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A case study in Colombia

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Fully integrated CO_2 mitigation strategy for an existing refinery: A case study in Colombia

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HIGHLIGHTS

- A bottom-up estimation of CO_2 mitigation potential of combined options for a case-study refinery.
- A dynamic CO_2 mitigation potential over time is based on measure interactions for each pathway.
- Co-processing account for 60% of the portfolio followed by CCS with 23%, GE with 7%, and H_2 with 6%
- The oil and gas industry could reach carbon neutral operation at factory gate.
- The methodological approach brings insights to define optimal transition routes of the industry.

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ABSTRACT

The oil and gas industry is responsible for 6% of total global CO_2 emissions, from exploration to downstream petrochemical production and account for another 50% when including the use of its products. Thus, this industry has a significant role in realising the target of net “zero” CO_2 emissions by 2070, essential to limit global warming to 1.8 °C [2], as introduced under the Paris agreement. Currently, the interactions of an extensive set of individual and combined CO_2 mitigation measures along the value chain and over time are poorly assessed. This paper aims to assess a bottom-up CO_2 mitigation potential for a complex refinery, including portfolios of combined mitigation options, considering synergies, overlap, and interactions over time for more realistic insight into the costs and constraints of the mitigation portfolio. A total of 40 measures were identified, covering a wide range of technologies such as energy efficiency measures (EEM), carbon capture and storage (CCS), bio-oil co-processing, blue and green hydrogen (BH_2, GH_2), green electricity import, and electrification of refining processes linked to the transition of the Colombian energy systems. Five deployment pathways were assessed to achieve different specific targets: 1-base case scenario, 2-less effort, 3-maximum CO_2 avoidance, 4-INDC, and 5-measures below 200 €/t CO_2. Two scenarios (3 and 5) gave the highest GHG emission reduction potentials of 106% and 98% of refining process emissions, respectively. Although significant, it represent only around 13% of the life-cycle emissions when including upstream and final-use emissions of the produced fuels. Bio-oil co-processing options account for around 60% of the mitigation options portfolio, followed by CCS (23%), green electricity (7%) and green H_2 (6%). The devised methodological approach in this study can also be applied to assess other energy-intensive industrial complexes and shed light on the bias for estimating CO_2 mitigation potentials, especially when combining different mitigation options. This is turn is vital to define optimal transition pathways of industrial complexes.

1. Introduction

Under the Paris agreement and in line with the sustainable development scenario from the International Energy Agency (IEA), a global target of net “zero” CO_2 emissions by 2070 has been introduced as essential to limit the global average temperature rise to 1.8 °C [2]. Europe plans to reduce greenhouse gas (GHG) emissions in the

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Nomenclature

C_a	GHG avoidance cost, (€/t $CO_{2\text{-eq}}$)
C_a	GHG avoidance cost, [€/t $CO_{2\text{-eq}}$]
EF^{st}_{eB}	Emission factor for steam production from a electric boiler, (kg CO_2 /kg steam)
EF^{st}_{gB}	Emission factor for steam production from a gas-fired boiler, (kg CO_2 /kg steam)
$LCOS_{eB}$	Levelized cost of steam production from a electric boiler, [€/kg steam]
$LCOS_{gB}$	Levelized cost of steam production from a gas-fired boiler, [€/kg steam]
$\Delta C_{O\&M}$	Net change in O&M cost (€/y)
ΔGHG_a	Annually avoided GHG emissions, (t $CO_{2\text{-eq}}$/y)
ΔGHG_{down}	Net change in annual GHG emissions for downstream processes, [$tCO_{2\text{-eq}}$/y]
ΔGHG_{plant}	Net change in annual GHG emissions for a plant facility, [$tCO_{2\text{-eq}}$/y]
ΔGHG_{up}	Net change in annual GHG emissions for upstream processes, [$tCO_{2\text{-eq}}$/y]
ADU	Atmospheric distillation unit
BAU	Business as usual
BG	Biomass gasification
BH_2	Blue hydrogen
BioC	Bio-oil co-processing route
BioHi	Biomass supply high scenario
BioLo	Biomass supply low scenario
bpd	barrel of crude oil per day
CCAC	CO_2 avoidance cost, [€/t CO_2]
CCS	Carbon capture and storage
CHP	Combined heat and power
$CO_{2\text{-eq}}$	CO_2 equivalent
CPO	Catalytic pyrolysis oil
DCK	Delayed coking
Eboiler	Electric boiler
EEM	Energy efficiency measures
EF	Emissions factor, (kg CO_2 /kg steam)
Efurn	Electric furnace
EOR	Enhanced oil recovery
FCC	Fluid catalytic cracking
FPO	Fast pyrolysis oil
FPOe	Esterified fast pyrolysis oil
FT	Fischer-Tropsch
GE	Green electricity
GH_2	Green hydrogen
GHG	Greenhouse gases
GHGa	Annually avoided GHG emissions, [t $CO_{2\text{-eq}}$/y]
GT	Gas turbine
HCK	Hydrocracking
HDO	Hydro-deoxygenated pyrolysis oil
HDT	Hydro-treatment
HRSG	Heat recovery steam generator
HTLO	Hydrothermal liquefaction oil
I	Upfront investment, (€)
INDC	Intended Nationally Determined Contributions
kbpd	Thousands of barrels per day
LCOE	Levelized cost of electricity production, [€/kWh]
LCOH	Levelized cost of hydrogen production, [€/Nm^3 H_2]
LCOS	Levelized cost of steam production, [€/kg steam]
LPG	Liquid petroleum gas
Lt	Lifetime, (years)
LT	Long term
MACC	Marginal abatement cost curve
MO	Mitigation option
MT	Medium term
MTM	Miscellaneous technological measures
Mbpd	Million barrels per day
NGL	Natural gas liquid
PEM	Proton exchange membrane
PPC	Process plant cost
PRV	Pressure-reducing valves
PSA	Pressure swing adsorption
r	Discount rate, [%]
SDG	Sustainable development goal
SF	Scaling factor
SMR	Steam methane reforming
SO	Solid oxide electrolyser
ST	Short term
TcPL	Technological co-processing limit
TCR	Total capital requirement
TRL	Technology readiness level
VBK	Visbreaking unit
VGO	Vacuum gas oil
VO	Vegetable palm oil
α	Annuity factor

petroleum refineries by 83–87% below the 1990 level by 2050 [3]. Colombia has committed to reduce its greenhouse gas emissions by 51% by 2030 compared to a projected baseline [4].

The oil and gas (O&G) industry has a significant role in realizing these GHG mitigation targets. This industry is directly responsible for 6% of total global CO_2 emissions, from exploration and production, to refining and downstream petrochemical production. In addition, the use of its products in power generation, heating and transportation represents another 50% of global GHG emissions [1].

A deep decarbonization strategy for the O&G industry should address the direct GHG emissions of its operations and the emissions from its products. The resulting complexity for a system assessment beyond individual-own boundaries of a sector may affect the effectiveness and efficiency of a broad mitigation strategy [5]. It is this connectivity with other sectors of our society that would make the energy transition much more difficult and expensive without the O&G industry [6]. A central role of the oil industry could help certain strategic clean energy technologies reach maturity faster due to the oil industry's ability to quickly scale up these technologies and its skills in large-scale engineering and project management [6].

Given the importance of the industrial sector, and the O&G industry in particularly, there is a considerable amount of literature on reducing GHG emissions. Technological measures such as energy efficiency, carbon capture and storage (CCS), bioenergy and fuel switching have been considered in the mitigation portfolio for industrial sectors. Fais et al. [7] proposed different technological portfolios to estimate CO_2 reduction potentials for the UK industry, but without giving insights into suitable strategies and associated investment cost. Boulamanti and Moya [8] estimated the mitigation potential for the chemical industry in Europe by 2050 by focusing on best available and innovative technologies.

Johansson et. al. [9] assessed the CO_2 mitigation potential for the oil industry in Europe without determining deployment pathways or interactions between different mitigation options. The authors do acknowledge that there might be an effect on the CO_2 reduction potential when different options are implemented in tandem. Berghout et.

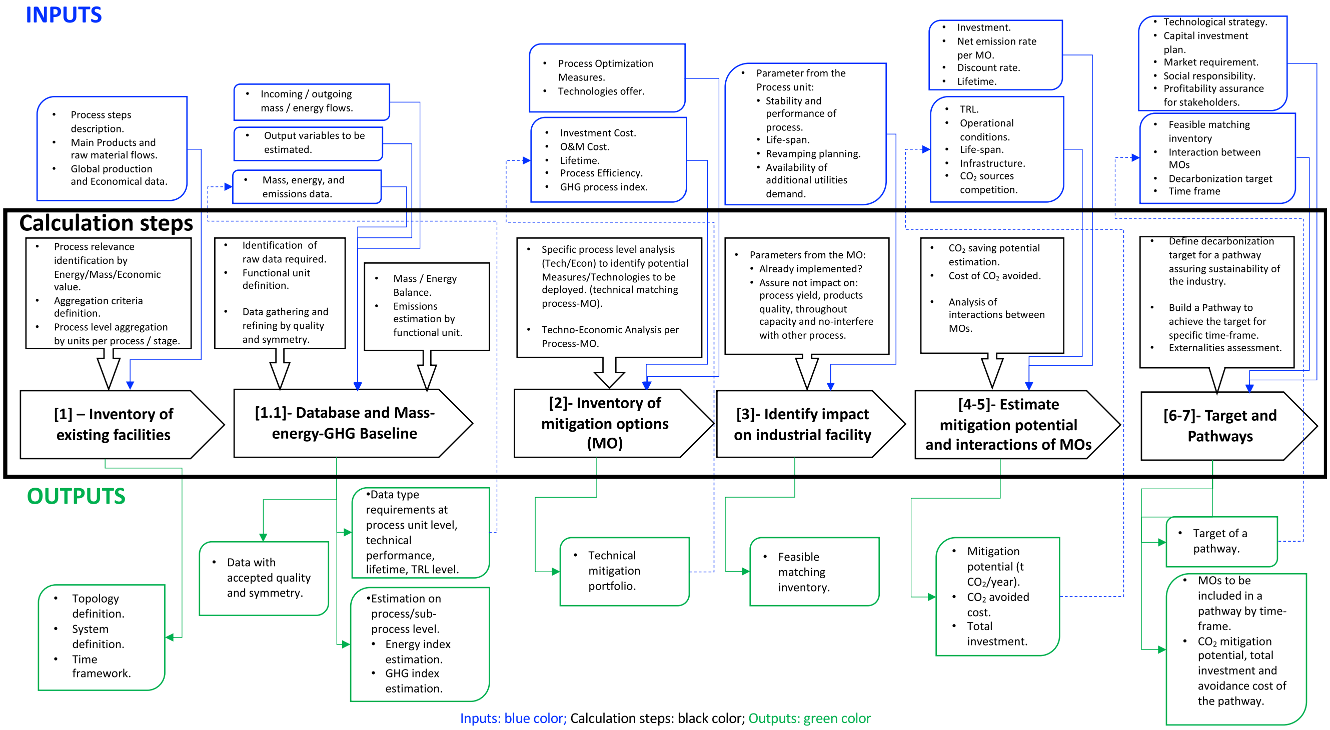

Fig. 2–1. Step plan for developing mitigation pathways in complex industries.

al. [10] assessed combined deployment pathways for GHG reduction in a complex oil refinery, from measures such as EEM, CCS, biomass gasification, and pyrolysis oil-based biofuels. All these studies are constrained by the low level of detail and the limited number of options covered.

Recent studies on decarbonization pathways look at the typical time horizons which addressed near or long term in one or more industrial sectors. These studies tend to focus on a higher-level assessment using a highly detailed bottom-up approach for a near term analysis but order-of-magnitude estimates for the long-term. A key example of these studies is the *Deep Decarbonization Pathways Project-DDPP* [11] aimed at examining decarbonization options for the world's sixteen largest greenhouse emitting countries. This study uses a bottom-up approach and has detailed decarbonization pathways up to 2030. However, for 2030–2050 there is limited integration analysis between sectors, a limited number of emerging technologies considered and no quantification of cost and benefits. Other examples are ICEF [12] which investigated energy efficiency and saving potentials in eight energy-intensive industrial sectors, while Lechtenbohmer et. al. [13], studied the impact of full electrification on the energy system. These studies used a bottom-up approach, but some emerging technologies were not explicitly defined in the model and based on a back-of-the-envelope method (an order of magnitude estimate) without assessing bottlenecks or synergies between mitigation options.

Similarly, the study from DNV-GJ in 2018 [14] estimated the CO_2 reduction potential of the Dutch refineries assuming a long-term simplified scenario (2030–2050) using a top-down assessment. They assumed the infrastructure for CCS, electricity, hydrogen and heat supply would be available without considering the sector's connectivity beyond the sector's boundaries. In addition, they assumed a products output and fractions constant for maximum development and implementation of the mitigation technologies, ignoring potential synergies or conflicts between combined options during its deployment. The study, however, did recognize that these assumptions are uncertain due to the significant uncertainty about technological development and the influence of external factors.

Although the need for a whole industrial value chain assessment is frequently recognized, most system analyses remain rather ad-hoc in nature and have a reduced scope [5]. For instance, an Ecofys study [15] for the European chemical industry drew the system boundaries of the analysed systems around the production process without including emission from upstream (mining, agriculture transport) or downstream activities (use and end-of-life).

Sector coupling (SC) is a recent concept that looks for synergy potentials between a multi-energy system and tackles the gaps in knowledge regarding efficiency and carbon reduction through cross-sector boundaries [17]. There are two types of SC [16–17]. The first is the end-use sector coupling, which aims to the electrification of the energy demand. The second involves cross-vector coupling through the integrated use of various infrastructure and energy vectors. SC assess energy efficiency and decarbonisation gains by increasing direct use of renewable electricity or indirect application through transformation into a suitable energy carrier.

Interactions between mitigation options and roadmap behaviour are often ignored, overlooking synergies or bottlenecks with other technologies. This is also noticed by Oliveira et al. [18], who carried out an exploration of decarbonisation options for the current Dutch refinery sector considering a 2050 horizon. Every mitigation option was analysed individually to estimate the benefits and challenges of its implementation. However, this study stresses the necessity to assess a combination of technology options and external factors (such as carbon transport and storage infrastructure, green electricity and hydrogen supply, and biomass availability) under a holistic assessment of CO_2 mitigation pathways.

In summary, there is a need for a systemic assessment for deep decarbonization of the O&G industry. This analysis should include assessing the interactions of mitigation options along the value chain and establishing a timeframe for an extensive set of individual and combined measures on a much more detailed level. As a result, a strong insight of decarbonisation pathways for the O&G industry can be achieved, based on a better understanding of barriers, lock-in impacts, and avoiding overestimating reduction potentials or underestimating the costs.

This paper aims to assess a bottom-up CO_2 mitigation potential for a complex refinery. It is extremely significant to get insights on the full

Table 2–1
Key characteristics of the refinery study case [21].

	Unit	Value
Crude oil throughput	Mt/year	12.13
Annual CO_2 emissions	Mt $CO_{2\text{-eq}}$/year	3.7
Electricity production	PJ_e/year	2.42
Steam production	PJ_{th}/year	24,843
Hydrogen production	kt/year	5.83
Total Conversion Yield	%	84.62
Distillation throughput	kt/year	12,131
Fluid Catalytic Cracking (FCC) throughput	kt/year	5065
Hydrotreating (HDT) throughput	kt/year	1047

mitigation potential for an oil refinery identifying appropriate deployment pathways. This is due to the highly conservative nature of the oil industry related to implementing new technologies at the refining facilities and its key role to boost energy transition and achieving global mitigation targets. The assessment included portfolios of combined mitigation technologies considering synergies, overlap, and interactions over the short, medium, and long term for a more realistic insight into the costs and constraints of the mitigation potential. Relevant mitigation options were included such as energy efficiency measures (EEM), CCS, EOR and biomass integration into an existing refinery, process electrifications measures, blue and green hydrogen, green electricity, and combinations of these mitigation options. The electrification options were assessed in relation to a potential transition of the Colombian energy system towards a sustainable system as described by Younis et. al. [19] as the first step to a sector coupling assessment.

The novelty of this paper is based not just on using actual refinery process data, but on the methodology proposed which brings more detailed insights into the CO_2 mitigation potential for deployment pathways (DP) determined by the timing and the interactions between mitigation options. These aspects are not considered in an integrated and comprehensive analysis in recent key studies for the industry, described above in detail, such as Oliveira et al. [18], Berghout et al. [10], Johansson et al. [9], and DNV-GJ [14]. Timing and interactions between mitigation option are due to the lifetime of existing process equipment, the cost development over time of mitigation options, and interdependency of mitigation options (either providing synergy, limiting impact or incompatibility). The implementation order of mitigation options (MOs) relies on its life-span, space availability, technical constraints, technological maturity (based on TRL), economic parameters (total investment), retrofitting order, facility units affected, and industrial utilities demand. As a result, these insights define a more detailed and possible transformation route of a refinery over time concerning a specific mitigation target.

A key contribution of this study reflects in the methodological approach that could be used for analysing the decarbonisation portfolio of other oil refineries or even other energy-intensive industrial complexes for a better understanding of their mitigation potential and cost. The refinery case used in this study represents the most common scale-sized and complexity-level refinery worldwide, following the complexity classification presented by Kaiser [20]. These studies are usually based on identifying mitigation options for a specific process (when using bottom-up) or globally, based on technology readiness, CO_2 mitigation potential and cost (CapEx or mitigation cost). Usually, this approach assumes all options can be fully implemented without any negative interactions such as space availability, CO_2 source competition, performance impact on process or refinery, replacement or decommission of assets in a lifetime, or deployment order in time.

2. Method

2.1. General approach

The assessment of the mitigation options for a decarbonization strategy followed seven main steps (Fig. 2–1):

1. Inventory of existing facilities and key parameters of core process of refinery (e.g. CO_2 emissions, capacity, energy flows);
2. Identification and data collection of GHG emissions mitigation options (MO);
3. Identification of impact on industrial facilities due to MO deployment;
4. Identification of interactions between mitigation options (GHG reduction potential, cost synergies, economies of scale, lock-in effect);
5. Estimation of GHG reduction potential and GHG avoidance cost of individual and combined mitigation options;
6. Determination of a target and technology portfolio for each mitigation pathway;
7. Estimation of the mitigation potential for each pathway.

The mitigation options were classified by time frame to be deployed and potential impact on the current plant layout. Besides technological readiness criteria, the current INDC by the Colombian government [4] was used to define the time frame for short-, medium- and long-term mitigation options. The deployment time was divided into short-term (<5 years), medium-term (5–15 years), and long-term (>15 years) measures. The complexity of the measure was classified as add-on, retrofit, replacement, or new concept.

The identification of promising deployment pathways combines several technology mitigation options for oil refining. Each portfolio considers non-mutually exclusive options that differ with respect to criteria such as CO_2 avoidance cost, GHG emission reduction potential, investment, technological maturity, and their impact on the core process. The output of the refinery was assumed as constant. Nevertheless, there are some minor changes in outputs, especially when Co-processing bio-oils. In this regard, fractions yields might change at the top streams, increasing the investment cost for downstream gas managing.

A more detailed explanation of the step-plan followed in this study for developing the mitigation pathways is presented in the Appendix.

2.2. Case study and performance indicators

North America and Europe hold 47% of refining capacity worldwide, followed by Asia-Pacific with 34%, the Middle East with 10%, and Central and South America with 6%. Refineries are classified by their technical complexity [20]. In the US, refineries are commonly referred to as simple or complex. The latter is split by “cracking” and “coking” refineries or as “complex” or “very complex” refineries, respectively. In Europe and elsewhere, it is common to refer to complex refineries as “conversion” or “deep conversion” refineries. According to OGCI, in 2014, global refining capacity reached 4482 Mt/y (90 Mbpd), and approximately half of the 646 refineries worldwide were conversion facilities. In the United States, most refineries are conversion facilities, while in Asia, the Middle East, and South America, almost all new constructions are conversion and deep conversion facilities.

The case study refinery is the largest oil refinery in Colombia with an average capacity of 12.4 Mt/y (250 kbpd) and processes medium-to-heavy crude oils. This refinery is a complex or cracking-type refinery. This study is based on company data. However, in order to maintain data

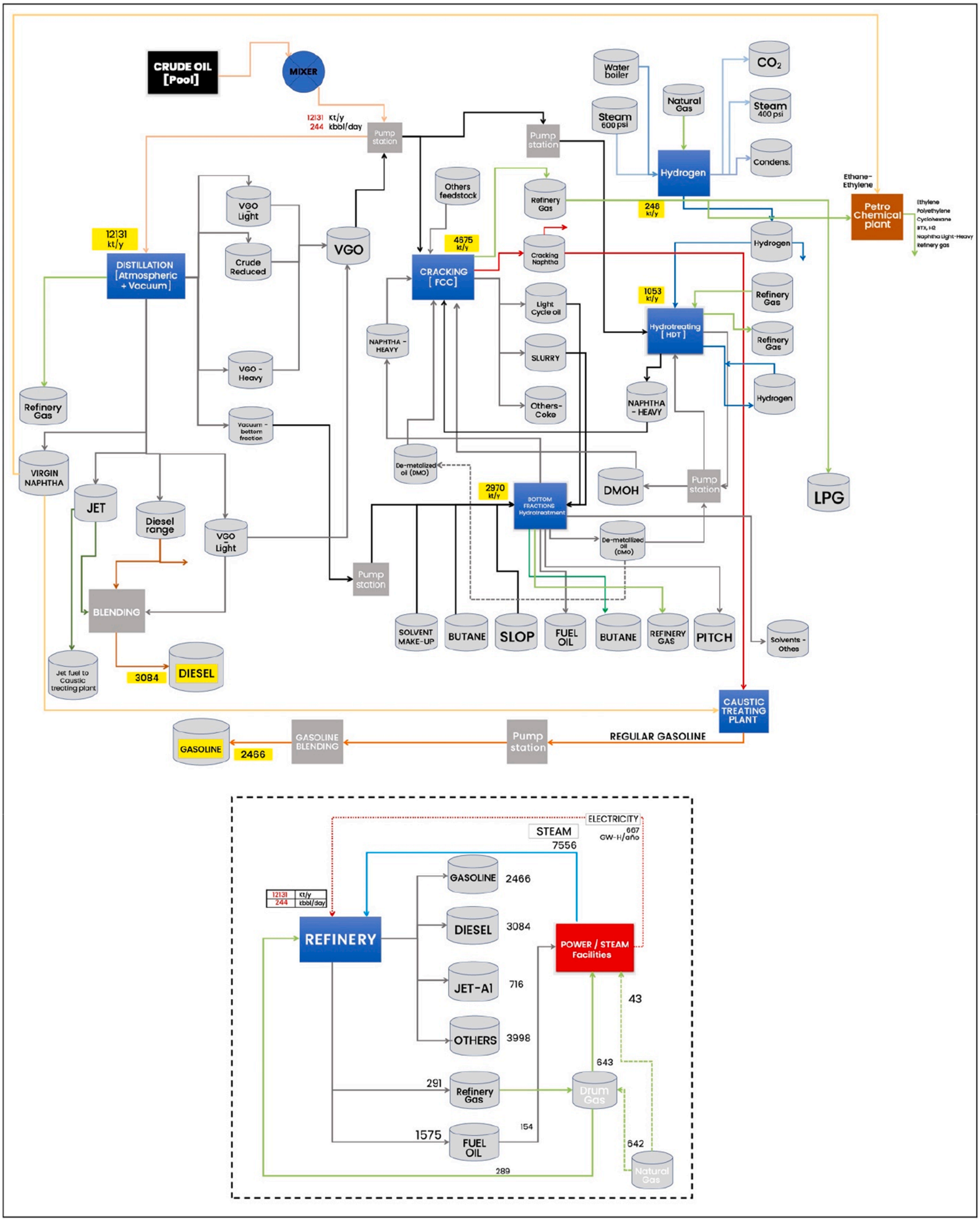

Fig. 2–2. Schematic diagram of the refinery case study (as described by Yáñez et al. [22].

Table 2–2
General techno-economic parameters used in this study.

Parameter	Unit	Value	References
Real discount rate [1]	%	12	[21]
Total plant cost [2] (TPC)	%PPC	130	[10]
Total Capital Requirement (TCR)	%TPC	110	[10]
Calorific values			
Bio-oil (crude palm oil)	MJ_{LHV}/kg	37.0	[26]
Diesel	MJ_{LHV}/kg	45.2	[27]
Gasoline	MJ_{LHV}/kg	46.0	[27]
Crude oil	MJ_{LHV}/kg	44.3	[27]
Natural gas	MJ_{LHV}/kg	52.2	[27]
Energy prices			
Hydrogen	$/thousand scf	0.887	[28]
Natural gas	$/MBTU	5.4	[27]
Electricity (national grid)	€/kWh	0.085	[29]
Electricity from combined heat and power (CHP)	€/kWh	0.065	[30]
CO_2 emissions factors			
Natural gas	kg CO_2/GJ	56.6	[27]
Electricity (national grid-2018)	t CO_2/MWh	0.128	[31]
Electricity (national grid-policy 2050)	t CO_2/MWh	0.021	[19]
GHG Life Cycle emission			
Fossil Diesel (Oil production) [5]	g $CO_{2\text{-eq}}$/MJ Diesel	1.91	[32]
Fossil Diesel (Oil transport) [5]	g $CO_{2\text{-eq}}$/MJ Diesel	0.76	[32]
Fossil Diesel (Oil refining) [5]	g $CO_{2\text{-eq}}$/MJ Diesel	10.43	[32]
Fossil Diesel (Refined transport)	g $CO_{2\text{-eq}}$/MJ Diesel	0.068	[32]
Fossil Gasoline (Oil production)	g $CO_{2\text{-eq}}$/MJ Gasoline	1.88	[32]
Fossil Gasoline (Oil Transport)	g $CO_{2\text{-eq}}$/MJ Gasoline	0.92	[32]
Fossil Gasoline (Oil Refining)	g $CO_{2\text{-eq}}$/MJ Gasoline	7.09	[32]
Fossil Gasoline (Refined transport)	g $CO_{2\text{-eq}}$/MJ Gasoline	0.07	[32]

[3] The CO_2 emissions factor is calculated for the hydrogen production via SMR (steam methane reformer) in the Barrancabermeja's refinery.

[4] The CO_2 emissions factor for electricity was calculated for the refinery industrial services department based on a combined heat and power cogeneration (CHP) process using gas turbines and heat recovery steam generation (HRSG). Allocation of the CO_2 emissions for the electricity and steam production uses the allocation guidance for the GHG protocol [33] and refinery energy production from [21].

[1] A discount rate (r) of 12% was used since Ecopetrol S.A. is a company with national state interest and participates in the stock market. A social perspective assessment might use lower values between 6% and 8% (Laitner et al., 2003) or even lower (Kesicki and Strachan, 2011). Industrial and commercial projects might use higher values of 20%, 30% or even 50%. (DeCanio, 1993; Jaffe and Stavins, 1994).

[2] The total plant cost (TPC) is estimated from the process plant cost (PPC) and engineering fees, contingencies. PPC include the cost of equipment and installation.

[5] The CO_2 emissions for the diesel production referred by Martinez et al. [32] is based on diesel that has been hydrotreated to reduce sulphur content to 500 ppm. CO_2 emission factors for regular diesel up to 3000 ppm S is estimated at 1.83, 0.79, and 7.02 g CO_2/MJ for the production, transport and refining process respectively.

confidentiality, aggregated data of mass, energy and CO_2 emissions of the refinery were extracted from a refinery model as described by Yanez et al. [21]. Table 2–1 provides an overview of key performance parameters.

Fig. 2–2 illustrates a simplified schematic of the different process units in the refinery, excluding the petrochemical section.

This study uses annual avoided GHG emissions, ΔGHG_a (t $CO_{2\text{-eq}}$/y) as the main technical indicator. See Equation 2–1.

Equation 2–1

$$\Delta GHG_a = \Delta GHG_{up} + \Delta GHG_{plant} + \Delta GHG_{down}$$

where ΔGHG_{plant}, ΔGHG_{up}, ΔGHG_{down} correspond to the net change in annual GHG emissions [$tCO_{2\text{-eq}}$/y] of the target process or plant, and upstream (*up*) and downstream (*own*) process, respectively. The focus of this study is on the performance of the oil and gas industry. This includes the production of the feedstock and conversion into products. It does not include the final use of these products. However, the majority of GHG emissions regarding petroleum products comes from the final combustion of the products. Therefore, two different CO_2 emissions will be calculated. The cradle-to-gate emissions cover only the production and gathering of feedstock and the emissions at the refinery, including due to the production of imported energy carriers. Any carbon in the products is considered stored as the products leave the refinery as hydrocarbons and are not (yet) converted into CO_2. However, when assessing the impact of the oil and gas industry, the emissions associated with the final use and/or disposal should also be included. Therefore, a cradle-to-grave estimation of GHG emissions based on the literature is also included. This includes the production and gathering of feedstock, conversion into products, distribution and use of products to consumers and, if applicable, disposal of the products. Note that this means that biocarbon is considered negative carbon in the cradle-to-gate methodology and neutral carbon in the cradle-to-grave methodology. For the cradle-to-gate calculation the benefits of using biocarbon on the GHG balance are fully allocated to the refinery and not the products.

The GHG avoidance cost, C_a (€/t $CO_{2\text{-eq}}$) is the main economic indicator in this study and expressed as shown by Equation 2–2.

Equation 2–2

$$C_a = \frac{\alpha \times I + \Delta C_{O\&M}}{\Delta GHG_a}$$

where I is the upfront investment (€), with α as the annuity factor and $\Delta C_{O\&M}$ is the net change in O&M cost (€/y). Total capital requirement (TCR) represents the upfront investment, which includes equipment cost, installation, engineering fees, contingencies, owner cost and interest during construction. The TCR is calculated as a percentage of the total plant cost and, in turn, of the process plant cost (PPC) as shown in Table 2–2.

The annualized capital cost is calculated by multiplying the annuity factor (α) and the TCR (Equation 2–3). The annuity factor is a function of the discount rate r (%) and the economic lifetime Lt (years) of the technology.

Equation 2–3

$$Annualized\ \ capitalcost = \alpha * I = \frac{r * I}{1-(1+r)^{-Lt}}$$

2.3. Harmonization of key parameters

In order to allow a fair comparison between different technological pathways, several parameters used in this study were harmonized as described below:

1. Indexation. All figure costs are reported in $€_{2018}$. Costs reported in other currency are first converted to Euro using the year-average exchange rate data of OANDA [23] and then corrected to the year 2018 using the Harmonised Index of Consumer Prices (HICP) [24].
2. Normalisation. Since the costs of the components are not equally reported in the literature, a fixed percentage was applied to the capital cost figures to correct for these differences. The total capital requirement (TCR) was calculated as shown in Table 2–2.
3. Scaling of capital cost values. Capital cost is highly dependent on economies of scale, i.e. of the size (capacity) of the equipment. Capital costs were calculated by applying the exponent method to values from literature (See Equation 2–4).

Equation 2–4

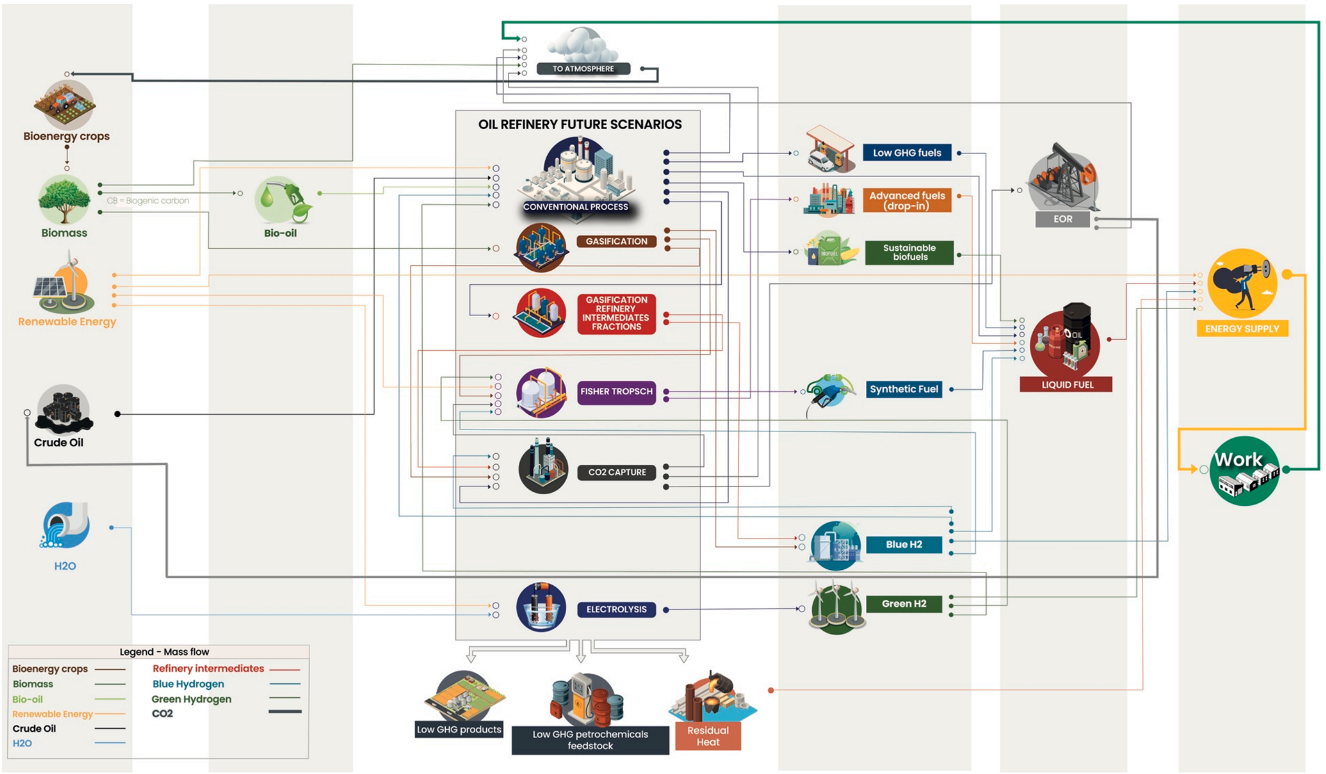

Fig. 2–3. The future layout of oil refineries due to GHG mitigation pathways-based transformation.

$$\frac{Cost_A}{Cost_B} = \left(\frac{Scale_A}{scale_B}\right)^{SF}$$

Where *SF* is defined as the scaling factor. A scaling factor of 0.67 was assumed according to Berghout et al. [25].

Table 2–2 provides an overview of the key parameters used in this study.

2.4. CO_2 mitigation options

The selected mitigation options are energy efficiency measures (EEM), CO_2 capture and storage with enhanced oil recovery (EOR), bio-oil co-processing at the refinery, miscellaneous technological measures (MTM) involving blue and green hydrogen, and electrification alternatives as well as green electricity (low-carbon) from the national grid. Fig. 23 depict how a future oil refinery looks like to reduce its GHG emissions through several technological alternatives integrated into the current oil refinery.

The mitigation options considered in this study are based on a bottom-up analysis carried out for the same refinery case study, using process field data. Mitigation options based on EEM, CCS, and bio-oil co-processing for the same refinery were investigated in precedent studies [21,34–35]. A description and time horizon of the CO_2 mitigation options considered in this study is given in the Appendix (Table 8–1).

2.4.1. Miscellaneous technological options

This category refers to the use of renewable options to replace a share of the fossil-based energy and hydrogen demand in the refinery.

2.4.1.1. Green electricity (GE). The refinery case study consumes around 2.4 PJ/y in electricity produced by CHP facilities which use refinery gas, fuel oil and natural gas. Replacing a share of this fossil-based electricity by a low-carbon intensity one (green electricity) is a potential mitigation alternative.

There is a significant difference in the carbon intensity of the on-site electricity production at the refinery and the national grid, which indicates a potential mitigation alternative by importing electricity into the refinery. The CO_2 emission factor for electricity production at the refinery is 0.41 kg CO_2/kWh while, according to the Colombia's Mining and Energy Planning Unit (UPME [31]), the carbon intensity for the Colombian electricity grid was 0.13 t CO_2/MWh in 2018, due to its high share of renewable sources (69%[1]). Nevertheless, the Colombian government, following international agreement such as SDG, COP21, COP25 and OECD, aims to further diversify the electricity generation matrix with renewable sources by 2050 [36]. This commitment would reduce the carbon intensity of the electricity even further. A forecast scenario for the mix of energy sources for the national electricity grid and the carbon intensity based on estimations of the national government and sustainable scenarios was developed by Younis et al. [19]. They investigated several renewable energy sources such as solar, wind, biomass and hydrogen to explore contributions of a bio-based economy to fulfil the energy and chemicals supply of Colombia by 2030 and 2050. Their modelling results estimate a reduction from 0.13 to 0.021 t CO_2/MWh (even to net zero) by 2050.

This study considers the scenario SSP1 proposed by Younis et al. [19], which aims to depict a sustainable development-oriented future with progressive measures to mitigate climate change. See a summary of the characteristic of this scenario in the Appendix. The SSP1 scenario estimates an increase in the total power generation from 250 PJ in 2015 to 550–1000 PJ by 2050, which represents an increase in the total installed capacity from 17 GW to 88 GW. Under a policy scenario with CO_2 emission constraints, the electricity mix of the national grid would reach a net-zero emission factor by 2050, or even by 2040 for the

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[1] The electricity in Colombia is produced mostly from renewable sources with hydro accounting for (68%), gas (11.9%), liquid fuel (8.6%), coal (9.5%), CHP (0.8%), solar (0.5%), and wind (0.1%) for an effective total capacity of 17.5 GW in 2019, according to the electric information system from UPME: http://www.siel.gov.co/Inicio/Generación/Generación1/tabid/143/Default.aspx

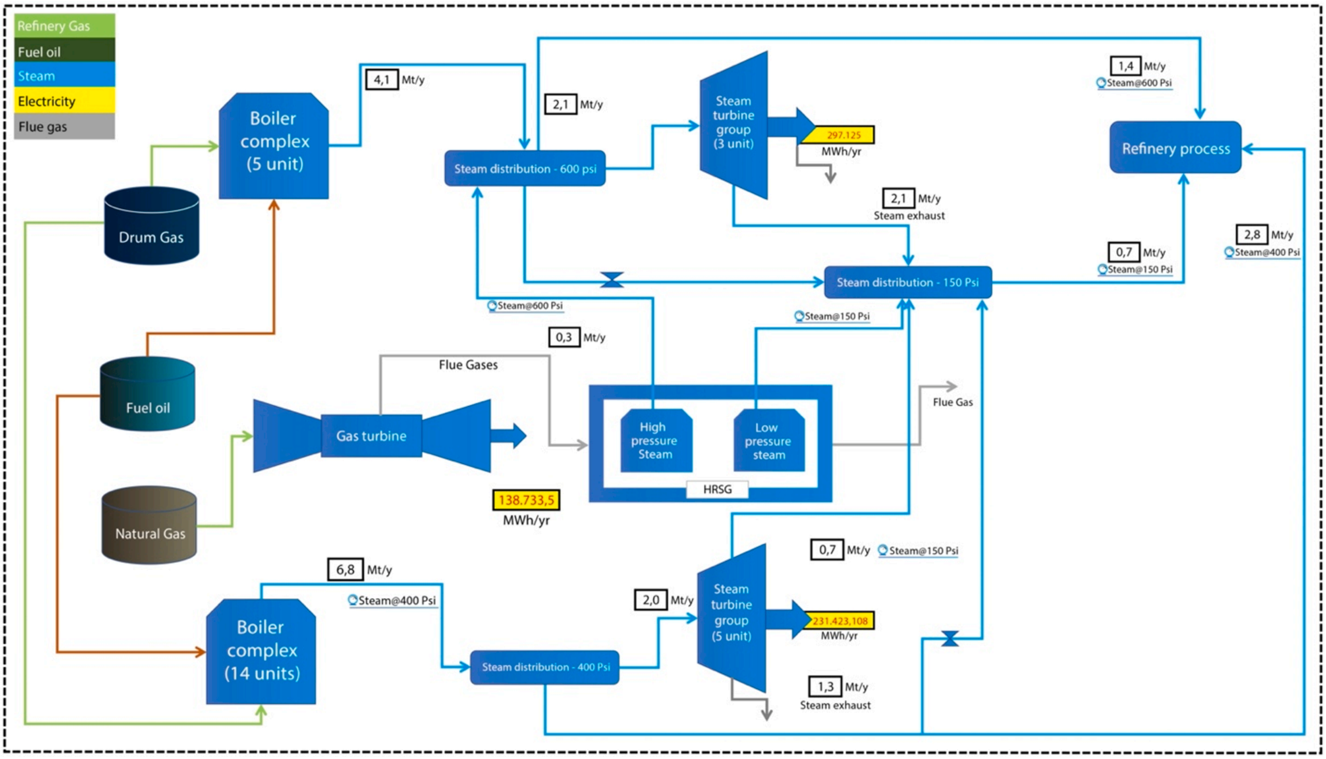

Fig. 2–4. Overview of the CHP system at the refinery study (Ecopetrol [37].

scenario with high biomass supply.

Even though there is a significant reduction potential from using electricity from the grid, identifying the electricity producers/consumers to be replaced at the refinery is challenging. Process control at the refinery is very conservative, avoiding any potential disturbance to the refining process. This is a result of high throughput volume, high utilization factor, complex reactions and high product values. Therefore, the reliability of the electricity supply must be assured in the refinery. This means that non-core processes are the first target of potential source of replacing fuels with electricity. For the refinery case study there is a significant consumption driven by non-core process-related consumers, which accounts for around 17% of the total electricity consumption (667 GWh/y). In the case study, steam and electricity are produced by a gas turbine (GT) integrated to a heat recovery steam generator (HRSG) and back-pressure steam turbines systems (see Fig. 2–4). These systems are divided into three leading facility groups. Group 1 includes five boilers and three steam turbines. Group 2 consists of 14 boilers and five steam turbines. In both groups there are natural gas fired-boilers, although there is a share of fuel oil used, representing around 28% and 17% of the energy supply, respectively. Group 3 represents the GT-HRSG system which produces, only high-pressure steam (@600 psi).

To determine which power facility group should be replaced the following merit order is used:

- High-carbon content fuel
- Low efficiency
- Low process control: instability might cause high fuel consumption (high emissions) and/or low steam production which could affect the refining process
- Older: High maintenance cost

Following this rationale, group 2 appears to be the group to be replaced first due to using fuel with higher carbon content. However, due to the high steam generation of group 2, it would be difficult for the other groups to make up for the lost steam production. Avoiding energy balance perturbation is essential. Therefore, a closed steam cycle (condensation turbine) would be the most interesting option to be replaced as there is no direct steam consumption. Groups 1 and 2 supply around 80% of the refinery steam demand. Replacing them would strongly affect the refining process and a new facility would be required to produce the considerable amount of steam demanded by the refinery. However, in our case study, there is no condensation turbine facility but a gas turbine integrated with an HSRG as a candidate to be replaced. The latter produces 21% of the total electricity consumption and only 2% of the total steam at the refinery. Other units would likely produce the small supply of steam from this facility. Instead, the electricity produced accounts for the buildings demand (which would not affect the refining process) and represents the electricity target to be replaced.

The small difference in the production of electricity and steam has to be produced elsewhere. It is possible to assume that boiler group 1 could produce a surplus of steam by increasing the feedwater temperature by 10 °C, which would also increase fuel consumption by around 5%. The electricity difference (26 GWh/yr) could be supplied by the national grid.

The CO_2 avoided cost, *CCAC* (€/t CO_2) was estimated based on the levelized production cost of electricity, *LCOE* (€/kWh), for the refinery reference case ($LCOE_{Ref}$) and the green national electricity grid scenario ($LCOE_{GE}$), as well as the CO_2 emissions factor, *EF* (kg CO_2/ MWh) for the reference case (EF_{Ref}) and green electricity (EF_{GE}), respectively. See Equation 2–5.

Equation 2–5

Table 2–3
Techno-economic performance data for CO_2 capture on SMR based standalone hydrogen plant (IEAGHG [38]).

	Unit	Base case	w/CO_2 capture
Inlet Stream			
Natural gas (NG) to Feedstock	t/h	26.23	26.23
NG to Fuel	t/h	4.33	7.347
Low Heating Value (LHV)	MJ/kg	46.50	46.50
Total energy input (A)	MW	394.77	433.72
Outlet Stream			
H_2 Mass	t/h	9.0	9.0
Volume	Nm^3/h	100,000	100,000
LHV	MJ/kg	119.96	119.96
Total energy in product (B)	MW	299.7	299.7
Power Balance			
Gross Power Output	MWe	11.50	11.7
H_2	MWe	−1.22	−1.314
Auxiliaries	MWe	−0.37	−1.677
Capture plant	MWe	NA	−2.001
Compression & Drying	MWe	NA	−6.282
Export to the grid	MWe	9.92	0.426
Specific Consumption			
NG to feedstock	MJ/Nm^3 (kg) H_2	12.197 (136)	12.197 (136)
NG to Fuel	MJ/Nm^3 (kg) H_2	2.014 (22)	3.416 (38)
Total	MJ/Nm^3 (kg) H_2	14.211 (158)	15.614 (174)
CO_2 performance			
Specific CO_2 Emissions	kg CO_2/Nm^3 (kg) H_2	0.8091 (9)	0.0888 (0.99)
Specific CO_2 Captured	kg CO_2/ Nm^3 (kg) H_2	NA	0.8004 (8.90)
Overall CO_2 avoided (%)		NA	89%
ECONOMIC			
TPC	million €	€ 171	€ 305
TCR	million €	€ 223	€ 398
Specific TPC cost	€/(Nm^3/h)	€ 1,710	€ 3,053
Opex			
Fixed cost	€/year	€ 7,545,514	€ 11,536,790
Variable cost	€/year	€ 71,484,752	€ 78,452,748
Total	€/year	€ 79,030,266	€ 89,989,538
Other Revenues (Electricity)	€/year	-€ 6,603,008	-€ 283,614
Other Cost-Transport and Storage	€/year		€ 6,661,077
Annual O&M Cost	€/year	€ 72,427,258	€ 96,367,001
CO_2 transport and storage	€/t CO_2 stored	NA	€ 10
Levelized Cost			
H_2	€/Nm^3 (kg)	€ 0.11 (1.25)	€ 0.16 (1.78)
CO_2 avoided cost	€/t CO_2	NA	€ 67

$$CCAC = \frac{\left(LCOE_{GE} - LCOE_{Ref}\right)}{\left(EF_{Ref} - EF_{GE}\right)} \times 10^6$$

The estimation of the levelized cost for the green scenario was based on the results from Younis et al. [19] for the energy matrix model of the national grid electricity and the investment cost for the energy sources biomass, hydro, solar and wind (see the Appendix).

2.4.1.2. *Blue hydrogen (BH_2).*

Fossil-based hydrogen produced at the refinery is called grey hydrogen. Blue hydrogen refers to the production of hydrogen using the conventional technology of steam methane reforming (SMR) but with CO_2 capture and storage (CCS) to reduce its carbon intensity.

There are two options to shift from grey to blue hydrogen for the refinery case study: 1) CO_2 capture at the current hydrogen production facilities which supplies hydrogen to the refining process, and 2) CO_2 capture at new hydrogen production units required for the co-processing of bio-oils.

For the first option, the hydrogen production facilities considered are composed of two primary units: one low-capacity unit (3.2 kt H_2/y) using conventional SMR technology and a second larger SMR-PSA which is energy-integrated with a hydrotreatment unit (9.1 kt H_2/y). CO_2 capture from these units are already considered as part of the CCS mitigation option cases (CCS-2 and CCS-4, see Table 8–1). The second option focuses on the bio-oil co-processing routes with upgrading and co-processing bio-oils through a hydrotreating process, which requires additional hydrogen. These two options could be deployed at the same time. However, it should the pathway aim and possible interactions within each time frame should be taken into account.

Bio-oil upgrading requires a significant hydrogen supply, which can be produced by a stand-alone SMR unit, as assumed in Yanez et al [35]. Blue hydrogen (BH_2) is produced when carbon capture is deployed on these hydrogen production units. Thus, the BH_2 mitigation option refers to the CO_2 capture process at the hydrogen production facilities used for bio-oil hydrotreating. The current commercial standard for CO_2 capture from an SMR based H_2 production plant is the capture of CO_2 from the shifted syngas using MDEA solvent. Techno-economic data reported by the IEAGHG [38] was used to estimate the capital investment and operation and maintenance cost. This data is summarized in Table 2–3.

CO_2 avoidance cost, *CCAC* (€/t CO_2), was calculated dividing the difference in levelized cost of hydrogen production, *LCOH* (€/Nm^3 H_2) with CCS ($LCOH_{CCS}$) and the reference case without CCS ($LCOH_{ref}$) by the difference in the CO_2 emission per Nm^3 of H_2 (*EF*) for with CCS (EF_{CCS}) and without CCS (EF_{ref}) (Equation 2–6).

Equation 2–6

$$CCAC = \frac{\left(LCOH_{CCS} - LCOH_{ref}\right)}{\left(EF_{ref} - EF_{CCS}\right)}$$

The technical performance indicator for bio-oil co-processing are provided in Table 2–4.

Table 2–4
Key technical indicators for bio-oil co-processing [35].

		BioC-1 (VO to HDT)	BioC-4 (CPO to HDT)	BioC-5 (HTL to HDT)
H_2 consumption	kg H_2/kg Bio-oil	0.035	0.097	0.051
Bio-oil consumption	kg Bio-oil/hr	15,820	94,919	182,892
	t Bio-oil/year	126,559	759,351	1,463,138
CO_2 emissions	kg CO_2/year	89,832,841	1,509,970,060	1,514,714,085
H_2 consumption	kg H_2/year	4,382,090	73,657,076	73,888,492
	t H_2/year	4,382	73,657	73,888

VO: Vegetable oil.
HDT: Hydrotreating.
CPO: Catalytic pyrolysis oil.
HTL: Hydrothermal liquefaction oil.

Table 2–5
Techno-economic data for PEM electrolyser [41].

		2020		2050	
		Reference	Optimistic	Reference	Optimistic
Capex	€/kW	€ 1,200	€ 900	€ 750	€ 400
Opex					
Fixed	€/kW	€ 36	€ 14	€ 23	€ 6
Variable	€/kWh				
	kWh/kg H_2	56	53	49	46
Efficiency	MW_{out}/MW_{in}	0.70	0.75	0.80	0.86
Availability factor		0.95	0.97	0.95	0.97
Lifetime	hours	50,000	60,000	80,000	100,000
	years	6.0	7.1	9.6	11.8

Table 2–6
Hydrogen production and CO_2 emissions at the refinery case study.

	H_2	CO_2 – Direct (Reaction)	CO_2 - Indirect (Energy)	CO_2 – Total	Emission Factor (EF) – Direct	Emission Factor (EF) – Indirect	Emission Factor (EF) – Total
Unit	t/y	t/y	t/y	t/y	kg CO_2/kg H_2	kg CO_2/kg H_2	kg CO_2/kg H_2
A	9,125	43,201	44,751	87,952	4.7	4.9	9.64
B	3,285	19,760	16,110	35,870	6.0	4.9	10.92
C	16,700	91,429	81,902	173,331	5.5	4.9	10.38
D(new project)	*175,791*		*862,124*	*862,124*	–	*4.9*	*4.90*
Total A + B + C	**29,110**	**154,390**	**142,764**	**297,154**	**5.3**	**4.9**	**10.21**

2.4.1.3. Green hydrogen (GH_2). Renewable hydrogen (green hydrogen-GH_2) can be produced using renewable electricity and water electrolysis through options such as alkaline solution (AS), proton exchange membrane (PEM) and solid oxide (SO) electrolysers. This hydrogen might replace the current grey hydrogen production and also the blue hydrogen production for bio-oil co-processing at the refinery.

Selection of electrolyser technology is based on TRL, the suitability to the production scale and time response. SO electrolysers are in the R&D stage. Alkaline electrolysers are the most common and mature technology (TRL = 9) to produce water electrolysis-based hydrogen. However, due to its limited current densities (0.2–0.4 A/cm^2), they might be challenging the higher production capacity required at refineries and with an extended system's response (seconds) to the power generation facilities [39–40].

Instead, although PEM is a less mature technology (TRL = 8–9), it has a higher current density (0.6–2.0 A/cm^2) and much shorter system time response (milliseconds) which makes this technology a more promising and flexible option (especially if used in power generation) for higher production capacity required at refineries [39–40]. Techno-economic data of the PEM electrolyser for the medium and long term is provided in Table 2–5.

For green H_2 alternatives, there are also two scenarios to be used at the refinery. First, it can replace the grey hydrogen produced by the three production units as depict in Table 2–6. However, replacing current hydrogen production might be challenging for the large hydrotreating plant (unit C) due to the energy integration between the hydrogen production unit and the hydrotreating facility. This means that shutting down the hydrogen production units could strongly affect the performance of the hydrotreating process. Second, GH_2 might be used to replace the hydrogen produced by the stand-alone units consider for the bio-oil hydrotreating process.

Current H_2 production and co-produced CO_2 emissions by the hydrotreating units at the refinery case study are provided in Table 2–6. Similarly to Equation 2–6, CO_2 avoidance cost, *CCAC* (€/t CO_2) was calculated by comparing the CO_2 emissions per Nm^3 H_2 and the *LCOH* (€/Nm^3 H_2) of hydrogen production plants based on PEM electrolysis with SMR without capture.

2.4.1.4. Electrification. Electricity generation at the refinery case study consumes overheated steam at 400 and 600 psi (@415 °C), while thermo-chemical processes demand steam at 400 and 150 psi. There are several technological options to introduce electrification in an oil refinery operation as described in the Appendix. This study considers e-boilers to replace low-pressure saturated steam (@150 psi, 186 °C), and e-furnaces for medium/high temperature (>400 °C).

A key aspect of these e-options is to use low-carbon intensity electricity, which, for this study, is considered as imported from the national grid electricity. Its deployment and CO_2 emissions contribution will depend on the price spread between electricity and conventional energy carriers. As a result, this option is currently preferable for flexible operations.

Electric boilers are commercially available. There are several types, but the dominant types are electric boiler (based on using an electric heating element) and electrode boiler (conductive/resistive of the water properties), although there are also infrared and induction boilers available at small-scale capacity. Electric boilers have lower thermal capacities (<5 MWe) than electrode boilers which range from 3 to 70 MWe [42]. Electric boilers might reach capacities of up to 70 MWe for saturated steam production up to 350 °C [43] @ 2383 psi or superheated steam up to 350 °C and > 1015 psi [42]. Industrial electrical boilers are a drop-in solution for low/medium temperature steam, with efficiencies up to 95–99% and a TRL of 9 (commercial level) [42]. Detailed techno-economic performance data is provided in Table 2–7.

Savings from using electrode boiler for power to heat applications involves the opportunity cost of typical heat generators such a gas-fired boiler or CHP installation. Advanced strategies for balancing steam production might result in further benefits which have been disregarded in this study.

Low-pressure steam (@150 psi) accounts for 51% [2]of total steam consumption by the refining processes, followed by medium-level steam (@400 psi) with 33% and high-pressure steam (@600 psi) with 16%. The low-pressure (LP) steam is set to be replaced by electric boilers-based steam, as detailed in Table 2–8. There are three generation points of steam (@150 psi): extraction from the steam turbine, pressure-reducing valves (PRV) and LP steam produced by the HRSG. For this study, HRSG-based steam is not considered as this unit only produces steam at @600 psi. Furthermore, steam production from the HRSG uses 'waste' heat from the flue gases from the gas turbine (GT), which means a reduction in steam production will result in lower overall efficiency.

Replacing the extraction steam from the steam turbine means higher electricity output as the mass flow increases throughout the turbine. However, as electricity demand remains constant, the steam mass flow should be reduced and, in turn, the fuel consumption will decrease and so will the CHP-related CO_2 emissions. In summary, CO_2 emission reductions from electrode boiler deployments, which produces low-

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[2] According to a study for oil refineries in the Netherlands [44], low-temperature steam (<200°C) represents around 15%, while 200-400°C steam accounts for 75% of a refinery's steam demand.

Table 2–7
Techno-economic performance data for Electric boilers.

	Electrode boilers	Electrode boilers	Electrode boilers
Pressure	Saturated conditions (2383 psi)	Superheated condition (1015 psi)	(652 psi)
Temperature	350 °C	350 °C	260 °C
Capacity	Up to 70 MWe	15 to 70 MWth (avg 20)	50–70 MW
Voltage	n.a.	n.a.	6–36 kV
Control range	n.a.	n.a.	0/10–100%
Ramp rates (0–100%)	n.a.	n.a.	3–10 min
Capacity utilization factor	n.a.	1.00	n.a.
Efficiency	99.9%	95–99%	99%
TRL	9 (Commercial)	9 (Commercial)	9 (Commercial)
Technical life time (years)		15	
Heat target to supply	n.a.	• All industrial heat demand 100–200 °C Depending on the process of up to 350 °C	n.a.
Investment cost	60 €/kW bare equipment or 150–190 €/kWe all in including electrical connection	0.17 million €/MWth (0.10–0.5). Bare equipment cost 17–60 €/kWe. Total investment can vary from 100 to 500 €/kW$_{output}$	0.19 M€/MW (incl. cables, installation and grid connection cost) 0.06 M€/MW average cost for a 20 MW and 0.13 M€/MW for grid connection 60,000 €/MW (Range of 50–70 k€/MW, incl. cables and installation) 0.06 M€/MW average cost for a 20 MW electric boiler
Fixed cost	1,100 €/MW/y		
Variable cost	0.5 €/MWh		
Source	[43]	[42]	[44]

Table 2–8
Low-pressure steam to be produced by electric boilers.

CHP Group	Source	kt/y	%
1	ST (3) extraction	555	15%
1	Valve Exp @600 psi	809	21%
3	ST (5) extraction	619	16%
3	Valve Exp @400psi	1,839	48%
Total		3,822	100%

CHP: Combined Heat and Power.
ST: steam turbine.

pressure steam, is due to low-carbon intensity process and lower steam consumption (i.e., lower boiler's fuel consumption) by the ST to maintain the same electricity output.

To estimate the steam consumption an online steam turbine tool[3] was used from the U.S. Department of Energy, keeping the same in/out thermodynamic properties of the steam but changing the mass inlet flow to generate the same electricity output. Thermodynamic parameters for the steam turbines system and emissions factors for the steam production are provided in the Appendix.

CO_2 avoided cost *CCAC* (€/t CO_2) was estimated using the levelized cost of steam production, *LCOS* (€/kg steam) for both the gas-fired ($LCOS_{gB}$) and electric boiler ($LCOS_{eB}$) and their CO_2 respective emission factors (kg CO_2 /kg steam) for the steam production (EF^{st}_{gB} and EF^{st}_{eB}) as described in Equation 2–7.

The calculation of the LCOS for a gas-fired boiler follows the steps suggested by the U.S. Department of Energy [45] to estimate the steam production cost at different pressure degradation levels (see Appendix).

Equation 2–7

$$CCAC = \frac{(LCOS_{eB} - LCOS_{gB})}{EF^{st}_{gB} - EF^{st}_{eB}} \times 1000$$

3. Results

3.1. Mitigation options (MOs)

Table 3–1 and Fig. 3–1 presents the CO_2 mitigation potential and avoidance cost of the mitigation options considered in this study. Additional information that describes potential, cost and capabilities is presented in Section 8.2 in the appendix, including Table 8–1 with the inventory and description of MO and in Section 8.4, a technological interaction matrix for mitigation options deployment.

The base case emission of 3.6 Mt CO_2/y is shown by the black bar in the figure, which may increase up to 4.8 Mt CO_2/y in the long term as a result of a revamping project to increase global conversion to around 93% but maintaining the same capacity. The theoretical potential of the mitigation options account for 22 Mt CO_2/y with a weighted average avoidance cost of 196 €/t CO_2. However, this is not the real potential as the MOs cannot be deployed all at the same time as shown by the deployment pathways in Section 3.2.

EEMs are mostly for the short term (low-hanging fruits), except for energy recovery in the cracking units (MT), due to the level of intervention in the processing units. These measures provide a negative CO_2 avoided cost (avg. −82 €/t CO_2), but have a low mitigation potential (around 0.4 kt CO_2/y). The highest share of mitigation potential (90%) comes from improving the steam loss management, which refers to a detect, measure and control of steam losses throughout the refinery network with a low investment. The EEM options were grouped and renamed depending on the processing unit it targets: EEM-1: Flaring, EEM-2: power and steam network and EEM-3: FCC.

CCS mitigation options include the capture, transport, and CO_2 storage through EOR processes. The estimated mitigation potential is 2.7 Mt CO_2/y with an average cost of 74 €/t CO_2. This mitigation option proposes CO_2 capture from the largest refinery sources, namely the cogeneration and cracking units. This mitigation option proposes CO2 capture from the largest refinery sources, namely the cogeneration and cracking units. These sources account for 50% of the CCS potential. The remaining potential is from the hydrogen production units from the revamping project (45) and the current production facilities (5%). The CO_2 avoided cost of these measures is reduced by the additional revenues from the oil produced through the EOR processes.

Blue hydrogen (BH_2) might be deployed to the current and future hydrogen production units, which are already considered for the CCS mitigation options. Besides BH_2 production can supply the bio-oil upgrading process for bio-oil co-processing of vegetable oil-VO (BioC-1), catalytic pyrolysis oil-CPO (BioC-4) and bio-oil from hydrothermal liquefaction-HTLO (BioC-5). Thermochemical bio-oils (CPO and HTLO) pose, compared to VO, the most significant mitigation potential (97%) of the 1.2 Mt CO_2/y, due to their high hydrogen consumption (0.09 and 0.05 vs. 0.03 kg H_2/kg bio-feed, respectively) and largest blending share from hydrotreatment (30% and 15% vs. 5%, respectively).

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[3] Steam turbine tool modelling from the U.S. Department of Energy. https://www4.eere.energy.gov/manufacturing/tech_deployment/amo_steam_tool/equipTurbine

Table 3–1
CO_2 mitigation potential and avoidance cost of the mitigation options considered in this study.

#	Mitigation option [3]	Process	Description	Time Frame	Scale	TCR [Million €, 2018]	CO_2 Avoided [t CO_2/y]	CO_2 Avoid Cost [€, 2018/t CO_2]
1	EEM-2	CHP	LPG and NGL recovery from refinery gas and its use optimization.	S	1,940,219 [GJ/y]	€ 39	8,400	€ –32
2	EEM-2	CHP	Tuning (excess air value, burners maintenance)	S	135,736 [GJ/y]	€ 1.8	6,250	€ 20
3	EEM-1	Flaring	Steam to air assist flares	S	66,697 [GJ/y]	€ 0.8	3,400	€ –29
4	EEM-2	CHP	Improved management of steam losses	S	5,355,355 [GJ/y]	€ 0.15	354,900	€ –93
5	EEM-1	Flaring	Improved management of Flaring by optimizing flare purge gas and reduce purge rates.	S	84,659 [GJ/y]	€ 0.085	6,500	€ –80
6	EEM-3	FCC	Waste heat recovery to produce low-pressure steam.	M	373,361 [GJ/y]	€ 0.8	17,215	€ –77
7	CCS-1	FCC + CHP	(FCC + CHP)	M	1.4 [Mt CO_2/y]	€ 1,541	1,352,999	€ 73
8	CCS-2	HDT	HDT-1	M	0.08 [Mt CO_2/y]	€ 201	80,458	€ 317.68
9	CCS-3	HDT	(HDT + HKC + DCK)	L	1.2 [Mt CO_2/y]	€ 1,375	1,242,577	€ 67.06
10	CCS-4	HDT	H_2	M	0.06 [Mt CO_2/y]	€ 12	62,961	€ –88
11	BioC	HDT	Process 1 + Current situation for Palm oil	M	0.13 Mt biofuel/y	€ 447	237,463	€ 497
12	BioC	HDT	Process 1 + Future B for palm oil	L	0.13 Mt biofuel/y	€ 447	380,627	€ 302
13	BioC-1	HDT	Process 2 + Current situation for Palm oil	S	0.13 Mt biofuel/y	€ 446	209,825	€ 651
14	BioC-2	HDT	Process 2 + Future B for Palm oil	M	0.13 Mt biofuel/y	€ 448	352,974	€ 375
15	BioC	FCC	VO to FCC	M	0.49 Mt biofuel/y	€ 535	921,678	€ 351
16	BioC	FCC	CPO to FCC	L	0.18 Mt biofuel/y	€ 536	646,129	€ 252
17	BioC	FCC	HDO to FCC	M	0.34 Mt biofuel/y	€ 535	1,300,251	€ 272
18	BioC-3	FCC	FPO to FCC	M	0.17 Mt biofuel/y	€ 536	695,245	€ 99
19	BioC-4	HDT	CPO to HDT	L	0.75 Mt biofuel/y	€ 448	2,980,281	€ 147
20	BioC	FCC	FPO-Est to FCC	L	0.36 Mt biofuel/y	€ 536	1,171,535	€ 321
21	BioC	HDT	FPO-E to HDT	L	0.51 Mt biofuel/y	€ 447	1,137,762	€ 337
22	BioC-5	HDT	HTLO to HDT	L	0.75 Mt biofuel/y	€ 447	2,544,312	€ 169
23	BioC-6	BG_FT	BG + FT [NO Capture]	L	0.74 Mt biofuel/y	€ 2,955	2,988,012	€ 124
24	GH_2-HDT	HDT	Green H_2 from electrolysis using future national grid to supply current Units	L	12,410 t H_2/y	€ 55	113,841	€ 303
25	GE-GT	CHP	Green electricity from national mix to replace GT	M	138 GWh/y	€ -	49,868	€ 214
26	GE-Mix_P	CHP	Green electricity from national mix [MIN EF for Policy Scenario]	L	138 GWh/y	€ -	64,669	€ 51
27	GE-Mix_BioH	CHP	Green electricity from national mix [MIN EF for SSP1 BioHi Scenario]	L	138 GWh/y	€ -	67,583	€ 46
28	BH2-BioC-1/2	BioC	Blue H_2 [1] to supply demand from BioC-1	L	4,382 t H_2/y	€ 59	35,095	€ 217
29	BH2-BioC-4	BioC	Blue H_2 [1] to supply demand from BioC-4	L	73,657 t H_2/y	€ 393	589,895	€ 68
30	BH2-BioC-5	BioC	Blue H_2 [1] to supply demand from BioC-5	L	73,888 t H_2/y	€ 394	591,749	€ 68
31	GH2-BioC-1/2	BioC	Green H_2 from electrolysis using future national grid to supply BioC-1	L	4,382 t H_2/y	€ 19	40,198	€ 159
32	GH2-BioC-4	BioC	Green H_2 from electrolysis using future national grid to supply BioC-4	L	73,657 t H_2/y	€ 327	675,682	€ 382
33	GH2-BioC-5	BioC	Green H_2 from electrolysis using future national grid to supply BioC-5	L	73,888 t H_2/y	€ 328	677,805	€ 382
34	GE-Eboiler	CHP	Replace a share of steam production using e-boilers [2]	L	395 MWth	€ 67	600,685	€ 170
35	GE-Efurn-HCK	HCK	Replace fossil-fired furnace by E-furnace in HCK	L	113 MWth	€ 412	186,898	€ 700
36	GE-Efurn-VBK	VBK	Replace fossil-fired furnace by E-furnace in VBK	L	36 MWth	€ 129	58,646	€ 700
37	BH_2-Furn-HCK	HCK	Replace fuel gas by BH_2 in furnace of HCK	L	29,774 t H_2/y	€ 214	157,501	€ 319
38	BH_2-Furnace-VBK	VBK	Replace fuel gas by BH_2 in furnace of VBK	L	9,343 t H_2/y	€ 98	49,422	€ 539
39	GH_2-Furnace-HCK	HCK	Replace fuel gas by GH_2 in furnace of HCK	L	29,774 t H_2/y	€ 132	156,096	€ 810
40	GH_2-Furnace-VBK	VBK	Replace fuel gas by GH_2 in furnace of VBK	L	9,343 t H_2/y	€ 41	48,981	€ 810

[1] The cost of CO_2 transport and storage for the BH_2 mitigation option was assumed as 10 $/t CO_2 according to the EIAGHG [38].

[2] An additional cost of 130 k€/MW [44] is required for grid connection in case there is a limited connection capacity present on site. In case where combined heat-power facilities are already in place, this grid connection can be avoided.

[3] The numbers/data given here are for the stand-alone implementation of each option. Although all MO could be applied to the refinery, interactions between different MO could affect the performance of these options. Possible interactions between MO and their effects are given in section 3.1.1.

The electrification alternatives (GE) include electricity import from the national grid (with future lower carbon intensity scenarios) and the implementation of electrode boilers. GE options account for 0.8 Mt CO_2/y with an average avoidance cost of 153 €/t CO_2. The use of electrode boilers represents the most significant mitigation option in this group (around 0.6 Mt CO_2/y). This potential could be higher as it is only based on the production of low-pressure steam (150 psi). Electricity import from the grid has a modest mitigation benefit since the replacement percentage is low (approx. 17%). The small difference in emission intensity between electricity import (0.13 t CO_2/MWh) and electricity from the GT (0.224 t CO_2/MWh) and the small scale of the electrode boilers results in relatively high CO_2 avoidance costs (214 €/t CO_2). The CO_2 avoided cost is substantially reduced to 46 €/t CO_2 when considering future scenarios of electricity generation with very low carbon intensity (0.021 t CO_2/MWh) or even net-zero grid electricity.

Co-processing of bio-oils shows the highest mitigation potential among the investigated mitigation options, with 9.7 Mt CO_2/y and with an average CO_2 avoided cost of 161 €/t CO_2. This high potential is mainly due to the GHG neutral effect of biogenic carbon and the relatively high blending ratios for coprocessing bio-oils (15% for HTLO and 30% for CPO and BG_FT). Co-processing in HDT units pyrolytic oils (CPO and HTLO) and fuels from the gasification-Fischer-Tropsch route, show the highest mitigation potential in the case study refinery (2.3 to 2.9 Mt CO_2/y) at CO_2 avoidance cost of 124 and 170 €/t CO_2. Instead, co-processing vegetable oils in HDT units offers lower mitigation potential (0.24 and 0.35 Mt CO_2/y) with higher avoidance costs (497 and 375 €/t CO_2) for current and future scenarios, respectively, based on technology improvements during the biomass production stage. The lower performance of this route is due to the low VO mixing ratio (5%) and the relatively high carbon intensity of bio-oils compared to those based on residual biomass.

The green hydrogen production using PEM electrolysers to supply hydrotreating processes shows the highest CO_2 avoidance costs with an average of 370 €/t CO_2. However, all the hydrogen options have a significant mitigation potential of around 1.5 Mt CO_2/y. The highest mitigation potential considered in this study is shown by grey hydrogen substitution consumed during bio-oil upgrading processes such as CPO and HTLO (0.67 Mt CO_2/y for each option), and to a lesser extent, by the current medium and low capacity hydrotreatment units (0.11 Mt CO_2/y).

Fig. 3–1 depicts the GHG reduction potential and GHG avoidance cost of each mitigation option identified for the case study oil refinery.

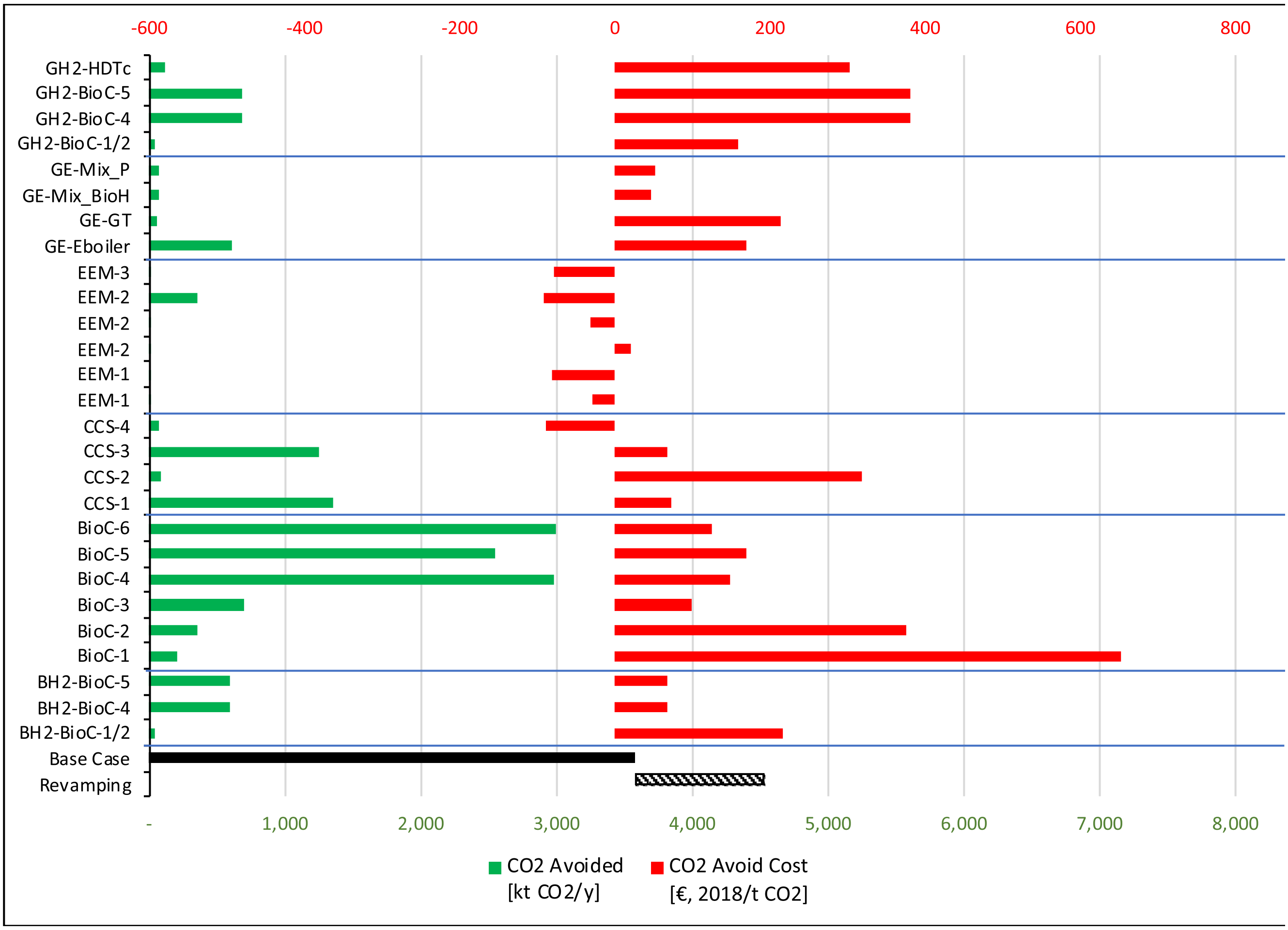
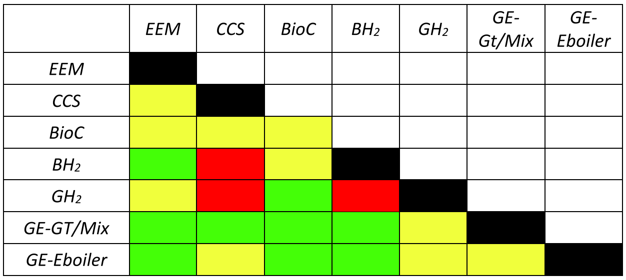


Fig. 3–1. GHG reduction potential and avoidance cost of the mitigation options. The MO are grouped by technology. The CO_2 avoidance potential is depicted in green and refers to the bottom axis. The CO_2 avoidance cost is displayed in red and refers to the top axis. CO_2 emission from the base case refinery and the additional emissions from the revamping project are shown in black and refer to the bottom axis. EEM's mitigation potential is low (<17 kt CO_2 /y, except for EEM-2), so the graph barely shows their values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3–2
Interaction matrix of mitigation options.



	EEM	*CCS*	*BioC*	*BH₂*	*GH₂*	*GE-Gt/Mix*	*GE-Eboiler*
EEM	⬛						
CCS	🟨	⬛					
BioC	🟨	🟨	🟨				
BH₂	🟩	🟥	🟨	⬛			
GH₂	🟨	🟥	🟩	🟥	⬛		
GE-GT/Mix	🟩	🟩	🟩	🟩	🟨	⬛	
GE-Eboiler	🟩	🟨	🟩	🟩	🟨	🟨	⬛

EEM: Energy efficiency measures; CCS: Carbon capture and storage; BioC: Bio-oil Co-processing; BH_2:Blue hydrogen; GH_2:Green hydrogen; GE: Green electricity; GT:Gas turbine ; Eboiler: Electric boiler

Table 3–3
Deployment pathways investigated for CO_2 mitigation in the case study oil refinery.

Deployment Pathway [DP]	Objective	Mitigation options (MO)		
		Short term [→ 2025]	Medium term [→ 2035]	Long Term [→ 2050]
DP-1	Baseline scenario	EEM-1, EEM-2	EEM-3,	
DP-2	Less effort	EEM-1, EEM-2, BioC-1	EEM-3, BioC-2 [Replaces BioC-1], CCS-4, GE-GT	GE-Mix_BioHi [Replaces GE-GT], BH_2 -BioC-2
DP-3	Maximum CO_2 avoidance	EEM-1, EEM-2, BioC-1	EEM-3, BioC-2 [Replaces BioC-1], BioC-3, CCS-4, CCS-1, CCS-2, GE-GT	BioC-4 [Replaces BioC-2], GH_2 -BioC4, GH_2-HDT [Replaces CCS-2 + CCS-4], BioC-6, CCS-3, GE-Mix_BioH [Replaces GE_GT], GE-EBoiler
DP-4	INDC target	EEM-1, EEM-2, BioC-1	EEM-3, BioC-2 [Replaces BioC-1], BioC-3, CCS-4, GE-GT	
DP-5	CO_2 avoided cost under 200 €/t CO_2	EEM-1, EEM-2	EEM-3, CCS-1, CCS-4, BioC-3	CCS-3, BioC-4, BioC-6, GE-Mix_BioHi, BH_2 -BioC4, GE-EBoiler

Mitigation options are shown by technology and compared to the base case refinery emissions as well as the future additional emissions from the revamping project.

3.1.1. Interaction for deployment.

A refinery is a highly integrated process facility where any modification on a specific part of the refinery might impact the mass and energy balance as well as the overall performance. Thus, mitigation option deployment must avoid affecting the steady-state of the processes but also possible negative interactions between them. Mitigation options can compete for the same CO_2 mass flow, process unit, and replacement time window. These interactions affect the CO_2 mitigation potential in the short, medium, and long-term.

Analysis of potential interactions between mitigation options should involve a detailed assessment based on current and future layout of the refinery, technological maturity, specific techno-economic parameters, life-span of facilities, and how they impact the local and global performance of the refinery. This would allow building real MOs portfolio and setting a merit order for their deployment. Since this study does not present an exhaustive assessment of these interactions, preliminary analysis is carried out instead and described below.

The traffic light in Table 3–2 exhibits the primary interactions between mitigation option categories. Green indicates that there is no interaction among the MOs and thus can be deployed simultaneously. Yellow indicates some restrictions might limit their joint deployment and red means significant constraints halt one or both implementations.

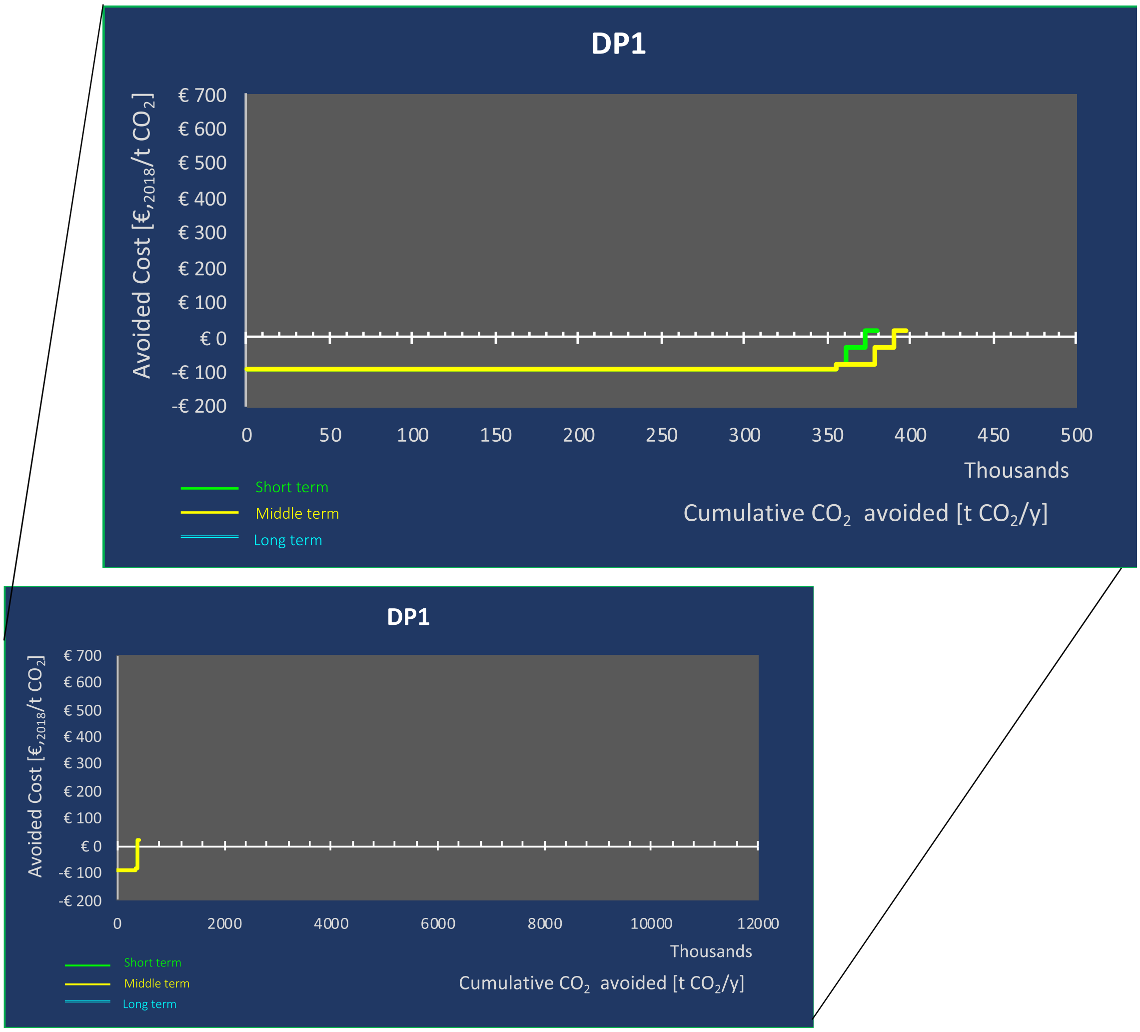
CCS options might interact with EEMs and as the energy demand increases. For instance, implementing a heat recovery unit would change the thermodynamic condition of the flue gas to be fed into a CO_2 capture unit. Besides, a CO_2 capture and storage project might need an economic lifetime of around 20 years (as considered in this study for a CO_2-EOR Project), which prevents any other measure deployment for the same CO_2 source unit in the medium and long term. In this study, EEM-3 and CCS-1 apply to the same unit (FCC). Therefore, EEM-3 should be implemented first for heat recovery and then removing CO_2 with the CCS-1 option, adjusting pressure loss and thermal requirement of the capture unit.

CCS-1 and BioC-3 apply to the same unit (FCC). By co-processing bio-oils, CO_2 emissions are increased, and therefore the capture capacity must be adjusted. Furthermore, impurities such as the heteroatoms S, N, and O must be monitored so that they do not affect the amines used in the carbon capture (post-combustion) process or the downstream refining process. Also, higher pressure drops in the downstream stream can be generated by both systems. CCS-2 and BioC-1,2,4, and 5 apply to the same HDT unit, but these two groups of MOs show synergies as they are deployed up and downstream of the H_2 production unit.

Any MO deployment would imply an additional load of power and/or steam (except for EEMs) to the internal energy network. As the energy network needs to keep the balance and proper distribution around the refinery this will result in some cases in increased capital investment.

Blue and green hydrogen (BH_2/GH_2) production might be overridden by CCS deployed on hydrogen production facility or delayed till after the lifetime expectancy of the CCS options (#8, 9 and 10 from Table 8–1). BH_2 with CCS-2 and CCS-4 are mutually excluding as they compete for the same CO_2 stream out of the HDT. BH_2 can be deployed if there is a BioC option already implemented. The CCS options already represents BH_2 for current hydrogen production units. BH_2 and GH_2 exclude each other as both aim to supply the hydrogen for the crude oil and bio-oil upgrading processes. Replacing CCS-4 by GH_2 would shut down the H_2 production facility (medium–low capacity) or supply hydrogen for new demand, e.g. to bio-oil co-processing. In the case study refinery the H_2 plant is a non-integrated facility at the end of its life-span. Decommissioning of the H_2 plant is, therefore, easier to realise than in refineries where this is not the case.

Electrification options and GH_2 increase the electricity demand at the refinery. These options affect the current energy balance and would require higher electricity import from the national grid due to its lower carbon intensity. This additional demand would represent an overload on the on-site power station at the refinery due to the significant electricity consumption and high voltage required. As a consequence, the power system would need a revamping project with additional investment and electrics load balance improvements. A simple estimation of this investment regarding a new power station cost was included but a detailed assessment needs to be further included. Another implication is that boilers electrification would reduce fuel consumption for steam and power generation but decrease the CO_2 capture potential assumed for CCS-EOR.



	Short-term (ST)	Medium-term (MT)	Long-term (LT)
CO_2 reduction [Mt CO_2 /y]	-→ 0.38	0.02	---
		-→ 0.39	
			-→0.39

Fig. 3–2. Marginal abatement cost curve for deployment pathway 1 (DP1). Green and yellow lines depict Short and Medium-term mitigation options, respectively. The cumulative CO_2 avoided (shown on X-axis) includes measures from short and medium terms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

CCS-1 might be negatively affected by imported green electricity if the GT is replaced by electricity import (GE-GT) which would eliminate the CO_2 stream available from the cogeneration process. Similarly, the CCS-1 option might also be affected by E-boilers deployment if CO_2 emissions from CHP are decreased by lower fuel consumption of the same unit.

Bio-oil co-processing and BG_FT alternatives are assumed as standalone facilities with minor interaction with EEMs and CCS. This is due as they should include their hydrogen and power supply plants. However, this is challenged by the space layout-constrained at the refinery.

Co-processing bio-oils represents a higher risk of increasing impurities during the refining process. Therefore, a maximum threshold of blending ratio (TcPL) is used to keep that risk low.

Co-processing bio-oils by HDT and FCC at the same time (which is the case of deploying BioC-1/2/4/5 and BioC-3) would increase the levels of impurities throughout the refinery, which have not been fully demonstrated yet.

BioC-1 and BioC-2 refer to the same co-processing route (VO to HDT), and the only difference is that on efficiency during the biomass production stage, which does not affect the refinery process.

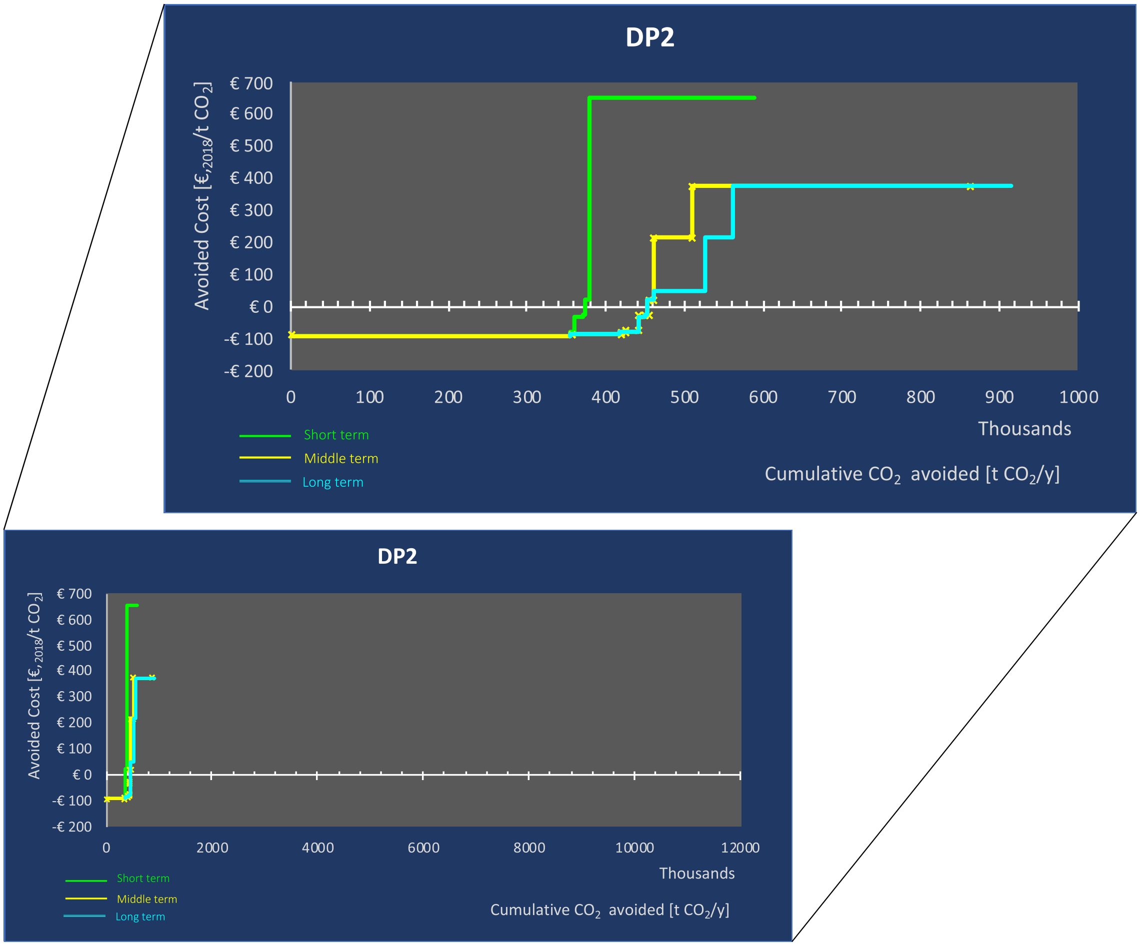
Co-processing options BioC-1, 4 and 5 are mutually exclusive as they compete for the same HDT processing unit. Nevertheless, they might be expected to be deployed in different periods (BioC-1 for ST and BioC-4 and 5 for LT).

In the long term, BioC-4 and BioC-5 are also mutually excluding options. However, BioC-4 is currently at higher TRL than BioC-5, so that might be deployed first. Nevertheless, both options are LT measures within a 15-year span, which is insufficient to plan a revamping project in the time frame considered in this study but to be assessed under any other condition.

GH_2 and BH_2 deployment to replace the grey-hydrogen is restricted by CCS implementation on the current hydrogen production plants and the bio-upgrading facilities, which means additional H_2 demand.

3.2. Deployment pathways

Five pathways were proposed to assess combined CO_2 mitigation options for the case study refinery. These pathways are based on several criteria such as technological maturity, CO_2 avoidance potential, CO_2 avoided cost, adaptation effort, and renewable energy sources (H_2 and



	Short-term (ST)	Medium-term (MT)	Long-term (LT)
CO₂ reduction [Mt CO₂ /y]	-→ 0.59	0.27	0.05
		-→ 0.86	
			-→0.91

Fig. 3–3. Marginal abatement cost curve for deployment pathway 2 (DP2). Green, yellow and blue lines depict Short, Medium and Long-term mitigation options, respectively. The cumulative CO_2 avoided (shown on X-axis) includes measures from short, medium and long-term. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrification options). Table 3–3 summarizes the mitigation options included by each deployment pathway investigated in this study. All pathways include EEMs due to their negative avoidance cost, easiness of implementation, low investment and technological maturity.

DP-1: Base line

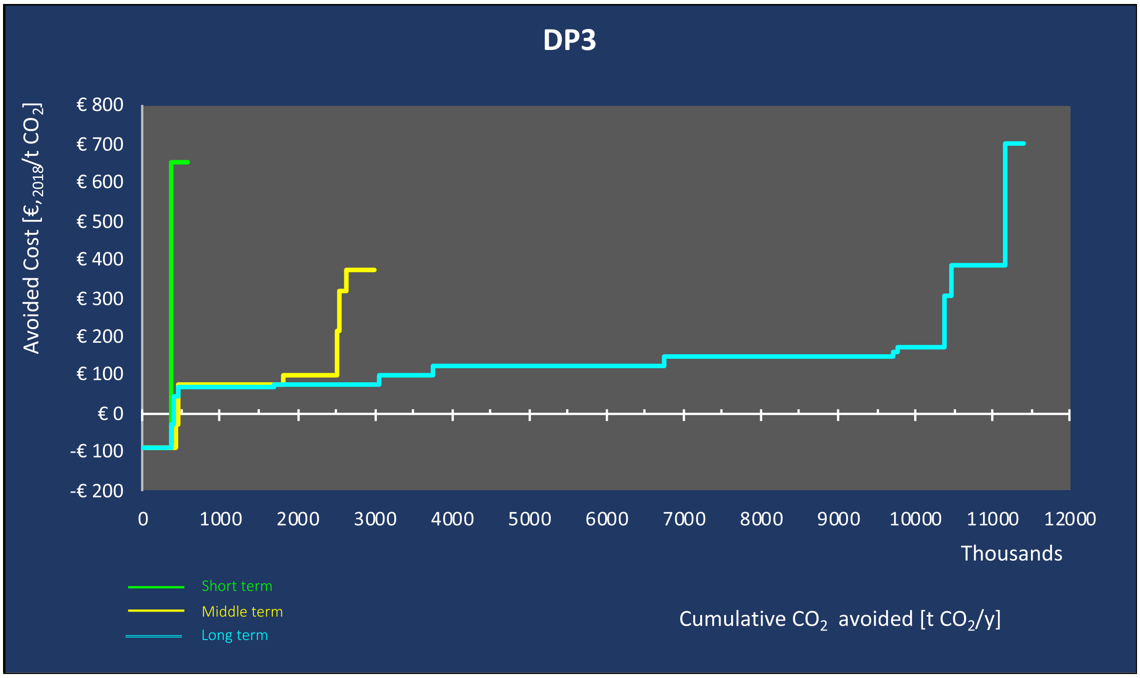
The energy efficiency improvements are included for the short and medium term as they have a negative investment cost for avoided CO_2 emissions and are easy to implement. There is no change in the refinery throughput, so the capacity remains constant at around 12.4 Mt/y (250 kbpd). Nevertheless, an oil refinery revamping project is assumed to be implemented in the MT period (2025–2035). This project aims to increase the refinery global conversion from around 82% to 93%, which represent a CO_2 emission increase of 1.16 Mt CO_2/year. The two oldest and smallest FCC units will be shut down due to the revamping project, which were included neither for CCS alternatives nor for co-processing potential.

Total CO_2 emissions from the refinery are barely affected by changes in the carbon intensity of the national grid electricity. This independence is a result of the very low electricity import from the grid (around 0.8% of 668 GWh total consumption in 2018). Despite this, there is a significant forecasted potential reduction in the carbon intensity of grid electricity from 0.13 to 0.021 t CO_2/MWh (even to net-zero) by 2050 according to Younis et al. [19]. Fig. 3–2 shows the CO_2 mitigation potential and avoidance cost using a marginal abatement cost curve (MACC) for the deployment pathway 1 (DP1). Most of the MOs depicts a negative cost of CO_2 avoided, which are based on energy efficiency measures.

DP-2: Less effort

The less effort scenario aims to deploy the low-hanging fruit options represented by improvements of EEMs but also include other mitigation options that comply with the highest TRL and minimum adaptation to the refinery, including import electricity from the national grid.

In the short term, vegetable oil co-processing is implemented as a way to reduce sulphur content and CO_2 emission intensity of diesel and increasing its cetane number as requested by international regulations. In the medium term, palm oil production is expected to significantly improve its sustainability performance as described by Ramirez et al. [26]. This will affect the CO_2 emissions intensity of co-processing-based



	Short-term (ST)	Medium-term (MT)	Long-term (LT)
CO₂ reduction [Mt CO₂ /y]	0.59	2.40	8.41
		-→ 2.99	
			-→ 11.39

Fig. 3–4. Marginal abatement cost curve for deployment pathway 3 (DP3). Green, yellow and blue lines depict Short, Medium and Long-term mitigation options, respectively. The cumulative CO_2 avoided (shown on X-axis) includes measures from short, medium and long-term. The total CO_2 mitigation for each term period is shown in the table above. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fuel. The amount of vegetable oil used for co-processing follows the maximum technological limits defined by the literature and discussed by Yanez et al. [3–5].

CCS is implemented for the easiest CO_2 capture sources at the refinery, which produce a concentrated stream of CO_2 (above 90%). The captured CO_2 is to be used for EOR projects. However, this option is considered for the medium term due to the fact that CO_2-EOR technology still needs to be regulated in the country and pilot projects must be carried out as there is no commercial experience of this technology in Colombia. By the medium term, BioC-2 replaces BioC-1. The improvements on CO_2 mitigation for BioC-2 compared to BioC-1 is based on better agricultural practices during palm oil production. This means, there is no additional retrofitting nor investment at the refinery but a higher CO_2 mitigation potential and lower CO_2 avoided cost.

Electricity import is increased in order to take advantage of the low CO_2 emissions intensity from the national grid (0.128 t CO_2 /MWh), which means supplying the administrative building (accounting for around 17% of total consumption in the refinery) and non-core operation at the refinery in order to avoid any disturbance of the performance operations and investment cost. In the long-term, the lower CO_2 emission intensity of the imported electricity result in even more CO_2 emission savings, without additional investments. Blue H_2 supplies the hydrogen demand of the upgrading in BioC-2. BioC-2 could also use green hydrogen, but since this DP scenario is considering the “Less Effort” options, blue H_2 remains used. Fig. 3–3 depicts the cost curve for CO_2 mitigation options for DP2. It must be noted that there is MOs replacement trough the time frames, which means the total cumulative CO_2 avoided for the considered measures are not the actual mitigation potentials. This potential changes over time (see table below Fig. 3–3).

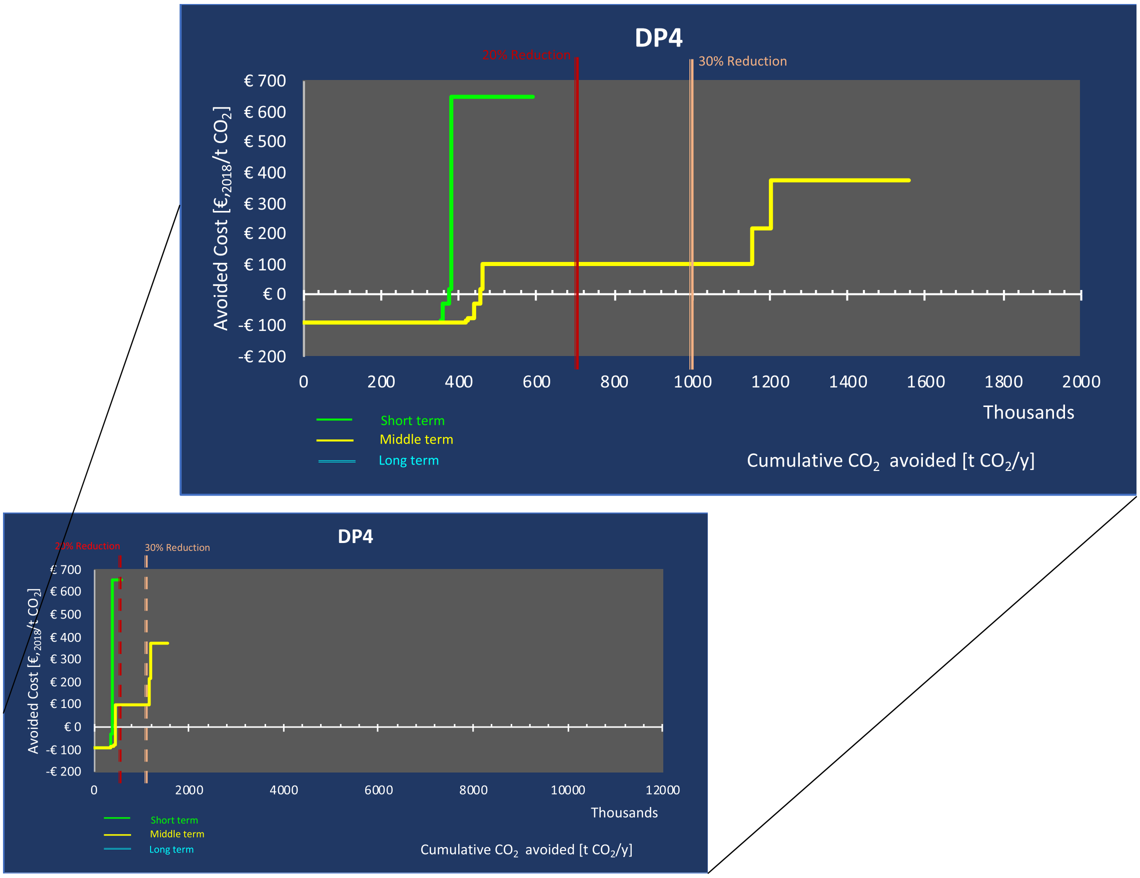
DP-3: Maximum CO_2 Avoidance

This deployment pathway (DP) aims to achieve maximum CO_2 avoidance potential. Included are EEMs, CCS options, bio-oil co-processing, green H_2 and electricity to achieve maximum CO_2 reduction. The highest CO_2 avoidance bio-oil co-processing routes reported by Yanez et al. [35] were included in this scenario. Due to the high TRL and current commercial-scale test, BioC-1 might be deployed in the short term and improve its CO_2 performance based on agricultural improvement expected for the medium term.

Even though the CO_2 captures projects could be implemented in the short term, CO_2-EOR is not available before the medium term due to the oil wells development assessment and infrastructure building. Besides, there are some technical challenges to be solved on the energy integration at the HDT unit due to the CO_2 capture unit. As a result, the CCS projects will be implemented in the medium term.

GE_GT is deployed to replace the fossil-based electricity used in the administrative building by electricity import for the national grid as described in DP2. But in the long term, it is replaced by GE-Mix_BioH with a lower CO_2 emission based on a energy matrix with a higher share of biomass-based electricity.

BioC-4 replaces BioC-2. It also includes green H_2 production for the upgrading process instead of blue H_2, as the latter results in lower CO_2 avoidance potential (although with lower CO_2 avoided cost). GH2-HDT replaces CCS-2 and CCS-4, although its volume of CO_2 avoided is slightly lower, and the cost per t CO_2 is higher than the CCS options. This is due after 20 years EOR project ending, which mean a different storage location for the CO2 must be found although hardly feasible. This will



	Short-term (ST)	Medium-term (MT)	Long-term (LT)
CO_2 reduction [Mt CO_2 /y]	0.59	0.97	---
		-→ 1.56	
			-→ 1.56

Fig. 3–5. Marginal abatement cost curve for deployment pathway 4 (DP4). Green and yellow lines depict short and medium-term mitigation options, respectively. The cumulative CO_2 avoided (shown on X-axis) includes measures from short, medium and long-term. The total CO_2 mitigation for each term period is shown in the table above. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lead to a significant increase in CO_2 avoidance cost. BioC-2 is upgraded using green hydrogen which allows a slightly higher mitigation potential and with lower avoidance cost than blue hydrogen. BioC-6 (BG-FT) can / will be deployed as a stand-alone plant inside the refinery.

CCS-3 is implemented as a retrofitted or re-design modernization project at the refinery which is expected for the MT-LT. Electrode type boilers are deployed in order to replace the low-pressure steam at the refinery (@150psi). Fig. 3–4 shows the CO_2 mitigation potential and avoidance cost using a marginal abatement cost curve (MACC) for the deployment pathway one (DP3).

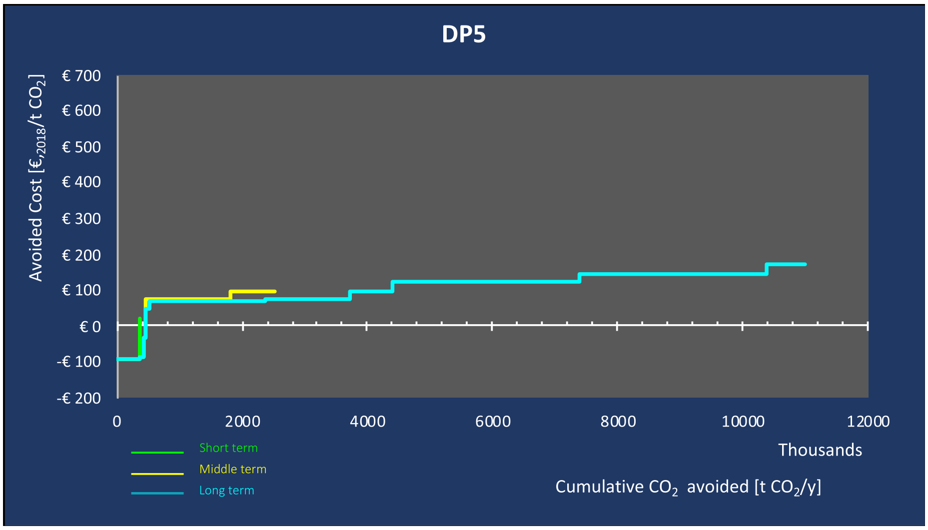
DP-4: INDC

According to the CO_2 emissions reduction goals defined by COP21, Colombia set an INDC commitment of 20% CO_2 emissions reduction by 2030 and a conditioned target of 30% for the same year. This pathway aims to comply with the CO_2 mitigation targets. MOs from the short and medium term were considered in this scenario. Fig. 35 shows the CO_2 mitigation potential and avoidance cost using a marginal abatement cost curve (MACC) for the deployment pathway one (DP4). A merit order was used to select MOs to be deployed following these criteria: 1) time frame of deployment, 2) less layout impacts, 3) low CO_2 avoidance cost, 4) low investment capital, and 5) high CO_2 avoided. The 20% and 30% target for CO_2 mitigation represents 0.7 and 1.05 Mt CO_2 per year, respectively. After ranking the MOs (see Appendix) the following options were considered. For the 20% reduction EEM-1, EEM-2, BioC-1, CCS-4, GE-GT can be deployed. This would result in emission reductions of 0.71 Mt CO_2. For the 30% reductionEEM-1, EEM-2, BioC-2 (replaces BioC-1 in MT), CCS-4, GE-GT, EEM-3 and BioC-3 can be deployed. The resulting emission reductions would reach 1.5 Mt CO_2, a reduction of 43% According to the ranking, CCS-1 would come before BioC-3. However, the latter is chosen first due to a lower investment compared to CCS-1.

DP-5: Lower CO_2 avoidance cost (<200 €/t CO_2)

This pathway chooses mitigation options with a CO_2 avoided cost below a threshold of 200 €/t CO_2. There are two reasons: First, the typical and significant CO_2 mitigation option at the refinery is CCS, and second, the cost of CO_2 capture at a large-capacity high-conversion refinery is in the range of 45–167 €/t CO_2 [10], while for a medium-capacity and conversion-level refinery the cost is 130–200 €/t CO_2 [34].

All the EEMs are included here since they have low or even negative avoidance costs. CCS-1 and CCS-3 show low avoidance cost (73 and 67 €/t CO_2, respectively) although they are in the top three highest



	Short-term (ST)	Medium-term (MT)	Long-term (LT)
CO₂ reduction [Mt CO₂ /y]	0.38	2.13	8.47
	-→ 2.51		
	-→ 10.97		

Fig. 3–6. Marginal abatement cost curve for pathway 5 (DP5). Green, yellow and blue lines depict Short, Medium and Long-term mitigation options, respectively. The cumulative CO_2 avoided (shown on X-axis) includes measures from short, medium and long-term. The total CO_2 mitigation for each term period is shown in the table above. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

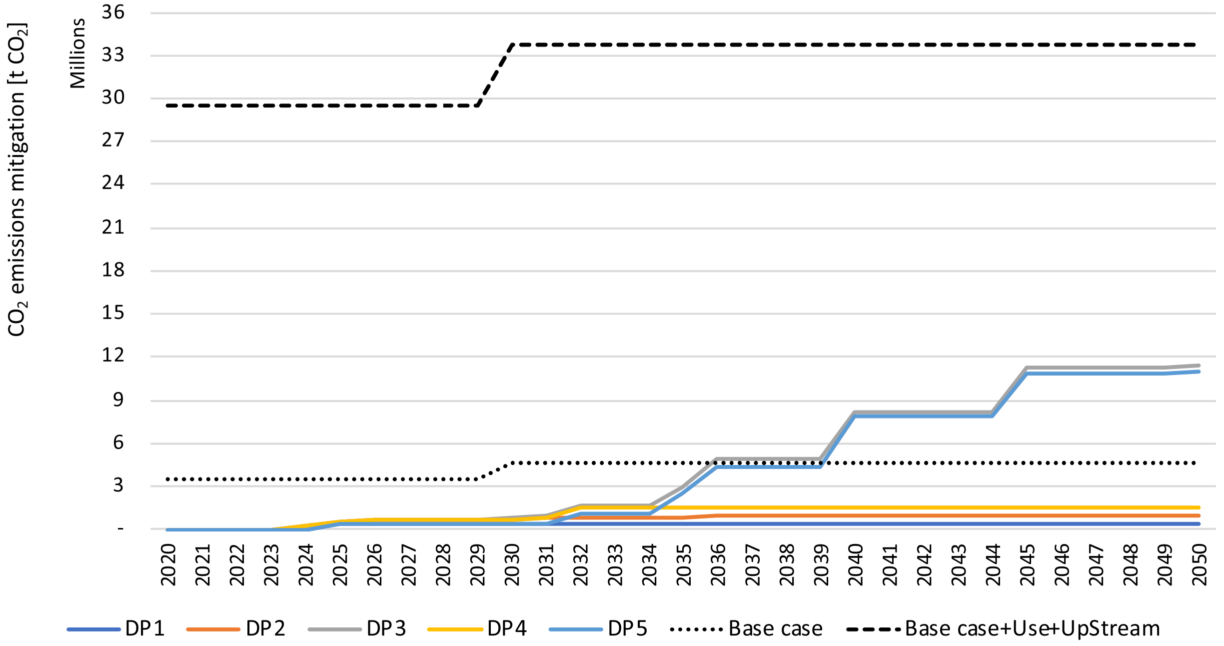
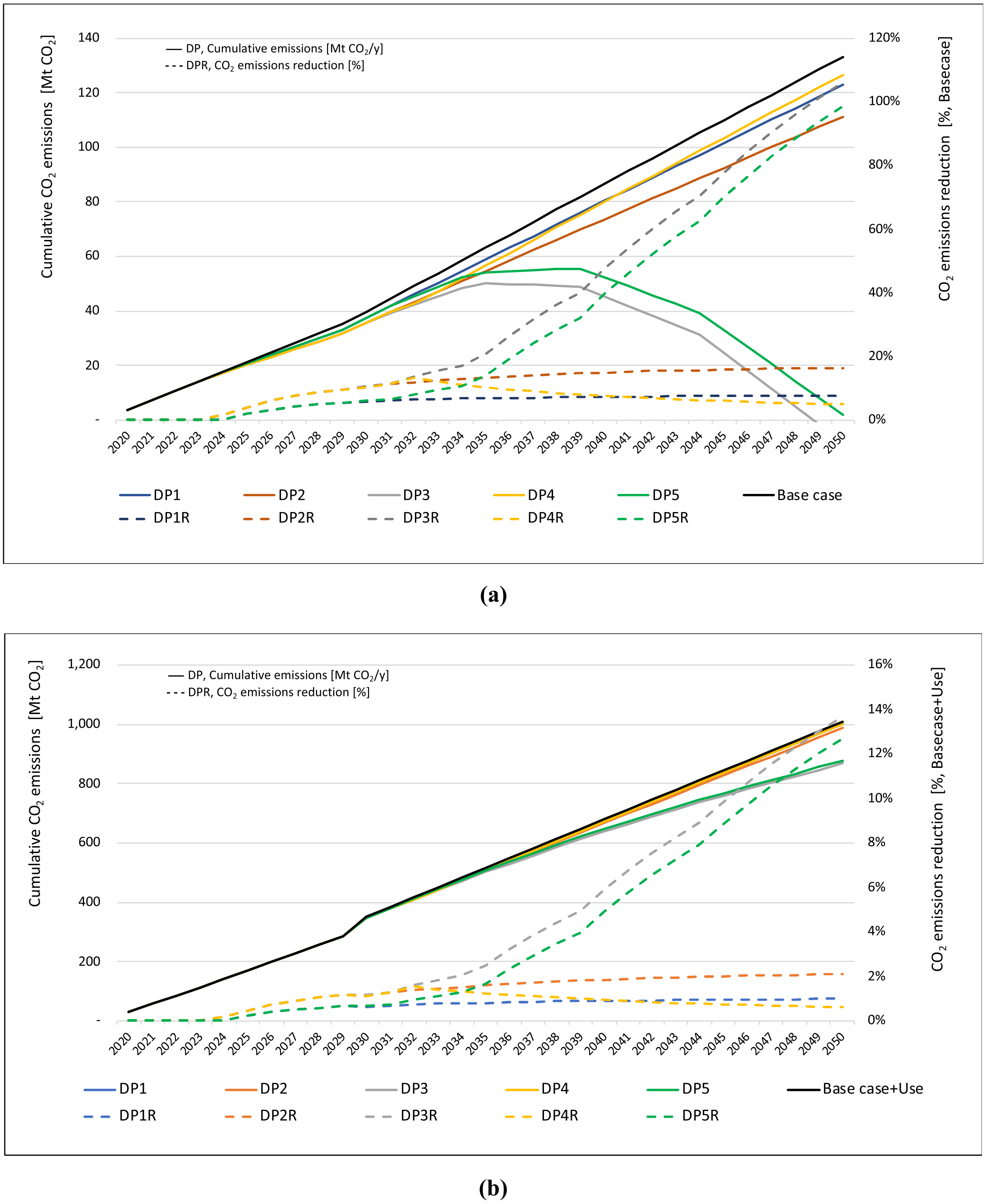


Fig. 3–7. Potential of CO_2 emissions mitigation to be achieved by the deployment pathways. Dashed lines refer to CO_2 emissions of the refinery base case (regular) and base-case emissions plus final use of liquid fuel (bold).

investments in the MO list (approx. 1.4 and 1.6 billion euro) due to the size of the CO_2 capture facilities to manage emission from delayed coke/hydrocracking and FCC/CHP facilities at the refinery. CCS-4 is also implemented as it refers to an easy-capture CO_2 source at the refinery with very low investment and CO_2 flow for the EOR project which result in a negative avoidance cost of −88 €/t CO_2.

Co-processing FPO in FCC and CPO in HDT (BioC3- and BioC-4, respectively) are also included with a CO_2 avoidance cost of 99 and 147 €/t CO_2, respectively. BioC-5 (HTLO to HDT) has a CO_2 avoidance cost lower than 200 €/t CO_2. However, this option is not included in this scenario as it competes with BioC4 for the same co-processing unit (HDT) and BioC-5 has higher avoidance costs, is a less mature technology and would require a new infrastructure facility instead of retrofitting a current process. In addition, blue hydrogen might be produced for the bio-oil upgrading in BioC-4, which also provides a lower CO_2 avoided of 68 €/t CO_2. BioC-6 is, despite having the 3rd highest investment costs (2.9 billion euro), the last co-processing option to be included as the significant CO_2 mitigation potential results in a lower CO_2 avoided cost (124 €/t CO_2).

For electricity import, a greener national grid is assumed based on a significant biomass-based electricity penetration of the energy matrix which would result in an avoidance cost of 46 €/t CO_2. Finally, electrode



Deployment Pathway (DP)	ST [Mt CO_2/y]	MT [Mt CO_2/y]	LT [Mt CO_2/y]	By 2050 [Mt CO_2/y]	CO_2 avoided cost [€/t CO_2]	Cumulative emission [Mt CO_2]		% Reduction Referred to:	
						Base case (Refinery+up+Down)	Base case (Refinery)	Base case (Refinery+up+Down)	Base case (Refinery)
1	0.38	0.02	-	**0.39**	- € 88	998	10.2	1.0 %	7.7 %
2	0.59	0.27	0.05	**0.92**	€ 213	986	21.9	2.1 %	16.5 %
3	0.59	2.40	8.41	**11.40**	€ 156	867	141.5	13.7 %	106.2 %
4	0.59	0.97	-	**1.56**	€174	1002	6.5	0.6 %	4.9 %
5	0.38	2.13	8.47	**10.98**	€ 106	877	131.4	12.7 %	98.6 %
Base case	---	---	---	**---**	---	1034	133.2	n.a.	n.a.

Fig. 3–8. Cumulative CO_2 emissions and the percentage of reduction for the mitigation deployment pathways. Figure a and b, depict the reduction percentage relative to the refinery base case emissions and the entire fuel cycle emissions (i.e. including upstream, refinery and final-use emissions), respectively.

boilers are considered for refinery electrification, which result in an avoided cost of 170 €/t CO_2. Fig. 3–6 shows the CO_2 mitigation potential and avoidance cost using a marginal abatement cost curve (MACC) for the deployment pathway one (DP5).

GH_2 for BioC1/2 is not considered for DP5 (despite its avoided cost $<$ 200€/t CO_2) because there is no consideration of BioC-1/2 for the ST or MT as their cost are much higher than 200 €/t CO_2.

Finally, GE-Mix-P is not considered here and any other pathway due to the similar CO_2 avoided and higher avoidance cost compared to GE-Mix_BioHi.

3.3. Net mitigation potential of deployment pathways

Fig. 3–7 depicts the CO_2 emissions mitigation potential for the deployment pathways considering interactions between alternatives and within specified periods. The deployment of new mitigation options, which might include replacing or decommissioning some facilities, change the mitigation potential over time.

Most of the total mitigation potential in DP2 (0.9 Mt CO_2/y) comes from short-term measures, which is in line with the "Less effort" objective of the pathway and in combination with the high level of maturity and easiness of implementation of the MOs. In contrast, the maximum avoidance scenario (DP3) estimates a significant mitigation potential of 11.4 Mt CO_2/y, which is based on long-term measures, including bio-oil co-processing routes which add significant CO_2 mitigation due to its carbon–neutral final use of the liquid fuels. The INDC scenario (DP4) shows it is possible to achieve the 20% and 30% CO_2 mitigation target (0.7 and 1 Mt CO_2/y, respectively), based on a portfolio of measures ranked following merit order of ease in deployment.

DP5 present a mitigation potential of 10.9 Mt CO_2/y, which is close to the DP3 potential, but based on measures with a CO_2 avoidance cost lower than 200 €/t CO_2. It is also primarily based on long-term measures, but shows less interactions and no replacements (except for GE_GT by GE_BioHi) between mitigation options throughout the time frame assessed.

Fig. 3–8 depicts the cumulative CO_2 emissions achieved for every DP compared to a) baseline emissions of the refinery and b) cradle to grave CO_2 emissions. The DP3 and DP5 scenarios depict the highest reduction potentials compared to the refinery emissions level with around 106% and 98%, respectively. Nevertheless, the mitigation potential, although significant, is lower (around 13%) when including the upstream and, especially, final-use emissions of the fuels. Negative emissions at the factory gate are achieved in DP3 due to bio-oil co-processing options combined with a substantial contribution of CCS.

From a 22 Mt CO_2/y mitigation option inventory, deployment pathways identified mitigation portfolios that could achieve a range of 0.4 to 11 Mt CO_2/y by 2050. In general, the mitigation potential increases over time, except for the less effort scenario. EEMs provide MOs potential from 0.01 to 0.37 Mt CO_2/y with CO_2 avoided cost in the range from −93 to 20 €/t CO_2. CCS presents a mitigation potential varying from 0.06 to 1.3 Mt CO_2/y and avoidance cost from −88 to 318 €/t CO_2. Co-processing bio-oil at the refinery provides the highest mitigation potential from 0.2 to 3 Mt CO_2/y, as a result of the carbon–neutral final use of the fuel, and avoidance cost of 98 to 651 €/t CO_2.

4. Limitation of the research

We identified five main limitations of the research. First, the potential deployment of mitigation options for an oil refinery depends on its complexity, feedstocks properties, product mix conversion level, lifetime, and refinery specific layout. Quantitative results will be affected by this and be specific per refinery. Integration of mitigation options to current refining infrastructure might have a significant impact at different levels, such as product yield, mass and energy balance, as well as the quality of products.

Second, simultaneous deployment of bio-oil co-processing alternatives might affect yields, composition, and quality of liquid fuels, even at a recommended technical co-processing limit (TcPL) as defined by literature. Co-processing options are usually assessed independently, and a combination strategy deployment might increase the risk level due to impurities or shifts in composition of the feed.

Third, the mitigation potential of electrification options relies on low-carbon electricity and availability from the national grid, its reliability, and cost to fulfil refinery processing demand to be competitive regarding fossil-based CHP electricity.

Fourth, co-processing alternatives of bio-oil represent the largest share of mitigation potential at the refinery, but also involve a high degree of uncertainty on biofuel yield and mitigation costs, especially for low yielding and early development stage technologies.

Fifth, technical and economic data for electrification options involve a large degree of uncertainty due to the lack of public data, which reflect the low TRL of these technologies.

Finally, it must be noted that the fractions of products out of the refinery were assumed to remain constant. Demand changes on fuel fractions might affect the mitigation potential of deployment pathways as some options would not be chosen due to a less significant role of a unit operation.

5. Conclusions

This paper estimates a bottom-up CO_2 mitigation potential for a medium-level conversion refinery for combined measures options, considering techno-economic interactions over short, medium, and long-term. A total of 40 measures were identified from a wide range of technologies such as energy efficiency measures (EEM), carbon capture and storage (CCS), bio-oil co-processing, blue and green hydrogen (BH_2, GH_2), green electricity import, and electrification of refining process connected to the transition of the Colombian energy systems. Five deployment pathways were assessed to achieve specific targets: DP1) base case scenario, DP2) less effort, DP3) maximum CO_2 avoidance, DP4) INDC commitment and DP5) competitive mitigation measures below 200 €/t CO_2.

There is a dynamic CO_2 mitigation potential through the time frame and for each deployment pathway (DP) based on MOs interactions. An implementation order of MOs relies on its life-span, space availability, technical constraints, technological maturity (based on TRL), economic parameters (total investment), retrofitting order, facility unit targeted for mitigation and utilities demand. This study used a fundamental and preliminary assessment of these parameters to identify potential interactions.

The findings show significant differences within the pathways, with all scenarios making improvements. However, there are two routes which represent a significant change in the mitigation potential: DP3 (maximum avoidance) and DP5 (measures below €200/t CO_2). Also, these results provide a technological strategy to comply with the 20% and 30% reduction target regarding the BAU scenario, as committed by Colombia's INDC.

Despite a relevant mitigation potential of medium-term measures, long-term options represent a significant and higher potential for CO_2 emission reduction. BioC options account for around 60% of the mitigation options portfolio for DP3 and DP5, followed by CCS with 23% GE with around 7%, and H_2 measures with 6%.

From a gross 22 Mt CO_2/y MOs inventory, based on all identified options, the mitigation portfolios used in the deployment pathways have a CO_2 mitigation potential of 0.4 to 11 Mt CO_2/y by 2050. In general, as more options become available, the mitigation potentials increases over time, except for the less effort scenario. EEMs provides MOs potential of 0.01 to 0.37 Mt CO_2 /y with CO_2 avoided cost ranging of −93 to 20 €/t CO_2. CCS has a mitigation potential varying from 0.06 to 1.3 Mt CO_2/y, and avoidance cost of −88 to 318 €/t CO_2. Co-processing bio-oil at the refinery provides the highest mitigation potential of 0.2 to 3 Mt CO_2/y, mainly as a result of the carbon–neutral emissions of fuel final use, with an avoidance cost of 98 to 651 €/t CO_2.

Despite the relevant mitigation potential (2.5–3 Mt CO_2/y) of short and medium-term (2025–2035) measures, the long-term (2035–2050) options represent a significant higher potential for CO_2 emission reduction (8.4 Mt CO_2/y). Combined options deployment can deliver very deep emissions reductions for existing refineries, and to a large extent to a relatively competitive cost. This is the case of the deployment pathway including measures below 200 €/t CO_2 (DP5), which has an almost equal mitigation potential as the maximum avoidance route (DP3), but with a lower avoidance cost.

Our findings show that the oil and gas industry could reach carbon neutral[4] operation without including final-use emissions. This methodological approach brings additional insights into and estimation of mitigation potentials compared to previous studies on aspects such as a broader portfolio of conventional and innovative technologies [5], decarbonization strategies and investment cost [7], deployment pathways including combined options [7], and an interactions assessment of mitigation options [8]. The results of this research show significant potential for conflicting activities throughout the implementation process. The main deployment constraints due to technical interactions result from competition for the same CO_2 stream or facility (e.g., heat recovery and CCS at FCC unit), exclusion of CO_2 sources (e.g., electrification options replace some boilers and furnaces which result in discarding CCS deployment for those combustion sources), and economic considerations (e.g., CO_2 sources with CCS options are locked-in for 20 years due to the economic life span of EOR projects).

A higher mitigation target leads to further investigation on increasing the share of biomass co-processing or gasification and use of green hydrogen for advanced conversion process such as e-fuels. Despite an exhaustive quantification of possibilities for normal refineries to bring CO_2 emissions down, fundamental changes in core process (in our case by 2050), should still be done. The mitigation strategies analysed in this paper do not fundamentally change the fact that these refineries are still oil processing facilities, which means that fossil carbon is embodied in the product output. In order to tackle this aspect, refineries can increase biomass gasification capacity or use more bio-oil into the process to replace crude oil. Also, adding more Green-H_2 and Green-electricity combined with CO_2 conversion processes to produce synthetic fuels or a mixture of synthetic and biofuels offers alternatives for crude oil. More research is required to investigate to what extent refurbishing existing refineries versus new low carbon fuel facilities is attractive from a technical, economic and environmental point of view.

CRediT authorship contribution statement

Édgar Yáñez: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft. **Hans Meerman:** Formal analysis, Validation, Writing – review & editing. **Andrea Ramírez:** Writing – review & editing, Validation. **Édgar Castillo:** Validation. **Andre Faaij:** Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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A. Appendix

A.1. Step plan for developing mitigation pathways in complex industries

A decarbonization strategy for the industry can be the result of different drivers such as technological, economic and policy drivers to reach a mitigation target. Based on the work presented in this study, potential deployment pathways can be developed by following the next steps (Fig. 2–1).

1. Inventory of existing facilities and value-chains. A detailed inventory of processing units, their performance data and lifetime, as carried out in this work, allows for identifying mitigation potential options not only for broad alternatives portfolio but also avoid under- or over estimation of this potential. More detailed data from the current processing infrastructure and future revamping projects can help to improve the bottom-up assessment of decarbonization potential for the sector full value-chain.
2. Inventory of mitigation options (MO): Map technological mitigation alternatives for processing units throughout the full value-chain of the industry with significant CO_2 emissions (PU) and identify the matches between CO_2 sources, process units and mitigation options. These options are to be rated for the short, medium and long-term based on their Technology Readiness Level. This inventory can include the following main categories:
   a. A first group covered in this study considered improvements to the heat generation system of the refinery and power demand by no-core related processes. The latter represents around 17% of the total consumption of electricity in the refinery, which can be supplied by low-carbon electricity import from the national grid (already low-carbon in Colombia and expected to reach net-zero by 2050) or by a dedicated renewable energy project. In addition, flaring reduction, CHP optimization process, pinch integration, and heat recovery from the steam network represent primary alternatives to be deployed in the first steps for a refinery.
   b. The second group covers co-processing options with a significant mitigation potential and lower infrastructure modification. Fossil carbon displacement by biogenic carbon due to biomass integration results on a large mitigation impact when considering the entire lifecycle of the CO_2 emissions of liquid fuels. However, the extent of this option is limited by the technical co-processing limit (TcPL) of blending bio-oils, in order to not only keep stable performance and low impurities level in the refinery, but also to assure the integrity of the infrastructure.
   c. The third group, CO_2 carbon capture, transport and storage (CCS) also shows significant mitigation potential for primary sources such as FCC, CHP, and H_2 production (blue hydrogen). This option is constrained by several factors such as the high investment capital, limited space available for new infrastructure deployment, and higher disturbance to core-process (compared to EEMs and bio co-processing options), which would affect process control and performance. Besides, CO_2 capture itself does not represent a complete mitigation option as a permanent

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[4] Carbon neutral is defined as net-zero emission from processing plants (industrial complex) at the refinery. This mean, total CO_2 emissions from a reference base scenario are offset through process efficiency measures, low-carbon energy vectors and material and CCS deployment

storage or fixation of CO_2 is still needed. This option might be excluded from the portfolio in a deeper analysis when it finds no region available for CO_2 storage or their cost is too high since most studies assume CO_2 can be stored somewhere at a fixed cost. An alternative to improve the economics of this option is using CO_2 for enhanced oil recovery (EOR), as considered in this study, which stores CO_2 underground while improving current oil production as a trade-off to the high investment of CO_2 capture. This option, however, shows an additional challenge related to an appropriate mass balance between source and sink to harmonize the CO_2 capture rate with its injection rate for a typically discontinuous CO_2 injection operation in EOR.

   d. The fourth group covers deploying green hydrogen, targeting mainly new hydrotreating facilities and high temperature level heat demand (e.g., furnaces). This option eliminates the need for finding a final use of CO_2 compared to blue hydrogen production. This is particularly important for those refineries which are not close to the oil fields where CO_2 can be used for EOR or any other final-use process.
   e. Process electrification is a fifth group to be considered for medium and long-term, which still show some barriers for implementation such as commercially available capacity, medium–high TRL, reliability, and Capex. A shorter-term option is steam production using electrode boilers but limited to a low-temperature heat. Then further longer-term applications need to be considered, such as heating of process streams and electro-refining processes. These developments require much stronger interventions in the core refining processes, first with the energy network and then with the core-process itself, which will require further in-depth study and development of a new concept refinery.
   f. Last, e-fuel production (synthetic fuels) is shown as a disruptive technology option to reduce CO_2 emissions by replacing or adding new fuel production capacity to existing refineries. This option (not included in this study) will allow refineries to produce liquid fuels from renewable electricity, green hydrogen, and biogenic CO_2.

3. Identifying impact on operation and assess required modifications to the refinery. The technical possibilities are combined with a feasibility analysis of covering the ease of implementation and impacts on the operation of the refinery. Determining these impacts of the MO's in processing units results in an impression of the complexity to implement them. The following aspects need to be considered:

- Stability of the process and good performance
- Life-span of the CO_2 source facility or plan for revamping
- Space availability at location-site for new infrastructure
- Availability of additional plant utilities
- Assure the MO implementation would not affect or have low impact on: process yield, products quality, throughput capacity, and also does not interfere with other processing units.

4. Estimate the mitigation potential, the investment cost, and CO_2 avoided cost for the deployment of each alternative.
5. Analysis of interactions between mitigation options. Techno-economic interactions and TRL of technology options as well as specific operation facilities conditions, define a potential deployment pathway. This analysis step takes into account the life-span of current and future infrastructure, and competition between CO_2 sources and process facilities for upgrading. Future revamping projects should also be considered, since some of the current facilities might be upgraded, replaced or decommissioned over time. These interactions mostly define the real mitigation potential of a deployment pathway in a decarbonization strategy of an industrial complex. Refineries are industrial complexes with a high degree of integration and, therefore, high interdependency between process units. This means any disturbance on any unit usually affects other operation units within the refinery, and could potentially disrupt the entire refinery. The highest share of CO_2 emissions in the refinery comes from energy use (around 65–75%), and most mitigation options reduce emissions from energy sources. However, due to the high energy-integration of the refinery, these options can represent risks for the stability and energy balance of the refinery. Main deployment constraints due to technical interactions result from competition for the same CO_2 stream or facility (e.g., heat recovery and CCS at FCC unit), exclusion of CO_2 sources (e.g., electrification options replace some boilers and furnaces which result on discarding CCS deployment for those combustion sources), and economic (e.g., CO_2 sources with CCS for EOR are locked-in for 20 years due to the life-economic span of EOR projects).
6. Determine the target of a pathway. A clear objective should be defined as a mitigation target for a decarbonization strategy. Will it be a technical target e.g., reducing CO_2 at any cost, any time, with any impact on current operations? An economic target e.g., CO_2 mitigation options with avoidance cost below 200 €/t CO_2? Or a policy target e.g., a 20% reduction of the business-as-usual emissions by 2030. These examples illustrate decarbonization targets from different perspectives, and so the mitigation potential and investment cost required will also be different. The mitigation target will dictate a specific strategy, which, in turn, will result in a particular deployment pathway, thereby impacting the mitigation potential at short, medium and long-term.
7. To design decarbonization pathways, the results on the feasible matching inventory of mitigation options, their interactions constraints and defined decarbonization target are used as follows: select MOs for a time frame by combining options, based on TRL, pathway's target (e.g. lower investment, lower CO_2 avoidance or higher mitigation first), and matrix of interactions. In addition, define a merit order to deploy MOs within the period based on ease of implementation, less layout impact, and lower commissioning time.
8. Calculate the result of the pathway for mitigation potential, total investment and CO_2 avoidance cost over time. The time dimension is particularly important for meeting targets, because despite potentially high mitigation potentials on longer term, the cumulative avoided GHG emissions in the selected timeframe may be constrained (and vice versa).
9. Last, assessment of externalities and their implications on the deployment of potential pathways should be included to bring comprehensive insights for decision making and an information base for investment decisions, including identification of key uncertainties, risks, and R&D priorities. Factors outside the company or industry might include government regulations (e.g. CO_2 emission targets and prices), availability, carbon-intensity and supply of energy carriers such as biomass, green electricity and H_2, presence of CO_2 network and a market for use and storage, licensing/permits, capital access cost, CO_2 price market, exchange rate, rate of the technology learning curves, among others.

A.2. Inventory of mitigation options (EEM, CCS, and co-processing)

A.2.1. Energy efficiency measures

A bottom-up approach study [21] of the oil industry process-chain (production, transport, and refining) was used to identify energy efficiency measures (EEM) based on operational data at the process unit level. This study estimated a potential energy saving of 16 PJ, which represents a GHG emissions reduction of 0.8 Mt CO_2 per year, which accounts for 25% and 19% reduction, respectively. In total, 20 measures were identified in 48 cases throughout the full process-chain of the case study for the oil industry in Colombia.

Around 60% of the total cases are short term measures. This means these measures are of low technological complexity, high implementation potential, and medium to low relative cost. Remarkably, this group represents 12% of the total portfolio investment but around 60% of the total energy and GHG savings.

The refinery accounts for about 66% of the total primary energy consumption and 73% of total GHG emissions for the full process-chain. For the case study refinery, were identified potential savings of 8 PJ (18%) and 0.4 Mt CO_2 per year (13%) for energy and GHG emissions, respectively.

The largest energy measure in the refinery represents 5.3 PJ in savings based on the improvement of the steam network in the refinery, followed by LPG and NGL recovery from the refinery gas network with 1.9 PJ. The former is an obvious focal point for improvements as the production of power and steam account for 78% of total primary energy consumption in the refinery. FCC and distillation units are the largest consumers with a steam share of 95% and 49% and electricity with 4% and 5%, respectively.

The EEMs were aggregated in four categories by aim and level of complexity of the technology involved as follow: process optimization, process upgrading, gas recovery, and power generation. Process optimization and gas recovery accounts for 80% and 74% of total energy and GHG saving, respectively. Power generation options accounts for 54% of the total portfolio investment for the oil process-chain but with a relatively low reduction potential in the total energy consumption (8%) and GHG savings (12%). In total, five EEMs were identified for the refinery which are describe in Table 8–1.

A.2.2. CO_2 capture and storage

The international energy agency (IEA) [46] has highlighted carbon capture and storage as a primary technology option for CO_2 mitigation in energy-intensive industries. However, its high investment cost led to non-competitive CO_2 avoided cost. CO_2 enhanced oil recovery (CO_2-EOR) allows for the use and storage of captured CO_2 while producing crude oil, which contributes to reducing the CO_2 avoidance cost. Yanez et al. [34] carried out a study to identify the techno-economic potential of integrated CCS-EOR projects for reducing greenhouse gas (GHG) emissions in the Colombian oil industry. This study estimated the potential CO_2 capture at the largest oil refinery in Colombia, which is considered in this study, and the CO_2-EOR potential from the nearest oil fields.

To this purpose, a source-sink matching process was carried out, including CO_2 capture potentials in sources from the petroleum, cement, power generation, and bioethanol industries, as well as from the CO_2 storage in suitable oil fields for EOR. The potentials for CO_2 storage and oil recovery were estimated at 142 Mt CO_2 and 465 MMbbl, respectively, through five CCS-EOR projects in four clusters identified around the country. From a national CO_2 capture potential of 11.8 Mt CO_2 per year (oil industry account for 33%), only 5.9 Mt CO_2 can be matched to be used in EOR projects. The oil industry represents 59% of the total CCS-EOR potential, with the largest oil refinery accounting for 80% of this sector.

CO_2 is captured in two out of four cracking units, which represents 66% of total cracking capacity, and shows the highest utilization factor and better performance control with suitable retrofitting availability. Besides, two small hydrogen production units are considering which release CO_2 at atmospheric pressure and high concentration (>95%) by using an old conventional SMR process. In addition, an energy-integrated hydrotreating unit with a SMR-PSA is also considered for CO_2 capture with a higher volume of CO_2 emissions. Finally, around 45% of the total CO_2 emitted by the refinery's power generation plants was considered for CO_2 capture. This CO_2 comes from the largest two central cogeneration units. Most of the power units are scattered within the refinery and show irregular operation, and are therefore considered less suitable for capture. Post combustion capture is deployed to the CO_2 sources at the refinery, which is considered an add-on technology with much lower retrofitting requirement. The final stage in the CO_2 capture process includes a train of compression (up to 13 MPa), separation, cooling, dehydration, and pumping to the injection and storage site. An economic lifetime of 25 years was used for the integrated CCS-EOR project.

A.2.3. Bio-oil co-processing

Since previous mitigation option are focus on reducing CO_2 emissions during oil production and refining, it must be noted that final fuel use accounts for ~ 80% of the total life-cycle emissions [47]. For lower net fuel-cycle emissions of liquid fuels, fuel production from sustainable biomass is a promising option. According to Hailey et al. [48] these fuels can achieved low net fuel-cycle emissions or even negative emissions if the CO_2 co-produced is capture and store underground.

Drop-in fuel integration to petroleum refineries through co-processing has been highlighted as the key to future deployment of low-carbon biofuels [49], which take advantages of the existing infrastructure. Yanez et al. [35] investigated the potential to reduce CO_2 emissions of thirteen bio-oil co-processing pathways, including vegetable oil (VO), fast pyrolysis oil (FPO), hydro-deoxygenated oil (HDO), catalytic pyrolysis oil (CPO), hydrothermal liquefaction oil (HTLO), and Fischer-Tropsch fuels. Each pathway identified matches the properties of bio-oil with the key restriction parameters from a refinery process unit in order to ensure co-processing suitability. This study showed that 15% of fossil fuel produced at the refinery could be replaced by bio-oil co-processing. This threshold was defined by a technical co-processing limit (TcPL), which lead to a minimum retrofitting of the process infrastructure and minimizes disturbance in the operational performance of the refinery [35].

The overall mass yield for biofuel production ranged from 9% (vegetable oils) to 33% (FPO co-processed in FCC) with thermochemical bio-oils in the range of 12–33% [35]. According to this study, Biofuels itself might reduce CO_2 emissions by 33–84% compared to equivalent fossil fuels, which would allow a 6–81% reduction of the oil refinery CO_2 emissions. Co-processing CPO in the HDT and FPO in the FCC showed the highest CO_2 avoidance and reduction in CO_2 emissions, respectively. For the highest CO_2 avoidance potential, the cost to avoid CO_2 ranged between 124 and 337 €/t CO_2. A summary of the bio-oil co-processing pathways consider in this study are provided in Table 8–1.

A.3. Inventory of mitigation options

Table 8–1

Inventory and description of mitigation options (MO) considered in this study.

#	Mitigation option	Target Process	Aim	Description	Deployment horizon
1	Energy efficiency measures (EEM)	Fuel gas network	Liquid petroleum gas (LPG) and Natural gas liquid (NGL) recovery from refinery gas and its use optimization.	This measure aims to recover liquid petroleum gas (LPG) and natural gas liquid (NGL) from the fuel gas network at the refinery, which is fed together with the intermediate products from refining process units. Furthermore, improved use of fuel gas at the refinery is considered, optimizing unnecessarily discharged quantities from processes to the leading fuel network, and optimizing process control so that appropriate quantities are used throughout the refinery [21]. CO_2 emissions reduction results from savings in natural gas and hydrogen import.	Short term:These measures represent best operational and maintenance practices or high maturity technologies (e.g., gas plant facility recovery of LPG and NGL), which are assumed as low-hanging fruits in a refinery.
2		Combined Heat and Power -CHP	Tuning (excess air value, burners maintenance).	A first step to improve boilers performance is to carry out combustion tests in order to identify tuning opportunities. Tuning practices include the implementation of an improved control system, which adjusts the air-to-fuel ratio based on fuel quality. It also includes regular manual checks of the thermal efficiencies using a portable combustion analyser. Due to its simplicity and ease of implementation, these are cost-effective alternatives to improve boiler performance [21]. CO_2 emission reductions results from savings in natural gas consumption.	
3		Flaring	Switching steam to air assist flares.	Aiming for a smokeless flare operation, the use of air instead of steam provides more oxygen and better-flaring conditions in the flare stack due to increases momentum and turbulence in the combustion zone. Eliminating the use of steam involves replacing the flare tip and possibly modifying the assist gas piping [21]. CO_2 emission reductions results from savings steam which in turn reduce natural gas consumption.	
4		Combined Heat and Power (CHP)	Improved management of steam losses.	Improving steam distribution systems might include blowdown reductions, steam distribution controls, improved insulation and maintenance, improvement and maintenance of steam traps, leak repairs, recovery of flash steam, and improvements in the management of steam losses. For this case study, it refers to the implementation of an enhanced leak management program to regularly detect and repair leaks from the steam network in the refinery [21]. CO_2 emission reductions results from savings steam, which in turn reduce natural gas consumption.	
5		Flaring	Improved management of flaring by optimizing flare purge gas and reduce purge rates.	Reducing gas flaring operations and thus CO_2 emissions might include alternatives such as the collection and compression of gas into pipelines for processing and sale, generation of electricity or cogeneration, and compression and reinjection of the gas into an underground reservoir. Optimizing this operation is based on operational practices such as a better flare purge gas control and reduced purge rates, which are considered to low investment and quick implementation measures. These kinds of options usually offer a potential gas recovery of 95% [21]. CO_2 emission reductions results from optimizing purge flow to the flares, which in turn reduces flue gas production.	
6		Fluid Catalytic Cracking (FCC)	Waste heat recovery to produce low-pressure steam.	Energy recovery from FCC catalyst regenerator exhaust can be done through a waste heat boiler and/or a power recovery turbine or turbo expander. This process would be characterized by large volumes of hot gases (around 700 °C)	Medium term:Despite this being a very mature technology, it is considered for a medium-term due to its relatively high impact on core process layout.

(*continued on next page*)

Table 8–1 (*continued*)

#	Mitigation option	Target Process	Aim	Description	Deployment horizon
				operating continuously over long periods at relatively low pressures [50]. A power recovery system can reduce the Energy Intensity Index of a refinery by 7%–10% [51,21]. CO_2 emission reductions result from saving natural gas consumption in boilers for steam production replaced by the heat recovery units.	
7	Carbon, capture and storage (CCS)	FCC + CHP	(FCC + CHP)	CO_2 capture is deployed in FCC and CHP units using a combined stack and considering MEA solvent-based post-combustion capture technology, which provides a 90% CO_2 capture efficiency for low CO_2 concentrations (4% to 16%) in the stream. FCC and CHP processes represent around 80% of the refinery's CO_2 emissions. However, this CCS option considers for this refinery case study only account for 49% of the CCS potential, as other CO_2 potential sources pose some techno-economic constraints [34]. CO_2 capture was deployed for the two newest and largest FCC and CHP facilities at the refinery. It must be noted that mitigation options including FCC units, are only considering two of the four cracking units at the refinery. These two are the newest units and account for around 65% of the cracking capacity.	Medium term:Post-combustion technology using MEA is considered at commercial level (technology readiness level –TRL[1]- of 9) [1]. This technology is the obvious first-generation technology for existing refineries [52]. Nevertheless, a few full chain CCS has been deployed on commercial scale [52], so thus it is assumed for a medium term. Besides, this measure requires CO_2-EOR infrastructure deployment for complete CO_2 mitigation.
8		Hydrotreating-HDT	(HDT)	CO_2 is captured in the largest hydrotreatment unit from flue gas in the SMR-PSA process at atmospheric conditions [34]. This measure considers post-combustion capture technology using MEA with a 90% CO_2 capture efficiency.	
9		HDT	(HDT + Hydrocracking (HKC) + Delayed coking (DCK))	From a future revamping project at the refinery, CO_2 is captured from a combined stack, which integrates three process unit such as hydrotreatment, hydrocracking and delayed coking. It is assumed a post-combustion CO_2 capture technology using MEA with a 90% CO_2 capture efficiency [34].	Long term:This measure is considered as a long term as it relies on a revamping project plan.
10		HDT	H_2 plant	CO_2 is captured in a combined stack from two small and old hydrogen generation units. There is no need of CO_2 capture facility, as CO_2 is produced at a high concentration level (>95%) and released to the atmosphere. It is assumed that no gas treatment is required but compression [34].	Medium term:Despite this being a low-hanging fruit option, this study assumes is a medium-term option due to requirement for CO_2-EOR infrastructure deployment.
11	Bio-oil Co-processing (BioC)	HDT	Vegetable palm oil (VO) to HDT	This measure refers to vegetable palm oil (VO) being co-processed in Hydrotreating units (HDT) as described by [35] to produce a low carbon diesel. Despite possible increased H_2 consumption and some heteroatoms reaching the final products, there is no significant restriction to VO co-processing in the HDT. VO is highly miscible with the fossil-based streams, which is an essential requirement for hydrotreatment. This option is the only route that has been commercialized [53].Pilot tests have shown that the blending ratio can range up to 20% of vegetable oil. However, blending VO at levels higher than 15% reduces the efficiency of desulphurization [54]. Industrial-scale tests carried out in a refinery used a blend of up to 5 v% of bleached palm oil without compromising the overall refinery yield and with neglectable impact on operations. For this case, a technological co-processing limit (TcPL)** of 5% is assumed. CO_2 emissions reduction results from introducing a biogenic carbon into the refinery processes, which is assumed as carbon	This measure is categorized as a short term for cases # 11 and #13, as the vegetable oil production is a very mature technology and co-processing by hydrotreating units has been proven successful at commercial scale [55]. Regarding cases #12 and #14, this measure is based on future lower carbon improvement in the palm oil production so that is considered a medium-term measure.
12		HDT	VO to HDT		
13		HDT	VO to HDT		
14		HDT	VO to HDT***		

(continued on next page)

Table 8–1 (*continued*)

#	Mitigation option	Target Process	Aim	Description	Deployment horizon
				neutral during final-use of fuels.For this co-processing measure there are four options considered in this study as presented in this table:#11: This measure option considers co-processing process reference 1* as described by Yanez et al. [35] and a current palm oil production scenario in Colombia, according to Ramirez et al. [26].#12: This measure option considers co-processing process reference 1* as described by Yanez et al. [35]and a future palm oil production scenario in Colombia, according to Ramirez et al. [26].#13: This measure option considers co-processing process reference 2* as described by Yanez et al. [35] and a current palm oil production scenario in Colombia, according to Ramirez et al. [26].#14: This measure option considers co-processing process reference 2* as described by Yanez et al. [35] and a future palm oil production scenario in Colombia, according to Ramirez et al. [26].	
15		FCC	VO to FCC***	This option considers vegetable-palm oil- (VO) co-processing in Fluid Catalytic Cracking (FCC) as described by [35], which use process reference 1* under current scenario for palm oil in Colombia [26]. TcPL** is 30%. Co-processing VO have shown similar yields of gasoline and coke as reported by [53,56]. VO is entirely miscible with the fossil fuel and can easily undergo cracking. Meanwhile, the FCC conditions are severe enough to ensure the catalytic decomposition of triglycerides in carbonic acids [54]. This co-processing option seems to show potential synergies between lipids an fossil feed which could increase conversion, octane number and oxidative stability of the products as described by [54].	Medium term:There is no significant restriction to VO co-processing in the FCC, VO is entirely miscible with fossil-based streams, VO can easily undergo cracking, and with severe enough conditions in the FCC can assure catalytic decomposition of triglycerides as described by [35]. However, there are few commercial developments of this measure as VO has been primarily co-processed by hydrotreating units.
16		FCC	Catalytic Pyrolysis (CPO) to FCC***	Catalytic Pyrolysis oil (CPO) co-processing in Fluid Catalytic Cracking (FCC) shows several positive aspect as described by Yanez et al. [35]. CPO is partially deoxygenated when compared to other pyrolysis oils so that there is no need of pre-treatment before co-processing. However, oxygen removal results in higher viscosity, which makes pumping more difficult [53]. Blending ratios of 10–20% yield results similar to those obtained with HDO and even pure VGO. A pilot-scale riser [57] exhibited similar yields for 10% CPO/VGO and 100% VGO. However, a threshold blending ratio of 15% was suggested to avert blockage by coking. This case uses a TcPL = 10%. **	Long term:Catalytic processes in pyrolysis technology are still in pilot scale (TRL = 5) [58] with also some co-processing test at pilot-scale riser with promising results reported by [57].
17		FCC	Hydro-deoxygenated oil (HDO) to FCC***	An upgrading alternative for FPO is hydrodeoxygenation which is often suggested in the literature to be co-processed in FCC with VGO. The refinery feed acts as diluent and hydrogen transfer source [59]. This measure refers to hydro-deoxygenated oil (HDO) co-processing in Fluid Catalytic Cracking (FCC) as described by [35]. Studies using mild HDO in FCC co-processing have shown similar gasoline yields and a slight increase in coke formation for bio-oils with oxygen content in the range of 17%–28% and a blending ratio of 20% [60,59,61]. This option considers a TcPL of 20. **	Medium term:This measure is categorized as medium term as the co-processing of fast pyrolysis oil have been proven successfully at pilot-scale (TRL = 6–7) [55] by Pinho et al [62].
18		FCC	Fast pyrolysis oil (FPO) to FCC***	This measure considers fast pyrolysis oil (FPO) co-processing in Fluid Catalytic Cracking (FCC) as described by [35]. Although some studies	

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Table 8–1 (*continued*)

#	Mitigation option	Target Process	Aim	Description	Deployment horizon
				have not recommended the co-processing of FPO in the refinery without prior deoxygenation (at least partial), this study follows the recent results by Pinho et al. [63–64], which proved it is technically feasible up to a blending ratio of 10 v%. Pinho et al. [63] carried out the co-processing of raw FPO with VGO in a fluid catalytic cracking (FCC) demonstration-scale unit using a commercial FCC equilibrium catalyst. Their results show a slight increase in the coke formation and non-significance changes in the naphtha (gasoline range) and LCO (diesel range) yield fractions at a 10% blending ratio. The TcPL use in this option is 10%.[**]	
19		HDT	CPO to HDT[***]	This option considers CPO co-processing in Fluid Catalytic Cracking (FCC) as described by [35]. CPO is an interesting alternative for co-processing due to its low oxygen content and good miscibility with fossil fuel. However, hydrotreating CPO requires a large amount of hydrogen to process the high content of aromatics, thus increasing the costs of refining [65]. TcPL = 30%. [**]	Long term:Catalytic processes in pyrolysis technology are still in pilot scale (TRL = 5) [58] with promising benefits from co-processing at HDT units due to its low oxygen content and high miscibility [65–66], but with a high H_2 consumption due to the high content of aromatics [65].
20		FCC	Esterified fast pyrolysis oil (FPOe) FPOe to FCC[***]	Esterified fast pyrolysis oil (FPOe) co-processing in fluid catalytic cracking (FCC) is considered as mitigation option as described by [35]. The esterification of bio-oils converts the organic acid compounds into the corresponding esters. Butanol reacts with carboxylic acids to produce esters such as butyl acetate, as a primary way to eliminate oxygenated compounds. The esterification method reduces acid number, water content and viscosity, while corrosion and stability is promoted [67]. Ecopetrol owns a patent of the esterification process for bio-oil based on oil palm residues. Process patented by Ecopetrol S.A. NC2016/0000689, NC2018/0000069. For this measure a TcPL of 20% is used.	Long term:The esterification of fast pyrolysis oil and its co-processing by hydrotreating is at lab-scale plant (TRL = 5) based on current development of Ecopetrol [68].
21		HDT	FPOe to HDT[***]	Esterified fast pyrolysis oil (FPOe) co-processing in Hydrotreating unit (HDT) is also a mitigation alternative as described by [35]. It follows the same esterification process but it is co-processed in the HDT unit that in turn primarily yield a diesel range fraction. TcPL = 20%. [**]	
22		HDT	Hydrothermal liquefaction oil (HTLO) to HDT[***]	Hydrothermal liquefaction is increasingly appointed as an effective technology to produce biofuels from wet biomass [69]. HTLO can be directly co-fed into the ADU in the refinery after upgrading, as described by [70]. However, it is not at a demonstration-scale level yet. HTLO is a promising bio-oil for co-processing in the refinery due to its thermal stability and fractional separation characteristics. Nevertheless, mild hydro processing is required to remove oxygenated components [71]. A concern about HTLO-based fuels is the aromatic content which has been reported as much as 60% more than FPO, which have to be reduced aggressively during hydrotreatment [72]. Hydrothermal-liquefaction oil (HTLO) co-processing in Hydrotreating unit (HDT) is considered for CO_2 mitigation at processing conditions described by [35]. TcPL = 15%. [**]	Long term:The HTLO production is categorized with a TRL of 5–6 [69].
23		Biomass gasification (BG)_ Fischer-Tropsch (FT)	BG + FT [w/o CCS] [***]	The production of biofuels through biomass gasification (BG) and Fischer-Tropsch (FT) process [without CCS] and final upgrading is	Long term:This technology is categorized as a of TRL = 5–6 [55], which means is at the early stage of a pilot-scale.

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Table 8–1 (*continued*)

#	Mitigation option	Target Process	Aim	Description	Deployment horizon
				considered as a CO_2 mitigation option for the refinery, as described by Yáñez et al. [35]. It is focused on a lignocellulosic biomass feedstock only scheme in a self-sufficient thermal design process. This process was scaled to produce 15% of mix fuel production at the case study refinery. The gasification and FT facility plant are considered as a stand-alone facility beside the refinery, which can produce the hydrogen required for the final upgrading to gasoline, diesel, and jet fuels through the hydrocracking process as described by Hailey et al. [48].	
24	Blue Hydrogen (BH_2)	HDT	Blue H_2	This mitigation option refers to hydrogen production through the conventional process of steam methane reforming (SMR) but including CO_2 capture and storage (CCS). In this way a low carbon intensity hydrogen is produced. For the case study refinery, there are two primary units to CO_2 capture during H_2 production, which are already considered for the CCS mitigation options. Nevertheless, additional H_2 demand by the refinery could be supplied by a new SMR facility with CO_2 capture.	Medium term:This measure refers to the CO_2 capture and storage during hydrogen production (CCS), which are considered in this study as medium-term measures.
25	Green Hydrogen (GH_2)	HDT	Green H_2	Green hydrogen refers to the hydrogen production using water electrolysis through a proton exchange membrane (PEM) electrolyser and renewable electricity. This mitigation option provides a lower carbon hydrogen compared to blue and grey hydrogen. This measure is included as a mitigation option with a stand-alone facility next to or inside the refinery.	Long term:The key electrochemical hydrogen production technologies are: alkaline, PEM and solid oxide (SO) electrolysers. SO electrolyser are in the R&D stage. Alkaline electrolysers are the most common and mature technology to produce water electrolysis-based hydrogen. However, due to its limited current densities (0.2–0.4 A/cm^2) and low systems response (seconds) compare to the less mature-PEM technology (0.6–2.0 A/cm [2] and milliseconds, respectively), make the latter more promising and flexible (especially in power generation) for higher production capacity required at the refineries [39–40]. Despite PEM being at commercial scale (TRL = 8–9), a large-scale deployment and integration into a refinery is still under development.
26	Green Electricity (GE)	Power generation	Green Electricity	This option aims to replace a share of the fossil-based electricity produced and consumed in the refinery by a lower carbon intensity electricity from the national grid. Due to the high share of hydropower generation (86% in 2017, accounting for as much as 53.7 TWh [73]in the national mix in Colombia, the carbon intensity of national grid electricity is as low as 0.13 t CO_2/MWh [31]. Nevertheless, Colombia is committed to a greener electricity scenario by 2050 [36], following the INDC commitment by 2030 [74]. A forecast of the future mix of electricity sources of the national grid and that of the carbon intensity is based on the Colombian government estimations and simulated scenarios described by Younis et al. [19] for the policy and high share of biomass scenarios.	Long term:There is a high renewable energy potential for electricity production in Colombia by 2050, which could reduce the carbon intensity for the electricity even more than today mix. Solar (PV), wind and biomass energy sources could play a significant role (56% share of electricity production in a high biomass supply scenario) in a cost-effective potential for a low-carbon scenario in Colombia [19]. This future scenario is considered in our study as a long-term measure to reduce CO_2 emission at the refinery.

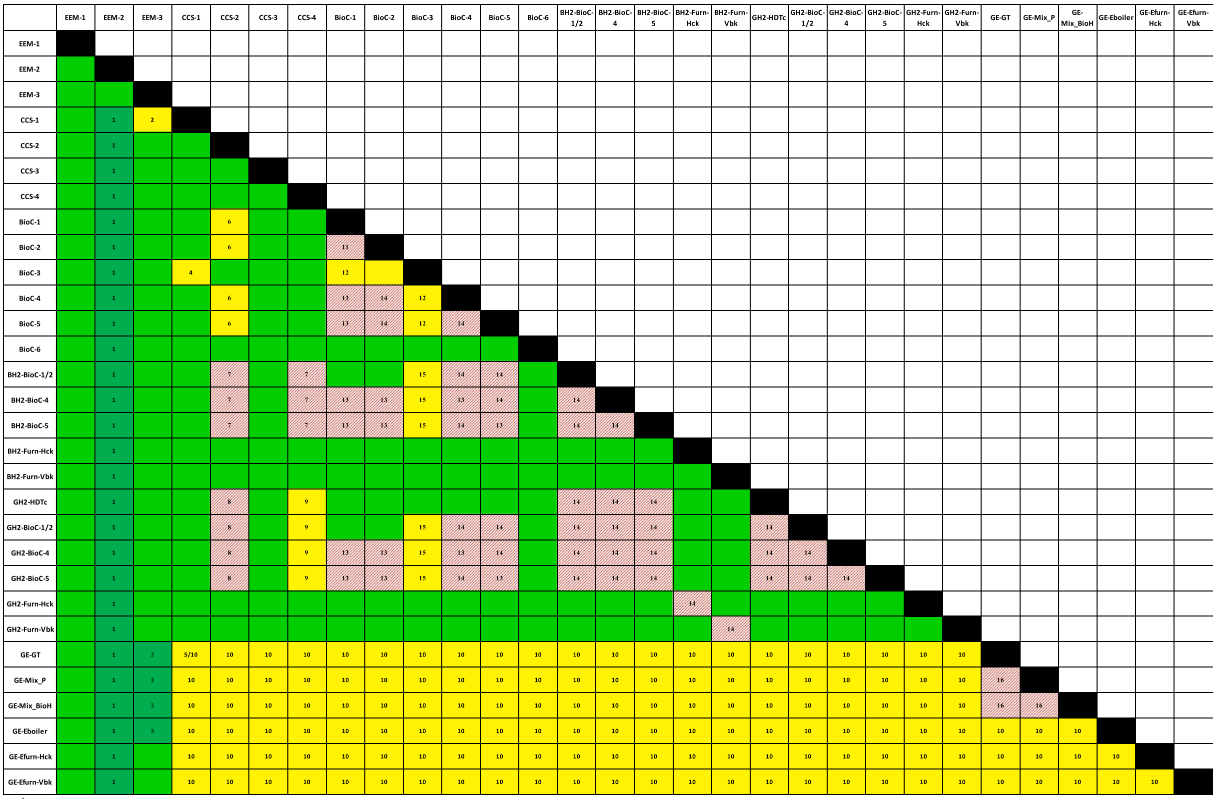
[*] VO co-processing in HDT that would require further (P1) or slight (P2) process modifications, respectively. Palm oil production was considered under two scenarios, as described by Ramirez et al. [26]: (1) current scenario and (2) a future scenario with a production chain optimized to reduce GHG emissions. Future scenario is assumed to be deployed in 2030.

[**] TcPL is defined as the maximum threshold ratio of bio-oil/fossil fed into a specific refinery process unit and can be determined based on lab or pilot tests (sourced from literature). This limit allows for minimum retrofitting of the process infrastructure and minimizes disturbance in the operational performance of the refinery [35].

[***] CO_2 emissions reduction results from introducing a biogenic carbon into the refinery processes, which is assumed as carbon neutral during final-use of fuels

[1] Technology readiness level (TRL) is a nine-point scaling system for tracking the status of maturity level of a technology, moving in a series of scale-up steps from a proof of concept to lab, pilot-scale, demonstration, and commercial scale [1].

A.4. Matrix of interaction for mitigation options deployment



	EEM-1	EEM-2	EEM-3	CCS-1	CCS-2	CCS-3	CCS-4	BioC-1	BioC-2	BioC-3	BioC-4	BioC-5	BioC-6	BH2-BioC-1/2	BH2-BioC-4	BH2-BioC-5	BH2-Furn-Hck	BH2-Furn-Vbk	GH2-HDTc	GH2-BioC-1/2	GH2-BioC-4	GH2-BioC-5	GH2-Furn-Hck	GH2-Furn-Vbk	GE-GT	GE-Mix_P	GE-Mix_BioH	GE-Eboiler	GE-Efurn-Hck	GE-Efurn-Vbk
EEM-1	■																													
EEM-2	🟩	■																												
EEM-3	🟩	🟩	■																											
CCS-1	🟩	1	2	■																										
CCS-2	🟩	1	🟩	🟩	■																									
CCS-3	🟩	1	🟩	🟩	🟩	■																								
CCS-4	🟩	1	🟩	🟩	🟩	🟩	■																							
BioC-1	🟩	1	🟩	🟩	6	🟩	🟩	■																						
BioC-2	🟩	1	🟩	🟩	6	🟩	🟩	11	■																					
BioC-3	🟩	1	🟩	4	🟩	🟩	🟩	12	🟨	■																				
BioC-4	🟩	1	🟩	🟩	6	🟩	🟩	13	14	12	■																			
BioC-5	🟩	1	🟩	🟩	6	🟩	🟩	13	14	12	14	■																		
BioC-6	🟩	1	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	■																	
BH2-BioC-1/2	🟩	1	🟩	🟩	7	🟩	7	🟩	🟩	15	14	14	🟩	■																
BH2-BioC-4	🟩	1	🟩	🟩	7	🟩	7	13	13	15	13	14	🟩	14	■															
BH2-BioC-5	🟩	1	🟩	🟩	7	🟩	7	13	13	15	14	13	🟩	14	14	■														
BH2-Furn-Hck	🟩	1	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	■													
BH2-Furn-Vbk	🟩	1	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	■												
GH2-HDTc	🟩	1	🟩	🟩	8	🟩	9	🟩	🟩	🟩	🟩	🟩	🟩	14	14	14	🟩	🟩	■											
GH2-BioC-1/2	🟩	1	🟩	🟩	8	🟩	9	🟩	🟩	15	14	14	🟩	14	14	14	🟩	🟩	14	■										
GH2-BioC-4	🟩	1	🟩	🟩	8	🟩	9	13	13	15	13	14	🟩	14	14	14	🟩	🟩	14	14	■									
GH2-BioC-5	🟩	1	🟩	🟩	8	🟩	9	13	13	15	14	13	🟩	14	14	14	🟩	🟩	14	14	14	■								
GH2-Furn-Hck	🟩	1	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	14	🟩	🟩	🟩	🟩	🟩	■							
GH2-Furn-Vbk	🟩	1	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	14	🟩	🟩	🟩	🟩	🟩	■						
GE-GT	🟩	1	3	5/10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	■					
GE-Mix_P	🟩	1	3	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	16	■				
GE-Mix_BioH	🟩	1	3	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	16	16	■			
GE-Eboiler	🟩	1	3	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	■		
GE-Efurn-Hck	🟩	1	🟩	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	■	
GE-Efurn-Vbk	🟩	1	🟩	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	■

1 Positive benefit might deliver even more energy to be used for the new measure (/= to EEM2)
2 Applied to the same unit (FCC). EEM-3 (waste heat recovery from regenerator; CCS-1: CO_2 capture from flue gas at regenerator. It shows higher pressure drops.
3 Positive benefit might make more energy available to produce electricity, so electricity import might be reduced
4 These measures are applied for the same unit (FCC), interaction on f the flue gas composition and flow rate as a consequence of bioC co-processing, might increase CO_2 production and affect energy balance. Besides, other impurities might be added to the flue gas (S, N) should be analysed for avoiding any impact on amines stability and efficiency during absorption. In addition, pressure change must be also checked.
5 CO_2 capture at CHP (EEM-3) might include the GT which is also considered to be replace by green electricity (GE-GT). In this case study EEM-3 address the larger CO_2 source at the CHP facilities.
6 It applies to the same HDT unit. CO_2 capture at the PSA unit, a potential energy unbalance at the furnace might increase temperature due to lower volume of recycle gas. This condition might affect hydrogen production.
7 These measure are competing for the same source of CO_2.
8 Due to a new green H_2 facility, the old current SMR-based H_2 facility should be isolated, affecting energy balance of the HDT unit.
9 Due to a new green H_2 facility, the old current SMR-based H_2 facility should be isolated. In this case this is a particularly unit which could be shut it down.
10 Any additional measures (Except for EEMs) will increase electricity demand at the refinery, which has to be compared to current cogeneration capacity, electricity import of new electrification alternatives.
11 BioC-1 and BioC-2 are related to VO co-processing in the HDT unit, but for a different time frame, short and medium term respectively.
12 Since this combination include two bioC options, it must be noted that potential increase of impurities throughout the refining operation units might occur. Current studies assessed only co-processing of one alternative at the time. More research is expected on this topic.
13 Theses measure are focus on the same unit (HDT),although in a different time frame. Life-span should be taken into account.
14 Theses measure are focus on the same unit (HDT) and the same time frame. So, they are exclude.
15 Similar situation of # 14, but BioC co-processing must be in place to propose the use of Blue/green Hydrogen
16 This two options aims to replace the same fossil-based electricity generation at the refinery.

A.5. Electrification options for an oil refinery

As combustion represent around 75% of the total CO_2 emissions at the refinery, an obvious option to reduce them is to shift from fossil-based boilers to an alternative source of heat. This option would prevent CO_2 formation from combustion but keeping the existing refinery process, with less intervention, known as Ex-ante adjustment. Among these alternatives are:

- Electrification of low heat demand by using high/very high temperature heat pumps (HTHP/VHTHP), which might replace heat demand below 80 °C and 165 °C, respectively.
- Electrification of low/medium temperature (<200 °C) steam production by using electric boilers.
- High temperature steam production using biomass (>200 °C) or H_2 (blue/green, >350 °C)-fired boilers.

There are other options that would require deep modifications of current infrastructure such as:

- Electrification of high temperature process heat (>350 °C) such as cracking process using electric furnaces.
- Apply pre-combustion CCS-technology
- Retrofitting current combustion furnace into biomass or H_2 (blue/green) to supply high temperature process heat above 350 °C.

Electrification options still face several challenges as a relevant alternative for refinery mitigation. TRL is still very low and most option are on TRL 3 to 5. Increasing the source of electricity supply to the core processes at the refinery would require to assure reliability of the system and avoid any negative effect on the process overall performance. In addition, electricity import would add significant cost to the new e-projects, as it would require extensive modifications of the refinery electrical infrastructure. Besides, having two parallel power systems would imply designing a mutual backup and load balancing system at the requested power. This option will require a significant amount of renewable electricity, which would be restrained by national production scenarios and competing with other sector as the electrification of passenger transport itself. Reliability of electricity supply is critical for the refinery and renewable energy is not due to intermittence generation. Also, would require a fossil-based or H_2 backup system, which mean higher investment and revamping of current on-site electricity station.

Refineries are highly energy integrated process, which means partial replacement/adjustment would highly affect the entire network. So, pinch analysis should be performed in order to keep energy efficiency level otherwise would mean higher fuel consumption on CHP facilities with more emissions added to the refinery. Refinery process itself co-produce and consume an important amount of fuels streams (e.g. low HC refinery gas and coke), which represent around 60–70% of total fuel consumption [75], and need to be consumed at the refinery or be transformed in valuable-products. Electrification options must consider this energy streams as a maximum threshold for replacement or consider downstream application with CO_2 emissions associated. Current e-technologies (except for e-furnace) do not reach medium–high temperatures level as required by the refinery (Distillation: 360; HDT: 315-398C; FCC: 540C; HCK: 400; DC: 500; SteamCracker:850), which limit their application.

Heat Pumps show a limited deployment potential, despite they are already at large scale 1–5 MW for District Heating to provide heat at 140C (capital cost of 800€/kWth, COP = 2–3) [75].Probable medium pressure steam might be produced. However, if HP steam is still needed, the prospect of viable Heat pump is remote. MP would be based on large-scale sources such as FCC and CDU air & water cooler, from which FCC is already used for EEM and direct electric heating and e-boilers would be preferred over heat pumps. Low-grade heat in refineries are typically in a range of 80 to 120 °C, which means a low thermodynamic efficiency (Carnot) between 10 and 20%. Higher temperature sources would better be used for refinery process heat integration instead [75].

In general, electrification options might face a maximum threshold on its deployment as refinery must consume their energy co-products such low-value fuel gas and FCC's coke, unless those find another use. This would limit the electrification potential up to 30% of the average energy refinery demand [75]. As a consequence of the low maturity level of the most of these alternatives and current low penetration in the industry, there are limited or none public techno-economic data [75].

Despite this study appraise short, medium and long-term technologies to reduce CO_2 emissions at the refinery, it also aims to a more feasible retrofitting and maximum use of current infrastructure in order to accelerate energy transition for the oil and gas industry. This means Ex-ante adjustment options are considered for alternative heat sources.

A.6. Ranking of mitigation options for the INDC scenario

Ranking criteria	
1	Time frame
2	Less layout impacts,
3	Low CO_2 avoidance cost,
4	Low investment capital and
5	High CO_2 avoided

#	Mitigation option	1-Time Frame (ST:1, MT:2, LT:3)	4-TCR [€, 2018]	5- CO_2 Avoided [t CO_2/y]	3- CO_2 Avoid Cost [€, 2018/t CO_2]	2- Layout impacts,	Cumulative CO_2 Avoided [t CO_2/y]

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(*continued*)

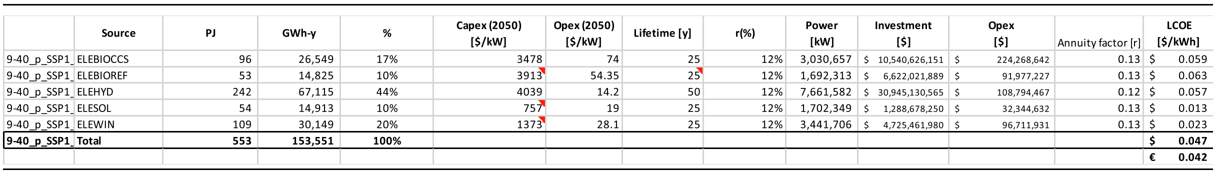
#	Mitigation option	1-Time Frame (ST:1, MT:2, LT:3)	4-TCR [€, 2018]	5- CO_2 Avoided [t CO_2/y]	3- CO_2 Avoid Cost [€, 2018/t CO_2]	2- Layout impacts,	Cumulative CO_2 Avoided [t CO_2/y]
4	EEM-2	1	€ 159,267	354,900	€ −93	L	354,900
5	EEM-1	1	€ 85,759	6,500	€ −80	L	361,400
3	EEM-1	1	€ 837,174	3,400	€ −29	L	364,800
2	EEM-2	1	€ 1,826,220	6,250	€ 20	L	371,050
13	BioC-1	1	€ 447,713,649	209,825	€ 651	L	580,875
1	EEM-2	1	€ 39,150,360	8,400	€ −32	L	589,275
10	CCS-4	2	€ 12,591,201	62,961	€ −88	L	652,236
25	GE-GT	2	€ -	49,868	€ 214	L	702,104
14	BioC-2	2	€ 447,713,649	352,974	€ 375	L	1,055,078
6	EEM-3	2	€ 818,797	17,215	€ −77	H	1,072,293
7	CCS-1	2	€ 1,541,597,167	1,352,999	€ 73	H	2,425,292
18	BioC-3	2	€ 535,803,662	695,245	€ 99	H	3,120,537
8	CCS-2	2	€ 201,656,193	80,458	€ 318	H	3,200,995
27	GE-Mix_BioH	3	€ -	67,583	€ 46	L	3,268,577
26	GE-Mix_P	3	€ -	64,669	€ 51	L	3,333,247
31	GH2-BioC-1/2	3	€ 19,455,552	40,198	€ 159	M	3,373,445
34	GE-Eboiler	3	€ 67,320,000	600,685	€ 170	M	3,974,130
28	BH2-BioC-1/2	3	€ 59,467,892	35,095	€ 217	M	4,009,225
24	GH2-HDT	3	€ 55,097,775	113,841	€ 303	M	4,123,066
9	CCS-3	3	€ 1,375,098,489	1,242,577	€ 67	H	5,365,643
30	BH2-BioC-5	3	€ 394,732,195	591,749	€ 68	H	5,957,391
29	BH2-BioC-4	3	€ 393,903,455	589,895	€ 68	H	6,547,287
23	BioC-6	3	€ 2,955,273,884	2,988,012	€ 124	H	9,535,299
19	BioC-4	3	€ 447,713,649	2,980,281	€ 147	H	12,515,580
22	BioC-5	3	€ 447,713,649	2,544,312	€ 169	H	15,059,892
32	GH2-BioC-4	3	€ 327,021,837	675,682	€ 382	H	15,735,575
33	GH2-BioC-5	3	€ 328,049,274	677,805	€ 382	H	16,413,380

A.7. SSP scenarios from Younis et al. [19]

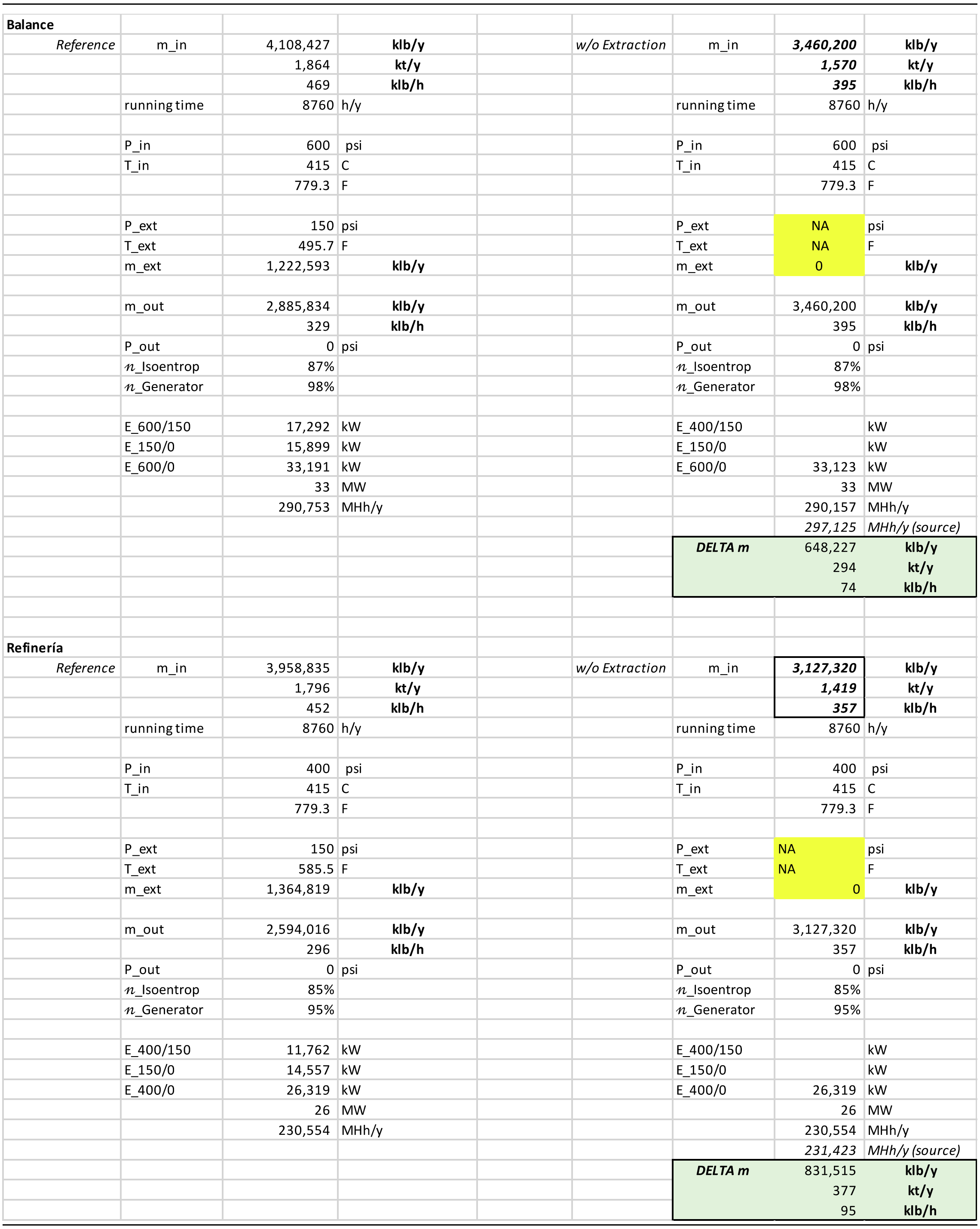
Quantitative description of the SSP scenarios used in this analysis.

Scenario variables	SSP1	SSP2	SSP3

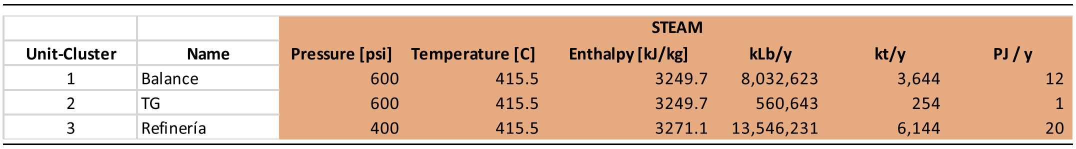
(*continued on next page*)



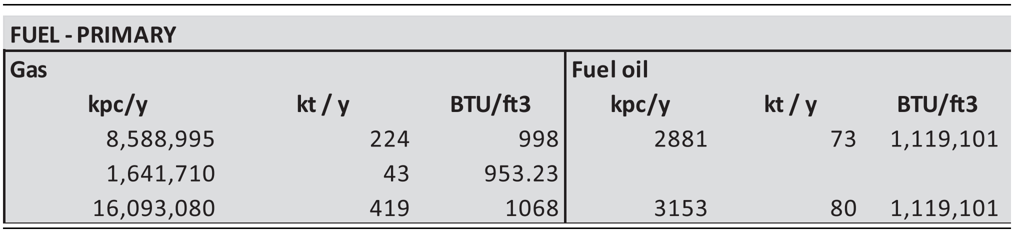
	Source	PJ	GWh-y	%	Capex (2050) [$/kW]	Opex (2050) [$/kW]	Lifetime [y]	r(%)	Power [kW]	Investment [$]	Opex [$]	Annuity factor [r]	LCOE [$/kWh]
9-40_p_SSP1_	ELEBIOCCS	96	26,549	17%	3478	74	25	12%	3,030,657	$ 10,540,626,151	$ 224,268,642	0.13	$ 0.059
9-40_p_SSP1_	ELEBIOREF	53	14,825	10%	3913	54.35	25	12%	1,692,313	$ 6,622,021,889	$ 91,977,227	0.13	$ 0.063
9-40_p_SSP1_	ELEHYD	242	67,115	44%	4039	14.2	50	12%	7,661,582	$ 30,945,130,565	$ 108,794,467	0.12	$ 0.057
9-40_p_SSP1_	ELESOL	54	14,913	10%	757	19	25	12%	1,702,349	$ 1,288,678,250	$ 32,344,632	0.13	$ 0.013
9-40_p_SSP1_	ELEWIN	109	30,149	20%	1373	28.1	25	12%	3,441,706	$ 4,725,461,980	$ 96,711,931	0.13	$ 0.023
9-40_p_SSP1_	**Total**	**553**	**153,551**	**100%**									**$ 0.047**
													€ 0.042



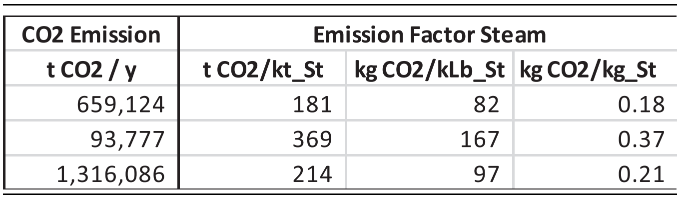
Balance								
Reference	m_in	4,108,427	**klb/y**		*w/o Extraction*	m_in	***3,460,200***	**klb/y**
		1,864	**kt/y**				***1,570***	**kt/y**
		469	**klb/h**				***395***	**klb/h**
	running time	8760	h/y			running time	8760	h/y
	P_in	600	psi			P_in	600	psi
	T_in	415	C			T_in	415	C
		779.3	F				779.3	F
	P_ext	150	psi			P_ext	NA	psi
	T_ext	495.7	F			T_ext	NA	F
	m_ext	1,222,593	**klb/y**			m_ext	0	**klb/y**
	m_out	2,885,834	**klb/y**			m_out	3,460,200	**klb/y**
		329	**klb/h**				395	**klb/h**
	P_out	0	psi			P_out	0	psi
	*n*_Isoentrop	87%				*n*_Isoentrop	87%	
	*n*_Generator	98%				*n*_Generator	98%	
	E_600/150	17,292	kW			E_400/150		kW
	E_150/0	15,899	kW			E_150/0		kW
	E_600/0	33,191	kW			E_600/0	33,123	kW
		33	MW				33	MW
		290,753	MHh/y				290,157	MHh/y
							297,125	*MHh/y (source)*
						DELTA m	648,227	**klb/y**
							294	**kt/y**
							74	**klb/h**
Refinería								
Reference	m_in	3,958,835	**klb/y**		*w/o Extraction*	m_in	***3,127,320***	**klb/y**
		1,796	**kt/y**				***1,419***	**kt/y**
		452	**klb/h**				***357***	**klb/h**
	running time	8760	h/y			running time	8760	h/y
	P_in	400	psi			P_in	400	psi
	T_in	415	C			T_in	415	C
		779.3	F				779.3	F
	P_ext	150	psi			P_ext	NA	psi
	T_ext	585.5	F			T_ext	NA	F
	m_ext	1,364,819	**klb/y**			m_ext	0	**klb/y**
	m_out	2,594,016	**klb/y**			m_out	3,127,320	**klb/y**
		296	**klb/h**				357	**klb/h**
	P_out	0	psi			P_out	0	psi
	*n*_Isoentrop	85%				*n*_Isoentrop	85%	
	*n*_Generator	95%				*n*_Generator	95%	
	E_400/150	11,762	kW			E_400/150		kW
	E_150/0	14,557	kW			E_150/0		kW
	E_400/0	26,319	kW			E_400/0	26,319	kW
		26	MW				26	MW
		230,554	MHh/y				230,554	MHh/y
							231,423	*MHh/y (source)*
						DELTA m	831,515	**klb/y**
							377	**kt/y**
							95	**klb/h**



		STEAM					
Unit-Cluster	Name	Pressure [psi]	Temperature [C]	Enthalpy [kJ/kg]	kLb/y	kt/y	PJ / y
1	Balance	600	415.5	3249.7	8,032,623	3,644	12
2	TG	600	415.5	3249.7	560,643	254	1
3	Refinería	400	415.5	3271.1	13,546,231	6,144	20



FUEL - PRIMARY					
Gas			Fuel oil		
kpc/y	kt / y	BTU/ft3	kpc/y	kt / y	BTU/ft3
8,588,995	224	998	2881	73	1,119,101
1,641,710	43	953.23			
16,093,080	419	1068	3153	80	1,119,101



CO2 Emission	Emission Factor Steam		
t CO2 / y	t CO2/kt_St	kg CO2/kLb_St	kg CO2/kg_St
659,124	181	82	0.18
93,777	369	167	0.37
1,316,086	214	97	0.21

(*continued*)

Scenario variables	SSP1	SSP2	SSP3
Population growth / Economic growth	Low/High	Intermediate	High / Low
Low carbon technology development [a]	Progressive	Intermediate	Modest
Energy Markets [b] (Oil price by 2050, $/GJ)	Low (12.8)	Interm.(22.2)	High (26.3)
GHG net emission target (Mt) by 2050 and reduction with respect to baseline (%) [c]	17 Mt (85%)	32 Mt (70%)	52 Mt (50%)
Blending of 1G biofuels [d] ($\%_{vol.}$) by 2050	B18 – E12	B13 – E09	B10 – E08
Carbon storage potential [e] (Mt CO_2)	Cumulative: 4,303 - Annual: 150 by 2050		
Biomass supply per scenario	*BioLo*: 650–1,000 PJ – *BioHi*: 6,800–13,900 PJ		

A.8. Levelized cost estimation for the national grid electricity

A.9. Steam turbine performance data

A.10. Thermodynamic parameters of steam production and CO2 emission factor

A.11. Steam production cost for a gas-fired boiler

Fuel cost (Cf) is aprox 90% of Steam cost	Source: DOE. How To Calculate The True Cost of Steam
Cf = €/kJ * (H_st – H_fw)/ n	

(*continued on next page*)

(*continued*)

Fuel cost (Cf) is aprox 90% of Steam cost			Source: DOE. How To Calculate The True Cost of Steam
Cf = €/kJ * (H_st – H_fw)/ n			
H_st	3.25	MJ/kg	@ 600 psi
H_fw	0.25	MJ/kg	@ 14.7 psi, 60 °C
n_boiler	85%		
NG Price	€ 0.004	€/MJ	Source: *UPME: Projección de precios de los energéticos para generación eléctrica. Enero 2019 – Diciembre 2039Versión Noviembre 2019* [76]
	€ 3.72	€/MMBTU	
Cf	€ 0.012	€/kg	
CG	€ 0.016	€/kg	
H_sl	2.96	MJ/kg	
CL = CH * (H_sl - hw) / (H_sh - hw)			
CL	€ 0.015	€ / kg	@ 150psi

A.12. Techno-economic performance data for electrolysers [41,77]

PEM Electrolysis		2020		2050		SOEC Electrolysis		Alkaline Electrolysis		
		Reference	Optimistic	Reference	Optimistic	2020	2050			
Capex	€/kW	€ 1,200	€ 900	€ 750	€ 400	785	€ 300	€/kW	€ 1,347	€ 1,012
Opex								€/kg H_2/y	€ 3,255	€ 2,066
Fixed	€/kW	€ 36	€ 14	€ 23	€ 6	66	€ 9	€/kW/y	€ 28	€ 21
Variable	€/kWh (elect)							€/kg H_2/y	€ 5	€ 4
	kWh/kg H_2	56	53	49	46	44		kWh/kg H_2	58	49
Efficiency	MW_{out}/MW_{in}	0.70	0.75	0.80	0.86	0.905			0.68	0.80
availability factor		0.95	0.97	0.95	0.97	0.95	0.95		*0.95*	*0.95*
Lifetime	hours	50,000	60,000	80,000	100,000	16,644	166,440	hours	90,000	90,000
	years	6.0	7.1	9.6	11.8	2	20		10.8	10.8

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