



Harvesting Renewable Energy for Carbon Dioxide Catalysis

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The use of renewable energy (RE) to transform carbon dioxide into commodities (i.e., CO₂ valorization) will pave the way towards a more sustainable economy in the coming years. But how can we efficiently use this energy (mostly available as electricity or solar light) to drive the necessary (catalytic) transformations? This paper presents a review of the technological advances in the transformation of carbon dioxide by means of RE. The socioeconomic implications and chemical basis of the transformation of carbon dioxide with RE are discussed. Then a general view of the use of RE to activate the (catalytic) transformations of carbon dioxide

with microwaves, plasmas, and light is presented. The fundamental phenomena involved are introduced from a catalytic and reaction device perspective to present the advantages of this energy form as well as the inherent limitations of the present state-of-the-art. It is shown that efficient use of RE requires the redesign of current catalytic concepts. In this context, a new kind of reaction system, an energy-harvesting device, is proposed as a new conceptual approach for this endeavor. Finally, the challenges that lie ahead for the efficient and economical use of RE for carbon dioxide conversion are exposed.

1. Introduction

The USA and P.R. China, the world's biggest emitters of greenhouse gases (GHGs), have recently announced (September 2016) that they will formally ratify the Paris climate deal within the United Nations Framework Convention on Climate Change (UNFCCC), which deals with GHG emissions mitigation. This fact will further push the identification of the most reliable strategies and solutions for climate change mitigation, although this aspect is part of the more general issue of energy transition, for example, to find cost-effective paths for the progressive substitution of fossil fuels as the key element for the energy system. From this perspective, the approach of CO₂ sequestration to reduce GHG emissions appears to be limiting because the key issue is to explore the link between renewable energy (RE) and CO₂ utilization, as discussed herein, as an opportunity to enable this energy transition rather than just implement a costly CO₂ sequestration option.^[1]

The often remarked upon question regards the dimension of GHG emissions. More than one ton of CO₂ per second is presently being released at a global scale, although it is the imbalance between emissions and sinks that is responsible for the increasing CO₂ concentration in the atmosphere. As a result of the increase in energy consumption from fossil fuels, an excess of 900 Gt of atmospheric CO₂ (compared with preindustrial levels) has been emitted so far.^[2] Environmental concerns related with the elevated atmospheric concentration of GHGs have motivated political action, which, in the case of the EU, looks for an 80% reduction of GHG emissions by 2050. These actions involve an increase in energy efficiency, more renewables in the energetic mix, and carbon capture. These three aspects have been typically con-

sidered to be disjointed. However, the use of captured CO₂ rather than its sequestration, when joined with the utilization of RE in the conversion process, leads to the critical possibility of extending the use of RE, as also discussed below.^[3] In this way, the utilization of CO₂ to produce energy vectors^[4] is a critical enabling element for the energy transition, with a potential impact, which, measured in terms of CO₂ equiva-

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lent saving tons, is equal to or even higher than what could be expected from CO₂ sequestration, but up to one-third of the cost.^[1]

From a broader perspective, the increasing share of solar and wind power in the energetic mix and the COP21 agreement pave the way for a new family of technologies based on RE. Storage of this energy is one of the most explored challenges necessary for a sustainable society. Several of these storage technologies are summarized in Figure 1. Long-term energy storage is the most challenging aspect due to factors such as costs, reliability, and maturity of the technologies available. Arguably, PHS is presently the most viable among the available long-term storage technologies. Nevertheless, the geographical conditions required are not widely available.

Therefore, to satisfy long-term energy storage requirements, synthesis of fuels or chemicals from RE (often indicated with the term solar fuels^[5]) is a central research subject.^[6] This is also a key element towards the transition to

sustainable and low-carbon-footprint chemistry; a topic of rapidly rising interest indicated by the general term “solar-driven chemistry”. The transition to this new energy and chemistry scenario requires, however, the development of new technologies and solutions, and, in general terms, a new type of synthetic approach based on the use of RE sources as energy input rather than thermal energy, as actually used in over 95 % of refinery and chemical processes. Therefore, an effective transition requires the development of new concepts to introduce RE sources in the paths of CO₂ conversion. Although there is increasing research activity into these aspects, a more comprehensive analysis of the novel existing opportunities and of the required knowledge to enable this transition is still missing.

Herein, we aim to present a succinct, yet critical, review of the present developments on the use of RE in chemical processes focused on the transformation of CO₂ from being a despicable waste into valuable fuels or chemicals. Thus, products such as methanol or methane could be obtained and used in the production of other compounds or as energetic vectors.^[8] These CO₂ valorization reactions are conventionally performed with thermal energy.

Thermochemical CO₂ conversion with concentrated solar energy is an attractive way to obtain fuels and chemicals in a sustainable way and has been broadly covered elsewhere in the scientific literature.^[9] The production of syngas through the dissociation of CO₂ and water requires very high temperatures (>2000 °C) and separation processes for hydrogen and oxygen obtained. The use of thermochemical cycles (mostly in two steps) based on metal oxides allows operation at lower temperatures (800–1200 °C) and the separation of oxygen from the syngas stream during the process.^[9] In the first step, oxygen is released from the metal oxide with solar energy. Subsequently, the reduced metal (or oxide) reacts exothermically with CO₂ to produce CO and the initial oxide state.^[9c] Some redox pairs used in this process include Fe₃O₄/FeO, ZnO/Zn, SnO₂/Sn, and nonstoichiometric ceria. Thermal management and materials are challenges of this technology that are currently under study.^[9a]

Devices based on the use of electricity through electrochemical transformations would be highly convenient for this endeavor. Therefore, electrocatalysis for CO₂ (fed together with water) conversion has been investigated in recent decades and, consequently, several thorough reviews have been written.^[9a,c,10] Copper has been identified as an attractive catalyst because it is able to yield methane, ethylene, or ethanol. However, electrocatalytic CO₂ conversion also has some drawbacks, such as high overpotentials, low reaction rate and selectivity, and low faradaic efficiency.^[9a,10c] One strategy to overcome such drawbacks is to first produce hydrogen through electrocatalytic water splitting and then feed this hydrogen into a CO₂ hydrogenation process (Figure 2).^[9a]

Owing to the fluctuating and distributed nature of renewables, it is necessary to develop technologies that are not only efficient, but also respond rapidly, are compact, and flexible. Therefore, this work will be directed towards microwave (MW), plasma, and photoactivation of CO₂ transforma-

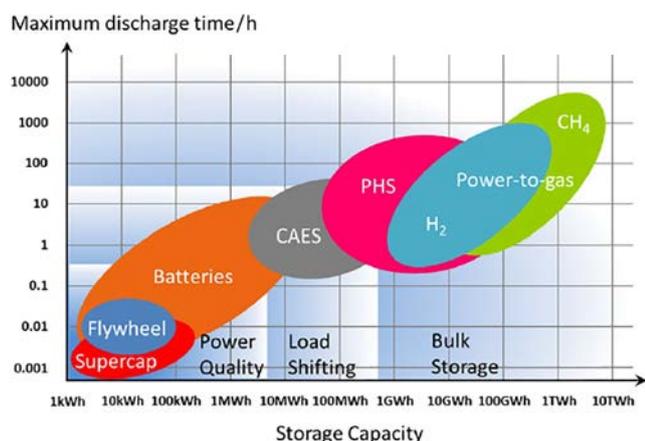


Figure 1. Feasibility of several energy storage technologies. CAES: compressed air energy storage, PHS: pumped hydroelectric storage. (Reproduced from Ref. [7] with permission from The Royal Society of Chemistry.)

Alexander Navarrete Muñoz earned his PhD at the University of Valladolid (Spain) in 2010, where he developed novel processes for biomass valorization by using microwaves. In 2012, he developed the first microwave plasma gasification processes in the Chair of Intensified Reaction and Separation Systems of Delft University of Technology with the support of the Bill and Melinda Gates Foundation. As postdoctoral researcher in the University of Valladolid has proposed and developed a new kind of microreactor that uses solar energy for CO₂ catalytic transformations and has patented a technology to store and release hydrogen in solid state. He is interested in the development of new materials and devices that capture and store renewable energy.



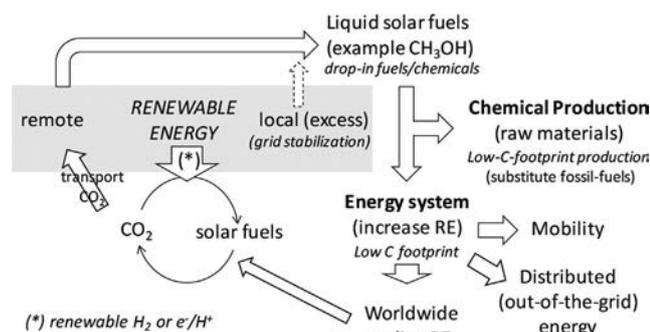


Figure 2. Simplified cartoon of the different roles inside the future energy and chemical production scenario of solar fuels derived from the conversion of CO_2 by using local or remote RE sources (adapted from Ref. [23]).

tion given the potential to overcome issues such as thermal inertia (e.g., solar thermochemical cycles)^[9a,c] or low reaction rates (e.g., electrocatalysis).^[9a,10c]

2. Chemical Processes to Introduce RE into the Economic Environment

As anticipated in the Introduction, realizing the energy transition requires implementation of the concept of the “renewable energy economy” as a key element for the future sustainable and low-carbon-footprint scenario of energy and chemical production.^[11] The key requirement is to develop new and efficient solutions for “chemical energy storage”.^[12]

The actual energy system requires the transport, storage, and distribution of energy on a global scale in an easy, low-energy-intensive, and cost-effective way. Although the “low cost” (with respect to alternatives) of fossil fuels is a relevant aspect of the actual fossil-fuel-centric energy system, it is not the only motivation. Relevant aspects are also easy processing to prepare the energy vectors suitable for a large variety of uses and their easy transport, storage, and distribution on large scale.^[13] Substituting fossil fuels (10% of which are used as carbon sources for chemicals^[14]) with other energy sources requires the maintenance of these characteristics, but the transition to new energy is possible (and in this sense sustainable) only when the cost of transition is minimized.

The energy is so pervasive that any minimal change to the energy infrastructure is very expensive. For example, the investment in energy infrastructure in Europe (just as a consequence of the rising share of renewable components in the energy mix) has been estimated to be about €200 billion up to 2020 by the European Commission.^[15] Changing in the actual energy infrastructure on a massive scale would imply huge investments. A “sustainable” energy transition would thus require that RE sources (sometimes also indicated as perennial) would be used to produce energy vectors that could be utilized in the actual energy infrastructure with minimal changes. There is a second critical aspect regarding the cost of transitions to the energy infrastructure that is illustrated by the fast increase in the market introduction of RE technologies (mainly photovoltaic (PV), and wind turbines).

The actual share is over twice that of predictions from 10–15 years ago.^[16] These technologies require a fixed capital cost of investment that is relatively low, with respect to centralized energy production systems and this allows a much wider base of investors to enter the market compared with the fossil-fuel energy system, for which a few large-scale investors (for refineries, power plants, etc.) exist.

This explains why predictions fail, but also demonstrates the role of the cost of investment in the transition to a new energy system. On the other hand, the rate of expansion of RE technologies is actually limited (at least in countries that introduce a larger extent of RE sources) by the possibility of introducing the produced RE in the distribution network (grid). Advanced energy storage technologies, in particular, chemical energy storage, is necessary as a further step. The latter, by producing energy vectors, would allow not only stabilization of the grid with respect to fluctuation in energy demand and RE production (thus minimizing the need for general reserve power plants), but also the actual (and likely also future) limit of long-range transport of electrical energy to be overcome. Energy vectors are thus the critical element to trade RE on a global scale; a step necessary to overcome the actual limit of RE distribution through the electrical energy grid.

There are different options to produce energy vectors by using RE sources, but let us focus our discussion on hydrogen, which is perhaps the most cited type of “clean” energy vector. In spite of various positive aspects, the great limit of hydrogen is storage and transport. Thus, the critical function for energy vectors (and to enable the energy transition) to create a worldwide trade of RE (an essential element to lower energy costs) is missing. In addition, the use of H_2 as an energy vector^[17] will require huge costs for changing the energy infrastructure (from infrastructure and distribution/storage to engines and conversion devices) with respect to the uncertainty in the market share and dynamics. We may also note that conceptually it is preferable to use the H_2 equivalent (e^-/H^+) to produce higher energy density vectors by converting CO_2 .^[3b,5]

In summary, further increasing the RE share would require massive investments in smart grids^[18] to address the two main weaknesses of PV/wind sources: intermittency and mismatch (time/geographical) between production/demand. Chemical storage is one of the elements that characterize and enable smart grids,^[12,19] and various solutions (from flow batteries to power-to-gas or -liquid, etc.) are under development, as shown in Figure 1.^[20] However, from a longer-term perspective, enabling the RE economy would require going beyond the limitation of a grid and realize a system of easy distribution and storage of RE out-of-the-grid and on a global scale, as actually occurs with oil and derived energy vectors.

This could only be realized when RE is converted into suitable energy vectors that integrate within the actual energy infrastructure and distribution to minimize investment as far as possible.^[4] The need for an out-of-the-grid distributed energy system is not only related to mobility (cars,

airplanes, etc.). Grids have a monopoly character, with only a shift from providers of energy vectors (as actual) to those of the grid services. The monopoly-like character in energy infrastructure (production, distribution) enhances costs due to the absence of (or very limited) competition. In addition, 1) when not convenient, some areas may be not reached by the grid; 2) a trade system of RE is required to be independent of the grid; and 3) RE sources far from the grid cannot be exploited. Distributed energy systems and the expected impact on the reduction of the energy cost can be effective only when an alternative exists to dependence on the grid. These represent some of the points for why enabling an out-of-the-grid distributed energy system is a strategic necessity to create a sustainable energy future, although it is a point often missed in a large part of the ongoing discussion on RE.^[21]

The concept of “solar fuels” is closely linked to the above questions.^[22] They are the energy vectors required to integrate RE into the actual energy system to make the transition to the new system faster, less costly, and sustainable (new infrastructures require energy for their production and have an impact on the environment).

Figure 2 shows in a simplified cartoon the possible integration of chemical energy storage technologies in the future energy and chemical production scenario.^[23] The indication of “drop-in” fuels or chemicals indicates the need for integration within the actual infrastructure.

The discussion on chemical energy storage is often centered on the utilization of excess (overproduction during some time, such as that produced by wind during the night) local resources of RE (in particular, in the case of power-to-gas (P2G), but also regarding H₂ storage^[24]), but the real role of chemical energy storage (solar fuels) will instead focus on different aspects:

- 1) enabling a system to trade RE on a global scale (out-of-the-grid) to allow the exploitation of currently unused remote resources;
- 2) developing a solar-driven, low-carbon, chemical production that reduces the use of fossil fuels;
- 3) creating a distributed energy production to go beyond the actual limitations and dependence on the grid; CO₂ conversion to liquid solar fuels (to methanol, for example, but not necessarily to only this chemical/energy vector) plays a relevant role in this scenario.

Production of methane is also an alternative possible chemical energy storage solution for local energy storage and grid stabilization (e.g., in P2G^[25]), but also shows great limitations for long-range transport. In addition, it is much less suitable for chemical uses, in contrast to methanol or derived products, such as dimethyl ether (DME).^[26]

Figure 2 also evidences that this scenario does not consider the production of H₂ (e.g., by water electrolysis), but rather of the H₂ equivalent: e⁻/H⁺. These are the elements necessary to reduce CO₂ and generate energy vectors. The produc-

tion of H₂ will introduce an energy penalty: overpotential to generate H₂ from e⁻/H⁺ and a further energy penalty in using H₂ that must be activated and catalytically converted. The catalytic processes for the conversion of CO₂ with H₂ require high pressure and relatively high temperatures to be effective (50–100 bar (1 bar = 1 × 10⁵ Pa) and 200–230 °C for methanol synthesis, for example). This scenario thus introduces the production of carbon-based solar fuels through the coupling of photo- and electrodriven processes.^[27] This area regards the development of artificial photosynthesis or leaf-type devices, with a focus on CO₂ conversion rather than H₂ production.^[28] The latter approach is instead actually performed in most of the studies reported in the literature. These devices are clearly also the basis for a distributed energy system.

A further aspect evidenced in Figure 2 regards the creation of a circular CO₂ economy in trading RE on a global scale. Methanol, for example, could be used in gas turbines, from which the recapture of CO₂ is relatively easy. These turbines allow high efficiencies (over 60%, in particular, by using combined cyclic systems with/without CO₂ capture based on methanol indirect combustion^[29] or solid oxide fuel cell–gas turbine (SOFC-GT) hybrid systems^[30]) together with the recovery of CO₂. In this way, an efficient closed-loop system for importing RE from remote areas will be possible.

Figure 3 shows a summary of the different possibilities and routes to convert CO₂ into solar fuels and chemicals, with the indication of the main possible uses of the products. RE may be used according to two main possibilities: 1) production of renewable H₂, or 2) production of electrons, or electron/protons (by water photo-oxidation), used in the electro- or photochemical routes. Although simplified, the scheme shown in Figure 3 evidences the larger spectrum of possible applications of methanol (or derived products, such as DME) with respect to formic acid or methane.

Figure 3 evidences also that syngas (a mixture of CO and H₂) is a key step to 1) methanol (or DME) synthesis, 2) the products of light (C₂–C₄) olefins or aromatics by a modified

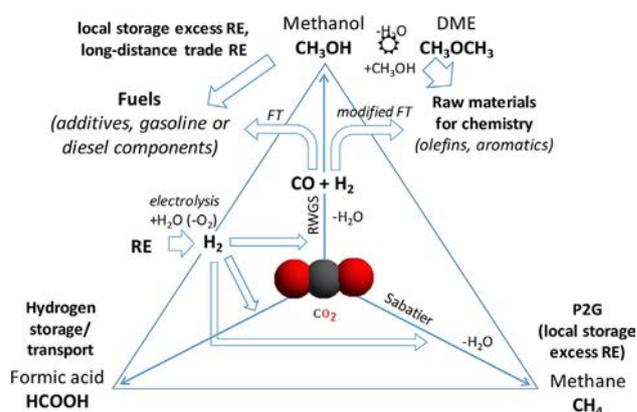


Figure 3. A summary of the current different possibilities and routes to convert CO₂ into solar fuels and chemicals, with the indication of the main possible uses of the products. RWGS: reverse water gas shift, FT: Fischer–Tropsch.

FT synthesis (both of these products are the base raw materials for chemistry), and 3) the production of synthetic fuels (>C₁ hydrocarbons or alcohols) by the FT process. The catalysts for the further conversion of syngas according to these routes are typically also active in the RWGS step of the production of syngas, so a one-step process may be possible. The routes indicated in Figure 3 may be considered established (particularly the catalytic ones that use renewable H₂) and already realizable on an industrial scale,^[8b] although some further development may be necessary. The routes that directly use the H₂ equivalents (e⁻/H⁺) generated in situ (by electro- and/or photocatalysis) require instead relevant development to be implemented on an industrial scale.

In addition to these catalytic routes, there are other possibilities to insert RE into the conversion chain from CO₂ to solar fuels and chemicals. These aspects are discussed in the following sections.

3. Use of RE to Activate CO₂ in Catalytic Reactions

In line with current technologies for energy storage, we can divide the use of renewables for chemical transformations in thermal- and electricity-based technologies.^[31]

Electric current is the main output from renewable technologies such as solar, wind, or hydroelectric energy. In addition, it is possible to harvest thermal energy directly from solar or geothermal energy, or to indirectly produce it from renewable electricity.

Another option is to look for other energy forms, such as MWs, plasmas, or light, which open up new opportunities for efficient and flexible transformations.

These methods of unconventional activation of chemical reactions have attracted recent attention owing to four main advantages:^[32] selectivity, bypass of reactions bottlenecks, new products or properties (added value), and improved process conditions.

Electromagnetic energy deployment to a catalyst is a radically new approach to activate catalytic reactions. The direct use of MWs or their use to create plasmas have been gathering interest owing to the increase in the reaction rates (up to

100-fold with MWs) and their high energy content (reactions induced by electrons with 1–3 eV in plasmas). In addition, the direct use of solar energy to locally activate the catalysts has been recently demonstrated and applied to an ever-increasing kind of reactions.

In the following sections, a brief description of these three unconventional energy forms is given. It is intended to give a broad view of the potential and results of these strategies for CO₂ conversion. Then a more phenomenological discussion and relevant results are presented in Section 4.

3.1. Microwaves

Microwaves (MWs) are in the region of the electromagnetic spectrum ranging from 300 MHz up to 300 GHz. MW heating takes place because of dipole rotation and ionic polarization during the interaction of the electromagnetic field and the matter exposed. The generation of MWs occurs in magnetrons. Once the electromagnetic field is generated, it is deployed by means of a MW applicator. Common MW applicators include waveguides, traveling-wave applicators, single-mode (monomode) cavities, and multimode cavities.^[33] The energy efficiency of this technology is very high and, depending on the conditions, can reach up to 90%.^[34]

Examples of MW activation of catalytic reactions for CO₂ conversion are not abundant, but there are some interesting examples. Owing to the localized thermal effects of MWs and the low energetic level of CO₂, endothermic reactions were investigated in particular. In heterogeneous catalysis, dry reforming of methane (DRM) and RWGS reactions are studied by using some MW-absorbing compound (characterized by high dielectric loss, for example, activated carbon (AC)) as part of the catalyst structure. Similarly, during homogeneous reactions, an absorbing liquid phase is used to transform and transmit the MW energy. Table 1 provides a summary of research into CO₂ catalytic conversion by using MWs.

Part of the potential of MWs is related to the possibility of selective energy delivery directly into the catalytic structures. This mere effect will increase reaction yields by diminishing the conduction–convection losses present in a conventional

Table 1. Catalytic CO₂ conversion by using MWs.

Reaction	Conditions	Reaction media	Conversion	Ref.
DRM	600–800 °C, 150–300 min; monomodal; no power reported	CO ₂ + CH ₄ (60–35% CO ₂) over AC (microplasmas reported)	100% CO ₂ conversion when feed 60% CO ₂ + 40% CH ₄	[35]
reverse Boudouard reaction	650–1200 °C; absorbed power 50–200 kW kg ⁻¹ , 30 min; multi- and monomodal	CO ₂ over AC OR charcoal	CO ₂ conversion > 95%	[36]
DRM	450–800 °C, input power ≈ 50–130 W	CO ₂ + CH ₄ (3:1–1:3) over Pt/γ-alumina (CeO ₂ or La ₂ O ₃ as promoters)	CO ₂ conversions 80–90% when T > 700 °C	[37]
RWGS	900–1100 °C, 280 W input power	H ₂ /CO ₂ /N ₂ = 1/1/2, over Al ₂ O ₃ /ZrO ₂ or Y ₂ O ₃ /ZrO ₂	49% CO ₂ conversion around 1000 °C	[38]
cycloaddition of CO ₂ and epoxides	200 W input multimodal MW power, 15 min	0.96 MPa of CO ₂ initial pressure + 18.6 mmol of allyl glycidyl ether; catalyst: HCOOH/KI (9:1)	94% conversion	[39]

heating system. Therefore, more initiatives are expected with reactions that use this technology to transform CO₂. Given the high conversion rates possible, it would be interesting to research the behavior with real flue gases or a representative mixture of industrially relevant cases.

3.2. Plasmas

In recent years, plasma technology has gained increasing interest for CO₂ conversion, as a possible energy-efficient alternative to classical thermal methods. Plasma is called the fourth state of matter, after solid, liquid, and gas. More than 99% of the visible universe is in the plasma state. Some examples of natural plasmas are the sun, other stars, the aurora borealis, and lightning. Plasma can, however, also be created artificially. Much research is performed on high-temperature plasmas (order of several hundred million Kelvin) for fusion applications. These plasmas are fully ionized and resemble the conditions of the sun.

The plasmas that are of interest for CO₂ conversion, however, operate at much lower temperature, that is, ranging from near room temperature (so-called nonthermal plasma) to about 1000 K (so-called warm plasma) and up to a few 1000 K (so-called thermal plasma). In particular, nonthermal and warm plasmas are of interest for CO₂ conversion. They are also called gas discharge plasma and they are typically partially ionized, consisting of a large number of molecules, but also ions and electrons, as well as radicals and excited species. All of these species can interact with each other, making this type of plasma a highly reactive chemical cocktail with high potential for affordable processes, certainly given its low temperature and cheap materials.^[40]

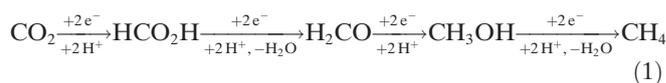
Simply speaking, such a gas discharge plasma is created by applying electric power to a gas, causing breakdown of the gas into the formation of electrons and ions. The electrons are easily heated by the applied electric power because of their small mass, whereas the gas itself typically remains near room temperature. The energetic electrons will then collide with the gas molecules, causing excitation, ionization, and dissociation collisions, thereby creating excited species, ions, and radicals. The latter species can easily react with each other, forming new molecules. Thus, due to the electron activation of the gas molecules, thermodynamically unfavorable reactions, such as CO₂ splitting and the DRM, can proceed under mild reaction conditions (i.e., atmospheric pressure and near room temperature).

Moreover, because plasma can easily be switched on/off, it also has great potential for the temporary storage of excess RE during peak production. Thus, plasma technology can contribute to the solution for the current imbalance between the supply and demand of energy, and for the integration of intermittent RE into the existing electricity grid, by using excess RE for the conversion of CO₂ into new fuels. Different examples of initiatives on the transformation of CO₂ with plasmas are included in Table 2.

3.3. Light for catalytic activation of artificial photosynthesis

Solar light is an immense and distributed energetic resource. It is the main energy input for living organisms and captured through photosynthesis. There is a huge variety of photosynthetic organisms, but, in general, they share some common elements: antenna compounds, usually constituted by a mixture of pigments that can absorb light at the different wavelengths at which natural sunlight is available, and photosynthetic reaction center proteins, which employ this energy to create charge-separated donor–acceptor states that are able to oxidize water or other electron donors in a redox reaction coupled with CO₂ reduction at catalytic centers. As a result of this complex set of processes, the overall reaction is the conversion of carbon dioxide and water into oxygen and carbohydrates. Artificial photosynthesis technologies mimic these natural photosynthetic CO₂ conversion systems.^[62] Although there are already industrial CO₂ catalytic conversion processes that operate at high temperature,^[63] from a global perspective, the widespread use of CO₂ as a chemical resource can only make sense if cheap or surplus RE is used for its transformation. Because CO₂ and solar light are universal resources, CO₂ photocatalytic conversion can contribute to the creation of a novel decentralized industrial structure that produces “just enough”.^[64]

The conversion of light into chemical energy for such fuels can be accomplished by using catalytic strategies that involve light capture, concentration, and catalytic reaction. More efficient light use for reactions involve the capture of the visible spectrum. Usually, this is achieved by means of organic or inorganic sensitization strategies. In particular, localized catalytic activation has enabled more efficient light energy use.^[65] Conversion reactions of CO₂ during artificial photosynthesis are usually represented as a sequence of gradual hydrogenation reactions from CO₂ to formic acid, formaldehyde, methanol, and methane [Eq. (1)]:



The simplified representation of the reaction scheme in Equation (1) is indeed useful, but recent studies indicate that the reaction pathway is more complex and involves the formation of several two-carbon species, such as glycolaldehyde, acetaldehyde, and methylformate [Eq. (2)]:^[66]

The key focus of research into artificial photosynthesis has been the production of methanol through the reactions shown in Equations (1) or (2), with the objective of producing a “solar”, carbon-neutral fuel, according to the concept of the “methanol economy”.^[64] Alternatives to fossil fuels are needed for chemical and energetic applications and, fol-

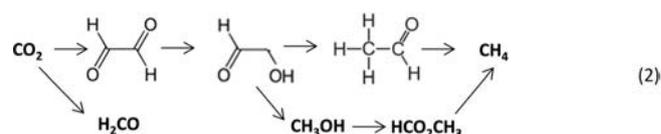


Table 2. CO₂ conversion with plasmas.^[a]

Reaction	Plasma conditions	Reaction media	CO ₂ conversion	Ref.
CO ₂ dissociation	glow discharge (411–906 V), 8.1 kHz	CO ₂ (0.5% to 4%) in He, Ar, or N ₂ ; flow 30–100 cm ³ min ⁻¹ ; coating of Au, Pd, Pt, or Rh	30.5% for a feed with 2.5% CO ₂ (in He); max. efficiency ≈ 1.95%	[41]
methanol synthesis	DBD, 100–1000 W, 30 kHz	mixture of H ₂ /CO ₂ (3:1). 0.1–4 L min ⁻¹ over CuO/ZnO/Al ₂ O ₃ ; 1–10 bar; 50–250 °C	14.0% (8 bar, 500 W, 0.5 L min ⁻¹); up to 1% yield of methanol	[42]
hydrocarbon synthesis from CH ₄ and CO ₂	DBD, 100–1000 W, 30 kHz	150–800 mL min ⁻¹ of a mixture of CH ₄ and CO ₂ (2:1–3:1) over 9 g of NaX, NaY, or NaA zeolites	51.0% (72% CH ₄) for a 150 mL min ⁻¹ feed with 66.7% CO ₂ and 500 W	[43]
CH ₄ reforming	DBD, 11–14 W, 300–600 Hz	100 mL min ⁻¹ of a mixture of CO ₂ /CH ₄ (1:1–5:1) and 50% water vapor; atmospheric pressure	20.9% at 13 W, 300 Hz and CO ₂ /CH ₄ 1:1	[44]
CO ₂ and H ₂ O dissociation	DBD, 0–3 W, 50 Hz	100 mL min ⁻¹ of a mixture of CO ₂ (1% in N ₂) and water vapor (up to 2.5%) at atmospheric pressure	38.0% at 3 W with no vapor	[45]
hydrocarbon synthesis from CH ₄ and CO ₂	DBD, 100 W, 25 kHz	60 mL min ⁻¹ of a mixture of CO ₂ /CH ₄ (2:1–1:5) at atmospheric pressure	52.0% when feeding 83.1% of CH ₄	[46]
oxidative dehydrogenation of ethane with CO ₂	corona discharge, pulse 330 ns, 7–70 kHz, 20 W	25 mL min ⁻¹ of C ₂ H ₆ and CO ₂ (0–100% CO ₂) over Pd/γ-Al ₂ O ₃ , La ₂ O ₃ /γ-Al ₂ O ₃ or CeO ₂ /γ-Al ₂ O ₃ ; atmospheric pressure	41.1% when C ₂ H ₆ and CO ₂ (1:1) flow over CeO ₂ /γ-Al ₂ O ₃	[47]
CH ₄ reforming	corona discharge, 18–42 W	60 mL min ⁻¹ of a mixture of CO ₂ /CH ₄ (2:1) over Ni/Al ₂ O ₃ or HZSM/5; atmospheric pressure	58.6% at 42 W no catalyst	[48]
hydrocarbon synthesis from CH ₄ and CO ₂	DBD, 18–19 W, 6 kHz	1–2 L h ⁻¹ of a mixture of CO ₂ /CH ₄ (2:1 or 1:1) over Al ₂ O ₃ , Pd/Al ₂ O ₃ , or Ag/Al ₂ O ₃ ; atmospheric pressure	35.7% no catalyst	[49]
CO ₂ dissociation	DBD, 100–200 W, 2–90 kHz	0.05–0.5 L min ⁻¹ of pure CO ₂ at atmospheric pressure; gas temperature up to 170 °C	30% at 0.05 L min ⁻¹ , 60 kHz, 100 °C and 200 W (14.75 W cm ⁻³)	[50]
CO ₂ dissociation	RF plasma, 13.56 MHz, 0–1000 W, 0–60 A	mixture of Ar (10 cm ³ min ⁻¹) and CO ₂ (15–100 cm ³ min ⁻¹); 80–280 mtorr	90% for 15 cm ³ min ⁻¹ at 1000 W (efficiency 0.2%)	[51]
CO ₂ dissociation	GA, 100–400 mA, 0–1000 W	14–40 L min ⁻¹ of pure CO ₂ in vortex flow; atmospheric pressure	9.0% at 14 L min ⁻¹	[52]
CO ₂ dissociation	MW plasma, 2.45 GHz, 1–2 kW	mixture of Ar (6–8 L min ⁻¹) and CO ₂ (1–31 L min ⁻¹) with or without a Rh/TiO ₂ catalyst; atmospheric pressure	45% without catalyst (5% efficiency) at 1 L min ⁻¹ and 1.75 kW	[53]
methanation of CO ₂	DBD, 9.4 kV, 1 kHz	mixture of H ₂ /CO ₂ (4:1) was flowed (15 000 cm ³ h ⁻¹) over Ni/β-zeolite (0–10 wt% Ni); 180–360 °C; atmospheric pressure	96.0% at 260 °C and Ni/β-zeolite 10 wt% Ni	[54]
hydrocarbon synthesis from CH ₄ and CO ₂	DBD, 0–50 W, 8 kHz	mixture of CH ₄ /CO ₂ (1:1) flowing at 200 cm ³ min ⁻¹	8% at 50 W	[55]
hydrocarbon synthesis from CH ₄ and CO ₂	DBD, 18–20 W, 6 kHz	1–2 L h ⁻¹ mixture of CH ₄ /CO ₂ (1:1) together with 50% Ar flowed over Fe/Al ₂ O ₃ , NaY zeolite or Na-ZSM-5 zeolite; pressure was 1.2 bar	40.1% at 240 °C and 1 L h ⁻¹ on Na-ZSM-5 zeolite	[56]
CO ₂ dissociation	DBD, 5–80 W, 60–130 kHz	pure CO ₂ 0.058–1.7 L min ⁻¹ ; atmospheric pressure	4.4% at 72 kJ mol ⁻¹	[57]
CO ₂ dissociation	DBD, 20–50 W, 5–20 kHz	50 mL min ⁻¹ of pure CO ₂ without packing or flowing over BaTiO ₃ or glass beads; atmospheric pressure	28.0% at 50 W and 9 kHz	[58]
CO ₂ dissociation	DBD, 35 W (quartz) or 39 W (alumina), 23.75 kHz	10–500 mL min ⁻¹ of pure CO ₂ without packing or flowing over quartz or alumina; atmospheric pressure	35.0% for S.E.I. > 200 J cm ⁻³ (quartz) at 10 mL min ⁻¹	[59]
CO ₂ hydrogenation	DBD, 35 W, 8.7 kHz	34.6 mL min ⁻¹ H ₂ /CO ₂ (1:1–4:1) over Cu/γ-Al ₂ O ₃ , Mn/γ-Al ₂ O ₃ , or Cu-Mn/γ-Al ₂ O ₃ at 150 °C, atmospheric pressure	22.5% when Cu/γ-Al ₂ O ₃ was present and H ₂ /CO ₂ = 4:1.	[60]
CO ₂ hydrogenation	MW plasma, 2.45 GHz, up to 200 W	100–400 mL min ⁻¹ H ₂ /CO ₂ (1:1–3:1). 20–50 mbar	82.0% at 400 mL min ⁻¹ , 20 mbar, 150 W; H ₂ /CO ₂ = 3:1	[61]

[a] S.E.I. (specific energy input): power/input flow rate; DBD: dielectric barrier discharge; GA: gliding arc; all flows are referenced to standard conditions.

lowing the example of nature, artificial photosynthesis based on CO₂ as a carbon source can be a key part of the solution. Application of the detailed reaction pathway suggested in Equation (2), which involves the formation of two-carbon species, is important for this purpose. Furthermore, recent developments of artificial photosynthesis involve the incorporation of other species, such as nitrogen to the reaction pathway, with the objective of producing derived substances, such as nitrogen compounds.

4. Harvesting RE for CO₂ Catalysis

The transformation of CO₂ into fuels and chemical intermediates represents a breakthrough to reduce carbon emissions.^[23,67] New options for energy storage and economic revenues can be created if this process is performed by using RE sources. In the following, the main results obtained with MWs, plasmas, and light, when used for CO₂ conversion, are considered from three different perspectives: the catalytic effects, reactor-level phenomena, and finally (Section 5) we suggest a systems integration into a single energy-harvesting device.

4.1. The catalytic level

4.1.1. MW effect

Both changes in the morphology of the solids and localized heating have been claimed as explanations for the increase in either selectivity or reaction rate when using MW energy in catalytic reactions.^[68] During chemical reactions in heterogeneous systems, a considerable increase (20–100-fold) in the reaction rate is not uncommon; this is sometimes explained by the MW effect. Detailed studies have identified two phenomena that give a rational explanation for these observations: selective heating and local hot spots.^[69]

Briefly, when two or more phases are involved, one material will absorb MWs more efficiently (selectively) than the others. This is the case for processes involving liquid–liquid, gas–solid, and solid–liquid systems.^[70] Therefore, higher energy efficiency and yields are observed in MW-activated reactions that are difficult to achieve under conventional heating.^[71] This effect can then be used as a strategy when reactions are limited by equilibrium, causing yield improvements by activation of the reacting phase with MWs, together with continuous removal of products by a solvent with low MW absorption, according to the Le Châtelier principle.^[72]

This selective heating in solid catalysts leads to the formation of hot spots in the catalyst bed and catalyst superheating, which altogether result in higher reaction rates as a consequence of local temperature increase. Selective heating is commonly observed when metallic or carbon materials are present in the catalyst particles (Figure 4).^[73] This opens up opportunities not only to develop more energy efficient and rapid processes, but also a way to couple energy and catalysts by means of smart catalytic structure engineering.

MW heating at the nanoscale has been analyzed by Keblinski et al.^[74] They proposed a characteristic time and temperature estimation method for electromagnetically heated nanoparticles [Eqs. (3) and (4)]. Another interesting finding is that the difference in temperature between the nanoparticles and fluid is not that big, but the superposition of the heating of a group of nanoparticles makes the temperature ramp up after a given characteristic time [Eq. (3)]. This theoretical finding is in agreement with experimental evidence, for which small differences were found.^[71a,75] Nevertheless, the phase transition of nanoparticles is not advised to

determine temperatures owing to the melting point depression characteristic of nanomaterials, which make the phase transition start hundreds of kelvin below the bulk melting temperature.^[76]

$$t_{\text{global}} = \frac{r_p^2}{\alpha} \quad (3)$$

$$T_{\text{system}} - T_{\text{fluid}} = \frac{\frac{dQ_{\text{particle}}}{dt} R^2 \rho_N}{2k} \quad (4)$$

t_{global} is the characteristic time for the system to get to a stable temperature; r_p is the radius of the particle; α is the thermal diffusivity of the fluid; $T_{\text{system}} - T_{\text{fluid}}$ is the difference between the surface of the particle and the colder fluid; $\frac{dQ_{\text{particle}}}{dt}$ is the power absorbed by each particle; R is the radius of the heated region; ρ_N is the density of particles; and k is the thermal conductivity of the fluid.

For a Cu/ZnO catalyst that could have Cu nanoparticles spaced by around 10 nm (ZnO nanoparticles), the characteristic time to heat it would be around 1 ns in an aqueous environment and 5 ps for steam (assuming thermal diffusivities of 1×10^{-7} and $2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, respectively).^[74,77] Nevertheless, for a 3 mm pellet,^[78] the characteristic time would be 22.5 and 0.11 s for water and steam, respectively.

In a given experiment, Equations (3) and (4) can be used to verify the scale of the thermal effect by first measuring the order of magnitude of the time required for temperature stabilization. Through quantification of the energy absorbed per particle, Equation (4) can be applied.

Another experimental evidence of the effect of localized heating came from studies to understand carbon formation on catalysts. Marotta et al.^[79] used an interesting strategy (Figure 5), which was to selectively heat the catalyst, while keeping the gas phase relatively cold, with the result of an increased yield, similar to that in MW heating. This principle has been applied for the local control of nanoscale reactions.^[80]

4.1.2. Plasma–Catalyst Interactions

Apart from pure plasma-based CO₂ conversion, there is also increasing interest for CO₂ conversion by plasma catalysis.

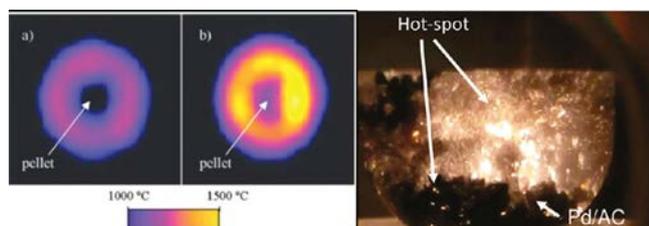


Figure 4. Left: Preferential absorption of MWs in graphite covering a much colder pellet (reproduced from Ref. [73a] with permission from The Royal Society of Chemistry). Right: Evidence of arcing on a Pd/AC catalyst suspended in toluene (low MW absorption solvent). (Reprinted with permission from Ref. [73b]. Copyright (2011) American Chemical Society.)

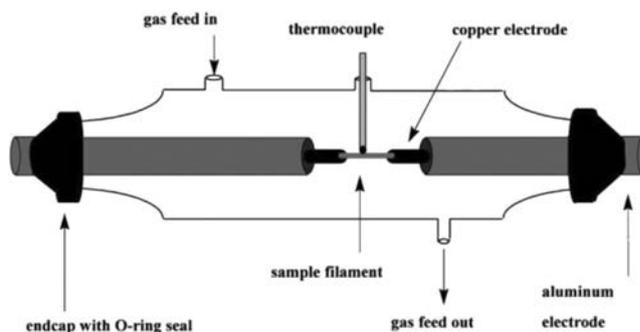


Figure 5. Localized catalyst heating unit. (Reproduced with permission from Ref. [79]. Copyright 2003, Elsevier.)

Indeed, because plasma is such a reactive environment, a variety of different compounds (chemicals, fuels) can be formed, but without selectivity. To obtain the selective production of targeted compounds, a catalyst can be inserted into the plasma, yielding so-called plasma catalysis.^[42,55,81]

When exposed to DBD plasmas, the catalyst particles will be subjected to filamentary discharges produced directly on the pellets owing to the high electric field (Figure 6).^[81e] The

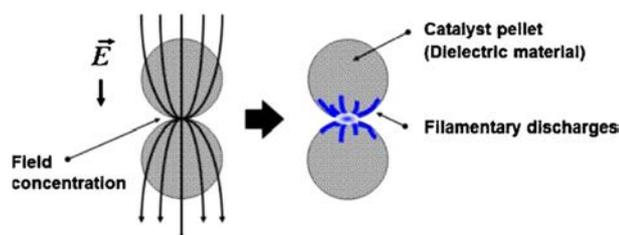


Figure 6. Generation of gas discharges between catalyst pellets. (Reproduced with permission from Ref. [81e]. Copyright 2013, Elsevier.)

latter typically arises due to polarization of the pellets in the DBD reactor. As a matter of fact, these phenomena can increase the effectiveness of a reaction, but they can also modify the catalyst.

The interactions of plasmas and catalysts take place in both ways. Changes to the plasma caused by the catalyst are enhanced electric field (and consequently, electron energy distribution) owing to geometric variations inside the reactor, formation of microdischarges (Figure 6), changes in the discharge type, and changes in reactant and product concentrations owing to adsorption on the catalyst.^[82] On the other hand, the main effects on the catalyst exerted by the plasma are increased dispersion of active sites; changes to the oxidation state; the formation of hot spots (together with higher reaction rates); activation by photons emitted by the plasma; and changes to the catalytic structure, surface area, and reaction pathways. The most common catalytic supports found in combination with plasmas are varieties of BaTiO₃, Al₂O₃, SiO₂, TiO₂, and MnO₂.^[83]

Electrons and active species can undergo both elastic and inelastic interactions with a catalyst. Inelastic interactions require energy transfer from the particles to the surface and are therefore of interest for chemical reactions. Electron-induced reactions in the plasma are usually performed with energies in the range of 1–3 eV. In this range, the inelastic collisions of electrons with matter can activate secondary electron emissions and phonons.^[84] Phonons represent vibrations of atoms in a crystal lattice, which are equivalent to heating the material. When an electron impacts on a material, resulting in an inelastic collision, the main result can be heating through phonon activation (i.e., local heating).

An interesting effect of electron interactions with semiconductors might be the generation of an electron–hole pair.^[84b] This represents an excited state that can possibly play a role in plasma catalysis. This could be an interesting opportunity to bridge disciplines through a deeper understanding of cata-

lytic processes in plasmas by the study of photocatalytic processes.

4.1.3. Light–catalyst interaction

Usually, photocatalytic systems based on a simple combination of a semiconductor and a cocatalyst can only operate over narrow light wavelength ranges. For example, it is known that TiO₂ is active in the UV range, but shows very limited activity when irradiated with light in the visible wavelength range.^[85] The development of composite photocatalysts suitable for light absorption over a wide wavelength band, and, in particular, in the visible light range, is a very challenging task because light absorption depends on many factors: the chemical composition of the catalyst, its crystalline structure and density of defects, the particle size, interactions at the interface between the photocatalyst and the oxidation catalyst, and so forth.

Control of the particle size of the semiconductor provides the first mechanism for adjusting the wavelength of light absorption. Following this approach, it has been found that titanium oxide nanoclusters dispersed within a silica glass framework are able to operate under visible-light irradiation.^[86] Modification of the chemical composition of the semiconductor through the incorporation of additives is another strategy frequently used by researchers.^[85b] Another approach is Z-scheme water splitting,^[87] which uses two different semiconductor photocatalysts coupled through a reversible donor/acceptor pair to utilize visible light more efficiently, in an approach inspired in the coupled photosystems I and II of green plants.

Despite these efforts, in general, inorganic systems are limited with respect to their ability to absorb light over a wide wavelength range, and particularly in the visible range. An alternative to overcome this limitation is to employ organic light sensitizers, which are usually inspired by natural pigments that perform this function in green plants. Following this approach, dye-sensitized solar cells (DSSCs) have achieved incipient commercialization, due to overall conversion efficiencies of light into electricity that surpass 10%. Metal–organic complexes based on porphyrins, which are natural light-harvesting pigments present in many plants, have been particularly studied.^[88] Porphyrins themselves strongly absorb light in the violet range and, as in natural systems, their light absorption range can be increased by combining them with other pigments, such as carotenoids.^[89] However, most light-sensitizer pigments currently available, such as porphyrin-based pigments, are expensive and difficult to manufacture because they are generally based on ruthenium complexes or similar materials,^[90] and they also show low stability, particularly if they are used in wet cells. Alternative metal-free organic dyes have been proposed, which are cheaper, but show limited efficiencies when compared with ruthenium-based catalysts.^[91]

The stabilization of charge separation induced by light is a key aspect that determines the photocatalytic activity of the material. An important method to stabilize charge sepa-

ration is to provide a nanostructure to the catalytic materials with appropriate and controlled sizes and shapes suitable for stabilization of charge separation.^[92] The development of such nanostructured materials is a key element of current research into artificial photosynthesis systems.

To obtain the desired sizes and dimensions, many of these catalytic materials are based on nanofibers or -rods, often arranged in ordered arrays. One of the most successful designs based on this idea was proposed by McKone et al.,^[93] who developed a double-layer structure consisting of silica nanowires deposited over both sides of a proton-exchange membrane (PEM), with nickel/molybdenum nanoparticles deposited over the nanowires acting as cocatalysts for the stabilization of charge separation. This catalytic material was able to induce water splitting under ambient conditions when exposed to natural sunlight. Other similar designs were presented by Yi and An,^[94] who deposited TiO₂-coated ZnO nanorods over a silicon substrate, and Shen et al.,^[95] who proposed the use of nanorods disposed in a pattern over a metal oxide substrate; a design that allowed them to act as nano-optical lenses, focusing light on catalytic centers. Titania nanotubes have also been used as supports for nanostructured photocatalysts,^[96] with enhanced properties when doped with elements such as nitrogen,^[97] metal cocatalysts,^[98] or porphyrin light sensitizers.^[99]

Careful control of catalyst particle size can also enhance the catalytic activity of the material through a plasmon resonance effect.^[100] Plasmon resonance is produced by the response of conduction electrons to the oscillations of the light radiation field. Increased energy absorption at narrow wavelength ranges is achieved with a proper particle size and shape of the catalyst nanoparticles; this depends on the surrounding media.^[65] One example is included in Figure 7 for which light concentration on nanoparticles has provided enough energy to activate the steam reforming of ethanol.^[101]

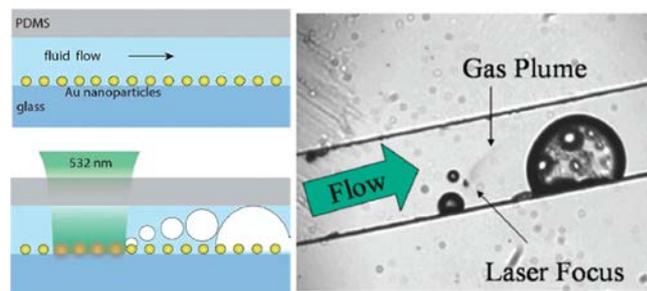


Figure 7. Ethanol steam reforming over gold nanoparticles as a result of the incidence of light. Left: Scheme of the vapor formed by the localized heating of the nanoparticles on the microfluidic channel. Right: Image of bubble formation when a laser is focused in the microchannel. (Reprinted with permission from Ref. [101]. Copyright (2009) American Chemical Society.)

4.2. The reactor level

4.2.1. MW-based reactor

The first concept to keep in mind when designing reactors for CO₂ transformation with MWs is that MW heating is not ruled by the transport of thermal energy, but by heat generation. Therefore, reactions taking place owing to MW heating cannot be studied in the same way as that of conventional reactions. Usually, chemical reactions are driven by heat transfer through a solid wall or by the convection of a fluid. Under MWs, heating occurs first inside the sample and then it is transmitted to the rest of the system. Therefore, in some cases, even if mixing is provided, temperature differences inside the reactor can still be significant (Figure 8).^[102]

One relevant aspect is the kind of thermometer used in the experiments. Metallic probes cannot be used due to their interaction with the MWs. Commercial apparatus usually installs IR detectors for external measurement of temperature, but, as already revealed, this is not advisable. Rather, fiber optic sensors can be used because their working principle is based on the change of temperature-dependent physical

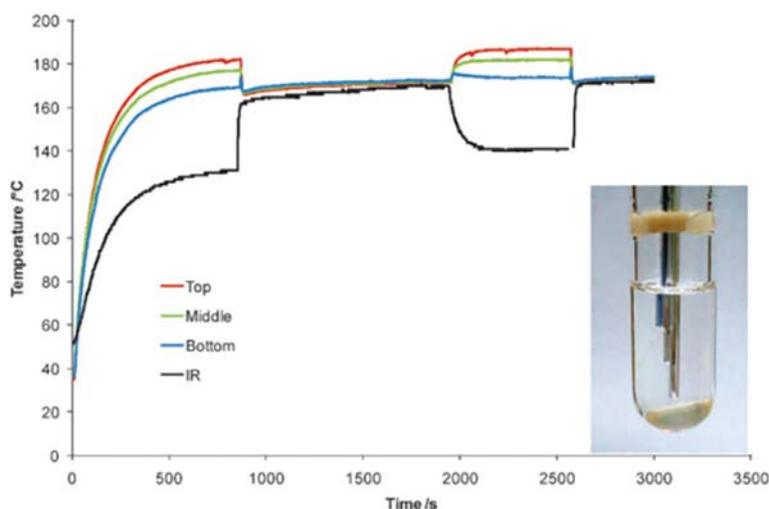


Figure 8. Influence of mixing and location on temperature measurements. The graph shows how the temperatures at different locations are similar when intense agitation is present. (Reproduced from Ref. [102] with permission from The Royal Society of Chemistry.)

properties measurable by light (band gap or luminescence decay).^[103] Raman spectroscopy can also be used to better elucidate not only temperatures, but also the reaction evolution.^[104]

Several reactor configurations have been proposed to study chemical reactions under MWs. For CO₂ transformations with MW catalysis, one interesting option is that presented by Silverwood et al.,^[105] who used a microreactor and followed the reaction by IR spectroscopy. This allowed close control of the reaction evolution and, at the same time, diminished the effects of transport phenomena. More recently, traveling electromagnetic waves have been proposed to overcome the interference phenomena and nonuniformities of resonant fields to allow precise control and optimization of the MW field.^[106]

4.2.2. Plasma-based reactors

Several types of plasma reactors are being investigated for CO₂ conversion, of which (packed bed) DBDs,^[42,50,55,58,59,81a,c-f,107] MW plasmas,^[53,108] and GA discharges^[52,109] are the most popular, although some research is also performed with ns-pulsed^[110] and spark^[81g,h,111] discharges. A DBD is a typical nonthermal plasma (gas near room temperature), whereas MW and GA are typical warm plasmas (gas temperature in the order of 1000 K). Research has focused on pure CO₂ splitting into CO and O₂, as well as on mixtures of CO₂ with a hydrogen source, that is, mainly CH₄, but sometimes also H₂O or H₂, to produce value-added chemicals, such as syngas, hydrocarbons, and oxygenated products. Key performance indicators are the conversion and energy efficiency of the process, as well as the possibility of producing specific value-added chemicals with good yields and selectivity. To realize the latter, the plasma should be combined with a catalyst,^[42,55,81] as mentioned above, because the plasma itself is too reactive an environment, and thus, produces a wealth of reactive species, which easily recombine to form new molecules, without any selectivity.

Plasma catalysis is mostly performed in a DBD reactor. In general, there are three basic configurations of plasma (catalysis) reactors: the plasma alone, the single-stage plasma catalysis reactor, and the two-stage plasma catalysis reactor. The single-stage reactor integrates the discharge and catalyst in the same volume. In the two-stage reactor, the plasma is physically separated from the catalyst. In plasma catalytic reactors, the most common way to introduce the catalyst is by means of a packed bed, but other catalyst structures include coatings, powder, and monoliths.

The integration of plasmas and catalysts allows an increase in the selectivity of the chemical reactions, while keeping the operating conditions at relatively low temperatures; this permits an increase in efficiency and diminishes the erosion and deactivation of both catalyst and electrodes. In a one-stage reactor, the direct contact of the catalyst surface with the short- and long-living species creates potential for the development of efficient processes. Nevertheless, it can also result

in a decay of the catalytic action due to erosion and transformation of the active sites.

The two-stage reactor, on the other hand, allows for a more controlled process development because plasma and catalyst conditions can be optimized separately, although the long-lived plasma species can still reach the catalyst sites, and thus, increase efficiency. Thus, through the study of the dynamic evolution of the active species, it could be possible to obtain the residence times necessary for them to reach the solid. This approach could open up the opportunity for a classical design based on previous knowledge of the catalytic system, together with the study of the plasma conditions.

The energy efficiency of CO₂ conversion might be the major criterion in the search for optimal plasma reactor design. The highest energy efficiency to date was reported for a MW plasma, namely, up to 90%,^[108a] but this was obtained under supersonic gas flow and reduced pressure (≈ 100 – 200 torr). Increasing the pressure to 1 atm ($= 101325$ Pa), which is desirable for industrial applications, causes a significantly lower energy efficiency, for example, around 40% under normal flow conditions and atmospheric pressure.^[112] Moreover, such high values have not yet been reproduced since then. The highest energy efficiency reported more recently for a MW plasma was 55%,^[108b] but this was again at reduced pressure under supersonic flow. Furthermore, an energy efficiency of 50% was recently obtained for a MW plasma at atmospheric pressure, by applying a reverse vortex flow.^[108d] A GA plasma also exhibits a rather high energy efficiency, even at atmospheric pressure, namely, around 43% for a conversion of 18% in the case of CO₂ splitting,^[52] and even around 60% for a conversion of 8–16%, for DRM.^[109g] Moreover, the combination of a GA plasma with catalysts in a heat-insulated reactor has shown to yield a dramatic rise in energy efficiency (up to 86%) with a CH₄ conversion of 92% and a CO₂ conversion of 23%.^[109d] The reason for the relatively high energy efficiencies of MW and GA plasmas is the role of the vibrationally excited levels of CO₂ in the splitting process. Indeed, under typical operating conditions of MW and GA plasmas, the electrons have sufficient energy to selectively excite CO₂ molecules into their lowest vibrational levels. By means of collisions among the vibrational levels, so-called vibration–vibration relaxation, the higher vibrational levels gradually become populated, until they dissociate into CO and O₂. This so-called ladder-climbing process is very energy efficient.^[112,113]

The energy efficiency of a DBD is more limited, that is, up to 10% for a CO₂ conversion of 30%.^[59] The reason is that the electrons in a DBD have a somewhat higher energy, so they will not selectively excite CO₂ molecules into their vibrational levels, but rather populate the electronically excited levels. This requires more energy, namely, in the order of 7–10 eV, whereas bond breaking requires only 5.5 eV. Hence, the extra energy is a waste of energy, which explains the lower energy efficiency of a DBD.^[112,113] However, energy efficiency can be improved by at least a factor two, by inserting (dielectric) packing into a DBD reactor, yielding a packed-

bed DBD reactor.^[58,107e] Moreover, when this packing is catalytically active, it enables the selective production of targeted compounds in plasma catalysis.^[42,55,81a,c-f] Plasma catalysis has indeed been investigated much more intensively in a DBD reactor than in the other plasma types.^[81g,h] Furthermore, a DBD reactor typically operates at atmospheric pressure, similar to a GA plasma, and has a very simple design, which makes it suitable for scale up. Therefore, it also has potential for industrial applications.

4.2.3. Light-activated reactor

The work of Fujishima and Honda introduced a catalytic system based on the combination of a semiconductor TiO₂ photocatalyst with Pt as a cocatalyst.^[116] Some of the most promising photocatalytic water-splitting systems available today are based on a similar combination of a semiconductor and a suitable cocatalyst that provides an active redox site.^[85a] However, it has been shown that these semiconductor photocatalyst/metal cocatalyst systems (e.g., Pt/TiO₂) can be directly coupled in a powder composite without the use of an external electrical circuit.^[85b] This configuration is more convenient than a cell with an external circuit, for the scale up of the process and reduction of costs.^[114] Employing those systems, overall water splitting has been described by several authors, in both liquid and gas phases.^[115]

Although, as described, considerable efforts have been made in the development of improved composites, as well as sensitized and nanostructured catalysts, progress in the development of reactors tailored for the CO₂ photocatalytic conversion reaction and, in particular, continuous-flow reactors, is very limited. In most cases, simple batch cell designs based on the original design of Fujishima and Honda^[116] are used. One of the few exceptions is the work of researchers from the Technical University of Denmark, who succeeded in the application of such composite catalysts for overall water splitting by employing silicon-based gas-phase microreactors into which the catalyst was dropped into the chamber.^[115a] Other researchers have used microliter-scale visual cells in which the catalyst was also deposited and the CO₂ transformation was performed.^[117]

In the work of Navarrete et al.,^[118] continuous-flow operation was also achieved by means of the integration of a transparent wall and a silica aerogel matrix as a catalytic structure into a single device, as discussed below. Additionally, some researchers have used reactor designs based on common solar collectors, with slight modifications, such as the use of semipermeable covers.^[119] Since the performance and, particularly, productivity of the system is strongly dependent on the reactor design—low productivity is one of the most common objections against photocatalytic CO₂ conversion systems—extensive additional research will undoubtedly be needed in this aspect.

5. RE Harvesting Device: Concept and First Initiatives in CO₂ Catalysis

The complete set of reactions necessary to activate CO₂ (including hydrogen generation from sustainable sources) is energy intensive; at the same time, equilibrium and kinetics could limit the process. These conditions constitute challenges for the development of efficient processes that can be finally put in place to use RE. Drastic reductions in energy consumption and reaction times have been achieved through the concept of process intensification by the smart use of catalytic structures, reactor design, and operation or the application of nonconventional energy forms.^[120] A successful application of this strategy requires novel reactor concepts that properly integrate the catalytic and energetic variables into a scalable process in a hierarchical way.^[121]

Therefore, we propose the concept of an energy-harvesting device that stores RE in chemical bonds by means of the CO₂ transformation. As a simile with microelectronics, we propose three elementary conditions for these devices:^[122] 1) efficient transformation of RE or green electricity, 2) a discontinuous energy capture process, and 3) the energy obtained is stored for further use.

Some advances in this sense are presently being made. We have selected devices from the examples presented in previous sections. They are all based on the RWGS reaction for three main reasons: its endothermic nature (energy storage); the possibility of obtaining hydrogen from renewable sources (sustainability); and finally its compatibility with further industrial reactions, such as methanol synthesis or the FT process. The devices are briefly introduced below.

5.1. MW-based devices

An interesting ongoing development is that made by Kayser et al., who have developed both a catalyst and a MW applicator to enable the homogeneous absorption of MW energy and, as a consequence, better control of the reaction evolution.^[38] The design has been improved based on numerical simulations of the MW field. Better coupling and absorption of MW energy in the catalyst bed provide a more efficient process. Although CO₂ conversions are still low (around 50% at 1000 °C), the initial results are promising and 60% conversion (as in the CAMERE process^[123]) should be achievable.

5.2. Plasma-based devices

To try to look for a better use of energy for chemical reactions, there have been different approaches on the subject of plasma-activated CO₂ transformation (Table 2). These usually involve a compromise between conversion and energy efficiency. Conversion generally rises upon increasing applied power and a lower flow rate (i.e., higher residence time), whereas energy efficiency typically shows the opposite behavior. One novel direction is the synergetic plasma catalysis integration to try to find an optimal process. The challenge is

to develop a structured catalyst coupled to the plasma-activated reaction system, in such a way that a synergy between both is obtained, that is, conversion and energy efficiency of the plasma catalytic system are higher than the sum of both the catalytic and plasma performance separately. It is, however, not yet clear which catalyst materials would be the most effective in combination with the plasma conditions. Much research is underway, for instance, to investigate whether the plasma can be formed inside catalyst pores, thereby increasing the catalytic surface area being exposed to the plasma species activities.^[124] A numerical study to investigate plasma formation inside catalyst pores has also been performed in that sense (Figure 9).^[124b]

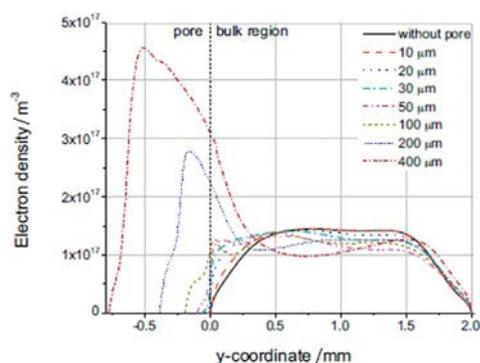


Figure 9. Simulation of microdischarge formations in porous catalyst structures. (Reproduced with permission from Ref. [124b]. Copyright 2016, Elsevier.)

5.3. Solar energy harvesting devices

It is also possible to integrate optical structures, local catalyst activation, and increased heat and mass transfer efficiency in microreactors. Recently, a proof-of-concept achieved the integration of three elements into just one device: light transmission, activation of catalyst with visual light, and observation of the reaction evolution (Figure 10). To do so, plasmonic catalytic composites based on mesoporous, transparent structures that allow high penetration of light (silica aerogels) were developed. Visual light activates the catalyst

owing to the concentration of the electric field on the metallic nanoparticles provided by the plasmon phenomenon. This catalyst is based on Cu/ZnO, which is commonly used for the synthesis of methanol from CO₂ and syngas. In addition, the composite was integrated into a glass-microchannel-based reactor to form a single device. The reaction was activated with visual light-emitting diode illumination.

The result showed that, by using plasmonic activation, it was possible to make the reaction proceed at lower temperatures (50–70 °C) with yields similar to those of other works obtained at higher temperatures (250 °C).^[118]

6. Summary and Outlook

The energy transition to a more sustainable energy (and chemistry) future with a largely reduced use of fossil fuels requires the production of C-carbon energy vectors from CO₂ and RE. We have remarked herein how this concept goes far beyond the often limited consideration of reducing CO₂ emissions and store excess RE. This chemical energy storage is an enabling element for a new vision for a low-carbon sustainable future, but, at the same time, considering how to minimize the costs for this transition.^[125] Although the current approach to produce C-carbon energy vectors is to produce renewable H₂ and use it in catalytic processes to convert CO₂, we have shown herein that realizing efficient use of RE in this conversion requires a redesign of current catalytic concepts. On one hand, it is necessary to explore how to make the in situ generation and use of e⁻/H⁺ (H₂ equivalent) in photo- and/or electrocatalytic processes more efficient. On the other hand, it is necessary to understand better how to use alternative energy sources (to thermal energy) to drive catalytic transformations of CO₂. We have focused the discussion herein on MW, plasma, and light.

In contrast with thermal catalysis, there is no established procedure for the design and scale up of chemical reactions when using RE through plasma, MW, or light. This is due to a lack of understanding of the intrinsic characteristics of electromagnetic transmission or plasma reactions and their interaction with materials by the chemical sciences community.

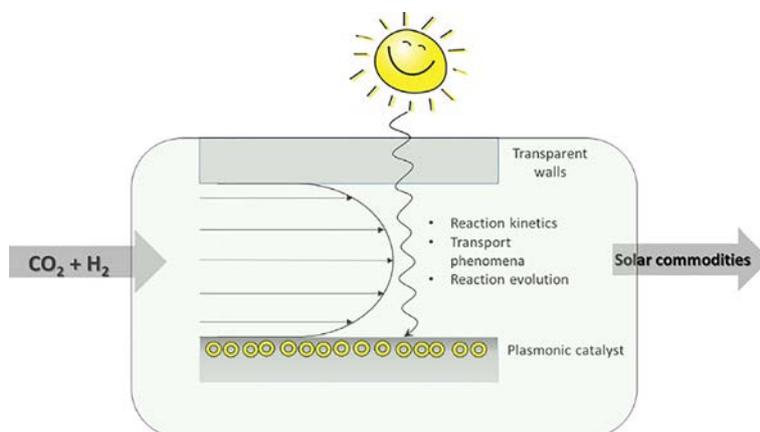


Figure 10. Concept of a plasmonic reactor as an energy-harvesting device. (Reproduced from Ref. [118] with permission from The Royal Society of Chemistry.)

Actually, it should be noted that the very fact that makes these technologies interesting, at the same time, causes non-uniformities and difficulties in design and scale up.^[126] Therefore, for the study and scale up of these kinds of processes, it is necessary to pay attention to energy, mass, and momentum transfer. On the other hand, the degree of mixing (or parameters, such as the Reynolds number) is critical to obtain reproducible results. If the timescales are not constant, derivatization of the compounds and detrimental effects on yields could be observed.^[126,127]

Timescales in heat delivery are key to obtaining reproducible and trustable reaction results. The bridge element in all of these technologies is the electric field, which is related to the geometry and dielectric properties of the material exposed, and thus, it will change with changing volume. Because of this reason, the electric field has to be either measured or calculated by means of numerical simulations.

Realizing the technologies to enable the energy transition thus requires an intense knowledge-based effort because it is not just the application of current knowledge and technologies, but requires conceptually new approaches and to explore novel areas. The use of RE in the conversion of CO₂ in new and unconventional ways is at the nexus of this revolution.

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Keywords: carbon dioxide • energy harvesting • plasmas chemistry • reaction mechanisms • renewable resources

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