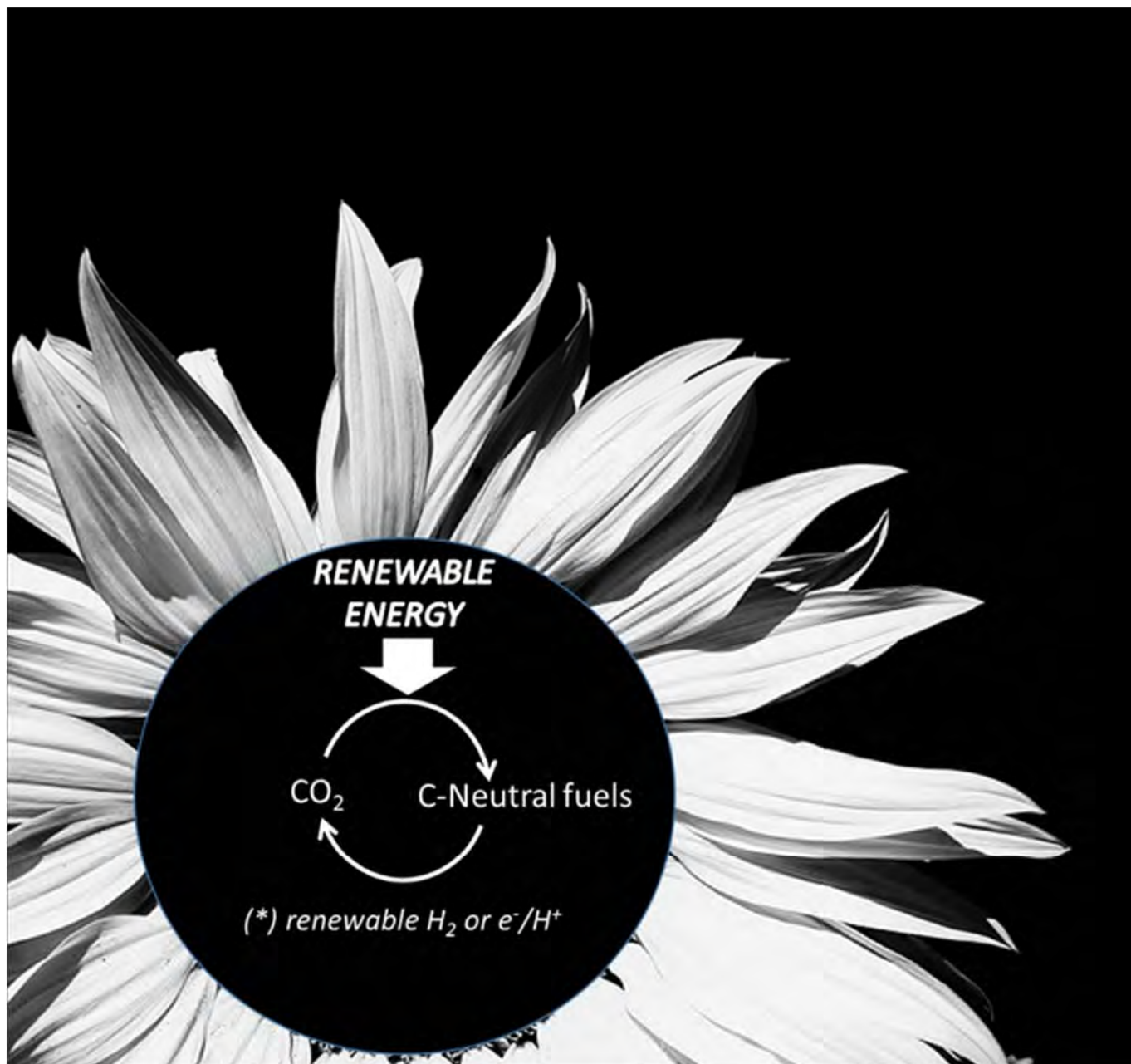


Harvesting renewable energy for CO₂ catalysis.

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Abstract: The use of renewable energy (RE) to transform CO₂ 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 CO₂ by means of RE. The socioeconomic implications and chemical basis of the transformation of CO₂ with RE are discussed. Then a general view of the use of RE to activate the (catalytic) transformations of CO₂ with microwaves, plasmas and light is presented. The fundamental phenomena involved are introduced from a catalytic and reaction device perspective presenting the advantages of this energy forms as well as the inherent limitations of the present state-of-the-art. It is shown that efficient use of RE requires to redesign 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 CO₂ conversion are exposed.

1. Introduction

United States and China, the world's biggest emitters of greenhouse gases (GHG), have recently announced (Sept. 2016) that they will formally ratify the Paris climate deal within the United Nations Framework Convention on Climate Change (UNFCCC) dealing GHG emissions mitigation. This fact will further push the identification of the most reliable strategies and solutions for climate change mitigation, even though this aspect is part of the more general issue of energy transition, e.g. to find cost-effective paths for the progressive substitution of fossil fuels as the key element for the energy system. From this perspective, it appears limitative the approach of CO₂ sequestration to reduce GHG emissions, because the key issue is to explore the link between renewable energy (RE) and CO₂ utilization, as discussed in this paper, as opportunity to enable this energy transition rather than just implement a costly CO₂ sequestration option^[1].

The often remarked question regards the dimension of GHG emissions. More than one ton per second of CO₂ is presently being released at a global scale, although it is the imbalance between emissions and sinks, the responsible for the CO₂ concentration increase 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 pre-industrial levels) has been emitted so far^[2]. Environmental concerns related with the elevated atmospheric concentration of greenhouse gases (GHGs) have motivated political action which, in the case of the EU, look for an 80% reduction of GHGs emissions by 2050. These actions involve increase of energy efficiency, more renewables in the energetic mix and carbon capture. These three aspects have been typically considered disjointed. However, the use of captured CO₂ rather than its sequestration, when jointed with the utilization of RE in the conversion process, leads to the critical possibility of extending the use of RE, as discussed also later^[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 CO_{2eq.} saving tons, is equal or even higher than what could be expected from CO₂ sequestration, but at a up to a one third of the cost^[1].

From a broader perspective, the increasing share of solar and wind 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 owed to factors such costs, reliability and maturity of the technologies available. Arguably, pumped hydro is presently the most viable among the available long-term storage technologies. Nevertheless, the geographical conditions required are not widely available. Therefore, in order to satisfy long-term energy storage requirements, synthesis of fuels or chemicals using 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 a sustainable and low carbon-footprint chemistry, a topic of rapidly rising interest indicated with 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 term of 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 on these aspects, a more comprehensive analysis of the novel existing opportunities and of the required knowledge to enable this transition is still missing.

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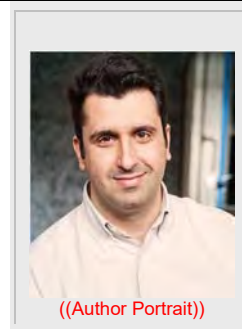
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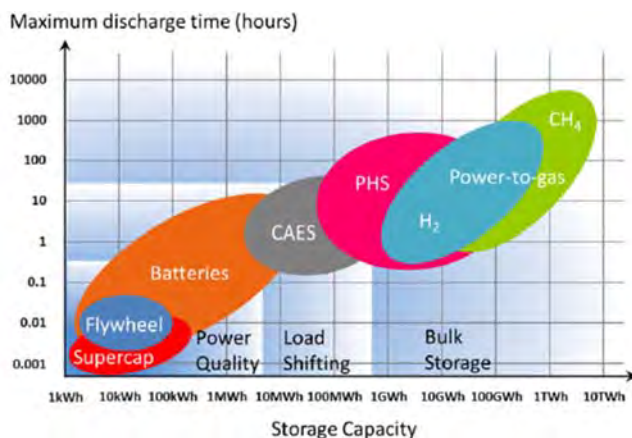


Figure 1. Feasibility of several energy storage technologies. (Reproduced from^[7] with permission from The Royal Society of Chemistry).

In this essay, 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 carried out 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 scientific literature^[9]. The production of syngas through the dissociation of CO₂ and water require very high temperatures (>2000°C) and separation processes for the hydrogen and oxygen obtained. The use of thermochemical cycles (mostly in two steps) based on metal oxides allows to operate at lower temperatures (800-1200C) and to separate oxygen from the syngas stream during the process^[9]. In the first step, the oxygen is released from the metal oxide with solar energy. Subsequently, the reduced metal (or oxide) reacts exothermically with CO₂ producing CO and the initial oxide state^[9c]. Some redox pairs used in this process include Fe₃O₄/FeO, ZnO/Zn, SnO₂/Sn and non-stoichiometric 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 during the last decades and consequently, several and thorough reviews have been written^[9a, 9c, 10]. Copper has been identified as an attractive catalyst as it is able to yield methane, ethylene or ethanol. However, electrocatalytic CO₂ conversion has also 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 using electrocatalytic water splitting and then feed this hydrogen into a CO₂ hydrogenation process^[9a] (outlined in Figure 2).

Owing to the fluctuating and distributed nature of renewables it is necessary to develop technologies that are not only efficient but also with a fast response, compact and flexible. Therefore, this work will be directed towards microwave, plasma and

photo-activation of CO₂ transformation given the potential to overcome issues such as thermal inertia (e.g. solar thermochemical cycles)^[9a, 9c] or low reaction rates (e.g. electrocatalysis)^[9a, 10c].

2. Chemical processes to introduce RE into the economic environment

As anticipated in the introduction section, realize the energy transition requires to implement the concept of "Renewable Energy Economy" a key element for the future sustainable and low-carbon footprint scenario for energy and chemical production^[11]. The key requirement is to develop new and efficient solutions for "chemical energy storage"^[12].

In fact, actual energy system requires to transport, store and distribute energy on a world scale in an easy, low energy-intensive and cost-effective way. Even though 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 the 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 to maintain these characteristics, but the transition to the 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 a massive way the actual energy infrastructure would imply huge investments. A "sustainable" energy transition would thus require that RE sources (sometimes also indicated as perennial) will be used to produce energy vectors which can 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, which is illustrated by the fast increase of the market introduction of RE technologies (mainly photovoltaic – PV, and wind turbines). The actual share is over twice the predictions of 10-15 years ago^[16]. These technologies require fixed capital cost of investment relatively low, with respect to centralized energy production systems and this allowed a much wider base of investors to enter the market as compared to the fossil-fuel energy-system where few large-scale investors (for refineries, power-plants etc.) exists.

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

the critical element to trade RE on a world 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 discussion on hydrogen, being perhaps the most cited type of "clean" energy vectors. In spite of various positive aspects, the great limit of H₂ is storage and transport. Thus the critical function for energy vectors (and in perspective to enable the energy transition) to create a worldwide trading of RE (an essential element to lower energy costs) is missing. In addition, the use of H₂ as 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 H₂-equivalent (e⁻/H⁺) to produce higher energy density vectors by converting CO₂^[3b, 5]. Summarizing, the further increase of RE share would require massive investments in smart grids,^[18] in order 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 to -liquid, etc.) are under development, as shown also in Figure 1^[20]. However, from a longer-term perspective, enabling the RE economy would require to go beyond the limitation of a grid and realize a system of easy distribution and storage of RE out-of-the-grid and on a world scale, as actually occurs with oil and derivative energy vectors.

This could be realized only when RE is converted to suitable energy vectors which integrate within the actual energy infrastructure and distribution, to minimize as much as possible the investments^[4]. The need of 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 the costs due to the absence of (or very limited) competition. In addition, i) when not convenient, some areas may be not reached by the grid, ii) a trade system of RE requires to be independent of the grid, and iii) 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 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 on-going 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, making faster, less costly and sustainable (new infrastructures require energy for their production, and have an impact on the environment) the transition to the new system.

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 of integration within the actual infrastructure.

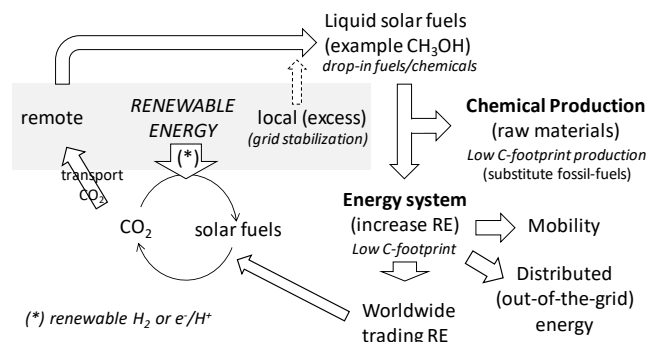


Figure 2. Simplified cartoon of the different roles inside the future energy and chemical production scenario of solar fuels deriving from the conversion of CO₂ using local or remote RE sources (adapted from^[23]).

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, but also regarding H₂ storage^[24]), but the real role of chemical energy storage (solar fuels) will be instead on different aspects:

1. enable a system to trade RE on a world scale (out-of-the-grid), allowing the exploit currently unused remote resources;
2. develop a solar-driven, and low-carbon, chemical production which reduces the use of fossil fuels;
3. create a distributed energy production, going 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 (in power-to-gas, for example^[25]), but for long-range transport shows also great limitations. In addition, it is much less suitable for chemical uses, in contrast to methanol or derived products such as DME^[26].

Figure 2 also evidences that this scenario does not consider the production of H₂ (for example, by water electrolysis), but rather of the H₂-equivalent: e⁻/H⁺. These are the elements necessary to reduce CO₂ and generate energy vectors. In fact, produce 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 of conversion of CO₂ with H₂ require high pressure and relatively high temperatures to be effective (50-100 bar and 200-230°C for methanol synthesis, for example). This scenario thus introduces the production of carbon-based solar fuels via coupling of photo- and electro-driven processes^[27]. This area regards the development of artificial photosynthesis or leaf-type devices, with focus on CO₂ conversion rather than H₂ production^[28]. The latter approach is instead actually done in most of the studies reported in literature. These devices will be clearly the basis also 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 worldwide scale. Methanol, for example, could be used in gas turbines, from which 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 SOFC-GT hybrid systems^[30] together with a 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 to solar fuels and chemicals, with the indication of the main possible uses of the products. RE may be used according to two main possibilities: (i) production of renewable H₂ or (ii) production of electron, or electron/protons (by water photo-oxidation), used in the electro- or photo-chemical routes. Although simplified, the scheme shown in Figure 3 evidences the larger spectrum of the 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 (i) methanol (or DME) synthesis, (ii) the products of light (C2-C4) olefins or aromatics by a modified Fischer-Tropsch synthesis (both these products are the base raw materials for chemistry) and (iii) the production of synthetic fuels (>C1 hydrocarbons or alcohols) by the Fischer-Tropsch process. The catalysts for the further conversion of syngas according to these routes are typically active also in the reverse water gas shift (RWGS) step of production of syngas, so a one-step process may be possible. The routes indicated in Figure 3 may be considered established (particularly those catalytic using renewable H₂) and already realizable on an industrial scale^[86], although some further development may be necessary. The routes using directly the H₂-equivalents (e⁻/H⁺) generated in-situ (by electro- and/or photo-catalysis) require instead still relevant development to be implemented on an industrial scale.

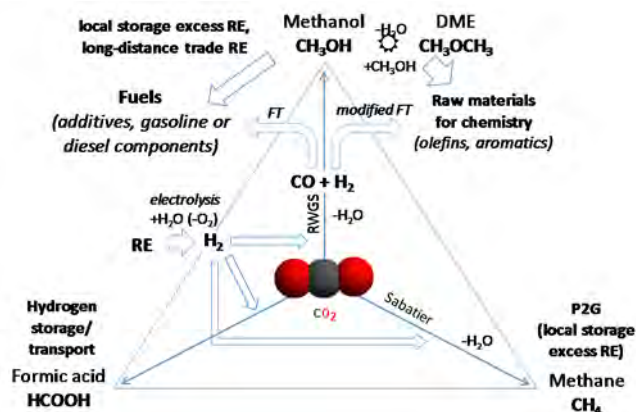


Figure 3. A summary of the current different possibilities and routes to convert CO₂ to solar fuels and chemicals, with the indication of the main possible uses of the products. RWGS: Reverse water gas shift. P2G: power to gas. FT: Fischer-Tropsch. DME: dimethyl ether.

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 will be discussed in the following sections.

3. Using RE to activate CO₂ in catalytic reactions

In line with the 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, geothermal or to indirectly produce it from renewable electricity.

Another option is to look for other energy forms such as microwaves, plasmas or light which open new opportunities for efficient and flexible transformations. These methods of non-conventional 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 the improvement of process conditions.

Electromagnetic energy deployment to catalyst is a radically new approach to activate catalytic reactions. The direct use of microwaves or their use to create plasmas have been gathering interests owing to the increases in the reaction rates (up to 100 fold with microwaves) 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 will be given on these three nonconventional energy forms. 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 are in the region of the electromagnetic spectrum, ranging from 300 MHz up to 300 GHz. Microwave heating takes place because of dipole rotation and ionic polarization during the interaction of the electromagnetic field and the matter exposed. The generation of microwaves occurs in magnetrons. Once the electromagnetic field is generated, it is deployed by means of a microwave applicator. Common microwave applicators include: waveguides, traveling wave applicators, single mode (mono-mode) cavities, and multi-mode cavities.^[33] The energy efficiency of this technology is very high and depending on the conditions can reach up to 90%^[34].

Examples of microwave activation of catalytic reactions for CO₂ conversion are not abundant, but there are some interesting examples. Owing to the localized thermal effects of microwaves and the low energetic level of CO₂, endothermic reactions were especially investigated. In heterogeneous catalysis, dry reforming of methane (DRM) and RWGS reactions are studied using some microwave-absorbing compound (characterized by high dielectric loss, e.g. Activated Carbon) as part of the catalyst structure. Similarly, during homogeneous reactions, an absorbing liquid phase is used to transform and transmit the microwave energy. Table 1 summarizes the research for CO₂ catalytic conversion using microwaves.

Part of the potential of microwaves is related with 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 conventional heating system. Therefore, more initiatives are expected with reactions using 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 the industrially relevant cases.

Table 1. Catalytic CO₂ conversion using microwaves.

Reaction	Conditions	Reaction media	Conversion	Ref
DRM	600-800C, 150-300 min. Monomodal No power reported.	CO ₂ +CH ₄ (60-35% CO ₂) over activated carbon (microplasmas reported)	100% CO ₂ conversion when feed 60% CO ₂ + 40% CH ₄ .	[35]
Reverse Boudouard reaction	650-1200C, Absorbed power 50-200 kW/kg, 30 min. Multi and monomode	CO ₂ over activated carbon OR charcoal	CO ₂ conversion >95%	[36]
DRM	450-800C, Input power 50-130 W Aprox.	CO ₂ +CH ₄ (3:1-1:3) over Pt/□- Alumina (CeO ₂ or La ₂ O ₃ as promoters).	CO ₂ conversions 80-90% when T>700C	[37]
RWGS	900-1100C, 280W 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 1000C	[38]
Cycloaddition of CO₂ and epoxides	200W input multimode microwave 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]

3.2. Plasmas

In recent years, plasma technology is gaining 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 plasma state. Some examples of natural plasmas are the Sun, other stars, the Aurora Borealis, and lightning. Plasma can, however, also be created artificially. A lot of research is performed on high temperature plasmas (order of several hundred million K) 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, i.e., ranging from near

room temperature (so-called non-thermal plasma) to ca. 1000 K (so-called warm plasma) and up to a few 1000 K (so-called thermal plasma). Especially the non-thermal 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 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, while 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 dry reforming of methane, can proceed at mild reaction conditions (i.e., atmospheric pressure and near room temperature).

Moreover, as 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 the 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.

Table 2. CO₂ conversion with plasmas.

Reaction	Plasma Conditions	Reaction media	CO ₂ Conversion	Ref
CO₂ dissociation	Glow discharge (411-906V), 8.1kHz	CO ₂ (0.5% to 4%) in He, Ar, or N ₂ . Flow 30-100cm ³ /min . Coating of Au, Pd, Pt, or Rh	30.5% for a feed with 2.5% CO ₂ (in He). Max. efficiency c.a. 1.95%	[41]
Methanol Synthesis	DBD, 100-1000W, 30kHz.	Mixture of H ₂ /CO ₂ (3:1). 0.1 – 4L/min over CuO/ZnO/AI ₂ O ₃ . 1-10 bar. 50-250C	14.0% (8bar, 500W, 0.5L/min). up to 1% yield of methanol	[42]
Hydrocarbon synthesis from CH₄ and CO₂	DBD, 100-1000W, 30 kHz.	150-800 mL/min of a mixture of CH ₄ and CO ₂ (2:1 – 3:1) over 9g	51.0% (72% CH ₄) for a feed with 66.7% CO ₂ and 500W.	[43]

CH₄ Reforming	DBD, 11-14W, 300-600Hz	of NaX, NaY or NaA zeolites. 100 mL/min of a mixture of CO ₂ :CH ₄ (1:1– 5:1) and 50% water vapor. Atmospheric pressure	20.9% at 13W, 300Hz and CO ₂ :CH ₄ 1:1.	[44]	CO₂ dissociation	RF plasma, 13.56MHz, 0-1000W, 0-60A	Mixture of Ar (10 cm ³ /min) and CO ₂ (15 cm ³ /min). 80 – 280 mTorr,	90% for 15 cm ³ /min at 1000W (efficiency 0.2%)	[51]
CO₂ and H₂O dissociation	DBD, 0-3W, 50Hz.	100 mL/min of a mixture of CO ₂ (1% in N ₂) and water vapor (up to 2.5%) at atmospheric pressure	38.0% at 3W with no vapor	[45]	CO₂ dissociation	Gliding arc, 100-400mA, 0-1000W	14-40 L/min of pure CO ₂ in vortex flow. Atmospheric pressure	9.0% at 14 L/min	[52]
Hydrocarbon synthesis from CH₄ and CO₂	DBD, 100W, 25kHz	60 mL/min 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]	CO₂ dissociation	Microwave plasma, 2.45GHz, 1-2kW,	Mixture of Ar (6-8 L/min) and CO ₂ (1-31 L/min) with or without a Rh/TiO ₂ catalyst. Atmospheric pressure	45% without catalyst (5% efficiency) at 1L/min and 1.75 kW.	[53]
Oxidative dehydrogenation of ethane with CO₂	Corona discharge, pulse 330ns, 7-70kHz, 20W	25 mL/min 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 /□-Al ₂ O ₃	[47]	Methanation of CO₂	DBD, 9.4kV, 1kHz	Mixture of H ₂ and CO ₂ (4:1) was flowed (15000 Cm ³ /h) over Ni/β-zeolite (0-10 wt.% Ni). 180-360C. Atmospheric pressure	96.0% at 260C and 10 wt.% Ni	[54]
CH₄ Reforming	Corona discharge, 18 - 42W	60 mL/min of a mixture of CO ₂ :CH ₄ (2:1) over Ni/Al ₂ O ₃ or HZSM/5. Atmospheric pressure.	58.6% at 42W no catalyst.	[48]	Hydrocarbon synthesis from CH₄ and CO₂	DBD, 0-50W, 8kHz	A mixture of CH ₄ and CO ₂ (1:1) flowing at 200 cm ³ /min	8% at 50W	[55]
Hydrocarbon synthesis from CH₄ and CO₂	DBD, 18-19W, 6kHz	1-2 L/h 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]	Hydrocarbon synthesis from CH₄ and CO₂	DBD, 18-20W, 6kHz	1-2 L/h of a mixture of CH ₄ and 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 240C and 1L/h on Na-ZSM-5 zeolite.	[56]
CO₂ dissociation	DBD, 100-200W, 2-90kHz.	0.05-0.5 L/min of pure CO ₂ at atmospheric pressure. Gas	30% at 0.05 L/min, 60 kHz, 100C and 200W (14.75W/cm ³)	[50]	CO₂ dissociation	DBD, 5-80W, 60-130kHz	Pure CO ₂ 0.058-1.7L/min. Atmospheric pressure	4.4% at 72 kJ/mol	[57]

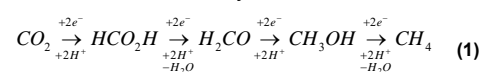
CO₂ dissociation	DBD, 20-50W, 5-20kHz	50 mL/min of pure CO ₂ without packing or flowing over BaTiO ₃ or glass beads.	28.0% at 50W and 9kHz	[58]
CO₂ dissociation	DBD, 35W (quartz) or 39W (alumina), 23.75kHz	10-500mL/min of pure CO ₂ without packing or flowing over quartz or alumina.	35.0% S.E.I. > 200J/cm ³ (quartz) at 10 mL/min	[59]
CO₂ hydrogenation	DBD, 35W, 8.7kHz	34.6 mL/min of H ₂ and 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 150C.	22.5% when Cu/□-Al ₂ O ₃ was present and H ₂ :CO ₂ =4:1.	[60]
CO₂ hydrogenation	Microwave plasma, 2.45GHz, up to 200W	100 - 400 mL/min of H ₂ and CO ₂ (1:1-3:1). 20 -50 mbar.	82.0% at 400mL/min, 20 mbar, 150W. H ₂ :CO ₂ =3:1	[61]

S.E.I. (Specific Energy input): Power/input flow rate; DBD: Dielectric Barrier Discharge; all the flows are referred to standard conditions.

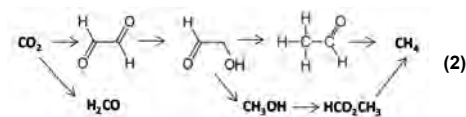
3.3. Light for catalytic activation of artificial photosynthesis.

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 which are able to oxidize water or other electron donors in a redox reaction coupled with CO₂ reduction at catalytic centers. As a result of these 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]. While 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. As 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 such fuels can be accomplished 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:



This simplified representation of the reaction scheme is indeed useful, but recent studies indicate that the reaction pathway is more complex and involves the formation of several two-carbon species as glycolaldehyde, acetaldehyde and methylformate, as sketched in reaction 2^[66]:



The key focus of research on artificial photosynthesis has been the production of methanol through reaction (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 following the example of nature, artificial photosynthesis based on CO₂ as carbon source can be a key part of the solution. Application of the detailed reaction pathway suggested in reaction equation 2, which involves the formation of 2-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 economical revenues can be created if this process is carried out using RE sources. In the following, the main results obtained with microwaves, plasmas and light when used for CO₂ conversion are considered from three different perspectives: the catalytic effects, the reactor level phenomena and finally (in section 5) we suggest a systems integration into a single energy-harvesting device.

4.1. The catalytic level

4.1.1. Microwave 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 microwave energy in catalytic reactions [68]. During chemical reactions in heterogeneous systems a considerable increase (20-100 fold) in the reaction rate is not uncommon, and this is explained sometimes by the so called microwave effect. Detailed studies have identified two phenomena that give a rational explanation to these observations: selective heating and local hot spots [69]. Briefly, when two or more phases are involved, one material will absorb microwaves 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 microwave 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 yields improvements by activation of the reacting phase with microwaves together with continuous removal of products by a solvent with low microwave absorption, according to the Le Châtelier's 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 catalysts particles (Figure 4) [73]. This opens opportunities not only to develop more energy efficient and rapid processes but also a way to couple energy and catalyst by means of smart catalytic structures engineering.

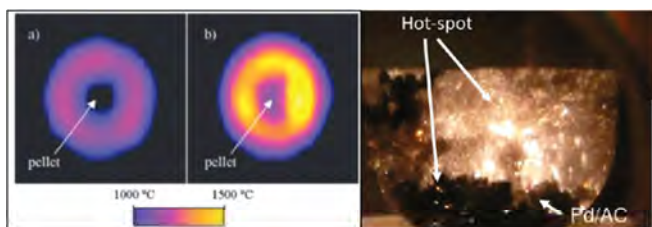


Figure 4. Left: Preferential absorption of microwaves in graphite covering a much colder pellet (Reproduced from [73a] with permission from The Royal Society of Chemistry). Right: Evidence of arcing on a Pd/AC catalyst suspended in toluene (low microwave absorption solvent). (Reprinted with permission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

Microwave heating at the nanoscale has been analysed by Koblinski et al. [74]. These authors proposed a characteristic time and a temperature estimation method for electromagnetically heated nanoparticles (Eq.s 3 and 4). Another interesting finding is that the difference in temperature between the nanoparticles and the fluid is not that big, but the superposition of the heating of a group of nanoparticles makes the temperature to ramp up after a given characteristic time (Eq. 3). This theoretical finding is in agreement with the experimental evidence where 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 to start hundreds of kelvin below the bulk melting temperature [76].

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

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

where, 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. $T_{system} - T_{fluid}$ is the difference between the surface of the particle and the colder fluid. $\frac{dQ_{particle}}{dt}$ is the power absorbed by each particle, R is the radius of the heated region. ρ_N is the density of particles. k is the thermal conductivity of the fluid.

For a Cu/ZnO catalyst which could have Cu nanoparticles spaced by around 10nm (ZnO nanoparticles), the characteristic time to heat it would be around 1 ns in a liquid water environment and 5 ps for steam (assuming thermal diffusivities of $1e-7$ and $2e-5$ m²/s respectively) [74, 77]. Nevertheless, for a 3 mm pellet [78] the characteristic time would be 22.5 s and 0.11 s, for water and steam respectively.

In a given experiment, these equations 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. And then by quantification of the energy absorbed per particle, applying Eq. 4.

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, just like in microwave heating. This principle has been applied for the local control of nanoscale reactions [80].

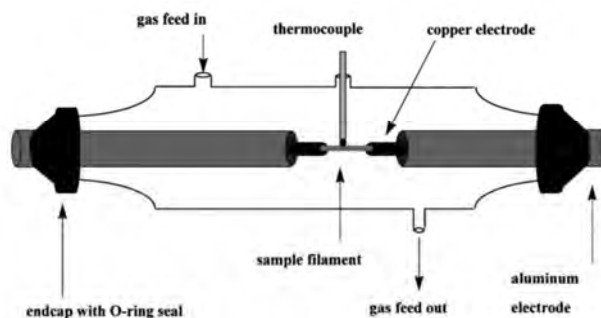


Figure 5. Localized catalyst heating unit. (Reproduced with permission from [79], Copyright 2003, Elsevier).

4.1.2. Plasma –Catalyst Interaction

Besides pure plasma-based CO₂ conversion, there is also increasing interest for CO₂ conversion by plasma catalysis. Indeed, because plasma is such a reactive environment, a variety of different compounds (chemicals, fuels) can be formed, but without selectivity. In order 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 dielectric barrier discharge (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 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.

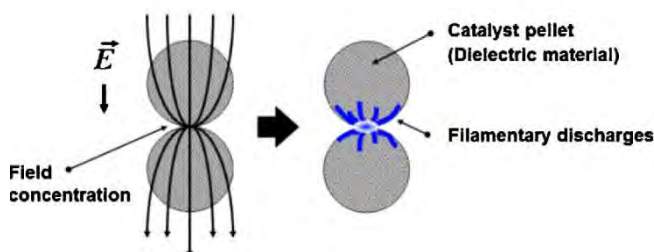


Figure 6. Generation of gas discharges in between catalyst pellets. (Reproduced with permission from^[81e]. Copyright 2013, Elsevier).

The interactions of plasmas and catalysts take place in both ways. The changes of the plasma caused by the catalyst are^[82]: enhanced electric field (and consequently electron energy distribution) owing to the geometric variations inside the reactor, formation of microdischarges (Figure 6), change in the discharge type, changes in reactants and products concentration owing to adsorption on the catalyst. On the other hand, the main effects on the catalyst exerted by the plasma are: increased dispersion of active sites, change of the oxidation state, formation of hot-spots (together with higher reaction rates), activation by photons emitted by the plasma, and changes of 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].

Electron and active species can undergo both elastic and inelastic interactions with a catalyst. Inelastic interactions require the energy transfer from the particles to the surface and are therefore of interest for chemical reactions. Electron-induced reactions in the plasma are usually carried out with energies in the range of 1-3 eV. In this range, the inelastic collisions of electrons with matter can activate secondary electron emission 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 interaction 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 by the deeper understanding of catalytic 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 co-catalyst can only operate at narrow light wavelength ranges. For example, it is well 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 in a wide wavelength band, and 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, the interactions at the interface between the photocatalyst and the oxidation catalyst, etc.

Control of the particle size of the semiconductor provides a 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^[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 the "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 capacity to absorb light in a wide wavelength range, and particularly in the visible range. An alternative to overcome this limitation is to employ organic light sensitizers, which usually are inspired on the natural pigments that perform this function in green plants. Following this approach, Dye-Sensitized Solar Cells (DSSCs) have achieved an 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 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, as 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 the ruthenium-based catalysts^[91].

The stabilization of the charge separation induced by light is a key aspect determining the photocatalytic activity of the material. An important method to stabilize charge separation 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 nano-structured materials is a key element of current research on artificial photosynthesis systems.

To obtain the desired sizes and dimensions, many of these catalytic materials are based on nanofibres or nanorods, 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 PEM membrane, with nickel/molybdenum nanoparticles deposited over the nanowires acting as co-catalysts for stabilization of charge separation. This catalytic material was able to induce water splitting at 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 to use 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 centres. Titania nanotubes have also been used as supports for nano-structured photocatalysts,^[96] with enhanced properties when doped with elements such as nitrogen^[97], metal co-catalysts^[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, which depends on the surrounding media^[65]. One example is included in Figure 7 where light concentration on nanoparticles has provided enough energy to activate the steam reforming of ethanol^[101].

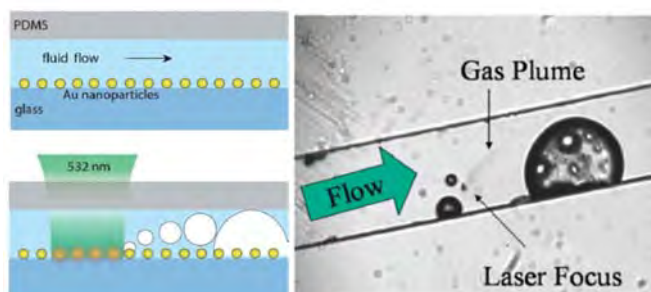


Figure 7. Ethanol steam reforming over gold nanoparticle as a result of the incidence of light. Left: Scheme of the vapor formed by the localized heating of the nanoparticles on the microfluidic channel. Right: Image of the bubble formation when a laser is focused in the microchannel. (Reprinted with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

4.2. The reactor level

4.2.1. Microwave based reactor

The first concept to keep in mind when designing reactors for CO₂ transformation with microwaves is that, microwave heating is not ruled by the transport of thermal energy, but by heat generation. Therefore, reactions taking place owing to microwave heating cannot be studied in the same way as conventional reactions. Usually, chemical reactions are driven by heat transfer through a solid wall or by the convection of a fluid. Under microwaves, 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].

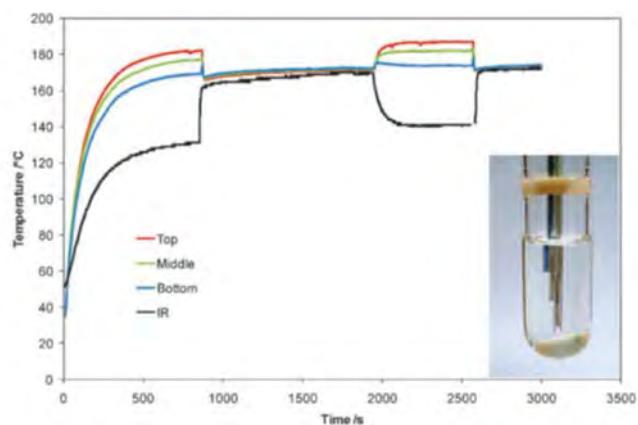


Figure 8. Influence of mixing and location on temperature measurement. The graph shows how the temperatures of different locations are similar when intense agitation is present. (Reproduced from^[102] with permission from The Royal Society of Chemistry).

One relevant aspect is the kind of thermometer to be used in the experiments. Metallic probes cannot be used due to their interaction with the microwaves. Commercial apparatus usually installs infrared detectors for external measurement of temperature but, as already exposed, this is not advisable. Rather, fiber optic sensors can be used since their working principle is based on the change of temperature-dependent physical 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^[105].

Several reactor configurations have been proposed to study chemical reactions under microwaves. For CO₂ transformations with microwave catalysis, one interesting option is the one presented by Silverwood et al.^[105], which uses a microreactor, and follows the reaction by IR-spectrometry. This allows to both control closely the reaction evolution and at the same time diminishing the effects of transport phenomena. More recently, traveling electromagnetic waves have been proposed in order to overcome the interference phenomena and non-uniformities of resonant fields which allows precise control and optimization of the microwave field^[106].

4.2.2. Plasma based reactor

Several types of plasma reactors are being investigated for CO₂ conversion, with (packed bed) dielectric barrier discharges (DBDs)^[42, 50, 55, 58-59, 81a, 81c-f, 107], microwave (MW) plasmas^[53, 108] and gliding arc (GA) discharges^[52, 109] being the most popular ones, although some research is also carried out with ns-pulsed^[110] and spark^[81g, 81h, 111] discharges. A DBD is a typical non-thermal plasma (gas near room temperature), while a MW and GA are typical warm plasmas (gas temperature in the order of 1000 K). Research focuses on pure CO₂ splitting into CO and O₂, as well as on mixtures of CO₂ with a hydrogen-source, i.e. mainly CH₄, but sometimes also H₂O or H₂, to produce value-added chemicals like syngas, hydrocarbons and oxygenated products. Key performance indicators are the conversion and the energy efficiency of the process, as well as the possibility to produce specific value-added chemicals with good yields and selectivity. To realize the latter, the plasma should be combined with a catalyst (e.g. ^[42, 55, 81]), as mentioned

above, because the plasma itself is a too reactive environment, and thus produces a wealth of reactive species, which easily recombine to form new molecules, without any selectivity.

Plasma catalysis is mostly carried out 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 the 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 to increase the selectivity of the chemical reactions while keeping the operating conditions at relatively low temperatures, which 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-living 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 as both plasma and catalyst conditions can be optimized separately, while the long-lived plasma species can still reach the catalyst sites and thus increase the efficiency. Thus, by 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 the opportunity for 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 up to now was reported for a MW plasma, i.e., up to 90%^[108a], but this was obtained under supersonic gas flow and reduced pressure (~100-200 Torr); and increasing the pressure to 1 atm, which is desirable for industrial applications, causes a significantly lower energy efficiency, e.g., around 40% at 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 and 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, i.e., 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 dry reforming of methane (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 efficiency of a MW and GA plasma is the role of the vibrationally excited levels of CO₂ in the splitting process. Indeed, at the typical operating conditions of a MW and GA plasma, the electrons have right enough energy to selectively excite the 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, i.e., up to 10% for a CO₂ conversion of 30% (e.g.,^[59]). The reason is that the electrons in a DBD have a somewhat higher energy, so they will not selectively excite the CO₂ molecules into their vibrational levels, but rather populate the electronically excited levels. This requires more energy, i.e., in the order of 7-10 eV, while the bond breaking requires only 5.5 eV. Hence, the extra energy is waste of energy, explaining the lower energy efficiency of a DBD^[112-113]. However, the energy efficiency can be improved by at least a factor 2, by inserting a (dielectric) packing into a DBD reactor, yielding a so-called packed bed DBD reactor (e.g.,^[58, 107e]). Moreover, when this packing is catalytically active, it enables the selective production of targeted compounds, in so-called plasma catalysis (e.g.,^[42, 55, 81a, 81c-f]). Plasma catalysis has indeed been investigated much more intensively in a DBD reactor than in the other plasma types^[81g, 81h]. Furthermore, a DBD reactor typically operates at atmospheric pressure, like a GA plasma, and has a very simple design, making it suitable for upscaling. 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 co-catalyst. 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 using 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 the reduction of costs^[114]. Employing those systems, overall water splitting has been described by several authors, both in liquid and gas phases^[115].

While, as described, considerable efforts have been made in the development of improved composite, 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 succeeded in the application of such composite catalysts for overall water splitting, employing silicon based gas phase microreactors where the catalyst was dropped in the chamber^[115a]. Others researchers have used □L-scale visual cells where the catalyst was as well deposited and the CO₂ transformation carried out^[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 catalytic structure into a single device as commented below. Besides this, some researchers use reactor designs that are based on common solar collectors, with slight modifications such as the use of semipermeable covers^[119]. Since the performance and,

particularly, the productivity of the system is strongly dependent on the reactor design, with the low productivity being one of the most common objections against photocatalytic CO₂ conversion systems, extensive additional research will be undoubtedly needed in this aspect.

5. The RE harvesting device. The 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 under 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 in a hierarchical way the catalytic and energetic variables into a scalable process [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]:

- Efficient transformation of RE or green electricity.
- The energy capture process is discontinuous.
- The energy obtained is stored for further use.

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

5.1. Microwave based devices

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

5.2. Plasma based devices

Trying to look for a better use of the 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. i.e., the conversion generally rises upon increasing applied power and lower flow rate (i.e., higher residence time),

while the energy efficiency typically shows the opposite behavior. One novel direction is the synergetic plasma-catalysis integration trying 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, i.e., that the 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. A lot of research is going on, 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 the plasma formation inside catalyst pores has also been carried out in that sense [124b] (Figure 9).

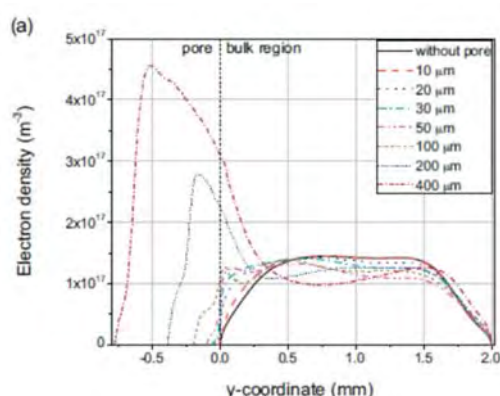


Figure 9. Simulation of microdischarge formations in porous catalyst structures. (Reproduced with permission from [124b]. Copyright 2016, Elsevier).

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 in just one device of three elements: light transmission, activation of catalyst with visual light and observation of the reaction evolution (Figure 10). In order 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 that is commonly used for the synthesis of methanol from CO₂ and syngas. In addition, the composite was integrated into a glass-microchannel based reactor forming a single device. The reaction was activated with visual LED illumination.

The result showed that using the plasmonic activation, it was possible to make the reaction proceed at lower temperatures (50-70°C) having yields that other works obtained at higher temperatures (250°C) [118].

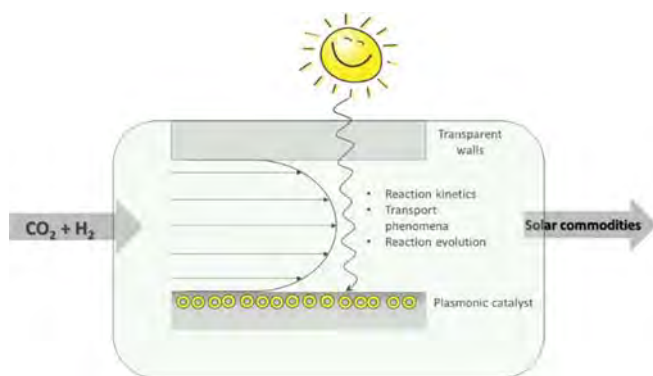


Figure 10. Concept of a plasmonic reactor as an energy harvesting device. (Reproduced from^[118] with permission from The Royal Society of Chemistry).

6. Summary and outlook

The energy transition to a more sustainable energy (and chemistry) future with a largely reduced use of fossil fuels requires to produce C-carbon energy vectors from CO₂ and renewable energy. We have remarked here 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 here that realize efficient use of RE in this conversion requires to redesign current catalytic concepts. From one side it is necessary to explore how to make more efficient the in-situ generation and use of e⁻/H⁺ (H₂-equivalent) in photo- and/or electro-catalytic processes. From the other side, it is necessary to understand better how to use alternative energy sources (to thermal energy) to drive catalytic transformations of CO₂. We have focused here discussion on microwave, 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, microwaves 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. Actually, it should be noted that the very fact which makes these technologies interesting is at the same time causing non-uniformities and difficulties in design and scale-up^[126]. Therefore, in order to study and scale up this kind of processes it is necessary to pay attention to energy, mass and momentum transfers. On the other hand, the degree of mixing (or parameters such as Reynolds number) is critical to obtain reproducible results. If the time scales are not constant, derivatization of the compounds and yield detriments could be observed^[126-127].

Time scales in heat delivery are the key to obtain reproducible and trustable reaction results. The bridge element in all 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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What a waste!

CO₂ valorization with renewable energy requires of novel “Energy-harvesting” devices that accomplish with three basic conditions:

- Efficient transformation of renewable energy
- Capability for a discontinuous energy capture.
- Chemical storage for further use



Alexander Navarrete, Gabriele Centi, Annemie Bogaerts, Ángel Martín, Andrew York, Georgios Stefanidis)*

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Harvesting renewable energy for CO₂ catalysis.

Layout 2:

REVIEW

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