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System analysis and optimization of replacing surplus refinery fuel gas by coprocessing with HTL bio-crude off-gas in oil refineries.

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ABSTRACT

This study evaluates the introduction of Carbon Capture and Utilization (CCU) process in two Colombian refineries, focusing on their potential to reduce CO_2 emissions and their associated impacts under a scenario aligned with the Net Zero Emissions by 2050 Scenario defined in the 2023 IEA report. The work uses a MILP programming tool (Linny-R) to model the operational processes of refinery sites, incorporating a net total cost calculation to optimize process performance over five-year intervals. This optimization was constrained by the maximum allowable CO2 emissions. The methodology includes the calculation of surplus refinery off-gas availability, the selection of products and CCU technologies, and the systematic collection of data from refinery operations, as well as scientific and industrial publications. The results indicate that integrating surplus refinery fuel gas (originally used for combustion processes) and HTL bio-crude off-gas (as a source of biogenic CO_2) can significantly lower scope 1 and 2 CO_2 emissions, aligning with long-term decarbonization goals. However, these advantages carry additional costs due to significant increases in utility demands. In the high-complexity refinery, electricity consumption increases by a factor of 16, steam demand by a factor of 2.5, and water usage by a factor of 3. Similarly, in the medium-complexity refinery, electricity consumption rises by a factor of 19, steam demand by a factor of 7, and water usage by a factor of 4. These increases are primarily driven by the renewable energy requirements for water electrolyzers and CO_2 capture units. Furthermore, despite achieving CO_2 neutrality in scope 1 and 2 emissions by 2050, scope 3 emissions increase due to additional CO_2-based methanol production.

Economic analyses highlight profit opportunities in the long term, as the production costs of CO_2-based methanol is lower than forecasted fossil-based cost of production , enhancing their economic viability in the long term.

The study emphasizes the critical influence of refinery complexity levels on the scale and timeline for implementing these technologies to achieve short- and long-term CO_2 reduction targets. However, further evaluation is necessary to align these results with national electrical grid capacity, water supply availability, and expansion plans.

Keywords: Modelling and Simulations, Optimization, Refining, sustainable process, oil refinery decarbonization.

1. INTRODUCTION

Reducing CO_2 emissions and reaching CO_2 neutrality in the long term , are pledged his study focus on two oil refineries, which together contribute with more than 50% of their Scope 1 &2 CO_2 emissions from Ecopetrol (the Colombian oil and gas industry). Within the refineries, process heating requirements via refinery fuel gas are responsible for 50 to 60% of the total scope 2 emissions.

Previous studies on this topic have found that for reducing CO_2 emissions, refineries require a combination of technologies, including low-carbon hydrogen (Low-C H2), sustainable energy, carbon capture, utilization, and storage (CCUS), bio-feedstocks, and product changes. Colombia's biomass resources offer opportunities for deploying advanced biofuel technologies like Hydrothermal Liquefaction (HTL) in the refineries. HTL produces bio-crude compatible with the existing refinery infrastructure, however, co-processing with fossil streams is challenging and is a topic of on-going research [1]

Alongside biocrude production, the process delivers a rich-biogenic CO2 gas stream with untapped potential to be used in CCU processes and off-gas with biogenic carbon that could be used in CCU processes. This research is grounded on the opportunity to repurpose the surplus refinery fuel gas that is generated by switching into more sustainable fuels such as Low-C H_2, and utilize this refinery fuel gas and (HTL) biocrude off-gas in a conversion processes to produce more valuable and sustainable products (see Figure 1 for the simplified system block diagram). This research aims to evaluate the impact of introducing CCU processes for methanol synthesis using alternative carbon sources and by-products as feedstock on the refinery performance considering both short and long-term targets.

2. METHODOLOGY

This research evaluates the future integration of alternative feedstock in methanol production /CCUS/biogenic C from biomass, into two Colombian refineries and redirecting their CO_2 to storage. A simplified process flow diagram of the system evaluated is presented in Figure 1.

The methodology comprised five steps. In the first step surplus refinery fuel gas was estimated. Note that HTL bio-crude off-gas was selected as source of biogenic CO2 from a biorefinery which we assume to be installed next to the refinery[1] and convert via thermocatalytic processes into methanol based on previous study [2]. Second, potential CCU technologies were screened, which resulted in the selection of steam reforming and thermocatalytic hydrogenation to convert refinery fuel gas and biocrude off gas into methanol.

Next, data was collected. the techno-economic data sourced from literature and Aspen Plus simulations, therefore, a detailed techno-economic assessment [2] was used as input for this study. Lozano's work identified that up to 44 % of HTL Bio off-gas can be mixed with Refinery fuel gas without an external H_2 supply.

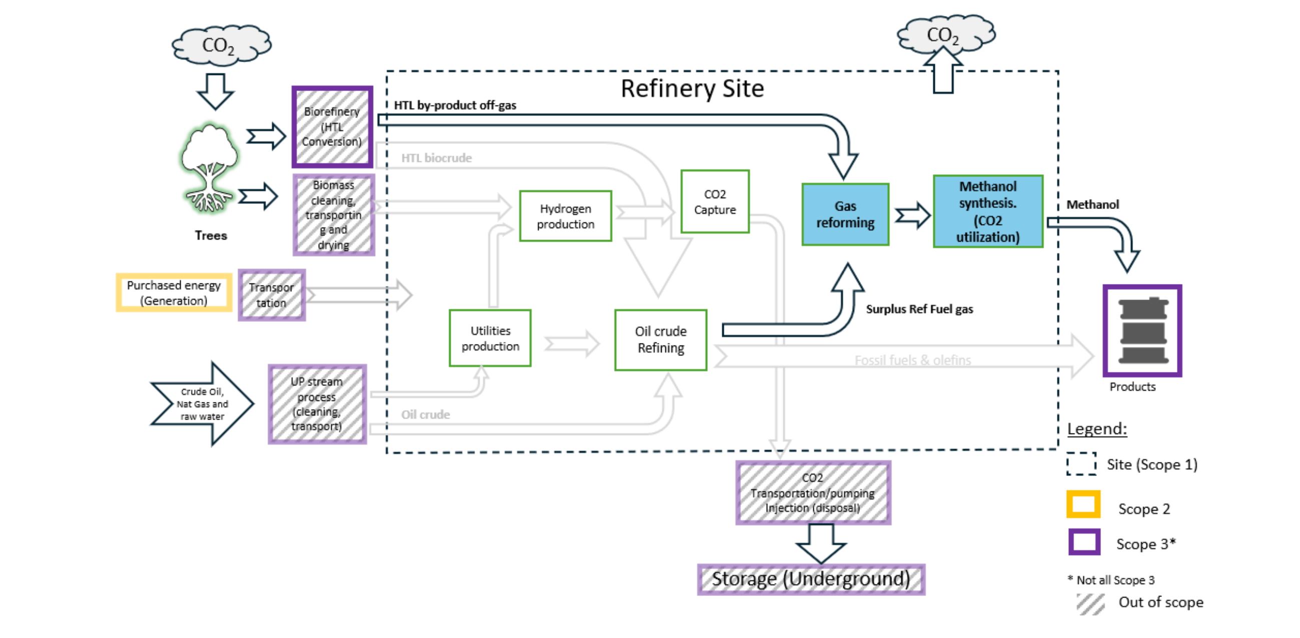

Figure 1. Simplified system block diagram.

[1] The impacts on direct and indirect emissions that could be generated from biorefinery is out the scope of this work.

Furthermore, this research uses data from two refineries owned by Ecopetrol. The two refineries, one with a medium level of process complexity and one with a high level of process complexity, process 11.95 Mtpd and 11.45 Mtpd of crude oil, respectively. The main characteristics of the two refineries are shown in Table 1.

Table 1. Main characteristics of the refinery 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	2.6	3.3
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 %

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 [3].

In the fourth step a mixed-integer linear programming (MILP) in Linny-R software was used to model and evaluate techno-economic and environmental parameters and energy and material balances at system level. Linny-R works with a Gurobi solver for minimizing the system costs under CO_2 emission constraints over time. The model was built based on previous work which optimized the basket of low-carbon H_2 production technologies and CCS for the two Colombian refineries to achieve the CO_2 reduction emissions targets [4]. In the final step the results were analysed.

We evaluated this system under a favorable decarbonization scenario aligned with the Net Zero Emissions by the 2050 Scenario (NZE Scenario) defined in the 2023 IEA report [5]. In this scenario, the world moves towards decarbonization by significantly reducing fossil fuel use, having fewer incentives to explore and produce natural gas, and promoting the adoption of renewable energy sources. The parameters defined in scenario are summarized in Table 2.

The mass and energy balances obtained from the model were compared to the 2019 material and energy balances of the refineries. The model results varied less than 5% from real-world data. The model performs a single objective optimization aiming to achieve the largest total cash flow through total cost minimization in every period In this works every period involve 5 years). To minimize the total cost (eq 1).

Objective function = min $OC_t = \left(\sum_{p=1}^{n}[C_o - C_i]p\right)_t$, (1)

Where, OC is the overall costs [€], C_o is cost output [€], C_i is cost input [€], and p is a process in the refinery, t is time period.

Cost input is the sum of all cost, including the cost of raw materials, feedstocks, utilities, and Capex and Opex of the new technologies, as well as an carbon taxes/penalties that increase as in the IEA scenario[5]; while the cost output category is the sum of the income associated with selling the products. Furthermore, Net margin[2] is calculated as total cost divided by crude oil processing throughput. Techno- economic parameters and the calculation of annualized Capex and Opex are described in detail in the supplementary data files [6].

There are some assumptions in this work. First, the processing capacity of the Cartagena refinery will be expanded from 155 kbbl to 235 kbbl in the period between 2020-2025 according to existing plans. Additionally, to be able to use the maximum capacity for both oil refineries, there is a plan to expand the H_2 production capacity in the medium term. In the short term, there is a project to interconnect the refineries to the Colombian electric grid through a 70 MW line to reduce their carbon footprint. The Colombian electrical grid has a lower carbon footprint compared with the auto-generated electricity generated at the refineries through natural gas power combined cycles because 70% approximately of Colombian electricity is hydropower. Additionally, as a consequence of the increase in energy efficiency initiatives, there is a goal to achieve the best performance in the peer group (North and South America) in 2035. Thus, the Cartagena refinery will reduce 11% of energy consumption and Barrancabermeja will reduce 9% of total energy consumption [7], in the short and medium term horizon.

The methanol production is considered to be expanded to fulfill the demand in modules of 500 t/d of methanol.

3 . RESULTS AND DISCUSSION

The results show that using HTL biocrude off gas (as a source of CO_2) with surplus refinery gas utilization (as a source of H_2), can significantly reduce scope 2 CO_2 emissions. Table 3 shows that the refinery's fuel gas consumption is projected to decrease significantly by 2050 by down to 12% and 30% of the 2020 levels for high-complexity and medium-complexity refineries,

[2] Net Margin (or Refining Margin) refers to the profitability of the refinery after accounting for operating costs, often expressed per unit of crude oil processed (e.g., USD per barrel).

respectively. This substantial reduction is due to the substitution of conventional refinery fuel gas with low-carbon hydrogen, which is produced within both refineries. The hydrogen demand for fuel uses would account for 59% and 93% of the total hydrogen requirement by 2050 in the high-complexity and medium-complexity refineries, respectively.

The results show significant reductions in scope 1 and scope 2 CO_2 emissions for both refinery types, as detailed in Table 4. However, when scope 3 CO_2 emissions are taken into account, the results show an increase in net emissions due to the introduction of CCU processes, which produce methanol from a external source of mass (HTL biocrude off gas) and the use of refinery fuel gas changes from scope 2 (combustion) to products (scope 3)—as shown in Table 5.

Furthermore, utilizing surplus refinery fuel gas and coprocessing with HTL bio-crude off-gas, significantly increases resource demand in both refineries. Electricity demand rises by 16 and 19 times, respectively, primarily due to the reliance on renewable electricity to power water electrolyzers for the additional low-carbon hydrogen. Consequently, water demand increases by 3 and 4 times for the high-complexity and medium-complexity refinery, respectively. In addition, steam demand increases by 2.6 and 7 times for high-complexity and medium-complexity refineries, respectively, which is driven by the requirements of the CO_2 capture units integrated with the steam methane reforming (SMR), and biomass combustion and gasification for Low-C H_2 production.

Table 2: Parameters considered in the scenario of evaluation

Parameter	2020	2030	2040	2050	Source
Natural Gas price, €/GJ	4.5	13.2	14.2	15.0	Based on [8]
CO_2 market price, €/t	0	90	120	160	
CO_2 transport, pumping, and injection Cost, €/t	26.7		3% LR		Based on [11]
CO_2 reduction target (scope 1 &2 and carbon removals in company supply chains).	0%	25%		Neutrality	Based on Ecopetrol Goals and [12]
Syngas production via SMR	€ 6850/t H2 based on [9]		1% LR		Based on [11]
CCU. CO_2 to Methanol; Catalytic process. Capex	€ 582/t based on source:[13]		10% LR		Based on [14] and [15]
CCU. CO_2 to Methanol; Catalytic process. Yield	51% Current			69% (2050)	Based on [16] and [17]

LR: Learning Rate. PV: Photovoltaic. €: 2020 euros

Table 3: Impacts on utility balance

High Complexity	2020	2030	2050
Oil refinery throughput, kbld	155	189	189
Kty	7718	9436	9436
Utilization capacity, %	100%	122%	122%
Refinery gas as fuel , TJd	26	0	1
Total Hydrogen Demand, t/d	205	313	747
As feedstock, t/d	205	313	313
As fuel, t/d	0	0	434
Total electricity demand, MWh	**92**	**811**	**1466**
Renewables, MWh	0	505	1117
PV and wind electricity, MWh	0	504	1094
Biomass electricity, MWh	0	1	23
Total steam demand, kt/d	**5**	**12**	**13**
Raw water demand, kt/d	**11**	**28**	**38**

Medium Complexity	2020	2030	2050
Oil refinery throughput, kbld	240	242	242
Kty	11931	12034	12034
Utilization capacity, %	99%	99%	99%
Refinery gas as fuel, TJd	60	41	29
Total Hydrogen Demand, t/d	104	111	1261
As feedstock, t/d	104	111	111
As fuel, t/d	0	0	1150
Total electricity demand, MWh	**134**	**468**	**2526**
Renewables, MWh	0	155	2058
PV and wind electricity, MWh	0	139	1839
Biomass electricity, MWh	0	15	119
Total steam demand, kt/d	**5**	**11**	**36**
Raw water demand, kt/d	**17**	**30**	**64**

The optimized solution identified for both refinery sites can achieve the long-term CO_2 emissions reduction targets regarding scope 1 and 2. However, this result is accompanied by a significant reduction in net margin, with reductions estimated in the order of 59% (high complexity) and 77% (medium-complexity) over the long term.

Table 5 also highlights a potential profit opportunity, as the current cost of methanol production of is competitive, falling within in the same range of fossil-based methanol. In the middle and the long-term, our methanol is expected to be cheaper than the fossil-based methanol due to increasing carbon taxes [5] and the expected limited availability of fossil fuels, particularly in the region of this case study [8] and [9]; however, the current production cost is higher than the European cost (+10% compared to Europe Methanol, export contract price, fob, Netherlands)[10].

4. CONCLUSIONS AND RECOMENDATIONS

In this study, we conducted a comprehensive system analysis and optimization of introducing a CCU technology to produce methanol and olefins using surplus refinery fuel gas and HTL/FP off biogas in two Colombian oil refineries operating at different levels of complexity. The results revealed the significant impact of the refinery's complexity level on the scale and timeline required for implementing these technologies to achieve the committed CO_2 emissions reduction goals in the short and long term.

As shown in the results, the introduction of CCU technologies using surplus refinery fuel gas and biogenic CO_2 source (HTL/FP off biogas) enables long-term CO_2 emissions reduction for refineries. However, this transition generates a substantial financial cost, with a significant decrease in Net Margin (60% for high-complexity refineries and 77% for medium-complexity refineries). Furthermore, the adoption of CCU technologies significantly increases electricity demand, primarily due to renewable electricity requirements for water electrolyzers producing low-carbon hydrogen as a substitute for refinery fuel gas. Water and steam demand also rise considerably, driven by CO_2 capture units.

The results also indicate that both refineries can achieve scope 1 and scope 2 CO_2 neutrality by 2050 as modelled assuming a favorable scenario. However, scope 3 CO_2 emissions increase due to the production of additional products like methanol through CCU processes. However, in contrast to the increased emissions associated with scope 3, the production of CO_2-based methanol can result in a modest profit opportunity. The production costs of the CO_2-based methanol presented

Table 5: CCU. Methanol production

	High Complexity					Medium Complex				
	2020	2025	2030	2040	2050	2020	2025	2030	2040	2050
Net margin, €/bbl	6.6	3.2	1.2	2.2	2.7	5.2	3.5	1.4	0.4	1.2
MeOH synthesis production, t/d	0	337	1121	1345	1440	0	374	912	489	1969
Cost of methanol production. €/t	-	371	353	285	261	-	376	336	318	274
Cost of fossil-methanol production. €/t	200 to 340	*250 to 400	300 to 450	350 to 500	†450 to 600					

€ euros 2020. * depending on natural gas prices and location. †due to carbon taxes and limited availability of fossil fuels.
Current Methanol cost of prouction. 307 €/t. Methanol, EUR (Europe): Methanol, export contract price, fob, Netherlands. [10]

Table 4: CO_2 emissions

	2020	2030	2050	2020	2030	2050
CO_2 emissions balance. (Scope 1 and 2 minus removals) **, kt CO2/y**	**2596**	**2155**	**0**	**3295**	**3007**	**0**
Reduction compared to 2020 CO_2 emissions	0	18%	100%	0	6%	100%
Direct Emissions, fossil and biogenic (Scope 1). kt CO_2/y	2597	2069	1269	3295	3260	2475
Purchased Electricity (Scope 2). kt CO_2/y	0	114	114	0	114	114
CO_2 removed via photosynthesis. kt CO_2/y	0	28	1383	0	367	2589
Total CO_2 emissions balance. Scope 1, 2 &3. kt CO_2/y	28106	33330	31074	42671	42781	39619
Use and end life products (in scope 3). kt CO_2/y	25473	31175	31074	39377	39671	39619
CO_2 to geologic storage (fossil and biogenic). kt CO_2/y	0	25	1139	0	333	2352

in this study align with the projected cost range of electrochemical-methanol and are lower than current fossil-based methanol in the long term, thereby enhancing its economic competitiveness.

Finally, the results should be further verified against the existing capacities of the national electrical grid and water supply in these specific areas, as well as the national expansion plans for both. Additionally, uncertainty analysis should be include in further works to evaluate the impact of it on the results.

DIGITAL SUPPLEMENTARY MATERIAL

Model files and supplementary data, material, and calculations to this article can be found online at: https://repository.tudelft.nl/person/Person_eec0cc1f-4ec6-4156-aed1-f593802cfaee?page=1

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