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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 CO_2 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 10, and steam demand and water usage each increase by a factor of 2.5 and 3, respectively. Similarly, in the medium-complexity refinery, electricity consumption rises by a factor of 11, steam demand by a factor of 4, and water usage by a factor of 6. The renewable energy requirements for water electrolyzers and CO_2 capture units primarily drive these increases. 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. The production costs of CO_2-based methanol are lower than the forecasted cost of production of fossil-based methanol, 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, Biofuels, Process Design.

INTRODUCTION

Reducing CO_2 emissions and reaching CO_2 neutrality in the long term are the objectives of this study, which focuses on two oil refineries that together contribute with more than 50% of their Scope 1&2 CO_2 emissions from

Ecopetrol (the Colombian state oil and gas industry). The process heating requirements via refinery fuel gas are responsible for 50 to 60% of the total scope 1 emissions.

Previous studies on this topic have found that for reducing CO_2 emissions, refineries require a portfolio 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 biocrude compatible with the existing refinery infrastructure; however, co-processing with fossil streams is challenging and is a topic of ongoing research [1]

Alongside biocrude production, the process delivers a rich-biogenic CO_2 gas stream with untapped potential to 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 H2, and utilize this refinery fuel gas and (HTL) biocrude off-gas in a conversion processes to produce more valuable and sustainable products, such as Methanol (see Figure 1 for the simplified system block diagram).

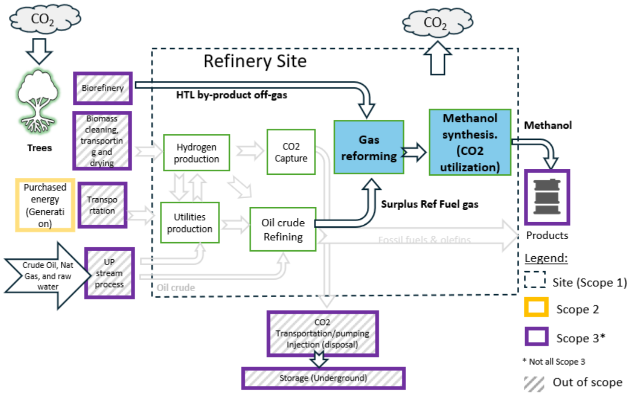

Figure 1. Simplified system block diagram.

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.

METHODS

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 the source of biogenic CO_2 from a biorefinery, which we assume to be installed next to the refinery and converted via thermocatalytic processes into methanol based on a 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 was 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. 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 7.7 Mtpd and 11.5 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	7.7	11.9
Annual CO_2 emissions	Mt CO_2-eq /y	2.5	3.4
Gas fuel consumption	PJ/y	19.8	30.4
Electricity production	PJe/y	3.2	4.9
Steam production	PJth/y	16.8	25.3
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 the system level (see Figure 2). Linny-R works with the Gurobi solver for minimizing the system costs under CO_2 emission constraints over time. The model was built based on previous work that optimized the basket of low-carbon H2 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 analyzed.

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 the scenario are summarized in Table 2.

The mass and energy balances obtained from the model were compared to the refineries' 2020 material and energy balances. 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 work, every period involves 5 years. To minimize the total cost (eq 1).

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

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

Cost input is the sum of all cost, including the cost of raw materials, feedstocks, utilities, and Capex and Opex and maintenance 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 is calculated as total cash flow 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 document [6].

There are some assumptions in this work. First, the processing capacity of the Cartagena refinery will be expanded from 155 kbbl to 205 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 H2 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% 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 horizons.

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

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 1 CO_2 emissions. Table 3 shows that the refinery's fuel gas consumption is projected to decrease significantly by 2050 by down to 0% and 39% of the 2020 levels for high-complexity and medium-complexity refineries, respectively. This substantial reduction is due to the substitution of conventional refinery fuel gas with low-carbon hydrogen produced within both refineries. The hydrogen demand for fuel uses would account for 41% and 85% of the total hydrogen requirement by 2050 in the high-complexity and medium-complexity refineries, respectively.

The results show significant reductions in Site direct and Indirect CO_2 emissions (Scope 1&2) for both refinery types, as detailed in Figure 3. However, when use of products CO_2 emissions (scope 3) 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 1 (combustion) to products (scope 3)—as shown in Figure 3.

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 10 and 11 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 6 times for the high-complexity and medium-complexity refinery, respectively. In addition, steam demand increases by 2.5 and 4 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 H2 production.

The optimized solution identified for both refinery sites can achieve the long-term CO_2 emissions reduction targets regarding scopes 1 and 2, as shown in Figure 3. However, this result is accompanied by a significant Underground storage capacity demand of 33 Mt for the HC refinery and 57 Mt CO2 for the MC refinery at 2050. Furthermore, the net margin is reduced in the order of 34% (high complexity) and 65% (medium complexity) over the long term.

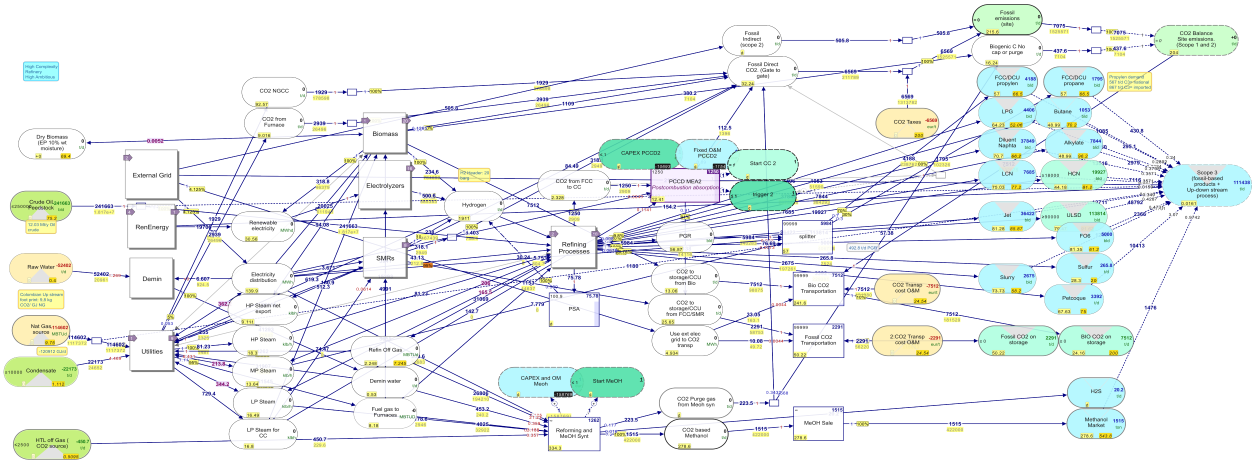

Figure 2. Modeled system in Linny-R. Main Layer view High complex refinery. Numbers displayed correspond to optimization result by 2050. Detailed layers in the supplementary material Apendix A.

Table 2: Parameters considered in the scenario of evaluation

Parameter	2020	2030	2040	2050	Source
Natural Gas price, €/GJ	4.5	8.6	9.2	9.8	HC and MC Based on [8]
CO_2 market price, €/t	0	90	160	200	
CO_2 transport, pumping, and injection Cost, €/t	26.7	3% LR			Based on [11]
CO_2 reduction target (scope 1 &2 minus carbon removals).	0%	25%		Neutrality	Based on Ecopetrol targets 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]	5% LR			Based on [14] and [15]
CCU. CO_2 to Methanol; Catalytic process. Yield	51% Current			60% (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	196	196
Kty	7718	9749	9749
Refinery offgas as fuel, TJd	24	0	0
Total Hydrogen Demand, t/d	**221**	**306**	**518**
As feedstock, t/d	221	306	306
As fuel, t/d	0	0	212
Total electricity demand, MWh	**100**	**861**	**1007**
Renewables, MWh	0	494	626
Total steam demand, kt/d	**15**	**35**	**37**
Raw water demand, kt/d	**15**	**36**	**38**
Dry Biomass, TJd	**0**	**0**	**58**

Medium Complexity	2020	2030	2050
Oil refinery throughput, kbld	240	242	242
Kty	11931	12034	12034
Refinery offgas as fuel, TJd	59	56	23
Total Hydrogen Demand, t/d	**104**	**111**	**733**
As feedstock, t/d	104	111	111
As fuel, t/d	0	0	622
Total electricity demand, MWh	**157**	**210**	**1665**
Renewables, MWh	0	12	1178
Total steam demand, kt/d	**8**	**7**	**34**
Raw water demand, kt/d	**13**	**13**	**46**
Dry Biomass, TJd	**0**	**0**	**63**

Figure 3. CO_2 emissions Balance. Sankey diagram

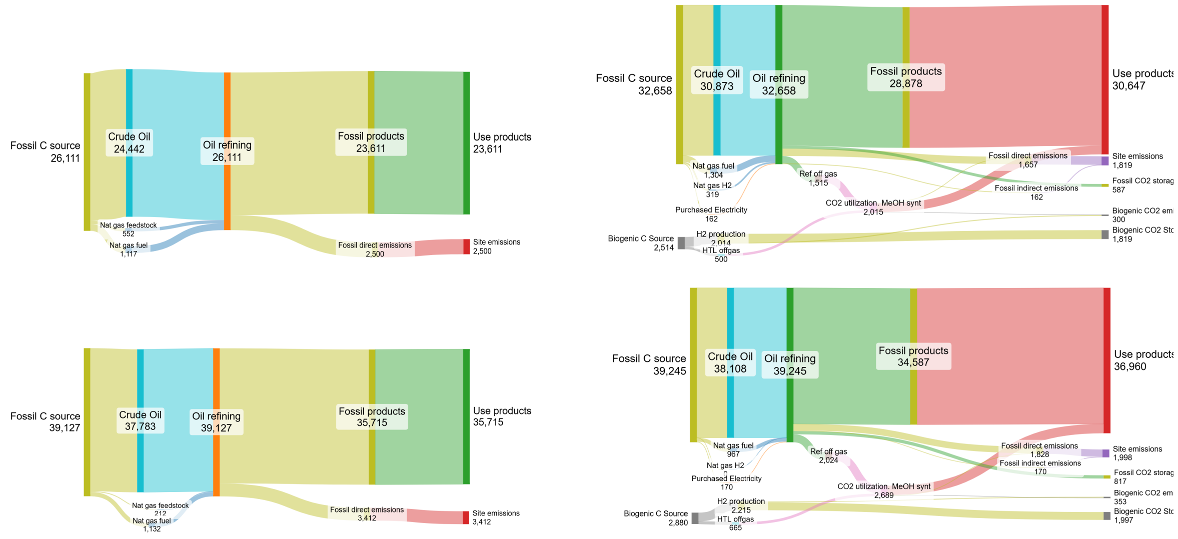

Table 4: CCU. Methanol production

		High Complexity				Medium Complexity				
	2020	**2025**	**2030**	**2040**	**2050**	**2020**	**2025**	**2030**	**2040**	**2050**
Net margin, €/bbl	5.9	4.1	1.4	2.8	3.9	5.2	4.0	2.5	2.0	1.8
MeOH synthesis production, t/d	0	614	1291	982	1291	0	401	168	1024	1689
Cost of methanol production. €/t	-	339	333	311	307	-	335	338	354	366
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 production. 307 €/t. Methanol, EUR (Europe): Methanol, export contract price, fob, Netherlands. [10]

Table 4 also highlights a potential profit opportunity, as the current cost of methanol production is competitive, falling within 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].

CONCLUSIONS

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 CO2 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 (34% for high-complexity refineries and 65% 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 modeled, 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 CO2-based methanol can result in a modest profit opportunity,

The production costs of the CO_2-based methanol presented 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 included in further works to evaluate the impact of it on the results.

DIGITAL SUPPLEMENTARY MATERIAL

The supplementary material can be consulted at http://PSEcommunity.org/LAPSE with the LAPSE ID LAPSE:2025.0041

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