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Assessing bio-oil co-processing routes as CO_2 mitigation strategies in oil refineries

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Abstract: The oil industry needs to reduce CO_2 emissions across the entire lifecycle of fossil fuels to meet environmental regulations and societal requirements and to sustain its business. With this goal in mind, this study aims to evaluate the CO_2 mitigation potential of several bio-oil co-processing pathways in an oil refinery. Techno-economic analysis was conducted on different pathways and their greenhouse gas (GHG) mitigation potentials were compared. Thirteen pathways with different bio-oils, including vegetable oil (VO), fast pyrolysis oil (FPO), hydro-deoxygenated oil (HDO), catalytic pyrolysis oil (CPO), hydrothermal liquefaction oil (HTLO), and Fischer–Tropsch fuels, were analyzed. However, no single pathway could be presented as the best option. This would depend on the criteria used and the target of the co-processing route. The results obtained indicated that up to 15% of the fossil-fuel output in the refinery could be replaced by biofuel without major changes in the core activities of the refinery. The consequent reduction in CO_2 emissions varied from 33% to 84% when compared with pure equivalent fossil fuels replaced (i.e., gasoline and diesel). Meanwhile, the production costs varied from 17 to 31€/GJ (i.e., 118–213\$/bbl$_{eq}$). Co-processing with VO resulted in the lowest overall performance among the options that were evaluated while co-processing HTLO in the hydrotreatment unit and FPO in the fluid catalytic cracking unit showed the highest potential for CO_2 avoidance (69% of refinery CO_2 emissions) and reduction in CO_2 emissions (84% compared to fossil fuel), respectively. The cost of CO_2 emissions avoided for all of the assessed routes was in the range of €99–651 per tCO_2. © 2020 The Authors. *Biofuels, Bioproducts, and Biorefining* published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

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Key words: oil industry; biomass; CO_2 mitigation; pyrolysis oil; refinery; co-processing; bio-oil

Introduction

Crude oil will maintain its dominance in the world energy matrix sector for the next several decades. It is expected that the share of oil in the world's demand for primary energy will decrease steadily from 31% in 2018 to 29% in 2040, but with an absolute increase of 25% to 5626 Mtoe in 2040.[1] The transport sector (road, aviation, and shipping) represents 49% of the total oil demand and this figure is expected to increase to 60% by 2040 (79 Mbbl/d).[1] The dominance of crude oil in the transport sector may be attributed to the vast established infrastructure, the large scale of production, low cost, and the availability of high energy-density fuels.[2]

Nevertheless, a target of net 'zero' CO_2 emissions by 2050 or 2070 is essential to limit the rise in global average temperature to below 2 °C, with or without an implied reliance on global net negative CO_2 emissions.[1,3] Several regions are responding to this objective with different targets; for instance, Europe and Colombia have committed to 40% and 20% reductions[*] by 2030, respectively, under the Paris agreement.[†] On the liquid fuel-based emissions for the transport sector, there is a range of choices to achieve this target, from fuel efficiency and low-carbon fuels to electric/hybrid vehicles. Regarding low-carbon intensity fuels, to date, several technological options have been proposed to reduce CO_2 emissions during oil production and refining. However, final use accounts for ~80% of the total life-cycle emissions.[4] Liquid fuels therefore still have to achieve lower net fuel-cycle emissions. One potential solution to this problem lies in the final use of fuels produced from sustainable biomass, as they release carbon that has been absorbed during plant growth through photosynthesis. These fuels can provide low net fuel-cycle emissions or even negative emissions if the co-produced CO_2 is captured and stored underground, as described by Hailey *et al.*[2]

There are several technological options for biomass-based fuel production but their high cost and low production volumes, coupled with sustainability concerns, have halted their deployment. Biofuel production was initially focused on the so-called first-generation fuels to produce gasoline and diesel based on the fermentation of carbohydrates (sugars) and esterification of fatty acids, respectively. However, land-use competition for food production and other adverse effects inhibited the production of first-generation biofuels and spurred interest in 'second-generation' fuels. These are fuels produced from agricultural wastes, thereby avoiding direct land-use competition and resulting in a better sustainable performance.[5]

Faaij[6] identified three main thermochemical conversion routes for biomass, viz. pyrolysis, gasification, and combustion. Drop-in fuel production is mainly achieved via gasification and pyrolysis / hydrothermal liquefaction.[7–9] Despite several decades of successful research and development regarding gasification to develop coal-based drop-in fuels, its adaptation for processing biomass feedstock faced several challenges such as investment cost, syngas clean up, and limited scale of facilities.[7] Research on bio-based fuel production has therefore veered towards pyrolysis, as the technology is commercially available, requires relatively low investment, and has adequate scaling capacity.[7,10] Several factors, however, have affected the deployment of drop-in fuels produced by pyrolysis / hydrothermal liquefaction, such as the high cost of bio-refinery infrastructure, low yields and production volumes, low quality, and limited stability, technology-scaling challenges, low petroleum prices, and high logistics costs.

Co-processing of bio-oil in refineries has been proposed as an alternative to cope up with these challenges.[11] The integration of petroleum refineries and drop-in biofuel production through co-processing has been highlighted by the International Energy Agency (IEA)[7] as the key to future deployment of low-carbon biofuels by creating a commodity market for intermediates. This option takes advantage of the existing infrastructure, which may be retrofitted for bio-oil co-processing. Nevertheless, several technical issues and economic aspects should be resolved with respect to the biomass-conversion process and refinery units under consideration.

There are two key parameters for assessing feedstock suitability for co-processing – production volumes and ease of integration with the refinery process. Lipids are usually considered the first alternative for co-processing given their large production volumes (~185 Mt in 2017) and their easy integration in the refinery process.[12,13] In contrast, current lignocellulosic-derived bio-oils are not readily available in significant volumes, and the integration of their production with the refiner process is highly complex.[13]

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[*] INDC: Intended Nationally Determined Contributions. https://www4.unfccc.int/sites/submissions/indc/Submission%20Pages/submissions.aspx.

[†] *'The Paris Agreement is the first ever universal legally binding global climate change agreement and was adopted at the Paris climate conference (COP21) in December 2015'*. https://ec.europa.eu/clima/policies/international/negotiations/paris_en.

Most studies on co-processing bio-oils / bio-crudes have focused on two primary refining processes, such as hydro treatment (HDT) and fluid catalytic cracking (FCC). The former has been widely used in the production of advanced fuels, especially from lipids, and the process has reached technological maturity on a commercial scale, as demonstrated by Preem, Cepsa, Repsol, and Kern Oil.[11,14] Its greatest strength is based on the flexibility to manage different bio-feedstocks without compromising the quality of the biofuel.[15] The second is also a promising process that is used by the vast majority of refineries worldwide for the conversion of heavy fractions into gasoline and propylene.[16] Research on co-processing at FCC has been carried out mainly at a technology readiness level[‡] (TRL) of 4–6, which have shown deviations compared to their performance at commercial scale, especially to coke formation tendency.[17] Results from Pinho *et al.*[17,18] have shown that pyrolysis oil could be co-processed up to 20 wt% along with vacuum gas oil (VGO) in FCC lab-scale units (TRL 4–5) and these results could later be confirmed on a FCC test unit at TRL 7, using a commercial FCC equilibrium catalyst.

As described by Bezergianni *et al.*,[16] most of these studies focus on stand-alone biofuel production, whereas studies on the implementation of co-processing for so-called hybrid fuels (simultaneously processing of bio-oils and petroleum fraction) are scarce. The latter have focused on the chemistry and catalytic processes of the transformation of biomass to biofuels in conventional refineries, as shown by Melero *et al.*[19] and kinetics and energy balance in fluid catalytic cracking (FCC) by Cruz *et al.*,[20] which did not include operating conditions, type of catalyst, and blending ration in the analysis. Sabawi *et al.*[21,22] compared the co-processing performance in the HDT and FCC processes of individual bio-oils or model compounds but did not discuss technological aspects. Stefanidis *et al.*[23] focused their research on co-processing in FCC for bio-oils prepared in different ways. Even more recently, Bhatt *et al.*[24] examined air emission changes due to raw bio-oil co-processing in FCC from existing refineries, and Wu *et al.*[25] assessed a superstructure model to analyze the optimum biomass feedstock, comparing fast pyrolysis and catalytic pyrolysis oil, and the integration scheme of the co-processing process. Bezergianni *et al.*[16] focus on analyzing the co-processing of bio feedstock with petroleum fractions in both HDT and FCC, considering different potential feedstocks, catalysts, operating conditions, products, and benefits presenting a general technological analysis. Concawe[26] has also described promising potentials with some limitations on using biomass gasification and co-processing pyrolysis oil (best-developed technology) and HTL oil (emerging technology, TRL 5–7) in the hydrotreating unit as a strategy to produce low carbon fuels.

A robust research project is being conducted by the US Department of Energy (USDOE),[27,28] which aims to accelerate co-processing biomass feedstock in existing refineries to achieve a range fuel production cost <3$/GGE. This project involves developing efficient technologies for co-processing 5–20 wt% bio-oil into the FCC and HC/HT process, looking to identify blend levels, modifying compatible catalysts, and developing accurate biological carbon measurements.

However, little attention has been given to the techno-economic analysis (TEA) of the co-processing alternatives. As stated by the IEA,[7] the next step for the promotion and use of drop-in fuels requires the techno-economic assessment of different co-processing combinations of feedstock and reactor to determine the economic viability of refinery integration. Several TEA studies[20,29–37] focus on individual bio-oil co-processing on a specific refinery process unit, without including key aspects such as bio-oil production technique, biofuel production cost, or even a comparison between HDT and FCC processes.

None of these studies has evaluated co-processing alternatives in a more comprehensive approach, such as an energy system analysis, as discussed by Ramirez *et al.*[38] This assessment would consider, at first, the technological performance based on bio-oil production techniques and co-processing units suitability, including mass and energy yields under operating conditions and blending restrictions of the refinery units. Besides, a broader techno-economic assessment and CO_2 mitigation potential estimate would be based on process-chain related CO_2 emissions and economic analysis of the most promising bio-oil co-processing pathways.

Focusing on this problem, in this study we assessed the CO_2-mitigation potential of bio-oil co-processing in an oil refinery. A comparative assessment of promising pathways was performed via TEA to estimate their mitigation potential. A medium-conversion refinery in Colombia with a capacity of 250 kbpd (thousand barrels per day) was used as the case study.

Methodology

General approach

The approach used in this study consists of two parts: (1) identification of technological pathways for bio-oil

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[‡] Technology readiness level (TRL) is a nine-point scaling system for tracking the status of the maturity level of a technology, moving in a series of scale-up steps from a bench or laboratory scale (3–5), to pilot-scale (6), demonstration (7), and commercial scale (8–9).[134]

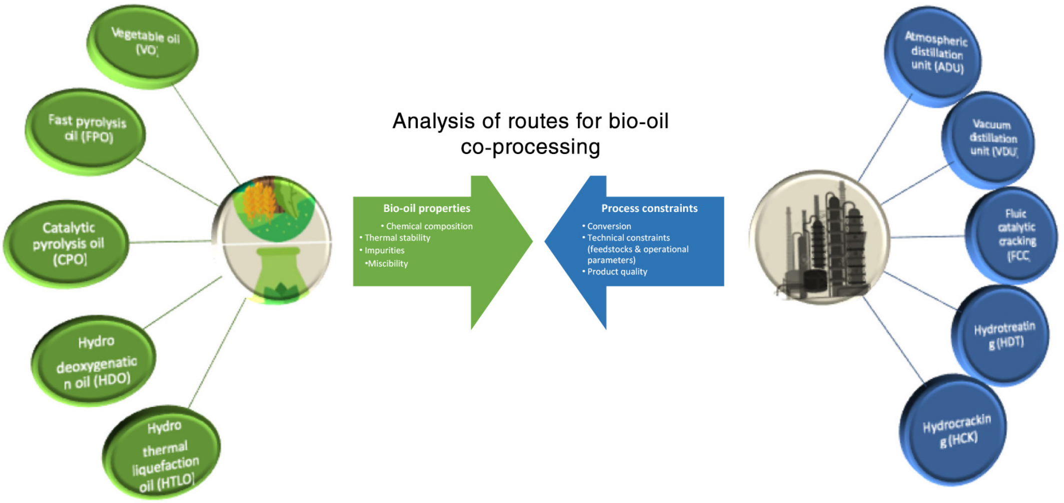

Figure 1. Analysis of bio-oil properties and potential insertion points in the refinery.

co-processing in the refinery and (2) TEA and analysis of the CO_2-mitigation potential of the most promising routes.

The identification of bio-oil co-processing pathways was carried out based on a qualitative analysis to match the properties of bio-oils with the key restriction parameters in refinery processing units (RUs) (see Fig. 1). Based on the insertion points into the refinery process for bio-oils described in the literature, this study addresses the lack of conclusive information on the suitability of bio-oils to be co-processed by specific RUs.

Each pathway (PW) matches a RU with a specific type of bio-oil for co-processing. The identification of potential PWs was accomplished using steps 1 to 5 as described below. The data and sources corresponding to steps 1 to 4 are discussed below.

1. Identification of bio-oils (mechanical and thermochemical) proposed in the literature for co-processing at the refinery.
2. Identification of suitable RUs from the literature as potential insertion points for bio-oil co-processing.
3. Inventory of the typical properties of the identified bio-oil and crude oil and its fractions.
4. Identification of the properties of the bio-oil that might affect the performance of the RUs selected as insertion points.
5. Qualitative ranking of bio-oils using typical properties and their suitability for co-processing in refinery units. A qualitative criterion was used to analyze the impact of each property on refinery performance.

In the TEA of bio-oil co-processing pathways, the steps described below were followed:

1. Set up system boundaries for mass and energy balance, cost, and CO_2 emission estimation.
2. Inventory the key parameters of the primary processes in each pathway and for fossil reference (for, e.g., CO_2 emissions, capacity, yield, energy, and mass flow).
3. Capex and Opex data collection for the production of the bio-oil selected in this study.
4. Scaling the mass and cost data related to bio-oil production to the bio-feed volume required in the co-processing pathways.
5. Estimation of CO_2 emissions from RUs based on the new reaction conditions generated from the co-processing parameters.
6. Assessment of greenhouse gas (GHG) reduction potential and avoidance costs corresponding to each bio-oil co-processing pathway.
7. Sensitivity analysis of the key parameters.

Case study

Ecopetrol's refinery, located in Barrancabermeja, Colombia, was considered as the case study in this investigation. This is a medium conversion and complexity-level oil refinery with an average capacity of 250 kbpd. Oil refineries are usually technologically described as simple and complex. The former include topping (very simple) and hydro-skimmer (simple) facilities; meanwhile, complex refineries refer to cracking (complex) and coking (very complex) refineries. In Europe, complex refineries are also referred to as 'conversion' facilities and 'deep conversion' refineries.[39] The Nelson complexity index is a common measure to assess the complexity level of a refinery, which compares the secondary conversion capacity to a primary distillation capacity. In 2014, half of the 646 world refineries were medium complexity level (cracking), 33% were high complexity level, and 15% were simple refineries (10% hydroskimmers and 5% topping).[39] Aggregated data corresponding to the mass, energy, and CO_2 emissions of the refinery were extracted from the basic refinery model[40] and verified against the operational data. Table 1 presents an overview of the current key performance parameters of the refinery.

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

Table 1. Key characteristics of the Ecopetrol refinery at Barrancabermeja.[40]

	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	2402
Steam production	PJt_h/year	24 843
Hydrogen production	kt/year	29.11
Total conversion yield	%	84.62
Distillation throughput	kt/year	12 131
FCC throughput	kt/year	5065
HDT throughput	kt/year	4814

FCC: Fluid catalytic cracking unit.
HDT: Hydro-treatment processing unit. The low capacity of this unit is related to a mild hydrotreating process which results in high-sulfur diesel production. So, there is a relatively low hydrogen consumption of 5.5 kg H_2 per t of input load.

System boundaries

In addition to using the most recent data available from studies at TRL 3–6, in this investigation, we considered several expert insights as commercial-scale data are not available. Nevertheless, the data aggregated from demonstration-scale tests of the co-processing routes patented by Ecopetrol are included in this study. It must be noted that this route is a bio-oil upgrading process currently under development with a medium maturity scale (lab test: TRL 4–5), based on restricted research by Ecopetrol, which has not been published yet. Ecopetrol S.A. owns several patents on hydrotreating vegetable oil and esterification of FPO for co-processing in oil refineries. Patents No: 07127669, 08132107, 09138358, 13 231 978, NC2016/0000689, NC2018/0000069. https://www.sic.gov.co/base-de-datos. Figure 3 depicts the system boundaries corresponding to the mass and energy analysis of the primary processes considered in the study. The following assumptions were used:

- To avoid any disturbance in refinery operations and performance, the throughput capacities of the co-processing RUs were maintained as constant as possible when co-processing bio-oils.
- The fraction of bio-oils co-processed was such that changes in the yield of the process unit were as minimal as possible. The amount of bio-oil for co-processing in each pathway was therefore determined based on the technical co-processing limits (TcPL). A TcPL is defined as the maximum threshold ratio of bio-oil / fossil fed into a specific RU with the minimum impact on product's yield, which is determined based on TRL 3–6 tests (sourced from literature). This limit allows for minimum retrofitting of the process infrastructure and minimizes disturbance in the operational performance of the refinery.
- Small changes in the yield of gasoline and diesel-range fractions were considered. However, it was assumed that they did not critically affect the performance of other process units or the refinery itself. There occurs a multi-integration effect on RU performance due to potential changes in the gas and liquid-fraction output. The RUs are interconnected and therefore any change in the fraction output might affect the performance of other process units. It is important to note that co-processing bio-oils at a refinery also yields other fractions (heavy, light, and gaseous) that might affect the refinery yield and downstream petrochemical conversion. These effects are outside the scope of this study.
- The required biomass for bio-oil production was based on the TcPL ratio for co-processing and the yield of the biomass-conversion process.
- The baseline reference used in this study is the equivalent fossil fuel produced in the refinery that can potentially be replaced by the biofuel processed.

Carbon dioxide emissions from scope 2, corresponding to bio and fossil fuels, were estimated for the process chain in each pathway. Each chain included stages related to production, transport, co-processing at the refinery, and final use. A general scheme of the CO_2-emission flow considered in this study is shown in Fig. 3.

Carbon dioxide emissions from fossil fuels were evaluated from the life-cycle assessment (LCA) for diesel production in Colombia as described by Martinez *et al.*[42] This LCA included the stages of crude-oil extraction, oil pipeline transport, oil refining, refined transport, and final use. A breakdown of CO_2 emissions from the fossil fuels is presented in Table 6. Carbon dioxide emissions from the refinery were calculated at level 2 of methodological complexity (tiers) and level 3 for hydrogen production, electricity, and steam production based on current operations. According to IPCC[135], 'a tier represents a level of methodological complexity' for estimating CO2 emissions. Three tiers are suggested starting from Tier 1 as the basic method followed by Tier 2 and Tier 3, which is the most demanding in terms of complexity and data requirement. Tier 1 uses average and default values whereas

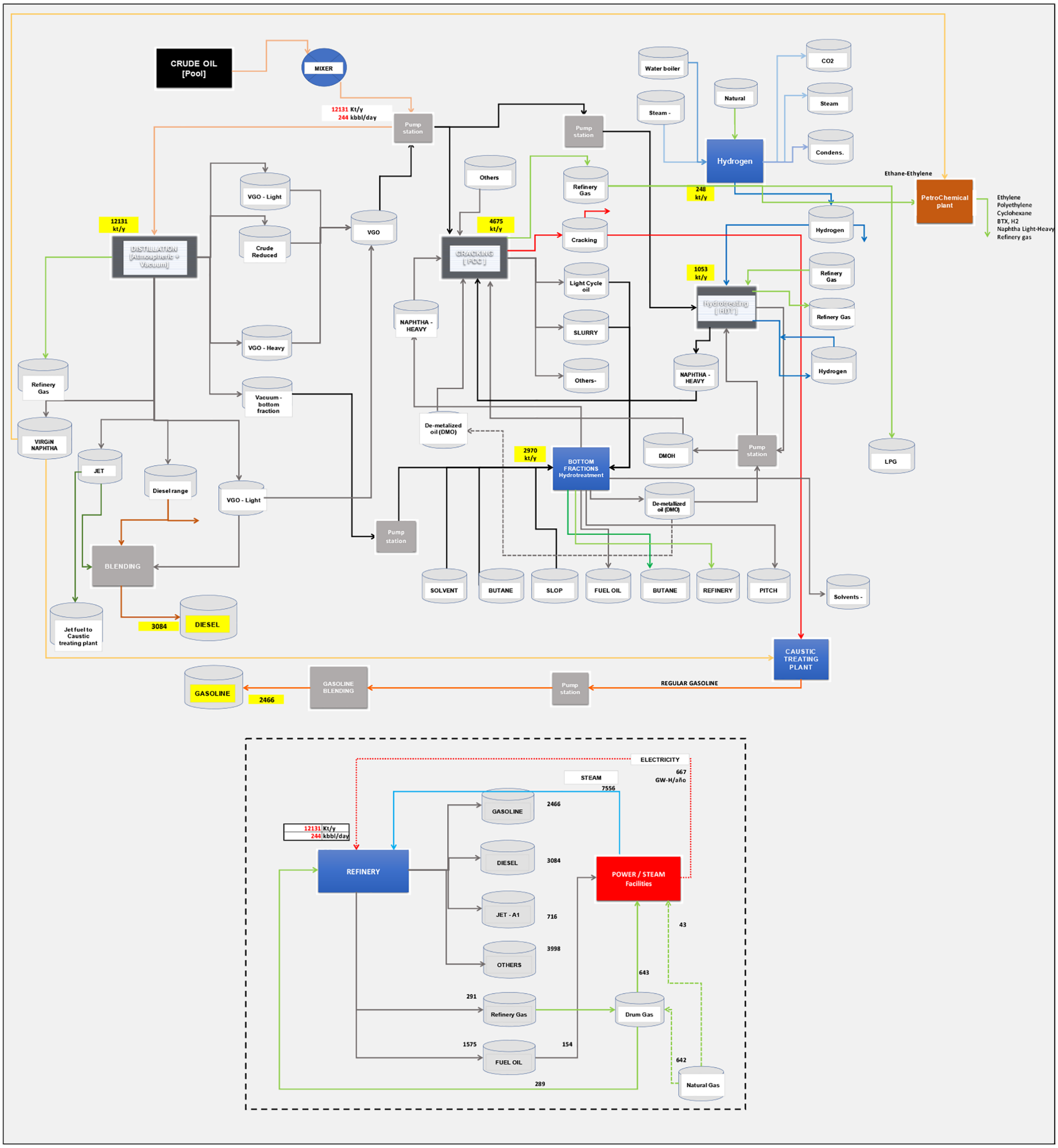

Figure 2. Schematic diagram of the refinery case study (Adapted from internal report by Ecopetrol).[41]

Tier 2 relies on country-specific data and Tier 3 is based either on detailed emission models or measurements.

Carbon dioxide emissions corresponding to upstream biomass and bio-oil production were calculated based on LCA studies as well as CO_2-specific emissions reported in the literature. Carbon dioxide emissions due to biomass transport were also estimated for an average fixed location of the biomass crop in a region near the case-study refinery. Emissions due to the co-processing of bio-oils were calculated using results from TRL 3–6 tests. This resulted in new CO_2 emission factors for the RUs. The final use of biofuels may indicate low net fuel-cycle emissions as they release carbon that has been absorbed during the photosynthesis process.[2] Nevertheless, CO_2 emissions from biogenic carbon might differ for different pathways as the types of biomass and planting conditions vary. Carbon dioxide emissions from fuel use were fixed at 94 g CO_2/MJ, as suggested by Martinez-Gonzalez *et al.*[42] for Colombian conditions.

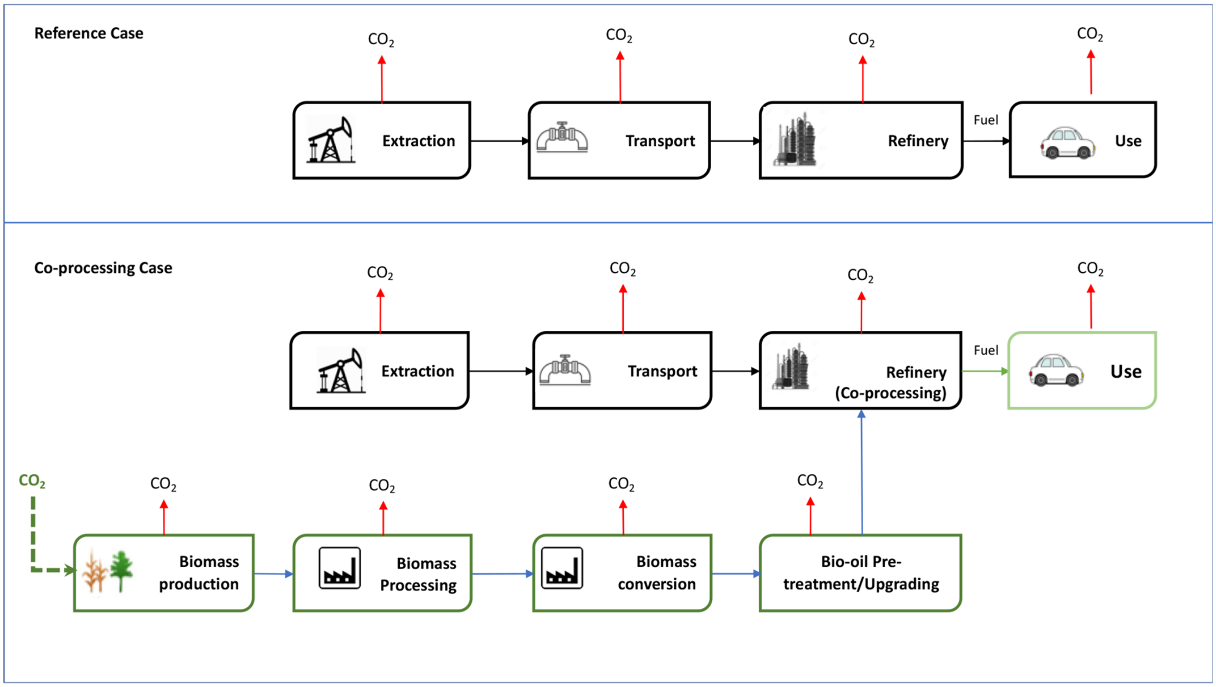

Figure 3. System boundaries and CO_2 emissions from the primary stages considered in this study. The black boxes indicate the fossil-fuel production chain, dark-green boxes represent the bio-oil chain, and the light-green box represents the final use of the blend liquid fuel. The red arrows indicate CO_2-emission mass flow, black arrows represent crude-oil flow, blue arrows indicate biomass / bio-oil flow, and the green arrow indicates the use of the blended biofuel. The dashed green arrow indicates CO_2 absorbed by the crop.

Key performance indicators

The main technical indicator used in this study is the net change in annual emissions ΔGHG (tCO_2/y), which was calculated using Eqn (1):

$$\Delta GHG = \left[\begin{array}{l} \left(\Delta GHG_{ff} \times M_{ff} \times H_{V_{ff}}\right) \\ -\left(\Delta GHG_{bf} \times M_{bf} \times H_{V_{bf}}\right) \end{array} \right] \times 10^{-3} \qquad (1)$$

Here, ΔGHG_{ff} and ΔGHG_{bf} represent net changes in the life-cycle GHG emissions ($gCO_{2\text{-eq}}$/MJ) during the production of fossil fuels and biofuels, respectively ($CO_{2\text{-eq}}$ is the mass of the CO_2 equivalent of GHG with the same global warming potential). M_{ff} is the mass of petroleum fuel to be replaced and M_{bf} is the amount of biofuel needed to replace M_{ff} (t/y). The high heating values (HHVs) of the fossil fuel ($H_{V_{ff}}$) and biofuel ($H_{V_{bf}}$) are expressed in MJ/kg.

The net changes in annually avoided GHG emissions for each fuel, GHG_f ($tCO_{2\text{-eq}}$/y), were calculated using Eqn (2). Life-cycle GHG emissions associated with bio-oil production and the co-processing pathway as well as fossil-fuel extraction, transport, and refining were included in the analysis.

$$GHG_f = \Delta GHG_{upstream} + \Delta GHG_{plant} + \Delta GHG_{downstream} \qquad (2)$$

Here, $\Delta GHG_{upstream}$, ΔGHG_{plant}, and $\Delta GHG_{downstream}$ represent net changes in annual GHG emissions (tCO_2/y) in the upstream, processing plant, and downstream, respectively.

The main economic indicator considered in this study was the GHG avoidance cost, C_a (€/t $CO_{2\text{-eq}}$), which was estimated using Eqn (3).

$$C_a = \frac{\left(C_{P_{bf}} - C_{P_{ff}}\right) \times 10^3}{\left(GHG_{ff} - GHG_{bf}\right)} \qquad (3)$$

In this equation, $C_{P_{bf}}$ and $C_{P_{ff}}$ represent production costs (€/GJ) of the biofuel and fossil fuel, respectively. The levelized production cost of the biofuel ($C_{P_{bf}}$) was estimated using Eqn (4).

$$C_{P_{bf}} = \frac{\left[\sum\left(E_i * P_i\right) + \sum\left(M_j * P_j\right) + \left(\alpha * I\right) + O\,\&\,M_{cost}\right]}{\left(M_{bf} \times H_{V_{bf}}\right)} \qquad (4)$$

Here, i represents the energy carrier (for e.g., electricity, natural gas, or steam), E_i is the annual energy consumption (GJ/y), P_i represents the energy prices (€/GJ), M_j is the annual feedstock input per feedstock type j (for, e.g., feedstock, catalyst, amine, or hydrogen) (t/y), P_j is the feedstock price (€/ t), α is the annuity factor (/y), I is the total upfront investment cost (€), and $O\&M_{cost}$ represents operational and maintenance costs (€/y). I was calculated as the total capital requirement (TCR), which was estimated as a percentage of the total plant cost (TPC) plus owner cost and interest during construction. The TPC, in turn, was estimated from the process plant cost (PPC), engineering fees, and contingencies. The PPC included the cost of equipment and installation (see Table 5).

The annualized capital cost ($\alpha * I$) was calculated as shown in Eqns (2)–(5). The annuity factor is a function of the discount rate r (%) and economic lifetime LT (years) of the technology:

$$annualized\ capital\ cost = \alpha * I = \frac{r}{1-(1+r)^{-LT}} * I \tag{5}$$

In the reference case, to estimate fossil-fuel production costs, official data reported by Ecopetrol were used as depicted in Table 5. Capital investment for co-processing at the refinery was estimated based on the retrofitting cost of the current infrastructure and not for an entirely new facility as required by a stand-alone bio-refinery. There is a significant difference between the capital investment for biofuel production and retrofitting investment for the petroleum industry. Van Dyk *et al.*[7] reported that the capital investment for biofuel production using FPO and CPO might range from 33 to 99 and 64 to 110 k€/bbl per day capacity, respectively. As described by Tsagkari *et al.*,[136] gasification-derived biofuels require higher investment in the range of 153 to 289 k€/bbl per day capacity. Van Dyk *et al.*[7] also described a cost reported by NREL of 183 k€/bbl per day capacity. Meanwhile, ethanol and biodiesel production might range from 17 to 121 k€/bbl per day capacity.[136] The investment required for upgrading a refinery depends on many factors, especially when it comes to additional hydrogen supply and use. For this study, the refinery process unit's adaptation for co-processing would not involve a significant retrofitting process. This assumption is based on some factors such as the throughput capacity remaining constant, pumping and heating requirements are assumed to be similar (depending on miscibility, viscosity, and density of bio-oils and blending), and the yields of the fractions are expected to keep in the same range (although some increase is expected in the top streams, which could increase the investment cost for downstream gas managing). As there are no data available on investment costs for this type of retrofitting process, it is assumed to be 50% of the retrofitting cost reported by the IEA,[43] which is of 17 k€/bbl per day of oil refining capacity. This assumption follows an estimate of the US National Energy Modeling System (NEMS), which assumes that the capital cost of refurbishing is about 50% of the cost of adding a new unit.[44] The cost of additional industrial services facilities (such as H_2, power, steam, and cooling water) was assumed to be included in the retrofitting cost estimated for the capital investment required for each pathway.

Standardization of key parameters

For a fair comparison of different technological pathways, several parameters used in this study were standardized as described by Berghout *et al.*[45] The standardization procedure is as follows:

1. Indexation. All figure costs were reported in €2018. Costs reported in other currencies were first converted to Euro using the year-average exchange rate data from Oanda[46] and escalated to the year 2018 using the Harmonized Index of Consumer Prices (HICP).[47]
2. Normalization. Component costs are not equally reported in the literature, so a fixed percentage was applied to the capital cost figures to correct any differences. The upfront investment cost was calculated as the TCR; the results are shown in Table 5.
3. Scaling of capital cost figures. The capital costs are highly dependent on the plant size (capacity). Capital costs are calculated by applying a generic scaling relation to figures reported in the literature (see Eqns (2)–(6), where SF is a scaling factor). A SF of 0.67 was assumed according to previously presented information.[48]

$$\frac{Cost_A}{Cost_B} = \left(\frac{Size_A}{Size_B}\right)^{SF} \tag{6}$$

Data

Bio- and crude-oil properties

The typical properties used to characterize crude oil and bio-oils are presented in the supporting information. The physical and chemical properties of the crude oil and its fractions were measured to determine their value and processability.[49] Several considerations were included, such as compatibility, processability, processing options, potential problems, and expected product quality.[50] In addition to these considerations, crude oil is usually analyzed by specific tests such as Saturated, Aromatic, Resins, and Asphaltenes (SARA) and Paraffins, Isoparaffins, Aromatics, Naphthenes, and Olefins (PIANO).

Screening analysis of the influence of bio-oil properties in the RUs

To define the co-processing pathways, the primary processing units in the refinery were defined as atmospheric distillation unit (ADU), vacuum distillation unit (VDU), FCC, HDT, and hydrocracking (HCK), to then assess the ability of these units to co-process bio-oil based on ranking, established in Tables 2 and 3. Thus, the final step in determining the most feasible pathway for biomass use in the refinery should consider the ranking of bio-oils by suitability (Table 3) and employ the least sensitive RU (Table 2). These pathways will be identified in the results section for different tiers of co-processing success. Tier 1 or the highest suitability for co-processing matches the bio-oil with the processing unit that offers the best alternative of what is required by the bio feedstock to make optimum biofuels. In other words, the properties of the bio-oil are favorable and induce minimal disturbance during co-processing (green cells in Table 3); likewise, the RU does not impose significant restrictions on this parameter (black cells in Table 2). This tier also employs the most mature technology for co-processing bio-oils in the refinery.

Tier 2 (medium co-processing success) was defined by the bio-oil properties highlighted in green cells and the RUs marked in gray cells. Meanwhile, Tier 3 is defined by yellow cells related to the properties of bio-oils and gray cells for RUs. Finally, Tier 4 is defined by yellow and red cells corresponding to bio-oil properties with gray and black cells for RUs, representing the least favorable matches between the bio-oils and RUs.

The impact of the properties of the bio-oil on the RU performance was assessed by a qualitative assessment approach described in the literature (Table 2). This analysis aims to identify the main properties of the bio-oils that affect process unit performance using different color codes. The cells in black represent the high relevance (negative impact) of the property on the RU analyzed. The gray color indicates slight impact while white cells represent a low or insignificant impact on the processing unit. A detailed explanation on the assigned impacts is provided in the footnote of Table 2.

The bio-oils were ranked by suitability using a qualitative criterion for the impact of each property on the refinery performance and the results are presented in Table 3.

Key mass and energy data from primary bio-oils used for co-processing

The key process data related to bio-oil production for co-processing are summarized in Table 4.

General techno-economic parameters used in this study

Table 5 shows a summary of the general input parameters used in this study.

CO_2 emissions associated with fossil-fuel production

A breakdown of the CO_2 emissions during fossil-fuel production from the chosen refinery in Colombia is provided in Table 6. These results were used as a reference system.

Results

Bio-oil co-processing routes

There are three basic insertion points for biomass co-processing as proposed by several researchers[13,59] (Fig. 4).

The potential risk of inserting bio-oils into the refinery plays a significant role in the choice of the insertion point. Biofuels in the form of finished fuels represent the lowest risk to the refinery; blending with crude oil prior to distillation poses the greatest risk.[7]

Insertion point 1 (IP_1) feeds the bio-oil into distillation units (ADU/VDU). However, it is not considered to be viable for three main reasons. First, it would require that the bio-oil is purely C and H_2, with minimal or zero levels of olefins, carbonyls, alcohols, and aldehydes. In other words, it should be virtually free of oxygen. However, ADU and VDU are used to separate and do not chemically alter molecules. Second, using IP_1 means that contaminants would be spread to the entire refinery. [13,59] Third, many bio-oils may contain non-volatile compounds, such as sugar and oligomeric phenols, which are not suitable for distillation. An increase in the temperature leads to an increase in the viscosity and solid residual formation due to the unstable nature of the bio-feedstocks.[13] Nevertheless, there are some recent studies suggesting that the HTL can undergo fractional distillation after mild deoxygenation.[36]

Insertion point 2 (IP_2) uses the current refinery infrastructure to mix bio-oils with intermediate streams at the refinery immediately after the distillation units. Bio-oils can often help in upgrading low-value refinery streams to meet the desired specifications. Higher capital savings may be accrued if IP_2 is used. Meanwhile, IP_3 is the

Table 2. Impact of bio-oil properties on RU performance.

Property	Concept	Refinery Process Units			
		Atmospheric distillation unit (ADU)	Fluid catalytic cracking (FCC) [12-15]	Hydrotreating (HDT) [4,17-19]	Hydrocracking (HCK) [4,17,20]
TAN[1]	Low is +	▨	▨	▨	▨
Water[8]	Low is +	▨	■	■	■
Blending ratio[5]	High is +	▩	▩	▩	▩
Coke yield[3,18]	Low is +	*n.a*	▨	■	■
Hydrogen consumption[9]	Low is +	*n.a*	□	■	■
Oxygen[2,12,20]	Low is +	■	▨	■	■
Sulphur[10]	Low is +		▨	■	■
Nitrogen[19]	Low is +			■	■
Contaminants[6, 21]	Low is +	■	▩	■	■
MCR/CCR[14]	Low is +	■	▨	n.d.	n.d.
Miscibility with fossil-based feeds[7,19]	High is +	▨	▨	■	■

[a] Refineries can cope with the acidity of bio-oils using 317 stainless steel cladding. This, however, is not standard in a RU.[51]

[b] The catalyst in the FCC is more tolerant to higher levels of oxygen than the catalyst in hydro-processing (HDT)[31] units. Furthermore, the zeolite catalyst in the FCC shows higher capacity for oxygen removal.[52] Bio-oils are more prone to cracking at elevated temperatures in the ADU due to their high oxygenate content.[53] In the HDT, oxygen removal increases the temperature, which in turn could lead to unwanted reactions, increased coking and decreased pressure, and low fluid distribution.[13]

[c] Coke formation deactivates catalysts. The FCC catalysts are continuously regenerated on site, unlike hydrotreatment catalysts, which must be taken to other locations (which involves higher costs).[13] Increasing coke formation could increase the temperature and affect the energy balance; it also damages the FCC catalyst.[13] However, it seems that the experimental results led to higher coke formation in the FCC when compared to that expected in realistic setups.[22,33,54]

[d] The effective hydrogen index (EHI) measures the H_2 required to remove heteroatoms with respect to the H_2 content of the oil. Fossil-based feedstocks have EHI values higher than 1, while bio-oils are <=1. Bio-oils with EHI <=1 are expected to increase coke formation.[52]

[e] Regarding the FCC,[23] it is suggested that a blending ratio of 3%–5% be adopted[31] although some tests were previously conducted at 15%[55,56] and 20%;[17] the latter resulted in an increased coke formation and reduced gasoline yield. Wang *et al*.[57] suggested that a blending ratio of 15% is optimal before blockage by coking.

[f] Contaminants refer to olefins, carbonyls, alcohols, aldehydes, and metals (discussed in numeral 21). The HCK cannot manage oxygen and impurities in its feedstock.[13] These contaminants may lead to a rapid pressure drop buildup and catalyst deactivation during hydrotreatment.[50] Chlorine, sulfur, and nitrogen are contaminants that cause catalyst poisoning in upgrading.[58] Unlike other processes, FCC provides an integrated *in situ* catalyst regeneration, which makes it less vulnerable to contaminants in bio-feedstock.[7] Meanwhile, contaminants in the atmospheric distillation unit / vacuum distillation unit (ADU/VCU) are spread to the entire refinery and affect its operation.[13,59]

[g] Miscibility is a primary requirement for co-processing, specifically for the HDT and HCK.[13] Immiscibility is a critical problem as hydrotreating reactions occur only when mixing takes place. Although many studies used model compounds to analyze this property, the results cannot be easily extrapolated to actual bio-oils.[16] The literature indicates that immiscibility has a more severe impact on the HDT and HCK than on the FCC.[16]

[h] Water in pyrolysis bio-oils is hard to separate and can be attributed to both the original moisture and reaction products. It can reduce the viscosity, stability, catalyst performance, and miscibility of bio-oils and fossil feeds.[13,60] The HDT and HCK use highly specialized catalysts under severe operating conditions, which means that these processes exhibit lower tolerance to contaminants. Water may affect alumina-supporting catalysts in a manner similar to that observed in the FCC.

[i] VO co-processing in HDT might increase H_2 consumption due to the presence of oxygen and unsaturated carbon chains.[21]

[j] As shown in the supplementary material, the sulfur content in the bio-oil is lower than of the crude oil, which may be considered a minor issue. However, sulfur is associated catalyst poisoning.[60] Mutual inhibition (deoxygenation and desulfurization) can lead to an unsatisfactory performance in the HDT/HCK[52] and a negative impact on diesel quality due to the presence of heteroatoms.[21] Unlike HDT/HCK processes, the FCC is not designed to remove sulfur and thus its presence and deoxygenation inhibition can have different impacts.[16,52]

[k] Vegetable oil co-processing in the HDT might deactivate the catalyst faster due to contact-time adjustment to maintain high conversion rates for nitrogen and sulfur. The water produced may also deactivate the catalyst.[61]

[l] Oxygen removal from the FCC occurs via hydrogen transfer from the fossil feeds, which increases the content of aromatics in products with high levels of phenols in the naphtha.[17,18]

[m] There is no external hydrogen consumption in the FCC but H_2 transfer occurs from the crude oil, which renders the FCC very suitable for co-processing. In addition, its catalyst (zeolite) it is more tolerant to higher levels of oxygen and exhibits a higher oxygen-removal ability.[31,52] Fluid catalytic cracking catalysts are continuously regenerated on site unlike hydrotreatment catalysts that must be taken to other locations.[13]

[n] Microcarbon residue (MCR) and Conradson carbon residue (CCR) tests are standard procedures carried out in the oil industry. The MCR measures the amount of solid produced once the feedstock is slowly evaporated in an inert atmosphere.[52] Castello *et al*.[52] suggested that the MCR is a more comprehensive indicator than oxygen content for assessing bio-oil processability in the FCC. A relationship between coke formation in the FCC and MCR was established previously.[62] A low MCR value is associated with better bio-oil co-processing in the FCC.[63] The MCR is also an indicator of the tendency for polymerization,[52] which is a critical factor in distillation. The CCR measures the tendency of a feedstock to form coke at elevated temperatures[54] and hence it represents the processability of bio-oils in the FCC. It is still unclear how bio-oils contribute to CCR values during co-processing.[54]

[o] Bio-feedstock co-processing in the FCC leads to lower H/C ratio products compared to 100% vacuum gas oil (VGO) processing.[13,34]

[p] Thermal and oxidative stability are important factors in analyzing bio-oils. A lack of stability in the bio-oil might cause problems, such as polymer formation, during storage, as several properties, such as density, viscosity, and acidity, undergo changes.

[q] Catalysts in the HDT/HCK are regenerated off-site in a typical cycle of 12 to 60 months, which means that these process units are less tolerant to contaminants than the FCC.[13]

[r] Hydrotreatment is an exothermic reaction associated with hydrogen consumption and oxygen removal. It leads to increased coking, decreased pressure, and poor liquid-flow distribution.[13]

[s] Like other heteroatoms, nitrogen should be removed from the crude oil and bio-oil[13] as it may poison acid catalysts during co-processing[60]; this is more critical for the HCK than for the HDT.[54] It also leads to nitrogen oxide emissions if present in the fuel during combustion.

[t] The HCK is comparatively less tolerant than the HDT to oxygen content in the bio-oil due to more severe operating conditions with highly sensitive catalysts.

[u] Metal content in heavier petroleum fractions is usually referred to as a contaminant that must be removed. In contrast, bio-oil does not contain metals, so, co-processing might lead to lower contaminant content (usually nickel and vanadium) in the final products.[64] Alkali metal presence in vegetable oil might affect cracking process due to fatty-acid composition,[64] and also promote secondary reactions during storage.[31] In the case of VO co-processing in FCC, metal content associated with petroleum feedstock, usually, nickel, might be attractive as that metal incorporation onto the base FCC catalyst is not required to improve gasoline yield.[65] Nevertheless, catalyst deactivation is a consequence of metal deposition during the upgrading process such as HDO.[66]

Table 3. Suitability ranking of bio-oils by property.

Parameter	Concept for co-processing	Bio-oil for co-processing					
		VO	FPO	FPO-E	CPO	HDO	HTLO
Total acid number (TAN)	Low is +	🟩	🟥	🟨	🟩	🟨	🟨
Water[b]	Low is +	🟩	🟥	🟩	🟨	🟩	🟩
Cetane[a]	High* is +	🟩	🟥	🟥	🟥	🟥	🟥
Octane[c]	High* is +	🟩	🟥	🟨	🟨	🟨	🟨
Bio-oil yield from biomass	High is +	🟩	🟩	🟨	🟨	🟨	🟩
Coke formation[e]	Low* is +	🟩	🟩	🟨	🟩	🟨	🟩
Blending ratio[d]	High is +	🟩	🟪	🟨	🟨	🟨	🟩
Oxygen	Low is +	🟩	🟪	🟨	🟨	🟨	🟩
Sulfur	Low is +	🟩	🟩	🟨	🟨	🟨	🟩
Nitrogen	Low is +	🟩	🟨	🟨	🟩	🟥	🟩
H/C ratio	High is +	🟩	🟥	🟩	🟨	🟩	🟩
EHI	High is +	🟩	🟥	🟩	🟥	🟨	🟨
MCR	Low is +	n.d.	🟥	🟨	🟥	🟨	🟩
Miscibility with fossil-based feed[f]	High* is +	🟩	🟥	🟨	🟩	🟨	🟩

[a] The cetane number describes the tendency of a fuel to undergo auto-ignition during compression. The oxygen content in lipids and acids results in a high cetane number when VO is co-processed, which is reflected in terms of higher alkene yields.[61] In addition to the increase in the cetane number, the *n*-paraffin content may increase, resulting in the appearance of a cloud point corresponding to diesel.[21] Pyrolysis oil exhibits poor ignition properties. Information on the cetane numbers of bio-oils is scarce in the literature, but it may be assumed that they tend to be low, in the range of 5 to 25, when compared to values greater than 40 for diesel and 47 for biodiesel.[67,68]

[b] The water content (moisture) in vegetable oil might not be an issue as oil refining includes a dehydration stage, which also eliminates some contaminants to produce refined oils, termed RBD (refined, bleached, and deodorized) oils.[69]

[c] The octane number is a spark-ignition engine characteristic used to characterize gasoline. This test is not appropriate for raw pyrolysis oils as it does not fulfill the requirements of high volatility, good stability, and miscibility with hydrocarbon, pH neutrality, and low deposited carbon among others.[70] However, it has been described that oxygenated components present in partially hydrotreated bio-oils have a positive impact on the cetane number due to the presence of 4-methyl anisole and other methyl aryl ethers.[71] The potential benefits of VO co-processing in the FCC include increased conversion, octane number, and oxidative stability.[13]

[d] Although VO has been tested in the FCC and HDT at different blending ratios up to 80%,[16] a maximum blending ratio of 10% is recommended for the HDT because at ratios greater than 15%, the liquid yield and sulfur removal decrease.[13] Processing 20% VO in the HDT increases the bromine and acid numbers to 8.4 g Br_2/100 g and 2.2 mg KOH/g, respectively.[21] Based on HTLO properties, co-processing with HTLO can be carried out at higher blending ratios than currently possible.[52] Studies with a 20% HDO blending ratio in the FCC resulted in similar gasoline yields and a slight increase in coke formation for bio-oils with an oxygen content of 17%–28%.[33,55,56] A blend with 10%–20% of FPOe in the FCC and HDT exhibited results similar to that of the reference case.[72] Although the bio-feedstocks considered for FCC are assumed to be at least partially deoxygenated, some studies used FPO without any treatment. The oxygen content of FPO was ~32%–38% (dry basis) as compared to HDO and CPO (~20%). Due to its high oxygen content, a low blending ratio is assumed. Recently, CPO has been used for FCC co-processing with blending ratios of 10%–20% to obtain results similar to those of the HDO. A 15% blending ratio results in an oxygen content of 22%[31] and results in a similar performance as pure VGO for gasoline production; this also resulted in a slight reduction in coke formation[35] as compared to HDO and CPO with similar oxygen content (21% and 27%, respectively) and 10% blending ratio. The results indicate higher gasoline production for CPO when compared to HDO and pure VGO. The overall yield of CPO-FCC is higher than that of HDO-FCC (30% and 24%, respectively). A pilot-scale riser[57] found similar yields with a 10%/90% CPO/VGO mixture when compared to 100% VGO. However, the researchers reported a threshold blending ratio of 15% due to blockage by coking. Another study used a demonstration-scale FCC unit and compared it with commercial-scale applications.[17] This study successfully used an FPO/VGO mixture with a maximum blending ratio of 10% and the authors observed similar yields of gasoline. However, a 20% mixture showed a significant drop in gasoline formation with an increase in coke formation. CO and CO_2 production were higher with FPO than with CPO and HDO. Case studies of FPO, HDO, and CPO were compared,[62] with similar oxygen content (~20%) at a blending ratio of 20%. In general, the gasoline yields were similar. However, there existed a relationship between coke formation and the MCR; in the case of VGO, a zero MCR was obtained. This suggests that this indicator helps in the evaluation of bio-feedstock suitability in FCC.[35] The overall yield of CPO-FCC was higher than that of HDO-FCC (30% and 24%, respectively). The low blending ratio during FCC co-processing (up to 20%) resulted in a decrease in the EHI but a reasonable level of internal hydrogen (for example, from the VGO) could be maintained to compensate for the low hydrogen content of the bio-oil.[52]

[e] The feedstock in the hydrotreatment process undergoes several reactions, including polymerization, which leads to coke formation, particularly with a catalyst based on alumina.[73] Non-hydrotreated FPO should not be processed because it might result in reactor plugging and high coke formation due to polymerization.[13] Co-processing HDO with FCC (28 wt.% of oxygen and 20% blending ratio) did not result in a significant increase in coke formation.[56] However, at the same blending ratio, a higher formation of coke was reported.[55] Vegetable oils are less prone to coking than thermochemical bio-oil. Co-processing VO in the FCC increased coke formation due to the polymerization of aromatics.[61] Co-processing CPO in the FCC resulted in a slightly lower coke formation when compared to the case with the HDO.[35] As data on the behavior of HTL co-processing are not widely available, minimal coke formation due to a low oxygen content and the possibility of fractional distillation of the crude oil are expected.[52] Blending FPO-E with VGO for co-processing in the FCC resulted in no significant increase in coke formation and the total conversion could be maintained at a constant level, even with a slight reduction in the heavy phase.[72] In general, after upgrading FPO, CPO and HTLO should result in the same coke formation based on their similar stoichiometry.

[f] Miscibility with petroleum has been described as poor for FPO and good for CPO (excellent for severe CPO).[74] Meanwhile, VO is entirely miscible, undergoes cracking easily, and the FCC conditions are severe enough to ensure the catalytic decomposition of triglycerides.[13] Slight immiscibility issues were found with HTLO during fractional distillation, which implies that it could be eliminated by mild deoxygenation.[75] Under FCC conditions, unlike FPO, CPO, and HDO experienced less immiscibility.[13] In the FCC, CPO and VGO exhibited good miscibility.[57]

*Compared to fossil-based feedstock.

n.a. Not applicable.

n.d. No data.

Table 4. Key characteristics of biomass use for co-processing in the case-study refinery.

	Unit[a]	Vegetable oil (VO)	Fast pyrolysis oil (FPO)[e]	Catalytic pyrolysis oil (CPO)	Hydrothermal liquefaction oil (HTLO)
Biomass (Bm)					
Type of biomass	–	Fresh fruit bunch (FFB-oil palm)	Wood	Beechwood	Wood
Energy content	MJ_{LHV}/kg	14.61	18.6	16.02	18.6
Cost	€/t $_{Bm}$	74.2[b]	62.6[d]	46.6[d]	67.8[d]
Carbon	(w%)		50.9[d]	48.4[g]	50.9[d]
Oxygen	(w%)		41.9[d]	45.7[g]	41.9[d]
Hydrogen	(w%)		6.1[d]	5.8[g]	6.1[d]
Bio-oil (Bo)					
Mass yield of oil	t $_{Bo}$ / t $_{Bm}$	0.204[c]	0.63[d]	0.259	0.38
Density	kg / L	0.88	1.2	1.1	1.1
Energy content	MJ_{LHV}/kg	37	16.9	29.1	27.4
Elemental composition					
Carbon	(w%)	77.6[f]	56.6	68.3	76.1
Oxygen	(w%)	10.4[f]	36.7	24.2	15.7
Hydrogen	(w%)	11.7[f]	6.6	7.5	7.9
Overall energy yield	MJ_{Bo}/MJ_{Bm}	0.52	0.57	0.45	0.56
References		11, 76–78	33, 79, 80	81	8

[a] The abbreviations Bm and Bo stand for biomass and bio-oil, respectively.
[b] Refers to the production cost of a tonne of fresh fruit bunch (FFB) in Colombia in 2016.[77]
[c] Based on the average oil extraction rate in Colombia for 2016. Oil extraction rate was calculated as the amount of vegetable oil extracted from 1 t of FFB.
[d] Based on dry biomass.
[e] For FPO,[82] estimated −0.854 k CO_2/kg FPO without land use change (direct + indirect).[80] estimated −1.15 to −1.64 kg CO_2/kg FPO including carbon absorption in crops.
[f] Based on soybean oil as described by Van Dyk, S. et. al.[11]
[g] Moisture and ash free as reported by Vasalos, IA. et. al.[81]

most accessible pathway to the blendstock. However, due to significant technical challenges, high capital costs, and low oil prices, this insertion point has failed to reach commercial maturity.[13]

The most promising pathways are described in Table 7.

In summary, co-processing bio-oils in a refinery is mainly restricted by their miscibility with fossil-based feedstock and, in processes strongly relying on elevated temperatures, by their low thermal stability. In this sense, bio-oils may be upgraded by removing oxygenated components (including organic acids), which are responsible for their immiscibility and low thermal stability. Furthermore, a low oxygen content in the fuels may improve the combustion process and lead to reduced soot formation.[96] Figure 5 depicts the most promising pathways for vegetable oil (VO), fast pyrolysis oil (FPO), catalytic pyrolysis oil (CPO), hydro-deoxygenated pyrolysis oil (HDO), and hydrothermal liquefaction oil (HTLO) co-processing in refineries.

TEA

The results of TEA for different pathways are presented in Table 8.

Mass and energy yields

Details of the process mass and energy data can be found in Appendix S1 in the supporting information. Table 9 presents the results corresponding to mass and energy yields, CO_2 emissions, and costs per processing stage for each pathway. For the chosen case study, it was estimated that ~2%–15% of the total fuel production (5.2 Mt/year) could be replaced by bio-oil co-processing, after taking into account the technical limitations of each pathway. These yields represent a biomass demand of ~0.5–5 Mt/year and the biofuel production varied from 33 to 116 gal of gasoline-equivalent per tonne of biomass. Co-processing of FPO in the FCC (PW6) and CPO in the HDT (PW7) resulted in the highest and lowest energy yields of 0.76 and 0.39, respectively, in the entire fuel

Table 5. General techno-economic input parameters used in this study.

Parameter	Unit	Value	References
Real discount rate[a]	%	12	40
Total plant cost[b]	% of PPC	130	45
Total capital requirement	% of TPC	110	45
Running time	Hours/year	8000	Own value
Calorific value			
Crude palm oil	MJ_{LHV}/kg	37.0	83
Diesel	MJ_{LHV}/kg	45.2	41
Gasoline	MJ_{LHV}/kg	46.0	41
Crude oil	MJ_{LHV}/kg	44.3	41
Natural gas	MJ_{LHV}/kg	52.2	41
Energy prices			
Hydrogen	$/Thousand scf	0.887	76
Natural gas	$/GJ	5.4	41
Electricity	$/kWh	0.12	76
Steam	$/t	9.5	76
Production cost – fossil fuel			
Finding + development	€/bbl	28.44	
Lifting	€/bbl	8.94	84
Transport	€/bbl	3.44	84
Refining	€/bbl	4.97	84
Dilution for transport	€/bbl	4.65	84
CO_2 emissions factor			
Natural gas	kg CO_2/GJ	56.6	41
Electricity (grid)	t CO_2 / MWh	0.21	85
Electricity (CHP)	t CO_2 / MWh	0.252	This study
Life cycle emission			
Hydrogen[c]	kg CO_2/t H_2	20.5	This study
Electricity (CHP)[d]	t CO_2/GWh	252	This study
Steam (CHP)	t CO_2/GWh	144	This study

[a] The interest rate has a significant influence on the economic analysis. This parameter is strongly influenced by the specific industry sector and the economic region. This study uses 12% as commonly used in Colombia by the state-owned oil company, which also reflects economic conditions for Latin America. A recent study by the IEA[86] uses 8% for the European oil refining industry.

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

[c] The CO_2 emission factor was calculated for the hydrogen production via SMR (steam methane reformer) in the Barrancabermeja's refinery.[87]

[d] 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 efficiency method suggested by the allocation guidance for the GHG protocol[88] and refinery energy production data.[40]

production cycle. The highest mass yield was obtained with PW6 (0.33) while the lowest was obtained in the vegetable oil co-processing route (0.09).

The high fuel-production efficiency of PW6 is due to the high oil yield obtained during the pyrolysis process (even though there is no evidence of a sharp increase in the fuel output from catalytic cracking). Furthermore, there is no clear evidence of a better yield by FCC or HDT co-processing. Instead, the mass and energy yields during co-processing seem correlated with the oxygen content in the bio-oil. The lower the oxygen content (due to deeper pre-upgrading), the higher is the mass yield obtained during co-processing, which is primarily related to the stoichiometry of the overall upgrading reaction. In contrast, the higher the oxygen content in the bio-oil, the greater is the chemical transformation needed. A high energy yield is therefore observed in PW6 (expressed per kg of fuel).

This study assumed a technical co-processing limit to maintain the current refinery performance; however, the gasoline and diesel yields of some routes were slightly affected. These changes were less than 6% of the total fuel output at specific RUs, which represented a change of less than 2% in the total fuel yield.

Table 6. Intensity of CO_2 emissions during fossil-fuel production from the refinery in Colombia.[42,89,90]

Stage	Gasoline ($g\ CO_2$ / MJ)	Diesel[a] ($g\ CO_2$ / MJ)
Oil extraction	1.88	1.83
Oil transport	0.92	0.79
Oil refining	7.09	7.02
Refined transport	0.068	0.068
Use	94.2	94.2
Well to tank (WTT)	9.96	9.71
Well to wheel (WTW)	104.2	103.9

[a] It should be noted that Martinez-Gonzalez *et al*.[42] assessed the LCA for two different quality diesel blends based on sulfur content (500 and 3000 ppm). The CO_2 emissions from 3000 ppm diesel were used in this study. Diesel with lower sulfur content requires additional hydro-treatment, leading to higher energy consumption and GHG emissions: 1.91, 0.76, and 10.43 g CO_2/MJ for production, transport, and refining, respectively.

CO_2 emissions

A breakdown of CO_2 emissions per unit of biofuel in each processing stage is shown in Fig. 6 and Table 9. PW6 (FPO to FCC) and PW7 (CPO to HDT) exhibited the lowest net CO_2 emissions of ~17 gCO_2/MJ for the entire lifecycle. Meanwhile, vegetable oil resulted in the highest emissions (70 gCO_2/MJ) in the technological conditions used. Ramirez et. al.,[83] estimated the lifecycle CO_2 emissions of the current and future technological scenarios for palm-oil production in Colombia. Future emissions are expected to be 40% less than the emissions in the current technological scenario. Next to vegetable oils, esterified fast pyrolysis oil (FPOe) showed the highest CO_2 emissions (56 gCO_2/MJ) for biofuel production. This is due to a high butanol consumption during the esterification process (even when using biobutanol) and in the case of PW8/B (FPOe to HDT) it is due to a high fossil fuel-based hydrogen consumption.

The results also highlight a key difference between the use of palm oil and thermochemical oil for co-processing. The latter is based on forestry residues which, can be assumed as to be a by-product with allocated emissions. Meanwhile, the former is a primary economic mass and energy component of the oil palm crop; almost all emissions are attributed to it during refining. Palm oil therefore contributes to a significant share of CO_2 emissions for the upstream biomass compared with other pathways.

Oil production represents the highest share (~85%) of CO_2 emissions per energy unit of biofuel, excluding the final use. Low mass and energy yields in the production stage are responsible for the high CO_2 intensity as it involves

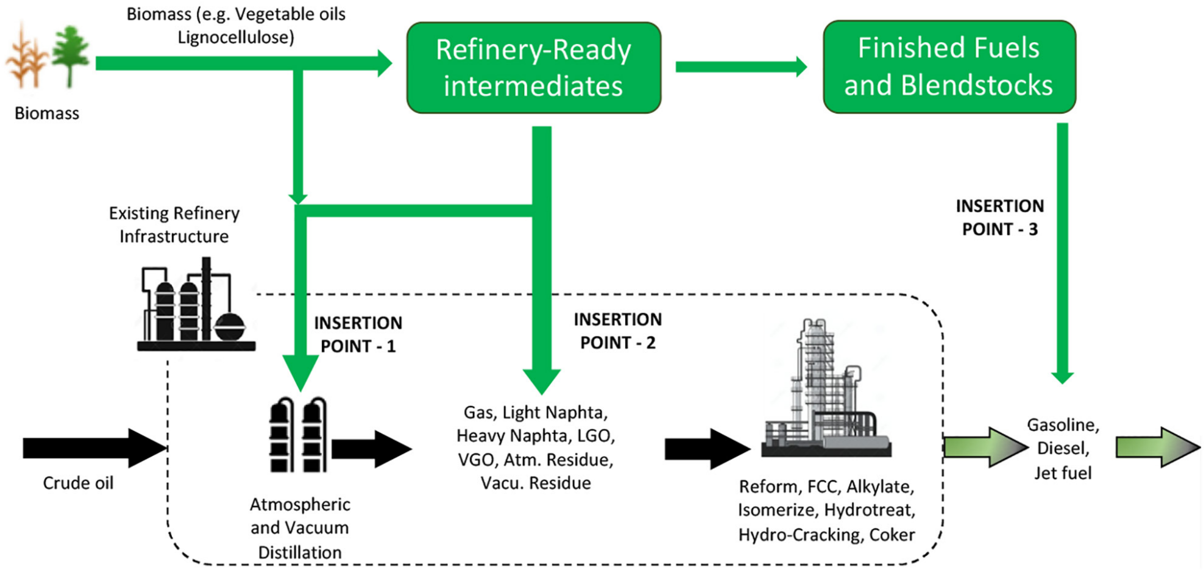

Figure 4. Potential insertion points for biomass co-processing in oil refineries, adapted from National Advanced Biofuels Consortium (NABC),[91] Van Dyk *et al*.,[13] and Pacific Northwest National Laboratory (PNNL).[59]

Table 7. Pathways (PW) for bio-oil co-processing in oil refineries.

Tier	PW	Bio-oil	RU	Notes
1	1	VO	HDT	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 commercialised [13]. Blending VO at levels higher than 15% reduces the efficiency of desulphurisation [16].
	2	VO	FCC	As there is no significant restriction to VO processing in the FCC, this route seems to be a successful co-processing alternative. Similar yields of gasoline and coke have been reported [13,63]. Still, there is some contradiction in terms of the yield of this process, which could be due to the setup of the experiment [13]. 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 carboxylic acids [16].
	3	VO-HDT	HCK	Reactions similar to hydrotreatment occur in the HCK but it is more sensitive to oxygen and impurities. This is a costly upgrading process as specialised catalysts may be needed but the products require less intensive downstream processing to reach the final specifications [13]. The HCK is recommended as a second step for bio-oil upgrading following stand-alone hydrotreatment. This process was described as the most promising and versatile process due to its flexibility and ability to control reactions [96].
2	4	CPO	FCC	CPO is partially deoxygenated when compared to other bio-oils and meets most of the parameters required for co-processing. Thus, CPO does not need pre-treatment before FCC processing [13]. However, oxygen removal results in higher viscosity, which makes pumping more difficult [13]. Lately, CPO has been used for FCC co-processing. Blending ratios of 10%–20% yield results similar to those obtained with the HDO. A 22% oxygen content [52] with a 15% blending ratio yielded results similar to those obtained with pure VGO for gasoline production but exhibited a slight reduction in coke formation. HDO and CPO of similar oxygen contents (21% and 27%, respectively) and 10% blending ratios were compared [35]. The results showed a higher gasoline production for CPO compared to HDO and pure VGO. Compared to VGO processing, the overall yield obtained with CPO-FCC is higher than that obtained with HDO-FCC (30% and 24%, respectively). A pilot-scale riser [59] exhibited similar yields for 10% CPO/VGO and 100% VGO. However, a threshold blending ratio of 15% was suggested to avert blockage by coking.
	5	HDO	FCC	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% [57,58,33]. Severe hydro-deoxygenation (HDO-HDT) represents the production of an almost finished drop-in fuel, and therefore, it is not a co-processing alternative to FCC [97].
	6	FPO	FCC	Some studies on co-processing FPO in the FCC indicated an increase in coking and reactor plugging, thus necessitating a partial removal of oxygen [23]. This may be due to the set-up of the experiment on a MAT, unlike a pilot-scale FCC, which led to different conclusions [13]. Nevertheless, recent studies [17,18], in which the set up was more similar to actual FCC conditions, showed that FPO (O_2: 50%) blending up to 10% with VGO is technically feasible and resulted in no significant changes in coke formation and gasoline yield. The drawbacks of this process included an increase in the pressure drop, apparently due to ageing of the bio-oil and increased production of alkyl phenols in gasoline and diesel. The FCC catalyst is tolerant to low levels of contaminants and medium-range oxygen levels. Besides, the catalyst is regenerated on-site, which makes catalyst regeneration less costly when compared to HDT or HCK catalysts.
	7	CPO	HDT	CPO is a good alternative co-processing route 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 [77].
	8	FPO-E	FCC/HDT	Process patented by Ecopetrol S.A. NC2016/0000689, NC2018/0000069
3	9	HTLO	FCC	Similar to CPO co-processing in the FCC, HTLO can be fed directly to the FCC without deoxygenation. In addition, the oxygen content of HTLO is lesser than that of CPO, which makes HTLO co-processing in the FCC more feasible when compared to CPO co-processing. Deoxygenated bio-oils decrease coke formation in the FCC as compared to fossil feeds [57,58]. It is a promising option for achieving higher blending ratios as the oxygen content is comparable (10%–20% [98]) to that of the feedstock used for co-processing in the FCC [53]. Experimental data are, however, currently not available [53].
	10	HTLO	HDT-VDU	HTLO is a promising, but less mature technology, bio-oil for co-processing route in the refinery due to its thermal stability and fractional separation characteristics. Nevertheless, mild hydro processing is required to remove oxygenated components [95]. Fractional distillation resulted in a 53% yield and equivalent fractions of gasoline (12%), diesel (25%), and jet fuel (16%) [99]. This bio-oil
4	11	VO	ADU	VO presents a good profile for most of the bio-oil parameters analysed. However, its low thermal stability and the possibility of spreading contaminants throughout the refinery hinder this option.
	12	FPO	HDT/HCK	FPO properties, such as a high acidity, water content, oxygen content, and immiscibility with fossil feed make this bio-oil unfit to be processed in the HDT or the HCK (Appendix; Table 8-1).

processing significant volumes of wet biomass and, in some cases, requires additional energy and hydrogen.

Carbon dioxide emissions from co-processing are the second-largest emissions (~8% of the total emissions). These emissions are mainly due to the intensive hydrogen consumption by the HDT to remove impurities and break double bonds as well as the CO_2 emitted due to carbon removal via coke regeneration and dry gas emissions from the FCC. None of the pathways assessed in this study considered CO_2 capture at the refinery, which may significantly reduce

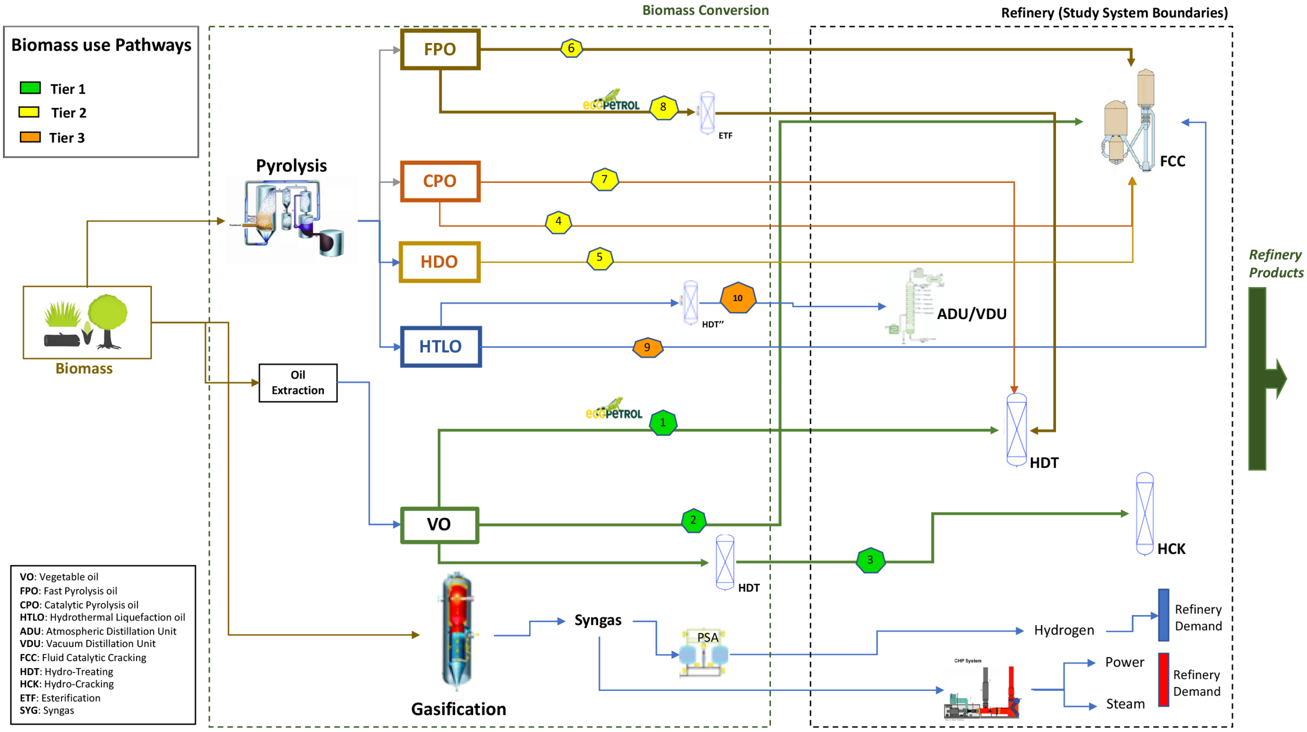

Figure 5. Technological routes for the potential use of biomass as feedstock in a refinery.

Table 8. Description of the pathways analyzed in this study.

Pathway (PW)	Route	Description
PW 1	VO to HDT	Vegetable oil (VO) to Hydrotreating units (HDT) – process reference 1 + current scenario for palm oil in Colombia
PW 1-A	VO to HDT	Vegetable oil (VO) to Hydrotreating units (HDT) – process reference 1 + future scenario for palm oil in Colombia
PW 1-B	VO to HDT	Vegetable oil (VO) to Hydrotreating units (HDT) – process reference 2 + current scenario for palm oil in Colombia
PW 1-C	VO to HDT	Vegetable oil (VO) to Hydrotreating units (HDT) – process reference 2 + future scenario for palm oil in Colombia
PW 2	VO to FCC	Vegetable oil (VO) to fluid catalytic cracking (FCC)
PW 4	CPO to FCC	Catalytic pyrolysis oil (CPO) to fluid catalytic cracking (FCC)
PW 5	HDO to FCC	Hydro-deoxygenated oil (HDO) to fluid catalytic cracking (FCC)
PW 6	FPO to FCC	Fast pyrolysis oil (FPO) to fluid catalytic cracking (FCC)
PW7	CPO to HDT	Catalytic pyrolysis oil (CPO) to fluid catalytic cracking (FCC)
PW 8-A	FPOe to FCC	Fast pyrolysis oil-esterified (FPOe) to fluid catalytic cracking (FCC)
PW 8-B	FPOe to HDT	Fast pyrolysis oil-esterified (FPOe) to hydrotreating unit (HDT)
PW9	HTLO to HDT	Hydrothermal-liquefaction oil (HTLO) to hydrotreating unit (HDT)
PW 15A	BG + FT (w/o CCS)	Biomass gasification (BG) + Fischer–Tropsch (FT) (without CO_2 storage) + upgrading

CO_2 emissions. As a reference, Hailey et. al.,[2] estimated a CO_2-reduction potential of 39%–94% using a post-combustion capture process during biofuel production via biomass gasification according to the Fischer–Tropsch reaction.

Compared to petroleum fuels, CO_2 emissions were reduced by 33% for VO co-processing in the HDT (PW1) to 83% for CPO in the HDT (PW7) and BG-FT fuels and 84% for FPO in the FCC (PW6) (see Fig. 9). The biomass gasfication to Fischer-Tropsch (BG-FT) pathway (PW15) showed a significant reduction in CO_2 emissions (expressed as a percentage of the carbon intensity, g CO_2 / GJ)compared to the fossil reference as this process was entirely thermal and H_2 self-sufficient; furthermore, the factors contributing

Table 9. Key indicators of bio-oil co-processing in the refinery.

Stage \ pathway	Description	Unit	PW 1 VO to HDT-P1[a,e] (current scenario for palm oil)	PW 1-A VO to HDT-P1[a,e,M] (future scenario for palm oil)	PW 1-B VO to HDT-P2[a,c] (current scenario for palm oil)	PW 1-C VO to HDT-P2[a,c] (future scenario for palm oil)	PW 2[k] VO to FCC	PW 4[k] CPO to FCC	PW 5[h,j] HDO to FCC	PW 6[h,k] FPO to FCC	PW7 CPO to HDT	PW 8-A[k, l, n] FPOe to FCC	PW 8-B[l, n] FPOe to HDT	PW9[p] HTLO to HDT	PW 15A[o] BG + FT (w/o capture)
Technical co-processing limit		%w	5%	5%	5%	5%	30%	10%	20%	10%	30%	20%	20%	15%	15%
Photosynthesis	CO_2 emissions	kg CO_2 / GJ fuel	−86.95	−86.95	−86.95	−86.95	−102.50	−224.57	−231.14	−123.38	−236.87	−196.20	−176.01	−145.72	−181.57
Upstream biomass	CO_2 emissions	kg CO_2 / GJ fuel	28.31	23.08	28.31	23.08	33.38	5.81	2.24	1.19	6.13	1.90	1.70	1.31	7.08
Bio-oil production	Energy content														
	Biomass	MJ HHV / kg	14.6	14.6	14.6	14.6	14.6	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
	Bio-oil	MJ / kg	37.0	37.0	37.0	37.0	37.0	29.5	31.3	16.8	29.5	29.6	29.6	35.2	n.a.
	Yield														
	Mass	kg oil / kg biomass	0.20	0.20	0.20	0.20	0.20	0.26	0.27	0.56	0.26	0.39	0.39	0.38	n.a.
	Energy	MJ oil / MJ biomass	0.52	0.52	0.52	0.52	0.52	0.38	0.42	0.47	0.38	0.52	0.52	0.66	n.a.
	Production cost	€ / GJ	€ 15.5	€ 15.5	€ 15.5	€ 15.5	€ 18.3	€ 16.5	€ 24.7	€ 5.2	€ 13.7	€ 24.8	€ 20.5	€ 12.7	n.a.
	CO_2 emissions	kg CO_2 / GJ	23	3	23	3	27	139	149	37	147	127	114	82	99
Bio-oil co-processing	Yield														
	Mass	kg bio-fuel / kg bio-oil	0.79	0.79	0.79	0.79	0.47	0.70	0.43	0.59	0.85	0.60	0.67	0.69	0.24
	Energy	MJ bio-fuel / MJ bio-oil	0.94	0.94	0.94	0.94	0.79	1.09	0.96	1.60	1.03	0.92	1.03	0.97	n.a.
	Production cost	€ / GJ	€ 12.6	€ 12.6	€ 15.5	€ 15.5	€ 4.2	€ 11.5	€ 6.1	€ 12.0	€ 7.6	€ 5.8	€ 4.2	€ 8.0	€ 12.6
	CO_2 emissions	kg CO_2 / GJ	5.4	5.4	10.4	10.4	11.3	11.7	7.0	7.8	6.9	8.2	22.1	n.a	n.a
Total biofuel production	Overall energy yield	MJ bio-fuel / MJ biomass	0.48	0.48	0.48	0.48	0.41	0.42	0.40	0.76	0.39	0.48	0.53	0.64	0.51
	Biofuel cost[b,i]	€ / GJ	€ 29	€ 29	€ 31	€ 31	€ 23	€ 28	€ 31	€ 17	€ 22	€ 31	€ 25	€ 21	€ 19
	Biofuel-net CO_2 emissions[d,q]	kg CO_2 / GJ fuel	65	39	70	44	64	27	22	17	37	35	56	32	19
	CO_2 avoided cost[g] (at 8.8€/GJ fossil fuel cost[f])	€ / t CO_2	€ 497	€ 302	€ 651	€ 375	€ 351	€ 252	€ 272	€ 99	€ 188	€ 321	€ 337	€ 169	€ 124
	CO_2 avoided cost[g] (at 15€/GJ fossil fuel[f])	€ / t CO_2	€ 328	€ 199	€ 458	€ 263	€ 184	€ 165	€ 191	€ 22	€ 87	€ 224	€ 198	€ 76	€ 45
	Avoided CO_2[f]	kt CO_2 / year	237	381	210	353	922	646	1300	695	2335	1172	1138	2544	2988
	TCR	k€ per bbl/day capacity	k€ 157	k€ 157	k€ 157	k€ 157	k€ 44	k€ 121	k€ 64	k€ 127	k€ 26	k€ 61	k€ 39	k€ 24	k€ 155

[a] VO co-processing in the HDT would require further (P1) or slight (P2) process modifications. Palm-oil production was considered under two scenarios, as described by Ramirez *et al.*[83] – (1) the current scenario and (2) a future scenario with a production chain optimized to reduce GHG emissions.

[b] The upfront investment in the RUs required for co-processing was based on the capacity addition cost for a refinery, as reported by the IEA.[103] Retrofitting cost was assumed to be 50% of the capacity addition cost in a refinery. Capital investment was estimated at 17.2 k€/bbl of capacity.

[c] Vegetable oil co-processing in the HDT for P2 might require a very low upfront investment of $€_{2018}$ 1.2 M€. For this investment, co-processing and biofuel-production costs were estimated at 1.3 and 17.2 €/GJ, respectively, for both scenarios (current and future). The CO_2-avoided cost was estimated at 242 and 139 €/tCO_2, respectively, for the current and future scenarios of palm-oil production. It should be noted that in addition to diesel production, there is a slight increase in the light naphtha fraction. This additional yield (~22.6 kg per t of biofuel produced[104]) could potentially increase the dry gas and gasoline output. These changes could affect mass flow and CO_2 emissions downstream of the top-side of the hydrotreatment unit. However, this additional yield was not included in this study.

[d] Carbon dioxide emissions were calculated from the CO_2 produced by decarboxylation reactions and hydrogen consumed during hydrotreatment. Emissions from additional energy consumption were not considered as hydrotreatment reactions are exothermic and produce heat proportional to the hydrogen consumed for oxygen removal.[13] The CO_2 emission factors for hydrogen production and co-processing of vegetable oil in the hydrotreating process were calculated as 20.5 kg CO_2/t H_2 and 67.8 kg CO_2/t biofuel, respectively. The emission factor for hydrogen production was calculated using direct and indirect CO_2 emissions (according to the guidelines of ISO 14064)[87] for yearly processing operations by the hydrogen-production units in the refinery.

[e] Process conditions of P2 include additional consumption of electricity, natural gas, and steam when compared to process P1. The CO_2 emissions are listed in the supplementary material.

[f] The fossil-fuel-production cost considered the following stages – finding and development, production, transport, and refining for Colombian conditions. See the supplementary material

[g] Carbon dioxide emissions from fossil fuels were taken from a LCA of the production of gasoline and diesel in Colombia,[42] which included production, transportation, and refining of crude oil. See Table 6.

[h] The TCR was calculated as suggested by the Pacific Northwest National Laboratory (PNNL) report[79] and was based on the estimation of direct and indirect costs. The latter were assumed to be 60% of the indirect cost, which corresponds to the total installed equipment cost. Direct costs included building, piping, and site-development costs, which are estimated as a percentage of the equipment cost, (4%, 4.5%, and 10%, respectively). Opex was calculated as 15% of the TCR, which included the cost of the feedstock and handling, natural gas, electricity and utilities, fixed cost, and waste disposal. The cost of bio-oil transport to the refinery was based on current crude palm-oil transport in Colombia[105] and was estimated as 0.4 €/GJ (see appendix 8.10).

[i] The same transport cost was used for each bio-oil-production pathway. This cost was based on the average transportation cost in oil-palm plantations in Colombia (0.4 €/GJ).[77,105]

[j] It was assumed that the CH_4 co-produced during oil production and upgrading was burnt before being released to the atmosphere.

[k] Only two of the four existing FCC units at the refinery were considered suitable for the co-processing of bio-oils, given their performance and process stability. This assumption implies lower bio-gasoline production as these units process only 61% of the total cracking throughput. It was assumed that 15% of diesel production from the refinery can be attributed to the diesel-range fraction produced in the FCC.

[l] The biomass used for PW8A/B was empty fruit bunch (EFB), a biomass residue produced during palm-oil extraction.

[m] Ramirez *et al.*[83] assumed a future scenario with 'zero' emissions from palm-oil-mill effluents (POME). However, CO_2 emissions do occur from the CH_4 released during effluent treatment. These emissions were included in this study and account for 2.3 gCO_2/MJ.

[n] Biofuels produced by the PW8A/B routes require a significant amount of butanol for oil esterification (0.36 kg butanol/kg FPOe), which increases production costs and CO_2 emissions. The cost is partially offset by the price of the by-products (char and butyl acetate) of the esterification process. For instance, butanol-associated CO_2 emissions represent ~68% of the net CO_2 emissions from PW8B.

[o] The total amount of BG-FT biofuels produced was set as the maximum volume produced by other co-processing pathways, which is PW7 in this study.

[p] Carbon dioxide emissions reported for oil production include upgrading (1.78 gCO_2/MJ) as there is no co-processing stage in this route.

[q] Carbon dioxide emissions for the upstream biomass were considered.

to emissions during production and co-processing were eliminated in this pathway. In a scenario where fuel is exported to EU, biofuel transport must meet a GHG-saving threshold of at least 65% as mandated by RED II (Renewable Energy Directive – Recast to 2030 (RED II) issued by the European Commission and enforced in December 2018, https://ec.europa.eu/jrc/en/jec/renewable-energy-recast-2030-red-ii). This requirement implies that the majority of co-processing pathways-based biofuels assessed in this study would meet the prescribed regulations, except for those produced via co-processing of VO and esterified FPO.

Van Dyk *et al.*[8] carried out a comparison LCA using the GENIUS model for the production of biojet fuels using FPO, CPO and HTLO as bio feedstock, evaluating two different upgrading methods. Results show reductions from 51% to 74% and from 5.4% to −2.6% when a dedicated hydroprocessing and fossil-blend hydrotreatment, respectively, are used. The low reduction of the latter was related to GHG emissions associated with the use of additives for improving miscibility and viscosity. Previous work[97] found reductions for the HTLO in a range from 66 to 69% and for the FPO between 46 to 65%. Tzanetis *et al.*[98] using SimaPro, estimated an 85% reduction for the allocated GHG emissions for the production of HTLO-based bio-jet fuel. In a related work, a 61% reduction for HTLO and 54% for FPO were reported, while other work claimed a 68–76% when using FPO. A study using the Greenhouse gases, Regulated Emissions, and Energy use in Technologies (GREET) model or SimaPRO, estimated reductions between 59–62% when looking at the pyrolysis oil from logging residues. Connor[99] report a 43% reduction for gasoline production using pyrolysis oil and 70% for HTLO-based diesel production. Similarly, The National Renewable Energy Laboratory (NREL) report,[100] found a 53% reduction in GHG emissions for the pyrolysis fuels compare to gasoline GHG emissions in 2005 using GREET data. Dupuis *et al.*[101] assessed five types of biomass which were gasified and reformed at a TRL 3–5 study to produce gasoline. LCA results using the GREET model show reduction between 79% for the switchgrass to 90% for the forest residues.

Based on these results, it seems that CO_2 mitigation potential would be slightly higher for the assessed co-processing pathways. It should be note that none of previous studies evaluated biofuel production throughout co-processing at the refinery. Instead, considered dedicated hydrotreatment facilities for the upgrading of bio-oils to produce drop-in biofuels. Nevertheless, as described by Van Dyk *et al.*,[8] several factors can have a strong influence on the estimation of the CO_2 reduction potential from the geographical location, type of feedstock, supply chain, source of electricity to LCA process design, co-products allocation, and source of hydrogen.

Economics

A breakdown of the levelized production cost of biofuels is provided in Fig. 7. The cost includes different stages of the bio-oil production process (including biomass cost), transport, and co-processing at the refinery. The lowest production cost was obtained with PW6 (FPO to FCC); 17

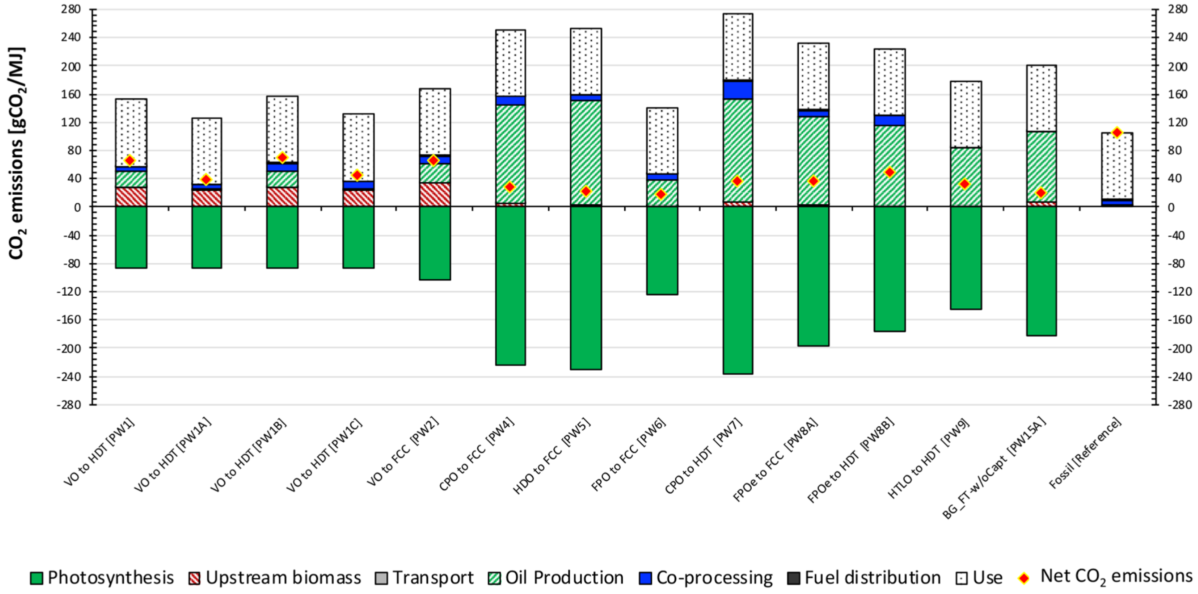

Figure 6. Breakdown of CO_2 emissions in different biofuel-production pathways with respect to a fossil-fuel reference.

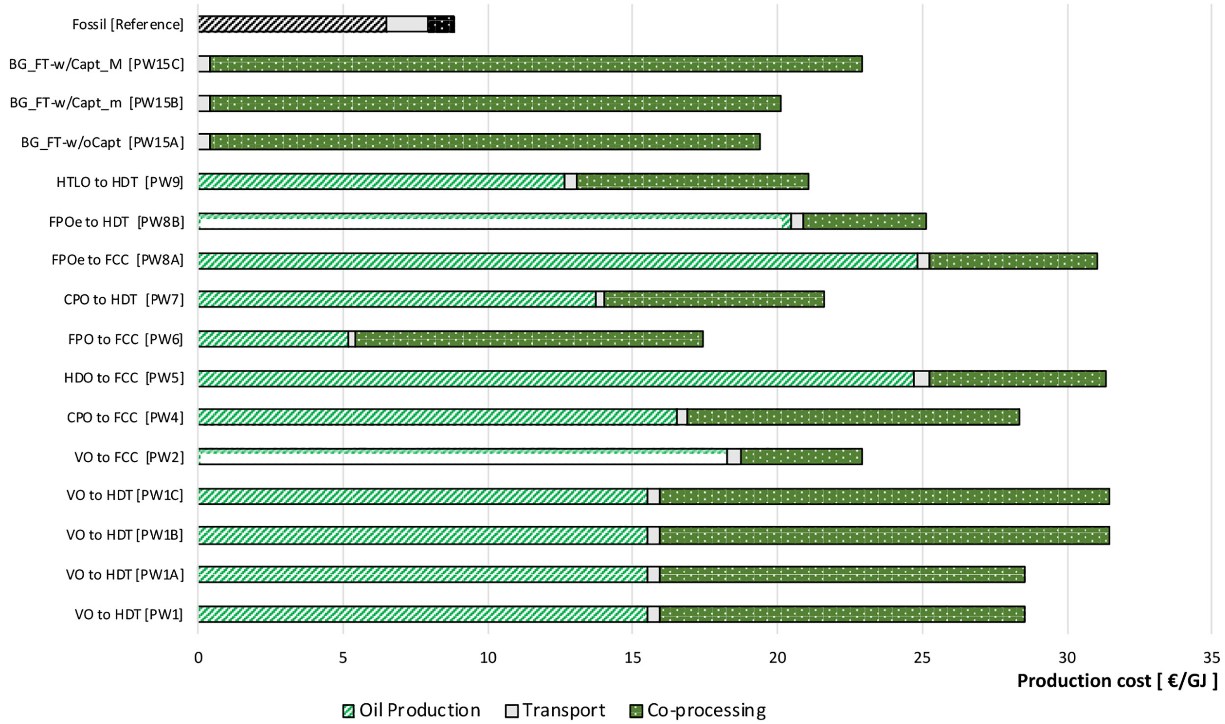

Figure 7. Biofuel-production cost compared to a fossil-fuel reference using different bio-oil co-processing pathways. *In the total production cost of the reference fossil fuel value-chain, co-processing represents the refining stage. Transport cost includes a dilution cost with naphtha (0.8 €/GJ).[84]

€/GJ), followed closely by PW7 and PW2 with ~22 €/GJ (to convert production cost from $€_{2018}$ /GJ to $US\$_{2018}$ /bbl-eq multiply by 6.77.). The highest costs were observed for PW1 (VO to HDT), PW5, and PW8 with a value of ~31 €/GJ. Interestingly, VO co-processing by FCC is less costly than hydrotreatment, as the latter leads to a high level of hydrogen consumption.

The cost of thermochemical oil production (except for HTLO) is higher than that of vegetable oils due to the lower energy yield during pre-treatment. However, the cost of co-processing thermochemical oils at the refinery is lower, due to their higher energy efficiency and co-processing limits. Thermochemical routes involve capital-intensive processes with catalytic reactions and high investments due to the inclusion of high-pressure reactors and high temperatures. Furthermore, these processes inherently contain high variable costs due to catalyst and hydrogen consumption.

The results indicate a significantly higher cost of oil production (up to five times) when compared with co-processing, with the exception of vegetable oils, in which case the costs were similar. Interestingly, PW6 showed the opposite relation, i.e., the cost of co-processing was higher than the cost of bio-oil production. This is because, unlike other routes, PW6 uses a raw pyrolysis oil (i.e., without upgrading). Critical chemical transformation is carried out during co-processing, resulting in a large energy transformation, which generates a high specific cost per unit of energy in the final fuel.

The cost of biofuel production would account for 10% to 50% of the cost of the final blended fuel, depending on the technical co-processing limits, bio-oil, and co-processing pathway. As described by Zacher *et al.*,[102] reducing biofuel-production cost is possible by improving the catalyst lifetime for both the activity and support stability.

The cost and potential of CO_2 avoided (defined as CO_2 emissions avoided by biofuels from bio-oil co-processing pathways compared to the total CO_2 emissions from the refinery) in each pathway is presented in Fig. 8. PW6, PW15A, and PW7 showed the lowest CO_2-avoidance cost of 99, 124, and 147 €/t CO_2, respectively. However, PW7 and PW15A showed the highest amount of CO_2 avoided as they produced the largest amount of biofuel and, consequently, their (relative) carbon footprint was low (~83% reduction compared to fossil fuel). Co-processing with vegetable oils resulted in the highest avoidance cost and the lowest amount of CO_2 avoided. Such low performance may be attributed to the high co-processing cost of this route due to hydrogen consumption, lower energy yield, and low co-processing

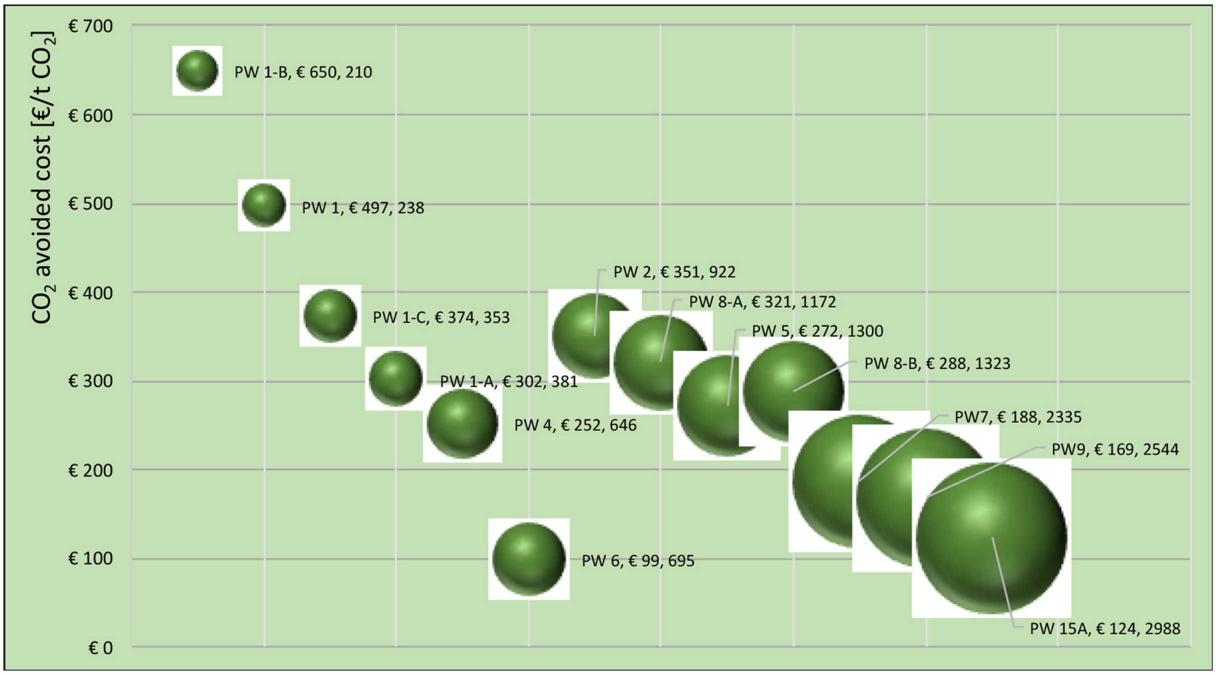

Figure 8. Potential amount of CO_2 avoided (kt/year) and CO_2-avoidance cost (€/t CO_2) for each of the assessed bio-oil CO-processing routes. The larger the circle, the higher is the CO_2 avoided potential.

limit. The TcPL for co-processing VO is constrained by the risk of low sulfur removal, acidity, higher H_2 pressures and catalyst deactivation.

The cost of CO_2 avoided depends on the production costs of bio and fossil fuels, as well as their carbon footprints. The low costs of co-processing CPO in the HDT (PW7) and CO_2 avoided can be ascribed to two main factors – the low hydrogen consumption driven primarily by the low oxygen content of the CPO and the high technical co-processing limit that allows the feeding of large amounts of bio-oils with better miscibility, acidity, and improved thermal stability.

Because all bio-oils are competing for the same RUs, it is not viable to estimate a combined potential of CO_2 avoided for all co-processing pathways. However, theoretically, it might be possible to combine some routes that use different processing units (FCC and HDT) and even a BG_FT unit, considering the least performance disturbance for each unit. This strategy would increase the amount of biofuel produced and reduce CO_2 emissions from the refinery.

The total CO_2 emissions avoided, specific biofuel emissions, and biofuel production costs are shown in Fig. 9. The emissions avoided are presented as a percentage of the total CO_2 emissions from the refinery. Biofuel emissions are expressed as a percentage of the reference fossil fuel. As for the production cost, fossil cost is reported as a percentage of the biofuel-production cost. This means that the higher the percentage of any category in the figure, the better is the pathway is for bio-oil co-processing.

Lower biofuel emissions do not necessarily mean a higher amount of CO_2 avoided. Co-processing vegetable oil reduces CO_2 emissions by less than 60%, while thermochemical routes cut emissions by 70%–84%, as compared with fossil-fuel processing. Nevertheless, there are some thermochemical options such as CPO to FCC, HDO to FCC, FPO to FCC, FPO_e to FCC, and FPO_e to HDT with a low percentage of avoided CO_2 emissions at the refinery, despite reporting a high reduction in CO_2 emissions compared to the reference fossil fuel. In contrast, other routes, such as CPO to HDT, HTLO to HDT, and BG_FT, result in a large reduction in CO_2 emissions when compared to the fossil fuel, as well as large amounts of CO_2 avoided in the refinery.

Co-processing of FPO in the FCC led to the lowest production cost followed by BG_FT-based biofuels, hydrothermal liquefaction, and CPO co-processing by FCC. Nevertheless, the production cost of BG_FT and HTLO biofuels was strongly influenced in our study by the assumed fuel-production scale. The mass and energy yield results indicate that PW6 (FPO to FCC) exhibited the highest efficiency, while CPO and VGO hydrotreating showed the lowest performance for this criterion. Regarding the total mitigation potential compared to the current CO_2 emissions from the refinery, co-processing CPO in the hydrotreating

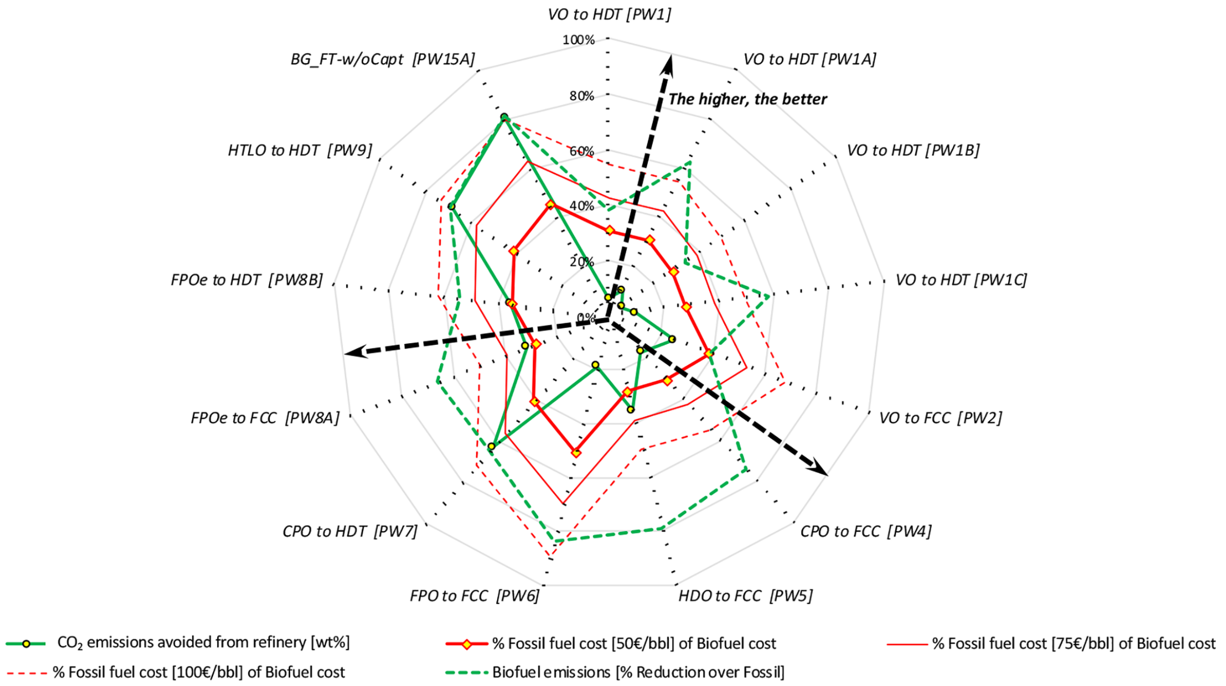

Figure 9. Percentage of CO_2 emissions avoided at the refinery and relative changes in biofuel emissions and production cost compared to fossil-fuel production. The higher the percentage of the category, the better is the CO-processing pathway compare to the fossil reference.

units (PW7) showed a higher CO_2 reduction potential, mainly due to its largest co-processing limits. In contrast, PW6 showed a reduced mitigation potential despite its low carbon footprint compared to fossil fuel, which might be attributed to its low feeding ratio in the FCC.

There are several pathways, such as FPO to FCC, CPO to HDT, HTLO to HDT, and BG_FT, which exhibit superior performance in most of the categories analyzed. These pathways include FCC, HDT, and a stand-alone process. This indicates that there is no specific suitable co-processing unit at the refinery. Co-processing FPO in the FCC (PW6) yields considerable advantages due to its very high mass and energy yield; further, raw FPO can be fed to the FCC unit without any upgrading, as described by Pinho *et al.*[17] This reduces the bio-oil co-processing cost and CO_2 emissions associated with the upgrading process. Nevertheless, the technical co-processing limit is low due to the miscibility and oxygen-content characteristics of the bio-oil. These parameters affect catalyst activity by promoting coke deposition, and influence energy balance in the cracking catalytic unit by inducing coke regeneration and decreasing gasoline yield.

In contrast, vegetable oil co-processing (PW1 and 2) showed the lowest performance in most of the categories except for energy yield. Although the energy yield reported for co-processing vegetable oil in the HDT is not poor, its low technical co-processing limit and high CO_2 emissions along the oil-production chain are responsible for its poor CO_2-mitigation performance. The use of fertilizer and wastewater-treatment processes contribute to the very high CO_2 emissions during bio-oil production and co-processing. This study considered palm oil, which is the principal economic energy and mass component of the fruit of oil palms, to analyze the co-processing of vegetable oil. All emissions from the crop activity are therefore allocated to palm oil in contrast to thermochemical pathways based on forestry residues (where no emissions are allocated to the residue).

Figure 10 shows the results of a sensitivity analysis of the CO_2-avoided cost with respect to the fossil- fuel price in key co-processing pathways. The analysis considered three cases: The highest CO_2-avoided cost (PW8A), the lowest CO_2-avoided cost (PW6), and the highest amount of CO_2 avoided (PW7). Negative CO_2-avoidance costs, which are economically the most attractive options, were obtained with fossil-oil prices higher than 18 €/GJ for the pathway with the lowest CO_2-avoidance cost (PW6). It must be noted that the crude oil price in the last 10 years has reached a top average monthly price of around 16 €/GJ (i.e., 110 $/bbl) with a maximum daily peak of around 23 €/GJ (i.e., 160 $/bbl) with a decreasing trend in the same period. The IEA[1] estimated a maximum crude oil price under current policies

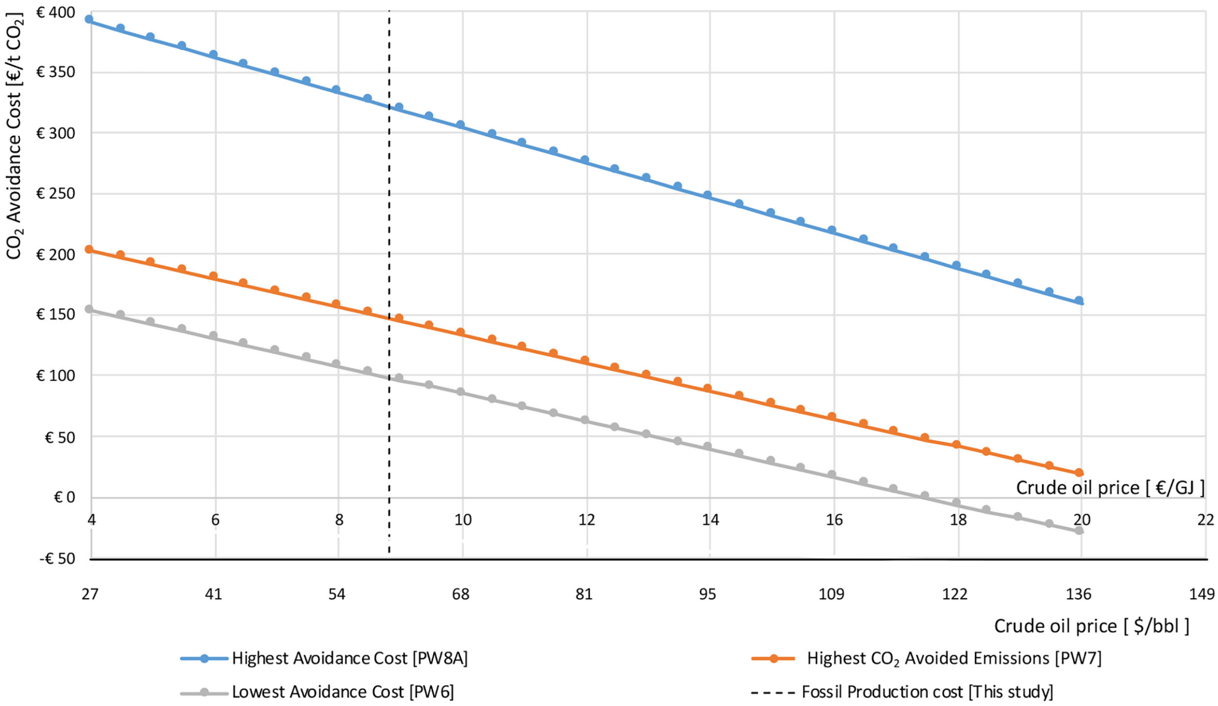

Figure 10. Sensitivity analysis of CO_2-avoidance cost versus fossil-fuel-production cost.

scenarios of 19.8 €/GJ (134 $/bbl) and with stated policies of 15.2 €/GJ (103$/bbl) by 2040. This means biofuel production by co-processing hardly reaches a break-even point when compared with the crude oil price unless a CO_2 credit is introduced.

Discussion

Based on the results described in the previous section, we identified five main points of discussion. First, estimates of biofuel production and mitigation costs involve a high degree of uncertainty, especially for pathways with low-yielding and early development-stage technologies. Although critical techno-economic data underlying bio-oil production can be sourced from key reference studies, co-processing costs are not tailored to specific process units in a refinery. As detailed data on investment costs for co-processing are not available, costs were derived from a specific investment for retrofitting. However, this estimation yields results within the range of production costs expected in the literature for biofuel production. More detailed data are needed on investment costs for retrofitting a specific process unit for bio-oil co-processing to further understand the potential of individual options.

A second limitation concerns several factors that affect the CO_2 emissions estimated for biomass production. This study assumed that biomass is produced under sustainable conditions. This is an important assumption as the contribution of photosynthesis, biomass type, yield, indirect land-use, and agro-ecological conditions might significantly affect the performance of biofuels in reducing CO_2 emissions.

Third, some parameters related to refinery performance, such as catalyst deactivation, removal of sulfur and nitrogen, and content of phenols and aromatics in the final biofuel, are uncertain. In particular, the long-term effects of co-processing are still being evaluated at the TRL 3–5 level and further TRL reproducibility should be investigated.

The fourth limitation is related to data availability as the majority of the pathways included in this study were not evaluated at a commercial scale except for PW1B/C. Most of the information used comes from research studies at TRL 3–5, except for PW6 (from a pilot plant simulating real conditions). Most lab tests on FCC co-processing are based on microactivity test (MAT), which do not fully represent the actual performance in a refinery in terms of coke deposition and gasoline yield.[11] The technical options currently being evaluated at a theoretical TRL 3–5 level should also be evaluated at larger scales. As technologies move along the TRL level, such evaluation would allow a more accurate estimate of the performance of co-processing routes and biofuel-production costs.

Fifth, neither the availability of biomass nor logistic constraints were considered in this study. As described by Hailey *et al.*[2] a maximum biomass load of ~1 Mt/year may be brought to a single plant site due to transportation constraints, which needs to be explored in more detail to account for the local conditions around the refinery. The impact of these aspects, in addition to emissions from land use change (LUC), on the net CO_2-mitigation potential of each route should be included in future research.

The cost of CO_2 capture at a large-capacity high-conversion refinery is in the range of 45–167 €/t CO_2.[45] Meanwhile, in a medium-capacity and conversion-level refinery,[106] similar to the one considered in this study, the cost was 130–200 €/t CO_2, which is within the cost range for pathways with the highest CO_2 avoidance potential. Berghout *et al.*[45] reported a CO_2-avoidance cost of 41–65 €/t CO_2 for BG-FT fuels, which is lesser than our reported value of 124 €/t CO_2. This difference might be attributed to the oil price assumed (we assumed an oil price of 8.8 €/GJ while Berghout *et al.*[45] used a price of 16 €/GJ).

Finally, as described by Van Dyk *et al.*,[13] specific bio-oil co-processing routes are strongly dependent on refinery configuration, the final product required, bio-feed characteristics, crude oil assays, and process-unit conversion. Ideally, the co-processing of bio-oils should be carried out with the least degree of bio-oil upgrading. This approach would reduce co-processing costs and mass losses due to process inefficiencies. However, difficulties such as miscibility with fossil streams, acidity, coke formation, polymerization, and catalyst deactivation, require improvement in bio-oil properties. A better option would be to produce bio-oils with properties similar to those of the crude oil. This seems to be the case with HTLO, as described by Jensen *et al.*[36,95] However, the inhomogeneous distribution of impurities in the bio-crude (unlike the homogeneous distribution in crude oil) presents new technical challenges that should be overcome.

Conclusions

In this study, the potential of bio-oil co-processing to reduce CO_2 emissions from existing refineries was analyzed. Thirteen co-processing pathways for vegetable oils, thermochemical bio-oil (FPO, CPO, and HTLO), and Fischer–Tropsch fuels, were evaluated. None of the paths selected for this study included CO_2 capture. Several important conclusions can be drawn from the analysis.

Among the co-processing options evaluated, it was not possible to determine a clear and unique winner. The choice depends on the criteria used (energy and mass yield, cost, CO_2 emissions, and CO_2 avoided) and the target of co-processing (mitigation, volume, and blending policy). For instance, in a biomass-scarcity scenario, biofuel co-processing pathways with higher yield might be valuable whereas in an abundant-biomass scenario, a high CO_2-mitigation potential might be the target.

Bio-oil co-processing would accelerate the transition of refineries towards the production of more sustainable fuels. In the case study chosen, up to 15% of fossil fuel could be replaced by bio-oil co-processing. This threshold was defined by technical co-processing limits based on modifications in the operational conditions and additional infrastructure. Biofuels reduced CO_2 emissions by 33%–84% compared to pure equivalent fossil fuels (i.e., gasoline and diesel). The bio-oil co-processing pathways analyzed in this study can reduce CO_2 emissions by 6%–81% for the case-study refinery. The overall mass yield for biofuel production ranged from 9% (vegetable oils) to 33% (FPO co-processed in FCC). Thermochemical bio-oils resulted in yield in the range of 12%–33%. These results agree with the yields reported by Van Dyk *et al.*[8] for jet-fuel production using FPO, CPO, and HTLO (21%–37%). The same study reported a GHG reduction of 74%, whereas, in our study, thermochemical bio-oils resulted in a GHG reduction of 46%–84%.

Biofuel-production costs were estimated at 17–31 €/GJ. Recently, Van Dyk *et al.*[7] reviewed the production costs of biofuels using thermochemical oils and reported costs of 17–42 €/GJ (adjusted to $€_{2018}$). Our findings are also consistent with the production costs reported by Maniatis *et al.*[107] regarding the hydrotreatment of vegetable oils and FT fuels (14–25 and 25–39 €/GJ, respectively).

Based on a conservative capital-cost estimate for refinery co-processing, the final blended fuel production cost would increase by 10%–50%, depending on the technical limits of co-processing.

The cost of CO_2 avoidance may vary from 99–651 €/t CO_2. In pathways with the highest potential for avoided CO_2 (PW5, 7, 8, 9, and 15), the cost varied in the range of 124–337 €/t CO_2. Avoided CO_2 costs for bio-oil co-processing are relatively close to those reported for CO_2 capture in a refinery.

Routes PW6, 7, 9, and 15 showed the highest potential for mitigating emissions from the refinery. Co-processing HTLO in the HDT (PW9) and FPO in the FCC (PW6) led to the highest CO_2 avoidance (69% of refinery CO_2 emissions) and reduction in CO_2 emissions (84% compared to the fossil fuel), respectively. Moreover, these routes showed good performance for criteria such as production cost and energy and mass yields. Co-processing with vegetable oils resulted in the lowest overall performance among the options that were evaluated.

Further investigation and scaling up should be conducted on the selected key co-processing routes. Such research should focus on providing more accurate information on the yield, costs, and quality of fuels produced. Their impact on the performance of other RUs and downstream petrochemical processes should also be analyzed. Better quality fuels may be produced by bio-oil co-processing, which would otherwise require additional investment for further refining of crude oil.

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