hs,init} - H_{hs,final}) \quad (24)$$

Where $\dot{m}_{hs}$ is the mass flow rate of the heating fluid, $H_{hs,init}$ and $H_{hs,final}$ are the specific enthalpy of the heating fluid at its initial state (before heat recovery) and final state (after heat recovery) respectively.

When trying to recover heat, it is critical to consider the quality and usefulness of the energy that can be extracted, that is exergy. Each steam generation method is modelled in Aspen Plus to estimate the recovered reboiler duty and in cases, where necessary, is used for exergy analysis. In the following subsections, the methods considered for heat and steam generation in this work are described.

3.1.3.1 Boilers

Steam could be generated with a natural gas-fired, process gas-fired or an electric boiler.

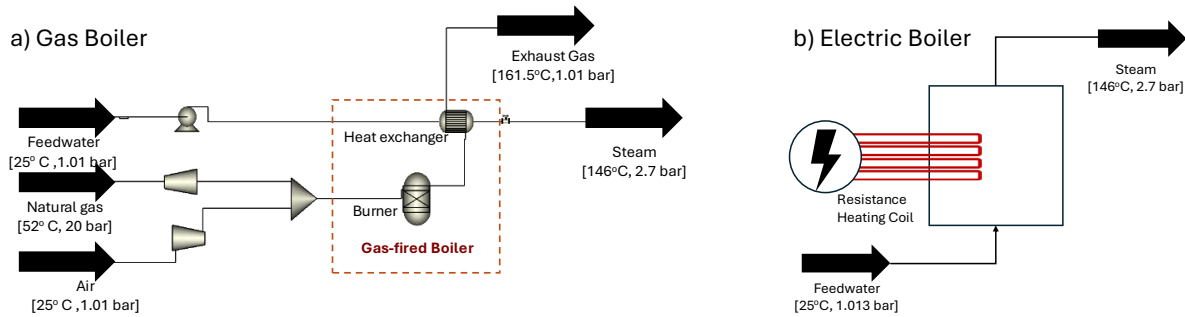


Figure 10: Production of steam through a) Gas-fired boiler b) Electric boiler

For gas-power generation, the steam could be generated in the existing power plant or from a field-erected boiler, incurring extra investment. Instead of natural gas, process gas is supplied by combining unused process streams with the high calorific value which are currently flared wastefully in the existing process. As seen in Figure 10a, the natural gas is subjected to a pressure reducing turbine to 1.5 bar, generating electricity and the air compressed to 1.5 bar to be fed to the boiler. The air is adjusted using a design specification so that the volume fraction of O_2 in the exhaust gas is 0.05. In the case where the natural gas is replaced with process gas, no turbine is included in the assessment. Both fuel and air are fed to a burner and used to heat the feedwater.

The electric boiler uses electricity to heat water into steam. As shown in Figure 10b, an electric resistance coil is used, which passes an electric current through a resistive element to heat the feedwater. This is a mature technology with sizes up to 73 MWe in operation [170] and energy efficiencies ranging from 95 – 99%. 97% energy efficiency is assumed in this study.

3.1.3.2 Heat Recovery Steam Generator (HRSG)

The HRSG is a special type of boiler, which can recover heat from low-quality sources like exhaust gases and circulating gases from quenching processes. The basic components of a HRSG unit, as shown in Figure 11, include ductwork, an outer casing (enclosure) and a series of heat exchangers. The first heat exchanger, the economizer, heats water nearly to saturation point. The following exchanger, the evaporator, converts this saturated water into partial steam and water mixture and is fitted with a steam drum to separate the steam from any remaining water. Last, the superheater increase the steam temperature beyond saturation.

In the Aspen Plus model, the hot gas is circulated through the shell of the HRSG exchangers, to generate steam at 146°C and 3.2 bars from feedwater at 25°C and 1 bar. The selected steam pressure and temperature is to allow for pressure losses up to 0.5 bar during transport and still arrive at the saturated steam conditions of 130°C and 2.7 bars needed in the reboiler.

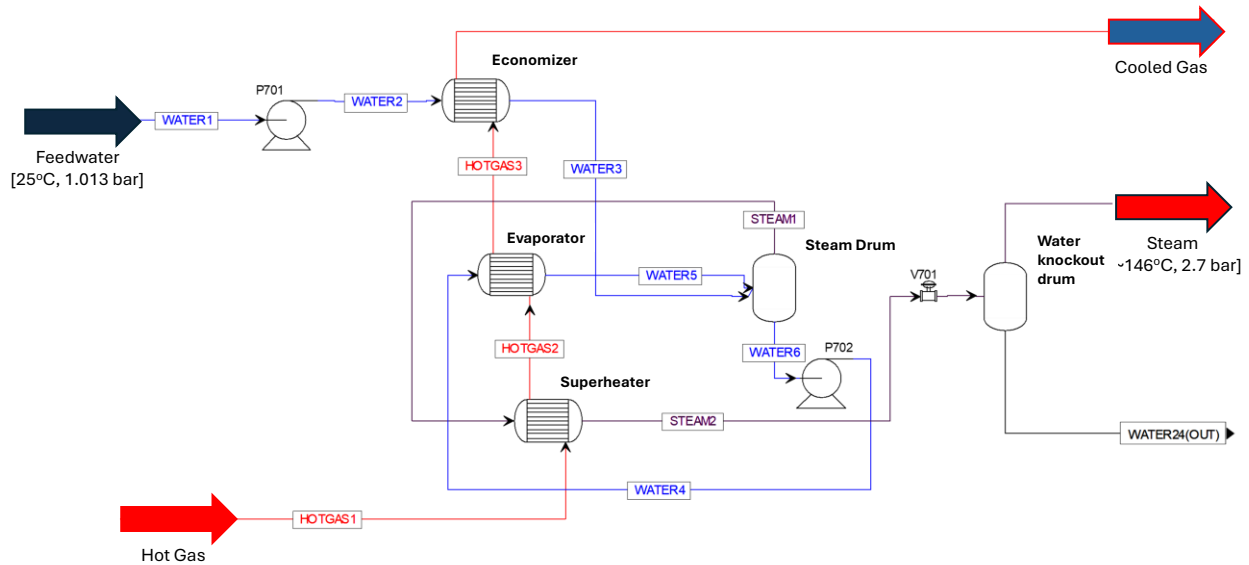


Figure 11: Heat Recovery Steam Generator Process Flow Diagram

The purpose of the HRSG is to achieve the maximum recoverable enthalpy at a reasonable cost. This cost is optimized by specifying a minimum temperature difference between the two streams that helps balance energy recovery with equipment size, based on the practical designs of unfired HRSG. The pinch point is the point of closest approach between the hot and cold composite curves. The minimum approach temperature is the smallest gap in temperature across which heat transfer will occur in the system.

The feedwater flow rate is varied and set using a design specification to meet an evaporator pinch temperature of 10°C (the temperature difference between the waste heat gas leaving the evaporator and the steam temperature). An approach temperature of 10°C between the economizer outlet feedwater and the saturated steam temperature is assumed for the HRSG design. Table 18 outlines the specifications for the units within the HRSG.

Table 18: HRSG equipment specifications

Unit	Specification
Boiler feedwater Pump	Pressure outlet = 5 bar
Economizer	Cold stream outlet vapor fraction = 0; Cold Stream Pressure drop = 0.5 bar; Hot Stream Pressure drop = 0 bar;
Evaporator	Cold stream outlet vapor fraction = 0.5; Cold Stream Pressure drop = 0.5 bar; Hot Stream Pressure drop = 0 bar;
Steam Drum	Pressure drop = 0 bar, Duty = 0 W

Superheater	Cold stream superheat temperature = 10°C; Cold Stream Pressure drop = 0.5 bar; Hot Stream Pressure drop = 0 bar;
-------------	--

3.1.3.2.1 Waste heat sources

The hot gas fed to the HRSG, is the heating fluid extracted from the waste heat streams, either directly e.g hot flue gas, or indirectly e.g circulating gas. The streams evaluated for heat recovery used in the HRSG include:

- exhaust gas streams
- flared process gas streams
- high temperature solid product streams

The gas stream properties for waste heat recovery are compiled in Table 1, as referenced from the existing steel plant. These gases are fed directly to the HRSG and are modelled individually to determine the recoverable enthalpy.

The solid stream properties were determined using a material balance model of the iron production process built in Aspen Plus. Figure 12 describes two processes considered to recover heat from the solid product streams in addition to the HRSG.

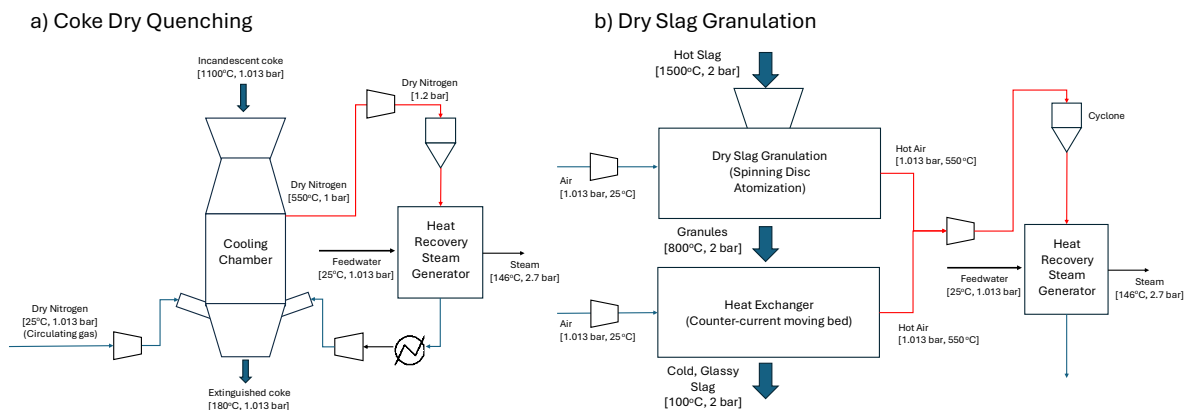


Figure 12: Heat recovery from solid streams a) Coke Dry Quenching, b) Dry Slag Granulation

The coke quenching process circulates water or dry inert gas (e.g. nitrogen) through the coke to recover the sensible heat. The inert gas ensures there is no combustion of the incandescent coke or the volatile matter in it. The traditional wet quenching used to cool hot coke loses high-quality heat. Thus, dry coke quenching (CDQ) has been recommended. Several studies [160], [171], [172] have been conducted to demonstrate the feasibility of heat recovery integrated with CDQ, and the technology has been successfully adopted in several plants worldwide [173], [174], [175]. In this study, the process shown in Figure 12a, is used to cool the coke from 1100°C to 180°C.

Molten slag from the blast furnace and basic oxygen furnace is currently left to air cool at the facility in slag dumps. Wet granulation is an established technology which uses water spray to create granulated blast furnace slag from molten slag, consuming large quantities of water,

creating polluting acid mist and losing high-grade waste heat. Recently, dry slag granulation (DSG) using air has been proposed since 1980s and has been evaluated to be better in terms of cost and emissions impacts [176], [177]. CSIRO [178] has developed this technology for commercial use in China where 60% of the world's blast furnace iron is produced. Their process produces glassy slag for cement production. Recently, an alternative DSG technology, paired with heat recovery has also been demonstrated at industrial scale [179] using electric arc furnace slag and ladle slag, with better performance than the traditional wet method. The CSIRO technology [180] shown in Figure 12b is used in this study – a two-step process which includes a dry granulation chamber and a moving bed heat exchanger. In the dry granulation chamber, a spinning disc separates the molten slag into droplets under centrifugal forces and uses air to quench and solidify the granules to 800°C. In the moving bed heat exchanger, air is used to further cool the granules to 180°C.

The circulating gas through both the dry quenching – nitrogen, and slag granulation process – dry air, are heated to 550°C and delivered to the HRSG.

These processes are individually analyzed with exergy balance to determine the flow rate of the circulating gas used in the quenching and granulation process.

3.1.3.2.2 Exergy Analysis

The exergy analysis method henceforth described is based on the presentation by Kotas [181]. Eq. 25 shows the exergy balance with a specified control region formed by combining the first and second laws of thermodynamics.

$$\text{Exergy input} - \text{Exergy output} - \text{Exergy consumption} = \text{Exergy accumulation} \quad (25)$$

At steady state, the terms in Eq. 25 can be mathematically formulated as follows;

$$\sum_i Ex_i \dot{m}_i - \sum_e Ex_{ie} \dot{m}_e + \sum \dot{E}_Q - \sum W - I = 0 \quad (26)$$

The first term on the left side of the equation refers to the exergy transfer associated with mass transfer into the control region and the second term is for out of the control region. Exergy for material flows is described with respect to a reference environment ($T_0 = 25^\circ\text{C}$, $P_0 = 1.01325 \text{ bar}$).

Without nuclear effects, magnetism, electricity and surface tension, the exergy of a flowing stream of matter consists of four elements (in order of Eq. 27): kinetic, potential exergy, physical and chemical.

$$Ex_i = Ex_{kin,i} + Ex_{pot,i} + Ex_{ph,i} + Ex_{ch,i} \quad (27)$$

Kinetic and potential exergy are higher-ordered forms of energy that can be fully converted to work. The potential exergy is neglected because the equipment is assumed to be installed on the earth's surface. The kinetic exergy is neglected since we are dealing with stationary systems and fluid velocities low enough to consider their kinetic energy negligible.

Thus, the exergy of each stream is estimated as the sum of the physical and chemical exergy. Physical exergy (in Eq. 28) represents the maximum work recoverable when the substance under consideration is brought from its initial state to the environmental state (i.e. in thermal and mechanical equilibrium with the environment), which involves only thermal interaction with the environment.

$$Ex_{ph,i} = (H_i - H_{0,i}) - T_0(S_i - S_{0,i}) \quad (28)$$

Where H is the enthalpy and S is entropy. Chemical exergy represents the maximum work recoverable when the substance under consideration is brought from the environmental state to the dead state (i.e. in thermal, mechanical and chemical equilibrium with the environment) by processes involving heat transfer and the exchange of substances with the environment.

$$Ex_{ch,i} = \sum_i x_i Ex_{ch,i} + RT_0 \sum_i x_i \ln x_i \quad (29)$$

Where the x_i is the mole fraction of the i -th component of the mixture.

Other flow streams considered in the exergy balance in Eq. 27 are the useable energy forms - heat and work. The exergy associated with heat transfer at a control surface is estimated from the maximum work that can be obtained from the transfer while using the environment as a reservoir for zero-grade thermal energy. For heat transfer rate $\dot{Q}_r$ and control region temperature T_r , the exergy of heat transfer is:

$$\dot{E}_Q = W_{MAX} = \dot{Q}_r * \left(1 - \frac{T_0}{T_r}\right) \quad (30)$$

The exergy associated with work transfer, W , including shaft work and electricity is equal to the supplied energy with no useable energy loss.

Exergy is consumed (destroyed) due to irreversibility such as friction, and unrestrained expansion amongst other non-idealities. The irreversibility rate term, I , based on the Gouy-Stodola theorem, is a product of the entropy production rate, S , and the temperature of the environment:

$$I = T_0 S = T_0 \left[\sum_{OUT} \dot{m}_e s_e + \sum_{IN} \dot{m}_i s_i - \sum_r \frac{\dot{Q}_r}{T_r} \right] \quad (31)$$

The exergy of all the material streams are estimated in Aspen Plus. The iron production process is modelled to assess the exergy of coke and slag produced from 1 t/h of coal and 1.4 t/h of iron and limestone ore. 0.2 t of slag/t of pig iron is used to determine the amount of slag. The coke and slag specific mass exergy at the boundary of the control region is then estimated within the Aspen simulation. Further specifications of this simulation are detailed in Appendix A:.

The CDQ and DSG processes are assumed to be sufficiently insulated such that the exergy associated with heat losses to the environment is set at 10% of total input. The exergy efficiency

of 70% is assumed based on studies of existing coke dry quenching process [171], [172]. So, the irreversibility is estimated as 30% of the input exergy to the control region.

The electricity needed in the CDQ process is primarily the electricity required for circulating gas handling. The electricity for the DSG process consists of the spinning disc in the granulator, the moving bed and the air handling system. Based on pilot studies, the total electricity consumption is assumed to be 9.5 kWh/t slag [182]. The circulating gas is transported using centrifugal fans with an efficiency of 0.97.

3.1.3.3 Heat Pump

Instead of using electricity for resistance heating, it can be used via heat pump to supply the heat needed in the reboiler. Mechanical Vapor Compression (MVC) is a heating strategy for reboilers that involves compressing vapour from the process to increase its temperature and pressure. Since the CO₂ must be compressed for storage, the compression process is integrated with a heat recovery generator as seen in Figure 13, to produce steam at each stage of compression.

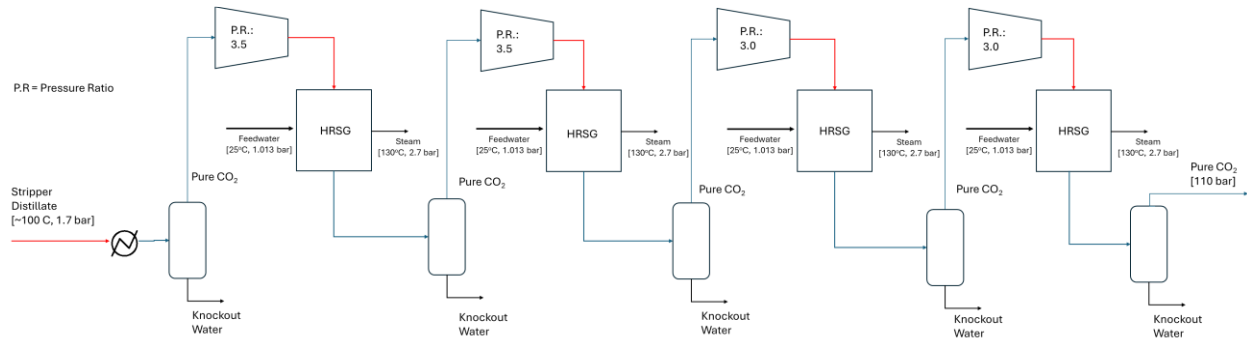


Figure 13: Integration of CO₂ compression with Heat Recovery Steam Generator

3.2 Hybrid VPSA-LTP Model Building

This hybrid process combines vacuum pressure swing adsorption (VPSA) with low-temperature purification (LTP). The VPSA recovers the CO₂ from the flue gas at a low purity (> 50%) and the LTP process further purifies the CO₂ rich flue gas to > 95%. Figure 14 shows the subsystems involved in the hybrid model. The flue gas is first dehydrated continuously in temperature swing adsorption process and fed continuously to a batch-process VPSA process. The adsorptive separation process is a cyclic batch system in which the bed is alternately saturated with CO₂ and regenerated cyclically. The adsorbed CO₂ rich material is desorbed in a discontinuous and dynamic manner, then supplied to the LTP for further purification, after which, the CO₂ is compressed for transport and storage.

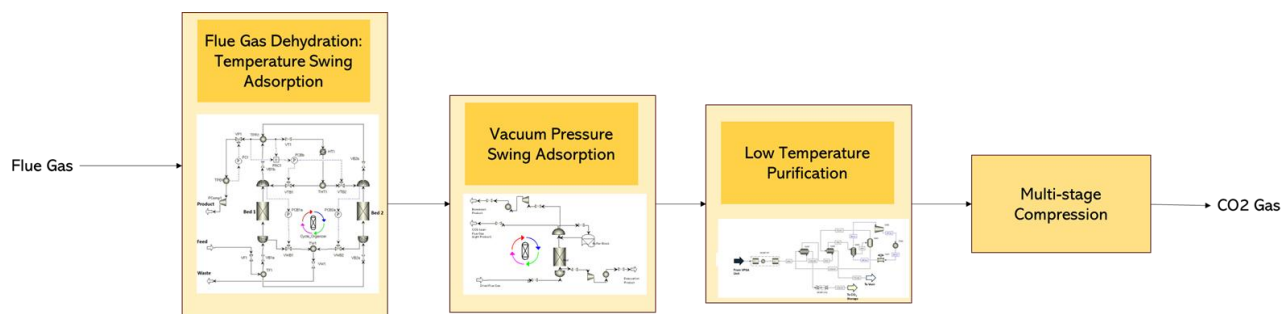


Figure 14: Hybrid VPSA-LTP Process Flow Diagram

3.2.1 Rigorous Model Development

The following subsections describe the development of the rigorous subsystem models within the hybrid process:

1. Vacuum Pressure Swing Adsorption
2. Flue Gas Dehydration
3. Low Temperature Purification

3.2.1.1 Vacuum Pressure Swing Adsorption

3.2.1.1.1 Literature Review

Several VPSA processes have been developed for post-combustion carbon capture. Several steps over several beds must occur in rapid succession for the process to operate continuously. In 1958, the simplest PSA configuration was introduced by Skarstrom [183] which consisted of bed pressurization, a high-pressure adsorption step, a blowdown, and a low-pressure purge of the adsorbed product using the light product. Shortly after, Montgareuil and Domine [20] introduced the regenerative vacuum step to achieve a higher concentration of the product stream without the need of a light product purge or extra heating. The Exxon Research Group [184] developed the pressure equalization steps to reduce product losses in blowdown step.

Activated carbon and zeolites have been the commercial adsorbents used for CO₂ capture. The capacity of zeolites for CO₂ is higher than that of activated carbon [185], [186]. On the other hands, zeolites are highly selective for the water in the flue gas, which is strongly adsorbed and difficult to remove. To simplify laboratory-scale experiments and simulation works, mixtures of CO₂ and N₂ have been used to mimic actual flue gas. More recently MOFs like MIL-120 [187]

and CALF-20 [188] have caught attention due to their high CO₂ loading capacity and selectivity even in the presence of moisture.

Rajagopalan et al. [189] conducted a study on activated carbon, UTSA-16, Zeolite 13x and Mg-MOF-74, and showed that overall process performance goes beyond just the sorbent performance. Beyond the sorbent ability, the VPSA performance also depends on the optimization of a myriad of operating conditions affecting different steps such as the evacuation pressure, the adsorption time, the vacuum flow rates, feed velocity amongst many others. Several commercial programs such as ASPEN Adsorption, COMSOL, gProms, PROSIM have been used to simulate different scenarios and evaluate the factors that improve the performance of a VPSA process. Here, ASPEN Adsorption is used to create a dynamic model of the VPSA process.

Chou and Chen [190] simulated the VPSA process cycling between 1 and 0.05 atm, using the 4-step process of adsorption, blowdown, evacuation and a heavy product rinse step. On Zeolite 13x sorbent, this process achieved 90% recovery but only concentrated the CO₂ from 20% to 30 – 40%.

In a bid to reduce product loss and increase purity, heavy reflux and pressure equalization steps were introduced and multistage VPSA units have been considered. Zhang et al. [191] studied a 3-bed 6-step configuration including two pressure equalization steps and a 3-bed 9-step configuration adding a heavy product reflux and a light product pressurization. They found the 9-step to achieve higher purity but with higher energy consumption. Khurana and Farooq [192] developed a 6-step cycle that can achieve high recoveries and purities at higher vacuum levels of 0.1 bar. Krishnamurthy [53] and Henrotin [193] setup a pilot plants capable of reaching 96% and 86% recovery at vacuum pressure of 0.011 and 0.1 bar respectively. The result of pilot and simulation studies are compiled in Table 19:

Table 19: Literature Overview of VPSA Cycles

VPSA Cycle	Study Type	Adsorbent	Feed flowrate [Nm ³ /h]	CO ₂ Mole %	Adsorption pressure [bar]	Intermediate Evacuation pressure [bar]	Low Evacuation pressure [bar]	Sorbent mass per column [kg]	Recovery	Purity	Productivity [tCO ₂ /m ³ ads/day]	Energy [MJ/kg-CO ₂]	Reference
3-bed 6-step ⁽¹⁾	P	Zeolite 13x	0.30	15	2.00	0.60	0.10	0.80	85.00	79.70	1.88	1.23	Henrotin (2024)
3-bed 6-step ⁽¹⁾	P	MIL-160	0.15	15	2.00	0.60	0.10	0.69	92.70	75.30	2.11	1.32	Henrotin (2024)
2-bed 4-step ⁽¹⁾	P	Zeolite 13x	55.90	15	1.50	0.07	0.03	41.00	85.40	94.70	1.40	1.84	Krishnamurthy (2014)
2-bed 4-step ⁽²⁾	P	Zeolite 13x	55.90	15	1.50	0.07	0.03	41.00	93.30	92.90	1.17	1.71	Krishnamurthy (2014)
2-bed 4-step ⁽²⁾	S	Zeolite 13x	170.41	15	1.76	0.22	0.03		90.00	90.00	3.04	0.73	Hagnagapah (2013)
4-step ⁽²⁾	S	CALF-20	5.4 - 108.2	15	1.00	0.07	0.03	5.60	88.30	91.60	0.53	0.63	Nguyen (2023)
6-step ⁽²⁾	S	Zeolite 13x	162.30	15	1.00	0.24	0.10	18.00	>90	>95	8.82	0.22	Khurana and Farooq (2016)
4-step ⁽²⁾	S	Zeolite 13x	162.30	15	1.00	0.08	0.02	18.00	>90	>95	3.80	0.52	Khurana and Farooq (2016)
6-step ⁽²⁾	S	UTSA-16	162.30	15	1.00	0.27	0.10	18.00	>90	>95	18.06	0.20	Khurana and Farooq (2016)
2 stage 4-step ⁽²⁾	S	Zeolite 13x	13.20	15	1.50		0.06		91.86	96.03	3.03	0.79	Jiang (2020)
6-step ⁽²⁾	P	Zeolite 13x	3.9 - 6.8	8 - 22	1.35		0.03 - 0.06	3.61	60 - 80	82 - 83		0.79	Zhang (2008)
9-Step	P	Zeolite 13x	3.9 - 6.9	8 - 22	1.35		0.03 - 0.07	3.61	60 - 70	90 - 95		0.28 - 0.43	Zhang (2008)
4-bed 9-step	P	Zeolite 13x	0.32	15	1.10		0.05	0.19	74 - 89	88 - 98	1.16 - 2.15	0.43 - 0.61	Webley (2017)
4-step ⁽²⁾	S	Zeolite 13x	108.20	15	1.00	0.11 - 0.14	0.03	18.50	80 - 99	80 - 98	1.37 - 3.50	0.48 - 0.56	Rajagolapan (2016)
4-step ⁽²⁾	S	UTSA-16	108.20	15	1.00	0.17-0.18	0.03	9.60	80 - 99	80 - 98	2.18 - 2.81	0.42 - 0.43	Rajagolapan (2016)
Study Type: P – Pilot; S – Simulation 4-step (1): Adsorption-Countercurrent Evacuation-Light Rinse-Pressurization 4-step (2): Adsorption-Cocurrent Blowdown-Countercurrent Evacuation-Light Pressurization 6-step (1): Adsorption-Heavy Reflux-Cocurrent Evacuation-Countercurrent Evacuation-Light Reflux-Light Product Pressurization 6-step (2): Adsorption-Equalization-Heavy Reflux-Countercurrent Evacuation-Light Reflux-Light Product Pressurization													

For the development of the simulation in this report, a 4-step cycle configuration is adopted due to its operational simplicity despite its relatively low purity. The 4-step VPSA cycle with light product pressurization has been shown to have advantages over the traditional 4-step cycle in meeting the purity and recovery constraints while minimizing the energy requirement [59], [194]. The cycle in Figure 15 consists of the following steps: (1) adsorption, (2) co-current blowdown, (3) counter-current evacuation and (4) light product pressurization.

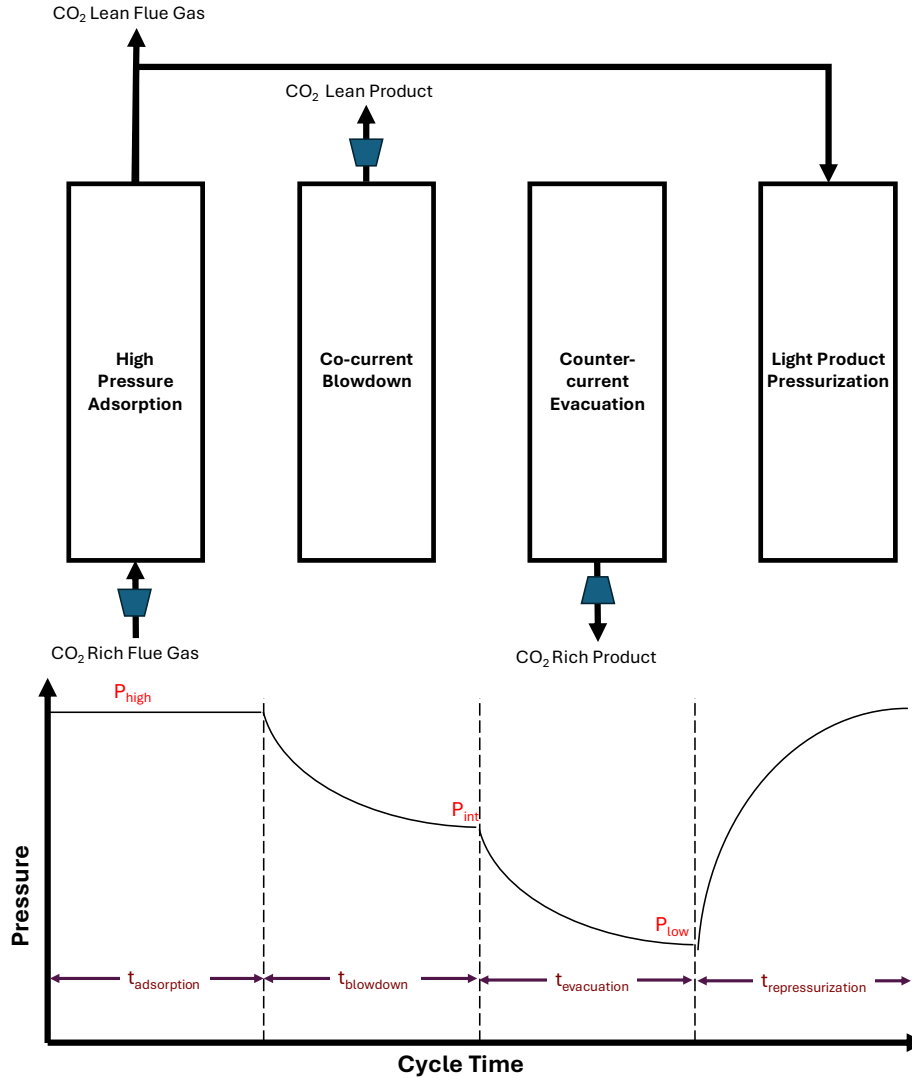


Figure 15: VPSA Cycle showing the 4 steps and the pressure swings

The approach to modelling this cycle must extend beyond the dynamic simulation of a single bed to scheduling of different beds, steps and parallel trains to achieve a continuous operation. There is a startup process from an empty bed and after several cycles, the system approaches a pseudo-steady state when the cyclical difference in the bed's thermal and material properties converges

to null. The sizing of the system is conducted based on this cyclic steady-state operation. The simulation development is organized as shown in Figure 16.

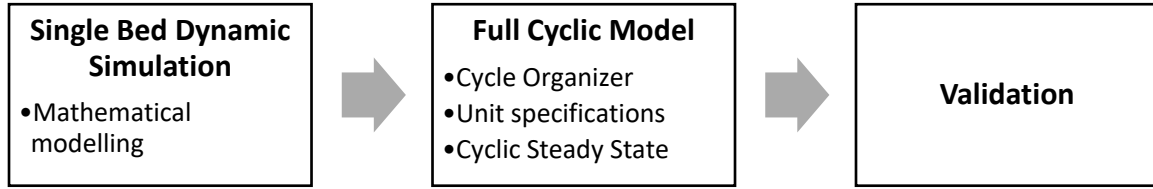


Figure 16: VPSA Simulation Development Framework

3.2.1.1.2 Single-bed Dynamic Simulation

The following assumptions were made for the dynamic simulation of CO₂ adsorption in the packed bed:

1. Radial effects are neglected in both the gas and solid phase.
2. The particle size and voidage are constant throughout the bed
3. The linear driving force model is used to describe gas diffusion into the adsorbent.
4. The energy balance on the bed assumes adiabatic and non-isothermal conditions.
5. There are no reactions taking place in the system.

Below is a summary of the equations that represent the transport behaviour of the fixed bed modelled in ASPEN Adsorption:

Momentum conservation equation

The gas phase momentum balance is represented by the Ergun Equation.

$$-\frac{dP_g}{dz} = 150 \frac{\mu_g(1 - \varepsilon_i)^2}{\varepsilon_i^3 4R_p^2 \psi^2} v_g + 1.75 \frac{M\rho_g(1 - \varepsilon_i)}{\varepsilon_i^3 2 R_p \psi} v_g^2 \quad (32)$$

Mass conservation equation

The convection-only assumption drops the dispersion term from the material balance, so the model represents plug flow. The mass balance for each component in the gas phase is:

$$\rho_s \frac{\partial c_k}{\partial t} + \frac{\partial(v_g c_k)}{\partial z} + J_{ads,k} = 0 \quad (33)$$

The mass transfer driving force is expressed as a function of the solid phase loading.

$$J_{ads,k} = -\rho_s \frac{\partial w_k}{\partial t} \quad (34)$$

$$\frac{\partial w_k}{\partial t} = MTC_{g,k}(w_k^* - w_k) \quad (35)$$

Where $MTC_{g,k}$ is the mass transfer coefficient and w^* is the loading which would be at equilibrium with the actual gas phase composition. The isotherm used to estimate the equilibrium loading is the Extended Langmuir isotherm. The isotherm uses the pure component isotherm data which is more readily available to describe the behaviour of a mixture. The Extended Langmuir isotherm is described as a function of temperature and partial pressure, in the form:

$$w_i^* = \frac{IP_{1i} \exp\left(\frac{IP_{2i}}{T_s}\right) P_i}{1 + \sum_k \left(IP_{3k} \exp\left(\frac{IP_{4k}}{T_s}\right) P_k\right)} \quad (36)$$

Energy conservation equation

The gas phase energy balance includes terms for thermal conduction, energy convection, heat accumulation, compression, heat transfer from gas to solid and the heat of adsorption.

$$-k_{ga}\varepsilon_i \frac{\partial^2 T_g}{\partial z^2} + C_{vg}v_g\rho_g \frac{\partial T_g}{\partial z} + \varepsilon_B C_{vg}\rho_g \frac{\partial T_g}{\partial t} + P \frac{\partial v_g}{\partial z} + HTC a_p (T_g - T_s) + \frac{4H_w}{D_B} (T_g - T_o) = 0 \quad (37)$$

The solid phase energy balance includes terms for thermal conduction, heat accumulation, adsorbed phase enthalpy accumulation, heat transfer from gas to solid and the heat of adsorption.

$$-k_{sa} \frac{\partial^2 T_s}{\partial z^2} + \rho_s C_{ps} \frac{\partial T_s}{\partial t} + \rho_s \sum_{i=1}^n (C_{pa,i} w_i) \frac{\partial T_s}{\partial z} + \rho_s \sum_{i=1}^n \left(\Delta H_i \frac{\partial w_i}{\partial t} \right) - HTC a_p (T_g - T_s) = 0 \quad (38)$$

Material and Bed Properties

Only two gas components, CO₂ and N₂ are considered. O₂ is neglected because it is relatively negligible in flue gas, and it is assumed that any present behaves like N₂ due to similarity in kinetic diameters. H₂O is neglected because it is assumed that the flue gas is “completely” dried before the VPSA process as described in Section 3.2.1.2. The fluid mixture thermodynamic properties are described using the Peng Robinson equation of state (EOS). The sorbent and adsorbate properties are defined as given in Table 20.

Table 20: VPSA Sorbent Properties

	Units	Value
Sorbent material		Zeolite 13x
Sorbent bulk density	kg m ⁻³	750
Sorbent particle radius	m	0.00125
Interparticle voidage (ε_i)		0.38
Intraparticle voidage (ε_p)		0.37
Shape factor (ψ)		1
Constant mass transfer coefficients (MTC)		
MTC_{CO_2}	1/s	0.1
MTC_{N_2}	1/s	0.5

Constant heat of Adsorption (ΔH)		
ΔH_{CO_2}	MJ/kmol	-37.0
ΔH_{N_2}	MJ/kmol	-18.5
Sorbent thermal conductivity	W/m/K	0.12
Sorbent specific heat capacity	kJ/kg/K	0.92

Table 21 presents a summary of experimental studies predicting the adsorption equilibrium loading of pure CO₂ at 0.2 - 0.3 bar and 25 – 40°C:

Table 21: Literature Overview of Equilibrium loading of pure CO₂ on 13x Zeolite

CO ₂ Pressure [bar]	Temperature [°C]	Equilibrium Loading [mol/kg]	Reference
0.3	20	2.5	Lee (2002) [185]
0.29	20	3.9	Park (2012) [195]
0.3	25	4.1	Krishnamurthy (2014) [196]
0.3	25	4.5	Perez (2019)[194]
0.3	30	4.9	Mondino (2019) [197]
0.29	25	3.2	Jiang (2020) [61]

The Extended Langmuir isotherm model was fitted to experimental data and validated by Jiang and coworkers for the adsorption of CO₂ on Zeolite 13x sorbent [61]. This model and the conditions it was fitted for yield an acceptable prediction of the CO₂ loading of Zeolite 13x compared to the other studies shown in Table 21. Thus, the Jiang model was selected. The model covered temperature ranges 298 K – 423 K and was limited to the CO₂ partial pressures between 0 – 1 bar, which cover the vacuum swing operating conditions. Table 22 shows the fitted isotherm constants used in Eq. 36.

Table 22: 13x Zeolite Langmuir Isotherm Constants

	IP_1	IP_2	IP_3	IP_4
CO ₂	2.60E-7	3574	6.18E-5	3603
N ₂	7.18E-7	1670	6.21E-4	1359

Vacuum Pump Specifications

The vacuum pump is described by an isentropic model with a fixed volumetric rate and an efficiency of 75%. This is specified to replicate the behaviour of industrial dry screw pumps [198], [199] which are capable of ultra-low vacuum conditions below 0.01 bar.

Numerical Methods

The partial differential equations are discretized using the Upwind Differencing Scheme (UDS) due to its unconditional stability and cheaper use of simulation time. UDS approximates spatial derivatives by considering the direction of the flow. The derivative at a given point is computed

using values from upstream (in the direction opposite to the flow) to account for the transport nature of the problem.

For a 1D linear advection equation,

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} = 0 \quad (39)$$

the UDS discretizes the spatial derivative $\frac{\partial u}{\partial x}$ as:

$$\frac{\partial u}{\partial x} \approx \frac{u_i - u_{i-1}}{\Delta x} \quad (40)$$

where u_i is the solution at the current grid point and u_{i-1} is the value at the upstream neighbor.

Because the UDS is only first-order accurate, it is critical to increase the number of nodes for improved accuracy and less “false” diffusion. As part of the verification and validation, a sensitivity test was conducted on the number of nodes. The time integration technique adopted is the Implicit Euler method. For a more accurate and stable simulation, variable time stepping is employed with an initial step size of 1×10^{-1} and a minimum step size of 1×10^{-10} .

After the differential equations have been decomposed and discretized, the MA48 method is used to solve the linear equations, and the Mixed Newton method solves the non-linear ones. The MA48 is an optimized implementation of the unsymmetric multifrontal method proposed by Davis and Duff [200] for solving sparse linear equations. The Mixed Newton method alternates between the Newton-Raphson method for initialization and steady-state steps and the Fast Newton method for dynamic steps.

During the initialization phase, the system is often far from equilibrium, and precise, stable iterations are crucial to ensure the method converges towards a viable solution. The Newton-Raphson method’s robust handling of large residuals and nonlinearities makes it the ideal choice for this stage. Similarly, in steady-state steps, where the system reaches a quasi-equilibrium and changes are minimal, the Newton-Raphson method provides accurate and stable convergence without requiring high computational speed.

In dynamic steps, the system evolves over time and often requires rapid calculations to track changes in state variables. The Fast Newton Method sacrifices some accuracy by relying on approximations (e.g., simplified Jacobians, preconditioners) but compensates with computational speed and convergence aids like preconditioning and iterative refinement. This method recalculates derivatives less frequently and thus updates the Jacobian matrix only when convergence is poor, thus making it faster.

3.2.1.1.3 Full Cyclic Model

Rigorous modelling of each step on individual beds is computationally expensive. To simplify, a single-bed approach is adopted, where each step is modelled using one bed. For coupled steps, a buffer temporarily stores the outlet stream properties from the supplying bed. These properties

are later fed into the coupled receiving step on the same bed, maintaining the process flow. The bed is initialized with the following conditions:

Table 23: Initial Bed Conditions

Initial Bed Conditions	$y_{CO_2} = 0;$ $y_{N_2} = 1$ $T = 25\text{ }^{\circ}\text{C}$ $P = 1\text{ bar}$
------------------------	--

Table 24 outlines the terminating conditions for each step in the VPSA units

Table 24: VPSA step terminating conditions and bed profile conditions

Step	Condition	$z = 0$	$z = L$
Adsorption	$t_{\text{step}} = t_{\text{adsorption}}$	$\dot{F} _{z=0} = \dot{F}_{\text{feed}}$	$P _{z=L} = 1\text{ atm}$
Concurrent Blowdown	$P _{z=L} = P_{\text{blowdown}}$		$\dot{V}F _{z=L} = V\dot{F}_{\text{vacuum pump}}$
Counter current Evacuation	$P _{z=0} = P_{\text{evacuation}}$	$V\dot{F} _{z=0} = V\dot{F}_{\text{vacuum pump}}$	
Light Product Pressurization	$t_{\text{step}} = t_{\text{adsorption}}$		

Dynamic models are run until they reach a pseudo-steady state, selected based on material and thermal conditions in the bed across the cycle. A specified tolerance of 1×10^{-4} is used to assess the average difference in the composition and thermal profile of the bed between consecutive cycles. Once this tolerance is reached, it is assumed that steady operating state conditions have been achieved and the run is completed. The simulation results at steady-state are used to evaluate the criteria in Table 25:

Table 25: VPSA Evaluation Criteria

Recovery	%	$\frac{\int_0^{t_{\text{evacuation}}} \dot{F}_{CO_2, \text{Product}} dt}{\int_0^{t_{\text{adsorption}}} \dot{F}_{CO_2, \text{Feed}} dt}$
Purity	%	$\frac{\int_0^{t_{\text{evacuation}}} \dot{F}_{CO_2, \text{Product}} dt}{\int_0^{t_{\text{evacuation}}} \dot{F}_{\text{Product}} dt}$
Productivity	Mt-CO ₂ /m ³ -day	$\frac{\int_0^{t_{\text{evacuation}}} \dot{F}_{CO_2, \text{Product}} dt}{t_{\text{cycle}} \times V_{\text{catalyst}}}$
Energy Consumption	MJ/kg-CO ₂	$\frac{\int_0^{t_{\text{blowdown}}} P dt + \int_0^{t_{\text{evacuation}}} P dt}{\int_0^{t_{\text{evacuation}}} \dot{F}_{CO_2, \text{Product}} dt}$

3.2.1.1.4 Model Validation

To validate the selected model parameters, cyclic steady state (CSS) modelling strategy and simplifying assumptions, pilot data sourced from literature (as shown in Table 26) was used to assess the model's effectiveness. First, the ability of the full model to describe the adsorption was assessed using a breakthrough curve from a VPSA pilot study by Henrotin [193].

Table 26: Pilot Study Specifications

Pilot Specifications	Case A	Case B
Reference	Henrotin et al. [193]	Krishnamurthy et al. [53]
Sorbent	13x zeolite	13x zeolite
Height (cm)	30	86.7
Diameter (cm)	7.0	30
Feed volumetric flow rate (Nm ³ /h)	1	56
CO ₂ Volume %	15	15
Feed Pressure (bar)	1.38	1.5
Feed Temperature (C)	30	30

The breakthrough curves in Figure 17a show similar fast adsorption kinetics, with the breakthrough (10% of CO₂ inlet concentration) achieved at 485 s. The isotherm model can reasonably predict the adsorption behaviour. The temperature peak in the bed corresponds to the period before the breakthrough point where there is a steep adsorption increase. The temperature increase, however, causes a reduction in the adsorption capacity and adsorption subsequently slows beyond breakthrough. There is a deviation from the experiment data during the steep rise in the outlet CO₂ mole fraction, which could lead to the underestimation of the sorbent's adsorption capacity. The temperature estimates of the simulation in Figure 17b at the peak are 20 - 40 K lower than the experimentally estimated values. The temperature profile does not exhibit a plateau in the outlet temperature suggesting that the pilot column might not be long enough to assume adiabatic behaviour. The model deviates from the thermal profile in the pilot beds beyond the breakthrough point. The fact that the deviation is more significant in the top sensor suggests that the assumed heat dissipation and thermal conductivity might not sufficiently describe the pilot column's behaviour at the end of the column compared to the bottom. The pilot column is also extremely short. Thus, it is critical to evaluate how this discrepancy impacts the overall model prediction of key criteria on a larger scale.

a)

b)

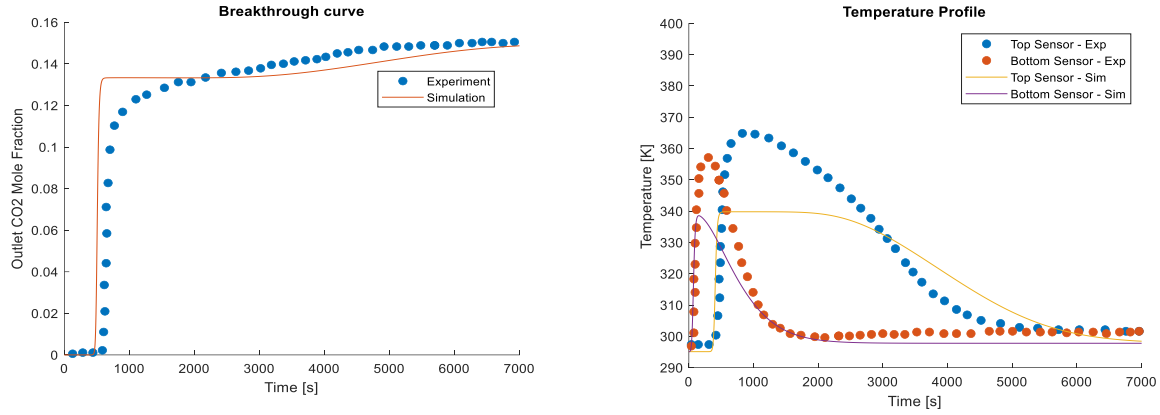


Figure 17: Breakthrough curves: a) Composition Profile b) Temperature Profile

Next, the 4-step cyclic modelling was validated using the 8 pilot runs of a similar cycle process (Case B) with a larger and longer column, published by Krishnamurthy et al. [53]. The following criteria were observed: recovery, purity and productivity. There is not sufficient information about the operating conditions of the vacuum pump in the study, so the energy consumption is not assessed. The average absolute error of the simulation results, presented in Table 27, shows that the model is sufficiently accurate in its estimation of recovery, purity and productivity:

Table 27: Average absolute error for rigorous model

Criteria	Average Absolute Error
Recovery	4.5%
Purity	2.0 %
Productivity	11.8%

3.2.1.1.5 VPSA Scheduling

The adsorption model accounts for the behaviour in individual steps and their interaction based on a single feed stream. In practice, several beds will operate in parallel to resemble a continuous operation.

In 1988, Chiang [201] proposed an arithmetic representation of the PSA schedule based on its cycle time and feed and production rate constraints. Smith and Westenberg [202] applied a mixed linear programming to estimate the minimum number of beds needed for a set of cycle times and constraints. Mehrotra and coworkers [203], [204] formulated an algebraic optimization and graphical approaches to account for idle times and couplings needed for PSA Scheduling. Based on these approaches for the special case on continuous feed supply, Khurana and Farooq [192] developed the formula in Eq. 41 – 43, used in this work to determine the number of beds and the required idle times to ensure minimal disruption of the concentration profile.

$$N_{beds} = Ceiling \left(\frac{\sum_{i=steps} t_i}{t_{adsorption}} \right) \quad (41)$$

$$t_{idle} = (N_{beds} * t_{adsorption}) - \sum_{i=steps} t_i \quad (42)$$

$$Number\ of\ blowdown\ vacuum\ pumps = Ceiling \left(\frac{t_{blowdown}}{t_{adsorption}} \right) \quad (43)$$

$$Number\ of\ desorption\ vacuum\ pumps = Ceiling \left(\frac{t_{evacuation}}{t_{adsorption}} \right) \quad (44)$$

A buffer is introduced after the VPSA unit to ensure continuous and constant flow to the purification unit. This buffer should ideally be sized to accommodate excess flow and supplement under flow such that a constant flow rate to the low-temperature purification (LTP) unit from the VPSA can be achieved. To be conservative in the continuing assessment, the buffer will be sized to accommodate the flow from all desorbed beds within a cycle time. For example, a VPSA train with 12 beds of which 8 are being evacuated at the same time will have a buffer sized to hold the contents of the 8 beds at a set maximum pressure.

3.2.1.2 Flue Gas Dehydration

Due to the use of Zeolite 13x, the wet flue gas must be dehydrated before feeding it to the pressure swing adsorption units. Zeolite 13x absorption capacity for CO₂ reduces in the presence of water because the sorbent has a greater affinity for H₂O, exhibiting an average uptake for pure water vapour of 6.98 mol/kg at pressures as low as 10 Pa over a 25 – 100°C range [205]. To achieve negligible water uptake of less than 0.1 mol/kg capacity in a CO₂/H₂O mixture, the vapour pressure of water must be lower than 0.1 Pa [206]. With flue gas feed at 2 bars, this means that the H₂O composition must be reduced to below 0.5 ppmv, corresponding to a dew point temperature of -80°C, which is very low. Therefore, temperature swing adsorption has been selected as a more practical technology.

A 5-step 2-bed process shown in Figure 18 has been designed using an alumina sorbent to dehydrate the flue gas. It is assumed that only water is adsorbed by the sorbent. The process is modelled in Aspen Adsorption, using a 1D model.

Flow and pressure controllers in Figure 18 are introduced to set the pressure and flowrates on different streams. First, a pressure controller (PCB1a and b) is used to achieve a 1.5 bar pressure drop across the columns. Using a flow controller (FCBb), the output of the adsorption in the first column is split from the product stream to use as a purge stream in the heating and cooling of the second column. The ratio of the purge stream to the product stream is set as 0.3. Another controller (FC1) is used to control flow into the buffer tank which maintains consistent flow to the VPSA unit.

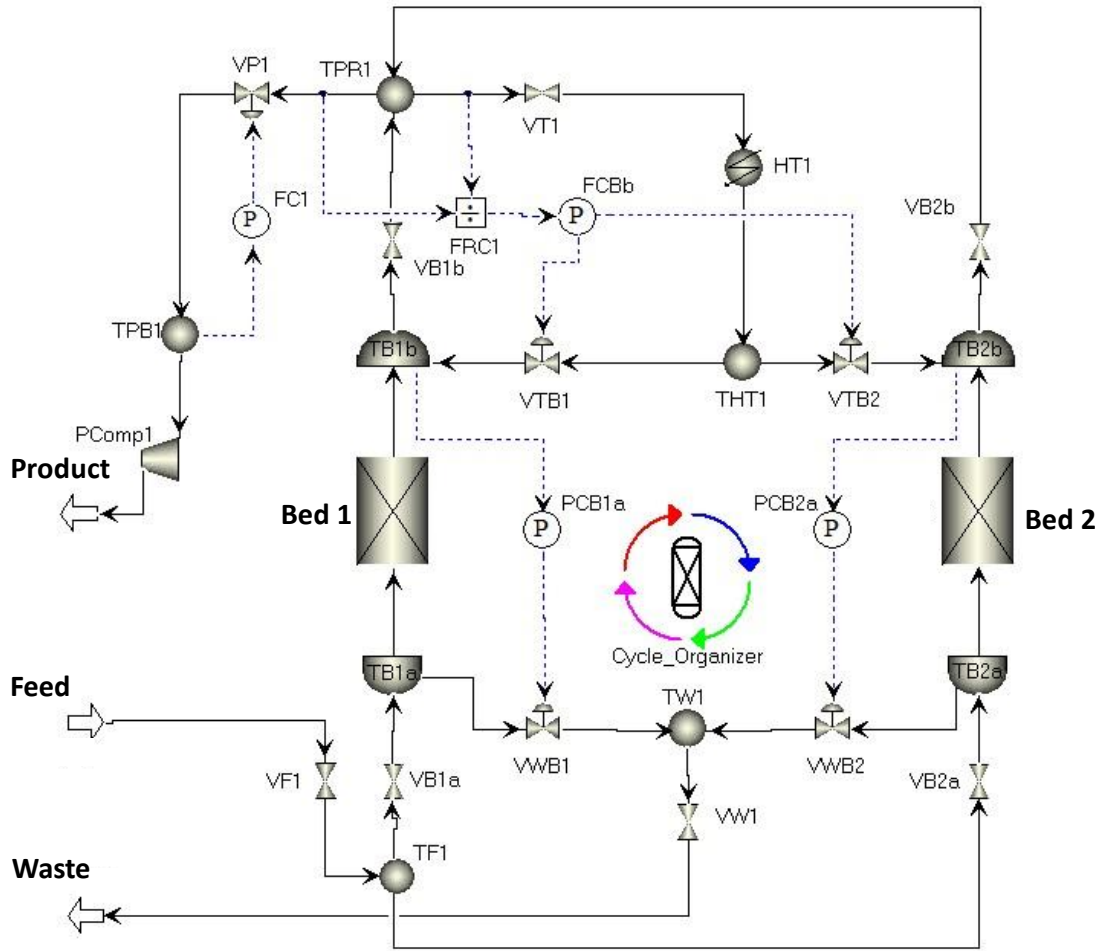


Figure 18: TSA Dehydration Schematic

The sorbent properties for air dehydration, are given in Table 28:

Table 28: TSA Bed Specifications [207]

	Units	Value
Sorbent material		Silica Type 3A
Sorbent bulk density	kg m ⁻³	770
Sorbent particle radius	m	0.0045
Interparticle voidage (ϵ_i)		0.35
Intraparticle voidage (ϵ_p)		0
Shape factor (ψ)		1
Molecular Diffusivity of all compounds	m ² /s	2.206E-5
Constant mass transfer coefficients (MTC)		
MTC_{H_2O}	1/s	9.823E-4
MTC_i for all other compounds, i , except H_2O	1/s	1
Heat of Adsorption (ΔH_{H_2O})	MJ/kmol	-45.15

Heat Capacity of Adsorbed Phase (Cpa_{H_2O})	MJ/kmol/K	0.075
Sorbent thermal conductivity	W/m/K	0.174
Sorbent specific heat capacity	kJ/kg/K	0.921
Specific surface area of adsorbent	1/m	433

It is assumed that convection occurs with axial dispersion estimated using the Kast correlation. The Ergun equation is used to describe the momentum balance. A solid film model and a pressure-dependent Arrhenius equation is used for the kinetics. Due to low concentration of water, Henry's law is used to describe the equilibrium loading in kmol/kg:

$$w_{H_2O} = IP_1 \times \exp\left(\frac{IP_2}{T}\right) * y_{H_2O} \times P_{sat,H_2O} \quad (45)$$

The isotherm constants are specified as in Table 29:

Table 29: TSA Sorbent Isotherm Specifications [207]

Isotherm Constant	Value
IP_1 [kmol/kg/bar]	2.89×10^{-8}
IP_2 [K ⁻¹]	5152.75

The bed is assumed to be adiabatic and non-isothermal with gas and solid conduction. All equipment involved in the pre-drying process is made from stainless steel SS316L for its corrosion resistance. Other process conditions for the TSA unit are given in Table 30:

Table 30: TSA Dehydration specifications

Cycle Step Times [hrs] – Total time	9.61
Step 1 – Adsorption [min]	288
Step 2 – Depressurization [min]	5
Step 3 – Heating [min]	168
Step 4 – Cooling [min]	110
Step 5 – Repressurization [min]	5
Low Temperature [C]	6.8
High Temperature [C]	207
Feed Temperature [C]	10
Feed Pressure [bar]	5
Feed flux [kmol/s/m ²]	4.1×10^{-2}
Diameter [m]	5
Height [m]	10

Based on the column flow rate, the number of 2-bed trains needed to handle the feed volume without exceeding the recommended feed flux is evaluated using Eq. 45:

$$N_{trains} = ceiling \left(\frac{\dot{F}_{overall}}{\dot{F}_{column}} \right) \quad (46)$$

The bed mass, momentum and energy transfer PDEs are discretized using Upswing Discretization Scheme with a discretization level of 10 nodes/m

3.2.1.3 Low-Temperature Purification (LTP)

The low-temperature purification process is assembled as depicted in Figure 19

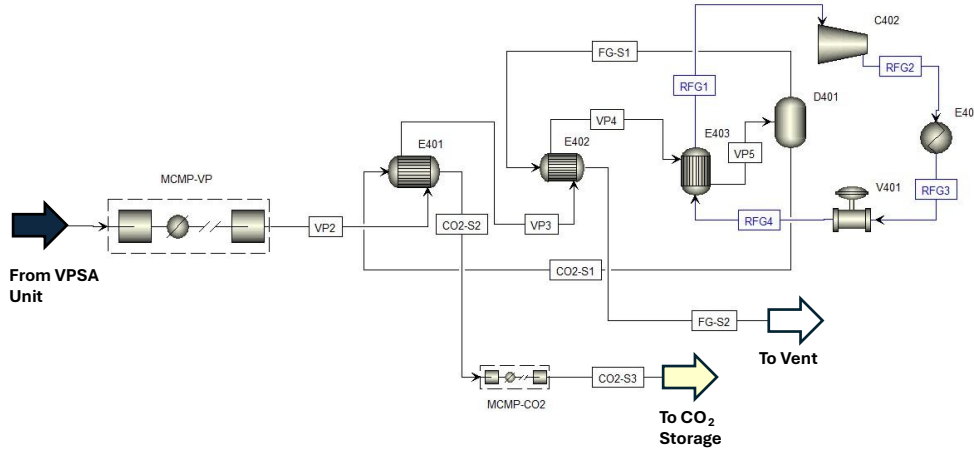


Figure 19: Low Temperature Purification Process Flow Diagram

After the VPSA unit, the CO₂-rich product is fed to this section to be further purified to over 95% CO₂ purity required for storage. First, the CO₂-rich stream is compressed to a specified pressure in a multi-stage compressor (MCMP-VP), that is fitted with intercoolers. The product (VP2) is cooled through a series of heat exchangers to the low-temperature flash temperature. The LTP flash temperature is set as 5°C higher than the temperature of the refrigerant entering the final heat exchanger (E403). Ideally the refrigerant heat exchanger (E403) should cool the CO₂ rich stream. However, the integration of cooler temperature flash (D401) products is used to reduce the duty and the amount of refrigerant through exchangers E401 and E402. The first exchanger (E401) and the second exchanger (E402) use the bottom and top products, respectively, to cool the CO₂ rich stream to within 5°C of the coolant stream.

The refrigeration cycle – coloured blue – is used to supply the cold refrigerant to the E403 through C402. The refrigerant used is propylene, labelled as R-1270. It is selected due to its thermodynamic efficiency, low Global Warming Potential of 3 and zero ozone depletion potential. However, it is highly flammable, correspondingly categorized as an A3 refrigerant under the CSA B52 and ASHRAE 34 Standards. Using propylene requires strict safety measures, including leak-proof installations, non-sparking tools for servicing, and proper ventilation in areas where it is used.

The refrigerant is first compressed to 15 bars in a compressor with isentropic efficiency of 0.75 and mechanical efficiency of 0.97. The hot compressed refrigerant is then cooled with cooling water to 35°C. The cooled product is then abruptly expanded in a thermal expansion valve

(V401) to atmospheric pressure, consequently cooling it to the flash (D401) temperature of -48°C. This throttling process is considered inefficient. Using an expansion turbine could theoretically replace the throttling process, as it would recover some of the pressure energy as work, improving exergy efficiency. However, turbines are often impractical in typical refrigeration applications due to their higher costs, added complexity, and potential reliability issues.

Table 31 shows how the overall heat transfer coefficient changes based on the phase of the fluid in the heat exchangers in the LTP system.

Table 31: Phase-specific Overall Heat Transfer Coefficient

Hot side	Cold side	U value [W/m ² /k]
Liquid	Liquid	850
Liquid	Boiling	850
Liquid	Vapor	600
Condensing	Liquid	300
Condensing	Boiling	850
Condensing	Vapor	850
Vapor	Liquid	600
Vapor	Boiling	850
Vapor	Vapor	30

3.2.2 Surrogate Model Development

When these rigorous sub-models were integrated to form the overall hybrid process, we encountered the problems associated with combining continuous and batch process models, as illustrated in Figure 20. These processes have different orders of computing (CPU) time, and the different combinations of unknown variables could yield a wide range of result and impact the computation time.

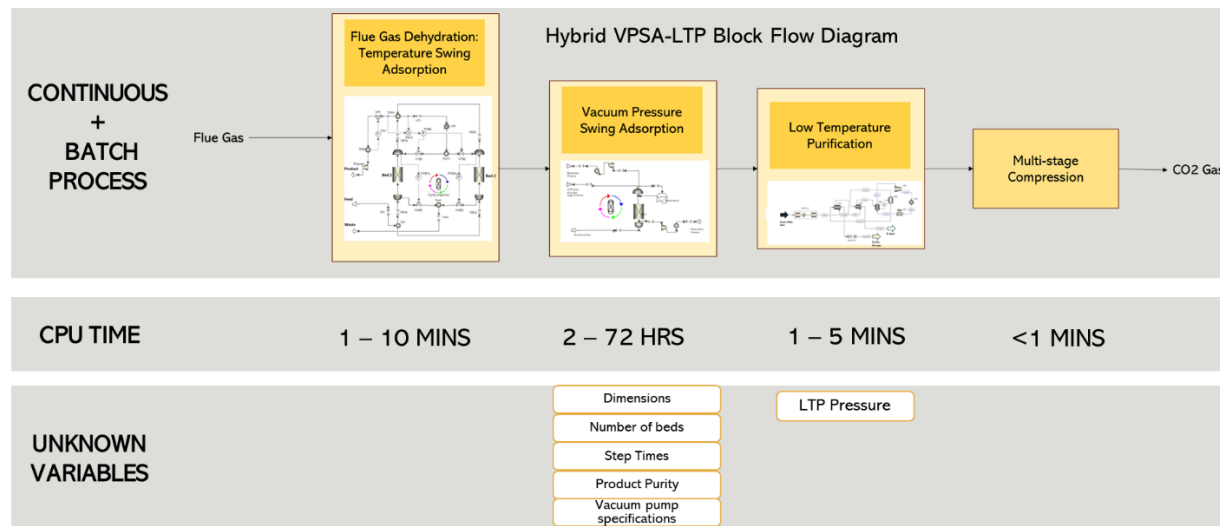


Figure 20: Hybrid VPSA-LTP Model showing CPU times and unknown variables

To estimate the best configurations for the hybrid process, several combinations of design parameters must be tested to minimize the cost of capture, while subject to efficiency and purity constraints.

The unknown variables are broken down into the following decision variables: The **residence time** refers to the duration the gas spends in the adsorption column, influencing the contact between the gas and adsorbent. **Adsorption time**, expressed as a percentage of the breakthrough time for a fresh bed, is the type the bed spends with flue gas fed to it. The **number of trains** indicates how many parallel processing units handle the overall flow, affecting scalability and the flue gas flow distribution. The **evacuation flowrate** is the volumetric rate of gas removed during the desorption phase to regenerate the adsorbent. **Blowdown pressure** is the pressure reduction applied during blowdown, to clear the void spaces. **Desorption pressure** is the low pressure used during desorption to maximize adsorbent regeneration. The **H/D ratio** (height to diameter of the column) influences gas flow and residence time, affecting the column's efficiency and performance. Together, these variables play key roles in optimizing the adsorption and desorption processes for effective system operation. The **LTP pressure** is the pressure to which the product of the VPSA is compressed for further purification.

The bottleneck of this optimization is the batch adsorption model, which is computationally expensive in Aspen Adsorption, requiring hours, sometimes nearly 3 days to reach steady state. Hence a reduced order surrogate model was developed based on a defined design space to get reasonably acceptable sizing results at a lower computational cost. Figure 21 shows how the

operating conditions for the LTP and VPSA process were chosen. The surrogate model of the dynamic VPSA system will be fitted and validated using results from several runs of the rigorous model. The results from this surrogate model will be fed alongside the low-temperature model results to a costing model which delivers the overall cost per ton of CO₂ captured. This result will be minimised using an optimization algorithm that will determine the best operating conditions.

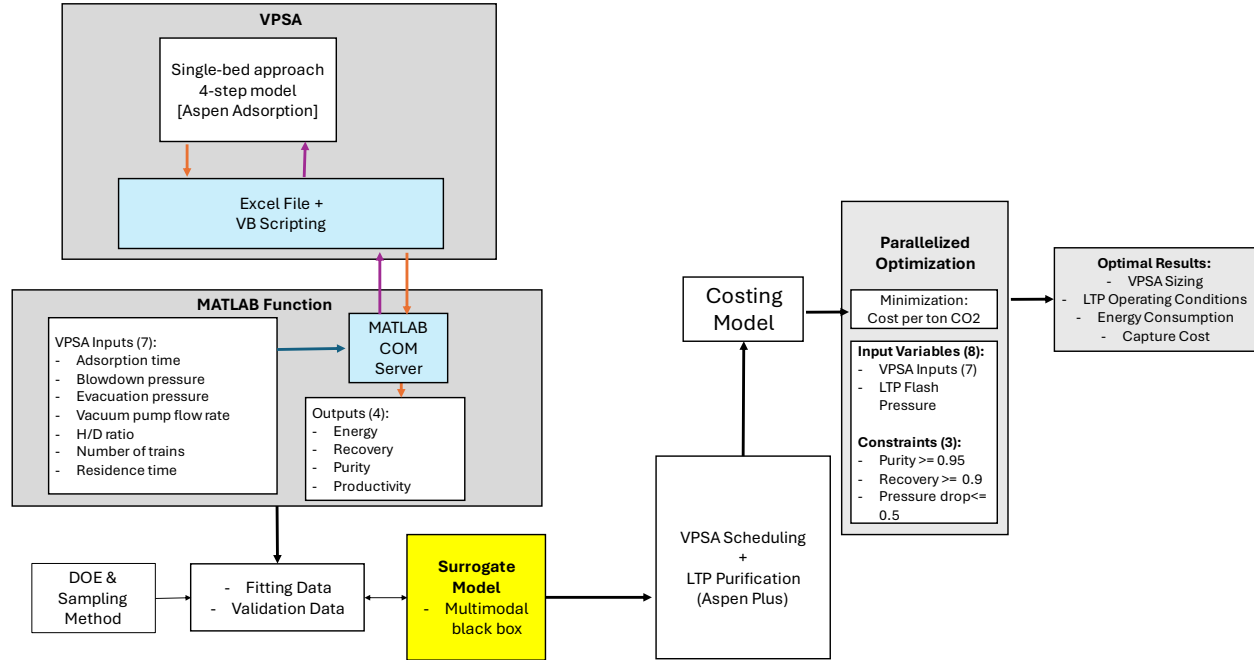


Figure 21: Surrogate Model Development

3.2.2.1 Design of Experiment

The design points were generated for fitting the model and for validating the model using JMP statistical software, which is a powerful tool for designing experiments, analyzing data, and creating predictive models. The process of generating design points ensures that the data used to develop and validate the model are both representative of the VPSA system's behavior and optimized for statistical analysis. The constrained Fast Flexible Filling (FFF) design was adopted, which seeks to maximize the product of the distances between design points for efficient coverage of the design space. The algorithm was developed by Joseph et al. [208] to accommodate continuous and discrete factors, as well as constrained factors. It begins by generating many random points within the specified design region. These points are then clustered using a Fast Ward algorithm, into several clusters of runs. The final cluster of design points is selected using the maximum projection optimality criterion.

The generation of design points is done in two stages. In the first stage, the data set of 360 runs was generated with 7 variables shown in Table 32. This is exploratory pre-sampling, which was done to gain a better understand of the design space at different residence times. Thus, the residence time was considered as categorical/discrete.

Table 32: Stage 1 Experiment Design Variables, Type and Range

Variable	Type	Design range
Residence time [s]	Categorical	4,7,10
Adsorption time [% of breakthrough time]	Continuous	0.1 - 0.7
Number of trains	Continuous Integer	20 - 1000
Evacuation flowrate [m3/h]	Continuous Integer	600 - 3600
Blowdown Pressure [bar]	Continuous	0.3 - 0.9
Desorption Pressure [bar]	Continuous	0.01 - 0.3
H/D ratio	Continuous	2 - 5

In the second stage, the residence time was considered continuous, and the data set was supplemented with 200 runs within a finely tuned range for the design variables to expand the representation of the optimization target region (CO_2 recovery > 0.9) within the design space.

Table 33: Stage 2 Experiment Design Variables, Type and Range

Variable	Type	Design range
Residence time [s]	Continuous	2 - 10
Adsorption time [% of breakthrough time]	Continuous	0.1 - 0.7
Number of trains	Continuous	20 - 1000
Evacuation flowrate [m3/h]	Continuous	600 - 3600
Blowdown Pressure [bar]	Continuous	0.3 - 0.9
Desorption Pressure [bar]	Continuous	0.01 - 0.3
H/D ratio	Continuous	2 - 5

In both stages, the following constraint was introduced when generating the design points:

$$\text{Blowdown Pressure \{bar\}} \geq \text{Desorption Pressure\{bar\}} + 0.01 \quad (47)$$

Each stage was repeated separately for the fitting and the validation design points. Thus, 700 sample runs were conducted over 4 weeks, 80% of the sample runs were used to train the model and 20% were used to validate the model.

Based on breakthrough runs, upon discovering that the breakthrough time was linearly related to the residence time, the breakthrough time was used to bound and scale the adsorption time. By

doing this, the possibility of exceeding the breakthrough time, thus reducing the CO₂ recovery and purity, could be limited. An equation relating the residence time to the breakthrough time was developed using breakthrough run data:

$$t_{breakthrough}\{s\} = t_{residence}\{s\} * 167.97 + 38.006 \quad (48)$$

Since the overall flue gas flow rate is known, the number of trains was used to evaluate the feed flowrate to each adsorption column:

$$\dot{F}_{column} = \frac{\dot{F}_{ov}}{N_{trains}} \quad (49)$$

The residence time was used to determine the bed volume:

$$V_{bed} \{m^3\} = \dot{V}_{feed} \left\{ \frac{m^3}{s} \right\} * \frac{t_{residence}\{s\}}{\varepsilon_{bed}} \quad (50)$$

The bed height was calculated as follows:

$$H_{bed} = \left(\frac{V_{bed}}{\frac{\pi}{4} * \left(\frac{1}{HD_{ratio}} \right)^2} \right)^{\frac{1}{3}} \quad (51)$$

The bed diameter could then be estimated with the calculated height and the specified H/D ratio.

3.2.2.2 Surrogate Model Building

Surrogate modelling approaches are divided primarily into 2 categories: interpolation and regression. Interpolation approaches produce a surrogate model that matches the true function value at every single point in the training data set. Regression methods do not match the function but attempt to minimize the error through smooth approximations. Regression methods smoothly approximate noisy data, and they include polynomials, splines, artificial neural networks (ANN), and support vector regression (SVR). Interpolation/ Gaussian process model methods attempt to fit non-noisy data smoothly and accurately, and they include inverse distance weighting (IDW), radial basis functions (RBFs), and kriging.

The regression methods were selected for two reasons. First, the goal is optimization and to approximate function to a broader unknown domain thus the overfitting of the interpolation methods might not allow flexibility, generalization and extrapolation. Second, interpolation requires storing all data points to make a single prediction which is computationally inefficient, unlike the regression models which when trained can predict output without the reference dataset.

The four regression models described in the following sections were fitted in MATLAB on the training data set. The hyperparameters tuned for each model are also highlighted.

1. Linear Regression Model

The linear regression models use analysis of variance to determine the relationship between design variables and the response. A linear polynomial is used to approximate the implicit limit state equation shown in Equation 51 by minimizing the error. The terms in the linear model can be linear, multiple-term interaction, quadratic, or even higher order. The coefficients of each term in the polynomial is fitted on the training dataset, and can give an idea of the importance of each predictor.

The form of the equation used to predict new values is

$$f(x) = \beta_0 + \sum_{i=1}^m \beta_i x_i + \sum_{i=1}^m \sum_{j \geq 1}^m \beta_{ij} x_i x_j + \dots + \varepsilon \quad (52)$$

$$f(x^i) = X^i \boldsymbol{\beta} + \varepsilon \quad (53)$$

Where $\beta_0, \beta_i, \beta_{ij}$ are parameters to be estimated that form a vector column $\boldsymbol{\beta}$; x_i is the i -th component of the m -dimensional problem; X^i is the row vector formed from the x_i components and ε is the error

2. Support Vector Machines Model

This model applies a support vector machine introduced by Cortes and Vapnik [209], to a regression problem. Unlike traditional regression methods that minimize the error between predicted and actual values, support vector regression tries to fit a function within a specified error margin, known as the epsilon margin, while keeping the model as flat as possible. Within this margin, all errors are ignored which helps prevent overfitting. The form of the equation used to predict new values is

$$f(x) = \sum_{i=1}^n (\alpha_i^* - \alpha_i) K(x_i, x) + b \quad (54)$$

Where x is the input vector for which we want a prediction, x_i are the support vectors from the training data, α_i^* and α_i are the Lagrange multipliers that weigh the contribution of each support vector, $K(x_i, x)$ is the kernel function that computes the similarity between x and each support vector and b is the bias term.

During the training, α_i^* , α_i and b are estimated by minimizing the loss function to find the function that fits within the epsilon margin for the most points.

$$L_\varepsilon = \begin{cases} 0 & \text{if } |y - f(x)| \leq \varepsilon \\ |y - f(x)| - \varepsilon & \text{otherwise} \end{cases} \quad (55)$$

The optimization problem is reformulated as

$$\min \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (\alpha_i - \alpha_i^*)(\alpha_j - \alpha_j^*) K(x_i, x_j) + C \sum_{i=1}^N (\xi_i + \xi_i^*) \quad (56)$$

The value of the Lagrange multipliers is limited by the box constraint to ensure that no support vector can dominate the model's output:

$$0 \leq \alpha_i^*, \alpha_i \leq C \quad (57)$$

The box constraint, also known as the regularization parameter, C , is a hyperparameter that controls the trade-off between the model's tolerance for errors and how closely it fits the data. ξ_i and ξ_i^* are slack variables representing the deviation from the epsilon margin. When the **loss function** for a given training point (i.e., the error outside ε) exceeds C , the model is no longer influenced by this point's error. A higher box constraint means the model is more sensitive to errors outside the margin and excludes more points.

Support vector regression can use various kernel functions to map data to a higher-dimensional feature space, making it capable of handling non-linear relationships. The kernel function, K , can be linear, polynomial, Gaussian, sigmoid or non-homogenous polynomials. Depending on the kernel function adopted, more tunable parameters might exist. Refer to Hastie et al's [210] work for more details on the theory.

3. Gaussian Process Regression Models

In Gaussian process regression (GPR), the predictions assume that the observed data points are drawn from a multivariate Gaussian (normal) distribution. The objective of the regression is to correlate the finite number of functions that define this distribution.

To predict a new point x , the observed output responses (n) are treated like they are results from a random process, Y , more specifically a multivariate normal one with a mean function μ :

$$\mu(Y) = \mathbf{h}(x)\boldsymbol{\beta} \quad (58)$$

and covariance

$$\text{Cov}(Y, Y) = \sigma^2 \mathbf{R}(X, \theta) \quad (59)$$

Where $\mathbf{h}(x)$ is the regression function vector, used if the mean function is linear, $\boldsymbol{\beta}$ is the regression coefficient vector, $\mathbf{R}(X, \theta)$ is the covariance (kernel) function that depends on the absolute distance between any two sample points and other parameters specific to the basic function selected, θ is the kernel scale, a parameter which indicates the rate at which the correlation between design points decays to zero and denotes the importance of the variable, σ^2 is the process variance (sigma), the vertical span of the function.

A key characteristic of GPR is its use of a covariance (kernel) function to capture the relationships between data points, allowing it to model complex, non-linear function smoothly. Common kernel functions are linear, squared exponential kernel, Matern kernel, polynomial kernel. For added flexibility and because the inputs have different scales, a non-isotropic GPR is used which does not assume the same scale or correlation across all input dimensions.

The hyperparameters to be estimated through fitting and validation, thus, include a mean (basis) function, a covariance (kernel) function, a correlation length scale and the standard deviation (sigma). They are derived by finding the maximum likelihood estimates: $\hat{\beta}, \hat{\sigma}^2, \hat{\theta}$ and then tuned using cross-validation.

For a more detailed overview of the theory see Rasmussen et al [211].

Due to computational constraints, iterative GPR updates during optimization are infeasible. Thus, in this work, the mean and variance estimates will be fixed based on the assumption that the model is trained on a large and representative dataset and the fact that the objective function in the optimization is deterministic. Validation with a representative dataset will be used to justify that the estimates are reliable.

4. Neural Network Models

A neural network model is structured in layers, beginning with an input layer (where predictor data enters), followed by hidden layer(s) (where transformations are applied), and ending with an output layer (where predicted responses are generated). The layer size is the number of neurons in each layer. Increasing neurons enhances the model's ability to learn complex patterns, but it also raises computational costs and can lead to overfitting. The model adopted is a feedforward network, meaning only has neuron connection in one direction.

The neural network consists of interconnected neurons with associated weights and biases that make up each layer. Each neuron in the network receives an input and generates an output. This output is produced by processing the input through an activation function. Common activation functions include Rectified Linear Unit (ReLU), Sigmoid, Tanh, and SoftMax. Neurons within a layer generally use the same activation function, while different functions may be applied to neurons in different layers. For example, a linear function is often used in the output layer for regression problems, whereas SoftMax is typical in classification. Nonlinear activation functions like Sigmoid, Tanh, and ReLU are commonly used in hidden layers.

The input to a neuron is multiplied by the weight before the activation function and a bias is added to it as it enters the next layer. Training involves iteratively adjusting the weights associated with each neuron to reduce error. Training may stop based on meeting a specific error threshold, maximum number of iterations, or a defined training time. See Goodwell et al [212] for more comprehensive details.

3.2.3 Genetic Algorithm Optimization

For global optimization of the black box surrogate model, evolutionary computation methods were considered. Evolutionary computation refers to all population-based methods of random variation and selection. The evolution process is driven by reproduction, mutation, competition, and selection. Evolutionary algorithms use different evolutionary-style operators to choose the design variables until the stopping criterion is met, through recombination, mutation and elitist selection. Genetic algorithm (GA) is a type of evolutionary algorithm based mostly on recombination. The elitist variation of GA also selects the next generation based on fitness from

both the parent and offspring population. The fitness scores here refer to the raw, scaled or transformed results of the optimized variable function.

The genetic algorithm involves 3 steps, as described by Golberg [213]:

1. Initial population generation: This is done based on random sampling of the design space and evaluation of the fitness function. This forms the first parent generation.
2. Creating the next generation: This process consists of three stages conducted iteratively:
 - a. Elitist Selection: A specified fraction (elite count) of the top-performing individuals from the parent generation, based on fitness, is directly passed to the next generation.
 - b. Recombination: Another fraction (crossover fraction) of the next generation is created through a weighted average of variables from randomly selected pair of parent individuals, producing new sets of design variables.
 - c. Mutation: The remaining individuals are generated by altering randomly selected design points in the parent generation to introduce variability.
3. Stopping the algorithm: The genetic algorithm terminates based on several stopping conditions, including:
 - a. Maximum Number of Generations: Sets an upper limit on the number of iterations of step 2 that the algorithm can perform.
 - b. Maximum Stall Generations: Defines the maximum number of consecutive generations allowed without improvement in the fitness value.
 - c. Fitness Function Tolerance: If the maximum stall generations have been reached, the algorithm stops if the average relative change in the best fitness value is less than or equal to a specified fitness function tolerance.

The optimization problem solved using the genetic algorithm is formulated as a Mixed Integer Non-Linear Programming problem to accelerate the optimization process. Table 34 outlines the optimization problem. It also shows the optimization decision variables, type, bounds and scaling factor. Each variable is multiplied by a scaling factor to convert non-integer variables to integers.

Table 34: Optimization Problem showing the objective, constraints and the decision variables

Optimization Objective		
Minimize: <i>Specific Cost</i> ($\mathbf{x}$)		
#	Type	Optimization Constraints
1	Non-linear	$0.9 \geq CO_2 \text{ Mass Recovery } (\mathbf{x}) \geq 1.0$
2	Non-linear	$0.95 \geq CO_2 \text{ Mass Purity } (\mathbf{x}) \geq 1.0$
3	Linear	$Blowdown \text{ Pressure } \{bar\} \geq Desorption \text{ Pressure } \{bar\} + 0.01$
4	Non-linear	$VPSA \text{ Bed Pressure Drop } (\mathbf{x}) \{bar\} \leq 0.5$
Where $\mathbf{x}$ is the vector of the decision variables		

Decision Variable (8)	Type	Scaling Factor	Optimization bounds
Residence time [s]	Integer	10	2 - 10
Adsorption time [% of breakthrough time]	Integer	100	0.05 - 0.7
Number of trains	Integer	1	10 - 1000
Evacuation flowrate [m ³ /h]	Integer	1	600 - 3600
Blowdown Pressure [bar]	Integer	100	0.1 - 0.9
Desorption Pressure [bar]	Integer	1000	0.01 - 0.3
H/D ratio	Integer	10	2 - 5
Low-Temperature Purification Flash Pressure [bar]	Integer	1	20 - 50

Because of the constraints introduced, the described algorithm is implemented using the constraint-handling method proposed by Deb [214]. In this context, the genetic algorithm focuses on minimizing a penalty function instead of the fitness function. The penalty function incorporates a term for infeasibility and is used with binary tournament selection to choose individuals for the next generation. The penalty function value is determined as follows:

- For feasible members, the penalty function is equal to the fitness function.
- For infeasible members, it consists of the maximum fitness function among feasible individuals, plus the sum of the constraint violations of the infeasible point.

This approach helps to reflect and manage constraint violations within the optimization process. The population consists of 200 design points, randomly generated and widely distributed across the design space to avoid premature convergence to local optima. The elite count is set to 20 design points, representing 10% of the population. Crossover generates 80% of the individuals in each new generation. The remaining 10% of the population is generated by mutation. The algorithm will be terminated when one of the following criteria is met: a maximum of 800 generations, a maximum of 50 stall generations, or a fitness function tolerance of 1×10^{-2} and a constraint tolerance of 1×10^{-2} .

For robustness, the stochastic optimization is conducted multiple times independently. The optimal results are aggregated by finding the mean of the solutions to find the optimal design point. The number of independent optimization runs is estimated based on the effect size variation with increasing sample runs and hypothesis testing which checks if there is a significant difference in the mean and variance among different aggregates of optimization runs and effect size variation with increase in sample runs.

The effect size is estimated as a difference in mean divided by the pooled standard deviation:

$$effect\ size = \frac{\mu_1 - \mu_2}{\sigma_p} \quad (60)$$

where μ_1 is the mean of one group of runs and μ_2 is the subsequent group with 1 additional run, and σ_p is the pooled standard deviation.

3.3 Economic Model Specification

3.3.1 Economic Assumptions

The key economic assessments in this study are the cost of CO₂ captured, and the cost of CO₂ avoided, described for the reference plant as shown in Figure 22:

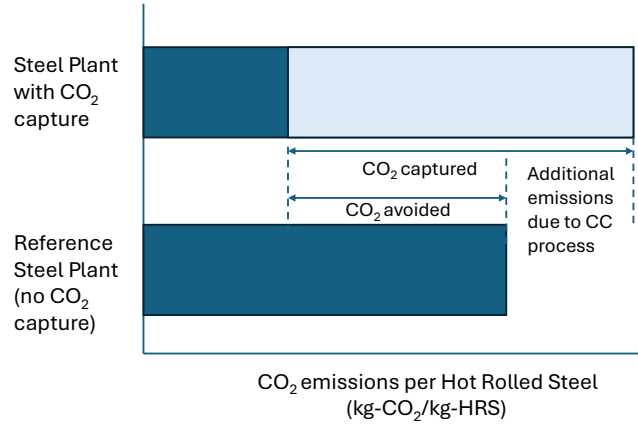


Figure 22: Comparison of steel plant with and without CO₂ capture

CO₂ captured refers to the total amount of carbon dioxide that is physically removed from an emission source through a CO₂ capture process. CO₂ Avoided measures the net reduction in CO₂ emissions achieved by the capture process, taking into account the CO₂ emissions generated due to the capture processes.

$$CO_{2,avoided} = CO_{2,before\ capture} - CO_{2,after\ capture} \quad (61)$$

$$CO_{2,avoided} = CO_{2,before\ capture} + CO_{2,emitted\ from\ energy\ source} - CO_{2,captured\ CO_2\ plant} \quad (62)$$

This distinction is crucial because the CO₂ capture process itself often requires energy, which might generate additional CO₂ emissions if the energy comes from fossil fuels. CO₂ avoided provides a more accurate picture of the process's net impact on reducing greenhouse gas emissions. The boundary for CO₂ avoided calculations include the emissions from the iron and steel production process, the emissions from the capture plant, the emissions from external energy supply including steam production and electricity. It does not account for emissions from construction, equipment manufacturing, CO₂ transport or storage.

The emission intensity of delivered natural gas is 0.575 kg CO₂e/kg CH₄ [215], evaluated based on the gross heating value of methane. The electricity grid intensity is 0.490 kg CO₂e/kWh [216].

Each cost per tonne of CO₂ captured/avoided consists of the capital cost annualized over the plant's useful life and the annual operating cost:

$$\text{\$ per tonne of } CO_2 = \frac{CAPCOST * \left(\frac{i * (1 + i)^n}{(1 + i)^n - 1} \right) + OPCOST}{CO2RATE * OPHOURS} \quad (63)$$

where i is the interest rate (in %), n is the plant's useful life (in years), OPCOST is the total annual operating cost (in \\$/yr), CAPCOST is the total capital investment (in \\$), CO2RATE is the ton of CO₂ captured or avoided (in Mt/hr). All costs in this paper are estimated in 2024 USD. It is assumed that the plant's useful life is 20 years. The 2024 exchange rate of 1 USD for 0.74 CAD was used when needed. The interest rate is the weighted average cost of debt and equity, as shown in Eq. 64.

$$i = DR * i_D + (1 - DR) * i_E \quad (64)$$

where DR is the debt ratio or the % of capital investment covered by debt, assumed as 60%, i_E is the expected return on equity, assumed as 30% and i_D is the loan interest rate/cost of debt, assumed as 8%.

The total capital investment is based on equipment costs which are primarily estimated using Aspen Process Economic Analyzer 2019 prices and adjusted for inflation using the Chemical Engineering Plant Cost Index. The direct cost of each equipment consists of both the equipment and installation costs.

The equipment cost (C_M) is based on key design characteristics of each equipment e.g. operating temperature, pressure, flow rate etc. The direct cost (C_D) is estimated simply by multiplying the equipment cost by an installation factor (F).

$$C_M F = C_D \quad (65)$$

This factor, retrieved from costing models and engineering design literature, accounts for the cost of labour per hour (C_L) and the manpower hours (T_i) in producing the finished units as shown:

$$1 + \frac{T_i C_L}{C_M} = F \quad (66)$$

The per-unit costing approach is used to estimate the installed cost for few multiple units under 10 units. With this approach, the total cost estimate results from multiplying the purchase cost per unit (C_M) by the number of units (N).

However, in scenarios where multiple units over 10 units are created, a learning curve cost estimation proposed by T.P Wright [217] is used. This approach assumes that workers become more efficient over time, and the time required decreases and consequently, the labour cost reduces. Thus, the average time required for the N^{th} unit, T_N is estimated as:

$$T_N = (T_1)(N)^b \quad (67)$$

Where T_1 is the time spent on the first unit and b , the learning curve exponent, defined as:

$$b = \frac{\log(\text{learning curve rate})}{\log(2.0)}$$

The learning curve rate is quantified by Rodney Stewart as 80% for processes that involve 75% hand assembly and 25% machining, repetitive electrical work. The overall cost of the multiple units ($C_{D,N}$) are estimated as:

$$\sum_{i=1}^N C_M + T_i(i)^b C_L = C_{D,N} \quad (68)$$

When accounting for learning and experience, a new installation factor (F^l) is used, which is derived as shown in Eqs. 69-71:

$$C_M N + T_i C_L \sum_{i=1}^N i^b = C_{D,N} \quad (69)$$

$$\frac{C_M N + T_i C_L \sum_{i=1}^N i^b}{C_M N} = \frac{C_{D,N}}{C_M N} \quad (70)$$

$$1 + \frac{T_i C_L \sum_{i=1}^N i^b}{C_M N} = F^l \quad (71)$$

The cumulative labour time factor can be approximated using the Hurwitz zeta function which was proposed [218] to approximate an infinite sum of a shifted reciprocal integer k , to the power s , as follows:

$$\zeta(s, a) = \sum_{k=0}^{\infty} \frac{1}{(k+a)^s}, \quad \text{for } \text{Re}(s) > 1 \text{ and } a > 0 \quad (72)$$

A finite sum of powers, $H_F^{(s)}$, can be defined as based on the standard formulation [219]:

$$H_F^{(s)} = \sum_{k=1}^F \frac{1}{(k)^s} \approx \zeta(s, 1) - \zeta(s, F+1) \quad (73)$$

The cumulative labour time factor in Eq. 69 can be rearranged to apply this approximation as shown:

$$\sum_{i=1}^N i^b = \sum_{i=1}^N \frac{1}{i^a} = H_N^{(a)} \quad (74)$$

where $a = -b$ and $b \neq 1$

The generalized harmonic function $H_N^{(a)}$ in Eq. 73 is subbed into Eq. 74 to give:

$$\sum_{i=1}^N \frac{1}{i^a} \approx \zeta(a, 1) - \zeta(a, N+1) \quad (75)$$

And Eq. 75 can be subbed in to Eq 71 to approximate the summation term:

$$1 + \frac{T_i C_L (\zeta(a, 1) - \zeta(a, i + 1))}{C_M N} = F^l \quad (76)$$

Because the labour time and cost are unknown, Eq. 76 is rearranged into a function of known terms. Then, Eq. 66 can be subbed in Eq. 76 to get the new installation factor expression:

$$F^l = 1 + \frac{F - 1}{N} (\zeta(a) - \zeta(a, i + 1)) \quad (77)$$

The total capital investment structure used is shown in Figure 23:

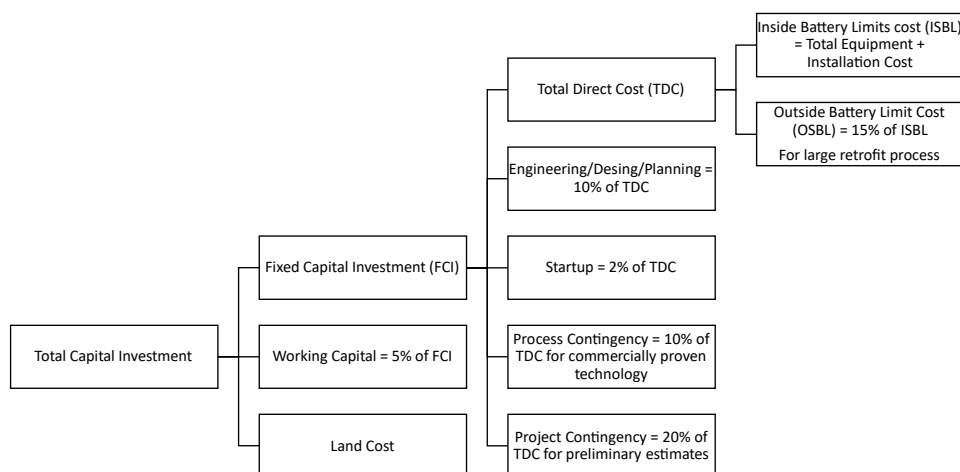


Figure 23: Capital cost levels and elements

The total operating cost accounts for variable and fixed operating costs. The variable operating cost is mostly estimated based on hourly rates from the material balance. It is assumed the plant operates for 8322 hours, equivalent to 95% capacity. The variable operating cost includes the cost of all utilities and feedstock to the process. The catalyst and sorbent are assumed to be replaced every 5 years. The solvent and sorbent prices are estimated based on published wholesaler prices and Aspen Capital Cost estimator 2019 prices respectively, adjusted for inflation using the Canadian industrial product price index. The electricity prices are assumed to be fixed and reflect Ontario's average industrial electricity prices. It is assumed that a large body of water is available to be treated and used as cooling water. The cooling tower and water treatment exist in the current plant. The prices for the feedstock and utilities are shown in Table 35.

Table 35: Feedstock and utility prices

Feedstock	Unit	Cost Year	Price
Coolant: Ethylene Glycol	TSA Dehydration System	2019	\$ 0.78/kg [220]
Solvent: Monoethanolamine	MEA Scrubbing	2019	\$ 1.10/kg [221]
Sorbent: 13X zeolite	Vacuum Pressure Swing Adsorber	2024	\$ 1.5/kg
Refrigerant: Propylene	Refrigeration Unit	2020	\$ 0.78/kg [222]
Sorbent: Silica gel	TSA Dehydration System	2024	\$ 0.5/kg
Utilities			Price
Natural gas (mass)		2024	\$ 0.58 /GJ [223]
Electricity		2022	\$ 0.07 /kWh [224]

The fixed operating costs include labour, maintenance and administrative costs. The labour costs were calculated based on the assumption that the plant requires a plant manager [225], engineer

[226], maintenance supervisor, 3 shift supervisors [227] with 12 operators per shift [228]. Their salaries were referenced from similar roles in the 2024 Canadian labour market. The annual maintenance cost was calculated as 5% of the fixed capital investment (FCI). Administrative costs and the salary overhead were set to 30% and 60% of the labour plus supervision cost, respectively. The annual insurance and taxes were set to 2% of FCI.

3.3.2 Surrogate Cost Model

In the surrogate optimization, several cost models were generated to simplify the optimization process. These costs were generated based on 2019 cost data from the Aspen Capital Cost Estimator.

Table 36: Surrogate Cost Model Equations and Validation Results

Equipment	Installed Cost Equation and Range	b1	b2	b3	b4	R ²	RMSE
Heat Exchanger	$b_1 * (\text{Area } \{\text{m}^2\}^{b_2}) * b_3^{\text{Vessel Pressure } \{\text{kPa}\}}$ Area: 100 – 10000; Vessel Pressure: 475 – 4272	2.336E+02	1.029E+00	1.008E+00		0.99	1.11E+05
LTP Multi-stage compressors	$b_1 * \text{Flowrate } \{\text{m}^3/\text{h}\}^{b_2} * \text{Inlet Pressure } \{\text{bar}\}^{b_3} * \text{Pressure Ratio}^{b_4}$ Flowrate: 3000 – 500000; Inlet Pressure: 1 – 30; Pressure ratio: 1 – 3.5	1.703E+03	7.036E-01	1.188E-01		0.97	3.87E+06
Multi-stage CO ₂ Conditioning compressor	$b_1 * (\text{Flowrate } \{\text{m}^3/\text{h}\}^{b_2}) * ((\text{Inlet Pressure } \{\text{bar}\} * \text{Pressure Ratio})^{b_3}) * (b_4^{\text{Pressure Ratio}})$ Flowrate: 3000 – 500000; Inlet Pressure: 5 – 50; Outlet Pressure: 80 – 120	2.907E+03	6.875E-01	-2.837E-01	4.626E-01	0.95	3.57E+06
Refrigeration Unit Compressor	$b_1 * (\text{Flowrate } \{\text{m}^3/\text{h}\})^{b_2} + b_3$ Flowrate: 1000 – 500000	1.022E+05	6.874E-01	-5.860E+06		0.97	3.89E+06
Adsorption Tower	$\exp\left(b_1 * \text{Diameter } \{\text{m}\} + b_2 * \frac{H}{D} + b_3 * \text{Packed Height}\{\text{m}\} + b_4\right)$ Diameter: 0.2 – 4.8; H/D: 2 – 5; Packed height: 0.7 – 10;	2.907E-01	-5.999E-02	9.956E-02	1.133E+01	0.99	1.30E+04
Flash Drum	$b_1 * \text{Liquid Volume } \{\text{m}^3\} * (b_2^{\text{Pressure } \{\text{bar}\}}) + b_3$ Volume: 0.35 – 100; Pressure: 1 – 50;	6.346E+03	3.902E+03	1.149E+05		0.97	3.49E+04
Vacuum Pump: Mechanical Booster	$b_1 * (\text{Flowrate } \{\text{m}^3/\text{h}\})^{b_2} + b_3$ Flowrate: 205 - 3375	4.044E+01	9.138E-01	1.176E+03		0.99	1.96E+03
Vacuum Pump: Mechanical Screw	$b_1 * (\text{Flowrate } \{\text{m}^3/\text{h}\})^{b_2} + b_3$ Flowrate: 55 - 1150	7.515E+01	9.369E-01	3.017E+04		1.00	8.82E+05

3.3.3 Special Unit Costing

This section covers custom costs that were not evaluated using the Aspen Capital Cost Estimator. The capital cost is fitted using the power law on the 2018 cost of electric boiler collated by Zuberi et al. [229] for boilers within 2.9 – 73 MW:

$$\frac{2018 \$}{\text{kW}} = 243.62 * (\text{Power capacity in MW})^{-0.393} \quad (78)$$

The capital cost for the dry slag granulation is estimated with an order of magnitude costing based on the cost of a CSIRO demonstration unit. For granulation of 300,000 t/yr of slag, the cost of the dry granulation and the moving bed heat exchanger was \$2,684,170 [182]. A 0.6 scaling exponent was applied.

4 Results

4.1 CO₂ capture using chemical absorption

4.1.1 Base Case - CO₂ capture using MEA Absorption at different emission points

As highlight in section 1, within the integrated steel mill, there are several direct sources of emissions with varying compositions and locations. *Figure 24* illustrates seven distinct direct emission streams where the CO₂ capture could be implemented. These direct CO₂ emissions can broadly be categorized into two types: the exhaust gases and the flared gases

The exhaust gases, represented by black solid lines, includes the steady flow of flue gases, that are vented directly into the atmosphere at each unit. They account for 84% of the CO₂ emissions from the process. In contrast, flared gases, shown in red solid lines, are unsteady flow streams produced during pressure control flaring. These streams have low volumes, are discontinuous, and contribute to 16% of the emissions, representing a lost heat source within the system.

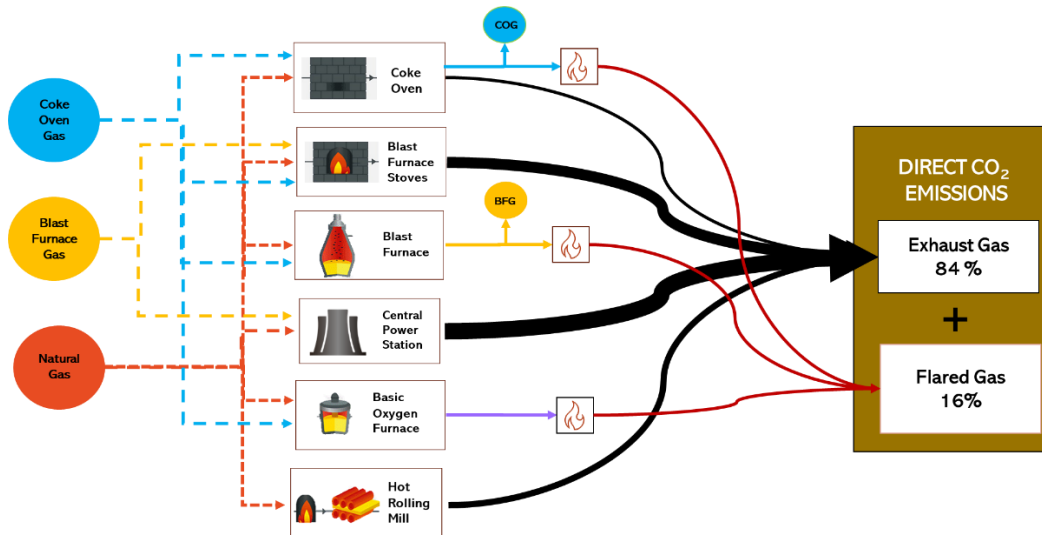


Figure 24: Direct CO₂ emission sources within the steel plant

Given these characteristics, it is evident that designing a CO₂ capture system to address all direct emissions is impractical. Instead, the focus must be on exhaust gases, which are more consistent and voluminous. Certain logistical constraints must be considered. For example, the hot rolling/strip mill is located far from other units, and some streams, like the coke oven exhaust gas, exist in small volumes. Despite these challenges, combining all exhaust gas streams for single-point capture is evaluated as an extreme scenario where carbon capture serves as the sole emission reduction strategy. It is assumed that the blast furnace stoves, coke oven, basic oxygen furnace, and central power station are located near each other, making a single capture plant for these emissions feasible

Table 37 outlines various retrofit scenarios for CO₂ capture, including single-point sources and their combinations.

Table 37: Single point and combined points of capture and the % of the overall direct emissions

Type	Capture Points % of Overall Direct CO ₂ emissions			
	Single Point Source	Central Power Station (CPS)	Blast Furnace Stoves (BFS)	Hot Rolling/Strip Mill (HSM) Coke Oven Gas (CO)
Combined Sources	All Exhaust Gases = CPS + BFS + HSM + CO			

In this section, monoethanolamine (MEA) absorption technology is applied across six scenarios to capture 90% of the CO₂ emissions at a minimum purity of 95 vol%. The technical and economic performance of each design, as well as its impact on steel production, is evaluated based on the selected capture points.

4.1.1.1 Technical Assessment

The designs presented in Table 38, are considered as the base-case for CO₂ capture at different locations in the steel plant. In this base case, the reboiler duty is supplied from a natural gas-fired boiler, erected alongside the retrofitted CO₂ capture facility and all electricity used is purchased from the grid.

Table 38: Technical performance of the MEA Absorption Process designed to capture different emission points in the steel plant

Technical Performance	Units	Coke Oven	Hot Strip Mill	Central Power Station	Blast furnace Stoves	BFS + COG + CPS	All Exhaust Gas
CO ₂ Molar Composition	%						
Total Flue Gas Flowrate	Nm ³ /hr						
CO ₂ Emissions captured	MMt/yr			~2.0			
Natural Gas-fired Boiler Emissions	Mt-CO ₂			~80			
% of total CO ₂ captured	%						
% of total CO ₂ avoided	%						
Electrical energy per CO ₂ captured	kWh/kg	0.35	0.30	0.19	0.20	0.20	0.21
Thermal energy per CO ₂ captured	MJ-th/kg	8.26	5.23	4.33	4.47	4.40	4.57
Dimensions							

Technical Performance	Units	Coke Oven	Hot Strip Mill	Central Power Station	Blast furnace Stoves	BFS + COG + CPS	All Exhaust Gas
# of Absorbers	-			2			
Absorber Height	m			12			
Absorber Diameter	m			8.2			
# of Wash Columns	-			2			
Wash Column Height	m			7			
Wash Column Diameter	m			4.9			
# of Strippers	-			1			
Stripper Height	m			12			
Stripper Diameter	m			10.2			
Column Packing		MELLA PAK 250Y	MELLA PAK 250Y	MELLAPA K 250Y	MELLAP AK 250Y	MELLAP AK 250Y	MELLA PAK 250Y
Absorber Performance							
Absorber feed temperature	C	40	40	40	40	40	40
Absorber feed pressure	bar	1.3	1.3	1.3	1.3	1.3	1.3
Absorber rich stream outlet temperature	C	40.1	40.1	40.1	40.1	40.1	40.1
Absorber flue gas outlet temperature	C	45.1	52.8	60.2	59.3	59.6	58.0
Absorber mac. Colum liquid temperature	C	45.4	59.8	67.5	66.5	67.2	64.3
Absorber pressure drop	bar	0.03	0.01	0.01	0.01	0.01	0.01
Liquid Circulation	m3-solvent /Mt-CO ₂	75.6	30.9	20.4	21.5	21.0	23.3
Rich Loading	kmol/kmol	0.35	0.42	0.47	0.47	0.47	0.46
Wash Performance							
MEA Recovery		1.00	1.00	1.00	1.00	1.00	1.00
MEA Loss	kmol/s	2.26E-07	1.16E-07	5.94E-08	6.05E-08	6.30E-08	1.02E-07
Stripper Performance							
Lean loading	kmol/kmol	0.30	0.30	0.30	0.30	0.29	0.30
Stripper feed temperature	C	104.0	104.0	104.0	103.9	103.8	104.0
Stripper feed pressure	bar	1.8	1.8	1.8	1.8	1.8	1.8
Reboiler pressure	bar	1.7	1.7	1.7	1.7	1.7	1.7
Reboiler temperature	C	116.0	116.6	116.7	116.6	116.8	116.5
Reboiler duty	MW-th			~300			

Technical Performance	Units	Coke Oven	Hot Strip Mill	Central Power Station	Blast furnace Stoves	BFS + COG + CPS	All Exhaust Gas
Natural gas Combustion Emissions	t-CO ₂ /hr			~80			
Emissions released per Emissions Captured	kg-CO ₂ /kg-CO ₂	0.61	0.38	0.32	0.33	0.32	0.34

The performance criteria in Table 38 show that the Central Power Station (CPS) and Blast Furnace Stoves (BFS) are the most efficient standalone capture points due to their high CO₂ molar compositions, lower energy requirements (0.19–0.20 kWh/kg and 4.33–4.47 MJ-th/kg CO₂), and significant emissions capture potential. These points also have lower liquid circulation rates (20.4–21.5 m³-solvent/Mt-CO₂), indicating the efficient utilization of the solvent for absorbing CO₂ which should translate into lower specific operating and capital expenditure.

Combined scenarios, such as BFS + COG + CPS or capturing all exhaust gases, achieve higher overall emissions captured but face challenges due to larger infrastructure requirements and higher reboiler duties (up to 520 MW-th).

In contrast, sources with lower CO₂ concentrations, like the Coke Oven, are less favourable for standalone capture due to their high liquid circulation rate (75.6 m³-solvent/Mt-CO₂), higher energy demands, and low capture efficiency.

In meeting the reboiler duty demands, it was found that for every kg of CO₂ captured, 0.32 – 0.61 kg of CO₂ is emitted, depending on the composition of CO₂ and the volume of the streams that is treated. The upper bound, 0.77 in this range corresponds to capturing emissions from the coke oven which has the lowest flow rate. While the lower bound, 0.62 correspond to the CPS stream with the higher composition streams. This stresses the need for emission-free methods of supplying this heat duty to make the most of the capture benefits.

4.1.1.2 Economic Assessment

Table 39 outlines the benchmark cost of CO₂ capture at different points in the plant. Note that combining the emission sources does not account for the transportation and storage costs.

Table 39: MEA Absorption Economic Performance at different emission points

Economic Performance	Coke Oven	Hot Strip Mill	Central Power Station	Blast furnace Stoves	BFS + COG + CPS	All Exhaust Gas
CO ₂ Mole Composition [%]						
Capital Cost [\$]	95,441,000	481,875,000	525,489,000	276,719,000	807,686,000	961,081,000
Annualized Capital Cost [M\$/yr]	15.1 [56%]	76.1 [63%]	83.0 [55%]	43.7 [57%]	128 [56%]	152 [56%]

[% of Total Cost]						
Annual Operating Cost [M\$/yr] [% of Total Cost]	12.0 [44%]	44.2 [37%]	67.0 [45%]	33.1 [43%]	99.0 [44%]	117 [44%]
Total Annualized Cost [M\$/yr]	27.0	120.34	150.01	76.82	226.7	269.3
Overall Cost per CO ₂ captured [\$/Mt-CO ₂]	397	326	77.0	109	80.2	83.4

Figure 25 describes the captured and avoided cost using MEA solvent absorption from all the emission sources in an integrated steel mill. It also shows the amount of the plant's pre-capture emissions that are removed by designing the CO₂ capture unit for each of the emission points.

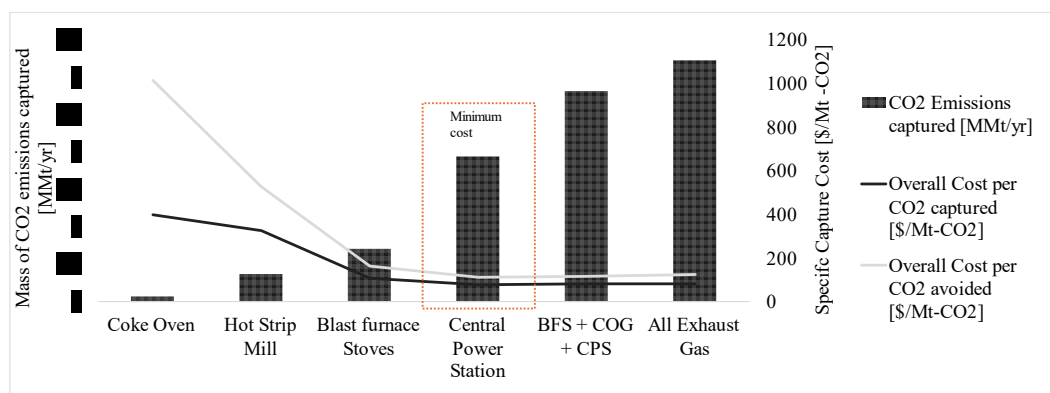


Figure 25: MEA Absorption at different emission points in a steel plant showing the cost and emission reduction

The capture costs (left axis) show both the cost per CO₂ captured and the cost per CO₂ avoided. The difference in cost for each emission source is attributed to the direct emissions of energy production within the carbon capture process. Capturing each exhaust gas stream can range from \$77 to \$398 per Mt of CO₂ captured. When considering the least costly point of capture, the scale of capture process presents an advantage, when we observe that for the two streams with the same CO₂ composition, the larger volume is captured at lower cost. It is critical to consider if the benefits of scale are worth it to combine emissions sources into a single point of capture. In Figure 25, we can follow the variation in the capture cost (right axis) as larger quantities of CO₂ are captured. There are no capture cost reduction benefits to combining the exhaust gases. This could be attributed to the dilution of the CO₂ in the feed stream that happens as more streams of varying composition are combined.

From the specific cost breakdown for the different emissions points in Figure 26, for the high-volume streams like the central power station, blast furnace stoves and the combined exhaust streams, the capital cost and fixed operating costs form a smaller fraction of the overall specific

cost due to the larger amounts of CO₂ recovered. Chemical absorption is impractical for low volume streams and alternative means of decarbonizing the hot strip mill and coke ovens must be pursued.

Outside the fixed cost, the key opportunities for cost reduction at large scale absorption is in the electricity consumption since electricity accounts for the largest variable operating cost. In each case, 99% of the electricity is consumed by the flue gas and the CO₂ compressors in this process, thus any significant improvement in cost could be achieved by improving the energy efficiency of compressor

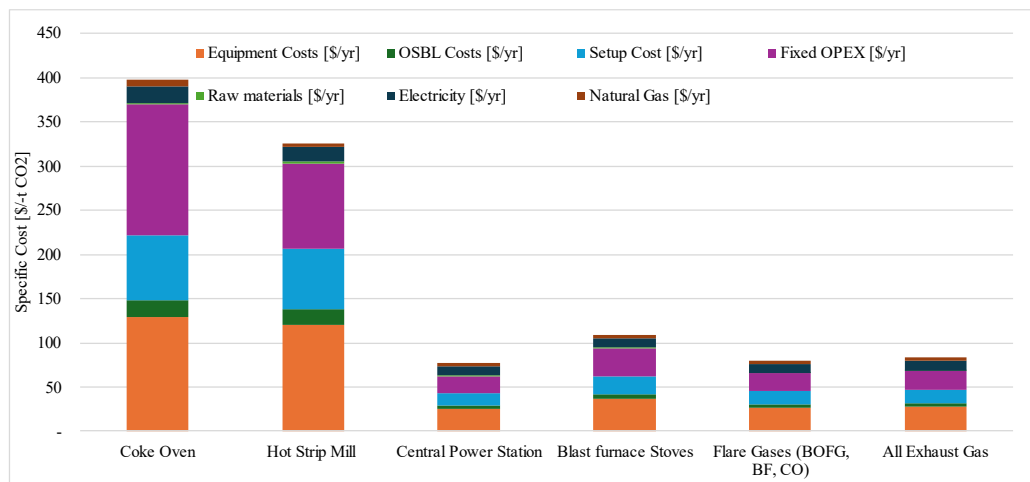


Figure 26: Specific cost breakdown of MEA absorption cost at different emission locations

4.1.1.3 Impact on steel production

The assessment of the different points of capture was then extended to the impact on the steel production cost. While there are several finishing applied, hot rolled steel (HRS) is the highest shipped product and is the basis for other finished product, thus it is used as the reference product. The 2024 production cost of hot rolled steel from a Canadian integrated steel mill is estimated as \$630/Mt-HRS.

In Figure 27, the added cost of capturing CO₂ emissions to the production cost of 1 tonne of Hot Rolled Steel (HRS) is presented. Relying solely on the base case MEA absorption to reduce the exhaust gas emissions would add 111 – 574 \$/Mt-HRS to the steel production cost. In the lowest capture cost scenario, the central power station, the production cost would increase by 18%. In

the highest cost scenario, the coke oven, the production cost would increase by 91%, almost double the current cost.

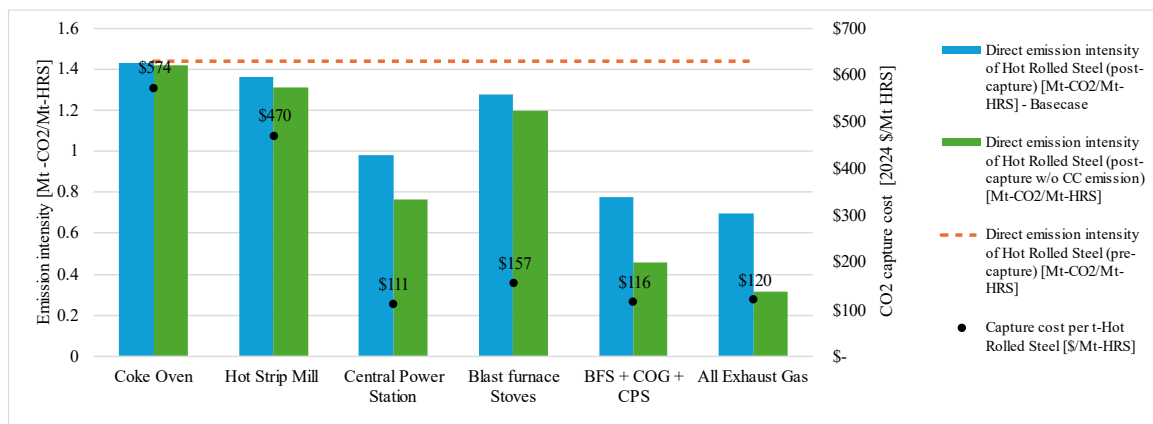


Figure 27: Impact of MEA absorption on the post-capture emission intensity of steel

Also included in Figure 27 is the direct carbon emission intensity that could have been reached without the additional emissions of the reboiler steam production, which stresses the need for alternative methods of supplying the reboiler duty. Varying degrees of low carbon-emission steel products can be produced at different capture locations at different cost. Based on the difference between the post-capture and pre-capture intensity, we can estimate the cost of each Mt-CO₂ reduction in intensity as shown in Table 40, to understand the marginal cost of reducing the emission intensity at each location.

Table 40: Marginal CO₂ intensity reduction

Emission Sources	Marginal cost of intensity reduction [\$/Mt-CO ₂]
All Exhaust Gas	161
BFS + COG + CPS	174
Central Power Station	240
Blast furnace Stoves	955
Hot Strip Mill	5926
Coke Oven	61633

Using this metric to compare the different emission points, it is cheapest to reduce the emission intensity with MEA scrubbing by capturing larger amounts of CO₂. This marginal cost of CO₂ intensity reduction could be used to comparing different methods of decarbonization.

4.1.2 Reboiler Heat Substitution

As seen in section 4.1.1.1, providing heat to the reboiler is a significant energy penalty. This heat can be provided in different ways such as heat integration or by external heating via natural gas burning or electrical heating. For the MEA absorption, additional direct emissions arise from burning natural gas to meet the reboiler duty demands. So, to reduce these emissions, three

approaches were considered: 1) electrification of heating using electric boilers, and 2) heat integration 3) oxy-combustion

The iron and steel production process has different grades of waste heat streams, from which heat could eventually be recovered to generate steam. For this study, those heat streams, outlined in Table 41, are classified as L1, L2, L3 based on accessibility:

- a. **L1 streams** are the “low-hanging fruit” streams such as flared gas, which require no additional equipment and do not modify the existing process and its product streams.
- b. **L2 streams** require additional capital investment for heat recovery such as HRSGs but do not alter the existing process.
- c. **L3 streams** require significant alterations to the existing process and its process streams.

The technologies have also been commercially demonstrated and adopted.

Each heat recovery process was modelled to estimate the recovered reboiler duty and the recovery efficiency.

Table 41: Waste heat streams in the existing steel plant, stream properties and heat recovery performance

Waste Heat Streams	Accessi- bility	P	T	Recovery Process	Max recoverable enthalpy (MWth)	Recovered reboiler duty (MWth)	% Recovery Efficiency
		[bar]	[C]				
Flared Gas	L1	1.10	82	Existing Steam Boiler	0.14	0.12	84.9%
Coke Oven Exhaust Gas	L2	1.75	250	HRSG	0.13	0.11	82.9%
Blast Furnace Stove Exhaust Gas	L2	1.75	250	HRSG	0.37	0.30	82.8%
Hot Strip Mill Exhaust Gas	L2	1.75	400	HRSG	0.37	0.04	82.8%
Central Power Station Exhaust Gas	L2	1.75	190	HRSG	1.75	1.05	11.5%
Blast Furnace Slag	L3	2.20	1500	HRSG + DSG + MBHX	2.81	2.00	60.0%

Incandescent coke	L3	1.50	1100	HRSG + CDQ	5.41	4.14	67.8%
Total							61.1%

It is estimated that of all existing heat streams, 61% of their recoverable enthalpy can be extracted to generate steam at 130°C and 2.7 bars for the stripping column reboiler.

To further improve the efficiency of the carbon capture process, we considered recovering heat from the CO₂ distillate within the CO₂ compression unit by replacing the compressors with high-temperature heat pumps. Taking the CO₂ compression unit (CCU) as the control volume, the exergy analysis for the CCU modifications at the central power station is presented in Table 42:

Table 42: Exergy analysis of CCU modifications - Compressors vs Heat Pumps

Stream	Exergy (MW) - CCU	% of Total Input Exergy - CCU	Exergy (MW) - Heat Pump CCU	% of Total Input Exergy Heat Pump CCU
CO ₂ Distillate (Material)	13.92	32%	13.92	18%
Condensate (Material)	-0.02	0%	0.00	0%
CO ₂ to storage (Material)	-14.65	-33%	-14.65	-19%
Feedwater (Material)	0.00	0%	0.00	0%
Reboiler steam duty (Material)	0.00	0%	-29.52	-39%
Heat transfer (Q)	-0.94	-2%	0.00	0%
Work (W)	29.85	68%	61.56	82%
Irreversibility	-28.16	-64%	-31.31	-41%
Total	0.00		0.00	

The exergy input to the CCU consists primarily of the exergy of the hot distillate leaving the stripper and the work supplied to rotating equipment including compressors and pumps. The modification to the process reduces the exergy losses from 64% to 41%. Much of the previously lost exergy is recovered as steam for the reboiler. It is important to note that the high-temperature heat pump technology providing heat exceeding 100°C is still under commercial development with few technologies providing up to 200°C [230].

The following sections present three design case study on heat substitution within the MEA absorption process.

4.1.2.1 Case Study 1: 90% Capture of the Central Power Station with waste heat utilization

In this case, different strategies for using both recovered waste heat and electrification to meet reboiler demand, are explored. The objective is to capture 90% of the central power station's emissions, equivalent to 46% of the overall process emissions. The required reboiler duty for the point of capture is 297 MWth, which exceeds even the maximum recoverable enthalpy available for all identified waste heat streams in Table 41. Any reboiler duty requirements that cannot be met with waste heat utilization here, is supplemented using a gas-fired or an electric boiler.

Case 1A: Total Electrification

First, we considered a total electrification of the heating process, where electric boilers are used to supply the steam needed and compared it to the natural-gas fired base case in Figure 28.

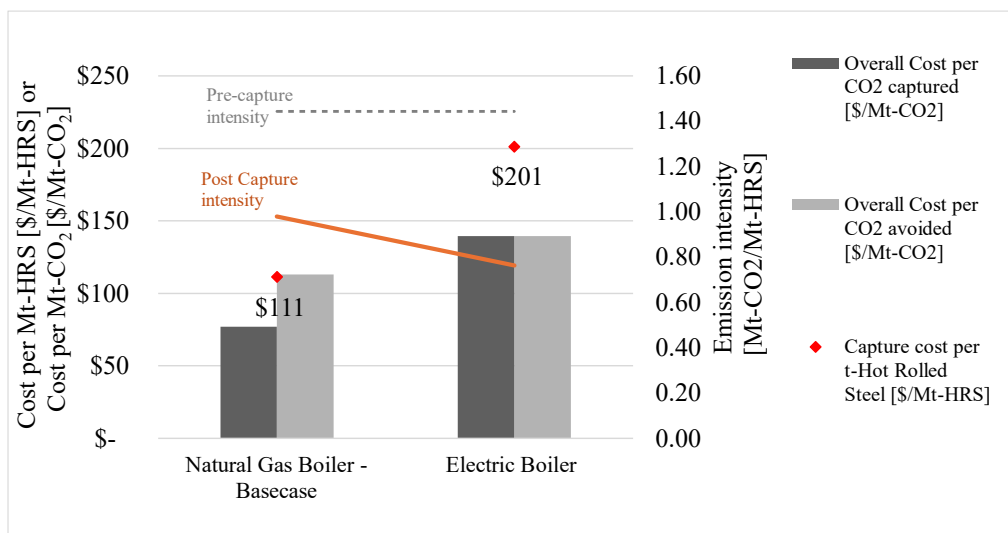


Figure 28: Comparison of the impact of steam production from gas-fired boilers vs electric boiler on the capture costs and the post-capture emission intensity of hot metal

Using electric boilers would significantly reduce the direct emission intensity of the processed steel to nearly 0.76 Mt-CO₂/Mt-HRS. However, it will add \$90 to the cost to production, almost double the cost of using just natural gas. In this case, the overall cost of thermal energy supplied by natural gas is 2 \$/GJ and that of the electric boiler is 16 \$/GJ. Considering that electricity is a higher-grade form of energy, using it to generate low grade heat (~130°C) likely does not make economic sense.

Case 1B: Different levels of Waste Heat Utilization + Gas-fired boiler steam

In this case, different levels of waste heat utilization to reduce the amount of fuel burnt in the natural gas boiler, are evaluated. In Figure 29, the reboiler duty sources in each scenario are shown. As expected, as we use more waste heat, the amount of CO₂ avoided increases, and this is reflected in the reducing emission intensity of the steel that is produced.

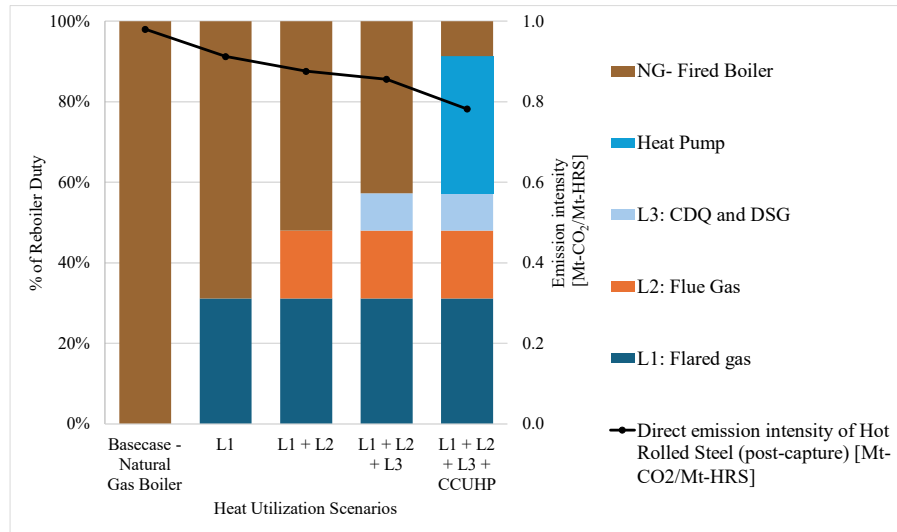


Figure 29: Comparing different combination of gas-fired boiler steam and waste heat utilization at 90% Capture of the Central Power Station, showing a breakdown of reboiler heat duty sources and the impact of the emission intensity

Figure 30 depicts how each heat utilization scenario impacts the production cost of hot rolled steel. the reliance on natural gas shifts to waste heat, the cost of avoiding CO₂ reduces up till a minimum case where 91% of the reboiler heat is recovered form flared gas, flue gas and process streams. Generating extra steam using heat pump leads to such a significant increase in capital and operating cost, such that it outweighs the added advantage of emission reduction, consequently causing to a sharp rise in the avoidance cost.

By recovering heat from the flared gas streams and the flue gases we can reduce the added cost to steel production by \$1/Mt-HRS. This suggest the potential of using easily accessible waste stream to reduce the natural gas consumption without significant capital cost penalties. When recovering with “L1 scenario”, it is important to note that flared gas streams are not consistent and would vary based on the process condition and depressurization needs. Thus, any adoption would demand advanced resource scheduling to ensure a steady steam supply.

Relative to the other natural gas-based scenarios, investing in dry coke quenching units and dry slag granulation units in “L1+ L2 + L3 scenario”, while adding more to the cost of production, offers the lowest cost of CO₂ avoided.

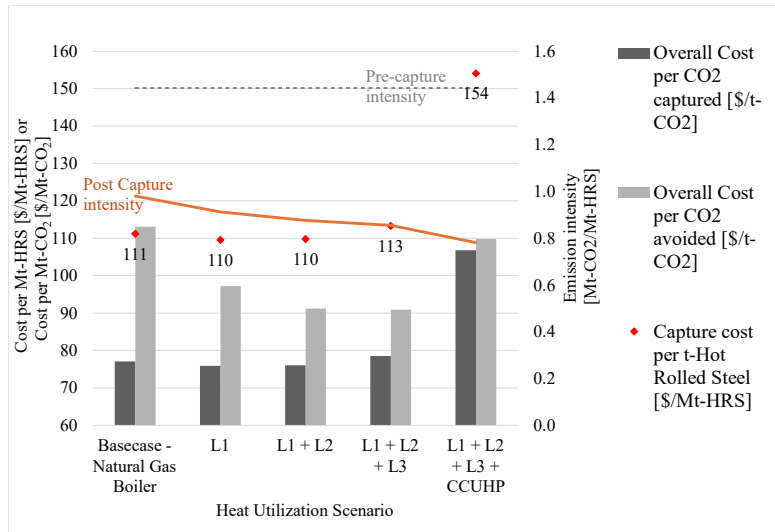


Figure 30: Impact of waste heat utilization supplemented with natural gas boilers on the capture costs

By adding a CCU-integrated heat pump (CCUHP), we get the lowest emission intensity of steel, albeit at a steep price of \$154/t-HRS. This heat integration offers that largest amount of waste heat, but the high capital and operating cost incurred, make it impractical.

Case 1C: Different levels of Waste Heat Utilization + Electric boiler steam

There is value in figuring out how best to capture the same level CO₂ without additional fossil fuel consumption, especially if the steel producer's natural gas supply is constrained. In Figure 31, the different heat utilization scenarios where extra heat is supplemented with electric boiler steam, are presented.

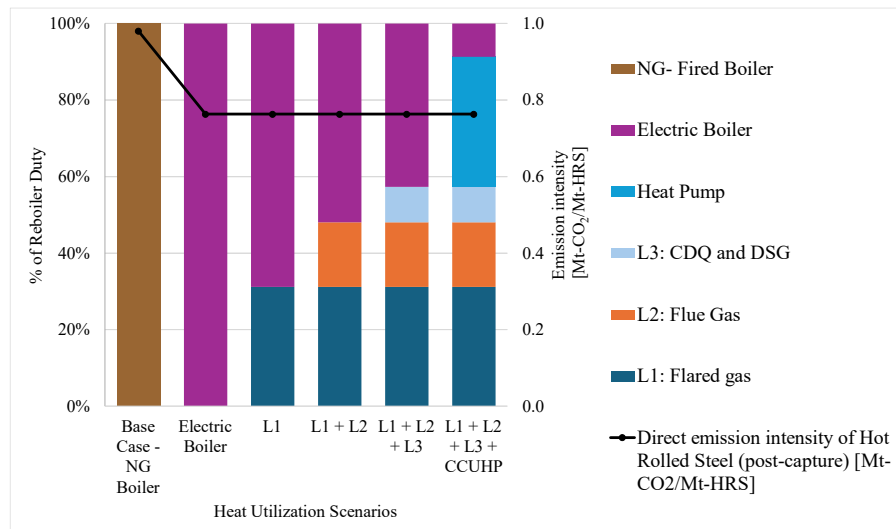


Figure 31: Comparing different combination of electric boiler steam and waste heat utilization at 90% Capture of the Central Power Station, showing a breakdown of reboiler heat duty sources and the impact of the emission intensity

Figure 32 depicts how each heat utilization scenario impacts the production cost of hot rolled steel. the reliance on the electric boiler shifts to waste heat, the cost of avoiding CO₂ reduces up

till a minimum case where 91% of heat is recovered from flared gas, flue gas and process streams.

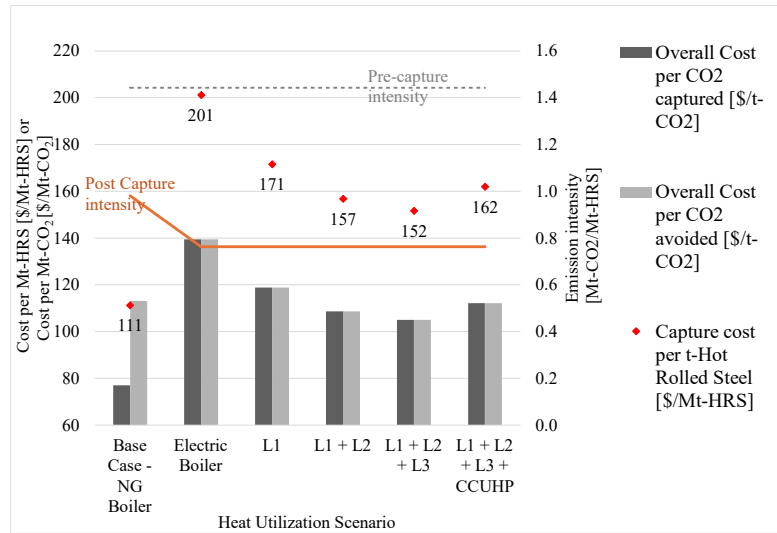


Figure 32: Impact of waste heat utilization supplemented with electric boilers on the capture costs

The scenarios that are supplemented with electric boilers have no additional emissions, so the avoidance and capture cost are identical as expected. Just as in Case 1B, there is a strong argument for recovering heat from not only the waste gas but also high-grade heat streams such as coke and slag. In this lowest cost scenario “L1 + L2 + L3”, the CO₂ capture cost for each tonne of hot metal is 40% more than the base case. Here, using a heat pump that is integrated with the CO₂ compression offers a cheaper means of CO₂ avoidance than total electrification.

In summary, for the lower emission intensity of steel production using 90% capture from the central power station, one could incur between 152-201 \$/Mt-HRS in extra production cost using electric boilers, compared to the cheaper range, 110-154 \$/Mt-HRS, determined for the gas-fired absorption. At the lowest cost bound, using an electric boiler with heat utilization, is equivalent to raising the production cost by 24%. This reduced the economic penalty of an electricity-dependent reboiler.

If it is critical to sell a greener steel product that is cost-competitive, the electric boiler-supplemented scenarios offer a cost of avoidance within the range: \$105 - 118 that is comparable to gas fired options at \$91 – 110, given that waste heat is utilized.

4.1.2.2 Case Study 2: Varying CO₂ capture level constrained by waste heat utilisation

In this case, we attempt to answer the question, *What if we selected the carbon capture level based on the recoverable waste heat?* Each capture point shown in Table 43 was selected based on the available waste heat at each level of waste utilization. For example, on reaching the second level on waste heat utilization, where L1 and L2 streams are recovered, we’d have enough heat to capture either the coke oven, hot strip mill or blast furnace stove gas or part of the central power station. In Table 43, we consider two scenarios, where the capture location is constrained by the waste heat available.

Table 43: Description of different heat integration-constrained capture scenarios

Case: Capture Point – Level	Heat utilization level	Recovered enthalpy [MWth]	Capture Point	Reboiler duty needed [MWth]	% of overall CO ₂ emissions avoided
HSM – HI	L1	■	Hot Strip Mill [Full Load]	■	8.9%
BFS – HI	L1 + L2	■	Blast Furnace Stoves [Full load]	■	17.0%
HSM – Hot Strip Mill, BFS – Blast Furnace Stoves, HI – Heat Integration					

Figure 33 and Figure 34 describe the performance of a heat integration-constrained CO₂ capture approach.

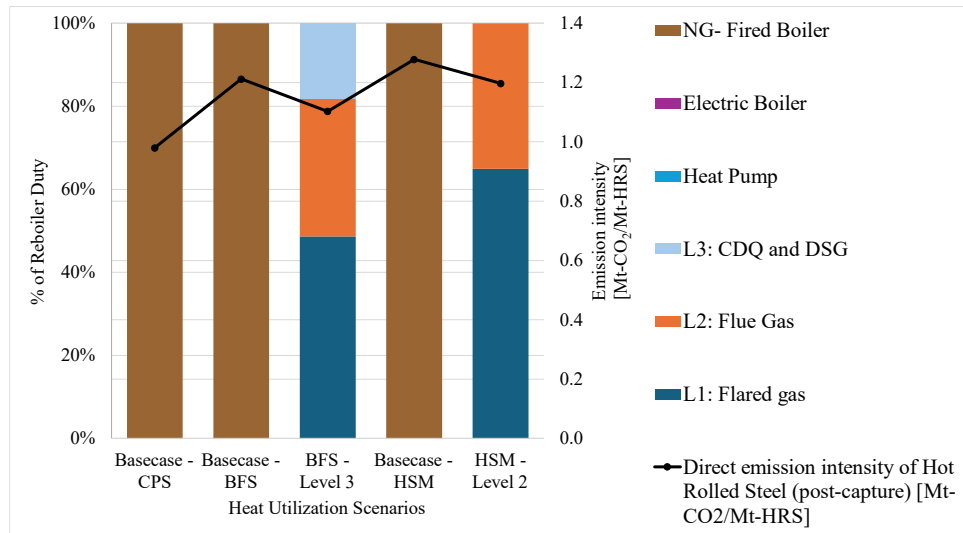


Figure 33: Reboiler duty breakdown at varying capture levels contained by waste heat utilization

First, the merits of sole waste heat utilization are evident in the CO₂ avoidance cost, shown in Figure 33. Relative to a natural gas-fired base case for the same capture point, there is almost always a 6 - 9 % reduction in the steel emission intensity. Based on the lowest avoidance cost of 87 \$/Mt-CO₂, the cheapest means of avoiding CO₂ emissions with the MEA absorption process is to capture directly and only from the hot strip mill (HSM), while generating steam from heat recovered from flared gas and flue gas.

Next, when we consider the impact on steel production as shown in Figure 34, the impacts of a waste-heat constrained capture process are less substantial. In the blast furnace stove (BFS), the added capital investment for the heat recovery to meet the larger duty demands increased the capture cost by nearly 2.5%. Conversely, in the hot strip mill, the lower capital investment needed to recover waste heat from the flared gas and the flue gas reduced the capture cost by about 2%.

Waste heat constrained capture is an economically competitive means of avoiding CO₂ emissions. However, capturing large emission volumes such as the central power station emissions at full load, even with natural gas fired boilers, still offers the lowest reduction in the emission intensity of steel and lower additional production cost at 111 \$/Mt-Hot Rolled Steel

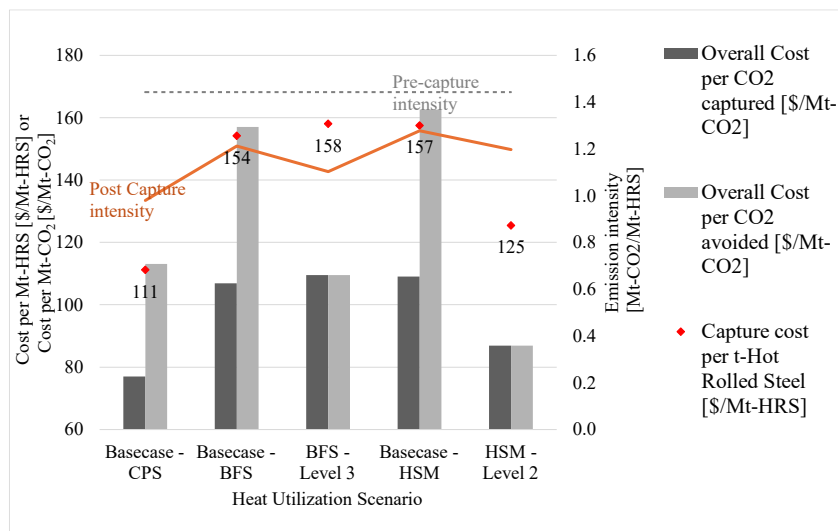


Figure 34: Capture cost at varying capture levels constrained by waste heat utilization

4.1.2.3 Case Study 3: Oxy-combustion w/ waste heat utilization

This case focuses on capturing 90% of the central power station emissions. Here, the reboiler steam is produced in an oxy-combustion boiler. 99.5% pure oxygen is supplied to the boiler from an Air Separation Unit (ASU). The highly concentrated product stream (over 95% purity) is compressed alongside the CO₂ captured with the MEA absorption process.

Figure 35 shows the reboiler duty sources and the steel emission intensity achieved by implemented each scenario. The use of oxy-combustion process reduces the emission intensity of the steel even though it is capturing the same quantity of the plant's emissions.

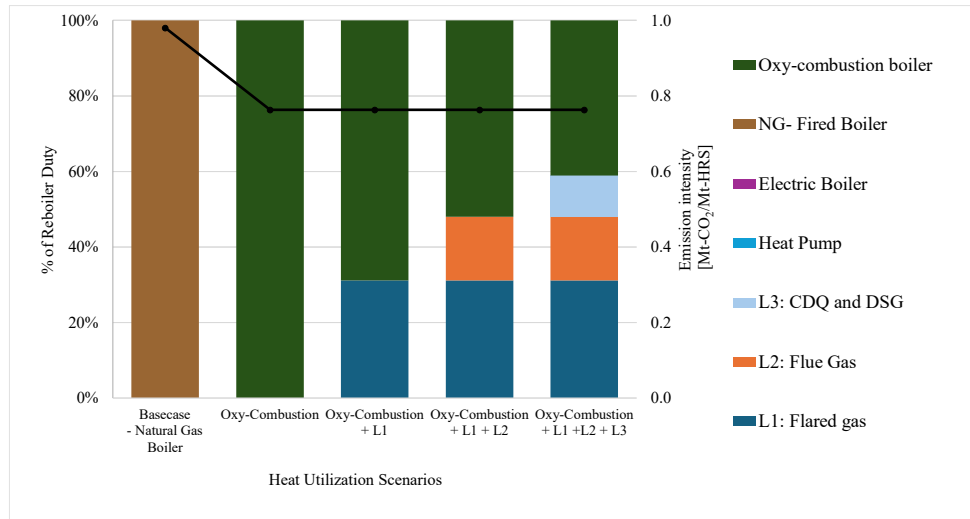


Figure 35: Comparing different combination of an oxy-combustion boiler and waste heat utilization at 90% Capture of the Central Power Station, showing a breakdown of reboiler heat duty sources and the impact of the emission intensity

Figure 36 explores the impact on the steel production costs. Substituting the natural gas boiler with oxy-combustion boiler comes with a cost penalty of 10%, due to the oxygen production costs. We find that adding the heat integration, reducing this cost up to a minimum after with further heat integration incurs a higher cost. The combination of steam generated via oxy-combustion and recovery of the flared gas and the flue gas waste heat gives the lowest capture cost yet at \$109/Mt-HRS, equivalent to increasing the production cost by 17%. This point also offers the lowest cost of CO₂ avoided.

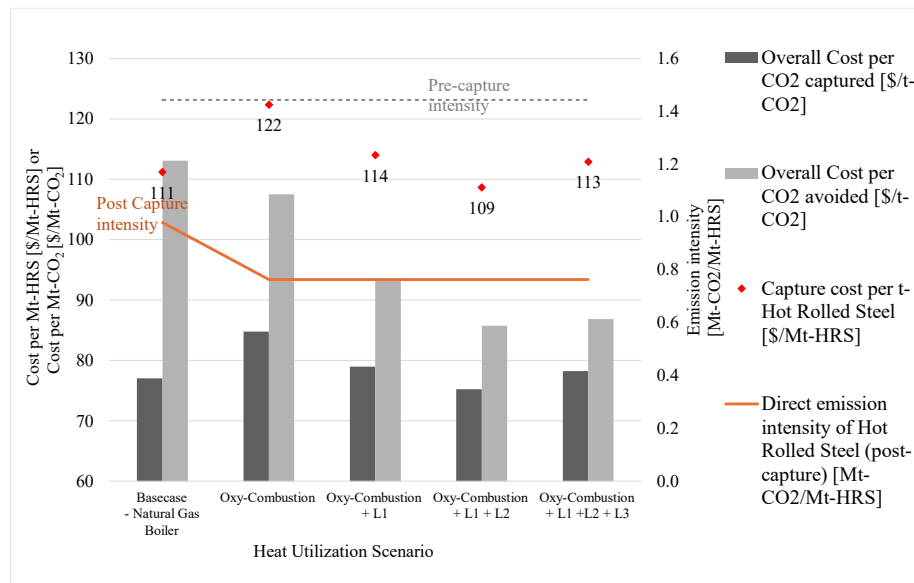


Figure 36: Impact of waste heat utilization supplemented with electric boilers on the capture costs

4.2 CO₂ Capture using a hybrid vacuum pressure swing adsorption

The central power station has been shown to be the best point for CO₂ capture based on its volume and high CO₂ composition. The vacuum pressure swing adsorption (VPSA) process takes advantage of the high CO₂ composition of the flue gas to recover CO₂ without the heat duty demands of the chemical absorption process. Using a surrogate-based optimization model, a hybrid VPSA and low temperature purification (VPSA-LTP) process and a standalone VPSA process were designed as lower-emitting alternatives to the base case.

The following section describe the surrogate model development and validation, the optimization results and an assessment of the adopted methodology.

4.2.1 Surrogate Model Validation

The goal in developing the surrogate model was to find the best fit of all the models described in section 3.2.2.2 that relates all the input variables to each output variable (7) as described in Figure 37. In this multi-modal approach, the different regression models were fitted and each model's hyperparameters were tuned based on a training data set of 556.

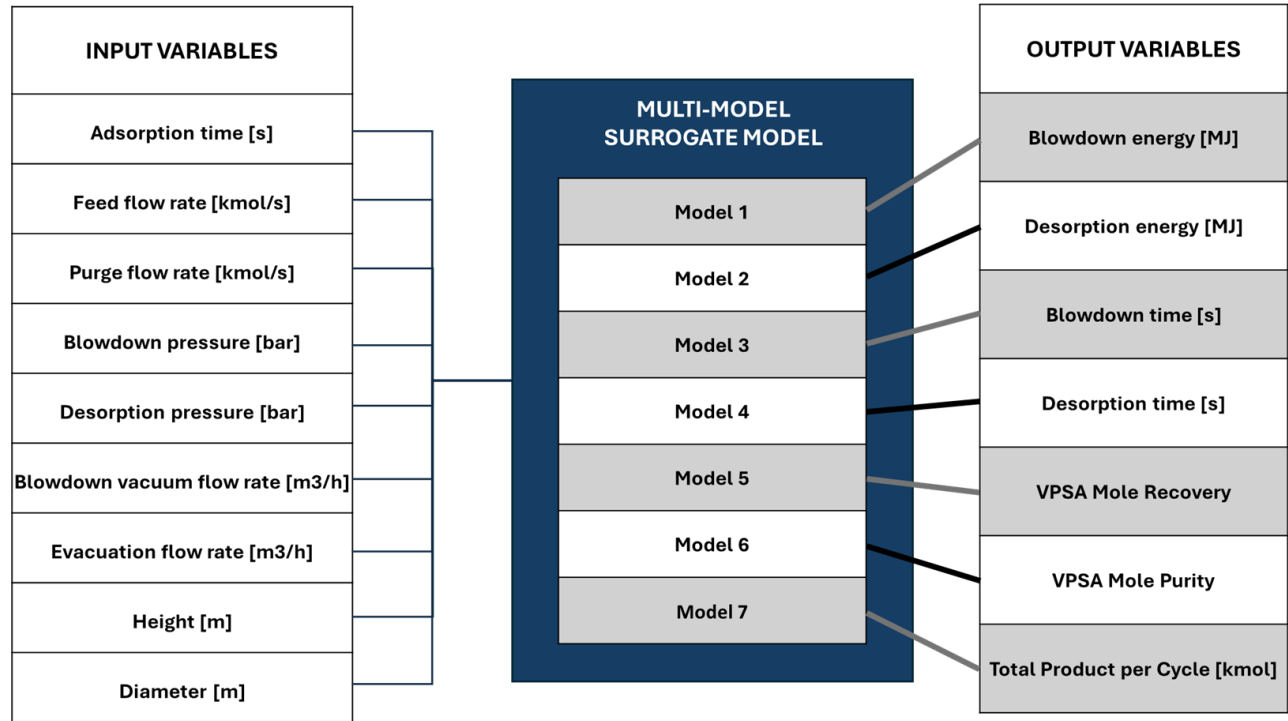
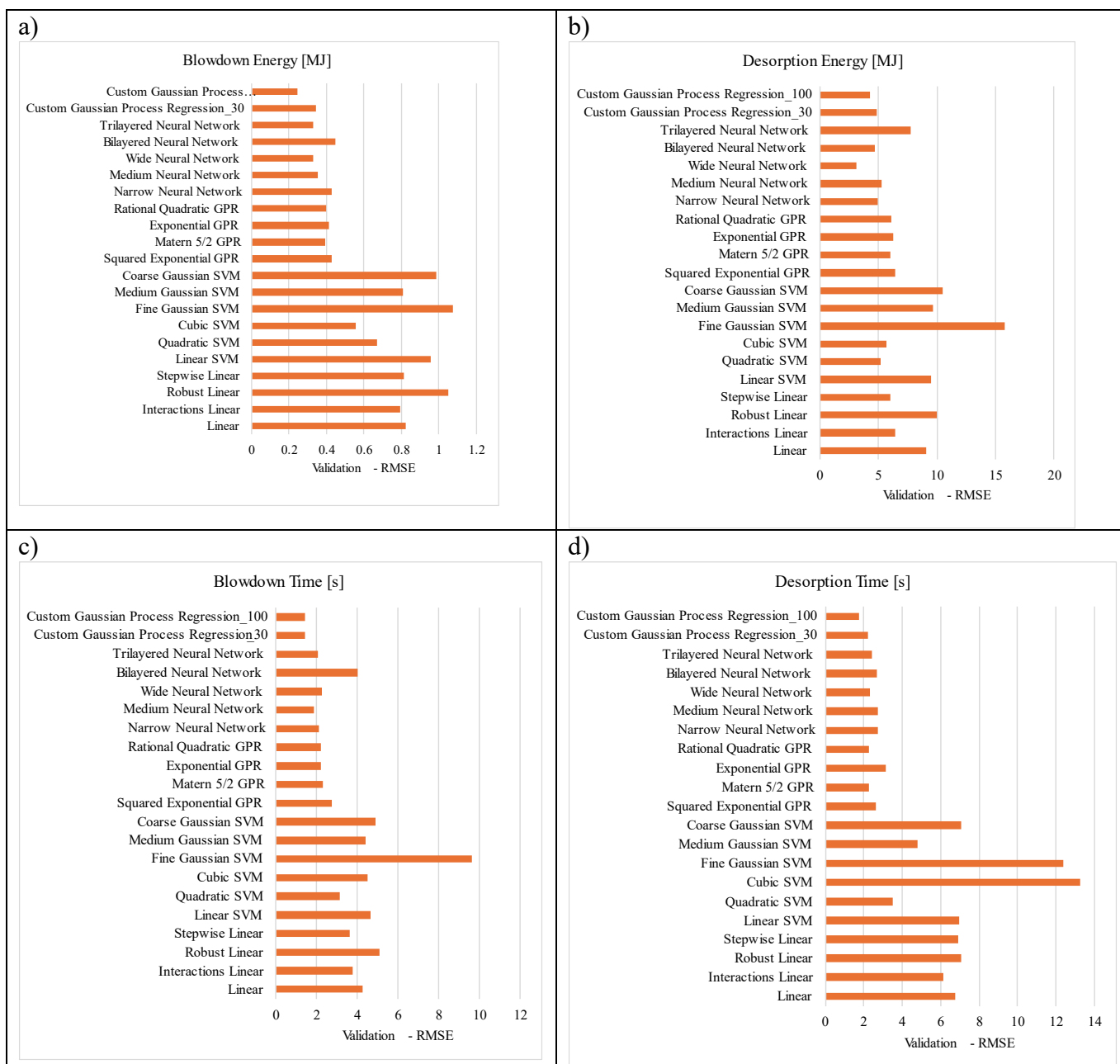


Figure 37: Multimodal surrogate model approach

To ensure that certain output variables that cannot feasibly be negative, square root transformations were applied to the output variable so that only non-negative values could be generated. Different combinations of regression model was trained for each output variables. The prediction speed, RMSE and R^2 values were evaluated for each trained model.

The RMSE of the different models for each output variable are presented in the Figure 38 a-g .



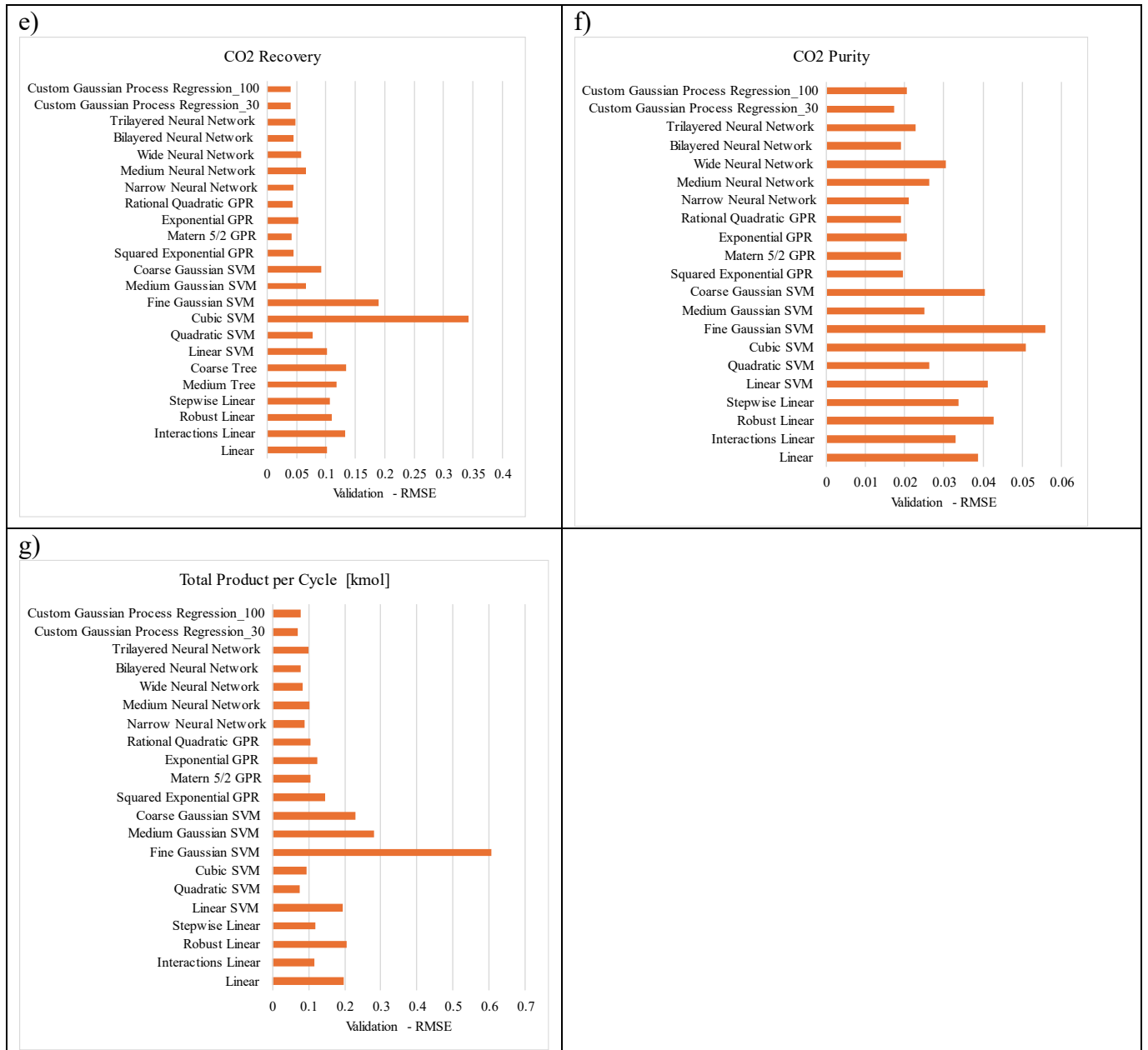


Figure 38: RMSE for different surrogate model type for different output variables a) Blowdown energy b) Desorption energy c) Blowdown time d) Desorption time e) CO₂ Recovery f) CO₂ Purity g) Total Product per Cycle

The Gaussian Process Regression (GPR) models and the Neural Network (NN) models provide superior predictive performance compared to Support Vector Machine (SVM) models and Linear Regression (LR) models in the context of multidimensional model. This can be attributed to their inherent flexibility and ability to capture the non-linear relationships present in the datasets. GPR's ability to provide uncertainty quantification alongside predictions makes it even more suitable for surrogate modeling, where the standard deviation (σ) is as critical as the predictions themselves. It's kernel-based structure can adapt to the complexity in the underlying data. The regression models with the lowest RMSE selected for each output variable, are shown in Table 44 alongside their hyperparameters, transformations, and different performance criteria:

Table 44: Multi-model Surrogate Models, Parameters and Validation Results

#	Regression Model	Parameters	Output Variable	Output Variable Transformation	Training Data Mean	Training Data RMSE	Validation Data RMSE	Training Data R ²	Validation Data R ²
1	Gaussian Process Regression	Basis function: Linear; Kernel function: Nonisotropic Exponential; Kernel Scale: 80.136, Sigma: 8.1979	Blowdown energy [MJ]	None	5.40E-01	4.15E-01	2.43E-01	0.833	0.915
2	Wide Neural Network	Number of layers: 1 Layer size: 100 Activation: ReLU Iteration limit: 1000	Desorption energy [MJ]	None	1.18E+01	1.92E+00	3.52E+00	0.994	0.972
3	Gaussian Process Regression	Basis function: Linear; Kernel function: Nonisotropic Squared Exponential; Kernel Scale: 3.0029 Sigma: 0.56199	Blowdown time [s]	Square root	3.84E+02	6.47E+01	2.06E+02	0.990	0.866
4	Gaussian Process Regression	Basis function: Linear; Kernel function: Nonisotropic Matern 3/2; Kernel Scale: 3.0197, Sigma: 138.8664	Desorption time [s]	Square root	6.50E+02	1.97E+02	2.07E+02	0.954	0.943
5	Gaussian Process Regression	Basis function: Linear; Kernel function: Nonisotropic Exponential; Kernel Scale: 29.9763 Sigma: 2.4306	VPSC Mole Recovery	Square root	4.82E-01	4.79E-02	5.63E-02	0.982	0.971

6	Gaussian Process Regression	Basis function: Linear; Kernel function: Nonisotropic Exponential; Kernel Scale: 16.0058 Sigma: 0.00042148	VPSA Mole Purity	Square root	8.39E-01	2.21E-02	3.15E-02	0.978	0.943
7	Gaussian Process Regression	Basis function: Linear; Kernel function: Nonisotropic Exponential; Kernel Scale: 1672.9226, Sigma: 0.0001004	Total Product per Cycle [kmol]	Square root	1.72E+00	7.87E-01	5.94E-01	0.947	0.955

The average prediction speed for the combined multimodal surrogate model is 8685 runs per second. The R^2 values indicate a goodness of fit for the fitted and validation data set. However, the RMSE values in some cases are a large fraction of the mean value, in the cases of the blowdown energy and the blowdown time. It is not enough that the surrogate model independently predicts the output variables of the VPSA accurately. We needed to be certain the error is tolerable for the optimization. Since an optimization will be conducted with this surrogate model, it is essential that the overall results when the surrogate output is fed to the subsequent purification model and then to the overall costing model, is accurate. Thus, the performance of the overall surrogate model was further assessed based on its impact on the following optimization objective and constraint variables:

1. Specific Cost [\$/Mt CO₂]
2. Specific Energy [MJ/kg CO₂]
3. Overall CO₂ Recovery
4. Overall CO₂ Purity

Figure 39 shows the surrogate vs the rigorous results and the R^2 and RMSE results with a fixed LTP pressure of 25 bars.

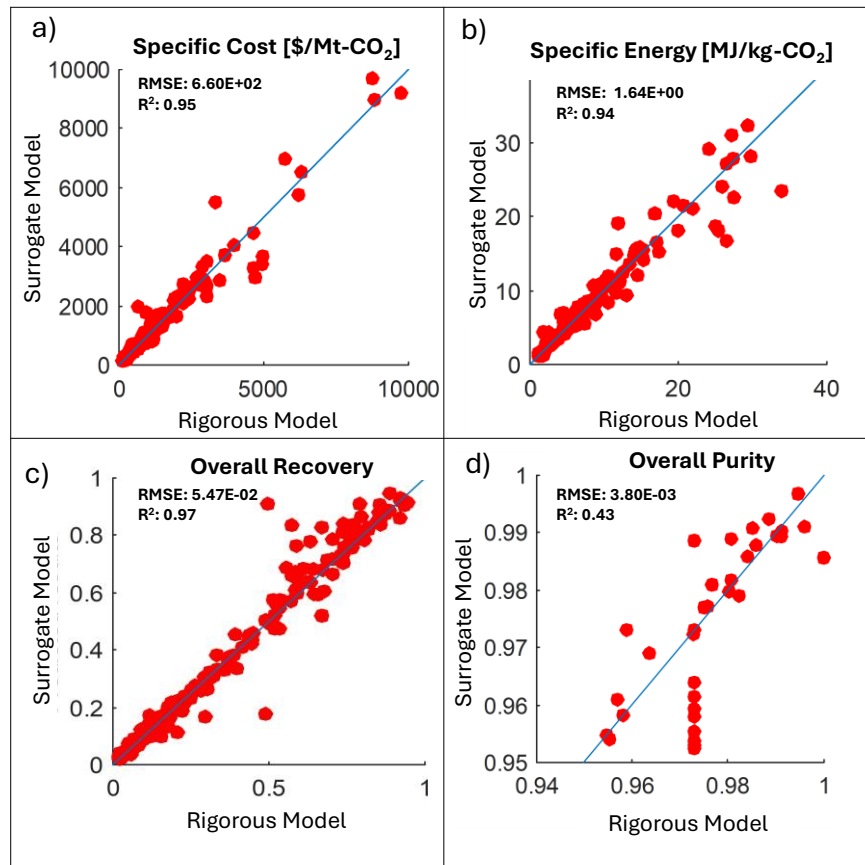


Figure 39: Surrogate Model Validation a) Specific Cost b) Specific Energy c) Overall Recovery d) Overall Purity

As seen in Figure 39, the surrogate model predicts the cost, energy and the overall recovery sufficiently based on the magnitude of errors and the plotted data. The purity levels, which range

from 0.94 to 1, are influenced by the flash pressure in the low-temperature purification unit. However, this flash pressure is not included in the surrogate model, meaning the model does not account for it as a variable or parameter. As a result, the narrow purity range is more reflective of the effectiveness of the high low-temperature purification (LTP) pressure rather than the model's accuracy. This limited range distorts the R^2 values, making them less reliable for evaluating the model's performance. In contrast, the RMSE, which accounts for the magnitude of errors and is less sensitive to the low data variance, provides a more accurate representation of the model's behavior.

The surrogate model's accuracy declines at higher cost points. Considering that we intend to minimize the cost, the model performs well to ensure the optimization objective is met. We can assume that the variables with higher RMSE values in Table 44, have a negligible impact on the final prediction of the optimized variables and constraints. Considering the blowdown time and energy are significantly lower than the desorption time, it makes sense that their impact on the prediction error is also significantly lower and can be accepted. Still, while the surrogate model can guide the optimization, the rigorous model must be used to predict the final performance.

4.2.2 Design Variable Analysis

To recall, the optimization function is given, a set of 9 input variables described in section 3.2.2.2 and delivers a set of 11 variables which include the surrogate model outputs and the overall model outputs shown in Figure 39. Another feature built into this function is its ability to predict based on the surrogate model results, whether a design should be a VPSA or a VPSA-LTP.

The distinction here, is that if the input variables for a design point result in a VPSA recovery and purity that meets the 90% recovery and 95% purity constraints, there is no need for further purification, the LTP process is neglected and a VPSA process is established. If the VPSA product stream regardless of the CO_2 recovery level falls below the 95% purity, then further purification is done and a VPSA-LTP process is established. This is implemented strictly within the costing model, where for design cases that meet the constraint using VPSA only, the LTP is excluded from the cost.

During each cost optimization run, several design points beyond the ones that met the required 90% recovery and 95% purity constraints, were generated. This set of runs consists of 12227 points. All these points are shown in Figure 40A, which plots the CO_2 purity of the product stream leaving the VPSA against the recovery of CO_2 in just the VPSA. Note that this is different from the overall recovery in the case of VPSA-LTP, which has an added purification system. During optimization generations, VPSA standalone process can be recommended, if the VPSA purity meets the 95% constraint. If it doesn't, a VPSA-LTP process is recommended with uses the low temperature purification to raise the purity of the stream.

From Figure 40A, we find that the VPSA delivers the 90% CO_2 recovery at purity levels ranging from 50% to 100%. There are design points that might meet the constraints with a VPSA standalone system in the topmost right corner of the plot. Figure 40B takes a closer look at the overall specific costs for only the design options that meet 90% recovery from the VPSA (points

to the right of the 90% CO₂ recovery line in Figure 40A. The few points which also satisfy the 95% purity constraint using the VPSA alone are left in orange, while the ones subjected to further purification in the LTP are in blue. Clearly, it will be more costly to achieve high purity stream with only the VPSA, emphasizing the need for a post purification system to increase the purity at a lower cost.

Even though the surrogate model is a black box, the way the optimization searches the design space gives some insight into the VPSA and the hybrid VPSA-LTP process. Figure 41 - Figure 44 show response plots between the design variables and the optimization objective – the specific capture cost. For presentation purposes, the cost have been filtered to show only cost lower than \$1000/Mt-CO₂ captured.

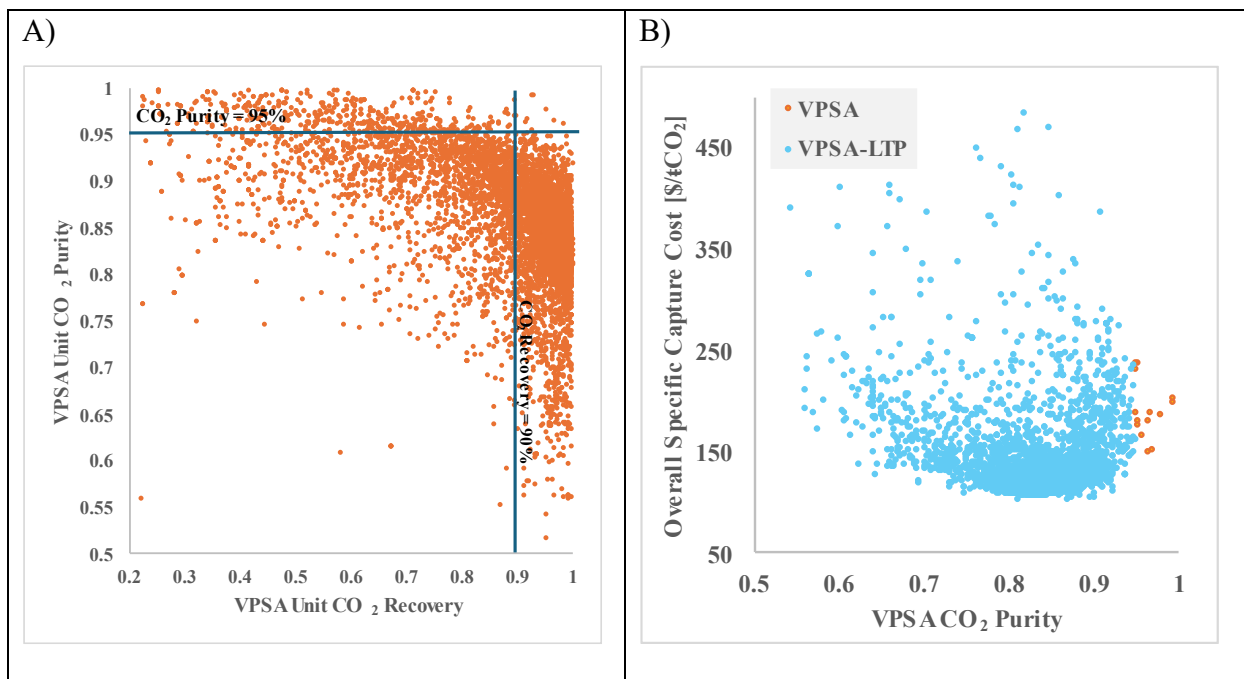


Figure 40: A) VPSA CO₂ Purity vs VPSA CO₂ Recovery B) Specific cost vs VPSA CO₂ Purity for design points with recovery > 90%

First, we look at the adsorption step times in Figure 41, there is no strong linear correlation between the adsorption time and the cost. The adsorption time is estimated based on the residence time and the breakthrough time. This estimation exploits the linear correlation between the residence and the breakthrough time identified in section 3.2.2.1. So, the optimizer selects a residence time, as one of the design variables and uses Equation 48 in section 3.2.2.1 to find the breakthrough time for a fresh bed.

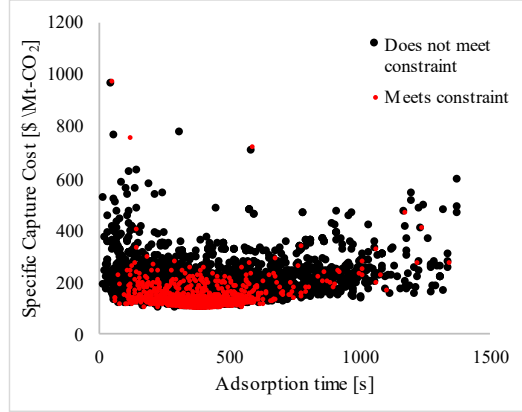


Figure 41: Specific CO₂ capture cost vs adsorption time

The blowdown time and the evacuation time in Figure 42 show a range of shorter times, less than 3 s for the blowdown step and less than 100 s for the evacuation step, that deliver the minimum cost. This indicates that a rapid cycling process is best means of operating the VPSA as longer times would increase the number of beds in a train needed for continuous production. It is unrealistic to have such low duration for the blowdown step so it is likely that in practice, the valve switches or the vacuum conditions would delay the transition between steps.

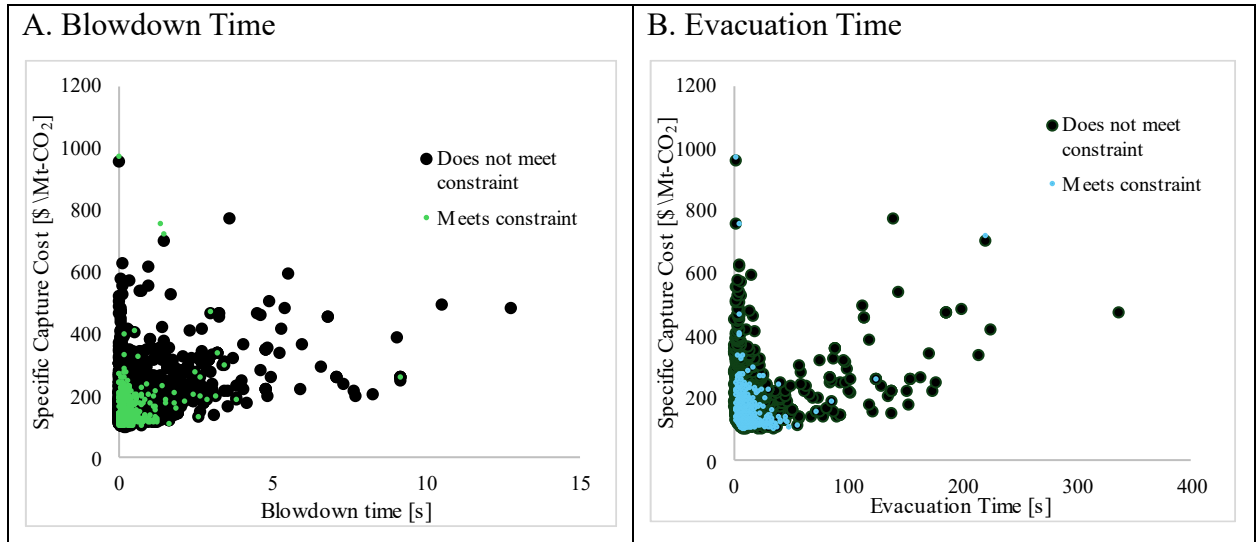


Figure 42: A) Specific CO₂ capture cost vs blowdown time B) Specific CO₂ capture cost vs evacuation time

Since it is optimal to create conditions that reduce the blowdown and product evacuation step times, the variables needed to achieve this are presented in Figure 43 A-C, namely the blowdown pressure, the evacuation pressure and the evacuation flowrate. For the blowdown step, since the flowrate is fixed at 150 m³/h, the time can be reduced through higher blowdown pressures (> 0.2 bars) as seen in Figure 43A. The higher blowdown pressures are critical to reducing the CO₂ losses as well. For the product evacuation step, the time can be reduced through higher evacuation flow rates and higher evacuation pressure. This becomes a balancing act since the higher evacuation pressure would reduce the recovered CO₂, and higher flow rate would increase the size of the vacuum pumps, all contributing to higher costs. Figure 43B shows that there is

some flexibility in the vacuum pressures that can be selected for VPSA capture. Working with pressure < 0.03 bars, usually require special vacuum pump configurations that might be more expensive in practice. Deep vacuum conditions (< 0.02 bar) are also likely to increase the cost because of the energy demands and pressures above 0.06 bar are likely to impede high recovery, so it makes sense that all the design points that satisfy the constraints are concentrated between the 0.02 – 0.06 bars bounds. Figure 43C also shows the evacuation flowrate optimal flowrate concentrated with higher bounds for the flowrate between 1000 – 35000 m^3/hr . All these factors, together create conditions that optimize the cost based on the blowdown and evacuation times.

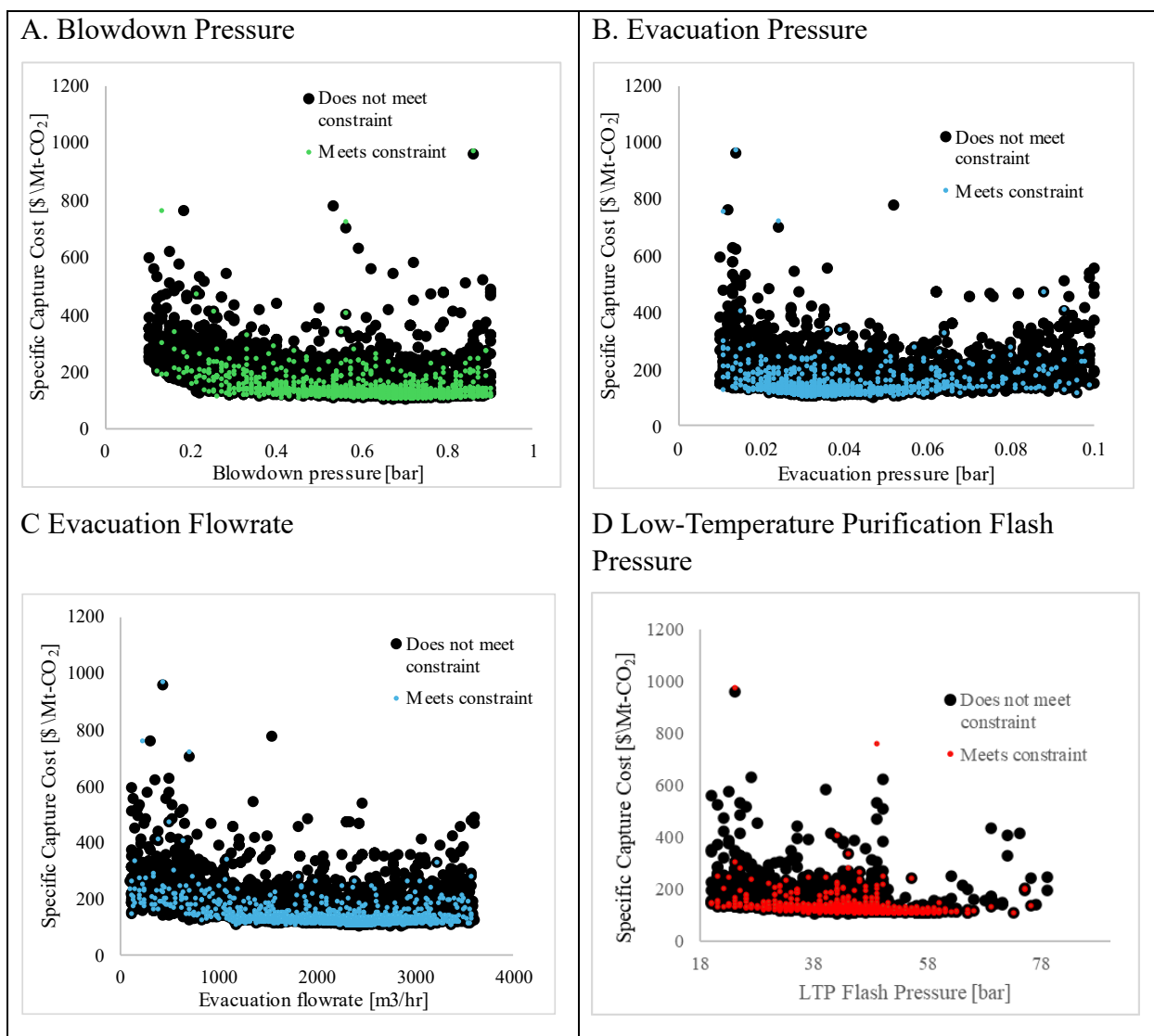


Figure 43: A) Specific CO₂ capture cost vs blowdown pressure B) Specific CO₂ capture cost vs evacuation pressure C) Specific CO₂ capture cost vs evacuation flowrate D) Specific CO₂ capture cost vs LTP flash pressure

Also included in the Figure 43D, is the flash pressure in the low-temperature purification process. The refrigeration cycle temperature is fixed so really the only variable here that could impact the cost is the pressure to which the VPSA product is compressed. Too low pressures will lead to significant CO₂ loss in the flash vapor, reducing the overall recovery. Too high pressures

would incur high capital and electricity cost. Yet another balancing act for our optimization guy to handle.

Now on to the dimensions of the columns that contribute to the significant capital cost of this process. The number of trains is determined by the column feed flow rate. Figure 44A-B shows the decision variables that impact to the size and number of the columns including the column feed rate and the height to diameter ratio. Also displayed alongside in Figure 44C-D the generated height and diameter of the column. From Figure 44A-D, designs with lower flow rates and smaller beds yield lower costs. There is no clear partiality toward any height to diameter ratios even though few higher cost points are observed at the H/D ratio of 5. The one thing we can be certain of is that dimension would be small with lower costs observed at lengths less than 7 m and diameters less than 2 m. Based on the optimization done, the VPSA operation is cheaper when configured with many small beds operating in parallel than with fewer and larger beds.

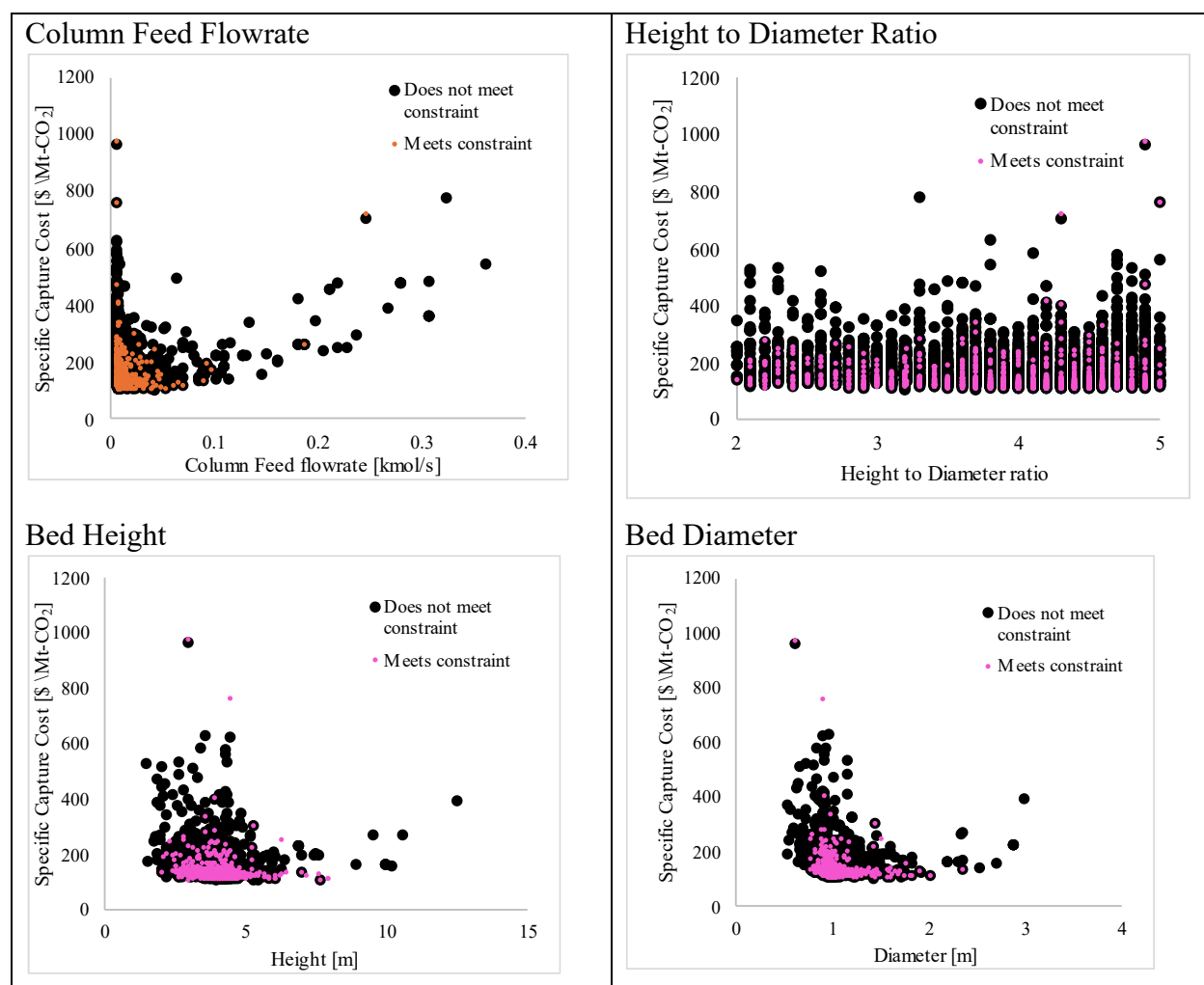


Figure 44: A) Specific CO₂ capture cost vs column molar flowrate B) Specific CO₂ capture cost vs H/D ratio C) Specific CO₂ capture cost vs Height D) Specific CO₂ capture cost vs Diameter

This is opposite to the chemical absorption process which benefits from larger volumes within a fewer large sized bed. This is a cause of concern because of the space required for the equipment.

However, it does allow flexibility in load as the trains could be activated depending on the volume of flue gas supplied. In the case of drop in flue gas supply, the chemical absorption columns would be significantly impacted by lower interfacial interaction of the flue gas with the solvent, stagnant zones in the column that can cause fouling, and the low velocities that could cause maldistribution of the solvent within the column.

4.2.3 Surrogate-Based Optimization Model Assessment

The optimization model is stochastic, so to understand the impact of this randomness and to determine a robust design option, several independent runs were conducted and collected. The effect size, a normalized difference between the average value of two sets of runs, is used as a metric to describe the variation in the optimal variables as more runs are added. Figure 45 and Figure 46 depict the changes in the effect size for the design variables and the output variables respectively. After 10 runs, the effect size for the design variables fluctuates less and converges to less than 0.05.

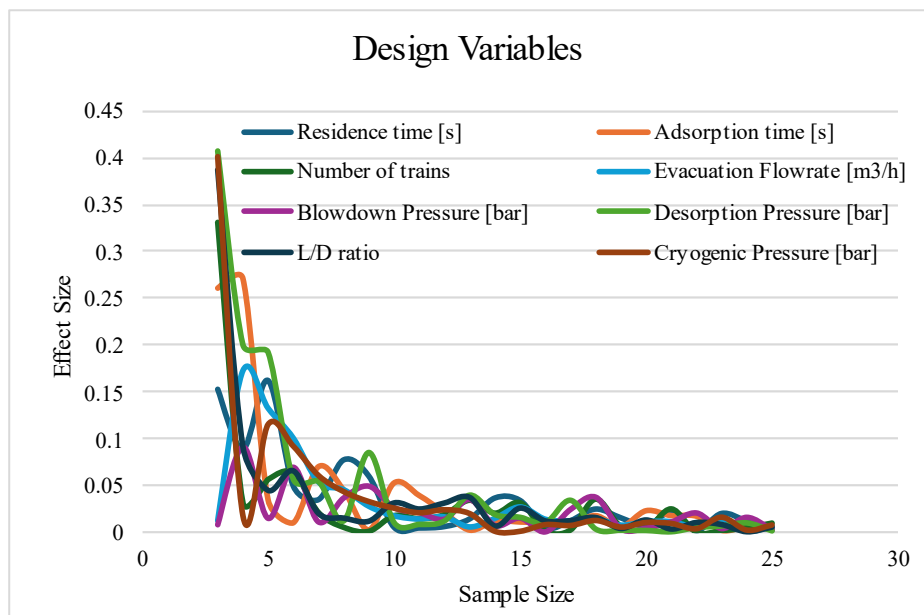


Figure 45: Impact of the sample size on the effect size for design variables

After 12 runs, the effect size for the output variables fluctuates less and converges to less than 0.05. This suggests that the observed differences between optimization runs become smaller and less significant as we collect more data. The small effect size, according to Cohen's guidelines (< 0.1), shows that the difference in adding extra runs is practically insignificant after 8 runs for all variables.

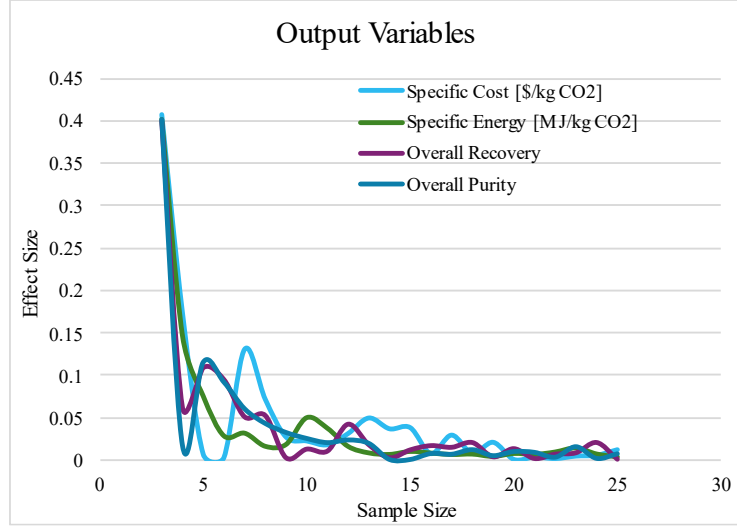


Figure 46: Impact of the sample size on the effect size for output variables

After the normality of the results and the independence of the samples was confirmed, hypothesis tests were conducted on the specific cost, the result of the optimization objective function. The F-test was done to test the null hypothesis that the variances in specific cost were not significantly different after additional runs. The equation for this hypothesis is given as:

$$H_{01}: \sigma_{s1}^2 = \sigma_{s2}^2 \quad (79)$$

Where $s1$ refers to the number of independent runs in the first sample and $s2$ refers to the number of independent runs in the second sample.

After checking if the variances was equal, a t-test was conducted to test the null hypothesis, that there was no significant difference in the mean predicted based on two set of independent runs. The equation for this hypothesis is given as:

$$H_{02}: \mu_{s1} = \mu_{s2} \quad (80)$$

A 95% significance level was used in testing these hypotheses. The t-tests results are interpreted, keeping in mind that the small sample size means that that only large effects can be observed without falsely rejecting the null hypothesis.

Table 45 shows the results and conclusions of the final hypothesis tests:

Table 45: Hypothesis test results for difference due to number of runs

Hypothesis	S1	S2	Test	Test Statistic	Criteria	P-value	Result	Conclusion
H_{01}	20	25	F-test	1.10	2.04	0.410	Fail to reject H_{01}	Equal variance
H_{02}	20	25	t-test	0.40	2.02	0.693	Fail to reject H_{02}	Equal mean

From the effect size plots and the hypothesis tests results, there is no significant difference in the design variables and the optimal cost after 20 runs. There is no benefit to including more runs. The design variables were aggregated as an average to estimate the robust optimal design result. Table 46 outlines the results of two approaches to finding the optimum design. It first shows the global minimum amongst all the conducted runs, next to the mean of all the optimum designs of the 25 independent runs. Also included in this table are the coefficient of variation (the ratio of the standard deviation to the mean) and the 95% confidence interval, in which we expect the true robust mean optimum to lie.

The global minimum is ideal only under perfect deterministic conditions, without accounting for variability in parameters. The robust optimum, however, accounts for uncertainties, ensuring consistent performance within a confidence interval despite input variations. A comparison of the two results shows the impact of uncertainties on the performance of the VPSA-LTP process.

Table 46: Surrogate-based GA optimization results

	Global Minimum Cost Design	Mean of Optimum Designs	Coefficient of Variation	Confidence Interval
Design Variables				
Residence time [s]	4.30	6.34	0.26	5.69 - 7
Adsorption time [% of Initial Breakthrough time]	0.36	0.34	0.13	0.32 - 0.35
Number of trains	320	408	0.37	349 - 468
Evacuation Flowrate [m ³ /h]	1535	1901	0.28	1690 - 2113
Blowdown Pressure [bar]	0.57	0.59	0.18	0.55 - 0.63
Desorption Pressure [bar]	0.029	0.030	0.14	0.028 - 0.031
Height to Diameter ratio	3.20	3.46	0.21	3.2 - 3.7
LTP Flash Pressure [bar]	38	37	0.05	37 - 38
Output Variables				
Specific Cost [\$ / kg CO ₂]	105.92	111.84	0.03	110.61 - 113.07
Specific Energy [MJ / kg CO ₂]	0.983	1.014	0.12	0.966 - 1.062
Overall Recovery	0.923	0.928	0.02	0.921 - 0.935
Overall Purity	0.953	0.954	0.00	0.953 - 0.956

Amongst the design variables, the residence time, the number of trains and the evacuation flowrate show the highest variability based on their relative coefficient of variation (CV). This indicates that there is significant room for flexibility in these variables in achieving a low-cost design.

The adsorption time, height to diameter ratio, blowdown pressure, desorption pressure and the LTP flash pressure exhibit lower variance. Even the global optimum lies within the slim

confidence interval for each variable. These observations suggest that these variables should be more tightly controlled when selecting a low-cost design. The optimization converged toward 40% of the initial breakthrough time as the adsorption time. From this, we can extrapolate that it is optimal to not operate the bed at the start to its breakthrough point, however it can't be too low as this would be a waste of the sorbent's capacity, leading to a lower sorbent/process productivity that increases the capital cost.

For the output variables, the specific cost with its low CV indicates a stable prediction across varying optimal scenarios. The specific energy has the highest variability of all the results. The CO₂ recovery shows that with the selection of design variables within the set interval will yield a reliable capture performance. There is an exceptional consistency in the purity which proves that this metric is nearly unaffected by design changes. This could be attributed to the tightly controlled flash pressure 37 – 38 bars.

These mean results can guide the fine-tuning of design variables to achieve cost-effective and energy-efficient CO₂ capture with high purity and recovery levels. A conservative approach is adopted, whereby the mean value is selected for variables with high variability and the global optimum for variables with low variability. This approach attempts to balance robustness and optimality.

The mixed approach design was fed to the rigorous VPSA model in Aspen Adsorption to yield the results shown in Table 47 for comparison.

Table 47: Optimized design point validation for the VPSA-LTP process

Design Variables			
Residence time [s]	6.34		
Adsorption time [% of Initial Breakthrough time]	0.36		
Number of trains	408		
Evacuation Flowrate [m ³ /h]	1901		
Blowdown Pressure [bar]	0.57		
Desorption Pressure [bar]	0.029		
Height to Diameter ratio	3.2		
LTP Flash Pressure [bar]	38		
Output Variables	Surrogate Model	Rigorous Model	% Error
Specific Cost [\$ /Mt-CO ₂]	110.68	120.45	8.5%
Specific Energy [MJ/kg CO ₂]	0.92	0.97	5.3%
Overall Recovery	0.93	0.90	-3.8%
Overall Purity	0.97	0.97	0.0%

The absolute relative error of the overall capture cost less than 10 %, shows the validity of this surrogate model-based approach in predicting the performance of the VPSA process for preliminary design.

This approach is also effective in exploring the design space of dynamic systems with many interacting variables at lower computational cost. This work was completed using two computers containing a 12th Gen Intel® Core™ i9-12900K CPU with 16 cores and 32 GB of installed RAM each. Table 48 shows the duration of time the optimization would take without parallelization, to illustrate the advantage of the surrogate-based optimization.

Table 48: Optimization CPU times based on the rigorous model vs the surrogate model

	Units	VPSA Rigorous Model	VPSA Surrogate Model
Aspen Adsorption CPU time	s	25129	
Surrogate model CPU time	s		0.1
Aspen Plus CPU time	s	187	187
Communication time	s	15	15
Total time for 1 full model run	s	25331	202
	hr	7.0	0.06
Estimated model building time for 785 rigorous model runs = 545 training + 240 validation	hrs		5524
Estimated GA Optimization time for 12227 optimization runs with 10% for communication overhead	hr	94637	755
Estimated Total time	days	563	37
Process Speed up		15	

Using the surrogate model reduced the optimization time by 15 times. With parallelization, the training only took about 2.5 weeks without accounting for frequent system lapses. Because there were system lapses, using this approach allowed us to troubleshoot the optimization function and better understand the black box at each stage of development, since the training set, the surrogate model and the design variables could be analyzed and altered quickly to adapt to different errors and disruption, without having to restart the development process. During the actual optimization, despite system crashes and errors, it was possible to restart the process as needed, while using previously generated results to improve the optimization function. If a brute-force optimization was done with just the rigorous model, failures would have been more expensive and difficult to troubleshoot.

4.2.4 Optimal VPSA-LTP Process Configuration

Table 49 shows the lowest cost design from the surrogate model-based optimization for hybrid VPSA-LTP and a VPSA capture system. Based on the insights drawn from the runs (individuals) generated during the optimization process in section 4.2.2, arriving at this recommended configuration makes sense; for example, the low height and diameter of the columns and the low evacuation pressure at around 0.03 bar.

Table 49: Minimum cost configuration for the VPSA-LTP process (Inlet CO₂ 28 vol %)

	Unit	Robust Optimum
Operating Configurations		
Adsorption time	s	397
Blowdown time	s	139
Evacuation time	s	914
Purge time	s	397
Idle time	s	138
Adsorption flow rate	kmol/s	0.015
Purge flow rate	kmol/s	0.002
Maximum feed pressure	bar	1.1
Feed temperature	C	30.00
Blowdown pressure	bar	0.57
Evacuation pressure	bar	0.028
Column height	m	4.59
Column diameter	m	1.20
Blowdown pump flow rate	m ³ /h	150
Evacuation pump flow rate	m ³ /h	1901
Train Configuration		
Number of parallel trains		408
Number of columns per train		5
Blowdown pumps per train		1
Evacuation pumps per train		3
Additional Setup		
Low temperature purification flash pressure	bar	38
Process Performance		

VPSA Recovery		93.1%
VPSA Purity (mole basis)		93.4%
Overall Recovery		90.0%
Overall Purity (mole basis)		97.0%
Productivity	Mt-CO ₂ /m ³ /day	0.417
Overall power consumption	MWe	■
Specific energy penalty	MJ/kg-CO ₂	0.97
Specific electricity penalty	kWh/kg-CO ₂	0.27
Costs		
Total Capital Investment	\$	895,980,000
Annual Operating Cost	\$/yr	92,244,391
Specific Capture cost	\$/Mt-CO ₂	120.46
CAPEX	\$/Mt-CO ₂	72.93 [61%]
OPEX	\$/Mt-CO ₂	47.53 [39%]

The daily productivity compared to literature cases shown in Table 19, typical of 13x zeolite but could be improved through advanced sorbents like the UTSA-13 with its higher CO₂ selectivity and capacity.

In the hybrid case with over 300 trains with 6 columns each are needed, this is equivalent to about 2130 m² of land for just the columns. A standard premier league football field is 7140 m², so these columns would require about 30% of a football field. With these many units, the process is capital intensive, the capital cost accounting for 58% of the annualized cost.

Figure 47 shows an overall cost breakdown of the VPSA-LTP capture processes compared to variations of the benchmark MEA scrubbing process for the central power station. The first case is the MEA scrubbing of the central power station flue gas with heat supplied by fuel-air fired boilers. The **MEA-EL only** case is MEA Scrubbing with total electrification of the heating using electric resistance boilers. The **MEA-EL-L3** case is MEA Scrubbing with partial heating using electric boilers supplemented with heat recovered from flared gas streams, hot flue gases, incandescent coke and molten blast furnace slag. This is the lowest cost electrification scenario. The **MEA-OXY-L2** case is MEA Scrubbing with partial heating using oxy-combustion boilers supplemented with heat recovered from flared streams and hot flue gases only.

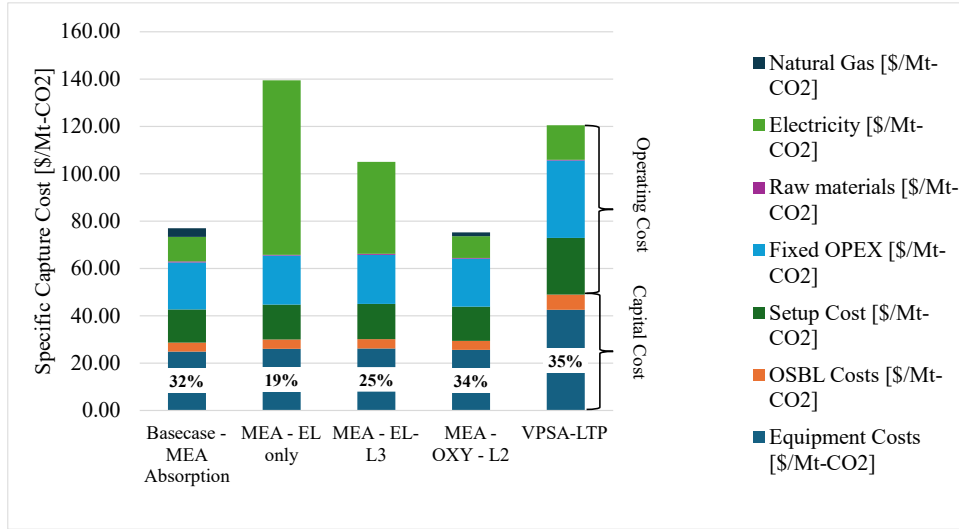


Figure 47: Overall Cost Breakdown of MEA Scrubbing and VPSA-LTP processes

There is a larger contribution of equipment cost for the VPSA-LTP process, which also impacts the setup and outside battery limit (OSBL) costs, leading to the large capital cost investment. When comparing the VPSA-LTP to the electrification scenarios, we find that the electricity cost accounts for significantly smaller fraction of the cost. In a natural gas constrained scenario, VPSA presents great alternative if the plant does not seek to expand their electricity consumption and can make the capital investment needed. If there are no constraints on natural gas available, VPSA-LTP performs poorly in comparison to the lowest cost hybrid oxy-combustion alternative. This attributed mostly to the high capital cost. When we break down the equipment cost into the different sections, as in Figure 48, it is found that VPSA unit accounts for 47% of the cost in the hybrid VPSA-LTP process.

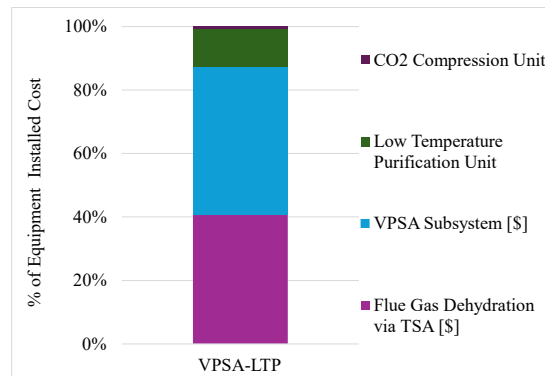


Figure 48: Capital Cost Breakdown for the MEA Scrubbing and VPSA-LTP processes.

The dehydration cost is also significant at about 41% of the cost. This further highlights the need for commercial sorbents that highly selective for CO₂ over water eliminating the need for dehydration process. To evaluate the impact on steel production, in Figure 49, we see that in terms of avoidance cost, the VPSA-LTP process performs worse than the base case. It will achieve a lower steel emission intensity than the chemical absorption, by 17%, while capturing the same volume of CO₂, albeit at a price tag that is 57% more.

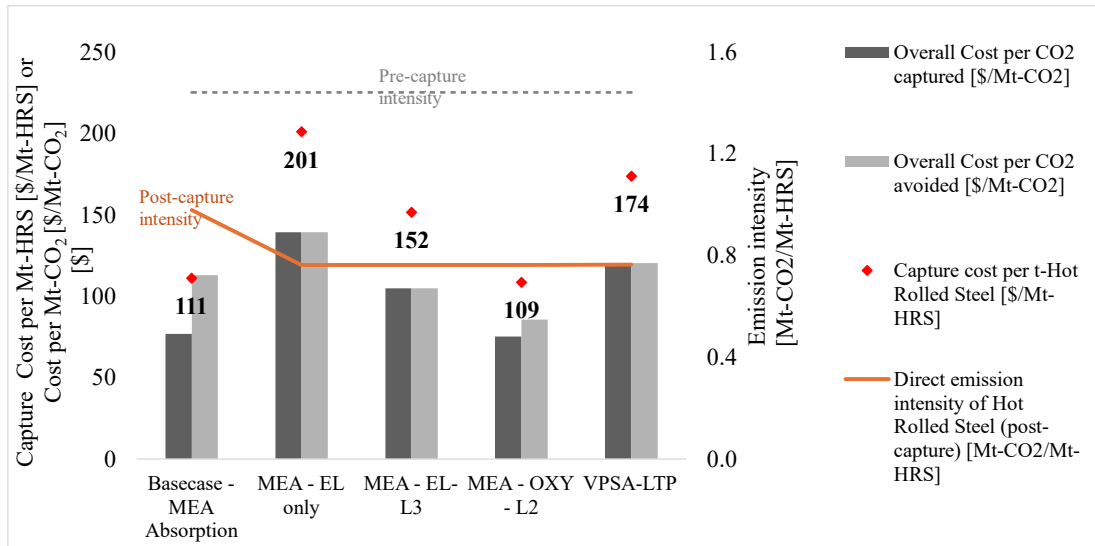


Figure 49: Comparison of the Impact of the VPSA, VPSA-LTP and the MEA Scrubbing Base case on steel emission intensity and capture costs

In summary, the cost of the VPSA-LTP process would increase the steel production cost by 57% compared to an MEA adsorption process. Given its advantage of no additional direct emissions generated, this process offers the cost of avoidance that is about 7% more expensive than the base case. In a natural gas constrained scenario, it is recommended choice of technology to reduce the operating cost of the plant.

5 Conclusions

This study investigates the feasibility and economic viability of implementing carbon capture technologies within integrated steel mills, with a focus on achieving mid-term decarbonization goals. Two primary approaches were analyzed: chemical absorption using Monoethanolamine (MEA) and a hybrid vacuum pressure swing adsorption with low-temperature purification (VPSA-LTP). The findings provide a comparative framework that highlights the trade-offs between technological maturity, operational costs, and energy requirements.

MEA Absorption

The Monoethanolamine (MEA) absorption process was shown to be a robust and mature technology for capturing CO₂ from high-concentration emission sources, such as the central power station (CPS) and blast furnace stoves. The central power station was identified as the best single point of capture due to its volume and composition. At a capture rate of 90%, the process achieves costs ranging from **\$77 to \$398 per tonne of CO₂ captured**, depending on the emission source. The regeneration energy demand, ranging from **4.3 to 8.2 MJ/kg CO₂**, can be partially offset by integrating waste heat recovery. For instance, recovering heat from sources like hot strip mills and coke ovens reduces external energy requirements by up to **61%**, significantly lowering operational costs.

However, the energy-intensive nature of MEA absorption poses challenges, particularly when powered by air-fired natural gas boilers, which increase CO₂ avoided costs due to the associated emissions. Alternative energy solutions, including oxy-combustion boilers, electric boilers, and waste heat recovery, were evaluated:

- **Oxy-combustion boilers** reduce avoided costs by **22%** through the provision of high-purity CO₂ streams.
- **Electric boilers**, though environmentally favorable, increase specific capture costs by **80%** and are thus deemed economically inefficient.
- **Waste heat recovery** proves to be a critical cost-reduction strategy. For example, partial substitution of the air-fired reboiler duty at the CPS with heat from flared gases achieves a **14–19% reduction in CO₂ avoided costs**. Despite the high capital costs, heat recovery from slag and coke using Coke Dry Quenching (CDQ) and Dry Slag Granulation (DSG) reduces avoided costs by **20%**.

Hybrid VPSA-LTP

The hybrid VPSA-LTP process provides an alternative for capturing CO₂ with a modular design that balances energy efficiency and recovery performance. Using a surrogate-based optimization approach, combining Gaussian Process Regression and Neural Network models, the process achieved significant computational efficiency by reducing simulation time by a factor of **15** while maintaining prediction accuracy within **10%**. While several variables like the adsorption time, blowdown and desorption pressures, purification flash pressure must be tightly controlled, there is some flexibility in selecting the modularity of units (number of trains) and the evacuation

flow rates, without impacting the minimum cost significantly. For robustness, the optimal design is evaluated based on an average aggregate of multiple independent runs

The optimized VPSA-LTP design achieves:

- A capture cost of **\$120 per tonne of CO₂**.
- Electricity consumption of **0.27 kWh/kg CO₂**, which is uses **80%** less electricity, compared to fully electrified MEA systems.

Although the VPSA-LTP process offers flexibility in modularity and cost-efficient electricity usage, it remains **60% more expensive** than the lowest-cost MEA hybrid configuration that incorporates oxy-combustion and waste heat recovery.

Comparative Insights

Among all evaluated scenarios, the combination of **MEA absorption, oxy-combustion heating, and waste heat recovery** from flared and flue gases was identified as the most cost-effective strategy for CO₂ capture from the central power station. This configuration achieves:

- A CO₂ capture cost of **\$75 per tonne** and an avoidance cost of **\$86 per tonne**.
- A reduction in the steel mill's emission intensity to **0.76 tonnes of CO₂ per tonne of hot rolled steel slabs**.
- An increase in production costs by **17%**, from **\$633 to \$741 per tonne** of steel.

For comparison, applying carbon tax of 87 CAD per tonne of CO₂ on the total direct emissions of the unabated process would increase the production cost by **14% to \$722 per tonne of steel**. Here the emission tax would cost less than the partial CO₂ capture implementation. A reduction of the interest rate to 5%, through reliance on low interest loans, could result in up to 40% reduction in the avoided cost. With an annual escalation rate of 3%, by 2030, this cost will be \$93 per tonne of CO₂ the carbon tax will be \$130 per tonne of CO₂, offering more room for investment in other decarbonization methods to handle 100% of emissions. This example highlights the role of policies such as the stricter carbon pricing and supportive financial incentives for decarbonization project, in making carbon capture cost-competitive

Contributions

This research provides a detailed techno-economic assessment of carbon capture strategies for integrated steel mills in Canada. The findings emphasize that a multi-pronged approach—leveraging waste heat recovery, optimizing energy-intensive operations, and employing hybrid capture systems—is essential for cost-effective decarbonization. Additionally, the surrogate-based optimization framework developed in this study offers a scalable approach for evaluating processes that require computationally intensive models and can be applied to other industrial decarbonization efforts.

6 Future Work

Future work should focus on the following areas to enhance the carbon capture process and explore new avenues for improvement:

1. **Heat Integration and Utility Optimization:** Investigate opportunities for heat integration, such as utilizing a central power station to supply steam for the MEA absorption process, instead of supplementing the plant's electricity supply. This could reduce operational costs of the capture plant but have trade-offs for the existing plants that must be assessed.
2. **Advanced Solvents and Sorbents:** Explore advanced materials, such as AMP (2-amino-2-methyl-1-propanol) and UTSA-16, which offer the potential to overcome the technical limitations of the benchmark materials such as the energy penalty of MEA and the productivity of 13x zeolite.
3. **Enhanced Surrogate Model:** Extend the surrogate model to include isotherm parameters, enabling performance predictions for alternative sorbents. This expansion would facilitate a broader search for ways to improve the VPSA-LTP (Vacuum Pressure Swing Adsorption - Low-Temperature Purification) process.
4. **Surrogate-base Optimization Improvement and Uncertainty Analysis:** The probabilistic models with the current surrogate model assumes fixed mean and standard deviation. Future studies should explore the impact of uncertainty to develop a more robust optimization framework. Conduct sensitivity analyses of Genetic Algorithm (GA) parameters, such as mutation and crossover rates, to enhance the algorithm's ability to locate global optima.
5. **Cryogenic Temperature Exploration:** Investigate the potential of operating at cryogenic temperatures below -100°C to reduce the compression work required in the purification process.
6. **Alternative Carbon Capture Technologies:** Expand the scope to include promising methods like chemical looping, which could significantly reduce the energy penalty associated with carbon capture.
7. **Impact of DSG and CDQ:** Further study the effects of Dry Slag Granulation (DSG) and Coke Dry Quenching (CDQ) on the steel production process, particularly regarding changes in the physical properties of slag and coke.
8. **Economic Sensitivity and Policy Assessment:** Conduct a multidisciplinary evaluation of carbon capture's economic potential, focusing on sensitivity to economic parameters, policy impacts, and uncertainty in cost assumptions. Identify optimal conditions for a cost-competitive implementation of carbon capture in the iron and steel industry.
9. **Life Cycle Assessment (LCA):** Perform a comprehensive LCA to account for emissions beyond direct emissions, ensuring a holistic understanding of environmental impacts of the capture plant.

10. **Mid-to-Long-Term Emission Strategies:** Develop strategies to address the remaining 54% of emissions such as fuel substitution, while optimizing for cost reduction.
11. **CO₂ Utilization Opportunities:** Explore the integration of CO₂ capture strategies into industrial applications, such as using captured CO₂ for sustainable aviation fuel production or other value-added processes.

These directions will help build a more efficient, sustainable, and integrated approach to carbon capture and emission reduction, addressing both technical and economic challenges.

References

- [1] IEA, 'Iron and Steel Technology Roadmap', IEA, Paris, 2020. doi: 10.1787/3dcc2a1b-en.
- [2] 'Canada's Greenhouse Gas and Air Pollutant Emissions Projections 2021', Environment and Climate Change Canada, Gatineau QC, 2022. [Online]. Available: <https://www.canada.ca/en/environment-climate-change/services/climate-change/greenhouse-gas-emissions/projections.html>
- [3] S. Canada, 'Net-zero emissions by 2050'. Accessed: Jun. 03, 2024. [Online]. Available: <https://www.canada.ca/en/services/environment/weather/climatechange/climate-plan/net-zero-emissions-2050.html>
- [4] 'Crude steel production in Canada 2021', Statista. Accessed: Jun. 03, 2024. [Online]. Available: <https://www.statista.com/statistics/184542/crude-steel-production-in-canada-since-2000/>
- [5] B. Griffin, 'Energy Use and CO₂ Emissions in Canadian Iron and Steel and Ferro-Alloy Manufacturing Industries', Canadian Energy & Emissions Data Centre, February, 2019.
- [6] D. of F. Canada, 'Economic Growth and Productivity'. Accessed: Jun. 03, 2024. [Online]. Available: <https://www.canada.ca/en/departement-finance/news/2024/04/economic-growth-and-productivity.html>
- [7] 'Steel Demand Forecasts', worldsteel.org. Accessed: Jun. 03, 2024. [Online]. Available: <https://www.worldsteel.org/data/short-range-outlook-new/STEELDEMAND-FC-PERC/>
- [8] 'World Steel in Figures 2024', worldsteel.org. Accessed: Dec. 10, 2024. [Online]. Available: <https://worldsteel.org/data/world-steel-in-figures-2024/>
- [9] M. T. Ho, A. Bustamante, and D. E. Wiley, 'Comparison of CO₂ capture economics for iron and steel mills', *Int. J. Greenh. Gas Control*, vol. 19, pp. 145–159, Nov. 2013, doi: 10.1016/j.ijggc.2013.08.003.
- [10] IEA, 'Age profile of global production capacity for the steel sector (blast furnaces and DRI furnaces)', *IEA*. [Online]. Available: <https://www.iea.org/data-and-statistics/charts/age-profile-of-global-production-capacity-for-the-steel-sector-blast-furnaces-and-dri-furnaces>
- [11] M. A. Khan, M. Powell, M. Tampier, E. Thorn, and D. Layzell, 'Hydrogen and the Decarbonization of Steel Production in Canada', vol. 5, no. 2, 2023.
- [12] P. R. Shukla, J. Skea, and R. Slade, 'Working Group III Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change'.
- [13] Golder Associates and Thorn Associates, 'Canadian Steel Industry Energy & Greenhouse Gas Emissions Intensity, Technology and Carbon Reduction Roadmap', Canadian Steel Producers Association, 2021.
- [14] S. Canada, '2030 Emissions Reduction Plan – Sector-by-sector overview'. Accessed: Dec. 26, 2024. [Online]. Available: <https://www.canada.ca/en/services/environment/weather/climatechange/climate-plan/climate-plan-overview/emissions-reduction-2030/sector-overview.html>
- [15] S. A. Usas and L. Ricardez-Sandoval, 'An optimal sustainable planning strategy for national carbon capture deployment: A review on the state of CO capture in Canada', *Can. J. Chem. Eng.*, vol. 102, no. 7, pp. 2332–2351, 2024, doi: 10.1002/cjce.25249.
- [16] S. Canada, '2023 Progress Report on the 2030 Emissions Reduction Plan: Part II'. Accessed: Oct. 21, 2024. [Online]. Available: <https://www.canada.ca/en/services/environment/weather/climatechange/climate-plan/climate-plan-overview/emissions-reduction-2030/2023-progress-report/part-ii.html>

- [17] H. Paxton, 'Steel', in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2004. doi: 10.1002/0471238961.1920050516012420.a01.pub2.
- [18] E. Worrell, L. Price, M. Neelis, C. Galitsky, and N. Zhou, 'World Best Practice Energy Intensity Values for Selected Industrial Sectors', LBNL--62806, 927032, Jun. 2007. doi: 10.2172/927032.
- [19] J. Schenk, 'Iron', in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2021, pp. 1–41. doi: 10.1002/0471238961.0918151412051609.a01.pub3.
- [20] H. Michishita and H. Tanaka, 'Prospects for Coal-based Direct Reduction Process'.
- [21] R. H. Tupkary, V. R. Tupkary, and R. H. Tupkary, *Modern steel making handbook*. in MLI handbook series. Dulles, Virginia: Mercury Learning and Information, 2018.
- [22] NSC, 'An introduction to steelmaking', newsteelconstruction.com. Accessed: Dec. 10, 2024. [Online]. Available: <https://www.newsteelconstruction.com/wp/an-introduction-to-steelmaking/>
- [23] J. C. M. Farla, C. A. Hendriks, and K. Blok, 'Carbon dioxide recovery from industrial processes'.
- [24] E. Tsupari, J. Kärki, A. Arasto, and E. Pisilä, 'Post-combustion capture of CO₂ at an integrated steel mill – Part II: Economic feasibility', *Int. J. Greenh. Gas Control*, vol. 16, pp. 278–286, Aug. 2013, doi: 10.1016/j.ijggc.2012.08.017.
- [25] S. Yun, M.-G. Jang, and J.-K. Kim, 'Techno-economic assessment and comparison of absorption and membrane CO₂ capture processes for iron and steel industry', *Energy*, vol. 229, p. 120778, Aug. 2021, doi: 10.1016/j.energy.2021.120778.
- [26] C. Guedard, D. Picq, F. Launay, and P.-L. Carrette, 'Amine degradation in CO₂ capture. I. A review', *Int. J. Greenh. Gas Control*, vol. 10, pp. 244–270, Sep. 2012, doi: 10.1016/j.ijggc.2012.06.015.
- [27] P. Luis, 'Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives', *Desalination*, vol. 380, pp. 93–99, Feb. 2016, doi: 10.1016/j.desal.2015.08.004.
- [28] F. A. Tobiesen, H. F. Svendsen, and T. Mejdell, 'Modeling of Blast Furnace CO₂ Capture Using Amine Absorbents', *Ind. Eng. Chem. Res.*, vol. 46, no. 23, pp. 7811–7819, Nov. 2007, doi: 10.1021/ie061556j.
- [29] Neveux T., Le Moullec Y., Corriou J.P., and Favre E., 'Energy performance of co₂ capture processes: interaction between process design and solvent', *Chem. Eng. Trans.*, vol. 35, pp. 337–342, Sep. 2013, doi: 10.3303/CET1335056.
- [30] X. Ding, H. Chen, J. Li, and T. Zhou, 'Comparative techno-economic analysis of CO₂ capture processes using blended amines', *Carbon Capture Sci. Technol.*, vol. 9, p. 100136, Dec. 2023, doi: 10.1016/j.ccst.2023.100136.
- [31] A. Bandyopadhyay, 'Amine versus ammonia absorption of CO₂ as a measure of reducing GHG emission: a critical analysis', *Clean Technol. Environ. Policy*, vol. 13, no. 2, pp. 269–294, Apr. 2011, doi: 10.1007/s10098-010-0299-z.
- [32] J. Du *et al.*, 'Review on post-combustion CO₂ capture by amine blended solvents and aqueous ammonia', *Chem. Eng. J.*, vol. 488, p. 150954, May 2024, doi: 10.1016/j.cej.2024.150954.
- [33] T. E. Akinola, E. Oko, and M. Wang, 'Study of CO₂ removal in natural gas process using mixture of ionic liquid and MEA through process simulation', *Fuel*, vol. 236, pp. 135–146, Jan. 2019, doi: 10.1016/j.fuel.2018.08.152.

- [34] M. Aghaie, N. Rezaei, and S. Zendehboudi, 'A systematic review on CO₂ capture with ionic liquids: Current status and future prospects', *Renew. Sustain. Energy Rev.*, vol. 96, pp. 502–525, Nov. 2018, doi: 10.1016/j.rser.2018.07.004.
- [35] M. Wang, A. S. Joel, C. Ramshaw, D. Eimer, and N. M. Musa, 'Process intensification for post-combustion CO₂ capture with chemical absorption: A critical review', *Appl. Energy*, vol. 158, pp. 275–291, Nov. 2015, doi: 10.1016/j.apenergy.2015.08.083.
- [36] A. S. Joel, M. Wang, C. Ramshaw, and E. Oko, 'Modelling, simulation and analysis of intensified regenerator for solvent based carbon capture using rotating packed bed technology', *Appl. Energy*, vol. 203, pp. 11–25, Oct. 2017, doi: 10.1016/j.apenergy.2017.05.157.
- [37] J. Choi *et al.*, 'Process design and optimization of MEA-based CO₂ capture processes for non-power industries', *Energy*, vol. 185, pp. 971–980, Oct. 2019, doi: 10.1016/j.energy.2019.07.092.
- [38] E. Mostafavi, O. Ashrafi, and P. Navarri, 'Assessment of process modifications for amine-based post-combustion carbon capture processes', *Clean. Eng. Technol.*, vol. 4, p. 100249, Oct. 2021, doi: 10.1016/j.clet.2021.100249.
- [39] D. Gielen, 'CO₂ removal in the iron and steel industry', *Energy Convers. Manag.*, 2003.
- [40] M. T. Ho, G. W. Allinson, and D. E. Wiley, 'Comparison of MEA capture cost for low CO₂ emissions sources in Australia', *Int. J. Greenh. Gas Control*, vol. 5, no. 1, pp. 49–60, Jan. 2011, doi: 10.1016/j.ijggc.2010.06.004.
- [41] K. Onarheim and A. Arasto, 'Staged implementation of alternative processes in an existing integrated steel mill for improved performance and reduced CO₂ emissions – Part I: Technical concept analysis', *Int. J. Greenh. Gas Control*, vol. 45, pp. 163–171, Feb. 2016, doi: 10.1016/j.ijggc.2015.12.008.
- [42] 'Fundamental Factors for Designing Adsorbent', in *Adsorbents: Fundamentals and Applications*, John Wiley & Sons, Ltd, 2003, pp. 8–16. doi: 10.1002/0471444409X.ch2.
- [43] F. Huhe, J. King, and S. S. C. Chuang, 'Amine-based sorbents for CO₂ capture from air and flue gas—a short review and perspective', *Res. Chem. Intermed.*, vol. 49, no. 3, pp. 791–817, Mar. 2023, doi: 10.1007/s11164-022-04902-7.
- [44] S. Lillia, D. Bonalumi, C. Grande, and G. Manzolini, 'A comprehensive modeling of the hybrid temperature electric swing adsorption process for CO₂ capture', *Int. J. Greenh. Gas Control*, vol. 74, pp. 155–173, Jul. 2018, doi: 10.1016/j.ijggc.2018.04.012.
- [45] R. K. Sahu, S. K. Roy, and P. K. Sen, 'Applicability of Top Gas Recycle Blast Furnace with Downstream Integration and Sequestration in an Integrated Steel Plant', *Steel Res. Int.*, vol. 86, no. 5, pp. 502–516, May 2015, doi: 10.1002/srin.201400196.
- [46] W. H. Saima, Y. Mogi, and T. Haraoka, 'Development of PSA System for the Recovery of Carbon Dioxide and Carbon Monoxide from Blast Furnace Gas in Steel Works', *Energy Procedia*, vol. 37, pp. 7152–7159, 2013, doi: 10.1016/j.egypro.2013.06.652.
- [47] M. Abdul Quader, S. Ahmed, S. Z. Dawal, and Y. Nukman, 'Present needs, recent progress and future trends of energy-efficient Ultra-Low Carbon Dioxide (CO) Steelmaking (ULCOS) program', *Renew. Sustain. Energy Rev.*, vol. 55, pp. 537–549, Mar. 2016, doi: 10.1016/j.rser.2015.10.101.
- [48] A. Arasto, E. Tsupari, J. Kärki, J. Lilja, and M. Sihvonen, 'Oxygen blast furnace with CO₂ capture and storage at an integrated steel mill—Part I: Technical concept analysis', *Int. J. Greenh. Gas Control*, vol. 30, pp. 140–147, Nov. 2014, doi: 10.1016/j.ijggc.2014.09.004.

- [49] J. Zhang, P. A. Webley, and P. Xiao, 'Effect of process parameters on power requirements of vacuum swing adsorption technology for CO₂ capture from flue gas', *Energy Convers. Manag.*, vol. 49, no. 2, pp. 346–356, Feb. 2008, doi: 10.1016/j.enconman.2007.06.007.
- [50] M. T. Ho, G. W. Allinson, and D. E. Wiley, 'Reducing the Cost of CO₂ Capture from Flue Gases Using Pressure Swing Adsorption', *Ind. Eng. Chem. Res.*, vol. 47, no. 14, pp. 4883–4890, Jul. 2008, doi: 10.1021/ie070831e.
- [51] P. A. Webley, A. Qader, A. Ntiamoah, J. Ling, P. Xiao, and Y. Zhai, 'A New Multi-bed Vacuum Swing Adsorption Cycle for CO₂ Capture from Flue Gas Streams', *Energy Procedia*, vol. 114, pp. 2467–2480, Jul. 2017, doi: 10.1016/j.egypro.2017.03.1398.
- [52] P. Xiao, J. Zhang, P. Webley, G. Li, R. Singh, and R. Todd, 'Capture of CO₂ from flue gas streams with zeolite 13X by vacuum-pressure swing adsorption', *Adsorption*, vol. 14, no. 4–5, pp. 575–582, Oct. 2008, doi: 10.1007/s10450-008-9128-7.
- [53] S. Krishnamurthy *et al.*, 'CO₂ capture from dry flue gas by vacuum swing adsorption: A pilot plant study', *AIChE J.*, vol. 60, no. 5, pp. 1830–1842, May 2014, doi: 10.1002/aic.14435.
- [54] R. Haghpanah, R. Nilam, A. Rajendran, S. Farooq, and I. A. Karimi, 'Cycle synthesis and optimization of a VSA process for postcombustion CO₂ capture', *AIChE J.*, vol. 59, no. 12, pp. 4735–4748, Dec. 2013, doi: 10.1002/aic.14192.
- [55] M. Khurana and S. Farooq, 'Integrated Adsorbent Process Optimization for Minimum Cost of Electricity Including Carbon Capture By a VSA Process', *AIChE J.*, vol. 65, no. 1, pp. 184–195, Jan. 2019, doi: 10.1002/aic.16362.
- [56] D. Danaci, M. Bui, N. Mac Dowell, and C. Petit, 'Exploring the limits of adsorption-based CO₂ capture using MOFs with PVSA – from molecular design to process economics', *Mol. Syst. Des. Eng.*, vol. 5, no. 1, pp. 212–231, 2020, doi: 10.1039/C9ME00102F.
- [57] M. Khurana and S. Farooq, 'Simulation and optimization of a 6-step dual-reflux VSA cycle for post-combustion CO₂ capture', *Chem. Eng. Sci.*, vol. 152, pp. 507–515, Oct. 2016, doi: 10.1016/j.ces.2016.06.033.
- [58] S. B. Peh, S. Farooq, and D. Zhao, 'Techno-economic analysis of MOF-based adsorption cycles for postcombustion CO₂ capture from wet flue gas', *Chem. Eng. Sci.*, vol. 268, p. 118390, Mar. 2023, doi: 10.1016/j.ces.2022.118390.
- [59] S. G. Subraveti, S. Roussanaly, R. Anantharaman, L. Riboldi, and A. Rajendran, 'Techno-economic assessment of optimised vacuum swing adsorption for post-combustion CO₂ capture from steam-methane reformer flue gas', *Sep. Purif. Technol.*, vol. 256, p. 117832, Feb. 2021, doi: 10.1016/j.seppur.2020.117832.
- [60] J. C. Li Yuen Fong, C. J. Anderson, G. Xiao, P. A. Webley, and A. F. A. Hoadley, 'Multi-objective optimisation of a hybrid vacuum swing adsorption and low-temperature post-combustion CO₂ capture', *J. Clean. Prod.*, vol. 111, pp. 193–203, Jan. 2016, doi: 10.1016/j.jclepro.2015.08.033.
- [61] N. Jiang *et al.*, 'CO₂ capture from dry flue gas by means of VPSA, TSA and TVSA', *J. CO₂ Util.*, vol. 35, pp. 153–168, Jan. 2020, doi: 10.1016/j.jcou.2019.09.012.
- [62] K. Wu, S. Deng, S. Li, R. Zhao, X. Yuan, and L. Zhao, 'Preliminary experimental study on the performance of CO₂ capture prototype based on temperature swing adsorption (TSA)', *Carbon Capture Sci. Technol.*, vol. 2, p. 100035, Mar. 2022, doi: 10.1016/j.ccst.2022.100035.

- [63] J. Mérel, M. Clausse, and F. Meunier, 'Carbon dioxide capture by indirect thermal swing adsorption using 13X zeolite', *Environ. Prog.*, vol. 25, no. 4, pp. 327–333, 2006, doi: 10.1002/ep.10166.
- [64] L. Wang, Z. Liu, P. Li, J. Yu, and A. E. Rodrigues, 'Experimental and modeling investigation on post-combustion carbon dioxide capture using zeolite 13X-APG by hybrid VTSA process', *Chem. Eng. J.*, vol. 197, pp. 151–161, Jul. 2012, doi: 10.1016/j.cej.2012.05.017.
- [65] G. Hofer, J. Fuchs, G. Schöny, and T. Pröll, 'Heat transfer challenge and design evaluation for a multi-stage temperature swing adsorption process', *Powder Technol.*, vol. 316, pp. 512–518, 2017, doi: 10.1016/j.powtec.2016.12.062.
- [66] B. Golparvar, H. Niazmand, A. Sharafian, and A. Ahmadian Hosseini, 'Optimum fin spacing of finned tube adsorber bed heat exchangers in an exhaust gas-driven adsorption cooling system', *Appl. Energy*, vol. 232, pp. 504–516, Dec. 2018, doi: 10.1016/j.apenergy.2018.10.002.
- [67] C. A. Grande, R. P. L. Ribeiro, E. L. G. Oliveira, and A. E. Rodrigues, 'Electric swing adsorption as emerging CO₂ capture technique', *Energy Procedia*, vol. 1, no. 1, pp. 1219–1225, Feb. 2009, doi: 10.1016/j.egypro.2009.01.160.
- [68] M. Gholami, B. Verougstraete, R. Vanoudenhoven, G. V. Baron, T. Van Assche, and J. F. M. Denayer, 'Induction heating as an alternative electrified heating method for carbon capture process', *Chem. Eng. J.*, vol. 431, p. 133380, Mar. 2022, doi: 10.1016/j.cej.2021.133380.
- [69] Y. Gomez-Rueda, B. Verougstraete, C. Ranga, E. Perez-Botella, F. Reniers, and J. F. M. Denayer, 'Rapid temperature swing adsorption using microwave regeneration for carbon capture', *Chem. Eng. J.*, vol. 446, p. 137345, Oct. 2022, doi: 10.1016/j.cej.2022.137345.
- [70] M. G. Plaza and F. Rubiera, 'Evaluation of a novel multibed heat-integrated vacuum and temperature swing adsorption post-combustion CO₂ capture process', *Appl. Energy*, vol. 250, pp. 916–925, Sep. 2019, doi: 10.1016/j.apenergy.2019.05.079.
- [71] A. S. Holmes, B. C. Price, J. M. Ryan, and R. E. Styring, 'Pilot tests prove out cryogenic acid-gas/hydrocarbon separation processes', *Oil Gas J U. S.*, vol. 81:26, Jun. 1983, [Online]. Available: <https://www.osti.gov/biblio/5285797>
- [72] H. Herzog, D. Golomb, and S. Zemba, 'Feasibility, modeling and economics of sequestering power plant CO₂ emissions in the deep ocean', *Environ. Prog.*, vol. 10, no. 1, pp. 64–74, Feb. 1991, doi: 10.1002/ep.670100118.
- [73] D. Clodic and M. Younes, 'A new Method for CO₂ Capture', in *Greenhouse Gas Control Technologies - 6th International Conference*, J. Gale and Y. Kaya, Eds., Oxford: Pergamon, 2003, pp. 155–160. doi: 10.1016/B978-008044276-1/50025-8.
- [74] X. Pan, D. Clodic, and J. Toubassy, '**CO₂ capture by antisublimation process and its technical economic analysis**', *Greenh. Gases Sci. Technol.*, vol. 3, no. 1, pp. 8–20, Feb. 2013, doi: 10.1002/ghg.1313.
- [75] D. Clodic, 'CO₂ capture by anti-sublimation Thermo-economic process evaluation'.
- [76] M. J. Tuinier, H. P. Hamers, and M. Van Sint Annaland, 'Techno-economic evaluation of cryogenic CO₂ capture—A comparison with absorption and membrane technology', *Int. J. Greenh. Gas Control*, vol. 5, no. 6, pp. 1559–1565, Nov. 2011, doi: 10.1016/j.ijggc.2011.08.013.
- [77] A. Ali, K. Maqsood, N. Syahera, A. B. M. Shariff, and S. Ganguly, 'Energy Minimization in Cryogenic Packed Beds during Purification of Natural Gas with High CO₂ Content',

- Chem. Eng. Technol.*, vol. 37, no. 10, pp. 1675–1685, Oct. 2014, doi: 10.1002/ceat.201400215.
- [78] C. F. Song, Y. Kitamura, and S. H. Li, ‘Evaluation of Stirling cooler system for cryogenic CO₂ capture’, *Appl. Energy*, vol. 98, pp. 491–501, Oct. 2012, doi: 10.1016/j.apenergy.2012.04.013.
 - [79] L. L. Baxter, ‘Carbon dioxide capture from flue gas’, US20110226010A1, Sep. 22, 2011 Accessed: Jun. 14, 2024. [Online]. Available: <https://patents.google.com/patent/US20110226010A1/en>
 - [80] M. Jensen, ‘Energy Process Enabled by Cryogenic Carbon Capture’.
 - [81] L. Baxter, A. Baxter, and S. Burt, ‘Cryogenic CO₂ Capture as a Cost-Effective CO₂ Capture Process’.
 - [82] B. Bellaissaoui, Y. Le Moullec, D. Willson, and E. Favre, ‘Hybrid membrane cryogenic process for post-combustion CO₂ capture’, *J. Membr. Sci.*, vol. 415–416, pp. 424–434, Oct. 2012, doi: 10.1016/j.memsci.2012.05.029.
 - [83] A. F. Ismail, K. C. Khulbe, and T. Matsuura, ‘Gas Separation Membrane Materials and Structures’, in *Gas Separation Membranes: Polymeric and Inorganic*, A. F. Ismail, K. Chandra Khulbe, and T. Matsuura, Eds., Cham: Springer International Publishing, 2015, pp. 37–192. doi: 10.1007/978-3-319-01095-3_3.
 - [84] A. F. Ismail, K. C. Khulbe, and T. Matsuura, ‘Fundamentals of Gas Permeation Through Membranes’, in *Gas Separation Membranes: Polymeric and Inorganic*, A. F. Ismail, K. Chandra Khulbe, and T. Matsuura, Eds., Cham: Springer International Publishing, 2015, pp. 11–35. doi: 10.1007/978-3-319-01095-3_2.
 - [85] T. C. Merkel, H. Lin, X. Wei, and R. Baker, ‘Power plant post-combustion carbon dioxide capture: An opportunity for membranes’, *J. Membr. Sci.*, vol. 359, no. 1–2, pp. 126–139, Sep. 2010, doi: 10.1016/j.memsci.2009.10.041.
 - [86] Y. Huang, T. C. Merkel, and R. W. Baker, ‘Pressure ratio and its impact on membrane gas separation processes’, *J. Membr. Sci.*, vol. 463, pp. 33–40, Aug. 2014, doi: 10.1016/j.memsci.2014.03.016.
 - [87] S. Roussanaly, R. Anantharaman, K. Lindqvist, and B. Hagen, ‘A new approach to the identification of high-potential materials for cost-efficient membrane-based post-combustion CO₂ capture’, *Sustain. Energy Fuels*, vol. 2, no. 6, pp. 1225–1243, May 2018, doi: 10.1039/C8SE00039E.
 - [88] R. W. Baker, B. Freeman, J. Kniep, Y. I. Huang, and T. C. Merkel, ‘CO₂ Capture from Cement Plants and Steel Mills Using Membranes’, *Ind. Eng. Chem. Res.*, vol. 57, no. 47, pp. 15963–15970, Nov. 2018, doi: 10.1021/acs.iecr.8b02574.
 - [89] Á. A. Ramírez-Santos, C. Castel, and E. Favre, ‘Utilization of blast furnace flue gas: Opportunities and challenges for polymeric membrane gas separation processes’, *J. Membr. Sci.*, vol. 526, pp. 191–204, Mar. 2017, doi: 10.1016/j.memsci.2016.12.033.
 - [90] Á. A. Ramírez-Santos, M. Bozorg, B. Addis, V. Piccialli, C. Castel, and E. Favre, ‘Optimization of multistage membrane gas separation processes. Example of application to CO₂ capture from blast furnace gas’, *J. Membr. Sci.*, vol. 566, pp. 346–366, Nov. 2018, doi: 10.1016/j.memsci.2018.08.024.
 - [91] H. Zhai and E. S. Rubin, ‘Techno-Economic Assessment of Polymer Membrane Systems for Postcombustion Carbon Capture at Coal-Fired Power Plants’, *Environ. Sci. Technol.*, vol. 47, no. 6, pp. 3006–3014, Mar. 2013, doi: 10.1021/es3050604.

- [92] S. Roussanaly and R. Anantharaman, ‘Cost-optimal CO₂ capture ratio for membrane-based capture from different CO₂ sources’, *Chem. Eng. J.*, vol. 327, pp. 618–628, Nov. 2017, doi: 10.1016/j.cej.2017.06.082.
- [93] J.-Y. Jeon, B.-R. Park, and J.-H. Kim, ‘Numerical Simulation and Optimization of 4-Component LDG Separation in the Steelmaking Industry Using Polysulfone Hollow Fiber Membranes’, *Membranes*, vol. 12, no. 1, p. 97, Jan. 2022, doi: 10.3390/membranes12010097.
- [94] C. Song *et al.*, ‘Reducing the energy consumption of membrane-cryogenic hybrid CO₂ capture by process optimization’, *Energy*, vol. 124, pp. 29–39, Apr. 2017, doi: 10.1016/j.energy.2017.02.054.
- [95] S. Lee and J.-K. Kim, ‘Sub-ambient membrane process for CO₂ removal in the industrial sector: Iron and steel, cement, and refinery’, *J. Membr. Sci.*, vol. 686, p. 122018, Nov. 2023, doi: 10.1016/j.memsci.2023.122018.
- [96] P. T. Chang, Q. H. Ng, A. L. Ahmad, and S. C. Low, ‘A critical review on the techno-economic analysis of membrane gas absorption for CO₂ capture’, *Chem. Eng. Commun.*, vol. 209, no. 11, pp. 1553–1569, Nov. 2022, doi: 10.1080/00986445.2021.1977926.
- [97] C. A. Scholes, ‘Membrane gas-solvent contactor process for efficient carbon capture from multiple emission sources within an industrial complex’, *Chem. Eng. Sci.*, vol. 278, p. 118915, Aug. 2023, doi: 10.1016/j.ces.2023.118915.
- [98] J. A. Lie, T. Vassbotn, M.-B. Hägg, D. Grainger, T.-J. Kim, and T. Mejdell, ‘Optimization of a membrane process for CO₂ capture in the steelmaking industry’, *Int. J. Greenh. Gas Control*, vol. 1, no. 3, pp. 309–317, Jul. 2007, doi: 10.1016/S1750-5836(07)00069-2.
- [99] M. Micari, M. Dakhchoune, and K. V. Agrawal, ‘Techno-economic assessment of postcombustion carbon capture using high-performance nanoporous single-layer graphene membranes’, *J. Membr. Sci.*, vol. 624, p. 119103, Apr. 2021, doi: 10.1016/j.memsci.2021.119103.
- [100] J. K. Adewole, A. L. Ahmad, S. Ismail, and C. P. Leo, ‘Current challenges in membrane separation of CO₂ from natural gas: A review’, *Int. J. Greenh. Gas Control*, vol. 17, pp. 46–65, Sep. 2013, doi: 10.1016/j.ijggc.2013.04.012.
- [101] L.-S. Fan, L. Zeng, W. Wang, and S. Luo, ‘Chemical looping processes for CO₂ capture and carbonaceous fuel conversion – prospect and opportunity’, *Energy Environ. Sci.*, vol. 5, no. 6, p. 7254, 2012, doi: 10.1039/c2ee03198a.
- [102] J. Li, H. Zhang, Z. Gao, J. Fu, W. Ao, and J. Dai, ‘CO₂ Capture with Chemical Looping Combustion of Gaseous Fuels: An Overview’, *Energy Fuels*, vol. 31, no. 4, pp. 3475–3524, Apr. 2017, doi: 10.1021/acs.energyfuels.6b03204.
- [103] K. Katayama, H. Bahzad, M. Boot-Handford, C. F. Patzschke, and P. S. Fennell, ‘Process Integration of Chemical Looping Water Splitting with a Sintering Plant for Iron Making’, *Ind. Eng. Chem. Res.*, vol. 59, no. 15, pp. 7021–7032, Apr. 2020, doi: 10.1021/acs.iecr.9b05945.
- [104] J. Hu, V. V. Galvita, H. Poelman, and G. B. Marin, ‘Advanced Chemical Looping Materials for CO₂ Utilization: A Review’, *Materials*, vol. 11, no. 7, p. 1187, Jul. 2018, doi: 10.3390/ma11071187.
- [105] J. Blamey, E. J. Anthony, J. Wang, and P. S. Fennell, ‘The calcium looping cycle for large-scale CO₂ capture’, *Prog. Energy Combust. Sci.*, vol. 36, no. 2, pp. 260–279, Apr. 2010, doi: 10.1016/j.pecs.2009.10.001.

- [106] R. C. Toledo, G. L. A. F. Arce, J. A. Carvalho, and I. Ávila, 'Experimental Development of Calcium Looping Carbon Capture Processes: An Overview of Opportunities and Challenges', *Energies*, vol. 16, no. 9, p. 3623, Apr. 2023, doi: 10.3390/en16093623.
- [107] S. Tian, J. Jiang, F. Yan, K. Li, and X. Chen, 'Synthesis of Highly Efficient CaO-Based, Self-Stabilizing CO₂ Sorbents via Structure-Reforming of Steel Slag', *Environ. Sci. Technol.*, vol. 49, no. 12, pp. 7464–7472, Jun. 2015, doi: 10.1021/acs.est.5b00244.
- [108] S. M. Hashemi, M. H. Sedghkardar, and N. Mahinpey, 'Calcium looping carbon capture: Progress and prospects', *Can. J. Chem. Eng.*, vol. 100, no. 9, pp. 2140–2171, Sep. 2022, doi: 10.1002/cjce.24480.
- [109] H. Xie, Q. Yu, Y. Zhang, J. Zhang, J. Liu, and Q. Qin, 'New process for hydrogen production from raw coke oven gas via sorption-enhanced steam reforming: Thermodynamic analysis', *Int. J. Hydrog. Energy*, vol. 42, no. 5, pp. 2914–2923, Feb. 2017, doi: 10.1016/j.ijhydene.2016.12.046.
- [110] D. Xiang and S. Zhao, 'Parameter optimization and thermodynamic analysis of COG direct chemical looping hydrogen processes', *Energy Convers. Manag.*, vol. 172, pp. 1–8, Sep. 2018, doi: 10.1016/j.enconman.2018.07.007.
- [111] M. H. Ibrahim, M. H. El-Naas, A. Benamor, S. S. Al-Sobhi, and Z. Zhang, 'Carbon Mineralization by Reaction with Steel-Making Waste: A Review', *Processes*, vol. 7, no. 2, p. 115, Feb. 2019, doi: 10.3390/pr7020115.
- [112] A.-M. Cormos, S. Dragan, L. Petrescu, V. Sandu, and C.-C. Cormos, 'Techno-Economic and Environmental Evaluations of Decarbonized Fossil-Intensive Industrial Processes by Reactive Absorption & Adsorption CO₂ Capture Systems', *Energies*, vol. 13, no. 5, p. 1268, Mar. 2020, doi: 10.3390/en13051268.
- [113] J. K. Stolaroff, G. V. Lowry, and D. W. Keith, 'Using CaO- and MgO-rich industrial waste streams for carbon sequestration', *Energy Convers. Manag.*, vol. 46, no. 5, pp. 687–699, Mar. 2005, doi: 10.1016/j.enconman.2004.05.009.
- [114] W. J. J. Huijgen, R. N. J. Comans, and G.-J. Witkamp, 'Cost evaluation of CO₂ sequestration by aqueous mineral carbonation', *Energy Convers. Manag.*, vol. 48, no. 7, pp. 1923–1935, Jul. 2007, doi: 10.1016/j.enconman.2007.01.035.
- [115] I. Martínez, J. R. Fernández, J. C. Abanades, and M. C. Romano, 'Integration of a fluidised bed Ca–Cu chemical looping process in a steel mill', *Energy*, vol. 163, pp. 570–584, Nov. 2018, doi: 10.1016/j.energy.2018.08.123.
- [116] J. R. Fernández, I. Martínez, J. C. Abanades, and M. C. Romano, 'Conceptual design of a Ca–Cu chemical looping process for hydrogen production in integrated steelworks', *Int. J. Hydrog. Energy*, vol. 42, no. 16, pp. 11023–11037, Apr. 2017, doi: 10.1016/j.ijhydene.2017.02.141.
- [117] J. R. Fernández, V. Spallina, and J. C. Abanades, 'Advanced Packed-Bed Ca-Cu Looping Process for the CO₂ Capture From Steel Mill Off-Gases', *Front. Energy Res.*, vol. 8, p. 146, Jul. 2020, doi: 10.3389/fenrg.2020.00146.
- [118] S. Tian, K. Li, J. Jiang, X. Chen, and F. Yan, 'CO₂ abatement from the iron and steel industry using a combined Ca–Fe chemical loop', *Appl. Energy*, vol. 170, pp. 345–352, May 2016, doi: 10.1016/j.apenergy.2016.02.120.
- [119] 'The Lens - Free & Open Patent and Scholarly Search', The Lens - Free & Open Patent and Scholarly Search. Accessed: Jun. 16, 2024. [Online]. Available: <https://www.lens.org/lens>

- [120] ‘Al Reyadah Carbon Capture, Use, and Storage (CCUS) Project | Carbon Sequestration Leadership Forum’. Accessed: Jun. 12, 2024. [Online]. Available: <https://fossil.energy.gov/archives/cslf/Projects/AlReyadah.html>
- [121] ‘Carbon capture for steel?’ Accessed: Jun. 12, 2024. [Online]. Available: <https://ieefa.org/resources/carbon-capture-steel>
- [122] M. Loughrey, H. Barlough, and S. Shahi, ‘State of the Art: CCS Technologies 2023’, Global CCS Institute, 2023. [Online]. Available: <https://www.globalccsinstitute.com/resources/publications-reports-research/state-of-the-art-ccs-technologies-2023/>
- [123] N. Parkinson, ‘Steps to capture economic viability’, *CARBON CAPTURE*.
- [124] N. E. L. Haugen *et al.*, ‘Building the world’s largest Chemical Looping Combustion (CLC) unit’, *Int. J. Greenh. Gas Control*, vol. 129, p. 103975, Oct. 2023, doi: 10.1016/j.ijggc.2023.103975.
- [125] ‘Final Report Summary - SCARLET (Scale-up of Calcium Carbonate Looping Technology for Efficient CO₂ Capture from Power and Industrial Plants) | FP7’, CORDIS | European Commission. Accessed: Jun. 17, 2024. [Online]. Available: <https://cordis.europa.eu/project/id/608578/reporting>
- [126] D. D. Kearns, ‘TECHNOLOGY READINESS AND COSTS OF CCS’.
- [127] R. Krishnamurthy and R. Taylor, ‘A nonequilibrium stage model of multicomponent separation processes. Part I: Model description and method of solution’, *AIChE J.*, vol. 31, no. 3, pp. 449–456, 1985, doi: 10.1002/aic.690310312.
- [128] Y. Zhang, H. Chen, C.-C. Chen, J. M. Plaza, R. Dugas, and G. T. Rochelle, ‘Rate-Based Process Modeling Study of CO₂ Capture with Aqueous Monoethanolamine Solution’, *Ind. Eng. Chem. Res.*, vol. 48, no. 20, pp. 9233–9246, Oct. 2009, doi: 10.1021/ie900068k.
- [129] M. Afkhamipour and M. Mofarahi, ‘Comparison of rate-based and equilibrium-stage models of a packed column for post-combustion CO₂ capture using 2-amino-2-methyl-1-propanol (AMP) solution’, *Int. J. Greenh. Gas Control*, vol. 15, pp. 186–199, Jul. 2013, doi: 10.1016/j.ijggc.2013.02.022.
- [130] J. W. (Josiah W. Gibbs, J. Tyndall, Connecticut Academy of Arts and Sciences, and donor D. Burndy Library, *On the equilibrium of heterogeneous substances : first [-second] part*. [New Haven : Published by the Academy], 1874. Accessed: Jul. 02, 2024. [Online]. Available: <http://archive.org/details/Onequilibriumhe00Gibb>
- [131] G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*. Courier Dover Publications, 2020.
- [132] C.-C. Chen and L. B. Evans, ‘A local composition model for the excess Gibbs energy of aqueous electrolyte systems’, *AIChE J.*, vol. 32, no. 3, pp. 444–454, 1986, doi: 10.1002/aic.690320311.
- [133] J. M. Smith, *Introduction to chemical engineering thermodynamics.*, 7th ed. / J.M. Smith, H.C. Van Ness, M.M. Abbott. in McGraw-Hill chemical engineering series. Boston ; McGraw-Hill, 2005.
- [134] M. D. Hilliard, ‘A predictive thermodynamic model for an aqueous blend of potassium carbonate, piperazine, and monoethanolamine for carbon dioxide capture from flue gas’, May 2008, Accessed: Jul. 03, 2024. [Online]. Available: <http://hdl.handle.net/2152/3900>
- [135] *Aspen Physical Property System*. (2021). Aspen Technology Inc., Bedford, MA.
- [136] M. Amirkhosrow, J.-F. Pérez-Calvo, M. Gazzani, M. Mazzotti, and E. Nemati Lay, ‘Rigorous rate-based model for CO₂ capture via monoethanolamine-based solutions:

- effect of kinetic models, mass transfer, and holdup correlations on prediction accuracy', *Sep. Sci. Technol.*, vol. 56, no. 9, pp. 1491–1509, Jun. 2021, doi: 10.1080/01496395.2020.1784943.
- [137] K. R. Putta, H. F. Svendsen, and H. K. Knuutila, 'CO₂ absorption into loaded aqueous MEA solutions: Impact of different model parameter correlations and thermodynamic models on the absorption rate model predictions', *Chem. Eng. J.*, vol. 327, pp. 868–880, Nov. 2017, doi: 10.1016/j.cej.2017.06.134.
- [138] R. Ramezani, I. M. Bernhardsen, R. Di Felice, and H. K. Knuutila, 'Physical properties and reaction kinetics of CO₂ absorption into unloaded and CO₂ loaded viscous monoethanolamine (MEA) solution', *J. Mol. Liq.*, vol. 329, p. 115569, May 2021, doi: 10.1016/j.molliq.2021.115569.
- [139] N. Razi, O. Bolland, and H. Svendsen, 'Review of design correlations for CO₂ absorption into MEA using structured packings', *Int. J. Greenh. Gas Control*, vol. 9, pp. 193–219, Jul. 2012, doi: 10.1016/j.ijggc.2012.03.003.
- [140] N. Razi, H. F. Svendsen, and O. Bolland, 'The Impact of Design Correlations on Rate-based Modeling of a Large Scale CO₂ Capture with MEA', *Energy Procedia*, vol. 37, pp. 1977–1986, 2013, doi: 10.1016/j.egypro.2013.06.078.
- [141] N. Razi, H. F. Svendsen, and O. Bolland, 'Validation of mass transfer correlations for CO₂ absorption with MEA using pilot data', *Int. J. Greenh. Gas Control*, vol. 19, pp. 478–491, Nov. 2013, doi: 10.1016/j.ijggc.2013.10.006.
- [142] A. Aboudheir, P. Tontiwachwuthikul, A. Chakma, and R. Idem, 'Kinetics of the reactive absorption of carbon dioxide in high CO₂-loaded, concentrated aqueous monoethanolamine solutions', *Chem. Eng. Sci.*, vol. 58, no. 23–24, pp. 5195–5210, Dec. 2003, doi: 10.1016/j.ces.2003.08.014.
- [143] P. V. Danckwerts, 'The reaction of CO₂ with ethanolamines', *Chem. Eng. Sci.*, vol. 34, no. 4, pp. 443–446, Jan. 1979, doi: 10.1016/0009-2509(79)85087-3.
- [144] J. E. Crooks and J. P. Donnellan, 'Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution', *J. Chem. Soc. Perkin Trans. 2*, no. 4, p. 331, 1989, doi: 10.1039/p29890000331.
- [145] G. F. Versteeg, L. A. J. Van Dijk, and W. P. M. Van Swaaij, 'ON THE KINETICS BETWEEN CO₂ AND ALKANOLAMINES BOTH IN AQUEOUS AND NON-AQUEOUS SOLUTIONS. AN OVERVIEW', *Chem. Eng. Commun.*, vol. 144, no. 1, pp. 113–158, Feb. 1996, doi: 10.1080/00986449608936450.
- [146] H. Hikita, S. Asai, H. Ishikawa, and M. Honda, 'The kinetics of reactions of carbon dioxide with monoethanolamine, diethanolamine and triethanolamine by a rapid mixing method', *Chem. Eng. J.*, vol. 13, no. 1, pp. 7–12, 1977, doi: 10.1016/0300-9467(77)80002-6.
- [147] S.-Y. Horng and M.-H. Li, 'Kinetics of Absorption of Carbon Dioxide into Aqueous Solutions of Monoethanolamine + Triethanolamine', *Ind. Eng. Chem. Res.*, vol. 41, no. 2, pp. 257–266, Jan. 2002, doi: 10.1021/ie010671l.
- [148] X. Luo, A. Hartono, S. Hussain, and H. F. Svendsen, 'Mass transfer and kinetics of carbon dioxide absorption into loaded aqueous monoethanolamine solutions', *Chem. Eng. Sci.*, vol. 123, pp. 57–69, Feb. 2015, doi: 10.1016/j.ces.2014.10.013.
- [149] G. P. Towler and R. Sinnott, Eds., *Chemical engineering design: principles, practice and economics of plant and process design*. Amsterdam Boston: Elsevier/Butterworth-Heinemann, 2008.

- [150] R. Notz, H. P. Mangalapally, and H. Hasse, 'Post combustion CO₂ capture by reactive absorption: Pilot plant description and results of systematic studies with MEA', *Int. J. Greenh. Gas Control*, vol. 6, pp. 84–112, Jan. 2012, doi: 10.1016/j.ijggc.2011.11.004.
- [151] F. A. Tobiesen, H. F. Svendsen, and O. Juliussen, 'Experimental validation of a rigorous absorber model for CO₂ postcombustion capture', *AIChE J.*, vol. 53, no. 4, pp. 846–865, Apr. 2007, doi: 10.1002/aic.11133.
- [152] F. A. Tobiesen, O. Juliussen, and H. F. Svendsen, 'Experimental validation of a rigorous desorber model for CO₂ post-combustion capture', *Chem. Eng. Sci.*, vol. 63, no. 10, pp. 2641–2656, May 2008, doi: 10.1016/j.ces.2008.02.011.
- [153] C. Madeddu, M. Errico, and R. Baratti, *CO₂ Capture by Reactive Absorption-Stripping: Modeling, Analysis and Design*. in SpringerBriefs in Energy. Cham: Springer International Publishing, 2019. doi: 10.1007/978-3-030-04579-1.
- [154] D. S. Mallapragada *et al.*, 'Decarbonization of the chemical industry through electrification: Barriers and opportunities', *Joule*, vol. 7, no. 1, pp. 23–41, Jan. 2023, doi: 10.1016/j.joule.2022.12.008.
- [155] S. Giannaris, B. Jacobs, W. Srisang, C. Bruce, and D. Janowczyk, 'Heat integration analysis and optimization for a post combustion CO₂ capture retrofit study of SaskPower's Shand Power Station', *Int. J. Greenh. Gas Control*, vol. 84, pp. 62–71, May 2019, doi: 10.1016/j.ijggc.2019.02.018.
- [156] Y. Hu, G. Xu, C. Xu, and Y. Yang, 'Thermodynamic analysis and techno-economic evaluation of an integrated natural gas combined cycle (NGCC) power plant with post-combustion CO₂ capture', *Appl. Therm. Eng.*, vol. 111, pp. 308–316, Jan. 2017, doi: 10.1016/j.applthermaleng.2016.09.094.
- [157] Z. Huang *et al.*, 'Thermal Integration of Postcombustion CO₂ Capture in Existing Natural Gas Combined Cycle–Combined Heat and Power Plant', *J. Energy Eng.*, vol. 143, no. 5, p. 04017025, Oct. 2017, doi: 10.1061/(ASCE)EY.1943-7897.0000455.
- [158] T. Bullen and S. Ferguson, 'Efficiency improvements in fossil-fired power generation with post-combustion carbon capture via improved heat integration and reuse of low grade heat'.
- [159] D. P. Hanak, C. Biliyok, H. Yeung, and R. Białlecki, 'Heat integration and exergy analysis for a supercritical high-ash coal-fired power plant integrated with a post-combustion carbon capture process', *Fuel*, vol. 134, pp. 126–139, Oct. 2014, doi: 10.1016/j.fuel.2014.05.036.
- [160] M. Sundqvist, M. Biermann, F. Normann, M. Larsson, and L. Nilsson, 'Evaluation of low and high level integration options for carbon capture at an integrated iron and steel mill', *Int. J. Greenh. Gas Control*, vol. 77, pp. 27–36, Oct. 2018, doi: 10.1016/j.ijggc.2018.07.008.
- [161] M. Biermann, H. Ali, M. Sundqvist, M. Larsson, F. Normann, and F. Johnsson, 'Excess heat-driven carbon capture at an integrated steel mill – Considerations for capture cost optimization', *Int. J. Greenh. Gas Control*, vol. 91, p. 102833, Dec. 2019, doi: 10.1016/j.ijggc.2019.102833.
- [162] Y. Yang *et al.*, 'Techno-economic assessment and exergy analysis of iron and steel plant coupled MEA-CO₂ capture process', *J. Clean. Prod.*, vol. 416, p. 137976, Sep. 2023, doi: 10.1016/j.jclepro.2023.137976.
- [163] Y. S. Jeong, J. Jung, U. Lee, C. Yang, and C. Han, 'Techno-economic analysis of mechanical vapor recompression for process integration of post-combustion CO₂ capture

- with downstream compression’, *Chem. Eng. Res. Des.*, vol. 104, pp. 247–255, Dec. 2015, doi: 10.1016/j.cherd.2015.08.016.
- [164] T. Harkin, A. Hoadley, and B. Hooper, ‘Reducing the energy penalty of CO₂ capture and compression using pinch analysis’, *J. Clean. Prod.*, vol. 18, no. 9, pp. 857–866, Jun. 2010, doi: 10.1016/j.jclepro.2010.02.011.
- [165] K. Zhang, Z. Liu, S. Huang, and Y. Li, ‘Process integration analysis and improved options for an MEA CO₂ capture system based on the pinch analysis’, *Appl. Therm. Eng.*, vol. 85, pp. 214–224, Jun. 2015, doi: 10.1016/j.applthermaleng.2015.03.073.
- [166] R. Zhai, H. Liu, H. Wu, H. Yu, and Y. Yang, ‘Analysis of Integration of MEA-Based CO₂ Capture and Solar Energy System for Coal-Based Power Plants Based on Thermo-Economic Structural Theory’, *Energies*, vol. 11, no. 5, Art. no. 5, May 2018, doi: 10.3390/en11051284.
- [167] A. Qadir, N. Abdul Manaf, and A. Abbas, ‘Analysis of the integration of a steel plant in Australia with a carbon capture system powered by renewable energy and NG-CHP’, *J. Clean. Prod.*, vol. 168, pp. 97–104, 2017, doi: 10.1016/j.jclepro.2017.09.001.
- [168] C. Brunner, ‘Solar Heat Integrations in Industrial Processes’, IEA Solar Heating and Cooling Technology Collaboration Programme, May 2020. [Online]. Available: <https://task49.iea-shc.org/Data/Sites/1/publications/IEA-SHC-Technology-Position-Paper--Solar-Heat-Integrations-Industrial-Processes--May2020.pdf>
- [169] S. Moran, ‘Section: 21.6.2 Where’s the Harm? The Downside of Academic “Process Integration”’, in *Applied Guide to Process and Plant Design (2nd Edition)*, Elsevier. [Online]. Available: <https://app.knovel.com/hotlink/pdf/id:kt0122VU49/applied-guide-process/wheres-harm-downside>
- [170] C. Schoeneberger, J. Zhang, C. McMillan, J. B. Dunn, and E. Masanet, ‘Electrification potential of U.S. industrial boilers and assessment of the GHG emissions impact’, *Adv. Appl. Energy*, vol. 5, p. 100089, Feb. 2022, doi: 10.1016/j.adapen.2022.100089.
- [171] P.-H. Lin, P.-H. Wang, and A.-T. Huang, ‘Exergy Analysis of a Coke Dry Quenching System’.
- [172] M. R. Errera and L. F. Milanez, ‘Thermodynamic analysis of a coke dry quenching unit’, *Energy Convers. Manag.*, vol. 41, no. 2, pp. 109–127, Jan. 2000, doi: 10.1016/S0196-8904(99)00090-4.
- [173] ‘Coke Dry Quenching Plants’. Accessed: Nov. 06, 2024. [Online]. Available: <https://www.thyssenkrupp-uhde.com/en/products-and-services/coke-plant-technologies/coke-dry-quenching-plants>
- [174] ‘Coke Dry Quenching (CDQ) System | NIPPON STEEL ENGINEERING’. Accessed: Nov. 06, 2024. [Online]. Available: https://www.eng.nipponsteel.com/en/business/steelplants/ironmaking/coke_dry_quenching/
- [175] ‘Clean Coal Technologies in Japan’, Japan Carbon Frontier Organization; New Energy and Industrial Technology Development Organization (NEDO); the Japan Coal Energy Center (JCOAL), 2004. Accessed: Nov. 06, 2024. [Online]. Available: https://www.jcoal.or.jp/eng/upload/cctin_japan_2_3A5.pdf
- [176] I. J. McDonald and A. Werner, ‘DRY SLAG GRANULATION WITH HEAT RECOVERY’, in *Anais dos Seminários de Redução, Minério de Ferro e Aglomeração*, Rio de Janeiro: Editora Blucher, Sep. 2017, pp. 286–295. doi: 10.5151/2594-357X-26526.

- [177] H. Wang, J.-J. Wu, X. Zhu, Q. Liao, and L. Zhao, 'Energy–environment–economy evaluations of commercial scale systems for blast furnace slag treatment: Dry slag granulation vs. water quenching', *Appl. Energy*, vol. 171, pp. 314–324, Jun. 2016, doi: 10.1016/j.apenergy.2016.03.079.
- [178] CSIRO, 'Dry slag granulation: producing valuable by-products from waste'. Accessed: Nov. 30, 2024. [Online]. Available: <https://www.csiro.au/en/work-with-us/industries/mining-resources/Processing/Dry-slag-granulation>
- [179] M. Guzzon, M. Bissoli, E. J. Chiarullo, and E. Malfa, 'Tenova's dry slag granulation process: The experience on EAF and LF slag in steel industry'.
- [180] S. Jahanshahi, Y. Pan, and D. Xie, 'Some Fundamental Aspects of the Dry Slag Granulation Process'.
- [181] T. J. Kotas, *The exergy method of thermal plant analysis*. London ; Butterworths, 1985.
- [182] T. Norgate, D. Xie, and S. Jahanshani, 'Economic and Environmental Evaluation of Slag Dry Granulation', presented at the SCANMET IV - 4th International Conference on Process Development in Iron and Steelmaking, Lulea, Sweden: CSIRO Minerals Down Under Flagship, 2012. [Online]. Available: https://www.researchgate.net/publication/281372721_Economic_and_environmental_evaluation_of_slag_dry_granulation
- [183] C. W. Skarstrom, 'Method and apparatus for fractionating gaseous mixtures by adsorption', US2944627A, Jul. 12, 1960 Accessed: Aug. 07, 2024. [Online]. Available: <https://patents.google.com/patent/US2944627A/en>
- [184] W. D. Marsh, F. S. Pramuk, R. C. Hoke, and C. W. Skarstrom, 'Pressure equalization depressuring in heatless adsorption', US3142547A, Jul. 28, 1964 Accessed: Aug. 07, 2024. [Online]. Available: <https://patents.google.com/patent/US3142547A/en>
- [185] J.-S. Lee, J.-H. Kim, J.-T. Kim, J.-K. Suh, J.-M. Lee, and C.-H. Lee, 'Adsorption Equilibria of CO₂ on Zeolite 13X and Zeolite X/Activated Carbon Composite', *J. Chem. Eng. Data*, vol. 47, no. 5, pp. 1237–1242, Sep. 2002, doi: 10.1021/je020050e.
- [186] K. T. Chue, J. N. Kim, Y. J. Yoo, S. H. Cho, and R. T. Yang, 'Comparison of Activated Carbon and Zeolite 13X for CO₂ Recovery from Flue Gas by Pressure Swing Adsorption', *Ind. Eng. Chem. Res.*, vol. 34, no. 2, pp. 591–598, Feb. 1995, doi: 10.1021/ie00041a020.
- [187] R. P. Loughran *et al.*, 'CO₂ capture from wet flue gas using a water-stable and cost-effective metal-organic framework', *Cell Rep. Phys. Sci.*, vol. 4, no. 7, p. 101470, Jul. 2023, doi: 10.1016/j.xcrp.2023.101470.
- [188] T. T. T. Nguyen, J.-B. Lin, G. K. H. Shimizu, and A. Rajendran, 'Separation of CO₂ and N₂ on a hydrophobic metal organic framework CALF-20', *Chem. Eng. J.*, vol. 442, p. 136263, Aug. 2022, doi: 10.1016/j.cej.2022.136263.
- [189] A. K. Rajagopalan, A. M. Avila, and A. Rajendran, 'Do adsorbent screening metrics predict process performance? A process optimisation based study for post-combustion capture of CO₂', *Int. J. Greenh. Gas Control*, vol. 46, pp. 76–85, Mar. 2016, doi: 10.1016/j.ijggc.2015.12.033.
- [190] C.-T. Chou and C.-Y. Chen, 'Carbon dioxide recovery by vacuum swing adsorption', *Sep. Purif. Technol.*, vol. 39, no. 1–2, pp. 51–65, Oct. 2004, doi: 10.1016/j.seppur.2003.12.009.
- [191] J. Zhang, P. A. Webley, and P. Xiao, 'Effect of process parameters on power requirements of vacuum swing adsorption technology for CO₂ capture from flue gas', *Energy Convers. Manag.*, vol. 49, no. 2, pp. 346–356, Feb. 2008, doi: 10.1016/j.enconman.2007.06.007.

- [192] M. Khurana and S. Farooq, 'Simulation and optimization of a 6-step dual-reflux VSA cycle for post-combustion CO₂ capture', *Chem. Eng. Sci.*, vol. 152, pp. 507–515, Oct. 2016, doi: 10.1016/j.ces.2016.06.033.
- [193] A. Henrotin *et al.*, 'Lab-scale pilot for CO₂ capture vacuum pressure swing adsorption: MIL-160(Al) vs zeolite 13X', *Carbon Capture Sci. Technol.*, vol. 12, p. 100224, Sep. 2024, doi: 10.1016/j.ccst.2024.100224.
- [194] L. Estupiñan Perez, P. Sarkar, and A. Rajendran, 'Experimental validation of multi-objective optimization techniques for design of vacuum swing adsorption processes', *Sep. Purif. Technol.*, vol. 224, pp. 553–563, Oct. 2019, doi: 10.1016/j.seppur.2019.05.039.
- [195] Y. Park, Y. Ju, D. Park, and C.-H. Lee, 'Adsorption equilibria and kinetics of six pure gases on pelletized zeolite 13X up to 1.0 MPa: CO₂, CO, N₂, CH₄, Ar and H₂', *Chem. Eng. J.*, vol. 292, pp. 348–365, May 2016, doi: 10.1016/j.cej.2016.02.046.
- [196] S. Krishnamurthy *et al.*, 'CO₂ capture from dry flue gas by vacuum swing adsorption: A pilot plant study', *AIChE J.*, vol. 60, no. 5, pp. 1830–1842, May 2014, doi: 10.1002/aic.14435.
- [197] G. Mondino, C. A. Grande, R. Blom, and L. O. Nord, 'Moving bed temperature swing adsorption for CO₂ capture from a natural gas combined cycle power plant', *Int. J. Greenh. Gas Control*, vol. 85, pp. 58–70, Jun. 2019, doi: 10.1016/j.ijggc.2019.03.021.
- [198] L. GmbH, 'DRYVAC DV 1200 | Leybold', Leybold Online Shop. Accessed: Nov. 25, 2024. [Online]. Available: <https://www.leyboldproducts.com/products/dry-compressing-vacuum-pumps/dryvac/pumps/704/dryvac-dv-1200>
- [199] A. Copco, 'GHS with VSD technology - Atlas Copco Canada'. Accessed: Nov. 25, 2024. [Online]. Available: <https://www.atlascopco.com/en-ca/vacuum-solutions/products/oil-sealed-vacuum-pumps/oil-sealed-screw-pumps/ghs-with-vs-d-technology>
- [200] T. A. Davis and I. S. Duff, 'An Unsymmetric-Pattern Multifrontal Method for Sparse LU Factorization', *SIAM J. Matrix Anal. Appl.*, vol. 18, no. 1, pp. 140–158, Jan. 1997, doi: 10.1137/S0895479894246905.
- [201] A. S. T. Chiang, 'Arithmetic of PSA process scheduling', *AIChE J.*, vol. 34, no. 11, pp. 1910–1912, Nov. 1988, doi: 10.1002/aic.690341118.
- [202] O. J. Smith and A. W. Westerberg, 'Mixed-integer programming for pressure swing adsorption cycle scheduling', *Chem. Eng. Sci.*, vol. 45, no. 9, pp. 2833–2842, 1990, doi: 10.1016/0009-2509(90)80176-F.
- [203] A. Mehrotra, A. D. Ebner, and J. A. Ritter, 'Simplified graphical approach for complex PSA cycle scheduling', *Adsorption*, vol. 17, no. 2, pp. 337–345, Apr. 2011, doi: 10.1007/s10450-011-9326-6.
- [204] A. Mehrotra, A. D. Ebner, and J. A. Ritter, 'Arithmetic approach for complex PSA cycle scheduling', *Adsorption*, vol. 16, no. 3, pp. 113–126, Aug. 2010, doi: 10.1007/s10450-010-9211-8.
- [205] K. N. Son, T.-M. J. Richardson, and G. E. Cmarik, 'Equilibrium Adsorption Isotherms for H₂O on Zeolite 13X', *J. Chem. Eng. Data*, vol. 64, no. 3, pp. 1063–1071, Mar. 2019, doi: 10.1021/acs.jced.8b00961.
- [206] L. Joos, J. A. Swisher, and B. Smit, 'Molecular Simulation Study of the Competitive Adsorption of H₂O and CO₂ in Zeolite 13X', *Langmuir*, vol. 29, no. 51, pp. 15936–15942, Dec. 2013, doi: 10.1021/la403824g.

- [207] K. C. Ng *et al.*, ‘Experimental investigation of the silica gel–water adsorption isotherm characteristics’, *Appl. Therm. Eng.*, vol. 21, no. 16, pp. 1631–1642, Nov. 2001, doi: 10.1016/S1359-4311(01)00039-4.
- [208] V. R. Joseph, E. Gul, and S. Ba, ‘Designing computer experiments with multiple types of factors: The MaxPro approach’, *J. Qual. Technol.*, vol. 52, no. 4, pp. 343–354, Oct. 2020, doi: 10.1080/00224065.2019.1611351.
- [209] C. Cortes and V. Vapnik, ‘Support-Vector Networks’, *Mach Learn*, vol. 20, no. 3, pp. 273–297, Sep. 1995, doi: 10.1023/A:1022627411411.
- [210] T. Hastie, R. Tibshirani, and J. Friedman, ‘Support Vector Machines and Flexible Discriminants’, in *The Elements of Statistical Learning: Data Mining, Inference, and Prediction*, T. Hastie, R. Tibshirani, and J. Friedman, Eds., New York, NY: Springer, 2009, pp. 417–458. doi: 10.1007/978-0-387-84858-7_12.
- [211] C. E. Rasmussen and C. K. I. Williams, *Gaussian Processes for Machine Learning*. The MIT Press, 2005. doi: 10.7551/mitpress/3206.001.0001.
- [212] I. Goodfellow, Y. Bengio, and A. Courville, *Deep Learning*. MIT Press, 2016.
- [213] D. E. Goldberg, *Genetic Algorithms in Search, Optimization, and Machine Learning*. Addison-Wesley, 1989.
- [214] K. Deb, ‘An efficient constraint handling method for genetic algorithms’, *Comput. Methods Appl. Mech. Eng.*, vol. 186, no. 2, pp. 311–338, Jun. 2000, doi: 10.1016/S0045-7825(99)00389-8.
- [215] E. and C. C. Canada, ‘Pre-publication: Proposed update to the carbon intensity of natural gas – early notice’. Accessed: Sep. 30, 2024. [Online]. Available: <https://www.canada.ca/en/environment-climate-change/services/managing-pollution/fuel-life-cycle-assessment-model/pre-publication-proposed-update-carbon-intensity-natural-gas-early-notice.html>
- [216] E. and C. C. Canada, ‘Emission factors and reference values’. Accessed: Sep. 30, 2024. [Online]. Available: <https://www.canada.ca/en/environment-climate-change/services/climate-change/pricing-pollution-how-it-will-work/output-based-pricing-system/federal-greenhouse-gas-offset-system/emission-factors-reference-values.html>
- [217] T. P. Wright, ‘Factors Affecting the Cost of Airplanes’, *J. Aeronaut. Sci.*, vol. 3, no. 4, pp. 122–128, Feb. 1936, doi: 10.2514/8.155.
- [218] A. Hurwitz, ‘Einige Eigenschaften der Dirichletschen Functionen $F(s) = \sum (\frac{D_n}{n}) \cdot \frac{1}{n}$, die bei der Bestimmung der Klassenanzahlen binärer quadratischer Formen auftreten’, *Z. Für Math U Phys.*, vol. 27, pp. 86–101, 1882.
- [219] ‘DLMF: §25.11 Hurwitz Zeta Function ▶ Related Functions ▶ Chapter 25 Zeta and Related Functions’. Accessed: Dec. 09, 2024. [Online]. Available: <https://dlmf.nist.gov/25.11#E1>
- [220] ‘Triethylene Glycol (TEG) Prices, News, Chart and Demand’. Accessed: Sep. 30, 2024. [Online]. Available: <https://www.imarcgroup.com/triethylene-glycol-pricing-report>
- [221] I. Alerts, ‘Monoethanolamine Prices | Historical and Current’, Intratec.us. Accessed: Nov. 06, 2024. [Online]. Available: <https://www.intratec.us/chemical-markets/monoethanolamine-price>
- [222] I. Alerts, ‘Propylene Prices | Current and Forecast’, Intratec.us. Accessed: Nov. 06, 2024. [Online]. Available: <https://www.intratec.us/chemical-markets/propylene-price>
- [223] ‘Natural Gas Prices | Alberta Economic Dashboard’. Accessed: Sep. 30, 2024. [Online]. Available: <https://economicdashboard.alberta.ca/dashboard/natural-gas-price/>

- [224] 'Industrial electricity prices in major Canadian cities', Statista. Accessed: Nov. 06, 2024. [Online]. Available: <https://www.statista.com/statistics/579159/average-industrial-electricity-prices-canada-by-major-city/>
- [225] E. and S. D. Canada, 'Manager, Gas Supply Operations in Canada | Wages - Job Bank'. Accessed: Sep. 30, 2024. [Online]. Available: http://www.jobbank.gc.ca/explore_career/job_market_report/wage_occupation_report.xhtml
- [226] E. and S. D. Canada, 'Engineer, Natural Gas in Canada | Wages - Job Bank'. Accessed: Sep. 30, 2024. [Online]. Available: http://www.jobbank.gc.ca/explore_career/job_market_report/wage_occupation_report.xhtml
- [227] E. and S. D. Canada, 'Petroleum Processing Shift Supervisor in Canada | Wages - Job Bank'. Accessed: Sep. 30, 2024. [Online]. Available: http://www.jobbank.gc.ca/explore_career/job_market_report/wage_occupation_report.xhtml
- [228] 'Hydrogen Process Plant Operator in Canada | Wages - Job Bank'. Accessed: Sep. 30, 2024. [Online]. Available: <https://www.jobbank.gc.ca/marketreport/wages-occupation/20423/ca>
- [229] M. Zuberi, A. Hasanbeigi, and W. Morrow, 'Electrification of Boilers in U.S. Manufacturing', None, 1867393, ark:/13030/qt98r4r9r5, Nov. 2021. doi: 10.2172/1867393.
- [230] R. de Boer *et al.*, 'Strengthening Industrial Heat Pump Innovation: Decarbonizing Industrial Heat', Report, 2020.
- [231] B.-H. Choi *et al.*, 'Nuclear-Driven Chemical Conversion Pathways'.
- [232] R. Wang, 'Energy saving technologies and optimisation of energy use for decarbonised iron and steel industry', Durham University, 2022.
- [233] R. Q. Wang, L. Jiang, Y. D. Wang, and A. P. Roskilly, 'Energy saving technologies and mass-thermal network optimization for decarbonized iron and steel industry: A review', *J. Clean. Prod.*, vol. 274, p. 122997, Nov. 2020, doi: 10.1016/j.jclepro.2020.122997.
- [234] 'Blast Furnace Slag - Material Description - User Guidelines for Waste and Byproduct Materials in Pavement Construction - FHWA-RD-97-148'. Accessed: Jan. 18, 2025. [Online]. Available: <https://www.fhwa.dot.gov/publications/research/infrastructure/structures/97148/bfs1.cfm>

Appendices

Appendix A: Coke and Slag Specification

The amount of coke is determined from a process model of the coke oven built in Aspen Plus. In the Aspen Plus model, coal is a nonconventional solid that cannot be described by a molecular formula. Thus, it is described by attributes of its components: Proxanal, Ultanal, Sulfanal. The values are referenced from Pittsburgh coal in the Idaho National Laboratory report [231].

Table A - 1: Coal Properties

PROXANAL					
Fixed Carbon	Volatil e Matter	Ash		Moistur e	
53.34	36.01	10.65		2.52	
ULTANAL					
C	H	N	Cl	O	S
72.85	5.47	2.92	0.10	5.57	2.44
SULFANAL					
Pyritic		Sulfate		Organic	
1.50		0		0.94	

The coking plant involves a burner, a coke oven and a separator. The coke oven is a modelled with an RYield reactor operating at 1100°C and atmospheric pressure. The yield model is based on the results of the coking yield equations given by Wang et al [232], [233]:

Table A - 2: Coking yield

Component	Yield (wt%)
COKE	83.41
SULFUR	0.23
WATER	1.78
AMMONIA	0.23
COAL TAR	0.00
COG	0.13

The model is validated by comparing the coke oven gas compositions as compiled in **Error! Reference source not found.**:

Table A - 3: Coke Oven Gas compositions in the reference plant vs model plant

	Molar % Composition
--	---------------------

Components	Reference Plant	Aspen Plus Model
CO		5.63
CO ₂		1.22
H ₂ O		0
H ₂		56.3
N ₂		11.6
CH ₄		23.8
C ₂ H ₄		1.71
C ₂ H ₆		0.22
C ₃ H ₈		0.01

The following coke attribute is used for the exergy analysis of the Coke Dry Quenching process:

Table A - 4: Coke properties

PROXANAL					
Fixed Carbon	Volatil e Matter	Ash	Moistur e		
89.7	3.17	7.13			
ULTANAL					
C	H	N	C l	O	S
89.7	1.62	0.62	0	0.62	0.31
SULFANAL					
Pyritic		Sulfate		Organic	
0.1		0.1		0.11	

The amount of slag produced is collected from the reference plant. The slag composition was estimated based on a mean aggregation for National Slag Association Data [234] from 1949 – 1985:

Table A - 5: Blast Furnace Slag Composition

Composition	Mean Weight % Composition	
	Mean	Range
Calcium Oxide (CaO)	40	31 – 43
Silicon Oxide (SiO ₂)	36	27 – 38
Aluminum Oxide (Al ₂ O ₃)	12	8 – 20
Magnesium Oxide (MgO)	9.25	1 – 15

Iron Oxides (Fe ₂ O ₃)	0.63	0.1 – 1.6
Manganese Oxide (MnO)	0.64	0.1 – 2.3
Sulfur (S)	1.48	0.6 – 2.3

The properties of the coke and slag used in the exergy analysis is given in Table A - 6 below:

Table A - 6: Coke and slag exergy analysis properties

	Coke	Slag
Temperature [C]	1100	1500
Pressure [bar]	1.01	2.20
Mass Exergy [kJ/kg]	1510	1337
Mass [t/day]		

Appendix B: Software Interlinking

An essential part of the hybrid model is the connection between the different software that are used.

B1. Excel-MATLAB

The following steps are involved in connecting Excel with MATLAB:

1. Ensure that Excel can be accessed without any hindrance.
Open Excel: *File > Options > Trust Center*. Go to the *Trust Center Settings* and ensure that location of the excel file is specified as a “Trusted Location”. Check that the *Add-Ins* tab has “Disable all Application Add ins” option is unchecked. Enable External Content to be accessed without. In the *External Content* tab, enable all data connections, workbook links, dynamic data exchange. Ensure that VBA Macros are enabled.
2. Setup a component object model (COM) Server, a program that allows software components to communicate with each other. A new server must be established in MATLAB for outward communication. The code below shows how this server can be initialized to create an instance of the excel application, changing the visibility of the app and allowing alerts from the app

```
% Initialize Excel COM server
try
    excelApp = actxserver('Excel.Application'); % Set up Excel COM server
    excelApp.Visible = false; % Set to true for debugging
    excelApp.DisplayAlerts = false;
```

3. Open a workbook within the app. Include a debugging statement to decipher if the workbook can be opened.

```
% Open the workbook
workbooks = excelApp.Workbooks;
excelWbk = workbooks.Open(fileName);
catch ME
    disp('Error interacting with Excel:');
```

```

        disp(ME.message);
    end

```

4. If needed, macros can be run through the following instructions;

```

try
    % Run the macro
    macroName = 'Cry_Model'; % Macro name
    macroFullPath = sprintf('%s!\s', excelWkbk.Name, macroName);
    excelApp.Run(macroFullPath);
catch ME
    % Handle errors if the macro cannot be run
    disp('Error running macro:');
    disp(ME.message);
end

```

5. Save and close the workbook as shown.

```

% Save the workbook if needed
try
    excelWkbk.Save(); % Uncomment if modifications need saving
catch ME
    disp('Error saving workbook:');
    disp(ME.message);
end

% Close workbook and quit Excel
try
    excelWkbk.Close(false); % Close without saving changes

catch ME
    disp('Error saving workbook:');
    disp(ME.message);
end

```

6. Close the COM server after the instruction is complete.

```

% Clean up COM server references
excelApp.Quit();
delete(excelApp);
clear excelApp;

```

B2. Excel-Aspen Plus

The following steps are involved in connecting Excel VBA to Aspen Plus:

1. Ensure that you have the necessary libraries in the Microsoft VBA application: Tools>References

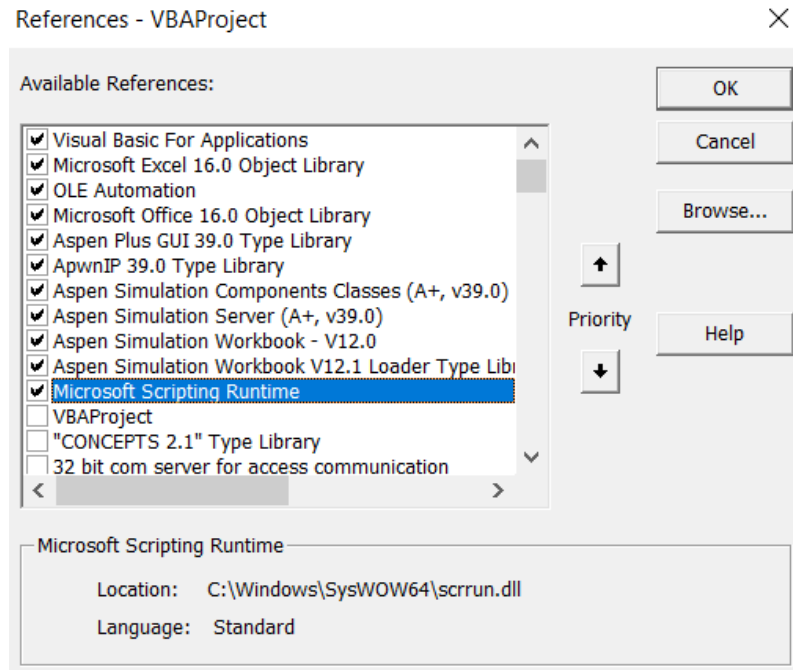


Figure B - 1: Reference library for VBA methods

2. Define objects that include Aspen Plus simulation document and the application.

```
Sub Test_Model()  
    Dim APSim As Object  
    Dim ihAPsim As IHapp
```

3. Create an instance of the Aspen Plus Application and open the simulation document. The simulation can be visible. Confirm the Aspen Plus Programmatic Identifier. Here it is: *Apwn.Document.39.0*. With newer versions, this value can be different.

```
'Create App Instance  
Set APSim = CreateObject("Apwn.Document.39.0")  
  
'Open Simulation document  
APSim.InitFromFile2 (NewFile)  
  
' display the GUI  
APSim.Application.Visible = False
```

4. Inputs and output can be communicated from the file a shown by this example. Here the mass flow of CO₂ in the FEED stream is changed to 20.

```
'Import inputs  
APSim.Application.Tree.FindNode("\Data\Streams\FEED\Input\FLOW\MIXED\CO2").Value = 20
```

This means that within Aspen Plus every variable or parameter has a unique node address which must be found before communication can happen. Each node has different attributes including name, value, units amongst others.

Within Aspen Plus, the node attributes can be found from the top navigation ribbon: *Customize > Variable Explorer > Root*.

An example of a node attributes are shown in the figure below:

Attribute	Value
Path to Node	Application.Tree.Data.Streams.HOTGAS1.Output.MASSFLOW.MIXED.CO2
Call	Application.Tree.FindNode("\\Data\\Streams\\HOTGAS1\\Output\\MASSFLOW\\MIXED\\CO2");
Dimension	0
Value	68801.1727
Physical Quantity	10
Unit of Measure	3
Basis	MASS
Record Type	No Attribute
Output	1
Enterable	
Upper Limit	No Attribute
Lower Limit	No Attribute
Default Value	No Attribute
Completion Status	
Port In or Out	No Attribute
Port Gender	No Attribute
Multiport	No Attribute
Port Type	No Attribute
Has Children	0

Figure B - 2: Node tree and attributes in Aspen Plus V12.1

The *Call* attribute is what is used to access the values needed.

- Simulation can be run from Excel VBA as shown:

```
APSim.Application.Run
```

- After result extraction, the application simulation can then be saved and closed.

```
APSim.Save
```

```
APSim.Quit
```

B3. Excel-Aspen Adsorption

Aspen Adsorption belongs to different set of the Aspen Custom Modeler process modelling programs which communicate differently with Microsoft Visual Basic. There are automation methods and properties used to control the simulation document in the Aspen Modeler Reference Guide.

- Ensure that macros are enabled. Define the app, document and simulation as objects.

```
Dim ADSApp As Object
```

```
Dim ADSDocument As Object
```

```
Dim ADSSimulation As Object
```

2. Create the application object and select whether to make the user interface visible or not. Visibility is useful in debugging errors. However, turning off the visibility uses less memory and makes it run faster. Create and open the document and simulations,

```
Set ADSApp = CreateObject("ADS Application")
ADSApp.Visible = False
Set ADSDocument = ADSApp.OpenDocument(newFile)
Set ADSSimulation = ADSApp.Simulation
```

3. Define input and output variable by using the node path as shown:

```
ADSSimulation.Flowsheet.Blocks("Product").P.Value = 10
```

4. The following methods show instruction to running a dynamic model

- a. First, the cycle organizer is activated

```
ADSSimulation.Flowsheet.Cycle1.Active = True
```

- b. The simulation is initialized from a snapshot in the dynamic model that specifies all the model input values.

```
ADSSimulation.Results.Refresh
```

```
Set aSnapshot = ADSSimulation.Results.FindResult("File saved")
```

```
ADSSimulation.Results.CopyValues aSnapshot, False, True, True, False, True, True,
" ", "~"
```

- c. Run the model in Initialization model.

```
ADSSimulation.RunMode = "Initialization"
```

```
ADSSimulation.Flowsheet.Bed.Initialize_unit
```

```
ADSSimulation.Run (True)
```

- d. Set the integration step size and run the model in Dynamic mode.

```
ADSSimulation.Options.Integration.InitStepSize = 0.0000001
```

```
ADSSimulation.termination = "Never"
```

```
ADSSimulation.RunMode = "Dynamic"
```

```
ADSSimulation.Run (False)
```

```
msgcount = ADSSimulation.OutputLogger.MessageCount
```

```
finmessage = "Clear"
```

```
i = 0
```

5. Extract the output results such as the simulation time, simulation status and other variables.

```
Sheets("Output").Range("C2").Value = ADSSimulation.Time
```

```
Sheets("Output").Range("B3").Value = ADSApp.StatusBar
```

```
num = 0
```

```
For Each s In ADSSimulation.Flowsheet.Forms("cycle_times").VariablesPaths
```

```
    num = num + 1
```

```
    Set v = ADSSimulation.Flowsheet.Resolve(s)
```

```
    cycle_time.Offset(num, 0) = v.Value
```

```
    cycle_time.Offset(num, -1) = v.units
```

```
Next
```

6. Create an error handler that resolves every type of error than might come up. The code below shows examples of ways to handle errors.

```
msgcount = ADSSimulation.OutputLogger.MessageCount
```

```
finmessage = "Clear"
```

```
i = 0
```

```
Do While (ADSSimulation.State = "Running")
```

```
    finmessage = ADSSimulation.OutputLogger.MessageText(msgcount - 1,  
    msgcount - 1)
```

```
    If finmessage = "Cyclic steady state has been achieved and the simulation  
    has been automatically paused" Then
```

```
        ADSSimulation.Pause
```

```
    ElseIf finmessage = "The batch of 200 cycles has been executed." Then
```

```
        ADSSimulation.Pause
```

```
    ElseIf finmessage = "Group 1: Nonlinear solver failed." Then
```

```
        ADSSimulation.Pause
```

```
        ADSSimulation.Options.Integration.InitStepSize = 0.0000001
```

```

        ADSSimulation.Run (False)
    ElseIf finmessage = "Integrator step size is too small" Then
        ADSSimulation.Pause
        ADSSimulation.Options.Integration.InitStepSize = 0.00001
        ADSSimulation.Run (False)
    ElseIf finmessage = "Integrator step size is too large" Then
        ADSSimulation.Pause
        ADSSimulation.Options.Integration.InitStepSize = 0.0000001
        ADSSimulation.Run (False)
    ElseIf (i = 0 And (finmessage = "Integrator corrector failed" Or
        finmessage = "Initialization failed at time 0")) Then
        i = i + 1
        ADSSimulation.Pause
        ADSSimulation.Restart
        'Activate Cycle
        ADSSimulation.Flowsheet.Cycle1.Active = True
        ADSSimulation.Results.Refresh
        Set aSnapshot = ADSSimulation.Results.FindResult("File saved")
        ADSSimulation.Results.CopyValues aSnapshot, False, True, True,
        False, True, True, " ", "~"
        ADSSimulation.RunMode = "Initialization"
        'ADSDocument.Flowsheet.Bed.Initialize_unit
        ADSSimulation.Options.Integration.InitStepSize = 0.0000001
        ADSSimulation.Run (True)
        'Set Simulation mode to Dynamic
        ADSSimulation.termination = "Never"
        ADSSimulation.RunMode = "Dynamic"
        ADSSimulation.Run (False)
    Else
        On Error GoTo ErrorHandler
    End If
Loop

```

7. Save and close files.

ADSAApp.SaveDocument

ADSAApp.Quit

Appendix C: Supplementary Information: Lessons Learned in Building VPSA and TSA Models

C1. Setting User Subroutines for Custom Kinetic Models for RADFRAC

This is the process of going from a user sub-routine to an Aspen library file. The process can be divided into 3 main steps:

- Writing the user model
- Compiling the user model
- Linking the user model to Aspen
-

1. Step 1: Writing the user model

According to the Aspen Plus User Models Manual,

For RadFrac, the kinetics subroutine calculates the rate of generation for each component on a given stage. It should also calculate the individual reaction rates in each phase if you use this routine for rate-based calculations.

The unit for the reaction rate: **kmol/s**

This section addresses converting kinetic model of any time into a Fortran77 User Routine file

- 1) Open the user kinetic template “usrknt.f” found in “C:\Program Files\AspenTech\Aspen Plus V12.1\Engine\User”
- 2) Save the file with a unique name in the form {new name}.f
- 3) Replace the subroutine name “USRKIN” with the name you will enter on the *Reactions/Subroutine* sheet in Aspen Plus. It must contain no more than 6 alphanumeric characters.
- 4) Confirm that the template includes calls for common block variables for RADFRAC/RATEFRAC:

```
#include "rxn_disti.cmn"  
#include "rxn_distr.cmn"
```

- 5) Declare the arguments and local variables for your model as integer, real or double number as well as their dimensioning. See Fortran 90 syntax for further guide on this.
- 6) Include the executable codes.
 - a. The components and individual reaction rates in each phase should be set as a 0

- b. The molar concentration of each component (J) can be determined using the following function:

$$C_{\text{molar}}(J) = X(J,1)/VMX$$

where,

the mole fraction (X) is one of the argument extracted from the RADFRAC block.
the molar volume (VMXL) is retrieved using a physical proper monitor e.g
MON_LL that extracts the liquid mixture molar volume as follows:

- c. The output here is the RATES for each component and the RATEL/RATEV for each reaction in each phase.
- 7) For further insight into the arguments, data structures of Aspen Plus variables and physical property monitors, refer to the **Aspen Plus' User Model** reference manual for details.

2. Step 2: Compiling the user model

The Compilation process involves the following steps

- a) Select your compiler for Aspen.

First, in the Start search bar, input = “**Set Compiler for {Aspen Version Number e.g V12.1}**”. A command line interface window should open. This window should display a list of compiler configuration section as seen below:

```

Set Compiler for V12.1

30 compiler sections in C:\Program Files\AspenTech\APrSystem V12.1\Engine\xeq\Compilers64.cfg

## Section      State Description
-----
1 IVF10_VS9      ERROR Intel Fortran 10.x and Microsoft Visual Studio 2008 WITH x64 Compiler
2 IVF11x_VS9      ERROR Intel Fortran 11.x and Microsoft Visual Studio 2008 WITH x64 Compiler
3 IVF11x_VSB      ERROR Intel Fortran 11.x and Bundled VS 2008 Shell ONLY
4 IVF12x_VS9      ERROR Intel Fortran 12.x/2011 and Microsoft Visual Studio 2010
5 IVF12x_VS10     ERROR Intel Fortran 12.x/2011 and Microsoft Visual Studio 2010
6 IVF12x_VSB      ERROR Intel Fortran 12.x/2011 and Bundled VS 2008 Shell ONLY
7 IVF12x_VSB2     ERROR Intel Fortran 12.x/2011 and Bundled VS 2010 Shell ONLY
8 IVF13_VSB      ERROR Intel Fortran 13/2013 and Bundled VS 2010 Shell ONLY
9 IVF13_VS11      ERROR Intel Fortran 13/2013 and Microsoft Visual Studio 11/2012
10 IVF13_VS12     ERROR Intel Fortran 13/2013 and Microsoft Visual Studio 12/2013
11 IVF14_VSB      ERROR Intel Fortran 2013SP1 and Bundled VS 2010 Shell ONLY
12 IVF14_VS12     ERROR Intel Fortran 2013SP1 and Microsoft Visual Studio 12/2013
13 IVF15_VS12     ERROR Intel Fortran 15/2015 and Microsoft Visual Studio 12/2013
14 IVF16_VS12     ERROR Intel Fortran 16/2016 and Microsoft Visual Studio 12/2013
15 IVF15_VS14     ERROR Intel Fortran 15/2015 and VS 2015 WITH C++ (and express)
16 IVF16_VS14     ERROR Intel Fortran 16/2016 and VS 2015 WITH C++ (and express)
17 IVF17_VS14     ERROR Intel Fortran 17/2017 and VS 2015 WITH C++ (and express)
18 IVF17_VS15     ERROR Intel Fortran 17/2017 and VS 2017 WITH C++ (and community)
19 IVF18_VS14     ERROR Intel Fortran 18/2018 and VS 2015 WITH C++ (and express)
20 IVF18_VS15     ERROR Intel Fortran 18/2018 and VS 2017 WITH C++ (and community)
21 IVF19_VS14     ERROR Intel Fortran 19/2019 and VS 2015 WITH C++ (and express)
22 IVF19_VS15     ERROR Intel Fortran 19/2019 and VS 2017 WITH C++ (and community)
23 IVF19_VS16     ERROR Intel Fortran 19/2019 and VS 2019 WITH C++ (and community)
24 IVF191_VS14    ERROR Intel Fortran 19.1/2020 and VS 2015 WITH C++ (and express)
25 IVF191_VS15    ERROR Intel Fortran 19.1/2020 and VS 2017 WITH C++ (and community)
26 IVF191_VS16    ERROR Intel Fortran 19.1/2020 and VS 2019 WITH C++ (and community)
27 IVF192_VS15    ERROR Intel Fortran 2021/2022 and VS 2017 WITH C++ (and community)
28 IVF192_VS16    ERROR Intel Fortran 2021/2022 and VS 2019 WITH C++ (and community)
29 IVF193_VS17    ERROR Intel Fortran 2021/2022 and VS 2022 WITH C++ (and community)
30 IVF2023_VS2022 OK Intel Fortran 2023 and VS 2022 WITH C++ (and community)

The current compiler option settings in order of searching
IVF2023_VS2022 for current user in HKEY_CURRENT_USER registry
Not set for current machine in HKEY_LOCAL_MACHINE registry
IVF17_VS15 in file C:\Program Files\AspenTech\APrSystem V12.1\Engine\xeq\Compilers64.cfg WILL BE IGNORED

Enter option (1:30) for current USER, 0 to skip, -1 to delete:

```

Figure C - 1: Window for Setting compiler for Aspen Plus V12.1

The list provides the following columns of information: the Number (#), Section, State and Description. This information is obtained from the configuration file found in the file location in Figure C - 2

Aspen Plus on Windows uses Intel Fortran compilers and Visual Studio as a linker. If any of the program is not available for use, its status will be “ERROR”. Otherwise, it will say “OK”.

Beneath the list of compiler options, the window tells you the current selected compiler setting for your User Profile and the machine. If neither of these are set, in the last line you can select any section that has its status as “OK” by inputting its option Number. A successful setup will show the updated compiler setting and tell you to restart as shown below:

```

The current compiler option settings in order of searching
IVF2023_VS2022 for current user in HKEY_CURRENT_USER registry
Not set for current machine in HKEY_LOCAL_MACHINE registry
IVF17_VS15 in file C:\Program Files\AspenTech\APrSystem V12.1\Engine\xeq\Compilers64.cfg WILL BE IGNORED

You need to restart Aspen Plus simulation Window or Aspen Plus run
for the compiler switching to take effect.
Press any key to exit:

```

Figure C - 2: Snippet from compiler setting command window

If no section has an “OK” status, go to Section: Installing a compiler package, before proceeding to the next section.

b) Convert the Subroutine Fortran (*.f) file to an object file using the Aspen compiler.

Go the start menu and type in “**Customise Aspen Plus {Version e.g V12.1}**”. A command line interface window should open up.

In this window, input the following command:

```
aspcomp {*} {*}.obj
```

where {*} should be replaced the subroutine file address relative to the current location on the command line e.g C:/.../.../...file.f.

This **aspcomp** command compiles the subroutine file into an object file with same name {*.obj} will be created in the location of the source file. The dbg is optional but gives insight on any error that could prevent compiling.

c) Convert the object file into a library or executable file using the Aspen linker.

Within the same window, input the following command:

```
link {*}.obj {**}.ext
```

This converts the object file into a file with the defined name “{**}” and file type that corresponds with the preferred extension {ext}. Some examples of extensions to us include:

- To create a library file for Aspen simulation, use extension: .dll
- To create an executable file , use extension: .exe

3. Step 3: Linking the User model to Aspen

There are 2 means of linking the subroutine to the Aspen model

1. Through an object file

- Place the object file created during the compilation (See part b of Step 2) in the same directory as the Aspen file.
- Specify the subroutine NAME (this is not the file name but the assigned name in the *.f code) in **Reactions > [Reaction Name]> Subroutine: Name**
- Reset the model and run. This allows Aspen to self link to the object file.
- Check the logs generated in Aspen if this process fails.

The drawback of this method is that for every new Aspen model created, the object file must be manually added, a compiler option must be set (as in Step 1) to give Aspen access to a linker. Without a linker, the object files cannot be used by another user.

2. Through a shared library [RECOMMENDED]

Installing a compiler package

If there is no available compiler setting, this means that either the compiler or the linker or both are not available on your system.

- Check the configuration file in the address section of section 4. It will also contain further instruction for debugging your compiler and linker setup.
- A snippet of the file format for the compiler setting is shown below:

```

Begin IVF2023_VS2022 "Intel Fortran 2023 and VS 2022 WITH C++ (and community)"
IFDir=HKLM(SOFTWARE\WOW6432Node\Intel\Compilers\Fortran\192.####\ProductDir)
INTEL_TARGET_ARCH_IA32=
VS2022=$(ProgramFiles)\Microsoft Visual Studio\2022
VSDir=Exist($(VS2022)\Enterprise)||Exist($(VS2022)\Professional)||Exist($(VS2022)\Community)
# !!! Replace the line above with proper one below for A+ before V9 !!!
#VSDir=$(VS2022)\Enterprise
#VSDir=$(VS2022)\Professional
#VSDir=$(VS2022)\Community
KitDir=HKLM(SOFTWARE\WOW6432Node\Microsoft\Microsoft SDKs\Windows\v10.0\InstallationFolder)
KitVer=HKLM(SOFTWARE\WOW6432Node\Microsoft\Microsoft SDKs\Windows\v10.0\ProductVersion).0
VCRVer=GetVer($(VSDir)\VC\Tools\MSVC\14.3?.**)
INCLUDE=$(IFDir)\Compiler\Include;$(IFDir)\Compiler\Include\Intel64;$(VSDir)\VC\Tools\MSVC\$(VCRVer)\Include
LIB=$(IFDir)\Compiler\lib\Intel64;$(VSDir)\VC\Tools\MSVC\$(VCRVer)\ATLMFC\lib\x64;$(VSDir)\VC\Tools\MSVC\$(VCRVer)\lib\x64
PATH=$(IFDir)\bin\Intel64;$(VSDir)\VC\Tools\MSVC\$(VCRVer)\bin\HostX64\x64;$(KitDir)\bin\x64;$(VSDir)\VC\Tools\MSVC\$(VCRVer)\bin\HostX64\x64
USE_COMPAQ_FORTRAN=
IFDir=
VS2022=
VSDir=
KitDir=
KitVer=
VCRVer=
End

```

- Confirm the following in the configuration file:
 - o It is the updated version as supplied by Aspen: solution 66002462 on <https://esupport.aspentech.com>. If it is not, replace the file with the most updated file uploaded on the Aspen support web page.
 - o It is compatible with your operating system's i.e a 64-bit or the 32-bit. This would be specified in the header comments of the file.
- In the updated configuration file, based on any of the listed setting options (the latest compiler is recommended)
 - o Install the Intel Fortran Compiler from www.intel.com/products
 - o Install the recommended version of the linker i.e Visual Studio IDE from www.visualstudio.microsoft
- Ensure that the installed file location matches the location in the configuration file.
- Repeat part a) of Step 1: Writing the user model

According to the Aspen Plus User Models Manual,

For RadFrac, the kinetics subroutine calculates the rate of generation for each component on a given stage. It should also calculate the individual reaction rates in each phase if you use this routine for rate-based calculations.

The unit for the reaction rate: **kmol/s**

This section addresses converting kinetic model of any time into a Fortran77 User Routine file

- 8) Open the user kinetic template "usrknt.f" found in "C:\Program Files\AspenTech\Aspen Plus V12.1\Engine\User"

- 9) Save the file with a unique name in the form {new name}.f
- 10) Replace the subroutine name “USRKIN” with the name you will enter on the *Reactions/Subroutine* sheet in Aspen Plus. It must contain no more than 6 alphanumeric characters.
- 11) Confirm that the template includes calls for common block variables for RADFRAC/RATEFRAC:

```
#include "rxn_disti.cmn"
#include "rxn_distr.cmn"
```

- 12) Declare the arguments and local variables for your model as integer, real or double number as well as their dimensioning. See Fortran 90 syntax for further guide on this.
- 13) Include the executable codes.
 - a. The components and individual reaction rates in each phase should be set as a 0
 - b. The molar concentration of each component (J) can be determined using the following function:

```
Cmolar(J) = X(J,1)/VMX
```

where,
the mole fraction (X) is one of the argument extracted from the RADFRAC block.
the molar volume (VMXL) is retrieved using a physical proper monitor e.g
MON_LL that extracts the liquid mixture molar volume as follows:

- c. The output here is the RATES for each component and the RATEL/RATEV for each reaction in each phase.
- 14) For further insight into the arguments, data structures of Aspen Plus variables and physical property monitors, refer to the **Aspen Plus’ User Model** reference manual for details.

- **Step 2: Compiling the user model** to check that the compiler settings are available to be used.

C2. Convergence of Aspen Plus Model

Building a robust rate-based model which does not crash is a product of experience and the right modelling specifications. The instructions detailed here are specific to Aspen V12.1 and assumed the reader has an intermediate level of navigating the program. Beyond the specifications in the Convergence setup in the overall model, each block type can also have their individual convergence setups.

- a) RadFrac Columns: The convergence algorithm and initialization methods are defined based on the **Convergence** option in the **Specifications | Setup** form. Refer to Aspen Manual for further details on the default settings for each option. The “Standard” method suffices for the amine absorption and stripping.

Further modifications can be made to the selected method settings:

- i) Increasing the maximum number of iterations: The default number of iterations in aspen is 20-30. Increasing the maximum number of iterations allows the solver more iterations to find the solution that achieves the specified error tolerance or to proceed beyond regions of minor oscillation. This change can be executed under the **Convergence | Convergence** form.
- ii) Introduce damping: The default damping level is None. Gradually increasing the level of damping, takes longer to converge but achieve more stable convergence. This change can be executed under the **Convergence | Convergence** form.
- iii) Specify estimates: After the initial initialization according to the modelling approach (i.e Sequential Modular or Equation-Oriented), subsequent runs are initialized with the solution of the previous run. Using these solutions might hinder convergence if they were solved from extremely differing specifications or a diverged simulation. In the **Convergence | Estimates** form, estimates can be generated for stage temperatures, liquid and vapor mole flows and component mole fractions from previous solutions. The following are alternative estimates that could improve convergence:
 - a. Previously converged equilibrium solutions
 - b. Experimental data estimates
 - c. Analytical hand calculations

Other ways of ensuring convergence:

1. Multi-step Changes

When introducing a significant change in a numerical variable e.g feed flow rate, temperature etc. The abrupt change might lead to divergence due to the sensitivity of the solver. For example, instead of changing a flow rate from 10 km/h to 1000 km/h in a single step, change it in increments of 50 i.e 10, 60, 110, 160....1000. It will take longer but it stabilizes the solution process by gradually guiding the solver to the solutions.

2. Recycle Stream Setup

Before coupling the amine recycle stream, set up a dummy stream to represent recycle stream feed and set up equation blocks to adjust any purge or makeup streams based on a mass/mole balance that equates the dummy feed stream to the recycled output.

3. Selecting Design Specification Solvers

When adopting several design specifications, change the convergence method to the Broyden method, which is less sensitive to initial specifications. If this fails, deactivate the design specifications, re-initialize the simulation and individually turn on a single design spec at a time. Then for each design specification, use the Secant method with bracketing to test different initial guesses and boundaries for the independent variable and to find better initial bracket points that will improve convergence.

C3. Convergence of Aspen Adsorption Models

Some methods of achieving convergence in cyclic Aspen Adsorption Models:

1. Using older solver MA43 if the new solver runs in errors relating to the dropped variables
2. Avoiding 0 as a specification, instead use a very negligible number that approaches 0
3. Instead of closing the valves with a 0 specification, specify extremely low CV values
4. Increase the initial time step to as large as possible and let the program refine it as needed.
5. Specify valves with a stop action as “Yes” to prevent back flow
6. Increase the communication interval and remove unnecessary snapshots
7. Test that steady state tolerance isn't too large that it impacts accuracy but too small that it increases the run time significantly
8. Use a working snapshot to run the model, instead on re-initializing the model