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The use of solar energy can enhance the conversion of carbon dioxide into energy-rich products: stepping towards artificial photosynthesis

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The need to cut CO₂ emission into the atmosphere is pushing scientists and technologists to discover and implement new strategies that may be effective for controlling the CO₂ atmospheric level (and its possible effects on climate change). One option is the capture of CO₂ from power plant flue gases or other industrial processes to avoid it entering the atmosphere. The captured CO₂ can be either disposed in natural fields (geological cavities, spent gas or oil wells, coal beds, aquifers; even oceans have been proposed) or used as a source of carbon in synthetic processes. In this paper, we present the options for CO₂ utilization and make an analysis of possible solutions for the conversion of large volumes of CO₂ by either combining it with H₂, that must be generated from water, or by directly converting it into fuels by electrolysis in water using solar energy. A CO₂–H₂-based economy may address the issue of reducing the environmental burden of energy production, also saving fossil carbon for future generations. The integration of CO₂ capture and utilization with CO₂ capture and storage would result in a more economically and energetically viable practice of CO₂ capture.

1. Introduction

Fossil carbon, in its various forms (as solid coal, liquid hydrocarbons or gaseous liquified natural gas) will represent for the next 30–40 years the major source of energy for humankind. Today, approximately 85 per cent of the used energy is derived from the conversion of the chemical energy of fossil carbon [1], whereas the combustion of wood or residual biomass contributes approximately 1.5 per cent of the worldwide used energy. Such continuous emission of CO₂ into the atmosphere is causing continuous accumulation as the natural carbon cycle is not able to convert it into usable products, despite the anthropogenic carbon being less than 3 per cent of the total carbon cycled in the natural cycle. The alarming parallel trend existing for ‘growth of population-increase of energy consumption-atmospheric concentration of CO₂’ (US EPA; www.epa.gov) is raising serious concerns about the future of our planet for the potential occurrence of extreme events that are out of human control. CO₂ is considered to be the major contributor to climate change (CC) so that science and technology are much involved in finding remedies that may stabilize its actual concentration in the atmosphere or even reduce it to lower values. The target is to keep under control the increase of the average temperature of our planet that should not be more than 2°C until 2050 [2].

The adoption of severe efficiency technologies, both in the *conversion* of fossil fuels into other forms of energy and in the *use* of the produced energy, would represent the most effective way to reduce the emission of CO₂. Anyway, such solution may require huge investment for upgrading the existing plants or even better building new ones incorporating energy-saving technologies. Efficient technologies alone, although their contribution is of fundamental importance, especially for the aspect of correct use of energy, may not be able to cut the amount of CO₂ necessary for its atmospheric stabilization.

2. The capture of carbon dioxide

The capture of CO₂ from flue gases emitted from continuous point sources, such as power plants or industrial processes [3], that represent approximately 60 per cent of the total emitted CO₂, is a mature technology. The capture of CO₂ may be performed using solid or liquid phases, or membranes [4,5]. Innovation in this field is continuous, and new materials are being developed, such as metallic organic frameworks or polymeric amines or functionalized silicates originated from silylamines or hybrid materials, that may reduce the high cost (energetic and economic) of the capture. Captured CO₂ can be either disposed of or used.

3. The carbon dioxide capture and storage technology

The CO₂ capture and disposal in natural sites have been considered with much attention in recent years. Such technology has been presented as the ‘solution’ to the problem of avoiding the produced CO₂ reaching the atmosphere because, in principle, the disposal capacity of our planet is larger than the total amount of CO₂ that would be produced by burning all fossil carbon available [4,5]. Unfortunately, the carbon dioxide capture and storage (CCS) technology presents some barriers, such as the high cost, not only economic (13–20 US\$ per tCO₂) but also energetic, and the fact that its implementation requires sites that are not ubiquitous. In fact, if the distance of the disposal site from the CO₂ source is of the order of 50 miles, then a minimum 20 per cent penalty must be considered on the efficiency of the power plant. Such favourable ‘vicinity of the disposal with respect to the production-site’ is not usual: in general, penalties of the order of 40 per cent or higher can be foreseen for the majority of cases, which means that substantial amounts of excess fossil carbon (with respect to the energy requirements) must be extracted! This makes CCS one of the technologies, but not ‘the technology’, for CO₂ reduction, also because issues such as the transportation and housing safety are still open questions.

Table 1. Technological utilization (25 Mt yr⁻¹).

additive to beverages	mechanical industry (moulding)
cereal preservation (<i>bactericide</i>)	fire extinguishers
food packaging/conservation	air-conditioning
dry-cleaning	
extraction (fragrances and enhanced oil recovery)	water treatment

4. The carbon dioxide capture and utilization technology

An alternative to CCS is the utilization of CO₂. Carbon dioxide capture and utilization encompasses *technological use*, *enhanced biological fixation* and *chemical conversion*. The *technological utilization* (table 1) does not convert CO₂ but makes use of it with final venting, or recycling, of the gas.

In all such applications, CO₂ is used instead of chemicals that have a much higher CC power than CO₂ itself [6] with large benefits in terms of CC reduction.

The *biological conversion* of CO₂ into micro- or macro-algae under non-natural conditions (concentration of CO₂ up to 150 times higher than the atmospheric) [7] can recycle large volumes of CO₂ and can be economically viable if a ‘biorefinery’ approach is used that makes use of chemicals and fuels derived from the biomass. The use of aquatic biomass for energy scope only is not economically viable today.

The first examples of CO₂ *conversion into chemicals* were: the Solvay process (1861) for the synthesis of NaHCO₃ and Na₂CO₃, the urea synthesis (1869) and the synthesis of salicylic acid (leading to aspirin, 1870). All such processes are pure ‘thermal’ processes. Almost one hundred years elapsed before catalytic processes were introduced in the 1970s: for example, the conversion into methanol by addition to syngas [8] and the carboxylation of ethene epoxide to afford cyclic carbonates [9]. The discovery in 1975 of the first transition metal complex of CO₂ [10] opened the door to the synthesis of new metal systems able to activate CO₂ and to the exploration of new catalytic routes for its conversion. The interest towards the chemical conversion of CO₂ has experienced in the past 40 years a *waving* trend, typically with an increase on the occasion of any oil crisis! Today, urgent environmental issues are calling for any useful action for limiting the CO₂ emission into the atmosphere: the attention towards CO₂ utilization is growing. Interestingly, the chemical utilization of CO₂ adds value to CO₂.

5. Used and avoided carbon dioxide

The chemical utilization of CO₂ is not *per se* a guarantee that CO₂ is avoided: in fact, when we use the produced compounds, in general, CO₂ will be re-emitted. Avoiding CO₂ requires the development of ‘less-carbon and energy-intensive’ synthetic methodologies than those on stream today: the new methodologies must be characterized by a higher carbon fraction utilization. On the other hand, avoiding CO₂ is not synonymous with a more environmentally friendly process! The environmental impact of a product or process follows a complex pattern. Table 2 gives the impact categories of a chemical emitted in soil, water or the atmosphere: in order for a new technology to be more environmentally friendly than the one on stream it must reduce the overall environmental impact, not simply decrease the CC impact.

If the new production technology reduces the CO₂ emission (i.e. the ‘carbon footprint’ of a product) and, thus, the CC impact, but increases the impact on other categories listed in table 2, the global effect may not be beneficial at all! The ‘carbon footprint’ does not tell the entire story of the environmental impact of a process product.

Table 2. Impact categories for emissions in soil, water and atmosphere.

carcinogens (non-carcinogens)	respiratory inorganics
ionizing radiations	ozone layer depletion
respiratory organics	aquatic ecotoxicity
terrestrial acidification	terrestrial nutrification
land occupation	aquatic acidification
climate change	aquatic eutrophication
non-renewable energy	mineral extraction

6. Catalytic conversion of carbon dioxide

The catalytic conversion of CO_2 into useful chemicals can be driven by homogeneous, heterogenized, heterogeneous and enzymatic systems either thermally or electrochemically or photochemically or else photo-electrochemically. CO_2 being a molecule lying in a potential energy well ($\Delta G^\circ = -394.4 \text{ kJ mol}^{-1}$; it is, with water, the end product of all combustion processes, either biotic or abiotic), it is a common belief that any chemical conversion of such a molecule will require energy. This is not completely true, as two processes can be clearly distinguished for its use.

- (i) Low-energy processes: any time the entire CO_2 moiety is incorporated into an organic or inorganic substrate.
- (ii) High-energy processes: any time the oxidation state of the carbon atom is reduced from +4 in CO_2 down to -4 in methane, such as in the series CO_2 , HCOOH , CO , CH_2O , CH_3OH , CH_4 .

The two classes of reactions can, in principle, lead to different products. class (i) processes will mostly produce products of the chemical industry, whereas class (ii) processes may give fuels. Chemicals and fuels used today are responsible for the production of CO_2 : fuels emit roughly 12 times more CO_2 than organic chemicals derived from fossil carbon. This means that if the synthetic use of CO_2 is confined to the synthesis of chemicals (figure 1a), more limited amounts of CO_2 will be recycled than if fuels (figure 1b) are produced.

Figure 1 shows the processes on stream, those under development that are of interest for the chemical industry and the reactions that may be of interest for the energy industry.

In the latter case, the key issue is the source of energy necessary for CO_2 conversion, an issue that has prevented so far the conversion of large volumes of CO_2 .

It is worth emphasizing that the benefit of using CO_2 is not represented that much by the amount of converted CO_2 , but is given by the amount of 'avoided CO_2 ', i.e. by the amount of *non produced* CO_2 if new, clean, less-carbon and energy-intensive processes are exploited, based on the use of CO_2 [6]. The most interesting innovative chemical processes that may 'avoid CO_2 ' with respect to those on stream are:

- the synthesis of *organic carbonates*, both acyclic and cyclic: this will avoid the synthesis and use of phosgene, an energy-intensive, toxic and pollutant chemical;
- the synthesis of *carbamates*, today equally obtained from phosgene; and
- the synthesis of *carboxylates*, such as acids, esters, lactones, pyrones, etc., obtained today through long multi-step (cyanation, hydrolysis) or non-selective (oxidation) processes.

Such compounds have each a market more than 1 Mt yr^{-1} and are responsible for the emission of tens of Mt yr^{-1} of CO_2 . Their synthesis has been discussed elsewhere [11,12]. In this paper, we shall concentrate on the conversion of large volumes of CO_2 into energy products such as: CO ,

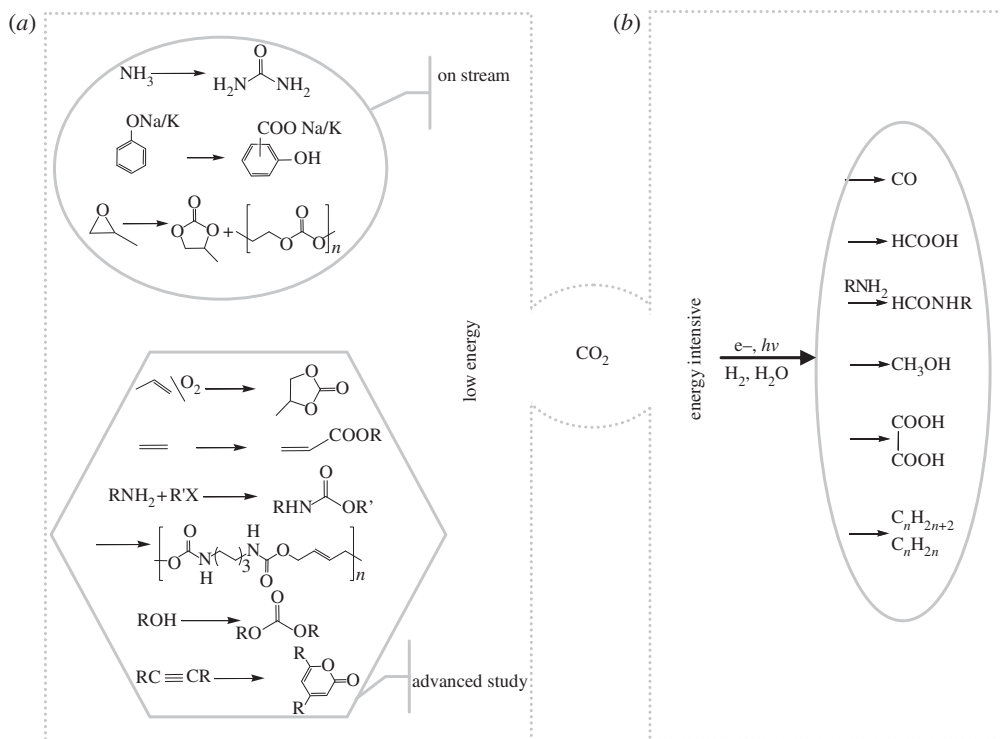
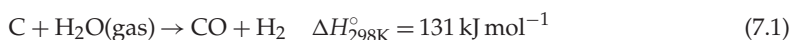


Figure 1. Synthetic processes for the production of chemicals from CO_2 .

CH_3OH and higher alcohols, CH_4 and higher hydrocarbons up to $\text{C}_{10}\text{--C}_{18}$, usable as transport fuels, and others.

7. The energy issue in the production of energy products from carbon dioxide

The conversion of CO_2 into fuels requires energy in the form of heat, electrons or else dihydrogen: such energy is today mainly derived from fossil carbon. As a matter of fact, 90 per cent of dihydrogen is produced from fossil carbon according to

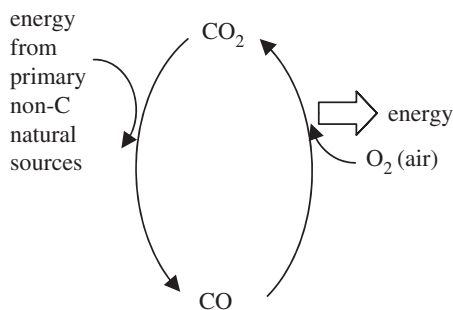


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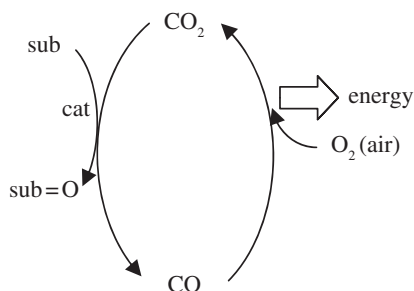


that also generate heat and electricity. Both reactions are strongly endergonic and occur at high temperature (more than 800°C). Obviously, such a route cannot be used for converting back CO_2 into energy-rich molecules: the amount of produced CO_2 would be higher than that converted! As a consequence, so far the conversion of large volumes of CO_2 into energy products has not been taken into consideration. A business-as-usual approach is, thus, ruled out and new C-free strategies must be implemented: water must, indeed, be used as a source of H_2 and perennial primary energy sources must be used to power the processes!

We are now seeing a change of paradigm in the utilization of primary perennial energy sources (such as solar, wind, hydro, geothermal energy). It makes sense, thus, to evaluate possibilities of using such C-free energy available on a large scale for converting back CO_2 into energy-rich compounds, mimicking Nature! Furthermore, the conversion of CO_2 may represent a route to the use of H_2 and produce fuels that would use the existing network of distribution and the existing



Scheme 1. Energy from cycling on CO–CO₂.



Scheme 2. Use of CO₂ as oxidant in a cycle that produces energy.

cars. Such H₂–CO₂ integration may become usable in the short- and medium-term and may lead to the production of fuels with C-recycling and fossil carbon saving for future generations.

Let us now consider the tools we have at hand for CO₂ conversion into energy products and how we can make use of the various primary energy sources.

8. Reduction of carbon dioxide to carbon monoxide

The simplest way to convert CO₂ into an energetic product is its deoxygenation to afford CO (scheme 1), a reaction that can be carried out either by a thermal or by a radiative route. Such non-catalysed process is very energy demanding, as shown in equation (8.1).



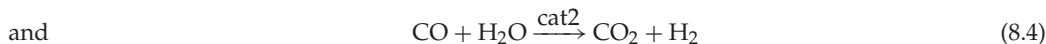
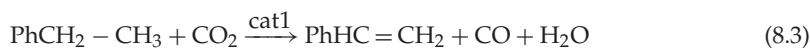
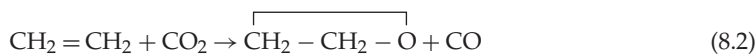
The produced CO can be burnt with air to give energy and CO₂.

The thermal decomposition of CO₂ into CO and oxygen (equation (8.1)) can be carried out using concentrators of solar power (CSP) [13]. Temperatures up to 1500 K can be generated in CSP that are suited for CO₂ dissociation. The drawback of such technology is its periodicity due to the light–dark daily cycle.

It is worth noting that when CO₂ is coordinated to a metal system the deoxygenation may occur at room temperature [10] or also just above 14 K in a gas matrix [14] with oxygen transfer to a substrate. Such catalysed deoxygenation process (scheme 2) would be of interest if a cyclic ‘reduction of CO₂–oxidation of CO’ could be implemented on a large scale with production of useful materials (during the reduction of CO₂ to CO) and energy (during the re-oxidation of CO to CO₂).

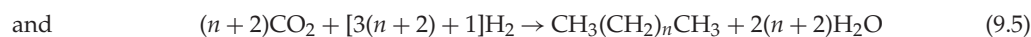
Obviously, such application is limited by the volume of the species ‘sub=O’ that can be produced and used. Among the O-acceptors, olefins and hydrocarbons can be identified as the most suitable as their ‘oxidized’ forms (epoxides, equation (8.2), and unsaturated hydrocarbons,

equations (8.3) and (8.4)) have large, but not unlimited, application ($\gg \text{Mt yr}^{-1}$) as monomers for polymers. While equations (8.3) and (8.4) have been demonstrated to be possible and could be exploited as the use of CO_2 results in a more selective and more controlled process than the dehydrogenation based on the use of only O_2 , equation (8.2) is not of practical use for its tendency to afford other products.

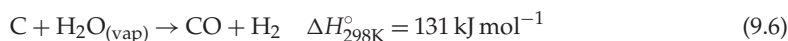


9. Reduction of carbon dioxide to other C1 or Cn molecules

The CO_2 -reduction process can be further continued beyond CO and a number of interesting chemicals can be obtained according to the catalysts and conditions used:



The issue is the availability of H_2 . Actually, 90 per cent of dihydrogen is produced from fossil carbon, according to the water gas reaction (equation (9.6)) and wet-reforming of methane (equation (9.7)):



and



Both reactions are strongly endergonic and occur at high temperature (more than 800°C). This route cannot be taken into consideration for producing H_2 for CO_2 conversion. A business-as-usual approach is, thus, ruled out. A new approach is needed that does not make use of fossil carbon for both producing H_2 and driving the conversion reaction: this is the use of water (water splitting) as source of H_2 and the use of perennial energies or 'waste' energy for powering the conversion process. Various technologies can be considered based on high-temperature (thermal) or low-temperature (electrophotocatalytic) reactions. Examples of the former are (i) the thermal scission of water; (ii) the use of thermodynamic cycles (table 3) [15]; (iii) the use of excess electric energy for H_2O electrolysis or for the direct reduction of CO_2 in water; and (iv) the application of solar energy for the electrochemical, photocatalytic or photo-electrochemical water splitting or for the direct conversion of CO_2 in water.

Table 3 reports the *sulfur–iodine thermodynamic cycle*: the net reaction of such cycle would be equation (9.8):



but H_2 is eventually produced from water.

The *direct thermal water splitting* (equation (9.9)), an endergonic process ($\Delta G^\circ = 237.2 \text{ kJ mol}^{-1}$), can be produced by using the CSP technology, as seen before for CO_2 splitting:



Table 3. Sulfur–iodine cycle.

cycle	<i>T</i> (°C)	reactions
sulfur–iodine	850	$2\text{H}_2\text{SO}_4(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$
	450	$2\text{HI} \rightarrow \text{I}_2(\text{g}) + \text{H}_2(\text{g})$
	120	$\text{I}_2 + \text{SO}_2(\text{a}) + 2\text{H}_2\text{O} \rightarrow 2\text{HI}(\text{a}) + \text{H}_2\text{SO}_4(\text{a})$

The other routes to H₂ or direct CO₂ reduction in water will be discussed in more detail below. However, in the case of a large availability of dihydrogen a number of products can be derived from the hydrogenation of CO₂, each having potential application in a different sector with a market ranging from a few (HCOOH, H₂CO) to tens (CH₃OH) or hundreds (HC) Mt yr^{−1}.

In particular, formic acid can also be considered as a H₂ carrier as equation (9.1) is easily reversed, and methanol can find use as a fuel (in fuel cells or in combustion engines in cars) or as a bulk chemical (synthesis of acetic acid, ethene, ethers, hydrocarbons, etc.). The synthesis of methanol is mastered at the plant level and is characterized by a high selectivity (100%) under relatively mild conditions (420 K and 3.0–5.0 MPa of pressure) with energy recovery and re-use [16]. The conversion of methanol into other chemicals or fuels is a mature technology practiced for many years.

The reaction of CO₂ with dihydrogen is, thus, a ‘multi-purpose’ application that can give positive solutions to two problems: the cycling of CO₂ and the storage of H₂, its transportation and use. In fact, coupling CO₂ and H₂ would allow the use of existing energy storage and transport infrastructures making more attractive and less problematic an eventual H₂ economy. In addition, the hydrogenation of CO₂ would represent a solution to the storage of electric energy as discussed below.

10. Use of excess electric energy and storage of electric energy

Nowadays, the electro-reduction of CO₂ is considered with particular interest as it can really contribute to recycling large volumes of CO₂ and to store electric energy, an old issue without any practical solution. It is obvious that we cannot produce electricity from fossil fuels expressly for such application, but such an option can be used for avoiding the electric energy produced from fossil carbon being wasted or in the case where perennial primary energy sources are used. Excess electric energy (e.g. energy produced during the night or holidays, for example, when less energy is used by consumers) could be conveniently converted into chemical energy (fuels) to be used in cars (substituting fuels produced from fossil carbon) or for regenerating electric energy during peak hours. A similar practice is already implemented in several power stations that pump water uphill during the night and use the falling water during the day at peak hours for electricity production: in this way, the excess energy produced during the time when lower power is demanded by the grid is conveniently stored and used when the demand is higher.

Furthermore, the conversion of electric energy into fuels by simultaneous reduction of CO₂ also gives an answer to an old issue: the conservation of electric energy. The storage of electricity into batteries is not a practical solution as batteries have a quite low energy density by volume (or even by mass) that ranges from 0.3 to 2.8 GJ m^{−3}, depending on the kind of battery considered (the most efficient are the Li batteries). Figure 2 gives an idea of how the storage of energy into batteries compares with the storage into chemicals that can be derived from CO₂.

Chemicals such as methanol or gasoline have an energy density that is from 10 to even 100 times higher than batteries. It is obvious that the two processes (battery charging and conversion of CO₂ into chemicals) may present a different energy conservation efficiency and this must be taken into consideration in order to assess the real benefit. Assuming that H₂ is first electrochemically produced from water and then used for the reduction of CO₂ into methanol, one should take into consideration that the electrolysis of water is today performed with an efficiency

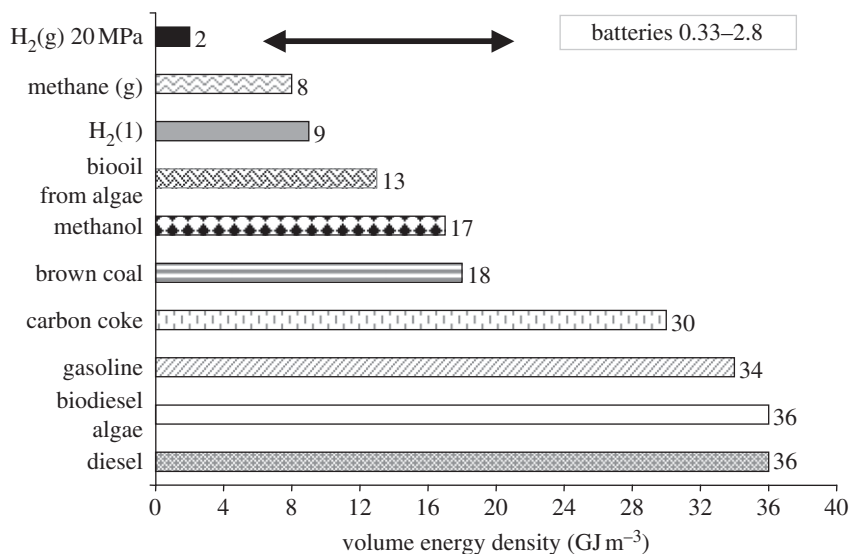


Figure 2. Volume energy density of different classes of chemicals.

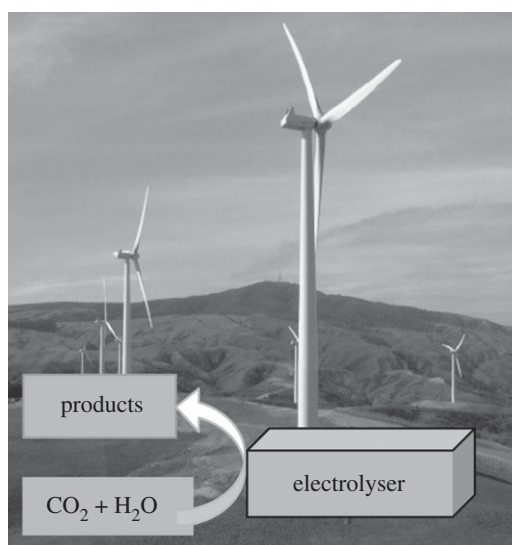


Figure 3. How to couple wind energy with CO₂ reduction through wind towers.

close to 80 per cent. The synthesis of methanol is quite efficient and very selective (100%). A loss of energy is encountered in the pressurization of H₂ from atmospheric pressure (production) to the utilization (methanol synthesis) that requires 2.0 to 5.0 MPa: the energy consumption is of the order of 3.6 kWh kg⁻¹ of H₂ [17].

The energy spent for H₂ production (electrolysis) is in the range 33–37.5 GJ per t_{CH₃OH} and the energy necessary for the compression of H₂ is 1.52 GJ per t_{CH₃OH}. All together, the energy required for the production of methanol via electrolysis of water is in the range 35–40 GJ per t_{CH₃OH}. Considering that methanol has an associated energy close to 20 GJ t⁻¹, the energy consumption ratio ($E_{\text{out}}/E_{\text{in}}$) is around 0.5–0.6. It may be worth recalling that the charge of a battery has an efficiency close to 80–90%.

Another possible approach is to use perennial energy, such as wind power, to run an electrolyser for CO₂ electro-reduction in water: a deeper insight into this topic is given in the next section. Figure 3 shows how one can figure out the coupling of a wind tower with CO₂ reduction. Wind towers are often stopped, because the grid is saturated: they could be kept in continuous operation and the excess electric energy they generate could be used for the reduction of CO₂ produced nearby or, even better, locally captured from the atmosphere. In fact, if non-fossil energy is used for CO₂ entropy reduction (separation from N₂ and O₂), then atmospheric CO₂ could conveniently be used for conversion into fuels. In a frame in which an effective electrochemical conversion of water is identified, the production of fuels from CO₂ and H₂ becomes of great interest for both the storage of energy and recycling of carbon.

Moreover, the recycling of carbon will bring to the reduction of the extraction of equivalent (if not higher!) amounts of fossil carbon.

11. The direct electro-reduction of carbon dioxide in water

An alternative to the production of dihydrogen from water is the direct reduction of CO₂ in water to afford C₁ or C_n molecules.

The electro-reduction of CO₂ in water is strongly dependent on the electrode used. Table 4 lists a number of electrodes and the products obtained (the yield is given in parentheses in one specific case). In any case, the electrodes are affected by the electrolysis and severe losses are observed.

In order to improve the efficiency of the process and the life of the electrodes, the *electrocatalytic* approach can be used. In this case, a catalyst is used that avoids reactions occurring at the electrodes' surface, expanding their life. Under homogeneous catalysis, soluble catalysts are used that catalyse the reaction out of contact with the electrodes. In this way, the electrodes are only involved in the transfer of electrons to and from the catalysts but are not the site where the reactions occur [18]. A particular case is the deposition on the electrode of electro-catalysts that protect the electrode surface from a chemical attack.

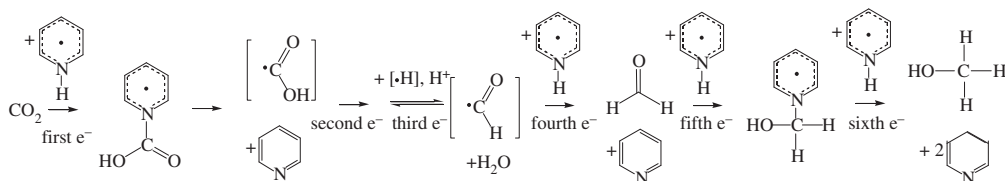
Aspects of paramount importance in the electro-catalytic reduction of CO₂ to fuels are the kinetics of reaction and the electron transfer, processes in which the catalyst is involved: this requires that the catalyst must have energy levels that match the reduction potential of CO₂ to the desired species (table 5).

Homogeneous catalysts are particularly suitable for adaptation to the different potentials required as the properties of the metal system can be quite finely tuned through ligands.

A key point is, thus, to design metal catalysts that may work as close as possible to the thermodynamic conditions, avoiding the high over-potential that often is generated when a direct reduction of CO₂ occurs at an electrode surface. Under the latter conditions, surface deterioration and low efficiency are very often encountered with a substantial reduction of the efficiency of the process of reduction. The ligands used to stabilize metal centres usually bear either P- or N-donors. Such anchoring sites are part of molecular structures of quite different complexity: by controlling the structural parameters of the ligands, it is possible to control the utilization of the metal complexes in the reduction of CO₂. Mono-, di- and poly-dentate phosphines with moieties of various basicity and acidity strongly influence the properties of the catalyst [19]. N-macrocyclic ligands have been intensively investigated [20–22] as well as dipyridine [23]. Cluster-soluble complexes have been efficiently used [24]. Electro-catalysis under homogeneous conditions has good potential, and either metal systems or organic catalysts may be used [18,25,26]. Sophisticated metal systems bearing complex ligands such as porphyrins [27] have been used. Polycyclic ligands have also been supported on the electrode [28].

All the systems above suffer an important limitation due to the possible oxidation of the ligand that may deactivate the catalyst. Recently, interesting results of more long-lived catalysts have been reported [29,30].

The organic catalysts based on the use of pyridine [25] have shown so far a good stability, most probably due to their extreme simplicity (scheme 3).



Scheme 3. Proposed mechanism for the pyridinium-catalysed reduction of CO_2 to methanol.

Table 4. Electrodes and products of reduction of CO_2 in water.

electrodes	products
Cu	C_2H_4 (32–80%) $\text{C}_n\text{H}_{2n+2}$
Zn, Au, Ag, p-InP, p-GaAs, Pt-Pd-Rh	CO CO + HCOOH
RuO_x on conductive diamond, B-doped C	MeOH, EtOH, $\text{C}_n\text{H}_{2n+1}\text{OH}$

Table 5. Multi-electron versus one-electron reduction of CO_2 .

$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	$E_0 = -0.53 \text{ V}$
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCO}_2\text{H}$	$E_0 = -0.61 \text{ V}$
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	$E_0 = -0.48 \text{ V}$
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	$E_0 = -0.38 \text{ V}$
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	$E_0 = -0.24 \text{ V}$
$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^{\cdot-}$	$E_0 = -1.90 \text{ V}$

Interestingly, they can afford not only C_1 species (CH_2O , CO, HCOOH , CH_3OH , CH_4), but also C_2 , C_3 and probably C_n molecules. A radical mechanism is most probably active in such systems which show a promising potential for application.

12. The changing paradigm: use of solar energy for carbon dioxide reduction

This decade is and will be characterized by an enormous jump of the installed photovoltaic (PV) technology, another way to use solar energy in addition to CSP already discussed. PV power installed is growing beyond any expectation as the cost of materials and installations is going down and the payback time is decreasing from the actual 8–11 to foreseen 2 years. This is mainly due to the shift from the actual mono-crystalline-Si technology to *thin-film* technologies. The amount of electric energy produced using thin-film technologies for solar light capture and conversion is estimated by the International Energy Agency to cover 20–25% of the electricity market by 2050. Table 6 gives the observed trend of PV power installation worldwide. The expected 9000 TWh of PV and CSP in 2050 clearly shows that PV technologies will soon reach a level of maturity that will enable the exploitation of solar energy for various purposes, among which is electric energy production [32].

Figure 4 shows that PV energy utilization is applicable all over the world: such application seems more limited by political decisions than by natural conditions, if it is true that Germany is leading now the exploitation of such technology.

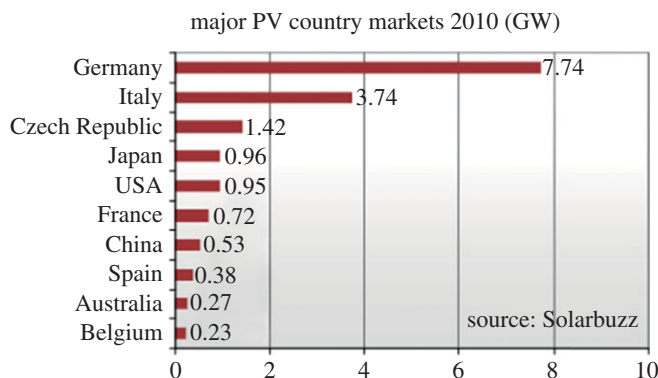


Figure 4. Worldwide installed PV power (2011). (Online version in colour.)

Table 6. Rate of growth of the power of installed PV [31].

year	power (GW)
2009	7.2
2010	16.6
2011	40
2020	200
2030	2000
2040	3000

Such a new paradigm is essential for the development of new strategies of H_2 production from water using PV or for the direct electrochemical conversion of CO_2 in water, as discussed earlier. The two options will be briefly discussed.

The key parameters in the water electrolysis based on PV are the overvoltage for H_2 production and the electrolysis efficiency (ranging from 55 to 80% with a good average at 73%). The existing electrodes allow an average solar-to-hydrogen (StH) conversion efficiency in the range 5–15%, with a best performance of 20 per cent observed when GaInP/GaAs/Ge junction is used, which has a low over-potential. The area necessary for the production of 1 t per day of H_2 is in the range 20–40 km², with a best figure of 10 km² in the case of the best performing junction given above. The US DoE target is to produce H_2 at a cost of 2–3 US\$ kg⁻¹ (1.5–2.3 € kg⁻¹). This requires that the capital costs of installations must be lower than 800 US\$ kW⁻¹ and an electricity cost of 0.055 US\$ kWh⁻¹ (0.042 € kWh⁻¹) [33]. Today, for a 1 t of H_2 per day production, with a solar input of 6.55 kWh m⁻² d⁻¹, a StH conversion of 15 per cent, using 1885 reactors each of 18 m² that require a total area of 33 930 m² for photon capture (using tracking concentrators) and a capital cost of 3.5 MUS\$, the H_2 production cost ranges around 4.5–5 US\$ kg⁻¹, still too high. An abatement of costs is possible using better concentrators, improving the StH conversion efficiency and reducing the overvoltage, doing better than 53 kWh kg⁻¹ H_2 necessary today.

If the direct conversion of CO_2 in water is considered, keeping the PV conversion efficiency of solar light into electric energy equal to 16–20% [34], and considering an 80 per cent efficiency in the electrolysis and 80 per cent selectivity in a product (table 7), then one can conclude that it would be possible to convert solar energy into chemical energy (as a single product!) with a global efficiency equal to more than 10 per cent. Such a value is higher than the efficiency of any bioprocess! In fact, plants show an efficiency close to 1.5–2% and microalgae, the most efficient solar energy users, have an efficiency close to 6–8%.

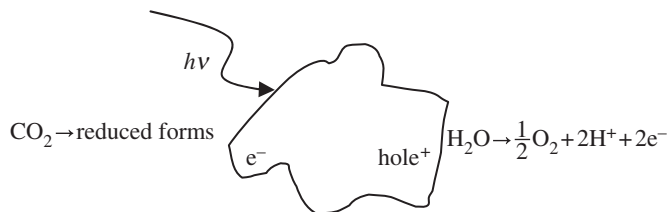


Figure 5. Use of semiconductors for CO_2 reduction using solar light.

Table 7. Comparison of two approaches for solar energy storage into chemicals obtained from CO_2 reduction.

technology	H_2 production from H_2O followed by the catalysed reaction with CO_2	direct photo-electrochemical reduction of CO_2 in water
solar light conversion efficiency, %	15–20	15–20
electrolysis efficiency	70–80	60–70
PH_2 (MPa) in the electrolyser	1	n.a.
PH_2 (MPa) in the chemical conversion	30	n.a.
temperature for CO_2 conversion	150°C	room temperature
products (selectivity)	CH_3OH (100)	H_2 –CO (approx. 20) CH_3OH $\text{CH}_2=\text{CH}_2$ (approx. 80)

13. Photochemical technologies for carbon dioxide reduction in water

The reduction of CO_2 in water can be carried out *photochemically*, in the presence of suitable photocatalysts. The *photochemical* reduction makes use of semiconductors which are able to absorb light and generate a ‘hole plus electron’ (figure 5).

The *electrons* reduce CO_2 , whereas water is oxidized at the positive *hole*. This is a quite appealing solution but, for practical application, it requires that: (i) sunlight is used and (ii) O_2 (the oxidized form of water) is efficiently produced and separated from the reduction products of CO_2 . At present, the efficiency of water oxidation is still low [35] and represents a barrier to the development of the system. Moreover, while several semiconductors are known to be able to work under UV light [36], very few are able to work efficiently under solar light irradiation. The goal here is to develop new photocatalysts such as mixed oxides that may be able to drive the target reaction using solar light and working as much as possible close to thermodynamic conditions for avoiding overvoltage phenomena and loss of efficiency. Mixed oxides seem to be a quite promising solution as the modification of the electronic properties of the photoactive oxide can be driven by adding a second oxide. So, for example, the band gap for TiO_2 is approximately 3.85 eV, far away from being usable for visible light conversion. By modifying the original TiO_2 lattice by adding ZnO one gets a band gap of 3.26 eV that is more close to the domain of visible light utilization [37]. Therefore, the combination of various oxides or the deposition of metals and ligands on the surface of a given oxide may lead to a material with the correct band gap that may use visible light for CO_2 reduction in water.

As pointed out earlier (table 5), the multi-electron reduction of CO_2 is energetically more easy than the one-electron reduction.

Considering the fast growth of knowledge in the area of solar light utilization, it is not incorrect to foresee a potential growth of such strategy to an application level in the medium term.

14. Comparison of the photovoltaic-electrochemical, photochemical and photo-electrochemical reduction of carbon dioxide

However, should we use the PV-electrochemical, the photochemical or the photo-electrochemical approach to the conversion of CO₂? Is it better to make use of the PV energy for producing dihydrogen from water or for a direct reduction of CO₂ in water? It must be pointed out that the use of solar energy is limited by the availability of space for solar light collection. With 6935 MJ m⁻² per year as average capacity of solar energy collection and 193 kWh m⁻² per year of produced electricity the actual PV technology is winning as there are not yet photochemical systems that may directly use solar light at the same level of efficiency. The expectation in this field is that with thin films the solar conversion efficiency into electric energy may be increased from 20 to 40 per cent. PV may support the conversion of large volumes of CO₂ in the short term, but possibly photochemical systems will become the winning option in the medium term. The specific space requirement per tonne of converted CO₂ and the investment costs will determine the most effective option.

Converting solar energy into liquid fuels would represent a great opportunity for reducing the CO₂ emission in the atmosphere while maintaining the actual transportation infrastructure.

Table 7 compares the two options: (i) making H₂ from water and using it for CO₂ chemical reduction and (ii) the direct reduction of CO₂ in water. Which of the two is thus the winning option?

From the data shown in table 7, it comes out that there are pros and cons for each technology. As said earlier, the preliminary production of dihydrogen has a weak point in the low pressure at which it is generated, compared with the pressure necessary for its use in the methanol plant. Energy is necessary for pressurizing H₂ to the working pressure in the methanol plant, which will reduce the overall efficiency. The high selectivity in methanol is a strong point in favour of the first technology. The variety of products obtained as a function of the electro-catalysts used or the electrode used may become (it is not now!) a point in favour of the direct reduction.

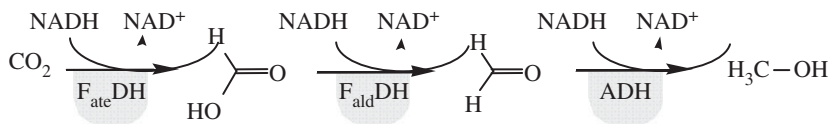
The production of CO in mixture with H₂ is not a negative case [6]; in fact, if the two gases could be produced in the correct H₂ : CO = 2 molar ratio, or close to it, then the mixture would find application as syngas. Either component could anyway independently be added to the gas mixture produced by electrolysis of CO₂ in water in order to reach the best ratio for its use in the synthesis of gasoline or other compounds.

The photo-electrochemical approach results, thus, in an interesting combination of the two approaches discussed earlier, electrochemical and photochemical, for the recycling of CO₂.

A critical point with PV is the high environmental impact due to the technologies of production of the used materials. As a matter of fact, today, the production of H₂ via PV has an impact that is some two times higher than the production using CSP and five times higher than the production from wind [38,39]. This case is an example of what was said above about the environmental impact assessment of the new technologies: the conversion of CO₂ into fuels is a positive fact as it reduces the accumulation of CO₂ into the atmosphere, consequently reducing the CC, but the production of the materials necessary for such conversion to occur generates important impacts on other key categories: the total result is not so positive. More environmentally friendly materials are needed that can make acceptable the production of H₂ via PV.

15. Coupling chemistry and biotechnology

The reduction of CO₂ in Nature occurs in several organisms, under anaerobic or aerobic conditions. The methanation of organic substrates involves, among others, enzymes that are able to reduce CO₂ to CO (carbon monoxide dehydrogenases) or to formic acid (formate dehydrogenases, F_{ate}DH). CO₂ can be reduced to the methyl group –CH₃ in a tetrahydrofolate-mediated process. CO and –CH₃ are coupled to give the acetyl moiety (–COCH₃) using a Fe₄S₄–Ni enzyme and vitamin B₁₂. Formate can be reduced to formaldehyde using the formaldehyde



Scheme 4. CO₂ reduction to methanol in water promoted by F_{ate}DH, F_{ald}DH, and ADH.

dehydrogenase (F_{ald}DH) enzyme, and formaldehyde can be converted into methanol by the alcohol dehydrogenase (ADH) enzyme. An interesting network of reactions that produce energy-rich C1-molecules from CO₂.

Interestingly, the three enzymes that convert CO₂ into methanol (scheme 4; F_{ate}DH, F_{ald}DH and ADH) are commercial. In an attempt to mimic Nature, a biotechnological approach to the conversion of CO₂ into methanol has been investigated based on the use of the enzymes described earlier. It has been shown that the trilogy of enzymes F_{ate}DH, F_{ald}DH and ADH are able to reduce CO₂ in water at ambient temperature [40]. Three moles of NADH are consumed per mole of CH₃OH produced (scheme 4).

This approach, though quite appealing, is not economically and energetically viable, unless NAD⁺ formed upon oxidation of NADH is efficiently recycled increasing, thus, the ratio CH₃OH/NADH to limits that can be acceptable for a biotechnological production of methanol.

More robust enzymes were obtained [41] by encapsulation in tetraethylorthosilicate. Co-encapsulated enzymes work better than singly encapsulated ones [42,43].

The artificial reduction of NAD⁺ to NADH can be performed in different ways, by using: (i) cheap chemicals that act as reducing agents [44]; (ii) metal systems that may use dihydrogen for the reduction under thermal or irradiated conditions; (iii) semiconductors, water and (solar) light as source of energy for the reduction; and (iv) electrocatalysts that may reduce NAD⁺ under electrochemical conditions. Among the methodologies listed earlier, the use of semiconductors in water or in cheap H-donors, such as bioglycerol, under solar light irradiation is by far the most attractive technology. So far, a proof of concept of such application has been reported with a production of 100 mol of CH₃OH per mole of NADH used [45]. The photo-electrochemical reduction of NAD⁺ is also an interesting route that still requires research for assessing its real potential.

16. Conclusions

The use of fossil fuels as energy sources in power generation and in industrial processes demands the maximization of yield and selectivity in order to save resources. Moving to the use of perennial energies (such as wind, waves, tides, solar) one can ask whether such strict rules will still stand or whether it will be possible to use a less stringent approach. If we assume that the conversion/utilization of such primary energies is a clean process and does not emit pollutants, then the use of such energies, that otherwise would be anyway lost, may allow one to run processes that do not respond to the strict efficiency criteria listed earlier and they can be run also if the best efficiency is not implemented. All together, Nature uses solar light with an efficiency that is very low: only a few units per cent. It is approximately 1.5 per cent in superior plants such as trees and approximately 2.2 per cent in sunflower or similar plants. The efficiency can reach 6–8% in microalgae, that often are unicellular microorganisms and, thus, more simple. Noteworthy, the above values represent the efficiency towards the production of ‘biomass’: if we look at a single product, then the efficiency is much lower. Nature is not very efficient, it does not need to be!

The existing PV systems, coupled to the best electrochemical techniques for a direct conversion of solar light in water lead to much more efficient systems. As discussed earlier, it would be possible to convert solar energy into a single chemical with an efficiency of the order of more than

10 per cent, which is much better than Nature! The key issue is the durability and productivity of the new devices that, at present, have a limited capacity for CO₂ conversion due to either low capacity or to limited lifetime. Durability and capacity: these are the parameters on which great research efforts must be placed. If the life of devices is made much longer and large-scale applicability of new catalysts is implemented, then the use of solar energy will be able to convert large volumes of CO₂ into fuels, saving natural resources and, what is very important, using the existing infrastructures within the industrial sector, in mobility, in home heating and energizing.

Artificial photosynthesis, that is, any non-natural conversion of CO₂ into energy products, may play a key role in our future, contributing to cleaning the atmosphere and to making natural resources available for a longer time to humankind.

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