

## CHAPTER 1

# *Turning CO<sub>2</sub> into Fuels and Chemicals: An Introduction*

G. CENTI<sup>\*a,b</sup> AND S. PERATHONER<sup>a,b</sup><sup>a</sup>Dept. ChiBiofarAm, V.le F. Stagno D'Alcontres 31, 98166 Messina, Italy;<sup>b</sup>ERIC aisbl (European Research Institute of Catalysis), Rond Point Robert Schuman, 14, B-1040 Brussels, Belgium

\*E-mail: centi@unime.it

## 1.1 Introduction

The increase in interest in CO<sub>2</sub> conversion to chemicals and fuels is impressive. Using as a simple index the entries in SciFinder on keywords “CO<sub>2</sub> utilization catal” (journals and review), 78 entries were reported for the 2000–2010 period, 120 in the 2011–2015 period, and 653 in the 2016–2021 period (up to August 2021). This is just a fraction of the much larger number of publications on the general area of CO<sub>2</sub> conversion to chemicals and fuels, but it represents a useful index to mark the exploding interest. Among the different motivations for the interest in this topic, besides the general aim of developing solutions to mitigate climate change and societal relevance, we may indicate:

- CO<sub>2</sub> is a relevant carbon source that cannot be considered a waste, but should be rather used as a sustainable feedstock for the chemical industry<sup>1</sup> with an additional decisive role to create a convenient path to introduce renewable energy in the industrial value chain (particularly for the refinery and chemical industries).<sup>2</sup>

---

Green Chemistry Series No. 74

Chemical Valorisation of Carbon Dioxide

Edited by Georgios Stefanidis and Andrzej Stankiewicz

© The Royal Society of Chemistry 2023

Published by the Royal Society of Chemistry, [www.rsc.org](http://www.rsc.org)

- The use of CO<sub>2</sub> as an alternative to CCS (carbon capture and storage) could be the preferable solution from both the economic and environmental perspectives<sup>3</sup> even in short term applications.<sup>4</sup>
- CO<sub>2</sub> conversion is a bundle of key technologies crucial in developing solutions to close the C-cycle, especially in energy intensive industries,<sup>5</sup> a topic of increasing relevance both to meet targets in GHG reduction (Europe aims to have zero-emissions in 2050) and to develop a more sustainable and resilient industry.<sup>6</sup>
- CO<sub>2</sub> conversion to chemicals and fuels (by electrocatalytic routes) is one of the components to develop artificial-leaf type devices,<sup>7</sup> which in the future will likely play a relevant role in transforming centralized energy and chemical production systems to a decentralized model (energy valleys or districts with integrated production of chemicals using local resources) with large societal impacts and benefits.

Many books and review articles have been published on CO<sub>2</sub> conversion to chemicals and fuels, and on the novel value chain they can induce. A limited selection of these books and reviews is given in the following citations<sup>8-28</sup> and the references thereof. We can generally classify the main research areas of CO<sub>2</sub> utilization as follows:

- Thermocatalytic conversion of CO<sub>2</sub>, including the large sector of the so-called *power-to-X* technologies; the latter defines multistep approaches where a first step is typical H<sub>2</sub> production by electrolysis (using renewable energy) which is followed by one or more thermocatalytic steps to make gaseous (methane) or liquid (methanol, DME, hydrocarbons) fuels acting as chemical energy storage (CES) agents.
- (Catalytic) routes to include CO<sub>2</sub> in organic products (polymers, for example) or inorganic products (mineralization – a route that, however, has seen decreasing interest in recent years, due to the energy costs).
- Photochemical conversion of CO<sub>2</sub>, that, even if potentially highly interesting, suffers from quite low productivity and thus is still very far from application.
- Electrochemical conversion of CO<sub>2</sub>, which may include a photoactive element, thus photoelectrochemical (PEC or PV/EC) conversion of CO<sub>2</sub>, also called artificial photosynthesis or artificial leaf. There are already quite advanced electrochemical processes to convert CO<sub>2</sub> to industrially valuable chemicals, particularly formic acid/formate, that are at an advanced prototype experimentation stage.<sup>29</sup>
- CO<sub>2</sub> conversion by (non-thermal) plasma routes, either in the presence of co-fed H<sub>2</sub> or in the presence of H-donor species (H<sub>2</sub>O or methane).
- Thermal conversion of CO<sub>2</sub> using concentrated solar power (CSP); experimentation in various pilot units has been reported, but many technical issues have decreased interest in this route in recent years.
- Enzymatic routes of CO<sub>2</sub> utilization which also include photo- and electro-assisted enzymatic routes (such as electro microbial cells) to

avoid the use of co-factors such as ATP and NADH; costs of downstream separation, and low productivity (per reactor volume) are the main issues to solve.

- Other minor CO<sub>2</sub> uses, for example as soft oxidants for dehydrogenation.

When solar energy is used in these processes, a popular term is “solar fuels” (or chemicals). Numerous reviews have discussed this topic, and just a few can be cited.<sup>30–40</sup>

## 1.2 Role of CO<sub>2</sub> to Chemicals and Fuels Paths in a Future Sustainable Scenario

As preamble, it is useful to remember that CO<sub>2</sub> is already a large volume commodity chemical, around 230 million tonnes per year of which ~56% accounts for urea (fertilizers) production, ~34% for EOR and the remaining for a series of other uses (beverages, food, fabrication of metals and others).<sup>41a</sup> However, the new paths for the use of CO<sub>2</sub> in the production of fuels and chemicals are generating global interest, although when they will start playing a significant role in contributing to overall GHG targets is a matter of intensive debate. While many still have the idea that even up to 2050 their contribution will remain small (IEA indicates around 1% in 2050<sup>41b</sup>), others consider a faster market penetration by these technologies.<sup>3</sup> The SUNERGY initiative ([www.sunergy-initiative.eu](http://www.sunergy-initiative.eu)) considers feasible in its roadmap the initial commercial introduction of solar fuels by 2030–2035. There are some main reasons behind this different impact assessment: (i) the method of accounting for the impact, (ii) the role that CCS and related technologies will play to meet targets on GHG emissions fixed at political levels and (iii) the cost of technologies and how scientific developments can make them competitive. While a full discussion of these aspects is going beyond the scope of this introductory chapter (some aspects will be also discussed in the other book chapters), some comments are necessary to evaluate better the impact of the technologies under development and the preferable routes.

### 1.2.1 How to Account for the Impact of CO<sub>2</sub> Utilization

The first question regards how to account for the impact. Many consider CO<sub>2</sub> utilization routes as a complementary solution to CCS and in fact, a common way is to indicate CO<sub>2</sub> utilization as CCU or CCUS (thus directly recalling CCS). Following this approach, the impact is accounted for in terms of the amount of CO<sub>2</sub> sequestered and for how long. This is not a correct approach, because it does not consider the overall effect on GHG reduction. The impact of CO<sub>2</sub> utilization routes should be rather in terms of GHG reduction related to the services that are provided in converting CO<sub>2</sub>.<sup>2,3</sup> If CO<sub>2</sub> is converted to fuels, through the use of renewable energy, the important elements are (i) the net amount of renewable energy that is

introduced in the value chain, (ii) the reduction in the impact due to substitution of fossil fuels (and derived products) for an equivalent service (thus estimating the significant impact on GHG related to extraction, transport, conversion of fossil fuels, fugitive emissions), (iii) the additional benefits (and related impact on GHG) derived from the use of solar rather than fossil fuels (lower emissions, use of local resources and reduced impact on transport, *etc.*). Looking from this perspective, which is also often accounted for only partially in LCA studies on CO<sub>2</sub> to chemicals and fuels,<sup>42–46</sup> the impact appears completely different. For example, CO<sub>2</sub> to fuels or chemical routes become much more relevant than technologies such as mineralization. The latter, after attracting significant interest some years ago, has lost scientific interest. Notwithstanding it may be considered a mature technology, mineralization never become a widely used industrial practice, only in some specific cases.<sup>47,48</sup> Estimations of the impact on GHG emissions of CO<sub>2</sub> mineralization processes do not properly account for the whole process. Ostovari *et al.*,<sup>49</sup> for example, reported an average negative footprint of about 1.15 t of CO<sub>2eq</sub> (indicates the equivalent amount of CO<sub>2</sub>) per ton CO<sub>2</sub> sequestered (they indicate that this value can be even higher in optimized ideal processes), assuming the use of the mineralization products as a cement substitute. They assumed that the mineralization products produced in the mineralization process can be used directly as a component for Portland cement. However, both the energy necessary for the whole mineralization process (from transporting the starting mineral to grinding, *etc.*) and the energy necessary (in processing) to compensate for the alteration in Portland characteristics due to the addition of the mineralization products have to be better considered. The result is that in the industrial practice the addition of CO<sub>2</sub> mineralization processes is not made, in contrast to the apparent large benefits claimed. In addition, a large availability of the starting minerals (olivine, serpentine) is assumed while the practice is different. The Carbon Capture Machine (CCM) company proposed this technology commercially for over a decade, and still the development is at a scale of 10 t day<sup>-1</sup>, thus about 0.1% of an industrial-size cement plant. The SkyMine® process, developed by Skyonic (now Eaton), is also among the first-of-its-kind proposed in the area, but is still at the stage of proposing, rather than implementing the technology. Thus, although forecasts predict nearly half of the world cement production being substituted by CO<sub>2</sub> mineralization, *i.e.* about 3.3 billion tonnes per year,<sup>50</sup> the current reality is that CO<sub>2</sub> mineralization is still not a significant part of the cement industry strategy towards GHG reduction. In the EU, for example, the cement industry is committed to reach zero emissions by the year 2050, but the plan does not consider CO<sub>2</sub> mineralization even as a minor complementary technology.<sup>51</sup> Thus, there is a large discrepancy between what is reported in the papers as the outlook for the technology and the industrial practice. This example evidences the difficulties in assessing the impact of CO<sub>2</sub> utilization paths, with often over- or under-estimations of the effective costs, applicability, and contribution to GHG reduction, leading to an intrinsic

difficulty in properly understanding gaps, limits, and effective possibilities of the different routes.

### 1.2.2 Putting CO<sub>2</sub> Conversion to Chemicals and Fuels in the Right Scenario

As it can be seen from the above discussion, it is not simple to clearly identify the emerging routes from the literature, and indications are still often based on estimations made decades ago that are currently no longer supported by the practice. Among these are the contribution of CCS and related technologies to meet targets on GHG emissions determined at the political level. IEA in its “Net Zero by 2050” report<sup>41b</sup> considers in detail the contribution of new technologies (under development) to meet this target, indicating that nearly half of the cut in the annual CO<sub>2</sub> emissions (about 7.6 Gt CO<sub>2</sub> emission reduction) should be provided by these emerging technologies by the year 2050. While the report uses the term CCUS, thus includes storage and utilization as a single technological option, it indicates that “around 3.5 Gt CO<sub>2</sub> emissions are captured from fossil fuels in 2050”. Thus, CO<sub>2</sub> storage rather than utilization is considered by IEA as the largely dominant solution to decarbonize the energy–chemistry system even in 2050. This conclusion, however, is in partial conflict with the other indications given by the IEA itself regarding (i) the technologies for “hard to abate” sectors (energy intensive industries), (ii) the degree of substitution of fossil fuels with renewables, and (iii) how to minimize the costs for the transitions. All these aspects require a significant role of solar fuels. In contrast, IEA<sup>41b</sup> indicates as key pillars to reach NZE (net zero emissions) by the year 2050: (i) energy efficiency, (ii) behavioural change, (iii) electrification, (iv) renewables, (v) hydrogen and hydrogen-based fuels, (vi) bioenergy, and (vii) CCUS. The latter will globally contribute to around 18.5% of the global reduction to reach the NZE target, but “around 95% of total CO<sub>2</sub> captured in 2050 is immitted in permanent geological storage sites and 5% is used to provide synthetic fuels.” Thus, the IEA report<sup>41b</sup> considers that CO<sub>2</sub> conversion to fuels (and chemicals) will contribute <1% of the total cut of GHG necessary to reach the NZE target by year 2050, essentially a negligible contribution compared to the dominant storage role in CCUS technologies. IRENA (another major international agency on energy) estimations for the year 2050<sup>52</sup> indicates instead that up to about half of the contribution in GHG reduction should derive from the “indirect use of clean electricity *via* synthetic fuels & feedstocks”, *e.g.*, from solar fuels (they use the alternative term of e-fuels).

We believe that likely the true indications will be in the middle with respect to negative and optimistic IEA and IRENA estimations, respectively. Our elements of the analysis are the following. First, CCS is expensive. Although there is a quite large spread of data, and it is almost impossible to have reliable indications, the few large scale storage plants, essentially related to EOR, demonstrate that effective costs are significantly larger than estimations,

and above €100 per tonne stored CO<sub>2</sub>, which becomes even larger when the energy costs for CO<sub>2</sub> capture and storage are considered, accounting for up to 30–40% of the GHG reduction (*i.e.* for each ton of CO<sub>2</sub> captured, the effective CO<sub>2eq</sub> impact is about 0.6–0.7). By evaluating the impact in the correct way, the CO<sub>2eq</sub> cost reduction for CO<sub>2</sub> to chemicals and fuels could reach half of that for CCS. Even if some of the technologies are still not mature, there is no reason why they should have a minimal impact with respect to CCS. However, there is a need to develop improved, second-generation technologies of CO<sub>2</sub> utilization with respect to those actually in development, such as *power-to-X* technologies.

In addition, CO<sub>2</sub> to chemicals and fuels technologies will also play an essential role in the chemical energy storage (CES) of renewable sources<sup>53</sup> and the integration of the latter in energy intensive industries (EIIs, steel, cement, refineries, chemical production and fertilizers).<sup>5,54</sup> The targets in using renewable energy indicated in the NZE report of the IEA<sup>41b,52</sup> cannot be met without a significant contribution of CO<sub>2</sub> to chemicals and fuels routes in CES and in closing the carbon cycle in EIIs. It is thus likely that IEA estimations lack the capability for proper accounting of the emerging technologies and the very interconnected energy (and chemistry) future panorama. On the other hand, the fraction of the current energy uses requiring solar fuels, rather than other solutions (direct electrification, for example), may range between 20 and 30%. Thus, the IRENA estimation<sup>52</sup> appears too optimistic. The European Commission report “Towards net-zero emissions in the EU energy system by 2050”<sup>55</sup> analysing 18 scenarios to NZE for Europe, remarked on the exceptionally large differences in the estimations of CO<sub>2</sub> emission trajectories (ranging from about a negligible reduction with respect to the current situation, up to 100% reduction) and in the estimation of the different contributions including the role of e-fuels (term used to indicate *power-to-X* technologies), of CES and solar fuels, and of CCS. In general, a nearly complete phase-out of the use of fossil fuels by 2050 and a parallel increase in the use of renewable energy sources is assumed in scenarios reaching at least 90% emission reduction by 2050 (as necessary for the NZE target). However, an analysis of their integration reveals that due to their geographical and temporal mismatch with respect to uses, and due to the too large investments necessary to fully change the industrial and energy infrastructures to use over 60–70% of the energy mix constituted by renewables, the targets cannot be reasonably reached without a significant role for CES and solar fuels, *e.g.*, by CO<sub>2</sub> to chemicals and fuels routes. Thus, looking from this perspective, the future of a sustainable society cannot disregard the significant role of CO<sub>2</sub> to chemicals and fuels technologies. The role of science and technology is to enable their effective realization at affordable costs. On the other hand, this discussion, even if limited to only a part of the broader range of aspects to consider, evidences the difficulty in making precise estimations about the future, the gaps to overcome, and the priorities for R&D. The rule of thumb is to have an open mind approach, not limited to considering few aspects.

### 1.2.3 The Cost of CO<sub>2</sub> Conversion Technologies

Cost plays a crucial role, although it is not the only parameter in assessing the applicability of CO<sub>2</sub> to chemicals and fuels technologies. However, even here, which could appear a more precise way to evaluate technologies, there are extremely large uncertainties. An example of this issue was given in analysing cost estimations for the CO<sub>2</sub> to methanol process.<sup>56</sup> From an industrial perspective, assessing the techno-economic feasibility is a fundamental step to deciding whether to invest in the development of a technology, even at low TRL (technology readiness levels). While this is typically done by the in-house engineering expertise within the companies, an abundant literature also exists on these aspects with the aim to demonstrate the feasibility (or not) of certain routes. Various papers have assessed the techno-economic feasibility of CO<sub>2</sub> utilization routes, with a selection of them being reported in the following citations.<sup>4,57–76</sup> However, the conclusions are quite contradictory. Hence, a question remains concerning the reliability and robustness of these studies, and whether significant barriers exist for the implementation and deployment of CO<sub>2</sub> to chemicals and fuels routes.

In general, anyone active in the field in the last decade is well aware that the scenario for CO<sub>2</sub> utilization, in terms of both cost and technical feasibility, has dramatically changed. What appeared some years ago as an academic exercise<sup>11,12</sup> is now often seriously considered as an industrial option. Various industrial pilot plants or demo-size units have been constructed to evaluate better the techno-economic feasibility. An example is given by CO<sub>2</sub> methanation<sup>77–79</sup> or CO<sub>2</sub> conversion to methanol.<sup>80</sup> Among the companies, (a) Haldor Topsoe announced a 50 t per year methanol plant based on their eSMR Methanol™ technology to produce sustainable methanol from biogas in an electrified reactor, (b) Carbon Recycling International (CRI), together with other partners of the MefCO<sub>2</sub> project, are building in Germany a ~300 t per year CO<sub>2</sub>-to-methanol demo unit, (c) Thyssenkrupp, as part of the Carbon2Chem project, is building 50 t per year of methanol from CO<sub>2</sub> for their steel mill in Duisburg (Germany), (d) the Audi e-Gas pilot plant produces 1000 t per year of methane from CO<sub>2</sub>, (e) Climeworks AG (one of the first companies pushing the CO<sub>2</sub> direct air technology) and other companies have built a pilot for producing 1400 m<sup>3</sup> day<sup>-1</sup> of synthetic methane from CO<sub>2</sub> captured from the air, as part of the STORE & GO project.

There are many other activities running at demo scale (TRL > 5–6) in the area of CO<sub>2</sub> conversion to fuels and chemicals, including by electrocatalytic routes.<sup>29</sup> In contrast to that, the general conclusions that can be derived from techno-economic assessments (reported in the literature) are that the barriers for the implementation and deployment of CO<sub>2</sub> to chemicals and fuels routes are still too large. This agrees with indications of international agencies such as IEA,<sup>41b</sup> forecasting an essentially negligible role of these technologies even in 2050, as commented on before. So why do various companies invest in costly pilot units when forecasts are so negative? In analogy to the assessment of economics for the CO<sub>2</sub> conversion routes, the evaluation of

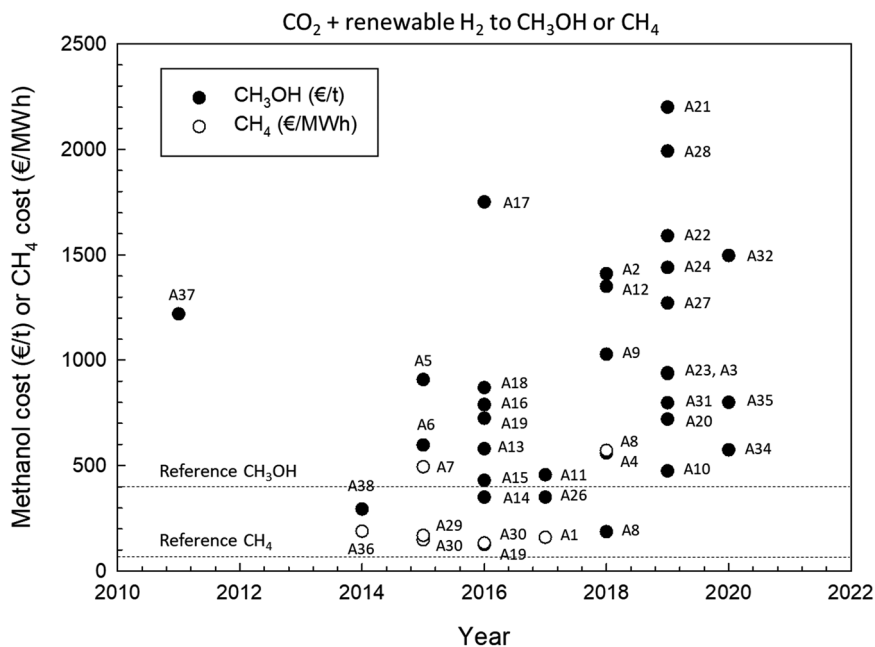
the environmental impact with LCA-type methodologies also resulted in a spread of indications.<sup>46,81–83</sup> It may be thus surprising why different conclusions can be obtained for the same problem.

The general comment is that techno-economic and environmental assessments require complex methodologies with the final result highly depending on several parameters, assumptions and boundary limits used for the evaluation. Some of them may be critical and thus even if the methodology appears rigorous and often follows a standardized approach, as in LCA, different conclusions can be derived. However, without specific experience and sensitivity on these aspects (and the use of the results in the proper context and limits), it is quite difficult for a reader to derive the correct indications. A further general issue is that often the methodologies used, particularly those based on LCA, are not able to include the innovation gap correctly, *i.e.* the effective possibility of improvement based on a further technological development. This innovation gap is crucial in periods where a full change of the system is present, as currently occurring with energy transition. The innovation gap appears when a proper pipeline between current and next generation technologies is missing. In addition, the strong nexus existing between energy and chemical production will change as a consequence of the transition.<sup>84</sup> This system change is completely transforming the set of production, transformation, transport and distribution processes of raw materials and products. It is not possible to analyse the techno-economic feasibility of CO<sub>2</sub> conversion routes making reference to the current system and using assessment parameters that do not account for the system change, including this evolving nexus.<sup>85</sup> A broader-view approach which explores new solutions, synergies and possibilities is necessarily guided by an industrial vision on targets, issues, integration, and solutions, including new possibilities not currently existing, such as new models of integrated solar- and bio-refineries.<sup>86–88</sup>

To support these indications, it is good to analyse the specific case of economic assessment of CO<sub>2</sub> conversion to methane or methanol routes (power-to-X).<sup>56</sup> Figure 1.1 summarizes the results of this analysis (for specific indications on related references see the original paper<sup>56</sup>). The results are reported as cost of production of methanol (€ h<sup>-1</sup>) or of methane (€ MW h<sup>-1</sup>) from CO<sub>2</sub> by using renewable energy sources as a function of the year of publication of the related paper. Even considering that the input data are not homogeneous in terms of database for costs of raw materials, technologies, approach, and boundary limits, it is evident from this analysis of the literature on the economic assessment of CO<sub>2</sub> to methane or methanol routes that the variability of the results falls far beyond the variation range ( $\pm 30\%$ ) considered acceptable for preliminary techno-economic evaluations. There is an intrinsic basic issue in these estimations.

Figure 1.1 refers only to those power-to-X technologies that are currently at a more advanced stage of development (TRL > 5–6) and at demo/pilot scale. For other, less mature technologies, like electrocatalytic and even less so photocatalytic, the level of uncertainties is even higher and also





**Figure 1.1** An overview of the results in terms of costs of methanol production ( $\text{€ t}^{-1}$ ) and of methane production ( $\text{€ MW h}^{-1}$ ) in CO<sub>2</sub> conversion using H<sub>2</sub> produced from renewable energy sources. For indications on the references (A1–A38) see the original paper.<sup>56</sup> Reproduced from ref. 56, <https://doi.org/10.3389/fenrg.2020.567986>, under the terms of the CC BY 4.0 license <https://creativecommons.org/licenses/by/4.0/>.

techno-economic assessments are limited. While more specific comments and analysis of literature results are reported in the paper by Centi *et al.*<sup>56</sup> on CO<sub>2</sub> economics, here the relevant point is that great care must be taken when using these literature assessments in order to judge whether further investigation of the CO<sub>2</sub> to chemicals or fuels routes make sense.

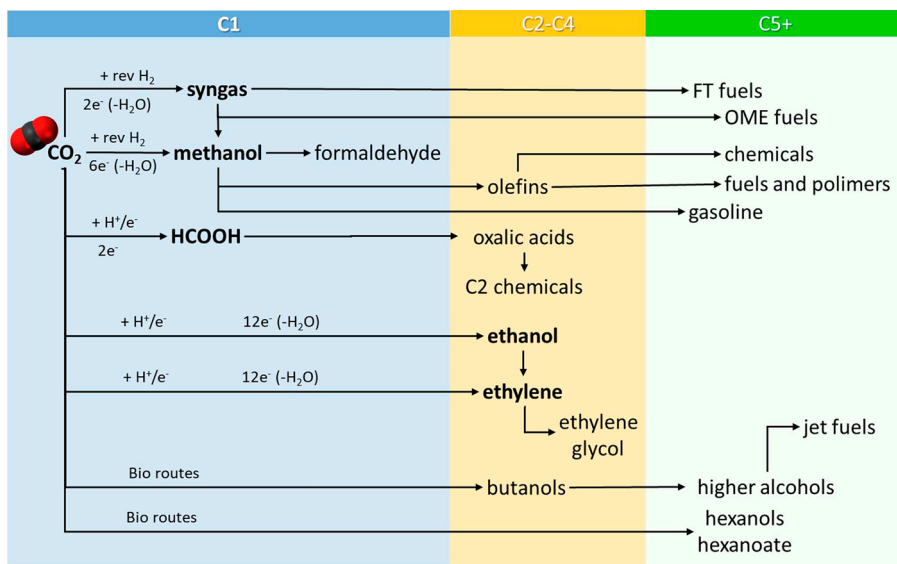
Our personal opinion is that a technological gap is still present. The speed in overcoming this gap will determine the role played by CO<sub>2</sub> to chemicals and fuels technologies in the evolving scenario for energy transitions and depends on the investments in R&D. These will be determined from the push from public and industrial stakeholders to overcome the current technological gaps. However, we consider that the conditions exist to accelerate this push and we are thus confident that CO<sub>2</sub> to chemicals and fuels technologies (in synergy with other solutions, but as an alternative to CO<sub>2</sub> storage) will have an increasing role even in the near future (next decade). Thus, these technologies will play an increasing role even starting from 2030 and not only in the year 2050 and beyond. However, a requirement is to start investigating them today. In a transition period, technologies related to *power-to-X*, and some biotech routes of CO<sub>2</sub> utilization, will be important. However, reaching the targets for NZE requires to surpass these technologies (that we

can indicate as first generation) with more efficient and less costly solutions, using directly solar energy, rather than (renewable) electrical energy. Substitute fossil fuels with renewable energy sources, beyond a degree of penetration in the energy mix higher than about 50–60%, also require the effective deployment of economic and reliable technologies for CES and production of solar- and e-fuels. CO<sub>2</sub> conversion to chemicals and fuels will be also crucial in closing the C cycle (and foster circularity) in EIIs. To fully proof these indications using the current techno-economic and LCA methods is not possible, due to the intrinsic weaknesses of these methodologies in the light of a full system change. However, at the same time it is not possible to wait for more reliable and robust assessment methodologies. Thus, at this stage, it is necessary to create more solid scientific and technological bases, and at the same time improve the assessment methodologies. This has to be realized both on the (i) shorter-term (mature) power-to-X, (ii) the medium-term (electrocatalysis and photoelectrocatalysis, playing both a crucial role in moving to a distributed production of chemicals and energy), and (iii) the long-term (photocatalysis and some of the biotech approaches, such as electro microbial cells). For thermal conversion of CO<sub>2</sub> using CSP we believe that there are intrinsic barriers limiting applicability, but nevertheless they should be further investigated to prove or disprove their applicability, and in which specific cases (and within which boundary limits) they could eventually be preferable over alternative options. Still indications do not allow to clarify this aspect.

### 1.3 Paths in CO<sub>2</sub> to Chemicals and Fuels Conversion

Many reviews have analysed and compared the different paths in CO<sub>2</sub> to chemicals and fuels conversion, a selection of them being cited before. For a recent analysis from an industrial perspective, two reviews prepared by Johnson Matthey scientists may be cited (Alcasabas *et al.*<sup>89,90</sup>). In part I, they discuss biological, catalytic and electrocatalytic routes, while in part II photochemical, photoelectrochemical, plasma and microbial electrosynthetic routes are analysed. Among the recommendations and conclusions of these reviews are:

- Research needs to be focussed on developing routes to synthesize molecules not competing with existing high TRL processes; for example, to produce syngas from CO<sub>2</sub> (and H<sub>2</sub>O) and further produce fuels by the FT (Fischer–Tropsch) process or *via* methanol. These technologies are not suggested as being worthy of investigation, while it is better to produce CO or formic acid (where electrochemical routes offer promise) or especially molecules in the C<sub>2</sub>–C<sub>4</sub> range (where electrochemistry appears well suited at present) or in the C<sub>2</sub>–C<sub>8</sub> range (by biological processes). Figure 1.2 reports the possible value chains in multistep conversion of CO<sub>2</sub> to fuels and chemicals.<sup>89,90</sup>



**Figure 1.2** Creation of a value chain to chemicals and fuels in multiple steps from CO<sub>2</sub>. Key intermediates in bold. Original figure created from data reported in ref. 89,90.

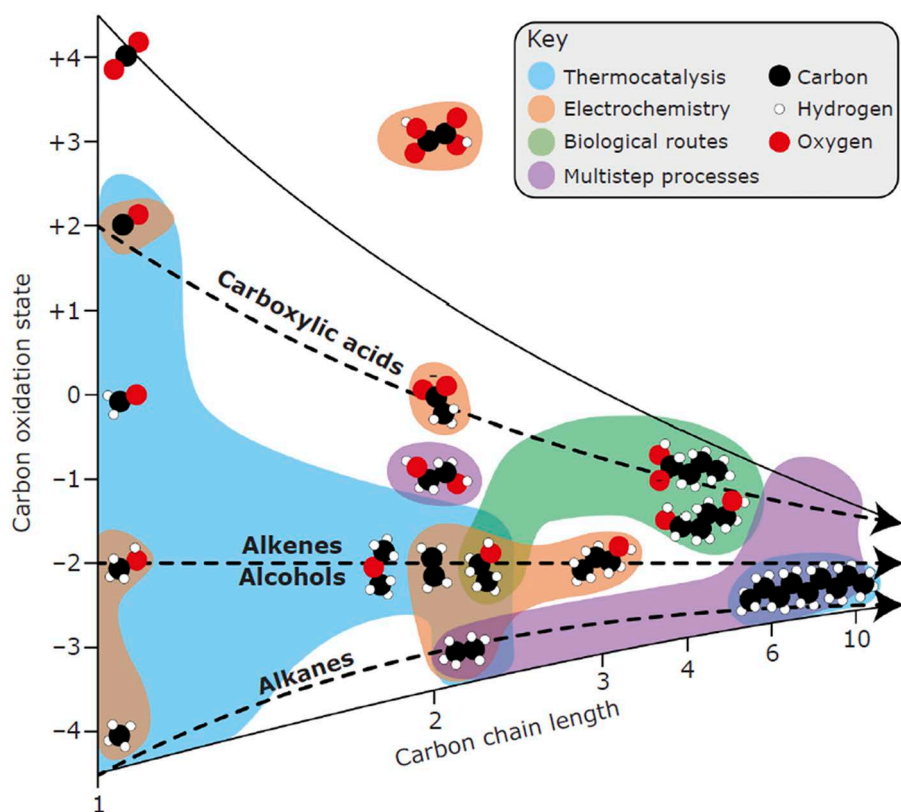
- Some target molecules such as CO, formate and ethylene have shown good FEs (Faradaic efficiencies), close to industrially relevant current densities. Cell geometries (suitable for industrial scale-up) are fundamental (together with electrodes) to achieve these conditions at relevant current densities for industrial exploitability (>0.5 A cm<sup>-2</sup>). However, among the issues to be solved are: scale-up, stability and identification of degradation routes, production costs, reduction of additional downstream steps and separation units. We may further add that the use of a different reaction at the anode to produce more valuable products than O<sub>2</sub> (from water oxidation) is another relevant target.
- Integration in complete processes and full value chains (some examples of this multistep processes are given in Figure 1.2) is crucial. Identifying the optimal integration of electrocatalytic, thermocatalytic or biochemical steps is the challenge to be addressed.
- Plasma technologies are one of the options to consider, being possibly the direct coupling with renewable energy, but still requiring specific energy inputs (SEI > 60%) at industrially relevant conditions, *i.e.* under ambient or higher pressures, not at pressures below the atmospheric one. In addition, they should operate with realistic CO<sub>2</sub> streams. Scalability of the different plasma reactors under investigation is also a main fundamental aspect to be solved.

A comparison of the different technology options in CO<sub>2</sub> conversion to chemicals and fuels was made by Alcasabas *et al.*<sup>89,90</sup> (Figure 1.3). It represents a good way to overview the different options discussed later in this book.

## 1.4 Conclusions

This introductory chapter of the book on chemical valorisation of carbon dioxide aims to provide some elements to consider going beyond the specific technical aspects discussed in the various chapters to analyse the role of the various discussed technologies in the context of the future scenario.

For this reason, the main point analysed is whether this research area is relevant to shape future sustainable chemical production and related energy aspects to meet agreed targets (net-zero emissions in Europe), or will it play a minor practical role, notwithstanding the fact that this is one of the areas to which the largest scientific attention in the literature is addressed. While some reports from international agencies are rather pessimistic about the relevance of CO<sub>2</sub> conversion to chemicals and fuels path, even for the year 2050, we stress here that a series of misleading aspects determine this impact.



**Figure 1.3** Carbon oxidation state *versus* carbon chain length with identification of the main domains of the main technologies for converting CO<sub>2</sub> to chemicals and fuels. The carbon oxidation state relates to the number of electrons needed to convert. Reproduced with permission from ref. 90 with permission from Johnson Matthey Plc.

Although a thorough analysis goes beyond the scope of this chapter, we discussed here some of the relevant elements: (i) how to account for the impact on CO<sub>2</sub> utilization, (ii) the need to put these routes in the right scenario, and (iii) the validity and limits of current techno-economic and life-cycle assessment results. Together with a short analysis of the paths in CO<sub>2</sub> conversion to chemicals and fuels, this discussion aims to give intellectual nourishment to put the specific technical elements discussed in the following chapters in a more general context, which can provide indications about the relevance (and limits) of the various studies.

We consider CO<sub>2</sub> conversion to chemicals and fuels an ensemble of technologies that will play a crucial role in shaping the future, in particular (i) in providing chemical energy storage solutions to store and transport renewable energy, (ii) in realizing a distributed production of chemicals and fuels, and (iii) in closing the carbon cycle in energy intensive industries. We propose that technologies for CO<sub>2</sub> conversion to chemicals and fuels will be a part of the backbone solutions to meet net-zero emission targets in 2050, and as such will start playing a significant role from 2030, notwithstanding the different ideas present in the literature and in the public debate. However, this target can be reached only when current fundamental and applied studies are intensified and carried out in closer cooperation. Books such as the present will certainly play a relevant role in reaching this objective.

## List of Abbreviations

ATP	Adenosine triphosphate
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CCUS	Carbon capture, utilization and storage
CES	Chemical energy storage
CO <sub>2eq</sub>	CO <sub>2</sub> equivalent (the equivalent amount of CO <sub>2</sub> which is reduced)
CSP	Concentred solar power
DME	Dimethyl ether
EIIs	Energy intensive industries
EOR	Enhanced oil recovery
FT	Fischer-Tropsch
GHG	Greenhouse gas
IEA	International Energy Agency
IRENA	International Renewable Energy Agency
LCA	Life cycle assessment
NADH	Nicotinamide adenine dinucleotide
NZE	Net zero emissions
PEC	Photoelectrochemical or photoelectrocatalytic
PV/EC	Devices combining a photovoltaic (PV) and an electrocatalytic (EC) cell

R&D	Research and development
SEI	Specific energy input
TRL	Technology readiness levels

## Acknowledgements

This work was carried out in the framework of the ERC Synergy SCOPE (project 810182) and PRIN 2017 project MULTI-e nr. 20179337R7 and CO<sub>2</sub> ONLY project no. 2017WR2LRS, which are gratefully acknowledged.

## References

1. M. De Falco, G. Iaquaniello and G. Centi, *CO<sub>2</sub>: A Valuable Source of Carbon*, Springer, London, 2013.
2. G. Centi and S. Perathoner, *Green Carbon Dioxide: Advances in CO<sub>2</sub> Utilization*, Wiley, Hoboken (NJ, US), 2014.
3. R. Schlögl, C. Abanades, M. Aresta, A. Azapagic, E. A. Blekkan, T. Cantat, G. Centi, N. Duic, A. El Khamlichi, G. Hutchings, M. Mazzotti, U. Olsbye and H. Mikulcic, *Novel Carbon Capture and Utilisation Technologies: Research and Climate Aspects*, SAPEA (Science Advice for Policy by European Academies), Evidence report no. 2, SAPEA, Berlin, 2018.
4. L. Barbato, G. Centi, G. Iaquaniello, A. Mangiapane and S. Perathoner, *Energy Technol.*, 2014, **2**, 453.
5. S. Perathoner, K. M. Van Geem, G. B. Marin and G. Centi, *Chem. Commun.*, 2021, **57**, 10967.
6. F. Cavani, G. Centi, S. Perathoner and F. Trifiró, *Sustainable Industrial Chemistry*, Wiley VCH, Weinheim – Germany, 2009.
7. S. Bensaid, G. Centi, E. Garrone, S. Perathoner and G. Saracco, *ChemSusChem*, 2012, **5**, 500.
8. P. Styring, E. A. Quadrelli and K. Armstrong, *Carbon Dioxide Utilisation*, Elsevier, Amsterdam – The Netherlands, 2014.
9. M. A. Scibioh and B. Viswanathan, *Carbon Dioxide to Chemicals and Fuels*, Elsevier, Amsterdam – The Netherlands, 2018.
10. F. Winter, R. A. Agarwal, J. Hrdlicka and S. Varjani, *CO<sub>2</sub> Separation, Purification and Conversion to Chemicals and Fuels*, Springer, Singapore, 2019.
11. G. Centi and S. Perathoner, *Catal. Today*, 2009, **148**, 191.
12. E. A. Quadrelli, G. Centi, J. L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194.
13. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal and J. Pérez-Ramírez, *Energy Environ. Sci.*, 2013, **6**, 3112.
14. G. Centi, E. A. Quadrelli and S. Perathoner, *Energy Environ. Sci.*, 2013, **6**, 1711.
15. J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem. Soc. Rev.*, 2014, **43**, 631.

16. R. S. Norhasyima and T. M. I. Mahlia, *J. CO<sub>2</sub> Util.*, 2018, **26**, 323.
17. H. Mikulčić, I. Ridjan Skov, D. F. Dominković, S. R. Wan Alwi, Z. A. Manan, R. Tan, N. Duić, S. N. Hidayah Mohamad and X. Wang, *Renewable Sustainable Energy Rev.*, 2019, **114**, 109338.
18. C. Ampelli, S. Perathoner and G. Centi, *Philos. Trans. R. Soc., A*, 2015, **373**, 20140177.
19. M. D. Porosoff, B. Yan and J. G. Chen, *Energy Environ. Sci.*, 2016, **9**, 62.
20. S. C. Peter, *ACS Energy Lett.*, 2018, **3**, 1557.
21. J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, *Chem. Rev.*, 2018, **118**, 434.
22. S. M. Jarvis and S. Samsatli, *Renewable Sustainable Energy Rev.*, 2018, **85**, 46.
23. S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo and I. Chorkendorff, *Chem. Rev.*, 2019, **119**, 7610.
24. S. Samanta and R. Srivastava, *Mater. Adv.*, 2020, **1**, 1506.
25. A. Mustafa, B. G. Lougoua, Y. Shuai, Z. Wang and H. Tan, *J. Energy Chem.*, 2020, **49**, 96.
26. W. Gao, S. Liang, R. Wang, Q. Jiang, Y. Zhang, Q. Zheng, B. Xie, C. Y. Toe, X. Zhu, J. Wang, L. Huang, Y. Gao, Z. Wang, C. Jo, Q. Wang, L. Wang, Y. Liu, B. Louis, J. Scott, A.-C. Roger, R. Amal, H. Heh and S.-E. Park, *Chem. Soc. Rev.*, 2020, **49**, 8584.
27. Y. Wang, L. R. Winter, J. G. Chen and B. Yan, *Green Chem.*, 2021, **23**, 249.
28. R. Cauwenbergh and S. Das, *Green Chem.*, 2021, **23**, 2553.
29. S. Perathoner and G. Centi, *Catal. Today*, 2019, **330**, 157.
30. S. Nandy, S. A. Savant and S. Haussener, *Chem. Sci.*, 2021, **12**, 9866.
31. X. Zhao, J. Li, X. Li, P. Huo and W. Shi, *Chin. J. Catal.*, 2021, **42**, 872.
32. X. Guo, L. Liu, Y. Xiao, Y. Qi, C. Duan and F. Zhang, *Coord. Chem. Rev.*, 2021, **435**, 213785.
33. H. J. Sayre, L. Tian, M. Son, S. M. Hart, X. Liu, D. M. Arias-Rotondo, B. P. Rand, G. S. Schlau-Cohen and G. D. Scholes, *Energy Environ. Sci.*, 2021, **14**, 1402.
34. J. R. Galan-Mascaros, *Catal. Sci. Technol.*, 2020, **10**, 1967.
35. M. A. Lumley, A. Radmilovic, Y. J. Jang, A. E. Lindberg and K.-S. Choi, *J. Am. Chem. Soc.*, 2019, **141**, 18358.
36. K. E. Dalle, J. Warnan, J. J. Leung, B. Reuillard, I. S. Karmel and E. Reisner, *Chem. Rev.*, 2019, **119**, 2752.
37. X. Li, J. Yu, M. Jaroniec and X. Chen, *Chem. Rev.*, 2019, **119**, 3962.
38. B. C. Marepally, C. Ampelli, C. Genovese, E. A. Quadrelli, S. Perathoner and G. Centi, *Stud. Surf. Sci. Catal.*, 2019, **178**, 7.
39. H. Yamashita, K. Mori, Y. Kuwahara, T. Kamegawa, M. Wen, P. Verma and M. Che, *Chem. Soc. Rev.*, 2018, **47**, 8072.
40. P. Lanzafame, S. Abate, C. Ampelli, C. Genovese, R. Passalacqua, G. Centi and S. Perathoner, *ChemSusChem*, 2017, **10**, 4409.

41. (a) International Energy Agency (IEA), *Putting CO<sub>2</sub> to Use: Creating Value from Emissions*, IEA, Paris, France, 2019, available on 28 August 2021 at DOI: 10.1787/dfeabbf4-en; (b) International Energy Agency (IEA), *Net Zero by 2050 - A Roadmap for the Global Energy Sector*, IEA, Paris, France, 2021, available on 8 October 2021 at <https://www.iea.org/reports/net-zero-by-2050>.
42. Y. Khojasteh-Salkuyeh, O. Ashrafi, E. Mostafavi and P. Navarri, *J. CO<sub>2</sub> Util.*, 2021, **50**, 101608.
43. M. Tomatis, A. Mahmud Parvez, M. T. Afzal, S. Mareta, T. Wu, J. He and T. He, *Fuel*, 2019, **254**, 115627.
44. X. Zhang, C. Bauer, C. L. Mutel and K. Volkart, *Appl. Energy*, 2017, **190**, 326.
45. N. von der Assen, P. Voll, M. Peters and A. Bardow, *Chem. Soc. Rev.*, 2014, **43**, 7982.
46. N. von der Assen, J. Jung and A. Bardow, *Energy Environ. Sci.*, 2013, **6**, 2721.
47. J. Meng, W. Liao and G. Zhang, *Minerals*, 2021, **11**, 274.
48. C. D. Hills, N. Tripathi and P. J. Carey, *Front. Energy Res.*, 2020, **8**, 142.
49. H. Ostovari, A. Sternberg and A. Bardow, *Sustainable Energy Fuels*, 2020, **4**, 4482.
50. H. Ostovari, L. Müller, J. Skocek and A. Bardow, *Environ. Sci. Technol.*, 2021, **55**(8), 5212.
51. CEMBUREAU (The European Cement Association), *Cementing the European Green Deal*, Cembureau, Brussels, 2020, available on 24 August 2021 at [https://cembureau.eu/media/kuxd32gi/cembureau-2050-roadmap\\_final-version\\_web.pdf](https://cembureau.eu/media/kuxd32gi/cembureau-2050-roadmap_final-version_web.pdf).
52. IRENA (International Renewable Energy Agency), *Reaching Zero with Renewables*, available on 8 October 2021 at [https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2020/Sep/IRENA\\_Reaching\\_zero\\_2020.pdf](https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2020/Sep/IRENA_Reaching_zero_2020.pdf).
53. R. Schlögl, *Chemical Energy Storage*, De Gruyter, Berlin – Germany, 2nd edn, 2022.
54. S. de Bruyn, C. Jongsma, B. Kampman, B. Görlach and J.-E. Thie, *Energy-intensive Industries. Challenges and Opportunities in Energy Transition*, European Parliament, 29 – Luxembourg, 2020, available on 24 August 2021 at [https://www.europarl.europa.eu/RegData/etudes/STUD/2020/652717/IPOL\\_STU\(2020\)652717\\_EN.pdf](https://www.europarl.europa.eu/RegData/etudes/STUD/2020/652717/IPOL_STU(2020)652717_EN.pdf).
55. I. Tsiropoulos, W. Nijs, D. Tarvydas and P. Ruiz, *Towards Net-Zero Emissions in the EU Energy System by 2050*, European Commission, Bruxelles – Belgium, 2020.
56. G. Centi, S. Perathoner, A. Salladini and G. Iaquaniello, *Front. Energy Res.*, 2020, **8**, 567986.
57. J. D. Laumb, J. P. Kay, M. J. Holmes, R. M. Cowan, A. Azenkeng, L. V. Heebink, S. K. Hanson, M. D. Jensen, P. A. Letvin and L. J. Raymond, *Energy Procedia*, 2013, **37**, 6987.



58. I. Dimitriou, P. Garcia-Gutierrez, R. H. Elder, R. M. Cuellar-Franca, A. Azapagic and R. W. K. Allen, *Energy Environ. Sci.*, 2015, **8**, 1775.
59. M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti and E. Tzimas, *Appl. Energy*, 2016, **161**, 718.
60. H. Naims, *Environ. Sci. Pollut. Res.*, 2016, **23**, 22226.
61. M. De Falco, M. Capocelli and G. Centi, *Chem. Eng. J.*, 2016, **294**, 400.
62. T. P. Senftle and E. A. Carter, *Acc. Chem. Res.*, 2017, **50**, 472.
63. A. Navarrete, G. Centi, A. Bogaerts, Á. Martín, A. York and G. Stefanidis, *Energy Technol.*, 2017, **5**, 796.
64. G. Iaquaniello, S. Setini, A. Salladini and M. De Falco, *Int. J. Hydrogen Energy*, 2018, **43**, 17069.
65. E. I. Koytsoumpa, C. Bergins and E. Kakaras, *J. Supercrit. Fluids*, 2018, **132**, 3.
66. A. González-Garay, M. S. Frei and A. Al-Qahtani, *Energy Environ. Sci.*, 2019, **12**, 3425.
67. C. Hepburn, E. Adlen, J. Beddington, E. A. Carter, S. Fuss, N. Mac Dowell, J. C. Minx, P. Smith and C. K. Williams, *Nature*, 2019, **575**, 87.
68. C. M. Jens, L. Müller, K. Leonhard and A. Bardow, *ACS Sustainable Chem. Eng.*, 2019, **7**, 12270.
69. C. Zhang, R. Gao, K.-W. Jun, S. K. Kim, S.-M. Hwang, H.-G. Park and G. Guan, *J. CO<sub>2</sub> Util.*, 2019, **34**, 293.
70. H. Zhang, L. Wang, J. van Herle, F. Maréchal and U. Desideri, *Energies*, 2019, **12**, 3742.
71. R. G. Grim, Z. Huang, M. T. Guarnieri, J. R. Ferrell III, L. Tao and J. A. Schaidle, *Energy Environ. Sci.*, 2020, **13**, 472.
72. H. Zhang and U. Desideri, *Energy*, 2020, **199**, 117498.
73. N. Meunier, R. Chauvy, S. Mouhoubi, D. Thomas and G. De Weireld, *Renewable Energy*, 2020, **146**, 1192.
74. A. W. Zimmermann, J. Wunderlich, L. Müller, G. A. Buchner, A. Marxen, S. Michailos, K. Armstrong, H. Naims, S. McCord, P. Styring, V. Sick and R. Schomäcker, *Front. Energy Res.*, 2020, **8**, 5.
75. I. U. Din, M. Usman, S. Khan, A. Helal, M. A. Alotaibi, A. I. Alharthi and G. Centi, *J. CO<sub>2</sub> Util.*, 2021, **43**, 101361.
76. A. Bogaerts, X. Tu, J. C. Whitehead, G. Centi, L. Lefferts, O. Guaitella, F. Azzolina-Jury, H.-H. Kim, A. B. Murphy, W. F. Schneider, T. Nozaki, J. C. Hicks, A. Rousseau, F. Thevenet, A. Khacef and M. Carreon, *J. Phys. D: Appl. Phys.*, 2020, **53**, 443001.
77. S. Schiebahn, T. Grube, M. Robinius, V. Tietze, B. Kumar and D. Stoltenm, *Int. J. Hydrogen Energy*, 2015, **40**, 4285.
78. M. Bailera, P. Lisbona, L. M. Romeo and S. Espatolero, *Renewable Sustainable Energy Rev.*, 2017, **69**, 292.
79. T. Chwola, T. Spietz, L. Wieclaw-Solny, A. Tatarczuk, A. Krotki, S. Dobras, A. Wilk, J. Tchorz, M. Stec and J. Zdeb, *Fuel*, 2020, **263**, 116804.
80. M. Son, M.-J. Park, G. Kwak, H.-G. Park and K.-W. Jun, *Korean J. Chem. Eng.*, 2018, **35**, 355.

81. M. Aresta, A. Caroppo, A. Dibenedetto and M. Narracci, in *Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century*, ed. M. M. Maroto-Valer, C. Song and Y. Soong, Springer, Singapore, 2002, p. 329.
82. I. Garcia-Herrero, R. M. Cuellar-Franca, V. M. Enriquez-Gutierrez, M. Alvarez-Guerra, A. Irabien and A. Azapagic, *ACS Sustainable Chem. Eng.*, 2016, **4**, 2088.
83. M. A. N. Thonemann, *Appl. Energy*, 2020, **263**, 114599.
84. S. Abate, G. Centi, P. Lanzafame and S. Perathoner, *J. Energy Chem.*, 2015, **24**, 535.
85. G. Centi, G. Iaquaniello and S. Perathoner, *BMC Chem. Eng.*, 2019, **1**, 5.
86. S. Abate, P. Lanzafame, S. Perathoner and G. Centi, *ChemSusChem*, 2015, **8**, 2854.
87. P. Lanzafame, G. Centi and S. Perathoner, *Catal. Today*, 2014, **234**, 2.
88. P. Lanzafame, G. Centi and S. Perathoner, *Chem. Soc. Rev.*, 2014, **43**, 7562.
89. A. Alcasabas, P. R. Ellis, I. Malone, G. Williams and C. Zalitis, *Johnson Matthey Technol. Rev.*, 2021, **65**, 180.
90. A. Alcasabas, P. R. Ellis, I. Malone, G. Williams and C. Zalitis, *Johnson Matthey Technol. Rev.*, 2021, **65**, 197.