A Combined Electrochemical-Biological System for the Production of Liquid Fuel from CO_2

Link Foundation Energy Fellowship Final Report
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Introduction

Biological photosynthesis is the origin of our liquid transportation fuels, from petroleum to corn ethanol. Biological photosynthesis has an efficiency of approximately 1% for the conversion of photons from sunlight to biomass[1]. Increasing the energy efficiency of biomass production (solar-to-biomass conversion) would allow for biomass, and biofuels, to be produced using less resources. Artificial photosynthesis seeks to overcome the limitations of biological photosynthesis, including low efficiency of solar energy capture and poor carbon dioxide reduction, and could provide an alternative route for biomass production. A two-step electrochemical process converts CO_2 to acetate. Acetate is a soluble, two-carbon substrate that can serve as the sole carbon and energy source for the heterotrophic cultivation of algae, an oil-producing feedstock for the production of drop-in liquid fuels. Coupling this system of carbon fixation to photovoltaics offers an alternative, more energy efficient approach to biomass production for biofuels.

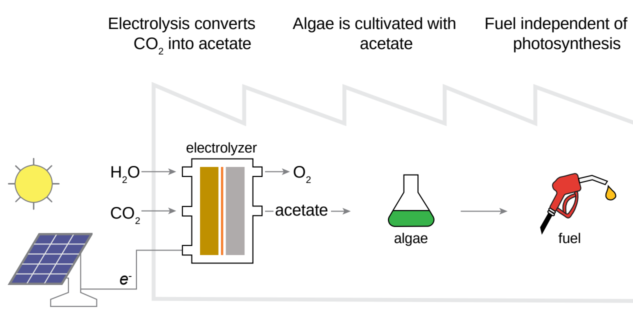

Figure 1. *Using electricity created from photovoltaics, the electrolyzer system converts CO_2 into acetate, the acetate is then used to cultivate algae heterotrophically. Algae can be used as a feedstock for biofuel.*

Results

An electrocatalytic process was designed to produce acetate from CO_2. To achieve maximum selectivity and production of acetate from a direct CO_2 feed, a two-step electrolyzer system was demonstrated to convert CO_2 to CO and then CO to acetate through a tandem process[2]. The liquid product of this process, the effluent, contains acetate and other by-products. We used the effluent in growth media of *Chlamydomonas reinhardtii*, a green algae, to reach an acetate concentration of typical growth media (17.5 mM)[3]. The algae did not grow initially, so each component of the effluent was added to individual growth media and it was observed that the only component that prohibited algal growth was the electrolyte salt ($KHCO_3$ or KOH) (Figure 2a-b). Using multiple iterations of electrolyzer produced effluent as a carbon source for algal growth allowed me to identify an ideal acetate-to-electrolyte salt ratio, above 0.4 was shown to support growth. The acetate selectivity of the electrocatalysis system was increased by over a factor of 3 by introducing a 5 M NaOH scrubber between the CO_2 and CO electrolyzers. The scrubber prevents unreacted CO_2 produced in the first electrolyzer from reaching the CO electrolyzer. Overall, 57% of reacted CO_2 formed acetate at a production rate of 0.7 g day^{-1} cm^{-2}, representing the highest conversion of CO_2 feed to acetate reported to date[4]. The electrolysis system was optimized to produce improved effluents with acetate-to-electrolyte salt ratios as high as 0.75, well above the ratio determined necessary to support biological growth. *Chlamydomonas* grown on an effluent with an improved acetate-to-electrolyte salt ratio (0.75 M acetate: 1 M KOH) had a yield of 0.28 g algae per g acetate (Figure 2c-e), which is comparable to yields reported from non-effluent medias[5].

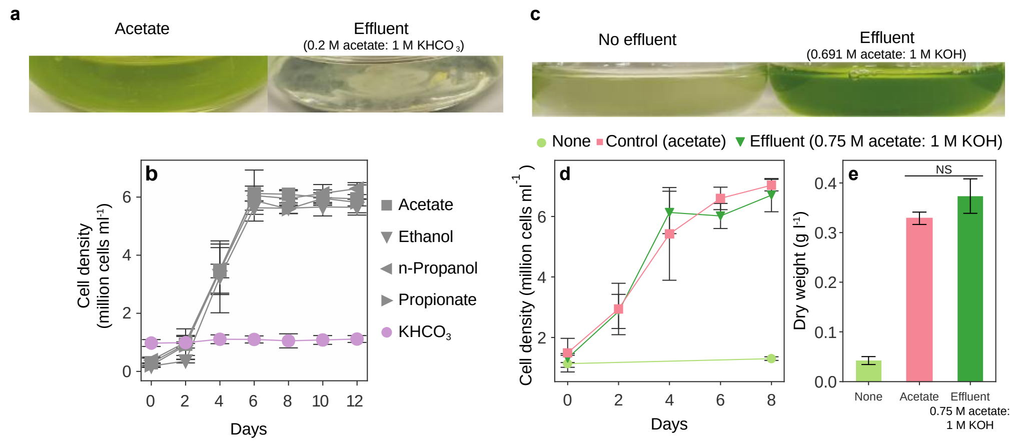

Figure 2. **a)** *The algae did not grow originally when electrolyzer-produced effluent was used as the sole carbon and energy source in heterotrophic growth medium*. **b)** *By growing algae in different media that each contained one component of the electrolyzer-produced effluent, the electrolyte salt ($KHCO_3$) was identified as growth prohibiting.* **c-e)** *Optimization of the tandem electrolysis system resulted in effluents with acetate-to-electrolyte-salt ratios higher than 0.4, which support heterotrophic growth of algae as the sole carbon and energy source.*

Significance and Impact

No products of photosynthesis (such as carbohydrates) or ancient photosynthesis (such as petroleum-derived carbon sources) were required for growth. This cultivation of a photosynthetic organism using carbon fixed through electrolysis is fully decoupled from biological photosynthesis. This process (photovoltaics to electrolysis to acetate to algae) is almost four-fold more solar-to-biomass energy-conversion efficient than biological photosynthesis (photosynthesis to algae) for algae production (Figure 3).

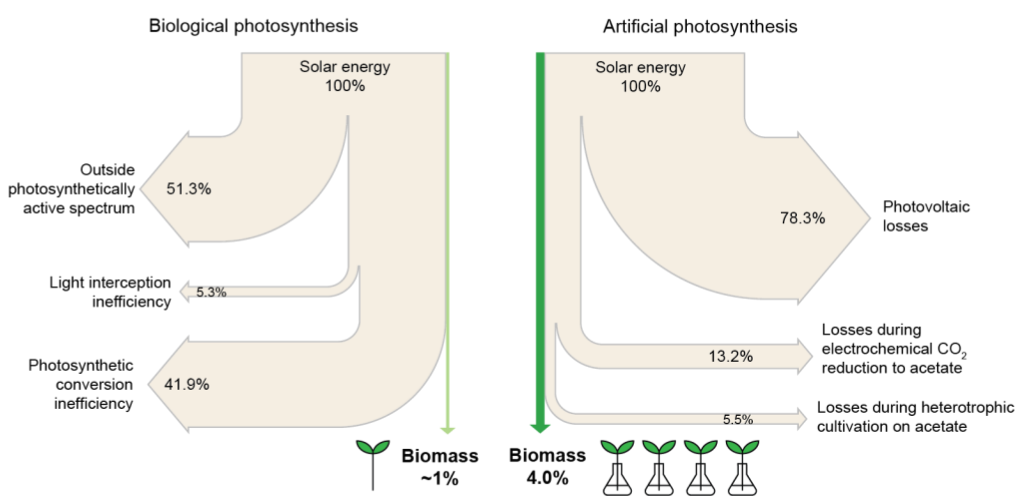

Figure 3. *Sankey diagrams of solar energy to plant and algae biomass compare the efficiencies of artificial and biological photosynthesis. Losses during energy conversion from sunlight (100% solar energy) to biomass are represented by arrows; the width of each arrow is proportional to the energy lost, and the percentage of the total energy lost at each step is indicated. The green arrows indicate the solar energy found in biomass; the width of each arrow is proportional to the energy, and the percentage of the total solar energy found in the biomass is indicated. The values for biological photosynthesis are from Zhu et al.*[6] *The value for photovoltaic losses is based on a commercially available solar cell*[7]*. The values for electrochemical CO_2 reduction to acetate and heterotrophic cultivation on acetate were determined in this work.*

Where will this lead?

We have developed an alternative system for the heterotrophic cultivation of organisms that does not rely on biological photosynthesis. There is potential for continued improvement to the system through advances in photovoltaics, electrolysis, and acetate utilization in biological organisms. In addition to growing *Chlamydomonas* in this system, we grew yeast and mushroom-producing fungus. We are working to engineer vascular plants to grow on acetate so that they can be integrated into this system as well. All these organisms can serve as food or as feedstocks for biofuels. Our approach to cultivation is ideally suited for applications where high energy efficiencies and low physical space usage are desired, such as on space flight missions or in controlled environments on Earth. Widespread adoption of this approach in conjunction with readily available solar energy could allow for more biomass to be produced in a given solar footprint, which will help to meet the rising demand for fuel without expansion of land needed to cultivate biomass.

References

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Link Foundation Energy Fellowship Outcome

The following have acknowledged the Link Foundation support:

Publications:

Hann, Elizabeth C.*, Sean Overa*, Marcus Harland-Dunaway*, Andrés F. Narvaez, Dang N. Le, Martha L. Orozco-Cárdenas, Feng Jiao, and Robert E. Jinkerson. "A hybrid inorganic–biological artificial photosynthesis system for energy-efficient food production." *Nature Food* 3, no. 6 (2022): 461-471. DOI: 10.1038/s43016-022-00530-x * indicates equal contribution

Hann, Elizabeth C., Marcus Harland-Dunaway, Jonathan E. Meuser, and Robert E. Jinkerson. "Alternative carbon sources for the production of plant cellular agriculture: a case study on acetate." In submission: *Frontiers in Plant Science Plant Biotechnology*.

Oral presentations:

"A hybrid inorganic-biological artificial photosynthesis system towards energy efficient food production"- Center for Industrial Biotechnology Group Meeting – University of California, Riverside (June 2, 2022)

"Artificial Photosynthesis for Food Production"- Lighting Talk- Celebrating Diversity in Botany Symposium- University of California, Riverside and Corteva (June 2, 2021)

Press highlights:

"Experiment in growing algae without sunlight- the future of biofuels in the dark"
https://news.ucr.edu/articles/2020/09/15/experiments-growing-algae-without-sunlight

"Researchers working to grow algae for biofuels in the dark using solar energy"
https://www.forbes.com/sites/jeffkart/2020/09/21/researchers-working-to-grow-algae-for-biofuels-in-the-dark-using-solar-energy/?sh=7797aada517d

"Artificial photosynthesis can produce food without sunshine"
https://news.ucr.edu/articles/2022/06/23/artificial-photosynthesis-can-produce-food-without-sunshine

"Can food crops grow in the dark? Scientists are working out how."
https://www.nationalgeographic.com/environment/article/can-food-crops-grow-in-the-dark-scientists-are-working-out-how

How did the Fellowship make a difference?

Having the support of the Link Energy Foundation during two years of my PhD study was monumental to my success. I received this funding at the beginning of my university's response to the COVID-19 pandemic. During a tumultuous time, the support of the foundation allowed me the security to pursue research that was truly fulfilling to me. I believe this fellowship will help me transition into the workforce after graduating with my PhD. I am honored to have been chosen for this fellowship among so many impressive early career scientists also interested in energy, but from a diversity of backgrounds and fields.