



Innovative photocatalysts integrated in flow photoreactor systems for direct CO₂ and H₂O conversion into solar fuels

Deliverable 1.2

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1 Introduction

Photocatalytic CO₂ reduction has been intensely investigated since the beginning of the century. However, the CO₂ reduction photoefficiency into valuable chemicals is rather poor.¹ Despite the great efforts for increasing the solar-driven CO₂ conversion, there are still major drawbacks. One of its limitations consist in the low solubility of CO₂ in water (0,034 M at r.t.).²

This report is about the performed CO₂ solubility experiments in water stream using different techniques in order to achieve the proposed KPI, 5 % solar-to-CO efficiency which results in a 0,6 M CO₂ concentration. The strategies proposed to this end are:

- Solubilize the CO₂ in form of nanobubbles to increase its dissolution rate in water. The nanobubbles with controlled size, excellent stabilization and better solubilization in H₂O will be studied to increase the literature results.
- Use of near neutral pH values to increase the CO₂ solubility in water stream. At high pH values the CO₂ is converted to carbonate and becomes unreactive and at low values, the H₂ transformation becomes predominant.
- Add salts to increase the CO₂ solubility due to the salting-in effect.
- Pressurize in both batch and flow condition. In gas solutions, an increase of pressure involves an increase of solubility.
- Use porous membranes to facilitate the permeation the CO₂ in the water stream.

2 Experimental work

The mentioned parameters and some others were applied for solubility experiments in batch first. Afterwards, the parameters that resulted in significant changes were applied in flow.

All the experiments have been performed using MiliQ water and a cylinder of commercial CO₂.

¹ Dimitrijevic, N. M., Vijayan, B. K., Poluektov, O. G., Rajh, T., Gray, K. A., He, H., & Zapol, P. (2011). *Journal of the American Chemical Society*, 133(11), 3964-3971.

² Parvanian, A. M., Sadeghi, N., Rafiee, A., Shearer, C. J., & Jafarian, M. (2021). *Energies*, 15(1), 63.



2.1 Solubility experiments in batch

As reported before, initial experiments were performed in batch to see general trends and gather information to apply later in continuous flow.

2.1.1 General procedure

MiliQ Water and CO₂ were mixed in batch using a high-pressure reactor. First, water was placed in the reactor and then it was closed. Later, CO₂ was bubbled up directly inside the reactor through the injector until the desired pressure was obtained. Samples were collected measuring the extracted volume and subsequently capturing the solubilized CO₂ by adding an excess of sodium hydroxide solution. The mixture was then stirred overnight.

A titration method to determine the amount of solubilized CO₂ was developed based in the literature.³ Therefore, the CO₂ was trapped first as carbonate anion through sodium hydroxide quenching, and then the carbonate was titrated with HCl.

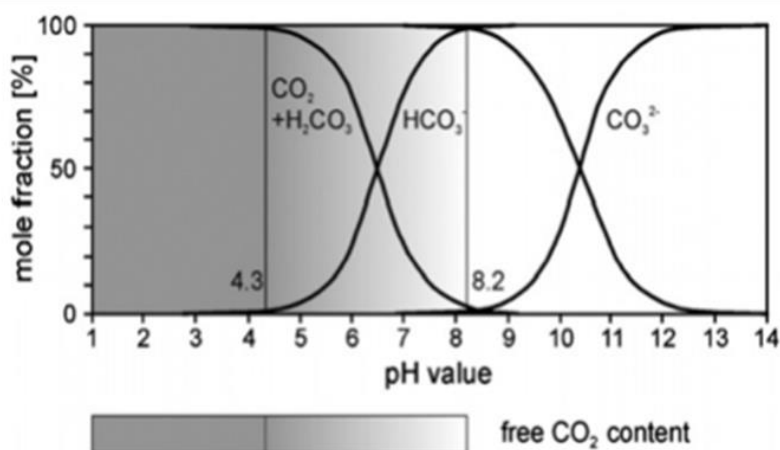
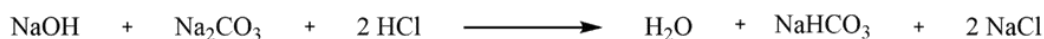


Figure 1. Carbonate titration process⁴

³ Crossno, S. K., Kalbus, L. H., & Kalbus, G. E. (1996). Determinations of Carbon Dioxide by Titration: New Experiments for General, Physical, and Quantitative Analysis Courses. *Journal of Chemical Education*, 73(2), 175.

⁴ Zosel, J; Oelßner, W; Decker, M; Gerlach, G; Guth, U (2011). The measurement of dissolved and gaseous carbon dioxide concentration. *Measurement Science and Technology*, 22(7), 072001.



Specifically, the mixture was titrated with HCl 1 M. The titration started with the quenching of the remaining sodium hydroxide and the conversion of carbonate into bicarbonate until pH 8,2 using phenolphthalein as indicator. Furthermore, bicarbonate was titrated with methyl orange as indicator until pH 4,3. Finally, the concentration of CO₂ was equal to the amount of solved bicarbonate.

In order to avoid visual errors that could be generated by the indicators in the manual titration, an automatic titrator Metrohm 888 titrando (Figure 2) was used.



Figure 2. Metrohm automatic titrator

2.1.2 Optimization of the process

The residence time of CO₂ and water in the reactor was found irrelevant. Experiments from 15 minutes to 1 hour showed the same results (Figure 3) so, 15 minutes were considered enough for this process.

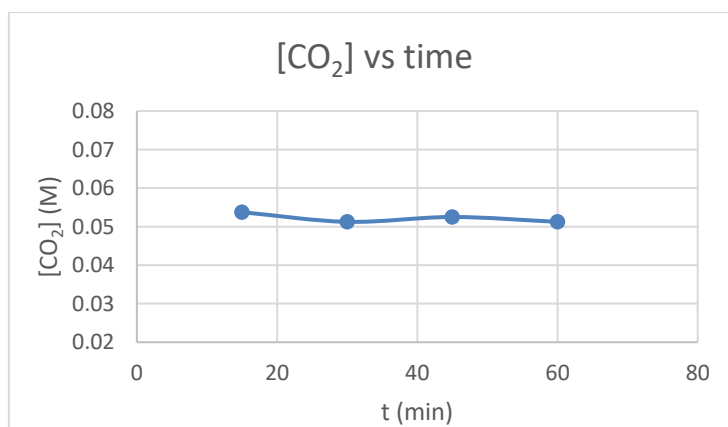


Figure 3. CO₂ concentration vs time



To ensure the complete capture of CO₂ as carbonate solution, the reaction time with the excess of NaOH was optimized. The mixture was stirred for two, four and six hours, overnight and for four days at room temperature. As seen in Figure 4, the results keep increasing with time, but overnight (20 h) was considered enough for the next tests.

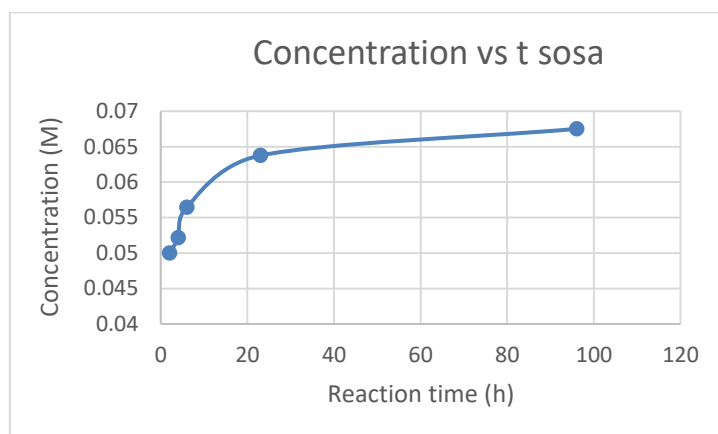


Figure 4. Sodium hydroxide reacting time

For experiments with pressure, sample collection process was optimized to minimize the pressure loss during the quenching process. At first, the sample was collected in a cold tube to measure de volume and immediately was added to the NaOH solution (Figure 5). Using this method, most of the CO₂ that could be solved because of the pressure influence, was evaporated before got trapped by the NaOH due to the pressure drop.

To fix this problem, instead of collecting the sample in a tube, the sample was collected directly in a three-necked flask with NaOH inside. Two necks were sealed with empty balloons (Figure 5). When the sample was collected the system was quickly closed and the balloons absorbed the pressure of the mixture, keeping most of the CO₂ inside. The flask contained a known volume of NaOH mixture and after stirring the mixture overnight, the total volume was measured and titrated to determinate the amount of CO₂ in the original sample. Three samples were collected for each experiment to reduce the error, so an average result is shown in all the tables.



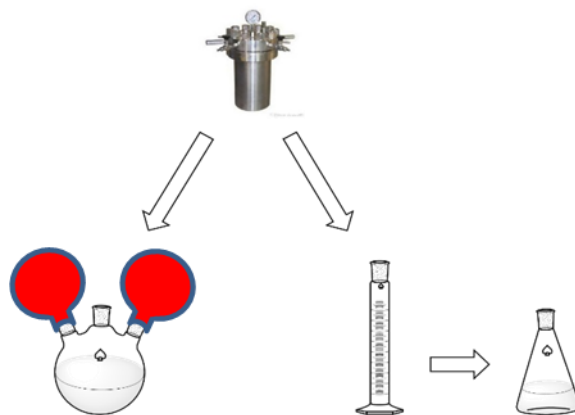


Figure 5. Sample collecting

2.1.3 Temperature and pressure effect

According to literature,⁵ lowering the temperature increases the solubility of CO₂ (Figure 6). Hereby, water was cooled down using an ice bath prior to the addition into the reactor. The sample was collected as reported in Figure 5.

<i>P</i> (bar)	<i>T</i> (K)		
	273.15	303.15	333.15
1	0.0693	0.0286	0.0137
5	0.3368	0.1442	0.0803
10	0.6463	0.2809	0.1602
50		1.0811	0.6695

Figure 6. Literature solubility data.⁵

As expected, lower temperatures resulted in better solubility. At 4° C, solubility increased a 45 % compared to room temperature experiments (Table 1), achieving comparable results to the literature.

⁵ Duan, Z., & Sun, R. (2003). An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical Geology*, 193(3-4), 257–271.



Essay	Temperature (°C)	Concentration (M)
Control	25	0,0478
1	8	0,0638
2	4	0,0693
3	4	0,0696

Table 1. Solubility data at different temperatures

Temperature played a key role to increase CO₂ solubility but had to be combined with other parameters to achieve the solubility goals. Moreover, pressure is described⁴ as the most influencing parameter for CO₂ solubility. Results around 1 M concentration have been described at 50 bar pressure and room temperature (Figure 6).

Therefore, several experiments were performed at different pressure values, going from 1 bar up to 50 bar (Table 2) at room temperature. Although many experiments were performed, only few of them could be successfully carried out due to the loss of CO₂ in the sample collecting process, especially the ones performed at high pressure.

Essay	Pressure (bar)	Concentration (M)
Control	1	0,0478
1	10	0,1030
2	20	0,1704
3	40	0,3619

Table 2. Solubility data at different pressures

Despite increasing the solubility, results were not comparable to the literature (Figure 6). Therefore, experiments applying optimal conditions in terms of pressure and temperature were performed (Table 3) to see the length of the solubility tests, achieving a CO₂ concentration of 0.83 M in the best attempt, reaching in this case the goal of the task.

Essay	Pressure (bar)	Temperature (°C)	Concentration (M)
Control	1	25	0,0515
1	50	4	0,8264

Table 3. Solubility data at optimal conditions



In conclusion, pressure and temperature were able to enhance CO₂ solubility. Further tests using flow chemistry and compatible pressure conditions with the reactor set-up are detailed in chapter 2.2.

2.1.4 Ionic liquids

Ionic liquids (IL) were described⁶ as CO₂ solubility enhancers in water. Higher amounts of solubilized CO₂ were supposed to obtain in pure IL. Since water was needed to be the larger phase, diluted IL were used.

Among all IL, 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM) was the IL selected to perform the experiments. As shown in Table 4, two different BMIM concentrations were used (BMIM 1 M and 0,1 M). The experiments were performed at room temperature and atmospheric pressure.

Essay	IL (M)	Concentration (M)
Control	0	0,0524
1	0,1	0,0542
2	1	0,1079

Table 4. Solubility data with different IL concentration

Ionic liquids had a huge impact in high concentration. Even though, concentrations above 0.1 M are too high to perform the syngas formation reaction and will conclude in further purification problems.

2.1.5 Salting in effect

As reported in literature,⁷ adding certain salts could enhance CO₂ solubility. Sodium chloride and potassium bicarbonate were selected to improve solubility. As shown in (Figure 7), the bicarbonate favours the equilibrium of water and CO₂ to carbonic acid.

⁶ Yang, D., Zhu, Q., & Han, B. (2020). Electroreduction of CO₂ in Ionic Liquid-Based Electrolytes. *The Innovation*, 1(1), 100016.

⁷ Al-Anezi, K., Somerfield, C., Mee, D., & Hilal, N. (2008). Parameters affecting the solubility of carbon dioxide in seawater at the conditions encountered in MSF desalination plants. *Desalination*, 222(1-3), 548–571.



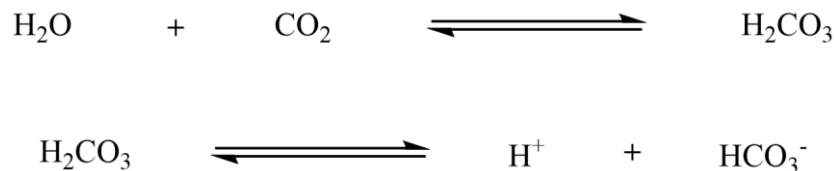


Figure 7. CO₂ an HCO₃⁻ equilibrium

Although bicarbonate increases the amount of captured CO₂, when the solution pH is too basic, the CO₂ becomes unreactive so, a small amount of bicarbonate must be used. First, sodium chloride 0,1 M was tested as solubility enhancer.

Essay	NaCl (M)	Concentration (M)
Control	0	0,0533
1	0,1	0,0511

Table 5. Solubility data with different NaCl concentration

As seen in Table 5, results with NaCl were similar and even a little worse than the control so, NaCl was discarded for further experiments.

The same process was applied for KHCO₃ 0,1 M. In this case, the pH of this solution was 8,6 compared to 6,3 of MiliQ water.

Essay	KHCO ₃ (M)	Concentration (M)
Control	0	0,0558
1	0,1	0,0587

Table 6. Solubility data with different KHCO₃ concentration

As shown in Table 6. Solubility data with different KHCO₃ concentration, KHCO₃ resulted in a small increase of CO₂ solubility. Thus, both salts were discarded for further experiments.



2.2 Solubility experiments in flow

All the information collected from the batch experiments was used to discard the techniques with lower or non relevant results and to emphasize and improve the most promising ones.

2.2.1 General procedure

As the main goal of the project was to use the power of flow chemistry to develop an integrated system capable of transforming CO₂ and water into fuels, the solubilization process of CO₂ was adapted to flow chemistry. Moreover, continuous flow CO₂ solubilization provided many different possibilities to achieve the desired KPI.

In a general set-up, water was pumped through the system and simultaneously, CO₂ was added from the commercial cylinder using a mass flow controller (MFC) to monitor the amount of gas added. Both phases got mixed in a glass microreactor and went through the continuous separator (Zaiput). This device was needed to get rid of the non-solubilized CO₂ from the aqueous phase⁸, to only measure the CO₂ that was solubilized. This aqueous phase was then directly mixed with sodium hydroxide and went through another glass microreactor to ensure the complete CO₂ trapping as carbonate species. The mixture was collected to measure the amount of CO₂ solubilized by titration, following the same method that was used in batch experiments.

For pressure needed experiments, two back pressure regulators (BPR) were placed in both system outcomes, one on the Zaiput gas phase output and the other at the liquid phase output.

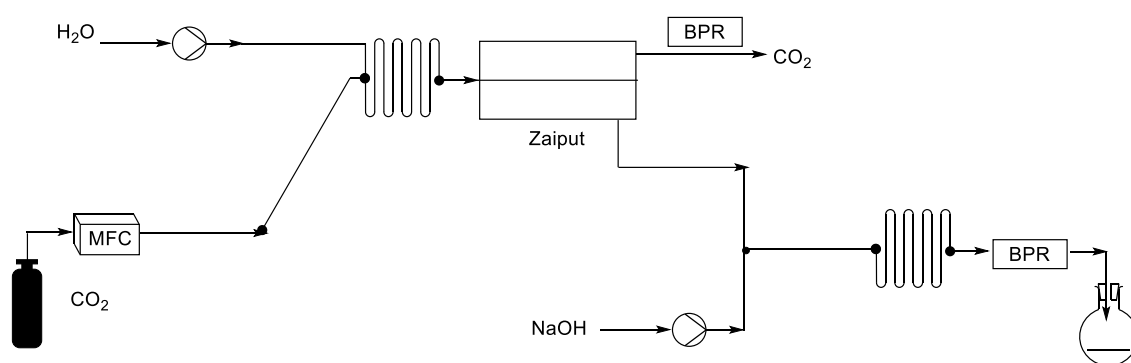


Figure 8. Flow system for solubility experiments

⁸ Zhang, J., Teixeira, A. R., Kögl, L. T., Yang, L., & Jensen, K. F. (2017). Hydrodynamics of gas-liquid flow in micropacked beds: Pressure drop, liquid holdup, and two-phase model. *AIChE Journal*, 63(10), 4694–4704.



To obtain better results, an excess of CO₂ was required. Hereby, the flow rate ratio was set between 1/1 to 1/4 (water/CO₂) achieving the best results as the CO₂ ratio increased. Higher ratios were avoided due to less homogeneous mixture and phase separation problems so, 0,5 mL/min of water and 2 mL/min of CO₂ were set as standard conditions.

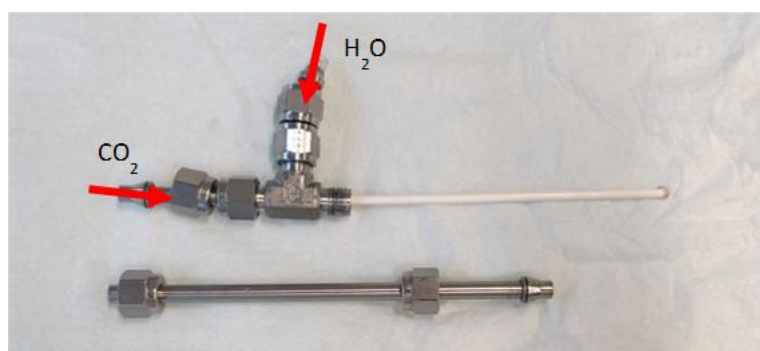


Figure 9. Ceramic membrane

As described in the proposal, a ceramic membrane was used to facilitate the permeation of CO₂ into the water stream and improve the solubility. The cylindrical membrane was placed concentrically inside a stainless steel tube as seen in **iError! No se encuentra el origen de la referencia.** Figure 9, before getting into the glass microreactor. Specifically, the gas is pumped through the ceramic membrane and permeates into the water phase throughout the tube, increasing the solubility.

2.2.2 Pressurizing CO₂ in flow reactors

As shown in Figure 8, two back pressure regulators (BPR) were placed in both system outcomes trying to enhance the amount of solubilized CO₂. Since the flow system could not reach as high pressures as used in batch experiments, 10 bar was set as the maximum working pressure because the Zaiput separator could not endure harder pressure conditions.

Different problems arose when pressure was applied regarding the correct separation of the excess of CO₂ and the constant maintenance of the flow rate. Experiments were performed directly at 4 °C changing the CO₂ flow rate to find the optimal conditions (Table 7).



Essay	Flow rate H ₂ O/CO ₂ (mL/min)	Pressure (bar)	Concentration (M)
Control	0.5/2	1	0,0468
1	0.5/7	5	0,1422
2	0.5/14	10	0,1804

Table 7. Solubility experiments at different pressures in flow

An improvement of solubility results in flow against the batch results could be seen comparing Table 2 with Table 7. Even though, the results were still far from the literature.

Since the results were not good enough at those conditions, two more experiments were performed without removing the excess of non-solubilized CO₂ to see the maximum amount of CO₂ that could be ideally captured if either the aqueous CO₂ or gas CO₂ could be used to obtain syngas (Table 8).

Essay	Flow rate H ₂ O/CO ₂ (mL/min)	Pressure (bar)	Concentration (M)
1	0.5/7	5	0,7227
2	0.5/14	10	1,4686

Table 8. Solubility experiments at different pressures in flow using a biphasic system

In both cases, all the CO₂ added, including the excess, got trapped by NaOH. As reported before, this experiments were performed to see the maximum amount of CO₂ that could react using this flow rates if both, gas and liquid CO₂ transformations into syngas were feasible.

2.2.3 CO₂ nanobubbles

Nanobubbles emerged as an alternative method to increase the solution lifetime and the gas solubility, increasing, in some cases, 30 times more the gas solubility.⁹ It was

⁹ Patel, A. K., Singhania, R. R., Chen, C. W., Tseng, Y. S., Kuo, C. H., Wu, C. H., & Di Dong, C. (2021). Environmental Technology & Innovation, 23, 101729.



reported that by using this methodology, the CO₂ solubility increased 15% (0.039 M at 1 bar, r.t.),¹⁰ and when 4 bar was applied, it could rise to 40% (0.048M, r.t.).¹¹

According to all the parameters shown in Figure 10 such as the reactor design, reactor flux (0.1 mL min⁻¹), rate of carbon source (R(C_{source})), the change in the Gibbs free energy that accompanies the CO₂ photoreduction to CO ($\Delta G^\circ = 64.1 \times 10^3 \text{ J mol}^{-1}$), the energy intensity of the solar light irradiation ($P = 0.1 \text{ W cm}^{-2}$) and the irradiation area ($S = 12.5 \text{ cm}^2$),¹² the CO₂ solubility and therefore the solar-to-CO efficiency (n(%)) could be calculated.

$$n (\%)_{max} = \frac{R(C_{source})(\Delta G^\circ)}{(P)(S)} (100)$$

Figure 10. Equation to calculate solar-to-CO efficiency.

Nevertheless, the significant increase of solubility is not enough for achieving the proposed KPI, 5% solar-to-CO efficiency (**iError! No se encuentra el origen de la referencia.**), so nanobubbles were discarded for this purpose.

Process	Conditions	CO ₂ solubility (M)	R (C _{source}) (mol s ⁻¹)	n (%) _{max}
Ambient	r.t., 1 bar	0.034		0.29
Nanobubbles	r.t., 1 bar	0.039		0.33
Nanobubbles	r.t., 1 bar	0.048		0.41
Goal		0.585	9.75 x 10 ⁻⁷	5.00

Table 9. Theoretical CO₂ solubilities using nanobubbles

3 Conclusions

Although several experiments and techniques were attempted for CO₂ solubility in water stream, solubility goals using working flow conditions were not achieved in aqueous phase in order to obtain the 5 % solar-to-CO efficiency. To reach the proposed theoretical solar-to-CO efficiency in a liquid-phase reaction, the CO₂ solubility should be increased to around 0.6 M using no more than 20 bar due to the reactor specifications.

¹⁰ Zhou, Y., Han, Z., He, C., Feng, Q., Wang, K., Wang, Y., Luo, N., Dodbiba, G., Wei, Y., Otsuki, A. & Fujita, T., (2021). *Materials*, 14(7), 1808.

¹¹ Phan, K. K. T., Truong, T., Wang, Y., & Bhandari, B. (2021). *Food Engineering Reviews*, 13(1), 3-14.

¹² Jiao, X., Li, X., Jin, X., Sun, Y., Xu, J., Liang, L., Ju, H., Zhu, J., Pan, Y., Yan, W. & Lin, Y. (2017). *Journal of the American Chemical Society*, 139(49), 18044-18051



To the best of our knowledge, there is no more available technology that can achieve this solubility in this specific conditions. Therefore, two different options emerge as the best candidates to address the problem. On one hand, with the results obtained in Table 8, the reaction could be carried out in a biphasic system, considering that solubilized and non-solubilized CO₂ will be reactive. On the other hand, the process can be accomplished in gas phase using moist CO₂, increasing the CO₂/H₂O ratio.¹³ An example of the gas phase proposed set-up is illustrated in Figure 11.

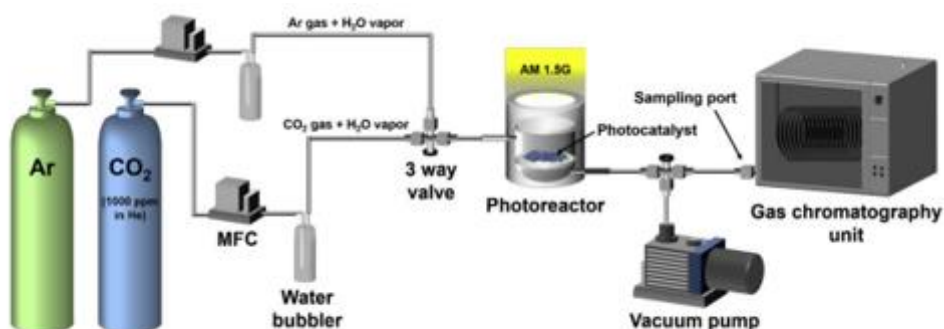


Figure 11. Gas phase set-up used for the photocatalytic CO₂ reduction.¹⁴

¹³ Ali, S., Flores, M.C., Razzaq, A., Sorcar, S., Hiragond, C.B., Kim, H.R., Park, Y.H., Hwang, Y., Kim, H.S., Kim, H. & Gong, E.H., (2019). *Catalysts*, 9(9), 727.

¹⁴ Sorcar, S., Hwang, Y., Grimes, C. A., & In, S. I. (2017). *Materials Today*, 20(9), 507-515.

