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On the climate change mitigation potential of CO_2 conversion to fuels

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CO_2 capture and conversion to fuels using renewable energy is being promoted as a climate change mitigation measure that reduces fossil fuel use by effectively recycling carbon. We examine this claim, first for a typical CO_2 capture and utilization (CCU) system producing methanol (MeOH), and then for a generalized system producing fuels from fossil carbon. The MeOH analysis shows CCU to be an inferior mitigation option compared to a system with CCS producing the same fuel without CO_2 utilization. CCU also is far more costly. The generalized analysis further reveals that the mitigation potential of CCU for fuels production is limited to 50% of the original emissions of the reference system without CCU. We further highlight that the main challenge to CCU cost reduction is not the CO_2-to-fuel conversion step but the production of required carbon-free electricity at very low cost.

Broader context

Carbon dioxide (CO_2) capture and storage (CCS) is a major climate change mitigation option applicable to large point sources of CO_2 such as power plants and industrial processes. Most research to date has focused on storing captured CO_2 in deep geological formations. However the concept of CO_2 capture and utilization (CCU) is gaining attention as a potential means of using the CO_2 to economically produce desired products while avoiding the extraction of additional fossil carbon resources. In this paper, we analyze the manufacture of transportation fuels from CO_2, a major proposed CCU pathway. To avoid increasing CO_2 emissions from process energy requirements, CCU systems require large quantities of zero-carbon electricity with high availability and low cost—systems not generally available today. Even if such electricity were available, the maximum mitigation potential of any CCU system is shown to be only 50% compared to an equivalent system with geological storage of CO_2. A preliminary economic analysis further shows mitigation costs for CCU to be much higher than CCS-based systems delivering the same fuel product. So while large-scale CO_2 utilization sounds attractive, our analysis shows that this concept has severe limitations as a mitigation measure or cost-effective strategy for reducing CO_2 emissions.

Introduction

Studies by the Intergovernmental Panel on Climate Change (IPCC) indicate that in order to limit global warming to around 1.5–2 °C by the end of the 21st century there is a need to drastically limit emissions of CO_2 and other greenhouse gases by mid-century and beyond.[1] Potentially, this could require leaving much of the known reserves of carbon underground as stranded assets[2] with economic consequences.[3,4] Considering current CO_2 emission trends, achieving climate mitigation targets may even require negative emissions of CO_2 (*i.e.*, extracting CO_2 from the atmosphere and storing it underground) at some point in the second half of the century.[1,5]

Paradoxically, however, in recent years new fossil fuel exploitation techniques such as hydraulic fracturing have substantially expanded the production of natural gas and crude oil resources, and future developments could tap into even larger fossil resources such as methane hydrates.

CO_2 capture and storage (CCS) could in theory allow the continued use of fossil fuels in a manner compatible with the aggressive targets for CO_2 emission reductions over the coming decades.[1,6] CCS is also an enabling technology for negative emission systems that extract carbon from the atmosphere. However, relative to expectations a decade ago, the deployment of CCS has been delayed by a lack of regulatory requirements and economic incentives (*e.g.*, an adequately high price for carbon or CO_2 avoided), as well as by issues of public acceptance in many countries.[7,8]

The growing interest in CO_2 utilization

In principle, CO_2 capture and utilisation (CCU) could be considered as an alternative or a complement to CCS with deep

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geological storage. The idea of a closed carbon cycle with CO_2 reuse can be traced back to at least the 1970s, involving processes using hydrogen generated electrolytically from nuclear power and CO_2 captured from industrial processes (cement, steel, power) or air.[9] More recently, scientists such as Nobel laureate Olah have advocated the vision of a "methanol economy"[10–13] that employs a carbon cycle involving CO_2 capture from air, H_2 production from renewable energy and transformation of CO_2 to methanol (MeOH) to power the transport sector. Major reviews imparting an optimistic outlook for the future role of CCU in a carbon-constrained world continue to appear in the scientific literature.[14–16] Ambitious statements about the "teraton challenge"[17] or the notion of "a carbon dioxide neutral world"[18] usually are emphatically linked to CO_2 chemical conversion routes using renewable energy (as well as advanced concepts such as artificial photosynthesis or artificial leafs). Public and private R&D funding agencies are supporting large research programmes on CCU, and several projects are demonstrating a variety of CCU concepts at pilot scale.[19,20] There are also proposals that consider CCU as a thermochemical energy storage process by maintaining a closed loop of carbon (as CO_2 or CH_4) in caverns or reservoirs (see for example Jensen *et al.*[21]).

The main driver of climate change mitigation claims for CO_2 conversion to fuels is the notion that, provided with carbon-free energy, the CO_2 molecule can be used as a carbon source instead of fossil carbon in a wide variety of processes and end uses (including fuels for transportation). Such substitution of the carbon source would avoid the extraction of additional

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Marco Mazzotti

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fossil carbon. This line of thinking is summarised in a recent review of CCU systems by Aresta *et al.*:[20] "Each atom of C we can recycle is an atom of fossil carbon left in the underground for next generations that will not reach the atmosphere today."

Prior assessments of CCU for climate change mitigation

The quantification of CO_2 credits gained or CO_2 emissions avoided by specific CCU products is not straightforward and requires careful analysis. Over two decades ago, for example, Herzog *et al.*[22] pointed out the large inefficiencies inherent in the conversion of CO_2 to liquid fuels. In 2005, the IPCC Special Report on CCS[23] systematically evaluated CCU relative to CCS for climate change mitigation, including claims by CCU advocates regarding carbon credits gained by product substitution.[24] The IPCC study concluded from overall mass and energy balances that the avoided emissions reported for CCU were generally overestimated and sometimes misleading. The report concluded that none of the major existing industrial uses of CO_2 (in applications other than enhanced oil recovery, EOR) could properly claim a credit for mitigating CO_2 emissions because of the short storage life of most carbon products currently produced from CO_2. For those few products with a sufficiently long (century-scale) carbon storage life (such as polycarbonate products), an increase of several orders of magnitude in their market demands would be needed to achieve a scale relevant for climate change mitigation (see Table 1). Also other niche uses of CO_2 for mineralisation or carbonation of industrial alkaline wastes are problematic[23] as their affinity for CO_2 usually comes from a previous calcination step of a natural carbonate that has released CO_2 (such as CaO produced from $CaCO_3$ as a raw material for clinker manufacture). Thus, the net impacts of a CCU process could be assessed only from a detailed, rigorous and transparent life cycle analysis (LCA) of each specific CCU product and process.[23] Overall, the IPCC study concluded that, "The scale of the use of captured CO_2 in industrial processes is too small, the storage times too short and the energy balance too unfavourable for industrial uses of CO_2 to become significant as a means of mitigating climate change."

In contrast with the large number of publications looking at fundamental aspects of CO_2 reactions to synthesize marketable products, there are few LCA studies on CCU processes quantifying their climate change mitigation potential from a whole system perspective. Recently, von der Assen *et al.*[25–27] and Van der Giesen *et al.*[28] discussed several pitfalls and common misconceptions in the CCU literature when assessing the mitigation potential of processes for CO_2 conversion to fuels. The results from recent LCA studies of specific CCU process schemes[25–27] also suggest that the avoided emissions from a "cradle-to-grave" perspective tends to be much smaller than in studies focused more narrowly on the "gate-to-gate" CO_2 conversion step that looks only at the utilization process and not at the full system. While some recent studies of specific CCU processes[28–36] have included sufficient detail to allow for full carbon accounting and economic analysis, generalisation of such results remains a challenge because of the large number of assumptions regarding specific process parameters.

In addition to process-specific studies, a recent paper by MacDowell *et al.*[37] reviewed the limitations of CCU from a global emissions reduction perspective, expanding upon the earlier IPCC analysis. Their work distinguished among different CCU concepts, such as the use of CO_2 for enhanced oil recovery, for biofuels production using algae, and for conversion processes using hydrogen—all of which are considered to be CO_2 utilisation technologies in various studies.[37] Overall, their analysis of global markets and emissions reduction potential concluded that: "CCU may prove to be a costly distraction, financially and politically, from the real task of mitigation".

Table 1 A perspective on CO_2 utilization for non-EOR applications showing approximate current amounts of relevant quantities (based on ref. 7, 23 and 35)

Annual amount (million tonnes of CO_2)	Description
~40 000	CO_2 worldwide anthropogenic emissions to atmosphere
~200	CO_2 utilized for products & chemicals, of which...
~20	CO_2 stored in products for a few decades
~1	CO_2 stored in products for a century or more

Objectives of this study

Given this background, our main objective is to propose and illustrate a simple but robust framework for assessing the true mitigation potential of CCU processes relative to two key alternatives: a "reference system" producing the same product without any CO_2 mitigation, and a "CCS system" that also mitigates CO_2 while providing the same fuel product.[6] Thus, we emphasize the need for—and value of—a proper comparative analysis of systems with and without CCU. Such a comparison also reduces or obviates the need for a full life cycle analysis of components that are identical for competing systems. It also allows a simple comparison of mitigation costs of the competing systems.

We first apply this methodology to a well-known example of CCU, namely, a CO_2-to-methanol process. Then, we generalise the discussion to other CO_2 conversion schemes by defining and utilizing an idealized systems analysis framework.

Calculating avoided emissions: a case study of CO_2 to methanol

Methanol (MeOH) is one of the major target products in studies of CO_2 conversion or CO_2 capture and utilization. Detailed process simulations of MeOH synthesis from CO_2 captured from large industrial sources or power plants, plus H_2 produced using renewable energy, have recently been published.[31,34–36,38,39] We have adopted as a base case a recent paper by Perez-Fortes *et al.*[31] from the European Commission, which gives overall carbon balances consistent with other recent studies.[34–36,38,39]

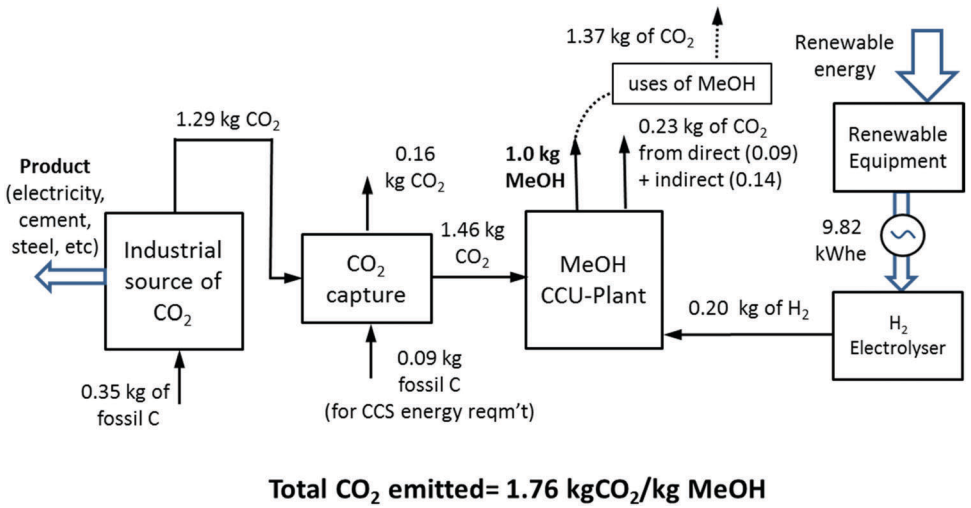

Fig. 1 Full CCU system capturing industrial CO_2 and using it to produce MeOH using carbon-free renewable energy.

We illustrate in Fig. 1 the full CCU system to deliver 1 kg of MeOH, using input and output flows for the CCU plant as in ref. 31. However, we also include all the necessary subsystems to produce the CO_2 and H_2 entering the MeOH CCU plant. As a result, the remaining flows into the components of Fig. 1 are natural resources only. The industrial source of CO_2 is a slave process providing exactly the amount of CO_2 needed by the CCU plant (*via* a CO_2 capture plant with 90% removal efficiency, requiring 25% additional fossil carbon to meet the energy requirements for capture). To facilitate comparisons, all energy requirements linked to the CO_2 capture step are connected to the CO_2 capture box in Fig. 1. The energy required for hydrogen production (142 MJ_{HHV} per kg H_2) is supplied to an electrolyzer with an assumed efficiency of 80%.

The total CO_2 emission rate of this full CCU system is 1.76 kg CO_2 per kg MeOH, thus indicating that it is still a source of greenhouse gas emissions. This is mainly a consequence of the short life of carbon in the MeOH product. Thus, the captured CO_2 used to produce fuel is not permanently stored but rather emitted to the atmosphere once the fuel is burned.

To evaluate the mitigation potential of this system we compare it to two alternatives that are illustrated in Fig. 2. The first is a "reference system" with unabated CO_2 emissions producing the same amount of MeOH as the CCU system (elements marked in green in Fig. 2). This consists of a MeOH reference plant fed by fossil fuel (typically natural gas) plus a separate industrial source of CO_2, emitting 1.29 kg CO_2, as in Fig. 1. The carbon flows for the reference MeOH plant are the weighted-average values of conventional MeOH plants in Europe[31] and include both direct process emissions plus indirect emissions from fossil fuel power plants supplying electricity to the process.[31] The total CO_2 emissions of this reference system is 3.43 kg CO_2 per kg MeOH (= 1.29 + 1.37 + 0.77).

The second option illustrated in Fig. 2 is a "full equivalent system with CCS"—which we refer to as the full CCS system. This also produces 1 kg of MeOH product using identical components as the reference system, but mitigates CO_2 emissions by capturing and storing the same amount of CO_2 utilized by the CCU system, using the same CO_2 capture technology. Most importantly, the full CCS system also includes a stand-alone renewable energy power system producing the same amount of carbon-free electricity as used by the CCU system. The total CO_2 emitted by this system is given by the equation shown in Fig. 2 and explained below.

Quantifying avoided emissions

Avoided emissions is defined in the literature as the reduction in emissions of a mitigation option relative to a reference case without mitigation, while still producing a unit of useful product (in this case, 1 kg MeOH). In this context, both the full CCU and CCS systems seek to avoid CO_2 emissions with respect to the reference system (green components of Fig. 2).

However, a full accounting of avoided emissions requires an assumption about the mitigation potential of the 9.82 kW h of renewable-based electricity available to the full CCS system in Fig. 2. The impact of alternative assumptions is plotted in Fig. 3. This figure plots on the vertical axis the avoided emissions of the CCU and CCS systems relative to the reference case with no CO_2 capture. The horizontal axis represents the emission rate (ER) of the power grid elements replaced by the 9.82 kW h of carbon-free electricity available in the full CCS system.

The solid (blue) line in Fig. 3 shows the emissions avoided by the full CCS system. This is the difference between the reference case emissions of 3.43 kg CO_2 per kg MeOH and the CCS system emissions given by the equation in Fig. 2. At the high end, if the carbon-free electricity of the full CCS system were used to offset emissions from an uncontrolled coal-fired power plant (E_R = 0.8 kg CO_2 per kW h) it would avoid 9.0 kg CO_2 per kg MeOH (shown by the blue symbol in Fig. 3). If instead the renewable power replaced a natural gas combined cycle (NGCC) plant (E_R = 0.4) the avoided emissions would be 5.0 kg CO_2 per kg MeOH (green symbol in Fig. 3). The dotted

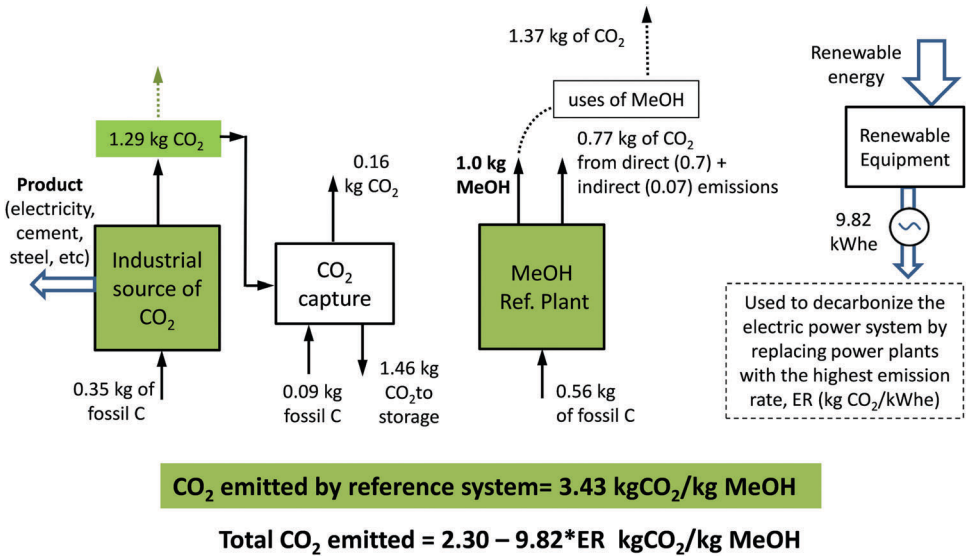

Fig. 2 The reference system with no CO_2 mitigation (shown by elements marked in green), plus the full CCS system producing the same products as the CCU system in Fig. 1.

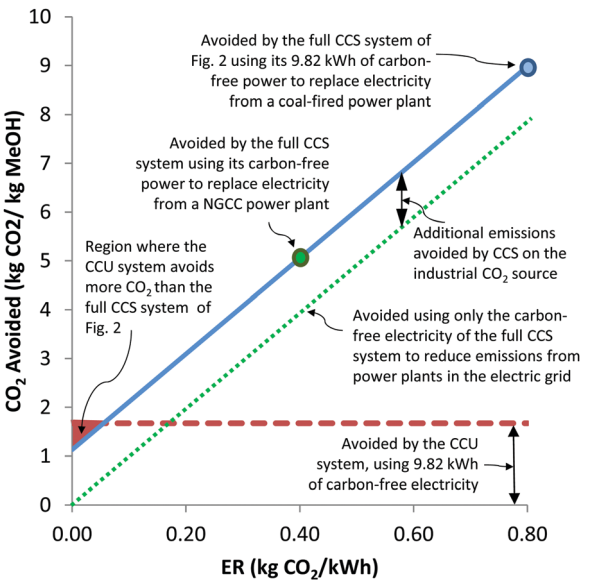

Fig. 3 Total CO_2 avoided per kg of MeOH product as a function of the emission rate, ER (kg CO_2 per kW h) of the power grid elements replaced by the 9.82 kW h of carbon-free electricity available in the full CCS system in Fig. 2.

(green) line shows the portion of avoided emissions of the full CCS system contributed by using the 9.82 kW h of carbon-free electricity to offset emissions in the power sector. As can be seen the major portion of avoided emissions in the full CCS case is due to the substitution of renewable-based power.

In contrast, the dashed (red) line shows the constant value of 1.67 kg CO_2 per kg MeOH calculated earlier for the avoided emissions by the full CCU system of Fig. 1. Note that this value assumes that the renewable energy used for the conversion process is a dedicated component of the CCU system with negligible life cycle emissions, and that it does not avoid any other CO_2 release.†

Fig. 3 shows that the CCS option avoids far more emissions than the CCU system as long as fossil fuel power plants remain on the grid. Not until the CO_2 emission rate of the most carbon-intensive components of the power system falls below 0.055 kg CO_2 per kg MeOH—a point at which the electric power system is effectively decarbonized[40]—does the CCU system begin to avoid more emissions than the full CCS system.

Variations in the numerical assumptions used here would not alter the qualitative results of this analysis showing CO_2-to-methanol to be an inferior mitigation option relative to the full CCS alternative. So too, the use of CO_2 to produce other hydrocarbon fuels such as methane ("power to gas"), diesel, or gasoline ("power to liquids") would further diminish the mitigation potential of CCU because these fuels have much higher energy content than MeOH (typically 44–47 MJ_{HHV} per kg for diesel and gasoline, and 55.5 MJ_{HHV} per kg for methane—*vs.* 22.7 MJ_{HHV} per kg for MeOH). Thus, they would require even more carbon-free electricity than the methanol system of Fig. 1. The key take away is that the mitigation potential of the carbon-free electricity required for the CCU system of Fig. 1 dominates the analysis.

Finally, we note that the concept of avoided extraction of fossil fuel resources (*e.g.*, keeping coal in the ground) also is often cited by CCU proponents as a key benefit of CO_2 utilization.[20] However, the data in Fig. 1 and 2 show that the total fossil fuel extracted by the CCU system is smaller than for

† We note that any quantitative allocation of this emission reduction to individual CCU system components would require criteria linked to a careful life cycle assessment. However, a substantial portion of the mitigation benefit is clearly due to the supply of renewable-based electricity, without which avoided emissions from the CO_2 conversion process would be unattainable.

the CCS system only if one (incorrectly) ignores the 9.82 kW h of carbon-free electricity available in the full CCS case. The use of that renewable energy to offset CO_2 emissions in the power sector also avoids the associated fossil fuel extraction for those power plants. Based on Fig. 2, one can easily show that as long as the 9.82 kW h of renewable energy replaces fossil fuel plants emitting more than 0.21 kg CO_2 per kW h the full CCS system avoids more fossil fuel extraction than the CCU system of Fig. 1. Thus, using that carbon-free energy to avoid emissions from a coal-fired or gas-fired power plant avoids far more fossil fuel extraction than the CO_2 utilization system.

Economic considerations

Economic considerations are inevitable in a rational discussion of climate change mitigation options. While a detailed assessment of mitigation costs (cost of CO_2 avoided) is outside the scope of this paper, we present a preliminary estimate of such costs by exploiting the great similarity between the CCU system of Fig. 1 and the two systems without CCU included in Fig. 2. Thus, we focus on the difference in avoided emissions and cost between the systems illustrated in Fig. 1 and 2.

Following common conventions,[41] the cost of CO_2 avoided (AC, in € per kg of CO_2 avoided), is defined as the difference in cost per unit of MeOH product (C_{MeOH}, in € per kg MeOH) between the CCU system and a reference system without CCU, divided by the difference in specific CO_2 emissions (CO_2, in kg CO_2 per kg MeOH) of the two systems:

$$AC_{CCU\text{-}Ref} = \frac{C_{MeOH\_CCU} - C_{MeOH\_Ref}}{(CO_2)_{Ref} - (CO_2)_{CCU}} = \frac{\Delta C_{CCU\text{-}Ref}}{\Delta(CO_2)_{Ref\text{-}CCU}} \quad (1)$$

We apply this equation to compare the full CCU system of Fig. 1 against the reference system of unabated emissions (green elements of Fig. 2). We consider the differences in annualized capital cost (CAPEX) and operating cost (OPEX) between the two systems. We estimate the latter difference as arising mainly from the costs of electricity and direct fuel supplies. Then, the difference in specific cost in the numerator of eqn (2) can be estimated as:

$$\begin{aligned}\Delta C_{CCU\text{-}Ref} &= \Delta(CAPEX) + \Delta(ElecCost) + \Delta(FuelCost) \\ &= \frac{\Delta(TCR) \times FCF}{CF \times 8760} + \Delta(kW\ h) \times COE + \Delta(FuelCost)\end{aligned} \quad (2)$$

where the Δ(TCR) is the difference in total specific capital requirement to build the two systems, FCF is the fixed charge factor (assumed to be 0.08 in this analysis, as in ref. 31), CF is the annualized plant capacity factor (= 8000/8760, as in ref. 31), Δ(kW h) is the 9.82 kW h of renewable-based electricity required per kg of MeOH in the system of Fig. 1, COE is the unit cost of electricity (assumed to be 0.0951 € per kW h in 2015, from ref. 31) and Δ(FuelCost) is the difference in total fuel cost between the CCU and reference systems based on a European natural gas cost of 8€ per GJ for the reference plant.

For CCU capital costs we assume 2000 € per kWe for a CO_2 capture unit applied to a power plant source of CO_2.[41] Based on ref. 31 we further assume 800 € per kWe for the CCU electrolyzers,[42] 450 € per t MeOH per year for the CCU methanol system, and 850 € per t MeOH per year for the conventional methanol plant. Translating these values to compatible units in eqn (2) and dividing by the avoided emissions of 1.67 kg CO_2 per kg MeOH yields a mitigation cost for the CCU system of approximately 520 € per tCO_2 avoided. Roughly 90% of this is due to the cost of renewable-based electricity used by the CCU system. The TCR is more than twice that of the unabated reference system, with more than half that cost coming from the electrolyzers.

Similarly, one can apply eqn (2) to estimate the avoidance cost of the full CCS system in Fig. 2 relative to the uncontrolled reference system. A "worst case" analysis assumes that the cost of the 9.82 kW h of renewable electricity supply is 0.095 € per kW per h (the current European price), with no credit for the savings in fossil fuel generation displaced. The resulting mitigation cost for the full CCS system ranges from approximately 200 € per t CO_2 to 110 € per t CO_2 based on avoiding emissions from either a NGCC plant or a coal-fired plant, respectively. Thus, even for this extreme case, the CCS system is a far less costly mitigation option than the CCU system. The CCS system cost is even lower if an economic credit is taken for the savings in generation costs for the fossil-based electricity displaced. In the bounding case where the full cost of the renewable electricity supply is recovered (*i.e.*, no net cost), the mitigation cost of the full CCS system falls by an order of magnitude.

Of course, the cost estimates above would differ for other assumptions for the cost of renewable electricity used in Fig. 1 and 2. A sensitive analysis of this issue was conducted by Antsonios *et al.* as part of their analysis of a methanol production process *via* CO_2 hydrogenation.[35] Overall, the important qualitative conclusions from the analysis above are that: (1) mitigation costs for the case study CCU system are substantially (roughly an order of magnitude) higher than typical mitigation costs for CCS applied to coal-fired power plants or other large industrial processes;[41] and (2) CCU costs are substantially higher than those of an equivalent CCS-based system delivering the same fuel product.

The analysis further shows that the key to major cost reductions for CCU lies not in reducing the conversion process cost, but in reducing the cost of a continuous (high capacity factor) renewable-based electricity supply. We note too that this conclusion would not change if the source of CO_2 were a facility capturing CO_2 from ambient air (as investigated in other studies[43,44]), as such a technology would also be included in the system with CCS. For the assumptions in this analysis, the CCU system of Fig. 1 would have to operate with zero cost of electricity for at least 2000 h per year to have lower mitigation costs than the CCS system of Fig. 2.

A general systems analysis of the concept of CO_2 conversion to fuels

Even for the option of CO_2 conversion to fuels, it is beyond the scope of this paper to analyze the variety of process concepts

and scenarios proposed in the CCU literature. Nonetheless, a simplified systems analysis framework can provide useful insights for comparing CO_2 conversion-to-fuels concepts against alternative systems without CCU.

Here, we consider a "thought experiment" in which a carbon resource extracted from the earth is the only raw material used to supply energy to the two main sectors of the economy (in amounts C_1 and C_2, as shown) and CO_2 is the only resulting emission. Fig. 4 represents the complete energy system for this hypothetical case, with all emissions of CO_2 to the atmosphere assumed to be from flue gases. For this idealized case we further assume that thermodynamic efficiency limits have been achieved for all energy conversion technologies, and that chemical processes are reversible (including the reduction of CO_2 to C). Thus, the energy requirements for CO_2 reduction to carbon are identical to the energy obtained *via* the combustion of carbon fuel.

With the aim of mitigating climate change by drastically avoiding CO_2 emissions to the atmosphere, two main approaches may be adopted to decarbonize both the transport and industrial/power sectors in the absence of CCU:

• The renewable electricity solution. The variability of renewable energy would be managed by upgrading electrical grids and by deploying energy storage technologies at appropriate scale and duration to ensure a continuous and reliable supply of electricity.

• The CCS solution. This would capture CO_2 from the flue gases of large industrial processes and power plants, followed by permanent storage of CO_2 away from the atmosphere. The idealized system is assumed to approach 100% capture of the CO_2 from the flue gases. Power plants would thus provide carbon-free electricity, just as renewable energy sources.

In both cases, electrification would require new technologies for the transport sector, as well as for other distributed and industrial sources. The CCS option, however, would allow large industrial sources and power plants to continue functioning with fossil fuels (with some process modifications).

As an alternative, the CCU solution shown in Fig. 5 would convert captured CO_2 back into C using electricity from a renewable energy source. This solution is intended to overcome some of the limitations of the electrification scenario since the production of liquid fuels using "recycled carbon" would allow continued use of existing combustion-based transportation technology (*i.e.*, no need for batteries or other electric-based components). The CCU solution in Fig. 5 includes all elements of the renewable and the CCS systems needed to supply both

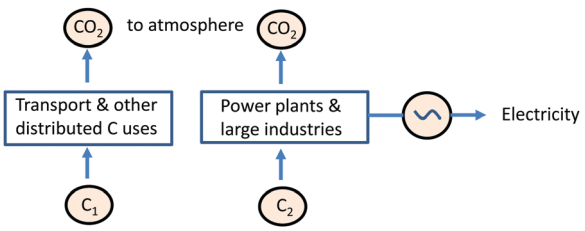

Fig. 4 Schematic of the reference energy system of an idealized carbon-based society emitting CO_2 to the atmosphere from the two major sectors with carbon inputs C_1 and C_2, respectively.

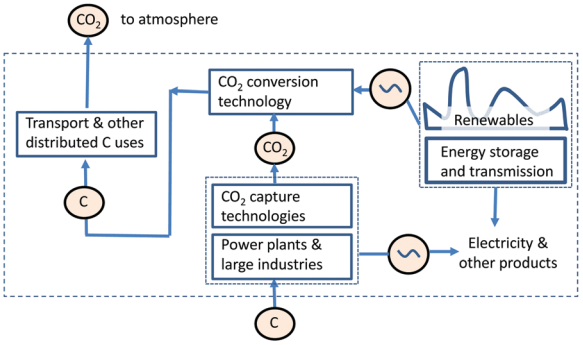

Fig. 5 Representation of the carbon mass balances in a full CCU system to convert CO_2 to C. The dotted boundary highlights the unavoidable carbon leakage for this option (unless CO_2 is captured from air).

the CO_2 and the additional electricity demanded by the CO_2 conversion technology.

Nonetheless, the carbon balance around the CCU solution of Fig. 5 reveals some fundamental limitations, regardless of the CO_2 conversion technology used to reduce CO_2 to C:

• When compared to the reference system of Fig. 4, the utilization of CO_2 can at best mitigate only 50% of the overall emissions from the use of fossil fuels (C_1 + C_2). This occurs when the carbon input to the industrial/power sector (C_2) equals the input to the transport/distributed sector (C_1). Utilization of the captured CO_2 then provides all the energy needs for transport, thus avoiding half of the reference system emissions.‡

• In order to achieve a closed carbon recycle loop with the CO_2 conversion technologies of Fig. 5 it would be necessary to avoid the use of fossil fuel as a source of carbon. Utilization of CO_2 captured from air, or from carbon produced from natural photosynthesis (idealized as pure carbon biomass), could be such options. However, such technologies, if available, would also compete directly with the CCU option (for example, by yielding negative emissions using air capture or bio-carbon with CCS, or by converting bio-carbon to transport fuels).

In any case, the CO_2 conversion step is a relatively minor element of the full CCU system in Fig. 5. Rather, the steady state supply of electricity from intermittent renewable energy sources, and/or the cost of CO_2 capture from air, will likely be the main challenges for the overall CCU system. If successfully developed, however, those technologies will compete directly with CCU as a climate change solution, as noted above.

The benefits of CCU for climate change mitigation thus are potentially significant only if the CO_2 storage option is not available, or if CCU can be deployed in the short term by exploiting its "substitution effect" as an alternative to fossil carbon sources. However, in order for this to scale it would require the near-term availability of large amounts of renewable power on a continuous basis, as well as plentiful sources of

‡ If the original C_1 exceeds C_2, fewer emissions are mitigated by CCU since the industrial sector CO_2 supply is insufficient to produce all transport sector energy. Thus, some direct use of fossil fuel is required, which increases CO_2 emissions. Similarly, if the original C_2 exceeds C_1, the CO_2 not utilized again results in less mitigation *via* CCU.

captured CO_2. Neither of these is immediately available in the "pre-mitigation" world of Fig. 4. On the other hand, for longer-term scenarios where substantial amounts of renewable-based energy are available, the substitution benefits of CO_2 conversion to fuels become increasingly irrelevant because widespread decarbonisation will already have occurred, and the limitation on maximum avoidable emissions noted above makes CCU less attractive for deep decarbonisation than other options.

Summary and conclusions

Capture and conversion of CO_2 to carbon-based fuels using electricity from renewable energy, CCU, is being advocated as a climate change mitigation strategy that can avoid significant emissions of CO_2 from vehicles and other distributed sources. However, a case study of methanol production showed that while CCU does have the potential to mitigate some CO_2 emissions (provided that a continuous supply of carbon-free electricity is available), an alternative system employing CCS together with the same carbon-free electricity is a far more effective mitigation option than CCU over a broad range of assumptions. A preliminary economic analysis further showed mitigation costs for CCU to be much higher than for a CCS-based system delivering the same fuel product. In all cases, the dominant contributor to CCU cost was the cost of the renewable-based electricity supply rather than that of the CO_2 conversion process.

More generally, we showed that the mitigation potential of CCU processes producing fuels for transportation and other distributed sources is limited to no more that 50% of the CO_2 emissions originating from fossil fuel energy supplies when the CO_2 is captured from an industrial source or power plant fuelled by fossil carbon. In all cases, the mitigation potential of CCU systems is dominated by assumptions regarding the carbon-free energy used by the utilization process. In general, alternative systems employing the same technological elements offer greater mitigation potential at substantially lower cost *via* more effective use of the carbon-free energy commonly assumed to be available for CCU processes.

Conflicts of interest

There are no conflicts to declare.

References

1 IPCC, Climate Change 2014: Synthesis Report. *Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. Core Writing Team, R. K. Pachauri and L. A. Meyer, IPCC, Geneva, Switzerland, 2014, p. 151.
2 C. McGlade and P. Ekins, *Nature*, 2015, **517**, 187–190.
3 Carbon Tracker, Unburnable Carbon 2013, Wasted capital and stranded assets, 2013.
4 S. Fuss, *Nat. Clim. Change*, 2016, **6**, 2.
5 P. Smith, S. J. Davis, F. Creutzig, S. Fuss, J. Minx, B. Gabrielle, E. Kato, R. B. Jackson, A. Cowie, E. Kriegler, D. P. Van Vuuren, J. Rogelj, P. Ciais, J. Milne, J. G. Canadell, D. McCollum, G. Peters, R. Andrew, V. Krey, G. Shrestha, P. Friedlingstein, T. Gasser, A. Grübler, W. K. Heidug, M. Jonas, C. D. Jones, F. Kraxner, E. Littleton, J. Lowe, J. R. Moreira, N. Nakicenovic, M. Obersteiner, A. Patwardhan, M. Rogner, E. Rubin, A. Sharifi, A. Torvanger, Y. Yamagata, J. Edmonds and C. Yongsung, *Nat. Clim. Change*, 2016, **6**, 42–50.
6 H. J. Herzog, K. Smekens, *et al.*, Cost and economic potential; IPCC Special Report on CO_2 Capture and Storage, IPCC, Geneva, Switzerland, 2005, ch. 8.
7 M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, M. J. Blunt, S. Brandani, N. Mac Dowell, J. R. Fernández, M. C. Ferrari, R. Gross, J. P. Hallett, R. S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R. T. J. Porter, M. Pourkashanian, G. T. Rochelle, N. Shah, J. G. Yao and P. S. Fennell, *Energy Environ. Sci.*, 2014, **7**, 130–189.
8 J. Gale, J. C. Abanades, S. Bachu and C. Jenkins, *Int. J. Greenhouse Gas Control*, 2015, **40**, 1–5.
9 M. Steinberg, *Fuel*, 1978, **57**, 8.
10 G. A. Olah, *Angew. Chem., Int. Ed.*, 2005, **44**, 2636–2639.
11 G. A. Olah, A. Goeppert and G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, 2nd edn, 2009.
12 G. A. Olah, A. Goeppert and G. K. S. Prakash, *J. Org. Chem.*, 2009, **74**, 487–498.
13 G. A. Olah, G. K. S. Prakash and A. Goeppert, *J. Am. Chem. Soc.*, 2011, **133**, 12881–12898.
14 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
15 M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709–1742.
16 J. M. Thomas and K. D. M. Harris, *Energy Environ. Sci.*, 2016, **9**, 687–708.
17 M. Mikkelsen, M. Jørgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43–81.
18 J. A. Martens, A. Bogaerts, N. De Kimpe, P. A. Jacobs, G. B. Marin, K. Rabaey, M. Saeys and S. Verhelst, *ChemSusChem*, 2017, **10**, 1039–1055.
19 M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert and T. Kolb, *Renewable Energy*, 2016, **85**, 1371–1390.
20 M. Aresta, A. Dibenedetto and E. Quaranta, *J. Catal.*, 2016, **343**, 2–45.
21 S. H. Jensen, C. Graves, M. Mogensen, C. Wendel, R. Braun, G. Hughes, Z. Gao and S. A. Barnett, *Energy Environ. Sci.*, 2015, **8**, 2471–2479.
22 H. J. Herzog, H. E. Drake, J. Tester and R. Rosenthal, *A Research Needs Assessment for the Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants*, Energy Laboratory, MIT, Cambridge, MA, 1993.
23 M. Mazzotti, J. C. Abanades, R. Allam, K. S. Lackner, F. Meunier, E. Rubin, J. C. Sanchez, Y. Katsunori and R. Zevenhoven, IPCC Special Report on Carbon Dioxide Capture and Storage, Cambridge University Press, 2005, ch. 7.
24 M. Aresta and M. Galatola, *J. Cleaner Prod.*, 1999, **7**, 181–193.

25 N. von Der Assen, P. Voll, M. Peters and A. Bardow, *Chem. Soc. Rev.*, 2014, **43**, 7982–7994.
26 N. von Der Assen, J. Jung and A. Bardow, *Energy Environ. Sci.*, 2013, **6**, 2721–2734.
27 N. V. von der Assen, A. M. L. Lafuente, M. Peters and A. Bardow, in *Carbon Dioxide Utilisation*, ed. E. A. Quadrelli and K. Armstrong, Elsevier, Amsterdam, 2015, pp. 45–56, DOI: https://doi.org/10.1016/B978-0-444-62746-9.00004-9.
28 C. van Der Giesen, R. Kleijn and G. J. Kramer, *Environ. Sci. Technol.*, 2014, **48**, 7111–7121.
29 S. J. Bennett, D. J. Schroeder and S. T. McCoy, *Energy Procedia*, 2014, **63**, 7976–7992.
30 I. Dimitriou, P. García-Gutiérrez, R. H. Elder, R. M. Cuéllar-Franca, A. Azapagic and R. W. K. Allen, *Energy Environ. Sci.*, 2015, **8**, 1775–1789.
31 M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti and E. Tzimas, *Appl. Energy*, 2016, **161**, 718–732.
32 W. Schakel, G. Oreggioni, B. Singh, A. Strømman and A. Ramírez, *J. CO_2 Util., 2016,* **16***, 138–149.*
33 N. von Der Assen and A. Bardow, *Green Chem.*, 2014, **16**, 3272–3280.
34 F. Pontzen, W. Liebner, V. Gronemann, M. Rothaemel and B. Ahlers, *Catal. Today*, 2011, **171**, 242–250.
35 K. Atsonios, K. D. Panopoulos and E. Kakaras, *Int. J. Hydrogen Energy*, 2016, **41**, 2202–2214.
36 M. Rivarolo, D. Bellotti, L. Magistri and A. F. Massardo, *Int. J. Hydrogen Energy*, 2016, **41**, 2105–2116.
37 N. Mac Dowell, P. S. Fennell, N. Shah and G. C. Maitland, *Nat. Clim. Change*, 2017, **7**, 243–249.
38 D. Mignard, M. Sahibzada, J. M. Duthie and H. W. Whittington, *Int. J. Hydrogen Energy*, 2003, **28**, 455–464.
39 É. S. van-Dal and C. Bouallou, *J. Cleaner Prod.*, 2013, **57**, 38–45.
40 T. Gibon, A. Arvesen and E. G. Hertwich, *Renewable Sustainable Energy Rev.*, 2017, **76**, 1283–1290.
41 E. S. Rubin, J. E. Davison and H. J. Herzog, *Int. J. Greenhouse Gas Control*, 2015, **40**, 378–400.
42 G. Gahleitner, *Int. J. Hydrogen Energy*, 2013, **38**, 2039–2061.
43 D. W. Keith, *Science*, 2009, **325**, 1654–1655.
44 K. Z. House, A. C. Baclig, M. Ranjan, E. A. van Nierop, J. Wilcox and H. J. Herzog, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 20428–20433.