CHAPTER 1

Perspectives and State of the Art in Producing Solar Fuels and Chemicals from CO₂

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1.1 INTRODUCTION

The last United Nations Climate Change Conference (COP17/CMP7, Durban, Dec. 2011) and the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report under preparation [1], two of the actual reference points regarding the strategies for the reduction of greenhouse gas (GHG) emissions, are still dedicating minor attention to the question of reusing CO₂. We discuss here how reusing CO₂ is a key element in strategies for a sustainable development as well as a nonnegligible mitigation option for addressing the issue of climate change. There is a somewhat
rigid separation between the discussion on the reduction of the emissions of GHG, based mainly on the introduction of renewable or alternative sources of energy and on the increase of efficiency in the use/production of energy, and the strategies for cutting current GHG emissions, based essentially only on the carbon capture and sequestration (CCS) option. The use of carbon dioxide as a valuable raw material is considered a minor/negligible contribution for the issue of climate change and thus not a priority to address.

The World Energy Outlook 2010 [2] report prepared by the International Energy Agency (IEA) has discussed different options and scenarios for GHG emissions, proposing a reduction of CO\(^2\) emissions in the 2.3–4.0 Gt·y\(^{-1}\) range within one decade (by the year 2021) and in the 10.8–15.4 Gt·y\(^{-1}\) range in two decades (by the year 2031) with respect to the business-as-usual scenario. About 20% of this reduction would derive from CCS. According to this estimation, about 400–800 Mt·y\(^{-1}\) of CO\(^2\) in a decade and about 2100–3000 Mt·y\(^{-1}\) of CO\(^2\) in two decades will be captured. The McKinsey report [3] estimated the global potential of CCS at 3.6 Gt·y\(^{-1}\) and the potential in Europe at 0.4 Gt·y\(^{-1}\) — around 20% of the total European abatement potential in 2030.

With these large volumes of CO\(^2\) as raw material at zero or even negative cost (the reuse of CO\(^2\) avoids the costs of sequestration and transport, up to about 40–50% of the CCS cost, depending on the distance of the sequestration site from the place of emission of CO\(^2\)) soon becoming available, there are clear opportunities for the utilization of CO\(^2\). In addition to direct use, many possibilities exist for its conversion to other chemicals, in addition to already-existing industrial processes.

A number of recent articles, reviews, and books have addressed the different options for converting CO\(^2\) [4–15]. Scientific and industrial initiatives toward the chemical utilization of CO\(^2\) have increased substantially over the last few years [6a], and there is increasing attention to the use of CO\(^2\) to produce

- Advanced materials (for example, a pilot plant opened at Bayers Chempark in Leverkusen, Germany in February 2011 to produce high-quality plastics—polyurethanes—based on CO\(^2\) [16]);
- Fine chemicals [5,10,11,14] (for example, DNV is developing the large-scale electrochemical reduction of carbon dioxide to formate salts and formic acid [17]);
- Fuels [6,9,15] (for example, Carbon Recycling International started in September 2011 in Svartsengi, Iceland, a plant for producing 5Mt·y\(^{-1}\) of methanol from CO\(^2\) using H\(_2\) produced electrolytically from renewable energy sources—geothermal, wind, etc. [18]).

The chemical transformation of CO\(^2\) is a dynamic field of research, in which many industrial initiatives also thrive, even if it is not always straightforward to grasp the real opportunities and limitations of each option. CO\(_2\) utilization as a raw material is expected in a short- to medium-term perspective to continue its progression, with several new products coming onto the market (e.g., polycarbonates). In the long term, CO\(_2\) recycling can become a key element of sustainable
carbon-resource management in chemical and energy companies, combined with curbing consumption. CO₂ can also become a strategic molecule for the progressive introduction of renewable energy resources into the chemical and energy chain, thus helping to slowly lessen our consumption of fossil fuels. Thus the prospects for large-scale utilization [6a] indicate that CO₂ recycling can become an important component of the strategy portfolio necessary for curbing CO₂ emissions (with an estimated potential impact of hundred millions of tons of CO₂ recycling, similar to the impact of CCS) and at the heart of strategies for sustainable chemical, energy, and process industries, for a resource and energy efficiency development, for example, as a key enabling technology and backbone for the resource-efficient Europe flagship initiative of the Europe 2020 Strategy [19].

The concept of “Green Carbon Dioxide” [20], considering CO₂ not a “devil” molecule (a problem or even a possible reuse of a waste) but a key element for sustainable strategies of energy and chemical companies, is thus the new emerging vision that we emphasize in this chapter, because the new strategies toward resource and energy efficiency development need to be advanced in both the industrial and scientific communities. The concept of solar fuels is a key part of this vision [21–26], but we will not limit the discussion on the state of the art and perspectives to this area, because CO₂ recycling is an enabling element for a low-carbon economy and the efficient introduction of renewable energy in the production chain. This chapter thus analyzes these aspects and describes the opportunities offered by CO₂ recycling and solar fuels in this more general vision and context.

1.1.1 GHG Impact Values of Pathways of CO₂ Chemical Recycling

For a correct evaluation of the real impact of recycling CO₂ via chemical conversion with respect to alternative options such as storage (CCS) or even direct use in applications such as enhanced oil recovery (EOR), which, however, can be applied only in specific locations, food use, and intensive agriculture (to enrich the atmosphere in greenhouses), etc. it is necessary to discuss the impact value of the chemical recycling of CO₂.

The GHG impact value (GIV) indicates the effective amount of CO₂ eliminated from contribution to the GHG effect (over a given time frame, for example, 20 years) on a life-cycle assessment (LCA) basis. For example, for CO₂ storage (CCS) the energy necessary for the recovery, transport, and storage of CO₂ must be calculated for each ton of stored CO₂. GIV for CCS clearly depends on a number of factors, from the type and composition of the emissions, to the distance of the capture site from the storage site, the modalities of transport, etc. Detailed studies are not available, but on average, it is a realistic estimate that around 0.5–0.6 tons of CO₂-equivalent energy is necessary for the capture, transport, and storage of 1 ton of CO₂ sequestered [21,27]. In fact, capture with the amine-absorption technologies (the most used today) accounts for about 0.2 tons of CO₂ and transport/storage accounts for an additional 0.3–0.4 tons of CO₂ (per ton of CO₂ sequestered). These are average values, because in many places, such as in various areas of Europe, it is necessary to transport CO₂ for over 150–200 km and pipelines are not available.
The storage will be long term, and thus over a time frame of 20 years the average GIV for CCS will be around 0.4–0.5.

There are different options for the reuse of CO₂. We may roughly distinguish two main routes for reusing CO₂ to produce commercially valuable products, apart from the routes involving bacteria and microorganisms:

1. Those reactions incorporating the whole CO₂ moiety in organic or inorganic backbones;
2. Those involving the rupture of one or more of the C–O bonds.

This classification is important in term of energy balance and applications. The first class of reactions (both organic and inorganic) is not energy intensive and sometimes may also occur spontaneously, although with low kinetics, as in the production of inorganic carbonates. The second class, reactions involving the cleavage of the C–O bond, is energy intensive and requires the use of reducing agents, typically H sources such as H₂. For a CO₂ resource- and energy-efficient management, the energy necessary for these reactions should derive from renewable (solar, wind, geothermal energy, etc.), or at least from non-carbon-based (nuclear energy) sources or, eventually, waste-energy sources.

There are two typical potentially large-scale examples for the first class of reactions [6a], the production of saleable precipitated carbonate and bicarbonates or carbonates from minerals and the production of polymers incorporating CO₂ units. An example of the first case is the mineralization via aqueous precipitation (MAP) process developed by Calera [28] in a 10MW demonstration unit in Moss Landing, California (US) and followed by an Australian demonstration project in Latrobe Valley, Victoria (Australia). The flue gas from fossil fuel combustion is reacted with alkaline solutions heavy in calcium and/or magnesium, such as certain minable brines, to form a stable carbonate solid with a by-product of relatively fresh water that would be suitable for desalination. When suitable brines are not readily available, an alkaline solution of sodium hydroxide must be manufactured via, for example, chemical electrolysis. Once the CO₂ has been absorbed into a bicarbonate solution, it can be stored underground or transformed into a carbonate (building material). A full LCA does not exist, and also in this case the exact value depends on the specific process characteristics (the alkalinity sources, for example) and use of the final product [29]. The production of the alkaline solution is the energy-intensive step, and energy estimation indicates a GIV value of about 0.6–0.8 [30] for the production of building materials (with thus a lifetime over 20 years). This average value is similar for the other CO₂ mineralization technologies, where, for example, the critical energy-intensive step is the mining and crushing of the minerals (for example, olivine) used as the raw material.

For the production of CO₂-based polymers, correct LCA assessments also do not exist, and the GIV value depends on specific process characteristics that have not yet been developed on a commercial scale, apart from Asahi Kasei’s phosgene-free process to produce aromatic polycarbonate starting from ethylene epoxide, bisphenol-A, and CO₂ [31]. Polypropylene and polyethylene carbonate as
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well as polyhydroxyalkanoate (PHA) from CO\textsubscript{2} and linear epoxides are currently developed by Novomer on a pilot-plant scale \[32\], while Bayer is developing on a pilot scale a process for producing polyurethane from polyether polycarbonate polyols, as already cited \[16\]. These are the more relevant examples of CO\textsubscript{2}-based polymers, but additional examples also exist \[6a\].

The difference with respect to inorganic carbonates is that these polymers will substitute for polymers derived from fossil fuel sources, although it must be noted that the weight content of CO\textsubscript{2} ranges from about 17\%wt. for aromatic polycarbonate to about 30\%wt. for polyurethane and about 50\%wt. for polypropylene carbonate. In addition, the use of these polymers will bring further benefits. For example, polyurethane foams are one of the most efficient insulation materials on the market today for roof and wall insulation, insulated windows and doors, and air barrier sealants. Spray polyurethane foams can cut yearly energy costs upwards of 35\% with respect to alternative insulation material, but their use is still limited by their cost. The expansion of their market through larger availability at low cost from production using CO\textsubscript{2} as raw material will thus have direct benefits in terms of use of CO\textsubscript{2} as raw material and reduction of the use of fossil fuels and indirect benefits in terms of energy saving. Polycarbonate multiwall structures also offer a real advantage in thermal insulation. As clear as glass, polycarbonate has superior characteristics as to energy savings, safety, and practicality for civil and industrial buildings, with the use of panels in structures that need reduced weight, abundant light, and high resistance to atmospheric agents. The indirect impact on energy saving is difficult to estimate, because it will depend on market development, incentives for energy saving, etc. It may be thus given only a very approximate estimation. We consider realistic a conservative average GIV value (the lifetime of these CO\textsubscript{2}-based polymers is over 20 years) of about 2–4.

Production of fuels from CO\textsubscript{2}, which involves the rupture of one or more of the C–O bonds and thus the need to supply renewable energy to make the conversion sustainable, is a different case. In fact, CO\textsubscript{2} recycling via incorporating renewable energy introduces a shorter path (in terms of time) to close the carbon cycle compared to natural cycles and an effective way to introduce renewable energy sources in the chemical/energy chain. In addition, it will reduce the use of fossil fuels for these chemical/energy uses. Let us consider the simple case of methane production from CO\textsubscript{2}, although as discussed below this is not the ideal energy vector into which carbon dioxide can be transformed. However, it is the simplest example for considering the fuel life cycle and the related GIV. If we capture CO\textsubscript{2} from the emissions deriving from the combustion of methane, we must spend energy in the capture (similar to the CCS case), but if we use renewable energy for the conversion of CO\textsubscript{2} to methane (as discussed below), the net effect is that we introduce renewable energy into the energy chain. Considering that (i) 0.2 tons of CO\textsubscript{2} are necessary for capturing each ton of CO\textsubscript{2} (in terms of CO\textsubscript{2}-equivalent energy), (ii) 0.2 tons of CO\textsubscript{2} are associated with the loss of energy in the conversion process, and (iii) 0.1–0.2 tons of CO\textsubscript{2} are necessary to produce the renewable energy necessary for the conversion of CO\textsubscript{2} to fuels, we have still a positive value of saving about 0.4–0.5 tons of CO\textsubscript{2}. We must note that the carbon footprints for the different renewable
resources are different and on the average not negligible, but to simplify the discussion we consider only an average value. When an excess of energy is used in the transformation, for example, to store the excess of energy in the form of chemical fuel, the impact value could be even better. Each time that a cycle is completed (capture of CO$_2$, conversion of CO$_2$ to CH$_4$, for example, by using H$_2$ produced from a renewable energy sources—photovoltaic, wind, etc., storage/transport of methane, use of methane to produce energy and CO$_2$), there is a saving of at least 0.4–0.5 tons of CO$_2$ per amount of CO$_2$ sequestrated. However, the cycle could be repeated several times. In a 20-year time frame, a single molecule of CO$_2$ is recycled virtually several thousand times, with thus a continuous mechanism of reintroduction of renewable energy. From a practical aspect, the number of cycles will depend on the cost differential with respect to use of fossil fuels, incentives in limiting GHG emissions, carbon taxes, technology development, etc. It is thus quite difficult to estimate a correct GIV, but we consider a conservative average a GIV value of about 10–12 over 20 years. There is thus a large amplification of the impact value of chemical utilization of CO$_2$ to produce polymers or fuels, with respect to the CCS or mineralization cases, even within the limits resulting from the absence of more specific studies.

Figure 1.1 summarizes the discussed average impact value on GHG for the different routes of chemical CO$_2$ recycling with respect to CCS and CO$_2$ mineralization. It may be noted that this concept is the opposite of that used in the IPCC report [33] which indicated that “the lifetime of the chemicals produced is too short with respect to the scale of interest in CO$_2$ storage. Therefore, the contribution of industrial uses of captured CO$_2$ to the mitigation of climate change is expected to be small.” This statement is not correct, because the chemicals/fuels produced from

![Figure 1.1](image)

**Figure 1.1** Average indicative impact values estimated for the different routes of chemical CO$_2$ recycling with respect to CCS and CO$_2$ mineralization.
the conversion of CO$_2$ and incorporation of renewable energy have an effective impact value for the reduction of GHG emissions at least one order of magnitude higher than that for CCS. Thus the effective potential of carbon capture and recycle (CCR) technologies in GHG control is at least similar to that of CCS technologies and estimated to be around 250–350 Mt·y$^{-1}$ in the short to medium term [6a]. This amount represents about 10% of the total reduction required globally and 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), and (iii) acceleration of the introduction of renewable energy into the chemical production and energy chains.

1.1.2 CO$_2$ Recycling and Energy Vectors

Solar energy is abundant, accounting for over three orders of magnitude the current global consumption of primary energy, but it must be converted to electrical, thermo-mechanical, or chemical energy to be used. Energy must be also stored/transported to be used when and where it is necessary. Storage of energy in chemical form, that is, fuels, is still the most efficient way for storage and transport of energy, in terms of energy density and cost-effectiveness [21]. Energy density in a typical fuel is about two orders of magnitude larger than in batteries, and even with the possible future developments in batteries, it will be not possible to fill this gap. This is the main reason that (chemical) energy vectors will be still dominating the future energy scenario. Even in the blue-sky scenarios of the IEA [2], chemical energy will still have a predominant role with respect to other forms (electrical, etc.) in the year 2050. Thus our society is and still will be in the future largely based on the use of liquid hydrocarbons as the energy vector. Even today, with a very limited fraction of energy produced from renewable energy sources (solar, wind, etc.), it is not possible to fully use the renewable energy produced outside peak hours. When this fraction of renewable energy will exceed about 5–10%, it will become imperative to find efficient ways to convert electrical to chemical energy [34,35].

Suitable energy vectors must fulfill a number of requirements: (i) have a high energy density both by volume and by weight; (ii) be easy to store without need of high pressure at room temperature; (iii) be of low toxicity and safe in handling and show limited risks in their distributed (nontechnical) use; (iv) show a good integration in the actual energy infrastructure without need of new dedicated equipment; and (v) have a low impact on the environment in both their production and use.

H$_2$ has been often presented as the ideal energy vector [36,37], but still has two main drawbacks: (i) it has too low energy density for practical large-scale use, and the expected targets in H$_2$ storage materials to overcome this issue are very difficult to be met, and (ii) too large investments are necessary to change the energy infrastructure required for its use. Solar H$_2$ [38] may be a better and more sustainable alternative, when combined with the possibility of forming liquid fuels that are easily transportable and with high energy density [9,39]. This possibility is offered by the use of solar H$_2$ to produce fuels from CO$_2$ or, even better, to integrate directly a
solar cell able to produce protons/electrons (the equivalent of $H_2$) from water oxidation using sunlight with an electrocatalyst able to use the protons/electrons to convert $CO_2$ efficiently to fuels. This is the photoelectrocatalytic (PEC) approach, in which the two reactions of water oxidation using sunlight and $CO_2$ reduction using the electrons/protons generated in the light-illuminated side occur in two different cell compartments separated by a proton-conducting membrane [21c,40]. Producing solar fuels by recycling $CO_2$ is a carbon-neutral approach to store and transport solar energy that can be well integrated into the current energy infrastructure. It is an effective path to introduce renewable energy into the energy chain and, as has been discussed recently, also in the chemical production chain [41].

1.2 SOLAR FUELS AND CHEMICALS FROM $CO_2$

The actual average global energy consumption is about 16 TW, and it is estimated to increase to about 25 TW by the year 2050 [2]. A conservative estimation of the potential for solar energy is at least 5–10 times higher than this estimated consumption, while significantly lower for other renewable sources: 2–4 TW for wind, 2–3 TW for tides, 5–7 TW for biomass, and 3–6 TW for geothermal energy [42]. Of these different renewable energy sources only biomass can be converted to liquid fuels, while almost all the others produce electrical energy. The biomass-to-fuel approach, however, is complex and costly, and there are many concerns regarding its effective contribution to limiting GHG emissions. It is thus a transitional, not long-term, solution for the GHG question. As pointed out in the previous section, the issue is thus how to convert electrical to chemical energy in a resource- and energy-efficient approach.

The main example of the use solar light of to convert $CO_2$ to chemicals is photosynthesis. Plants or algae use solar energy and $CO_2$ to generate the several molecules necessary for life (cellulose, hemicellulose, lignin, starch, lipids, oils, etc.) through quite complex machinery. It is then necessary to convert these molecules to fuels according to different possible routes, all characterized by many steps and a large energy consumption [43–46]. The efficiency in using solar light for the chemical transformation is low, around 1% or less for green plants. Some algae are more efficient in the process, up to about 10%. When the LCA efficiency is considered, including the energy necessary to grow and harvest the biomass and its transformation to useful chemicals, the efficiency is drastically reduced (below 0.1%) because of the many steps necessary, reflecting also in the effective impact on the reduction of the emissions of $CO_2$. For example, LCA shows that production of biodiesel from algae may be even negative compared with production of diesel from fossil fuels in terms of global warming potential (GWP) or climate change power (CCP), if the emissions of $N_2O$ associated with the intensified use of fertilizers, the effect of substitution in land use, and other factors are taken into consideration in the LCA [47].

Bio-solar fuels may be directly produced from bio-organisms, and not through the transformation of the primary bio-products (lipids, cellulose, starch, etc.),
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but current developments are essentially limited to the production of H$_2$ using cyanobacteria or some green algae [48,49]. Interesting recent results showed that genetically modified cyanobacteria (Synechococcus elongatus PCC7942) consume CO$_2$ in a set of steps to produce directly a mixture of isobutaraldehyde (primarily) and isobutanol [50]. However, productivities are still quite low. Carbon Sciences [51] has announced that it has developed a breakthrough enzyme-based technology to transform CO$_2$ into low-level fuels, such as methanol, but more precise information and data are lacking. Other biotech companies, such as Joule Biotechnologies, Gevo, and Global Bioenergies, have also announced that they have developed genetically modified microorganism pools able to use CO$_2$ to produce directly fuels or chemicals, but data are not available to estimate productivities and pro/cons of the proposed technologies. Thus biotech routes will probably have a relevant role in converting CO$_2$ to solar fuels and chemicals in the future, but currently available data are not sufficient to really prove the potential. Algae and plants are already used in producing some very high-value chemicals industrially, but this has not had a significant impact on CO$_2$ emissions, because of the very low value of these products. We discuss here the case of solutions using CO$_2$ for potentially large-volume products (fuels) or chemicals having a large impact value.

1.2.1 Routes for Converting CO$_2$ to Fuels

There are different routes to convert CO$_2$ back to fuels. The most-studied area is the hydrogenation of CO$_2$ to form oxygenates and/or hydrocarbons. Methanol (CH$_3$OH) synthesis from CO$_2$ and H$_2$ has been investigated up to pilot-plant stage, with promising results [6a,b]. The CAMERE process [carbon dioxide hydrogenation to methanol via a reverse water-gas shift (RWGS) reaction] is based on a first stage in a RWGS reactor where part of the CO$_2$ feed is converted to CO (>60%). After elimination of the water produced, the resulting H$_2$/CO$_2$/CO mixture is then fed to a methanol synthesis (MS) reactor, where it is converted to CH$_3$OH, according to:

\[ \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (1.1a) \]

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (1.1b) \]

The two-step process allows 25% reduction of volume of the MS reactor with respect to a single stage, higher process efficiency, and lower operational costs. Zinc aluminate- and Cu/Zn/Al$_2$O$_3$-based catalysts are used in the two steps. The CAMERE process was developed on a bench scale (50–100 kg MeOH/day) [52]. The Japanese company Mitsui Chemicals Inc. completed in 2009 a pilot (100 t·y$^{-1}$) methanol plant in Osaka [53]. Mitsui Chemicals is also planning a first commercial-scale (600,000 t·y$^{-1}$) methanol plant based on Mitsui’s Green House Gases-to-Chemical Resources (GTR) technology. Methanol is intended as feedstock for olefins and aromatics. The previously cited company Carbon
Recycling International [18] also started in September 2011 a plant in Svartsengi, Iceland for producing 5 Mt-y\(^{-1}\) of methanol from CO\(_2\).

The alternative possibility is the production of dimethyl ether (DME), a clean-burning fuel that is a potential diesel pool additive. Kansai Electric Power Co. and Mitsubishi Heavy Industries (Japan) have developed a bench-scale unit (100 cm\(^3\) catalyst loading) for DME synthesis via the reforming of methane by CO\(_2\) and steam [54]. Ni/MgO-Al\(_2\)O\(_3\) and Ru/MgO-Al\(_2\)O\(_3\) catalysts were used for the methane reforming with a CH\(_4\) conversion almost complete over 1073 K in 800-h durability tests; carbon deposition on the catalyst was very low.

Ethanol formation, either directly or via methanol homologation, and conversion of CO\(_2\) to formic acid are also potentially interesting routes. Methanol, ethanol, and formic acid may be used as feedstock in fuel cells, providing a way to store energy from CO\(_2\) and then produce electricity. Alcohols are in principle preferable over hydrocarbons because their synthesis requires less hydrogen per unit of product. In fact, the key problem in this route is the availability of H\(_2\). If the latter is produced from hydrocarbons (the main current route is by steam reforming of methane) there are no real advantages in converting CO\(_2\). H\(_2\) must thus derive from renewable sources. The possible options are the following:

- **Water electrolysis**, coupled with a renewable source of electrical energy (photovoltaic cells, wind, or waves, etc.). This technology is already available, but the need for multiple steps, the overpotential in the electrolyzer, and other issues limit the overall efficiency. The technology is mature, with a limited degree of further possible improvements.

- **Biomass conversion**, preferably using waste materials and in conditions that require low energy consumption. An example is the catalytic production of H\(_2\) directly in liquid phase from aqueous solutions (ethanol waste streams, for example). This option could be a way for valorization of side waste streams in biorefinery, but it is not an efficient way if considered alone. In fact, if we consider the whole life cycle including growing the plant, harvesting, fermentation, etc., and finally H\(_2\) production (from bioethanol, for example), the overall energy consumption (and thus amount of CO\(_2\) produced) is higher than the advantage in hydrogenating CO\(_2\) back to fuels.

- **Production of H\(_2\)** via biogas produced from anaerobic fermentation of biomass. Also in this case, it could be a valuable option using waste biomass, but it is a quite complex process considering the whole production chain. There are also problems of purification of biogas.

- **Production of H\(_2\)** using cyanobacteria or green algae. This is an interesting option, but still with low productivity and under development.

- **Direct H\(_2\)** production by water photoelectrolysis, which still suffers from low productivity and in some cases the need for further separation/recovery of hydrogen but has great potentiality for development to reach industrial feasibility.

The following section further discusses the production of H\(_2\) using renewable energy, abbreviated as “renewable H\(_2\)” hereinafter. Hydrogen, after eventual
compression and heating to the requested reaction temperature, may then be used for the hydrogenation of CO\textsubscript{2} to produce CO via the RWGS reaction. Carbon monoxide and hydrogen, the so-called syngas, may then be converted to methanol and/or DME, or Fischer–Tropsch (FT) products (hydrocarbons, mainly) by known catalytic processes [6]. These processes may be also combined in a single process with the RWGS reaction, but the formation of water in the latter is an issue in syngas transformation. The cited transformations are technologies essentially available, although some further improvement is necessary in terms of both catalysts and reactor technologies. The key aspect in all these routes is to produce renewable \( \text{H}_2 \) through economic and eco-/energy-efficient processes. Dry reforming of methane with CO\textsubscript{2} is an alternative possibility to produce syngas:

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \tag{1.2}
\]

However, this is a strong endothermic reaction suffering from fast deactivation due to carbon formation. Coupling with the reaction of steam reforming of methane and of partial methane combustion (the so-called tri-reforming process) reduces the issue of deactivation and allows autothermic operations. The process is interesting and is developed up to pilot-scale operations [12]. However, the CO\textsubscript{2} recycling effectiveness is low, even if specific LCA studies are not present in the literature.

There are other routes and options in converting CO\textsubscript{2} to fuels, as discussed in detail elsewhere [5a,6a,7,9,12,21]. When sources of renewable \( \text{H}_2 \) below a cost of about $2–3/kg are available, either because it is used as excess energy or for other reasons, these processes of CO\textsubscript{2} conversion to fuels could be already close to commercialization, with minor technological aspects that still need to be developed further [6a]. However, different process steps and large chemical plants are necessary, and in general terms it is not an energy-efficient process technology. A longer-term vision would be a technology that will couple and integrate directly the stage of hydrogen generation (from water using solar energy) to the stage of CO\textsubscript{2} reduction and conversion to fuels in mild reaction conditions. This is the concept of artificial leaf discussed in the following section.

### 1.2.2 \( \text{H}_2 \) Production Using Renewable Energy

Converting CO\textsubscript{2} to fuels or chemicals via breaking of the C–O bond requires \( \text{H}_2 \), and the latter should be produced with the use of renewable energy sources to make the process effective in terms of GHG impact, as discussed in the previous sections. The current method of producing \( \text{H}_2 \) is mainly based on methane (or other fossil fuels) steam reforming:

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2 \tag{1.3}
\]

Four moles of \( \text{H}_2 \) are produced per mole of CO\textsubscript{2}, that is, 5.5 kg CO\textsubscript{2} per kg \( \text{H}_2 \), but including the energy required in this endothermic reaction this value rises to about 9 kg CO\textsubscript{2}/kg \( \text{H}_2 \) [55]. The impact on CO\textsubscript{2} emissions of producing \( \text{H}_2 \) from
biomass needs to include many factors, from the growing of biomass to biomass harvesting/transport, conversion etc. On average 5–6 kg CO$_2$ per kg H$_2$ are produced [56].

For the direct production of H$_2$ using renewable energy, LCA data are not very reliable, because all technologies are still at the development stage. For wind/electrolysis, a value below 1 kg CO$_2$/kg H$_2$ was estimated [57]. Utgikar and Thiesen [58] reported life-cycle CO$_2$ emissions for various hydrogen production methods and indicated values for hydroelectric/electrolysis or solar thermal production of H$_2$ around 2 kg CO$_2$/kg H$_2$ and values for photovoltaic/electrolysis production around 6 CO$_2$/kg H$_2$. However, the latter value appears overestimated and does not include the latest developments in the field. We thus assume an average of 1–2 kg CO$_2$/kg H$_2$ for hydrogen produced via electrolysis using excess electrical energy.

The production of H$_2$ by electrolysis is already well established, with the electrical energy deriving from photovoltaic (PV) cells, wind turbines, etc. Today, the efficiency of the PV-electrolysis system is at best about 12% [59]. H$_2$ could be produced under pressure in modern electrolyzers, while other routes produce H$_2$ at atmospheric pressure. Polymer electrolyte membrane (PEM) water electrolysis technology is today a safe and efficient way to produce renewable hydrogen, with stack efficiencies close to 80% at high (1 A·cm$^{-2}$) current densities [60], but overpotential is still a major problem limiting the cost-effectiveness. PEM electrolyzers show a number of advantages over the alternative and well-established alkaline technology: the absence of corrosive electrolytes and better integration with solar and wind power. A target cost of about $2–4/kg H$_2$ necessary to make the technology competitive has still not been reached, but the current trend in cost reduction looks promising, especially when the problem of overpotential could be solved by a better understanding of the processes at the electrode surface.

### 1.2.3 Converting CO$_2$ to Base Chemicals

Light olefins (ethylene and propylene), currently produced in an amount of about 200 Mt·y$^{-1}$, are the building blocks of current chemical production. They are synthetized today from fossil fuels, but this process is the single most energy-consuming production in the chemical industry, and the specific emission of CO$_2$ per ton of light olefin ranges between 1.2 and 1.8 [61]. It is thus interesting to explore the possibility of using CO$_2$ as the carbon source to produce olefins, using H$_2$ produced from renewable energy sources [61]. Because of their high energy of formation, C2-C3 olefins represent an excellent opportunity to store solar energy and incorporate it into the value chain for chemical production instead of that for energy. The high value of the energy of formation of olefins also explains why their actual process of formation is the most energy-consuming process in the chemical industry, with a large impact on CO$_2$ emissions.

The largest part of ethylene and propylene production is currently used to produce polymers, directly (polyethylene and polypropylene; polypropylene production, for example, accounts for >60% of the total world propylene consumption)
or indirectly (for example, main products of propylene are acrylonitrile, propylene oxide, acrylic acid, and cumene, which are intermediates in the production of polymers).

The synthesis of light olefins from CO\textsubscript{2} requires the availability of H\textsubscript{2}. Ethylene and propylene have a positive standard energy of formation with respect to H\textsubscript{2}, but water forms in the reaction and thus the process essentially does not need extra energy with respect to that required to produce H\textsubscript{2}. From the energetic point of view, the energy efficiency of the process is thus related to the energy efficiency of the production of H\textsubscript{2}. The process for olefin synthesis from CO\textsubscript{2} may be described as the combination of a stage of RWGS (Eq. 1.1b) and a consecutive stage of FT synthesis:

\[
\text{CO} + \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + \text{C}_n\text{H}_{2n+2} + \text{H}_2\text{O} + \text{CO}_2 (n = 1, 2, \ldots) \tag{1.4}
\]

The FT catalyst should be modified in order to minimize the formation of alkanes (especially CH\textsubscript{4}) and increase selectivity to C2-C3 olefins. The above two stages may be combined together, but water should be preferably removed in situ to shift the equilibrium and avoid FT catalyst reversible inhibition. Current catalysts, derived mainly from the doping with alkaline metals of conventional FT catalysts or catalysts combining a zeolite with a methanol or FT catalyst, give at best selectivities around 70–80% and around 40% conversion [61]. Further improvements in catalysts, reactor design, and process operations are thus necessary, but it is reasonable to consider possible a further optimization with a target in selective synthesis of light olefins over 80% at higher conversion (>70%).

The process flow sheet in light olefin production from CO\textsubscript{2} [61] (Fig. 1.2) is based on a first step of production of H\textsubscript{2} by electrolysis and electrical energy derived from renewable sources. The core of the process is the combination of RWGS and modified FT reactions. The two steps are in separate stages for the optimization.

![Figure 1.2](image.png)
of the relative catalysts and reaction conditions. Inorganic membranes permeselective to water are integrated in the reactors to improve the performance of the process. \( \text{H}_2 \) is added in part between the two stages, and the methane, light alkanes, and >C5 hydrocarbons produced in the process are recycled. The overall process, because of the formation of water, results in a slightly exothermic process. After thermal recovery, the light olefins are separated in a sequence of columns similar to the steam cracking process, while CO and \( \text{CO}_2 \) are recycled to the RWGS unit.

A techno-economic analysis of this possibility [61] indicates that for a predicted renewable \( \text{H}_2 \) cost as target for the year 2020 (US$2–3/kg \( \text{H}_2 \)), the process is economically valuable. The current renewable \( \text{H}_2 \) cost is still higher, but not so high not to consider in more detail the possibility of producing light olefins from \( \text{CO}_2 \).

### 1.2.4 Routes to Solar Fuels

Although the concept of solar fuels is broad and typically also includes \( \text{H}_2 \) production using solar energy, we do not here consider hydrogen strictly a solar fuel but an intermediate to produce the true solar fuels in the form of liquid (easily storable and with high energy density) chemicals, that is, energy vectors that can be more easily stored and transported (see Section 1.2). As briefly discussed in Section 2.1, there are different possible energy vectors that derive from the hydrogenation of \( \text{CO}_2 \), either directly or through the intermediate stage of the RWGS reaction (Eq. 1.1b), to produce syngas (mixture of \( \text{CO}/\text{H}_2 \)), which can be then converted through already-established and commercially applied routes, although the syngas is produced from hydrocarbons instead of from \( \text{CO}_2 \) and \( \text{H}_2 \):

- Formic acid, which may be used in formic acid fuel cells or as a vector to store and transport \( \text{H}_2 \) (the reaction of synthesis is reversible, and formic acid can be catalytically decomposed under mild conditions to form back \( \text{H}_2 \) and \( \text{CO}_2 \) [62])
- Methanol and dimethyl ether (DME)
- Methane (substituted natural gas, SNG)
- >C1 alcohols or hydrocarbons

These different routes have been discussed in detail elsewhere [6a]. The main routes are chemical (catalytic), but electrochemical or solar thermal routes are also possible, even if the latter two routes are still not sufficiently developed. Syngas may also be produced by reaction with hydrocarbons (particularly methane) through so-called dry reforming. The main potential advantage of this route is that it can be applied directly to flue gases (even if technical problems exist), while all the other routes require a first step of separation of \( \text{CO}_2 \) from the flue gases. However, dry reforming is an endothermic reaction occurring at high temperature (about 900–1000°C) and with formation of carbon (which deactivates the catalyst) as a side reaction. An overview of the different routes is given in Figure 1.3.

The catalytic chemistry of the RWGS reaction, the following transformation to methanol/DME, or hydrocarbons via Fischer–Tropsch synthesis, and the
subsequent production of gasoline (methanol to gasoline, MTG) or of diesel via hydrocracking of the alkanes produced in the FT process (using Co-based catalysts) is well established, even if there is still need for development because of the change of feed composition starting from CO\textsubscript{2} rather than from syngas. Also, in terms of process development, most of the necessary knowledge is available. Minor technological barriers to development of these routes are thus present. Only for the synthesis of formic acid, either catalytically or electrocatalytically, is there still need for development in terms of productivity and stability.

The main gap in the catalytic routes of CO\textsubscript{2} conversion to fuels is economic, with the cost of production of renewable H\textsubscript{2} as the key factor. However, opportunities already exist in terms of available (low cost) sources of renewable H\textsubscript{2} that make the production of fuels from CO\textsubscript{2} interesting. Mitsui Chemicals and Carbon Recycling International are two companies that are running pilot plant projects to exploit the conversion of CO\textsubscript{2} to methanol, as discussed above, while Mantra Venture Group and DNV are exploring at pilot-plant scale the electroreduction of CO\textsubscript{2} to formic acid. RCO\textsubscript{2} AS has instead developed at pilot scale a process based on recovery of CO\textsubscript{2} from flue gas and its conversion to methane using renewable H\textsubscript{2}. Details on these processes and the related chemistry and catalysis are provided elsewhere [6]. A book discussing the various possible routes for CO\textsubscript{2} conversion was recently published by Aresta [5a]. Other authors have also recently published reviews on this topic [6–15].

The catalytic synthesis of higher alcohols from CO\textsubscript{2} is an interesting route but is still not competitive. New interesting catalysts, however, have been developed.
Conversion of CO$_2$ to higher alcohols and hydrocarbons (≥C2) by biocatalysis or electrocatalysis methodologies is also an interesting route, but is still at a preliminary stage [21]. Genetically modified cyanobacteria have been recently reported to consume CO$_2$ in a set of steps to produce a mixture of isobutyraldehyde (primarily) and isobutanol. With a gas-phase electrocatalysis approach CO$_2$ may be reduced to a mixture of ≥C2 hydrocarbon and alcohols, mainly isopropanol [63]. Artificial metabolic pathways involving enzymes or cyanobacteria have been proposed to use NADPH and ATP from photosynthesis for the synthesis of n-butanol (UCLA) or isobutene (Global Bioenergies) directly from CO$_2$ and water.

1.3 TOWARD ARTIFICIAL LEAVES

The leaf is a highly complex machinery that utilizes solar light to oxidize water and produce electrons/protons used in a different part of the cell to reduce CO$_2$ to carbohydrate, lipid, and other components necessary for plant life and growth. In an artificial leaf it is necessary to mimic the various steps in this hierarchical process (capture of sunlight photons, electron–hole separation with long lifetimes, energy transduction, etc.) while developing a new functional and robust design that realizes two goals:

- Intensify the process, thus allowing higher productivity and efficiency in converting sunlight (in plants the quantum yield is typically below 1%);
- Use solid components that keep functionalities but are more robust, scalable, and cost-effective.

It is also necessary to separate the two reactions, water oxidation using sunlight and CO$_2$ reduction using the electrons/protons generated in the light-illuminated side. They should occur in two different cell compartments separated by a proton-conducting membrane [21c], in order to reduce back reactions, achieve high efficiency, and, importantly from the practical perspective, have separate production of O$_2$ and of the products of reduction of CO$_2$. This is a critical issue both for safety and to avoid the costs of separation. The same is valid in the simpler case of production of O$_2$ and H$_2$ in two compartments. This is the photoelectrocatalytic (PEC) approach. An artificial leaf should thus be composed of the following main elements:

- An anode exposed to sunlight carrying a photocatalyst able to oxidize water and supported on a conductive substrate that allows fast collection of the electrons and is permeable to protons, in order to transport the electrons and protons to the cathode side;
- A membrane enabling fast transport of protons with a minimum transfer resistance, good contact with the anode and cathode sites, and an effective barrier action to O$_2$ diffusion;
- A cathode, which is formed in the simplest approach by a conductive substrate (in contact with the membrane and permeable to protons) containing active
centers for proton and electron recombination to \( \text{H}_2 \). In a more challenging approach, the cathode contains centers able to chemisorb \( \text{CO}_2 \) and convert it catalytically (in the presence of electrons and protons) to fuels or valuable chemicals.

An alternative for the anode side is to have an electrocatalyst able to perform water electrolysis, with the electrons supplied by semiconductor, preferably active in the visible region of the sunlight and in direct contact with the electrocatalyst. This alternative solution is preferable to the first case, because the issues related to charge separation are in principle lower. Sensitizers for the semiconductor, if robust enough to anodic oxidation conditions and not quenching the water oxidation processes, allow extension of the range of wavelengths of activities (antenna effect).

1.3.1 PEC Cells for \( \text{CO}_2 \) Conversion

A number of proposals have been made recently for artificial leaf solar cells, although often they are still at a conceptual level and their feasibility of realization and behavior have not been proved [64]. Most of them are designed only for producing \( \text{H}_2 \) from water, and often also without separate production of \( \text{O}_2 \) and \( \text{H}_2 \). In principle, an artificial leaf-type PEC solar cell for converting \( \text{CO}_2 \) using sunlight requires a different design [40]. One of the few examples reported specifically for this objective has a design close to that of commercial PEM fuel cells, to take advantage of the large knowledge portfolio on their engineering and mass/charge transfer optimization. The scheme of the solar fuel cell is shown in Figure 1.4, which also shows the practical realization of the cell that is currently under testing [63,65].

The cathodic part operates in gas phase, because this (i) simplifies the recovery of the reaction products (they can be collected by cooling the gas outlet from the flowing cell), (ii) allows continuous operations and the use of large concentrations of \( \text{CO}_2 \), (iii) greatly reduces mass transfer limitations, and especially (iv) changes the type of products that are formed.

The electrochemical reduction of \( \text{CO}_2 \), in both aqueous or organic electrolytes, gives mainly \( \text{C}_1 \) products of reduction and is limited in productivity by the solubility of \( \text{CO}_2 \) in the electrolyte and the mass transfer in solution [66]. Conversely, gas-phase operations allow formation of \( >\text{C}_2 \) products [21,63,65] (never detected in liquid-phase operations) and eliminate the problem of solubility of \( \text{CO}_2 \) and mass transfer in liquid phase, as well as avoiding the formation of a double layer and related effects. The electrocatalyst, however, should be different. Instead of using conventional electrodes, the solar PEC cell shown in Figure 1.4 uses an electrode based on metal nanoparticles dispersed over conductive doped carbon nanotubes (CNT) and then deposited over a carbon-cloth (CC) conductive material acting as electron transport net [40,67]. With a Fe/N-CNT-based gas diffusion electrode, it was shown that isopropanol is formed, being the main reaction product of the \( \text{CO}_2 \) electrocatalytic reduction [21,63].
CO₂ reduction to fuels
or CH₃CH(OH)CH₃

H₂ Production

2H⁺

H₂

O₂

Light

Electrocatalyst
Photoanode
Proton membrane

Assembly of photoanode with the Nafion membrane

PEC cell

Solar simulator

Quartz window

Filter

Figure 1.4  PEC solar cell. Top: scheme of the cell with electron microscopy images of an example of the TiO₂-nanotube array electrode and of the Fe-nanoparticles on N-doped carbon nanotubes, used as photocatalyst for water oxidation and electrocatalyst for CO₂ reduction, respectively. It is also shown that it may be possible to use this cell for the production of H₂/O₂ in separate compartments by water photoelectrolysis. Bottom: photo of the experimental cell and the assembly of a photoanode with a Nafion membrane. Adapted from refs. 40,63,65.

The photoanode is instead based on an array of vertically-aligned doped titania nanotubes, produced by anodic oxidation of thin Ti layers [68], in order to meet the following demanding requirements for a porous photoanode for PEC solar cells:

- Cost-effective and easily scaled to large operations;
- Robust for stable operations;
- Having an optimal nanostructure allowing (i) enhanced light harvesting (possible over the entire sunlight spectrum, with effective use of the radiation for creating a photocurrent), (ii) low rate of charge recombination and reduced interfaces/grain boundaries, which favors the charge recombination, (iii) negligible defects and centers that favor thermal or radiative pathways (which reduce quantum efficiency), and (iv) fast transport of the electrons to a conductive substrate;
- Having a porous nanostructure that allows fast transport of protons (generated from water oxidation) to the underlying proton-conductive membrane,
avoiding surface recombination between protons and electrons (which should have different paths of transport), and an optimal interface with the membrane.

Because of self-doping during preparation and/or the creation of surface phononic heterostructures (by deposition of very small gold nanoparticles), these titania nanotubes ordered thin films are active in the visible light region [69], although still with not enough performance. Commercial Nafion is used as the proton-conductive membrane. There are still a number of problems at the interface between this membrane and the titania photo anode, and the effectiveness in the transport of protons is limited. In addition, transient measurements [63b,70] indicate the presence of significant surface quenching processes (associated to the formation of surface peroxo-species) that limit the steady-state productivity in water oxidation. This cell design could be transferred to application as an artificial leaf, but productivity of both electrodes must be improved in terms of (i) response to visible light, (ii) reducing surface self-quenching during reaction, (iii) presence of several interfaces that limit the mass/charge transfer and cell efficiency, and (iv) rate of CO₂ reduction. A new advanced cell design has been proposed and is under investigation to solve these issues [64].

1.4 CONCLUSIONS

This brief discussion of the perspectives and state of the art of production of solar fuels and chemicals from CO₂ has presented some of the trends and issues regarding the recycling of CO₂ as an enabling element for a low-carbon economy and the efficient introduction of renewable energy into the production chain. The aim was not to provide a systematic review of the state of the art but only to highlight the opportunities offered by this new vision of CO₂ recycling to solar fuels and chemicals.

After introducing the general context and the motivations, and general issues regarding the energy vectors and the problem of introducing renewable energy in the energy and chemical production chains, this chapter has analyzed two main aspects:

- The challenge of using CO₂ for the production of light olefins (ethylene, propylene) as an example of the possible reuse of CO₂ as a valuable carbon source and an effective way to introduce renewable energy into the chemical industry value chain, improve resource efficiency, and limit greenhouse gas emissions;
- The conversion of CO₂ to fuels using sunlight (solar fuels), with a concise presentation of the possible routes with some indication also of the industrial developments in the field, in order to highlight the possible routes for the storage of solar energy and discuss briefly the pro/cons and how they integrate into the existing energy infrastructure for a smooth, but fast, transition to a more sustainable energy future.
These examples show that it is possible to create \( \text{CO}_2 \)-based resource-efficient chemical and energy production. Thus \( \text{CO}_2 \) must no longer be a waste, but rather an enabling factor for the effective introduction of renewable energy into the chemical production chain, and solar fuels are an effective driving force toward a more sustainable energy.

From a longer-term perspective, the objective should be the photoelectrochemical activation of \( \text{CO}_2 \) in artificial leaf-type PEC cells to fully enable the potential of solar radiation by collecting energy in the same way that natural leaves do, but in an intensified process directly producing chemicals/fuels. Because of the complexity of the problems, a fundamental understanding is the key for advancing, taking into consideration system engineering and integration. The fast advances in the development of nano-tailored materials will be key to progress in this field, but only when combined with the integration between catalysis and electrode concepts to achieve a real breakthrough in the understanding of the reaction mechanisms of these fast surface processes.

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