Assessing bio-oil co-processing routes as CO₂ mitigation strategies in oil refineries

Édgar Yáñez, Hans Meerman, Andrea Ramírez, Édgar Castillo, André Faaij

Received June 10 2020; Revised September 16 2020; Accepted October 01 2020; View online November 28, 2020 at Wiley Online Library (wileyonlinelibrary.com); DOI: 10.1002/bbb.2163; Biofuels, Bioprod. Bioref. 15:305–333 (2021)

Abstract: The oil industry needs to reduce CO₂ 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 CO₂ 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 CO₂ 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 CO₂ avoidance (69% of refinery CO₂ emissions) and reduction in CO₂ emissions (84% compared to fossil fuel), respectively. The cost of CO₂ emissions avoided for all of the assessed routes was in the range of 99–651 per tCO₂. © 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.
Key words: oil industry; biomass; CO₂ 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’ CO₂ 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 CO₂ emissions.¹³ 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.⁷ 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 CO₂ 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 CO₂ 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

Faaij⁶ 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 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 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 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

¹INDC: Intended Nationally Determined Contributions. https://www4.unfccc.int/sites/submissions/indc/Submission%20Pages/submissions.aspx.
²The 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 (HTD) 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. Its greatest strength is based on the flexibility to manage different bio-feedstocks without compromising the quality of the biofuel. 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.

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. Results from Pinho et al. 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., 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. and kinetics and energy balance in fluid catalytic cracking (FCC) by Cruz et al., which did not include operating conditions, type of catalyst, and blending ration in the analysis. Sabawi et al. 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. focused their research on co-processing in FCC for bio-oils prepared in different ways. Even more recently, Bhatt et al. examined air emission changes due to raw bio-oil co-processing in FCC from existing refineries, and Wu et al. 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. focus on analyzing the co-processing of bio feedstock with petroleum fractions in both HTD and FCC, considering different potential feedstocks, catalysts, operating conditions, products, and benefits presenting a general technological analysis. Concawe 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), 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 technoeconomic analysis (TEA) of the co-processing alternatives. As stated by the IEA, the next step for the promotion and use of drop-in fuels requires the technoeconomic assessment of different co-processing combinations of feedstock and reactor to determine the economic viability of refinery integration. Several TEA studies 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 HTD 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. 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 technoeconomic assessment and CO₂ mitigation potential estimate would be based on process-chain related CO₂ emissions and economic analysis of the most promising bio-oil co-processing pathways.

Focusing on this problem, in this study we assessed the CO₂ 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 250kbdp (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
co-processing in the refinery and (2) TEA and analysis of the CO₂-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 CO₂ emission estimation.
2. Inventory the key parameters of the primary processes in each pathway and for fossil reference (for, e.g., CO₂ 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 CO₂ 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 kbdpd. 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. 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% hydroskimers and 5% topping).\textsuperscript{39} Aggregated data corresponding to the mass, energy, and CO\textsubscript{2} emissions of the refinery were extracted from the basic refinery model\textsuperscript{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.

### 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, NC2018/000069. 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 CO2-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.\textsuperscript{42} This LCA included the stages of crude-oil extraction, oil pipeline transport, oil refining, refined transport, and final use. A breakdown of CO\textsubscript{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\textsuperscript{135}, ‘a tier represents a level of methodological complexity’ for estimating CO\textsubscript{2} 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

| Table 1. Key characteristics of the Ecopetrol refinery at Barrancabermeja.\textsuperscript{40} |
|---------------------------------------------------------------|
| **Crude oil throughput** | Unit | Value |
| **Annual CO\textsubscript{2} emissions** | Mt CO\textsubscript{2}-eq/Year | 3.7 |
| **Electricity production** | PJ/year | 2402 |
| **Steam production** | PJ\textsubscript{u}/year | 24843 |
| **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 cracking 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\textsubscript{2} per t of input load.
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. 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. for Colombian conditions.
Key performance indicators

The main technical indicator used in this study is the net change in annual emissions $\Delta GHG$ (tCO$_2$/y), which was calculated using Eqn (1):

$$\Delta GHG = \frac{(\Delta GHG_{ff} \times M_{ff} \times H_{V_{ff}}) - (\Delta GHG_{bf} \times M_{bf} \times H_{V_{bf}})}{10^3}$$

(1)

Here, $\Delta GHG_{ff}$ and $\Delta GHG_{bf}$ represent net changes in the life-cycle GHG emissions (gCO$_2$-eq/MJ) during the production of fossil fuels and biofuels, respectively (CO$_2$-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$_2$-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.

$$GHG_f = \Delta GHG_{upstream} + \Delta GHG_{plant} + \Delta GHG_{downstream}$$

(2)

Here, $\Delta GHG_{upstream}$, $\Delta GHG_{plant}$, 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$_2$-eq), which was estimated using Eqn (3).

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

(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).

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

(4)

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.
Here, $i$ represents the energy carrier (for e.g., electricity, natural gas, or steam), $E_i$ is the annual energy consumption (GJ/yr), $P_i$ 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/yr), $P_j$ is the feedstock price (€/t), $\alpha$ is the annuity factor (t/yr), $I$ is the total upfront investment cost (€), and $O&M_{\text{cost}}$ represents operational and maintenance costs (€/yr). $I$ 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:

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

(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.\textsuperscript{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.,\textsuperscript{136} gasification-derived biofuels require higher investment in the range of 153 to 289 k€/bbl per day capacity. Van Dyk et al.\textsuperscript{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.\textsuperscript{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,\textsuperscript{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.\textsuperscript{44} The cost of additional industrial services facilities (such as H₂, 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.\textsuperscript{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\textsuperscript{46} and escalated to the year 2018 using the Harmonized Index of Consumer Prices (HICP).\textsuperscript{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.\textsuperscript{48}

$$\frac{\text{Cost}_A}{\text{Cost}_B} = \left(\frac{\text{Size}_A}{\text{Size}_B}\right)^{SF}$$

(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.\textsuperscript{49} Several considerations were included, such as compatibility, processability, processing options, potential problems, and...
expected product quality. 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.

CO₂ emissions associated with fossil-fuel production

A breakdown of the CO₂ 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 (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. 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 H₂, 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. 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. Nevertheless, there are some recent studies suggesting that the HTL can undergo fractional distillation after mild deoxygenation.

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...
Biofuels, Bioproducts and Biorefining (2021) 13, 305–333
DOI: 10.1002/bbb.2163

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

| Property | Refinery Process Units |
|----------|------------------------|
|          |                        |
|                      | Atmospheric distillation unit (ADU) | Fluid catalytic cracking (FCC) | Hydrotreating (HDT) | Hydrocracking (HCK) |
| Concept |                      |                        |                     |                     |
| TAN\(^1\) | Low is + |                        |                     |                     |
| Water\(^8\) | Low is + |                        |                     |                     |
| Blending ratio\(^2\) | High is + |                        |                     |                     |
| Coke yield\(^{1,18}\) | Low is + |                        |                     |                     |
| Hydrogen consumption\(^8\) | Low is + |                        |                     |                     |
| Oxygen\(^{1,12,20}\) | Low is + |                        |                     |                     |
| Sulphur\(^{10}\) | Low is + |                        |                     |                     |
| Nitrogen\(^{19}\) | Low is + |                        |                     |                     |
| Contaminants\(^{6,21}\) | Low is + |                        |                     |                     |
| MCR/CCR\(^{14}\) | Low is + |                        |                     |                     |
| Miscibility with fossil-based feeds\(^{5,19}\) | High is + |                        |                     |                     |

\(^{1}\)Refineries can cope with the acidity of bio-oils using 317 stainless steel cladding. This, however, is not standard in a RU.\(^{51}\)

\(^{2}\)The catalyst in the FCC is more tolerant to higher levels of oxygen than the catalyst in hydro-processing (HDT)\(^{11}\) 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 oxygen content.\(^{25}\) 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.\(^{11}\)

\(^{3}\)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).\(^{11}\) Increasing coke formation could increase the temperature and affect the fluid balance; it also damages the FCC catalyst.\(^{15}\) However, it seems that the experimental results led to higher coke formation in the FCC when compared to that expected in realistic setups.\(^{22,30,54}\)

\(^{4}\)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 close to 1. Bio-oils with EHI < 1 are expected to increase coke formation.\(^{52}\)

\(^{5}\)Regarding the FCC, it is suggested that a blending ratio of 3%-5% be adopted\(^{11}\) although some tests were previously conducted at 15%.\(^{50,56}\) and 20%,\(^{17}\) the latter resulted in an increased coke formation and reduced gasoline yield. Wang et al.\(^{31}\) suggested that a blending ratio of 15% is optimal before blockage by coking.

\(^{6}\)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.\(^{55}\) Chlorine, sulfur, and nitrogen are contaminants that cause catalyst poisoning in upgrading.\(^{36}\) Unlike other processes, FCC provides an integrated in situ catalyst regeneration, which makes it less vulnerable to contaminants in bio-feedstock.\(^{21}\)

\(^{7}\)Meanwhile, contaminants in the atmospheric distillation unit/vacuum distillation unit (ADU/VCU) are spread to the entire refinery and affect its operation.\(^{13,59}\)

\(^{8}\)Miscibility is a primary requirement for co-processing, specifically for the HDT and HCK.\(^{17}\) 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.\(^{56}\)

\(^{9}\)Water in pyrolysis bio-oil is hard to separate and for 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.

\(^{10}\)VO co-processing in HDT might increase H\(_2\) consumption due to the presence of oxygen and unsaturated carbon chains.\(^{21}\)

\(^{11}\)As shown in the supplementary material, the sulfur content in the bio-oil is lower than the crude oil, which may be considered a minor issue. However, sulfur is associated catalyst poisoning.\(^{20}\) Mutual inhibition (deoxygenation and desulfurization) can lead to an unsatisfactory performance in the HDT/HCK\(^{32}\) 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.\(^{16,52}\)

\(^{12}\)Vegetable oil co-processing in the FCC 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.\(^{31}\)

\(^{13}\)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.\(^{17,18}\)

\(^{14}\)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) is more tolerant to higher levels of oxygen and exhibits a higher oxygen-removal ability.\(^{17,18}\) Fluid catalytic cracking catalysts are continuously regenerated on site unlike hydrotreatment catalysts that must be taken to other locations.\(^{17}\)

\(^{15}\)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.\(^{26}\) Castello et al.\(^{31}\) 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.\(^{55}\) A low MCR value is associated with better bio-oil co-processing in the FCC.\(^{55}\) The MCR is also an indicator of the tendency for polymerization,\(^{26}\) which is a critical factor in distillation. The CCR measures the tendency of a feedstock to form coke at elevated temperatures\(^{19}\) 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.\(^{55}\)

\(^{16}\)Bio-feedstock co-processing in the FCC leads to lower H/C ratio products compared to 100% vacuum gas oil (VGO) processing.\(^{13,54}\)

\(^{17}\)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.

\(^{18}\)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.\(^{33}\)

\(^{19}\)Hydrotreatment is an exothermic reaction associated with hydrogen consumption and oxygen removal. It leads to increased coking, decreased pressure, and poor liquid-flow distribution.\(^{17}\)

\(^{20}\)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.\(^{14}\) It also leads to nitrogen oxide emissions if present in the fuel during combustion.

\(^{21}\)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. Metal content in heavier hydrocarbons 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.\(^{14}\) Alkaline metal presence in vegetable oil might affect cracking process due to fatty-acid composition,\(^{26}\) and also promote secondary reactions during storage.\(^{37}\) 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.\(^{26}\) Nevertheless, catalyst deactivation is a consequence of metal deposition during the upgrading process such as HDO.\(^{48}\)
The table below ranks the suitability of bio-oils for co-processing in oil refineries based on various parameters:

| Parameter                        | Concept for co-processing | Bio-oil for co-processing |
|----------------------------------|---------------------------|---------------------------|
| Total acid number (TAN)          | Low is +                  | VO                        |
|                                  |                           | FPO                       |
|                                  |                           | FPO-E                     |
|                                  |                           | CPO                       |
|                                  |                           | HDO                       |
|                                  |                           | HTLO                      |
| Water                            | Low is +                  |                           |
| Cetane                           | High is +                 |                           |
| Octane                           | High is +                 |                           |
| Bio-oil yield from biomass       | High is +                 |                           |
| Coke formation                   | Low* is +                 |                           |
| Blending ratio                   | 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 | High* is +       |                           |

The table indicates the suitability of bio-oils for co-processing in oil refineries based on various parameters such as total acid number (TAN), water, cetane, octane, bio-oil yield from biomass, coke formation, blending ratio, oxygen, sulfur, nitrogen, H/C ratio, EHI, MCR, and miscibility with fossil-based feed. High values indicate better performance, while low values indicate lesser suitability.

For instance, high total acid number indicates poor ignition properties, which is undesirable for bio-oil feedstock. Similarly, high sulfur content can cause plugging and high coke formation, impacting refinery efficiency. Miscibility with fossil-based feed is crucial for smooth blending and overall performance of the co-processing.

The table is a comprehensive guide for refinery operators to select the most suitable bio-oil feedstock for co-processing, ensuring optimal performance and efficiency.
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.\textsuperscript{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.\textsuperscript{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.

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

| Biomass (Bm) | Unit\textsuperscript{a} | Vegetable oil (VO) | Fast pyrolysis oil (FPO)\textsuperscript{b} | Catalytic pyrolysis oil (CPO) | Hydrothermal liquefaction oil (HTLO) |
|-------------|-----------------|---------------------|-------------------------------|-------------------------------|-------------------------------------|
| Type of biomass | — | Fresh fruit bunch (FFB-oil palm) | Wood | Beechwood | Wood |
| Energy content | MJ\textsubscript{LHV}/kg | 14.61 | 16.8 | 16.02 | 18.6 |
| Cost | €\textsubscript{Bm}/t | 74.2\textsuperscript{b} | 62.6\textsuperscript{d} | 46.6\textsuperscript{d} | 67.8\textsuperscript{d} |
| Carbon (w%) | | 50.9\textsuperscript{d} | 48.4\textsuperscript{g} | 50.9\textsuperscript{d} |
| Oxygen (w%) | | 41.9\textsuperscript{d} | 45.7\textsuperscript{g} | 41.9\textsuperscript{d} |
| Hydrogen (w%) | | 6.1\textsuperscript{d} | 5.8\textsuperscript{g} | 6.1\textsuperscript{d} |
| Bio-oil (Bo) | | | |
| Mass yield of oil | t\textsubscript{Bo}/t\textsubscript{Bm} | 0.204\textsuperscript{c} | 0.63\textsuperscript{d} | 0.259 | 0.38 |
| Density | kg/L | 0.88 | 1.2 | 1.1 | 1.1 |
| Energy content | MJ\textsubscript{LHV}/kg | 37 | 16.9 | 29.1 | 27.4 |
| Elemental composition | | | | | |
| Carbon (w%) | | 77.6\textsuperscript{f} | 56.6 | 68.3 | 76.1 |
| Oxygen (w%) | | 10.4\textsuperscript{f} | 36.7 | 24.2 | 15.7 |
| Hydrogen (w%) | | 11.7\textsuperscript{f} | 6.6 | 7.5 | 7.9 |
| Overall energy yield | M\textsubscript{Bo}/M\textsubscript{Bm} | 0.52 | 0.57 | 0.45 | 0.56 |
| References | | 11, 76–78 | 33, 79, 80 | 81 | 8 |

\textsuperscript{a}The abbreviations Bm and Bo stand for biomass and bio-oil, respectively.
\textsuperscript{b}Refers to the production cost of a tonne of fresh fruit bunch (FFB) in Colombia in 2016.\textsuperscript{77}
\textsuperscript{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.
\textsuperscript{d}Based on dry biomass.
\textsuperscript{e}For FPO,\textsuperscript{82} estimated $-0.854$ k CO\textsubscript{2}/kg FPO without land use change (direct + indirect).\textsuperscript{80} estimated $-1.15$ to $-1.64$ kg CO\textsubscript{2}/kg FPO including carbon absorption in crops.
\textsuperscript{f}Based on soybean oil as described by Van Dyk, S. et. al.\textsuperscript{11}
\textsuperscript{g}Moisture and ash free as reported by Vasalos, IA. et. al.\textsuperscript{81}

**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\textsubscript{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
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

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

| Parameter                        | Unit       | Value  | References |
|----------------------------------|------------|--------|------------|
| Real discount rate               | %          | 12     | 40         |
| Total plant cost                 | % 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  | 84         |
| Lifting                          | €/bbl      | 8.94   | 84         |
| Transport                        | €/bbl      | 3.44   | 84         |
| Refining                         | €/bbl      | 4.97   | 84         |
| Dilution for transport           | €/bbl      | 4.65   | 84         |
| CO₂ emissions factor             |            |        |            |
| Natural gas                      | kg CO₂/GJ  | 56.6   | 41         |
| Electricity (grid)               | t CO₂ / MWh| 0.21   | 85         |
| Electricity (CHP)                | t CO₂ / MWh| 0.252  | This study |
| Life cycle emission              |            |        |            |
| Hydrogen                         | kg CO₂/t H₂| 20.5   | This study |
| Electricity (CHP)                | t CO₂/GWh  | 252    | This study |
| Steam (CHP)                      | t CO₂/GWh  | 144    | This study |

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 uses 8% for the European oil refining industry.

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.

The CO₂ emission 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 CO₂ emissions for the electricity and steam production uses the efficiency method suggested by the allocation guidance for the GHG protocol and refinery energy production data.
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.

**CO₂ emissions**

A breakdown of CO₂ 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 CO₂ emissions of ~17 gCO₂/MJ for the entire lifecycle. Meanwhile, vegetable oil resulted in the highest emissions (70 gCO₂/MJ) in the technological conditions used. Ramirez et al. estimated the lifecycle CO₂ 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 CO₂ emissions (56 gCO₂/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 CO₂ emissions for the upstream biomass compared with other pathways.

Oil production represents the highest share (~85%) of CO₂ emissions per energy unit of biofuel, excluding the final use. Low mass and energy yields in the production stage are responsible for the high CO₂ intensity as it involves

---

**Table 6. Intensity of CO₂ emissions during fossil-fuel production from the refinery in Colombia.**

| Stage                  | Gasoline (g CO₂ / MJ) | Diesel (g CO₂ / 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               |

*It should be noted that Martinez-Gonzalez et al. assessed the LCA for two different quality diesel blends based on sulfur content (500 and 3000 ppm). The CO₂ 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 CO₂/MJ for production, transport, and refining, respectively.*
Table 7. Pathways (PW) for bio-oil co-processing in oil refineries.

| Tier | PW | Bio-oil | RU | Notes |
|------|----|---------|----|-------|
| 1    | VO | HDT     |    | Despite possible increased H₂ consumption and some heteroatoms reaching the final products, there is no significant restriction to VO co-processing in the HDT. VO is highly miscible with the fossil-based streams, which is an essential requirement for hydrotreatment. This option is the only route that has been commercialized. Blending VO at levels higher than 15% reduces the efficiency of desulphurisation. |
| 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. Still, there is some contradiction in terms of the yield of this process, which could be due to the setup of the experiment. 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. |
| 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. 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. |
| 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. However, oxygen removal results in higher viscosity, which makes pumping more difficult. 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 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. 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 26%, respectively). A pilot-plant trial exhibited similar yields for 10% CPO/VGO and 100% VGO. However, a threshold blending ratio of 15% was suggested to avert blockage by coke. |
| 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%-50%. 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. |
| 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. This may be due to the set-up of the experiment on a MAT, unlike a pilot-scale FCC, which led to different conclusions. Nevertheless, recent studies in which the set-up was more similar to actual FCC conditions, showed that FPO (O₂: 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. |
| 8    | FPO+E | FCC/HDT | | Process patented by Ecopetrol S.A. NC2016/0000689, NC2018/0000669. |
| 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 CO co-processing. Deoxygenated bio-oils decrease coke formation in the FCC as compared to fossil feeds. It is a promising option for achieving higher blending ratios as the oxygen content is comparable (10%-20%) to that of the feedstock used for co-processing in the FCC. Experimental data are, however, currently not available. |
| 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 hydroprocessing is required to remove oxygenated components. Fractional distillation resulted in a 53% yield and equivalent fractions of gasoline (12%), diesel (25%), and jet fuel (16%). This bio-oil |
| 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 CO₂ emitted due to carbon removal via coke regeneration and dry gas emissions from the FCC. None of the pathways assessed in this study considered CO₂ capture at the refinery, which may significantly reduce...
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) |
| PW 7         | 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) |
| PW 9         | HTLO to FCC | Hydrothermal-liquefaction oil (HTLO) to hydrotreating unit (HDT) |
| PW 15A       | BG + FT (w/o CCS) | Biomass gasification (BG) + Fischer-Tropsch (FT) (without CO₂ storage) + upgrading |

CO₂ emissions. As a reference, Hailey et. al.² estimated a CO₂-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, CO₂ 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 gasification to Fischer-Tropsch (BG-FT) pathway (PW15) showed a significant reduction in CO₂ emissions (expressed as a percentage of the carbon intensity, g CO₂ / GJ) compared to the fossil reference as this process was entirely thermal and H₂ self-sufficient; furthermore, the factors contributing
Table 9. Key indicators of bio-oil co-processing in the refinery.

| Stage \ pathway | Description | Unit | PW 1 | PW 1-A | PW 1-B | PW 1-C | PW 2 | PW 4 | PW 5 | PW 6 | PW 7 | PW 8 | PW 9 | PW 15A |
|----------------|-------------|------|------|--------|--------|--------|------|------|------|------|------|------|------|--------|
| Technical co-processing limit | %w | 5% | 5% | 5% | 5% | 5% | 5% | 5% | 10% | 20% | 20% | 30% | 20% | 20% |
| Photosynthesis CO2 emissions | kg CO2 / GJ fuel | -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 CO2 emissions | kg CO2 / 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 |
| | Bio-oil | MJ / kg | 37.0 | 37.0 | 37.0 | 37.0 | 37.0 | 29.5 | 31.3 | 29.5 | 29.5 | 29.5 | 35.2 | n.a. |
| | 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 |
| | 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 |
| | 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 |
| | CO2 emissions | kg CO2 / 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 | 0.79 | 0.79 | 0.79 | 0.43 | 0.59 | 0.85 | 0.60 | 0.67 | 0.69 |
| | 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 |
| | CO2 emissions | kg CO2 / 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 | 0.48 | 0.41 | 0.42 | 0.40 | 0.76 | 0.39 | 0.48 | 0.53 | 0.64 |
| | Biofuel cost | € / GJ | 2.9 | 2.9 | 3.1 | 3.1 | 2.3 | 2.8 | 3.1 | 17 | 22 | 31 | 25 | 21 | 19 |
| | Biofuel-net CO2 emissions | kg CO2 / GJ fuel | 65 | 39 | 70 | 44 | 64 | 27 | 22 | 17 | 37 | 35 | 56 | 32 | 19 |
| | CO2 avoided cost | € / t CO2 | 497 | 302 | 651 | 375 | 351 | 292 | 272 | 99 | 188 | 321 | 337 | 169 | 124 |
| | CO2 avoided cost | € / t CO2 | 328 | 199 | 458 | 263 | 184 | 165 | 191 | 22 | 87 | 224 | 198 | 76 | 45 |
| | Avoided CO2 | kt CO2 / 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 |

*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. (1) the current scenario and (2) a future scenario with a production chain optimized to reduce GHG emissions.
It was assumed that the CH$_2$$_2$$_2$$_2$ could potentially increase the dry gas and gasoline output. These changes could affect mass flow and CO$_2$ emissions downstream of the hydrotreatment unit. However, this additional yield was not included in this study.

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. 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 87.8 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) for yearly processing operations by the hydrogen-production units in the refinery.

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.

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. 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.

Vegetable oil co-processing in the HDT for P2 might require a very low upfront investment of €0.18 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) 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.

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

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

The TCR was calculated as suggested by the Pacific Northwest National Laboratory (PNNL) report 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 and was estimated as 0.4 €/GJ (see appendix 8.10).

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). It was assumed that the CH$_4$ co-produced during oil production and upgrading was burnt before being released to the atmosphere.

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.

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

Ramirez et al. 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.

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.

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.

Carbon dioxide emissions reported for oil production include upgrading (1.78 gCO$_2$/MJ) as there is no co-processing stage in this route.

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 hydropyrolysis 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 work27 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.

Connor99 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 reforming 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 CO₂ 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 CO₂ 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
€/GJ), followed closely by PW7 and PW2 with ~22 €/GJ (to convert production cost from €\textsubscript{2018}/GJ to US$/bbl-equivalent 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., reducing biofuel-production cost is possible by improving the catalyst lifetime for both the activity and support stability.

The cost and potential of CO\textsubscript{2} avoidance (defined as CO\textsubscript{2} emissions avoided by biofuels from bio-oil co-processing pathways compared to the total CO\textsubscript{2} emissions from the refinery) in each pathway is presented in Fig. 8. PW6, PW15A, and PW7 showed the lowest CO\textsubscript{2}-avoidance cost of 99, 124, and 147 €/t CO\textsubscript{2}, respectively. However, PW7 and PW15A showed the highest amount of CO\textsubscript{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\textsubscript{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
limit. The TcPL for co-processing VO is constrained by the risk of low sulfur removal, acidity, higher H₂ pressures and catalyst deactivation.

The cost of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ emissions from the refinery.

The total CO₂ 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 CO₂ 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 CO₂ avoided. Co-processing vegetable oil reduces CO₂ 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, FPO₄ to FCC, and FPO₂ to HDT with a low percentage of avoided CO₂ emissions at the refinery, despite reporting a high reduction in CO₂ 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 CO₂ emissions when compared to the fossil fuel, as well as large amounts of CO₂ 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 CO₂ emissions from the refinery, co-processing CPO in the hydrotreating process...
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 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 compared to the fossil reference.
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. 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\(_2\).\(^{15}\) 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 hydro treatment 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.

Acknowledgements

A personal stipend was awarded to the lead researcher from Ecopetrol S.A. in the form of a loan-scholarship to pursue postgraduate studies. The views expressed in this paper do not necessarily reflect those of Ecopetrol S.A.

References

1. IEA. World Energy Outlook 2019. [Online]. (2019). Available: https://webstore.iea.org/download/summary/24677?file=Japanese-Summary-WEO2019.pdf [10 March 2020]
2. Hailey AK, Meerman JC, Larson ED and Loo YL, Low-carbon “drop-in replacement” transportation fuels from non-food biomass and natural gas. Appl Energy. 183:1722–1730 (2016).
3. IPCC. IPCC, 2018. Global Warming of 1.5 °C. An IPCC Special Report on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change [Online]. (2018). Available: http://www.ipcc.ch/sr15/ [05 March 2020]
4. (S&T) Squared Consultants Inc. GHGenius [Online]. (2020). Available: https://ghgenius.ca/index.php [27 April 2020]
5. Darda S, Papalas T and Zabaniotou A, Biofuels journey in Europe: currently the way to low carbon economy sustainability is still a challenge. J Clean Prod 208:575–588 (2019). https://doi.org/10.1016/j.jclepro.2018.10.147.
6. Faaiz A, Modern biomass conversion technologies. Mitig Adapt Strateg Glob Chang 11:343–375 (2006).
7. Dyk S v, Su J, Mcmillan JD and Saddler JN, Drop-in biofuels: the key role that co-processing will play in its production. IEA Bioenergy Task 39 (2019). http://task39.org/files/2014/01/Task-39-drop-in-biofuels-report-summary-FINAL-14-July-2014-ecopy.pdf.
8. Dyk S, Van SJ, Ebadian M, Connor DO and Lakeman M, Potential yields and emission reductions of biojet fuels produced via hydrotreatment of biocrudes produced through direct thermochemical liquefaction. Biotecnol Biofuels 12:1–12 (2019). https://doi.org/10.1186/s13068-019-1625-2.
9. Karatzos S, Mcmillan J and Saddler J, The potential and challenges of “drop in” biofuels. IEA Bioenergy - Task 39:202 (2014) Available: http://task39.org/files/2014/01/Task-39-drop-in-biofuels-report-summary-FINAL-14-July-2014-ecopy.pdf.
10. Ramirez JA, Brown RJ and Rainey TJ, A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels. Energies. 8(7):6765–6794 (2015).
11. van Dyk S, Su J, Mcmillan JD and Saddler J, Potential synergies of drop-in biofuel production with further co-processing at oil refineries. Biofuel Bioprod Biorefin 13(3):760–775 (2019).
12. Bezergianni S, Dimitriadi A and Karonis D, Diesel decarbonization via effective catalytic co-hydroprocessing of residual lipids with gas-oil. Fuel 136:366–373 (2014). https://doi.org/10.1016/j.fuel.2014.07.038.
13. van Dyk S, Su J, Mcmillan JD and Saddler J, Potential synergies of drop-in biofuel production with further co-processing at oil refineries. Biofuels. Bioprod Biorefin 13(3):760–775 (2019).
14. Greenea, New players join the HVO game. Biofuels Waste Based Biofuels (2017) Available: https://www.greenea.com/publication/new-players-join-the-hvo-game/ [3 July 2020].
15. Bezergianni S and Dimitriadi A, Comparison between different types of renewable diesel. Renew Sustain Energy Rev 21:110–116. Available: [2013]. https://doi.org/10.1016/j.rser.2012.12.042.
16. Bezergianni S, Dimitriadi A, Kikhtyanin O and Kubi D, Refinery co-processing of renewable feeds. Prog Energy Combust Sci. 68:24–69 (2018).
17. Pinho A d R, MBB d A, Mendes FL, Casavechia LC, Talmadge MS, Kinchin CM et al., Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. Fuel 188:462–473 (2017). https://doi.org/10.1016/j.fuel.2016.10.032.
18. Pinho ADR, De Almeida MBB, Mendes FL, Ximenes VL and Casavechia LC, Co-processing raw bio-oil and gasoil in an FCC unit. Fuel Process Technol 131:159–166 (2015). https://doi.org/10.1016/j.fuproc.2014.11.008.
19. Melero JA, Iglesias J and Garcia A, Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. Energy Environ Sci. 6(6):7393–7420 (2012).
20. Cruz PL, Montero E and Dufour J, Modelling of co-processing of HDO-oil with VGO in a FCC unit. Fuel 196:362–370 (2017). https://doi.org/10.1016/j.fuel.2017.01.112.
21. Al-Sabawi M and Chen J, Hydroprocessing of biomass-derived oils and their blends with petroleum feedstocks: a review. Energy Fuel. 26(9):5373–5399 (2012).
22. Al-Sabawi M, Chen J and Ng S, Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: a review. Energy and Fuels. 26(9):5355–5372 (2012).
23. Stefanidis S, Kalogiannis KG and Lappas AA, Co-processing bio-oil in the refinery for drop-in biofuels via fluid catalytic cracking. Wiley Interdiscip Rev Energy Environ. 7(3):1–18 (2018).
24. Bhattacharya, Zhang Y and Heath G, Bio-oil co-processing can substantially contribute to renewable fuel production potential and meet air quality standards. Appl Energy 268:114937 (2020). https://doi.org/10.1016/j.apenergy.2020.114937.
25. Wu L, Wang Y, Zheng L, Shi M and Li J, Design and optimization of bio-oil co-processing with vacuum gas oil in a refinery. Energy Convers Manag. 195:620–629 (2019).
26. Gudde N, Larivé J and Refinery YM, Conceptual assessment. Exploring opportunities and challenges for the EU refining industry to transition towards a low-CO2 intensive economy. Concawe Special Task Force Refinery 2050:2019 (2050).
27. Baldwin B, Li Z, Magrini K, Wang H and Investigators P, DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review Strategies for Co-Processing in Refineries (SCR). (2019).
28. Chum HL, DOE bioenergy technologies office (BETO) 2015 project. peer review 1–32 (2015).
29. Ali Asmaa AM, Mustafa Mustafa A and Yassin Kamal E, A techno-economic evaluation of bio-oil co-processing within a petroleum refinery. Biofuels. 1–9 (2016). https://doi.org/10.1080/17597269.2018.1519758.

30. Wu L, Wang Y, Zheng L, Wang P and Han X, Techno-economic analysis of bio-oil co-processing with vacuum gas oil to transportation fuels in an existing fluid catalytic cracker. Energy Convers Manag. 197(1):111901 (2019).

31. Agblevor Foster A, Mante O, McClung R and Oyama ST, Co-processing of standard gas oil and biocrude oil to hydrocarbon fuels. Biomass and Bioenergy. 45:130–137 (2012). http://dx.doi.org/10.1016/j.biombioe.2012.05.024.

32. Choi YS, Elkasabi Y, Tarves PC, Mullen CA and Boateng AA, Co-cracking of bio-oil distillate bottoms with vacuum gas oil for enhanced production of light compounds. J Anal Appl Pyrolysis 132:65–71 (2018). https://doi.org/10.1016/j.jaap.2018.03.014.

33. Fogassy G, Thegarid N, Schuurman Y and Mirodatos C, From biomass to bio-gasoline by FCC co-processing: effect of feed composition and catalyst structure on product quality. Energy & Environmental Science 4(12):5068 (2011). http://dx.doi.org/10.1039/c1ee00201a.

34. Lappas AA, Bezergianni S and Vasalos IA, Production of biofuels via co-processing in conventional refining processes. Catalysis Today. 145:55–62 (2009). http://dx.doi.org/10.1016/j.cattod.2008.07.001.

35. Thegarid N, Fogassy G, Schuurman Y, Mirodatos C, Stefanidis S, Ilipoulou EF, et al., Second-generation biofuels by co-processing catalytic pyrolysis oil in FCC units. Applied Catalysis B: Environmental. 145:161–166 (2014). http://dx.doi.org/10.1016/j.apcatb.2013.01.019.

36. Hoffmann J, Jensen CU and Rosendahl LA, Co-processing potential of HTL bio-crude at petroleum refineries – Part 1: Fractional distillation and characterization. Fuel. 165:526–535 (2016). http://dx.doi.org/10.1016/j.fuel.2015.10.094.

37. Auerswald M, Shumeiko B, Vrščika D, Straka P, Staš M, Šimáček P et al., Hydrotreatment of straw bio-oil from ablative fast pyrolysis to produce suitable refinery intermediates. Fuel 238:98–110 (2019). https://doi.org/10.1016/j.fuel.2018.10.090.

38. Ramírez A, Blok K, Faaj A, Meeran H, Worrell E, Gert JK, et al., System approach for a sustainable industry. Understanding the need for systems analysis to support the energy transition of the industrial sector. (2019). Available: https://www.topsectorenergie.nl/sites/default/files/uploads/FinalReport-System-approach-for-a-sustainable-industry_0.pdf

39. Kaiser MJ, A review of refinery complexity applications. Pet Sci. 14(1):167–194 (2017).

40. Yáñez E, Ramírez A, Uribe A, Castillo E and Faaj APC, Unravelling the potential of energy efficiency in the Colombian oil industry. J Clean Prod. 176:604–628 (2018).

41. Ecopetrol S.A. Informe-Integrado-Validado-ACV. (2011).

42. Martínez-Gonzalez A, Casas-Leuro O, Acero Reyes J and Ecopetrol S.A. Informe-Integrado-Validado-ACV. (2011).

43. 40. Yáñez E, Ramírez A, Uribe A, Castillo E and Faaj APC, Unravelling the potential of energy efficiency in the Colombian oil industry. J Clean Prod. 176:604–628 (2018).

44. Energy Information Administration (EIA), Petroleum Market Module (PMM) of the National Energy Modeling System: Model Documentation. U.S. Department of Energy: Washington, DC (2013). https://www.eia.gov.
catalytic pyrolysis oil, and hydrotreated bio-oil in a micro activity test unit. *Energy and Fuels.* 29**(6)**:3707–3714 (2015).
63. Venderbosch RH and Heeres HJ. Coprocessing of (upgraded) pyrolysis liquids in conventional oil refineries, in *Biomass Power for the World: Transformations to Effective Use*, Singapore: Pan Stanford Publishing Pte. Ltd. pp. 515–540 (2015).
64. Melero JA, Clavero MM, Calleja G, García A, Miravalles R and Galindo T. Production of biofuels via the catalytic cracking of mixtures of crude vegetable oils and nonedible animal fats with vacuum gas oil. *Energy Fuel.* 24**(1)**:707–717 (2010).
65. Malleswara Rao TV, Dupain X and Makkee M. Fluid catalytic cracking; processing opportunities for Fischer-Tropsch waxes and vegetable oils to produce transportation fuels and light olefins. *Micropor Mesopor Mater.* 164:148–163. Available: (2012). https://doi.org/10.1016/j.micromeso.2012.07.016.
66. Si Z, Zhang X, Wang C, Ma L and Dong R. An overview on catalytic hydrodeoxygenation of pyrolysis oil and its model compounds. *Catalysts.* 7**(6)**:1–22 (2017).
67. Van De Beld B, Holle E and Florijn J. The use of pyrolysis oil and pyrolysis oil derived fuels in diesel engines for CHP applications. *Appl Energy* 102:190–197 (2013). https://doi.org/10.1016/j.apenergy.2012.05.047.
68. Yang Y, Brammer JG, Ouadi M, Samanya J, Hornung A, Xu HM et al., Characterisation of waste derived intermediate pyrolysis oils for use as diesel engine fuels. *Fuel.* 103:247–257 (2013).
69. Santori G, Di Nicola G, Moglie M and Polonara F. A review analyzing the industrial biodiesel production practice starting from vegetable oil refining. *Appl Energy.* 92:109–132 (2012). https://doi.org/10.1016/j.apenergy.2011.10.031.
70. Oasmaa A and Peacocke C. Properties and fuel use of biomass-derived fast pyrolysis liquids. *A Guide 731:739 (2010).*
71. McCormick RL, Ratcliff MA, Christensen E, Fouts L, Luecke J, Chupka GM et al., Properties of oxygenates found in upgraded biomass pyrolysis oil as components of spark and compression ignition engine fuels. *Energy Fuel* 29**(4)**:2453–2461 (2015).
72. Ecopetrol SA. Caracterización cargas y productos coprocesamiento biocauce HDT y FCC. [Internal document by Jose Aristóbulo Sarmiento-Unpublished.] (2018).
73. Wildschut J, Mahfud FH, Venderbosch RH and Heeres HJ. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. *Ind Eng Chem Res.* 48**(23)**:10324–10334 (2009).
74. Meerman JC and Larson ED, Negative-carbon drop-in transport fuels produced via catalytic hydropyrolysis of woody biomass with CO2 capture and storage. *Sustain Energy Fuel.* 1**(1)**:866–881 (2017) Available: http://dx.doi.org/10.1016/j.sefe.2016.09.007.
75. Jensen CU and Rasmussen KM. Co-processing Bio-crude at Petroleum Refineries. Aalborg: Aalborg University, (2014).
76. Ecopetrol SA. Economic analysis for Biocetano production. (2018).
77. Mosquera Montoya M, Valderrama Villabona M, Ruiz Álvarez E, López Alfonso D, Enrique Castro Zamudio L, Andrés Fontanilla C et al., Economic production costs for the fruit of oil palms and crude palm oil in 2016: estimation in a Group of Colombian Producers Palabras. *Fedepalma* 38**(2)**:11–27 (2017) Available: http://web.fedepalma.org/media/01-Palmas-38-2-2017_VF_sin_marcas.pdf.
78. NL Agency. Ministry of Economic Affairs A and I. Valorization of palm oil (mill) residues. (2013).
79. Jones S, Meyer P, Snowden-Swan L, Pmadapeurma A, Tan E, Dutta A et al., Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and hydrotreating bio-oil pathway. *PNNL-23053*. PNNL (2013) Available: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-23053.pdf%5Cnhttp://www.nrel.gov/docs/fy14osti/61178.pdf.
80. Peters JF, Iribarren D and Dufour J, Life cycle assessment of pyrolysis oil applications. *Biomass Converv Biorefin Process Biog Mater Energy Chem TA - TT* 5**(1)**:1–19 (2015).
81. Vasalos IA, Lappas AA, Kapolidou EP and Kalogiannis KG, Biomass catalytic pyrolysis: process design and economic analysis. *Wiley Interdiscip Rev Energy Environ.* 5**(3)**:370–383 (2016).
82. Iribarren D, Peters JF and Dufour J, Life cycle assessment of transportation fuels from biomass pyrolysis. *Fuel* 97:812–821 (2012). https://doi.org/10.1016/j.fuel.2012.02.053.
83. Ramirez-Contreras NE, Munar-Florez D, García-Nuñez J, Mosquera-Montoya M and APC F, GHG balance and economic performance of palm oil production in Colombia: current status and long-term perspectives. *J Clean Prod 258*:120757 (2019). https://doi.org/10.1016/j.jclepro.2020.120757.
84. Ecopetrol S.A. Resultados 2018. 2019. Available: https://www. ecopetrol.com.co/wps/portal/es/ecopetrol-web/nuestra-empresa/sala-de-prensa/boletines-de-prensa/boletines-2019/ boletines-2018/ resultados-groupo-ecopetrol+2018
85. (UPME) U de PME. Doc. _Calculo_del_FE_del_SIN_2016_. (2017). Available: https://www1.upme.gov.co/ ServicioCiudadano/Documents/Proyectos_normativos/Doc_calculo_del_FE_del_SIN_2016.docx.
86. IEAGHG. Understanding the Cost of Retrofitting CO2 capture in an Integrated Oil Refinery 2017/TRB. (2017).
87. Ecopetrol S.A. Sistema de gestión de emisiones atmosféricas-SIGEA. (2018).
88. GHG Protocol. Allocation of GHG emissions from a combined heat and power (CHP) plant. CalculationTools. (2006). Available: https://ghgprotocol.org/sites/default/files/ CHP_guidance_v1.0.pdf.
89. MINMINAS, IDB, EMPA. Evaluación del ciclo de vida de la cadena de producción de biocombustibles en Colombia. (2012). Available: https://www.minenergia.gov.co/ documentos/10180/488888/Capitulo_0_Resumen_ejecutivo_de_la_cadena_de_produccion_de_biocombustibles_en_colombia+2012.pdf%5Cnhttps://www.minenergia.gov.co/documents/10180/488888/Capitulo_0_Resumen_ejecutivo_de_la_cadena_de_produccion_de_biocombustibles_en_colombia/19d0f223-e319-4ac6-bc8d-5462e18e41a7
90. Peters JF, Iribarren D and Dufour J, Life cycle assessment of transportation fuels from biomass pyrolysis. *Fuel* 97:812–821 (2012). https://doi.org/10.1016/j.fuel.2012.02.053.
91. National Renewable Energy Lab. (NREL). National Advanced Biofuels Consortium. Biofuels for advancing America. (2010).
92. Worrell E and Galitsky C, Profile of the Petroleum Refining Industry in California, California Industries of the Future Program. Lawrence Berkeley National Laboratory, Berkeley, CA (2004) Available: http://ies.lbl.gov/iespubs/55450.pdf. Available: http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Profile+of+the+Petroleum+Refining+Industry+in+California+&func=buy&cad=cite&start=1&num=10&hl=en&safe=off
93. Valle B, Remiro A, García-Gómez N, Gayubo AG and Bilbao J, Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review. *J Chem Technol Biotechnol TA - TT* - 94**(3)**:670–689 (2019).
94. Peterson AA, Vogel F, Lachance RP, Fröling M, Antal MJ and Tester JW, Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. *Energy Environ Sci.* 1**(1)**:32–65 (2008).
95. Jensen CJ, Hoffmann J and Resendahl LA, Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study. Fuel 165:536–543 (2016). https://doi.org/10.1016/j.fuel.2015.08.047.

96. Ardiyanti AR, Hydrotreatment of Fast Pyrolysis Oil: Catalyst Development and Process-Product Relations. Groningen, NL: University of Groningen, (2013).

97. De Jong S, Antonissen K, Hoefnagels R, Lonza L, Wang M, Faaij A et al., Life-cycle analysis of greenhouse gas emissions from renewable jet fuel production. Biotechnol Biofuel 10(1):1–18 (2017).

98. Tzanetis KF, Posada JA and Ramirez A, Analysis of biomass hydrothermal liquefaction and biocrude-oil upgrading for renewable jet fuel production: the impact of reaction conditions on production costs and GHG emissions performance. Renew Energy 113:1388–1398 (2017). https://doi.org/10.1016/j.renene.2017.06.104.

99. Connor DO, Advanced biofuels – GHG emissions and energy balances. A report to IEA bioenergy task 39. (2013).

100. Hsu D, Life Cycle Assessment of Gasoline and Diesel Produced via Fast Pyrolysis and Hydroprocessing - Technical Report NREL-TP-6A20-49341. (2011).

101. Dupuis DP, Grim RG, Nelson E, Tan ECD, Ruddy DA, Hernandez S et al., High-octane gasoline from biomass: experimental, economic, and environmental assessment. Appl Energy 241(February):25–33 (2019). https://doi.org/10.1016/j.apenergy.2019.02.064.

102. Zacher AH, Olarte MV, Santos DA, Elliott DC and Jones SB, A review and perspective of recent bio-oil hydrotreating research. Green Chem. 16(2):491–515 (2014).

103. IEA, Oil Refineries. ETSAP-Technology Brief P04. (2015).

104. Castillo E, Biocombustibles avanzados a partir del aceite de palma. Palmas. 37(II):191–194 (2016).

105. Mosquera-Montoya M, Ruiz-Alvarez E and Mesa-Fuquen E, Economic assessment of technology adoption in oil palm plantations from Colombia. Int J Financ Res. 8(3):74 (2017).

106. Yáñez E, Ramírez A, Núñez-López V, Castillo E and Faaij A, Exploring the potential of carbon capture and storage-enhanced oil recovery as a mitigation strategy in the Colombian oil industry. Int J Greenh Gas Control 94(October):102938 (2020).

107. Maniatis K, Landläv I, Waldheim L, Van Den Heuvel E and Kalligeros S, Building Up the Future-Sub Group on Advanced Biofuels-Sustainable Transport Forum. (2017).

108. Castello D, Pedersen TH and Rosendahl LA, Continuous hydrothermal liquefaction of biomass: a critical review. Energies. 11(11):3165–3197 (2018). http://dx.doi.org/10.3390/en11111365.

109. Karmakar A, Karmakar S and Mukherjee S, Properties of various plants and animals feedstocks for biodiesel production. Bioresour Technol 101(19):7201–7210 (2010). https://doi.org/10.1016/j.biortech.2010.04.079.

110. He BB and Van Gerpen JH, Analyzing biodiesel for contaminants and moisture retention. Biofuels. 3(3):351–360 (2012).

111. Holmgren J, Marinangelli R, McCall M, Marker T, Czernik S, Elliott D et al., Opportunities for Biorenewables in Petroleum Refineries. PyNe Newslett. Richland: Pacific Northwest National Lab. (PNNL) 24 (2008). https://www.osti.gov/biblio/963247-opportunities-biorenewables-petroleum-refineries.

112. Guzman A, Torres JE, Prada LP and Nuñez ML, Hydroprocessing of crude palm oil at pilot plant scale. Catal Today. 156(1–2):38–43 (2010).

113. Karatzos S, van Dyk JS, McMillan JD and Saddler J, Drop-in biofuel production via conventional (lipid/fatty acid) and advanced (biomass) routes. Part I. Biofuels Bioprod Biorefin TA - TT -. 11(2):344–362 (2017).

114. Otten M, Hoen M ‘t and Boer E den, STREAM Freight transport 2016 - Emissions of freight transport modes. (2016). Available: http://www.cedelft.eu/publicatie/stream_freight_transport_2016_/1855

115. Ahmed Y, Benders R, Delgado R, Lap T, Gonzalez-Salazar M, Cadena A, et al., Systems analysis of the biobased economy in Colombia: A bottom-up energy system model and scenario analysis. n.a. (2020).

116. Henson IE, Ruiz Romero R and Romero HM, c. The greenhouse gas balance of the oil palm industry in Colombia: a preliminary analysis. II. Greenhouse gas balances and the carbon budget [Balance de gases de efecto invernadero de la agroindustria de la Palma de aceite en Colombia: Análisis preliminar]. Agron Colomb 30(3):370–378 (2012) Available: http://www.scopus.com/inward.record.url?eid=2-s2.0-84875449121&partnerID=40&md5=78303c0f1cc6b16204f5edefc4f5881fc.

117. Henson IE, Ruiz Romero R and Romero HM, The greenhouse gas balance of the oil palm industry in Colombia: a preliminary analysis. II. Greenhouse gas emissions and the carbon budget. Agron Colomb. 30(3):370–378 (2012).

118. Rivera-Méndez YD, Rodríguez DT and Romero HM, Carbon footprint of the production of oil palm (Elaeis guineensis) fresh fruit bunches in Colombia. J Clean Prod. 149:743–750 (2017).

119. Dupain X, Costa DJ, Schaverien CJ, Makkee M and Moulijn JA, Cracking of a rapeseed vegetable oil under realistic FCC conditions. Appl Catal B Environ. 72(1–2):44–61 (2007).

120. Doronin VP, Potapenko OV, Lipin PV and Sorokina TP, Catalytic cracking of vegetable oils and vacuum gas oil. Fuel 106:757–765 (2013). https://doi.org/10.1016/j.fuel.2012.11.027.

121. Ng SH, Al-Sabawi M, Wang J, Ling H, Zheng Y, Wei Q et al., FCC coprocessing oil sands heavy gas oil and canola oil. 1. Yield structure. Fuel 156:163–176 (2015). https://doi.org/10.1016/j.fuel.2015.03.077.

122. Pinho ADR, De Almeida MBB, Mendes FL and Ximenes VL, Production of lignocellulosic gasoline using fast pyrolysis of biomass and a conventional refining scheme. Pure Appl Chem. 86(5):859–865 (2014).

123. Vasileios F, Ioannis P, Nikolaos S, Ioannis E and Kostas T, Analysis of logging forest residues as an energy source. J Agric Informatics. 9(1):14–25 (2018).

124. Roy P and Dias G, Prospects for pyrolysis technologies in the bioenergy sector: a review. Renew Sustain Energy Rev. 77(May 2016):59–69 (2017). https://doi.org/10.1016/j.rser.2017.03.136.

125. Gollakota ARK, Reddy M, Subramanyam MD and Kishore N, A review on the upgradation techniques of pyrolysis oil. Renew Sustain Energy Rev 58:1543–1568 (2016). https://doi.org/10.1016/j.rser.2015.12.180.

126. Ecopetrol S.A. Informe con la actualización de la factibilidad técnica y económica para la producción de combustibles líquidos para transporte a partir de la pirólisis de la biomasa y su posterior upgrading. (2014).

127. Brito M and Martins F, Life cycle assessment of butanol production. Fuel 208:476–482 (2017). https://doi.org/10.1016/j.fuel.2017.07.050.

128. Royne F, Ringström E and Berlin J, Life Cycle Assessment of forest based raw materials for the Stenungsund chemical industry cluster. (2015).

© 2020 The Authors. Biofuels, Bioproducts and Biorefining published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Biofuels, Bioprod. Bioref. 15:305–333 (2021); DOI: 10.1002/bbb.2163
129. De Miguel Mercader F, Groeneveld MJ, Kersten SRA, Geantet C, Toussaint G, Way NWJ et al., Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units. Energy Environ Sci. 4(3):985–997 (2011).
130. Zhu Y, Biddy MJ, Jones SB, Elliott DC and Schmidt AJ, Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. Appl Energy 129:384–394 (2014). https://doi.org/10.1016/j.apenergy.2014.03.053.
131. Biller P, Sharma BK, Kunwar B and Ross AB, Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae. Fuel 159:197–205 (2015). https://doi.org/10.1016/j.fuel.2015.06.077.
132. Nie Y and Bi XT, Techno-economic assessment of transportation biofuels from hydrothermal liquefaction of forest residues in British Columbia. Energy 153:464–475 (2018). https://doi.org/10.1016/j.energy.2018.04.057.
133. Xue Y, Chen H, Zhao W, Yang C, Ma P and Han S, A review on the operating conditions of producing bio-oil from hydrothermal liquefaction of biomass. Int J Energy Res. 40:865–877 (2016).
134. Bui M, Adijman CS, Bardow A, Anthony EJ, Boston A, Brown S et al., Carbon capture and storage (CCS): the way forward. Energy Environ Sci. 11(5):1062–1176 (2018).
135. IPCC. Volume 2: Energy. Chaper 1. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. (2006). Available: https://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf2_ Volume2/V2_1_Cht1_Introduction.pdf
136. Tsagkari M, Couturier JL, Kokossis A and Dubois JL, Early-stage capital cost estimation of biorefinery processes: a comparative study of heuristic techniques. ChemSusChem. 9(17):2284–2297 (2016).

Edgar Yáñez
Edgar Yáñez is a PhD candidate at the Energy and Sustainability Research Institute Groningen-ESRIG (University of Groningen), focusing on assessing the techno-economic and environmental potential of a decarbonization strategy for the oil and gas industry. Edgar also holds a project leading position at the Colombian Petroleum Institute-Ecopetrol, where he works on the realization of energy transition pathways.

Hans Meereman
Hans Meereman is a post-doctoral researcher at the Energy and Sustainability Research Institute (ESRIG) at the University of Groningen. His research focuses on modeling energy systems related to advanced biofuels production, CO₂ capture and storage (CCS), and CO₂ mitigation in energy-intensive industries.

Andrea Ramírez
Dr Andrea Ramírez is full professor of low carbon systems and technologies at Delft University of Technology in the Netherlands. Her research focuses on the early evaluation of novel low-carbon technologies and the design of methodologies and tools to assess their potential contribution to sustainable energy and resource systems. The research is interdisciplinary in character and integrates her chemical engineering background with ex ante techno-economic analysis, environmental life-cycle assessment and system analysis.

Édgar Castillo
Édgar Castillo is currently an energy expert working for Instituto Colombiano del Petróleo, a specialized unit from Empresa Colombiana de Petróleos (Ecopetrol). Dr Castillo obtained his degree in chemical engineering at 1986 and then he received his PhD in 2000. He had developed roles as production engineer, associate professor, titular professor, head of research program at CENICAÑA (the most important research center in Colombia, focused on sugar cane and biomass) and now is playing the role of conducting and assessing technical assistance and research activities in biofuels and energy efficiency at the National Oil Company in Colombia.

André Faaij
André Faaij is Director of Science of TNO Energy Transition, the largest energy research organization in the Netherlands, and distinguished professor of energy system analysis at the University of Groningen. Current research includes energy system integration, scenario analysis, model development, transition towards low carbon energy systems, and related innovation and policy questions.