CO₂ utilization: an enabling element to move to a resource- and energy-efficient chemical and fuel production

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CO₂ conversion will be at the core of the future of low-carbon chemical and energy industry. This review gives a glimpse into the possibilities in this field by discussing (i) CO₂ circular economy and its impact on the chemical and energy value chain, (ii) the role of CO₂ in a future scenario of chemical industry, (iii) new routes for CO₂ utilization, including emerging biotechnology routes, (iv) the technology roadmap for CO₂ chemical utilization, (v) the introduction of renewable energy in the chemical production chain through CO₂ utilization, and (vi) CO₂ as a suitable C-source to move to a low-carbon chemical industry, discussing in particular syngas and light olefin production from CO₂. There are thus many stimulating possibilities offered by using CO₂ and this review shows this new perspective on CO₂ at the industrial, societal and scientific levels.

1. Introduction

CO₂ has long been considered a waste and a cost (in countries applying carbon taxes), but interest is rising in the possibility of chemical utilization as well as in producing solar fuels. Many reviews and books have discussed the different options for converting CO₂. A selection covering the different aspects of the broad
range of CO₂ chemical use is presented in [1–20]. The rising academic and industrial interest is shown, for example, by the number of results in a SciFinder search with the keywords ‘CO₂ conversion’. In 2003, the number of entries were about 180 for books, journals and reviews and about 15 for patents; these entries rose to approximately 650 and 100, respectively, in 2013. Scientific and industrial initiatives towards the chemical utilization of CO₂ have increased substantially over the last few years [8] and there is increasing industrial attention to produce different types of chemicals and fuels from CO₂:

— **Advanced materials**: a pilot plant opened at Bayers Chempark in Leverkusen, Germany, in February 2011 [21] to produce high-quality plastics (polyurethanes) based on CO₂; other industrial initiatives are in the area of the production of polycarbonates from monomers derived from the reaction of epoxides (propylene oxide, for example) and CO₂.

— **Fine chemicals**: DNV (now DNV GL) has developed a pilot unit for the electrochemical reduction of CO₂ to formate salts and formic acid [22]; various fine chemicals of industrial interest (carbamates, urethanes, isocyanates, etc.) may also be produced using CO₂ as a co-reactant.

— **Intermediate chemicals**: BASF is actively working to develop catalysts to produce acrylic acid from ethylene and CO₂ [23,24], as an alternative to the bio-based route developed by Arkema and BASF—acrylic acid from glycerol; both these routes are proposed to overcome high propylene prices in the current oxidation route. Other intermediates produced using CO₂ involve biotechnology routes; for example, acetone synthesis (Evonik) or succinic acid production (Bioamber, Roquette, BASF, Mitsubishi Chemicals, etc.).

— **Base chemicals/fuels**: in September 2011 CRI opened a plant in Svartsengi (Iceland) for synthesizing 5 Mton yr⁻¹ of methanol from CO₂ using H₂ produced electrolytically from renewable energy (RE) sources—mainly geothermal [25]; other companies, such as Mitsui Chemical, are exploring the production of base chemicals from CO₂.

Notwithstanding these positive indications, the general opinion about the chemical use of CO₂ is of an area with (and that will still have in the future) a very minor impact in terms of its contribution to the reduction of greenhouse gas (GHG) emissions. For example, the Intergovernmental Panel on Climate Change (IPCC) reported that: ‘the use of captured CO₂ in industrial processes could have only a minute (if any) effect on reduction of net CO₂ emissions’ [26]. Also, in terms of the specific impact on the chemical and energy industry, it is often argued that the utilization of CO₂ will be limited to small, niche applications and in general will not have a major impact on chemical production. A general remark is that CO₂ is the end product of chemical or energy production and has a low thermodynamic energy value. Thus, a lot of energy is required to transform CO₂ into useful chemical or energy products (energy may be transferred directly or through a reaction with high-energy molecules). This is supposed to determine the high costs of production. It is possible to turn this limitation into an opportunity, by using the process of converting CO₂ to higher energy density compounds as an effective way to insert RE into the chemical production chain, as discussed later. The supposed low potential impact of CO₂ chemical utilization is derived from the wrong vision of its potential uses, as also discussed later. The field of CO₂ chemical utilization is thus still largely influenced by misconceptions about the real potential and impact.

The objective of this review is thus quite different from the many reviews and books on CO₂ utilization mentioned before. The aim is not to provide a systematic overview of the different possibilities and reactions of CO₂ and/or of related aspects such as the characteristics of the catalysts necessary to efficiently perform these reactions. However, novel opportunities will be highlighted to evidence how the use of CO₂ will be a critical enabling element for the sustainable future of chemical production and to move to a resource- and energy-efficient production. We will discuss how large the impact on GHG emissions will be—potentially no less than that expected
from carbon capture and storage (CCS) technologies or the use of biofuels, but with significantly lower costs [27].

A further objective is to show how some of the grand challenges faced by our society (mitigate climate change, preserve the environment, use of RE and replace fossil fuels) share a common aspect [28]: the (re)use of CO₂ to produce fuels and chemicals is an enabling factor to overcome these challenges. Reusing CO₂ not only addresses the carbon balance in the Earth’s atmosphere with the related negative aspects on the quality of life and the environment, but also represents a valuable C-source to substitute fossil fuels [18,19]. By using RE sources for the conversion of CO₂, it is possible to introduce RE into the production chain, in a more efficient way than alternative possibilities [7,29]. The products derived from the conversion of CO₂ (such as methanol, light olefins, etc.) effectively integrate in the current energy and material infrastructure, thus allowing a smooth and sustainable transition to a new economy without the very large investments required to change this infrastructure [29,30]. In close collaboration with the use of biomass, the use of CO₂ provides a new sustainable scenario for chemical production [31–33] and to move biorefineries to biofactories [34,35].

Often in discussions on the possible ways to use CO₂, the need to employ long-term sequestration of CO₂ to reduce GHG emissions has been considered necessary, because having a short cycle time means that carbon is returned to the atmosphere quickly. This is not a correct analysis, when RE is incorporated in the final molecule of CO₂ transformation. A short cycle time, for example when CO₂ is converted to methanol using the H₂ produced by RE sources and then methanol is used as a fuel, means that in every cycle there is a minus delta in carbon emissions that is derived from the substitution of fossil fuels with less-carbon-intensive sources. On a certain time scale (20 years, for example), the long-term sequestration of CO₂ has a single impact, while for short-time cycles there is a cumulative effect. The exact value derives from a life cycle analysis (LCA), but, on average, the effect is at least one order of magnitude higher in short-time cycles than in long-term sequestration. As discussed below, the reason to incorporate RE in CO₂ transformation molecules (fuels) derives from the need to store/transport energy and to extend its range of utilization. Thus, recycling of CO₂ with incorporation of RE in the transformation process enables new routes for using low-carbon energy sources.

In a longer term visionary idea, it is possible to create a CO₂ economy, where it will be possible to achieve full circle recycling of CO₂ using RE sources, in analogy with how plants convert CO₂ to carbohydrates and O₂ through photosynthesis but intensifying the process and especially being able to control the type of final products [36–39]. Capture and conversion of CO₂ to chemical feedstock could provide new routes to a circular economy and move to Economy 3.0. One of the pillars of the latter is the realization of a distributed and personalized energy (and perhaps chemical) production.

This review aims not only to show and discuss this new vision on CO₂ at the industrial, societal and scientific levels but also to provide evidence on how CO₂ conversion will be at the core of the future of chemical industry. It will start by briefly introducing the future of the chemical industry and the role of CO₂ in enabling a sustainable scenario, moving then to an analysis of some of the recent developments in the industrial chemical use of CO₂. Emphasis is placed especially on CO₂ hydrogenation with H₂ produced from RE sources. Some limited indication is given on the use of CO₂ to produce advanced materials. This topic is discussed in various other reviews and books [8,13,17–19]. Some new possible routes of CO₂ utilization, although still at the laboratory scale, are also discussed in §3.4, together with new possibilities offered by revising well-established routes such as urea synthesis (§3.5). Emphasis is placed on the emerging opportunities for CO₂ utilization by biotechnological routes (§3.6), because this is an aspect that is still not adequately covered, despite having a large potential for innovation.

A technological roadmap for CO₂ chemical utilization based on this survey of emerging possibilities as well other state-of-the-art analyses is discussed. Aspects discussed in this section include assessing the different routes, the social perception of CO₂ utilization paths and an analysis of the emerging patent literature. The next section deals with the key question of the use of...
Figure 1. A model of CO$_2$ circular economy and its impact on the chemical and energy value chain. (Online version in colour.)
2. What is the future for the chemical industry and the role of \( \text{CO}_2 \) in this industry?

Discussing the role of \( \text{CO}_2 \) utilization, as an enabling factor to move to a resource- and energy-efficient chemical production, requires analysing briefly what the future may hold for the chemical industry, that is, a short discussion on the new scenario [31–33] and the driving elements determining the evolution. We limit the discussion here to some aspects that put the discussion about the technology roadmap for \( \text{CO}_2 \) utilization in the right perspective and that help to understand the effective impact. Some further aspects can be found in [31–33].

It must be remarked that scientists commonly do not use scenario analysis, even though it is a typical economic tool. However, it is an important tool to anticipate priorities. In general, it allows (i) early identification of key technology bottlenecks, (ii) recognition of opportunities, R&D paths and barriers, and (iii) anticipation of research macro-trends. It is thus clear that a discussion on the impact of \( \text{CO}_2 \) utilization paths on the future of the chemical industry should be linked to an analysis of our future scenario, the correct assessment of which could allow us to identify early the possible routes that have a higher probability of becoming effective industrial routes (out of minor uses). On the other hand, scenario analyses are often based on a nearly linear extrapolation of future directions as well as a limited understanding of the possible impact of new technologies and how they can open new paths or what are the bottlenecks limiting these paths. It is thus not possible to use only the developed scenarios, but it is necessary to analyse them in more detail.

Various studies have been carried out recently on the future of the chemical industry [40–42], mainly from an economic perspective, although it should be made clear that they also suffer from some of the remarks made earlier. A main observation is that the evolution trends in the chemical industry are not linear, being the result of

— **Pushing forces**: related to raw materials, technology developments, etc.
— **Pulling forces**: related to social demand (market demand, security, environment and quality of life).

The consequence is a nonlinear evolution due to the different dynamics of these forces [43] and the synchronisms with developments in other industrial areas. There is a cyclic evolution with periods of renewal, prosperity, recession and depression, which are known as macro-economic cycles of Kondratieff [44,45]. We are at the end of one of these cycles [45]. The new one will be dominated by a change in raw materials (with respect to the dominant use of oil; this has happened in all the preceding cycles), reorganization of the energy and resource infrastructure, switch to renewable energies and drivers for sustainability, largely influencing the market and industrial objectives [45]. The consequence is that the chemical industry is at a turning point with a major change expected in its structure within a relatively short time (one to two decades maximum). Science and technology should provide the basis to enable this transition, and there is thus an increasing need to find new raw materials to substitute for fossil fuels in the production of chemicals and polymers (and energy), and new production methodologies which decouple production from the scale-economy. The latter was the characterizing element of the last economic cycle of chemical production, and also one of the limiting factors in the move to sustainable production [44].

There are many major changes in chemical production that are necessary for the industry to respond to the need for a resource- and energy-efficient sustainable future and to move to a low-carbon economy. The use of alternative raw materials is among these driving forces, as are biomass as chemical feedstock, (re)use of \( \text{CO}_2 \), waste valorization, use of RE, use of fossil fuel alternatives to oil (actually accounting for the majority of petrochemistry production), and use of shale gas instead of coal [31–34]. Figure 2 schematically represents the change from the current (oil-centred) petrochemistry to the future of chemical production based on a larger use of
alternative raw materials and of RE sources. We will discuss in the following sections the role of CO2 utilization in this general panorama.

Globalization of chemical production is a major element characterizing the current landscape, but there are several indications of how moving to a de-globalization will characterize the future of chemical production. In fact, widening the type of raw materials, with emphasis on local resources (due to various economic and social pushes), will determine a move towards de-globalization and tighter integration with other industrial sectors (symbiosis, synergy, etc.), as already observed in some cases. This will determine different regional ‘pressures’ to use alternative raw materials. In regions such as Europe that lack other resources, CO2 (re)use will play a major role in maintaining competitiveness and in moving to a low-carbon economy [31–34].

It is important to take account of all these aspects when considering the role of CO2 in a future scenario for chemical production, which may be different in Asia with respect to Europe or the USA. The following considerations will apply especially to Europe, due to the higher social and political pressure (translating into targets for substituting fossil fuels, use of RE, etc.) on addressing the GHG issue, use of renewable energies and the move to a low-carbon economy. Furthermore, there is a lack of other raw materials; therefore, waste biomass and CO2 can be considered as Europe’s own resources. However, it is likely that Europe will be the driving force behind spreading the chemical utilization of CO2 worldwide.

3. Recent advances in the industrial chemical use of CO2

CO2 as a feedstock for producing chemicals represents an interesting challenge both commercially (as low-cost alternative raw materials, to produce novel valuable materials and to lower the impact of production) and for innovation (to explore new concepts and new opportunities for catalysis and industrial chemistry). The utilization of CO2 is an excellent opportunity to inject RE in the energy or chemical production chains, as discussed below. This is a major problem faced by the chemical industry, which is looking at new possibilities to increase its efficiency in the use of resources and energy.
The chemical transformation of CO₂ is a dynamic field of research, in which many industrial initiatives also thrive, even if it is not always easy to understand the real opportunities and limitations of each option [8]. The next section on the technology roadmap will attempt to define the panorama for the industrial utilization of CO₂ based on the analysis of the state of the art, including recent trends in patents.

In a short-to-medium-term perspective, CO₂ utilization will continue its progression especially in areas that are technologically more advanced (e.g. CO₂-containing polymers, CO₂ hydrogenation). The use of CO₂ conversion to exploit unused RE resources or to mitigate instabilities on the grid (related to the discontinuous production of energy by renewable sources; thus, chemical conversion is a way to store and distribute energy) will play a future relevant role, as discussed below. These driving elements will lead the way to increased use of CO₂.

In the long term, CO₂ utilization will become a key element in sustainable low-carbon economy in chemical and energy companies, combined with curbing consumption [27]. CO₂ will become especially a strategic molecule for the progressive introduction of RE resources into the chemical and energy chain [7,31], thus helping to lessen fossil fuel consumption. CO₂ utilization will become an important component of the strategy portfolio necessary for curbing CO₂ emissions (with an estimated potential impact of gigatons equivalent CO₂ emissions, similar or even superior to the impact of CCS and biofuels, but with a lower cost for society [27]). CO₂ utilization will thus be at the heart of strategies for sustainable chemical, energy and process industries, for resource- and energy-efficient development.

In terms of potential application, the time to market (in relation also to the degree of technological maturity), bottlenecks and limiting factors, market incentives and potential impact on chemical production are among the main factors to be considered. The discussion in the next section on the technology roadmap for CO₂ chemical utilization will address some of these aspects.

(a) CO₂ hydrogenation

CO₂ catalytic hydrogenation is the technology with the greatest possibility of shortly being commercialized on a large scale. There are many possible routes, to methanol or DME, methane, light olefins, above C2 hydrocarbons or alcohols, etc. An overview of the different CO₂
conversion routes by hydrogenation is shown in figure 3. The routes are multi-step (e.g. H\(_2\) is produced, for example, by water electrolysis using electrical energy from renewable sources and then it is used in a catalytic process) or integrated (with formation of H\(_2\) equivalents, e.g. protons and electrons are produced in the electro- and photocatalytic processes as well as in bio-catalytic processes). In all these processes, RE is incorporated in the final product of CO\(_2\) hydrogenation. Production of renewable H\(_2\) (by electrolysis using RE) and then its use in catalytic processes is the current state of the art, with various processes (methanol, DME, methane, syngas and FT processes) at a semi-commercial stage of development. In the future, integrated processes will grow in relevance, because they allow a potential better efficiency, but productivities are still too low.

Between the various routes outlined in figure 3, we believe that methanol formation is the preferable one. There are various reasons related to the degree of maturity of the technology such as the formation of a liquid product that is easy to store and distribute as well as very versatile use in applications going from fuels to chemicals and not least because it uses relatively easy technology (reduced steps, high selectivity and simpler separation). A semi-commercial unit in Iceland run by CRI is in operation and pre-commercial industrial plants are under evaluation (for example, by Mitsui Chemicals in Singapore).

Methane from CO\(_2\) (P2G) is another area in which there is strong R&D effort, particularly in Germany, in relation to the local storage of excess electrical energy (from wind) and the production of methane for automotive use (Audi e-gas process). A 6-MW P2G, located in the Lower Saxony city of Werlte, started operations in 2013. As methane is a gas, storage and distribution is more difficult than for methanol (even considering the large pipeline net; there are also issues of purity for introduction in the pipeline system) and chemical use is quite difficult, if not passing through syngas (but then direct production of syngas from CO\(_2\) would be preferable).

While various stakeholders, in particular in Germany, consider that this option will play a major role in future energy systems as the infrastructure already exists and the storage capacity (mainly underground in salt caverns, but present only in some areas) is very large, we do not feel that this indication is fully correct. First, P2G is limited to using excess RE production, for example from wind during the night. Therefore, the impact itself is limited. Second, from the energy efficiency perspective, the synthesis of methanol, working at milder conditions and using less H\(_2\), is more efficient. Third, a gas in comparison with a liquid fuel has many constraints in terms of storage, distribution and uses, including for chemical purposes.

The challenge for a future energy sustainability system is to enable an oil-equivalent energy system, where RE can be traded on a world scale [27]. It is thus necessary to produce a liquid fuel, rather than a gas, as demonstrated by the comparison between oil and natural gas (NG). There are many countries worldwide where RE sources can be traded by converting them into a liquid fuel that is easy to transport and store. The need for a pipeline infrastructure, as for methane, greatly limits the type of exploitable RE sources. Thus, we believe that P2G will have a minor impact on the chemical production value chain, although it will play a role in a future energy system.

Formic acid has minor uses for chemical production, if it is not being used as a carrier for transporting H\(_2\). The synthesis of higher alcohols and hydrocarbons through Fischer–Tropsch-type reactions leads to a broad range of products, with resulting high costs of separation. However, the production of light olefins (C2–C4) through a Fischer–Tropsch-to-olefin is an industrially interesting process [46,47], for the higher added value of olefins with respect to methanol. It is estimated that methanol synthesis from CO\(_2\) will become commercial within a few years (see later section, in relation to the use of this reaction to import remote RE sources), while light olefins from CO\(_2\) will require more time, because of other competitive possibilities including from biomass [32].

The main issue is the cost (and carbon footprint) of H\(_2\) necessary for the reaction. Actual electrolyzers allow an efficiency of approximately 70–85% with energy consumption of 4–6 kWh Nm\(^{-3}\) of H\(_2\) produced. Using RE, the efficiency decreases to about 60%, but the hydrogenation of CO\(_2\) decreases the intrinsic energy by only a minimal amount, and thus the main parameter influencing the carbon footprint is the production of H\(_2\). Improvement
in the production of renewable H₂, however, is a necessary key element to establish the commercialization of the CO₂ hydrogenation processes.

(b) CO₂ use to produce monomers for advanced materials

For the use of CO₂ in producing advanced materials, particularly polymers, and also fine chemicals, the driving factor is the possibility to develop alternative synthesis routes, rather than to reduce GHG emissions. There are various industrial initiatives in this sector, among which are the above-mentioned Bayer initiative (focused especially at producing polyols for polyurethane), BASF initiative (for polypropylene carbonate) and Novomer Inc. initiative (for a polypropylene carbonate) [8]. Although it is already commercial, the Asahi Kasei’s process for phosgene-free production of aromatic polycarbonate starts from ethylene epoxide, bisphenol-A and CO₂ [48].

(c) Sources of CO₂ and costs

Often there is a problem regarding the recovery of CO₂ and its purity. This is an important aspect, but we do not feel that it is a critical one, at least in the initial stage of commercialization of CO₂ utilization technologies. In fact, there are many large-volume sources of rather pure CO₂ in refinery and chemical processes (ammonia production, ethylene oxide production, gas processing, H₂ production, liquefied natural gas, Fischer–Tropsch synthesis coal) as well as from biorefineries (fermentation processes [35]). In the initial phase of introduction of technologies for CO₂ chemical utilization, the recovery of CO₂ from the flue gases of combustion processes, with the related problems of purification from contaminants, is thus not necessary.

It is estimated that globally approximately 500 million tons of low-cost (less than US$20 per ton) high-concentration CO₂ is available annually as a by-product from natural gas processing, fertilizer plants and some other industrial sources. This amount does not include the CO₂ emissions from biorefineries, which can double this figure. CO₂ emissions from fermentation processes are characterized by a high-purity level. At a higher cost, over 18 000 million tons could also be captured annually from the dilute CO₂ streams currently emitted by power, steel and cement plants.

As commented at the end of the Introduction, the incorrect belief that the value of the contribution of CO₂ to climate change goals is limited to its sequestration effect must be overcome. Instead, the key is its value to enable new low-carbon routes of RE use, with the related decrease in GHG emissions. Account should be taken not only of the ‘sequestration’ of CO₂, but also of how its reuse enables the reduction of GHG emissions on an LCA basis. By accounting in this way, the misconception that the use of CO₂ to make fuels (by using RE) does not contribute to climate change goals when CO₂ derives from fossil fuels is overcome.

The cost of CO₂ capture is decreasing rapidly and market prices for CO₂ will decrease when restrictions on CO₂ emissions are introduced worldwide. The revenue generated from reuse will be inadequate to drive the development of CCS for power, steel and cement plants, but is a current incentive for developing chemical reuse of CO₂ as a C-source, to prepare advanced materials (polymers), to develop new synthetic routes and in storage/transport of RE. Therefore, the perspectives on CO₂ utilization are quite positive.

(d) New routes for CO₂ utilization

The last 2–3 years have seen a rapid increase in the number of publications, with many proposed new routes for activating CO₂ using homogeneous catalysts [49], for example

— hydrosilanes used to convert CO₂ into methane or methanol using zirconium phenoxide borane complexes or N-heterocyclic carbenes as catalysts [50,51];
— borane reduction of CO₂ to form boryl formats using nickel diphosphine complexes as catalysts [52];
— frustrated Lewis pairs for homogeneous hydrogenation of CO\textsubscript{2} [53,54];
— non-metal-mediated homogeneous hydrogenation of CO\textsubscript{2} to CH\textsubscript{3}OH [55]; and
— indirect conversion of CO\textsubscript{2} to methanol based on the use of Ru pincer complexes as catalysts for the hydrogenation of carbonates, carbamates and formats [56].

Although all these reactions represent interesting achievements, and good turnovers are reported (Milstein and co-workers [56] showed turnover numbers up to 4400 h\textsuperscript{−1} under mild reaction conditions; 10–60 atm H\textsubscript{2}, 110–145°C, 1–14 h), the productivity (e.g. the tons of methanol of per h and per reactor volume) is largely lower than that of conventional heterogeneous catalytic routes. The exploitability of these discoveries to develop industrially competitive processes is thus still to be verified. However, the many new proposed paths are indicative of the vitality of the topic.

Also in the area of the use of CO\textsubscript{2} in organic synthesis, a number of recent breakthroughs have been made; for example, in the area of carboxylation, the catalytic hydrocarboxylation of styrene and the copper-catalysed hydrocarboxylation of alkynes using CO\textsubscript{2} in the presence of a hydrosilane [57]. These reactions open up new interesting perspectives for organic synthesis, but all have low-volume productions. Therefore, they will not have a significant impact in shifting chemical production to a low-carbon economy.

Electrocatalysis is offering new possibilities, either to produce small organic molecules to be used in conjunction with or integrated into solar devices (for artificial leaf-type systems [36–38]) or as a valuable synthetic procedure. The number of new discoveries after years of stagnation is remarkable. There is the need to go beyond the conventional metal-type electrodes operating in liquid phase. Gas-phase [58] or liquid-phase operations in the presence of molecular catalysts (such as pyridinium ions) [59–62] are two promising directions to form either methanol or even long-chain alcohols, but scientific effort in these areas is still too limited. The use of non-conventional electrolytes, such as ionic liquids, is another attractive direction [63,64]. New electrocatalysts have also been recently discovered; for example, a nanoporous silver electrocatalyst that is able to electrochemically reduce CO\textsubscript{2} to carbon monoxide with approximately 92% selectivity at a rate over 3000 times higher than its polycrystalline counterpart under moderate overpotentials of less than 0.50 V [65]. Electrocatalytic carbonylation on novel catalysts (metal organic frameworks, e.g. [66]) is another interesting possibility (relevant for organic syntheses).

This short panorama evidences that there are plenty of new ideas and emerging opportunities in the area of CO\textsubscript{2} (re)use, thus confirming that the CO\textsubscript{2} challenge is not only relevant for industry and society, but is an excellent opportunity to explore new concepts and new opportunities for catalysis and industrial chemistry. However, many of the recent discoveries, particularly in the area of homogeneous catalysis and electrocatalysis, have still to be proven to be exploitable at the industrial level. Several of them appear to still have a productivity and cost-effectiveness that are too low to consider industrial feasibility or aspects such as stability (particularly for electrocatalysts) have still not been adequately investigated.

(e) Revising old routes: urea synthesis

There are also interesting new industrial possibilities in revising old routes, particularly urea production, which is well established on a large scale (over 120 Mton yearly production). However, opportunities to improve it are emerging. Urea boosting indicates the capture of an external current of fossil CO\textsubscript{2} for urea production in an integrated ammonia–urea manufacturing plant, and that uses natural gas as a feedstock in the reforming process to produce CO\textsubscript{2} and NH\textsubscript{3}. When natural gas is used as a feedstock, an excess of NH\textsubscript{3} is produced. An external source of CO\textsubscript{2} can be delivered via a pipeline to the urea plant and reacted with surplus ammonia to form urea. This solution mitigates GHG emissions in various ways: (i) feedstock switch (avoidance of the emission of a fossil CO\textsubscript{2} current through its capture and utilization as input for urea production) and (ii) thermal energy savings (through the reduction of fossil fuel combustion needed to produce the CO\textsubscript{2} input for urea production).
The synthesis of substituted ureas [67] is also of industrial interest, for their application in a wide variety of fields, from refinery and petrochemicals to agrochemicals and pharmaceuticals. Ureas are also useful in the production of carbamates. The use of CO₂ as a starting material in the synthesis of substituted ureas represents an intriguing alternative to classical phosgenation methods and several possible approaches have been explored to date.

(f) Emerging opportunities for CO₂ utilization: biotechnological routes

Bio-catalytic industrial routes for CO₂ valorization represent an emerging opportunity. Evonik is developing a CO₂-based acetone fermentation process using industrial waste-gas streams that contain carbon monoxide (CO) and hydrogen (H₂) in addition to CO₂. They use genetically modified acetogens, e.g. bacteria strains (Clostridium ljungdahlii, C. carboxidivorans and C. aceticum), that are able to utilize CO₂. The stage of development is the successful production of acetone and its scale-up from flask into lab-fermenter. Figure 4 reports the schematic mechanism, part natural and part synthetic, developed by Evonik to produce acetone from CO₂ [68]. Evonik developed specific strains able to insert in the Wood–Ljungdahl natural pathway of transformation, converting the intermediate acetyl-CoA into acetone.

Bio-succinic acid from glucose and CO₂ is another interesting product derived from engineering strategies [69,70]. At least five groups are developing (semi)commercial plants for bio-succinic acid. Bioamber is starting a facility in Pomacle, France, with an annual capacity of 2000 tonnes. Their process uses an Escherichia coli strain developed specifically to produce succinic acid, with wheat-derived glucose currently being used as the substrate. DSM (now Sabic) is also actively investigating the production of bio-succinic acid. In early 2008, DSM formed a partnership with France’s Roquette Frères to develop bio-succinic acid, and the two companies have been supplying kilo-scale samples for over a year from a pilot plant at Roquette’s site (Lestrem, France). Myriant is building a commercial-scale facility in Louisiana, USA. The company is currently making bio-succinic acid at the 20 000 litre bioreactor scale using E. coli and unrefined sugar as a feedstock. BASF linked with Purac subsidiary CSM is planning to produce bio-succinic acid using a BASF-developed bacterial strain (B. succiniproducens) and glycerine or glucose as a feedstock. Finally, Mitsubishi Chemical Holdings Corporation has also developed its own process for making bio-succinic acid from biomass.
Another interesting metabolic pathway is the production of longer chain alcohols from CO₂. Mitsubishi Chemical Holdings Corporation is developing the original results of researchers at the University of California, Los Angeles (UCLA) on CO₂ conversion, in particular for the production of butanol and hexanol by applying genetic manipulation techniques to modify algae. Liao and co-workers [71] at UCLA developed engineered bacteria to convert CO₂ into alcohols, in particular genetically modified E. coli bacteria to produce various alcohols and modified cyanobacterium to produce isobutanol. Using a non-natural metabolic engineering approach, the branched-chain amino acid pathways are extended to produce abiotic longer chain keto acids and alcohols by engineering the chain elongation activity of 2-isopropylmalate synthase and altering the substrate specificity of downstream enzymes through rational protein design [71]. When introduced into E. coli, this non-natural biosynthetic pathway produces various long-chain alcohols with carbon number ranging from 5 to 8. The feasibility of this approach was demonstrated by optimizing the biosynthesis of the 6-carbon alcohol, (S)-3-methyl-1-pentanol. Later, the same group [72] showed the possibility of direct photosynthetic recycling of CO₂ to isobutyraldehyde. They have genetically engineered Synechococcus elongatus PCC7942 to produce isobutyraldehyde and isobutanol directly from CO₂ and increased productivity by overexpression of ribulose 1,5-bisphosphate carboxylase/oxygenase (RuBisCO). Isobutyraldehyde is a precursor for the synthesis of other chemicals, and isobutanol can be used as a gasoline substitute. The high vapour pressure of isobutyraldehyde allows in situ product recovery and reduces product toxicity. The engineered strain remained active for 8 d and produced isobutyraldehyde at a higher rate than those reported for ethanol, hydrogen or lipid production by cyanobacteria or algae.

Rather interesting developments in biotech routes for CO₂ valorization are also in the area of syngas fermentation. Although industrial developments are still on the use of syngas (CO/H₂) rather than CO₂, the modification of the path could lead to direct use of CO₂. It is known that carbon monoxide dehydrogenase (CODH) from C. thermoaceticum (a Ni and Fe containing metalloenzyme) catalyses the reversible oxidation of CO to CO₂. It is possible to couple this enzyme with a semiconductor such as TiO₂, which produces the electrons necessary for the reduction. A hybrid enzyme–nanoparticle system was used to achieve an efficient CO₂ to CO reduction using visible light as the energy source. Armstrong and co-workers [73–75] used

— TiO₂ nanoparticles modified by attachment of CODH and a Ru photosensitizer; this system produces CO at a rate of 250 μmol of CO (g of TiO₂)⁻¹ h⁻¹ when illuminated with visible light at pH 6 and 20°C.
— Assemblies of CODH with CdS nanocrystals; in this case, the CO production rate at best is approximately 0.5 μmol h⁻¹, but the turnover frequency per enzyme molecule is better. A total of 0.35 M 2-(N-morpholino)ethanesulfonic acid was used to buffer the acidifying effect of CO₂ in solution and to act as the electron donor.

In a different approach, several purple non-sulfur bacteria were used to convert CO to H₂ in a process similar to the water gas shift (WGS) reaction. Lazarus et al. [76] reported the use of redox enzymes on conducting graphite platelets to perform the WGS reaction efficiently at room temperature. The H⁺ reduction reaction is catalysed by a hydrogenase, Hyd-2, from E. coli, and CO oxidation is catalysed by a carbon monoxide dehydrogenase (CODH-I) from Carboxydothermus hydrogenoformans. This system is claimed to have a turnover frequency (at 30°C about 2.5 s⁻¹ per minute functional unit, e.g. a CODH/Hyd-2 pair) comparable to conventional high-temperature catalysts, although the productivity per reactor volume (the industrially relevant parameter) is quite superior for the heterogeneous catalyst under optimized reaction conditions.

The following step of syngas fermentation is well established at the (semi)commercial level. The production of fuels and chemicals through syngas fermentation offers some advantages over metal catalytic conversion: the higher specificity of the biocatalyst, lower energy costs, greater resistance to catalyst poisoning and independence of a fixed H₂:CO ratio. However, process costs are still higher. There are several microorganisms which can produce fuels and chemicals by
syngas utilization. These microorganisms are mostly known as acetogens including C. ljungdahlii, C. autoethanogenum, Eurobacterium limosum, etc. [77]. Most use the Wood–Ljungdahl pathway. The fermentation of syngas to ethanol by C. ljungdahlii was developed into a commercial process that combines biomass gasification, syngas fermentation and distillation of ethanol from the reactor effluent. Syngas is cooled before it can be introduced into the bioreactor and is coupled to heat recovery (BRI Energy; www.brienergy.com). The Lanzatech (www.lanzatech.com) process of CO fermentation is currently applied on a 0.4 Ml demonstration facility (Shanghai, China) using steel mill off-gas from a working steel mill [78]. INEOS Bio (www.ineosbio.com) also began in 2011 the construction of its first commercial-scale plant, the Indian River BioEnergy Center in Florida, USA. Gas fermentation is thus an established technology, but clearly it would be interesting to directly use CO2 along the lines outlined above. There are interesting scientific bases to develop hybrid systems for this fascinating opportunity.

4. A technological roadmap for CO2 chemical utilization

The previous section gave a brief overview of the main aspects and tendencies for industrial utilization of CO2 to develop new sustainable productions. As mentioned in the Introduction, this interest is confirmed by the rising number of patents in this area and various new companies created to find opportunities from this novel area of technology. A further important aspect to consider is that the possible market for CO2 reuse is dependent on the possibility of developing drop-in processes and products, because the cost for the introduction of new technologies/processes is quite high. Different institutes have examined the possible scenario and technology roadmap for the utilization of CO2 [79–84]. We feel, however, that the complexity of the scenario was not always correctly identified, including the many socio-economic aspects and the potential for technological development, market incentives and constraints (including investment costs), etc.

Figure 5 reports our estimations for the ‘technology roadmap’ to commercialize CO2 reuse paths. It was based on the above inputs, but was corrected by taking into account the results of recent workshops, meetings, reports etc. as well as considerations regarding the possible market, costs for implementation of the technology, perspectives in incentives on reuse of CO2 in relation to the different impact of the various technologies, drop-in characteristics of the
technology/products, exploitability and technical constraints, etc. In figure 5, the light blue circle represents technology at the pilot/demonstration scale, while the bar represents the expected timeframe when commercial operation of the technology is likely. Owing to different uncertainties in the conversion paths, the range of years when commercial operations will start changes from path to path.

In terms of impact, the Parsons Brinckerhoff/Global CCS Institute [82] estimated that the main path for CO₂ use in 2020 will be non-chemical, e.g. by enhanced oil recovery (EOR), with a cumulative demand (in year 2020) higher than 500 Mton and gross revenue higher than US$ 7500 M. It should be commented, however, that EOR could not be properly considered a low-carbon route because (i) EOR enhances the use of fossil fuels being used for oil displacement and (ii) part of the CO₂ used in EOR will be remitted owing to soil porosity.

A second main path will be related to urea yield boosting, mineral carbonation and enhanced coal bed recovery with cumulative demand between 20 and 100 Mton and gross revenue up to US$ 1500 M. For polymers, renewable methanol (RM), concrete curing, bauxite residue carbonation and algae cultivation, the Parsons Brinckerhoff/Global CCS Institute [82] estimated a cumulative demand between 5 and 20 Mton and gross revenue up to US$ 1500 M. Formic acid and enhanced geothermal systems account for less than 5 Mton cumulative demand and less than US$ 75 M gross revenue (all referring to year 2020).

It should be noted that this scenario is strongly dependent on CO₂ reuse as complementary technology to CCS to favour legislative and regulatory regimes, as well as to accelerate CCS by providing an economic driver. However, we feel that the potential for polymers and particularly for RM (or DME) as vectors to transport RE as well as additive for fuels or to produce renewable fuel components is not correctly estimated. The potential for CO₂ as a C-source (in particular, for producing light olefins) is also underestimated. A more correct estimation for these technologies is that the cumulative demand to 2020 is at least 30–50 Mton with a gross revenue of up to US$ 500–700 M, but it is expected to rapidly increase in the following decade.

It is worthwhile mentioning that the European Chemical Industry, through the SPIRE PPP (Sustainable Process Industry Public–Private Partnership) initiative [85] and other relevant documents [86], aims to reduce (by year 2030) fossil energy intensity by up to 30% and renewable and primary raw material intensity by up to 20%. It is estimated that a significant part of these targets (nearly half) could derive from CO₂ valorization technologies.

(a) Assessing the different routes for CO₂ utilization

The implementation of the different solutions will depend not only on techno-economic aspects but also on other criteria. A comparison of the different routes, according to six criteria, is
presented in figure 6 [84]. These criteria allow a first quick overview of the degree of development and the main issues of the various options to valorize CO2. The criteria are the following.

(i) Potential development: this criterion indicates the length of time required to open the first industrial facility. This duration depends on the R&D effort.

(ii) Economic perspectives: this criterion represents the prospect of achieving an economic return. It also reflects the anticipated level of difficulty to remove economic blocks that actually exist.

(iii) External use of energy: this criterion assesses the energy consumption per cost of the product. This consumption takes into account energy requirements (electrical and thermal) associated with the manufacture of the reagents (especially the production of hydrogen or grinding of minerals) and energy requirements associated with processes. The step to capture CO2 from industrial flue gases is not taken into account. Energy consumption is a major issue, particularly for dry reforming and mineralization. Some routes, such as microalgae or photo-electrocatalysis, present the significant advantage of direct use of photons from the Sun and have little productivity cost depending on the energy.

(iv) Potential volume of use of CO2: this criterion represents the maximum amount of CO2 that could be potentially used—by year 2050—per year without any other consideration. Emissions of CO2 released by the industrial process or during the use of the product are not taken into account.

(v) Time of sequestration: related to the time of sequestration of CO2 before it is reintroduced into the atmosphere.

(vi) Other environmental impacts: this criterion is related to the use of solvents or toxic chemicals in the process, catalysts with negative impact on the environment and use of scarce natural resources.

Figure 6 represents the visual summary of the indications given in the study by Thybaud & Lebain [84] for the French Environment and Energy Management Agency, but some of their indications may be questionable. For example, as remarked before, CO2 use for EOR cannot be properly considered as a route for decreasing CO2 emissions, because the main effect is to stimulate a larger use of fossil fuels.
(b) The perception of the role of CO₂ utilization paths on the future of society

A proper analysis of the technology roadmap for CO₂ utilization requires evaluation of the public and industrial managers’ perception of the role of CO₂ utilization paths on the future of society. There are not many specific studies on these aspects, but the graphs reported in figure 7 are useful to raise some relevant issues on this topic. The first graph [81] is the relation between the stage of development and market value for some technologies of CO₂ reuse, while the second graph [83] reports a comparison of the public perception of CO₂ reuse with respect to the case of aspirin and CCS, according to seven key parameters. It is interesting to observe how, in terms of public perception, CO₂ reuse (for chemicals and/or fuels) is considered a largely more relevant area with respect to carbon sequestration (CSS) and aspirin in terms of market capacity and value, but a less relevant area for sustainable catalysts. The latter aspect is clearly connected to poor public understanding of catalysis, because, for example, no catalysis at all is involved in CO₂ sequestration (thus questioning the impact on sustainable catalysts). Another interesting result is that all three technologies are considered nearly equivalent in terms of net CO₂ capture, while CCS is considered much less energy efficient. CO₂ reuse results are also better in terms of sustainable feedstocks. On average, CO₂ reuse is thus considered by the public as a positive technology and better than CCS, favouring the social push to this technology as a significant contribution to a low-carbon economy. However, the results in figure 7b also demonstrate the need to raise awareness among general public of the methodologies of CO₂ chemical utilization.

The results of figure 7a also provide some interesting, but questionable, aspects. Catalysis, for example, is not a mature technology, at least in the aspects related to moving to a low-carbon economy, realizing a more efficient use of resources and energy, and developing novel processes for the use of renewables [87,88]. The market value and scientific maturity of electrochemical technologies is definitively lower than that of catalytic reduction routes and not slightly superior, as indicated in figure 7a. This figure is reproduced from a market study prepared by Frost & Sullivan [81], which is a business consulting firm offering market analyses, research, etc. The firm’s team consists of industry experts, consultants, market analysts and research executives. The study is thus indicative of the perception of decision-makers on the economic potential of CO₂ utilization routes. Figure 7a and the cited report [81] indicate positive perspectives, but the need to strengthen research. However, as commented above, there is still a lack of clarity on research bottlenecks and effective impact. It is thus necessary from the scientific perspective to increase effort not only to develop new scientific routes but also to effectively assess the issues in moving from idea to innovation. In fact, only when enough critical mass of research effort is dedicated to the topic of CO₂ utilization will it be possible to translate to fact the technology roadmap tentatively identified in figure 5. A combination of public and private funds is necessary to reach this goal. From this perspective, it is important to mention that the cited SPIRE initiative [85] is a public–private partnership, which has seen CO₂ utilization as one of the pillars to move to a sustainable, but competitive, future for the chemical industry.

(c) An analysis of emerging patent areas in relation to the technology roadmap

In order to complete the analysis of the technology roadmap in CO₂ utilization technologies, it is useful to analyse briefly the emerging patent literature trends, limited to the last 5 years (2008–2013) and patents in English. The search was made with SciFinder as the main search mechanism, using different keywords, based on the combination of CO₂ and a second word from the following list: (i) type of product (syngas, methanol, formic acid, urea, polymer, epoxide, etc.), (ii) type of reaction (carboxylation, photo, electro, Fischer–Tropsch, plasma, reverse water gas shift, etc.), (iii) company (Basf, Bayer, etc.), and (iv) generic (conversion, use, etc.). The entries derived from these searches were then manually selected. In addition, the results were integrated with additional searches using different patent databases: Google patents, USPTO, Patentdocs, etc. In total, 230 entries were identified in the 2008–2013 period (year of publication of the patent) relevant to the various sectors of CO₂ catalytic conversion for chemical use.
It must be noted that the patents identified included only those where the use of CO₂ was a key element. For example, the patents for methanol or Fischer–Tropsch synthesis typically report the use of syngas as feedstock, and also indicate the possible presence of CO₂ in the feed. These patents were not considered here because the catalysts for using pure CO₂ (+H₂) are different from those using syngas (CO + H₂) or syngas containing small amounts (typically less 4%) of CO₂.

The patents identified were all classified according to 11 main classes of reactions. The results are summarized in figure 8. The three top areas in terms of number of patents are the conversion of CO₂ to syngas, the use of CO₂ for monomers/polymers and the photo/electrocatalytic processes for using CO₂. It should also be noted that the total number of patents appears to be limited. There are various reasons for this:

— there is a delay between scientific interest and the exploitation of the results;
— large companies still need to define their priorities in this area, and for this reason there is a delay in patents;
— small companies in some cases use patents as a way to increase visibility, but in several cases prefer to avoid patenting to avoid disseminating information.

The trend in the number of patents in the last 5 years, however, clearly shows that up to about 2010 the number of identified patents in this area was nearly constant (approx. 15–20 per year), but then rapidly rose to reach approximately 130 patents in 2013. This result confirms the suggestion that it is only very recently that companies are looking more seriously at this area as a potential business area.

(d) Indications from the technology roadmap

We conclude this section on the technology roadmap for CO₂ utilization by indicating that the area of CO₂ chemical utilization shows several topics of industrial interest, characterized by the different stages of development in the technology roadmap (figure 5). A significant gap exists between the stage of R&D development reported in the open literature, and the innovation and technology chain represented by patenting activity. This is an area in which patent activity is still significantly behind R&D. Several large companies need to fully develop their business strategies in this area, often delayed because of slow recognition of the potential, while start-up/venture capital companies have a more aggressive patenting policy. However, the assessment of the patents reveals how often patents have claimed system approaches (process or device design, often also based on established state of the art) rather than specific breakthroughs and discoveries.
5. Introducing renewable energy in the chemical production chain through CO₂ utilization

Moving to a resource- and energy-efficient chemical production requires finding effective ways to introduce renewable resources into the chemical production chain. There are two main possible routes to introduce RE in the process and chemical industries: (i) an indirect path via biomass and (ii) a direct use of RE sources such as solar, wind, hydro, etc. However, the latter path suffers from two main drawbacks:

— all these RE sources produce electrical energy as the output, while direct use of electrical energy in the actual chemical production accounts for only a small fraction (10–15% typically) of the energy input;
— these RE sources are discontinuous, while a continuous input is necessary in process and chemical industries.

The reaction of CO₂ catalytic hydrogenation to methanol with renewable H₂ (as mentioned before, we focus discussion here on this reaction [7,27,31], but other products may also potentially be exploited) solves both these issues, because it forms:

— a chemical, which may be introduced directly in the chemical production chain or after the eventual conversion to other building blocks for petrochemistry (light olefins, e.g. [46]); also note that these are products already in widespread use (drop-in products) and do not require large investments for their use differently from novel chemicals;
— a liquid product, which can be easily stored and distributed, bypassing the issue of RE production intermittency (this means that it may also be possible to use unexploited remote sources or excess of RE production; both of these are current relevant targets for R&D in the area of RE).

The advantage of short life cycles (for example, when converting CO₂ to ‘solar’ fuels) in contrast to long-term storage of CO₂ has been discussed above, but it may be useful to remark that the value of merit is related to enhancing the introduction of low-carbon energy in the energy value chain, rather than ‘storing’ CO₂. From this perspective, it is not relevant from which source the CO₂ derives. The perspective should thus be shifted from a direct reduction of CO₂ emissions by storage to the different, and more interesting, perspective of how the reuse of CO₂ contributes to enabling the new low-carbon economy.

With respect to bio-routes, CO₂ utilization paths are not in opposition, but in integration to move to a low-carbon economy [31–33]. Realizing a sustainable, resource-efficient and low-carbon economy requires integrating in the chemical production chain other forms of RE than those associated with the use of biomass. This emerges from the analysis of the different scenarios for a bio-based economy [89,90], taking into account the social and techno-economic constraints in developing some of the routes. In other words, it is necessary to analyse the integration of RE sources (solar, wind, hydro, etc.) in the chemical production chain along the lines indicated above.

A relevant question also regards the cost-effectiveness of the bio-based versus CO₂-based routes, although it is relevant to mention how a more specific analysis (case by case) would be necessary. In general terms, biofuel production and consumption have been expanded not in response to market forces, but rather to comply with government policies (for example, mandate in using biofuels). On average, the use of bioenergy allows a saving of approximately 50% of CO₂ emissions with respect to fossil fuels. This is an average value because many parameters affect LCA of the use of bioenergy [91,92]. Methanol produced from the reuse of CO₂ and RE has a potentially larger impact in terms of saving CO₂ emissions, as well as in terms of resource and energy efficiency. CO₂ chemical utilization to make (renewable) methanol, for example, has many advantages:
— The CO₂ to (renewable) methanol (and back to CO₂ during methanol use) has a short-time cycle; at each cycle, RE (used to produce the H₂ needed for the reaction) inserts RE in the energy/chemical system. Over a certain period (20 years, for example) each recycled CO₂ molecule saves CO₂ equivalent emissions corresponding to how many times the cycle is repeated multiplied by the effective energy introduced in the system, after subtracting the energy necessary to perform the cycle. While the effectiveness factor for geological storage of CO₂ is approximately 0.5 (considering the energy to capture and store CO₂), this factor is over 10–20 for CO₂ reuse incorporating RE in the conversion process [93].

— Trading RE through the conversion of CO₂ contributes to energy security, by diversifying the sources and valorizing local production.

— The chemical utilization of CO₂ improves innovation in industry, preserving competitiveness and jobs.

Another key question regards the economic sustainability of the route. Current methanol production from CO₂ and renewable H₂ involves a process based on multiple steps (figure 9).

— Electrical energy can be produced by different routes (hydro, solar, wind, etc.), but we consider here especially hydropower in remote (underexploited or unexploited) areas for the motivations discussed later.

— The (renewable) electrical energy is used in a water electrolyser, preferably operating at high pressure (greater than 30 bars). This is currently the state-of-the-art technology to produce H₂ by electrolysis, but there are fast and interesting developments in solid oxide electrolyser cells (SOECs) [94–96], indicating that this technology is promising for the future. It is also possible to co-electrolyse CO₂ and H₂ to produce syngas, which can be fed directly to a conventional methanol synthesis route [97, 98]. However, costs are still high [98] and a single unit does not produce the necessary H₂/CO ratio for feeding to the methanol unit.

— Renewable H₂ and CO₂ are then fed to a catalytic unit to synthetize methanol. It may be a single unit or two units (RWGS first and then methanol synthesis unit, with intermediate removal of water formed in the first step). By using suitable catalysts and reaction conditions, other chemicals (light olefins) and fuels (DME, methane, higher hydrocarbons or alcohols, etc.) could alternatively be produced.

The concept of using the conversion of CO₂ to methanol to import RE to Europe (as an example) from remote unexploited areas is schematically presented in figure 10. The technology can be
Figure 10. Concept of using the reaction of CO$_2$ conversion to methanol to import RE to Europe (as an example) from remote unexploited areas. (Online version in colour.)

Figure 11. Comparison of the methanol production cost from CO$_2$ and renewable H$_2$ with respect to the conventional production cost from fossil fuels (average cost estimated for Europe, methanol plant capacity of 2400 ton d$^{-1}$; typical fluctuation range in production costs is also indicated). For the production cost using renewable H$_2$ (methanol plant capacity of 2400 ton d$^{-1}$), the variability in production costs depending on the cost of CO$_2$ at site and the electricity consumption for H$_2$ production is also shown. (Elaborated from the data reported in [27].) (Online version in colour.)

considered nearly ready for commercialization, although scale-up aspects in electrolyser have to be solved and improvements in CO$_2$ conversion catalysts and in the stability of the electrolyser, particularly under high-pressure operations, would be necessary [7,27]. In the longer term (approx. 15 years), it will be possible to reduce the number of steps, realizing inverse fuel cells or directly solar fuel cells [37–39,99–101].

A techno-economic evaluation of this possibility [27] showed that methanol can be produced by this route at a cost that is competitive with conventional methanol production from fossil fuels (comparison made for a methanol plant with a capacity of 2400 tons per day, corresponding to one GWh hydropower plant). Figure 11 summarizes some of the key results, as well as some elements of the sensitivity analysis for the production cost using renewable H$_2$ (other elements of
sensitivity analysis and full details on techno-economic estimation are reported in [27]) and the variability in average costs for the production of methanol in Europe from fossil fuels (methane) for a comparable plant capacity. In remote areas, electricity from hydropower plants could be produced at rather low costs, giving rise to low renewable H₂ production cost (on average about 0.140€ Nm⁻³ H₂ with current electrolyser technology). With these costs, it is convenient to produce RM rather than from fossil fuels, enabling a range of applications, from direct use of methanol as a feedstock for the chemical industry (to produce light olefins, for example) to using methanol as an energy carrier for chemical production, in addition to various uses of methanol in transport applications. Edwards and co-workers [102] in collaboration with Lotus Engineering (UK), PARC (Palo Alto, CA), FSK Technology (UK) and GT-Systems (UK) presented a similar concept of methanol as a versatile energy carrier produced by recycling CO₂ and combining it with renewable H₂. They remarked how the synthesis and storage of carbon-neutral liquid fuels offers the possibility of decarbonizing transport without the paradigm shifts required by either electrification of the vehicle fleet or conversion to a hydrogen economy.

A recent study by the Science and Technology Options Assessment of the European Parliament [103] on methanol as a future transport fuel based on H₂ and CO₂ showed

— the benefits in terms of reduced dependence on conventional fossil fuels and lower risks to security of supply for this solution;
— how this solution would be attractive not only for the transport sector but also for other industries;
— how Europe’s increasingly limited and expensive access to fossil fuels makes it obligatory to consider policy options and smart strategies, combining market, regulatory and planning instruments to bring down the direct and indirect costs of alternative fuels, so that transport services remain affordable for citizens and companies during the transition to a less petroleum-dependent economy.

This document evidenced that making methanol from CO₂/renewable H₂ is a key priority for Europe and the need for specific research to enable this route.

(a) Advantages of producing renewable methanol

Methanol from CO₂/rH₂ is a renewable fuel as established by the Renewable Energy Directives of the European Union. We use here the term ‘renewable methanol’ to indicate methanol synthesized from CO₂ and H₂, the latter produced using only RE sources, by either electrolysis or other methodologies (bio-routes, solar thermal, using semiconductor photocatalysts, etc. [39]). While, in principle, the indication ‘renewable methanol’ should also be applied when CO₂ is not derived from fossil sources, we do not apply this restricted interpretation here because, as commented in the previous sections, the true value of converting CO₂ to fuels (methanol, but also other energy vectors such as methane) is not related to the sequestration of CO₂ itself (which is negligible in the case of fuels, because of their short life cycle), but to their enabling effect in introducing more low-carbon energy sources in the energy (or chemical) value chain.

The same conceptual scheme may be used (i) to produce different types of products (either fuels such as hydrocarbons, higher alcohols, DME, or chemicals such as light olefins, etc.) and (ii) to exploit other sources of RE than hydropower (solar, wind, geothermal, etc.). However, we believe that the combination of methanol and hydropower is a better initial choice to develop the technology for the following reasons.

— Methanol, in comparison with other solutions (such as FT hydrocarbons), has the advantage of less complex process technology, higher selectivity and flexibility in use; methanol is compatible with transport back on ships transporting CO₂, thus reducing transport costs; transport costs were included in the cited evaluation of costs of producing RM in remote areas [27].
— RM has a diversified market and use:

(a) it can be mixed (directly or after conversion to DME) with biofuels to reach renewable standards and/or can be used as a raw material to produce various additives for fuels (MTBE, as an example, which can be produced from isobutene and methanol; when both derive from renewable sources—isobutene could be produced from biomass—this is a high octane number component for gasoline; thus a great and boosting synergy with biofuels to meet European Union targets on RE and GHG reduction);

(b) it is a raw material for the process industry; for example, it may be used for producing the building blocks for petrochemical production, e.g. olefins, besides various other uses. In this way, methanol can contribute significantly to reaching low-carbon production targets in this sector, but also has a diversified and higher added value market;

(c) methanol allows a better flexibility in energy management to follow fluctuating energy demand, because, for example, methanol-fuelled turbines have a rapid switch off–on time. Methanol is a superior turbine fuel, with low emissions, excellent heat rate and high power output.

Methanol turbines have been demonstrated on pilot units to have low NOx emissions. For example, GE tested a MS6001B full-scale combustor representative of GE heavy-duty gas turbine combustors and an MS7001 developmental dry low-NOx combustor. The tests demonstrated that methanol fuel can be successfully burned in GE heavy-duty combustors without requiring major modifications to the combustor, and NOx emissions were approximately 20% lower. Other pilot unit tests showed that methanol-fuelled turbines reduce NOx emissions by 30% with respect to using methane as the feedstock [104]. Water content in the methanol provides further NOx reduction.

The use of methanol-fuelled gas turbines allows high efficiencies of over 60% to be obtained (in particular, by using combined cycle systems with/without CO2 capture based on methanol indirect combustion or solid oxide fuel cell combined with a gas turbine (SOFC-GT) hybrid systems [105]) together with recovery of CO2. In this way, an efficient closed-loop system for importing RE from remote areas will be possible.

(b) Potential sources of unexploited renewable energy

There is a large untapped hydropower potential. The global technically exploitable hydropower potential is estimated as approximately 16.4 PWh per year, e.g. over 80% of the unexploited potential [106]. A large part of this potential can be utilized only when effective ways to transport this RE over long distances (more than 500 km) are developed.

There is thus a large potential for increasing hydropower production by constructing dams in various remote areas, when effective technology to transport this RE over long distances is developed. This solution offers the great opportunity to combine a cost-effective increase in generation capacity with the diversification of energy sources and thus better energy security. With respect to alternative RE sources, hydropower shows distinct advantages: (i) it is still the cheapest production of RE on a large scale, (ii) it is a readily available technology, and (iii) it provides nearly a constant supply, while most of alternative RE sources (wind, solar, etc.) are discontinuous. The last aspect means that the fixed costs of the technology for converting electrical energy to chemical energy (methanol), as examined in depth below, can be amortized over the whole year, whereas this is possible for only a fraction of time for discontinuous sources of RE such as wind and solar. This is a key economic element for costs. There are some concerns regarding the environmental impact of hydropower, but there is a general consensus that it is among the cleaner technologies to produce energy.

The exploitation of hydropower untapped sources in remote areas is thus the preferable option in the initial stage of introduction of the proposed technology.
Table 1: Estimation for Europe by 2050 of the potential contribution to the reduction of CO2 emissions by CCS, use of biofuels and CO2/renewable H2 to CH3OH. (Adapted from [27].)

<table>
<thead>
<tr>
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<th>estimated cost per 1 Gton CO2 eq. removed (€)</th>
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<td>60</td>
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<tr>
<td>use of biofuels</td>
<td>700</td>
<td>35</td>
</tr>
<tr>
<td>CO2/rH2 to CH3OH</td>
<td>800</td>
<td>20</td>
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In addition to exploiting unused hydropower resources, deserts and arid regions offer also a large, unexploited potential for large-scale generation of RE (photovoltaics (PV), wind) which can be effectively exploited only when the problem of transporting the produced electrical energy over long distances is solved. The cost of the production of electrical energy by wind and by solar PV panels is rapidly falling and in desert/arid areas, where the density of population and fauna is limited, the impact on the land and environment is reduced. Finally, the conversion of electrical to chemical energy, by synthesizing liquid energy vectors such as methanol, allows the issue of intermittency in energy generation by wind and solar PV panels to be solved. The potential of wind and solar energy production costing less than 50€ MWh⁻¹ (in 2050) was estimated to be over 10 PWh [107].

Assuming that only a part of this potential RE can be exploited, there is still a potential of over 10 PWh yr⁻¹ of electrical energy which can be produced from unexploited renewable sources and whose use can significantly move the chemical industry towards low-carbon production.

(c) Impact on ecosystem and potential contribution to climate change control

Ten petawatt hours per year of electrical energy corresponds to a reduction of approximately 7 Gtons of CO2 equivalent emissions. In order to assess the relevance of this potential contribution to CO2 mitigation strategies, it is necessary to start with the Blue Map Scenario of the International Energy Agency (IEA) [108] for 2050 that CCS will remove about 8 Gtons of CO2. However, the effective contribution (by taking into account the energy requirement for CO2 capture and storage) will be nearly half. The conversion of CO2 to methanol using renewable H2, in order to use unexploited RE sources, will thus have a better impact than CCS in contributing to climate change mitigation.

Table 1 reports the estimate for Europe by 2050 of the potential contribution to the reduction of CO2 emissions [27] by

- CCS (not considering the energy needed for CO2 capture, transport and storage; the effective contribution will thus be lower);
- use of biofuels (average contribution, not considering land change use and other aspects such as intensified GHG emissions due to enhanced use of fertilizers consequent to monocultures);
- importing RE via conversion of CO2 to methanol (CO2/rH2 to CH3OH). In the latter case, this was based on considering 15% of unexploited RE, and includes about 0.2 tons CO2 per ton of avoided CO2 eq. emissions owing to the energy needs for conversion to methanol and transport. The impact avoids CO2 emissions by introducing RE into the energy chain.

Table 1 also compares the estimated cost (in 2050) per 1 Gton CO2 removed in these three cases [27]. The cost for CCS was based on the estimated average cost of capture and storage of CO2, while the cost for biofuels was based on the data from the IEA (Blue Map Scenario) [108] for the incremental costs for biofuels (approx. US$ 330 billion in the high-cost scenario, with oil estimated
at US$ 120 per bbl in 2050). The cost for the $CO_2/rH_2$ to $CH_3OH$ case was based on considering 20€ per ton subsidies (related to avoided carbon taxes) to make the methanol cost equivalent to the fuel projected cost. Table 1 shows that the proposed technology ($CO_2/rH_2$ to $CH_3OH$) is a cost-effective solution for GHG emission reduction and environmentally a more effective path for the following reasons:

- reduced emissions of pollutants (NOx, etc.) and GHG emissions, because the use of unexploited RE sources reduces the need for new power plants as well as for extraction of fossil fuels;
- better diversification of energy resources (with benefits in terms of energy security) and greater flexibility in use (methanol or DME can be used to produce components for the transport sector, for example);
- better flexibility in energy management to follow fluctuating energy demand, because, for example, methanol-fuelled turbines have a rapid switch off–on time. Methanol is considered a superior turbine fuel, with low emissions, excellent heat rate and high power output, as indicated before.

(d) Methanol uses and market perspectives

Methanol serves three key markets: chemicals, transportation and power generation. The dynamics of RM in each of these markets will depend on their respective demand and prices. Market segments that offer an advantage for RM, such as transportation and electricity generation, are more likely to see RM use. An estimated total of approximately 65 million tons of methanol and its derivatives are used annually in the world (in 2013), and China is on track to become the world’s leading methanol market. The chemicals market represents the traditional market of methanol, but energy uses are fast growing. Over one-third of the actual production is for energy use and is rapidly increasing, particularly in Asia. In China, petrol is mixed with methanol (15%) without the need for engines to be redesigned.

The uses of methanol are showing rapid growth, with world demand increasing from approximately 65 Mtons in 2013 to approximately 95 Mtons in 2016, driven by both energy uses and the production of olefins. The operating rate, e.g. plant capacity utilization rate, is expected to increase to approximately 70% (in 2013) to over 80% (in 2016). This indicates that there will be a progressive shortage in supply versus demand, with a consequent increase in the prices, higher in regions such as Europe and China, which are net importers of methanol [109]. Indications for Europe (and also China) are that this deficit of local production will increase in coming years. The net import of methanol in Europe is expected to increase from approximately 4150 to 5250 thousand metric tons between 2011 and 2016 [109]. In addition, the expected trends in average industry spot prices for methanol are significantly increasing in coming years. These results indicate that there exists a need and demand in Europe for an alternative production of RM and the economic perspectives in terms of prices are rather positive.

6. $CO_2$: a suitable C-source to move to a low-carbon chemical production

$CO_2$ has many possible uses to move to a low-carbon chemical production, but there will be a higher impact when basic raw materials (light olefins, syngas; as outlined in figure 2) are produced from $CO_2$.

(a) Syngas production from $CO_2$

Syngas is one of the major base chemicals produced worldwide, with a 2010 capacity of over 70 000 MWth, currently derived as approximately 51% (53 plants) from coal, followed by petroleum (including fuel oil, refinery residue and naphtha) with 25% of total gasification capacity, covering 56 plants [110]. NG provides 22%, with petcoke approximately 1% and
biomass/waste accounting for 0.5%. About 45% of the overall syngas production is used to produce chemicals, while 38% is used for producing liquid fuels. Chemicals are generated at 112 plants and liquid transportation fuels at five plants. Other products are power (11%) and gaseous fuels (6%). There is thus a potential large market for producing syngas from non-fossil fuel resources, in particular CO2.

The catalytic RWGS reaction using rH2 is the main route to produce syngas from CO2. This is a mildly endothermic reaction with enthalpy and free energy changes of $\Delta H_{298K} = 41.2 \text{ kJ mol}^{-1}$ and $\Delta G_{298K} = 28.6 \text{ kJ mol}^{-1}$, respectively. The reaction has been known for over two centuries, but there is still the need to develop improved catalysts, as, for example, iron–chromium catalysts are active at temperatures of 400°C or greater, but at this temperature the equilibrium constant, $K_p$, is low and it is not possible to drive the RWGS reaction to completion. The equilibrium can be shifted to the right by different options:

- Increasing the CO2 concentration to force the complete consumption of H2, then recycling the excess CO2 in the exhaust stream back into the reactor.
- Operating at high H2 concentration to force the complete consumption of the CO2, then recycling the excess H2 back into the reactor.
- Removing water vapour from the reactor, thereby driving the reaction to the right. Such a system could be realized either with a desiccant bed or with a water permeoselective membrane. Various studies have been reported recently on membrane application in FT synthesis reactors [111], where silico-alumina or zeolitic membranes are used for the selective removal of the by-product H2O, which deactivates FT catalysts and inhibits the reaction rate. The same concept could be applied for shifting the equilibrium in a RWGS reaction.

Given that RWGS is a reversible reaction, catalysts active in the direct WGS reaction are also active in the reverse reaction. Different classes of catalysts have been studied for this reaction:

- Copper-based catalysts, particularly CuO/ZnO oxides, modified by alumina, zirconia, titania and/or silica. Cu–ZnO based catalysts suffer from the drawback of being pyrophoric and highly susceptible to poisons.
- Iron-based catalysts, essentially modifications of the commercial high-temperature Fe–Cr catalyst. Iron-based catalysts require reaction temperatures above 400°C and are not suited for RWGS reactions.
- Cerium oxide-based catalysts. Most of the studies on cerium-based catalysts have been focused on noble metals (Pt mainly) supported on cerium. Other catalysts studied include ruthenium and iridium-based catalysts (supported over various oxides), gold-based catalysts (particularly Au/Fe2O3 and Au/TiO2) and nickel-based catalysts (e.g. Ni–Ce(La)Ox).

A review by Polychronopoulou et al. [112] provides an overview of the use of cerium-based catalytic materials with a focus on representative patenting activities in the past 10 years. For the specific use in RWGS reactions, particularly when coupled with integrated methanol production, Cu–ZnO/Al2O3-based catalysts are preferable or Pt or Au supported on CeO2, when a lower temperature activity is needed. Still debate exists about the reaction mechanism in RWGS reactions.

There are other possible routes for producing CO or syngas from CO2 using renewable sources of energy, in addition to the catalytic RWGS using H2 produced from RE sources (solar, wind, hydropower, etc.), although we do not discuss them in detail here:

- thermo-catalytic (solar-assisted) routes, where the Sun is essentially used to produce the heat of reaction necessary for endothermic processes (e.g. CO2 reforming) or to reduce metal oxide materials which are then re-oxidized by CO2;
Another interesting area that is growing in importance is high-temperature (in SOEC devices mentioned earlier) 'co-electrolysis' of CO_2 and steam to produce syngas (CO + H_2). The long-term operation of cells indicates a long lifetime (up to over 10 000–20 000 h [113]). Techno-economic estimations [114] indicate that, although not yet technologically mature, the high-temperature steam/CO_2 co-electrolysis process is a feasible and environmentally benign route. As an energy-intensive process, the availability of cost-effective electricity is crucial for its economic competitiveness. Graves et al. [115] indicated that high-temperature co-electrolysis of H_2O and CO_2 makes very efficient use of electricity and heat (near-100% electricity-to-syngas efficiency, but only when full heat integration is present, a rather difficult practical case), provides high reaction rates, and directly produces syngas (CO/H_2 mixtures) for use in conventional catalytic fuel synthesis reactors. A target for the competitiveness of the process is electricity at 4–5 US cents kWh\(^{-1}\), which is in line with the case discussed for methanol synthesis. SOEC and co-electrolysis are part of the Danish vision to reach a fossil-free economy by 2050.

(b) Light olefins production from CO_2

Light olefins (ethylene and propylene) can be produced from different sources, the main processes being the steam cracking of oil or natural gas fractions, while direct dehydrogenation of alkanes accounts for only a few per cent of the overall production [46]. New process routes include the dehydration of ethanol deriving from biomass fermentation and production via syngas (through the intermediate synthesis of methanol) from coal combustion or biomass pyrolysis/gasification [32]. The use of CO_2 is a new interesting option to produce light olefins, which have been shown to be economically valuable, when renewable H_2 could be produced at low costs, below about US$1–2 per kg [46].

There are different possible routes to produce light olefins from CO_2 and renewable H_2 (figure 12). Being promoted by the same catalysts of further conversion, RWGS is typically present. Direct routes converting CO_2 not involving the intermediate reversible reaction of RWGS
would be preferable to overcome thermodynamic constraints related to this equilibrium reaction.

Light olefins could be directly produced from syngas (CO + H₂), using modified FT catalysts, or indirectly, via the formation of methanol (using conventional commercial methanol catalysts) and then converting methanol to light olefins using the methanol to olefins (MTO) process based on small-pore zeolites. In the presence of an acid catalyst, two methanol molecules could be dehydrated to DME, which can also be converted to light olefins (it is an intermediate in the process).

The methanol catalysts are active also in the RWGS reaction and thus the two steps can be combined, but the water produced in the reaction inhibits the reaction rate and should thus preferably be removed in situ. It is also possible to combine the catalysts for methanol with the zeolite for MTO to have in one step the direct formation of light olefins from CO₂ and H₂.

The route for light olefins from CO₂ + H₂ via syngas and then modified FT catalysts is potentially simpler, but gives rise to a broader distribution of olefins. The route passing through methanol/DME and MTO/MTP processes is more complex, but it is based on already established catalysts/processes, whose economics are interesting for large-scale plants. The use of CO₂ + H₂ instead of syngas causes lower rates and selectivities in both cases. It would thus be necessary to develop novel and specific catalysts. They should be designed to contain selective sites for direct light olefin production by hydrogenation of CO₂.

An interesting route, still largely unexplored, involves the possibility of having a mixed mechanism between that present in methanol synthesis [116], leading to the formation of formate (HCOO) surface species from chemisorbed CO₂ and H, and that for the FT reaction, with a key step of C–C bond formation between the surface formate and ‘C1’ type species deriving from CO dissociation. A similar mechanism was proposed originally by Izumi [117] to explain the selective synthesis of ethanol from CO₂ + H₂ on [Rh₁₀Se]/TiO₂ catalysts. Rh/SiO₂ and Rh–Fe/SiO₂ are active in the hydrogenation of CO₂ to ethanol, although selectivities to ethanol are 30% at best. In CO₂ hydrogenation over supported [Rh₁₀Se] clusters, selectivity up to over 80% was observed, even if the conversion was not given. The ethanol may then be easily dehydrated selectively to form ethylene.

A new route was proposed recently by Ogura [118] based on the electrochemical conversion of CO₂ using Cu electrodes and rather specific conditions involving a three-phase (gas/solution/solid) interface, concentrated solution of potassium halide, low pH and copper or Cu(I) halide-confined metal electrode.

In general, the electrocatalytic reduction of CO₂ is attractive, but productivity is low, selectivity has to be improved (approx. 60% at the best), high potentials (~2.4 V versus Ag/AgCl) are required and stability is to be verified. A necessary condition to exploit electrocatalytic conversion of CO₂ on an industrial scale is to develop higher surface area (three-dimensional type) efficient electrodes. The heterogeneous catalysis approach, even if it also has to be improved, is currently preferable. All catalysts tested are based on catalysts for syngas (CO/H₂) adapted to operate with CO₂ and H₂, but not specifically developed to work with CO₂.

Although further improvements in catalysts, reactor design and process operations are necessary, these results show that it should be possible to modify FT or methanol catalysts to selectively form light olefins, or even develop new types of catalysts based on a novel reaction scheme. It is reasonable to consider a further optimization with a target in selective synthesis of light olefins of over 80% at higher productivity.

7. Conclusion

The utilization of CO₂ as a feedstock for producing chemicals is an interesting challenge to explore new concepts and new opportunities for catalysis and industrial chemistry. It is an excellent possibility to inject RE in the energy or chemical production chains. The latter is a major problem facing the chemical industry to increase its efficiency in the use of resources and energy. However, a major hurdle is the development of cheaper production of renewable H₂ by improving electrocatalysts and device technology in the current electrolysers (and in the long
term, integrating this step in a CO₂ conversion device). When rather cheap electrical energy from renewable sources is available, the use of CO₂ may already be economic.

In terms of the potential for application, the catalytic hydrogenation of CO₂ to methanol appears to have the highest maturity for commercialization. It may be already commercially interesting when cheap sources of renewable H₂ are available or when it may be used to store an excess of electrical energy. It may be estimated that this reaction could reach the industrial stage in less than 5 years. This development would be pushed by experience in pilot or pre-commercial industrial plants, such as the discussed Mitsui plant (pilot in Japan, and large unit expected in Singapore) and methanol plant in Iceland (Carbon Recycling Inc.). Methanol can be used both as a chemical (directly or as an intermediate for other products, including light olefins) and as a fuel (directly, or to produce fuel additives/components).

Many new routes are also explored for activating CO₂ by homogeneous routes, as discussed in §3.4. Although scientifically attractive, none of them appear to be industrially competitive. An alternative route recently proposed for the indirect conversion of CO₂ to methanol is based on the use of Ru pincer complexes as catalysts for the hydrogenation of carbonates, carbamates and formates. Although this reaction shows many attractive features (atom-economy and operates in the absence of solvent with good turnover numbers), the industrial exploitability has to be verified. It has been remarked how productivity rather than turnover is the parameter to consider for industrial exploitability.

There is a lot of interest in the development of new modified FT catalysts for selective light olefins synthesis from CO₂, preferably directly and not through the intermediate CO formation. The main scientific issue is related to the fact that the systems investigated are mainly modifications of conventional FT catalysts, rather than novel systems as probably required. The role of CO₂ in FT reactions remains contradictory. Hybrid FT–zeolite catalysts appear to be an interesting possibility, but they are still not being developed on a scientific basis. Yields of over 55% in C₂–C₄ olefins are possible, but they need to be further increased (more than 75–80%) [32] to exploit the process.

Significant advances in the co-polymerization of CO₂ with epoxides to form cyclic and/or polycarbonates or polyoils have been made. Various companies are exploring this route, which appears to be close to commercialization. This route is interesting in terms of new materials characteristics rather than in terms of its effective contribution to reducing GHG emissions.

Urea production is well established on a large scale, but there are further opportunities to improve it. Commercial applications of CO₂ conversion call for eco-sustainable synthesis of some useful substituted ureas, carbamate and isocyanate in order to substitute toxic reagents. It is evident that the key to CO₂ conversion is the activation of either CO₂ or co-reactants, under as mild conditions as possible. Reactions with poor catalytic performance and/or those that take place under severe conditions, such as isocyanate production from CO₂, need to be improved.

Electrocatalysis is offering new possibilities, either to produce small organic molecules to be used in conjunction with or integrated into solar devices or as a valuable synthetic procedure. There is the need to go beyond the conventional metal-type electrodes operating in the liquid phase. Gas-phase operations or liquid phase in the presence of molecular catalysts (such as pyridinium ions) are two promising directions to form either methanol or even long-chain alcohols, but scientific effort in these areas is still too limited. The use of non-conventional electrolytes, such as ionic liquids, is another attractive direction. Electrocatalytic carbonylation is also an interesting possibility, but further effort is necessary.

Many interesting bio-catalytic routes using CO₂ are also under development at an industrial scale, such as acetone production (Evonik), bio-succinic acid from glucose and CO₂ (many companies), longer chain alcohols (Mitsubischi Chem.) and modification of syngas fermentation processes to start from CO₂. Interesting developments are also in the area of hybrid enzyme–photocatalysts.

The concept of artificial photosynthesis or leaves must be cited among the long-term perspectives of CO₂ utilization. Although often used to discuss only the formation of H₂ by water splitting or analogous approaches, there is an emerging interest in the possibility of realizing
more advanced devices, which instead use photochemical water oxidation (generating protons and electrons, together with \( \text{O}_2 \)) to drive the electrocatalytic reduction of \( \text{CO}_2 \) to chemicals or fuels [36–38]. To focus discussion we have not discussed these aspects here, as they are already covered to a good extent in the cited reviews.

Often the approach above is confused with the photochemical reduction of \( \text{CO}_2 \), which was also not discussed here, but for different motivations. There is an increasing research interest in this topic [119–122]. The prospect of reaching the productivity necessary for a possible exploitation of this technology is quite low. To reach a higher level of productivity, it is not only a matter of developing better photocatalysts but also of using a different approach. It is necessary first to physically separate the reaction zone of \( \text{CO}_2 \) reduction from that of \( \text{O}_2 \) evolution (from water photo-conversion), otherwise \( \text{CO}_2 \) and the products of \( \text{CO}_2 \) reduction will compete and quench the latter reaction. In addition, it is necessary to operate under conditions where the recovery of the products is easy, at least requiring less energy than that incorporated in the products of \( \text{CO}_2 \) reduction. For these reasons, we have omitted to discuss the photocatalytic reduction of \( \text{CO}_2 \), because we do not believe that it is a relevant path to move to a resource- and energy-efficient chemical and fuel production.

This review has given a glimpse into the various novel possibilities that we believe will have a role in the future scenario for chemical and energy sustainable production. The aim was not a systematic survey, but rather to evidence how the use of \( \text{CO}_2 \) will be a critical enabling element for the sustainable future of chemical production. For this reason, a large part of the discussion was dedicated to analysing the technological roadmap for \( \text{CO}_2 \) chemical utilization and related aspects: (i) how to assess the different routes for \( \text{CO}_2 \) utilization, (ii) the critical question of the perception of the role of \( \text{CO}_2 \) utilization paths in the future of society, and (iii) a brief analysis of emerging patent areas in relation to the technology roadmap.

The introduction of RE in the chemical production chain through \( \text{CO}_2 \) utilization is a key element to move the chemical industry towards low-carbon production. For this reason, a relevant part of this review was dedicated to analysing this question and related aspects: (i) production of RM and (ii) its impact on the ecosystem and climate change control. We have discussed how the impact on GHG emissions will be large, and potentially not less than that expected from CCS technologies or the use of biofuels, but with significantly lower costs [27].

The discussion has also provided evidence of on how \( \text{CO}_2 \) utilization contributes to solving some of the grand challenges facing our society: (i) mitigating climate change, (ii) preserving the environment, (iii) using RE, and (iv) replacing fossil fuels. In tight integration with the use of biomass, the use of \( \text{CO}_2 \) provides a new sustainable scenario for chemical production [31–33] and moves biorefineries to biofactories [34,35]. In a longer term visionary idea, it is possible to create a \( \text{CO}_2 \) economy where it will be possible to achieve full circle recycling of \( \text{CO}_2 \) using RE sources, similar to how plants photosynthetically convert \( \text{CO}_2 \) to carbohydrates and \( \text{O}_2 \), but with an intensified process and the capacity to control the type of products formed [36–39].

There are thus many stimulating possibilities offered by using \( \text{CO}_2 \) and this review shows this new vision on \( \text{CO}_2 \) at the industrial, societal and scientific levels, but with some examples evidencing how \( \text{CO}_2 \) conversion will be at the core of the future of the chemical industry.

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References


17. Aresta M. 2010 CO\textsubscript{2} as chemical feedstock. Weinheim, Germany: Wiley-VCH.


43. Valencia RC. 2013 The future of the chemical industry by 2050. Weinheim, Germany: Wiley-VCH.


79. Dechema. 2009 Commercial biomass syngas fermentation. Frankfurt am Main, Germany: Verband der Chemischen Industrie e.V.
80. Dechema/IEA/ICCA. 2013 Technology roadmap ‘energy and GHG reductions in the chemical industry via catalytic processes’. Frankfurt am Main, Germany: Dechema.
83. Styring P. 2013 Carbon dioxide utilization off-setting the costs of CCS and providing a route to renewable energy storage. Presented at ‘CO₂ reuse workshop’ organized by DG Clima and DG JRC, 7 June 2013, Brussels, Belgium.
89. J. van Santen RA. 2009 Catalysis for renewables: from feedstock to energy production. Weinheim, Germany: Wiley-VCH.


**Glossary**

CH₃OH methanol  
CODH carbon monoxide dehydrogenase  
CCS carbon capture and storage  
CO₂ carbon dioxide  
CRI Carbon Recycling International  
DME dimethyl ether  
DNV Det Norske Veritas Inc.  
EOR enhanced oil recovery  
EU European Union  
FT Fischer–Tropsch  
GE General Electric  
GHG greenhouse gas  
Gton giga tons  
GWh giga watts per hour  
IPCC Intergovernmental Panel on Climate Change  
LCA life cycle analysis  
MTBE methyl tert-butyl ether  
Mton million tons  
MWth megawatt thermal  
NG natural gas  
P₂G power to gas  
PV photovoltaic  
RE renewable energy  
R&D research and development  
RM renewable methanol  
RWGS reverse water gas shift  
SOEC solid oxide electrolyser cell  
SPIRE Sustainable Process Industry through Resource and Energy Efficiency, a European Public–Private Partnership  
UCLA University of California, Los Angeles  
USPTO United States Patent and Trademark Office  
WGS water gas shift