The Economic Outlook for Converting CO_2 and Electrons to Molecules

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Broader Context

Recent reports from the Intergovernmental Panel on Climate Change find that decarbonizing our global economy through the development of carbon neutral and carbon negative technologies will be critical to reaching future environmental goals. With global CO_2 emissions approaching 40 gigatonnes per year, the conversion of CO_2 to fuels and chemicals powered by renewable electricity, as part of a broader Power-to-X strategy, represents an emerging pathway with the potential to both impact product markets on the global scale and significantly lower carbon emissions. While transformational technical advancements in CO_2 conversion have been made over the past decade, many critical questions around the economic viability of these technologies remain unanswered. In this contribution, we identify and conduct a comprehensive techno-economic analysis around five major electricity-driven CO_2 conversion technologies spanning 11 unique carbonaceous products. By establishing consistent techno-economic assumptions across multiple technologies and products, we enable cross-pathway and cross-product evaluations. Using this approach, we identify promising near-term opportunities for the deployment of CO_2 conversion as well as highlight critical R&D needs and the impact of CO_2 source and incentives on enabling longer-term adoption at price points competitive with existing markets.

ARTICLE

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Shifting towards a circular carbon economy in the face of rising global population and diminishing natural reserves represents one of the greatest challenges facing mankind. CO_2 reduction reactions powered by renewable electricity offer a possible route to transform our incumbent linear consumption economic model by tapping into the over 10 gigatonnes of carbon emitted globally each year in the form of CO_2. However, many critical questions for CO_2 reduction remain unanswered across the varied pathway-product combinations such as (1) what is the near-term economic viability? (2) what opportunities exist for transformational R&D to reduce cost? (3) what is the impact of CO_2 price? (4) how does renewable electricity intermittency affect the production costs? Herein we perform a comprehensive economic assessment of CO_2 reduction across five major electricity-driven technologies using a scale basis of a 200 million gallon per year bioethanol facility (ca. 600 kilotonnes CO_2/year) as the CO_2 source. From this framework we address these key issues and report the outlook for the near-, mid-, and long-term production of 11 promising carbonaceous products while providing guidance to the research community on key cost drivers and R&D needs. Our analysis shows that with modest technical advancements and an accompanying reduction in electricity price to \$0.03 / kWh and CO_2 price to \$20 per tonne, 8 out of 11 CO_2-derived products have the potential to reach production costs at parity with, or even lower than, current market prices.

Introduction

CO_2 captured from point sources or directly from the air can be utilized as a feedstock in CO_2 reduction (CO_2R) to make carbon-based products using renewable electricity, thereby minimizing further CO_2 emissions during conversion. With 10 gigatonnes of carbon currently emitted globally each year in the form of CO_2[1], CO_2R is poised to revolutionize the "green" chemicals and fuels industry. Specifically, if this carbon trapped in CO_2 were instead directed towards products in an economically feasible manner leveraging renewable energy sources, we could annually generate over 40 times the entire global production of ethylene and propylene[2] (the two largest carbonaceous industrial chemicals by volume) via complete recycle of the carbon without additional fossil resources[2].

Recent interest in CO_2R has surged, driven not only by the growing push for sustainability, but also by transformative changes in the global energy market. For instance, in 2019, power generation costs from fossil fuels were estimated at \$0.050–\$0.170/kWh[3] while the levelized cost of renewable electricity from new utility-scale solar photovoltaic and onshore wind fell to \$0.050–\$0.057/kWh[4], all while total installed renewable electricity capacity has increased to greater than 2,500 GW[5]. This rise of renewable energy deployment has also raised the need for longer-term seasonal energy storage, which is generally considered to be obtainable only through the formation of chemical bonds[6]. Whereas batteries may store up to 200 Wh/kg[7], which will work for transient storage on the order of seconds to weeks, species such as methane (CH_4) (15,000 Wh/kg) that can be derived from CO_2R may store energy on a seasonal basis, are easily transportable, and are compatible with existing infrastructure.

CO_2R technologies are likely to be pursued commercially first in locations where low-cost renewable electricity and high-purity CO_2 (i.e., low cost with minimal purification, such as at an ethanol biorefinery) are available. One promising location is in the Midwest of the United States, where there is a geographic overlap between existing ethanol biorefineries[2, 8] and abundant wind energy[9, 10]. Co-location of CO_2R processes with existing biorefinery assets in the form of bolt-on systems could also provide additional revenue streams and product diversification for this established industry.

CO_2R can be accomplished through a flexible suite of electricity-mediated reduction pathways capable of producing essentially all the top globally consumed carbonaceous products[2]. Demonstrated CO_2R technologies can utilize electricity directly in reduction pathways such as low-temperature electrolysis (LTE)[11, 12], high-temperature electrolysis (HTE)[13, 14], and microbial electrosynthesis (MES)[15, 16], or indirectly via energy carriers like electrolytic hydrogen (H_2) through biological conversion (BC)[17, 18] and thermochemical conversion (TC)[19, 20]. However, such diversity in pathways and

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products presents a challenge in understanding the long-term economic viability of CO_2R. Previous economic evaluations have generally targeted only a few products from a single conversion pathway[21-23] or studied only one scenario with select technical and economic assumptions[24, 25]. It remains unclear how the numerous pathway-product combinations compare with one another on a consistent technical and economic basis, and how that comparison is affected by short- to long-term technical, market, and policy factors.

In this study, we perform a comparative techno-economic analysis (TEA) across five major electricity-driven CO_2R technologies shown in Fig. 1. For the first time, we establish a consistent technical and economic basis for the five CO_2R pathways integrating current, future, and theoretical economic scenarios. This approach enables a comparative assessment of different CO_2R pathway-product combinations at the current state of technology (SOT) and projections of future scenarios across inter-connected technology, market, and policy dimensions. Ultimately, we provide quantifiable answers to critical lingering questions regarding the economic viability of CO_2R: (1) what is the near-term viability? (2) what opportunities exist for transformational R&D to reduce cost? (3) what is the impact of CO_2 price? (4) how does renewable electricity intermittency affect the production costs?

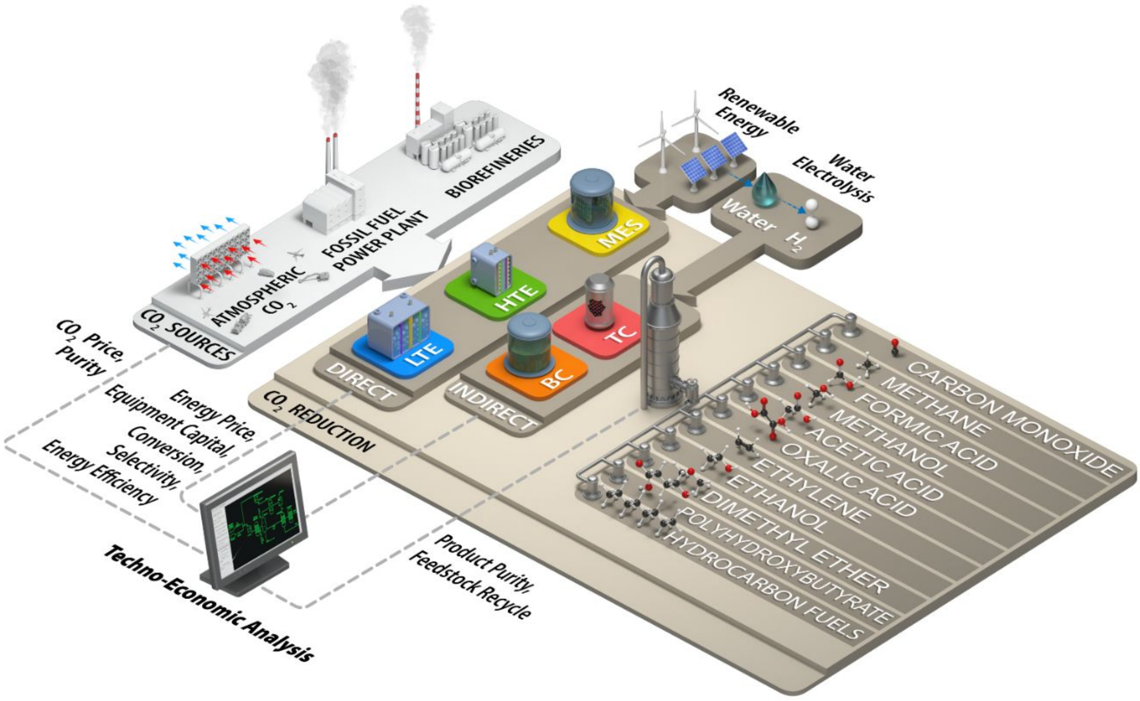

Fig. 1: Overview of studied renewable energy-powered CO_2 reduction pathways and possible near-term products. LTE = low temperature electrolysis, HTE = high temperature electrolysis, MES = microbial electrosynthesis, BC = biological conversion, TC = thermochemical conversion.

Methodology

The first stage of our CO_2R economic analysis involved identification of the major pathways and products through literature review and subject matter expert interviews[2]. Based on published reports, a database of major conversion technologies and the associated demonstrated products was generated. Although many of the identified products can also serve as intermediates (e.g., CO) for further conversion to additional products, to focus the scope of the TEA, we considered only single-step CO_2R processes.

Economic Scenarios

Recognizing that many CO_2R technologies are still in their infancy and technology-specific parameters (e.g., operating voltage, product selectivity, and CO_2 single-pass conversion) and market parameters (e.g., CO_2 and electricity price) are expected to improve over time, we consider three separate economic scenarios throughout the study: (1) a “current” scenario representing the SOT technical parameters and \$40/tonne CO_2 and \$0.068/kWh electricity; (2) a “future” scenario based on more aggressive technical parameters derived from subject matter expert interviews, comparison with similar but more mature systems (e.g., fuel cells or water electrolyzers), and engineering judgement with \$20/tonne CO_2 and \$0.03/kWh electricity (see Table S7 ESI† for more information); and

(3) a "theoretical" scenario with technical parameters based on thermodynamic limitations and/or best-case assumptions and \$0/tonne CO_2 and \$0.02/kWh electricity (Table 1).

Given that within a specific product-pathway combination the technical parameters and system design can vary between studies and are often conducted under different operating conditions, we acknowledge the definition of SOT can be subjective. Herein we attempt to define the SOT from the perspective of most commercially relevant design. Specifically, available studies were parsed and ranked initially on system stability, prioritizing processes that have been demonstrated commercially (e.g., thermochemical reverse water-gas shift reaction, Sabatier reaction) or studies demonstrating stabilities on the order of hundreds of hours as a minimum threshold. For the products where stability data was not reported and/or of insufficient duration (which comprised most low TRL data), studies with the highest reported productivity towards a given product were selected as SOT. Productivity is defined as partial current density for direct CO_2R pathways and volumetric/catalytic productivity for H_2-mediated indirect pathways. The reversible thermochemical reactions were evaluated at commercially relevant conditions operating near or at their thermodynamic conversion limits.

System boundary

Modelled CO_2R processing steps include the core CO_2 conversion, recycle of unconverted feedstocks, and product purification stages. For each CO_2R pathway, the materials and energy required to convert a fixed CO_2 stream are quantified and used to estimate capital and operating expenses with raw material unit prices (Table. S1, ESI†) from open literature[26, 27], EIA[28], and other commercial databases[29]. The modelled TEA system boundary does not include activities and processes common to all pathways such as electricity generation or the production and capture of waste CO_2 which are instead captured as constant operating expenses (Fig. S1, ESI†).

Process scale

The scale basis for all five CO_2R pathways is a 200 million gallon per year (MGY) bioethanol plant as it represents an appealing entry point for CO_2R with high purity and low-cost CO_2. The mass flowrate of emitted CO_2 (M_{co_2}, kg per hour) during ethanol fermentation is defined by ethanol production ($E_{g,f}$, 200MGY), CO_2 emissions factor ($\theta_{E.f}$, 6.6lb CO_2 per gal ethanol[30]) and operating hours per year (O_t, 7884 hours per year) resulting in a value of 75,931 kg CO_2/hr.

$$M_{co_2} = \frac{\sum(E_{g,f}\theta_{E.f}) \cdot 10^6}{2.205 \cdot O_t} \qquad \text{Equation 1}$$

The CO_2 mass flowrate from a 200 MGY bioethanol plant is also equivalent to (1) the amount of CO_2 emitted from a 100MW power plant with an emission rate of 820 kg CO_2/MWh[21] and ~90% CO_2 capture efficiency, which is 1 order of magnitude smaller than a typical 1000MW coal-fired power plant[31, 32] or (2) a direct air capture plant with air flow of ~100 million cubic meters (MCM) per hour at CO_2 concentration of 415ppm[2], which is about half of the largest 1 megatonne (Mt) CO_2/year direct air capture plant in development in the United States[33].

Variable operating cost

Variable operating costs are based on material and energy balance calculations under current, future, and theoretical scenarios (Table 1). Major raw material (i.e., CO_2 and H_2) and utility (i.e., electricity and heat) costs are also listed in Table 1. We assume a CO_2 price of \$40, \$20, and \$0/tonne for current, future, and theoretical scenarios, respectively. \$40/tonne CO_2 is selected as a middle ground of reported cost of CO_2 avoided among different carbon capture and storage (CCS) technologies[34, 35]; \$20/tonne CO_2 reflects high-purity CO_2 with minimal clean-up; and \$0/tonne CO_2 is modelled to reflect a best-case scenario in the absence of policy credits[36]. A more in-depth assessment of the impact of CO_2 price on production cost is shown in the "Impact of CO_2 Price and Incentives" subsection. Electricity is priced at \$0.068, \$0.030, and \$0.020/kWh for the current, future, and theoretical scenarios. For the current scenario, \$0.068/kWh is based on the 2017 average industrial electric rate in the United States[37], where \$0.030 and \$0.020/kWh are selected as reasonable long-term estimates for average deliverable electric rates[38]. All H_2 needed in the indirect CO_2R pathways is assumed to be produced via water electrolysis. The U.S. Department of Energy (DOE)'s H2A Hydrogen Production Cash Flow Analysis Tool V3.2018 for polymer electrolyte membrane (PEM) Electrolysis is used to calculate the electrolytic H_2 price[39, 40]. Applying the aforementioned electricity costs under current, future and theoretical scenarios in the DOE H2A model, estimated production costs for electrolytic H_2 are \$3.91, \$1.80, and \$1.20/kg for the three respective scenarios. All costs are inflation-adjusted to 2016 U.S. dollars (2016\$) using the Plant Cost Index from Chemical Engineering Magazine[41], the Industrial Inorganic Chemical Index from SRI Consulting[42], and the labor indices provided by the U.S. Department of Labor Bureau of Labor Statistics[43].

Fixed operating cost

For all five CO_2R pathways, annual maintenance costs are estimated at 2.5% of the total installed equipment costs, and annual fixed operating costs (i.e., salaries, property insurance and tax) are modelled at 3% of the total installed cost (TIC). Low temperature CO_2 electrolyzers are assumed to be replaced on 7 / 10 year intervals at 15% / 12% of total installed electrolyzer costs for current and future scenarios respectively based on previous water electrolyzer assumptions in DOE H2A model[39, 40]. High temperature solid oxide CO_2 electrolyzers are assumed to be replaced on 4 / 7 year intervals at 7.5% / 4% of total installed electrolyzer costs[44]. In the theoretical scenario, it was assumed that no electrolyzer replacement was required in either case.

Equipment cost

With a recent push towards higher current densities via electrolyzer designs featuring zero-gap configurations and ion conducting polymers in the form of membrane electrode assemblies[45-47], the current highest performing LTE reactor designs are most physically similar to PEM water electrolyzers[6, 21]. Consequently, electrolyzer capital costs were based on the established PEM water electrolyzer systems published by the DOE H2A program[39]. However, a notable difference between water electrolyzers and CO_2 electrolyzers is the use of non-precious metals on the cathode. Whereas PEM water electrolyzers typically use platinum on the cathode, CO_2R electrolyzers more often utilize cheaper metals such as copper, tin, and silver depending on the desired product. Installed electrolyzer capital costs were adjusted accordingly to account for these savings yielding installed PEM electrolyzer costs on a per m^2 basis of \$18,000, \$13,000 and \$6,000/m^2 for current, future, and theoretical scenarios (see Table S3 ESI† for more information). In the MES pathway, alkaline water electrolyzers are selected as the most similar configuration based on reported lower current density[48, 49] and aqueous environments due to constraints dictated by microorganisms. Using comparable H2A models, the installed alkaline electrolyzer costs on a per m^2 basis are estimated at \$1,400, \$1,100 and \$800/m^2 for current, future and theoretical scenarios[39]. CO_2 electrolyzers in HTE pathway are modelled based on the solid oxide electrochemical cell (SOEC)[39]. The calculated installed SOEC costs on a per m^2 basis are \$8,000, \$6,000 and \$4,000/m^2 for the three scenarios. The total electrode area needed for each CO_2R pathway-product combination is then defined by the total current needed to reduce the incoming CO_2 and current density (CD) under the three respective scenarios (Table1) where I is the current, z is the number of required electrons to produce one mole of product, n is the number of moles of the given product, FE is faradaic efficiency, F is Faraday's constant, t is the operating time and Q is the total charge in Coulombs per time.

$$Electrode\ Area = \frac{I}{CD} = \frac{Q}{CD \cdot t} = \frac{z \cdot n \cdot F}{FE \cdot t \cdot CD} \qquad \text{Equation 2}$$

The CO_2R reactor costs in BC and TC pathways and product separation equipment costs are primarily based on industry quotes found in published National Renewable Energy Laboratory (NREL) design reports[26, 27]. The key assumptions for bio- and thermo- reactor cost estimations are summarized in Table S4 (ESI†). The general equipment cost assumptions for product separation processes are contained in Table S5 (ESI†).

Discounted cash flow analysis and minimum selling price

With capital and operating cost data, a discounted cash flow rate-of-return analysis is generated using published engineering methods[50]. Major financial assumptions (Table S6, ESI†) include 40% equity financing and 3 years of construction plus 6 months for start-up. The CO_2R plant's life is assumed to be 20 years. The working capital is assumed 5% of the fixed cost investment (FCI) and income tax is 21%. For each CO_2R pathway-product combination, the calculated minimum selling price (MSP) is the minimum price at which the product must sell to generate a net present value of zero for a 10% internal rate of return. It should be emphasized that although MSP is calculated as a single point value (Tables S8-S12, ESI†), uncertainty exists around the conceptual cost estimates. Based on availability of data, TRL of these technologies, and our analysis approach, our analysis and data reported herein are analogous to a "Class 4" study of feasibility as defined by the Association for the Advancement of Cost Engineering (AACE) International Recommended Practice No. 18R-97[51]. As such, the implied accuracy of the estimates are likely similar to the expressed class 4 range of -30% to +50%[51]. To further address the underlying uncertainty of the calculations, a sensitivity analysis on both market parameters (i.e., CO_2 and electricity price) and technology-specific parameters (i.e., operating voltage, product selectivity, and CO_2 single-pass conversion) is developed in this study to understand not only key cost drivers but also key strategies for cost reduction across the five CO_2R pathways (Fig. S2–S6, ESI†).

Table 1: Summary of major process assumptions for five CO_2R pathways under current, future and theoretical scenarios

Pathway	Product	Current scenario				Future scenario				Theoretical scenario			
LTE		CD[a]	V[b]	FE[c]	Conv [d]	CD	V	FE	Conv	CD	V	FE	Conv
	Carbon monoxide[52]	200	3.00	98	20	1500	1.93	95	90	2000	1.33	100	100
	Formic acid[53]	140	3.50	94			2.08				1.48		
	Oxalic acid[54]	75	6.50	50			2.30				1.70		
	Methane[55]	225	2.94	48			1.66				1.06		
	Methanol[56]	41.5	2.67	77.6			1.80				1.20		
	Ethylene[57]	1550	3.23	60			1.74				1.14		
	Ethanol[58]	300	2.21	52			1.82				1.22		
	CO_2 electrolyzer cost	\$18,000/m^2				\$13,000/m^2				\$6,000/m^2			
HTE		CD	V	FE	Conv	CD	V	FE	Conv	CD	V	FE	Conv
	Carbon monoxide[59]	772	1.41	99.5	65	2500	1.30	95	90	3000	0.96	100	100
	Methane[60]	1800	1.45	12	11.1		1.25				1.05		
	CO_2 electrolyzer cost	\$8,000/m^2				\$6,000/m^2				\$4,000/m^2			

		CD	V	FE	Conv	CD	V	FE	Conv	CD	V	FE	Conv
MES	Formic acid[61]	6.8	2.20	5	20	100	2.08	95	90	200	1.48	100	98
	Acetic acid[62]	20.0	2.50	99			1.71				1.11		
	Methane[63]	1.2	2.50	70			1.66				1.06		
	Ethanol[64]	1.2	2.10	10			1.74				1.14		
	CO_2 electrolyzer cost	$\$1,400/m^2$				$\$1,100/m^2$				$\$800/m^2$			
BC		H_2: CO_2	Sel[e]	Prod[f]	Tit[g]	H_2: CO_2	Sel	Prod	Tit	H_2: CO_2	Sel	Prod	Tit
	Acetic acid[65]	2	100	1.3	25	2	100	2.6	60	2	100	10	100
	Methane[66]	4	100	1.1	n.a.	4	100	6.2	n.a.	4	100	10	n.a.
	Ethanol[67]	3.8	95	8.1	50	3	100	9.2	60	3	100	10	60
	Polyhydroxybutyrate[68]	2.5	100	1.0	56	2.25	100	2.4	121	2.25	100	10	200
TC		H_2: CO_2	Sel	Yield	Conv	H_2: CO_2	Sel	Yield	Conv	H_2: CO_2	Sel	Yield	Conv
	Carbon monoxide[69]	1:1	100	68	68	1:1	100	68	68	1:1	100	68	68
	Methanol[71]	3:1	68	18	27	3:1	90	24	27	3:1	100	27	27
	Methane[72, 73]	4:1	99	79	80	4:1	99	84	85	4:1	99	84	85
	Dimethyl ether[74]	3:1	73	23	31	3:1	90	31	34	3:1	100	34	34
	Fischer-Tropsch Liquids[75]	6:1	78	42	54	6:1	78	70	90	6:1	100	100	100
CO_2 price (\$/tonne)		40				20				0			
Electricity price (\$/kWh)		0.068				0.030				0.020			
Electrolytic H_2 price (\$/kg)		3.91				1.80				1.20			
Heat price (\$/MMBtu)		3				3				3			

a: CD is total current density (mA/cm^2)
b: V is overall cell voltage (V)
c: FE is faradaic efficiency (%)
d: Conv is single-pass CO_2 conversion (%)
e: Sel is product selectivity (%)
f: Prod is productivity (g product/L-hr)
g: Tit is product titer (g product/L)

Results and discussion

Economic viability of near-term products

After the initial literature screening process, 11 products were selected for comparative analysis based on their near-term technical viability[2] including carbon monoxide (CO), formic acid (FA), oxalic acid (OA), ethylene (C_2H_4), ethanol (EtOH), methane (CH_4), methanol (MeOH), acetic acid (AA), polyhydroxybutyrate (PHB), dimethyl ether (DME), and Fischer-Tropsch liquids (FT).

In Fig. 2A, the spread between calculated product MSP and the average 2014–2018 U.S. market price of each product (2016\$), represented by the midline, is shown for the three economic scenarios. A positive deviation from market price indicates the calculated MSP is greater than the current market price and conversely, a negative deviation from market price indicates the calculated MSP is under current market price and the product is potentially economically viable. Recognizing that market prices fluctuate with time, we include bars around the midline which reflect the observed range in market price over the past decade (2008-2018) where data was available. In the case of CH_4, two sets of bars are shown to differentiate the lower cost fossil natural gas (midline) from renewable natural gas (RNG, dotted) which can command a significantly higher market price.

Under current conditions (red squares in Fig. 2A), only PHB is projected to be cost competitive due to its high current market price (Fig. 2B). After applying the improved technological and market parameters of the future scenario (blue triangles in Fig. 2A), calculated product MSPs fall by an average of 74% across the five pathways as shown in Fig. 3A, resulting in 8 of the 11 products being potentially market competitive (Fig. 2A). Only CH_4, MeOH, and DME remain above the competitive market range. Under the theoretical scenario (green circles in Fig. 2A), all products are at or below current market prices except for CH_4, which is disadvantaged due to low U.S. natural gas (NG) prices. However, when compared against RNG prices (dotted bars), CH_4 does fall within the competitive range for some technologies in the future scenario and all technologies in the theoretical scenario. These results imply that near-term viability of CO_2R lies in high-value specialty chemicals (often with small market share); however, as technological and market parameters continue to improve, the production cost of many CO_2R-derived commodity chemicals and fuels can rival the market price of the incumbent fossil-based methods.

In addition to technological and market parameters, product specific factors such as theoretical mass yield and reaction stoichiometry also strongly influence the underlying economic viability. Specifically, in comparing chemical (e.g., FA) versus fuel (e.g., CH_4) products, hydrocarbon fuels have lower maximum theoretical mass yields as oxygen atoms are removed from the final product (Eq. 3) to improve fuel properties. For example, the theoretical mass yield of CO_2R-CH_4 is only 36% on a CO_2 basis whereas FA is 105% with all original carbon and oxygen elements retained in the final product along with added hydrogen (Eq. 4). With products commonly marketed on a per-mass basis, these differences in theoretical mass yields can play a significant role in determining product viability. Similarly, the number of electrons (e-) required in direct conversion pathways or mols of H_2 needed in indirect pathways can vary widely depending on the product. For example, eight e- (or four mol of H_2) are required to reduce CO_2 to CH_4 while only two e- (or one mol H_2) are required to produce one mol of FA. Thus, assuming an even baseline for conversion, oxygenated products are inherently more efficient, consuming up to 75% less feedstock(s) (electrons or H_2) while achieving higher mass yield, resulting in lower operating costs (OPEX) and often a more competitive MSP.

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad \text{Equation 3}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad \text{Equation 4}$$

For CO_2R to have an impact on the *global* circular carbon economy, it will be essential to not only reach cost competitiveness, but also target products that can be implemented at the gigatonne scale[6]. In Fig. 2B, a summary of annual global consumption (tonne/y) versus average 2014–2018 U.S. market price (2016$/kg) is shown, highlighting a four-order of magnitude variation in consumption across the 11 products.

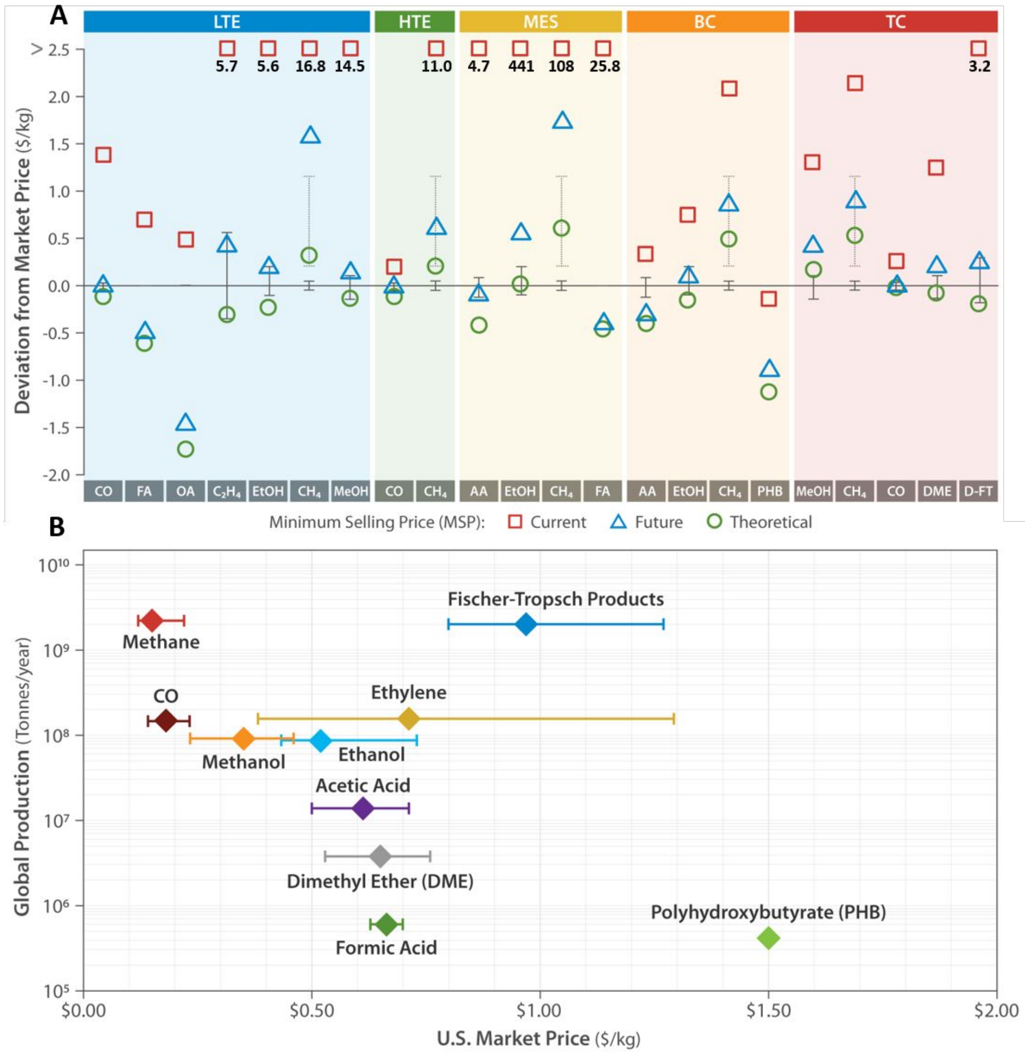

Fig. 2 A. Difference between calculated product MSP and 5-year (2014–2018) averaged U.S. market price in 2016 U.S. dollars (2016$) for selected chemicals in the current (SOT), future, and theoretical scenarios. Differences > \$2.5/kg are specified in bold. Bars depict lower and upper bound of recorded 2008-2018 market price (data in ESI† Table S2). Methane MSP data contains sets of bars, solid bars represent fossil CH_4 around the midline and dotted bars represent renewable natural gas pricing above the midline. **B.** A summary of 5-year (2014–2018) averaged annual global production reported versus 5-year (2014–2018) average U.S. market price in 2016$.

From a carbon utilization perspective, the top current products by mass are CH_4, FT products, CO, C_2H_4, EtOH, and MeOH. However, it should be noted that this is a snapshot based on currently available data and the relative demand for products may shift in the future as the demand for seasonal storage of renewable electricity grows and alternative markets for products continue to expand.

In considering both economic competitiveness and CO_2 utilization potential, FT products, C_2H_4, EtOH, and CO represent some of the most compelling near-term CO_2R products. In a previous study which examined the technical feasibility of CO_2R and the relative ease of formation of products, the top performing C_1-C_3 species in order were CO, MeOH, CH_4, FA, C_2H_4, and AA[2]. From the nexus of these two studies, CO and C_2H_4 stand out as strong candidates from both a near-term economic standpoint and technical standpoint[2]. Despite the low U.S. NG prices and the rise of shale gas, research and commercial interest into the sustainable methanation of CO_2 known as power-to-gas is also growing[72, 76], largely driven by its potential as an energy storage play for otherwise curtailed electricity, compatibility with existing NG infrastructure, and carbon intensity regulations for fuels and energy that are driving growth in global RNG markets, which value RNG at a higher price point than NG. Thus, these MSP values should not be taken as a statement of commercial viability or business cases; they solely represent cost estimates. Opportunities for providing value to multiple sectors as well as other ancillary benefits must be further considered.

Opportunities for Transformational R&D

CO_2R economics are dramatically improved in moving from current to future scenarios, on average reducing product MSPs by 54%–97%

depending on the pathway (Fig. 3A). In the higher technology readiness level (TRL) indirect pathways (i.e., TC and BC), which have benefited from years of infrastructure and R&D investments for syngas chemistry, the improvement to MSP is driven primarily by market parameters (i.e., feedstock costs), accounting for on average 84% ± 17% of the total cost reduction. Within the market parameters, H_2 production comprises the most significant fractional cost. Consequently, although separate from the core CO_2R conversion step, R&D efforts on large-scale electrolytic H_2 generation, such as H2@Scale[77] are poised to provide the greatest potential for near-term cost reduction in indirect pathways. Conversely, MSPs in the emerging LTE, HTE, and MES pathways are most sensitive to technical parameters comprising on average 77% ± 22% of the cost reduction. To move these low TRL direct pathways forward towards commercial readiness, transformational R&D is needed to advance the core conversion technology. At a high level, these findings are in agreement with other studies highlighting the importance of market parameters (i.e., H_2 price)[78] and technical parameters (i.e. CD and FE)[21] on the economics of indirect and direct pathways respectively; however, the breadth of our analysis allows for a deeper quantification of the impact of specific technical metrics on CO_2R economics to elucidate the most critical R&D needs as discussed below.

Using a sensitivity analysis around current technical parameters paired with cross-technology evaluation, the top technological cost drivers for CO_2R and areas for transformational R&D are identified for each pathway-product combination (Fig. S2–S6, ESI†). For the direct LTE and MES pathways, partial current density is consistently the most influential cost driver across the majority of products. Partial current density reflects the total amount of current utilized to produce a specific product per unit area of an electrode and directly impacts the size and capital cost of an electrolyzer. Presently, estimates for capital costs range from \$18,000/m^2 in the case of emerging PEM electrolyzers to \$1,400/m^2 for more mature alkaline electrolyzers[39]. When current densities are low, the electrode area needed to convert a fixed volume of CO_2 is increased, requiring larger equipment, and contributing to higher costs. Under current scenarios, electrolyzer capital costs account for on average 44% and 72% of the total MSP for LTE and MES processes respectively (Tables S8, S10, ESI†).

In Fig. 3B, the impact of partial current density on MSP is quantified for an LTE PEM electrolyzer and compared across products requiring the transfer of two, six, and eight electrons per carbon converted under current assumptions. Starting from a partial current density of 10 mA/cm^2, a series of 50 mA/cm^2 step changes are applied to the TEA models, allowing the change in MSP per step change to be calculated. At very low current densities (i.e., <100 mA/cm^2), modest improvements have a dramatic impact on MSP where, for example, a change of 10 → 60 mA/cm^2 for LTE ethylene production shows a \$73/kg reduction in MSP. A product's sensitivity to partial current density is strongly dependent on the number of electrons transferred per carbon during product synthesis (Fig. 3B and 3C), with products requiring eight e- per carbon being most affected and products requiring two e- being least affected. As partial current density continues to increase, the impact on MSP is reduced, with the slope reaching a "level-off point" dependent on the number of electrons transferred in the reaction. Applying a cut-off for the MSP/partial current density slope of Δ0.5 cents/mA, our analysis reveals that for LTE PEM systems level off points are reached at approximately 160–210 mA/cm^2 for products requiring two electrons per carbon and 360–510 mA/cm^2 for products requiring six to eight electrons per carbon (Fig. 3B). Applying the same analysis for MES alkaline electrolyzers, the level-off points in partial current density are approximately 40–70 mA/cm^2 for products requiring two to four electrons per carbon and 95–130 mA/cm^2 for products requiring six to eight electrons per carbon (Fig. 3C).

With partial current densities in the current scenario (i.e., CD x FE in Table 1) less than 200 mA/cm^2 for all but one product in the LTE pathway and on the order of, or less than, 1 mA/cm^2 in the MES pathway except for AA, these data suggest that improving partial current density to a minimum of the aforementioned level-off points represents one of, if not the greatest near-term opportunity for cost reduction. For products (e.g., C_2H_4) that currently exceed the targeted "cut-off" current density values, the economic return from increasing current density will be diminished and further improvement to technical parameters such as single-pass conversion and overpotential could enable a greater reduction in process costs depending on the specific case. A more detailed case-by-case evaluation of key cost drivers and a breakdown of process costs for all product-pathway combinations is provided in the supporting information (Tables S8–S12, ESI†). Although less sensitive to technical parameters, indirect pathways also have opportunities for transformational R&D, specifically in expanding the suite of CO_2R products via development of new (bio)catalysts that offer opportunities for CO_2R to capture market share in the commodity chemical or petrochemical markets. For example, the selective production of formate via TC pathway is still challenging nowadays but could be a game changer with new catalyst development. Accompanying the development of new products, technical parameters such as volumetric productivity and product titer are also influential cost drivers for indirect pathways (Fig. S2–S6, ESI†).

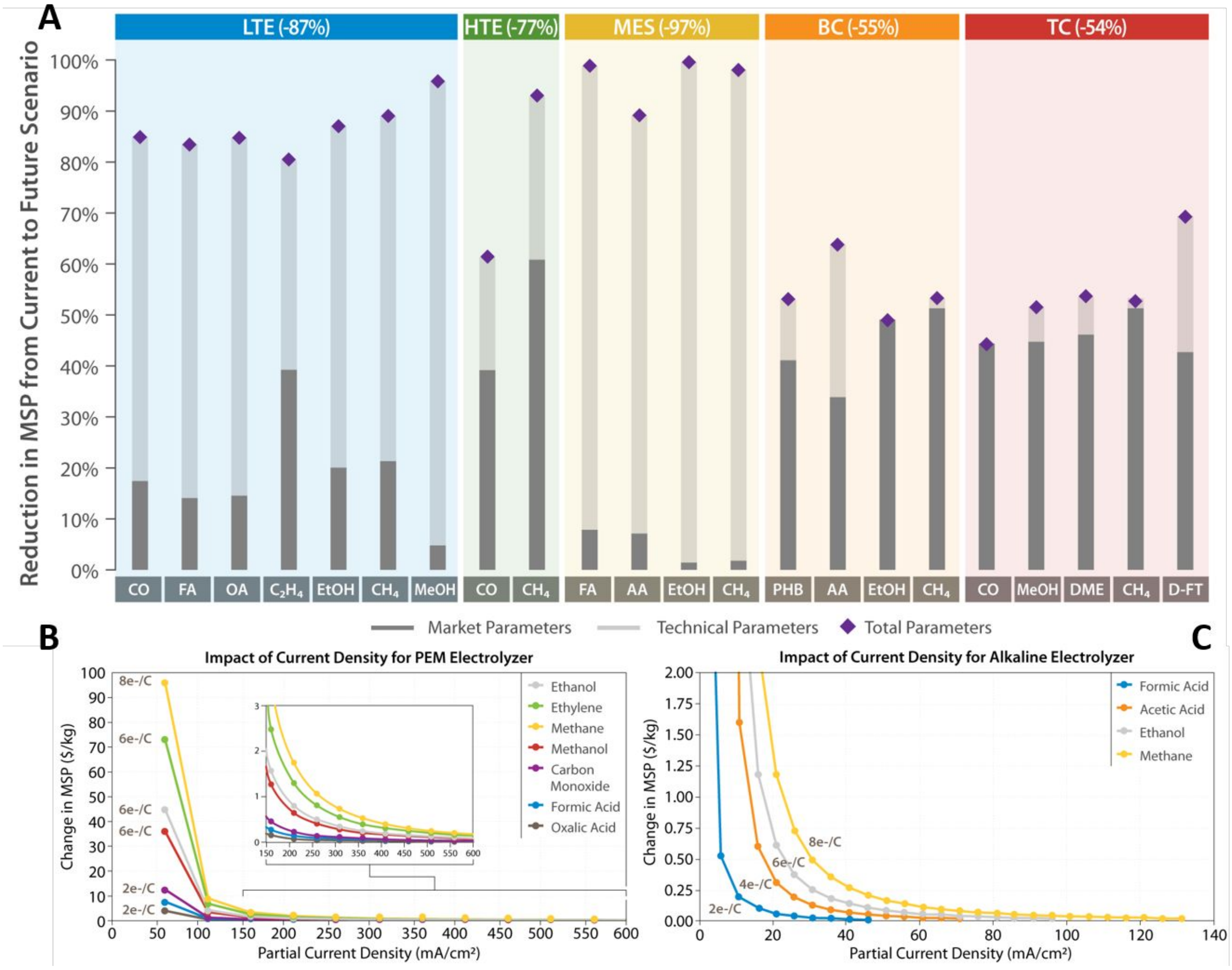

Fig. 3 A. The percentage reduction in calculated MSP moving from current to future scenario (detailed assumptions are listed in Table 1). Total reduction in MSP (diamond) reflects the summation of changes in market parameters (i.e., CO_2 and electricity price) shown in dark grey and technical parameters (i.e., conversion and selectivity) shown in light grey. The averaged change in price across all products in each pathway is shown in parentheses. **B.** Impact of increasing partial current density on MSP of LTE products using PEM electrolyzers. Data points reflect the change in MSP for a 50 mA/cm^2 step change in partial current density using demonstrated SOT product faradaic efficiencies and constant electrolyzer cost on a per m^2 basis. **C.** Impact of raising partial current density on the MSP of MES products using alkaline electrolyzers. Data points reflect the change in MSP for a 5 mA/cm^2 step change in partial current density using SOT product faradaic efficiencies and constant electrolyzer cost on a per m^2 basis.

Impact of CO_2 Price and Incentives

CO_2R technologies are considered a versatile option for converting CO_2, accepting a variety of sources ranging from the highly concentrated streams of fermenters down to the parts per million concentrations found in the atmosphere, assuming appropriate clean up and purification. However, the price per tonne of CO_2 varies dramatically depending on the source ranging from near free, or even negative with incentives[79], up to several hundreds of dollars for direct air capture[80]. The impact of CO_2 price on product MSP is dependent on variety of parameters including overall process efficiency, scenario assumptions (e.g., current, future, and theoretical), and product type. As one example, in our current scenario which assumes a fixed price of $40/tonne CO_2, the cost of CO_2 comprised only 1.5% of the total product cost on average in the less efficient and underdeveloped LTE/MES pathways (Tables S8 and S10, ESI†) compared to an average of 6.5% in the more mature and more efficient HTE/TC/BC pathways (Tables S9 ,S11, S12, ESI†). This finding was consistent across a range of CO_2 prices in the current scenario (Fig. S7, ESI†). Thus, as technological advancements are achieved and CO_2R pathways move closer towards commercialization, the impact of CO_2 price will become more significant and more clearly observed. In Fig. 4 we quantify the impact of CO_2 price in the future scenario on product MSP across some of the most common higher volume industrially relevant sources including: integrated gasification and combined cycle (IGCC), pulverized coal (PC), and natural gas combined cycle (NGCC) power generation, along with CO_2 from cement, iron and steel, and direct air capture sources[80, 81]. We also examine the impact of emerging federal-level credits such as the U.S. 45Q program, worth approximately \$35/tonne sequestered[79].

In Fig. 4 the percent change in MSP across CO_2 sources is shown for each product-pathway combination assuming (1) a baseline CO_2 price of \$20/tonne represented by the vertical midline and (2) future scenario technical and market parameters as noted in Table 1. Across the studied range of CO_2 prices from \$-35/tonne to \$250/tonne, we show that product MSPs in the future scenario vary by as much as -60% to +251% relative to the baseline value. In general, we note that processes requiring the fewest electrons (or H_2) along with those exhibiting higher energy efficiencies are most sensitive to CO_2 price such as in the case of HTE-CO and TC-CO. In other words, pathway-product combinations that operate more efficiently and/or start from a lower operating expense (OPEX) baseline will experience a larger percentage change in total OPEX, and consequentially larger change in MSP, when subjected to a like-for-like change in CO_2 price. Still, we show that increasing the CO_2 price by over a factor of three from \$20/tonne (baseline) to \$63/tonne (NGCC) resulted in an MSP change of on average just 15% across all future product-pathway combinations. These data emphasize that as technologies continue to improve and overall efficiencies rise, CO_2 price will become more influential to the overall economics; however, the magnitude of the impact is still minimal for most industrial point sources.

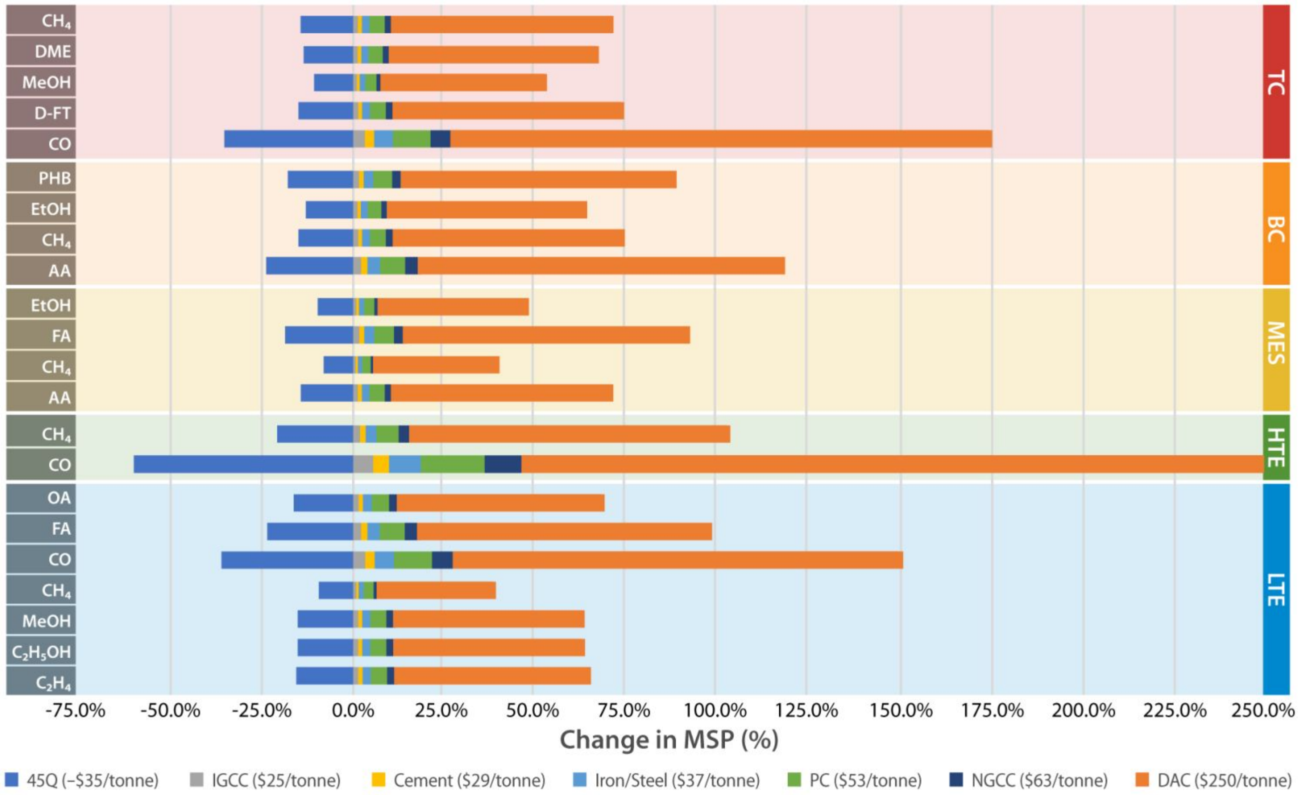

Fig. 4. The percent change in product minimum selling price (MSP) as a function of CO_2 capture cost assuming future scenario conditions and an initial capture cost of \$20/tonne. Assumed capture costs of -\$35/tonne (45Q), \$25/tonne (IGCC), \$29/tonne (cement), \$37/tonne (iron/steel), \$53/tonne (PC), \$63/tonne (NGCC), and \$250/tonne (DAC) are based on published literature reports[79-81].

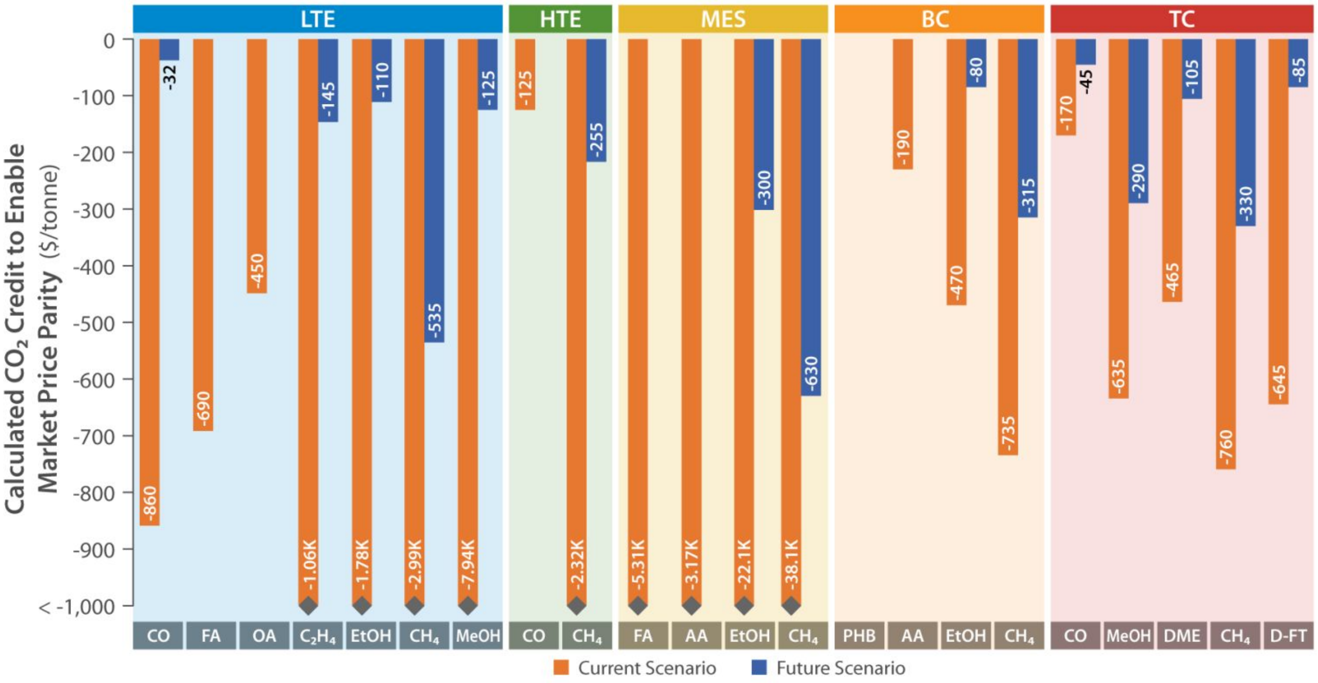

Fig. 5. Calculated CO_2 credit ($/tonne) to enable market price parity under current (orange) and future (blue) scenario assumptions. A value of zero represents products reaching market price parity without the assistance of credits. 7 of the 22 product-pathway combinations do not have blue bars, indicating they could potentially be cost competitive in the future without incentives. All CH_4 datasets were evaluated using fossil CH_4 market data.

In addition to the type of point source, the effective CO_2 price can also be impacted by the policies and incentives of local governments. In attempt to help drive the adoption of CO_2R and carbon neutral technologies, many governments worldwide are now giving high priority to climate change initiatives[82]. For example, in the United States, notable carbon mitigation credits include tradeable low carbon fuel standard (LCFS) credits in California ranging from $100–$200 per tonne of CO_2 transferred in 2017–2019[83] and the federal 45Q carbon capture and storage (CCS) tax credits at $35–$50 per tonne CO_2[84]. Canada has also recently enacted the Greenhouse Gas Pollution Price Act (GHGPPA) which sets a national tax on carbon emissions increasing from C$30 tonne CO_2/yr to C$170 tonne CO_2/yr by 2030[85]. Further, China, the world's largest energy consumer and carbon emitter, recently announced $360 billion in renewable energy investments by 2020 in an effort to reduce carbon emissions[86]. While these investments prioritize infrastructure for energy generation, the results of Fig. 2A suggest that the economic viability of CO_2R products can be enhanced through financial incentives and/or policy mechanisms.

In Fig. 5 we show the estimated credit in terms of $/tonne CO_2 converted required for each product-pathway combination to achieve an MSP equivalent to the current market selling price in the current and future scenarios. Note these values do not consider total life cycle emissions and are not intended to promote a specific level of policy; rather, the data estimate the level of subsidy that can help achieve market price parity of the calculated MSP if directly applied to the CO_2 utilized during the conversion step without other changes to the technologies or other model assumptions.

In the current scenario, CO_2 credits from $170/tonne to >>$1,000/tonne were shown to enable MSPs at market price parity for all product-pathway combinations other than PHB, which is outright competitive. For the majority of CO_2R technologies today, a carbon credit on the order of those that currently exist in the market (i.e., LCFS and 45Q) is unlikely to significantly impact their ability to reach cost parity. Consequently, these data suggest that major gains are still needed upfront from technological advancements to drive down costs before CO_2 credits can significantly contribute to closing the gap and achieving cost parity. Conversely, in the future scenarios which account for technological advancements as well as a reduction in feedstock costs (e.g., electricity and H_2), 7 of 22 product-pathway combinations are shown to be outright competitive with the current market price, and the calculated subsidy for the remaining are significantly reduced to $32–$630/tonne CO_2 in which case policy drivers and CO_2 price become more relevant as noted above.

Intermittent Operation Economics

Surging deployment of renewable electricity infrastructure has resulted in a rapid decrease in the price of renewable energy across technologies over the past decade. Specifically, data from the

International Renewable Energy Agency (IRENA) shows that over the past nine years the levelized cost of electricity (LCOE) for solar and onshore wind has fallen to c.a. \$0.050/kWh and \$0.057/kWh respectively, while simultaneously the global weighted-average capacity factors have increased to 18% (solar) and 36% (wind)[4]. With the rapid deployment of these technologies has also come concerns surrounding the risks of periods of overgeneration and lack of storage[87]. Intermittent utilization of CO_2R has been proposed as one possible strategy to mitigate these challenges where excess electricity could be purchased from the grid at negative or low cost and stored in the form of chemical bonds[6]. Although Intermittent operation of CO_2R processes to capitalize on transient low-cost electricity has the potential to significantly lower process costs, the true economic feasibility of intermittent operation is complex. In addition to potential OPEX savings, operators must also consider the electron demand of the product, losses in production, equipment lifetime with frequent cycling, and the ability to payoff recurring financing charges from fixed capital expenses (CAPEX). An in-depth system-level analysis is needed to assess the challenge and opportunity of using CO_2R for renewable electricity storage and higher-value chemicals or fuels production.

To illustrate the interplay between MSP (i.e., production cost), capacity factor, input electricity prices, and CAPEX, in Fig. 6 we present two case studies of intermittent operation for LTE derived C_2H_4 and SOEC derived CO under both current and future scenario conditions. CO and C_2H_4 were selected to show the impact of electron demand (2 e^- per carbon for CO and 6 e^- per carbon for C_2H_4) and due to the relatively high TRL of the two product-pathway combinations. Using the same models and assumptions as discussed above, Fig. 6A shows lines of constant MSP as a function of electricity price and capacity factor for the CO and C_2H_4 products under current scenario conditions across CAPEX values ranging from \$50M - \$500M based on modelled values. For reference, in the current case modelled CAPEX values were \$67M (LTE-C_2H_4) and \$68M (HTE-CO) while in the future case, modelled CAPEX values were \$219M (LTE-C_2H_4) and \$26M (HTE-CO) (note: electrolyzer CAPEX is dependent on total current (Amps) demand which can be much higher in the future scenarios due to higher assumed conversions, causing CAPEX to increase for some products despite improvements in efficiency). While keeping all product-specific technical parameters constant (i.e., voltage, current density, conversion), Fig. 6A illustrates that as capacity factor is stepped down from the baseline value of 90% to lower values representative of intermittent operation, there is a corresponding decrease in the required electricity price to maintain a constant MSP for the product(s). This drop in required electricity price stems from the fact that to offset losses in production from a lower capacity factor and pay off fixed financing charges, OPEX costs (i.e., cost of electricity) must also decrease.

In comparing the four CAPEX sets, the data shows that, for a given set of assumptions, processes with the lowest CAPEX were the least sensitive to electricity price and as CAPEX was increased, the required electricity price to maintain profitability decreased proportionally. For example, in the case of LTE-C_2H_4 (orange circles Fig. 6A), in moving from 90% capacity to 60% capacity, Fig. 6A shows that at a total CAPEX of \$50M, the electricity price must drop to ≤ \$0.060/kWh to maintain or lower the product MSP. However, for the same process but with a total CAPEX of \$500M (red circles Fig. 6A), the financing charges are significantly higher and to compensate, the required electricity price drops to ≤ \$0.015/kWh. With the global average capacity factor of renewable sources ranging between 18-36% for solar and wind energy, these data suggest that fully-renewable conversion processes with CAPEX greater than \$200M will currently struggle to find economic value in intermittent operation at the studied scale of a 200M gallon per year bioethanol facility (76 tonne CO_2/h) and may need to utilize higher-cost grid electricity from fossil sources to raise their capacity factor. However, with the use of grid electricity comes environmental trade-offs and an increase in CO_2 emissions as grid electricity is predominantly comprised of fossil energy sources in many locations[88]. Note that the reported \$200M CAPEX threshold in this case is specific to the incoming CO_2 flowrate of this analysis, and when normalized by the flowrate of 75,931 kg CO_2/hr is equivalent to approximately \$2,630/kg CO_2 hr^{-1}.

In moving from current scenario to future scenario assumptions in Fig. 6B, we show that the slope of the constant MSP lines vary more noticeably between the two products. Unlike in Fig. 6A where the technical parameters varied between products based on the current reported SOT data, under the future scenario the technical assumptions are more consistent for each product allowing for a truer like-for-like comparison of the two products (Table 1). A critical intrinsic difference between CO and C_2H_4 is the number of electrons required per mole of product with CO requiring only 2 e- and C_2H_4 requiring 12 e-. As a result, OPEX is a higher proportion of the total cost in higher electron processes (e.g., C_2H_4) and consequently, the penalty of underutilized CAPEX charges is lower. In other words, for an equivalent step change in electricity price the absolute change in feedstock cost for the 12 e- C_2H_4 case will be c.a. 6x greater than in the 2 e- CO case (assuming similar cell voltages) and thus a smaller move in electricity price is needed for C_2H_4 compared to CO due to this electron multiplier effect. These results suggest that processes with the greatest electron demand stand to benefit the most from intermittent operation.

Ultimately these data on intermittency collectively highlight that the development of future CO_2R processes should not be overly reliant on the transient utilization of low-cost or curtailed electricity as the loss of production and financing charges from capital-intensive processes can quickly erode the benefits of discounted electricity and intermittent operation. For most products, the reduction in MSP from intermittency will be insufficient to reach cost parity without also accompanying advancements in the underlying conversion technology. Further, previous studies have projected that more than 18.1 PWh (Petawatt Hour) of renewable electricity will be needed to decouple chemical production from fossil resources via CO_2R at a scale of 3.5 gigatonnes of CO_2 equivalent in 2030[89]. This suggests that although curtailed electricity could play a role in some cases, the total energy demand to drive CO_2R at industrially relevant scales is substantial and investments into dedicated energy infrastructure are likely to be required.

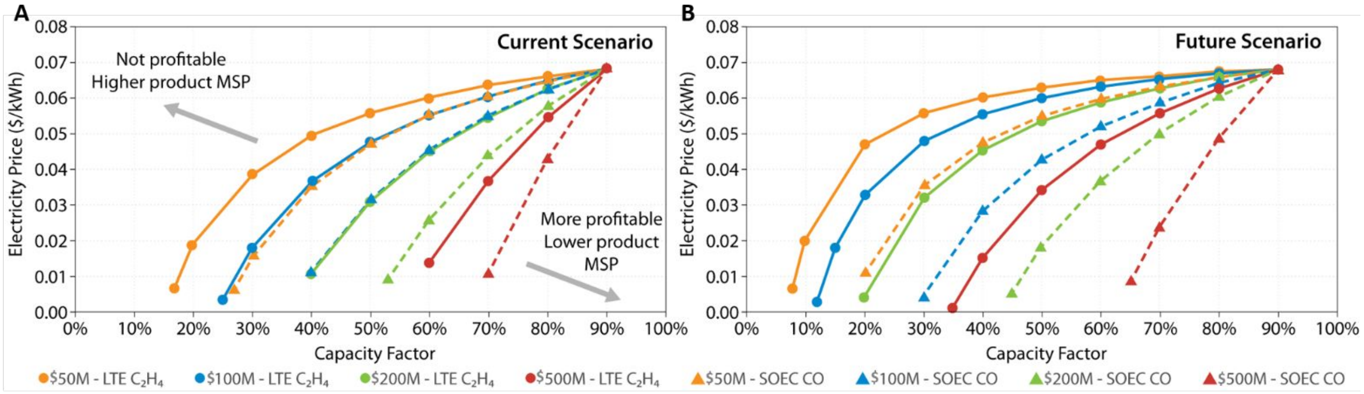

Fig. 6. Lines of constant MSP for the production of SOEC-derived CO (triangles) and LTE-derived C_2H_4 (circles) for (A) current scenario assumptions and (B) future scenario assumptions. Assumed CAPEX values range from \$50M to \$500M for a fixed incoming CO_2 flowrate of 75,931 kg CO_2/hr based on a 200M gallon per year bioethanol refinery.

Conclusion

Similar to the path taken by the bioenergy field over the past decade(s)[90, 91], the near-term viability of emerging CO_2R technologies will be linked to reducing feedstock (e.g., H_2 and electricity) and conversion costs. The data provided herein show that, in the current scenario, substantial upfront gains from technical advancements are possible to help close the gap with incumbent methods. High-value, high-margin products (e.g., PHB) or products that provide value to multiple sectors (i.e., CH_4) are likely to be the focus early on to overcome the higher costs associated with unoptimized technologies and first-of-a-kind plants. The techno-economic analysis provided herein can help guide the necessary R&D, such as prioritizing partial current density, in order to accelerate the development of these technologies and to identify the most economically advantaged products for initial targets. As CO_2R technologies evolve and more facilities come online and operating costs come down, it may allow for the expansion to higher-volume commodity products like fuels with smaller margins at more competitive price points. Although this strategy will not immediately impact overall CO_2 mitigation with an initial emphasis on smaller niche markets, it enables the field to grow more rapidly and allows for learning to occur at industrial scale so that those lessons combined with R&D advancements can lead to accessing some of the largest market chemicals and fuels at costs competitive with market prices.

With H_2 and renewable electricity costs identified as major contributors to the overall economics of CO_2R, an emerging theme across the CO_2R community has been to mitigate these challenges through intermittent operation to capitalize on the lowest-cost or curtailed electricity during periods of overgeneration. Although the usage of curtailed electricity can dramatically lower operating expenses, herein we highlight that often the accompanying losses in production from operating the CO_2 conversion step at a lower capacity factor can significantly impair the ability to pay back fixed charges, especially in capital intensive processes, raising the product minimum selling price per unit output. Consequently, the economic viability of intermittent operation must be evaluated on a case-by-case basis and future design choices should be driven not only by the net cost of electricity, but also the effective utilization of CAPEX. Moving forward, more analysis is needed to determine the total energy demand for CO_2R at scale and how to meet these demands through curtailed electricity, dedicated infrastructure, and systems integration to maximize product output per capital invested.

Conflicts of interest

There are no conflicts to declare.

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Abbreviations

45Q: United States federal CO_2 storage incentive program
AA: Acetic acid
AACE: Association for the Advancement of Cost Engineering
BC: Biochemical conversion
CAPEX: Capital expense
CCS: Carbon capture and storage
CD: Current density
CO: Carbon monoxide
CO_2R: CO_2 reduction
Conv: Single-pass CO_2 conversion
DME: Dimethyl ether
DOE: U.S. Department of Energy
EIA: U.S. Energy Information Administration
EtOH: Ethanol
FA: Formic acid
FE: Faradaic efficiency
FT: Fischer-Tropsch
GHGPPA: Greenhouse Gas Pollution Pricing Act
H2A: H_2 at scale
HTE: High temperature electrolysis
IGCC: Integrated gasification combined cycle
IRENA: International renewable energy agency
LCFS: California's low-carbon fuel standard
LCOE: Levelized cost of electricity
LTE: Low temperature electrolysis
MEA: Membrane electrode assembly
MeOH: Methanol
MES: Microbial electrosynthesis
MGY: Million gallon per year
MSP: Minimum selling price
NG: Natural gas
NGCC: Natural gas combined cycle
NREL: National Renewable Energy Laboratory
OA: Oxalic acid
OPEX: Operating expense
PC: Pulverized coal
PEM: Polymer electrolyte membrane
PHB: Poly-hydroxy butyrate
RNG: Renewable natural gas
SOEC: Solid-oxide electrochemical cell
SOT: State of technology
TC: Thermochemical conversion
TEA: Techno-economic analysis
TIC: Total installed cost
TRL: Technology readiness level
V: Voltage

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