Optimization of Retrofit Decarbonization in Oil Refineries

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ABSTRACT

The chemical industry is actively pursuing energy transition and decarbonization through renewables and other decarbonization initiatives. However, navigating this transition is challenging due to uncertainties in capital investments, electricity costs, and carbon taxes. Adapting to decarbonization standards while preserving existing valuable infrastructure presents a dilemma. Early transitions may lead to inefficiencies, while delays increase the carbon footprint. This research proposes a framework to find an optimal retrofit decarbonization strategy for existing oil refineries. We start with a generic process flowsheet representing the refinery's current configuration and operations, and consider various decarbonization alternatives. Through superstructure optimization, we identify the most cost-effective retrofit strategy over the next three decades to achieve decarbonization goals. We develop a Mixed-Integer Linear Programming (MILP) model, integrating simplified process equations and logical constraints to identify the most economical retrofit decarbonization strategy. The paper presents numerical results from the MILP model. Furthermore, the trends exhibited by the outcomes across various scenarios considering distinct electricity costs and carbon tax levels are presented. These results provide valuable insights into the economic feasibility of retrofit electrification strategies for decision-makers in the chemical industry.

Keywords: Optimization, Process Design, Electricity & Electrical Devices, Process Operations, Renewable and Sustainable Energy

INTRODUCTION

The 2021 UN Climate Change Conference (COP26) stressed the urgent need to reduce global greenhouse gas emissions to limit global warming to 1.5˚C [25]. This goal coupled with a global increase in energy consumption has urged nations to accelerate the adoption of low-emission energy systems. There is a pressure for the chemical industry to embrace emerging low-carbon technologies [16] [8].

Decarbonization of oil refineries is challenging due to their diverse configurations and high operational efficiencies. One potential pathway for decarbonization involves incorporating low-carbon feed into refinery operations. Retrofitting a fossil-based refinery to use a biomass-based feed over a time horizon of 10 years has been studied in [30] using a Mixed-Integer Linear Programming (MILP) model. Currently, significant effort is directed towards reducing scope 1 [32] emissions by electrification of process heat & hydrogen and the use of

carbon capture and storage techniques. Other possible pathways involve the use of carbon capture technologies and/or electrification of hydrogen production and steam generation integrated within existing refinery infrastructure (see Fig. 1 (a)) which are described below.

Carbon capture (CC) Techniques

Post-combustion, pre-combustion, and oxy-combustion are the primary techniques for carbon capture (CC) [18]. Post-combustion capture suits low CO_2 concentration flue gas, while pre-combustion applies to gasification plants. Oxy-combustion involves burning fuel in an oxygen-rich environment. This study exclusively focuses on pre- and post-combustion capture due to their ease of retrofitting existing operations. [22, 24, 28, 12]

H$_2$ production

One approach for decarbonizing H_2 production is through blue H_2 production, where SMR (Steam Methane Reforming) and WGS (Water Gas Shift) reactors are augmented with pre-combustion CC [9]. Alternatively, the flue gas

from these reactors, after extracting hydrogen through adsorption-based separation, can be mixed with flue gas from other plant sources. This mixture allows for absorption-based post-combustion CC. Another method for decarbonizing H_2 production involves using renewable electricity for the electrolysis of water, producing green hydrogen [21, 20, 15, 27] . We focus on the use of low-temperature electrolyzers, such as Alkaline Electrolyzers (AE) and Proton Exchange Membrane Electrolyzer (PEME), due to their level of maturity (AE), efficiency, and adaptability to handling variable operational conditions (PEME) [7].
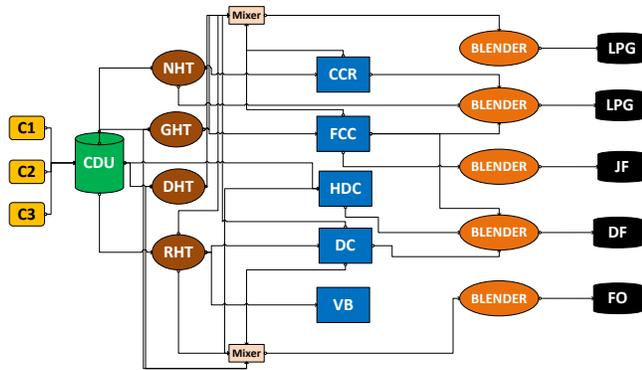
Fig 1(a) : Generic Flowsheet for an oil refinery; CT denotes different types of crude oil fed to Hydrotreating units—NHT (Naphtha Hydrotreater), DHT (Distillate Hydrotreater), GHT (Gas Oil Hydrotreater), and RHT (Residue Hydrotreater)—further treated in processing Units: CCR (Continuous Catalytic Reformer), HDC (Hydrocracking), FCC (Fluid Catalytic Cracking), DC (Delayed Coking), and VB (Visbreaking); Output streams are blended in desired proportions to produce LPG (liquified petroleum gas), JF (Jet Fuel), DF (Diesel Fuel), FO (Fuel Oil); adopted from [29]
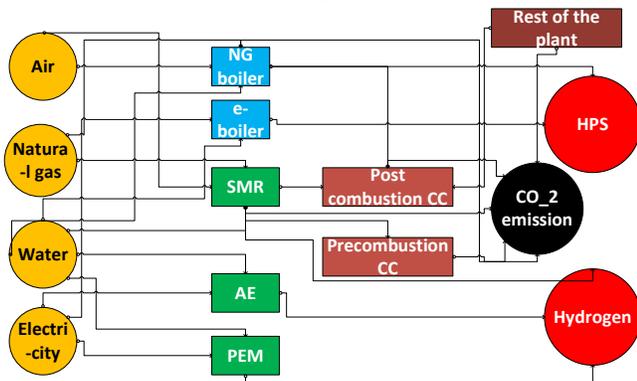
Fig 1(b): Superstructure with possible pathways for hydrogen and HPS (high-pressure steam) production: considered routes for H_2 production include Gray H_2, Blue H_2, and Green H_2 (using PEME or AE); HPS generation alternatives encompass utilization of Natural Gas (NG) Boilers or e-boilers; Blue hydrogen can be synthesized employing either pre-combustion or post-combustion

techniques; the flue gas released from the rest of the plant is captured by post-combustion CC.

Process heat

In the refinery, most of the heating demands are met using steam. Boilers in Fig 1 (b) generate only HPS. MPS and LPS are obtained from HPS by reducing the pressure with let-down valves. Other heating needs are fulfilled by furnaces tailored to individual unit operations in the refinery. To simplify the analysis, we assume that flue gas from these sources can be collected and treated by post-combustion CC units. Currently, steam production relies on gas boilers that burn natural gas. Electric boilers (e-boilers) are a possible greener replacement for gas boilers due to their easy installation, control, and maintenance, as well as higher thermal efficiency. e-boilers can also be easily retrofitted with renewable power sources, offering a more sustainable option for steam generation [26].

The gap: Electrification from a systems perspective

While market-ready technologies exist and technoeconomic analysis are available for individual decarbonization initiatives, there is a lack of literature on how these initiatives can be optimally combined to retrofit existing units cost-effectively. As emphasized in [33] since the heat and mass flow between units are interconnected in a chemical industry it is extremely critical to perform a systems level analysis to perform for decarbonization or electrification planning. This work develops a tool for planning a transition towards such a retrofit solution, which can cater to each specific oil refinery at a given location.

PROBLEM STATEMENT

Existing literature discusses some market-ready technologies for alternative decarbonized technologies [17] but lacks a clear framework for understanding which ones should be chosen, when these alternative technologies should be implemented, and how they could be optimally integrated. This paper aims to fill this gap by developing a comprehensive decarbonization plan that is applied to a given oil refinery operating over 29 years (2022-2050). The plan involves strategic selection and timely implementation of the best set of initiatives for retrofitting the supply of HPS and hydrogen to the given refinery (by addition and removal of units and interconnections), considering operating data for a typical crude-based refinery with a distillation capacity of 100 kbbl crude oil per day. The objective is to minimize the Present Value of the cost for decarbonization retrofit design, while meeting predefined environmental commitments.

METHODOLOGY

Fig. 1 (b) shows a superstructure representing potential pathways for High-Pressure Steam (HPS) generation, hydrogen production, and CC.

The variables used in the model are, $F_{i,j,k,yr}$, a positive continuous variable representing the amount of component k present in a stream flowing from unit i to unit j in year yr. $y_{i,yr}$ $(m_{i,yr})$, a binary variable indicating whether the installation of a specific unit of technology i (e.g. PEME, AE) is initiated (completed) in year yr. $z_{i,yr}$ $(p_{i,yr})$, a non-negative integer variable indicating the number of initiated (completed) installations in year less than or equal to yr for units of technology i. $Q_{i,yr}$; $(QE_{i,yr})$, a continuous variable indicating the total (expansion in) installed capacity of a technology i in a given year yr.

Logic Timing constraints

Eqs. (1) and (2) capture the relationships between the described binary variables.

$$\sum_{yr=1}^{l} y_{i,yr} = z_{i,l} \qquad \forall i, l \qquad (1)$$

$$\sum_{yr=1}^{l} m_{i,yr} = p_{i,l} \qquad \forall i, l \qquad (2)$$

These Eqs. are valid for all years in the range 1-29 unless specified otherwise. Furthermore, additional logical constraints are added to specify that z and p are time-lagged copies of y and m respectively depending on the duration of installation of each equipment. Flow to units of technology i is non-zero if the installation of any unit of i has been completed by a given year. This relationship can be expressed as an upper bound constraint, shown in Eq. (3):

$$F_{i,j,k,yr} \leq UB * p_{i,yr} \qquad (3)$$

Mass Balance constraints

The proposed formulation requires specifying that flow can take place only when the units are connected in the superstructure.

$$F_{i,j,k,yr} = 0 \ \forall j \notin Out(i), \forall k, \forall yr$$

Additionally, equations specify that air, natural gas, water, and electricity are obtained from their respective supply nodes.

Mass Balance constraints given by Eqs. (4) and (5) relate the amount of components present in inlet and outlet streams to reactors and separators through simplified yield-based models. In Eq. (6), $\mu_{in,j,k}$ represents the amount of reactant k reacting with a certain amount of reactant k' in unit j, denoted as $\mu_{in,j,k'}$. Similarly, in Eq. (5), $\mu_{out,j,k}$ denotes the amount of product k in the outlet stream of unit j, given a certain amount of reactant k' in the inlet stream.

$$\sum_{i \in In(j)} F_{i,j,k,yr} = \frac{\mu_{in,j,k}}{\mu_{in,j,k'}} \sum_{i \in In(j)} F_{i,j,k',yr} \qquad (4)$$

$$\sum_{i \in Out(j)} F_{j,i,k,yr} = \frac{\mu_{out,j,k}}{\mu_{in,j,k'}} \sum_{i \in In(j)} F_{i,j,k',yr} \qquad (5)$$

$$k \ \mathcal{E} \ \{Relevant\ Components, Electricity\}$$
$$\forall i\{ Reactors, electrolyzers, boilers\}$$

Here, the notations $In(j)$ and $Out(j)$ represent the set of nodes connected at the inlet and outlet of node j respectively.

For the CC units, a component-wise mass balance constraint is applied, as no reactions occur. The constraint is represented by Eq. (6)

$$\sum_{i \in Out(j)} F_{j,i,k,yr} = \sum_{i \in In(j)} F_{i,j,k,yr} \quad \forall j \in CC\ units \quad (6)$$

Additional constraints are imposed to guarantee the specified purity of the final streams.

Energy Balance Constraints

Energy balances for Natural Gas (NG) boiler, e-boiler, and electrolyzers are given by Eqs. (7), (8) and (9) respectively.

$$F_{NGSupply,\ NG\ Boiler,\ NG,\ yr} LHV_{NG\ Boiler} \eta_{NG\ boiler} =$$
$$F_{Water\ Supply,\ NG\ Boiler,NG,\ yr} \Delta H_{vap} \qquad (7)$$

$$F_{Grid,\ e-boiler,\ electricity,\ yr} \eta_{e-boiler} =$$
$$\Delta H_{vap} F_{H_2\ supply,\ e-boiler,\ H_2O,\ yr} \qquad (8)$$

$$F_{electrolyzer,\ H_2 requirement,Hydrogen,yr} \Delta H_{electrolysis}$$
$$= F_{grid,electrolyzer,Electricity,yr}\ \eta_{electrolyzer} \qquad (9)$$

η denotes the energy efficiency of equipment and LHV is the Lower Heating Value of natural gas.

Design Constraints

The values of the total HPS and hydrogen produced by all the different pathways must match the total hydrogen and HPS requirements of the refinery. The amount of CO_2 captured and emitted after passing through CC units are linearly related by a constant factor given by the efficiency of the respective CC equipment. Similarly, the steam produced and the losses through the purge stream (blowdown) from the boilers are linearly related by a constant factor.

The amount of CO_2 and other gases present in the flue-gas released from the rest of the operations in the refinery are specified by constraints. Decarbonization goals of the refinery impose an upper limit on the emissions as shown in Eq. (10)

$$\sum_{i \in In(CO_2\ emission)} F_{i,CO_2 emission,\ CO_2,yr} \leq CO2\ cap_{yr} \quad (10)$$

Eq. (11) imposes a logical constraint on the capacity expansion in any year $\forall i \in PEM, AE, e-boiler, CC\ units$.

$$LB_1 m_{i,yr} \leq QE_{yr} \leq UB_1 m_{i,yr} \qquad (11)$$

Eq. (12) evaluates the total capacity at the end of any year yr. [23, 19]

$$QE_{i,yr} + Q_{i,yr-1} = Q_{i,yr} \qquad (12)$$

Eqs. (13) and (14) state that the operating flowrate or power is less than the installed capacity.

$$F_{grid,i,electricity,yr} \leq Q_{i,yr} \qquad (13)$$

$$\forall i \in e - boiler,\ electrolyzer$$

$$F_{CC\ unit,CO_2\ captured,CO_2,yr} \leq Q_{CC\ unit,\ yr} \qquad (14)$$

We consider that the capacity expansion for e-boiler and CC facilities can take any value within a continuous range, whereas the expansion of electrolyzer capacity can only take discrete values based on available standard sizes. To handle this, we introduce binary variables $w_{i,h,s,yr}$ which denote whether, in year yr, the hth electrolyzer ($h\ \varepsilon\ \{1,\dots\dots H\}$) of type $i\ \varepsilon\ \{PEM, AE\}$ is of the sth size $s\ \varepsilon\ \{Available\ discrete\ sizes\}$, with $d_{i,s}$ denoting the available sizes for each type of electrolyzer.

Eq. (15) adds the size of all installed electrolyzers to calculate the total capacity expansion in any given year [10]. Eq. (16) ensures that at most one size is chosen for every electrolyzer. Eq. (17) is added in order to avoid degenerate solutions.[6]

$$\sum_{h=1}^{H} \sum_{s=d_{1,s}}^{d_{1,S}} w_{i,h,s,yr}\ d_{i,s} = QE_{i,yr}\ \forall i \in PEM, AE \qquad (15)$$

$$\sum_s w_{i,h,s,yr} \leq 1 \ \forall\ i \in PEM,\ AE \qquad (16)$$

$$\sum_s w_{i,h,s,yr} d_{i,s} \geq\ \sum_s w_{i,h+1,s,yr} d_{i,s} \qquad (17)$$

Cost Constraints and Objective function

Eq. (18) & (19) incorporate an upper limit on the annual capital expenditure (CAPEX) that can be allocated.

Eq (18) shows that the total CAPEX for an expansion is denoted by $\alpha + \beta\ QE$, where α represents the fixed cost and $\beta\ QE$ represents the variable cost.

$$CAPEX_{yr} = \sum_i \frac{\alpha_{i,yr}(z_{i,yr} - p_{i,yr})}{dur(i)} + \sum_{p=1}^{dur(i)} \frac{\beta_{i,yr}\ QE_{i,yr+p}}{dur(i)} \qquad (18)$$

$$CAPEX_{yr} \leq CAPEX\ CAP \qquad (19)$$

Here dur(i) is the time taken to install the unit i. The OPEX incurred for pursuing the decarbonization initiatives each year is given by Eq. (20). The OPEX consists of two primary components: the first pertains to the consumption of natural gas and electricity from their respective sources, while the second, linked to the CC units, is directly proportional to emission reductions.

$$OPEX_{yr} = \left(\sum_{j\epsilon Out(NG\ Supply)} F_{NG\ Supply,\ j,NG,yr}\ \$_{\frac{NG}{unit\ mass}} + \right.$$
$$\sum_{j\epsilon Out(NG\ Supply)} F_{Grid,\ j,Electricity,yr}\$_{\frac{electricity}{unitenergy}} +$$
$$\left. \sum_{i\epsilon CCS\ Units} F_{i,\ Captured\ CO_2,CO_2,yr}\ OPEX_i \right) time\ units$$

$$(20)$$

Finally, we formulate the objective function as the Present Value of the Cost of the decarbonization project in Eq. (21) which is subject to Eqs. (1) to (20), the constraints of the optimization problem.

$$Minimize\ \sum_{yr=1}^{29} (CAPEX_{yr} + OPEX_{yr})/(1+i)^{yr} \qquad (21)$$

RESULTS

The formulated retrofit MILP model was implemented in Pyomo Pyomo 6.6.1 with the Gurobi 10.0.1 solver [11], for a 29-year horizon containing 204,700 constraints and 102,918 variables (97,233 continuous, 5,684 integer). Discounting for the inequality constraints and dependent equations, there are ~3,900 degrees of freedom

Base Case

As shown in Fig. 2 (a) for the base case when predefined targets for reduction in CO2 emissions. (i.e. 50% reduction by year 10 and reduction to the minimum attainable value using the given superstructure by year 28) are implemented, carbon capture technology is favored over electrified options. Electrified technologies are not chosen due to the high operating costs associated with them [2, 1, 14, 3, 13, 31, 4]. Due to space constraints details regarding the data used for natural gas and electricity prices and capital costs for e-boilers, electrolyzers and CC technologies shall be disseminated in a full-length journal publication which is under preparation. Among the CC technologies, post-combustion capture is preferred for both SMR and other combustion-related flue gases, as the additional CAPEX for pre-combustion technology outweighs operational cost savings.

Transition to electrified technologies for both steam and H₂ production occurs in 2049 when stringent restrictions are enforced (as shown in Fig. 2 (a) and (c)) that limits the emissions to the minimum attainable value. For electrification of H₂, PEM electrolyzers are preferred at given electricity price forecasts due to the associated savings in OPEX.

As shown in Fig. 2 (b) the capital expenditure for CC alternatives was very high compared to electrified technologies and reached the upper limit. Fig. 2 (c) shows that carbon neutrality was not achieved in the final years as the current superstructure only allows post-combustion CC of the flue gas from the rest of the plant, which is not 100% efficient. Fig 2(c) also shows that the emission cap constraint is always active at the optima.

We can see in Fig. 2 (d) that lowering the maximum allowed CAPEX spending per year leads to a preference for installation and use of e-boilers until the CAPEX intensive capture facility is built. Hence, enterprise specific economic policies can alter the optimal solution.

However, adding a penalty for unused capital could alter the optima away from the presented solution.

To gain insight on scenarios that could lead to adoption of electrified options, we studied how the optimal solution varied when (i) Carbon taxes are applied, and (ii) Electricity prices are reduced by different percentages.

Case 2: Introduction of Carbon taxes

Given carbon tax implementation at specified rates as shown in Figure 3 (b), (mimicking Canadian rates) it was observed that transitioning to CC based decarbonization technologies relatively earlier is economically beneficial as shown in Fig 3(a), decreasing the overall CO_2 emissions. Fig 3(b) also shows that economically optimal emission levels are below the maximum allowed levels. However, C-taxes do not expedite the adoption of carbon-neutral electrified technologies at the optimal design as can be seen in Fig. 3 (a). Additional case studies have also shown us that the results remain qualitatively similar if carbon credits are introduced instead of carbon taxes.
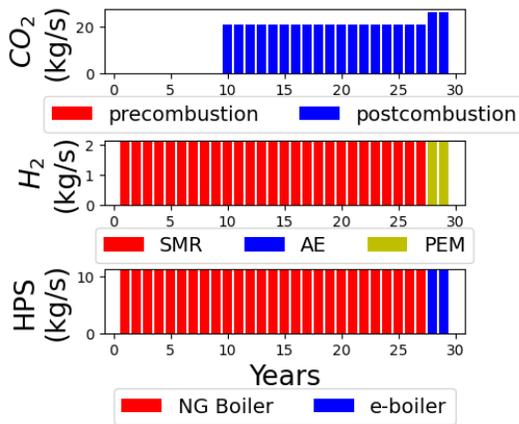
Fig 2 (a) The panels from top to down show the contribution of each technology in carbon capture; Hydrogen production and HPS production. Postcombustion CC is preferred over years 10-27; e-boilers and PEMS operated in years 28-29
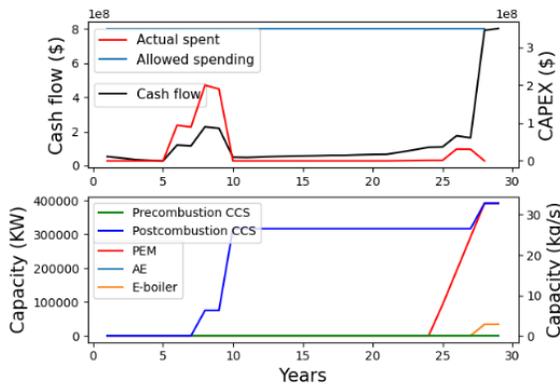
Fig 2 (b) Upper panel shows the actual CAPEX spending and the maximum CAPEX spending limit; along with the total cash outflow associated with hydrogen and HPS

production. The panel below shows the rate at which the electriied alternatived should be installed in KW capacity. It also shows the optimal rate of CC capacity installation in kg/s. CAPEX spending reaches maximum limit when CC infrastructure is built; CAPEX for electrified alternatives is relatively cheaper; large cash outflow after adoption of electrified alternatives
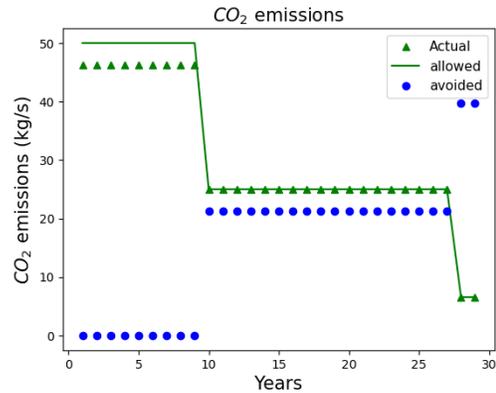
Fig 2(c) The total carbon-di-oxide emissions as compared to the maximum allowed emissions over the years. The emissions avoided as a result of the decarbonization initiatives are also shown. Emissions are restricted to 50% of current values from years 10-27; Emissions are capped at the minimum attainable value in years 28-29. Emission cap constraint is always active.
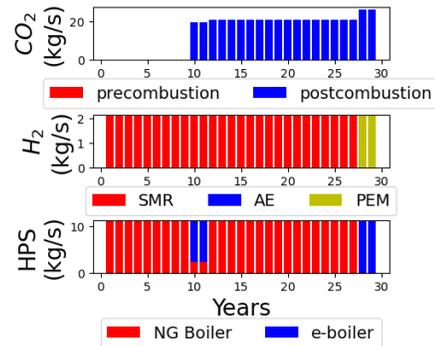
Fig 2(d) With $100,000,000 cap in annual capital expenditure e-boiler is operated until CC technology is built

Case 3: With reduction in electricity prices

Examining the impact of reductions in electricity costs, it was observed that with 25-70% reduction in electricity costs, the overall solution remained qualitatively similar to the base case. However, a mix of PEME and AE was chosen in the final solution due to the trade-off in CAPEX and OPEX as shown in fig 4(a). Fig 4 (b) shows that upon further reducing electricity costs to 80% below the forecasted levels, e-boiler technology is selected earlier. Nevertheless, the adoption of electrolyzer technology is delayed due to high energy requirements for electrolysis. Fig 4(c) shows that when electricity costs are reduced by 90%, a partial shift from SMR-based

hydrogen production to electrolysis-based hydrogen production is observed, suggesting the use of a mix of both types of electrolyzers. A higher capacity of AEs (Alkaline Electrolyzers) is chosen in the final mix due to the cheap electricity prices in this scenario.

Case 4: Electricity price reduction and carbon taxes

With reduction in electricity prices and carbon taxes implemented, we further analyze three sub-cases where the electricity prices are reduced by 85%, 90%, and 95% compared to the currently forecasted prices. In all the scenarios, the introduction of carbon capture units is accelerated due to carbon tax introduction as shown in figures 4(d)-4(f). Simultaneously, electrified technologies were also chosen earlier as compared to the base case. In other words, the trends observed are a superposition of the effects obtained in the 2 previous cases. In summary, while carbon taxes Encourage early transition to CC-based technologies, substantial electricity cost reductions or stringent environmental norms are needed for favoring electrified technologies.

CONCLUSION

This paper has proposed a MILP-based superstructure optimization model to minimize the Present Value of the Cost for retrofit decarbonization of an oil refinery. Higher electricity prices relative to natural gas favor CC over electrification alternatives. Lowering electricity costs by up to 70% has little impact, but further reductions significantly affect the optimal solution. Carbon taxes accelerate adoption of carbon capture technologies. Substantial electricity cost reductions make e-boilers financially attractive.

It should be noted that for the two different carbon capture technologies we have assumed MEA based absorption operating at different conditions and with different costs for dilute (post-combustion) and concentrated (pre-combustion) CO_2 concentrations of the flue gas. For each technology, the cost per unit of captured CO_2 was assumed to remain constant. Future work will enhance the tool by taking into account the differential pricing for carbon capture technologies as a function of the CO_2 concentration of the flue gas stream using piecewise linear approximations. In addition, future work may include the carbon intensity of the fuel and electricity as they are expected to change over time and affect the optimal retrofit plan.

Finally, obtaining accurate cost forecasts are challenging due to energy and carbon market uncertainties. Hence, an enhancement of the solution's robustness is needed. For this, we plan to explore stochastic programming techniques to account for uncertainties in the MILP model [5].

ACKNOWLEDGEMENTS

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Fig 3 (a) Optimal solution is heavily reliant on carbon capture alternatives and are adapted earlier as compared to base case; Electrified alternatives still chosen in years 28-29 **(b)** Actual emissions are below the maximum emission cap; Carbon taxes implemented mimicking Canadian rates
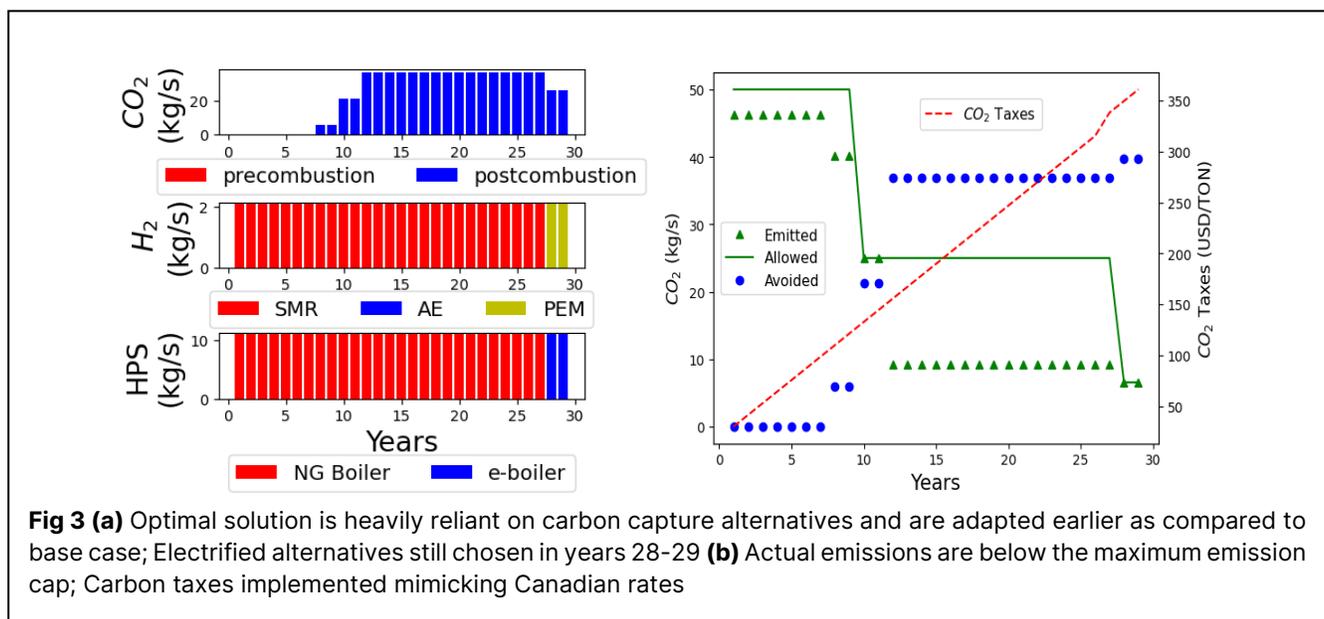
https://www.eia.gov/outlooks/aeo/data/browser/#/?id=1-AEO2023&region=0-0&cases=ref2023&start=2021&end=2050&f=A&linechart=~ref2023-d020623a.44-1-AEO2023&map=&ctype=linechart&sid=ref2023-d020623a.44-1-AEO2023&sourcekey=0

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Fig. 4(a) Optimal PEME and AE mix selected in years 28-29 with a 25% electricity price reduction; **4(b)** E-boilers chosen from year 10 onward with an 80% electricity price reduction; **4(c)** Electrolyzers selected from year 10 onward with a 90% electricity price reduction; **4(d)** Mix of PEME and AE chosen in years 28-29 with a 25% electricity price reduction and C-taxes; CC implemented from year 8; **4(e)** E-boilers chosen from year 6 with an 80% electricity price reduction and C-taxes; CC implemented from year 8; **4(f)** e-boilers selected from year 4 with a 90% electricity price reduction and C-taxes; partial shift to electrolyzers year 9; CC implemented from year 10.