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Impact assessment of CO_2 capture and low-carbon hydrogen technologies in Colombian oil refineries

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Abstract

This research uses system optimization to assess short, medium, and long-term scenarios to achieve the committed CO_2-emission goals of Ecopetrol while minimizing potential adverse impacts such as incremental operational costs and utility demand. Two Colombian refineries are used as a case study: a medium-complexity and a high-complexity refinery. The study explores whether the level of complexity plays a significant role in the results.

Potential technologies were ranked using a multi-criteria decision analysis. The system analysis and optimization were done in Linny-R, a mixed integer linear programming software package developed by TU Delft. In the short-term (2030) scenario, the selected technologies include low-carbon H_2 produced from Steam Methane Reformer units with carbon capture and storage and H_2 produced from renewable electricity sources. The medium and long-term (2050) scenario also included biomass gasification, naphtha reforming, and the cracking unit, all with carbon capture and storage. The refineries were modelled using on-site company data. The results indicate that using low-carbon H_2 and carbon capture and storage to flue gases would allow to reach the net zero target. Furthermore, the results show that the level of complexity in a refinery significantly impacts the decarbonization deployment pathways. The high-complexity refineries benefited from using low-carbon H_2 as feedstock while the medium-complexity refinery relied on a combination of carbon capture and low-carbon H_2 as an alternative fuel. This research highlights the potential to achieve substantial CO_2 emissions reductions with less impact on the total operational cost by using the amount of excess refinery gas generated when H_2 is used as fuel in boilers and process furnaces. A significant challenge remains in identifying suitable applications for surplus refinery fuel gas beyond its conventional use in combustion within boilers and furnaces.

Keywords: Carbon capture and storage, low-carbon hydrogen, oil refinery decarbonization, multi-criteria decision analysis, and system optimization

1. Introduction

The global commitment to reduce greenhouse gas emissions is driving a shift in our energy preference, moving away from fossil fuels towards cleaner energy sources with lower carbon footprints. This shift is expected to decrease the demand for fossil fuels in transportation. However, refineries play a crucial role beyond fuel supply; they serve as a source of raw materials for manufacturing base chemicals, speciality chemicals, and fuels for the shipping and aviation sectors. Due to the significance of these products, refineries will continue to play a pivotal role in the foreseeable future. Consequently, it is crucial to evaluate and develop a strategy for decarbonization (Oliveira & Schure, 2020).

In 2018, Ecopetrol was responsible for approximately 4% of the Colombian GHG emissions (IDEAM et al, 2022), and it has committed to reducing its GHG emissions to 75 % of the level emitted in 2019 **by 2030** (5.9 Mt CO_{2eq}/y), corresponding **to scopes 1 and 2**. In addition, the long-term strategy of Ecopetrol aims to achieve **net-zero carbon emissions for scopes 1 and 2 by 2050** (note that the target does not include scope 3 emissions i.e.,l indirect emissions not included in scope 2 that occur in the value chain of the reporting company, including both upstream and downstream emissions). Nowadays, the downstream sector is responsible for 55 % of the company's GHG emissions under scopes 1 and 2, with the refineries contributing to 98 % of those emissions (Canova, 2021). This study focuses on a case study based on two Colombian oil refineries that have different levels of complexity. An overview of the key characteristics of both refineries is shown in Table 1. Note that H_2 use differs between the refineries. In the high-complexity configuration refinery, H_2 production contributes 33% of the emissions, whereas, in the medium-complexity configuration refinery, it corresponds to 7 % of total CO_2 emissions. This study aims to a) assess the potential for decarbonization in each refinery by using low carbon H_2 as a feedstock and as a fuel, and by capturing CO_2 from flue gas streams and b) evaluate whether the level of complexity, which is often overlooked in this type of assessment, affects the results.

Table 1. Main characteristics of the refineries case study

		Cartagena	**Barrancabermeja**
	Unit	**Value**	**Value**
Complexity level[1]		High	Medium
Crude oil Capacity	Mt/y	11.45	11.95
Annual CO_2 emissions	Mt CO_2-eq /y	2.5	3.1
Gas fuel consumption	PJ/y	22.6	40.3
Electricity production	PJe/y	2.93	3.53
Steam production	PJth/y	3.5	28.63
Hydrogen production	kt/y	84	28.7
Total Conversion Yield	%	96.7 %	77 %
H_2 consumption index	t H_2-consumed / feedstock	0.015	0.0051

1: The refinery complexity is defined by the Nelson Complexity Index, which quantifies the type of process units in a refinery and their capacity relative to the atmospheric distillation unit by assigning a factor (Kaiser, 2017).

2. Methodology

The methodology is composed of three stages. In the first stage, promising low-carbon technologies for hydrogen production and CO_2 capture technologies were identified. The assessment considered three time periods, i.e., short-term (by 2030), medium-term (by 2040), and long-term (by 2050). The short-term period includes technologies with a TRL larger than 8 that could be deployed before 2030; the long-term period includes technologies currently at a TRL of 3 or larger. The second stage is composed of two steps: (i) selecting suitable technologies, and (ii) gathering data for case studies based on the complexity level of the refinery. Five technologies were selected for this study and are presented in Table 2 and Table 3.

In terms of CCS, post-combustion capture in flue gas from boilers, furnaces, reformers, and the FCC plant. The capture was done using MEA 30%wt with a 90% CO_2 capture rate based on work reported in (IEAGHG, 2017). For the SMR unit, it was considered a 95% CO_2 capture rate using ADIP-X solvent (45 %wt. MDEA conc. and 5 %wt. Piperazine conc.) in the out-stream from the water gas shift reactor(25 barg and 350 C) based on work done by Meerman et al. (2012). Table 4 shows the techno-economic parameters of the CO_2 capture technologies selected.

Table 2. Selected low-carbon H_2 process

	Technology	Produc.sub-method	Feedstock	Horizon
SMR+CC	Thermochemical	Steam Reforming	Natural Gas	Short term
Ren Elec + PEM El.	Electrolysis	PEM electrolysis	Water + Ren. elec	Short term
Biomass Elec + PEM El.	Electrolysis	PEM electrolysis	Water + Biomass	Short term
Biomass gasif. + CC.	Thermochemical	Gasification	Biomass	Long term
Naphtha Reforming + CC.	Thermochemical	Steam Reforming	Low-grade Naphtha	Long term

Table 3. General techno-economic parameters of low-carbon H_2 technologies.

	SMR	PEM El.	Biomass Elec	Biomass gasif.	Naphtha Reform.
Emission factor, kg CO2/kg H2	9.31	0	† (up) + 1.7 kg CO_2/ kWe	†(up) + 19.5 kg CO_2/kg H_2	-
Yield	2.95 % vol. H2/NG		1.13 MWe / t dry biomass	0.1 t H_2 / t dry biomass (IG)	0.0032 t H_2/bl
Electricity consump., MWe/t H2	0.36	*66.6 kWh/ kg H_2 (2030) 60.4 (2040) 54.7 (2050)	0	1.57	0.007 MWe/ bl
Steam consump., t Steam / t H2	7.3 (export)	0	0	11.6	0.035 t/bl
Fuel gas consump., GJ/ t H2	73.8	0	0	-	0.25 GJ/bl
Capex 2022, M€/ t/d H2	1.7-2.6	3.6-5.7	4.4-8.7 M€/MWe	4.3 – 5.9	15-17 M€ /kbld
Fix Opex (Capex %)	4%	3%	3%	3%	3.5%
Econ. Lifetime, year	25	20	20	25	30

12% Discounting rate ** Including 19% additional consumption for auxiliary equipment. † Upstream: 126.5 kg CO2 / t dry biomass kbld: Kilo Barrel per day*

Regarding CO_2 storage, the geological reservoir used in the model follows the estimation of capacity onshore and offshore potential in Colombia reported by Younis et al., (2023). Table 5 shows the calculated CO_2 footprint for transportation and storage alternatives. Data for the case studies used confidential information from the on-site refinery processes (e.g., yields, mass and energy balance, operational cost), as well as scientific and industrial publications available in the literature, and information gathered from expert interviews. The mass, energy, and emissions balances were estimated for the annual operation of each process unit under normal conditions. As the raw data used in this study is confidential, values are reported at the block process level.

In the final stage, a system model was developed that represents the process and interactions of the technologies under evaluation. They are designed to represent the capacity, limits, and availability of the case study in interaction with the existing processes in the oil refineries. The two case studies were modeled using Linny-R (Bots, 2022) a mixed-integer linear programming (MILP) with a Gurobi MILP solver. In this software, the refinery system can be represented by a block diagram. Each block corresponds to a process and the connections between blocks represent an energy or mass stream. The model was built in layers and at a section level of detail. Figure 1 shows a screenshot of the main layer in Linny-R. Additionally, all feedstocks/products were related to a process through a linear function. Finally, the balances shown in the model were made to represent a daily basis. The model runs 7 steps, every step corresponding to 5 calendar years, starting in 2020 and ending in 2050.

The main objective of the optimization function is centered on the maximization of cash flow within distinct blocks following the scheduling of CO_2 emissions reductions, products, and availability of feedstocks and technologies. Feedstocks, products, and processes are considered variables in Linny-R. Every process and feedstock/product can be set at a low and up limit (Capacity). A list of data sets allows to establish a schedule of production or capacity or prices in time to feedstocks, products, and processes. Two separate models were built, one for each refinery. The model is composed of 486 variables for the high-complex refinery and 461 for the medium-complex refinery model.

Table 4. Carbon capture processes

Process	CO_2 partial press., bar	Chem. solvent	Electricity demand, kWh/t CO_2 cap.	Heat demand, GJ/ t CO_2 cap.	Capex, € 2022/ t CO2	CO_2 cap. cost, €/t CO2
SMR+CC	3-6	ADIP-X. 50% wt.	2.1 (Absorber= 2.7 barg)	1.97 (Desorber= 1.9 barg/ 115 C)	124.4	54
SMR+CC	0.08	MEA. 30% wt.	64.55 (HC) 58.25 (MC)	3.68 (HC) 3.65 (MC)	142	56.7
Biomass gasification	0.1					
Boilers	0.05-0.09					
NGCC-CHP	0.043					
Process furnaces	0.08-0.10					
FCC	0.1-0.17					

Source of CO2 partial pressure data: Calculated based on SIGEA (2019). IRENA, (2021)
Economic lifetime: 20 years. Discount rate: 12%. Fix opex: 4% capex.

Table 5. CO_2 footprint of transportation and storage alternatives.

Refinery	On-shore pipeline, kg CO_2 /t CO_2 stored	Off-shore pipeline, kg CO_2 /t CO_2 stored	Off-shore shipping, kg CO_2 /t CO_2 stored
Cartagena. (HC))	2.5	2.9	18.3
Barrancabermeja. (MC)	1.8	9.6	22.5

Based on Younis et al., (2023), Khoo & Tan, (2006), (Knoope et al., 2015), (Yoo et al., 2013)

The baseline for CO_2 emissions and data collection was for the year 2019. Cost and prices for CAPEX and OPEX were updated to 2022 using the Chemical Engineering Plant Cost Index, and a currency conversion rate from dollars or Colombian pesos to euros in 2022. Prices associated with feedstocks, products, and production capacities were set according to the Colombian context. Technologies that involve biomass as feedstock considered tree species of Eucalyptus available in Colombia (E. camaldulensis, E. grandis, and E. globulus). The capacity of utilities and refining process represent the actual capacity of both oil refineries. Fuel production capacity (i.e. gasoline, diesel, and jet fuel) was defined according to the Ecopetrol long-term production scheduling strategy. Colombian electricity grid connection to refineries is 70 MW capacity, 85 €/ MWh (XM, 2020), and with a Carbon footprint of 186 kg CO_2 / MWhe (128 kg CO_2 / MWhe, according to Unidad de Planeación Minero Energética (UPME) (UPME., 2019).

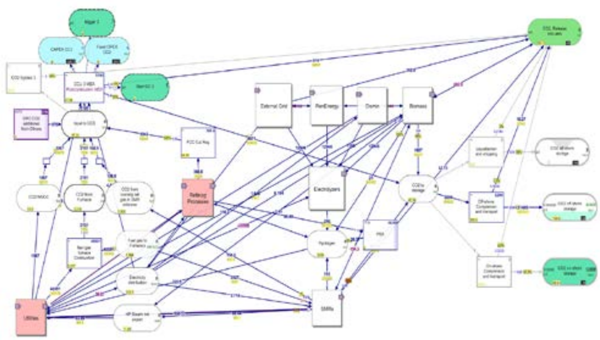

Figure 1. Linny-R Model. Screenshot of the main layer

3. Results and discussion

The impact of implementing the low-carbon H2 technologies on the energy and CO_2 balances of the two refineries is shown in Table 5. In both cases, the results show a significant reduction of CO_2 emissions in the short term (26% and 23% for HC and MC configurations, respectively) and they meet the target of CO_2 neutrality in 2050. The SMR with CC is the most cost-effective technology to produce hydrogen, with a production price between 1.0 and 1.5 €/kg lower than H_2 based on PEM electrolysis (using REN between 30-40 €/MWh). It reaches the same production price in the long-term horizon with a REN of 30 €/MWh and a forecasted incremental price of natural gas.

Hydrogen based on Biomass+ CC emerges as a viable option to achieve CO_2 emissions neutrality in the long term horizon, despite having a production cost that is 2-3 €/kg higher than the SMR-CC and REN-PEM electrolyzer alternatives. This is due to the significant advantage it provides as a "negative emissions process (NET)" when both biomass H_2 and the biomass electricity process are accompanied by CCS. Biomass processes alone (without CCS) contribute to a CO_2 reduction of 13% for both refinery configurations, with respect to the baseline. The results do not show any limitation concerning the availability of CO_2 underground reservoir. For the MC refinery, the onshore capacity (64 Mt CO_2) was enough until 2050 horizon. The HC Refinery will use 100 % onshore (12 Mt CO_2) and 32 % Colombian offshore of its CO_2 storage capacity by 2050. Similarly, the MC refinery will use 93 % of the on-shore of its CO_2 storage capacity by 2050.

Table 6. Energy and CO_2 impacts in oil refineries

High Complex	Base Line	Short Term	Long Term
Oil refinery throutput, kb/d	155	200	197
kt/y	7718	9959	9810
Total Hydrogen Demand, kt/d	211	287 136%	508 241%
H_2 Production processes			
SMR, kt/d	211	155	119
Biomass gasification, kt/d	0	0,0	23,0
Naphta Reformer, kt/d	0	0,0	106,4
Natural Gas Feedstock, TJd	28,2	20,7	15,9
Total Gas fuel demand, TJd	37	45,4 121%	49,7 133%
Natural Gas (external source), TJ/d	11,7	17,2 147%	3,4 29%
Refinery off-gas (internal source)	25,8	28,3 109%	46,4 180%
Total electricity demand, MWh	98	448 457%	646 658%
Fossil fuel source, MWh	98	45 46%	36 37%
External grid, MWh	0	67	70
Renewables, MWh	0	336	539
Total Steam Demand, kt/d	9	10,3 117%	21,2 241%
Total CO_2 emissions, kt CO_2/y	2493	1836 74%	0 0%

Medium Complex	Base Line	Short Term	Long Term
Oil refinery throutput, kb/d	239	242	242
kt/y	11891	12034	12034
Total Hydrogen Demand, kt/d	79	85 107%	358 454%
H_2 Production processes			
SMR, kt/d	79	19	39
Biomass gasification, kt/d	0	0	0
Naphta Reformer, kt/d	0	0,0	123,0
Natural Gas Feedstock, TJd	10,6	2,6	5,2
Total Gas fuel demand, TJd	78	79,8 102%	97,1 124%
Natural Gas (external source), TJ/d	14,9	16,8 113%	13,1 87%
Refinery off-gas (internal source)	63,1	63,0 100%	84,0 133%
Total electricity demand, MWh	93	261 280%	502 539%
Fossil fuel source, MWh	93	42 45%	25 27%
External grid, MWh	0	53	69
Renewables, MWh	0	166	408
Total Steam Demand, kt/d	8	8,8 115%	25,0 327%
Total CO_2 emissions, kt CO_2/y	3500,2	2704 77%	0 0%

The impact of the refinery's level of complexity on the utilization of low-carbon hydrogen is evident in the short-term scenario. In the high-complexity (HC) refinery, a substantial reduction (26%) in CO_2 emissions was achieved, with 36% attributed to bio-electricity with CC used in the electrolyzers. In contrast, the medium-complexity (MC) refinery achieved a 17% reduction in CO_2 emissions, with 74% credited to bio-electricity with CC. For the long term, MC refineries gained an edge through the implementation of CO_2 capture from flue gas produced by fossil fuel combustion, resulting in an 85% reduction in total CO_2 emissions, in comparison to the 72% reduction achieved in the HC refinery configurations. The decarbonization technologies for the high-complexity refinery are oriented towards renewable energy (REN) and electrolyzers; whereas for the medium-complexity refinery, the optimization focuses on biomass + CC electricity and gasification to produce low-carbon hydrogen. In both cases, the Naphtha reformer + CC process was shown to be the less expensive way to produce low-carbon hydrogen, playing a significant role in the decarbonization pathways in the long-term horizon. Biomass-based H_2 with CC emerges as a viable option post-2030, despite having a higher hydrogen production cost. The benefits will likely far outweigh the negative impact on the Oil refinery's cash flow.

4. Conclusions

The combination of low-carbon hydrogen production and CO_2 capture technologies provides for both types of oil refineries a pathway to achieve the CO_2 reduction target committed by Ecopetrol in the short-term (75 %) and CO_2 neutrality in the long-term.
The level of complexity in oil refineries significantly impacts the decarbonization process, with the high-complexity refinery benefiting from low-carbon H_2 as feedstock for the processes and the medium-complexity refinery relying more on CO_2 capture in combination with hydrogen as an alternative fuel. However, the CO_2 emissions reduction is limited because of the avoiding flaring of surplus fuel gas generated as a consequence of the fuel shifting process.
However, a significant challenge lies in identifying suitable applications for surplus refinery fuel gas beyond its conventional use in combustion within boilers and furnaces will be necessary in future research.

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