Electronic Supplementary Material (ESI) for Energy & Environmental Science.
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Supplementary Information

S1 - Calculation of relevant illuminated surface area in cyanobacteria-based product formation

This section describes the determination of the illuminated surface areas used in the calculation of solar-to-product efficiencies.

Erlenmeyer flasks

For the cyanobacteria-based approaches, several assumptions were made when calculating the total area and the resulting input energy for the studies using Erlenmeyer flasks, bottles, and column bioreactors. For studies using Erlenmeyer flasks and when no further specific detail was available, we calculated the maximum and minimum surface areas based on the assumption that light would either hit the sides and top of the culture flask (maximum possible surface area), or only hit the top (minimum possible surface area). The possible use of opaque caps was ignored.

Specifically, the maximum surface area was calculated as the sum of the lateral area and the top area of the frustum shape created in a typical Erlenmeyer flask by the volume of culture liquid (the 'culture frustum'). The flask itself was also represented as a frustum (the 'flask frustum'). To calculate the surface area of the culture frustum, we needed to know the culture volume's base radius, top radius, and height. The base radius is the same radius as the original flasks as given by the given dimensions in table S1. The top radius (r2 in figure S1) and height (h_culture) can be derived through trigonometry. To do so, we first had to use the given flask dimensions in table S1 to calculate the dimensions of the cone that results from extending the flask frustum with an upper part containing a vertex ('flask cone'). We then used the known culture volume to calculate the top radius of the culture frustum using the relationship:

$$V_{culture} = V_{cone} - V_{cone - culture} \quad (1)$$

In which $V_{culture}$ is the known volume of the culture (e.g. 25 mL) and V_{cone} is the volume of the extended flask cone. The latter two volumes are unknown, but can be derived from the relationship between a right circular cone's volume and its radius and height, specified as:

$$V_{cone} = ⅓ * \pi * r_1^2 * h_{cone}, \quad (2)$$

$$V_{cone\text{-}culture} = ⅓ * \pi * r_2^2 * h_{cone - culture} \quad (3)$$

The base radius of the extended flask cone, r_1, is given by the known flask dimensions. The height can be substituted for as follows:

$$h_{cone} = r_1 * \text{cotangent}(\beta) \quad (4)$$

To derive β, we first calculate the slant height, s_{flask}, of the flask frustum:

$$s_{flask} = \sqrt{((r_1 - r_3)^2 + h_{flask})} \quad (5)$$

With s_{flask}, we can calculate the sin(α) via:

$$\sin(\alpha) = h_{flask} / s_{flask} \quad (6)$$

With α, we can calculate the slant height of the flask cone, s_{cone}, as:

$$s_{cone} = r_1 / \cos(\alpha) \quad (7)$$

From the slant height s_{cone}, we then calculate the β as:

$$\sin(\beta) = r_1 * / s_{cone} \quad (8)$$

For $V_{cone - culture}$, the height, $h_{cone - culture}$, in equation (3) can similarly be substituted for:

$$h_{cone - culture} = r_2 * \text{cotangent}(\beta) \quad (9)$$

With r_2 also being the top radius of the culture frustum. Given these substitutions, equation (1) can be rewritten as:

$$V_{culture} = ⅓ * \pi * r_1^3 * \text{cotangent}(\beta) - ⅓ * \pi * r_2^3 * \text{cotangent}(\beta) \quad (10)$$

To calculate r_2, we can rewrite this to:

$$r_2 = (r_1^3 - (3 * V_{culture}) / (\pi * \text{cotangent}(\beta)))⅓ \quad (11)$$

Tthe height of the culture ($h_{culture}$) can then be calculated from $V_{culture}$ and r_1 and r_2 as follows:

$$h_{culture} = 3 * V_{culture} / (\pi * (r_2^2 + r_1^2 + r_2 * r_1)) \quad (12)$$

with r_1, r_2, and $h_{culture}$, we can finally calculate the lateral surface area as:

$$A_{lateral} = \pi * (r_1 + r_2) * √((r_1 - r_2)^2 + h_{culture}) \quad (13)$$

and the top area as:

$$A_{top} = \pi * r_2^2 \quad (14)$$

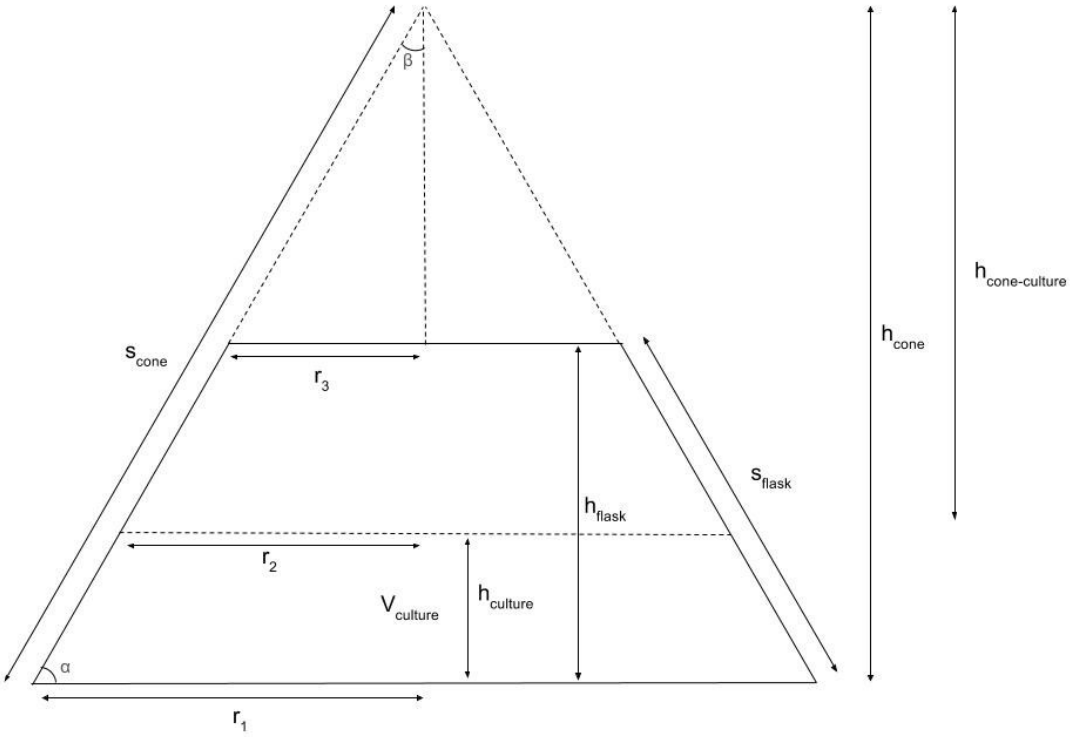

Figure S1: surface area representation of a culture volume in a flask. Both Erlenmeyer flasks and the culture volumes were approximated as frustum shapes. To calculate the surface areas of the culture volumes, its base radius, r_1, top radius, r_2, and height, $h_{culture}$, needed to be derived. s: slant height, r: radius, h: height.

Roux bottle

For the Roux bottle used by Atsumi et al. (2009), the relevant surface was calculated as the sum of the squares making up the sides and top of the culture volume within the rectangular bottle. The dimensions of the bottle were obtained from Sigma Aldrich[1].

For the column-photobioreactor used by Gao et al. (2012), the culture volume was approximated as a cylinder, calculated from the dimensions of the column specified in the paper (height: 0.255 m, bottom radius: 0.055 m). The surface area was subsequently calculated as a range from a lateral cross-section of the cylinder (minimum area; assuming the light were to only hit one side of the column), to the culture cylinder's total lateral surface (maximum area).

For the 1-liter culture bottle used by Ruffing et al, the culture was similarly approximated as a cylinder based on the specified dimensions of a 1-liter-capacity glass media bottle by Sigma Aldrich[2]. The surface area range was defined as ranging the bottom of the bottle (minimum area, assuming light were to hit from the top) to the sum of the lateral surface area and the bottom (maximum area).

Flat-panel bioreactor

The dimensions of the flat-panel bioreactor used by Zavrel et al. were specified in [3]. With these dimensions and light specified to hit from one side only, we calculated the rectangular total surface area.

S2 - Electrofuel studies: used surface areas

For the majority of electrofuel publications included in our analysis, the input energy was provided through direct current. The total energy input for these studies was therefore derived from the specified applied voltage (V) and the total charge in coulombs, which was in turn specified by the current (A) and the duration of the experiment. These metrics were specified directly in the publication, and a known surface area was therefore not required.

Two studies used light-sensitive electrodes and required surface area data to calculate the total energy input. For Nichols et al., the area dimensions of the light-sensitive electrodes were specified in the publication, which allowed for the calculation of total input energy based on the illumination data (W cm^{-2}). For Liu et al. (2015), the dimensions of the nanowire-array was not specified. The authors reported a peak efficiency of 0.38 %, with a photocurrent of 35 mA/cm^2. This translates into a total surface area of roughly 2 cm^2. This value was therefore used as the surface area in subsequent calculations.

S3 - efficiency calculations

Efficiencies were calculated based on the total input and output energy as follows:

$$\eta_{solar2product} = E_{out} / E_{in} * 100$$

The total input energy (E_{in}) for the cyanobacteria-based studies was derived from the total duration of the experiment in seconds (t), the light regime in mol photons m^{-2} s^{-1} (I), and the relevant surface area in m^2 (a), which together specified the total amount of input of photons in moles:

$$\text{mole photons} = I * a * t$$

For white light photons, a conversion factor of 226 kJ mol^{-1} photons was used to calculate the total input energy in joule:

$$E_{in} = \text{photon input} * 226 * 1000$$

while for red light photons the energy content used was 190.1 kJ * mol^{-1}.

For the electrofuel studies using a 2-step setup with a PV cell to convert solar energy to electricity, the total input energy in joule was determined by the current (A), voltage (V), and time in seconds (t):

$$E_{in} = V * A * t \quad (15)$$

For the electrofuel studies based on an integrated setup using light-sensitive electrodes, the input energy in J was quantified by the specified light intensity in W m^{-2} (I), the time in seconds (t), and the surface area of the electrodes in m^2 (a):

$$E_{in} = I * a * t \quad (16)$$

For all studies, the output energy (E_{out}) was quantified using the total amount of product formed in moles from the given titer (g L^{-1}), the molecular weight (g mol^{-1}), the volume (L), and using the heat of combustion ($\Delta_c H$) of each product in kJ mol^{-1}.

$$E_{out} = \text{mole product} * \Delta_c H * 1000 \quad (17)$$

For the free fatty acid product by Ruffing et al., palmitic acid was chosen as a representative FFA for output calculations.

Table S2 and S3 provide an overview of the main metrics used for each study to calculate the input and output energy for cyanobacterial- and electrofuel studies, respectively

Table S1: flask dimensions and calculated surface

Container type	*Container Volume (mL)*	*Culture volume (mL)*	*Flask Height (m)*	*Flask base radius(m)*	*Flask top radius (m)*	*lateral surface area (m2)*	*bottom surface area (m2)*	*top surface area (m2)*
Erlenmeyer flask	125	25	0,065	0,041	0,028	0,002	0,004	0,003
Erlenmeyer flask	250	50	0,08	0,053	0,032	0,002	0,006	0,005
Media bottle	1000	400	0,231	0,101	0,101	0,02932	0,00801	0,00801
Roux bottle	1000	600	0,153	0,055	0,12	0,054	0,0066	0,0066
Column-photobioreactor	410	300	0,58	0,03	0,03	0,04	0,0127 (side)	-
Flat-panel reactor	350	350	0,2	0,1	0,1	0,02	-	-

Table S2: cyanobacteria parameters used for efficiency calculations

Ref	**Time (h)**	**Culture volume (mL)**	**Min/max surface area (m2)**	**light intensity (uE/m2/s)**	**Product**	**Heat of combustion (kJ/mol)**	**Titer (g/L)**
Atsumi et al, 2009	192	600 ml	0.0066	55	Isobutyraldehyde	2509.918	1.1
Gao et al, 2012	624	300 ml	0.0127 - 0.0400	100	Ethanol	1370.7	5.5
Oliver et al, 2013	504	25 ml	0.00353 - 0.00481	55	2,3-butanediol	2461	2.38
Ruffing et al, 2014	480	400 ml	0.00801 - 0.0373	60	FFA**	10030.6	0.131
Ian et al, 2015	384	50 ml	0.00581 - 0.00782	50	3-HP	1419	0.665
Hirokawa et al, 2016	336	50 ml	0.00581 - 0.00782	100	1,3-propanediol	1859	0.2883811
Zavrel et al, 2016	-	350 ml	0,02	50	Ethylene	1387.4	-

Table S3: Electrofuel parameters used for efficiency calculations

Ref	Time (h)	Volume (mL)	Voltage (V)	Charge (Coulomb)	Surface area (m2)	Illumination (W / cm2)	Product	Heat of combustion (kJ/mol)	Titer (g/L)
Li et al, 2012	105	350	4	94500		-	C4 + C5	2994.3	0.15
Torella et al, 2015	120	25	3	5443.2			C3	2006.9	0.216
Nichols et al, 2015	72	150	-	-	0.0007	2.2	Methane	882	7.35701E-06
Liu et al, 2015	120	20	-	-	~0.0002	0.1	PHB (from acetate)	1903	1.2
Liu et al, 2016	144	100	2	2500		-	C3	2006.9	0.584
Liu et al, 2016	144	100	2	2400		-	C4+C5	2994.3	0.231
Liu et al, 2016	144	100	2	2100			PHB	1903	0.701

Table S4: Solar-to-product efficiency (averaged) and production rates

Ref	Organism	Product	Procedure; setup	Efficiency	Rate (g/l/h)
Atsumi et al., 2009	*S. elongatus* PCC7942	isobutyraldehyde	dcc; 1L-roux bottle	4,45	5,7
Gao et al., 2012	*Synechocystis sp*. PCC6803	ethanol	dcc; column reactor	5.01*	8,8
Oliver et al., 2013	*S. elongatus* PCC7942	2,3-butanediol	dcc; 125-ml Flask	1.77*	4,7
Ruffing et al., 2014	*Synechococcus sp*. PCC7002	free fatty acids	dcc; 1L-culture bottle	0.66*	0,3
Ian et al., 2015	*S. elongatus* PCC7942	3-hydroxy-propionate	dcc; 250-ml Flask	0.51*	1,7
Hirokawa et al., 2016	*S. elongatus* PCC7942	1,3-propanediol	dcc; 250-ml Flask	0.20	0,9
Zavrel et al., 2016	*Synechocystis sp*. PCC6803	ethylene	led; flat-panel reactor	3,58/0.36 (led/solar)	1,5
Li et al., 2012	*R. eutropha* H16	iso- & 3-methyl-1-butanol	sef; 2-step, formate	0,10	1,4
Torella et al., 2015	*R. eutropha* H16	*iso*-propanol	sef; 2-step, hydrogen	0,31	1,8
Liu et al., 2016	*R. eutropha* H16	PHB	sef; 2-step, hydrogen	7,38	4,9
Liu et al., 2016	*R. eutropha* H16	*iso*-propanol	sef; 2-step, hydrogen	7,80	4,1
Liu et al., 2016	*R. eutropha* H16	*iso*- & 3-methyl-1-butanol	sef; 2-step, hydrogen	3,55	1,6
Nichols et al., 2015	*M. barkeri*	methane	sef; integrated, hydrogen	0,00	0,05
Liu et al., 2015	*S. ovata*	acetate (+ PHB)	sef; integrated, direct et	0,2	4,08

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1. Pyrex® Roux culture bottle with offset neck capacity 1000 mL | Sigma-Aldrich. http://www.sigmaaldrich.com/catalog/product/aldrich/cls12901l?lang=en&region=US. Accessed August 5, 2017.
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3. Nedbal L, Trtílek M, Červený J, Komárek O, Pakrasi HB. A photobioreactor system for precision cultivation of photoautotrophic microorganisms and for high-content analysis of suspension dynamics. *Biotechnol Bioeng*. 2008;100(5):902-910. doi:10.1002/bit.21833.