

Conceptual design and feasibility assessment of photoreactors for solar energy storage

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ABSTRACT

The experimental results of testing with different irradiation power are compared and used as a basis for the feasibility assessment and conceptual design of a photoreforming reactor. The highest H₂ productivity (0.276 mol H₂/h kg_{cat}) was achieved with 1 g/L of 1 wt% Au/TiO₂ P25 catalyst by using a 113 W/m² UVA irradiation. Insufficient hydrogen productivity for practical deployment was achieved, following reactor design. However, the comparison with the state of the art evidenced that also the energy storage potential of the literature photocatalysts do not allow a short term feasibility of the proposed technology. The potential productivity of hydrogen, as well as solar energy storage efficiency are discussed both for the present experimental values and for the best results in the literature.

On the other hand, solar energy can be used to artificially fix CO₂, e.g. captured and stored from combustion processes that can be converted back to chemicals or regenerated fuels. The production of H₂, HCOOH, HCHO and CH₃OH by photoreduction of

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CO₂ has been evaluated as for daily production potential. CO₂ photoconversion to formaldehyde can be envisaged as solar energy storage mean with 13.3% efficiency, whereas for the other products the solar energy storage efficiency was below 1%..

Keywords: Photoreactor; Hydrogen production; Photocatalytic reforming; CO₂ photoreduction.

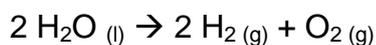
1 - INTRODUCTION

Solar energy is the most abundant primary source on Earth, which intercepts $180 \cdot 10^6$ GW of the total emitted power. The incident radiation is mainly constituted by visible ($\lambda=400-700$ nm) and infrared components of the spectrum, with a low but not negligible portion of UV rays, amounting to ca. 6% of the total incident radiation at sea level. UV radiation can be further classified into the UVA, UVB and UVC components, whose intensity varies widely depending on altitude, latitude, ozone layer depth and meteorological conditions. The UVA component ($\lambda=320-400$ nm) is by far the most abundant, being 10 to 100 times more intense than the UVB component ($\lambda=280-320$ nm) (Wald, n.d.).

In the last fifteen years, hydrogen has been proposed as promising energy vector, due to its possible use as clean fuel, characterised by high combustion enthalpy, whose combustion leads to water as only product. Nevertheless, it is currently produced at most from fossil sources, leading to net CO₂ emissions during its production. To improve the environmental sustainability of hydrogen production, different strategies were then proposed from renewables. On one hand, research is focused on adapting the existing thermocatalytic routes for the conversion of gas, liquid and solid fossil raw materials. For instance, efforts are put on the validation of biomass gasification, pyrolysis and on the steam reforming of various biomass derived biofuels, *in primis* bioethanol. All these routes can be seen as a way to exploit the solar energy stored in biomass in form of hydrogen, to

be used as intrinsically green fuel. On the other hand, the direct exploitation of solar energy would be appreciable and for this reason photocatalytic routes are being developed for hydrogen production.

The most direct reaction would be water splitting



which, however, is highly endothermic and endoergonic ($\Delta G^0 = 237 \text{ kJ/mol}$). Various attempts to split water photocatalytically have been reported, starting from the first pioneering studies by Fujishima and Honda (Fujishima and Honda, 1972). However, the productivity achieved for direct water photosplitting is largely insufficient for practical exploitation (Chiarello and Selli, 2014). This is mainly attributed to the water oxidation half reaction, which is a slow 4-electrons process. The use of organic electron donors was the key to improve productivity. Starting from methanol, the simplest molecule, up to carbohydrates and other biomass derived compounds, many examples have been reported for the use of oxygenate organic compounds as hole scavengers in a process that is conventionally defined photoreforming (Christoforidis and Fornasiero, 2017; Iervolino et al., 2017; Li et al., 2015; Rossetti, 2012; Serra et al., 2016; Vaiano et al., 2015).

Indeed, a separated electron-hole couple is photogenerated upon absorption of solar radiation by the semiconductor used as photocatalyst. The electron promotes the reduction of a proton to hydrogen (or of any other reducible substrate), while the organic molecule consumes the holes being progressively oxidised to CO_2 .

Many recent reports deal with materials synthesis and activity testing, but few papers propose photoreactors design or the conceptual design and sizing of the plant. Most importantly, besides defining specific productivity, no conceptual assessment of process feasibility is usually proposed. Therefore, the aim of this paper is to check the feasibility of

a photoreforming plant to produce hydrogen from different organic substrates, based either on original activity testing results and state of the art literature data.

Furthermore, the photoreduction of CO₂ is investigated as a mean to store solar energy in form of regenerated organic fuels, to be subsequently used as chemicals, fuels or even reactants for photoreforming.

To date, no conclusion on the feasibility of an integrated plant, not on photoreactor sizing is available for this application. Hence, the purpose of this work is to assess quantitatively the potential if the processes of i) photoreforming of organic substrates and ii) the photoreduction of CO₂. Both are intended as energy storage strategies. The investigation takes into account different geographic locations and both literature and experimental data on productivity for these reactions. The comparison and suggestion on feasibility is based on quantitative parameters appropriately set.

2 – EXPERIMENTAL

2.1 – Photocatalysts

Details on catalysts preparation and characterisation are reported elsewhere (Federico Galli et al., 2017; Rossetti et al., 2015, 2014a). Briefly, different commercial samples of TiO₂, constituted by pure anatase (A) (from Aldrich), pure rutile (R) (from Aldrich) or a mixture of them (Evonik P25) were used as photocatalysts. Au was added with 0.1 wt% amount through a deposition precipitation technique and used for photoreforming of methanol, whereas pure P25 TiO₂ was used for the photoreduction of CO₂.

For the preparation of Au/TiO₂, 2 g of TiO₂ were suspended in 200 ml water and added with 0.2 ml Au from NaAuCl₄ and 5 g urea and left under stirring for 4 h at 80 °C. The catalyst was filtered and washed several times with water. The material was then suspended in distilled water and a solution of NaBH₄ (0.1 M) was added (NaBH₄/Au = 4 mol mol⁻¹) under stirring at room temperature. The sample was filtered, washed and dried

at 100 °C for 4 h. Au content (0.1%) was confirmed by Atomic Absorption Spectroscopy (AAS) analysis of the filtrate, on a Perkin Elmer 3100 instrument.

2.2 – Photoreactor for photoreforming

A cylindrical 500 mL glass photoreactor was used, surrounded with a cooling jacket fed with water. Two different lamps were placed on the top of the reactor, irradiating the suspension through a quartz window. A Jelosil 250 W lamp was used, with maximum of emission at 365 nm and mean measured irradiance 113 W/m². A different lamp, with measured irradiance at the same wavelength of 0.5 W/m² was also used for comparison.

200 mL of solution with methanol concentration ranging from 1 to 15 wt% was added with 0.2 g of photocatalyst and magnetically stirred. Before switching on the lamp, the solution was outgassed by flushing with 200 NL/h of N₂ for 10 min.

The liquid phase was analysed either by means of an Agilent 6890 gaschromatograph, with a FID detector or by using a HPLC (Agilent 1220 Infinity) using a suitable column (Alltech OA-10308, 300 mm_7.8 mm) with UV and refractive index (Agilent 1260 Infinity) detectors. Aqueous H₃PO₄ solution (0.1 wt%) was used as the eluent. The gas phase was analysed with an Agilent 7890 gaschromatograph, furnished with a TCD detector and calibrated to quantify H₂, CO and CO₂.

Sampling of the liquid phase was periodically done (every 30 min at the beginning of the reaction, every 1-2 hours later). Sampling of the gas phase was carried out every 2-3 h by collecting 10 mL of gas to avoid excessive dilution of the sample.

2.3 – Photoreactor for CO₂ photoreduction

The photoreduction of CO₂ was carried out in a high pressure photoreactor as described in (Federico Galli et al., 2017; Rossetti et al., 2015, 2014a). The operation up to 20 bar

allowed to overcome one of the main limitations of the reaction, *i.e.* the poor CO₂ solubility in water, which limits the availability of the reactant on photocatalyst surface.

Specifically, the results here reported were collected at 7 bar CO₂ pressure and 80 °C. The reactor skeleton is made of AISI 316 stainless steel (volume = 1.7 L). A 125 W medium-pressure Hg vapour axial immersion lamp was used, emitting in the 254 - 364 nm range. The emitted power was experimentally measured as 104.2 W/m². The photoreactor was filled with 1.2 L of solution and the catalyst was suspended in it with 0.5 g/L concentration. Outgassing was performed before each test under a constant CO₂ flow of 15 mL/min at 13 bar. Then, CO₂ saturation was completed overnight by applying a static 7 bar pressure of CO₂ (Rossetti et al., 2014b).

An inorganic hole scavenger, sodium sulphite (2.0 g) was added. Whenever the sulphite was still present in the reaction medium it led to the accumulation of organic products in the solution. After its consumption organics were used as hole scavengers, with formation of hydrogen (consecutive photoreforming (F. Galli et al., 2017)).

3 – RESULTS AND DISCUSSION

3.1 – Photoreforming of methanol: effect of irradiance and of catalyst composition

The reaction was first tested by using the lowest power lamp, with measured irradiance 0.5 W/m². The photocatalyst was 0.1 wt% Au supported on TiO₂ P25, dispersed in a 1 wt% methanol solution.

TiO₂ was selected as semiconductor, due to presently unrivalled commercial availability at moderate cost, stability and appropriate band potentials for the proposed reaction. One major drawback is that all its polymorphs (anatase, rutile or brookite) have quite big band gap (3.0-3.2 eV) and thus it can absorb only the UV portion of the spectrum. This limits the possibility to exploit efficiently solar light. To account for this, UVA lamps were used during

testing and the useful fraction of solar spectrum, only, was considered during computation of solar energy storage efficiency and productive potential.

Metals addition on titania surface improved its absorption potential in the visible range (Aramendía et al., 2008, 2007; Ilie et al., 2011; Pichat et al., 1984; Rossetti et al., 2014a). Furthermore, the metal can entrap the photogenerated electrons by forming a Schottky barrier, so preventing its recombination with the valence band holes (Linsebigler et al., 1995). In addition, metals decrease the overpotential for H₂ occurring with bare TiO₂ (Lee and Mills, 2003). The amount of metal is typically below 1 wt%, because too high loading can act as a recombination centre for electrons and holes (Colmenares et al., 2011; Pichat et al., 1984) and shield the semiconductor surface limiting light harvesting.

22% conversion of methanol was achieved after 5 h irradiation, but hydrogen was undetectable in the surnatant gas. By contrast, when using *ca.* 200 times more intense power, *i.e.* a lamp with measured irradiance 113 kW/m² the conversion of methanol was slightly lower, reaching 18 % after 6 h, but the most important result was a significant H₂ productivity, reaching 0.062 mol/h kg_{cat}.

The increase of methanol concentration to 2 wt% improved the conversion to 23 % after 5 h, with a hydrogen productivity of 0.079 mol/h kg_{cat}. A further increase to 15 wt% of the starting methanol concentration decreased the conversion to 8.5 %, which however corresponded to an increase of the absolute amount of methanol converted per unit time (due to the much higher starting amount. A corresponding increase of hydrogen productivity was observed (0.276 mol/h kg_{cat}).

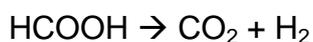
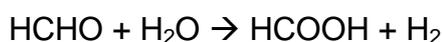
Therefore, an increase of the irradiance did not directly affect the conversion of the reactant, but it allowed to promote the consecutive oxidation reaction steps, which transform methanol into formaldehyde, formic acid and finally to CO₂. Thus, the small photon flux of the low power lamp was efficiently used to promote the first reaction step,

with accumulation of intermediates in the liquid phase, without allowing the formation of significant amounts of hydrogen in gas phase.

The general reaction for the photoreforming of organic compounds is indeed the following:



which declines in the following detailed steps in the case of methanol:



Insufficient power lamp was unable to provide holes to promote all the consecutive steps.

An increase of initial methanol concentration with the highest intensity source induced a maximum shaped conversion pattern, which however corresponds to an overall increasing conversion rate of methanol as reported in Fig. 1. Accordingly, hydrogen productivity increased with methanol initial concentration.

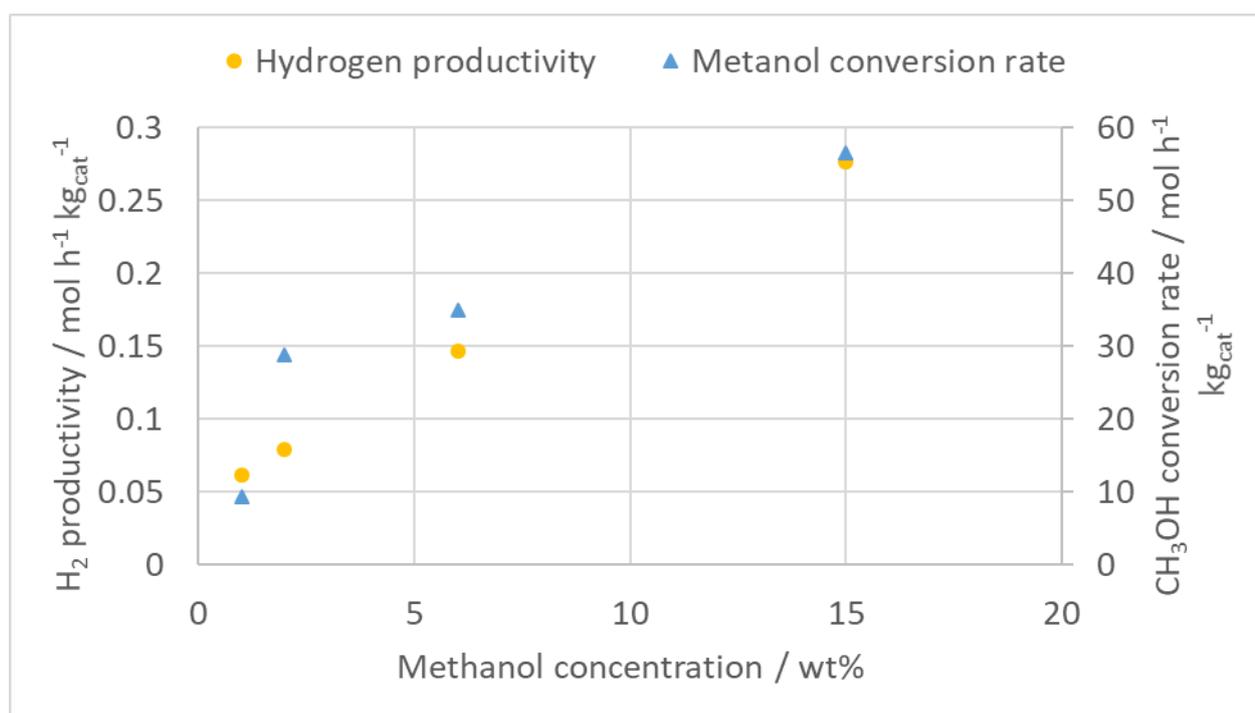


Fig. 1: Hydrogen productivity as a function of methanol concentration in the starting solution. The average methanol conversion rate is also reported.

Furthermore, 15 wt% methanol solutions were photoreformed with different TiO₂ polymorphs as photocatalysts.

Table 1: Methanol conversion and H₂ productivity of different Au/TiO₂ photocatalysts.

Catalyst	Initial CH₃OH concentration (wt%)	CH₃OH conversion (%)	H₂ productivity (mol/h kg_{cat})
0.1 wt% Au/TiO ₂ rutile	6	17.9	0.022
0.1 wt% Au/TiO ₂ rutile	15	17.7	0.089
0.1 wt% Au/TiO ₂ anatase	15	7.4	0.040
0.1 wt% Au/TiO ₂ P25	15	8.5	0.276

The highest methanol conversion was obtained with rutile, as already remarked elsewhere (Rossetti et al., n.d.). Lower conversions are attained with anatase and P25 photocatalysts, where the latter is a mixture ca. 60-80 % of anatase and rutile. This can be interpreted on the basis of the band gap of these samples, lower for rutile and increasingly higher for P25 and anatase, respectively. A lower band gap allows better light harvesting, which in turn favours the conversion of the substrate. However, the overall reaction steps consist of multielectronic processes, which can be efficiently brought to completion only when effective charge separation is achieved, which prevents charge recombination. P25

is reported as a multiphase catalyst, where the intimate mixture of the two titania polymorphs allows charge separation. Thus, despite the higher band gap, which implies lower light harvesting, the P25-based catalyst is more efficient to complete the reaction sequence, leading to higher hydrogen productivity. Another possible explanation is the higher dispersion of Au achieved with P25 than for the two single polymorphs.

3.2 – Photoreactor conceptual design for H₂ production by photoreforming of methanol

Based on the given maximum productivity, designing a continuously operating system which refills the liquid consumes and draws the gas accumulated, a productivity of 0.013 kg H₂/day kg_{cat} is achievable. However, this system relies on UV lamp for irradiation, which may be sustainable if renewable power is available. Nevertheless, the most interesting application is the direct exploitation of solar light. Therefore, in the following, different possible scenarios are examined in this sense.

Sunlight mapping has been considered for different world regions. We have selected four model locations, identified by the respective parallels, which are characterised by relatively high population density and/or high technological development. Thus, the local energy demand is expected to be high, as well as the need of locally available energy vectors. The four areas are characterised by widely different energy input by solar irradiation, so that the zones may be qualitatively identified as “very high”, “high”, “medium” and “low” potential zones for the construction of a solar-to-hydrogen conversion plant, as sketched in Table 2. Possibly higher potential is available in other zones (lower parallels), which are however less densely populated or unsuitable for a local production and use of hydrogen, which is the key, at the moment, for its economic and environmental sustainability as energy vector in distributed cogeneration.

Table 2: Identification of the four model zones. Average daily irradiance from (“<http://www.solarelectricityhandbook.com/solar-irradiance.html>,” n.d.). S. = Southern; N. = Northern; C. = Central.

Zone	Parallel	Avg. Daily irradiance (kWh/m²)	Examples
Low	52	2.6	England (S.); Germany; Holland; Belgium; Canada; Russia
Medium	45	3.7	Italy (N.); France (C., S.); Romania; USA (N.); Mongolia; China (N.)
High	37	5.0	Italy (S.); Spain (S.); Portugal; Greece; USA (C.); Japan; Korea (S); China (C.); Iran (N.)
Very high	30	5.4	Egypt (Cairo); Mexico (N.); USA (S.); China (S.); India (N.); Pakistan (C.); Iran (C.); Saudi Arabia (N.)

We have assumed the 6 % UV fraction of the total solar radiation, which is useful to photo-excite the above described TiO₂-based catalysts. The catalysts are sensitive to UVA irradiation, which is the main constituent of the UV fraction (ca. 60% UVA, 40% UVB on the 45th parallel). UVA are also more persistent and less variable during seasonal and hourly fluctuations.

The so calculated useful irradiance per day, *i.e.* the fraction of the daily irradiance that can be harvested by the semiconductor has been divided by the irradiance in kW/m² made available by the UV lamp used during the experiments, to calculate an equivalent time of reaction (τ_{eq}). This time represents the duration of a run carried out in the photoreactor irradiated with a 113 W/m² lamp, that would be equivalent to the light harvested for one day exposure to sunlight in each of the four zones. This parameter ranged from 1.4 to 2.9 h of experiment per one day of solar radiation for the “low” and “very high” potential zones, respectively.

$$\tau_{eq} \left(\frac{h}{day} \right) = \frac{\text{Daily irradiance zone} \times \left(\frac{kWh}{m^2 \text{ day}} \right) \times \text{Fraction harvested}}{\text{Lamp irradiance} \left(\frac{kW}{m^2} \right)}$$

Based on this equivalent time and on the maximum achieved experimental productivity (P_{H_2}) we calculated the amount of hydrogen that is possibly produced (Π_{H_2}) for one day solar irradiation.

$$\Pi_{H_2} \left(\frac{mol}{day \text{ kg}_{cat}} \right) = P_{H_2} \left(\frac{mol}{h \text{ kg}_{cat}} \right) \times \tau_{eq} \left(\frac{h}{day} \right)$$

The results are summarised in Table 3.

Table 3: Potential daily hydrogen production per zone for the best catalyst and conditions here reported.

Zone	Irradiance (kWh/m ² day)	Harvested energy (kWh/m ²)	τ_{eq} (h/day)	Π_{H_2} (mol/day kg _{cat})
Low	2.6	0.16	1.38	0.38
Medium	3.7	0.22	1.96	0.54

High	5.0	0.30	2.65	0.73
Very high	5.4	0.32	2.87	0.79

Based on the highest productivity $P_{H_2} = 0.276 \text{ mol/h kg}_{cat}$, the expected daily production per kg of catalyst was quite low under sunlight, of the order of magnitude of grams per day per kilogram of catalyst. The catalyst concentration used in the experiments was 1 kg/m^3 , so that, 1 m^3 photoreactor volume is envisaged for the above given hydrogen production.

In order to provide sufficient exposure to sunlight, a basic photoreactor design was basically shaped as a parallelepiped with 20 cm height (*i.e.* suspension/solution depth). Accordingly, to obtain 1 m^3 useful volume to host the desired 1 kg of catalyst, 5 m^2 of surface exposed to sunlight is needed.

The incident available light energy (total sunlight) has been calculated based on irradiance of the zone and this available reactor surface. On the other hand, the energy stored in form of hydrogen was also calculated based on both its lower (LHV = 120 MJ/kg) and higher heating values (HHV = 142 MJ/kg). The efficiency (η) of solar energy storage has been thus calculated as follows.

$$\text{Stored power} \left(\frac{\text{MJ}}{\text{day kg}_{cat}} \right) = \Pi_{H_2} \left(\frac{\text{mol}}{\text{day kg}_{cat}} \right) \times 0.002 \left(\frac{\text{kg}}{\text{mol}} \right) \times \text{LHV or HHV} \left(\frac{\text{MJ}}{\text{day kg}} \right)$$

$$\text{Incident light} \left(\frac{\text{MJ}}{\text{day kg}_{cat}} \right)$$

$$= \text{Irradiance} \left(\frac{\text{kWh}}{\text{day m}^2} \right) \times \text{Exp. photoreactor surf.} \left(\frac{\text{m}^2}{\text{kg}_{cat}} \right) \times \text{CF} \left(\frac{\text{MJ}}{\text{kWh}} \right)$$

$$\eta = \frac{\text{Stored power} \left(\frac{\text{MJ}}{\text{day kg}_{cat}} \right)}{\text{Incident light} \left(\frac{\text{MJ}}{\text{day}} \right)}$$

The results are reported in Table 4.

Table 4: Efficiency of solar energy storage based on the results of Table 3. available surface of the photoreactor = 5 m².

Zone	Stored energy (LHV) (MJ/day kg _{cat})	Stored energy (HHV) (MJ/day kg _{cat})	Incident energy on 5 m ² (MJ/day kg _{cat})	η (LHV)	η (HHV)
Low	0.091	0.108	46.8	0.0020 (0.16 UV)	0.0023 (0.19 UV)
Medium	0.130	0.154	66.6		
High	0.176	0.208	90.0		
Very high	0.190	0.225	97.2		

These results evidence that the amount of stored energy (and of H₂ produced) increases as expected with available irradiance, but the efficiency of energy storage (ca. 0.2%) and the expected production of H₂ per kg of catalyst are still insufficient for practical exploitation. If the efficiency is calculated by considering the UV fraction only of the incident light, 16 or 19 % efficiency of energy storage are calculated, depending on the use of LHV or HHV. This suggest that multiple improvements are needed to achieve feasibility. On one hand process and material improvement is needed (better charge separation, improved mixing, reactants adsorption, etc.). However, a key factor is the improvement of light harvesting that can be achieved by shifting the absorption edge of the material

towards the visible portion of the spectrum or by using means for concentration of the UV radiation fraction.

These results have been compared with the best ones reported in a recent review by Christoforidis and Fornasiero (Christoforidis and Fornasiero, 2017). An outstanding and unrivalled H₂ production rate has been obtained by Li et al. (Li et al., 2011) using hybrid catalysts, which include graphene nanosheets decorated with CdS and Pt. The advantage of this catalyst, besides its higher cost, complexity and possible durability problems with respect to TiO₂, is the much wider absorption of visible light ($\lambda < 500$ nm). The reported productivity is 1120 $\mu\text{mol/h}$ of H₂ under visible light irradiation and using 20 mg of catalyst and lactic acid as hole scavenger. This corresponds to a productivity $P_{\text{H}_2} = 56 \text{ mol H}_2/\text{h kg}_{\text{cat}}$, 200 times higher than the best value here achieved. Also, the fraction of light harvested can be considered up to 18% of the solar spectrum with respect to 6% of our above reported case. The expected daily production of H₂ and the relative storage efficiency are reported in Tables 5 and 6. The same concept for data elaboration can be further applied to other cases, in which different hole scavengers are tested, e.g. deriving from renewable materials, and for different catalysts.

Table 5: Potential daily hydrogen production per zone for the literature-derived case (Li et al., 2011).

Zone	Irradiance (kWh/m ² day)	Harvested energy (kWh/m ²)	τ_{eq} (h/day)	Π_{H_2} (mol/day kg _{cat})
Low	2.6	0.47	0.26	14.6
Medium	3.7	0.67	0.37	20.7
High	5.0	0.90	0.50	28.0

Very high	5.4	0.97	0.54	30.2
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In this case (Li et al., 2011) the intensity of the Xe lamp was 16 times higher than in our experiments, corresponding to 1.8 kW/m^2 . Furthermore, the concentration of the catalyst in the suspension was lower, $0.25 \text{ kg}_{\text{cat}}/\text{m}^3$, which implies a volume of the reactor 4 times higher than our base case to keep the same catalyst amount. This means that, to maintain 20 cm reactor depth, the exposed surface of the photoreactor to host 1 kg of catalyst would be 20 m^2 .

Even in the case of these unrivalled results, the productivity of H_2 attests on a maximum of $0.060 \text{ kg/day kg}_{\text{cat}}$, for a photoreactor extension that, though not optimised, can reach 20 m^2 . The feasibility, even based on these results, cannot be met.

Table 6: Efficiency of solar energy storage based on the results of Table 5 (Li et al., 2011).

Zone	Stored energy (LHV) (MJ/day kg_{cat})	Stored energy (HHV) (MJ/day kg_{cat})	Incident energy on 20 m^2 (MJ/day kg_{cat})	η (LHV)	η (HHV)
Low	3.5	4.1	187.2	0.019 (0.104 UV+Vis)	0.022 (0.123 UV+Vis)
Medium	5.0	5.9	266.4		
High	6.7	8.0	360.0		
Very high	7.3	8.6	388.8		

Also looking at the efficiency of solar energy storage, it attests on 2%. Furthermore, considering the only useful fraction of the incident light, the photocatalyst is able to convert a maximum of 12.3% of the useful incident light fraction (UV+Vis fraction), suggesting also in this case the need for important improvements.

Therefore, based on the present experimental results and on some of the best available ones in the literature, the conclusion is that small, distributed photoreactors for the delocalised production of hydrogen are still insufficiently efficient to ensure commercially interesting productivity and solar energy storage efficiency.

Issues to be solved are at first the need of a considerable improvement of light harvesting and of its conversion efficiency. A further complication arises from the widely variable irradiance during the year, which has to be accounted for to correctly size the plant. For instance, in London (UK) the daily irradiance varies from 0.6 (December) to 4.86 (June) kWh/m² whereas for Cairo (Egypt) it spans from 2.95 to 7.65 kWh/m². This means that an 8 times excursion between the minimum and maximum irradiance values occurs in the low potential zones, with respect to 2.5 excursion in the very high potential ones.

3.3 – Photoreactor conceptual design for CO₂ photoreduction

The photoreduction of CO₂ has been studied using a newly designed photoreactor operating up to 20 bar. This unique prototype allows to increase CO₂ pressure so to enhance its solubility in water, which is one of the factors physically limiting conversion (Federico Galli et al., 2017; Rossetti et al., 2015, 2014a).

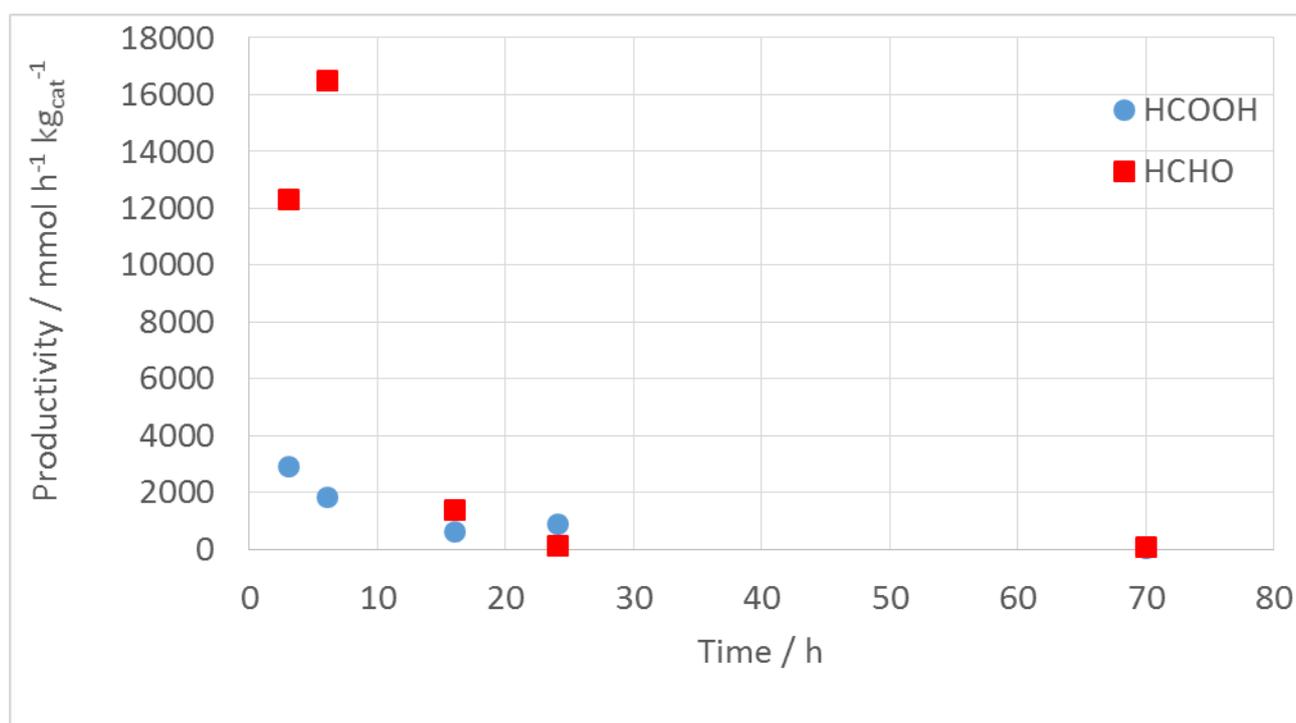
We here consider the productivity results relative to a TiO₂ P25 sample, undoped, tested for different reaction time with or without the addition of a hole scavenger as extensively described in previous reports. The highest productivities towards the various possible products are summarised in Table 7, together with the same design parameters above defined.

The photoreduction of CO₂ can bring to both liquid phase organic products with different reduction degree (HCOOH, HCHO and CH₃OH) and gas phase ones (CO, H₂, CH₄), depending on catalyst formulation and reaction conditions. Based on the reported productivities, a daily production of 0.15-0.82 mol/day kg_{cat} is envisaged, which is

comparable with the results reported for the direct photoreforming of methanol in the previous paragraph, being the catalyst and the irradiance substantially similar.

On the other hand, CO_2 is firstly fixed as HCOOH , HCHO and CH_3OH , remaining dissolved in liquid phase, and these compounds constitute the major products (Fig. 2) at least until the sacrificial inorganic hole scavenger (Na_2SO_3) adopted is completely consumed (Federico Galli et al., 2017). After sulphite consumption, the organic reduced products act as hole scavengers and are consumed with formation of syngas.

Fig. 2: Example of products distribution in liquid phase vs. reaction time for CO_2 photoreduction (F. Galli et al., 2017).



Therefore, this process presents the same concerns discussed in the previous paragraph as for the feasibility of a photoreactor under solar light irradiation. Nevertheless, the productivity of organic products is not minor and deserved major deepening. According to Table 7, insignificant daily production of CH_3OH (0.017-0.035 kg/day kg_{cat}) is achieved, something more for HCOOH (0.20-0.42 kg/day kg_{cat}), but very interesting productivity for

formaldehyde (0.7-1.5 kg/day kg_{cat}) (F. Galli et al., 2017). The results were achieved with 0.5 kg/m³ catalyst concentration, which implies 2 m³ reactor sizing to host 1 kg of catalyst and, according to the above mentioned hypothesis of 20 cm photoreactor depth, it would imply 10 m² exposed surface.

If UV lamps are used (24 h), the expected daily production in the “very high” potential zone for the four products is 0.015 kg/day kg_{cat} of H₂, 0.83 kg/day kg_{cat} for CH₃OH, 10.2 kg/day kg_{cat} for HCOOH and up to 35.0 kg/day kg_{cat} of HCHO, which is a very interesting productivity that deserves further attention.

Also in this case, however, the highest interest is focused on the possibility to drive the reaction with solar energy.

The solar energy storage efficiency has been calculated considering the LHV of H₂, CH₃OH (19.9 MJ/kg), HCHO (17.3 MJ/kg) and the combustion enthalpy of HCOOH (5.5 MJ/kg). Accordingly, η was 0.04 % for H₂ production, 0.33 % for methanol production, 1.2 % for the CO₂ fixation as formic acid, while it reached 13.3% in the case of HCHO synthesis, which is indeed the most interesting application. Considering that the catalyst formulation and operating conditions present further room for improvement, this latter seems the most promising route for the valorisation of CO₂ by photocatalytic fixation in the short term.

At last, a few economic assessment studies were proposed for H₂ production. In particular, four reactor types considered were a single bed particle suspension system, a dual bed particle suspension system, a fixed panel array and a tracking concentrator array were compared in a PEC configuration, *i.e.* using photoelectrochemical cells. The final cost of production of H₂ was estimated as \$1.60–\$10.40 per kg H₂, with the particle bed systems having lower costs than the panel-based systems (Pinaud et al., 2013). A maximum solar to H₂ maximum efficiency of 11.2% was proposed for materials having a band gap ca. 2.2

eV, dropping to ca. 2% for a bandgap higher than 3 eV (such as TiO_2). Such efficiency was calculated on the basis of the circuit current and the data refer to water splitting rather than photoreforming.

As for CO_2 fixation by photocatalytic reduction a very interesting comparison between the economic sustainability of photocatalytic vs. electrocatalytic reduction has been proposed recently (Herron and Maravelias, 2016). Besides the very deep description and sensitivity analysis on the cost items of the system, a definition of the solar to fuels efficiency has been set as sum of the productivities times the HHV. The most important goal to guarantee the economic sustainability of the process is to push the solar to fuel efficiency to 15%. In the present case, the efficiency calculated on HCHO, only, is already 13%. This supports this route as the most promising in the short term, though with the need of some further optimisation.

Table 7: Maximum productivity of various products of CO₂ photoreduction and relative solar energy storage efficiency. X= different products listed. Different lines represent the selected irradiance zones.

Product	Zone	Harvested energy (kWh/m ²)	τ_{eq} (h/day)	Π_x (kg/day kg _{cat})	Stored energy (LHV) (MJ/day kg _{cat})	Incident energy on 10 m ² (MJ/day kg _{cat})	η (LHV)
H ₂	Low	0.16	1.50	0.00031	0.037	93.6	0.0004
	Medium	0.22	2.13	0.00044	0.052	133.2	
	High	0.30	2.88	0.00059	0.071	180.0	
	Very high	0.32	3.12	0.00064	0.076	194.4	
HCOOH	Low	0.16	1.50	0.20	1.1	93.6	0.012
	Medium	0.22	2.13	0.29	1.6	133.2	
	High	0.30	2.88	0.39	2.2	180.0	
	Very high	0.32	3.12	0.42	2.3	194.4	
HCHO	Low	0.16	1.50	0.72	12.4	93.6	0.13
	Medium	0.22	2.13	1.02	17.7	133.2	
	High	0.30	2.88	1.38	23.9	180.0	
	Very high	0.32	3.12	1.50	25.8	194.4	
CH ₃ OH	Low	0.16	1.50	0.017	0.31	93.6	0.0033
	Medium	0.22	2.13	0.024	0.45	133.2	
	High	0.30	2.88	0.032	0.60	180.0	
	Very high	0.32	3.12	0.035	0.65	194.4	

4 – CONCLUSIONS

The photoreforming of methanol has been experimentally investigated over TiO₂ based catalysts doped with 0.1 wt% Au. More than 20% methanol conversion was achieved even with very low UVA lamp power, but negligible H₂ productivity was obtained. H₂ productivity and the methanol conversion rate increased with irradiance and initial methanol concentration and the best results were obtained by using P25 TiO₂.

The conceptual feasibility of a photoreactor based on these results has been investigated considering both a continuous apparatus with UV irradiation, and solar light. In both cases the hydrogen productivity and the efficiency of solar light storage seem insufficient for a practical exploitation. However, the same study was based on one of the best hydrogen productivities reported in the literature under visible light and also in such a promising case the feasibility does not seem guaranteed.

The photoreduction of CO₂ has been also considered as a process for the fixation of this greenhouse gas to useful fuels by storing solar energy. Hydrogen productivity was insufficient for practical interest, being similar to the results obtained by photoreforming. On the other hand, also reduced organic products accumulate in liquid phase, among which the productivity of formaldehyde is particularly interesting. When using UV lamps 35 kg/day kg_{cat} can be obtained, which decrease to 1.5 under solar light irradiation. This latter value corresponds to a 13% efficiency of solar light storage.

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