Supplementary Information

Most common products from wild-type algal strain

Most common products that can be derived from wild-type algal strains, shown in Table S1. Most of these components are not secreted into the medium and thus require biomass harvesting, product extraction, and purification.

Table S1. Products from Algae Photosynthesis, with Reported Quantum Requirement, Cell Biomass Productivities, and Product Productivities. For comparison, reported productivities were converted to mg/L/day and mmol carbon/L/day.

Product	Quantum Requirement (mol photon /mol CO_2 to Product)	Cell Biomass Productivity (mg/L/day)	Product Productivity (mg/L/day) / (mmol carbon/L/day)
Algae Neutral Lipid[a] $C_{13}H_{26}O_2$-$C_{20}H_{40}O_2$	8 [1]	580 [2]	350.0/21.7[2, 3]
Lipid[a]	8 [1]	500 [4]	121.0/n.a. [4]
Amino Acids	4.8[b] [5]	500 [4]	159.0/8.1 [4]
Fatty Acids (FA) $C_{16}H_{34}O_2$ – $C_{18}H_{34}O_2$	12 [5]	500 [4]	38.7/2.4 [4]
Docosahexaenoic Acid (DHA) $C_{22}H_{32}O_2$	12[c] [5]	720 [6]	13.6/0.8 [6]
Eicosapentaenoic Acid (EPA) $C_{20}H_{30}O_2$	12[c] [5]	221 [7]	12.3/0.9 [7]

a. Algal neutral lipids have higher productivities compared to other lipids, shown in the second row.
b. The quantum requirement is for alanine, but is assumed as a proxy for all other amino acids.
c. The quantum requirement for all fatty acids is assumed to be the same.

Most common products from cyanobacteria

Table S2 reports several products from genetically modified cyanobacteria, ranked according to their reported productivity. The table lists the quantum requirement (number of moles of photons required to convert per mole of CO_2 to the respective product). Additionally, the physical properties of the product (formula, molecular weight, density, and higher heating value) and its toxicity to the organism are summarized. Test conditions for productivity have not been standardized, and each laboratory measures productivity under different cultivation conditions.

Table S2. Reported Products from Genetically Modified Cyanobacteria.

Product	Formula	MW (g/mol)	Density[f] (g/mL)	HHV Energy Content (MJ/kg)	Toxicity to Cells (g/L)	Quantum Requirement (mol photons/mol CO_2 to product)	Productivity (mg/L/day)/ (mmol carbon/L/day)
Sucrose	$C_{12}H_{22}O_{11}$	342.30	1.59	16.49 [8]	>3 [9]	8 [10]	866.4/30.3 [9]
Ethylene	C_2H_4	28.05	0.57 (@-104°C)	50.30 [11]	NT [12]	12-30.5[g] [5, 13-16]	**739/52.7** [12]
2,3-butanediol	$C_4H_{10}O_2$	90.12	0.99	27.31 [17]	>30 [18]	11 [16]	236.3/10.5 [18]
Isobutyraldehyde	C_4H_8O	72.11	0.78	34.24 [19]	>1 [20]	11 [16]	149.5/8.3 [20]
Free Fatty Acid	$C_{10}H_{20}O_2$-$C_{18}H_{36}O_2$	243.02[b]	-	38.4[b]	NR	12 [5]	98.5/5.7 [18]
Ethanol	C_2H_5OH	46.07	0.79	29.67 [21]	>11 [22]	12 [5]	95.4/4.1 [22]
Isobutanol	$C_4H_{10}O$	74.12	0.80	36.00 [23]	>1 [20]	12 [5, 16]	74.9/4.0 [20]
Acetoacetate	$C_4H_6O_3$	102.09	1.07	22.56 [24]	NR	NR	72.5/2.8 [25]
Lactic Acid	$C_3H_6O_3$	90.08	1.20	15.13 [26]	>9 [27]	8 [5, 16]	38.5[e]/1.3 [27]
Acetoin	$C_4H_8O_2$	88.11	1.01	-	>1 [18]	NR	36/1.6 [18]
1,2-propanediol	$C_3H_8O_2$	76.10	1.03	23.95 [28]	NR	NR	15/0.6 [29]
Hydrogen	H_2	2.02	0.09 (g/L [30])	142.87 [31]	NR	4.2 mol photons/mol H_2 [32]	9.1 [32]
Acetone	C_3H_6O	58.08	0.79	31.06 [33]	>100 [34]	NR	9.0/0.5 [25]
Isopropanol	C_3H_8O	60.1	0.78	33.39 [35]	>5	12[c] [5]	2.9/0.1 [34]
Hydrocarbons[a]					NT	NR	2.6 [36]
Heptadecane[a]	$C_{17}H_{36}$	240.47	0.77	47.20 [37]	NT	12.5 [15]	2.4/0.2 [36]
Heptadecene[a]	$C_{17}H_{34}$	238.46	0.78	46.93 [38]	NT	12.5[d] [15]	0.2/<0.1 [36]
Acetol	$C_3H_6O_2$	74.08	0.82	-	NR	NR	2.2/0.1 [29]
1-butanol	$C_4H_{10}O$	74.12	0.81	36.11 [39]	>1 [40]	12 [5, 14]	1.9/0.1 [40]

NR=Not Reported, NT=Not Toxic

a. The hydrocarbons heptadecane and heptadecene are intracellular products.
b. Fatty acid product profile was from [18] and HHV values were found for each fatty acid from [41, 42]; the molecular weights and HHV were the weighted average of the product distribution. Density was dependent on temperature and no data set for common temperature was found.
c. The quantum requirement is assumed to be the same as that for 1-propanol.
d. The quantum requirement is assumed to be the same as that for heptadecane.
e. These values are reported on a dry weight basis instead of a volume basis. The units are mg/g dry weight/day.
f. Unless otherwise stated, the density values were taken from [43] at 25°C.
g. For the base TEA case the quantum requirement is assumed to be 12 mol photons per mol of CO_2 to product, the range of 12-31 mol photons per mole of CO_2 is used for sensitivity analysis.

Calculated average yearly solar irradiance based on location.

Table S3. Average Yearly Solar Irradiance for Various Example Locations

Location	Average yearly Solar Irradiance MJ/m^2/year
Columbia, SC	5696
Houston, TX	5749
Meridian, MS	5946
Denver, CO	6012
Jacksonville, FL	6053
Lafayette, LA	6085
Valparaiso, FL	6198
Great Bend, KS	6245
Miami, FL	6311
Ely, NV	6418
Key West, FL	6740
Clayton, NM	6974
Albuquerque, NM	7129
Honolulu, HI	7147
Phoenix, AZ	7621
Truth or Consequence, NM	7715

* Based on data from https://energyplus.net/weather

Growth and ethylene production measurement of *Synechocystis* 2X*efe* strain

This work was performed in the Angenent Lab, Cornell University, working with the *Synechocystis* 2X*efe* in semi-batch experiments.

BG-11 medium was augmented with 20 mM $NaHCO_3$ as additional carbon source and 4.6 g/L TES as buffering agent. All cultures have been grown in selective media with 25 mg/L spectinomycin and 200 mg/L kanamycin. Cultures were initially grown under atmospheric CO_2 levels. Cultures up to OD_{730} of 2.7 were achieved.

High-density cultures were achieved by raising the serum bottle headspace CO_2 concentration to 5% and augmenting standard BG-11 medium with 100 mM $NaHCO_3$. These cultures were grown in duplicate. 1 L Schott bottle reactors were used to allow sufficient headspace volume. Cell suspensions were recultured daily by centrifugation and resuspension of the cell pellet in fresh medium to original volume. To prevent cell damage sub-optimal centrifugation speed (4100 g) was used, resulting in daily partial loss of cell biomass. Over 66 days of experiment biomass increase has thus been noted. Between days 38 and 66 steady-state values of OD_{730} up to 60 have been achieved.

A gas-chromatography (GC) based method has been developed and implemented for quantification of ethylene formation. The GC used is optimized for ethylene measurement and is equipped with an alumina-silica column (181°C, He carrier gas at 20 mL/min), and a flame ionization detector (FID) with hydrogen fuel gas (25 mL/min H_2 at 204°C).

In the period between day 0 and day 11 of the experiment, product formation rates have been measured in 1 L Schott bottle reactors. During exponential growth phase (days 3 to 7), ethylene production rates up to 183 µL ethylene/L/h/OD_{730} have been measured. Due to relatively low corresponding culture density (OD_{730} of 1.8), the maximum volumetric production rate in the exponential phase equaled 611 µg ethylene/L/h (day 6).

From the 14th day of experiments, ethylene production rates have been measured by transferring an aliquot of the 1 L Schott reactor culture in a 250 mL serum bottle. This was necessary due to relatively thick and thus sub-optimal light path (order of 1 cm) in the 1 L Schott reactors, which prevented maximal ethylene production. Light path thickness in the serum bottles is in the order of 1 mm, comparable to the stacked reactors developed at Cornell. Thus, peak product formation rates up to 9106 µg/L/h have been measured. For over three weeks steady-state production rate of 3751 µg/L/h has been achieved in both duplicate semi-batch reactors.

Reference:

1. K. Weyer, D. Bush, A. Darzins and B. Willson, *Bioenerg Res*, 2010, 3, 204-213.
2. Y. Li, D. Han, M. Sommerfeld and Q. Hu, *Bioresource Technol*, 2011, 102, 123-129.
3. *WO Pat.,* WO 2009/005496 A1, 2009.
4. N. Hempel, I. Petrick and F. Behrendt, *J Appl Phycol*, 2012, 24, 1407-1418.
5. T. T. Vu, E. A. Hill, L. A. Kucek, A. E. Konopka, A. S. Beliaev and J. L. Reed, *Biotechnology Journal*, 2013, 8, 619-630.
6. J. Liu, M. Sommerfeld and Q. Hu, *Appl Microbiol Biotechnol*, 2013, 97, 4785-4798.
7. C.-Y. Chen, Y.-C. Chen, H.-C. Huang, C.-C. Huang, W.-L. Lee and J.-S. Chang, *Bioresource Technology*, 2013, 147, 160-167.
8. V. Ponomarev and L. Migarskaya, *Russ. J. Phys. Chem*, 1960, 34, 1182-1183.
9. D. C. Ducat, J. A. Avelar-Rivas, J. C. Way and P. A. Silver, *Applied and Environmental Microbiology*, 2012, 78, 2660-2668.
10. D. C. Ducat, J. C. Way and P. A. Silver, *Trends in Biotechnology*, 2011, 29, 95-103.
11. F. D. Rossini and J. W. Knowlton, *J. Res. NBS*, 1937, 19, 249-262.
12. Y. J. Ungerer J, Presentation: Photobiological ethylene production in Synechocystis 6803, Washington University, St. Louis, 2013.
13. D. E. Robertson, S. A. Jacobson, F. Morgan, D. Berry, G. M. Church and N. B. Afeyan, *Photosynth Res*, 2011, 107, 269-277.
14. E. I. Lan and J. C. Liao, *Metab Eng*, 2011, 13, 353-363.
15. J. Kämäräinen, H. Knoop, N. J. Stanford, F. Guerrero, M. K. Akhtar, E.-M. Aro, R. Steuer and P. R. Jones, *Journal of Biotechnology*, 2012, 162, 67-74.
16. H. Knoop and R. Steuer, *Frontiers in Bioengineering and Biotechnology*, 2015, 3, 47.
17. H. Moureu and M. Dode, *Bull. Soc. Chim. France*, 1937, 4, 637-647.
18. J. W. K. Oliver, I. M. P. Machado, H. Yoneda and S. Atsumi, *Proceedings of the National Academy of Sciences*, 2013, 110, 1249-1254.
19. A. Gubareva and P. Gerasimov, *Journal of Applied Chemistry of the USSR*, 1990, 63, 844-846.
20. S. Atsumi, W. Higashide and J. C. Liao, *Nat Biotech*, 2009, 27, 1177-1180.
21. J. Green, *Chem. Ind.(London)*, 1960, 1215-1216.
22. J. Dexter and P. Fu, *Energy & Environmental Science*, 2009, 2, 857-864.
23. H. A. Skinner and A. Snelson, *Transactions of the Faraday Society*, 1960, 56, 1776-1783.
24. G. Wypych, Knovel Solvents - A Properties Database, http://www.elsevier.com/, Accessed May 25, 2013.
25. J. Zhou, H. Zhang, Y. Zhang, Y. Li and Y. Ma, *Metab Eng*, 2012, 14, 394-400.
26. O. Meyerhof, *Biochem. Z.*, 1922, 129, 594-604.
27. S. A. Angermayr, M. Paszota and K. J. Hellingwerf, *Applied and Environmental Microbiology*, 2012, 78, 7098-7106.
28. P. Knauth and R. Sabbah, *Thermochimica Acta*, 1990, 164, 145-152.
29. H. Li and J. Liao, *Microbial Cell Factories*, 2013, 12, 4.
30. Knovel, Knovel Critical Tables (2nd Edition), http://www.elsevier.com/, Accessed May 25, 2013.
31. S. Ahmed and M. Krumpelt, *International Journal of Hydrogen Energy*, 2001, 26, 291-301.
32. G. Ananyev, D. Carrieri and G. C. Dismukes, *Applied and Environmental Microbiology*, 2008, 74, 6102-6113.
33. A. G. Emery and F. G. Benedict, *American Journal of Physiology--Legacy Content*, 1911, 28, 301-307.
34. T. Kusakabe, T. Tatsuke, K. Tsuruno, Y. Hirokawa, S. Atsumi, J. C. Liao and T. Hanai, *Metabolic Engineering*, 2013, 20, 101-108.

35. J. Chao and F. Rossini, *Journal of Chemical and Engineering Data*, 1965, 10, 374-379.
36. W. Wang, X. Liu and X. Lu, *Biotechnology for biofuels*, 2013, 6, 1-9.
37. E. Prosen and F. Rossini, *J Res NBS*, 1945, 36, 263-267.
38. E. V. Sagadeev, R. A. Kafiatullin, V. V. Sagadeev and V. I. Sagadeev, *Theoretical Foundations of Chemical Engineering*, 2003, 37, 524-526.
39. C. Mosselman and H. Dekker, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1975, 71, 417-424.
40. J. Anfelt, B. Hallström, J. Nielsen, M. Uhlén and E. P. Hudson, *Applied and Environmental Microbiology*, 2013, 79, 7419-7427.
41. N. Adriaanse, H. Dekker and J. Coops, *Recueil des Travaux Chimiques des Pays-Bas*, 1965, 84, 393-407.
42. L. Keffler, *The Journal of Physical Chemistry*, 1930, 34, 1319-1325.
43. C. L. Yaws, Yaws' critical property data for chemical engineers and chemists, http://www.elsevier.com/, Accessed May 25, 2013.