

Photocatalytic Approaches to Circular Economy: CO₂ Photoreduction to Regenerated Fuels and Chemicals and H₂ Production from Wastewater

I. Rossetti*, G. Ramis**

*Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, CNR-ISTM and ISTM Unit Milano-Università, Milano, Italy, **Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova, Genoa, Italy

Abstract

The photoreduction of CO₂ is an unconventional process to regenerate fuels and chemicals storing solar radiation. A new photoreactor has been designed recently to achieve high productivity during the process, *i.e.* up to 39 mol/h kg_{cat} of HCOOH or 1.4 mol/h kg_{cat} of CH₃OH, which are unprecedented results with respect to literature, especially with a very simple commercial TiO₂ catalyst.

The production of hydrogen through photoreforming of aqueous solutions of organic compounds is also considered as a way to exploit solar energy storage in the form of hydrogen. Different sugars were selected as substrates derived from the hydrolysis of biomass or from wastewater (food or paper industry). A significant amount of H₂ was obtained with very simple catalyst formulations, *e.g.* 14 mol kg_{cat}⁻¹ h⁻¹ were obtained at 4 bar, 80 °C over commercial TiO₂ samples, added with 0.1 mol% of Pt and using glucose as substrate. This result is very remarkable with respect to similar research in conventional photoreactors.

Both the routes represent a circular way to regenerate valuable products from gaseous or liquid wastes. Our attention was predominantly focused on the development of innovative reactors, possibly operating under unconventional conditions, with fine tuning of the operation parameters. The exploitation potential of these results under solar irradiation is presented.

Introduction

An historic agreement to fight against climate change and unleash actions and investments towards a low carbon, resilient and sustainable future was agreed by 195 nations in Paris in December 2015. This universal agreement aims to maintain a global temperature rise in this century well below 2°C and to drive efforts to limit the temperature increase even further to 1.5 °C above pre-industrial levels. According to the Intergovernmental Panel on Climate Change [1,2] our planet's surface temperature has raised by approximately 0.6 °C in the past century, strongly increasing in the last decades.

The largest contribution seems to derive from CO₂, one of the most abundant greenhouse gases emitted in the atmosphere. The main sources are industrial effluents, transportations and agriculture. The United States Environmental Protection Agency (EPA) in April 2017 reported that in 2014 CO₂ represented 76% of greenhouse gases and that the global production of these gases was divided as: 25% Electricity and Heat Production; 24% Agriculture; 21% Industry; 14% Transportations; 10% Other Energy; 6% Buildings.

Different approaches can be followed in order to reduce human and industrial emissions of carbon dioxide, such as a more efficient use of carbon-based fossil fuels, the use of alternative, carbon-less or carbon-free sources and the use of treatments to capture CO₂ before emission. Fossil fuels are still abundant and the existence of cost-effective alternative is still absent. Moreover, emerging countries are increasing their use of fossil energy sources with a rate that is becoming critical.

For this reason, research is passing from carbon capture and storage (CCS) to carbon capture and conversion (CCC) or Utilisation (CCU) [3,4], which seems the most convenient method in the near future, along with a strong commitment to reduce emissions.

CCS strategies refer to the removal of carbon dioxide from industrial flue gas, typically in stationary combustion plants, by a separation process prior to the release in atmosphere of the combustion exhausts

After CO₂ separation, several pathways can be followed:

- Storage by injection in depleted oil and gas wells, deep oceans and aquifers.
- Use as chemical for meat freezing, carbonated beverages, supercritical extraction and methanol production
- Injection in geological formations and subsequent recovery of fuel products with several techniques (EOR enhanced oil recovery, ECBM enhanced coal bed methane recovery, EGR enhanced gas recovery).

Several techniques are available [5] for the capture of CO₂ from flue gas, such as chemical absorption, membrane gas absorption, cryogenic treatments and solid adsorption; all these processes present advantages and disadvantages, but the main processes for CO₂ capture are absorption with a liquid solvent (usually alkanolamines [6]) or adsorption in solid adsorbents in a Pressure Swing Adsorption unit [7].

Carbon dioxide is a very stable compound that requires a huge amount of energy to be activated. For this reason, its conversion to organic molecules is challenging, needing harsh reaction conditions.

CO₂ photocatalytic conversion towards marketable chemicals such as hydrogen, methanol, methane, formaldehyde and formic acid. Photocatalysis seems to represent a valid and green method to reduce atmospheric concentration of carbon dioxide [8–12]. It is less energy demanding than traditional processes and does not produce harmful byproducts. For all these reasons photocatalysis appears to be a smart alternative for effective CO₂ conversion. Furthermore, the possibility to exploit solar energy represents a free energy source available worldwide.

An alternative path can be the combustion of a carbon free fuel, i.e. H₂, which can be used in adapted combustion furnaces or exploited in emerging high efficiency devices such as fuel cells. However, nowadays H₂ is mainly produced through thermocatalytic processes from fossil fuels, transferring the problems of CO₂ emissions from the exhausts emission moment to the fuel production one.

About 100 million metric tons of hydrogen are produced worldwide [13] which is not even the 3% of the world's primary energy demand. In addition, more than 95% of this amount derives from fossil fuels, with the generation of carbon dioxide.

Biomass is a renewable organic resource, which includes agriculture crop residues, forestry residues, animal wastes and organic municipal solid wastes, that can be used to produce hydrogen. Different options are currently under study, that can be overall divided in two main categories, thermo-chemical and biological routes [14,15].

The environmental advantage resides in the fact that biomass, while growing, consumes atmospheric CO₂, therefore its greenhouse impact is shrunked. Further environmental advantages can be envisaged if waste biomass derived materials are used as hydrogen source. Also in this case, photocatalytic, or better photosynthetic approaches have been proposed in order to further add the advantage of inexpensive solar energy to drive the reaction, which is "up-hill" as the photoreduction of CO₂, *i.e.* is characterised by $\Delta G > 0$ [16–22].

When using a solid semiconductor as photocatalyst, the absorption of a photon excites an electron (e⁻) from the valence band to the conduction band, provided that the photon energy ($h\nu$) equals or exceeds the band gap of the semiconductor. Simultaneously, an electron vacancy or a positive charge, called hole (h⁺), is generated in the valence band. The generated electron-hole pair migrates to the photocatalyst surface where it can recombine, dissipating thermal energy, or participate in a redox reaction with the compound(s) adsorbed onto the photocatalyst.

Despite the considerable interest for this reaction, limited attention has been devoted to the development of a process, scalable and economically advantageous for both the applications. This is particularly important since most literature reports, despite huge interest in mechanism and smart materials development, evidence unpractically low productivity of H₂ or organic reduced products, in the scale of micromoles per hour and gram of catalyst. Especially, insufficient demonstration of the applicability of the process to exploit solar energy is provided yet.

In the recent past, we have recently proposed an innovative photoreactor, able to operate up to 20 bar and 100°C for the photoreduction of CO₂. The advantage of the approach is found in the possibility to enhance CO₂ solubility in water (one of the main physical limitations of the process) and the surface adsorption of the reactant [23–28]. High pressure also allows to increase temperature of operation (while keeping sufficiently high concentration of CO₂ in liquid phase), with beneficial effects on all the auxiliary steps of the reaction, i.e. mass transfer, sticking probability, etc. This is beneficial in the case of photocatalytic H₂ production [17,29–34], where the environmental advantage add from a circular economy point of view if water containing biomass derived or waste organics is used. Therefore, the development of a unique high pressure device allows to explore unconventional reaction conditions for both applications, to boost the productivity.

Therefore, in this work, we are reporting some high productivity results for both the reactions, collected using simple and inexpensive photocatalysts, trying to focus on the expected efficiency under solar light irradiation. The case study is represented by irradiation in Northern Italy, specifically Milan, located on the 45.5° parallel, which is an intermediate situation with respect to the maximum and minimum values across Europe and for the northern hemisphere. Indeed, the mean daily irradiance in Northern Italy is 3.7 kWh/m², ranging from 5.0 in Southern Europe to 2.6 in Northern Europe.

Experimental

Catalysts

The materials that returned the best results for both the reactions are here described.

Commercial TiO₂ (Evonik P25, 50 m² g⁻¹) was used for most experiments. This is an abundant, cheap, non toxic and widely available material, typically used as benchmark for photocatalytic applications.

On a sample of TiO₂ P25, gold nanoparticles were added as co-catalyst through a modified deposition-precipitation method using urea and a chemical reductant. 1 g of titania was suspended in 100ml distilled water, while adding 5 g of urea (Aldrich, >99%) and a NaAuCl₄•2H₂O solution (Aldrich, 99.99%). The mixture was left under vigorous stirring for 4 h at 80°C, then the powder was collected and repeatedly washed. The catalyst was again suspended in distilled water and treated with 0.1 M NaBH₄ (Fluka, > 96%, NaBH₄/Au = 4 mol/mol) at room temperature. The sample was collected, washed and dried at 80°C for 4 h. Au loading was 0.2 wt%, determined from Atomic Absorption Spectroscopy (AAS, Perkin Elmer 3100) test on the filtrate [24,26].

On a second sample of TiO₂ P25, Pt was added by wet impregnation from a solution of Pt(II) acetylacetonate (Sigma Aldrich, 97%). The reduction was accomplished by reduction in pure H₂ at 700°C for 4 h.

Photo-catalytic testing: CO₂ reduction

The innovative photoreactor used for activity testing has been widely described in previous publications [23–27,35]. An AISI 316 stainless steel, batch type photoreactor was used, with co-axial immersion lamp and bottom stirrer. Testing is done on 1.2 L of solution, allowing ca. 0.1 L of head space for the gas. A thermal bath circulates water around the external heating wall, setting the operating temperature. A 125 W medium pressure Hg lamp was used as light source, emitting between 254 and 364 nm (main emission peak). A detailed mapping of the irradiance through the reactor is supplied by a radiometer, as detailed elsewhere [18]. Irradiance ranged between 133 and 157 W/m² for different tests. This datum is used as comparison with the sunlight irradiance.

The catalyst, 0.03 g/cm³, was suspended in demineralized and outgassed water. The suspension has been saturated with CO₂ at 7 bar pressure overnight before starting irradiation. Tests lasted 24 h at 7 bar pressure and 80°C[25,36].

Na₂SO₃ 0.85 g L⁻¹ has been used as hole scavenger. Sulfite conversion was determined by iodometric titration.

The liquid phase products (HCOOH, HCHO and CH₃OH) were analysed by HPLC (Agilent

1220 Infinity, column Alltech OA-10308, 300 mm-7.8 mm), with UV and refractive index (Agilent 1260 Infinity) detectors. HCHO, critical to analyse was also quantified in parallel by UV-Vis spectrophotometry through the Nash reactant and UV-Vis analysis (Perkin Elmer, Lambda 35). The gas phase products (H₂, CH₄ and polar/non polar light gases) were analysed by a gas chromatograph (Agilent 7890) equipped with HP Plot Q and MS columns through a TCD detector.

Photo-catalytic testing: H₂ production

The same photoreactor was used, setting temperature at 80°C, pressure at 4 bar and photocatalyst concentration at 0.25 g/L. Glucose (5 g/L) was used as hole scavenger as a model molecule for the hydrolysis of biomass.

Before starting the irradiation of the reaction mixture, the system was outgassed with nitrogen flow at a pressure of 8 bar for 15 minutes and the head space was constantly monitored by gas chromatography to ensure air elimination. The liquid sample for the analysis of the solution at t₀ was collected. The temperature was then raised to 80°C while reducing the pressure at 4 bar. After turning on the irradiation the kinetic test started. The typical duration of each reaction was 5h. Gas samples have been analyzed by GC every hour of reaction. At the end of the test, the lamp was switched-off and three liquid samples (t₅) have been collected for analysis, carried out both by HPLC, to calculate glucose conversion, and by Total Organic Carbon (TOC) to determine the overall amount of C-based material left in solution.

Results and discussion

From preliminary screening on a wide array of samples, we have identified the best results as for productivity of different liquid or gas phase products for both reactions. The results are reported in Table 1.

Table 1: Best catalysts for both the reactions and relative productivity.

Reaction	Catalyst	Irradiance (W/m ²)	Main products	Max productivity (mol / h kg _{cat})
CO ₂ photoreduction	TiO ₂	150	HCOOH	39.3
	0.2 wt% Au / TiO ₂	142	HCOOH	7.0
H ₂ production	0.1 mol% Pt / TiO ₂	157	H ₂ CH ₂ CH ₂ CH ₃ CH ₃	14.5 0.30 0.87

Data of daily irradiance have been collected for the Metropolitan City of Milan (Northern Italy) from ARPA Lombardia, the local agency for Environmental protection. The variability of the available sun power per unit surface is reported in Figure 1, relative to year 2018.

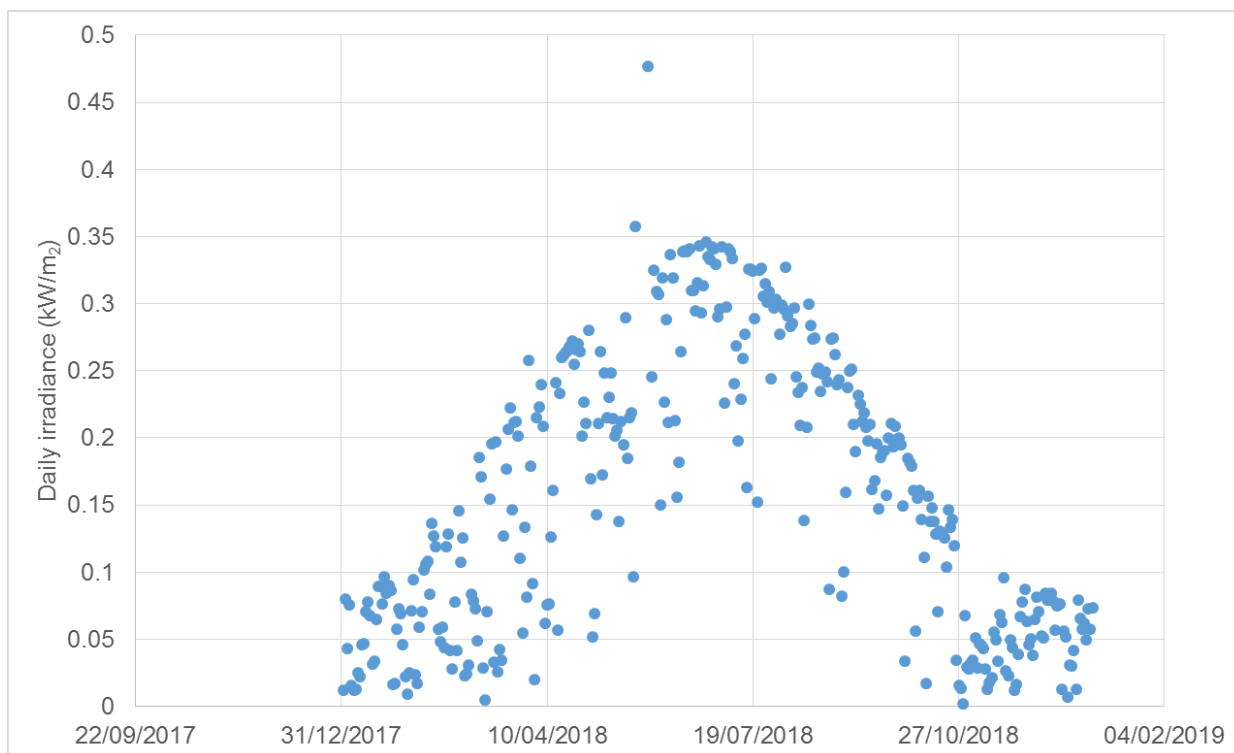


Figure 1: Daily irradiance averaged for the metropolitan city of Milan (Italy) in year 2018.

With an average value of 0.156 kW/m² day of solar irradiation, Fig. 1 shows a broad variance not only during the seasons (Table 2), but also within the same time period, depending mainly on weather conditions. This is a first issue with plant sizing, since the huge variability of the primary source induces not only a variable output of the products, but also control problems for the plant, which hardly reaches a stationary condition.

In addition, these data refer to the total radiation flux, of which only a portion can be affectively exploited by the photocatalyst, which is activated only by photons with energy higher than its band gap. Pure TiO₂ is a wide band gap material, able to harvest only part of the UV fraction of the radiation. Light harvesting can be improved by doping or by the addition of a co-catalyst, e.g. a noble metal with plasmonic effect. According to each catalyst band gap, we have calculated the fraction of UV light that could be exploited by each sample (Table 3).

Table 2: Average monthly irradiance for the Metropolitan City of Milan, with breakdown of the radiation UV, Vis and IR fractions.

Month	Average monthly irradiance (kW/m ²)	UV fraction	Visible fraction	IR fraction
January	0.053	0.003	0.022	0.028
February	0.078	0.005	0.033	0.040
March	0.109	0.007	0.046	0.057
April	0.201	0.012	0.084	0.105
May	0.211	0.013	0.089	0.110
June	0.295	0.018	0.124	0.153
July	0.286	0.017	0.120	0.149
August	0.248	0.015	0.104	0.129
September	0.195	0.012	0.082	0.101
October	0.108	0.006	0.045	0.056
November	0.044	0.003	0.018	0.023
December	0.058	0.003	0.024	0.030
Year 2018	1.885			

Table 3: Useful UV radiation fraction for different catalysts.

Sample	Band gap energy (eV)	λ_{max}	Useful UV fraction
TiO ₂	3.41	363.63	0.64
0.2 wt% Au / TiO ₂	3.12	397.43	0.97
0.1 mol% Pt / TiO ₂	3.12	397.44	0.97

The maximum wavelength of the radiation absorbable by each catalyst (λ_{max}) has been calculated as a function of the band gap as follows, which determines the useful fraction of UV radiation [37].

$$\lambda_{max} = \frac{1240}{band\ gap}$$

$$Useful\ UV\ fraction = \frac{\lambda_{max} - 300}{400 - 300}$$

From these data, for each catalyst the useful irradiance per day has been calculated as total irradiance, weighted by the UV fraction and its useful portion. This useful irradiance has been then compared with the lamp power to calculate an equivalent experiment time, τ (h/day), in the photoreactor, that would correspond to one day irradiation with the absorbable fraction of radiation, assuming in average 10 h of light per day of natural sunlight. From τ it is possible to calculate the expected daily productivity of a given product (Π), if the photocatalyst would be exposed to one day irradiation absorbing the useful fraction of light. Details on this calculation can be found elsewhere [20], we here recall only the main parameters.

$$\tau \left(\frac{h}{day} \right) = \frac{Solar\ UV\ useful\ radiation \left(\frac{kW}{m^2} \right) \times 10 \left(\frac{h}{day} \right)}{Lamp\ power \left(\frac{kW}{m^2} \right)}$$

$$\Pi \left(\frac{mol}{day\ kg_{cat}} \right) = Productivity\ in\ photoreactor \left(\frac{mol}{h\ kg_{cat}} \right) \times \tau \left(\frac{h}{day} \right)$$

The power stored in the product has been calculated from the Lower Heating Value (LHV) or

the Higher Heating Value (HHV). Then, based on the catalyst concentration in the experiments, the productivity referred to 1 m³ volume and the same amount of catalyst and reactor volume distributed in a reactor 0.2 m wide and with the extension of 5 m² was calculated.

$$\text{Stored power (LHV)} \left(\frac{\text{MJ}}{\text{day kg}_{\text{cat}}} \right) = \Pi \left(\frac{\text{mol}}{\text{day kg}_{\text{cat}}} \right) \times \text{molecular weight} \left(\frac{\text{kg}}{\text{mol}} \right) \times \text{LHV} \left(\frac{\text{MJ}}{\text{kg}} \right)$$

$$\text{Stored power (HHV)} = \Pi \times \text{molecularweight} \times \text{HHV}$$

Knowing the catalyst concentration in the suspension these data were then referred to the volume of solution, rather than the mass of catalyst. Supposing that 1 m³ of suspension could be allocated in a photoreactor formed as a parallelepiped with 5 m² exposed surface, the calculated value of stored power can be compared with the incident solar light per square meter to calculate process efficiency (η).

$$\eta \text{ (LHV)}(\%) = \frac{\text{Stored power LHV}}{\text{Incident radiation}} \times 100$$

$$\eta \text{ (HHV)}(\%) = \frac{\text{Stored power HHV}}{\text{Incident radiation}} \times 100$$

Table 4: Expected yearly productivity of HCOOH with different samples from CO₂ photoreduction. The efficiency is referred to the whole incident solar radiation or, in parenthesis, only to the useful UV fraction.

Sample	Mean Π (kg / day kg _{cat})	Yearly Π (kg / year kg _{cat})	Stored power LHV (MJ/year kg _{cat})	Stored power HHV (MJ/year kg _{cat})	$\eta\%$ (LHV)	$\eta\%$ (HHV)
TiO ₂	0.72	259	1,189	1,426	0.15 (9.3)	0.17 (11.2)
0.2 wt% Au / TiO ₂	0.22	74.4	342	410	0.044 (1.8)	0.052 (2.2)

From the results reported in Table 4 the following conclusions can be drawn. In average, 0.72 kg/day of HCOOH are expected supposing a photoreactor including 1 kg of catalyst, corresponding to 259 kg per year. The stored energy corresponds to 1.2-1.4 GJ/year per kg of catalyst. These results refer to a very simple, commercial, inexpensive and durable catalyst. The addition of Au, with consequent increase of catalyst cost, did not improve the productivity of the system, in spite of a higher potential light harvesting due to lower band gap. The improvement of light absorption achievable in this way is by far insufficient to constitute a breakthrough of productivity.

The efficiency of the process is very low when referred to the whole incident radiation, while it increases to ca. 10% when referred to the useful fraction of radiation exploitable by the photocatalyst. This suggests on one hand the need for improvement of the light harvesting ability of the sample. On the other hand, it leaves wide room for improvement of the intrinsic catalyst efficiency.

Similar results were obtained for hydrogen production, using glucose as hole scavenger. Referring always to 1 kg of catalyst, exposed hypothetically over a 5 m² irradiated surface, one can conclude that a limited H₂ yearly productivity can be achieved, corresponding to ca. 12 kg of H₂ per year. This in any case corresponds to a significant amount of stored energy thanks to the very high LHV and HHV of H₂. Again, the efficiency of the process is very low when referring to the total incident light, but it raises to ca. 30% while considering the only UV exploitable fraction. Furthermore, if the glucose hole scavenger (or any alternative organic

material) is a waste contained in water that should be in any case degraded by water treatment, this approach energetically valorizes a waste, in light of circular economy.

Table 5: Expected yearly productivity of HCOOH with different samples from CO₂ photoreduction. The efficiency is referred to the whole incident radiation or in parenthesis to the only useful UV fraction.

Sample	Mean Π (kg / day kg _{cat})	Yearly Π (kg / year kg _{cat})	Stored power LHV (MJ/year kg _{cat})	Stored power HHV (MJ/year kg _{cat})	η % (LHV)	η % (HHV)
0.1 mol% Pt / TiO ₂	0.033	11.9	1,428	1,688	0.015 (30)	0.017 (36)

Conclusions

Two popular uphill processes, e.g. the photoreduction of CO₂ and the photocatalytic hydrogen production by photoreforming of glucose, as example of biomass derived feedstock, have been considered.

Based on some of the best performing results for both reactions, we have calculated the process exploitation potential in Northern Italy, referring to the available irradiance data for year 2018 and calculating its useful fraction to be absorbed by the photocatalyst. Significant productivity of HCOOH has been achieved by photoreduction of CO₂ over a very simple TiO₂ commercial catalyst. The calculated efficiency of the process is still very low, even referring to the only UV useful fraction, leaving wide margins for improvement.

Lower H₂ productivity for the photoreforming of glucose has been obtained with a more complex and expensive Pt-loaded sample, but the yearly stored energy amount is comparable with the previous process.

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