

# Optimal retrofit decarbonization in oil refineries

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## Abstract

The chemical industry is making significant investments in clean energy technologies such as green hydrogen, carbon capture and storage, electric heating, and electrochemical processes to reduce carbon emissions. However, uncertainties regarding investments in nascent technologies, fluctuating electricity and carbon prices, and the need to balance existing infrastructure with new ones complicate the transition. In this study, we develop a Mixed-Integer Linear Programming (MILP) formulation to determine the most cost-effective transition for the decarbonization of oil refineries. Two case studies that consider different refinery configurations are presented. Overall, the results of our simulations indicate that (i) natural gas with carbon capture is more economically favorable than electricity-based options, unless there are significant reductions in electricity prices or stricter emission regulations are imposed; (ii) carbon taxes or credits drive earlier adoption of capture technologies but do not promote electrification.

# 1 Introduction

The 2024 UN Climate Change Conference (COP29)<sup>1</sup> made significant strides towards promoting the transition from fossil fuels to clean energy systems while focusing on energy security. It committed to achieving net zero emissions by 2050 by tripling the renewable energy capacity by 2030, following COP 28 and limiting global warming to 1.5°C. This ambitious goal, combined with a global increase in energy consumption, has prompted countries to accelerate the adoption of low-emission energy systems, with a growing pressure on the energy-intensive chemical industry to embrace emerging technologies.<sup>23</sup>

Decarbonizing the US industrial sector, particularly high carbon intensity subsectors such as iron and steel, chemicals, food and beverage, petroleum refining, and cement, presents unique challenges due to their diverse energy inputs and processes. Strategies for decarbonization include improving energy efficiency, adopting industrial electrification and low-carbon fuels as energy sources, and carbon capture, utilization, and storage. It is noted that the decarbonization of oil refineries, which represent 5% of industrial emissions in the US (the second largest emitter in the US industrial sector), is particularly challenging due to their varied configurations and high operational efficiencies<sup>2</sup>.

Several recent papers have explored potential future scenarios for the refining industry in the context of decarbonization efforts. Griffiths et al.<sup>4</sup> conducted a comprehensive review of decarbonization in the oil refining industry. The review draws attention to the need for customized decarbonization strategies, highlighting the importance of policy interventions such as carbon pricing, stricter emission controls, increased R&D investment in renewable technologies, and subsidies for the adoption of renewable energy. Byrum et al.<sup>5</sup> evaluated multiple pathways to decarbonize petroleum refining, advocating the adoption of low and zero-carbon hydrogen fuels, electrification of processes, and the integration of carbon capture and storage technologies as crucial measures to meet U.S. climate targets. Their study presents two conceptual low-emission refinery designs: one focused on co-processing various

feedstocks and refinery fuel gas, and another one on recycling  $CO_2$ . Both papers offer primarily qualitative information without providing quantitative guidance on the optimal combination of strategies for an effective transition.

Techno-economic assessments (TEAs) and Life Cycle assessments (LCAs) of different technologies for the decarbonization of refineries have also been addressed in the literature. Nixon et al.<sup>6</sup> performed an analysis for the case of a large conversion refinery, where the results suggest that post-combustion Carbon Capture and Storage (CCS) may only be feasible for large point emission sources, leaving around 30% of the emissions unaddressed. The authors also suggest that to achieve carbon-neutral refinery operations, a combination of high-efficiency CCS, fuel substitution, and emission offsets is necessary. However, the primary focus is on quantifying the emission reduction potentials for different configurations of CCS technologies, and no explicit comparison with other technologies is made.

Li et al.<sup>7</sup> examine  $CO_2$  emission control in China's petroleum refining sector under the potential emission trading scheme. The authors identify six  $CO_2$  abatement technologies, including waste heat recovery, new material-based technology, process optimization, intelligent system installation for optimized energy use, new equipment-based technology, and wastewater circulation technology with efficient energy usage. Their results show that most of the technologies are cost-effective, and new equipment technology contributes to the greatest emission reductions. The authors also find that, in the absence of a carbon trading market, these technologies can only reduce emissions by up to 40%. Sun et al.<sup>8</sup> examine the potential and cost of decarbonizing the U.S. refinery sector, highlighting three main strategies: switching to renewable energy sources, implementing carbon capture and storage, and using biocrude feedstock. The analysis suggests that a combination of these approaches could achieve negative life-cycle  $CO_2$  emissions, with costs of decarbonization ranging from \$ 113/ton to \$ 477/ton  $CO_2$ , primarily driven by the cost of biocrude feedstock. While the economics and  $CO_2$  reduction potential of technologies have been compared in these studies, it is hard to identify a transition pathway with an associated timeline based on them.

A few papers have explored the synergies between technologies to come up with a transition pathway. Yáñez et al.<sup>9</sup> present a case study on a comprehensive  $CO_2$  mitigation strategy for a refinery in Colombia, exploring various technologies such as carbon capture and storage, process optimization, and energy efficiency improvements. Their techno-economic analysis indicates significant potential for  $CO_2$  reduction but is limited by its applicability to the specific refinery studied. Furthermore, while synergies between technologies have been considered, some choices are eliminated based on an ad hoc interaction matrix. Sachs et al.<sup>10</sup> analyze global refinery decarbonization pathways, emphasizing the need for a diverse technology mix to meet 2°C and 2.5°C climate targets, and highlight that only the most efficient conventional refineries or those with CCS will stay competitive. However, the approach relies on simulating cases for different retrofitting decisions, and committing the most profitable ones to satisfy the market demands, which may not result in the most optimal retrofit solution.

Optimization-based approaches have also been used to study the decarbonization of oil refineries. de Maigret et al.<sup>11</sup> employ EnergyPLAN, an energy system simulation software coupled with a Multi-Objective Evolutionary Algorithm (MOEA) to balance the dual goals of minimizing  $CO_2$  emissions and annual cost on an Italian refinery. The analysis considers 22 technologies for electricity, thermal energy, hydrogen feedstock, and transport demand using a superstructure optimization framework. While a systematic framework is developed, the model minimizes the costs for a single year and does not provide insights into an implementable transition plan. Ofori-Atta and Oluleye<sup>12</sup> introduce an optimization model to assess the impact of combined policies on Carbon Capture Utilization and Storage (CCUS) uptake and cost reduction by 2030. Analyzing 512 refineries in 86 countries, the results show that global policy measures on carbon taxes, grants, and tax credits for CC infrastructure, revenues for  $CO_2$  sale and emission allowances can lower capture costs to less than \$40 /ton  $CO_2$  and achieve up to 33% cost savings, totaling \$46.3 billion. However, this study is focused on the adoption of CCUS based technologies, and their tool is directed more towards

policymakers rather than individual refineries that need to decarbonize. A study conducted by Zhang et al.<sup>13</sup> uses a multiperiod Mixed-Integer Linear Programming (MILP) model to obtain optimal ways to retrofit a fossil-based refinery to use a biomass-based feed over a ten-year horizon. However, the study does not consider pathways for decarbonization of scope-1 (emissions taking place within the plant boundaries) or scope-2 emissions (energy-related emissions outside the plant's immediate boundary).

Based on the literature review conducted above, it is found that while market-ready technologies and technoeconomic analyses are available for individual decarbonization initiatives<sup>869</sup>, a specialized tool that can find decarbonization strategies for individual refineries based on specific factors such as production capacity, plant structure, location, and availability and cost of renewable energy sources is needed. A tool like this would enable refineries to determine the optimal timing for implementing various decarbonization technologies, catering to their specific circumstances, and ensuring economic viability, while keeping the associated emissions from the plant in check.

This work develops such a decision-making tool based on a multi-period MILP model to plan the transition to retrofit solutions. The tool aims at reducing scope 1 emissions by decarbonizing process heating and hydrogen production, and implementing carbon capture techniques, while systematically searching through all possible combination of technologies. The tool can be used iteratively to generate optimal retrofit plans with more accurate forecasts as the time periods on the horizon are realized.

This paper is organized as follows: we begin with the description of a generic flowsheet of an oil refinery, the potential technologies for decarbonizing process heating and hydrogen production, and carbon capture. Next, we discuss the associated superstructure, the problem statement, and the associated MILP model formulation. The case study sections present the results obtained using the optimization-based tool for various scenarios, including different policy implementations and price forecasts. Finally, the conclusions of the study are summarized.

## 2 Background on oil refining and associated options for decarbonization

### 2.1 Illustration of a generic oil refinery

A conventional refinery processes various types of crude oil with variable compositions to produce various products such as liquified petroleum gas, gasoline, jet fuel, diesel, and paraffins. As seen in Figure 1, the refinery operations begin with an atmospheric crude distillation unit, which separates the raw crude into different streams. The heavier products at the bottom of the atmospheric distillation are heated in the vacuum crude distillation unit to further separate them. These streams can be blended directly into final products but typically undergo further processing to enhance quality. One of the first processing steps involves the hydrotreatment units, which produce low-sulfur fuel oils and prepare feeds for subsequent processes. The hydrotreated streams are then processed in various units, such as the catalytic reforming unit, the fluid catalytic cracking unit, the hydrocracking unit, and the delayed coking unit, to upgrade the intermediates into lighter and higher value products. The intermediates from these units are blended into final products.

### 2.2 Technologies for decarbonization

Analyses of scope 1 emissions in refineries have identified combustion of fossil fuels to generate heat to be the main source, accounting for 63% of the total emissions of the sector in 2018<sup>5</sup>. The second largest contribution is from the process emissions, accounting for 31%. The Fluid Catalytic Cracker (FCC), is responsible for 22% emissions, due to the  $CO_2$  produced during catalyst regeneration through combustion of the coke generated as a byproduct of cracking reactions. The Steam Methane Reformer (SMR), which uses steam to convert methane into hydrogen, releasing  $CO_2$  as a byproduct, contributes to 9% emissions. This hydrogen is later used in several units. As a summary, Table 1 outlines the high-pressure, medium-pressure, and low-pressure steam (used both as a heating agent and for process

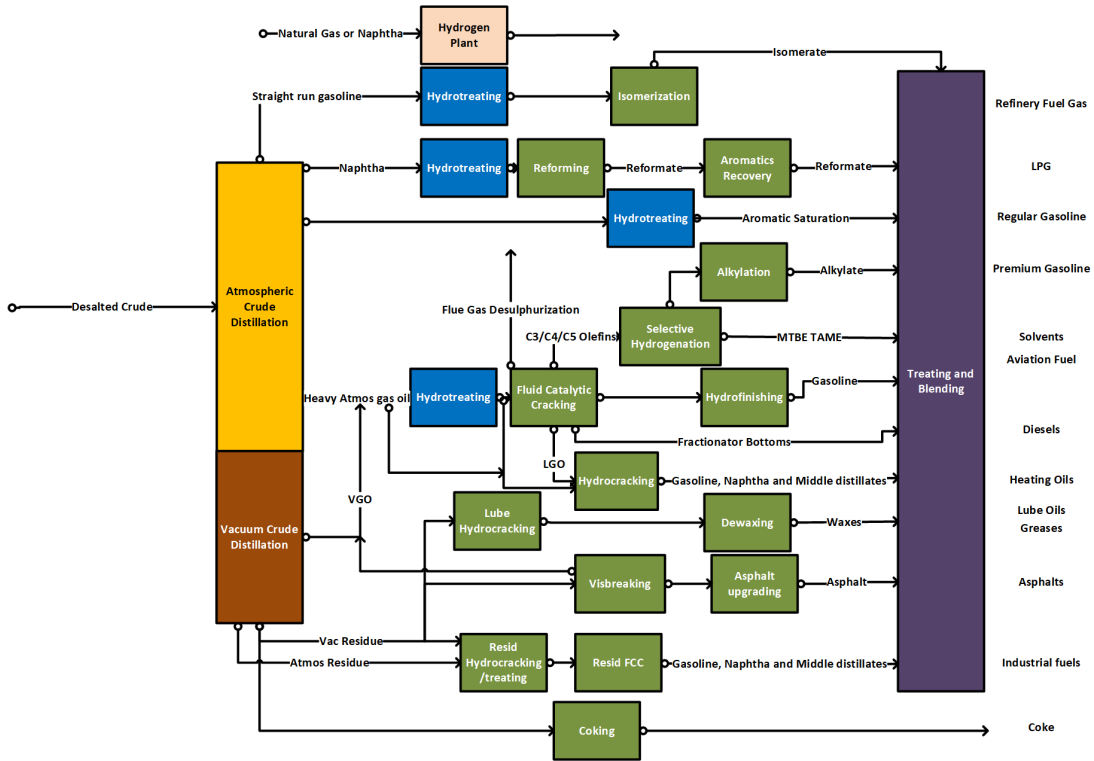


Figure 1: Flowsheet for a generic crude-based refinery. Adapted from<sup>14</sup>

requirements), furnace-based heating, and hydrogen needs for the various units illustrated in Figure 1. From here, it can be inferred that scope-1 emissions from a refinery can be greatly reduced by targeting the full decarbonization of the (centralized) production of hydrogen and steam. Such a solution preserves most of the current equipment, which is desirable, as completely discarding valuable assets is neither an economical nor an environmentally sound solution. Heating needs beyond HPS, i.e., those that require furnaces, can be partially decarbonized by the addition of carbon capture units. Next, we discuss the implementation of carbon capture technologies, the electrification of process heating, and alternative hydrogen production methods as the primary decarbonization techniques.

### 2.2.1 Carbon capture technologies

Carbon capture techniques such as post-combustion, pre-combustion, and oxy-combustion are the main methods for carbon capture, which differ in terms of operating flue gas concen-

Table 1: Heating and hydrogen requirements for refineries, crosses denote release, ticks denote requirement.

Unit	Furnace based heating	hydrogen	HPS	MPS	LPS
Hydrotreating	✓	✓	×		
Hydrocracking	✓	✓		✓	
Fluid Catalytic Cracking			✓		✓
Visbreaking	✓			✓	
Coking	✓			✓	✓
Isomerization	✓			✓	✓
Alkylation	✓			✓	✓
Asphalt upgrading					✓
Hydrodesulphurization	✓	✓			
Crude Distillation Unit	✓		✓		
Vacuum Distillation Unit	✓			✓	
Reforming	✓	×	✓	✓	✓
Selective Hydrogenation		✓	✓		
Hydrofinishing	✓	✓			
Dewaxing			✓		
Aromatic Recovery			✓		

tration, energy requirements, capital, and operating expenses<sup>15</sup>. Each of these technologies can involve absorption, adsorption, or membrane-based separation methods<sup>16</sup>. This study focuses on pre-combustion and post-combustion capture methods due to their compatibility with retrofitting existing operations, in contrast to oxy-combustion techniques, which demand energy-intensive air separation units, and pose challenges for retrofitting. Although pre-combustion carbon capture has lower energy requirements and is cheaper in terms of capital and operating expenses, it can operate only in conjunction with gasification units that produce flue gas with higher concentrations of  $CO_2$ <sup>17 15</sup>. Post-combustion capture  $CO_2$  has higher energy requirements, but can handle low concentration and pressure of  $CO_2$  in flue gas<sup>18-21</sup>. Solvent-based (MEA (monoethanolamine)/ MDEA (metyhldiethanolamine)) absorption is the most widely used technology for oil refineries<sup>12 22</sup>.



### 2.2.2 Decarbonization of hydrogen production

One method for achieving hydrogen production with reduced carbon emissions involves what is known as blue hydrogen production<sup>23,24</sup>. This process enhances Steam Methane Reforming (SMR) and Water Gas Shift (WGS) reactors with Carbon Capture (CC) units. Pre-combustion-based capture can be implemented on the shifted syngas or tail gas from the pressure-swing adsorption column. The Pressure Swing Adsorption (PSA) column is responsible for separating  $H_2$  from the syngas. Alternatively, residual  $CO$  and supplementary natural gas can be burned to obtain flue gas with a lower concentration  $CO_2$  that can be combined with flue gas from other combustion or cracking related emission points in the refinery. This mixture can then be treated using absorption-based post-combustion carbon capture.

Another method for decarbonizing  $H_2$  production uses renewable electricity for the electrolysis of water, leading to the production of green hydrogen. Various electrolyzer technologies have been discussed in the literature, with higher Technology Readiness Levels (TRLs) observed in Alkaline Electrolyzers (AEs), Proton Exchange Membrane Electrolyzers (PEMEs), and Solid Oxide Electrolyzers (SOEs)<sup>24</sup>. Low-temperature electrolyzers (AEs, PEMEs) are better suited to handle variable operation rates due to their shorter ramp-up and ramp-down times compared to high-temperature electrolyzers (SOEs) in case of fluctuations of power availability<sup>25</sup>. Alkaline electrolyzers (AEs) are less energy efficient and have a drawback related to their shutdown current, as they cannot operate at low current densities, limiting their minimum load rates to the range of 15-40%<sup>24</sup>, but are cheaper than PEMEs.

### 2.2.3 Decarbonization of process heating

In the refinery, most of the heating demands are met by using steam. Typically, steam is produced in an associated power and utility production plant that is placed in conjunction with the refinery. Most of the steam is currently produced using gas boilers and heat recovery units associated with gas turbines. Electrification of steam using clean electricity is an

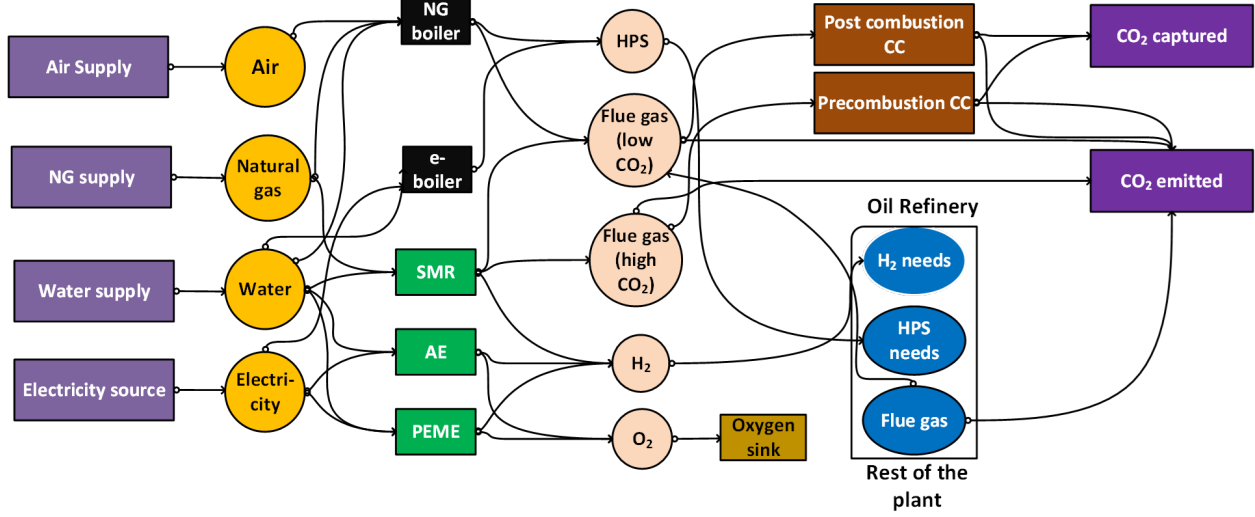


Figure 2: Associated superstructure for decarbonization of oil refineries with a focus on HPS generation and hydrogen production

effective zero emissions solution for low and medium temperature applications. Electric boilers (e-boilers), which offer easy installation, control, maintenance, and higher thermal efficiency, can be retrofitted in refineries<sup>26</sup>.

High-temperature electrified processes remain limited in availability and challenging to implement<sup>5</sup>. Resistive heating, inductive heating, the use of plasma technology, and the use of  $H_2$  fuel are possible alternatives<sup>27</sup>. However, some of these technologies have very low technological readiness levels, and the literature on modeling these processes at an industrial level is scarce. Hence, they are not considered in this work.

### 3 Problem statement and model formulation

Given the operating units in an existing refinery, our goal is to select the refinery configuration that minimizes the present value of the retrofit cost. We combine the discussed alternatives for decarbonization in the form of a superstructure, as shown in Figure 2. We consider current and decarbonized pathways for the production of High-Pressure Steam (HPS) and hydrogen ( $H_2$ ), including gray, blue, and green hydrogen. Blue hydrogen production can involve pre-combustion or post-combustion capture. Similarly, HPS generation alternatives include natural gas (NG) boilers, with or without post-combustion capture, and electric

boilers (e-boilers). For the flue gas released from the rest of the units in the refinery, it is assumed that post-combustion capture is implemented.

The retrofit problem then involves the following decisions:

1. When and how much capacity must be installed for the e-boiler, electrolyzers, and capture units.
2. Operational decisions about how much steam /  $H_2$  needs to be produced by a particular technology.

The following information is assumed to be given:

1. The steam requirements, hydrogen requirements, and the flue gas released (along with the associated  $CO_2$  concentration) from all the units in the refinery other than the boilers and steam methane reformers (including water gas shift reactors).
2. The yield of reaction for the SMR unit.
3. Price forecasts for natural gas and renewable electricity over a specified time horizon.
4. CAPEX forecasts as a function of size for boilers, electrolyzers, and carbon capture (CC) technologies as well as, available sizes for electrolyzers, energy efficiency of boilers and electrolyzers, and capture efficiency of CC technologies.
5. The total time horizon and discount rate for present value calculation along with the discrete time interval at which operating and investment decisions are made (a year in this case).
6. Annual  $CO_2$  emission limits and other policy details such as carbon tax/carbon credit rates or subsidies in renewable electricity.
7. Yearly CAPEX spending limits and upper bounds on annual capacity expansions in respective units (e.g., KW).

Next, we describe the deterministic multiperiod MILP model for this problem.

### 3.1 Mass, energy, design and capacity expansion constraints for each unit

The reader is referred to Nomenclature Section 8 for the symbols included in this section.

#### 1. Boilers

- (a) Mass balance equations: The mass balance constraints outlined in Equations (1) and (2) establish for every year,  $yr$ , a connection between the amounts of components within inlet and outlet streams to the boilers. In Equation (1) the total flow of component  $k$  from all units  $l$ ,  $(\sum_{l \in In(j)} F_{l,j,k,yr})$ , at the inlet of the boiler ( $j$ ), is related by a coefficient  $-\mu_{j,k}$ ,  $(\mu_{j,k} \leq 0)$ , to the total flow of key component  $k'_j$  to all the units  $i$  at the outlet  $(\sum_{i \in Out(j)} F_{j,i,k'_j,yr})$ .  $-\mu_{j,k}$  denotes the amount of component  $k$  that is consumed to produce a unit amount of  $k'_j$  (key component in block  $j$ ) in unit  $j$  (as shown in Figure S2). The key component is the product HPS for this case. Likewise, in equation (2),  $\mu_{j,k}$ ,  $(\mu_{j,k} \geq 0)$ , is used to relate the amount of byproduct  $k$  in the outlet stream of unit  $j$ , considering a certain amount of product  $k'_j$  in the outlet stream (as shown in Figure S3).

$$\sum_{l \in In(j)} F_{l,j,k,yr} = -\mu_{j,k} \sum_{i \in Out(j)} F_{j,i,k'_j,yr}, \quad \text{if } \mu_{j,k} \leq 0 \quad (1)$$

$$j \in \{\text{e-boiler, NG Boiler}\}$$

$$k \in \{\text{water, air, natural gas}\}$$

$$k' = \text{HPS}$$

$$yr \in \{1, \dots, YR\}$$

$$\sum_{i \in Out(j)} F_{j,i,k,yr} = \mu_{j,k} \sum_{i \in Out(j)} F_{j,i,k'_j,yr}, \quad \text{if } \mu_{j,k} \geq 0 \quad (2)$$

$$j \in \{\text{e-boiler, NG Boiler}\}$$

$$k = CO_2$$

$$k' = HPS$$

$$yr \in \{1, \dots, YR\}$$

Equation (3) states that the HPS stream supplied for the requirements of the refinery does not contain any other component.

$$\begin{aligned} F_{j,HPS \text{ needs},k,yr} &= 0, \\ \forall j &\in \{\text{e-boiler, NG boiler}\}, \\ k &\in \mathbb{K} \setminus \{HPS\}, \\ yr &\in \{1, \dots, YR\}. \end{aligned} \tag{3}$$

The boilers' blowdown (purge) is modeled as a linear function of the steam produced. It is related by a constant coefficient  $\gamma_j$  shown in Equation (4)

$$\begin{aligned} \gamma_j F_{j,HPS \text{ needs},HPS,yr} &= F_{j,\text{blowdown},HPS,yr} \\ j &\in \{\text{e-boiler, NG-Boiler}\} \\ yr &\in \{1, \dots, YR\} \end{aligned} \tag{4}$$

(b) Energy balance equations:

The power that needs to be drawn from the electricity source by the e-boiler to produce a given amount of steam is given by the energy balance equation for e-boiler is given by Equation (5). We do not include an energy balance for the gas boiler since the mass balance relating amount of natural gas to the amount of HPS already incorporates the energy balance.

$$\begin{aligned} P_{\text{e-boiler},yr} \cdot \eta_{\text{e-boiler}} &= \Delta H_{\text{vap}} \cdot F_{\text{H}_2\text{O supply,e-boiler,H}_2\text{O},yr} \\ yr &\in \{1, \dots, YR\} \end{aligned} \tag{5}$$

Here  $\eta_{\text{e-boiler}}$  represents the energy efficiency of e-boiler represented as a fraction and  $\Delta H_{\text{vap}}$  shows the enthalpy change involved in formation of HPS from water.

(c) Capacity expansion equations

For e-boilers Equation (6) states that the operational power should not exceed the installed capacity and is greater than fraction  $\chi$  of the installed capacity.

$$Q_{\text{e-boiler},\text{yr}} \cdot \chi_{\text{e-boiler}} \leq P_{\text{e-boiler},\text{yr}} \leq Q_{\text{e-boiler},\text{yr}} \quad (6)$$

$$\text{yr} \in \{1, \dots, \text{YR}\}.$$

Here we assume that electricity supplied to the e-boiler is generated from renewable sources. Hence, scope-2 emissions due to electricity consumption have been excluded from consideration. It is also assumed that renewable electricity is sourced from a stable and consistent supply, which is achieved through the use of storage technologies such as batteries to ensure continuous operation. The upstream costs associated with any such technology are assumed to be included in the electricity price. We do not include capacity expansion equations since no new NG boilers are installed in a transition towards a decarbonized future. Alternatively, equations can be included to keep track of the decommissioned capacities.

## 2. Steam methane reformers:

The SMR labeled superstructure node includes the SMR and WGS reactors, and a PSA column. Additionally, while the SMR unit typically releases High Pressure Steam (HPS) as a result of the exothermic nature of the reaction, this amount is negligible relative to the refinery's total steam requirement and has been disregarded. The superstructure can be modified to take this into account.

### (a) Mass balance equations:

Equations (7) and (8) are the mass balance equations for the SMR, they are similar to the ones used for boilers. The key product in this case is hydrogen. We assumed a fixed yield for the SMR.

$$\sum_{l \in \text{In}(j)} F_{l,j,k,\text{yr}} = -\mu_{j,k} \sum_{i \in \text{Out}(j)} F_{j,i,k',\text{yr}}, \quad \text{if } \mu_{j,k} \leq 0 \quad \forall \text{yr} \quad (7)$$

$$\begin{aligned}
& j \in \{\text{SMR}\} \\
& k \in \{\text{natural gas, water}\} \\
& k' = H_2 \\
& \text{yr} \in \{1, \dots, \text{YR}\} \\
& \sum_{i \in \text{Out}(j)} F_{j,i,k,\text{yr}} = \mu_{j,k} \sum_{i \in \text{Out}(j)} F_{j,i,k',\text{yr}}, \quad \text{if } \mu_{j,k} \geq 0 \tag{8} \\
& j \in \{\text{SMR}\} \\
& k' = H_2 \\
& k = CO_2 \\
& \text{yr} \in \{1, \dots, \text{YR}\}
\end{aligned}$$

Equation (9) denotes that the hydrogen sent to the refinery is 100% pure.

$$\begin{aligned}
& F_{SMR,\text{hydrogen needs},k,\text{yr}} = 0 \tag{9} \\
& k \in \mathbb{K} \setminus \{\text{hydrogen}\} \\
& \text{yr} \in \{1, \dots, \text{YR}\}
\end{aligned}$$

(b) Energy balance equations

We do not include energy balance equations because a portion of the natural gas used per unit mass of hydrogen in the mass balance equations for SMR accounts for the natural gas required both as fuel and as feedstock.

(c) Capacity expansion equations

Capacity expansion equations are not included for the SMR since no new investments are made on SMRs towards a transition to decarbonization.

### 3. Electrolyzers

(a) Mass balance equations

Equations (10) and (11), are the mass balance equations for the electrolyzers.

The key product in this case is hydrogen.

$$\sum_{l \in In(j)} F_{l,j,k,yr} = -\mu_{j,k} \sum_{l \in Out(j)} F_{j,i,k',yr} \quad \text{if } \mu_{j,k} \leq 0 \quad (10)$$

$$j \in \{\text{PEME, AE}\},$$

$$k = \{\text{Water, Electricity}\}$$

$$k' = H_2$$

$$yr \in \{1, \dots, \text{YR}\}$$

$$\sum_{i \in Out(j)} F_{j,i,k,yr} = \mu_{j,k} \sum_{i \in Out(j)} F_{j,i,k',yr}, \quad \text{if } \mu_{j,k} \geq 0 \quad (11)$$

$$j \in \{\text{PEME, AE}\}$$

$$k = O_2$$

$$k' = H_2$$

$$yr \in \{1, \dots, \text{YR}\}$$

We ensure here that no other components flow into the oxygen and hydrogen requirement streams as shown in Equations (12) and (13).

$$F_{j,\text{oxygen sink},k,yr} = 0 \quad (12)$$

$$j \in \{\text{PEME, AE}\}$$

$$k \in \mathbb{K} \setminus \{\text{oxygen}\}$$

$$yr \in \{1, \dots, \text{YR}\}$$

$$F_{j,\text{hydrogen needs},k,yr} = 0 \quad (13)$$

$$j \in \{\text{PEME, AE}\}$$

$$k \in \mathbb{K} \setminus \{\text{hydrogen}\}$$

$$yr \in \{1, \dots, \text{YR}\}$$

The assumptions associated with usage of renewable electricity and the associated scope-2 emissions carry forward to electrolyzers too as described for the electric boiler.

(b) Energy balance equations: Equation (14) denotes the energy balance equation for



electrolyzers. The rate at which electric power,  $P_{j,yr}$ , is drawn from the grid by electrolyzers is based on the enthalpy of electrolysis,  $\Delta H_{\text{electrolysis}}$ , times the mass flowrate upon the efficiency of the electrolyzer,  $\eta_j$ .

$$F_{j,\text{H}_2 \text{ needs,hydrogen,yr}} \cdot \Delta H_{\text{electrolysis}} = P_{j,yr} \cdot \eta_j \quad (14)$$

$$j \in \{\text{PEME, AE}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

- (c) Capacity expansion equations:  $w_{j,h,s,yr}$  shows if the  $s^{\text{th}}$  size is chosen for the  $h^{\text{th}}$  electrolyzer of the  $j^{\text{th}}$  electrolyzer technology in a particular year  $yr$ .  $d_{j,s}$  denotes the  $s^{\text{th}}$  discrete size available in the  $j^{\text{th}}$  electrolyzer technology. Equation (15) computes the overall capacity expansion of a specific technology  $j$  of electrolyzer,  $QE_{j,yr}$ , for any given year. This is the sum of the capacities of individual units  $h$ , where  $\sum_{s=d_{j,s}}^{d_{j,s}} w_{j,h,s,yr} d_{j,s}$  represents the size selected for a particular unit  $h$ .

$$\sum_{h=1}^H \sum_{s=d_{j,s}}^{d_{j,s}} w_{j,h,s,yr} d_{j,s} = QE_{j,yr} \quad (15)$$

$$j \in \{\text{PEME, AE}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

Equation (16) ensures that at most one size  $d_{j,s}$  is selected for each electrolyzer unit  $h$  designated for installation.

$$\sum_s w_{j,h,s,yr} \leq 1 \quad (16)$$

$$j \in \{\text{PEME, AE}\}$$

$$h \in \{1, \dots, H\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

Equation (17) enforces that a higher-indexed electrolyzer unit can only be installed if a lower-indexed unit is already selected<sup>28</sup>. This creates a logical ordering of installations. Equation (18) ensures that larger sizes have lower indices, thereby

preventing any permutation of size selections.

$$w_{j,h,s,\text{yr}} \geq w_{j,h+1,s,\text{yr}} \quad (17)$$

$$j \in \{\text{PEME, AE}\}$$

$$h \in \{1, \dots, \text{H}-1\}$$

$$s \in \{d_{j,s}, \dots, d_{j,S}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

$$\sum_{s=d_{j,s}}^{d_{j,S}} w_{j,h,s,\text{yr}} d_{j,s} \geq \sum_{s=d_{j,s}}^{d_{j,S}} w_{j,h+1,s,\text{yr}} d_{j,s} \quad (18)$$

$$j \in \{\text{PEME, AE}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

$$h \in \{1, \dots, \text{H}-1\}$$

Finally, Equation (19) imposes the constraints that the operational power must not exceed the installed capacity, and it must be at least a fraction  $\chi_j$  of the installed capacity.

$$Q_{j,\text{yr}} \chi_j \leq P_{j,\text{yr}} \leq Q_{j,\text{yr}} \quad (19)$$

$$j \in \{\text{PEME, AE}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

#### 4. Carbon capture units

Both post-combustion and pre-combustion carbon capture technologies are assumed to utilize absorption-based methods employing monoethanolamine (MEA) as a solvent. The flue gas is approximated to be composed of  $CO_2$  and air.

##### (a) Mass balance constraints:

For the carbon capture units, a constraint based on mass balance for each component as shown in Equation (20) is specified, which denotes that the amount of component  $k$  passed on from any of the sources of flue gas to the carbon capture

units is either emitted or captured.

$$F_{j,CO_2 \text{ emitted},k,yr} + F_{j,CO_2 \text{ captured},k,yr} = \sum_{l \in \text{In}(j)} F_{l,j,k,yr} \quad (20)$$

$$j \in \{\text{Pre-comb. CC, Post-comb. CC}\}$$

$$k \in \{\text{CO}_2, \text{air}\}$$

$$yr \in \{1, \dots, \text{YR}\}$$

The amount of  $CO_2$  captured and released through carbon capture units is proportionally linked by a  $\eta_j$  efficiency as shown in Equation (21).

$$(1 - \eta_j)F_{j,CO_2 \text{ captured},CO_2,yr} = \eta_j F_{j,CO_2 \text{ emitted},CO_2,yr} \quad (21)$$

$$j \in \{\text{Pre-comb. CC, Post-comb. CC}\}$$

$$k \in \{\text{CO}_2, \text{air}\}$$

$$yr \in \{1, \dots, \text{YR}\}$$

Furthermore, pre-combustion CC can only be used to treat the shifted syn gas or PSA tail gas, which accounts for 59% of  $CO_2$  emissions from the SMR unit as shown in Equation (22)<sup>22</sup>. The rest of the  $CO_2$  released by combustion of the natural gas based fuel gas can only be treated by postcombustion. Alternatively, if the PSA tail gas is recycled back into the SMR reactor to utilize the unburnt hydrocarbon as fuel, the resulting flue gas can be only treated by postcombustion CC.

$$\begin{aligned} & 0.59 (F_{\text{SMR,Precomb CC},CO_2,yr} + F_{\text{SMR,Post comb CC},CO_2,yr} + F_{\text{SMR, CO}_2 \text{ emitted}, CO_2,yr}) \\ & \geq F_{\text{SMR,Precomb CC},CO_2,yr} \end{aligned} \quad (22)$$

$$\text{where } yr \in \{1, \dots, \text{YR}\}.$$

(b) Capacity Expansion equations:

Equation (23) states that the operating flowrates have to be less than the total installed capacity of CC equipments as shown in.

$$F_{j,CO_2 \text{ captured},CO_2,yr} \leq Q_{j,yr} \quad (23)$$

$$j \in \{\text{Pre-comb. CC, Post-comb. CC}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

### 3.2 Overall mass balance equations

The combined amounts of total HPS and hydrogen generated through various methods must match the total HPS ( $r_1$ ) and the hydrogen needs ( $r_2$ ) of the refinery as specified in Equations (24) and (25). We assume that the needs for LPS and MPS are satisfied by HPS production and appropriate pressure reduction using let down valves.

$$\sum_{j \in \text{In(HPS needs)}} F_{j, \text{HPS needs, HPS, yr}} = r_1 \quad (24)$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

$$\sum_{j \in \text{In(hydrogen needs)}} F_{j, \text{hydrogen needs, hydrogen, yr}} = r_2 \quad (25)$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

We consider that furnaces, catalytic cracking units, and other processing units that do not have an electrification based alternative in our superstructure and emit flue gas containing a specific mix of components. We simplify this mixture to consist of air and carbon dioxide in specified amounts  $f_1$  and  $f_2$ , respectively, as shown in Equations (26) and (27). We assume that the only option for decarbonizing these units is by treating the flue gas released in post-combustion capture units.

$$\sum_{j \in \text{Out(rest of the plant (flue gas prod.))}} F_{\text{rest of the plant (flue gas prod.), } j, \text{CO}_2, \text{yr}} = f_1 \quad (26)$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

$$\sum_{j \in \text{Out(rest of the plant (flue gas prod.))}} F_{\text{rest of the plant (flue gas prod.), } j, \text{air, yr}} = f_2 \quad (27)$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

We also assume that blending of flue gas from natural gas boilers, hydrogen production using SMR, and from the rest of the plant do not significantly impact the Operational Expense (OPEX) for post-combustion capture.

### 3.3 Overall capacity expansion equations

#### 3.3.1 Capacity expansion constraints

Equation (28) specifies that the capacity at the end of each time interval, denoted as  $Q_{j,yr}$ , equals the cumulative capacity from the preceding period,  $Q_{j,yr-1}$  plus the expansion realized within the current period,  $QE_{j,yr}$ .

$$QE_{j,yr} + Q_{j,yr-1} = Q_{j,yr} \quad (28)$$

$$j \in \{\text{PEME, AE, e-boiler, Pre-comb CC., Post-comb CC.}\}$$

$$yr \in \{1, \dots, \text{YR}\}$$

Equation (29) states that expansion  $QE_{j,yr}$  should lie within the specified range defined by a lower bound  $LB_j$  and an upper bound  $UB_j$ . If no expansion takes place, the value of the expansion is exactly 0. If the installation of a particular unit is completed in the given year only then the capacity expansion can be set to non-zero<sup>29 30</sup>.

$$LB_j m_{j,yr} \leq QE_{j,yr} \leq UB_j m_{j,yr} \quad (29)$$

$$j \in \{\text{PEME, AE, e-boiler, Pre-comb CC., Post-comb CC.}\}$$

$$yr \in \{1, \dots, \text{YR}\}$$

#### 3.3.2 Logic timing constraints

Equations (30) and (31) describe the relationships between the binary variables and the non-negative integer variables keeping a count on the total number of installations initiated/completed in a particular year  $l$ .

$$\sum_{n=1}^{yr} y_{j,n} = z_{j,yr} \quad (30)$$

$$j \in \{\text{PEME, AE, e-boiler, Pre-comb CC., Post-comb CC.}\}$$

$$yr \in \{1, \dots, \text{YR}\}$$

$$\sum_{n=1}^{yr} m_{j,n} = p_{j,yr} \quad (31)$$

$$j \in \{\text{PEME, AE, e-boiler, Pre-comb CC., Post-comb CC.}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

Additionally, logical relations are implemented so that  $m$  is a delayed representation of  $y$ , contingent upon the installation period ( $dur(j)$ ) of each equipment component as shown in Equation (32).

$$y_{j,\text{yr}+dur(j)} = m_{j,\text{yr}} \quad (32)$$

$$j \in \{\text{PEME, AE, e-boiler, Pre-comb CC., Post-comb CC.}\}$$

$$\text{yr} \in \{1, \dots, \text{YR}-dur(j)\}$$

The flow of the key component  $k'_j$ , to a unit of technology block  $j$ , can be non-zero only if the installation of at least one unit of technology  $j$  has been completed by a given year as shown in Equation (33).

$$F_{j,i,k'_j,\text{yr}} \leq UB_j \cdot p_{j,\text{yr}} \quad (33)$$

$$j \in \{\text{PEME, AE, e-boiler, Pre-comb CC, Post-comb CC}\}$$

$$i \in \text{Out}(j)$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

Here, the symbol  $UB_j$  denotes an upper limit on the relevant flow rate.

### 3.4 Carbon dioxide emissions constraint

Each year, Equation (34) imposes a maximum limit on the amount of carbon dioxide ( $CO_2$ ) that can be produced. These are based on emission restriction goals set by the company or imposed by the government.

$$\sum_{j \in In(CO_2 \text{ emitted})} F_{j,CO_2 \text{ emission},CO_2,\text{yr}} \leq CO_2 \text{ CAP}_{\text{yr}} \quad (34)$$

$$\text{yr} \in \{1, \dots, \text{YR}\}$$

### 3.5 Capital expenses constraint

Equation (35) ensures that the annual CAPEX does not exceed the specified CAPEX  $CAP_{yr}$  set by the company.

$$CAPEX_{yr} \leq CAPEX CAP_{yr} \quad (35)$$

$$yr \in \{1, \dots, YR\}$$

### 3.6 Objective function

The objective function is defined as the present Value of the cost of the decarbonization project as shown in Equation (36) where  $int$  is the discount rate.

$$Z = \sum_{yr=1}^{29} \frac{(CAPEX_{yr} + OPEX_{yr})}{(1 + int)^{yr}} \quad (36)$$

In Equation (37) the total Capital Expenditure (CAPEX) for an expansion is represented by  $\alpha_{j,yr} + \beta_{j,yr}QE_{j,yr}$ , where  $\alpha_{j,yr}$  denotes the fixed cost in a particular year, and  $\beta_{j,yr}QE_{j,yr}$  denotes the variable cost associated to the amount of capacity expansion for installing a given technology  $j$  in a particular year. This type of a linear cost function with fixed charge accounts for the economies of scale as discussed in Biegler et al.<sup>31</sup>. Furthermore it is noted that the fixed cost is spent only during the period when an equipment is being built. Any costs associated with decommissioning of old equipments have been neglected.

$$CAPEX_{yr} = \sum_j \left( \frac{\alpha_{j,yr}(z_{j,yr} - p_{j,yr})}{dur(j)} + \sum_{c=1}^{dur(j)} \frac{\beta_{j,yr}QE_{j,yr+c}}{dur(j)} \right) \quad (37)$$

$$yr \in \{1, \dots, YR\}$$

$$j \in \{PEME, AE, e-boiler, Precomb CC., Postcomb CC.\}$$

The Operational Expenses (OPEX) incurred for decarbonization initiatives each year are included in Equation (38), and comprise of two primary components: the first one relates to the consumption of natural gas and electricity from their respective sources; the second one, associated with the carbon capture units, is directly proportional to emission reductions.

Part of the operating expense for carbon capture equipment is associated with the energy cost for separation. The steam required for  $CO_2$  stripping is assumed to be generated using

combustion of natural gas since cost data was available for this. This assumption is from the rationale that if CC is being implemented, NG based technologies are still in place and it would be more practical to consider natural gas for steam generation. Hence, we relate the amount of natural gas needed to capture a given amount of  $CO_2$ , and find the associated prices using natural gas price forecasts. The rest of the OPEX is assumed to be proportional to the amount of  $CO_2$  captured.

$$\begin{aligned}
OPEX_{yr} = & \left( \sum_{j \in \text{Out(NG Supply)}} F_{\text{NG Supply},j,\text{NG},yr} \$_{\text{NG/unit mass}} \right. \\
& + \sum_{j \in \text{Out(Electricity source)}} P_{j,yr} \$_{\text{electricity/unit energy}} \left. \right) \\
& + \sum_{j \in \text{CC. Units}} \left( F_{j,\text{CO}_2 \text{ Captured},\text{CO}_2,yr} \cdot \frac{NG_{\text{consumed}}}{\text{unit mass CO}_2 \text{ captured}} \cdot \$_{\text{NG/unit mass}} \right. \\
& \left. + F_{j,\text{CO}_2 \text{ Captured},\text{CO}_2,yr} \cdot \frac{\$_{\text{rest of the OPEX}_j}}{\text{unit CO}_2 \text{ captured}} \right) \\
& yr \in \{1, \dots, \text{YR}\}
\end{aligned} \tag{38}$$

### 3.7 Formulation of the optimization problem

Overall, the optimization problem is formulated as shown below:

$$\min Z \tag{39}$$

s.t. Equations (1) – (38)

The continuous decision variables are  $F$  (Material flow rate),  $P$  (Power),  $Q$  (Capacity), and  $QE$  (Capacity expansion). The binary decision variables are  $m$ ,  $y$ ,  $z$ ,  $p$  (showing timing for installation start and completion for individual units or cumulative number of units).  $w$  (showing sizing choices) is a non-negative integer decision variable. An illustration in the Supplementary Information (Figure S1) shows the physical significance of each of the variables.

The objective function and the constraints are linear functions of the decision variables for each period  $yr$ . Hence, this gives rise to a multiperiod Mixed-Integer Linear Program (MILP), which can be solved with state-of-the-art solvers like Cplex<sup>32</sup> and Gurobi<sup>33</sup>.



## 4 Case study 1: Complex high conversion refinery

### 4.1 Description and data

We consider the operational data for a refinery and the associated flowsheet shown in Figure S4 based on the simulations conducted by Anantharaman et al.<sup>34</sup> described in the associated project website. The high conversion refinery in this case study 1, with a capacity of 220,000 BPSD, includes additional process units beyond a simple hydroskimming refinery. These units convert Vacuum Gas Oil (VGO) and vacuum residue into distillates, which are then treated to meet the 10 ppm sulfur specification for automotive fuels. Hydrogen production from the heavy naphtha catalytic reformer is supplemented by a SMR. The refinery configuration features a second crude distillation train, an FCC block, and a DCU added in a second phase, improving both the capacity and the added options.

The cumulative requirements for hydrogen, LPS, MPS, and HPS are shown in Table 2. The amount of HPS, MPS and LPS required/released by each unit and  $H_2$  required are shown in Tables S1 and S2, respectively. The mass of the flue gas emitted and its associated concentration is shown in Figure S5.

Table 2: Case 1 : Steam and  $H_2$  requirements

<b>Utility requirement</b>	<b>Amount</b>
High Pressure Steam (HPS)	161 tons/hr
Medium Pressure Steam (MPS)	144 tons/hr
Low Pressure Steam (LPS)	52 tons/hr
$H_2$ requirements	2.75 tons/hr
Flue gas emissions	76.6 tons/hour
$CO_2$ concentration in flue gas	0.1523

The forecasts for the prices of natural gas and industrial electricity as obtained from the EIA website<sup>35</sup>, are shown in Figure 3. We note that these prices are in terms of 2020 dollars; hence, the original formulation has been slightly modified to discard any additional discounting for the NG and electricity prices. The operating costs associated with post-combustion capture are shown in Figure S8(a) and S8(b) for different refinery sizes<sup>36</sup>. The amount of natural

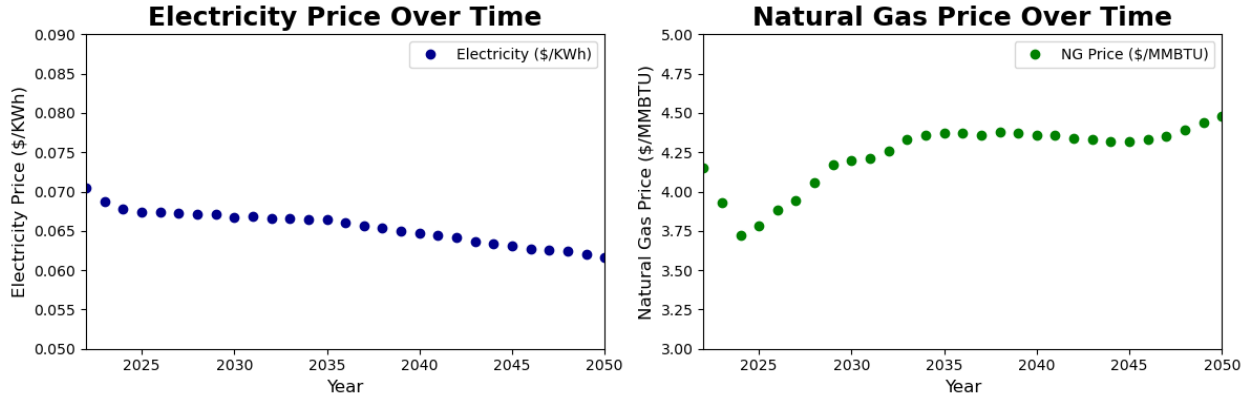


Figure 3: Electricity and natural Gas price forecasts for years 2022-2050

gas required for capture (to produce steam for stripping) is directly proportional to the net amount of  $CO_2$  captured<sup>36</sup>. The rate of natural gas consumption is fixed based on the slope of the line obtained in Figure S8(a)<sup>36</sup>. The remaining OPEX not associated with natural gas consumption is also assumed to be linearly related to the amount of carbon captured, as shown in Figure S8(b).<sup>36</sup> Considering the case of pre-combustion capture, operating expenses are modeled similarly based on the data obtained from the literature<sup>22</sup> as shown in Table S5. CAPEX for equipment are assumed to be linear functions of the processed net  $CO_2$  captured, or  $H_2$  or HPS produced with an intercept to consider economies of scale as in Biegler et al.<sup>31</sup>. Figures S9 (a), (b), (c) and (d) show the data we used to obtain the relevant coefficients for the modeling of the CAPEX of e-boilers<sup>37</sup>, AEs, PEMEs<sup>38</sup>, and post-combustion capture units<sup>36</sup>, respectively. For pre-combustion carbon capture of various capacities catering to SMRs, the CAPEX are shown in Table S5. For CAPEX related to pre-combustion capture, it was assumed that the slope of the CAPEX curve as a function of size remains consistent with that of post-combustion, but the intercept is adjusted to align with the data in Table S5. Linear fits give rise to the fixed cost coefficient  $\alpha_{j,yr}$ , and the variable cost coefficient  $\beta_{j,yr}$  for each newly installed technology unit.

## 4.2 Implementation and base case results

The proposed retrofit MILP model was implemented in Pyomo 6.6.1 with the Gurobi 10.0.1 solver<sup>33</sup>, for a 29-year horizon containing 204,729 constraints, and 102,918 variables (97,234 continuous, 5,684 integer). There are  $\sim 3,800$  degrees of freedom, and the CPU time to solve the model was 10-20 seconds.

In the base case scenario, where predetermined targets for reducing  $CO_2$  emissions are enforced (a reduction of 50% by year 10 and a reduction to the lowest achievable level by year 28), post-combustion and pre-combustion CC are preferred over electrified solutions in years 11-27. Among the carbon capture methods, pre-combustion capture is favored for SMRs, while post-combustion capture is implemented for other combustion-related flue gases. Although installation of pre and post-combustion capture unit requires diversifying capital investment, it is chosen due to its operational cost savings.

A shift towards electrified technologies is observed in 2049 for both steam and  $H_2$  production, prompted by the imposition of stringent emission restrictions that require them to be reduced to the minimum feasible level. In this context, Proton Exchange Membrane Electrolyzers (PEMEs) are favored for electrification of  $H_2$ , driven by the anticipated cost savings in operational expenditure based on predicted electricity prices. AEs are chosen if the efficiency of PEMEs decreases to 71% from 75%.

Figure 4(b) shows that carbon neutrality has not been achieved in the last years because the current superstructure allows only post-combustion CC of the flue gas from the rest of the plant, which is not 100% efficient. Figure 4(b) also shows that the emission cap constraint is always active at the optimal solution, meaning that the plant emits as much as it is allowed to.

Figure 5 shows the optimal installation timelines for various technologies. We note that the capital expenditure for CC alternatives is significantly higher than for electrified technologies. Still, electrification-based technologies are not selected due to their high operational costs.

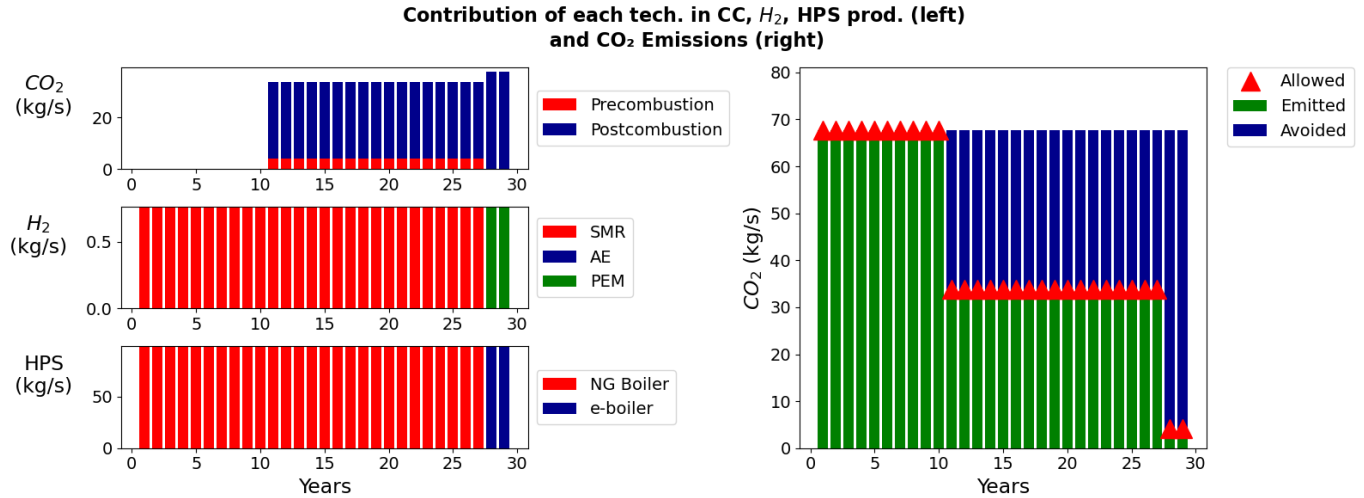


Figure 4: (a) Optimal results for base case simulation: The figures from top to down show the contribution of each technology in carbon capture; hydrogen production and steam production. (b) Figure shows the total  $CO_2$  emissions as compared to the maximum allowed emissions over the years. The emissions avoided as a result of the decarbonization initiatives are also shown.

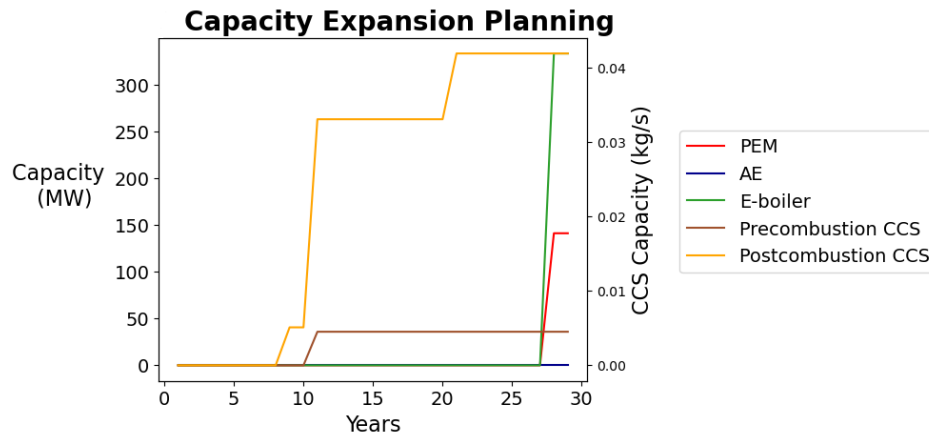


Figure 5: Rate at which the electrified alternatives should be installed in MW capacity and the optimal rate of CC capacity installation in kg/s.

### 4.3 Sensitivity analyses

To explore scenarios conducive to the adoption of electrified options, we investigate how the optimal solution varies in response to policy implementations such as (i) carbon tax, (ii) carbon credits, (iii) modified emission reduction goals, (iv) reduction in electricity prices or rates of subsidy application.

### 4.3.1 Policy implementation: Effect of carbon taxes

When carbon taxes are implemented at specified rates, as shown in Figure S10<sup>39</sup>, it is noted that transitioning earlier to carbon capture technologies proves to be economically advantageous. However, the introduction of carbon taxes does not accelerate the adoption of electrified technologies.

This transition, illustrated in Figure 6(a), results in a decrease in  $CO_2$  emissions of the plant. Furthermore, after year 20, emission levels fall below the maximum allowable levels as indicated in Figure 6(b). This indicates the point where paying for carbon taxes becomes more expensive than deploying decarbonization technologies.

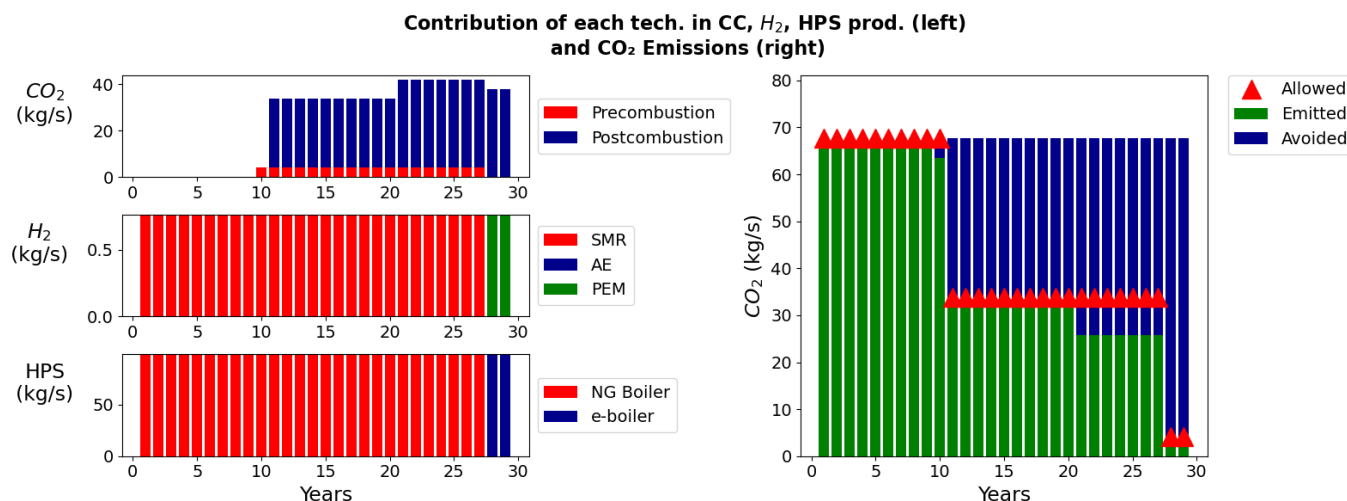


Figure 6: (a) With carbon taxes: Optimal solution is heavily reliant on carbon capture alternatives and are adapted earlier (from year 10) as compared to the base case, electrified alternatives still chosen in years 28-29. Canadian carbon tax rates were used in the simulations<sup>39</sup> (b) Emission constraints are inactive for a part of the time frame

### 4.3.2 Policy implementations: Effect of carbon credits

According to the 45Q tax credit rates under the Inflation Reduction Act, \$85/ton  $CO_2$  captured<sup>40 41</sup> and stored securely underground are provided. According to the 45 V tax credits, at least \$0.6 tax credits are provided per kg of clean  $H_2$  produced (if the life cycle emissions are between 2.5-4 kg  $CO_2e$ ). We have applied 45 V tax credits to green  $H_2$  in

our case study, and not to blue, carbon capture based  $H_2$ , as multiple incentives cannot be claimed together. The applicable amount is based on the expected lifecycle greenhouse gas emissions.

Figure 7 shows that the results are qualitatively similar when carbon credits are imposed instead of carbon taxes, in the sense that both initiatives promote the installation of carbon capture units but not electrification. Interestingly, the carbon credit initiatives considered promote emission levels well below the allowed ones. This indicates that this policy is more successful than the carbon taxes, at the discussed rates for accelerating decarbonization.

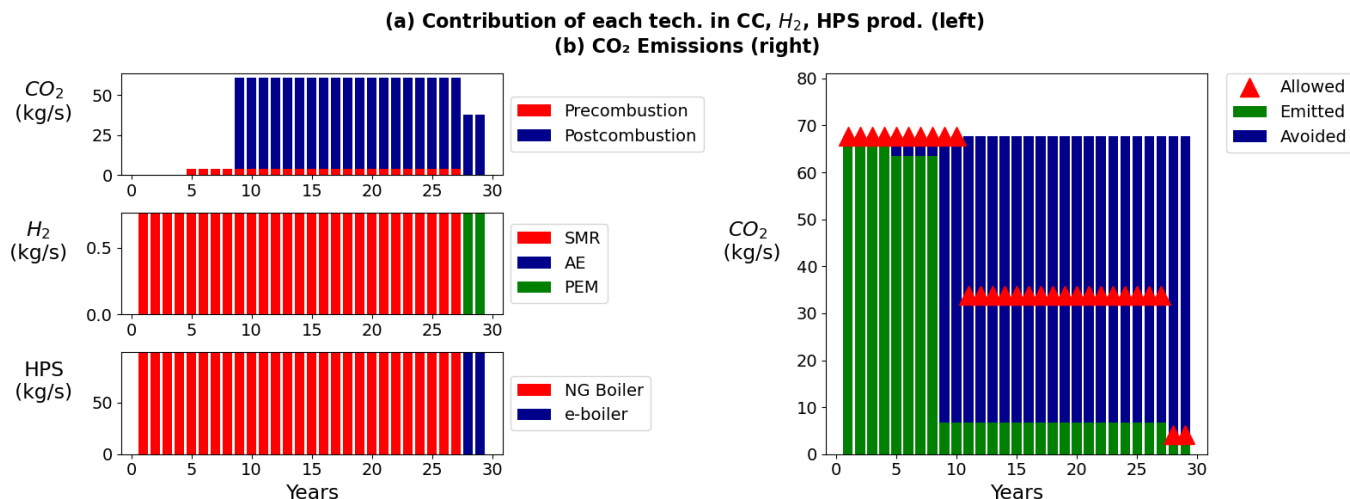


Figure 7: With 45 Q and 45 V carbon credits : (a) Optimal solution with carbon credits implemented at specified rates; carbon capture is implemented from year 5; e-boilers and electrolyzers still chosen in years 28-29 (b) Emission constraints are inactive similar to the case with  $CO_2$  taxes

### 4.3.3 Effect of changing emission reduction goals coupled with carbon taxes

The previous results indicate that the technological choices are primarily influenced by emission cap constraints. Although companies typically focus on setting long-term emission reduction goals rather than annual targets, policymakers could benefit from exploring whether incentivizing alternative emission reduction profiles can potentially accelerate decarbonization. We chose an emission cap profile that linearly decreases from 50% of current emissions

to the minimum achievable value by year 29.

In this setting, cumulative emissions, represented by the total area shaded in green, are significantly lower than those in Figure 6(b) (Section 4.3.1), as shown in Figure 8(b). However, the objective value (present cost) in this case is 1.59% higher than in the scenario with staggered reduction goals (shown in Figure 6(b)).

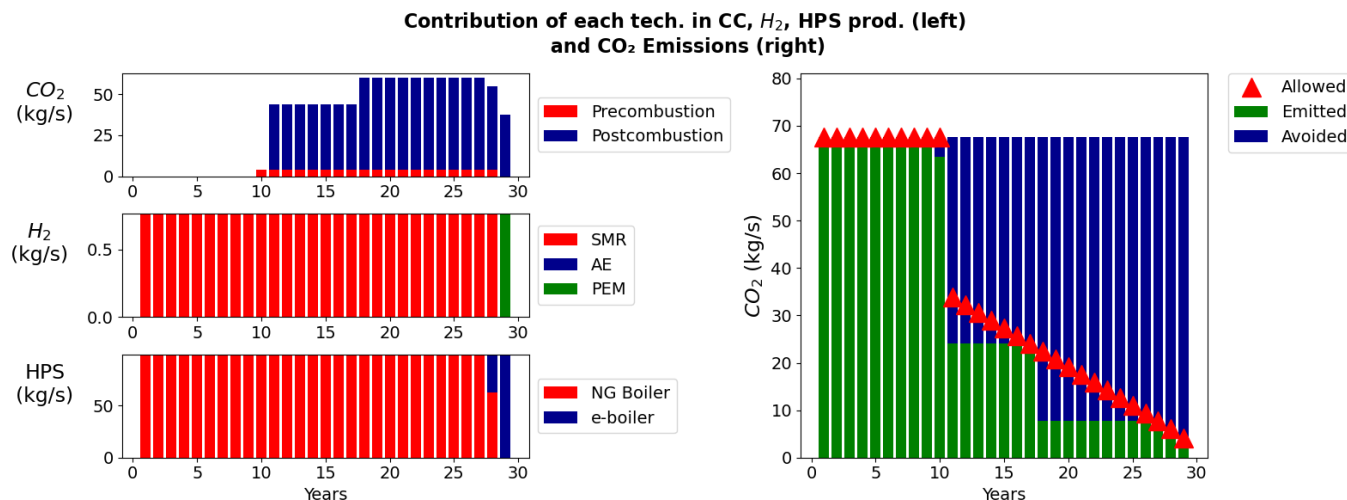


Figure 8: (a) With changing emission reduction goals and  $CO_2$  taxes : Optimal solution with linear reduction in emission cap from years 11 to 29 and  $CO_2$  taxes; e-boiler chosen from year 28 onwards (b) Lower cumulative emissions with reduction in emission cap from years 11 to 29

#### 4.3.4 Effect of a reduction in electricity prices/subsidized availability of renewable electricity

An analysis of the impact of reduced electricity costs reveals that with a reduction of up to 65%, the overall solution remains qualitatively similar to the base case. Figure 9 illustrates that when electricity prices are reduced further than 65% of the forecasted prices, e-boiler technology is selected earlier. However, the adoption of electrolyzer technology is still delayed as a result of its high energy requirements and associated operational costs. Figure 10 shows that when electricity costs are reduced by 80%, a transition to electrolysis-based hydrogen production occurs from year 11 onward. In this scenario, PEMEs are preferred over AEs

because of the operational savings dominating the extra CAPEX.

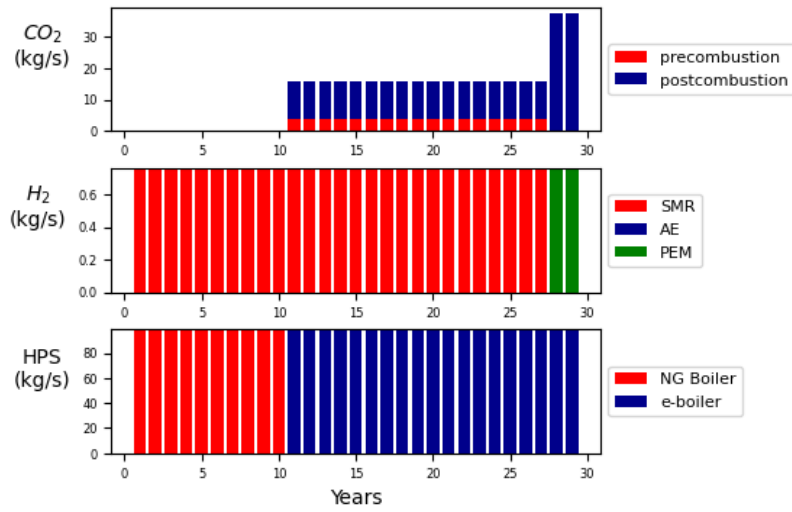


Figure 9: e-boiler chosen from year 11 with 65% drop in electricity prices

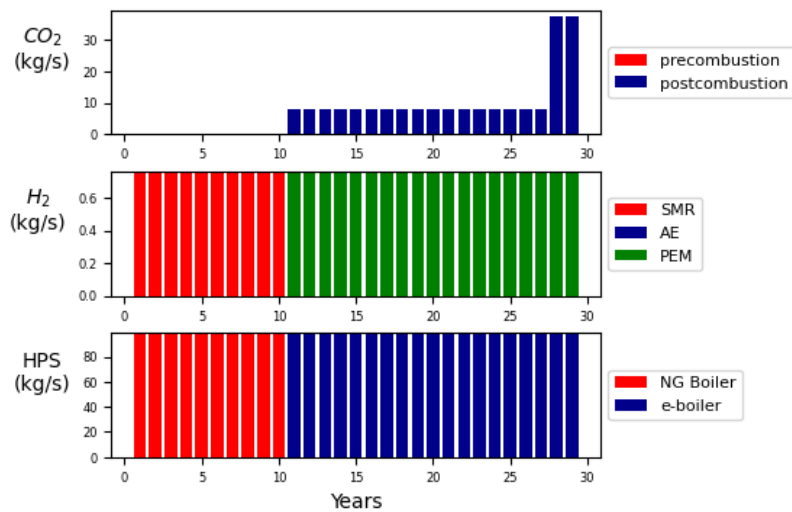


Figure 10: e-boiler chosen from year 3 with 80% drop in electricity prices; PEME are also chosen from year 11 in this case



## 5 Case study 2: Highly complex, large capacity, high conversion refinery

### 5.1 Description and data

Next, we consider a larger capacity refinery of 350,000 BPSD, with more advanced and integrated technology than the one in Case 1. This refinery is shown in Figure S6. It features two parallel crude distillation trains, and includes both FCC and High Pressure Hydrocracking (HCK) units for VGO conversion, each with a capacity of 60,000 BPSD. Additionally, case 2 incorporates a Solvent Deasphalting Unit (SDA) followed by a Delayed Coker Unit (DCU) for vacuum residue conversion, enhancing feedstock flexibility and product value. The hydrogen demand is met by two parallel SMR trains, reflecting a more organized and efficient design<sup>34</sup>.

The cumulative hydrogen, LPS, MPS, and HPS requirements are shown in Table 3. The amount of HPS, MPS and LPS required/released by each unit and the amount of  $H_2$  required are shown in Tables S3 and S4, respectively. Mass of the flue gas emitted and its associated concentration are shown in Figure S7.

Table 3: Case 2: Utility requirements for each unit

<b>Utility Requirement</b>	<b>Amount</b>
High Pressure Steam (HPS)	0 tons/hr
Medium Pressure Steam (MPS)	199.6 tons/hr
Low Pressure Steam (LPS)	213.6 tons/hr
$H_2$ requirements	9.8856 tons/hr
Flue gas	122.7 tons/hr
$CO_2$ concentration in flue gas	0.15189203

We explored 2 different scenarios for the alternate refinery (i) with  $CO_2$  taxes, (ii) with a reduction in electricity prices or increased rates of subsidy application.

## 5.2 Results for case study 2

### 5.2.1 With carbon taxes

Under the given emission restrictions (Figure 11(b)) and imposed carbon taxes (as per rates shown in Figure S10) the optimal solution is as shown in Figure 11. The results are similar to those of Case 1, in the sense that carbon capture technologies are favored over electrified technologies. We also observe that compared to Case 1, there is an earlier adoption of carbon capture. We see this as an indication that the higher amounts of carbon dioxide produced by the larger refinery, make paying carbon taxes less economical than deploying decarbonization technologies.

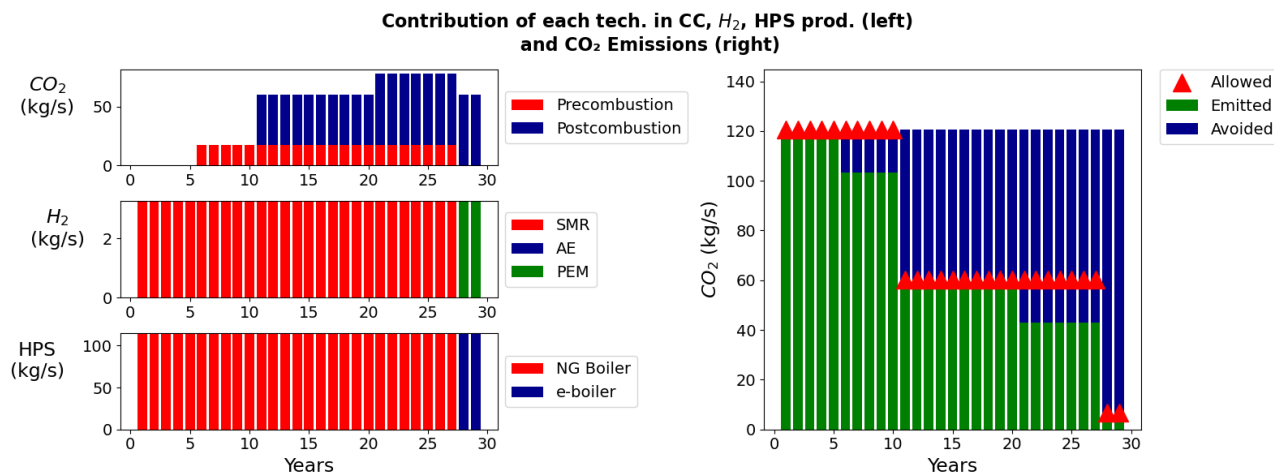


Figure 11: Optimal solutions for high throughput high conversion complex refinery: (a) Carbon capture alternatives heavily implemented from year 6 onwards (b) Actual  $CO_2$  emissions and allowed emissions show that the imposed emission restriction constraint is inactive

### 5.2.2 With reduced electricity prices

With 65% reduction in electricity prices, e-boilers are chosen from year 11 onward. However, the model also recommends reintroducing natural gas (NG) boilers for partial high-pressure steam (HPS) production from year 21 onwards, as natural gas prices decrease slightly between years 20 and 25, making them temporarily cost-effective. Despite being predicted as an optimal solution, it is impractical since decommissioned equipment, is unlikely to be

brought back after long periods of inactivity. This limitation can be addressed by tracking decommissioned equipment and ensuring that all installed systems are utilized at least at their minimum operating capacity. Additionally, this insight suggests that hybrid operation strategies could be explored using finer time discretization.

With 80% reduction in electricity prices, Figure 13 shows that the results are similar to those obtained for the previous refinery shown in Figure 10.

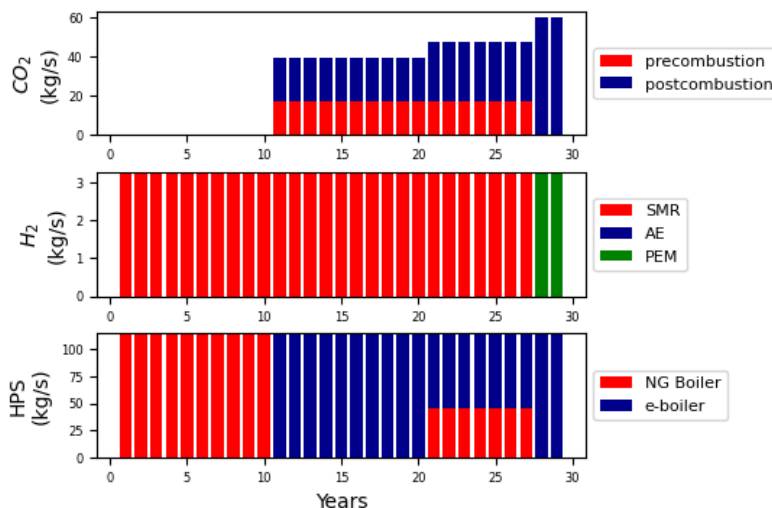


Figure 12: With 65% reduction in electricity prices (case study 2): e-boilers are chosen from year 11; however hybrid operation is favored from year 21-28 due to fluctuating prices

## 6 Conclusion

The paper proposes a multiperiod Mixed Integer Linear Programming (MILP) modeling framework to minimize the present value of costs associated with retrofit decarbonization in an oil refinery. The framework considers decarbonization via the electrification of hydrogen and steam production. It also considers the potential addition of pre-combustion or post-combustion carbon capture units. The framework is agnostic to the refinery configuration, only requiring heating (steam and non-steam), hydrogen needs, and flue gas specifications. Given the decarbonization goals, expenditure limits, electricity and natural gas price forecasts, in addition to carbon policies applicable to the industry's setting, the proposed framework selects the optimal technology switch strategy and timeline for implementation.

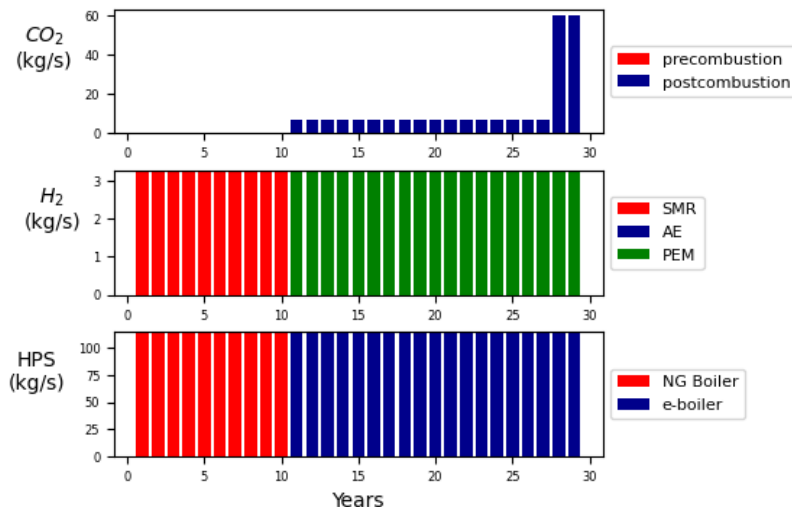


Figure 13: With 80% reduction in electricity prices (case study 2): PEME electrolyzers and e-boilers chosen from year 11.

We illustrate the use of the framework with two different refinery configurations assuming US as the location of operation. We find that due to significantly higher operating expenses associated with electricity, the optimal solution tends to select carbon capture technologies over electrification options. Further, we establish that up to 65% reductions in electricity costs, have a minimal impact on this overall trend. However, a more substantial decrease significantly impacts the optimal solution promoting electrification.

We also find that the implementation of carbon taxes or carbon reduction credits accelerates the adoption of carbon capture methodologies, but not electrification. In addition, carbon credits appear to be more effective in promoting a reduction in  $CO_2$  emissions for the rates used in the case studies. In addition, setting intermediate decarbonization goals has been shown to reduce  $CO_2$  emissions to a greater extent than aiming for a specific long-term emission reduction goal. However, these results are subject to enterprise-specific economic goals. More case studies considering different locations and policies are needed to claim generalization of these trends.

In the future, we plan to expand the framework by including the option of hybrid operation, which requires addressing the effects of variable pricing for electricity from renewable

intermittent sources and the inclusion of energy storage technologies. A rigorous analysis of uncertainties in energy prices, technology costs, and carbon prices should also be included in the framework.

## 7 Acknowledgments

This work was financed [in part] by a grant from the Commonwealth of Pennsylvania, Department of Community and Economic Development. We acknowledge the support and funding from Shell Global and Shell Polymers Monaca. This work was also partially financed by the Department of Chemical Engineering at CMU through AI Torres start-up package.

## 8 Nomenclature

### 8.1 Abbreviations

SDA: Solvent Deasphalting Unit

PTU: Post-treatment unit

KHT: Kerosene Hydrotreatment Unit

ISO: Isomerization unit

NSU: Naphtha Splitting Unit

CAPEX: Capital Expenses

OPEX: Operating Expenses

CDU: Crude Distillation Unit

VDU: Vacuum Distillation Unit

NHT: Naphtha Hydrotreating Unit

VHT: Vacuum oil Hydrotreating Unit

KHT: Kerosene Hydrotreating Unit

DCU: Delayed Coking Unit

MO GAS: Motor Gasoline

SRU: Sulphur Recovery Unit

ISO: Isomerization unit

CRF: Continuous Catalytic Reformer

FCC: Fluid Catalytic Cracking unit

HCK: Hydrocracking unit

SMR: Steam Methane Reformer

VGO: Vacuum Gas Oil

## 8.2 Notations

$F_{l,j,k,yr}$ : A positive continuous variable representing the flow of component  $k$  from unit  $l$  to unit  $j$  in year  $yr$ .

$P_{j,yr}$  denotes the power at which unit  $j$  operates in a particular year

$y_{j,yr}$ : A binary variable indicating whether the installation of a specific technology unit  $j$  is initiated in year  $yr$ .

$m_{j,yr}$ : A binary variable indicating whether the installation of a specific technology unit  $j$  is completed in year  $yr$ .

$z_{j,yr}$ : A non-negative integer variable indicating the number of installations initiated up to year  $yr$  for technology units of type  $j$ .

$p_{j,yr}$ : A non-negative integer variable indicating the number of completed installations up to year  $yr$  for technology units of type  $j$ .

$Q_{j,yr}$ : A continuous variable indicating the total installed capacity of technology  $j$  in a given year  $yr$ .

$QE_{j,yr}$ : A continuous variable that indicates the expansion in installed capacity of technology  $j$  in a given year  $yr$ .

$w_{j,h,s,yr}$ : A binary variable which denotes whether, in year  $yr$ , the  $h$ -th electrolyzer of type  $j$  is of the  $s$ -th size

$-\mu_{j,k}$ , ( $\mu_{j,k} \leq 0$ ): denotes the amount of reactant  $k$  consumed to produce unit amount of key product  $k'_j$  in unit  $j$

$\mu_{j,k}$ , ( $\mu_{j,k} \geq 0$ ): denotes the amount of byproduct  $k$  consumed to produce unit amount of

key product  $k'_j$  in unit  $j$

$k'_j$ : denotes the key product  $k'_j$  produced in unit  $j$

$d_{j,s}$ : denotes the available discrete size  $s$  for each type of electrolyzer,  $j$ .

$dur_j$ : denotes the specified time duration to build the  $j^{th}$  technology node.

$In(j)$ : denotes the nodes that are connected to the inlet of node  $j$

$Out(j)$ : denotes the nodes that are connected to the outlet of node  $j$

$\Delta H_{vap}$ : denotes the enthalpy change involved in the formation of HPS from water

$\Delta H_{electrolysis}$ : denotes the enthalpy change involved in the electrolysis of water

$\eta_j$ : denotes the energy efficiency (for the case of electrolyzers, e-boilers)/ capture efficiency (for the case of pre-combustion CC/ post-combustion CC) for equipment  $j$

$\chi_j$ : denotes the lowest possible turndown expressed as a fraction for equipment  $j$  (electrolyzers and e-boilers)

$f_1$ : denotes the amount of  $CO_2$  in the flue gas from the rest of the plant that does not have electrification-based decarbonization alternatives.

$f_2$ : denotes the amount of air in the flue gas from the rest of the plant that has no electrification based alternatives.

$r_1$ : denotes the requirement of  $H_2$  for the operational needs of the oil refinery

$r_2$ : denotes the requirement of HPS for the operational needs of the oil refinery

$YR$ : denotes the length of the time horizon for planning

$H$ : denotes the maximum number of electrolyzer units bought in a given year.

$S$ : denotes the maximum number of available sizes

### 8.3 Sets

$\mathbb{K}$ : denotes the set of material components present in the various streams (e.g., carbon dioxide, high pressure steam, water, hydrogen and natural gas).

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# S1 Supplementary Information

## S1.1 Figures

### S1.1.1 Illustrations for variables and equations

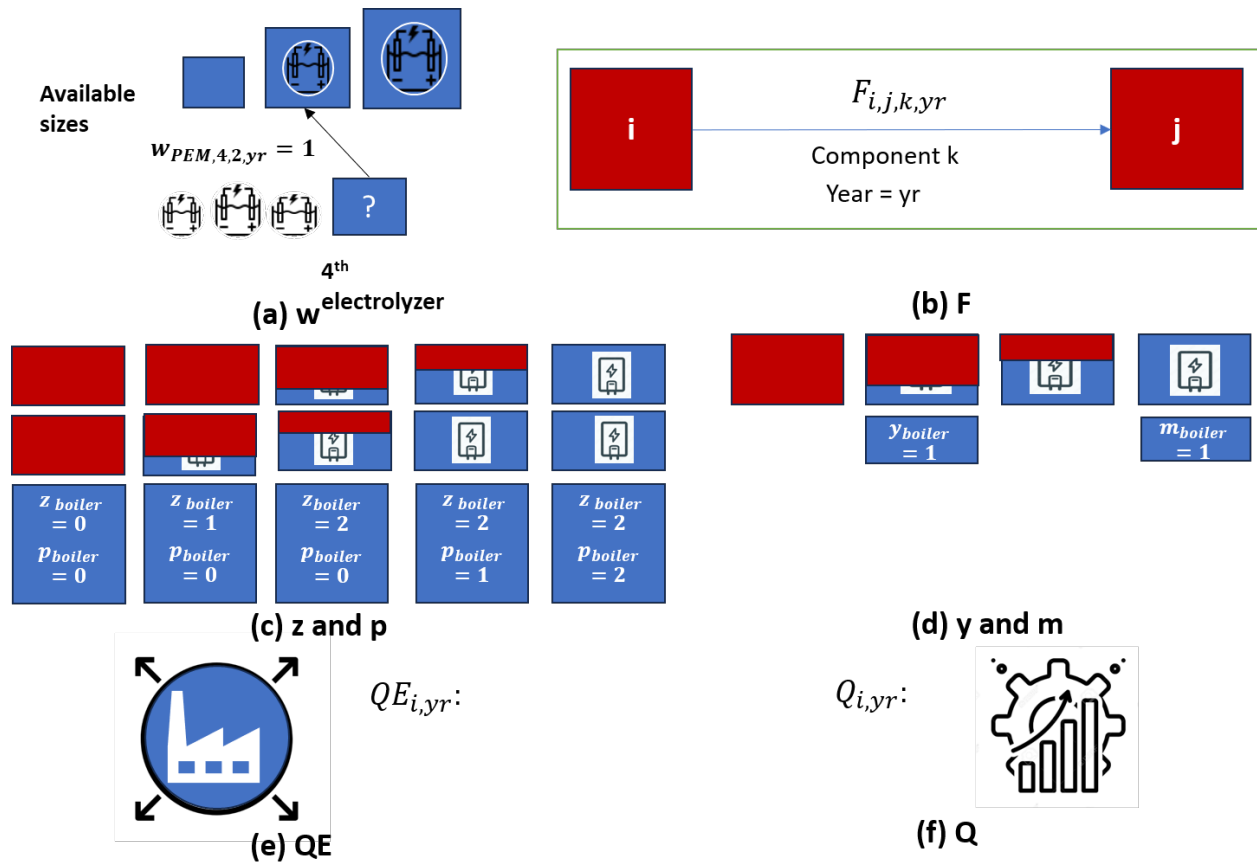


Figure S1: Illustration showing the physical meaning of w, F, z, p, m, y, QE and Q variables

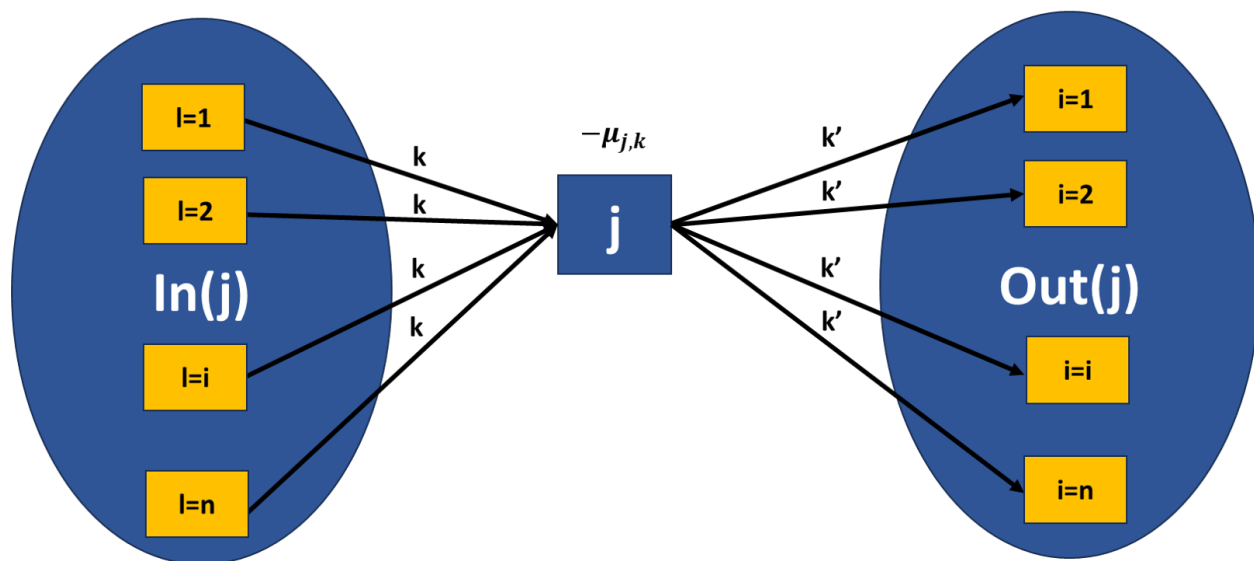


Figure S2: Illustration showing the physical meaning of Equation 1

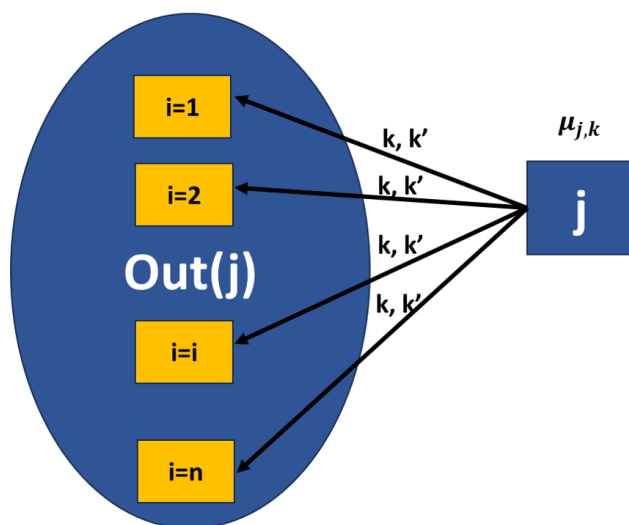


Figure S3: Illustration showing the physical meaning of Equation 2

S1.1.2 Data for refinery in Case Study 1: Complex high conversion refinery

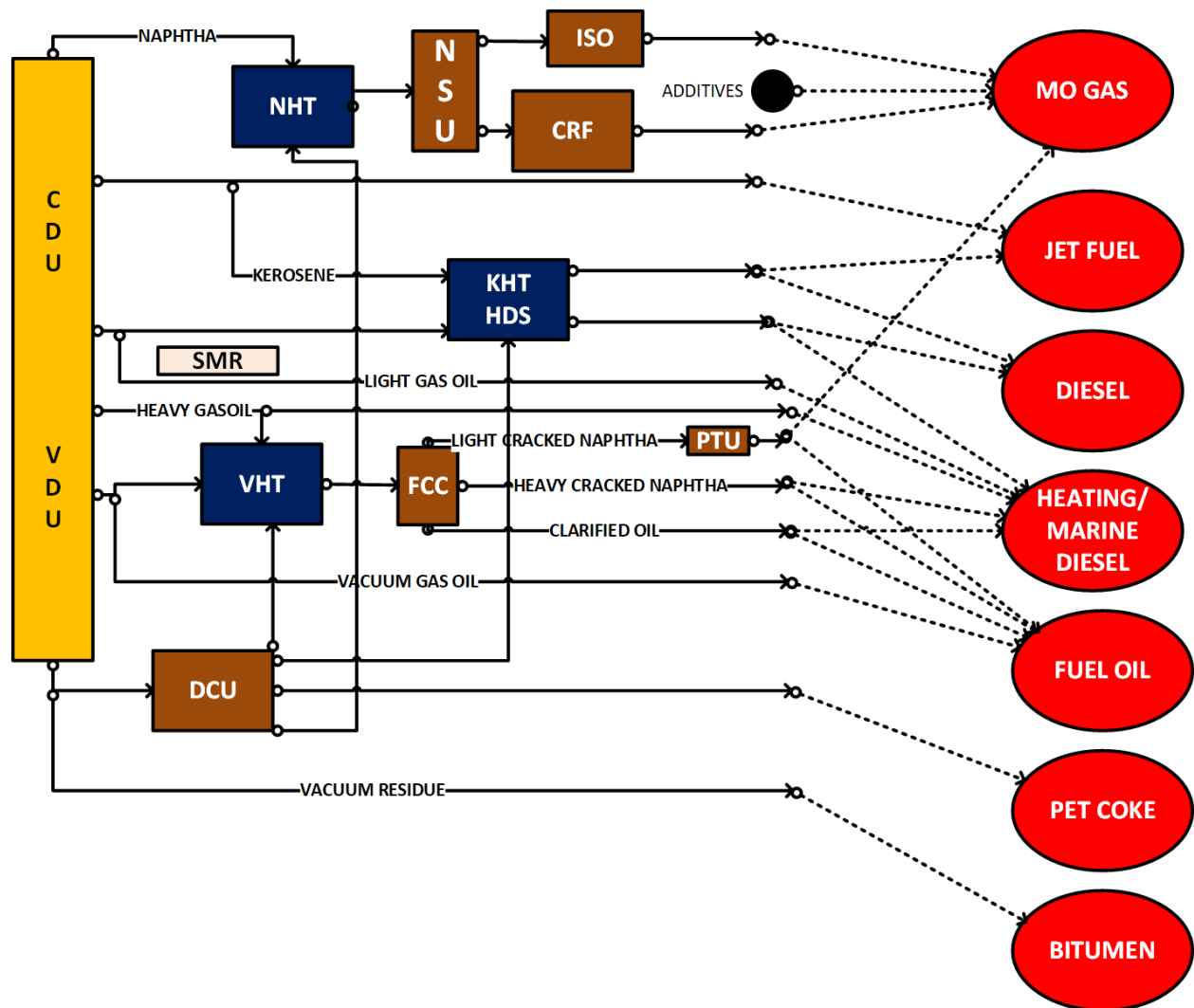


Figure S4: Case study 1: Flowsheet of the refinery



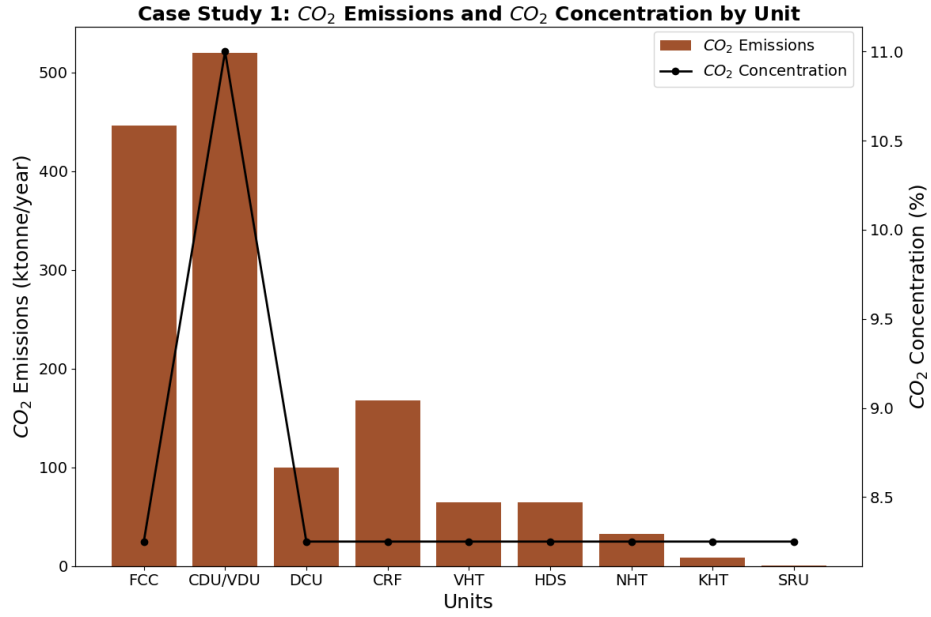


Figure S5: Case study 1: Emissions from the rest of the refinery; excluding steam generation and hydrogen production units

S1.1.3 Data for refinery in Case study 2: High-throughput complex high conversion refinery

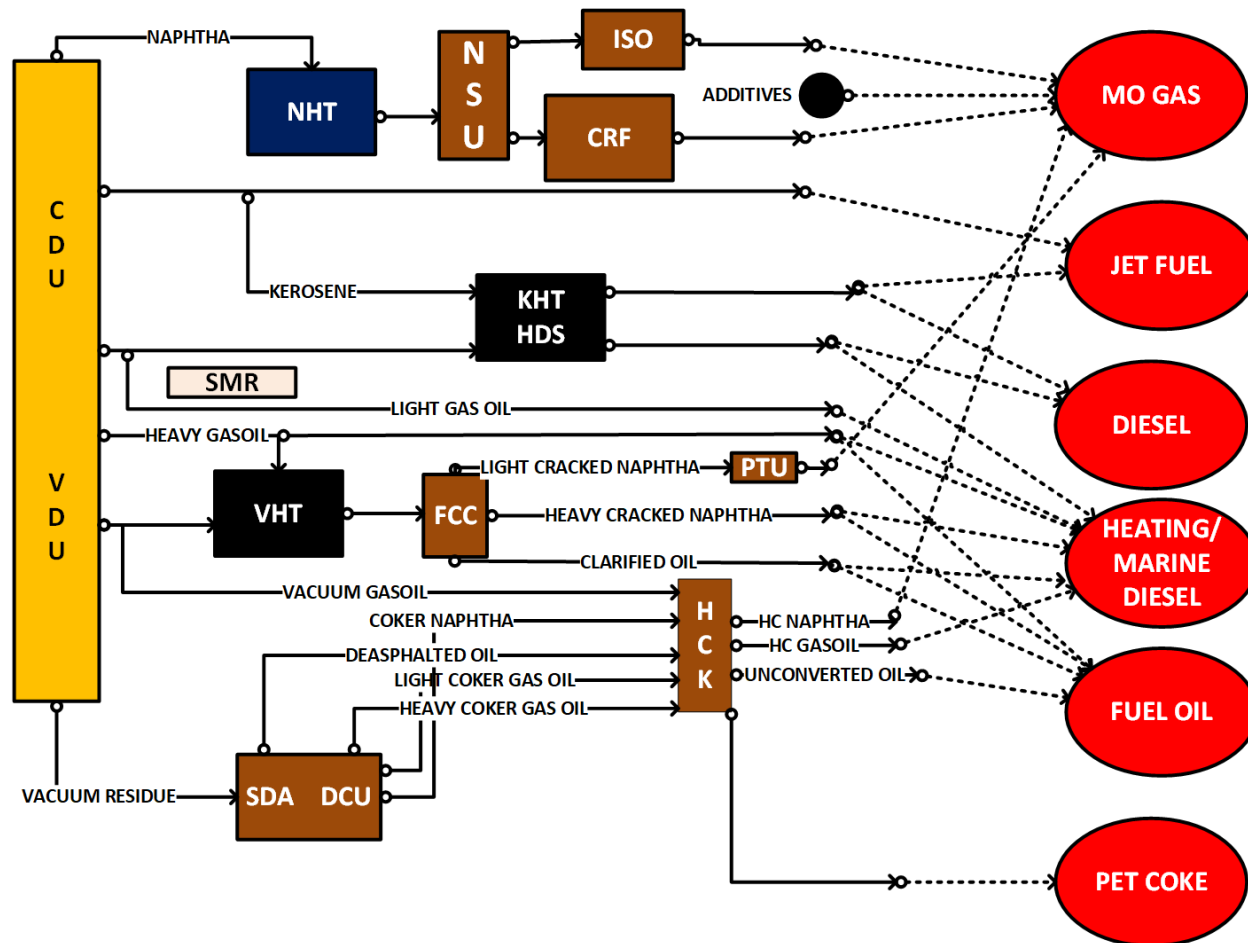


Figure S6: Case 2: Flowsheet of the refinery

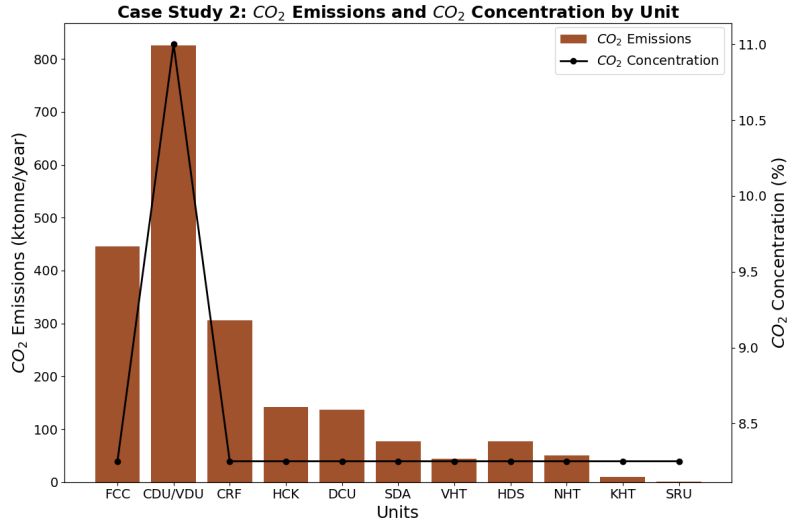


Figure S7: Case study 2: Emissions from the rest of the refinery; excluding steam generation and hydrogen production units

### S1.2 Common data used for both case studies

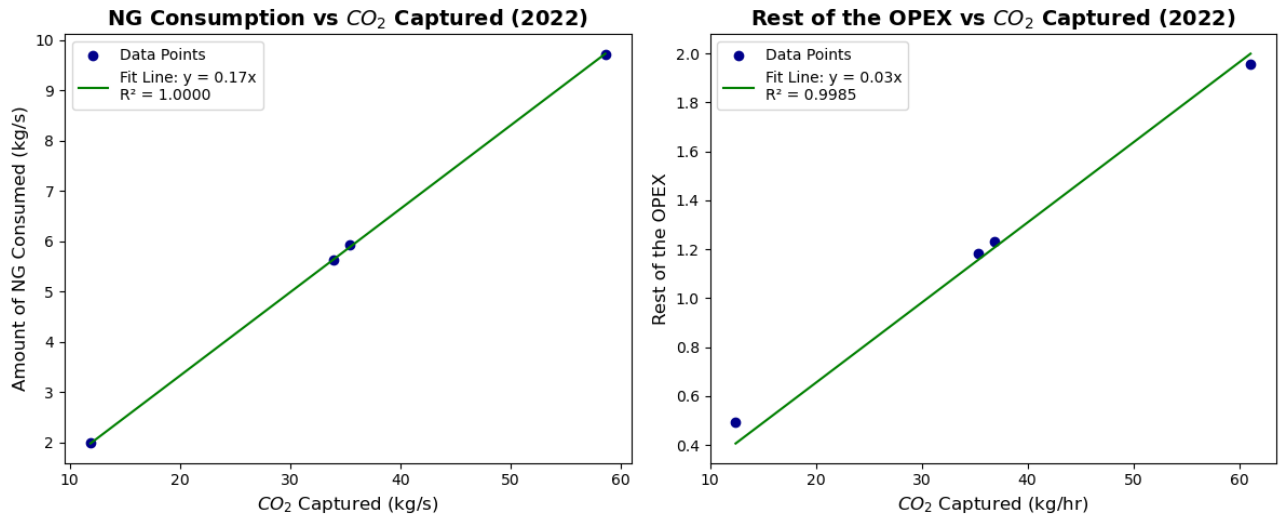


Figure S8: (a) Natural gas consumption as a function of post combustion carbon capture equipment size. (b) Rest of the OPEX as a function of amount of CO<sub>2</sub> captured.

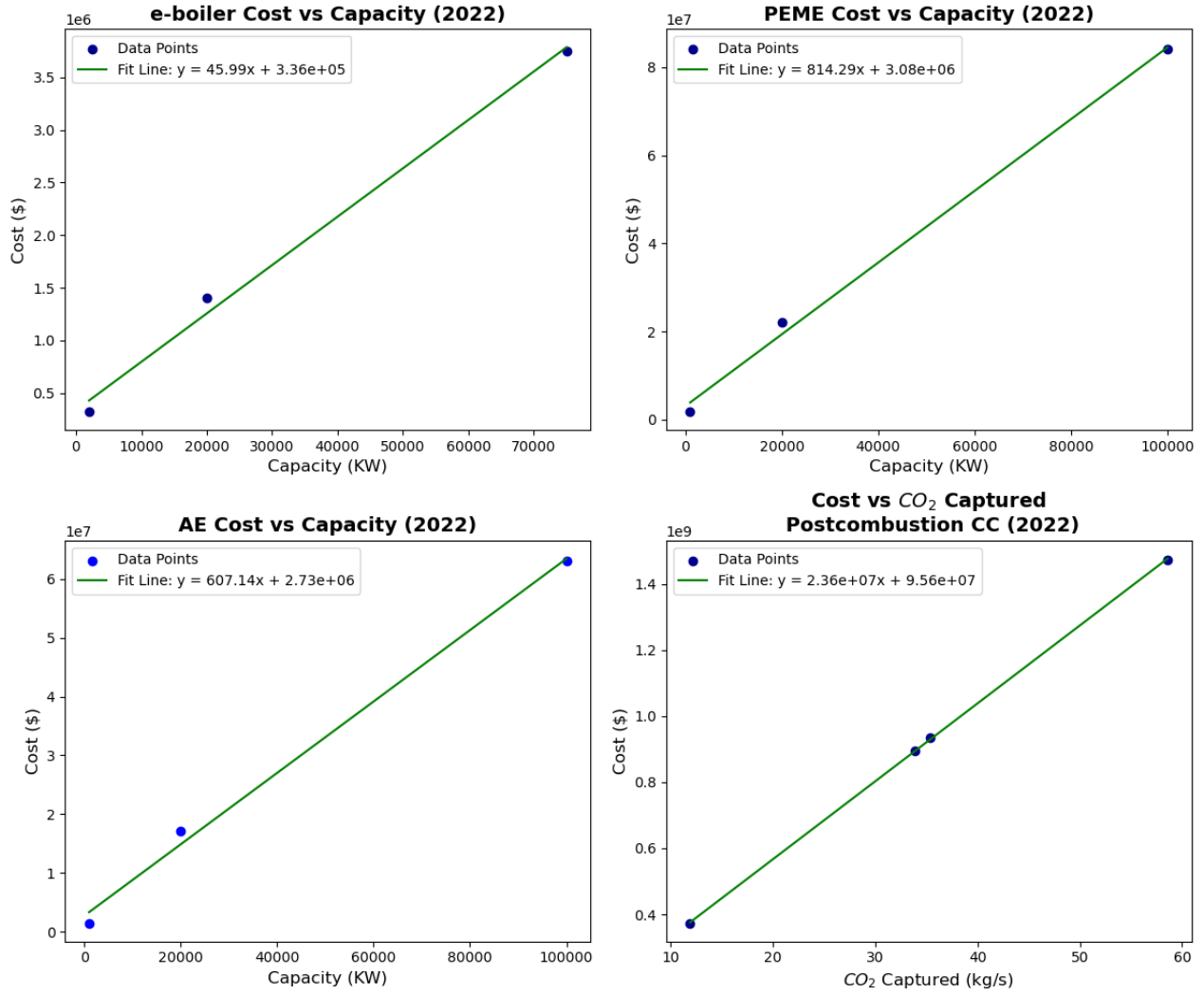


Figure S9: (a) e-boiler CAPEX as a function of boiler capacity<sup>37</sup> (b) Alkaline electrolyzer (AE) CAPEX as a function of capacity<sup>38</sup> (c) Proton Exchange Membrane Electrolyzer (PEME) size as a function of its capacity<sup>38</sup> (d) Post-combustion CC CAPEX as a function of processing capacity<sup>36</sup>

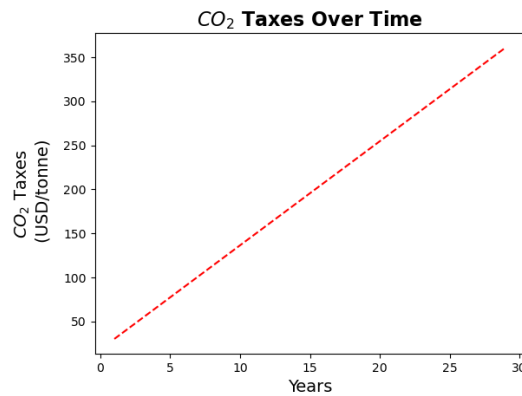


Figure S10: Carbon taxes implemented mimicking Canadian rates

### S1.3 Tables

#### S1.3.1 Data used in Case Study 1

Table S1: Case 1: Steam requirements for each unit  
numbering to S1, S2, etc.

Unit Name	HP Steam (t/h)	MP Steam (t/h)	LP Steam (t/h)
SRU	0.0	-1.59	0.0
ARU	0.0	0.0	6.04
KHT	0.0	7.8	0.0
HDS	0.0	2.8	0.0
CDU	5.0	22.5	71.2
NHT	0.0	13.5	0.0
NSU	0.0	-0.7	0.0
ISO	0.0	4.4	0.0
CRF	-10.5	0.0	0.0
Refinery Base Load	15.0	30.0	30.0
NHT	12.4	0.0	0.0
HDS	0.0	3.7	0.0
VHT	0.0	5.5	5.7
FCC	30.4	47.6	0.0
DCU	8.9	-9.8	0.0
SMR	-29.0	0.0	0.0
VDU	0.0	18.6	4.7

Table S2: Case 1: Unit  $H_2$  requirement in ktonne/year

Component	Value
NHT	2.4
KHT	2.2
HDS	20.2
VHT	32.4
PTU	2.3
ISO	4.1
CRF	-39.9
SMR	-24.1

### S1.3.2 Data used in Case study 2

Table S3: Case 2: Steam requirements for each unit

Unit Name	HP Steam (t/h)	MP Steam (t/h)	LP Steam (t/h)
NHT	40.6	0.0	-2.2
CRF	-19.5	0.0	0.0
ARU	0.0	0.0	10.8
DCU	12.4	-13.7	0.0
SDA	0.0	14.5	0.0
VDU	0.0	24.8	6.3
CDU	8.0	35.8	129.0
VDU	0.0	49.6	12.6
HDS	0.0	4.0	0.0
KHT	0.0	4.8	0.0
FCC	30.4	47.6	0.0
SMR	-99.8	0.0	0.0
ISO	27.4	7.4	53.3
SRU	0.0	-2.9	0.0
VHT	0.0	3.8	4.0
HCK	0.0	0.0	-34.1

Table S4: Case 2: Unit  $H_2$  requirement in kton/year

Component	Value
NHT	3.8
KHT	2.7
HDS	25.0
VHT	22.3
PTU	2.3
ISO	4.1
CRF	-74.1
SMR	-86.6
HCK	97.0

### S1.3.3 Common data used in both case studies

Table S5: Operating costs, capital costs and natural gas requirements for pre-combustion capture unit associated with SMR Reactor

<b>Parameter</b>	<b>Value</b>
$CO_2$ Avoided	23.234 kg/s
$H_2$ Produced	100,000 Nm <sup>3</sup>
Operating Costs	\$ 96,367,002 /year
Natural Gas Requirement for Capture	\$ 15.614 MJ/Nm <sup>3</sup> $H_2$
Capital Costs	\$ 398.48 Million

Table S6: Electrolyzer Size Index and Capacity

Electrolyzer size index	electrolyzer Capacity
1	20,000
2	100,000
3	200,000

Table S7: Efficiency Values for Different Units

<b>Unit</b>	<b>Efficiency</b>
Proton Exchange Membrane Electrolyzer (PEME)	75%
Alkaline Electrolyzer (AE)	70%
Natural Gas	95%
E-boiler	98%
Post-combustion Technology	90%
Pre-combustion Technology	90%