



# Economic and environmental assessment of directly converting CO<sub>2</sub> into a gasoline fuel

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## ABSTRACT

The threat posed by Climate Change demands urgent action on finding clean energy solutions with a view to cutting fossil fuel consumption. However, a sudden stop in the use of fossil fuels is not possible without a profound disruption of the economy. This transition is expected to take several decades, and therefore every type of renewable energy should be considered as part of the solution mix. In this work, we propose including gasoline synthesized from atmospheric CO<sub>2</sub> as one possible interim solution while the transition away from liquid fossil fuels intensifies. To that end, we have designed a novel process that produces green gasoline in one stage on an industrial scale. This contrasts with the two or three stages needed in the classical Fischer-Tropsch based processes. Furthermore, we have optimized this process through mass and heat integration, and propose three different options that make the most of the waste streams. Finally, we have studied a total of 144 realistic scenarios that take into account the origin of H<sub>2</sub> and CO<sub>2</sub> as well as their environmental impacts and costs. According to our findings, such a process will be capable of producing high-quality gasoline to be manufactured competitively in the near future. The significance of our findings is that it is realistic to reduce carbon emissions while also promoting the circular economy.

## 1. Introduction

The potentially detrimental effects of climate change could be so far-reaching and devastating that the Intergovernmental Panel on Climate Change (IPCC) was founded decades ago to advise policymakers on how best to make informed decisions and take action to mitigate it. The natural carbon cycle has been severely disrupted by mankind, especially in the last century which has seen an unprecedented rise in CO<sub>2</sub> concentration in the atmosphere [1]. Between the years 1000 and 1800 CE, the atmospheric concentration of CO<sub>2</sub> remained nearly constant at around 280 ppm, but starting in the 19th century, there has been a clear and pronounced increase in its level as a result of the so-called Industrial Revolution [2]. To contribute to mitigating climate change, all countries, especially the rich ones, need to quickly implement the use of renewable energies and systems that stabilize the intermittency of some of the existing technologies [3]. It is expected that solar and wind renewables will account for a total of 36% by 2050 in the European Union [3], a level that is clearly insufficient to mitigate the threats to energy

security posed by the EU's continued dependence on third countries for fossil fuels [4], not to mention the systemic risks posed by climate change itself. Yet, the pace at which desirable new regulations to control CO<sub>2</sub> emissions are established, and investment is undertaken to curb them in different parts of the world, seem inadequate. Not surprisingly, the latest report from the IPCC indicates that we urgently need to bend the curve on CO<sub>2</sub> emissions [5]. According to Razali et al [6], there are four main approaches that can be taken to reduce the amount of CO<sub>2</sub> that humans emit into the atmosphere through our industrial practices. They are: (a) to improve the efficiency of the energy that is used; (b) to replace fossil fuels with renewable sources of carbon-neutral fuels; (c) to capture and store CO<sub>2</sub> (CCS) by any chemical, physical or biological [7] means and (d) to use CO<sub>2</sub> as a feedstock and convert it into interesting and useful chemical carbon-containing products. The latter option implies the capture of CO<sub>2</sub> from either a concentrated point source (CPS), such as the chimneys of power stations, or directly from the air (DAC) [3] for subsequent use, i.e., carbon capture and utilization (CCU). DAC is an attractive technology because it sequesters CO<sub>2</sub> that has been

*Abbreviations:* IPCC, Intergovernmental Panel on Climate Change; ppm, parts per million; CCS, CO<sub>2</sub> Capture and Storage; CPS, Concentrated Point Source; DAC, Direct Air Capture; CCU, Carbon Capture and Utilization; CDU, Carbon Dioxide Utilization; HC, Hydrocarbon; EVs, Electric Vehicles; HEN, Heat Exchanger Network.

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released previously from mobile sources such as vehicles and fugitive emissions, though it is more expensive than CPS. In any event, it is essential that future industrial plants synthesizing new products from captured CO<sub>2</sub> only rely on renewable energy, relegating the use of fossil fuels to pilot-demonstration plants at the very most [3]. Over the past decade, there has been considerable research into carbon dioxide utilization processes (CDU) [8], for example, in the production of formic acid [8–10], methanol [6,8,10,11], carbonates [6,8,12], or other hydrocarbons (HC) [13]. There are also studies in the literature that report the production of fuel from the catalytic hydrogenation of CO<sub>2</sub> [14–16]. Mac Dowell et al [17] pointed out that we should not be distracted by CCU techniques because they do not have the potential to permanently sequester CO<sub>2</sub> and, moreover, that the real short-to-medium term objective should instead be to remove a very substantial amount of this gas from the atmosphere via CCS. Nonetheless, we should not forget about the worrying pace of present fossil fuel consumption, since it guarantees a permanent uptake of fossil CO<sub>2</sub> into the biosphere. The simplistic solution, then, would be to stop using fossil fuels altogether, but this will not be possible without a profound disruption of the economy our societies depend on, as illustrated starkly by the COVID-19 postpandemic energy supply crisis the EU currently finds itself immersed in [4]. For that reason, the transition to the use of another type of energy is unfortunately expected to take several decades; a time horizon that we can no longer afford. Hence, it seems reasonable that parallel to the implementation of a variety of CCS techniques (including its synergistic integration with renewables [18]), an urgent effort be undertaken to produce carbon-neutral fuels that will decrease the uptake of fossil CO<sub>2</sub> into the atmosphere. Thus, with a view to stimulating the circular economy, a logical next step would be to study the possibility of producing green gasoline directly from CO<sub>2</sub> and H<sub>2</sub> on an industrial scale. This CO<sub>2</sub> will then flow in an endless technical carbon cycle of CO<sub>2</sub>-gasoline-CO<sub>2</sub>.

Synthesizing carbon-neutral gasoline would be the sensible way to go even though the European Union is en route to phase out new gasoline and diesel vehicles. In our opinion, this would be the right thing to do because decarbonizing a global transport system that relies on fossil fuels cannot be accomplished overnight. Therefore, in the interim, it would be desirable to rely on synthetic gasolines that do not contribute to climate change, especially as the retrenchment of combustion engine vehicles globally will take much longer. For instance, many of the phase-out vehicles from rich countries are likely to end up in developing countries where new environmental regulations are not always strictly enforced; it seems highly unlikely that large developing countries such as India, Brazil, Indonesia, Nigeria, Bangladesh, etc. will make the transition to EVs within the same timeframe as the EU.

The aim of the present work is therefore to evaluate the prospects of a direct industrial-scale synthesis of green gasoline from atmospheric CO<sub>2</sub> and H<sub>2</sub>, i.e., to study the economic viability and the environmental impact of such a process. Furthermore, this approach supports a number of the United Nations Sustainable Development Goals (SDG), particularly, goal 7 (reliable, sustainable clean energy), goal 8 (decent work and economic growth), goal 9 (industry and innovation) and, goal 13 (climate action).

Our proposal depends on a successful chemical route that guarantees the single-stage synthesis of gasoline possessing the desired properties. To that end, we have chosen to use the data reported by Wei et al. [16]. They have demonstrated at a laboratory scale that it is possible to obtain gasoline fuels from a single-stage hydrogenation of CO<sub>2</sub> by virtue of the high selectivity of their catalyst towards C5-C11 fractions of hydrocarbons of adequate octane number. These authors employed the multifunctional Na-Fe<sub>3</sub>O<sub>4</sub>/HZSM-5 catalyst in their work. The product they obtained shows low selectivity towards CH<sub>4</sub> and CO—it does not follow the Anderson-Schulz-Flory distribution [19] typical of the Fischer-Tropsch synthesis, and instead exhibits a clear tendency towards the desired gasoline fraction. This is the great advantage of our proposed process synthesis if we compare it to the traditional procedure to making

synthetic gasoline via Fischer-Tropsch synthesis, which requires costly multistage refining processes to obtain a commercial gasoline [20].

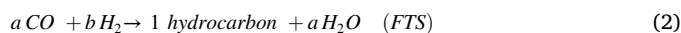
Choosing the right catalyst and designing a reactor that synthesizes gasoline fuel represent just the beginning of an industrial process design undertaking. To be competitive, industrial plants need to be properly optimized in terms of material and energy flows. Here, we present the optimal design of a process that makes gasoline fuel from CO<sub>2</sub> and H<sub>2</sub>, considering the most favorable feed materials and a proper heat integration strategy. Our objective is to design a process that manufactures gasoline fuel at a reasonable cost, but which, in addition, is a net consumer of CO<sub>2</sub> and net producer of electricity. This electricity can then go on to be sold to generate extra revenue. To demonstrate its feasibility, we optimize the energy use in three possible ways, all ultimately generating more energy than they consume. To undertake a realistic study from which representative conclusions can be drawn, we perform a thermo-economic evaluation of the entire optimized plant. To that end, we take into account various different scenarios related to the sourcing of H<sub>2</sub> and CO<sub>2</sub>, and also perform an environmental impact assessment of the overall CO<sub>2</sub> balance that not only accounts for direct, but also indirect, CO<sub>2</sub> emissions. The new contributions of this study are: the design of a process that produces green gasoline by means of a novel catalyst, in a single stage and on an industrial scale; the optimization of that process by means of mass and heat integration, with three different options that make the most of waste streams; and the calculation of the breakeven cost of production of the green gasoline together with the environmental impact of 144 different scenarios.

Our main conclusion is that it is worthwhile to synthesize green gasoline in this way because as climate change mitigation efforts intensify and the transition away from fossil fuels continues, it is likely to represent a profitable and environmentally-friendly option in the near future. Finally, we do expect that our proposal may be included as part of a mix of well-defined approaches that will contribute to decreasing manmade climate change, as well as providing decision-makers with an additional but useful alternative to consider.

## 2. Methods

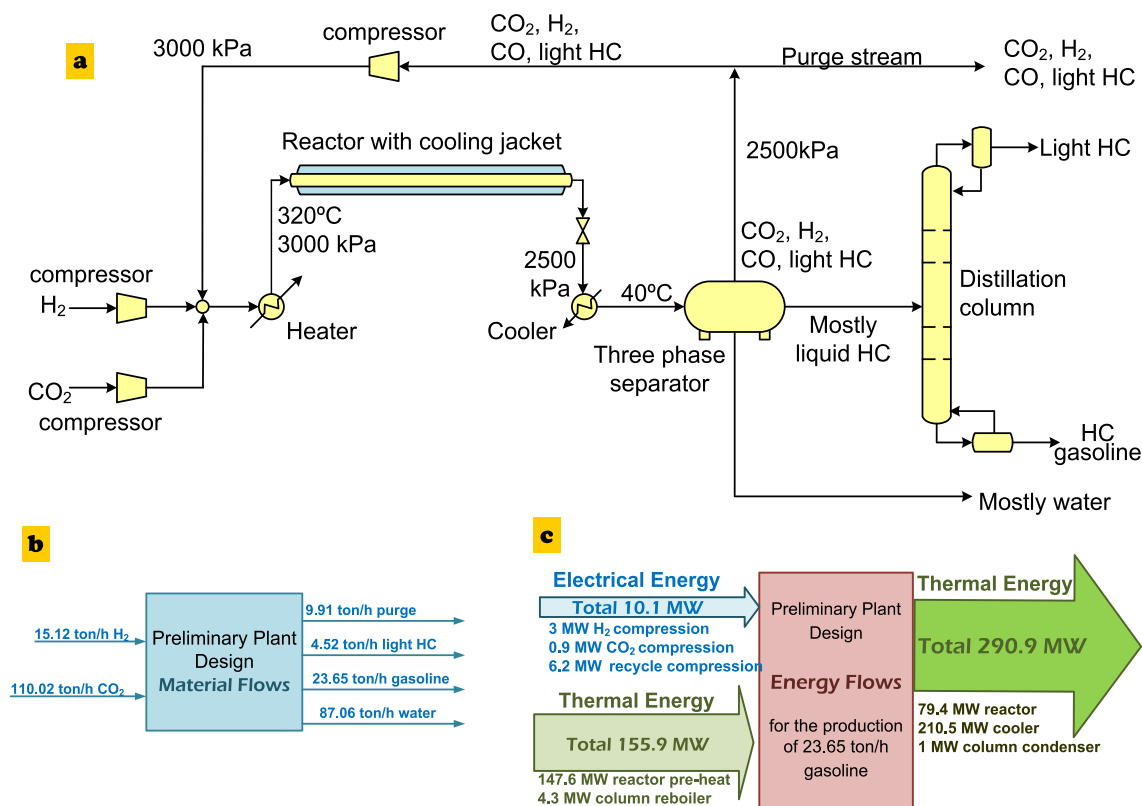
### 2.1. Industrial plant flowsheet development design and optimization

We use the simulator tool Aspen-HYSYS v11 to design and optimize an industrial plant that produces gasoline from CO<sub>2</sub> and H<sub>2</sub> based on the Peng-Robinson thermodynamic model which is widely known to properly estimate thermodynamic variables in hydrocarbons. The design of the plant comprises several stages. First, we simulate a reactor operating under the conditions described by Wei et al. [16], involving 68 species and 63 reactions (see [Supplementary Material](#)). Our reactor design accurately reproduces the product distribution obtained in the laboratory [16]. According to Wei et al. [16], the molecules of CO<sub>2</sub> are reduced to CO via a reverse water-gas shift (RWGS) reaction eqn (1). Subsequently, some CO undergoes hydrogenation via Fischer-Tropsch synthesis (FTS) to produce HC, eqn (2).



In our simulations we use two conversion reactors in series to reproduce the reactions shown in equations (1) and (2), but in practice they take place in a single catalytic reactor with a cooling jacket. The reaction unit operates under conditions given in ref. [16], i.e., 320 °C, 3 MPa and a ratio H<sub>2</sub>/CO<sub>2</sub> of 3 to 1, achieving the required single pass conversion of CO<sub>2</sub> of 34%.

Once the reactor unit has been simulated, the second step is to design a preliminary plant. Given that H<sub>2</sub> is a very expensive reactant, it becomes clear that a recycle stream will be necessary. We draft a preliminary plant flowsheet to accomplish the desired transformation on an industrial scale, see Fig. 1(a). The exit stream of the reactor requires a



**Fig. 1.** Key basic aspects, data, and diagram of the preliminary plant design before any optimization and energy integration steps. (a) Shows a diagram of the preliminary plant. (b) Shows the material flows. The water stream contains 0.25 wt% of impurities. (c) Displays the balance of the energy flows based on the production of 23.65 ton/h of gasoline, which includes the electric and thermal energy input demands as well as the thermal energy that needs to be removed (output) because the set of reactions in the reactor are exothermic.

three-phase unit to separate water from gaseous and liquid hydrocarbons (HCs). The recycle stream recovers the unconverted reactants. A purge stream is required to remove the excess  $H_2$  reactant and achieve a steady state. This setup is used as a foundation for optimizing the plant design in terms of energy and material flows. Simulating this system shows that (see [Supplementary Information](#)) the purge stream has a hydrogen molar flow rate of 217 kmol/h, which is 1.5% of the total molar flow rate of the purge stream (543.6 kmol/h) and 2.8% of the total molar flow rate of the fresh feed of hydrogen (7500 kmol/h). In this preliminary plant design, the hydrogen and light HC that leave the system (in the purge and light HC streams) may be considered to be byproducts, but we show below that they can be used as fuel for a combustor in the three proposed optimized plants. Subsequent verification of the resulting gasoline characteristics [21] yields the following excellent results: 95.9 RON (research octane number), 26.7 kPa RVP (Reid vapor pressure), and 45.0 MJ/kg HHV (high heating value). [Fig. 1](#) (b) is a sketch of the material flows in [Fig. 1](#)(a), whereas [Fig. 1](#)(c) outlines the energy flows and reveals a net excess of “energy generation”, even though the system experiences an overall shortage of electrical energy (see Results section).

The third step is optimization of the preliminary plant shown in [Fig. 1](#). Optimization is required because not all the carbon atoms fed to the system are transformed into a gasoline product. Notice, for instance, that the atom C occurs in many of the species leaving the system in the purge stream ( $CO_2$ , CO, and light hydrocarbons (HC)) and the distillation column (light HC). However, these species are all different from the desired product: gasoline. Also, the purge stream loses  $H_2$  which is an expensive reactant. Moreover, it is important to bear in mind that our simulations must not change the reactor product distribution because this information was obtained from Wei et al. [16] and depends on the use of a particular catalyst that makes the transformation possible.

**Table 1**

Cost of producing  $H_2$  (\$/kg) by different technologies (from Parkinson et al. [25]). Letters A to M are used for quick identification of the technologies.

	low	central	high
A = steam methane reforming	1.03	1.26	2.16
B = coal gasification	0.96	1.38	1.88
C = methane pyrolysis	1.36	1.76	1.79
D = thermochemical water splitting (S-I) cycle	1.47	1.81	2.71
E = steam methane reforming with carbon capture sequestration (CCS)	1.93	2.09	2.26
F = thermochemical water splitting (Cu-Cl) cycle	1.47	2.13	2.70
G = biomass gasification	1.48	2.24	3.00
H = coal gasification with CCS	2.24	2.46	2.68
J = Biomass gasification with CCS	3.15	3.37	3.60
K = Electrolysis – nuclear	4.99	6.79	8.21
L = Electrolysis – wind	4.61	7.86	10.01
M = electrolysis – solar	7.10	12.00	14.87

Therefore, in optimizing the preliminary plant it makes sense to take advantage, wherever possible, of the excess thermal energy of the unwanted streams (purge and light HC). In other words, it is sensible to make use of the energetic potential of these streams towards the production of electricity. Hence, we propose joining and then combusting the light HC and purge streams to harness the energy that will be released. To that end we study and optimize three options that make use of the energy potential of the unified waste streams: (a) oxy-combustion of waste streams plus Allam cycle [22,23], (b) oxy-combustion of waste streams plus Rankine cycle and (c) combustion of waste streams plus gas turbine together with additional heat recovery by steam generator in conjunction with a steam turbine.

**Table 2**

Costs of O<sub>2</sub> and CO<sub>2</sub> and the income from selling electricity. A currency exchange rate \$0.83/€ has been assumed.

	Optimistic scenario	Pessimistic scenario
Cost of O <sub>2</sub> (\$/kg) used in this study (from Eurostats [28]) for the oxy-combustion associated with technologies A to J in Table 1	0.02	0.25
Income from selling O <sub>2</sub> (\$/kg) product (from Eurostats [28]). K to M technologies produce O <sub>2</sub> (electrolysis) as a byproduct. The excess O <sub>2</sub> can be sold to earn income.	0.25	0.02
Cost of CPS CO <sub>2</sub> (\$/kg) used in this work (taken from Schlögl [3])	0.04	0.06
Cost of DAC CO <sub>2</sub> (\$/kg) used in this work (from Fasihi et al. [29])	0.1104	0.1843
Income from selling the electricity generated (\$/kWh) (from Eurostat [28])	0.0581	0.0083

**Table 3**

CO<sub>2</sub> emissions associated with the production of H<sub>2</sub> (kg CO<sub>2</sub>e/kg H<sub>2</sub>) in this work (from Parkinson et al. [25]).

	low	central	high
A = steam methane reforming	10.09	13.24	17.21
B = coal gasification	15.81	21.82	28.49
C = methane pyrolysis	4.20	6.10	9.14
D = thermochemical water splitting (S-I) cycle	0.41	1.20	2.20
E = steam methane reforming with carbon capture sequestration (CCS)	2.97	5.61	9.16
F = thermochemical water splitting (Cu-Cl) cycle	0.70	1.08	1.80
G = biomass gasification	0.31	2.60	8.63
H = coal gasification with CCS	2.18	4.16	7.93
J = Biomass gasification with CCS	-11.66	-14.58	-17.50
K = Electrolysis - nuclear	0.47	0.76	0.96
L = Electrolysis - wind	0.52	0.88	1.14
M = electrolysis - solar	1.32	2.21	2.50

## 2.2. Cost evaluation and environmental impact assessment

The cost evaluation of a process plant can be carried out on many levels. Given that H<sub>2</sub> is such an expensive reactant, it makes sense to start by simply checking the gross economic margin, i.e., whether the cost of the fresh feed can be compensated by the revenue from selling the gasoline produced under the best possible scenario. If this simple calculation provides a good figure for the breakeven point of green gasoline, then the rigorous evaluation that takes into account the capital and operational costs can be done following the procedure described in Turton et al. [24].

In terms of environmental impact, we have accounted for the direct and also the indirect CO<sub>2</sub> released by the process. The indirect CO<sub>2</sub> is that which is released during the production of H<sub>2</sub> [25] and O<sub>2</sub> [26] and also from capturing and concentrating CO<sub>2</sub> by means of two techniques, CPS and DAC [3,26]. Tables 1 to 4 collect all the information gathered from the literature and used in this study to estimate costs and CO<sub>2</sub> emissions.

We have also evaluated our process according to a set of environmental metrics [27]: mass economy, carbon efficiency and E factor as

**Table 4**

CO<sub>2</sub> emissions from the production of O<sub>2</sub> (from Ecoinvent [26]) and also from the capture of CO<sub>2</sub> (from Schlögl [3]).

CO <sub>2</sub> emissions from the production of O <sub>2</sub> associated with technologies A to J in Table 1	0.59247 (kg CO <sub>2</sub> e/kg O <sub>2</sub> )
CO <sub>2</sub> emissions from the production of O <sub>2</sub> . Technologies K to M produce O <sub>2</sub> as a byproduct (electrolysis) during the synthesis of H <sub>2</sub> . These emissions are already accounted for in the case of H <sub>2</sub>	0 (kg CO <sub>2</sub> e/kg O <sub>2</sub> )
CO <sub>2</sub> emissions from the capture of CO <sub>2</sub> (CPS technique) calculated from the thermal energy consumption in Schlögl [3]: 300 kWh/ton of CO <sub>2</sub> and using as heating agent, steam, 0.10344 kgCO <sub>2</sub> e/MJ [26]	0.11160 (kg CO <sub>2</sub> e/kg CO <sub>2</sub> )
CO <sub>2</sub> emissions from the capture of CO <sub>2</sub> (DAC technique) calculated from the thermal energy consumption in Schlögl [3]: 2000 kWh/ton of CO <sub>2</sub> using steam (0.10344 kgCO <sub>2</sub> e/MJ [26]) as heating agent	0.74399 (kg CO <sub>2</sub> e/kg CO <sub>2</sub> )

presented in equations (3) through (5).

$$\% \text{ Mass economy} = \frac{\text{Mass of desired product}}{\text{total mass of feed}} \times 100 \quad (3)$$

$$\% \text{ Carbon Efficiency} = \frac{\text{Moles of C in desired product}}{\text{Moles of C in feed}} \times 100 \quad (4)$$

$$E \text{ factor} = \frac{\text{Mass of waste produced}}{\text{Mass of desired product}} \quad (5)$$

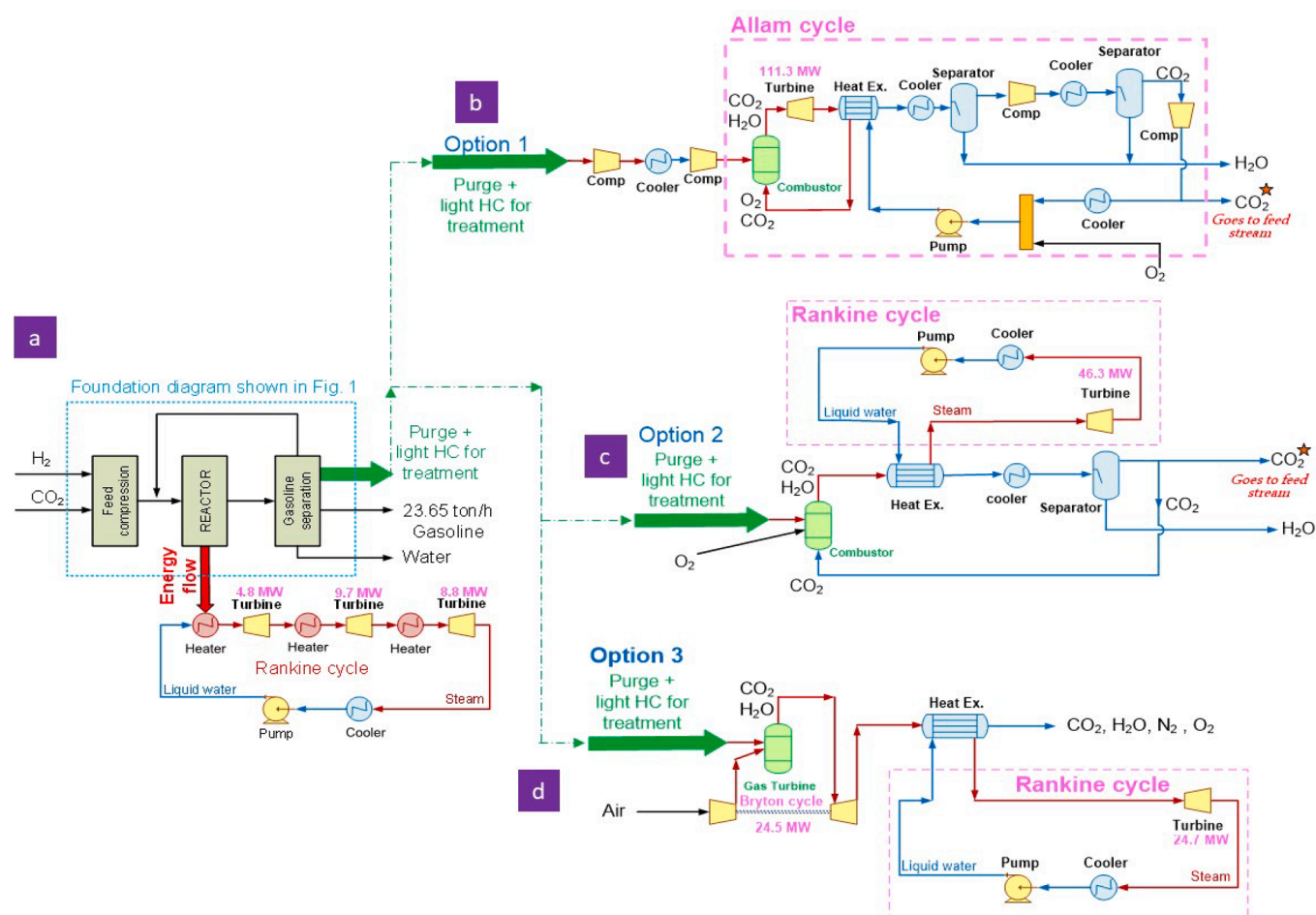
## 3. Results

In this section, we analyze our results to verify whether it is both economically feasible and environmentally sound to design and construct an industrial process plant that consumes H<sub>2</sub> and atmospheric CO<sub>2</sub> in order to produce green gasoline fuel that, in addition, can contribute to the circular economy.

### 3.1. Optimized flowsheets

From the preliminary plant design done in Aspen-Hysys and shown in Fig. 1(a), we have obtained the quantitative results shown in Fig. 1(b) and (c). These results provide the basis for the completion of an optimized flowsheet. For instance, Fig. 1(c) shows that the preliminary plant, which produces 23.65 ton/h of gasoline, requires, on the one hand, 3 MW and 0.9 MW, respectively, for the compression of the fresh H<sub>2</sub> and CO<sub>2</sub> feed streams, 147.6 MW for the feed pre-heater, 4.3 MW for the column reboiler and 6.2 MW for the compressor in the recycle stream; but on the other hand, the plant needs to release 1.0 MW from the distillation column condenser, 79.4 MW from the cooling jacket of the reactor and 210.5 MW from the cooler located next to the reactor. For the interchange of this energy, a heat exchanger network (HEN) [30] can be used. Since more energy needs to be released than is consumed, we propose (see Fig. 2(a)) that the extra energy be harnessed to move turbines and “generate” electricity. For example, the heat that the reactor needs to release can be used to drive a Rankine cycle, i.e., the excess heat can be used to vaporize water flowing in a closed circuit that, in turn, can move 3 turbines producing 4.8, 9.7, and 8.8 MW, respectively. Furthermore, we consider three energy producing options that take advantage of the purge and light HC streams that are burned in a furnace after first combining them (see Fig. 2(b), 2(c) and 2(d)):

*Option 1 - Fig. 2(b), oxy-combustion of waste streams plus Allam cycle [22,23]:* The stream that results from joining together the purge and light HC streams is burnt in the presence of O<sub>2</sub> (oxy-combustion) and the exhaust gases (CO<sub>2</sub> and H<sub>2</sub>O) are then used to drive a so-called Allam cycle. All the streams in this cycle are very rich in CO<sub>2</sub> for two reasons: one, a large flowrate of CO<sub>2</sub> dilutes the water after combustion, making it possible to employ the exhaust gases as a working fluid that exploits the supercritical conditions of CO<sub>2</sub>; and two, the high flowrate of CO<sub>2</sub> as compared to O<sub>2</sub> entering the combustion chamber helps to reduce the temperature in the combustor. As shown in the figure, the combustion gases move a turbine that provides 111.3 MW. The net electrical power generation from this option (foundational section of the plant together with option 1) is 2.924 kWh/L of gasoline. Finally, the purged CO<sub>2</sub> stream can be recycled and recombined with the fresh feed stream in



**Fig. 2.** Optimized plant design that includes energy integration and three options to deal with the purge and light HC streams. The core section in (a) corresponds to the foundational diagram already shown in Fig. 1(a). Sections (b), (c) and (d) correspond to three different options that connect to the core section (a) to harness the energy released during the combustion of the purge and light HC streams.

Fig. 2(a) because it consists of pure CO<sub>2</sub>. The overall CO<sub>2</sub> conversion in this option is close to a 100% but does not reach this value because the condensed water streams leaving the process carry some dissolved (therefore, unreacted) CO<sub>2</sub>. The exact conversion value is 99.0%.

**Option 2 - Fig. 2(c), oxy-combustion of waste streams plus Rankine cycle:** In this alternative, as in option 1, the resultant purge plus light HC stream is also burnt in the presence of O<sub>2</sub>. The resultant exhaust gases are cooled down by means of a heat exchanger and this energy can be employed in a Rankine cycle to generate 46.3 MW in the steam turbine. The net electrical power generation in this case (foundational section of the plant together with option 2) is 1.957 kWh/L of gasoline. The condensed water needs to be extracted. As can be seen in Fig. 2(c), the system is designed to recycle a stream of pure CO<sub>2</sub> that behaves as a refrigerant in the combustion chamber. The overall CO<sub>2</sub> conversion is 99.3% for the same reasons as in option 1 (condensed water carries some CO<sub>2</sub>).

**Option 3 - Fig. 2(d), combustion of waste streams plus gas turbine along with additional heat recovery by steam generator in conjunction with a turbine:** The final alternative considered in this study consists of burning in air the resultant stream (purge plus light HC) and employing the evolved exhaust gases (CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, and O<sub>2</sub>) to move a gas turbine. The energy that can be generated by this turbine is 24.5 MW. In addition, these exhaust gases can be cooled down further and the exchanged thermal energy utilized to drive a Rankine cycle with a steam turbine that harnesses 24.7 MW more. The net electrical power generation of this option (foundational section of the plant together with option 3) is 2.057 kWh/L of gasoline. The downside in this case is that the CO<sub>2</sub> exiting the heat

exchanger is not pure and cannot be directly recycled as part of the fresh feed. The overall CO<sub>2</sub> conversion is 69% in this case.

The optimized design (all three options) maximizes the heat recovery and simultaneously minimizes the consumption of external cooling services. It is important to point out that, as a simplification, only pure CO<sub>2</sub> enters the system in our simulations. However, the proposed design will work equally well provided that the feed-stream is rich in CO<sub>2</sub> and the other substances also present in the stream do not damage the catalyst inside in the reactor.

The three options described above have been successfully simulated and optimized in HYSYS. The resulting overall mass balance is presented in Fig. 3. This information will be useful for economic and sustainability metrics calculations. All other aspects of the results are detailed in the accompanying Supplementary Material. The input CO<sub>2</sub> streams in options 1 and 2, shown in Fig. 3, represent consumption of fresh CO<sub>2</sub>, i.e., the process can also consume CO<sub>2</sub> generated in the furnace, which appears in the exit streams in Fig. 2(b) and 2(c), and is recycled to re-join the fresh feed. In Option 3 the furnace uses air, which serves two purposes: to provide oxygen for the combustion and to cool down the reactant mixture in the furnace. The output gas mixture leaving this system cannot be directly recycled. Notice the difference between the mass percentages in the output streams of option 3 compared to the other two: in the third, the mass percentages of the output streams are 10.3% water, 2.8% gasoline and 86.9% gas mixture whereas the mass percentages in the first two options are 82% water and 18% of gasoline in both cases. This difference will affect the environmental metrics.

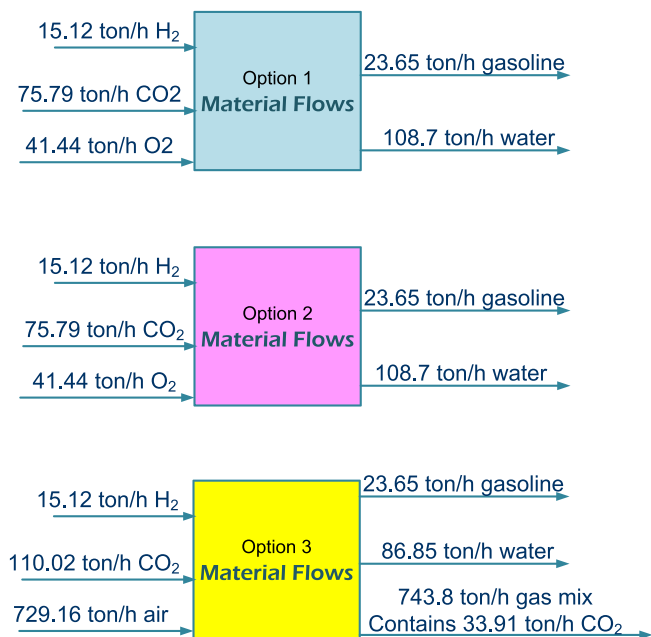


Fig. 3. Overall material balances for the three options presented in Fig. 2. Options 1 and 2 use pure O<sub>2</sub> to operate the furnace, therefore the diagrams referring to options 1 and 2 show the net balance of CO<sub>2</sub> input (or consumed) to the system. The stream of water leaving the system in any of the three options contains traces of CO<sub>2</sub>.

### 3.2. Optimized HEN (Heat Exchanger Network)

With the view to optimizing the three options described above to an even greater extent, the reliance on heating and cooling utilities has been minimized by means of a HEN [30]. This HEN has been estimated from the Pinch technology and posterior refinement based on a rigorous

method. In brief, a HEN makes use of hot process streams to heat cold ones, and vice versa: cold process streams are used to cool down hot ones. In other words, we achieve an optimal heat integration between hot and cold process streams, thus reducing the dependence on heating and cooling utilities as a consequence. This integration of hot/cold streams has been carried out for all three options shown in Fig. 2 and the full results and a brief description of each can be found in the Supplementary Material. Fig. 4 shows a diagram of the optimized HEN that has been obtained for option 2 shown in Fig. 2(c). All network streams are shown in color. Notice that the units that are already present in Figs. 1 and 2 appear in the color grey to avoid confusion with the HEN. All the heat exchangers shown in Figs. 1 and 2 are represented in Fig. 4 by a color-coded network.

### 3.3. Economic analysis

We start by first calculating the gross economic margin. To that end, we consider the cheapest cost of H<sub>2</sub> published in Parkinson et al. [25], i. e., \$0.96/kg of H<sub>2</sub>, which agrees with the data published on Eurostat’s website [28] or the data reported in Piebalgs et al. [31]. Recognizing that the hydrogen gas input required to produce 23.65 ton/h of gasoline is 15.12 ton/h (see Fig. 3), we find that it is necessary to spend at least \$116 million per year (M\$/y) only on hydrogen gas procurement. In the event that the CO<sub>2</sub> cost is negligible and that the combustion in the combustor-furnace (see Fig. 2) occurs in air, the breakeven price for gasoline before taxes will be \$0.48/L, which is not a bad figure (the density of gasoline obtained from the process simulator was: 0.7859 kg/L). However, in performing this back-of-the-envelope calculation, we have ignored important expenses such as the investment (capital cost) of the entire plant, the operational costs (direct and fixed manufacturing costs including labor costs, general expenses, depreciation, etc.), the cost of the O<sub>2</sub> in options 1 and 2 shown in Fig. 2(b) and 2(c), higher costs for hydrogen or even the cost of purchasing CO<sub>2</sub>. Nevertheless, we note that it is possible to obtain extra income from not only selling the gasoline but also from selling the net extra electricity generated by the process.

Because the value of the gross economic margin that is obtained is

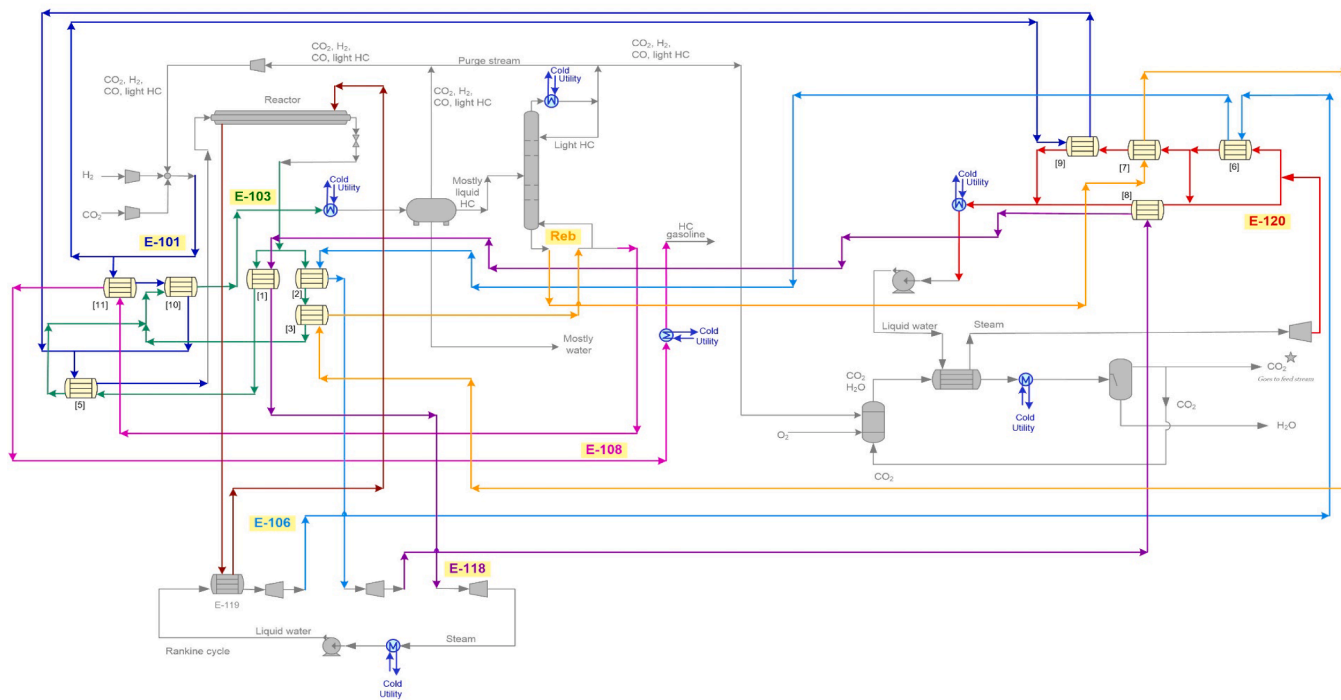


Fig. 4. Diagram of the optimized heat exchange network (HEN) for option 2 shown in Fig. 2(c). Notice (red arrows), as an example, that the cooler present in the Rankine cycle in Fig. 2(c) (denoted here as E-120) is replaced by four heat exchangers. Process units already shown in Figs. 1 and 2 appear here in grey color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reasonable, we can now proceed with a rigorous calculation of the breakeven cost of gasoline that includes labor costs, general expenses, depreciation, etc. To that end, we need to account for the capital and operational costs of the three options shown in Fig. 2. For that, we have followed the stepwise procedure described in Turton et al. [24]. The Supplementary Material provided illustrates this calculation for Option 3 which is shown in Fig. 2(d). The other two options are evaluated following the same approach. Thus, the calculated capital costs of the options are: 128 M\$ for option 1, 73 M\$ for option 2, and 122 M\$ for option 3. For the operational costs we need to include, among other considerations, a realistic variety of scenarios under which H<sub>2</sub> is sourced. Consequently, we have considered all the costs (and cost ranges) of obtaining hydrogen and their corresponding CO<sub>2</sub> equivalent emissions (and ranges) from the 12 different technologies studied in Parkinson et al. [25]. See Tables 1–4. They are labelled A to M for ease of reference and identification in Fig. 5 and in the subsequent discussion:

- A = steam methane reforming
- B = coal gasification
- C = methane pyrolysis
- D = thermochemical water splitting (S-I) cycle
- E = steam methane reforming with carbon capture sequestration (CCS)
- F = thermochemical water splitting (Cu-Cl) cycle
- G = biomass gasification
- H = coal gasification with CCS
- J = Biomass gasification with CCS
- K = Electrolysis – nuclear
- L = Electrolysis – wind
- M = Electrolysis – solar

Fig. 5 shows, in six different panels, a large portion of the results obtained in this study. We have considered a total of 144 realistic scenarios of the operational costs (3 options × 12 technologies × 2 CO<sub>2</sub> sources × 2 settings): for each of the three options depicted in Fig. 2, we have included the twelve technologies (A to M) that produce hydrogen as described in Parkinson et al. [25], two possibilities (DAC or CPS) for obtaining the CO<sub>2</sub> feed stream [3] and two settings (optimistic and

pessimistic). The optimistic setting places a lower bound on the operational cost because it considers the lowest costs of producing CO<sub>2</sub> and O<sub>2</sub> and the highest income from selling the electricity generated. The pessimistic setting implies the highest cost of CO<sub>2</sub> and O<sub>2</sub> and the least income from selling electricity. See Tables 1 and 2. Finally, the results of the breakeven costs of gasoline in the 144 scenarios are shown in Fig. 5 as a function of the CO<sub>2</sub> released or captured.

We assume here that both, DAC and CPS plants, are located near the gasoline fuel production plant, which immediately implies that we are ignoring any cost or environmental burden of transporting CO<sub>2</sub> once captured. This is a simplification that could affect the final decision of choosing between DAC or CPS because the costs of transporting CO<sub>2</sub> may be considered high [32], although capturing CO<sub>2</sub> is the stage in CCS that involves around 90% of the total cost [33]. For the year 2020, we use the two extreme values in the range of costs of DAC-obtained CO<sub>2</sub> reported by Fasihi et al. [29]. The corresponding costs for CPS are taken from ref. [3]. To reconcile figures in \$ and €, an exchange rate of \$0.83/€ has been assumed. For the cost of O<sub>2</sub>, we have used the range provided by Eurostat [28] for the year 2020.

It is important to point out that for the three electrolysis options under consideration (nuclear, wind, and solar or K, L, and M), the cost of producing O<sub>2</sub> and the corresponding CO<sub>2</sub> emissions are zero. This is because O<sub>2</sub> is a byproduct in the production of H<sub>2</sub> and those costs are imputed to hydrogen only. Finally, to estimate the revenue that can be earned from selling the electricity generated, we have also referred to Eurostat [28] for the year 2020.

A table containing the operational costs of each of the 144 evaluated scenarios is given in the Supplementary Material. These values range from 244 to 1951 M\$/y. The breakeven cost of gasoline has been calculated by taking into consideration capital and operational costs and is plotted on the y-axis in Fig. 5. The error bars in the y-variables represent the cost ranges reported in refs. [25,28]. The abscissa of this figure is calculated using the information provided in the next section (environmental assessment).

### 3.4. Environmental assessment

An overly-simplistic assessment of Fig. 3, which shows the details of

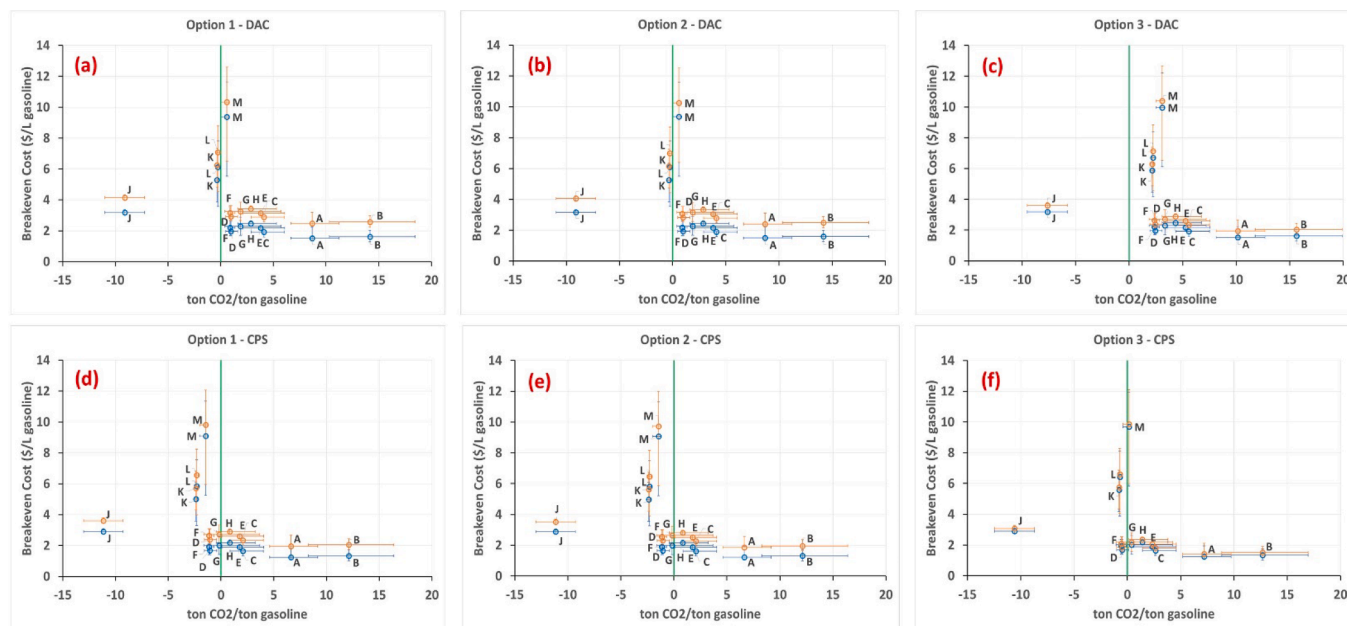


Fig. 5. Main results from the economic and environmental evaluation. Ranges of breakeven costs for gasoline and CO<sub>2</sub> emissions grouped according to the three options under consideration (shown in Fig. 2), the two technologies for capturing CO<sub>2</sub> (DAC and CPS) and the twelve technologies needed to produce hydrogen (A to M). The minimum in each range (blue dot) is calculated for the optimistic setting whereas the maximum (upper orange dot) corresponds to the pessimistic setting. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the overall material balance of the three options displayed in Fig. 2, could lead to the erroneous conclusion that there is a “net” consumption of 76 ton/h of CO<sub>2</sub> to produce 24 ton/h of gasoline. But this simple calculation ignores the indirect CO<sub>2</sub> that is released in the process. Therefore, we have also accounted for the indirect CO<sub>2</sub> emissions attributed to the 144 scenarios under study. The CO<sub>2</sub> equivalent emissions (and ranges) of the 12 different technologies that are used to produce H<sub>2</sub> have been taken from Parkinson et al. [25]. For the emissions of CO<sub>2</sub> during the production of O<sub>2</sub>, we have used the data in Ecoinvent, GWP 100a (global warming potential over a 100-year time horizon). The CO<sub>2</sub> emissions during the capture of CO<sub>2</sub> by the two technologies under consideration (DAC or CPS) can be estimated from the thermal energy that these technologies consume [3]. Summing up, the abscissa in Fig. 5 represents the tonnes of CO<sub>2</sub> released per ton of gasoline produced, which also includes the amount of CO<sub>2</sub> released during the production of H<sub>2</sub> and O<sub>2</sub> as well as the amount released during the CO<sub>2</sub> concentration process (DAC or CPS). Note that it can be positive or negative depending on whether the technology is a net producer or consumer of CO<sub>2</sub>. The error bars in the x-variables correspond to the CO<sub>2</sub> equivalent emissions ranges reported in ref. [25]. The green vertical line in Fig. 5 separates the scenarios that are net consumers of CO<sub>2</sub> (negative abscissas) from those that are not. The green line thus separates the environmentally desirable scenarios from the unwanted ones. Numerical information on these quantities are collected in the Supplementary Material.

We have also evaluated our process design based on the set of environmental metrics defined in equations (3) through (5) and summarized in Table 5. The Supplementary Material collects the information required to calculate these parameters. The desired product is gasoline. The % mass economy exhibits better results for options 1 and 2 (17.9%) than for option 3 (2.8%) which is penalized because of the large amount of air in the input stream. The % carbon efficiency is 99.0% for option 1 and 99.3% for option 2. It is not 100% because there is some CO<sub>2</sub> and traces of other light species present in the condensed water streams shown in Fig. 2. Option 3 exhibits a much lower value of the % carbon efficiency, 69.2%. The E factor should be zero for options 1 and 2 based on the consideration that water (the byproduct) is not really a waste stream and could be returned safely to the environment. But if water needs to be considered as a waste because it contains traces of light HC species, the E factor for options 1 and 2 becomes 4.6. This represents the worst-case scenario assuming that water cannot be recovered at all. Option 3 yields the poorest results because it produces a gaseous waste stream containing CO<sub>2</sub>. The E factor is 1.4 based solely on the CO<sub>2</sub> in the gaseous waste stream, but if we add to that the entire mass flow rate of water leaving the system, it rises to 6.

#### 4. Discussion

We start by scrutinizing in detail the various results shown in Fig. 5, where the calculated breakeven cost of gasoline is plotted against the tonnes of CO<sub>2</sub> consumed (if negative abscissas) or liberated (if positive abscissas) per ton of gasoline produced. As mentioned above, Fig. 5 collects results for a total of 144 realistic studied scenarios, properly grouped into six panels. The information has been plotted in the most

concentrated manner possible to allow easy identification of scenarios leading to the cheapest or the most expensive breakeven cost of gasoline (y-axis) while simultaneously permitting easy identification of the scenarios that release or consume the most CO<sub>2</sub> (x-axis). The three top panels correspond to the scenarios where the feed CO<sub>2</sub> is obtained from DAC while the bottom three correspond to CPS. The letters A to M help to identify which technology has been used to produce the required H<sub>2</sub>. For each letter A to M there are two points in each of the six panels, one on top (orange colour) and the other at the bottom (blue colour) which delimit the range of breakeven costs of gasoline according to the optimistic (blue dot) and pessimistic (orange dot) scenarios described previously.

From a mathematical point of view, there is clearly a set of undesired scenarios that are dominated by better ones in the sense that, at a similar cost, there is another scenario with better environmental metrics and vice versa. Whatever final decision is adopted with regard to any of these processes, one must always choose one that is not dominated in the above way. Fig. 5 permits making a clear distinction between processes that are inherently economical based on current technology and others that are inherently more environmentally sustainable.

Options 1 and 2 are seen to be very similar to each other (Fig. 5(a) is very similar to Fig. 5(d) and, likewise, Fig. 5(b) to 5(e)). Given that the capital cost of option 1 is higher than that of option 2, the latter appears to be the optimal choice. Furthermore, it becomes evident that Fig. 5(a), (b), and (c), corresponding to the DAC technology, exhibit less favourable results than Fig. 5(d), 5(e), 5(f), corresponding to the CPS technology.

The lowest breakeven cost of gasoline (\$1.22/L) is shown in Fig. 5(e), which corresponds to H<sub>2</sub> production technology A (steam methane reforming), under option 2, CPS, and an optimistic setting. However, this combination would lead to a net production (positive sign) of CO<sub>2</sub> (direct and indirect emissions) of + 6.64 tons CO<sub>2</sub>/ton gasoline. At the other end of the spectrum, the option that consumes the most CO<sub>2</sub>/ton gasoline is technology J in Fig. 5(e), in which the H<sub>2</sub> originates from biomass gasification with CCS. This combination will consume (negative sign) – 11.15 tons CO<sub>2</sub>/ton gasoline but the downside is that the cost of producing gasoline is bracketed between \$2.88/L (optimistic setting) and \$3.53/L (pessimistic setting). A possible compromise in terms of economic and environmental impact of a future industrial plant would thus be to use technology D in Fig. 5(e). It is based on CPS carbon concentration with H<sub>2</sub> generated from the thermochemical water splitting (S-I) cycle and results in a breakeven cost for gasoline of between \$1.65 and \$2.30/L and a capture of 1.06 ton CO<sub>2</sub>/ton of gasoline produced. Such a plant would have an operational cost of between 328 and 427 M\$/y. Another option would be to choose a mix of technologies instead of just a single one.

Given that option 2 offers the lowest capital cost, in Fig. 6 we show the breakeven cost of gasoline for this option compared to the base case or preliminary plant shown in Fig. 1(a) and 2(a). The top panel corresponds to the situation where the CO<sub>2</sub> in the feed stream is obtained from DAC while the bottom panel corresponds to CPS. Notice that the lack of optimization in the base case makes the breakeven cost of gasoline more expensive than for the optimized situation in option 2. Even though the differences in absolute values between the base case and the heat-integrated and optimized one in Fig. 6 seem small, the relative values can differ greatly, ranging from 7% to 40.4% for DAC and from 5.5% to 39.4% for CPS. But even a difference of just 5.5% is a very significant number when it comes to a large-scale industrial plant.

At this point of the discussion, the following consideration becomes pertinent: all monetary figures cited above have been calculated for the year 2020. It would therefore be unfair to directly compare the figures obtained in this study with those corresponding to the current production cost of fossil gasoline because it is a very well-established industry. Such a comparison might naively imply that the scenarios reported here are not financially attractive at all. However, there are other relevant aspects that could contribute to diminishing the final cost of the considered green gasoline in the long run:

**Table 5**

Environmental metrics calculated according to equations (3) to (5) for the three options presented in Fig. 2.

	Option 1	Option 2	Option 3
% mass economy eq. (3)	17.9%	17.9%	2.8%
% carbon efficiency eq. (4)	99.0%	99.3%	69.2%
E factor eq. (5) where water is not taken as a waste stream	0	0	1.4
E factor eq. (5) where water is considered to be a waste stream	4.6	4.6	6



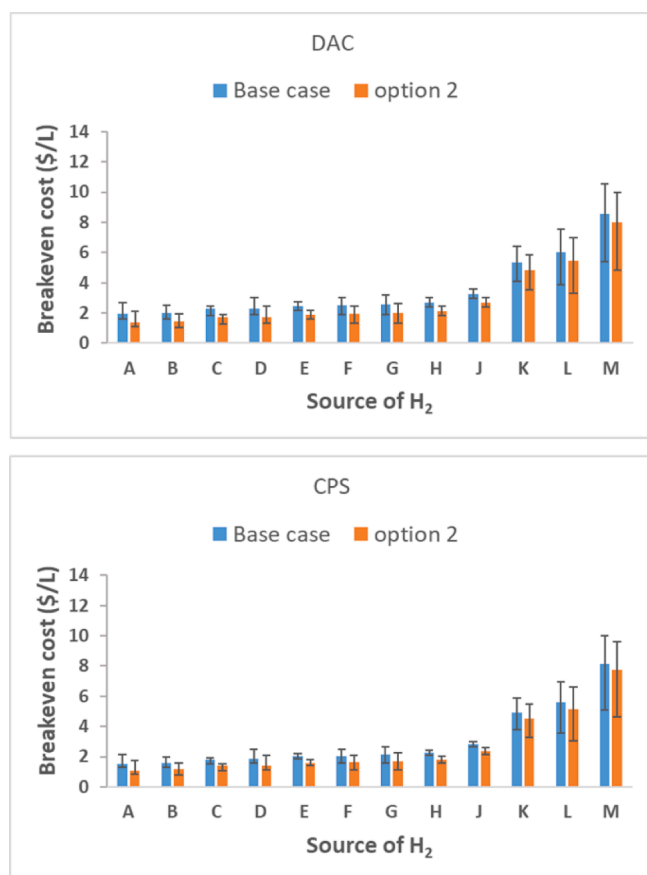


Fig. 6. Comparison between the breakeven cost of gasoline for the base case (without optimization) and the results obtained for option 2 as a function of the source of hydrogen (technologies A to M).

- The price of CO<sub>2</sub> is expected to fall dramatically over time: a 55% reduction by 2030, 70% by 2040, and 77% by 2050 [29]. The price of H<sub>2</sub> is also expected to decrease for two reasons: maturity of the production technology and economies of scale [3]. The report by Piebalgs et al. [31] expects the cost of H<sub>2</sub> to decrease by about 45% by 2030 and up to 65% by 2050. This is an expected outcome because hydrogen has become a key priority in terms of research and investment in the European Union [34]
- Our proposal can also generate extra income from the greenhouse gas (GHG) emission reduction credits that a future plant is likely to be eligible for in the corresponding Emission Trading Scheme (ETS).
- Contrary to the case of fossil gasoline, government taxation could be waived to incentivize the production of green gasoline based on its promising positive outcomes for society: first, it can stimulate the economy and create jobs during the construction and operation of future plants; second, these plants have the potential to reduce fossil fuel dependence, reducing, in turn, the reliance of countries on fossil fuel imports [4]; and third, it is a way to deal with man-made CO<sub>2</sub> emissions and contribute to the circular economy.

In terms of environmental considerations, we demonstrate quantitatively that all three options proposed here behave as a net producer of energy. This is possible because the results exhibit complete heat integration that, in addition, has been optimized. Option 2 is associated with the smallest capital cost and also exhibits remarkable outcomes from an environmental perspective: it is possible to achieve both close to 100% atomic carbon efficiency and 0% E factor waste.

## 5. Conclusions

We have demonstrated that it can be feasible to design an environmentally-friendly and eventually, in the near future, profitable process that produces an excellent green gasoline fuel at a cost similar to that of fossil fuel. But not only that, we have also shown that this process is a net producer of electricity and a net consumer of carbon dioxide, both in terms of direct and indirect emissions. This represents a very important achievement given the current pace of consumption of fossil fuel in the world. Every liter of green gasoline produced will avoid the extraction of oil from the lithosphere that is used to produce a liter of fossil gasoline. In the long run, we envision that transportation based on combustion-engine vehicles will become outmoded, but realizing that the transition from the present situation to a sustainable transportation system is not likely to occur fast enough, especially in large developing countries, we recommend using green gasoline in the interim as an alternative to fossil gasoline.

## Author Contributions

All authors contributed significantly to the research. All authors discussed the conception of the research idea and designed the details about the research requirements. J.A.C and M.J.F.T. performed the simulation of the process in Hysys and subsequent calculations. W.D. wrote the introduction, provided critical feedback and helped shape the manuscript. M.J.F.T. wrote the results. All the authors contributed to the analysis and discussion on the data to write the conclusions and abstract. J.A.C supervised the whole project.

## Declaration of Competing Interest

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

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.enconman.2021.115115>.

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