# SUPPORTING INFORMATION

# Solar-powered carbon fixation for food and feed production using microorganisms – a comparative techno-economic analysis

Marja Nappa<sup>a</sup>\*, Michael Lienemann<sup>a</sup>, Camilla Tossi<sup>b</sup>, Peter Blomberg<sup>a</sup>, Jussi Jäntti<sup>a</sup>, Ilkka Juhani Tittonen<sup>b</sup>, Merja Penttilä<sup>a</sup>

<sup>a</sup>VTT Technical Research Centre of Finland Ltd, <sup>b</sup>Aalto University, School of Electrical Engineering, Department of Electronics and Nanoengineering, Finland

\*Corresponding Author. E-mail: marja.nappa@vtt.fi, ORCID-ID: 0000-0002-6868-0503

#### **Supporting Information Contents**

Figure S1. Comparison of solar energy storing capabilities of different technologies	2
Data S1. Microalgae: estimation of photosynthetic efficiency (PE)	2
Data S2. Precipitation and evaporation estimates for Finland and Morocco	3
Table S1. Estimated monthly average precipitation and evaporation amounts	3
Data S3. Technology consideration, capital expenses and additional input parameters	4
Table S2a. Capital costs of concepts in million euros [M€], scenario Morocco	10
Table S2b. Capital costs of concepts in million euros [M€], scenario Finland	10
Table S3. Estimate for labor amount [persons] for different concepts and scenarios	11
Data S4. Parameter rangess for sensitivity analysis	11
Data S5. H <sub>2</sub> Storage assumptions	13
Data S6. State of the art of photoelectrochemical water splitting	14
Supplementary material references	15



Figure S1. Comparison of solar energy storing capabilities of different technologies.

#### Data S1. Microalgae: estimation of photosynthetic efficiency (PE)

Weyer et al<sup>1</sup> assess a total photosynthetic efficiency (PE) of 2.9% in their theoretical evaluation of a best-case scenario for microalgae cultivation, while other studies claim PEs of 4% and 5% <sup>2,3</sup>. The PE is affected by various terms, such as suboptimal conditions (temperature, light amount) and losses caused by construction or geometry (e.g., light reflection). PE values for other scenarios and cases are lower than 2.9% and estimated based on Weyer et al <sup>1</sup>. The PE of biomass production by open-cultivation of microalgae is estimated to be 20% lower than the PE of the production process using PBRs. The lower PE of the latter is likely due to the prolonged light path and increased light reflection at the liquid surface, which result in energy transfer losses. In addition, the PE for the scenario Finland is assumed to be 10% lower than the PE for the scenario Morocco due to its lower photon transmission efficiency caused by low angle of incident light and the resulting increased light reflection.<sup>1</sup> Based on these assumptions, the following PEs are obtained: Morocco PBR 2.9%, open pond 2.3%; Finland PBR 2.6% and open pond 2.0%.

#### Data S2. Precipitation and evaporation estimates for Finland and Morocco

Evaporation E [m s<sup>-1</sup>] in open ponds is evaluated based on this previously published equation <sup>4</sup>:

$$E = 1.84 * (0.37 + 0.22V) * (5T^{2} - 51T + 1282)^{0.88} * (1 - F)^{0.88}$$
 (eq. S1)

, where V is wind speed [m s<sup>-1</sup>], T is temperature [°C] and F is relative humidity. Monthly values are calculated for both locations. The rate at which fresh water needs to be added to balance compensate for evaporation is determined based on the monthly difference between evaporation and precipitation.

	Average		Average		Average difference	
	precipi	tation	Evaporation			
	mm m	onth <sup>-1</sup>	mm month <sup>-1</sup>		mm month <sup>-1</sup>	
Month	Helsinki	Agadir	Helsinki	Agadir	Helsinki	Agadir
January	44.0	23.4	52.2	104.3		80.9
February	33.0	34.8	49.1	113.4		78.6
March	33.0	27.9	73.7	128.0		100.1
April	37.0	18.7	75.2	122.4	38.2	103.7
May	36.0	8.2	116.7	156.0	80.7	147.8
June	47.0	0.1	140.1	133.4	93.1	133.3
July	72.0	0.0	140.4	142.5	68.4	142.5
August	78.0	3.3	103.9	142.5	25.9	139.2
September	71.0	7.3	54.3	137.4	-16.7	130.1
October	72.0	21.8	37.8	139.7		117.9
November	70.0	48.2	40.4	120.5		72.3
December	57.0	49.3	42.3	109.0		59.7

Table S1. Estimated monthly average precipitation and evaporation amounts.

The weather data from following sources are used:

 Wind Agadir and Helsinki; precipitation Agadir (accessed 11 Nov 2019): <u>https://www.weatheronline.co.uk/weather/maps/city?FMM=1&FYY=2000&LMM=12</u> <u>&LYY=2019&WMO=60252&CONT=afri&REGION=0011&LAND=MC&ART=WS</u> <u>T&R=0&NOREGION=0&LEVEL=162&LANG=en&MOD=tab</u>

- Humidity Agadir: <u>http://www.agadir.climatemps.com/humidity.php</u> (accessed 11 Nov 2019)
- Humidity Helsiki (accessed 11 Nov 2019): http://www.helsinki.climatemps.com/humidity.php
- Precipitation Helsinki (accessed 11 Nov 2019): <u>https://en.climate-data.org/europe/finland/helsinki/helsinki-5971/#climate-table</u>

#### Data S3. Technology consideration, capital expenses and additional input parameters

The cost of fermentation, downstream processing and CO<sub>2</sub> delivery were estimated from installed equipment costs while the fixed capital costs for all other processing steps were estimated directly from literature when available. The fixed capital cost (FCI) of these processing steps is the sum of direct costs and indirect costs. In addition to installed equipment costs, direct costs include the costs for buildings, service facilities and yard improvements, estimated here to be 20% of installed equipment costs equaling 11% of FCI. Indirect costs (contingency 10%, engineering & supervision 10%, legal expenses and construction expense 13%) is estimated 60% of installed equipment costs equaling 33% of fixed capital costs.

Cost, i.e. the cost of a certain equipment or processing step in design size of the study was calculated from reference costs according to equation S2. The scale factor F reflects the dependency of economy of scale and depends on the type of equipment. F ranges from 0.2 to 1 depending on the equipment, being on average 0.6.<sup>5</sup>

$$cost = reference \ cost \left(\frac{new \ size}{reference \ size}\right)^F$$
 (eq. S2)

#### **Biomass production systems**

Open-pond cultivation of microalgae for the production of edible biomass is attractive for its simple nature and the ability of the photosynthetic organisms to assimilate  $CO_2^{6}$ .

However, the open-pond process is considered to be particularly vulnerable to contamination by air-borne particulate matter with adverse effects on the food safety (e.g., photosynthetic toxin-producing microorganisms)<sup>7</sup>. The safety of the photosynthetically produced biomass can be increased by performing the microalgae cultivation in closed photobioreactors which however increases the process costs. When comparing the microalgal and HOB systems, it can be stated that the prior suffers from a lower volumetric product yield and cultivation concentration that is due to the low penetration depth of light and results in a comparably large production area. HOB's, on the other hand, require hydrogen, which in discussed HOB cultivation concepts is produced through energyintensive water electrolysis. However, water electrolysis is an attractive alternative to supply from external reservoirs because storage of large quantities of flammable gas can be avoided, zero-emission energy sources can be utilized and *in situ* production of gaseous substrates may result in more efficient utilization as found for other hydrogenotrophic microorganisms. However, in situ water electrolysis releases reactive oxygen species, has been shown to adversely affect growth of some HOB species<sup>8,9</sup> and is thereby restricted to HOB species that tolerate oxidative stress.

#### <u>CO<sub>2</sub> supply system</u>

Capital expenses for the CO<sub>2</sub> supply system were calcultated using reference data published by <sup>10</sup>, and included a CO<sub>2</sub> storage sphere, immersion heaters and piping to the cultivation area. The used reference cost for storage sphere and immersion heaters is 1.7 M€ with the scaling size of 1100 t of CO<sub>2</sub> per day. The used scaling exponent F is 0.6. The size of piping is estimated based on a constant CO<sub>2</sub> volumetric flow. However, the cultivation concentration affects to the area needed for biomass production, further which affects the length of needed piping. This is considered in CO<sub>2</sub> supply system cost estimate. The cost is based on reference cost of 4.3 M€. Used scaling exponent F is 1.

 $CO_2$  purified from fluegas was selected as  $CO_2$  supply strategy in this study. However, several  $CO_2$  supply strategies can be used for the considered concepts including the use of unpurified flue gas, the utilization of industrial flue gas streams from which  $CO_2$  can be purified and the use of other industrial sources like CO<sub>2</sub>-rich fermentation gas. In addition, atmospheric CO<sub>2</sub> can be used as such or accessed by direct air capture (DAC) technology. However, the CO<sub>2</sub> concentration in air is too low to sustain a high productivity of the considered processes. Moreover, according to Davis et al.<sup>10</sup> the use of flue gas as CO<sub>2</sub> source without purification in algae cultivation, is more expensive than the use of CO<sub>2</sub> purified from flue gas, and also highly uncertain in cost. In addition, in case of hydrogenotrophic fermentation, the use of unpurified flue gas would increase the gas amount fed to the fermenter and probably cause (i) challenges in gas circulation. Furthermore, DAC would remove restrictions with respect to the location of the concept as it would be independent of existing infrastructure providing CO<sub>2</sub>, i.e., CO<sub>2</sub> emitting industries. However, currently DAC technology faces both, energetic and financial constraints <sup>11</sup>, which have to be overcome for DAC to be considered as a viable CO<sub>2</sub> source.

#### Algae cultivation

Comprehensive but highly variable estimates for capital costs of CO<sub>2</sub> conversion into organic matter by microalgae in open raceway ponds can be found from literature <sup>10,12–15</sup>, with the lowest being 0.089 M€ ha<sup>-1 13</sup> and the highest being 0.612 M€ ha<sup>-1 14</sup>. Fixed capital cost of 0.136 M€ ha<sup>-1</sup> (including CO<sub>2</sub> delivery inside the pond area, water circulation and cultivation) and an additional  $6 \in m^{-2}$  for pond lining is used <sup>10</sup>.

There are only few studies reporting capital costs for closed pond algal cultivation systems of >100 ha in size. Therein, capital costs of 0.519 M $\in$  ha<sup>-1</sup> are stated for horizontal tubular systems <sup>16</sup> and capital costs of 0.262 M $\in$  ha<sup>-1</sup> for tubular reactors with airlift columns <sup>13</sup>. The higher cost was taken as an estimate for photobioreactor (PBR) capital cost, because the lower one appeared too optimistic.

The cost of inoculum system in both algae concepts was estimated to be 10% of the open pond capital costs. This may vary a lot, depending, among the others, on how easily and often system contaminate cause a need for a fresh algae inoculum.

A study of de Godos et al.<sup>17</sup> found that, when  $CO_2$  was delivered as flue gas, 66% of the incoming  $CO_2$  was fixed to biomass. Bao et al.<sup>18</sup> have measured a utilization efficiency of 79% with direct injection of pure  $CO_2$ . However, the definition of representative process parameters is complicated by the fact that a wide range of  $CO_2$  utilization efficiencies is utilized and that, in some cases, outgassed  $CO_2$  is left unaccounted for. According to review of Collet et al.<sup>19</sup>, only 44% of assessments take these losses into account among which the average  $CO_2$  utilization efficiency is stated to be as high as 82%. The utilization efficiency values used in this study are 75% in an open system and 90% in closed systems.

#### Dewatering and water circulation

Design and capital expenses of mechanical dewatering have been adopted from a research report by Davis et al. <sup>10</sup>. In accordance with this study, biomass settling is performed in tanks, which are located next to each pond or pond module, and from which 10 g L<sup>-1</sup> algae slurry is pumped to a centralized dewatering station. Settling tanks were designed to have a 4 h residence time, and the capital cost is based on peak season flow in each concept and scenario. Reference cost is 9 M€ with flow of 1.68 million m<sup>3</sup> d<sup>-1</sup>. After settling, water content is further decreased using advanced membrane filtration for which a reference cost is 13.5 M€ for flow of 76 266 m<sup>3</sup> d<sup>-1</sup> <sup>10</sup>. The final dewatering step is a centrifugation, which is estimated to be based on a reference cost of 2.89 M€ and a liquid flow of 252 m<sup>3</sup> h<sup>-1</sup> <sup>10</sup>.

Make-up water pumping and water circulation are estimated to consume electric energy at  $0.123 \text{ kWh m}^{-3 20}$  and  $0.04 \text{ kWh m}^{-3}$ , respectively, assuming a total pump efficiency of 67% and a pressure difference of 100 kPa.

#### Drying

The drying costs are estimated based on published reference capital cost of 2.48 M€ determined for an evaporation of 65 t water per day using a ring dryer. <sup>14</sup> Fuel cost of 35 € MWh<sup>-1</sup>, is used in both scenarios.

#### PV and inverter

The capital cost of photovoltaic (PV) has been determined as being 945  $\in$  kW<sup>-1</sup> DC <sup>21</sup>. The nominal power of 0.2 kW<sub>p</sub> m<sup>-2</sup> corresponds to an areal cost of 189  $\in$  m<sup>-2</sup>.

The capital cost of inverters was estimated as  $54 \in kW^{-1}$  DC according to Fu et al.<sup>21</sup>.

#### Polymer electrolyte membrane (PEM) electrolysis

Capital costs of PEM electrolysis were estimated to be  $1500 \notin kW^{-1}$  based on a IEA study stating costs that range from 1350 to  $3400 \notin kW^{-1}$ .<sup>22</sup>

#### HOB cultivation

HOB cultivation is performed in 1000 m<sup>3</sup> stirred tank reactors (STR). Needed H<sub>2</sub> and O<sub>2</sub> are generated by water electrolysis and then compressed while  $CO_2$  is fed from a pressurized storage. 10% of gas feed is assumed to be collected in the reactor headspace and circulated back to the gas feed. In addition, the HOB cultivation system contains media preparation tanks, fresh water and circulation water tanks and seed fermentation reactors.

The bioreactor cost is based on STR reactors with a size of 1000 m<sup>3</sup> including a 1000 kW stirrer motor (reference cost of 2.07 M $\in$ <sup>23</sup>). Filling degree 80% and installation factor 2.0 are used for bioreactors. The seed fermentation system is assumed to cost 10% of fermentation reactors, similarly to algae concepts.

Inlet gas compressors are evaluated as air cooled two stage compressor, which cost is based on equation C [2003] = 302 000\*S + 2500, where S is the inlet gas flow [m<sup>3</sup> s<sup>-1</sup>]<sup>5</sup>.

Recirculation and feed water pump costs are calculated from equation C [\$2006] = 3300 + 48 \* S<sup>1.2</sup>, where S is the water flow [1 s<sup>-1</sup>].<sup>24</sup>

The costs of media preparation tanks are calculated from equation C [\$2006] = 5800 + 1600 \* S<sup>0.7</sup>, where S is the tank volume [m<sup>3</sup>].<sup>24</sup>

Solar energy conversion using photoelectrochemical (PEC) fixed panel arrays

The capital costs of solar energy conversion using PEC fixed panel arrays have been reported to amount to  $260 \notin m^{-2}$ <sup>25</sup> and  $200 \notin m^{-2}$ <sup>26</sup> of which the latter value is used in the present study.

Electric energy consumption of PEC panel arrays in the concept PV-e-HOB is estimated to amount to 2.0 kW h kg<sup>-1</sup> H<sub>2</sub><sup>26,27</sup>.

Scenario Morocco	Algae-open	Algae-	PV-e-	PVGrid-	PEC-
		closed	biomass	e-	biomass
				biomass	
FCI of					
Downstream + CO <sub>2</sub> delivery	14.9	13.7	23.6	9.6	23.6
HOB cultivation			388.8	110.2	388.8
Algae cultivation + inoculum	28.4	59.5			
PV	1.0	3.8	142.7	43.7	56.9
PEC					109.7
Water electrolysis			141.2	38.8	
FCI	44.3	77.0	696.3	202.3	579.0
Working capital, of FCI <sup>1</sup>	2.2	3.9	34.8	10.1	29.0
Land cost <sup>2</sup>	1.1	0.9	0.6	0.2	0.7
TCI	47.7	81.8	731.7	212.6	608.6

## Table S2a. Capital costs of concepts in million euros [M€], scenario Morocco .

1. 5% of FCI; 2. 6672 € ha<sup>-1 10</sup>

## Table S2b. Capital costs of concepts in million euros [M€], scenario Finland .

Scenario Finland	Algae-open	Algae-	PV-e-	PVGrid-	PEC-
		closed	biomass	e-	biomass
				biomass	
FCI of					
Downstream + CO <sub>2</sub> delivery	23.4	21.3	42.4	9.6	42.4
HOB cultivation			898.8	110.2	898.8
Algae cultivation + inoculum	90.9	184.6			
PV	2.5	11.3	330.4	43.7	131.8
PEC					254.1
Water electrolysis			327.0	38.8	
FCI	116.8	217.2	1 598.6	202.3	1 327.0
Working capital, of FCI <sup>1</sup>	5.8	10.9	79.9	10.1	66.3
Land cost <sup>2</sup>	3.7	2.9	1.4	0.2	1.6
TCI	126.3	230.9	1 679.9	212.6	1 394.9

**1**. 5% of FCI; 2. 6672 € ha<sup>-1 10</sup>

	Finland	Morocco
Algae-open	85	53
Algae-closed	65	42
PV-e-HOB	96	50
PVGrid-e-HOB	25	25
PEC-HOB	143	70

Table S3. Estimate for labor amount [persons] for different concepts and scenarios.

#### Data S4. Parameter rangess for sensitivity analysis

The ranges within the process parameters were varied during the sensitivity analysis were chosen based on relevant cases described in literature.

The maximum PV efficiency depends, among other factors, on the type of used technology with the current benchmark for an experimental device exceeding 40% energy conversion efficiency <sup>28</sup>. Here, 40% is used as upper 17.5% as lower limit.

PEC efficiency was varied between the lower limit of  $5\%^{29}$  and the upper limit of  $25\%^{25}$ .

In the concept Algae-closed, PE was varied between 2% and 5% <sup>2,3</sup>. Similarly to baseline value in the Algae-open concept, the most and less favorable PE values in open-cultivation of microalgae is estimated to be 20% lower than the PE of the production process using PBRs, resulting the PE range varying from 1.6% to 4% in the concept Algae-open.

According to the International Energy Agency, the efficiency of current implementations of the PEM electrolysis technology ranges between 65% and 78% <sup>22</sup>, which were set as minimum and maximum values in the sensitivity analysis.

The efficiency of hydrogenotrophic fermentation was varied between 31% and 55%, which relates to  $H_2$ –CO<sub>2</sub> ratios of 5.9<sup>30</sup> and 3.3. A baseline figure of 4<sup>31</sup> and a most favorable value of 2.4 for this parameter is estimated, with the latter being based on the stated thermodynamic limit for hydrogenotrophic CO<sub>2</sub> assimilation <sup>30</sup>.

The fermentation dry content and productivity variation are estimated based on a recent study by Reed et al. <sup>32</sup>. More favorable values are set to 41 g L<sup>-1</sup> and 6.9 g L<sup>-1</sup> d<sup>-1</sup> (0.29 g L<sup>-1</sup> h<sup>-1</sup>), taken from high-concentration batch trial and less favorable values are set to 1.2 g L<sup>-1</sup> and 0.11 g L<sup>-1</sup> h<sup>-1</sup> originally determined for a continuous cultivation process. It should be noted that the higher concentration value is likely to be an overestimate because Yu and Munasinghe have previously found that gas transfer becomes limiting at biomass densities of >4.5 g L<sup>-1</sup> and atmospheric pressure and at >6.3 g L<sup>-1</sup> and 4 bars<sup>33</sup>.

The assumed PEC power range is based on a study by Pinaud et al. according to which the power consumption of a tracking concentrator array PEC system is 0.16 kWh kg<sup>-1</sup> H<sub>2</sub><sup>27</sup>. This figure is used here as more favorable value and the power consumption of single bed particle suspension PEC is 3.29 kW h kg<sup>-1</sup> H<sub>2</sub> used here as less favorable value.

The power consumption of the open pond system was estimated to lie within the range of 1 W m<sup>-3</sup> – 2.4 W m<sup>-3</sup>. The lower value is selected according to Acien Fernandez et al.<sup>34</sup> and the higher value is estimated to be double the baseline and based on literature reporting values between 1 W m<sup>-3</sup> and 2 W m<sup>-3 10,14,34</sup>. The more favorable value for the PBR power consumption is set to 0.0062 kW m<sup>-3</sup> and adopted from the PBR design<sup>10,14</sup>. The less favorable value of 0.5 kW/m<sup>3</sup> is an estimate for tubular photobioreactors <sup>34</sup>. The specific energy consumption of bioreactor typically ranges between 0.2 kW m<sup>-3</sup> and 3 kW m<sup>-3 35</sup> based on which 0.8 kW m<sup>-3</sup> and 2.5 kW m<sup>-3</sup> were selected as sensitivity limits including mixing and gas inlet.

Biomass dewatering includes settling (Dewatering 1) as initial step, in which electricity consumption in baseline is neglected while 0.1 kW h m<sup>-3</sup> is selected as a less favourable value to account for a possible alternative type of primary dewatering. The second dewatering step (Dewatering 2) is performed using hollow-fiber membrane technology with very low power consumptions and no more favourable value is considered here. A less favorable value is selected according to less power efficient technology, centrifugation, which is also used in the final dewatering step (Dewatering 3).

Capital charge is studied within the range of +50% to -30% of the baseline values, which are typical limits for concept level CAPEX estimates. The plant economic life time may change depending on the studied concept and process unit, a range of 10–30 years is assessed. In addition, the maintenance costs for different equipment types are studied within a range of 1–4% of the total capital investment.

Large differences of the grid electricity cost exist between different countries and in addition, in the case of Morocco significant seasonal and daytime-dependent variations exist. Anyhow, fixed unit cost for electricity is used in the evaluation and sensitivity analysis evaluates the possible effect of cost change on biomass production costs. A more favorable electricity cost of  $25 \in MW h^{-1}$  is adopted from a recent levelized cost report<sup>36</sup>, while a 50% cost increase is assumed to define the less favourable value.

#### Data S5. H<sub>2</sub> Storage assumptions

There are seasonal and daily variations in solar irradiation and solar irridation is estimated considering H<sub>2</sub> storage capacity, which allows to balance daily production fluctuations but does not compensate for seasonal variations of solar irradiation. To compensate for seasonal variations, the storage capacity would need to be significantly increased because solar irradiation in Morocco varies between 3.1 kWh m<sup>-2</sup> day<sup>-1</sup> and 7.4 kWh m<sup>-2</sup> day<sup>-1</sup> throughout the year. However, to be able to double the utility degree of bioreactors and DSP, it is estimated that H<sub>2</sub> storage tanks, capable to store 6-8 h H<sub>2</sub> production (corresponding 14 t H<sub>2</sub> or 552 MWh), are needed. The evaluated cost for the storage is 4.418 M€, assumed based on an IEA report <sup>22</sup> according which the cost of H<sub>2</sub> storage in pressurized tanks is 5400–9000 € MWh<sup>-1</sup> (the figure of 8000 € MWh<sup>-1</sup> used in evaluation). The decrease of 4% of electrolysis efficiency is introduced to this evaluation because H2 is stored in a pressurized state <sup>37</sup>. Further, doubling the utility degree of the bioreactor and DSP reduces the needed size (and cost due to decrease in equipment amounts rather than size) of this equipment roughly to the half of original. The usage of this kind of H<sub>2</sub> storage will decrease the TCI, e.g. in the scenario Morocco for concepts PV-e-HOB and PEC-HOB from 732 M€ to 520 M€ and from 609 M€ to 400 M€, respectively. Moreover the

production costs would reduce from  $10.7 \notin kg^{-1}$  to  $8.0 \notin kg^{-1}$  and from  $9.1 \notin kg^{-1}$  to  $6.2 \notin kg^{-1}$ , respectively. This is however a rough estimate because it neither includes the cost of grid electricity to sustain bioreactor operation and DSP at times when PV electricity is unavailable nor the savings from possible lower need of PV electricity. However, these considerations show a large potential for cost reduction by introducing of a H<sub>2</sub> storage facility.

#### Data S6. State of the art of photoelectrochemical water splitting

A concept based on photoelectrochemical water-splitting (namely PEC-HOB) was included in the present study in order to examine an emerging technology that has not yet been assessed from a techno-economical <sup>25,26</sup> point of view. However, they do not extend the analysis to consequential technologies like fuel or food production, and the following decade has seen a surge of interest and development in water-splitting research.

A PEC-cell in a single device <sup>38</sup> is the design of choice when maximizing the integrability of the H<sub>2</sub> production system. Currently, such design can be articulated into three kinds: single photo-electrode (where the other electrode is a metal), double photo-electrode (anode and cathode are both photoactive materials) and PEC/PV (PEC cell integrated with a photovoltaic system), which in turn can be divided between semiconductor PV, dyesensitized PV and perovskite PV.

Single photo-electrode designs present the necessity for an external electrical bias and stringent requirements on the band edges of the involved materials <sup>39</sup>, making it a disadvantageous choice in an industrial application such as the one contemplated in the present study. Double photo-electrode designs overcome such flaws and present a higher solar-to-hydrogen (STH) conversion efficiency <sup>40</sup>. Furthermore, they offer a variety of arrangements, with the two photoelectrodes either being separated or combined in a monolithic cell, and either presenting themselves to sunlight as a stack, or side-by-side (thus widening the choice of materials to include non-transparent ones). The materials investigated for the double-electrode configuration range from expensive but efficient semiconductors <sup>41</sup>, to inexpensive and less efficient metal oxides and chalcogenides <sup>42</sup>. In

this configuration, top STH efficiency is displayed by materials based on non-toxic and eco-friendly bismuth vanadate (BiVO<sub>4</sub>), approaching 1% <sup>38</sup>. This efficiency is still well below the theoretical limits estimated by <sup>29</sup> and presented in the main manuscript.

The third design (PEC/PV) reveals itself as the most efficient and the most versatile of the three, attaining 10% for a CdS/TiO<sub>2</sub> photoanode matched with a perovskite solar cell, and a platinum photocathode, with close runner-ups based on amorphous silicon, bismuth vanadate and multijunction semiconductors. This is in line with the commercialization requirements of a 10% STH, a 10-year lifetime, and a H<sub>2</sub> production cost of \$2-4 per kg.<sup>25,36,43</sup>

#### Supplementary material references

- Weyer, K. M.; Bush, D. R.; Darzins, A.; Willson, B. D. Theoretical Maximum Algal Oil Production. *Bioenergy Res.* 2010, *3* (2), 204–213. https://doi.org/10.1007/s12155-009-9046-x.
- (2) Slocombe, S. P. S.; Benemann, J. R. J. Microalgal Production for Biomass and High-Value Products, first.; Slocombe, S. P., Benemann, J. R., Eds.; CRC Press, 2017. https://doi.org/10.1201/b19464.
- Ward, A. J.; Lewis, D. M.; Green, F. B. Anaerobic Digestion of Algae Biomass: A Review. *Algal Res.* 2014, 5 (1), 204–214. https://doi.org/10.1016/j.algal.2014.02.001.
- (4) Climates to travel World climate guide www.climatestotravel.com (accessed Oct 13, 2019).
- (5) Peters, M.; Timmerhaus, K.; West, R. Plant Design and Economics for Chemical Engineering, 5th ed.; McGraw-Hill, 2004.
- (6) Le Quéré, C.; Andrew, R. M.; Friedlingstein, P.; Sitch, S.; Pongratz, J.; Manning, A. C.; Korsbakken, J. I.; Peters, G. P.; Canadell, J. G.; Jackson, R. B.; et al. Global

Carbon Budget 2017. *Earth Syst. Sci. Data* **2018**, *10* (1), 405–448. https://doi.org/10.5194/essd-10-405-2018.

- (7) Heussner, A. H.; Mazija, L.; Fastner, J.; Dietrich, D. R. Toxin Content and Cytotoxicity of Algal Dietary Supplements. *Toxicol. Appl. Pharmacol.* 2012, 265
  (2), 263–271. https://doi.org/10.1016/j.taap.2012.10.005.
- (8) Nyyssölä, A.; Ojala, L. S.; Wuokko, M.; Peddinti, G.; Tamminen, A.; Tsitko, I.; Nordlund, E.; Lienemann, M. Production of Endotoxin-Free Microbial Biomass for Food Applications by Gas Fermentation of Gram-Positive H2-Oxidizing Autotrophic Bacteria, Submitted for Publication.
- (9) Torella, J. P.; Gagliardi, C. J.; Chen, J. S.; Bediako, D. K.; Colón, B.; Way, J. C.;
  Silver, P. A.; Nocera, D. G. Efficient Solar-to-Fuels Production from a Hybrid Microbial-Water-Splitting Catalyst System. *Proc. Natl. Acad. Sci. U. S. A.* 2015, *112* (8), 2337–2342. https://doi.org/10.1073/pnas.1424872112.
- (10) Davis, R.; Markham, J.; Kinchin, C.; Grundl, N.; Tan, E. C. D.; Humbird, D. Process Design and Economics for the Production of Algal Biomass: Algal Biomass Production in Open Pond Systems and Processing Through Dewatering for Downstream Conversion; 2016.
- (11) Greene, C.; Huntley, M.; Archibald, I.; Gerber, L.; Sills, D.; Granados, J.; Beal, C.;
   Walsh, M. Geoengineering, Marine Microalgae, and Climate Stabilization in the 21st Century Charles. *Earth's Futur.* 2017. https://doi.org/10.1002/2016EF000486.Received.
- (12) Lundquist, T. J.; Woertz, I. C.; Quinn, N. W. T.; Benemann, J. R. A Realistic Technology and Engineering Assessment of Algae Biofuel Production; 2010; Vol. October. https://doi.org/10.1556/1848.2015.6.1.6.
- (13) Davis, R.; Aden, A.; Pienkos, P. T. Techno-Economic Analysis of Autotrophic

Microalgae for Fuel Production. *Appl. Energy* **2011**, *88* (10), 3524–3531. https://doi.org/10.1016/j.apenergy.2011.04.018.

- Beal, C. M.; Gerber, L. N.; Sills, D. L.; Huntley, M. E.; Machesky, S. C.; Walsh, M. J.; Tester, J. W.; Archibald, I.; Granados, J.; Greene, C. H. Algal Biofuel Production for Fuels and Feed in a 100-Ha Facility: A Comprehensive Techno-Economic Analysis and Life Cycle Assessment. *Algal Res.* 2015, *10* (June), 266–279. https://doi.org/10.1016/j.algal.2015.04.017.
- (15) Benemann, J. R. Systems and Economic Analysis of Microalgae Ponds for Conversion of CO2 to Biomass; 1996.
- Jonker, J. G. G.; Faaij, A. P. C. Techno-Economic Assessment of Micro-Algae as Feedstock for Renewable Bio-Energy Production. *Appl. Energy* 2013, *102*, 461–475. https://doi.org/10.1016/j.apenergy.2012.07.053.
- (17) de Godos, I.; Mendoza, J. L.; Acién, F. G.; Molina, E.; Banks, C. J.; Heaven, S.;
   Rogalla, F. Evaluation of Carbon Dioxide Mass Transfer in Raceway Reactors for Microalgae Culture Using Flue Gases. *Bioresour. Technol.* 2014, 153, 307–314. https://doi.org/10.1016/j.biortech.2013.11.087.
- Bao, Y.; Liu, M.; Wu, X.; Cong, W.; Ning, Z. In Situ Carbon Supplementation in Large-Scale Cultivations of Spirulina Platensis in Open Raceway Pond. *Biotechnol. Bioprocess Eng.* 2012, *17* (1), 93–99. https://doi.org/10.1007/s12257-011-0319-9.
- (19) Collet, P.; Hélias, A.; Lardon, L.; Steyer, J. P.; Bernard, O. Recommendations for Life Cycle Assessment of Algal Fuels. *Appl. Energy* 2015, *154*, 1089–1102. https://doi.org/10.1016/j.apenergy.2015.03.056.
- (20) Davis, R.; Fishman, D.; Frank, E. D.; Wigmosta, M. S.; Aden, A.; Coleman, A. M.; Pienkos, P. T.; Skaggs, R. J.; Venteris, E. R.; Wang, M. Q. Renewable Diesel from Algal Lipids: An Integrated Baseline for Cost, Emissions, and Resource Potential

from a Harmonized Model; 2012. https://doi.org/10.1017/CBO9781107415324.004.

- (21) Fu, R.; Feldman, D.; Margolis, R.; Woodhouse, M.; Ardani, K.; Fu, R.; Feldman, D.; Margolis, R.; Woodhouse, M.; Ardani, K. US Solar Photovoltaic System Cost Benchmark: Q1 2017; 2017. https://doi.org/10.2172/1390776.
- (22) IEA. Technology Roadmap Hydrogen and Fuel Cells; 2015. https://doi.org/10.1007/SpringerReference\_7300.
- Humbird, D.; Davis, R.; McMillan, J. D. Aeration Costs in Stirred-Tank and Bubble Column Bioreactors. *Biochem. Eng. J.* 2017, *127*, 161–166. https://doi.org/10.1016/J.BEJ.2017.08.006.
- (24) Towler, G. P.; Sinnott, R. K. *Chemical Engineering Design : Principles, Practice, and Economics of Plant and Process Design*; Butterworth-Heinemann, 2013.
- (25) Shaner, M. R.; Atwater, H. A.; Lewis, N. S.; McFarland, E. W. A Comparative Technoeconomic Analysis of Renewable Hydrogen Production Using Solar Energy. *Energy Environ. Sci.* 2016, 9 (7), 2354–2371. https://doi.org/10.1039/c5ee02573g.
- (26) James, B. D.; Baum, G. N.; Perez, J.; Baum, K. N. Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production. *DOE Contract Number GS-10F-*009J 2009, 22201 (December), 1–128.
- (27) Pinaud, B. A.; Benck, J. D.; Seitz, L. C.; Forman, A. J.; Chen, Z.; Deutsch, T. G.; James, B. D.; Baum, K. N.; Baum, G. N.; Ardo, S.; et al. Technical and Economic Feasibility of Centralized Facilities for Solar Hydrogen Production via Photocatalysis and Photoelectrochemistry. *Energy Environ. Sci.* 2013, *6* (7), 1983–2002. https://doi.org/10.1039/C3EE40831K.
- (28) Green, M. A.; Hishikawa, Y.; Warta, W.; Dunlop, E. D.; Levi, D. H.; Hohl-Ebinger, J.; Ho-Baillie, A. W. H. Solar Cell Efficiency Tables (Version 50). *Prog.*

Photovoltaics Res. Appl. 2017, 25 (7), 668-676. https://doi.org/10.1002/pip.2909.

- (29) Fountaine, K. T.; Lewerenz, H. J.; Atwater, H. A. Efficiency Limits for Photoelectrochemical Water-Splitting. *Nat. Commun.* 2016, 7 (1), 13706. https://doi.org/10.1038/ncomms13706.
- Yu, J.; Dow, A.; Pingali, S. The Energy Efficiency of Carbon Dioxide Fixation by a Hydrogen-Oxidizing Bacterium. *Int. J. Hydrogen Energy* 2013, *38* (21), 8683–8690. https://doi.org/10.1016/j.ijhydene.2013.04.153.
- Schink, B.; Schlegel, H.-G. Hydrogen Metabolism in Aerobic Hydrogen-Oxidizing Bacteria. *Biochimie* 1978, 60 (3), 297–305. https://doi.org/10.1016/S0300-9084(78)80826-8.
- (32) Reed, J.; Geller, J.; McDaniel, R. CO2 Conversion by Knallgas Microorganisms -Evaluation of Products and Processes; Kiverdi, Inc., California Energy Commission Publication: CEC-500-2017-005., 2017.
- (33) Yu, J.; Munasinghe, P. Gas Fermentation Enhancement for Chemolithotrophic Growth of Cupriavidus Necator on Carbon Dioxide. *Fermentation* 2018, *4* (3), 63. https://doi.org/10.3390/fermentation4030063.
- (34) Acien Fernandez, F. G.; Fernandez Sevilla, J. M.; Molina Grima, E.
  Photobioreactors for the Production of Microalgae. *Rev. Environ. Sci. Biotechnol.*2013, *12* (2), 131–151. https://doi.org/10.1007/s11157-012-9307-6.
- (35) Niazi, S. K.; Brown, J. L. Fundamentals of Modern Bioprocessing; CRC Press Taylor & Francis Group, 2017.
- (36) Lazard.com | Levelized Cost of Energy and Levelized Cost of Storage 2019 https://www.lazard.com/perspective/lcoe2019 (accessed Jun 22, 2020).
- (37) Le Duigou, A.; Bader, A.-G.; Lanoix, J.-C.; Nadau, L. Relevance and Costs of Large S19

Scale Underground Hydrogen Storage in France. *Int. J. Hydrogen Energy* **2017**, *42* (36), 22987–23003. https://doi.org/10.1016/J.IJHYDENE.2017.06.239.

- (38) Ahmed, M.; Dincer, I. A Review on Photoelectrochemical Hydrogen Production Systems: Challenges and Future Directions. *Int. J. Hydrogen Energy* 2019, 44 (5), 2474–2507. https://doi.org/10.1016/J.IJHYDENE.2018.12.037.
- (39) Minggu, L. J.; Wan Daud, W. R.; Kassim, M. B. An Overview of Photocells and Photoreactors for Photoelectrochemical Water Splitting. *Int. J. Hydrogen Energy* 2010, *35* (11), 5233–5244. https://doi.org/10.1016/J.IJHYDENE.2010.02.133.
- (40) Coridan, R. H.; Nielander, A. C.; Francis, S. A.; McDowell, M. T.; Dix, V.; Chatman, S. M.; Lewis, N. S. Methods for Comparing the Performance of Energy-Conversion Systems for Use in Solar Fuels and Solar Electricity Generation. *Energy Environ. Sci.* 2015, 8 (10), 2886–2901. https://doi.org/10.1039/C5EE00777A.
- (41) Kainthla, R. C.; Zelenay, B.; Bockris, J. O. Significant Efficiency Increase in Self-Driven Photoelectrochemical Cell for Water Photoelectrolysis. *J. Electrochem. Soc.* 1987, 134 (4), 841. https://doi.org/10.1149/1.2100583.
- (42) Zhang, K.; Ma, M.; Li, P.; Wang, D. H.; Park, J. H. Water Splitting Progress in Tandem Devices: Moving Photolysis beyond Electrolysis. *Advanced Energy Materials*. John Wiley & Sons, Ltd August 1, 2016, p 1600602. https://doi.org/10.1002/aenm.201600602.
- (43) Karuturi, S. K.; Shen, H.; Duong, T.; Narangari, P. R.; Yew, R.; Wong-Leung, J.; Catchpole, K.; Tan, H. H.; Jagadish, C. Perovskite Photovoltaic Integrated CdS/TiO2 Photoanode for Unbiased Photoelectrochemical Hydrogen Generation. *ACS Appl. Mater. Interfaces* 2018, *10* (28), 23766–23773. https://doi.org/10.1021/acsami.8b04855.