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Sustainability Assessment of Thermocatalytic Conversion of CO₂ to Transportation Fuels, Methanol, and 1-Propanol

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ABSTRACT

Using captured CO₂ as a chemical feedstock is widely considered towards establishing low carbon technologies to mitigate climate change. Process systems engineering analyses can help increase the chances of success by identifying attractive targets at early stages. Here, a comparative techno-economic and environmental analysis of three thermocatalytic CO₂-based plants individually producing liquid hydrocarbon transportation fuels (LHTF), methanol, and 1-propanol is introduced. While the 1-propanol plant generates a remarkable profit, the LHTF and methanol plants are not economically viable, mainly due to the CO₂ and H₂ input cost. Sensitivity analysis shows that the feedstocks prices need to drop by 80% for these two plants to break even. A tax structure is not a sensible option since it would be more than four times the highest carbon tax currently implemented in country. In term of the environmental performance, the CO₂ utilization efficiencies are 45.5%, 60.1%, and -33.8% for LHTF, methanol, and 1-propanol synthesis, respectively. The negative utilization efficiency in the 1-propanol plant highlights the need of a greener production of its raw material ethylene. When the entire life cycles of the products are considered, these emerging plants emit 85.9%, 77.4%, and 35.9% less CO₂ than their conventional counterparts for the same output. Our study provides the first evaluation of CO₂-based 1-propanol synthesis, highlighting its potential, and underscores gaps in the CO₂-based LHTF, methanol, and 1-propanol by comparing them on a uniform common basis, and sets future research directions.

KEYWORDS

CO₂ utilization; Transportation fuels; Methanol; 1-Propanol; Techno-economic analysis; CO₂ emission avoidance.

ABBREVIATIONS

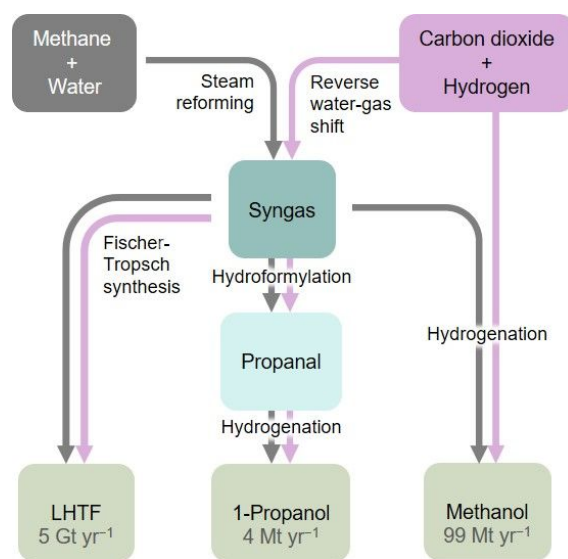
\$	U.S. dollar
\$MM	Million U.S. dollar
a ⁻¹	Per annum
CCS	CO ₂ capture and storage
CCU	CO ₂ capture and utilization
CEPCI	Chemical engineering plant cost index
EOR	Enhanced oil recovery
FTS	Fischer–Tropsch synthesis
HFM	Hydroformylation
LHTF	Liquid hydrocarbon transportation fuels
LHV	Lower heating value
Mt	Megatonne
RWGS	Reverse water-gas shift
t	Tonne
TEG	Triethylene glycol

INTRODUCTION

In order to achieve the target set by the Paris agreement, the global CO₂ emissions must steadily fall annually by 7.6% in the next decade¹. A consistent increase of renewable energy in the total energy mix² and increased adoption of CO₂ capture, storage, and utilization technologies³⁻⁵ are the crucial pre-requisites to accomplish this daunting task. As of late 2020, 26 commercial CO₂ capture and storage (CCS) facilities are operational worldwide, most of which use the captured gas for enhanced oil recovery (EOR)⁶. The recent closure of Petra Nova, the last active CCS-EOR coal plant in the USA, demonstrates the susceptibility of these facilities to the falling oil prices and emphasizes the importance of potentiating CO₂ capture and utilization (CCU) solutions as well as of diversifying the portfolio of CO₂-based applications. Indeed, only about 110 Mt of CO₂ is currently utilized per year (*i.e.*, 0.3% of the annual total emissions)⁵, mainly in the production of urea, CO-derived methanol, and inorganic carbonates. Toward a closed carbon cycle, CO₂ should become a major feedstock for methanol synthesis^{7,8}, and other products, such as methane⁹, ethylene¹⁰, ethanol¹¹, formate^{7,12}, dimethyl ether⁷, carboxylic acids^{13,14}, polymers^{15,16}, as well as liquid hydrocarbon transportation fuels (LHTF)¹⁷, shall enter the portfolio. The scale of CO₂ utilization must become significant in comparison to the global emissions to decarbonize the economy, but any strategy that involves large-scale production of low-demand specialty chemicals would eventually saturate the market and cause the product values to plummet. In addition, the routes envisioned shall be efficient in terms of energy and materials, with direct paths typically meeting these goals more easily. In this context, process systems engineering analyses are critical to define the actual potential of emerging CO₂ mitigation technologies and to permit their ranking and improvement.

LHTF (*i.e.*, gasoline, kerosene, and diesel), methanol, and 1-propanol are some potential candidates for large-scale CO₂ utilization (Figure 1), which are prioritized for sustainability assessment in this study. The global demand for LHTF was about 4.5 Gt in 2019¹⁸ and, while

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3 curtailed by the COVID-19 pandemic in 2020, is projected to rebound in 2022¹⁹. Low-or-
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5 negative carbon LHTF are of special interest to Singapore, a strategic oil hub of Asia. The
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7 global demand for methanol is among the highest in the chemical sector (99 Mt in 2020).
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9 Although the demand for 1-propanol is more modest (4.1 Mt in 2020), its price is *ca.* 3-times
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11 higher than that for methanol due to its manifold applications, which endows it with a particular
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13 prominence among short-chain alcohols. Moreover, the market volumes of methanol and 1-
14
15 propanol are estimated to grow annually by 5% for the next 5 years²⁰⁻²² and shall be further
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17 stimulated by the prospect of blending with or substitution of gasoline. Indeed, although
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19 methanol and 1-propanol have lower energy densities than gasoline (~ 22 and 33 *versus*
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21 45 MJ kg⁻¹, respectively), their higher octane numbers permit greater combustion efficiencies,
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23 thus partly compensating for their lower densities and making them suitable as gasoline
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25 substitutes²³.
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Figure 1. Production routes of LHTF, methanol, and 1-propanol, with their annual global market sizes indicated. In conventional industrially-practiced processes (black arrows), syngas is obtained from methane steam reforming, whereas it is produced from captured CO₂ and renewable H₂ in emerging processes (purple arrows).

Available processes to produce methanol and LHTF have been evaluated^{8, 23-26}, but each study followed a distinct methodology in term of costs of raw materials, plant capacity, and process boundary, rendering a direct comparison problematic. This issue also emerges when distinct

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2
3 technologies leading to the same product are contrasted across publications. Moreover, an
4 analysis of a full-scale process for producing 1-propanol *via* CO₂ utilization is yet to be reported
5 in the open literature. For rigorousness and to fill the lack of assessment of 1-propanol
6 production from CO₂, a common approach to unravel the performance of these three CO₂-
7 based processes is thus highly desirable.

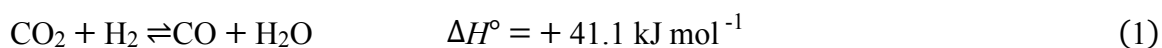
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10 Here, we introduce a comparative techno-economic and environmental assessment of large-
11 scale productions of LH₂, methanol, and 1-propanol using captured CO₂ and green H₂ as the
12 feedstocks. In the first stage, economic viability of the production of these three compounds is
13 discussed only based on raw material cost for a range of CO₂ and H₂ prices *i.e.*, neglecting
14 process and processing costs to convert them into the products. Therefore, this may be
15 considered as the best-case scenario giving the upper limit of expected profit – hence a solid
16 basis for our evaluating the outcomes of techno-economic analysis. In the next stage of the
17 study, we focus then on the design, optimization, and costing of the three plants, operated based
18 on technologies that are already commercial for conventional steps and viable for industrial
19 deployment for emerging transformations. Their energy demand and CO₂ emission avoidance
20 are examined in detail, along with the impact of carbon tax on profitability and its sensitivity
21 to other factors. The findings are then framed in a general context to demonstrate the power of
22 process systems engineering to assess known processes and develop new routes by
23 synergistically exploiting established and novel technologies. While other authors²⁷ have
24 evaluated the potential of CO₂ as a feedstock for various products based solely on the CO₂
25 utilization reactions, our approach distinguishes itself by comparing the complete production
26 processes of different CO₂-based products using a uniform common basis, *i.e.*, same raw
27 material cost, production capacity and process boundary. The analysis platform presented to
28 compare different key products of CO₂ utilization on the same basis stands as a critical tool to
29 direct further research efforts on this urgent topic.

METHODS

In this section, the three CO₂-based processes are first described (Figure 2), followed by their simulation, and economic and environmental evaluations.

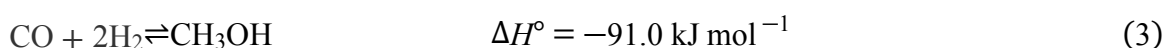
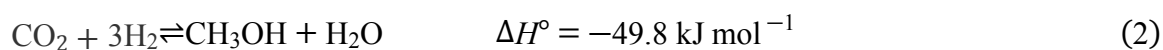
Process description

CO₂ to LHTF. CO₂ and H₂ are heated and fed to a multitubular reactor to carry out the reverse water-gas shift (RWGS) reaction (Equation 1) on a Ni/Al₂O₃ catalyst at 1173 K and 2.3 bar, *i.e.*, conditions reported to mitigate catalyst deactivation by coke deposition²⁸. This catalyst was selected instead of alternative low-temperature catalytic systems in view of the higher syngas yield and the verified benefit of the high reaction temperature for heat integration.



The syngas produced is cooled to 318 K and 4.0 bar before entering a gas-liquid separator for water removal. The exiting gas stream is compressed to 10.0 bar and heated to 500 K, and then sent to the Fischer–Tropsch synthesis (FTS) reactor hosting a Co/MgO/SiO₂ catalyst. The FTS products are cooled to 288 K and sent to a 3-phase separator. 92% of the gas stream is recycled to the RWGS reactor and the remaining is purged, whereas the liquid stream is sent to a fractional distillation column to be separated into light gases, gasoline, kerosene, diesel, and wax.

CO₂ to methanol. CO₂ and H₂ are compressed to 74.5 bar and preheated to 518 K before being sent to an adiabatic reactor, where a commercial Cu-ZnO-Al₂O₃ catalyst mediates the RWGS reaction (Equation 1) as well as the hydrogenation of the two carbon oxides to methanol (Equations 2 and 3).



The products are cooled to 318 K and sent to a gas-liquid separator. From there, the gas stream is recycled to the reactor and the liquid stream is directed to a distillation column for water

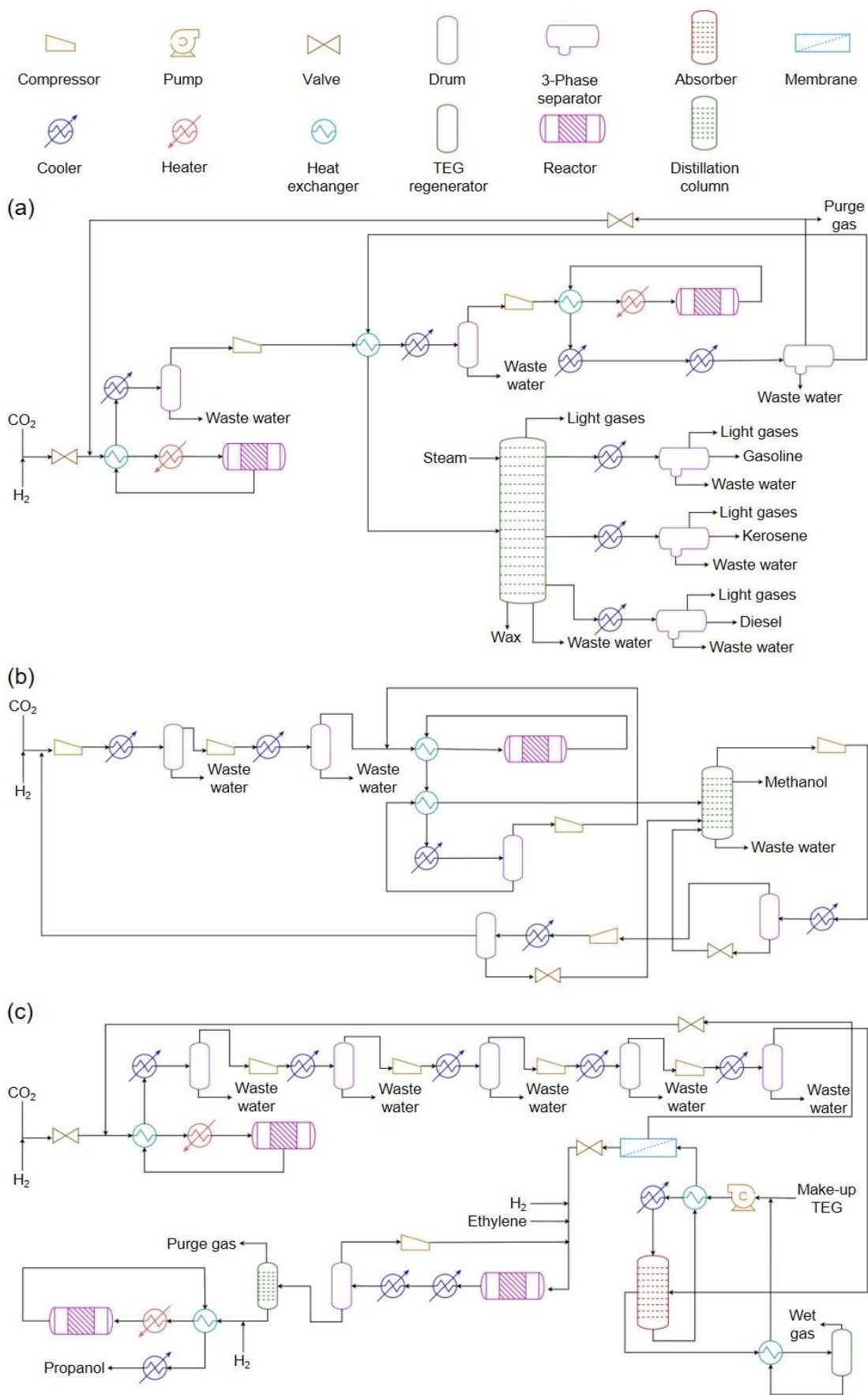


Figure 2. Process flow diagram of the CO₂-based synthesis plants: (a) LHTF, (b) methanol, and (c) 1-propanol.

removal. A partial condenser is used to withdraw methanol as the distillate, and recycle the overhead vapor.

CO₂ to 1-propanol. Similar to the CO₂-to-LHTF process, the RWGS reaction over Ni/Al₂O₃ produces syngas from CO₂ and H₂, however, the amount of H₂ is adjusted to attain a molar H₂:CO ratio of about 1. The syngas is compressed to 13.5 bar with intercooling and partial removal of water. Thereafter, it enters a triethylene glycol (TEG) dehydration section for further removal of water. The dry gas is sent to a membrane separation unit, where 80% of CO₂ is separated and recycled to the RWGS reactor. The syngas exiting from the membrane unit reacts with ethylene to form propanal (Equation 4) in the hydroformylation (HFM) reactor. In parallel, ethylene also undergoes hydrogenation, forming ethane as a byproduct (Equation 5).



The HFM reaction is catalyzed by a homogeneous rhodium triphenylphosphine (Rh/PPh₃) catalyst due to its milder operating temperature and pressure in comparison to cobalt-based alternatives^{29,30}. The catalyst concentration is assumed to be 0.270 kg m⁻³³¹. To compensate for catalyst bleeding, a make-up stream is required, and the catalyst amount replaced in one year is assumed to be equal to the original catalyst loading. Conversion of ethylene and selectivity towards aldehyde have been reported as 80-98% and >90%, respectively²⁹⁻³¹. The HFM reactor is assumed to adopt the configuration MK IV developed by the Union Carbide Corporation³⁰. The products of this reactor are cooled to 278 K, and the gas stream is separated for recycle. Since the liquid propanal stream still contains a substantial amount of CO₂, ethylene, and ethane due to their rather high solubilities in this aldehyde, distillation is required to remove these gases. The purified propanal stream is then brought to 2.5 bar and 448 K, and hydrogenated to 1-propanol (Equation 6). This reaction is catalyzed by a commercial supported nickel catalyst from the Jefferson Chemical Company (Ni-0101).



Process modeling

Since the conventional LHTF, methanol, and 1-propanol plants have different capacities, rendering a comparison difficult, we standardize a processing capacity of $0.704 \text{ Mt}_{\text{CO}_2} \text{ a}^{-1}$ (2000 kmol h^{-1}) for all three products. The feed gases (H_2 , CO_2 , and ethylene) were assumed to be available at 298 K and 17.0 bar. Process modeling based on the process layouts described in Figure 2 was performed using Aspen HYSYS V10®, unless otherwise stated. The Peng–Robinson equation of state with Boston–Mathias modifications and the Redlich–Kwong–Soave equation of state with the modified Huron and Vidal mixing rules were used as the fluid packages for the LHTF and methanol plants, respectively. For the 1-propanol plant, the UNIQUAC model was used, except for the dehydration section, for which the Glycol Package was employed. The FTS reactor was modeled by a Langmuir–Hinshelwood–Hougen–Watson type kinetic expression³² implemented in MATLAB R2018a interfaced with Aspen HYSYS V10 (see Supporting Information, SI). Due to the lack of process kinetics in the literature, the HFM was modeled using a conversion reactor with 90% conversion of ethylene and 90% selectivity towards the aldehyde. Other reactors were modeled with published kinetic parameters^{26,28,33}. Energy integration was achieved using pinch analysis³⁴.

Economic evaluation

The economics of the three grassroots plants were estimated based on (1) an annual operation of 8000 h, (2) 2020 CEPCI of 607.5, (3) a plant life of 15 years, and (4) carbon tax of $3.75 \text{ \$ t}_{\text{CO}_2}^{-1}$ (carbon tax rate in Singapore). Other parameters used in the economic evaluation are presented in Table S1 (SI). The equipment sizing was performed using the Aspen Process Economic Analyzer. Fixed capital investments were calculated based on the methodology³⁴ in Turton *et al.* The operating cost, COM ($\text{\$ a}^{-1}$), was estimated from Equation 7:

$$\text{COM} = 0.18C_{\text{GR}} + 2.73C_{\text{COL}} + 1.23(C_{\text{UT}} + C_{\text{RM}} + C_{\text{WT}}) + C_{\text{CT}} \quad (7)$$

where C_{GR} , C_{COL} , C_{UT} , C_{RM} , C_{WT} , and C_{CT} ($\text{\$ a}^{-1}$) are fixed capital investment (grassroots), labor cost, utilities cost, raw materials cost, waste treatment cost, and carbon tax, respectively.

The net present value (NPV), *i.e.*, the cumulative discounted cash position at the end of plant life³⁴, is used as the economic metric to determine the profitability of the plants.

Environmental evaluation

A comprehensive environmental metric for CO_2 emissions must take into account the emission associated with the supply chain of the raw materials and those from the end of life of the products. Accordingly, the total CO_2 emission to the atmosphere, $\text{CO}_{2,\text{ATMOS}}$, was defined based on Equation 8:

$$\text{CO}_{2,\text{ATMOS}} = \text{CO}_{2,\text{RM}} + \text{CO}_{2,\text{PR}} + \text{CO}_{2,\text{EOL}} \quad (8)$$

where $\text{CO}_{2,\text{RM}}$, $\text{CO}_{2,\text{PR}}$, and $\text{CO}_{2,\text{EOL}}$ are the emissions associated with raw materials, processes, and end-of-life of products, respectively. For conventional plants, $\text{CO}_{2,\text{RM}}$ originates from the extraction, purification, storage, and distribution of natural gas, and is estimated at $0.700 \text{ t}_{\text{CO}_2} \text{ t}_{\text{CH}_4}^{-1}$ ³⁵. For the emerging plants, $\text{CO}_{2,\text{RM}}$ mainly comes from carbon capture ($\sim 0.220 \text{ t}_{\text{CO}_2} \text{ t}_{\text{CO}_2 \text{ captured}}^{-1}$ ³⁶, assuming an amine-based absorption process), green hydrogen (assuming negligible emissions), and ethylene ($\sim 0.990 \text{ t}_{\text{CO}_2} \text{ t}_{\text{ethylene}}^{-1}$ ³⁷) production processes. $\text{CO}_{2,\text{PR}}$ represents the net emissions within the plants, and mainly results from the flue and flare gases leaving the plants, and electricity generation. Heat recovery (assuming 80% efficiency) from combustion of flare gases mitigates the consumption of natural gas within the plants, thereby improving both economic and environmental aspects. CO_2 emissions in conventional LHTF and 1-propanol plants were estimated at 5.21 and $0.535 \text{ t}_{\text{CO}_2} \text{ t}_{\text{product}}^{-1}$, respectively, by replacing the RWGS reactors in our simulations with methane steam reforming

reactors of the same capacity. This factor in the conventional methanol plant was set at 0.700 $t_{CO_2} t_{product}^{-1}$ based on the literature⁸. The last factor, $CO_{2,EOL}$, accounts for the fact that the products of the three plants are converted into CO_2 at the end of their lives and released into the atmosphere. We further defined the following two metrics:

$$CO_2 \text{ utilization efficiency} = (CO_2 \text{ feed} - CO_{2, RM} - CO_{2, PR}) / CO_2 \text{ feed} \times 100\% \quad (9)$$

$$CO_2 \text{ avoidance} = (1 - CO_{2, ATMOS, emerging \text{ plant}} / CO_{2, ATMOS, conventional \text{ plant}}) \times 100\% \quad (10)$$

RESULTS AND DISCUSSION

Preliminary evaluation

Prior to rigorous process design and simulation, a preliminary analysis was performed to justify the relevance of our study by examining the raw material cost for producing one tonne of LHTF, methanol, and 1-propanol (Figure 3). This analysis was solely based on mass balances and raw material costs, and independent of the routes transforming the feedstocks into the corresponding products. In the figure, the purple dot represents the CO_2 and H_2 costs used in this study. Each diagonal line is an equicost line, *i.e.* all points on a such line have the same total raw materials cost. In particular, the purple lines indicate the current market values of the products. The resilience of the economic viability of 1-propanol production against varying CO_2 and H_2 prices is very clear, since the purple dot is located within the triangular region formed by the purple line and the axes (Figure 3c). In contrast, the purple dots are outside of these triangular regions for LHTF and methanol plants (Figures 3a,b), showing that these are unattractive at present. However, LHTF and methanol syntheses could fall into profitable regions when CO_2 capture and green H_2 production technologies are further improved. It should be stressed that when methanol is priced in relation to its energy content with respect to gasoline, profitability based on the raw materials cost is already given, and the same holds for 1-propanol (green dashed lines).

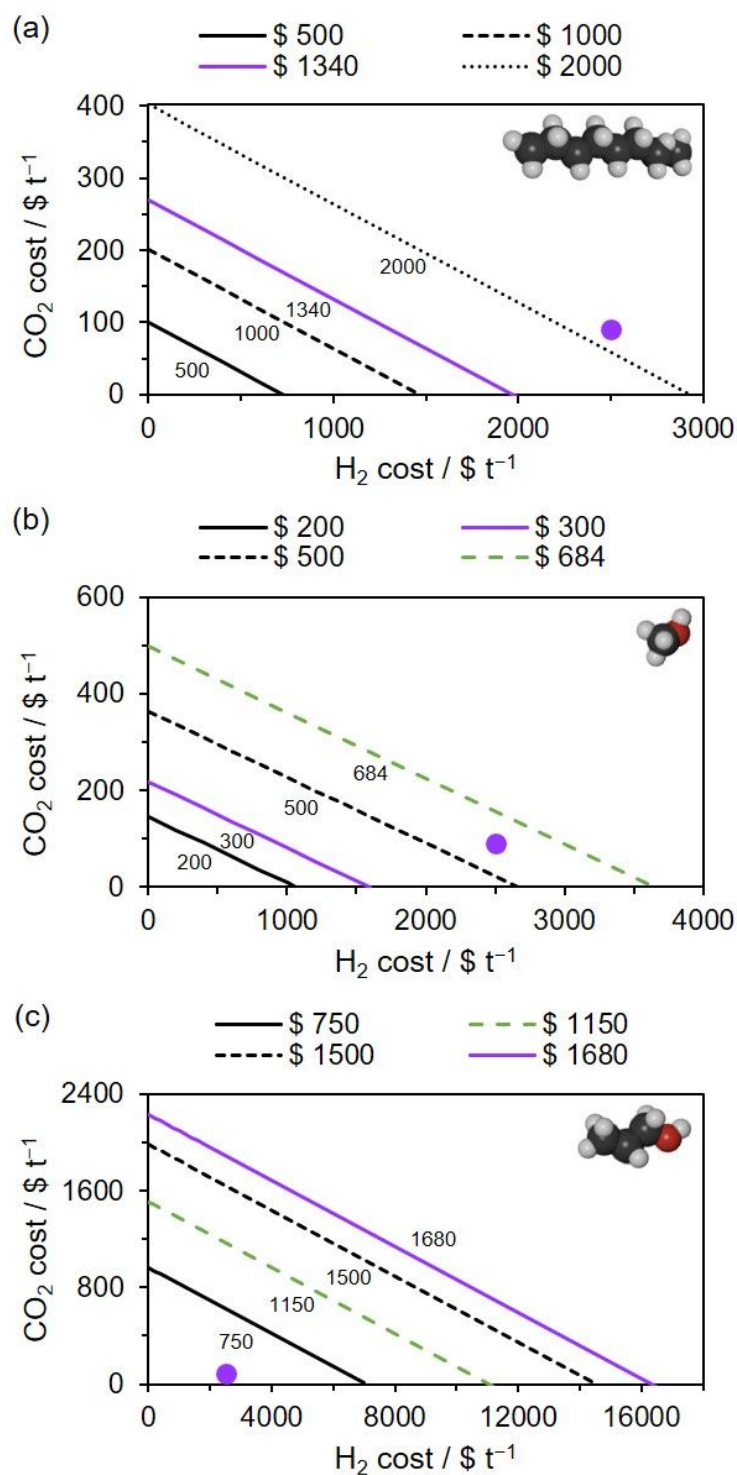


Figure 3. Total raw material cost to produce 1 tonne of (a) LHTF, (b) methanol and (c) 1-propanol as a function of H₂ and CO₂ prices. Each line represents the total raw material cost (indicated by the adjacent number) at specific combinations of H₂ and CO₂ prices. Solid purple lines mark the current market prices of the products. Dashed green lines indicate the prices of methanol and 1-propanol in relation to their energy contents, with respect to gasoline. 1 tonne of LHTF is assumed to contain 50% gasoline, 35% kerosene, and 15% diesel by weight. For 1-propanol, the price of ethylene is fixed at 106 \$ t⁻¹. The purple dots show the prices of H₂ and CO₂ used in this study (2500 and 90 \$ t⁻¹, respectively).

Technical evaluation

Based on the models outlined above, the three processes were simulated leading to the key results reported in Table 1. The design specifications for reactors and separation columns are compiled in Tables S2 and S3, respectively. Each t_{CO_2} is transformed into $0.210 t_{\text{LHTF}}$, $0.731 t_{\text{methanol}}$, or $1.18 t_{1\text{-propanol}}$. The LHTF product attained in our plant is composed of 50.1% of gasoline, 35.4% of kerosene, and 14.4% of diesel by mass (Figure S1), with an average lower heating value (LHV) of 43.14 MJ kg^{-1} . Methanol and 1-propanol are obtained with a purity of 99.57 and 99.97wt%, respectively. In the LHTF synthesis plant, the recycle percentage was determined to be 92% to minimize CO_2 emission (Figure S2, *vide infra*). In CO_2 -based 1-propanol production, upstream water removal is an essential step to ensure high purity of the final product, since 1-propanol and water can form an azeotrope. Two designs of the 1-propanol plant as alternatives to the configuration presented in Figure 2c were additionally considered aiming at economic improvements. The first involves the replacement of the TEG dehydration section with an adsorber column packed with a 3A zeolite, while the second transfers the TEG dehydration section to downstream of the hydrogenation reactor to separate the 1-propanol-water azeotrope. However, both alternatives resulted in configurations inferior to the original design due to higher operating costs.

From an energy perspective, the cooling duty is the greatest in the CO_2 -to-LHTF plant due to the highly exothermic FTS reaction, while the heating duty is the highest in the CO_2 -to-methanol plant. The latter is due to methanol and water formation in a 1:1 molar ratio, resulting in a large flow rate into the distillation column and, thus, an energy-intensive separation. In all three plants, heat integration and heat recovery from the combustion of the purge gases significantly reduce both heating and cooling duties. In particular, the flare gases can fully replace natural gas to provide heating duties in the syntheses of LHTF and 1-propanol (Table 1).

Table 1. Key simulation results for the CO₂-based LHTF, methanol, and 1-propanol synthesis plants. The numbers in parentheses indicate the values after heat integration and heat recovery from the combustion of the flare gases.

	LHTF	Methanol	1-Propanol
Raw materials (Mt a ⁻¹)			
Captured CO ₂	0.704	0.704	0.704
Green H ₂	0.097	0.097	0.089
Ethylene	N.A.	N.A.	0.450
Products			
Quantity (Mt a ⁻¹)	0.148	0.514	0.831
	Gasoline: 50.1		
Purity (wt%)	Kerosene: 35.4	99.57	99.97
	Diesel: 14.4		
Utilities (TJ a ⁻¹)			
Electricity	734	516	353
Heating	4711 (0)	5235 (1054)	3374 (0)
Cooling	8647 (5012)	7715 (3534)	7302 (5153)

Economic evaluation

Considering the CO₂-to-LHTF plant, the COM (490.8 \$MM a⁻¹, 3,313.7 \$ t_{LHTF}⁻¹) was determined at about 2.5-fold the revenue (198.4 \$MM a⁻¹, 1,339.5 \$ t_{LHTF}⁻¹), implying its economic unviability (Figure 4). The major contributor to the COM is cost of the raw materials, with a share of 76.5%. Gasoline generates 58.6% of the revenue due to its higher selling price and higher content (50.1 wt%) within the mixed fuel product. Reactors account for 42.3% of the fixed capital investment, reflecting the high cost of the FTS reactor. In terms of COM (excluding raw materials), utilities contribute 36.7% due to the high heating duties at the

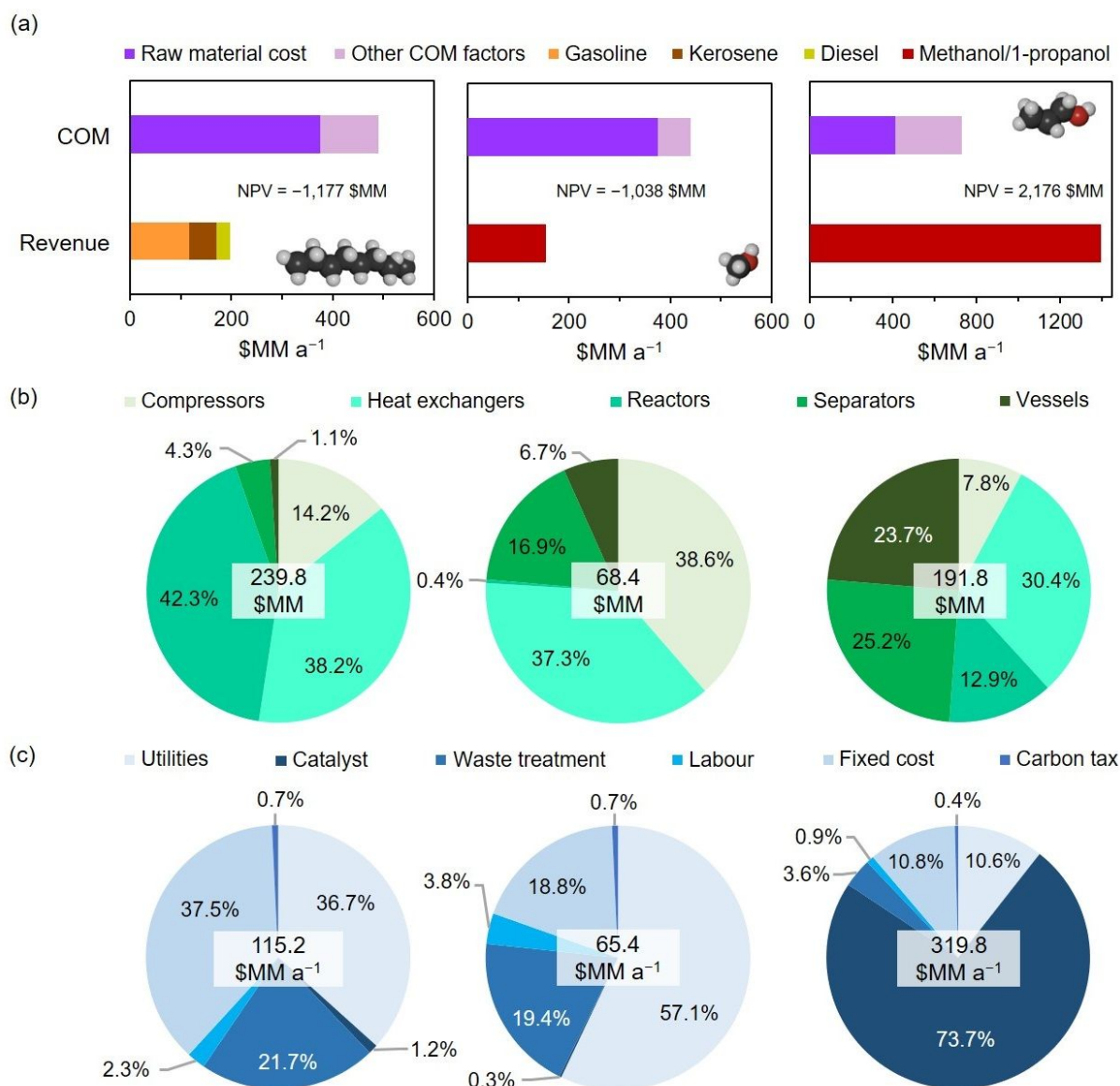


Figure 4. Economic analysis of the CO₂-based LHTF, methanol and 1-propanol synthesis plants, respectively. (a) Overview of cost of manufacturing (COM), revenue, and net present value (NPV), (b) breakdown of fixed capital investment, and (c) breakdown of COM (excluding raw materials).

RWGS reactor and the fractional distillation column, and the high cooling duty at the FTS reactor. Waste treatment determines a further 21.7% of this parameter due to the substantial amount (0.570 Mt a⁻¹) of aqueous waste produced in the RWGS and FTS reactors. Zhang *et al.*²⁴ performed a techno-economic assessment of the direct conversion of CO₂ to LHTF using an iron-based catalyst. Despite assuming a lower cost of captured CO₂ (35 *versus* 90 \$ t_{CO₂}⁻¹), their total production cost is *ca.* 30% higher than ours (~1,000 *versus* 697.2 \$MM Mt_{CO₂}⁻¹). Such

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3 discrepancy can be accounted for by the lower conversion of their one-step process and the
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5 about half design capacity (0.370 *versus* 0.704 Mt_{CO₂} a⁻¹).

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8 The COM and the revenue of the methanol synthesis plant are 441.0 and 154.3 \$MM a⁻¹ (857.2
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10 and 300.0 \$ t_{methanol}⁻¹), respectively. Similar to the LHTF process, this plant is economically
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12 unviable due to the high raw materials cost, which constitutes 85.2% of the COM. Since the
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14 plant operates at a high pressure (74.5 bar), the cost of compressors and utilities (specifically
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16 electricity) contribute the highest percentages to the fixed capital investment and COM,
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18 respectively. Alleviation of these costs calls for a catalyst showing equivalent performance at
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20 reduced pressures. As a significant amount of aqueous waste (0.286 Mt a⁻¹) is formed in
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22 methanol synthesis, the cost of waste treatment has a high share of 19.4% in the COM
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24 (excluding raw materials). Previous studies^{8,23,25} have also concluded that thermocatalytic CO₂-
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26 based methanol synthesis is economically unappealing, but estimates of the total production
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28 cost differ. Our value (857.2 \$ t_{methanol}⁻¹) is slightly higher than that by Pérez-Fortes *et al.*⁸
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30 (~800 \$ t_{methanol}⁻¹), possibly because the costs of CO₂ and H₂ were assumed to be 0 and
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32 ~3,700 \$ t⁻¹ instead of 90 and 2,500 \$ t⁻¹ here, respectively. Pérez-Ramírez *et al.*²⁵ employed
33
34 the same process design as Pérez-Fortes *et al.*, and calculated a production cost of 810-
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36 2,430 \$ t_{methanol}⁻¹ depending on the energy source for green H₂ production. Bellotti *et al.* reported
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38 a competitive ~500 \$ t_{methanol}⁻¹,²³ but their methanol plant was only represented by a reactor, *i.e.*,
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40 they totally neglected the fixed capital investment of other units, the cost of separation, and
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42 other operating costs.
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51 Despite a high COM (729.3 \$MM a⁻¹, 877.4 \$ t_{1-propanol}⁻¹), the plant converting CO₂ into 1-
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53 propanol generates sufficient revenue (1,396.5 \$MM a⁻¹, 1,680.0 \$ t_{1-propanol}⁻¹) to be
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55 economically profitable. In comparison to the aforementioned two plants, the materials cost
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57 accounts for a relatively smaller percentage (56.2%) of the total production cost. Heat
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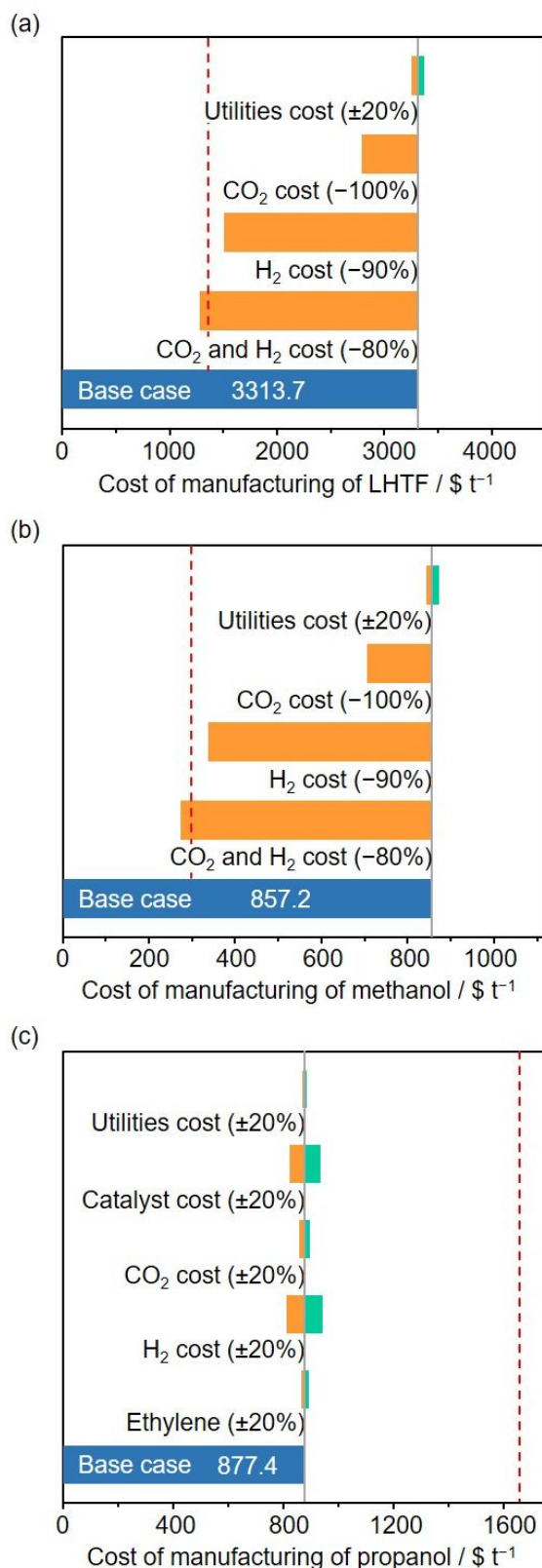
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3 exchangers and reactors contribute more than 43% of the fixed capital investment. Due to
4 several purification steps, separators account for another 25.2%. The COM (excluding raw
5 materials) is dominated by the cost of the catalyst used in the HFM reactor (73.7%). Indeed,
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7 the homogenous Rh/PPh₃ catalyst constantly bleeds out of the system, requiring a permanent
8
9 make-up stream.

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11 Overall, the NPV of the CO₂-based LHTF, methanol, and 1-propanol plant are -1,177, -1,038,
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13 and 2,176 \$MM, respectively. The assumed carbon tax contributes to a small portion (0.4-
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15 0.7%) of the COM (excluding raw materials) and has little impact on the economics of the
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17 plants. The cost breakdown reveals distinct aspects that should become focus of future research
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19 for the three plants. For the LHTF and methanol synthesis, the reduction in the raw materials
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21 cost is key to reach profitability. In other words, their success is contingent on the advances in
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23 CO₂ capture and production of green H₂. On the other hand, both raw materials and catalyst
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25 significantly contribute to the total production cost in the CO₂-to-1-propanol plant. While this
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27 plant will benefit from a lower raw materials cost, catalyst development, preferentially
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29 embracing a heterogeneous system, is essential for widening the profit margin. Although a
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31 plant life of 15 years was chosen for our economic evaluation, our conclusions qualitatively
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33 hold also for a longer plant life.

34 35 36 37 38 39 40 41 42 43 44 45 **Sensitivity analysis**

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47 The urgency regarding the reduction of raw materials cost to improve the economic
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49 performance of a CO₂-based production of LHTF and methanol has been previously asserted
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51 by other authors^{8, 24}. However, the extent of this reduction requires further investigation.
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53 Effects of different parameters on the total production cost of the three target chemicals were
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55 analyzed. The most impactful factors are shown in Figure 5. Varying the cost of CO₂ is
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57 equivalent to studying the impact of source-dependent variation in CO₂ capture cost as well its
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3 cost reduction from advances in CO₂ capture technology. In all cases, the impact of a 20%
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55 **Figure 5.** Sensitivity analysis for the = cost of manufacturing of CO₂-based (a) LHTF, (b) methanol,
56 and (c) 1-propanol, with indication of lower (orange) and higher (cyan) costs of parameters compared
57 to the base cases. Dashed red lines indicate the current market prices of the products.
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variation of the utilities cost is marginal. The same applies to an analogous change in ethylene

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3 cost, additionally relevant for 1-propanol production (Figure 5c). Focusing on the main raw
4 materials, the CO₂-to-LHTF and -methanol plants remain economically unviable even when
5 the price of CO₂ drops by 100% or that of H₂ drops by 90%. In both plants, the cost of the
6 gaseous feedstocks is *ca.* twice that of the product value. At 50% reduction of both CO₂ and
7 H₂ costs, the raw materials expenditure matches the revenue, leaving no margin for other
8 operating costs. These two plants only become economically viable when the costs of two raw
9 materials decrease by 80% (Figures 5a,b). In other words, the cost of green H₂ must fall below
10 that of fossil-derived H₂, which is an unrealistic scenario. Thus, a reduction in raw materials
11 cost alone is insufficient for LHTF and methanol to be potential products of CO₂ utilization,
12 and must be accompanied by an innovation in catalysis or an alternative reaction pathway.
13 While the catalysts used in this study have sufficiently high conversions for industrial
14 implementation, we remark the need of advances to reach milder operating temperature and
15 pressure while maintaining the high conversion in order to reduce the production cost further.
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34 35 **CO₂ emissions and avoidance**

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37 The CO₂ emissions of in the CO₂-based LHTF, methanol, and 1-propanol plants are 0.229,
38 0.126, and 0.341 Mt_{CO₂} a⁻¹, respectively (Figure 6a) and result from indirect emissions, mostly
39 related to electricity or steam generation, and direct emissions, owing to flare gas combustion.
40 Electricity usage is the greatest contributor to indirect emissions for LHTF and 1-propanol
41 syntheses accounting for 0.05-0.09 Mt_{CO₂} a⁻¹, while steam generation determines the
42 equivalent scenario in methanol production, being responsible for 0.0651 Mt_{CO₂} a⁻¹. Regarding
43 direct emissions, flare gas combustion contributes to CO₂ emissions more substantially for
44 CO₂-to-LHTF and -1-propanol processes (0.143 and 0.290 Mt_{CO₂} a⁻¹, respectively). The flare
45 gases consist mainly of C₁-C₅ paraffins in the former and by-product ethane in the latter. Since
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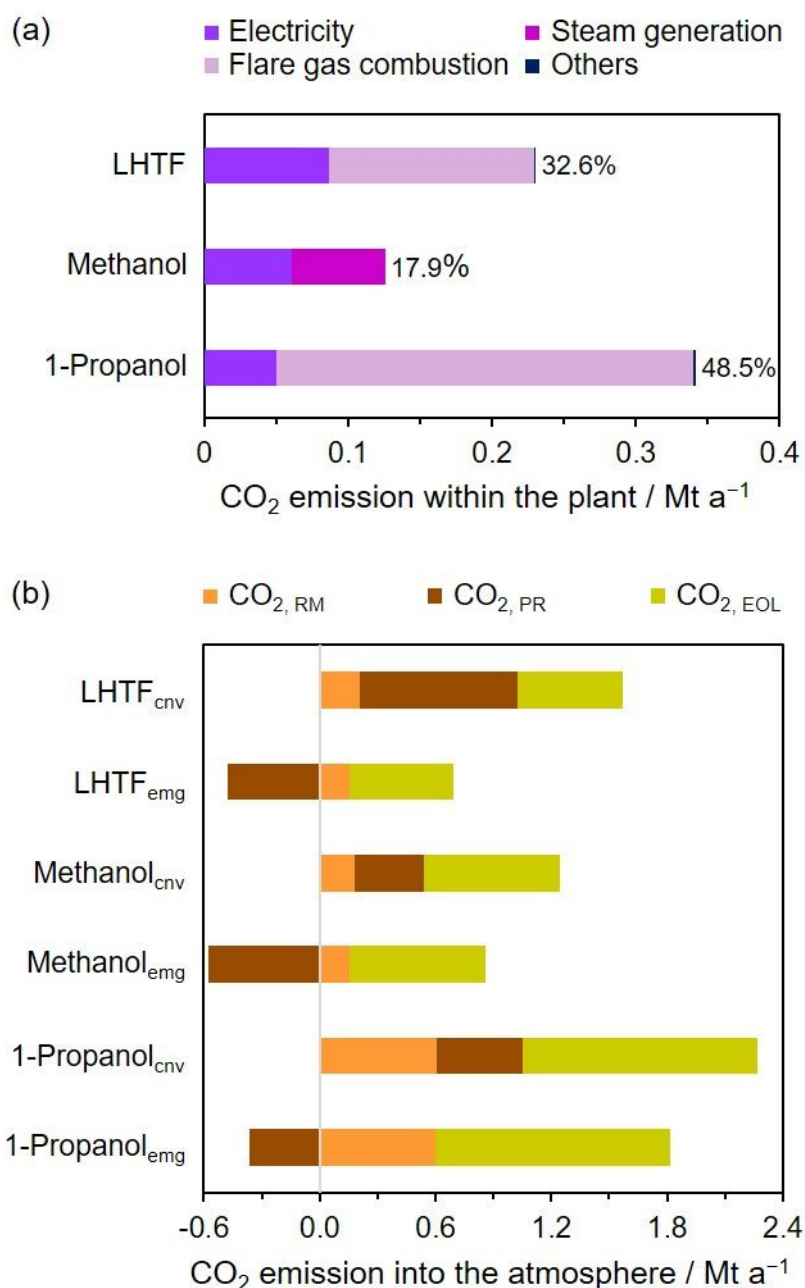


Figure 6. (a) Breakdown of CO₂ emissions within the plants and (b) CO₂ emissions into the atmosphere for the CO₂ based LHTF, methanol, and 1-propanol synthesis plants. The percentages in (a) indicate the proportion of CO₂ emission relative to CO₂ utilization (0.704 Mt a⁻¹). CO_{2, RM} is the emission associated with raw materials; CO_{2, PR} is the net emission within the plant (a negative value indicates a net utilization of CO₂); CO_{2, EOL} is the emission associated with the combustion of the products; cnv: conventional; emg: emerging.

the molar selectivity of ethane to propanal is 1 to 9, approximately 0.0556 t_{ethane} t_{1-propanol}⁻¹ are produced. The CO₂-based 1-propanol plant will hence benefit from a catalyst with a selectivity > 9 to lower its CO₂ emission. On the other hand, heat recovery from flare gas combustion can be used for direct heating or steam generation, thereby eliminating one CO₂ emission source

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3 from these plants. With the capacity to utilize $0.704 \text{ Mt}_{\text{CO}_2} \text{ a}^{-1}$, the CO_2 utilization efficiencies
4 of the three plants are 45.5%, 60.1%, and -33.8% , respectively. Negative utilization efficiency
5 in the case of 1-propanol plant was due to a higher CO_2 emission associated with the raw
6 material ethylene than CO_2 utilized by the plant. This highlights the need for a greener
7 production of ethylene. However, the negative utilization efficiency of the CO_2 -based 1-
8 propanol plant does not discredit its potential, since it still has lower CO_2 emissions than its
9 conventional counterpart, as shown hereafter.

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19 The CO_2 emissions to the atmosphere, accounting for all factors in the life cycle of the products,
20 for the emerging LHTF, methanol, and 1-propanol plants are 0.221, 0.280, and $1.45 \text{ Mt}_{\text{CO}_2} \text{ a}^{-1}$,
21 respectively (Figure 6b). In comparison, conventional plants with the same product capacities
22 have higher CO_2 emissions, estimated at 1.57, 1.24, and $2.27 \text{ Mt}_{\text{CO}_2} \text{ a}^{-1}$, respectively.
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28 Therefore, the CO_2 avoidances are 85.9%, 77.4%, and 35.9%, respectively.

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If the entire global demand of 1-propanol (4.1 Mt a^{-1}) were realized by the emerging
technology, the reduction in CO_2 emissions would be 4.02 Mt a^{-1} , which is equivalent to about
0.12% of the annual global emission. If 1-propanol was priced based on its energy content
relative to gasoline, its market value would drop to $1,150 \text{ \$ t}_{1\text{-propanol}}^{-1}$ but the plant would still
remain profitable. In this scenario, the reduction in CO_2 emissions to the atmosphere could
reach *ca.* 180 Mt a^{-1} , assuming that 1-propanol is produced by the emerging technology to
fulfil the global demand of gasoline (*ca.* 22 Mt a^{-1} ³⁸). Further production of 1-propanol will
saturate the market and bring down its price, with the plant becoming economically unviable
if the latter drops below its COM ($877.4 \text{ \$ t}_{1\text{-propanol}}^{-1}$).

Effect of carbon tax on profit

To examine the effect of carbon tax, two terms, *i.e.*, $\text{Market value}_{\text{CT}}$ and $\text{Profit}_{\text{CT}}$, were defined.
The first corresponds to the sum of the current market value of a product and the carbon tax

imposed on the conventional plant to produce such product. Essentially, this reflects the situation in which the producer transfers the carbon tax to the consumer in the form of a higher selling price. The second is defined as the difference between Market value_{CT} and COM in the emerging plant (inclusive of carbon tax). Figure 7 shows that the CO₂-to-1-propanol plant remains profitable at any carbon tax. The CO₂-based syntheses of LHTF and methanol can be economically viable if the carbon tax is set at about 500 and 1,230 \$ t_{CO₂}⁻¹, respectively, which are much higher than the current estimate of the social cost of CO₂ (55-417 \$ t_{CO₂}⁻¹^{39,40}). This social cost represents the expected economic damage from CO₂ emissions³⁹ and a carbon tax structure exceeding the social cost of carbon implies that CO₂ emitters would be paying beyond the damage they cause. Specifically, carbon taxes required to make the LHTF and methanol processes economically viable at the current CO₂ and H₂ prices is 4-fold greater than the highest carbon tax currently implemented in any country. In addition, a high carbon tax will inevitably increase the market value of the product, which in turn reduces the global demand. As a result, the amount of CO₂ utilized will also diminish.

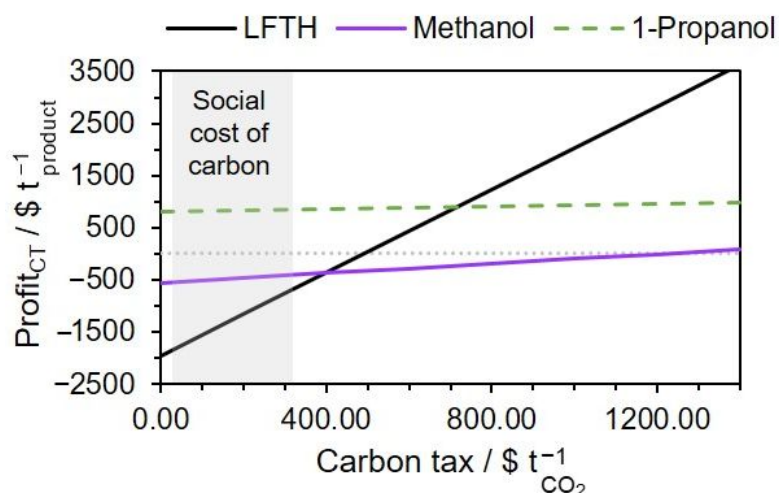


Figure 7. Effect of carbon tax on Profit_{CT}, where Profit_{CT} = (product selling price + carbon tax in conventional process) – (cost of manufacturing in emerging process). Profit_{CT} for LFTH and methanol processes enters the positive region at 500 and 1,230 \$ t_{CO₂}⁻¹, respectively, indicating that these emerging processes can be profitable at high carbon taxes. The region shaded in grey shows the range of the social cost of CO₂.

Green H₂ availability

The annual global capacity of electrolyzers is forecasted to reach 43,200 TJ a⁻¹ by 2023⁴¹, and, in the scenario of perfect efficiency, one kilogram of green H₂ will be generated using 140,400 kJ. Therefore, the global supply of green H₂ will at most equal 0.308 Mt_{H₂} a⁻¹. With a capacity of 0.704 Mt_{CO₂} a⁻¹, the CO₂-to-1-propanol plant will consume nearly 30% of the entire global supply of green H₂. Despite its profitability and the use of commercial or retrofittable technologies, the plant is thus not readily deployable, since it will consistently require a steady supply of green H₂. The limited availability of green H₂ is not a specific challenge to the 1-propanol synthesis plant, but extends to any other plant that utilizes this gaseous feedstock, urging accelerated progress in water splitting technologies. The CO₂-based 1-propanol synthesis plant, like any other H₂-mediated CO₂ conversion, shall be put on hold until green H₂ is available at the required scale.

CONCLUSIONS

With a myriad of innovations currently being studied to mitigate CO₂ emissions, the evaluation of their potential needs to move beyond the catalyst level to the process system level by determining both economic and environmental performances. In this study, three plants were thoroughly evaluated, which utilize 0.704 Mt_{CO₂} a⁻¹ of captured CO₂ and green H₂ to produce liquid hydrocarbon transportation fuels, methanol, and 1-propanol based on commercial and state-of-the-art incipient technologies. It should be noted that this study presents the first evaluation of a CO₂-to-1-propanol plant.

Since the total production costs of LHTF and methanol are about three times the respective product values, these perspective processes are deemed economically unviable at this time. The raw materials cost, *ca.* twice the product values, is highlighted as the bottleneck for these plants,

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3 which, based on sensitivity analysis, can only become attractive when both CO₂ and H₂ costs
4 drop by 80%, unless advances in catalysis open the door to lower operating temperature and
5 pressure without compromising the conversion. Increasing carbon tax in order to support
6 emerging CO₂ utilization technologies appears to be an unrealistic strategy for these
7 applications, since it would exceed the social cost of CO₂. Despite having a high production
8 cost, the 1-propanol plant stands as profitable due to the high market value of the product.
9 Replacing the homogeneous rhodium-based catalyst, dominating the operating cost, by a
10 cheaper and, preferably heterogeneous, catalyst has the potential to further increase the profit
11 margin.
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24 In terms of environmental benefits, the departure from methane-based syngas allows the three
25 emerging plants to have lower CO₂ emissions than their conventional counterparts. However,
26 the current global landscape of green H₂ production has not reached the maturity to support
27 this task.
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33 Not only our study centers on high volume and/or versatile products but also provides a
34 sustainability assessment based on a common platform thus enabling their direct comparison,
35 an approach that should be more broadly applied in future analyses. While emphasizing the
36 potential role of all emerging technologies in mitigating CO₂ emissions, our findings pinpoint
37 raw materials cost reduction, higher green H₂ production capacity, and catalyst improvement
38 as ubiquitous needs to move forward in the establishment of these processes and, due to their
39 transversal validity, for a carbon-neutral society in general.
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51 **Supporting information.** Modeling of the Fischer–Tropsch synthesis reactor; parameters used
52 in the economic evaluation; design specifications for the reactors and separation columns;
53 products distribution in the CO₂-based LHTF synthesis plant; and effect of recycle fraction on
54 the CO₂ emission of the CO₂-based LHTF synthesis plant.
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DECLARATION

The authors declare no competing financial interest.

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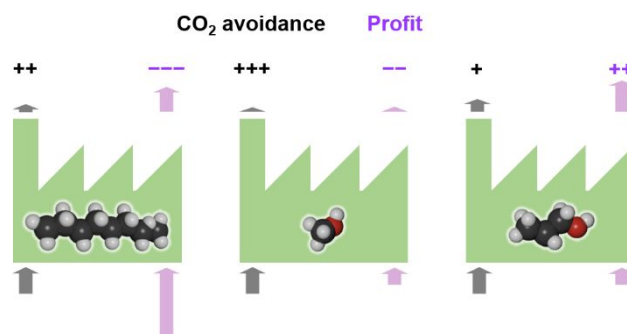
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FOR TABLE OF CONTENTS USE ONLY**GRAPHICAL ABSTRACT****SYNOPSIS**

Industrial-scale production of fuels, methanol, and 1-propanol from CO₂ and green H₂ can reduce CO₂ emissions but only 1-propanol seems profitable.