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Carbon Dioxide Recycling: Emerging Large-Scale Technologies with Industrial Potential

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This Review introduces this special issue of ChemSusChem dedicated to CO_2 recycling. Its aim is to offer an up-to-date overview of CO_2 chemical utilization (inorganic mineralization, organic carboxylation, reduction reactions, and biochemical conversion), as a continuation and extension of earlier books and reviews on this topic, but with a specific focus on large-volume routes and projects/pilot plants that are currently emerging at (pre-)industrial level. The Review also highlights how some of these routes will offer a valuable opportunity to introduce renewable energy into the existing energy and chemical infrastructure (i.e., "drop-in" renewable energy) by synthesis of chemicals from CO_2 that are easy to transport and store. CO_2 conversion therefore has the potential to become a key pillar of the sustainable and resource-efficient production of chemicals and energy from renewables.

1. Introduction

Nowadays, CO_2 recycling is under increased scrutiny as one of the possible contributions to CO_2 mitigation and as an opportunity to use a low-cost (or even negative-cost, when considering taxes on emissions) carbon source. When looking at the quantities of anthropogenic energy-related CO_2 emissions reported by the International Energy Agency (i.e., 28.8 Gt for 2007, which is expected to grow to 40.3 Gt by 2030 in its reference scenario[1] and to 50 Gt by 2050 in the absence of curbing actions) and comparing these amounts to the current largest CO_2-based chemical production process (urea, derived from CO_2 and NH_3, had a world production of 0.15 Gt in 2008), a clear mismatch in the scales involved can be seen. However, this is not the right way to consider the contribution of CO_2 recycling to greenhouse gas (GHG) emission control for a number of reasons:

- to limit the growth of the CO_2 concentration in the troposphere it is necessary to address only that fraction of the global carbon cycle that cannot be closed by natural cycles;
- in all scenarios developed to address GHG emissions, a portfolio of technologies is always necessary;
- CO_2 recycling introduces a shorter path (in terms of time) to close the carbon cycle compared to natural cycles and/or an additional way to store CO_2 in materials with a long life-time; in addition, it is a way to store renewable energy sources and/or use an alternative carbon source to fossil fuels, as discussed later; all these factors indicate that the net effect of recycling CO_2 is not simple, as in storage options, but multilevel;
- CO_2 recycling produces valuable products that can be marketed and thus add economic incentives to the reduction of CO_2 emissions, while options such as storage only add costs;
- all future scenarios to address GHG emissions include the contribution of carbon capture and storage (CCS) technologies to meet the target levels for the CO_2 concentration in the troposphere;[1] CO_2 recycling [i.e., carbon capture and recycling (CCR)] avoids the costs associated with transporting CO_2 (a critical factor: up to about 35–40% of the total cost when the capture site is more than ca. 100–150 km away from the storage site, a common situation in, for example, many countries in Europe). CCR is thus an economically valuable alternative in these cases.

Recycling of CO_2 is therefore a possible contributor, together with other technologies, to a solution for the global issue of GHG emissions, but has only started to be considered in detail in recent years. This Review article, which introduces this issue of *ChemSusChem* dedicated to CO_2 recycling, surveys this field with a general discussion on the emerging large-scale technologies around CO_2 recycling with industrial potential.

The industrial, large-volume conversion of CO_2 into added-value chemicals is well-established:[2,3]

- urea production from CO_2 amounted to 146 Mt in 2008 (International Fertilizer Industry Association);
- about 5 Mt of methanol were produced from CO_2 during CO hydrogenation in 2007[4];
- about 170 kTa^{-1} of salicylic acid, a pharmaceutical ingredient derived from sodium salicylate that is synthesized from sodium phenoxide and CO_2 at high pressure and temperature in the Kolbe–Schmitt reaction, are produced worldwide.

Options for directly using CO_2, without transformation, also exist. These take advantage of its physico-chemical properties, for example by using it as refrigerant or in enhanced oil recovery (EOR).

Some of these industrial processes utilizing CO_2 have market growth potential, as will be discussed later; others, despite having a long history like the 19th-century Kolbe–Schmitt process, are not expected to grow to the large volumes necessary to contribute significantly to the current challenge of CO_2 recycling. In this context of already established million-ton chemistries, novel needs and opportunities for CO_2 conversion are appearing, and will further grow in the next decades.

Due in part to societal pressure, but also to the need of saving energy and costs on emissions, there is a definite trend in recent years in the chemical and process industry to raise

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the issue of energy and CO_2 emissions to status of key priority.[5] A resource-efficient Europe is the flagship initiative of the Europe 2020 Strategy,[6] with the CO_2 emissions control issue as its backbone activity. The increasing support on climate-safer actions, the possibility of an increasing carbon-taxation and an overall possibility of tapping into CO_2 as a zero- or even negative-cost chemical feedstock are indeed attracting increasing attention for existing or novel emerging routes for chemical utilization of CO_2.

A market price for CO_2 at about 60 to 450 US$ per ton for a market of about 2.7 billion US$ per year, combined with a CCS (carbon capture and storage) potential estimated at $3.6\,\mathrm{Gt\,a^{-1}}$[7] means that CO_2 might become more and more available. At the same time carbon capture and recycling (CCR) is also under strong scrutiny. The risk of emitting more CO_2 in CCR than the amount actually recycled is an identified pitfall, and explains the necessity of renewable (e.g., solar, geothermal, wind) or decarbonated (e.g., nuclear) energy sources. The scope of this Review is to provide an update that integrates with previous books and Reviews on this topic,[3,4,8–21] but focuses on the large-volume routes and the projects/pilot plants for CO_2 chemical utilization that are currently emerging at the industrial or pre-industrial level. Where possible, the quantities that could potentially be used by the proposed routes will be stated. Reference to the life-cycle analysis (LCA) of the overall process,[22] to supply chain management (SCM), or to the carbon footprint of the potential route will be less systematic, although desirable, given the scarcity of public data, which remains an important point to be treated in techno-economic assessments (see Conclusion).

The lifetime of the products of CO_2 conversion is another important aspect. The IPCC report on CO_2 capture and storage[23] selected as a crucial parameter the time lapse between the moment of CO_2 conversion into a product and CO_2 release back into the atmosphere. A long lifetime of the CO_2-based product will fix the molecule for a long time, thus preventing its (re-)release into the atmosphere. Most product lifetimes range between several months and a few years, with the exception of inorganic carbonates and polymers based on organic carbonates that store CO_2 from decades to centuries. However, this approach focused on product lifetime is strictly necessary only from a pure storage perspective, while products

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deriving from recycled CO_2 will substitute for other products that are often derived from fossil fuels (i.e., there are direct and indirect effects on CO_2 emissions); their use can allow an energy saving (for example, foams produced from CO_2-based polymers may be used for a better thermal insulation of buildings). In addition, the energy use (and associated CO_2 emissions) of the CCR and CCS processes has to be considered. From this perspective CCR can be viewed as a way to introduce renewable energy into the chemical and energy chain,[15] by storing solar, geothermal, wind, or other energies in chemical form. The resulting chemical facilitates storage and transport of energy, and is particularly important if it is compatible with the existing energy infrastructure and/or can be easily integrated into the existing chemical chain. Therefore, recycling CO_2 is an opportunity to limit the use and drawbacks of fossil fuels, while avoiding the high costs (including energy) associated with a change in the current energy and chemical chain. In considering CO_2 recycling (CCR), the effect is thus not only direct, that is, subtraction of CO_2 from emissions as for CCS, but a combination of direct and indirect effects that amplifies the impact. Therefore, a quantitative estimation of the potential contribution of CCR technologies to GHG emissions requires new approaches, based on extended LCA. Reliable analyses from this perspective are still not available, but it is clear that more complex approaches have to be used in CCR compared to those used for CCS.

In the end, CO_2 finds utilization when there is a profitable cost/benefit trade-off linked to CO_2 (re)using in place of the existing technology, regardless of any considerations linked to capture and storage policies. However, the problem of CO_2 (re)use cannot be limited to an economic opportunity, since the energy and chemical infrastructures are so tightly interconnected and diffused throughout society. New methodologies to approach the issue are necessary to fully understand the real benefit of CCR compared to CCS approaches.

Several position papers by large funding bodies provide converging indications on the momentum building up around the topic of CO_2 utilization. Asian actors such as Japanese and Korean funding bodies and private investors have been involved in CO_2 utilization early on, as indicated for "Project for Chemical CO_2 Fixation & Utilization" (1990–1999) in Japan supported by NEDO/RITE. The 2009 paper "Utilization and Storage of CO_2"[26] by Germany's DECHEMA identified five options (polymer, fuel, chemical, microalgae, and artificial photosynthesis) and listed their stage of development and potential maximum quantities of CO_2 stored, ranging from ca. 200 $Mt\,a^{-1}$ for chemicals to about 2 $Gt\,a^{-1}$ for fuels. In 2010, the French ADEME agency commissioned an assessment on the development stage of different CO_2 valorization options. Out of the 12 identified routes, 10 can be related to chemical utilizations and several present a very significant potential for both using very large amounts of CO_2 and becoming economically profitable.[27] Figure 1 is a radar chart of the 12 different routes identified, organized according to the time-scale of application.

In this survey, the emerging large-scale CO_2 conversion routes have been organized into four main headings: inorganic mineralization, organic carboxylation, reduction reactions related to syngas formation, and biochemical conversion.

On top of the overarching mineral/organic/biochemical separation, we adopted a further subdivision among the organic reactions involved for the conversion of CO_2: on one side, reactions incorporating the whole CO_2 moiety in organic backbones, termed organic carboxylation reactions, which yield –COOR (carboxylates, esters, lactones), –N–COOR (carbamates), –NCO (isocyanates or ureas), and –RO–CO–OR (carbonates), …; on the other side, reactions incorporating only a fragment of the CO_2 substrate to other C1 (CO, CH_3OH) or C*n* molecules, termed reduction reactions. This subdivision is crucial in terms of energy balance and the applications of ensuing products. Carboxylation reactions (both organic and inorganic) are generally not energy-intensive, because they imply transfer of the whole molecule (this does not exclude the connected process to be energy consuming, e.g. grinding of the ore in mineral carbonation,…). Reduction reactions are energy-intensive, since they imply C–O cleavage by reducing agents (typically hydrogen sources, for example H_2). Therefore, the energy source—particularly in the present context of CO_2 management the need for renewable ones—is crucial for this latter class of organic reactions. The involvement of energy sources makes the molecules belonging to this class "CO_2-issued energy-storage molecules". They are related to the fuel markets, and more specifically to the concept of CO_2-based energy vectors for the storage of solar energy or other renewable energy sources.[14,15] Conversely, the first class of molecules, and their inorganic counterparts such as carbonates, do not find application in fuel synthesis but yield stable materials and become relevant in carbon management strategies for ensuring long-term storage.

Non-chemical industrial usages of CO_2 (e.g., as refrigerant, gasifier, EOR, extraction and reaction medium),[25] even though they represent sizeable markets (20 $Mt\,a^{-1}$) and some of them, such as EOR or the use of supercritical CO_2 as solvent, also have good market growth perspectives, will not be treated here, because the focus is on the chemical transformation of CO_2. Each section discusses emerging markets or related marketable chemicals, growth outlooks, and main technical issues, including those related to sustainability (LCA, carbon footprint and impact on the environmental), with overall 26 identified items.

2. Mineralization

2.1. Preliminary considerations

The cement industry is one of the largest CO_2 emitters. Around 3 billion tons of Portland cement are produced every year. Very coarsely, the very large CO_2 footprint (1 ton of CO_2 per ton of cement produced) is explained by the large fossil fuel consumption necessary to reach the ca. 1400 °C required for roasting, the first step of the process (Scheme 1). The roasting step also emits 1 mol of CO_2 per mole of carbonate converted to quicklime. Quicklime (CaO) is the main ingredient of cement. In total, cement production accounts for roughly 5%

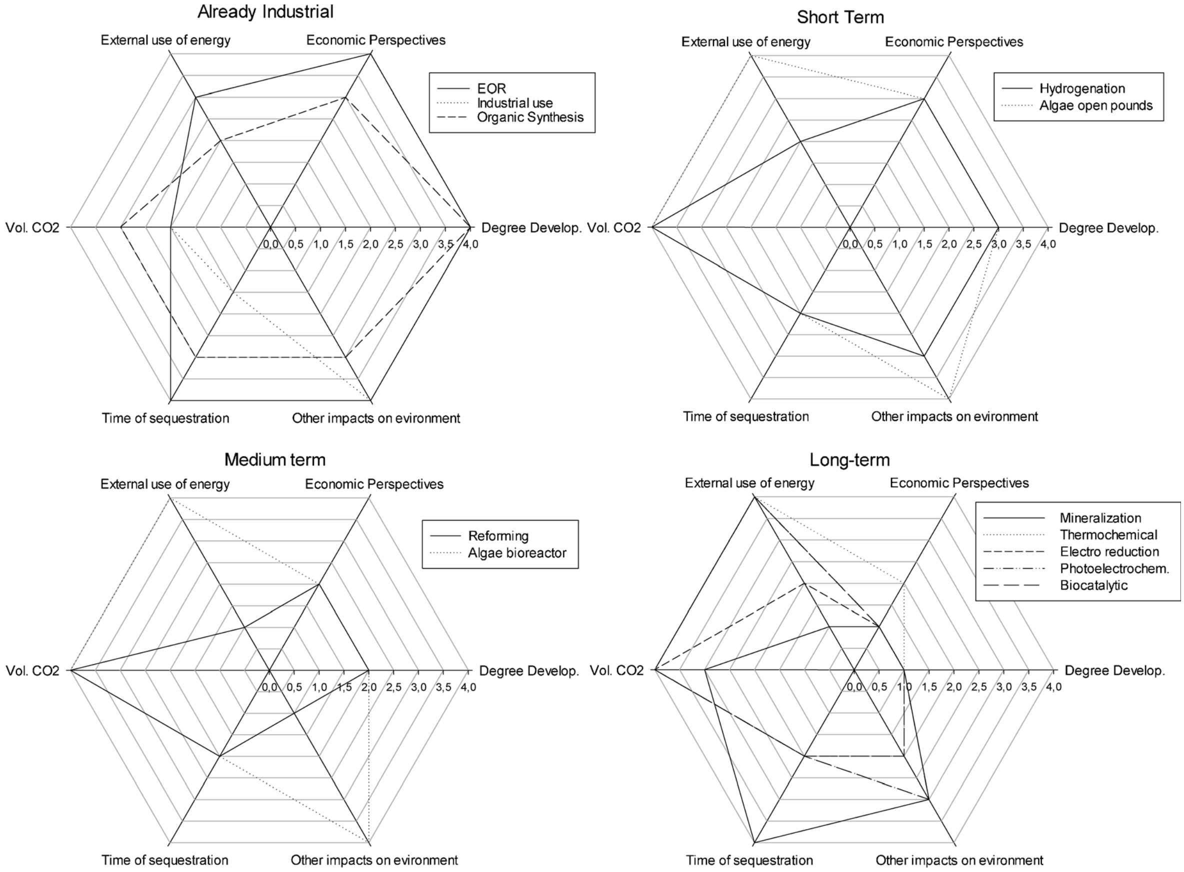
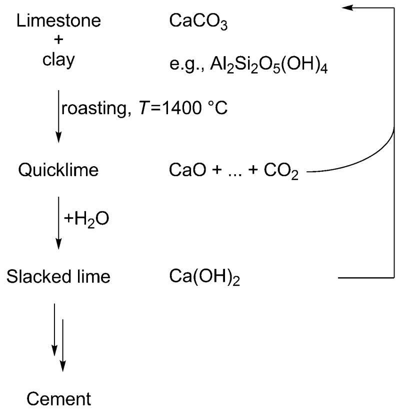


Figure 1. Summary of the different options for CO_2 the valorization. Data taken from Ref. [27]. Notes: *Necessary timeframe for development*: **1** More than 10 years → **4** Industrial; *Economic Perspectives*: **1** Difficult to estimate→**4** Available industrial data; *External use of energy*: **1** Difficult to decrease→**4** No need; *Volume CO_2 (potential)*: **1** Less than 10 Mt→**4** More than 500 Mt; *Time of sequestration*: **1** Very short→**4** Long term; *Undesirable impacts on environment (utilization of solvents, utilization or production of toxic or metallic compounds, utilization of scarce resources)*: **1** Significant→**4** Low.



Scheme 1. Simplified scheme of the cement manufacturing process.

of all anthropogenic CO_2 emissions. Some of the emitted CO_2 can be recovered by carbonation [see Equation (1a), M = Ca, Mg, ...).

$$M(OH)_2 + CO_2 \rightarrow MCO_3 + H_2O \qquad (1a)$$

When performed with slacked lime, a product associated with the cement industry, limestone can be regenerated and re-enter the production lines (see Scheme 1) with questionable marks in terms of carbon management. Precipitation with other cation-rich solutions would lead to commercial products such as $MgCO_3$ that can potentially be used as building materials or for road paving, but compliance with sector standards is not trivial.

The use of industrial residues rich in magnesium or calcium (or even iron), such as steel and blast furnace slags, cement kiln dust, fly ashes, municipal waste incineration ash, mining wastes, asbestos, coming from several industry sectors (e.g., iron and steel making, cement, incinerations, power production, the paper industry, the mining industry) for the synthesis of carbonates from emitted CO_2 allows to compound CO_2 emission reduction with improved waste disposal circuits in some industries and, most importantly, with production of potentially commercial materials. A CO_2 fixation potential of 60–170 $Mt\,a^{-1}$ was calculated based on a recent estimate of worldwide iron- and steel-making slag production of 315–400 $Mt\,a^{-1}$,[28] although the actual large-scale deployment of this technology is not foreseen in the next decade. A credible estimate of the percentage of commercial products issued form waste carbonation is also difficult. The most advanced industrial examples of CO_2 incorporation to inorganic materials are discussed in the following sections.

2.2. Commercial precipitated carbonates and bicarbonates

Calcium carbonate is a key product, for example of the Solvay process for production of Na_2CO_3 and $NaHCO_3$ (45 $Mt\,a^{-1}$), and can be mined as limestone. An extensive market exists also for synthetic or precipitated calcium carbonate (PPC) for applications in the paper industry, plastics, rubber and paint products, with an estimated global market of more than 15 $Mt\,a^{-1}$.[29]

Skyonic's patented CO_2 mineralization process Skymine,[30] the first for-profit system converting flue gas CO_2 into bicarbonate (baking soda) as main commercial product, was awarded a grant of 25 million US$ by the US Department of Energy (DoE) in 2010, to support the industrialization of this carbon capture technology that can be retrofitted to existing plant infrastructures. In addition to this CCS mineralization process, the DoE also supported mineralization for CCR by granting Alcoa Inc., a leading producer of aluminum, 12 million US$ for upscaling a CO_2-into-construction-fill-material process to pilot-plant scale. Alcoa recently reiterated its commitment to this technology based both on the use of a carbonic anhydrase enzyme and a flue scrubber, and further transforming the resulting carbonate into a useful construction material by reaction with alkaline clay, a bauxite residue of the aluminum refining industry.[31] DoE's share increased to 13.5 million US$ through the National Energy Technology Laboratory (NETL) award. The commercial destination of the "new, useful products" was recently rephrased as toward "environmental reclamation projects".

The Calera project, also selected in the same 2010 funding act (DoE share 20 million US$), clearly stated the commercial destination of its mineral end-products as building materials, such as carbonate-containing aggregates or supplementary cement-like materials (SCM, cements and clinkers, that can be mixed with cement up to 5%). Inspired by the biogenesis of coral reef, the heart of the technology coarsely consisted of precipitating captured CO_2 as novel (meta)-stable carbonates and bicarbonates with magnesium- and calcium-rich brines [see Equations (1)]; the CO_2 would originate from captured flue gas—from fuel combustion or other large plants—and the brine from seawater or alkaline industrial waste sources.[32]

$$CO_2 + Mg^{2+} + 2\,OH^- \rightarrow MgCO_3 + H_2O \tag{1b}$$

$$CO_2 + Ca^{2+} + 2\,OH^- \rightarrow CaCO_3 + H_2O \tag{1c}$$

The CO_2 capture step from flue gas is termed Mineralization via Aqueous Precipitation (MAP). Later developments led to the integration of an electrochemical step if the alkalinity of the system is not sufficient for precipitation of carbonates. The Calera's 10 MW demonstration unit in Moss Landing, CA (USA) was followed by an Australian government-supported demonstration project,[33] with additional funding of 40 million AUS$ in Latrobe Valley, VIC (Australia), where the Yallourn power station (ca. 1 MW) furnished the CO_2 to be captured. Since the available brines proved quantitatively and qualitatively unsuitable, Calera suspended the Latrobe Valley project in late 2010.[34] The lack of new incentive legislation on carbon prices was also given as part of the explanation for the suspension of the project and to the proposal for an alternative project. The process has been critically assessed both in terms of global energy balance and the quality of the product obtained.[27] A cost analysis of the technology showed that the cost of the end-products was critically dependent on, amongst others, the alkalinity sources. The carbon capture part of the Calera process resulted cost-competitive.[35] Likewise, balance of the carbon emissions appeared favorable for the first stage of the process, while the second stage of processing, which included the drying step of the calceous material to the final SCM, could revert to unfavorable carbon-footprint values.[34] Deployment of the technology closer to sites with adequate starting materials, with market drivers such a need for cementitious materials and/or partly desalinized water (one of the side effects of the technology) may make this CO_2 utilization route attractive. The salt-enriched concentrate can be utilized to produce NaOH and HCl.

Building materials and other products issued from electrochemically capturing CO_2 were also proposed by New Sky Energy [Boulder, CO (USA)]; a company that indicates itself as the first carbon-negative energy and manufacturing company.[36] In March 2010 it announced the start of an integrated drainage water treatment facility in California's Central Valley that will desalinate approximately 240 000 gallons of high-salinity water per day, and convert approximately five tons of waste brine salts into chemicals such as acid, caustic soda, and solid carbonates such as limestone and soda ash. These solids can in turn be incorporated into building materials, durable goods, fertilizers, and other manufactured products. In addition, the project is said to trap approximately 2.8 t of CO_2 daily and furnish fresh water for irrigation.

Another interesting approach is the concrete curing process, that limits heat and steam of precast concrete products, and consumes CO_2, bubbled through wet cement and sequestered as carbonate. Concrete Curing Carbon Sense Solutions is partnering with Air Liquide, the Shaw Group in Nova Scotia (Canada), and the Government of Nova Scotia to demonstrate and optimize this process. Several other companies are heavily investing in the greener cement and/or carbon capture materials. Because some of these efforts are more pertinent to CCS, no further details will be discussed here.

2.3. Carbonates from minerals

Mineral carbonation, that is, the formation of carbonate from naturally occurring minerals such as silicate-rich olivine and serpentine, is an already well-recognized carbon storage option.[37] While the in situ process is mainly used for geological storage, the ex situ mineral carbonation has been investigated in several CCR R&D projects. For example, the Energy Technologies Institute (ETI, hosted by the Midlands Energy Consortium of Birmingham, Loughborough and Nottingham Universities) is running a 1 billion GBP public–private partnership (i.e., a partnership between the British government and BP, Caterpillar, EDF, E.ON, Rolls-Royce, and Shell) to explore this route as an additional method for CO_2 sequestration. Last year the ETI announced 15 projects worth over 53 million GBP, among which studies on the viability of CCS and the economic benefits of CO_2 mineralization. The technology is proposed as an alternative to CCS when CO_2 storage sites are far from the CO_2 source (more than about 100 miles) but several problems remain, such as: (i) the process is slow and energy-demanding (grinding, dissolution),[38,39] leading to unfavorable energy balances; (ii) the transportation of solid reactant/products is not avoided; (iii) the cost (energetic and economic) associated with mining the minerals to be reacted with CO_2 remains high; (iv) the social/environmental impact of the mining activities associated with the process is critical.[27]

Some allotropes of the most prominent minerals suitable for the mineralization of CO_2, such as olivine [$(MgFe)_2SiO_4$], serpentine [$Mg_3Si_2O_5(OH)_4$], wollastonite ($CaSiO_3$), are picking up momentum as reacting minerals for the production of valuable products, and industrial applications are therefore emerging even in this unfavorable context.

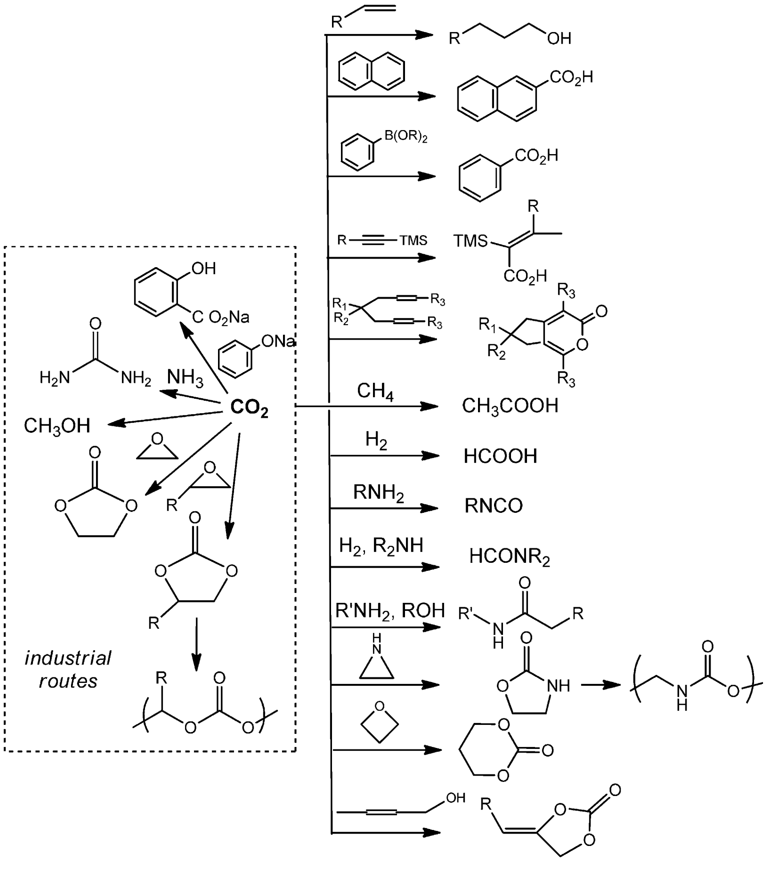


Figure 2. A summary of organic chemicals produced from CO_2. Elaborated from Ref. [40].

The company Novacem, founded in 2007 as a spin-off of Imperial College, London (UK), is developing a substitute for Portland cement not based on CO_2-emitting limestone technology, but on CO_2-absorbing magnesium silicates carbonation routes [see Equation (2) for a possible carbonation route of one of the lizardite components of serpentine]. With funding exceeding 1.5 million US$ from the Royal Society and others, and in partnership with the largest private British construction company (Laing O'Rourke), Novacem will test a pilot-plant-scale process in 2011.

$$Mg_3Si_2O_5(OH)_4 \rightarrow MgO + H_2O + SiO_2 \tag{2a}$$

$$MgO + CO_2 \rightarrow MgCO_3 \tag{2b}$$

In conclusion, these few emerging routes for CO_2 inorganic mineralization have the potential to tap into the gigaton volumes commonplace in the cement industry. However, in terms of access to marketable products, these routes to CO_2 recycling are thwarted by the very low costs of the competing materials (e.g., limestone) and adherence to standards in the construction sector. The cement industry is very conservative and it is extremely difficult to launch new products that have not proven themselves in long-term trials.

3. Organic Carboxylation Reactions

The synthetic routes from CO_2 to organic compounds that contain three or more carbon atoms number in the tens, as recently reviewed,[3,9,40–45] but only five are earmarked as industrialized. Figure 2 is an overview of some of the possible organic chemicals produced from CO_2. This section will review the organic compounds deriving from a full incorporation of the CO_2 moiety (or CO–N possibly formed by energy-facile ammonolysis) that are at an industrial or pre-industrial level of development.

3.1. Urea

The synthesis of urea (NH_2CONH_2) is the largest-volume industrial example of converting CO_2 into value-added products [Equations (3)].[46,47]

$$2\,NH_3 + CO_2 \rightarrow [H_2N\text{-}COO][NH_4] \tag{3a}$$

$$[H_2N\text{-}COO][NH_4] \rightarrow NH_2CONH_2 + H_2O \tag{3b}$$

The >100 Mt of urea produced worldwide yearly[4] is used for fertilizers and polymer synthesis, such as melamine and urea-formaldehyde resins, and in deNO$_x$ applications for diesel-engine vehicles.[46] Among the various technologies in use, the ammonia stripping (Snamprogetti) and CO_2 stripping (Stamicarbon) processes share approximately 70% of the world market,[48] while the "advanced process for cost and energy saving urea production" (ACES) from Toyo Engineering Corp. (TEP).[49] Several advancements in the urea process have been described in recent patents,[50] reporting increased CO_2 conversion and improved overall thermal efficiency with specific energy consumption reduction[51] that can be retrofitted to existing plants.

3.2. Acrylates, lactones, and carboxylic acids

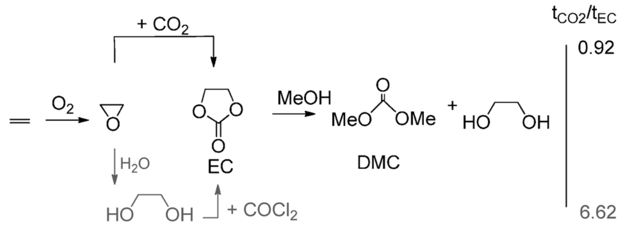
Sodium acrylate is a key basic intermediate for the large market of polyacrylates ($>25\,\mathrm{Mt\,a^{-1}}$); the super-absorbents used in diapers. A 39 million € project based at the Catalysis Research Laboratory (CarLA) sponsored by BASF (also via the AG), the Federal Ministry of Education and Research (BMBF), The Technische Universität München (TUM), and the Universität Stuttgart, is aimed at the conversion of CO_2 to acrylic acid via a reaction with ethene:[52]

$$H_2C{=}CH_2 + CO_2 \rightarrow H_2C{=}CH{-}COOH \tag{4}$$

Several catalytic pathways, some of them including nickel lactones, are known for syntheses of acrylic acid and derivatives thereof from ethylene and CO_2.[53–55] Although long-chain carboxylic acids and carbamates are amenable to a similar synthetic route and find use in different industrial sectors (e.g., solvents, pharmaceuticals, surfactants, cosmetics)[56,57] with some existing markets (e.g., currently $10\,\mathrm{Mt\,a^{-1}}$ for long-chain carboxylic acids) and well-established chemistry in some cases,[58] only very few demonstration-level developments have been reported. An exception is a pilot plant for the selective synthesis of lactones,[59] tailored towards the fragrance market.

3.3. Monomeric carbonates

Carbonates are becoming industrially viable alternatives to toxic phosgene ($COCl_2$, a toxic species with a world market larger than $8\,\mathrm{Mt\,a^{-1}}$)[60] through what has been termed the "green carbonyl route".[61] For example, carbonation of the ethylene oxide (Scheme 2) as opposed to phosgenation of ethylene glycol for ethylene carbonate (EC) synthesis is both a less toxic route and reduces CO_2 emissions seven-fold (0.92 t per ton vs. 6.62 t per ton).[4] Reaction of CO_2 with oxetanes (1,3-propylene oxide) rather than oxiranes (ethylene oxide derivatives) leads to six-membered carbonates. The high selectivity and yields of the cyclization reactions from CO_2 and oxiranes have allowed industrialization.



Scheme 2. Comparison of DMC synthesis routes with either CO_2 or phosgene, and corresponding carbon footprints. Adapted from Ref. [4].

The resulting EC is a marketable product by itself, finding use as organic solvent in pharmaceutical and cosmetic preparations and as electrolyte in lithium-ion batteries. The transterification of the resulting cyclic carbonate with methanol (Scheme 2) to dimethyl carbonate (DMC) is a relevant route to produce DMC and dry ethylene glycol. Current DMC production is about $0.5\,\mathrm{Mt\,a^{-1}}$. Its potential as fuel additive could boost its production to $30\,\mathrm{Mt\,a^{-1}}$ if a direct industrial CO_2-based synthesis route is found to replace the current phosgene or methanol carbonylation routes (see eni or UBE processes).[53] The CO_2-based process is still not cost-competitive.

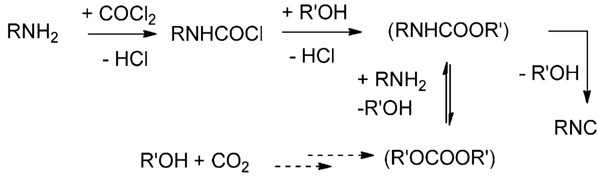
Transesterification of the cyclic carbonates with higher alcohols to linear carbonates, such as diethylcarbonate (DEC), diallylcarbonate (DAC), and diphenylcarbonate (DPC) is also pursued. The three carbonates DEC, DAC, and DPC are among the most interesting carbonates potentially amenable to CO_2 reaction with oxiranes/unsaturated substrates, because they find applications as alkylating and carbonylating agents.[9] The most advanced industrial application is the use of carbonates as comonomers in polymer syntheses (e.g., polycarbonates, polyols).

3.4. Isocyanates

Isocyanates (R–NCO), can be directly synthesized from an amine and CO_2 by, for example, using organometallic Ti^{IV} and U^{V} catalysts [Equation (5)].[62,63]

$$RNH_2 + CO_2 \rightarrow RNCO + H_2O \tag{5}$$

Although a recent process for isocyanate synthesis from CO and a nitro substrate in the presence of CO_2 has been reported,[64] amine phosgenation is the only current industrial route.[65] For example, methyl diphenyl diisocyanate (MDI), a key material in polyurethane synthesis, is produced by this route. Amine phosgenation involves carbamate intermediates, industrially interesting molecules per se (having end applications as foams, adhesives,[66] agrochemicals,[67] drugs, and prodrugs[68]) and precursors to ureas[69] and to isocyanate, with a market of several million tons per year.[57] Because carbamates are potentially amenable to CO_2 chemistry, their industrial development as well as related isocyanate production could become a frontier of the industrial utilization of CO_2 (Scheme 3).



Scheme 3. General production scheme of isocyanates.

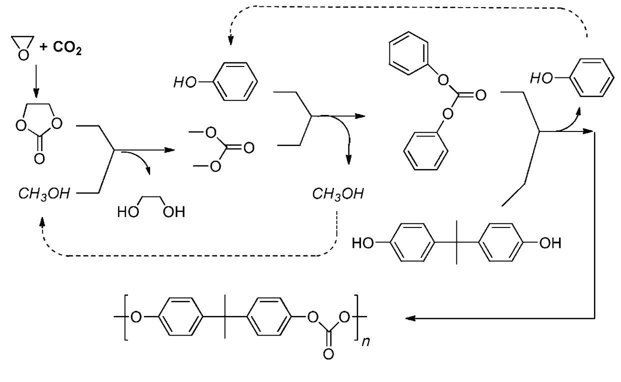
3.5. Polymeric materials

Many functional polymers can incorporate CO_2.[70,71] In the reaction of CO_2 with oxiranes, ring-opening polymerization (ROP) of the previously discussed intermediates have led to polymer synthesis. Adjustment of the catalytic conditions to directly steer the CO_2 reaction towards isolation of the polymers has also been possible, since the polymers are the kinetic products of the reaction while the cyclic carbonates are the thermodynamic ones.[72] Catalyst development has also been crucial to achieve process control and tunability of the polymeric end-product to ensure the establishment of industrial applications for these CO_2-to-polymers routes. Their industrialization has concerned mainly polycarbonate (by either ROP or directly) and polyether carbonate polyols (PPP).

3.5.1. Polycarbonate via monomeric cyclic carbonate

An industrial phosgene-free process to aromatic polycarbonates (APCs) from, inter alia, an epoxide reaction with CO_2 to yield ethylene carbonates[73] was developed by Asahi Kasei. Until the Asahi Kasei process, all of APC's carbonate groups were derived from CO and $>90\%$ involved phosgene. In the Asahi Kasei process, a glycol (e.g., a monoethylene glycol if the starting epoxide is ethylene oxide) and bisphenol-A (BPA) polycarbonate are produced in high yields from three starting materials (the epoxide, bisphenol-A, and CO_2), the intermediary phenol being recycled (see Scheme 4 for ethylene oxide). Fukuoka et al. discussed recent progresses in the APC process.[73]

The production volume at the Chimei Asai plant in Taiwan (resulting from a joint venture between Asahi Kasei and Chi Mei) has risen from 50 kt in 2002 to 150 kt in 2007. The Asahi Kasei process is now also run in Yeosu, Korea (two plants: Cheil Industries and Honam Petrochemical of 65 kta^{-1} each), and in Kazan, Russia (65 kta^{-1}).[73] The process was licensed in 2009 to Saudi Kayan Petrochemical Co, in Jubail, Saudi Arabia for a 260 kta^{-1} polycarbonate production plant that was due to commence in March 2011. In the traditional polycarbonate process, large amounts of water and CH_2Cl_2 are used, yielding large quantities of waste and Cl^-impurities in the final product.



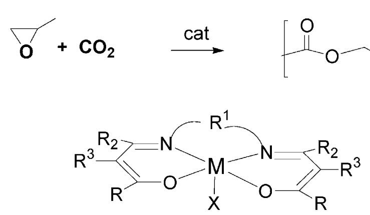
Scheme 4. Simplified Asahi Kasei phosgene-free process to BPA polycarbonate and dimethylglycol.

Conversely, in the Asahi Kasei process the CO_2 utilized is typically the by-product of ethylene oxidation to the epoxide, leading to a substantial reduction in CO_2 emissions for the whole process (0.173 t per ton polycarbonate). Partially driven by this new environmentally friendly process, the total market for polycarbonates has grown to 3 Mta^{-1}.[74] The route to polycarbonates could also increase the share of this specialty-turned-commodity polymer in the engineering plastics market, with an expected market growth of 35%. The low cost of CO_2 as starting material and the avoidance of toxic phosgene partly explains the successful industrialization.

3.5.2. Alternating polyolefin carbonate polymers

The reaction between an epoxide and CO_2 can be steered from yielding monomeric cyclic carbonates to polymeric organic carbonates depending, amongst others, on the catalytic systems used. As reviewed by Coates et al.,[72] the CO_2-into-polycarbonates technologies were based on the breakthrough paper by Inoue in 1969.[75] Their commercialization started in the late 1980s/early 1990s by several companies, such as Arco,[76] Air Products,[77] and Mitsui.[78] More recently, in part due to the development of more efficient catalysts for synthesis of alternating polycarbonate based materials (see Scheme 5),[72] the company Novomer, founded in 2004 as a result of Coates' research at Cornell university,[79] gained increasing visibility. The technology allows the synthesis of polymers containing up to 47 wt% CO_2. Amongst others, Novomer has secured a six-month phase I grant (2 million US$ for experiments and preliminary pilot design) and a two-year phase II grant (18.4 million US$ to design, construct, and operate materials creation at pilot-scale) by the US DoE in 2010. There are also investments by amongst others Albemarle, Kodak, and DSM venturing (the latter's share in 2007 being 6.6 million US$ for coating and resin development). Currently, a Novomer pilot plant uses CO_2 from an ethanol fermentation plant supplied by Praxair. Polypropylene and polyethylene carbonate are being developed. Novomer's first commercial polypropylene carbonate Novomer Binder 180 °C (NB-180) has commercial applications when requiring a binder that decomposes rapidly and cleanly. Beside potential cost reductions, these coating resins are said to perform well environmentally and technically.

Henan Tianguan Group, in Nanyang, PR China has announced the commercialization of alternating polypropylene carbonate (PPC), with a capacity of 5 kta^{-1}, linked to its tech-



Scheme 5. Schematized route to alternating polypropylene carbonates developed by Novomer, and one example of the catalyst family optimized by G. Coates (co-founder of the company).

nology involving a supported zinc glutarate catalyst for the copolymerization of CO_2 and propylene oxide.[80]

Although fixation in polymers achieves the long-term sequestration desired in carbon management strategies proposed by IPCC special report on CO_2 capture and storage,[23] the impact on the reduction of CO_2 emissions by year 2020—assuming that CO_2-PC will constitute 30% of world PC production (current world consumption of polycarbonates about 2.7 Mt a^{-1})—will be about 0.3–0.5 Mt a^{-1}. Although the market share could grow faster and the overall PC market could increase, the tonnages involved are not expect to go over the Mt a^{-1} mark for sequestration of CO_2.

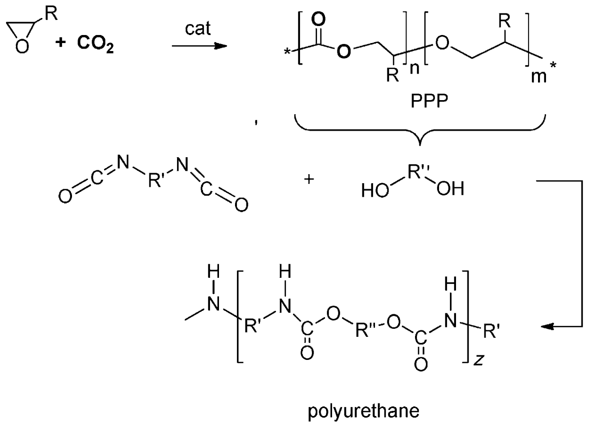
3.5.3. Polyhydroxyalkanoate

Novomer company has positioned itself also in the synthesis of polyhydroxyalkanoate (PHA) from CO_2 and epoxides. A pilot plant was planned near a producer of sugar-based ethylene oxide.[81] Global demand for bioplastics is expected to increase four-fold, to 900 kt in 2013, according to US market research firm Freedonia Group.[82] The Germany-based trade association European Bioplastics estimates that global bioplastics production will reach 1.5 Mt by 2011 from an estimated 300 kt in 2010, while global capacity is expected to reach 2.3 Mt by 2013.

3.5.4. Polyether carbonate polyols

Polyether carbonate polyols (PPP) find use in products with remarkable properties, such as plastics with improved compatibility for CO_2 blowing agents and fire-resistant foams. Haider et al.[83] patented a number of polyether carbonate polyols made from co-polymerizing CO_2 with a starter molecule (mono-, di- and poly-ols; alkoxylated oligomers of glycols) and an alkylene oxide, in the presence of a "substantially non-crystalline double metal cyanide catalyst" (such as a zinc hexacyanocobaltate/*t*-butyl alcohol complex prepared with a specific procedure to obtain a low-crystalline catalyst), wherein the polyol has an incorporated CO_2 content up to 40 wt%. Among the advantages claimed are the low levels of by-products (cyclic carbonates).

Bayer Material Science and Bayer Technology Services, in collaboration with the RWTH University of Applied Science in Aachen (Germany) and RWE Power have developed a process for polyether carbonates polyols (PPP) from CO_2. The project, named "Dream Production", has lead to the building of a pilot plant where PPP is produced on a kilogram scale.[84] The polyols consumption was about 6 Mt a^{-1} in 2003. The PPP resulting from the copolymerization of CO_2 with a starter molecule (mono-, di- and poly-ols; alkoxylated oligomers of glycols) and an alkylene oxide are characterized by low molecular weights and terminal OH functionalities, available for further reaction with isocyanates to lead to urethane groups (see Scheme 6). Since Inoue's original heterogeneous catalyst obtained from $ZnMe_2$, one of the scientific breakthroughs allowing industrialization of CO_2 polymerization to PPP was the development of a catalyst that is sufficiently stable and active under the process conditions (90 °C, 10 bar of CO_2), such as the double metal cyanide catalyst mentioned above. The process also requires low metal residues in the polymer as well as good recyclability and recovery.



Scheme 6. Schematized route to polyurethane from the polyether polycarbonate polyols (PPP), synthesized by Bayer's Dream production.

After reaction with isocyanates, polyurethane foams can be obtained that find application as elastomers, coatings, sealants, and adhesives. When used as insulating material, 1 kg of the polyurethane foam is claimed to save 70 kg of CO_2, due to the reduced energy consumption related to better thermal insulation of a building. Flame retardation is another valuable property of polyurethane foam. In 2003, polyurethane consumption had a volume of about 10 Mt, which represents 5% of the world's consumption of plastic materials. An optimistic estimate of the potential CO_2 consumption due to this route is 2–3 Mt a^{-1}, obtained by the non-realistic assumption that all polyurethane production will switch to the CO_2-containing polyols route.

3.5.5. Chlorinated polypropylene

China National Offshore Oil Corporation (CNOOC) started a plant for CO_2-based degradable chlorinated polypropylene carbonate (PPC) in Dongfang Chemical City, Hainan Province (PR China) in 2009.[85] The process is based on a patent developed by Changchun Institute of Applied Chemistry (Chinese Academy of Sciences) and will have a PPC production capacity of 3 kt a^{-1}. The project is said to have an annual CO_2 consumption amounting 2.1 kt and the ultimate product will be a degradable CO_2 copolymer.

3.6. Overall CO_2 reduction potential and LCA studies

Altogether, if one takes into consideration the amount of CO_2 that can be used in the syntheses of the above-mentioned organic carboxylation products, not including the already established urea synthesis (150 Mt a^{-1}), the amounts sum up a potential CO_2 use of 30–40 Mt a^{-1}, mostly driven by DMC's potential as fuel additive. CO_2 savings due to more efficient processes or better-performing materials are difficult to quantify from current published data, due to the lack of details for energy/

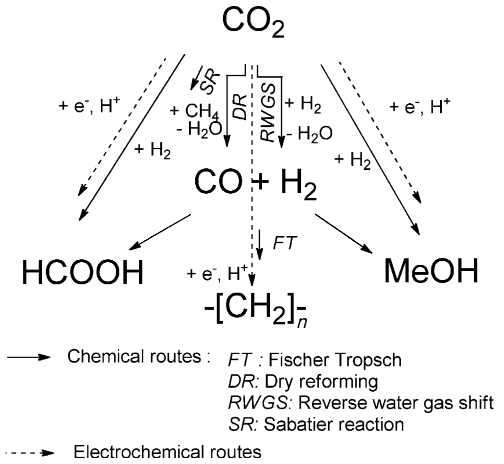
materials changes in the process and because most processes are still not optimized.

LCA studies on organic carboxylation products that allow a more detailed comparison of the different routes are also lacking, even if the need for this type of studies has been remarked.[86] When LCA is applied to an existing process and to a new one based on CO_2, it is possible to quantify the benefits or, possibly, the disadvantages of the new process by taking into consideration the various impact categories, and not only the carbon footprint.

4. Reduction Reactions related to Syngas Formation and Further Conversion

4.1. Preliminary considerations

The chemical reduction of thermodynamically stable CO_2 to low-molecular-weight organic chemicals requires high-chemical-potential reducing agents such as H_2, CH_4, electrons, and others. The hydrogenation of CO_2 can be connected to the well-established portfolio of chemicals synthesized from syngas (CO/H_2) via the reverse water–gas shift (RWGS) reaction, where methanol, formic acid, and hydrocarbons emerge as the three main products of interest (see Scheme 7). The distinction with respect to direct hydrogenation routes, which also exists, is only formal because the direct route always implies the coexistence RWGS as a side-reaction to some extent. An alternate source of reducing hydrogen can be methane.[87]



Scheme 7. CO_2 routes to chemistry and energy products via syngas.

The production of the reducing agents accounts for the biggest share of the energy cost and related carbon footprint of CO_2 reduction. For example, a simplified energy diagram for CO_2 conversion into methanol with H_2 produced by electrolysis (Figure 3) shows that the most significant energy cost is associated with H_2 production.[88] More precisely, energetic analysis[88] reveals that exergy losses are most severe in the parts of the system when electrical energy is converted to chemical energy (electrolysis), while the chemical reaction itself (methanol production) causes a minimal change in the intrinsic energy.

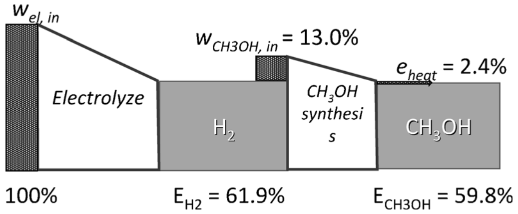


Figure 3. Simplified energy diagram for the energy chain of methanol production using H_2 from water electrolysis. Adapted from Ref. [88].

4.1.1. LCA analyses of carbon footprint for H_2 production routes

In hydrogenation routes, a critical parameter affecting the LCA results is the production of H_2. While direct production of renewable H_2 via solar energy (direct methods or indirect methods, for example using cyanobacteria or green algae) would be the preferable method, it is still a long-term goal. Currently available methods are thus essentially based on the production of electrical energy using renewable energy, and then water electrolysis. Electrolyzers allow efficiency of about 70–85% with energy consumption of about 4–6 kWh Nm^{-3}.

Utgikar and Thiesen have analyzed life-cycle CO_2 emissions for various hydrogen production methods (Table 1),[89] concluding that wind energy has the lowest CO_2 production per kg H_2 formed; about 2–4 times lower than with current solar routes (thermal or photovoltaic). Also nuclear-energy-based electrolysis shows a competitive carbon footprint, but a negative impact for other components of LCA analysis. There is a push in investigating nuclear energy as decarbonated energy supply for CO_2 conversion by the French government-funded research organization on atomic and alternatives energies (CEA).[90]

Table 1. CO_2 emissions from LCA studies on various H_2 production methods. Adapted from Utgikar and Thiesen.[89]

H_2 production method	CO_2 production [$kg_{CO_2} kg_{H_2}^{-1}$]
Wind/electric	1.2
Hydroelectric	2.1
Nuclear/steam electrolysis	2.0
Solar thermal	2.5
Biomass	3.1
Solar photovoltaic	6.5
Methane steam reforming	12.1

In some special situations, renewable energies are already cost-competitive[91] and the hydrogenation of CO_2 to syngas or syngas-related products is also becoming competitive with existing routes to syngas (steam reforming or steam cracking) if H_2 could be produced at costs below about 2–4 US$ gge (gallon gasoline equivalent),[92] such as in Iceland with electrical energy produced from geothermal sources. Figure 4 reports the projected data for H_2 production costs reported from the US Fuel Cell Technologies Program. The expectation for H_2 production from renewable energy sources, especially from wind energy, is that it may become competitive around 2015.

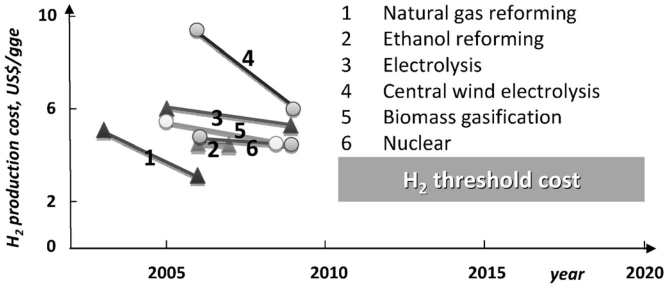


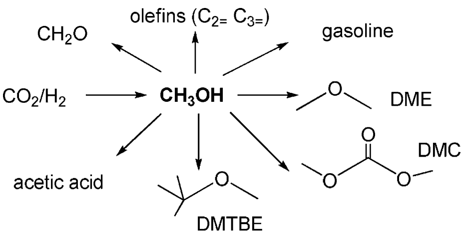
Figure 4. Projected cost of hydrogen production by different methods. Adapted from Ref. [93].

In summary, the reduction of CO_2 requires a high-energy reactant that needs to be produced using renewable energy to lower the carbon footprint of the whole CO_2 conversion process. De facto, CO_2 thus becomes an energy-storing molecule[14,15] through the synthesis/combustion loops of the resulting molecules issued for its reduction (methanol, formic acid, methane). In other words, CO_2 is an excellent energy-vector which stores renewable energy (e.g, from the sun) and thus enables the concept of solar fuels.[14] The solar-fuels concept may be extended to incorporate off-peak waste energies during the conversion of CO_2 to the above mentioned energy-carrier molecules. Some of these solar fuels could also be suitable not only as stationary energy storage, but also as fuel for transportation. The possibility of converting CO_2 into fuel market products related to energy and transportation sectors thus opens potentially gigaton-level applications for CO_2 utilization.

4.2. Methanol

Methanol is one of the chemicals with the largest potential to convert very large volumes of CO_2 into a valuable feedstock. It is already a commodity chemical, manufactured on a large scale (40 Mt in 2007)[19] mainly as a feedstock for the chemical industry towards chemicals such as formaldehyde, methyl tert-butyl ether (MTBE), and acetic acid, which makes CH_3OH a preferable alternative to the Fischer–Tropsch (FT) reaction, due to the broader range of chemicals/products, and hence their application fields (see Scheme 8) as well as higher productivity.

As popularized by Nobel laureate G. Olah, G. K. Prakash Surya, and A. Goeppert, in their contributions around the "methanol economy" concept,[18,19] methanol issued from CO_2 and renewable energy sources, or products thereof (e.g., DME, gasoline; see Scheme 8) are also a credible alternative to fossil fuels. If such an energy switch occurred, methanol produced from CO_2 could reach much larger volumes; as large as 1.5[11] or 3 $Gt\,a^{-1}$.[27] Although the technical feasibility of such a large production has not been demonstrated, it appears more realistic to implement than other possible routes. For example, while utilization of hydrogen as storage medium shows higher exergetic efficiency than the methanol route, the storage and use of hydrogen as fuel is clearly more complex and cost-intensive than the storage and use of methanol.



Scheme 8. Some conversion routes to methanol.

Methanol production from CO_2 and a renewable H_2 source has already been demonstrated at a large-pilot-plant level. In continuation of the dissemination efforts around the "methanol economy" concept, Olah is supporting the industrial manufacture of methanol from renewable energy and CO_2, carried out by Carbon Recycling International (CRI) located in Iceland, taking advantage of Icelandic geothermal plants. In fact, H_2 is produced from hydropower and wind is also present in the energy mix. CRI is currently constructing a methanol fuel plant at Svartsengi, and a new plant is expected at Krafla, for an expected methanol production of $2\times10^6\,L\,a^{-1}$.[94] CRI plans to expand the plant to more than $5\times10^6\,L\,a^{-1}$ by 2011 and build a larger plant for export (output 50 Mt) by 2013.

The Japanese company Mitsui Chemicals Inc. also completed a pilot methanol plant ($100\,t\,a^{-1}$) in Osaka in 2009,[95] developed in collaboration with the Research Institute of Innovative Technology for the Earth (RITE), Kyoto (Japan) in the Project for Chemical CO_2 Fixation & Utilization (1990–1999; supported by the New Energy and Industrial Technology Development Organization, NEDO).[96,97] The process utilizes CO_2 emitted in the exhaust of an adjacent petrochemical factory. In the pilot plant H_2 was a waste by-product of coke furnaces and other sources. In parallel, Mitsui Chemicals was developing photocatalysts for splitting water and solar cell materials for electrolysis on water in order to obtain H_2 from renewable resources. By 2010 the plant had been running for about 2000 h and Mitsui Chemicals aims to run it for 8000 h to verify the reliability of the catalyst. Mitsui Chemicals says it is looking for partners in a first commercial-scale ($600\,kt\,a^{-1}$) methanol plant based on Mitsui's Green House Gases-to-Chemical Resources (GTR) technology.[98] Methanol is intended as feedstock for olefins and aromatics.

CO_2 hydrogenation to methanol via a reverse water–gas shift reaction is also a route for CO_2 conversion to CH_3OH. This reaction is the basis of the CAMERE process developed on a bench-scale (50–100 kg per day) by the Korea Institute of Science and Technology (KIST) and operated by the Korean Institute of Energy and Research (KIER) and Korea Gas Corporation (KOGAS).[99] CAMERE is a two-step process: (1) reverse water–gas shift, and (2) CH_3OH synthesis after intermediate H_2O removal. Zinc aluminate and $Cu/Zn/Al_2O_3$-based catalysts are used in the two steps. Further research activities on this process are in progress.[100]

One of the few LCA studies specific to methanol production using CO_2 was reported by Aresta et al.,[101] showing that heat recovery during methanol synthesis from syngas has a very positive effect on reducing environmental impact and energy consumption The combination of steam and CO_2 reforming of methane is energetically interesting, and confirms that H_2 produced by water electrolysis powered by non-carbon-based fuels is the least energy consuming. An energetic analysis of the methanol synthesis with exhaust CO_2 for chemical storage of electrical energy[88] evaluated the exergetic efficiency of the overall energy conversion-storage system, including methanol as storage medium, to be between 16.2 and 20.0% depending on the applied conversion technology.

4.3. Ethanol

Ethanol (world demand in 2010 >70 Mt) is less toxic and a better intermediate for some chemicals than methanol, although its low-cost production by sugar fermentation makes its synthesis through CO_2 hydrogenation less attractive than its synthesis by fermentation. A techno-economic study of ethanol synthesis from CO_2, using a Cu–Zn–Fe–K catalyst at 300 °C, was reported recently.[102] The flow sheet considered the off-gas from a coal-based Integrated Gasification Combined Cycle as a source of CO_2.

4.4. Formic acid

Hydrogenation of CO_2 by H_2 in a 1:1 stoichiometry yields formic acid (HCOOH), which is actively investigated as a fuel for electrochemical fuel cells, that is, direct formic acid fuel cells (DFAFCs),[103] and as a suitable H_2 vector:[104]

$$CO_2 + H_2 \rightarrow HCOOH \qquad (6a)$$

An economy based on formic acid (FA) has been proposed by Leitner,[105] and repopularized by Ferenc.[106] FA is also obtained from CO_2 by direct electrochemical pathways. For example, a British consortium involving Huntsman ICI Chemicals and EPSRC funding investigates formic acid synthesis from CO_2, possibly applied as feedstock for fuel cells.[103]

Following studies at University of British Columbia, in part funded by the Canadian National Research Council—Industrial Research Assistance Program, a technology called electroreduction of CO_2 (ERC) has been developed by Mantra Energy Alternatives Ltd for the electrochemical production of formic acid (as first product) from water and captured CO_2.[107,108] Under industrially viable conditions, problems such as cathode stability and formate crossover exist as investigated by Oloman and Li[108] with the use of a trickle-bed continuous electro-chemical reactor. The type of product strongly depends on the electrode. Figure 5 is a conceptual chart of the ERC technology. The reactor's efficiency has been increased to 90% from the initial 46%, with improved and more stable electrocatalysts.[108] The technology has been deployed first at the prototype level (1 kg per day) and had been planned to be tested at the demonstrator plant level (100 kg) in collaboration with Lafarge North America. Kemira Oyj of Finland will work with Mantra in improving the formic acid concentration technology.

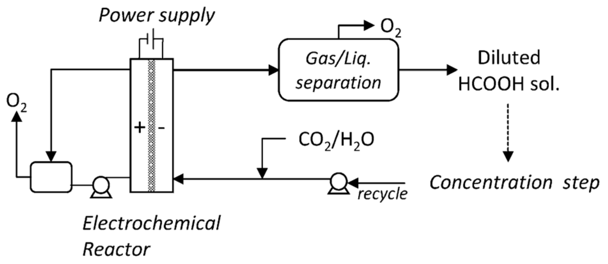


Figure 5. Conceptual diagram of ERC technology. Adapted from Ref. [108].

Since formic acid could act as H_2 vector, many recent studies investigate the catalytic decomposition of FA to produce H_2:

$$HCOOH \rightarrow CO_2 + H_2 \qquad (6b)$$

The current world demand for formic acid is 0.6 Mt. Larger-scale applications (e.g., as energy vector) would require to address the safety and toxicity issues posed by its large-scale utilization.

4.5. CO/H_2 mixtures

The reaction of CO_2 with CH_4 (also called dry reforming) to produce syngas [CO/H_2 mixtures; Equation (7)] is endothermic. The use of dry reforming at remote ('stranded') natural gas wells coupled to FT would yield easy-to-transport liquid hydrocarbons. Another target application for dry reforming is biogas upgrading.[109] Ti-reforming, that is, the combination of dry reforming with the oxidation of CH_4 [an exothermic reaction, Equations (9)] and ensuing simultaneous dry and wet reforming (methane steam reforming) reactions [Equations (7) and (8), respectively]) may be applied directly to flue gases:

$$CO_2 + CH_4 \rightarrow 2\,CO + 2\,H_2;\ \Delta H^0{}_{298} = +247.3\ \text{kJ mol}^{-1} \qquad (7)$$

$$CO_2 + H_2O \rightarrow CO + 3\,H_2;\ \Delta H^0{}_{298} = +206.3\ \text{kJ mol}^{-1} \qquad (8)$$

$$CH_4 + {}^1\!/_2\,O_2 \rightarrow CO + 2\,H_2;\ \Delta H^0{}_{298} = -35.6\ \text{kJ mol}^{-1} \qquad (9a)$$

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O;\ \Delta H^0{}_{298} = -880\ \text{kJ mol}^{-1} \qquad (9b)$$

A Yufutsu GTL pilot plant has been operating at a capacity of 7 barrels per day (bpd) in Hokkaido (Japan; JOGMEC GTL process).[110] Over the period 2001–2004, process stability ($>$ 6000 h) and high productivity (1300 $g\,kg_{cat}{}^{-1}\,h^{-1}$) were achieved. In April 2009 the Niigata Demonstration Plant (500 bpd) was completed as a result of a joint venture between Nippon Oil, JOGMEC, JAPEX, INPEX, and Chiyoda (Figure 6).

The Nippon GTL technology association[111] reported that a 15 000–20 000 bpd plant (Japan GTL process) is planned. A recent simulation showed that zero emission of CO_2 can be obtained with recycling of unreacted syngas.[112] A recent study[113,114] also proposed tri-reforming as a suitable approach to increase the energy efficiency of fossil-fired power plants (integrated tri-reforming power plants, ITRPPs). Similar approaches were proposed for applications combined to gas turbine power plants[115] or for coke/coal gasification combined with lime carbonation.[116]

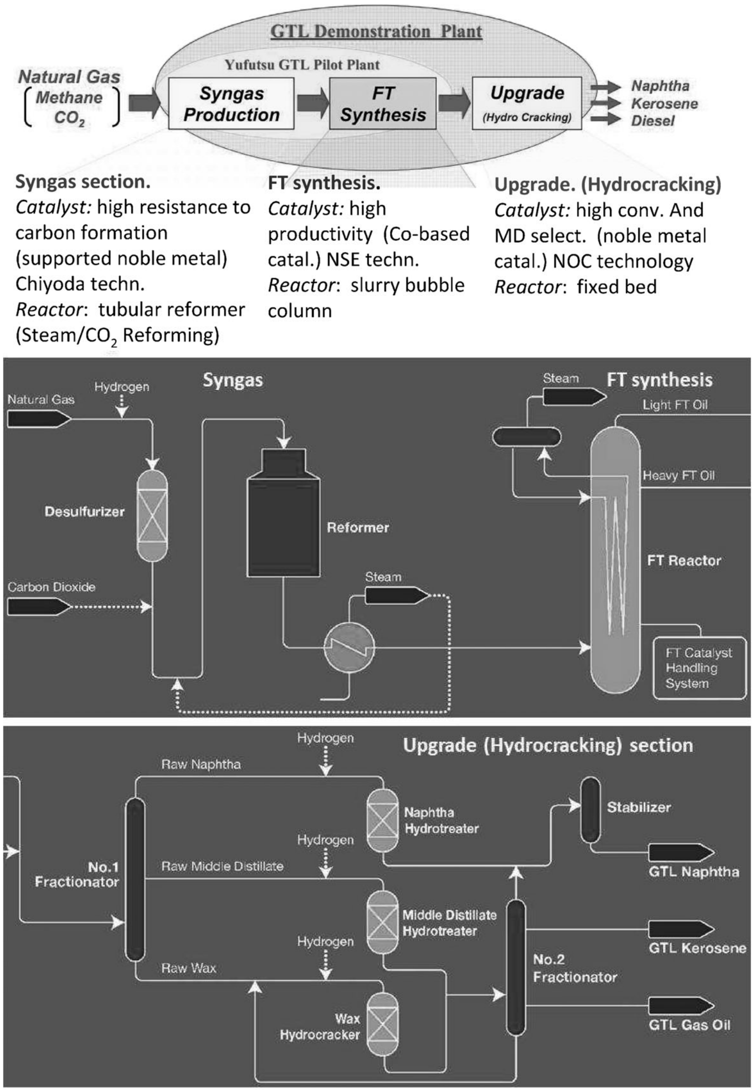


Figure 6. Characteristics of the Japan-GTL process. Adapted from Ref. [111].

4.6. Methane

The complete hydrogenation of CO_2 to methane is the Sabatier reaction:

$$CO_2 + 4\,H_2 \rightarrow CH_4 + H_2O \qquad (10)$$

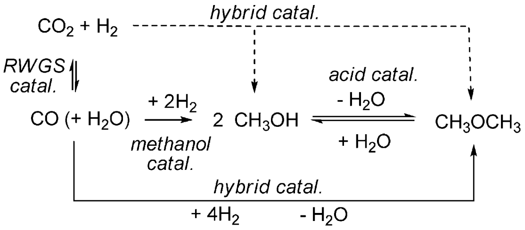
In terms of hydrogen consumption, and hence overall energetics (see 4.1.1), CO_2 reduction to methanol rather than to methane might appear favorable given the better ratio by energy value of the product relative to the starting H_2; nevertheless, specific conditions (for example, the need to produce substituted natural gas; SNG), know-how, and other local conditions have spurred industrial applications of the Sabatier reaction.

The Norwegian company RCO2 AS[117] has developed a pilot-scale process based on recovery of CO_2 from flue gas and its conversion to methane using renewable H_2. BP and Tohoku University of Technology (Japan) have developed a pilot plant based on the Sabatier reaction with very high selectivity ($<1\%$ ethane as major by product).[118] Hydrogen is produced by seawater electrolysis and produces about 25% *v/v* of methane [Equation (10)]. The Desert Research Institute (DRI) in the USA has also studied the reaction in a small pilot unit, (60% CO_2 conversion, 300–350 °C, H_2/CO_2 ratio 4:1).[119]

4.7. Dimethylether

Dimethyl ether, or DME (CH_3OCH_3; world demand about 5 Mt in 2010), has a high cetane number (a measurement of the combustion quality of diesel fuel during compression ignition; the equivalent of octane number for gasoline) and low boiling point, making it a clean and economic alternative fuel, particularly to LPG (light petroleum gas). DME is also a platform chemical for the selective production of olefins, especially propylene (as investigated by, for example UOP, Lurgi, JGC, and Idemitsu in Japan)[120] and of methyl acetate by carbonylation.[121] DME synthesis is directly connected to the methanol synthesis discussed above, making its synthesis from CO_2/H_2 a related reaction, accessible by using hybrid catalysts (see Scheme 9).

Korea Gas Corporation (KOGAS) is developing a new DME plant that starts from CO_2.[122,123] Unitel Technologies was recently awarded a contract by KOGAS to prepare the basic engineering and design package for a plant that will make 300 kt of DME per year.[124] KOGAS is the first organization in the world to successfully develop and demonstrate a commercially viable 'one step' process. The Aspen Plus simulation of the commercial DME plant (capacity 3 kt per day) for the process layout reported in Figure 7 has been reported.[125]



Scheme 9. General DME synthesis scheme.

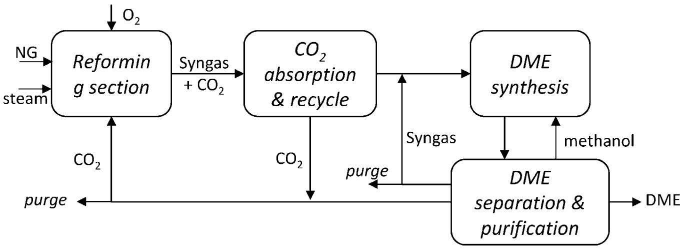


Figure 7. Block diagram of dimethyl ether production. Adapted from Ref. [125].

The KOGAS process is based on tri-reforming (CH_4, CO_2, and H_2O) as a first step and the direct conversion of the resulting syngas to DME as the second step. In the first bench-scale stage, research was performed by KIER and KIST, while KOGAS progressed into the second stage (50 kg day^{-1}) under a consortium of KIER, KIST, KRICT, and Samsung Engineering. Presently, a pilot plant has been constructed and is now operating to produce DME with a target of obtaining data for a demonstration unit (20 t per day). The demonstrator is currently working at 10 t per day.[126]

DME synthesis has also been obtained at bench-scale (100 cm^3 catalyst loading) via the reforming of methane by CO_2 and steam in a joint effort by Kansai Electric Power Co. and Mitsubishi Heavy Industries (Japan).[127,128]

5. Bioroutes

5.1. Preliminary considerations

Photosynthesis is the largest-scale CO_2 conversion process, since it is present in all plants and photosynthetic micro-organisms (including microalgae and cyanobacteria). Sunlight powers the CO_2 conversion reaction:

$$6\,CO_2 + 6\,H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6 + 6\,O_2 \qquad (11)$$

In terms of CO_2 consumption, a total of 1.8 tons of CO_2 is needed to produce 1 ton of algal biomass.[129] Microalgae need also nitrogen and phosphorus nutrients. We focus the discussion here on the production of terrestrial or aquatic biomass under non-natural photosynthetic conditions for chemicals and/or chemicals integrated with fuels (thus excluding biomass thermovalorization). In reality, the strict integration of these two is necessary for the economics of the process. The integration of chemicals and energy production in large scale industrial algal biofarms has led to the "algal biorefinery" concept.[130] The chemical products of the biorefinery include carbohydrate and protein extracts, fine organic chemicals (e.g., carotenoids, chlorophyll, fatty acids) for food supplements and nutrients, pharmaceuticals, pigments, cosmetics, and others, along with energy fuels, for example, biodiesel, bioethanol, and biomethane. The biochemical conversion finalized exclusively to energy (e.g., anaerobic digestion, alcoholic fermentation, photobiological hydrogen production) has recently been reviewed by Brennan and Owende.[131]

5.2. Nutrition, cosmetics, pharma, and other high-value sectors

Microalgal biomass is produced at a scale of a few thousand tons per year (ca. 5 kt of dry biomass; total market volume is 1.25 billion €), implying an average market price for microalgae of 250 € kg^{-1} dry biomass,[132] mostly produced in open systems.[133] The current commercial applications have been developed with relatively few species: *Chlorella vulgaris*[134] and *kessleri, Dunaliella salina, Botryococcus braunii*,[135] *Spirulina platensis*[136] and *sp*,[137] *Nannochloropsis, Arthrospira, and Haematococcus pluvialis*.[138] In terms of non-energy microalgae uses, the main area of sales (together with cosmetics) is related to human nutrition,[131] such as animal feed (especially in salmonids aquaculture for coloring), biofertilizer, as source of polyunsaturated fatty acids (PUFA), or other biomass extract derivatives (e.g., β-carotene, astaxanthin, and C-phycocyanin).[138,139] Some of these end-products are characterized by very high prices, niche-size markets, and very stringent regulations, particularly in terms of purity.

5.3. Bioenergy

A comprehensive survey of algal cultivations and their industrial utilization has been carried out by Edward,[140] while Singh and Gu[141] have discussed in detail the commercialization potential of microalgae for biofuels production. Table 2 lists some companies involved in the growth of algae for biofuel production. Over 150 companies worldwide are involved in algal biofuels,[142] including some major companies, such as ExxonMobil Corp (600 million US$ over the next five years for its partnership with Synthetic Genomics), BP Amoco plc (10 million US$ for a project with Martek Biosciences Corp), Dow Chemical Co. (with Algenol Biofuels Inc. in a joint algae-based pilot biorefinery for ethanol production). In addition, a number of companies are carrying out pilot-level algal carbon capture projects, where the biomass is in part devoted to fuel production (see Table 3).

The environmental burdens of algal production are compared with switchgrass, corn, and canola as source of biofuels.[143] Based on a stochastic life cycle model of algae cultivation processes, algae appear to have larger environmental impacts, energy use, and greenhouse gas emissions (in harvesting and processing) compared to conventional crops, regardless of cultivation method.[143] Algae cultivation performs poorly also with respect to water consumption.[144,145] Algae perform favorably only in total land use and eutrophication potential. Larson's review[146] on life-cycle analyses of liquid biofuel systems for the transport sector has evidenced the inefficiencies associated with biomass production and their subsequent conversion to biofuels.

In most LCA and environmental-impact studies on algae cultivation the upstream impacts, such as the demand for CO_2 and fertilizer, seem to drive the large environmental footprint. The utilization of flue gas and, more importantly, wastewater should reduce this negative carbon footprint.

Notably, one LCA analysis[143] was strongly condemned, amongst others by the Algal Biomass Organization (the trade association for the algae industry), for showing obsolete data and grossly outdated business models, and not having considered technology and processes improvements (e.g., photobioreactor design, water and nutrient provenance, energy source) across the production cycle (algae-growth system, co-location, energy). These topics have emerged early as cutting-edge research fields. For example, the Japanese research project entitled "Biological CO_2 Fixation and Utilization", sponsored by NEDO focused on aspects such as lipid production strains, open production systems (raceway ponds), and photobioreac-

Table 2. Examples of algae production companies around the world. Adapted from Edward[140] and Singh and Gu.[141]

Company	Strategies and comments
Cultivation method: open ponds	
LiveFuels Menlo Park, CA (USA)	Production of bio-crude oil to be used directly through the current refinery system (drop-in). Led by a US Dept. of Energy National Laboratory.
OriginOil Inc. Los Angeles, CA (USA)	Claims of cost-effective and rapid manufacturing process of algal oil production.
PetroSun Scottsdale, AZ (USA)	1100 acres of saltwater ponds in Texas. Extraction of algal oil is done on site before transport to company biodiesel refineries. Also created an algae-to-jet fuel venture with Science Applications.
Nestle Oil Helsinki (Finland)	Renewable fuel by refining imported vegetable oils and algae. Aim: 170 000 $t\,a^{-1}$ of biodiesel.
Ingrepro BV Borculo (Netherlands)	Large biotech company specialized in industrial-scale algae production. Algae production facilities in Malaysia in collaboration with BioMac Sdn Bhd.
Seambiotic Ashkelon (Israel)	Algae production for foods, fine chemicals, biofuels, etc. Working with Israel Electric company's (IEC) smokestack as source of CO_2.
Cultivation method: natural settings	
Kelco San Diego, CA (USA)	Natural kelp beds harvesting to produce alginic acid.
Neptune Industries Boca Raton, FL (USA)	Growth of algae for biodiesel and methane gas with aquaculture company's patented Aqua-sphere system on fish waste use.
Blue Marble Energy Seattle, WA (USA)	Hybridized bacteria to generate biochemicals, bioenergy and clean water.
AquaFlow Auckland (New Zealand)	Biofuel from wild algae harvested from open air polluted environments (settling ponds of standard effluent management systems and other nutrient rich waters).
Bio Fuel Systems Alicante (Spain)	Marine algae for 'biopetroleum' (e.g., biodiesel) from phytoplankton).
Cultivation method: closed systems	
A2BE carbon capture Boulder, CO (USA)	Combination of shrimp-culture algal CO_2 capture technology with biomass gasification.
Green fuel technologies Cambridge, MA (USA)	Algal Biofactory for daytime CO_2 capture from power plant. Claims: 7000 gallons of jet fuel per acre; 5000 gallons of ethanol per acre; 1000 tons of protein per acre; 200 pounds of specialized nutrients per acre; 20 pounds of pigments per acre.
Solazyme Inc San Francisco, CA (USA)	Specialty oils for cosmetic industry and algal diesel "solodiesel" tolerant to cold water obtained by microalgae growth in dark large tanks with sugar to supercharge their growth.
Algeneol Biofuels Fort Meyers, FL (USA)	Industrial-scale ethanol from algae on desert land using seawater and CO_2. Patented presence of N_2 fixating blue green algae, and cyanobacteria (reduce fertilizers). Plans to obtain excretion of biocrude. Aim: 100 million gallons of ethanol in Mexico's Sonaran Desert by end 2009 and 1 billion gallons by 2012.
Sapphire Energy San Diego, CA (USA)	Likely, genetically modified blue-green algae eng. for secretion of bio-crude-oil to be skimmed (cheaper harvesting and processing costs). Algal fuel claimed to be compatible with current energy infrastructure.
Solena Washington, DC (USA)	Patented plasma technology to gasify algae to syngas. Plans for 40 MW power plant.
Solix Biofuels Fort Collins, CO (USA)	Large-scale facility planned at nearby brewery, where CO_2 produced during beer production would be used.
Aurora Biofuels Hayward, CA (USA)	Genetically modified algae to yield biodiesel using patented technology (Univ. of California, Berkeley).
Cellana San Diego, CA (USA)	A Shell Oil and algae-to-biofuel start-up HR biopetroleum joint venture.

tor design (e.g., the use of fiber optics to bring light inside the systems) as early as in the 1990–1999 decade.

The use of wastewater and/or plant-emitted CO_2, besides improving the LCA and possibly producing clean water,[147] also improves the economics of the system. However, there are still contrasting views about the real economic perspectives (costs) of algae-to-fuel technologies and the time requested to arrive to commercialization.

Wijffels and Barbosa, in their outlook paper on microalgal biofuels,[148] indicated that at least 10–15 years are necessary for the development of a sustainable and economically viable process for the commercial production of biofuels from algal biomass. It is necessary to reduce production costs and energy requirements, while maximizing lipid productivity and increasing the biomass value by making use of all algal biomass components. For cost and energy reduction and maximization of lipid productivity, cell properties, bioreactor design, supply efficiency, and the use of nutrients and resources needs to be improved, and in order to make use of all biomass, a biorefinery infrastructure needs to be established. In addition, the commercial production of microalgae is still based on traditional technologies using a few strains. There are many more species yet to explore; in addition, genetic engineering offers the possibility for strain improvement. For this purpose, well-annotated genomes need to be available.

Thurmond, in its roadmap analysis of the commercialization perspectives of algal biofuels,[149] highlighted 11 key trends for the algae industry from 2011 to the year 2020. The first trend

Table 3. Examples of companies involved in algal carbon capture projects partly used for biofuel production.

Company	Comments
Columbia Energy Partners	Converts CO_2 from a coal-fired electricity plant into algal oil.
Linc Energy & BioClean-Coal	CO_2 from Australian coal-fired power plant. Algal biomass to be used as fuel or fertilizer, or to be re-burn to produce additional energy.
Seambiotic	CO_2 emissions from coal-burning power plant in Ashkelon (Israel Electric Company) senz to a pools of algae to produce biofuel.
Trident Exploration	Joint venture between the NG exploration company, and Menova Power-Spar, a company with focus on PV solar cells.
eni	Pilot scale on microalgae biofixation of fossil CO_2 emitted from a NGCC power plant located in Gela, Italy
Kolaghat Thermal Power Plant	Pilot project at the 1260 MW Kolaghat thermal power plant for algal farming (25% spirulina) and dry ice production
MBD Energy	For combined oil and meal production
RWE and E-On Hansa	Pilot algae plant (vertical bioreactor, 600 m^2, algae "fed" with flue gas from the power plant).
GreenFuel Technology	Proprietary algal photobioreactors (Harvard–MIT algae company, now closed).
CO_2 Solution Inc.	Enzymatic (carbonic anhydrase) CO_2 capture. Tested at pilot scale at Alcoa Inc.' s aluminum smelting facility at Deschambault (Canada) and as prototype at a Quebec City (Canada) waste incinerator.
ALG Western Oil	Pilot plant at Xstrata's Boschoek ferrochrome smelters near Rustenburg (South Africa) for CO_2 biocapture

regards the "brewery" model in algal biofuels ventures to develop low-cost, high-tech production using standard industrial fermenters. Solazyme is leading the field, followed by veteran algae producer Martek with support from BP. The second challenge regards the development of drop-in fuels, that is, fuels that are compatible with existing engines, pipelines, storage systems, and petrol stations. The diversification of biofuel companies beyond one fuel to include a portfolio of advanced biofuels represents another complementary aspect for the strategies to inspire investor confidence. However, due to uncertainties in economics, most of the algae ventures are moving from biofuels to high-value products including livestock and fishmeal, omega 3s, health products, cosmetic and pharmaceutical uses, shifting over time their plan to scale up operations for commercial biofuels production. Another clear trend is scalability. Of the 100 or so companies involved in the algae space, less than 25 have moved from the laboratory to the pilot phase. Few have been able to convince investors to risk 10 million US$ or more to make this necessary transition.

Therefore, even if there are still great expectations and governments in the USA, EU, Brazil, China, India, Canada, and other regions are funding collaborative algae R&D initiatives at different levels (universities, public–private partnerships, precommercial demonstration stage enterprises, pilot- and prototype-stage endeavors), algal venture companies are reconsidering their strategies to produce algal biofuels. Nevertheless, seaweed has gained favor with petrochemical majors Statoil, Dupont, and ENAP because it grows faster than terrestrial crops, has a high sugar content for conversion to ethanol and advanced biofuels, absorbs more CO_2 than land-based plants, has no lignin, can be easily harvested compared to microalgae, requires no pretreatment for ethanol production, and can be harvested up to six times a year in warm climates. Seaweed biofuels include ethanol, methanol, and biobutanol. BP–Dupont's Butamax will collaborate with BAL, a leader in the field to produce biobutanol for drop-in fuels and chemicals.

Some algae producers now have collaborative R&D partners with big industry players, such as the Exxon–Synthetic Genomics 600 million US$ collaborative for green crude development, the Algenol–Dow for bioproducts, BP–Martek for algae fermentation, Shell–HR Biopetroleum for hybrid PBR-pond development, Chevron–Solazyme for green crude and drop-in fuels, and Dupont–BAL for biobutanol from seaweed. An increasing number of partnerships are thus forming and leveraging advantages in technologies, economies, and geographies.

Thus, even if current stage of development in algal carbon capture at large emitter sites indicates an economic cost that is still too high, there are signals of a fast scientific and technological development in this area, including improvements in:

- photobioreactor design (e.g., surface area, light path, layer thickness),[133,150] where applicable
- harvesting and processing technologies, including substantial simplification due to self-excreting algae that allow 'milking' as exemplified by the Arizona State's milking blue-green algae that excrete a kerosene-type jet fuel and Algenol's blue-green algae that directly excrete ethanol fuel (Table 3)
- photosynthetic efficiency, productivity, compatibility with concentrated CO_2 streams, and tuning to desired end-product by genetic engineering[151,152]

These are among the promising leads for necessary breakthroughs and industrial advancements. As summarized by Thurmond:[153] algal biofuel production needs to be "fatter, faster, cheaper, easier".

The Algae 2020 study[149] reported that the estimated costs to produce algae oils and algae biodiesel today range between 9 and 25 US$ per gallon in ponds, and 15–40 US$ per gallon in photobioreactors (PBRs). The study indicates that an increase in the size of the plants by three orders of magnitude and a ten-fold drop in the production costs are necessary to turn algal biofuels/biolipids from demonstration programs to industrial processes, and that it will take over 10 years to reach these objectives.[148] According to the US "National Algal Biofuels Technology Roadmap"[154] (based on a workshop held in December 2008) the future of algae biofuels will be brighter, with a final indication that algal biofuels can be competitive with petroleum at approximately 100 US$ per barrel, even when considering the costs and uncertainties in algae production. However, after two years have elapsed since this roadmap appeared, the perspectives appear too optimistic.

The bottom line at the present moment is that analyses seem to suggest that the environmental burdens of producing energy from biomass could be greater than those associated with petroleum-based fuels with current technology. In light of these results, full-cost accounting via LCA has become critical for optimizing biomass-to-fuel production systems, and steering the necessary improvements.

5.4. Succinic acid

Succinic acid is currently only a niche product (30 $kt\,a^{-1}$, a market worth 225 million US\$), but with a strong potential, estimated at a six-fold expansion to 180 kt by 2015,[155] mainly due to biosuccinic acid production. The expected related drop in production costs could turn this specialty molecule into a commodity chemical due to its large portfolio of accessible derivatives (platform molecule). Most processes rely on *Escherichia coli* (E. coli) strains specifically developed for the desired metabolic engineering strategies based on glucose transformation routes.[156] Since the glucose is generally derived from wheat or unrefined sugars, these strategies are only indirectly CO_2 transformation routes.

Many joint ventures are being established around biosuccinic production, among which: Bioamber (joint DNP Green and ARD in Pomacle, France, 2 $kt\,a^{-1}$), DSM and Roquette Frères (Lestrem, France 10 $kt\,a^{-1}$), Myriant (20 $kt\,a^{-1}$ in Louisiana, USA, based on a 50 million US\$ grant from the US DoE), BASF and CSM (Purac, Spain). Mitsubishi Chemical Company currently uses fossil-based succinic acid to yield polybutylsuccinate (PBS), but plans to develop biosuccinic-based PBS in collaboration with the Thai company PTT.

5.5. Formic acid

Direct formic acid fuel cells (DFAFCs) can be fed with HCOOH which has been produced biochemically by a CO_2-assimilating micro-organism or by an encapsulated enzyme such as formate dehydrogenase in hydroxyapatite-polysaccharide capsules to promote stability of the system.[157]

5.6. Hydrocarbons

Global Bioenergies (France)[158] has developed a process for "bio-isobutene" production, which by-passes purification steps due to the product volatility. Other hydrocarbons could be obtained from renewable resources using similar artificial metabolic pathways.

5.7. Isobutyraldeyde and isobutanol

The KAITEKI Institute (TKI) from Japan, a strategic arm of Mitsubishi Chemical Holdings Corp.,[159] is investing in UCLA Prof. James Liao's research on engineering bacteria that convert CO_2 into alcohols, in particular genetically modified *E. coli* and cyanobacterium bacteria to produce various alcohols (among which isobutanol[160]) and genetically engineered *Synechococcus elongatus PCC7942* to produce isobutyraldehyde.[161] The latter is a valuable biorefinery platform molecule, while isobutanol can be used as a gasoline substitute. Butanol and hexanol synthesis are also among the targeted molecules.

5.8. Carbohydrates

Naturally Scientific,[162] a UK company, patented a photosynthetic approach to grow palisade layer plant cell culture that produces low-cost sugar-glucose and sucrose. They constructed a demonstration plant in Nottingham (UK) which started operations in May 2010, producing both sugars and oils.

6 Conclusions

The societal push to reduce CO_2 emissions has opened new opportunities for a sustainable, resource-efficient chemical and energy industry that considers CO_2 as an abundant, renewable, economic, non-toxic, non-flammable, and green carbon feedstock. In addition to the already established 150 Mt of industrial CO_2 chemical utilization, four fields have emerging potential for industrial CO_2 recycling: organic carboxylation to polymeric carbonates, mineralization, reduction to fuels, and biotransformations.

The transformation of CO_2 into polymeric materials, offsetting the related demand for petroleum-based resources, has matured to a point where it is being used in specific instances, albeit on a limited industrial scale (e.g., Novomer, Bayer, Empower Materials). The motivation for these industrial applications has primarily been the development of phosgene-free (and cheaper) routes, rather than to find a sink for CO_2. Although potentially capable of consuming several million tons of CO_2 per year (under optimistic assumptions) the field of plastic materials from CO_2 is not sufficiently large to substantially curb CO_2 emissions. At the same time, the development of CO_2-based advanced plastic materials can have a beneficial indirect effect on curbing these emissions. For example, polyurethane-based materials from polyols contain as much as 40 wt% CO_2. Their large insulating capacity can allow for the avoidance of 70 kg of CO_2 emissions for every kilogram of fixated CO_2. But such speculations on avoiding CO_2 emissions are perilous, and hereafter estimates will be limited to actual fixation values.

The inorganic mineral carbonation in commercial materials is almost in an opposite situation compared to the organic carbonation for polymeric materials just mentioned. While the market for inorganic carbonates is gigantic and could provide the gigaton sink necessary for climate-relevant disposal of CO_2, the very low costs of raw materials in the cement industry make CO_2-based technologies hardly economically competitive, that is, there is a lack of CO_2 price incentives/taxation. Taken together with concerns that have been voiced about the adherence of some of the potentially commercial carbonates to existing standards, the current industrially viable technology for CO_2 recycling via inorganic carbonation seems less a gigaton CCR option (carbonates as “green” cement) than an interesting CCS technology.

CO_2 recycling could lead to a meaningful impact on CO_2 emission if fuels, rather than chemicals, could be obtained by direct CO_2 conversion routes, since the worldwide market for fuels has a volume about two orders of magnitude bigger than that for chemicals, and CO_2 emissions are mainly associated to energy use. A first caveat, given the time-scale of CO_2 permanence in the fuels (whose destiny is to be burned shortly after synthesis and not to be stored indefinitely), is that the contribution to CO_2 mitigation made by CO_2 recycling into fuels is more toward the development of ‘low(er)-carbon’ economies, than toward CO_2 storage policies. Secondly, LCA analyses of these reduction routes, which require substantial energy inputs, reveal that the carbon footprint and environmental impact of the energy source are crucial, and for now generally not competitive. However, several industrial successes are emerging: CO_2 hydrogenation to methanol, DME, and hydrocarbons appear already economically viable industrial processes if cheap sources of renewable H_2/electrochemical power are available. A relevant aspect of this route, which also includes the conversion of CO_2 to large-volume chemicals such as light olefins, is that it is a valuable opportunity to introduce renewable energy (by conversion into chemical energy in a form that is easy to transport and store) into the existing energy and chemical infrastructures (drop-in renewable energy), thus becoming a key pillar towards the goal of realizing a sustainable and resource-efficient chemicals and energy production. In the long-term, this is a more strategically valuable and critical element of CO_2 recycling.

Finally, an evaluation of the biotechnological utilization of CO_2 (e.g., via microalgae) requires reliable data on energy, environmental, and societal costs. While the balance appears unfavorable for now when compared to fossil fuel alternatives, the massive R&D investments and the well-identified roadmap to “fatter, faster, cheaper and easier” microalgal biotechnology are encouraging.

Optimistically, assuming that all the options for CO_2 utilization can be fully implemented and considering that the use of CO_2 as carbon source partly prevents the use of fossil fuels and incorporates renewable energy into the chemicals and energy chain (and thus has a more widespread impact than only on GHG emissions, different from CCS), a potential reduction equivalent of 250–350 $Mt\,a^{-1}$ can be estimated in the short- to medium-term. This amount represents about 10% of the total reduction required globally, that is, it is comparable to the expected impact of CCS technologies, but with additional benefit in terms of (i) fossil fuel savings; (ii) additional energy savings (e.g., the cited insulating effect of polyurethane foams); (iii) accelerating the introduction of renewable energy into the chemicals and energy chain.

Thus, not considering the possible economic returns gained by using instead of wasting a carbon resource, recycling CO_2 will contribute to reducing fossil carbon extraction and consumption, taking into account that the use of CO_2 requires fewer precautions with a lower energetic and economic cost compared to several other chemicals. Clearly, CO_2 can be a green molecule that enables a sustainable and resource-efficient production of chemicals and energy.

At the same time, full analyses should go beyond these considerations, using methodologies such as LCA, exergy analysis, and similar approaches, which should be tightly integrated to the more classical techno-economic methods to evaluate opportunities in this field. The limited literature data available on these aspects evidence the need to dedicate much more effort to these topics and analysis and assessment methodologies.

There are other important aspects to consider, such as the expected trend in CO_2 prices, social pressure, environmental needs, and retaining a good public image for companies. A multicriteria methodology for selecting new energy-efficient CO_2 processes was applied by Xu et al.,[163] and is based on plant operating conditions, energy requirements for reactions, catalyst performance, product demand and revenue, market penetration, and economic, environmental, and sustainability costs. Only processes that, on the basis of this analysis, are advantageous compared to existing commercial process, were then analyzed more rigorously by using chemical process simulation, where criteria such as raw material cost and use, product price and potential sales, labor, and utility costs can be taken into account. This approach, which simplifies more rigorous economic and lifecycle assessments, can be an interesting alternative. Therefore, the thorough implementation of such a tool is a meaningful way to steer the field of CO_2 utilization towards large-scale impacts.

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