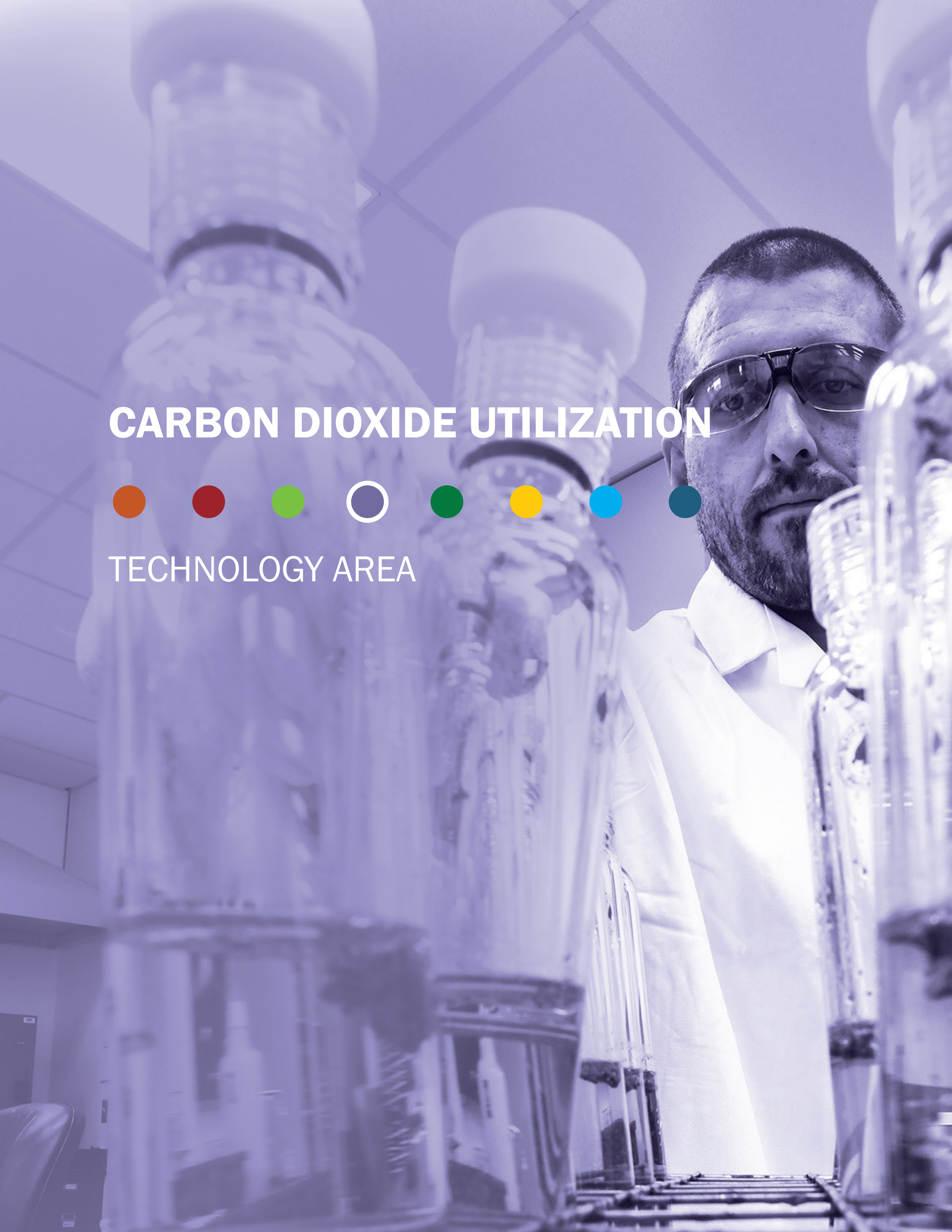


CARBON DIOXIDE UTILIZATION

TECHNOLOGY AREA

CONTENTS

INTRODUCTION

The Carbon Dioxide (CO_2) Utilization Technology Area is one of 14 related technology areas that were reviewed during the 2019 Bioenergy Technologies Office (BETO) Project Peer Review, which took place March 4–7, 2019, at the Hilton Denver City Center in Denver, Colorado. A total of 11 projects were reviewed in the CO_2 Utilization session by five external experts from industry, academia, and other government agencies.

This review addressed a total U.S. Department of Energy (DOE) investment value of approximately $6,590,000 (Fiscal Year [FY] 2016–2019 obligations), which represents approximately 0.8% of the BETO portfolio reviewed during the 2019 Peer Review. During the Project Peer Review meeting, the principal investigator (PI) for each project was given 20 to 30 minutes (depending primarily on the funding level) to deliver a presentation and respond to questions from the review panel.

Projects were evaluated and scored for their project approach, technical progress and accomplishments, relevance to BETO goals, and future plans. This section of the report contains the results of the Project Peer Review, including full scoring information for each project, summary comments from each reviewer, and any public response provided by the PI. Overview information on the CO_2 Utilization Area, full scoring results and analysis, the Review Panel Summary Report, and the Technology Area Programmatic Response are also included in this section.

BETO designated Dr. Ian Rowe as the CO_2 Utilization Technology Area Review Lead, with contractor support from Dr. Mark Philbrick (Allegheny Science & Technology). In this capacity, Dr. Rowe was responsible for all aspects of review planning and implementation.

CO_2 UTILIZATION OVERVIEW

The CO_2 Utilization Technology Area addresses research and development (R&D) barriers associated with the conversion of CO_2 to fuels and chemicals. To establish this recent addition to the Conversion R&D portfolio, BETO sought to learn from past and ongoing efforts in CO_2 utilization across DOE to determine the research area that best suits BETO capabilities. Notably, efforts exist within BETO's Advanced Algal Systems portfolio, the Office of Fossil Energy, and the Advanced Research Projects Agency–Energy (ARPA–E); BETO communicated closely with individuals in all of these programs when developing its CO_2 utilization strategy in an effort to avoid duplication and learn from previous results.

Traditionally, producing renewable fuels and products relies on biogenic carbon, and this renewable carbon feedstock has been largely limited to terrestrial plants or algal biomass and associated intermediates. In such strategies, plants use solar energy to chemically reduce CO_2 into biomass. This feedstock is then collected and deconstructed into simple intermediates (sugar, syngas, oil, etc.) before being upgraded to fuels and products. In contrast, the majority of this CO_2 Utilization R&D portfolio takes an alternative approach and specifically investigates technologies that perform CO_2 conversion through non-photosynthetic and abiotic means, substituting electricity for solar energy in powering CO_2 reduction. Such pathways generate one-carbon (C1) or two-carbon (C2) products or intermediates that can be further upgraded through biological or catalytic means that are quite similar to existing conversion efforts within the BETO portfolio.

This CO_2 Utilization Technology Area within BETO began in FY 2017; thus, many of the projects discussed below are new and focused on determining what the current state of technology is in the field. Projects generally fall within three categories: (1) non-photosynthetic or nonbiological CO_2 reduction for generating intermediates, (2) biological upgrading of CO_2-derived intermediates, and 3) enabling analyses to help inform R&D and the life cycle implications of products derived from CO_2. Given recent trends in renewable energy deployment and carbon capture, utilizing CO_2 as a feedstock is a field of research that is poised to grow, and BETO is well suited to investigate such technologies.

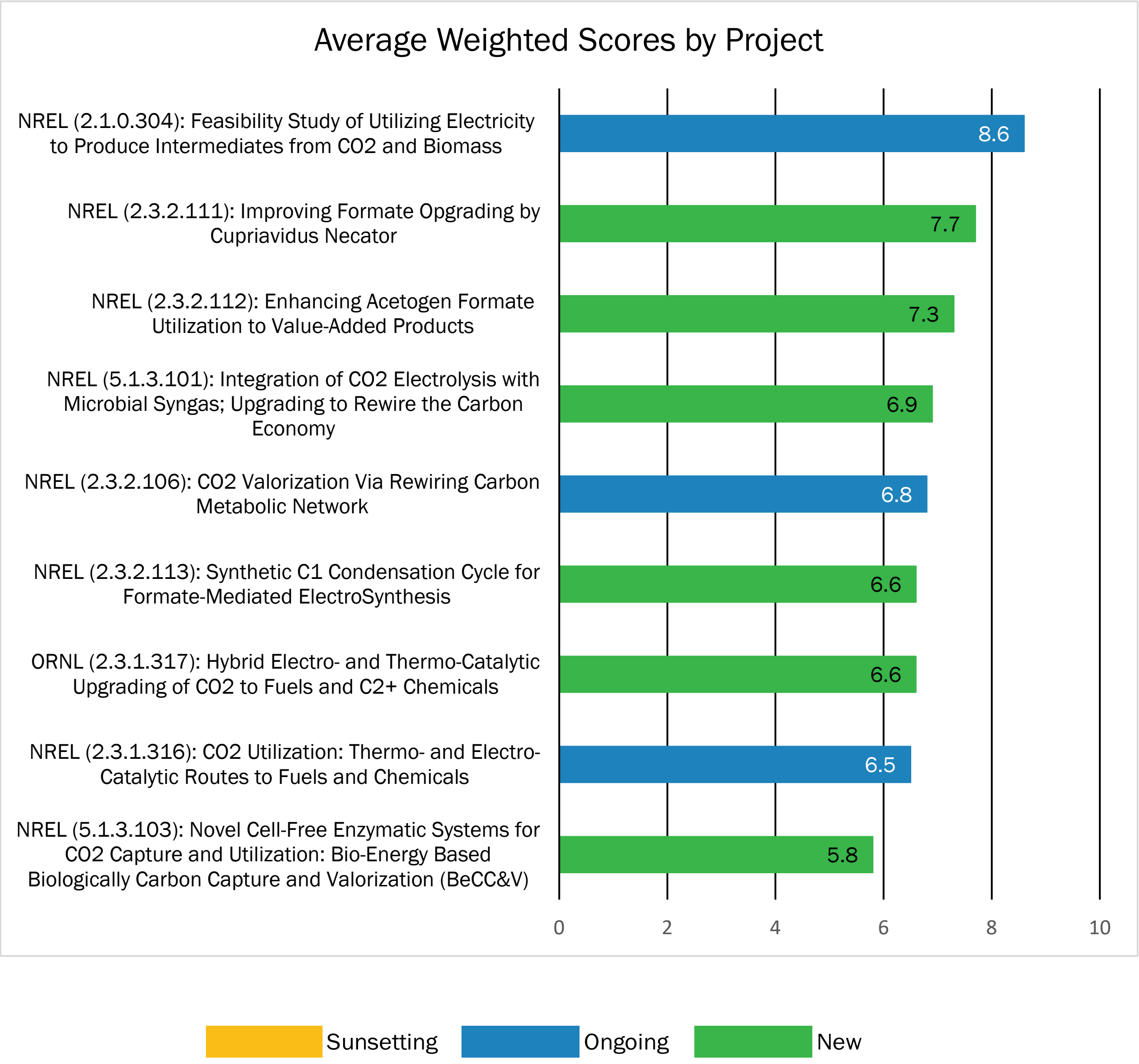
CO_2 UTILIZATION REVIEW PANEL

The following external experts served as reviewers for the CO_2 Utilization Technology Area during the 2019 Project Peer Review.

Name	Affiliation
Alissa Park [a]	Columbia University
Matt Lucas	Carbon180
Z. Jason Ren	Princeton University
Matthew Kanan	Stanford University
Igor Bogorad	Amyris

[a] Lead Reviewer

TECHNOLOGY AREA SCORE RESULTS



CO_2 UTILIZATION REVIEW PANEL SUMMARY REPORT

Prepared by the CO_2 Review Panel

The CO_2 Utilization program is a new endeavor by BETO to explore the opportunities and potential of converting carbon dioxide into biofuels, bioproducts, and biopower using non-photosynthetic pathways such as electrocatalytic, thermocatalytic, biocatalytic, and hybrid approaches. BETO's recent report, "Rewiring the Carbon Economy: Engineered Carbon Reduction Report," serves as the foundation and guideline of this program, and the panel agrees with the evaluation that "the CO_2 reduction and utilization technologies discussed have significant potential to impact carbon management and provide economic, environmental, and electric grid stability benefits."

The panel reviewed 9 slide decks and 11 presentations, and panelists conducted extensive Q&A and discussions with the PIs, BETO program managers, and other participants. Overall, the panelists were impressed by the organization of the program, the diversity of project topics, and some new findings presented by the groups. There are several areas that can be improved, such as finding synergies among different approaches and groups, collaborating with partners outside of national labs, and better utilizing techno-economic analysis (TEA) and other tools. The panel provides in this report summarized review comments and recommendations on program development.

IMPACT

Because this is a new topic that has an intrinsic nature of high risk, high reward, BETO funding is critical to advance the state of technology. Once technologies are advanced to higher technology readiness levels (TRLs) and risks are reduced, private sector investments will likely follow suit.

All projects are aligned with the BETO goals on carbon rewiring, and different pathways were well represented. All but one team presented in this program were from the National Renewable Energy Laboratory (NREL), which has been leading the efforts in helping BETO develop the carbon rewiring initiative. Many scientists and managers were involved in providing technical support, performing feasibility studies, and developing programs. The presentations were grouped in three main categories following a first presentation on TEAs. The three groups each focused on electrocatalytic and/or thermocatalytic pathways, biocatalytic pathways (focused on formate), and the BETO biopower annual operating plan (AOP) call, respectively.

The panel was impressed by the techno-economic analysis presented by NREL and thinks this project is strategically and technically important for carbon rewiring research and program development. The project "Feasibility Study of Utilizing Electricity to Produce Intermediates from CO_2 and Biomass" provided good analysis on state of the art of CO_2 valorization and identified challenges and opportunities to guide and support technology development. The panel suggests in the next period the team consider including more sensitivity analysis and, if possible, benchmarking evaluation metrics for different processes and technologies. However, the panel cautions that the findings should not be used to pick winners and losers. In addition to academic publications, it will be much more impactful for the tools and findings to be publicly available via a website or other platforms.

The projects on electrocatalytic and/or thermocatalytic CO_2 conversions were primarily focused on electrochemical catalysts development. Broadly speaking, the ability to access multi-carbon products through electrocatalytic or thermocatalytic CO_2 conversion is a key capability that must be advanced to make these processes viable. The focus on accessing multi-carbon targets is therefore relevant at a fundamental level to the BETO goals. The presentations reported on different types of catalyst development, but various challenges were reported. While C_{2+} products were targets, none of the catalysts have been able to demonstrate efficient conversion toward targeted products, and the conversion efficiency was low. It was not clear whether some of the catalysts such as bimetal cocatalysts would have a high impact on electrochemical CO_2 reduction. While some projects mentioned the plan of a CO_2 electrolyzer and other device development, little results were presented. The development of efficient reactor systems can be as critical as catalysts, and associated challenges including mass transfer and product separation need to be considered in future studies.

The projects on biocatalytic pathways include one project focused on developing the clustered, regularly interspaced short palindromic repeats-associated protein 9 (CRISPR-Cas9) tools for *Clostridium ljungdahlii* to directly convert CO_2/carbon monoxide (CO)/hydrogen (H_2) to 3-hydroxybutyrate (3HB). The CRISPR tool development can be very impactful, as such capacity is critical to enable targeted product generation from CO_2. Three other projects were funded via a formate AOP to convert a key CO_2 reduction intermediate formate to higher-carbon products. This includes using *Cupriavidus necator* to produce polymer precursor β-ketoadipate, using *Escherichia coli* to produce glycolate, and using *Clostridium ljungdahlii* to produce butanol. All these projects were just started with little data presentation. All the projects recognized the value of formate valorization using biological pathways because they can be complementary to the upstream electrochemical pathways, which can be highly efficient in converting CO_2 to formate. However, common areas that need improvement include better rationales and quantitative analyses why the proposed pathway makes sense in both technological and economic means. The project must also consider the potential markets and commercialization pathways for these chemicals.

The last group of projects were funded by the BETO biopower AOP, which focused on converting waste carbon into biopower. All projects were required to have industry partners, which the panel thinks is a very good approach. The projects spanned from CO_2 electrolysis with syngas fermentation to biogas upgrade, and to enzyme-accelerated solvents for waste gas scrubbing. While the panelists think that these projects may have potential in niche applications, a common concern is that the novelty of these projects is not clear. Much of the proposed work seems to have been carried out previously by industrial partners or other entities that the national lab team attempted to replicate to fit into the AOP scope. In addition, partially because of the early stage of these projects, it was difficult to evaluate the economic viability of these pathways. TEA and life cycle assessment (LCA) could be very beneficial.

INNOVATION

CO_2 utilization is a new program, and many of the funded projects were recently started without much data generated. However, the panel feels many projects presented innovative ideas and feasible research plans. The TEA project was ranked highly because it showed very interesting data and could provide critical insights in technology development, which may avoid unnecessary efforts and provide guidance on addressing critical barriers. The CRISPR-Cas9 tool development project also received positive feedback, as it can become a powerful in-house capacity to not only develop engineered *Clostridium ljungdahlii* strains but also other bacterial strains that are capable of producing targeted compounds that have never been accomplished before. The development of novel electrochemical catalysts with high conversion efficiency and selectivity can be a major milestone for CO_2 utilization, so even though the projects have not demonstrated success, further investigations will be critical.

SYNERGIES

So far, most projects have a focus on individual areas of CO_2 utilization such as catalyst development, strain development, and process engineering. However, there exist significant synergies among the groups with different expertise. The panel highly suggests BETO and researchers explore interdisciplinary collaborations. For example, chemists and material scientists could work together to develop more efficient catalysts for CO_2 reduction; microbiologists could collaborate with electrochemists to develop high-performing conversion systems; and scientists and engineers could work jointly to tackle major barriers such as mass transfer, system integration, and product separation.

Another synergy that should be explored is the collaboration between national lab scientists with university researchers and industry partners. Many university groups have been highly productive in CO_2 valorization R&D and increasing numbers of companies have demonstrated success in CO_2 utilization as well. Such collaboration will greatly accelerate the advancement of CO_2 research as well as facilitate the development and expansion of BETO’s carbon rewiring program.

FOCUS

Overall the CO_2 utilization program is well organized, and the portfolio contains diverse and complementary projects that covered most conversion pathways. The panel suggests BETO investigate several focus areas that have not been funded.

The program should consider funding projects that investigate hybrid CO_2 utilization approaches. As discussed in BETO’s report, a hybrid approach maybe the most efficient way to realize practical CO_2 utilization with renewable electrons, as it combines the efficient abiotic CO_2 reduction to intermediates (H_2, syngas, formate, methanol, etc.) followed by biological upgrade of the intermediates to high-value, long-chain products. Thermodynamically, the potential losses can be reduced by focusing on desired intermediate production in a CO_2 electrolyzer and overcoming surface area limitation in the bioreactor; kinetically, multiphase mass transfer can be increased by designing efficient gas production and delivery system in bioreactor; economically, high-purity and high-titer chemicals can be produced by taking advantage of the metabolic engineering tools; and engineeringly, scaleup systems can be relatively easily developed by modulating each unit and streamlining production.

The program could also consider funding projects that address gas solubility issues, mass transfer limitations, product separation, and issues in system development and integration. These are critical barriers in CO_2 utilization development, and the understanding and advancement of these topics will help steer the direction of fundamental science related to BETO goals, and they will help identify major technological and economic barriers that maybe overlooked by TEA.

The early TEA study presented a great opportunity to provide early intervention help for projects struggling with value proposition. Similar work can be supported for LCA as well, because some pathways seem to consume large amounts of energy, chemicals, materials, and water, and generate a significant amount of waste. The environmental benefits will be important to evaluate, considering these conversion processes are largely carbon neutral, yet the life cycle may pose negative environmental impacts.

TECHNOLOGY DEVELOPMENT PIPELINE

Given that the majority of the projects are still at low TRLs, it is reasonable for BETO to keep investing in different pathways until they become mature for early technology adoption by industry. The biopower AOP was a good approach that required collaboration between national labs and industry partners, but more guidance and clear expectations could be helpful to identify appropriate project objectives and deliverables. More applied projects on process and reactor development may be valuable to facilitate technology development.

RECOMMENDATIONS

Recommendation 1: The panel recommends that all projects conduct carbon and energy efficiency calculations as well as TEA, and, if possible, LCA. Such quantitative analysis should be done at the beginning, middle, and end of the project, because it can provide important insights in project development directions, identify critical barriers, and find new opportunities. The panel would recommend TEA-guided milestones and measurable deliverables for project management. The panel also cautions that sensitivity analysis should be included in TEAs, since most of the time assumptions were made to serve rather than check the project goals.

Recommendation 2: The panel supports establishing standardized matrices for project evaluation. Standard parameters may include carbon efficiency, energy efficiency, normalized cost, product titer, selectivity, scalability, etc. The calculation methods should be accessible to the public so the project results can be evaluated by using standardized methods. An open-source user interface and data platform will be helpful to achieve such a goal.

Recommendation 3: Interdisciplinary collaborations and applied research need to be encouraged and facilitated. Such partnerships will accelerate the translation of science understanding into technology and business development. Success measurements need to include both scientific publications and other accomplishments such as patent filings, technology licenses, and entrepreneurship.

CO_2 UTILIZATION PROGRAMMATIC RESPONSE

INTRODUCTION/OVERVIEW

The Conversion R&D program would like to thank the entire CO_2 Utilization Panel for their hard work and helpful discussion related to this emerging research area within BETO. As the above summary points out, the panel found the organization of this new program and the variety of projects within it to be commendable and aligned with BETO goals. The technology balance between biological and catalytic options was seen as well balanced. Specifically, the panel found the TEA associated with the "Feasibility Study" to be especially important for the strategic development of this program specifically as well as the broad field of CO_2 utilization.

The reviewers pointed out the synergistic opportunity for combining researchers that work on catalyst development with their counterparts that are engaged in process engineering and biological strain development. Such interdisciplinary collaboration was seen as key to developing robust conversion systems. Similarly, additional collaboration between those at the national labs and their university and industrial counterparts could be leveraged to overcome major barriers in CO_2 utilization.

The panel pointed toward opportunities in funding projects that integrate hybrid approaches to realize practical CO_2 conversion. This can allow catalysis researchers to specify their output stream for the proper engineering of the relevant bioreactors. Other opportunities in addressing mass transfer limitations, separations, and system integration were mentioned as items BETO should be considering.

The following section specifically addresses the three major recommendations from the review panel.

Recommendation 1: All projects are recommended to conduct carbon- and energy-efficiency calculations as well as TEA, and, if possible, LCA.

The program agrees with the importance of these assessments. The LCA of any product made from CO_2 is extremely important. We currently have an analysis project that broadly looks at the carbon footprint of various pathways related to CO_2 utilization. While we absolutely agree that initial LCAs should be considered when thinking about the portfolio, it is still quite early in the process for many of these technologies to dive very deeply into specific pathways; however, we are considering having projects explicitly point out what metrics would be needed to hit relevant TEA or LCA values.

Recommendation 2: The panel supports the establishment of standardized matrices for project evaluation.

The program wholeheartedly agrees with the importance of such assessments and metrics and this has been a point of regular discussion. The program is actively considering the specific metrics outlined by the panel as possible metrics for further work. One opportunity we are examining to get uniformity across the portfolio is to leverage the "Feasibility Study" as well as recent TEA/LCA guidelines from the National Energy Technology Library and The Global CO_2 Initiative.

Recommendation 3: Interdisciplinary collaborations and applied research need to be encouraged and facilitated.

BETO agrees with the importance of this integration. Of note is the FY 2018 BETO Funding Opportunity Announcement, which included a topic area titled “Rewiring Carbon Utilization” that specifically sought to connect catalytic experts and biologists to ensure that they are developing technologies that complement one another. This resulted in three awards that connected electrochemists and biologists. The projects did not begin in time to be presented to the review panel; however, they have since commenced. In general, this specific recommendation is well received and BETO considers the connection of interdisciplinary efforts to be essential to advancing CO_2 conversion technologies.

FEASIBILITY STUDY OF UTILIZING ELECTRICITY TO PRODUCE INTERMEDIATES FROM CO_2 AND BIOMASS

National Renewable Energy Laboratory

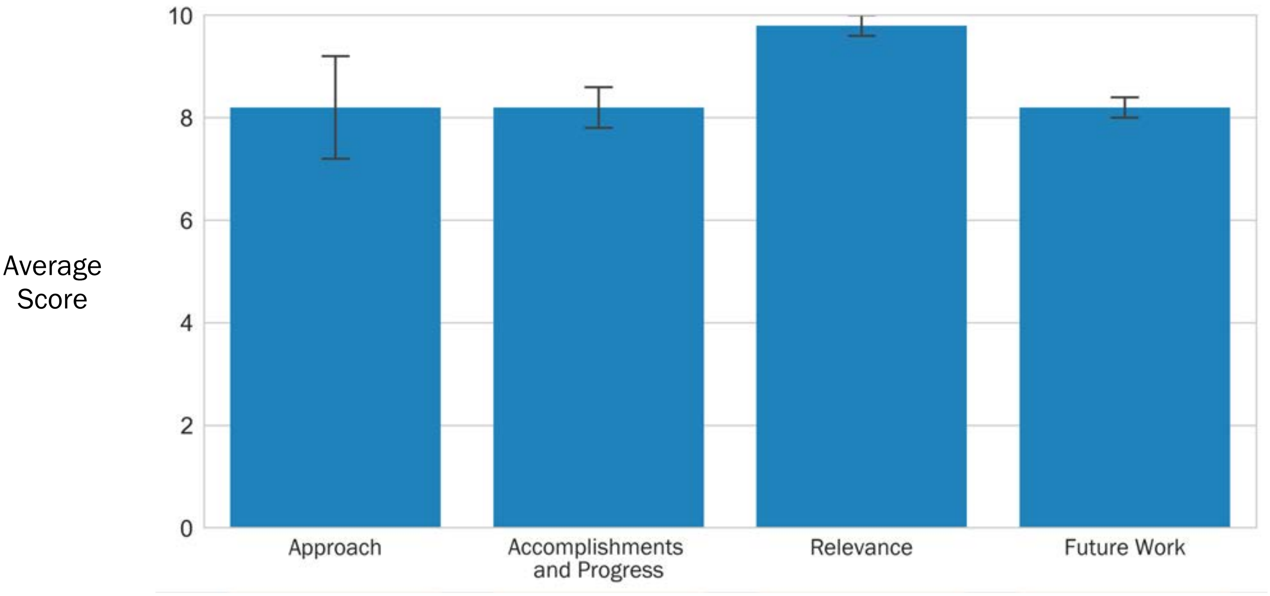
PROJECT DESCRIPTION

The primary objective of this project is to assess the technical and economic feasibility of utilizing electricity for (1) the reduction of CO_2 to C1–C3 intermediates and (2) the generation and upgrading of biomass-derived intermediates. Through critical literature review, subject matter expert interviews, collaboration with experimental projects, and both high-level comparative and detailed TEA coupled with biorefinery integration, this project will develop a roadmap for the effective utilization of electricity within existing and emerging biorefinery designs that can guide ongoing R&D activities towards cost reductions and carbon energy efficiency improvements.

WBS:	2.1.0.304
CID:	NL0033391
Principal Investigator:	Dr. Josh Schaidle
Period of Performance:	10/1/2017–9/30/2020
Total DOE Funding:	$800,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$400,000
DOE Funding FY19:	$400,000
Project Status:	Ongoing

Weighted Project Score: 8.6

Weighting for Ongoing Projects: Approach - 25%; Accomplishments and Progress - 25%; Relevance - 25%; Future Work - 25%



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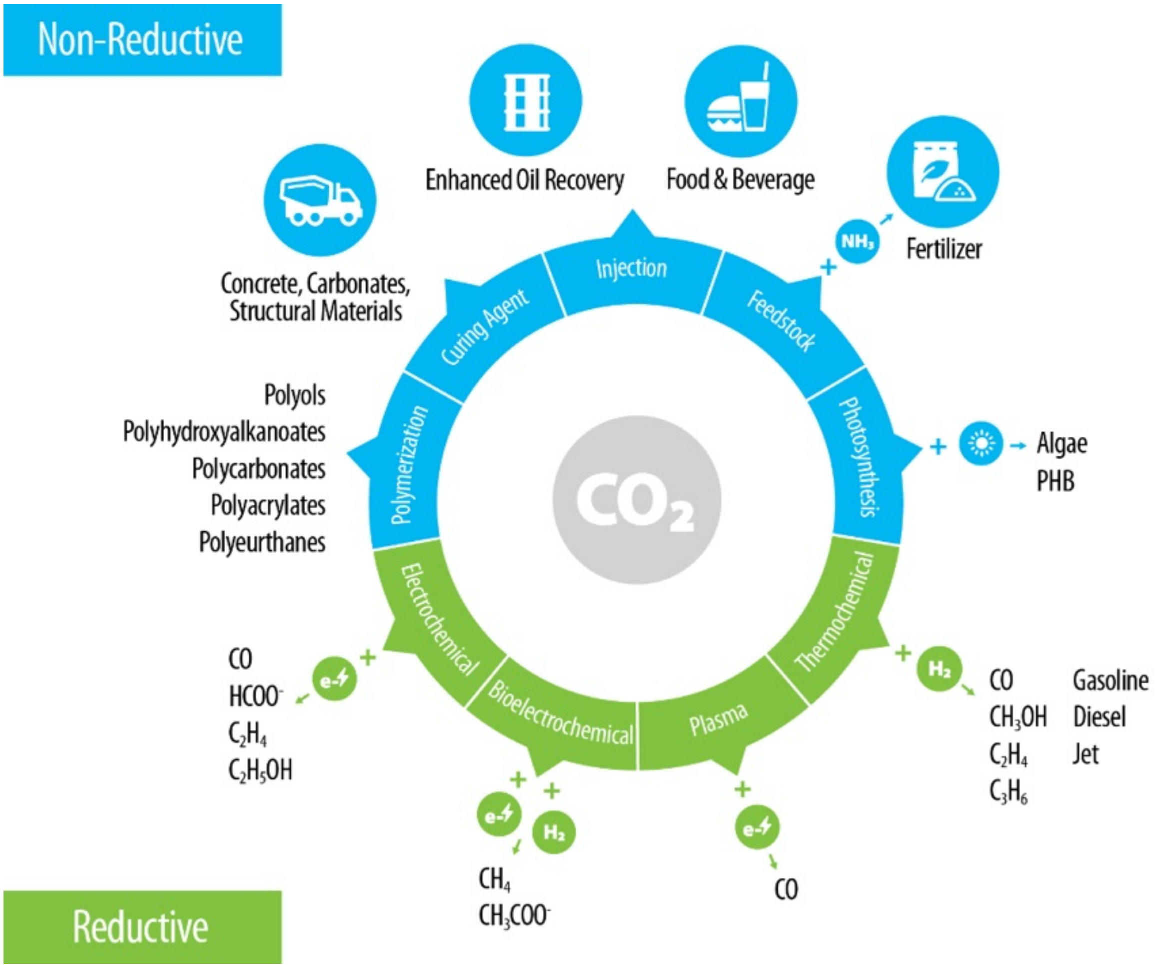


Photo courtesy of National Renewable Energy Laboratory

OVERALL IMPRESSIONS

- This is an important study that can set the important logical pathway toward the future technological development for CO_2 utilization. The team has developed a good platform to analyze different pathways to identify their challenges and opportunities. This project can be expanded to provide a better assessment platform for a broader user group.

- This project is timely and strategically important. The performers did a very good job organizing the project and delivering critical findings. The findings will be very valuable in understanding the challenges and opportunities in carbon rewiring R&D. Quantitative metrics will be desired for standardized evaluation. Uncertainty analysis and mitigation strategies will be helpful when making assumptions.

- This project evaluates the technical and economic feasibility of using CO_2 or biomass feedstocks and creating C1–C3 chemicals from them. This work could help identify targets for R&D.

- The project provides essential analysis to underpin BETO's goal of employing CO_2 utilization to improve the economic competitiveness of biofuels. The team has identified the critical success factors. Further depth on some of the technical issues will be necessary to clarify the research challenges.

- The performers have proposed to do an in-depth analysis of various technologies to upgrade CO_2, including electrochemical, thermochemical, and biological. The performers are covering a very wide space with many built-in assumptions to what the current state of technology is and potential for future improvements. During the presentation, the performers focused on electrochemical, which appears to be most in line with their expertise. The performers are encouraged to narrow the scope of their study to just electrochemical upgrading, which is already a challenging endeavor. Extending the analysis to biological upgrading may lose focus for the study and would be extremely challenging. For example, many potential bioproducts could be made such as *n*-butanol, fatty acids, ketoadipate, polyhydroxybutyrate, etc. Publishing their results early on would be very helpful for the other BETO teams, who also will be performing their own TEA on each project.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- We greatly appreciate the thoughtful analysis and constructive feedback provided by the reviewers. We have sought to assess the technical and economic feasibility of utilizing electricity to reduce CO_2 into C1–C3 intermediates, with the end goal of providing guidance to the R&D community. To that end, we agree with the reviewers that further depth is needed in specific technical areas and that the results need to be broadly disseminated through peer-reviewed publications; we are working diligently to address these comments. While we acknowledge that the scope of the study is fairly broad (spanning across five different direct and indirect CO_2 reduction technologies), we believe that the cross-cutting nature of this analysis is critical to its value creation for the research community. Due to the time allocated to the peer-review presentation, we decided to use electrochemical conversion as an example case; we have similar detailed studies and cost analyses for all five reduction technologies. Since the start of this project, we have engaged with subject matter experts across these included technologies, and our project team members have diverse technical backgrounds. In out-years, we plan to dive deeper into specific technologies, especially in regard to integration of these technologies with existing biorefinery designs.

CO_2 UTILIZATION: THERMOCATALYTIC AND ELECTROCATALYTIC ROUTES TO FUELS AND CHEMICALS

National Renewable Energy Laboratory

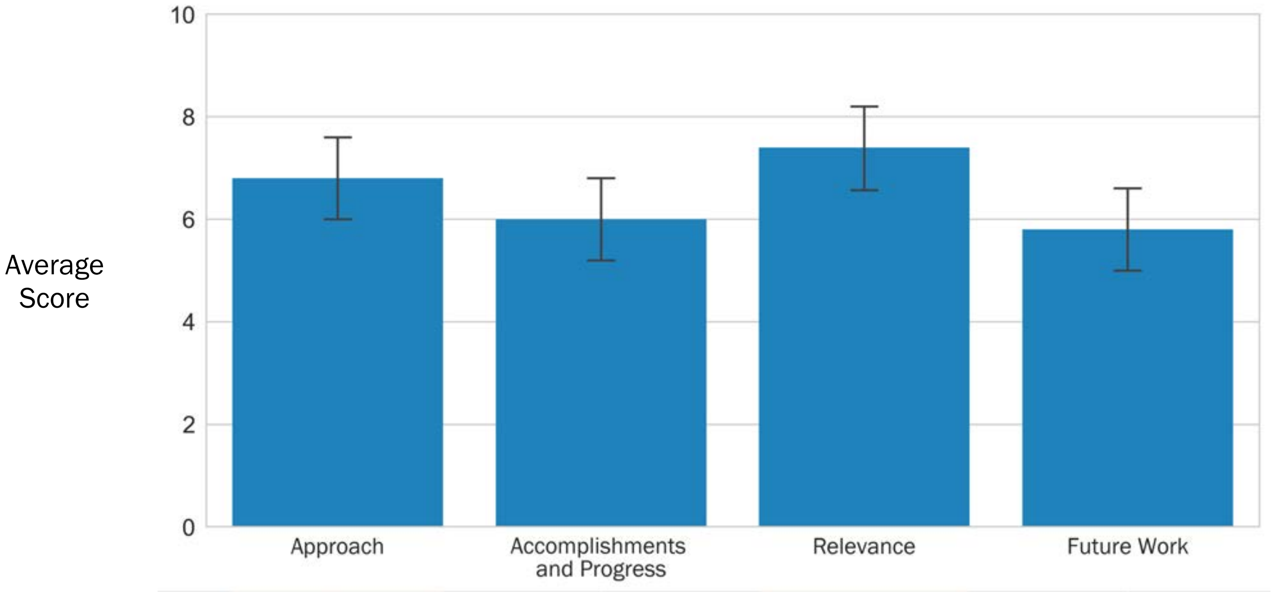
PROJECT DESCRIPTION

WBS:	2.3.1.316
CID:	NL0033403
Principal Investigator:	Dr. Jack Ferrell
Period of Performance:	11/1/2017–9/30/2020
Total DOE Funding:	$1,000,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$500,000
DOE Funding FY19:	$500,000
Project Status:	Ongoing

Over the past several years, it has become clear that the emergence of inexpensive and intermittent electricity provides an opportunity for electron-enabled conversions of CO_2. In this project, both direct electrochemical and thermochemical conversions of CO_2 are being investigated. Electricity provides the driving force for chemical reaction in the electrochemical pathway, while CO_2 is reacted with hydrogen (which can be produced from the electrolysis of water) in the thermochemical pathway. While the thermochemical pathway is the most developed for conversion of CO_2 (e.g., the production and utilization of syngas), these existing processes operate at a scale that is too large to match distributed CO_2 sources. Consequently, process intensification and scale-down is needed to enable distributed thermochemical CO_2 utilization. Development is needed to produce catalysts combining reverse water gas shift (RWGS) and C-C coupling functionalities. Over the past year, we have shown that bulk molybdenum carbide is a promising candidate to enable direct formation of C2+ products from CO_2. Subsequently, we have experimentally baselined existing molybdenum carbide catalysts, and synthesized and tested nanoscale molybdenum carbide catalysts that have achieved increased performance, including increased selectivity to desired C2+ products.

Weighted Project Score: 6.5

Weighting for Ongoing Projects: Approach - 25%; Accomplishments and Progress - 25%; Relevance - 25%; Future Work - 25%



Ι One standard deviation of reviewers' scores

For the electrochemical conversion pathway, we are focused on low-temperature (generally less than 100°C) electrochemical technologies. Copper remains the state-of-the-art catalyst and is the only catalyst that can produce C2+ products. However, catalyst development is needed to reduce overpotential and increase selectivity to individual C2+ products. We have begun the investigation of metal phosphide catalysts for electrochemical CO_2 conversion. These are tunable materials that have recently shown promise for CO_2 conversion and have produced novel C3 and C4 products. Beyond electrocatalyst development, we are investigating different scalable electrolyzer architectures. While electrochemical CO_2 conversion has been heavily studied, most of the work has been performed in aqueous solutions, where the low solubility of CO_2 prevents high-enough currents for scale-up. Therefore, it is widely held that electrolyzer configurations are needed where gas-phase CO_2 is used. While several different membrane-electrode assemblies have been tested, there remains no consensus on the best electrolyzer configuration. Furthermore, relevant electrolyzer setups are needed for catalyst evaluation in a relevant environment, as results obtained in aqueous solutions may not clearly translate to the electrolyzer environment. Overall, we aim to advance the state of the art for both electrochemical and thermochemical CO_2 conversion and help to enable the effective processing of this large biorefinery waste stream.

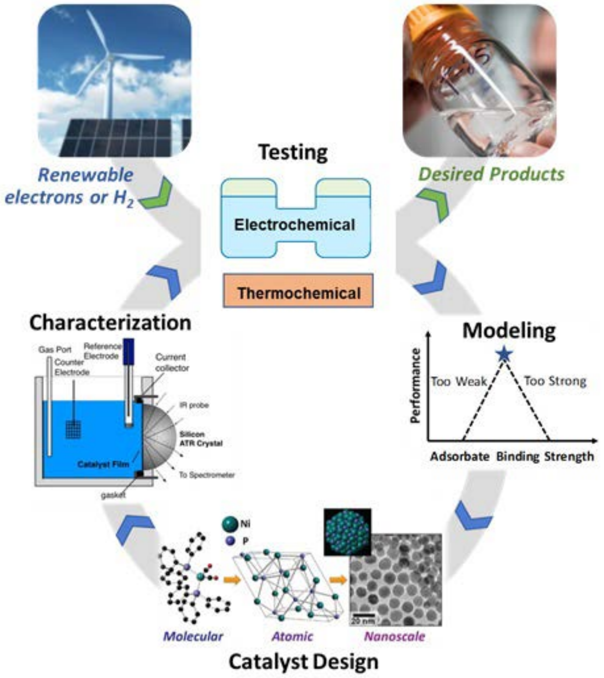


Photo courtesy of National Renewable Energy Laboratory

OVERALL IMPRESSIONS

- This project aims to benchmark and then further develop both electrochemical and thermochemical catalysts for the conversion of CO_2.
- This is a comprehensive project, and advancements were made in catalyst development. System design results can help demonstrate the variability of the approach. The connections between electrochemical and thermochemical pathways can be articulated to identify the synergies, and the linkage between the identified BETO barriers and deliverables can help shape future priorities.
- This is a great team leveraging the Chemical Catalysis for Bioenergy Consortium efforts and has active collaborations with other expert groups. Thus, the team has a great potential to significantly advance the

thermochemical and electrochemical catalysts for CO_2 conversion to C2+. The consideration of using a wide range of CO_2 sources (e.g., ambient to industrial sources beyond ethanol plants) and the investigation of challenges associated with different CO_2 waste streams would further improve the potential impact of this study.

- While the thematic goals are highly relevant to the BETO mission, the project has presented insufficient evidence to show that specific efforts in this project have a good chance of advancing the state of the art.
- The performers have proposed to improve both electrochemical and thermochemical conversion of CO_2 to C2+ products. The performers will be collaborating with the Feasibility Study from NREL. We suggest the performers focus on one of the two approaches (likely electrochemical) to maximize chance of success. The performers should also more clearly list out the metrics of success and the rationale for choosing those targets.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- We thank the reviewer for the feedback and agree that there are clear synergies between the CO_2 conversion routes such as the synthesis of catalyst materials that are being leveraged across both pathways and characterization efforts that focus on key intermediates that are similar in both cases. Future deliverables will have metrics that directly address BETO Multi-Year Plan barriers through the incorporation of TEA in upcoming years.
- We thank the reviewer for their positive comments and agree that the investigation of realistic CO_2 sources will bring additional value to the project. In the initial two years of the project we focused on developing a synthetic platform of catalyst materials and an understanding of the corresponding reactivity. Additionally, we have developed capabilities for the testing of different membrane-electrode assemblies that are required for performing relevant research (including the screening of different CO_2 sources).
- On the thermochemical side, we sought to develop a synthetic strategy for a tunable catalyst system to develop a fundamental understanding of the impact of catalyst features on the resulting product slate. We acknowledge that the metal carbide system is only one type of catalyst system used for CO_2 reduction, but we believe that it affords the ability to rationally tune the catalyst structure and advance the state of the art over industrial materials. On the electrochemical side, our catalyst development efforts have yet to find a material that can outperform the state-of-the-art copper catalyst. However, electrocatalyst development with a tunable materials platform (transition metal phosphides) have been useful for studying electrochemical CO_2 reduction, and we are actively exploring new materials systems. Additionally, much work has been spent developing capabilities for catalyst testing in the relevant environment (in a membrane-electrode assembly), and these capabilities are required to advance the current state of the art.
- In the future, we will more closely align metrics of success for the project with BETO Multi-Year Plan barriers, which will be facilitated with ongoing TEA efforts to compare electrochemical and thermochemical approaches.

HYBRID ELECTROCATALYTIC AND THERMOCATALYTIC UPGRADING OF CO_2 TO FUELS AND C2+ CHEMICALS

Oak Ridge National Laboratory

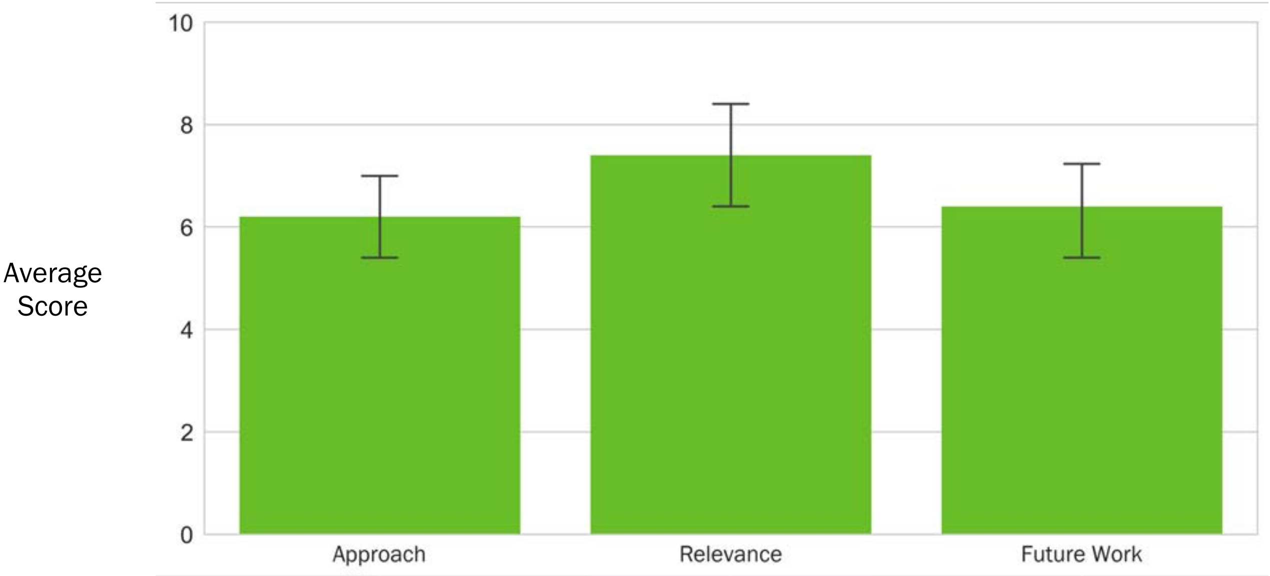
PROJECT DESCRIPTION

WBS:	2.3.1.317
CID:	NL0034400
Principal Investigator:	Dr. Adam Rondinone
Period of Performance:	10/1/2018–10/1/2020
Total DOE Funding:	$250,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$0
DOE Funding FY19:	$250,000
Project Status:	New

Electrocatalytic reduction of CO_2 to useful products is a possible pathway towards higher rates of CO_2 recycling and lower rates of fossil carbon utilization. It is also a means of using electrical energy to convert or reduce (in the chemical sense) CO_2 to useful products. In this approach, an electrochemical catalyst acts as a cathode in an electrochemical cell. Energy in the form of electricity removes oxygen from the carbon and replaces it with hydrogen or other elements, moving the carbon from a low energy state (CO_2) to a higher energy state (alkane, oxygenates). This strategy will become critically important in the future as an alternative to fossil carbon sources and as renewable electricity becomes more available. To fully utilize renewable electricity, we will need to develop appropriate catalysts and processes for the conversion of CO_2 to a variety of important industrial chemicals and fuels. Previous major R&D efforts in CO_2 electrocatalytic reduction have been targeting C1 products, such as CO, methane, and formate. There are strong interests and motivations to convert CO_2 to heavier (C2+) alcohols (e.g., ethanol and 1-propanol) and hydrocarbons (e.g., olefins) as a critical approach to directly produce liquid fuels.

Weighted Project Score: 6.6

Weighting for New Projects: Approach - 25%; Relevance - 25%; Future Work - 50%



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Recently, the Oak Ridge National Laboratory has developed a novel and efficient copper nanoparticle carbon nanospike (CNS) electrocatalyst to convert CO_2 to ethanol with high selectivity of 84% and high Faradaic efficiency (63% at −1.2 V versus reversible hydrogen electrode) that operates in water and at ambient temperature and pressure. Based on this groundbreaking technology, we propose to develop new bimetallic electrocatalysts supported on the carbon nanospike to further reduce the overpotentials and improve Faradaic efficiency and C2+ product selectivity. While there are only limited works on bimetallic approach for CO_2 conversion to C2+ products, a bimetallic catalyst has been computationally shown to break the linear relationship between the binding energies of CO and carboxyl groups (COOH) on the electrode surface. The addition of the second metal could modify both the electronic property and the geometry of the Cu metallic nanoparticle, which will impact the adsorption of reaction intermediates and potentially improve the Faradaic efficiency of C2+ products. In addition to the promise of a bimetallic cocatalyst for promoting C2+ products formation, we also expect a synergistic effect between the high localized electric fields of the carbon nanospikes and the bimetallic nanoparticle cocatalysts. The carbon nanospikes generate high localized electric fields that effectively convert CO_2 to CO, providing abundant CO for further oligomerization on the bimetallic cocatalyst. All of these suggest bimetallic nanoparticles coupled with CNS could offer a great solution to advance the current state of technology on CO_2 conversion.

In this proposed work, we aim at improving the selectivity of C2+ products at lower overpotential, especially alcohols and olefins, which can be either used as fuels or be converted to fuels and value-added products. Ethanol and 1-propanol, for example, can be used as fuels or fuel additives, or converted to produce other hydrocarbon fuels and important precursors for carbon fiber or polymers. Other products (ethylene, acetaldehyde, acetone, hydrogen, etc.) from the proposed electrocatalytic process can be further thermocatalytically upgraded to produce high-quality gasoline, jet diesel, or precursors for polymers, rubbers, detergents, plasticizers, or lubricants. If successful, this hybrid integrated pathway provides significant advantages compared with the current state of technology on CO_2 conversion.

OVERALL IMPRESSIONS

- The performers have proposed to electrochemically reduce CO_2 to C2+ products. The performers have developed new copper "nanospikes" that convert CO_2 to ethanol in favorable conditions. The performers aim to test other catalysts to reduce overpotential and produce molecules larger than ethanol. TEA will be extremely important for this work and the performers should determine ease of scalability of their new nanoparticle catalysts. Overall, the project is very promising and aligned with BETO's goals.

- Electrochemical conversion of CO_2 to C2+ chemicals is an important technical goal for making CO_2 utilization viable. The justification for the specific approach in this project is a speculative mechanistic hypothesis. Data at high current density is needed to properly assess the promise of the core technology.

- This project will use a carbon nanospike platform that previously showed interesting activity for CO_2-to-ethanol conversion to investigate electrochemical synthesis of new C2+ products.

- This is an interesting project combining carbon nanospikes with bimetal cocatalysts to produce C2+ products from CO_2. The catalyst development for the electrochemical conversion of CO_2 is a very important research field.

- The performers developed the unique structure of catalysts with nanospikes to convert CO_2 into alcohol. The science is interesting and technical approach is sound. Clear strategies on how cocatalysts will be synthesized can help guide future development. Identifying meaningful products and understanding the economic viability of the potential products will be helpful too.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- The recipients choose not to respond to the reviewers' overall impressions of their project.

CO_2 VALORIZATION VIA REWIRING CARBON METABOLIC NETWORK

National Renewable Energy Laboratory

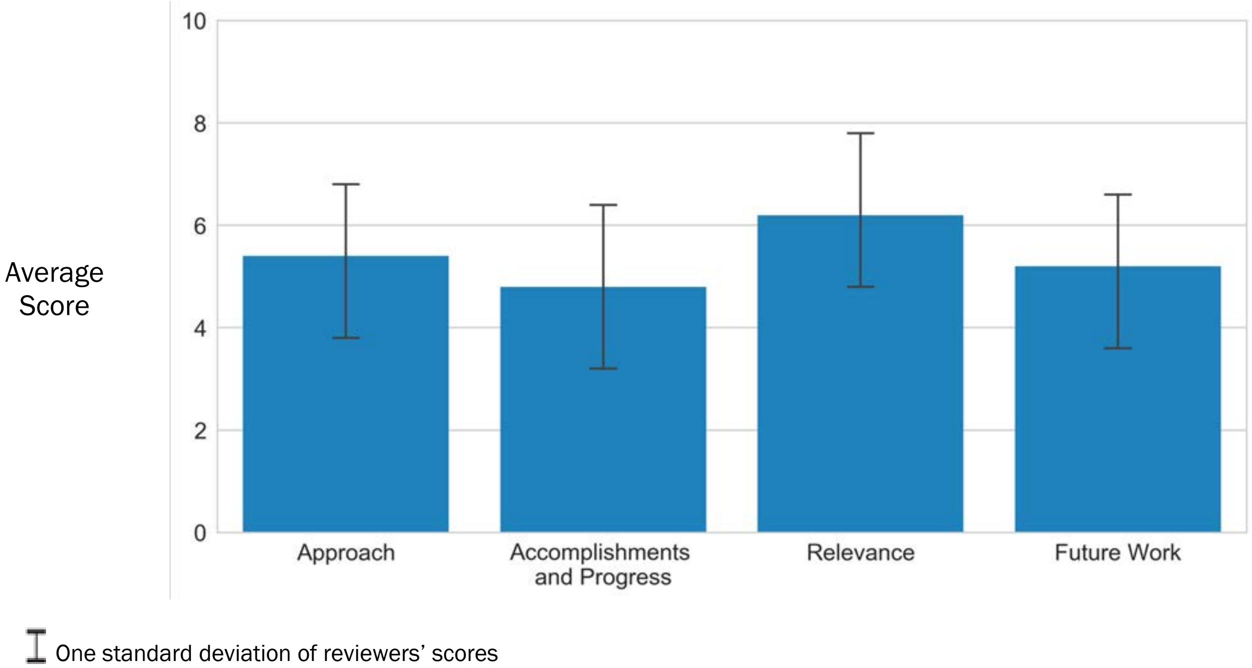
PROJECT DESCRIPTION

WBS:	2.3.2.106
CID:	NL0033406
Principal Investigator:	Ms. Pin-Ching Maness
Period of Performance:	10/1/2017–9/30/2020
Total DOE Funding:	$650,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$325,000
DOE Funding FY19:	$325,000
Project Status:	Ongoing

The overarching goal of this project is to perform strain development and preliminary TEA on a process valorizing CO_2 to high-value hydrocarbon products, including 3HB, using the renewable electrons from H_2. *Clostridium ljungdahlii* is the model CO_2-fixing autotrophic microbe to realize this goal. A BETO assessment report has concluded that gaseous waste streams represent a significant and underutilized set of carbon-based feedstocks for biofuels and bioproducts. We aim to develop a microbial-based strategy to upgrade CO_2 gaseous waste streams with its successful outcome, paving the way to a new waste-based bioeconomy. With the foreseeable abundance of renewable electrons in the form of H_2 generated from electrolysis, progress of this project aligns well with DOE BETO programmatic goals. Choosing the H_2-supported CO_2-fixing *C. ljungdahlii* microbe is another merit because it is genetically tractable with the highest rates of growth in syngas (H_2 CO) reported in the literature. NREL already has the genetic toolbox and further improvement is an ongoing research plan. A detailed 13C-metabolic flux analysis including under the autotrophic growth mode has not been conducted. This NREL project will provide more detailed insights to guide genetic engineering efforts and probe the strategies cells employed to manage its carbon and energy flow under autotrophic conditions, leading to high titer and yield of the targeted products in a more robust microbe.

Weighted Project Score: 6.8

Weighting for Ongoing Projects: Approach - 25%; Accomplishments and Progress - 25%; Relevance - 25%; Future Work - 25%



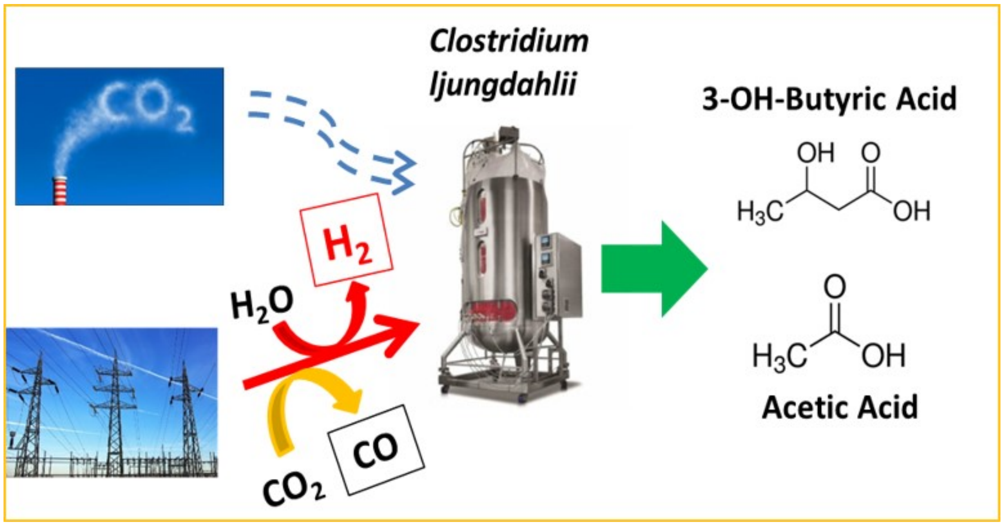


Photo courtesy of National Renewable Energy Laboratory

OVERALL IMPRESSIONS

- This project aims to produce 3HB, a platform chemical, using CO_2/CO and hydrogen. Initial data were taken under growth with sugar and have demonstrated small but increasing titers of the desired product.

- The concept is interesting, and the team has the appropriate expertise. The results with C1 co-fed with sugar are promising, but the performance with C1 only is critical moving forward.

- This study focuses on engineering *Clostridia ljungdahlii* to convert a CO_2 and H_2 to 3HB. The project is well aligned with the BETO goals and has a great potential to be high impact, although the overall economics of this process are not clear.

- The performers have proposed to engineer *Clostridia ljungdahlii* to convert a CO_2 and H_2 to 3HB. The performers have developed the CRISPR-Cas9 system and demonstrated a phosphate acetyltransferase knockout can increase titers. The performers are encouraged to carefully do all titer benchmarking in autotrophic conditions, not mixotrophic conditions. Also, it is unclear what the value is of performing 13C fluxomics work in mixotrophic conditions. The performers are encouraged to explore multiplexing with Cas9 to enable faster engineering and to maintain genome-integrated copies of all overexpressions. TEA should be very valuable to direct the performers to the market size of 3HB, and what the necessary titer/productivities should be in order to commercialize. The project has great potential, aligned with BETO's mission, and has a high chance of success to reach the goal of 2 g/L 3HB titers.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- We agree with the reviewers that performance with a C1-only substrate is critical moving forward.

- The project is well integrated with a TEA to evaluate the overall economics, which sets research targets and guides future research directions.

- We thank the reviewers for recognizing the great potential of this project, its alignment with BETO's mission, and the high chance of success to reach the goal of 2 g/L 3HB titers. Developing the CRISPR-Cas9 tool is the critical first step toward its multiplexing, aimed to modify microbial genome with higher throughput and efficiency, for which we are in full agreement with the reviewers. Thus far, genome integration has not been reported in this microbe and is a research goal of the project team. We also agree that the goal is to obtain final 3HB titers under autotrophic conditions. Current work conducted under mixotrophic conditions including the initial 13C-fluxomics work is solely to obtain baseline information. We plan to systematically probe and gain insights as to how this microbe manages carbon, energy, and electron flux under varying growth conditions. The outcomes will help guide the design of microbial pathways to maximize growth and product titers under autotrophic conditions. TEA is already an integral component of the research to determine market size, the needed titers/productivity, and coproducts to attain techno-economic feasibility. Indeed, the preliminary TEA has revealed a 3HB minimum selling price of $1.90/kg, provided a titer of 10 g/L and a productivity of 0.2 g/L/h can be achieved. This can set research targets. A minimum selling price for coproducts like acetate and 2,3-butanediol are $1.80 and $2.20/kg, respectively. The major cost drivers are H_2 and CO_2 feedstock cost and capital expenditure of biological conversion. The former can be addressed through improving the production yield to near theoretical maximums and the latter through increasing productivity and product titers. These findings guide R&D efforts carried out by the project team.

IMPROVING FORMATE UPGRADING BY *CUPRIAVIDUS NECATOR*

National Renewable Energy Laboratory

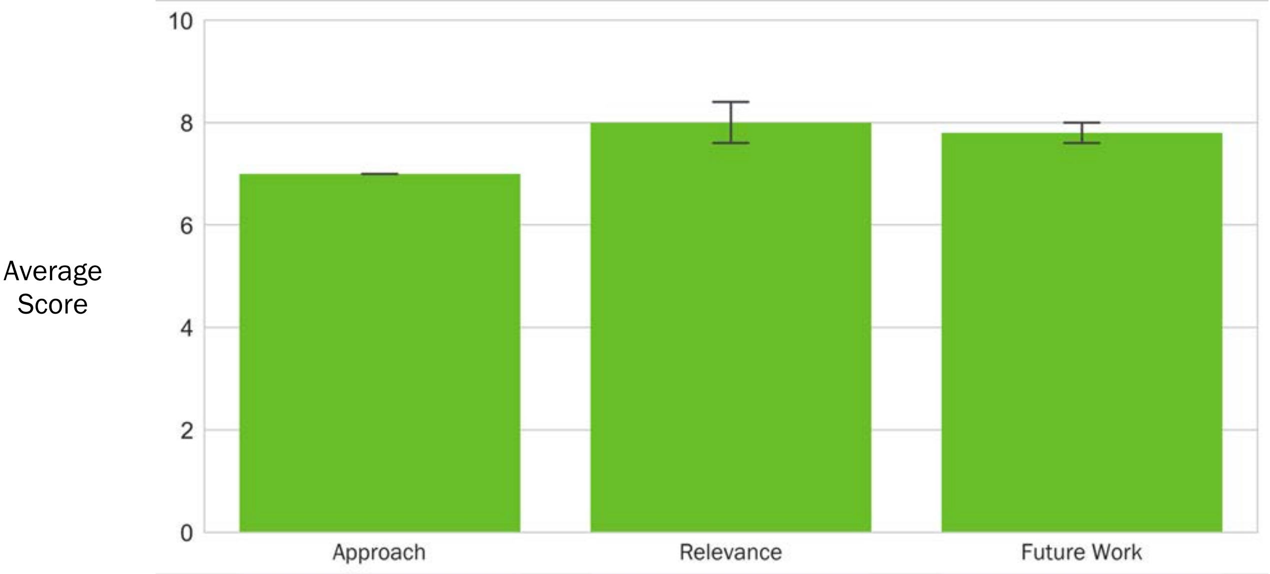
PROJECT DESCRIPTION

WBS:	2.3.2.111
CID:	NL0034713
Principal Investigator:	Dr. Christopher Johnson
Period of Performance:	10/1/2018–9/30/2021
Total DOE Funding:	$310,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$0
DOE Funding FY19:	$310,000
Project Status:	New

In support of BETO's interest in capturing and converting CO_2 into value-added products using low-cost electricity, this project aims to develop the natural formatotroph, *Cupriavidus necator*, as a robust microbial chassis for efficient production of value-added products from formate, which can be produced by electrocatalytic reduction of CO_2. To date, we have demonstrated and baselined growth of *C. necator* on formate as its sole source of carbon and energy in a format consistent with high-throughput evaluation. In future work, a combination of rational metabolic engineering and evolutionary approaches will be employed to improve *C. necator*'s ability to assimilate formate. Improved strains will be further engineered to convert formate to the polymer precursor β-ketoadipate as an exemplary product. Data from this project will be used to generate TEA and LCA that can inform the foci and direction of this and related technologies for biological formate conversion.

Weighted Project Score: 7.7

Weighting for New Projects: Approach - 25%; Relevance - 25%; Future Work - 50%



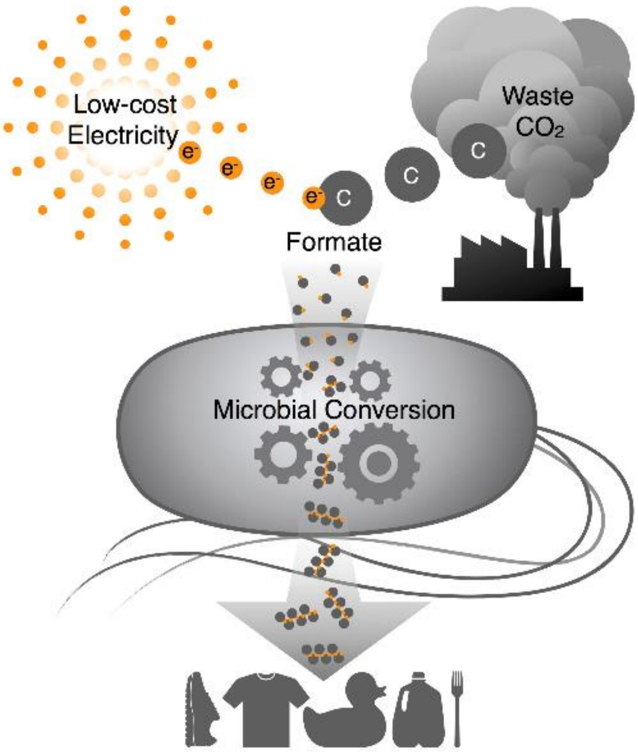


Photo courtesy of National Renewable Energy Laboratory

OVERALL IMPRESSIONS

- The performers have proposed to convert formate to beta-ketoadipate using engineered *Cupriavidus necator*. Though engineering the beta-ketoadipate pathway is promising, the performers seem too optimistic to improve the host's Calvin-Benson-Bassham (CBB) cycle, given this has been attempted for decades with little success. Additionally, the formolase will likely carry very little metabolic flux due to its extremely slow kinetics and should be reconsidered. The performers should consider setting higher milestone titers than 2 g/L of beta-ketoadipate given previous work showing 1.5 g/L of a branched alcohol. TEA will also be extremely important to validate the market size of beta-ketoadipate and what the titer/productivity levels should be for scale-up. Industrial fermentations typically have titers >50 g/L with productivities about 1 g/L/hr.

- The project is well designed and will generate useful baseline data to evaluate the feasibility of using *C. necator* for formate upgrading. More attention to the feasibility of operating at high formate utilization is needed to determine whether the overall approach is viable.

- This project aims to use a genetically engineered microbe to convert formate into beta-ketoadipic acid, a potentially performance-advantaged monomer for the production of nylons.

- This project is designed to convert formate to beta-ketoadipate using *Cupriavidus necator*. Formate is one of the target intermediates that can be produced through chemical synthesis, and beta-ketoadipate seems to be higher in value compared to other target products being considered. Thus, there seems to be a high potential for this project in terms of CO_2 to value-added products.

- This is a well-organized project. The performers clearly identified the project goals and approaches, as well as their relevance to BETO interests. The tasks are well defined, and the milestones are quantitative and clear. More considerations can be given on understanding and improving formate tolerance and improving carbon and energy efficiencies.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- This project aims to improve formate conversion by *Cupriavidus necator* using a combination of rational engineering, including increasing expression of the CBB cycle components and introducing the formolase pathway and evolutionary approaches aimed at enhancing assimilation of formate. We acknowledge that improving the CBB cycle has been a major focus of research for many years. Improved CO_2 fixation has been demonstrated in other organisms by merely overexpressing Rubisco and/or other pathway components, however, and this is the main focus of our rational engineering related to this pathway. In addition, it is likely that laboratory evolution may improve formate conversion without improving assimilation pathways themselves. For instance, it has been shown that higher concentrations of formate do not necessarily lead to higher biomass yields, likely because withstanding higher concentrations requires additional energy. Thus, improved tolerance to formate resulting from laboratory evolution could improve conversion of formate. β-ketoadipate is an exemplary product for formate conversion and is being investigated in other projects in the BETO portfolio as a performance-advantaged alternative to the incumbent petroleum-derived polymer precursor, adipic acid. TEA is an integral component of this project and will be employed to define titer, rate, yield, and downstream processing goals. We anticipate the need for higher titers, rates, and yields of products for economic viability but the main focus of this project is to improve formate conversion.

ENHANCING ACETOGEN FORMATE UTILIZATION TO VALUE-ADDED PRODUCTS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

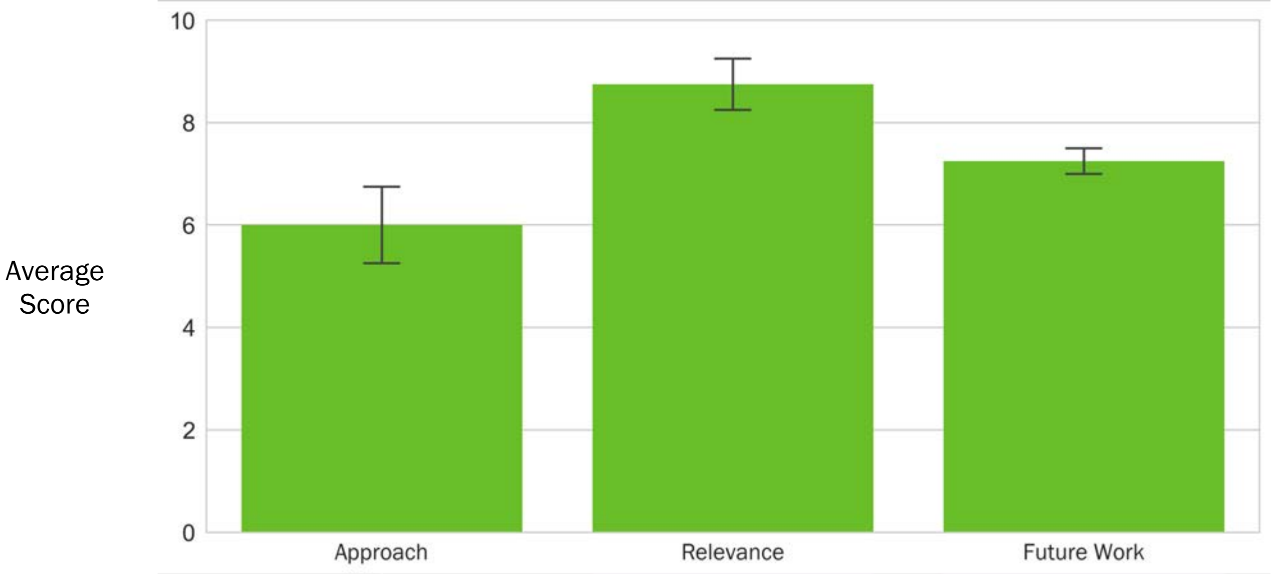
WBS:	2.3.2.112
CID:	NL0034714
Principal Investigator:	Dr. Jonathan Lo
Period of Performance:	10/1/2018–9/30/2021
Total DOE Funding:	$280,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$0
DOE Funding FY19:	$280,000
Project Status:	New

Electricity from a diversity of sources is increasingly utilized due to its low cost. However, since much of this energy is intermittently generated, there is a mismatch between energy demand and supply. Cheap intermittent energy offers opportunities to utilize this energy and generate value-added chemicals. Low-cost electricity can be used to electrochemically reduce CO_2 to formate, which then can be upgraded to useful chemicals. To utilize formate for production of valuable chemicals, we decided to focus on *Clostridium ljungdahlii* as our host organism due to several advantages: it can already utilize formate under some conditions, it has the most developed genetic system for acetogens, and is a model organism for the Wood-Ljungdahl pathway, the most efficient anaerobic carbon fixation pathway.

Formate is a feedstock for a variety of bacteria and has several advantages to gaseous electrochemical products, including ease of storage and miscibility in liquid. Acetogens naturally take C1 compounds and convert them to higher-chain products through acetyl coenzyme A (acetyl-CoA), which is a precursor to many valuable products including carboxylic acids and alcohols. For this project, as a proof of concept, we are focusing on converting formate to butanol. This task primarily relies on two parts: improving formate

Weighted Project Score: 7.3

Weighting for New Projects: Approach - 25%; Relevance - 25%; Future Work - 50%



I One standard deviation of reviewers' scores

utilization and installing a butanol pathway. First, we characterized the conditions of native formate utilization in *C. ljungdahlii*. We also have begun working on genetic tools to delete and express genes.

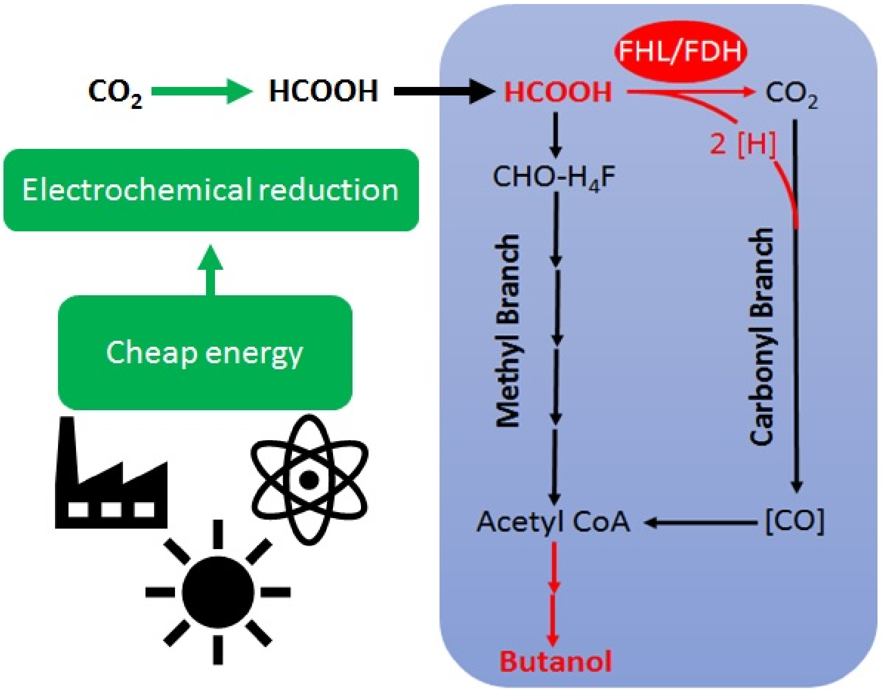


Photo courtesy of National Renewable Energy Laboratory

OVERALL IMPRESSIONS

- The performers have proposed to convert formate to butanol using *Clostridia ljungdahlii*. The performers have set a goal of 2 g/L titer and 0.18 g/L/hr productivity. The performers are encouraged to improve genetic tools in the organism to enable multiplex CRISPR-Cas9 engineering. It will also be important to integrate all overexpressed enzymes because plasmid-based systems are unstable during production. It is also unclear how 13C fluxomics in mixotrophic conditions (sugar and C1) will help the performers improve production in autotrophic conditions. Overall, the project aligns well with BETO's mission to upgrade C1 carbon sources.

- The project is investigating an interesting concept for hybrid electro-bio CO_2 conversion. The use of formate as a soluble reducing equivalent and CO_2 carrier for biological upgrading is conceptually appealing. However, the project would benefit from greater effort on system-level analysis to understand the key drivers of formate-based processes.

- This project uses a genetically engineered microbe to convert formate into butanol.

- This project aims to convert formate to butanol using *Clostridia ljungdahlii*. Formate is one of the target intermediates that can be produced via chemical synthesis. It is not clear whether butanol is the best target product considering their value and subsequent separation issues, etc. Thus, a better system engineering should be incorporated to fully evaluate the proposed technology.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- We are working on new strategies to improve transformation efficiency and hopefully bring rapid genome editing to *C. ljungdahlii*. Because formate is not natively completely growth supportive in *C. ljungdahlii*, it cannot be used alone to understand formate-related growth. However, it can be used in conjunction with other energy sources and 13C labeling helps identify how the organism is using formate. There has been one 13C formate study of a formatotrophic acetogen that shows that formate is utilized by both branches of the Wood-Ljungdahl pathway, when grown with CO. Our preliminary study shows that in contrast, formate is used by only one branch of the Wood-Ljungdahl pathway when grown with CO, showing a clear difference between an organism that can use formate only, versus our organism which can only use formate complementary.

- TEA/LCA is being utilized to examine drivers of formate-based processes and may be integrated into a larger "electrons to molecules" concept at NREL.

- The TEA analysis is utilized to evaluate which products could best be made from formate. In our system, formate is first converted into acetyl-CoA, which is a precursor to many other products that could be made instead of formate, including ethanol, butyrate, and mevalonate, which could be made instead of butanol.

SYNTHETIC C1 CONDENSATION CYCLE FOR FORMATE-MEDIATED ELECTROSYNTHESIS

National Renewable Energy Laboratory

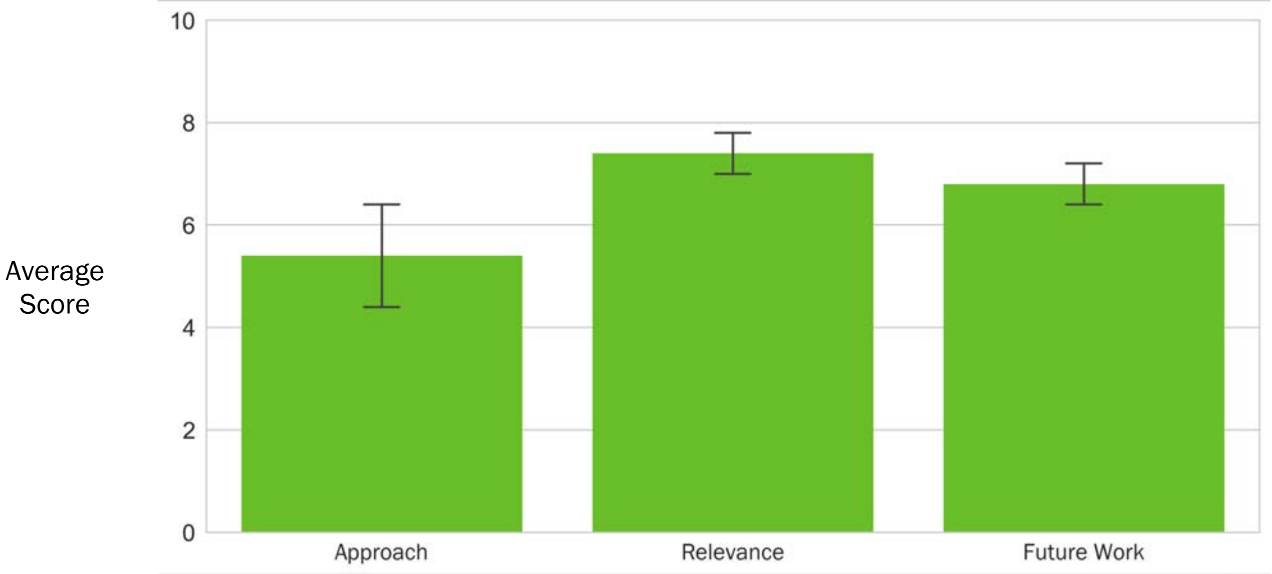
PROJECT DESCRIPTION

The innovative hybrid of biology and electrochemistry provides the potential to develop excelling bioenergy technologies. For instance, Formate-Mediated Electrosynthesis (FMES) offers a promising approach: excess electricity may reduce CO_2 to formate electrochemically and the latter could then serve as the feedstock for the cultivation of microbes and production of value-added chemicals. To facilitate the novel technology, this project leverages *E. coli* as a model organism, engineering its metabolism and enabling it to convert formate and CO_2 into C2 carboxylic acids. A synthetic pathway termed as the C1 Condensation Cycle will be constructed. Specifically, the cycle will achieve C1-to-C2 condensation and have three procedures. In net, it realizes a stoichiometry: formate (C1) + CO_2 (C1) = glyoxylate (C2) by engineering two heterologous enzymes: malate thiokinase (MTK) and malyl-CoA lyase (MCL). We will further engineer a glyoxylate reductase to convert glyoxylate to glycolate as a representative value-added chemical. This technical route has many apparent merits, such as bioenergetics feasibility, pathway simplicity, and production of industrially important chemicals.

WBS:	2.3.2.113
CID:	NL0034715
Principal Investigator:	Dr. Wei Xiong
Period of Performance:	10/1/2018–9/30/2021
Total DOE Funding:	$300,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$0
DOE Funding FY19:	$300,000
Project Status:	New

Weighted Project Score: 6.6

Weighting for New Projects: Approach - 25%; Relevance - 25%; Future Work - 50%



⌶ One standard deviation of reviewers' scores

OVERALL IMPRESSIONS

- The performers have proposed a novel pathway to convert formate to glycolate using engineered *E. coli*. A key reaction in their pathway is pyruvate formate lyase (PFL). The performers hope to utilize this enzyme in the reverse direction. Their pathway requires a constant source of adenosine triphosphate (ATP), which can be provided only in respiratory conditions. However, the PFL enzyme is very oxygen sensitive and may likely not function even in microaerobic conditions. The performers should fully evaluate the activity of this enzyme and determine if anaerobic respiration can be industrially scalable. Additionally, the performers have set low productivity targets (0.04 g/L/hr), which should be reevaluated based on their TEA. Most industrial fermentations run at productivities >1 g/L/hr. Electrochemical formate production will likely be a significant cost, and overall success will depend on high titers and productivity of any downstream upgrading.

- Leveraging selective CO_2-to-formate electrochemical conversion for biosynthesis is an interesting new strategy. *E coli* is appealing from the perspective of the availability of metabolic engineering tools, but the feasibility of engineering pathways that allow *E. coli* to thrive on formate alone has not been established.

- The project endeavors to engineer *E. coli* to use formate as a substrate and produce acetate and/or glycolate.

- The use of *E. coli* to convert formate and CO_2 to glycolate is an interesting approach and very challenging. Unfortunately, this project is still in the early stages and does not have enough data to prove the concept yet.

- The performers provide a straightforward approach to modify model strains for formate upgrading. The technical approach is clear, and the proposed tasks are relevant to BETO's goals. More thoughts could be given on which pathways to be prioritized and techno-economic feasibility.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- Thanks for reviewers' comments. (1) The PFL enzyme can work in microaerobic conditions. Our 13C-formate labeling data has confirmed its activity in both microaerobic and anaerobic conditions. When we use 13C formate and unlabeled glucose as the carbon sources for microaerobically growing *E. coli*, the carboxylic group of pyruvate is significantly 13C labeled, which aligns with strong PFL activity. The PFL activity in microaerobic conditions was also supported in literature.[1,2] (2) The entire pathway is not ATP expensive as it only costs one ATP for producing a glyoxylate/glycolate from formate and CO_2. We agree more ATP will be produced in the presence of oxygen. But there is still ATP generation in microaerobic and anaerobic conditions. In our case, it's too early to state that ATP is in shortage. We will investigate this in the study. (3) Down the road, we will do detailed TEA to guide experimental work. Currently, the productivity target is based on our protein cost analysis, which represents the biological expense for formate upgrading.

- We agree with the reviewer's statements of purpose.

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[1] Alexeeva, Svetlana, Bart de Kort, Gary Sawers, Gary, Klass J. Hellingwerf, and M. Joost Teixeira de Mattos. 2000. "Effects of Limited Aeration and of the ArcAB System on Intermediary Pyruvate Catabolism in *Escherichia coli*." *Journal of Bacteriology* 182, 4934–4940. http://doi.org/10.1128/JB.182.17.4934-4940.2000.

[2] Zhu, Jiangfeng, Sagit Shalel-Levanon, George Bennett, and Ka-Yiu San. 2007. "The YfiD Protein Contributes to the Pyruvate Formate-Lyase Flux in an *Escherichia coli arc*A Mutant Strain." *Biotechnology and Bioengineering* 97 (1): 138–143. https://doi.org/10.1002/bit.21219.

- We agree that the project is still in a very early stage, as we have just begun project work in FY 2019. Our project will have more outcomes to share in future reviews.
- Two primary tasks for this project are pathway design/engineering and TEA, which will inform the pathways to prioritize and provide insight into TEA feasibility.

INTEGRATION OF CO_2 ELECTROLYSIS WITH MICROBIAL SYNGAS; UPGRADING TO REWIRE THE CARBON ECONOMY

National Renewable Energy Laboratory

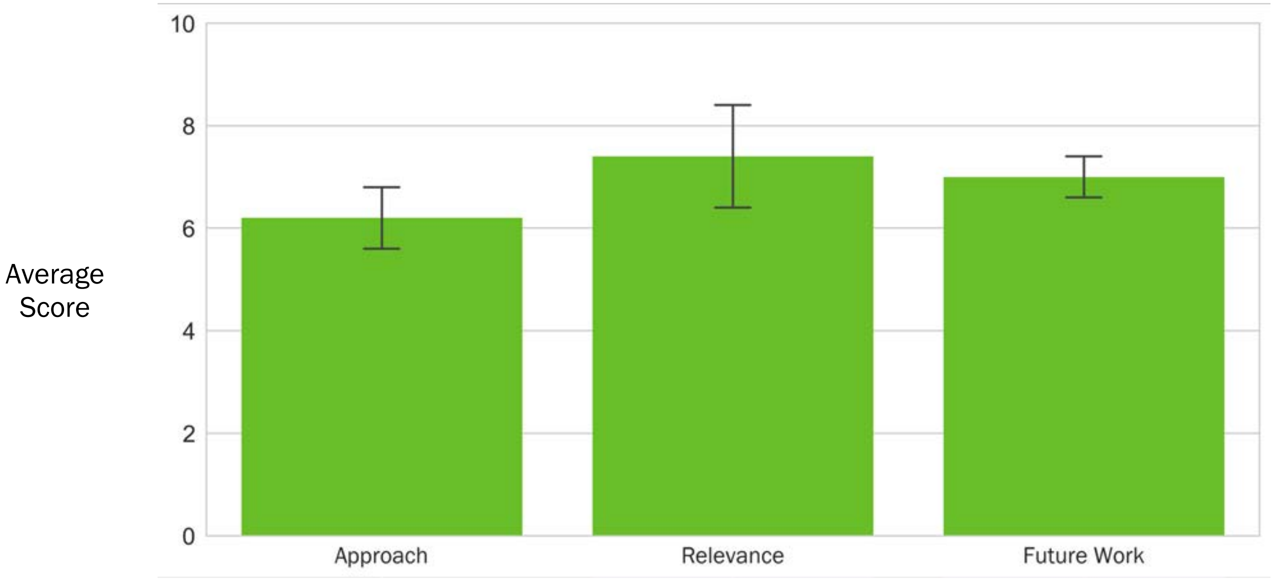
PROJECT DESCRIPTION

WBS:	5.1.3.101
CID:	NL0034004
Principal Investigator:	Dr. Michael Resch
Period of Performance:	6/30/2018–3/31/2021
Total DOE Funding:	$1,500,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$1,500,000
DOE Funding FY19:	$0
Project Status:	New

This project will work toward maximizing the carbon efficiencies and incentivizing carbon capture from industrial biopower processes and electricity generation technologies, where our bolt-on technology will produce valuable products from CO_2. In response to the lab call for biopower: topic area 5, this technology will incentivize bioenergy with CO_2 capture and sequestration through the integration of downstream electrolytic and biocatalytic upgrading of flue gases into fuels and chemical intermediates. The production of valuable products from flue gas-derived CO_2 will reduce the net cost of conventional carbon-capture technologies, leading to a more economically favorable and sustainable process. Two core technologies will be employed to demonstrate a novel process integration approach: electrolytic CO_2 conversion and biocatalytic syngas upgrading. Industrial partners 3M and Dioxide Materials have recently demonstrated electrolytic conversion of CO_2 and water to syngas using inexpensive renewable energy under an active ARPA-E subcontract. Concurrently, supporting partner LanzaTech has demonstrated industrial-scale CO fermentation using steel mill off-gas as a substrate. We will leverage these two technologies to examine integrated conversion of several industrial CO_2-rich flue gases from biopower sources to fuel and/or chemical intermediates such as alcohols, butanediol, acetate, or jet fuel. At scale, we envision this system would be co-

Weighted Project Score: 6.9

Weighting for New Projects: Approach - 25%; Relevance - 25%; Future Work - 50%



I One standard deviation of reviewers' scores

located at an industrial biopower facility and could either use CO_2 from conventional carbon capture and utilization (CCU) sources or avoid the large CCU capital expense and directly use flue gas.

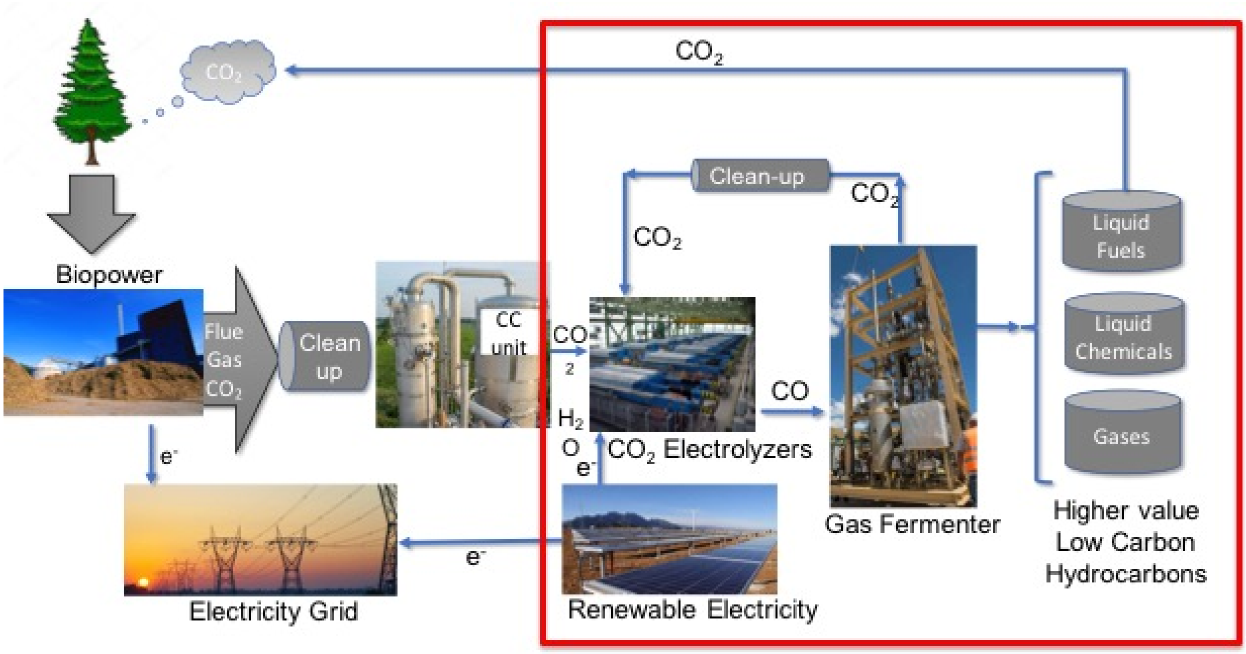


Photo courtesy of National Renewable Energy Laboratory

OVERALL IMPRESSIONS

- This project aims to demonstrate the integration of a CO_2-to-CO electrolyzer with a microbial gas fermenter using industrial flue gas.
- The performers have proposed to integrate electrolysis with biological upgrading. The performers aim to convert CO_2 to syngas (electrolyzer by 3M/Dioxide Materials) using electrolysis, which will then be fed to LanzaTech's *Clostridia* for upgrading to a product. NREL will focus on the integration of various parts that work independently but have not been tested together. The project will evaluate the effect of various CO_2 flue gases on the electrolyzer performance and perform strain engineering to adapt strains to the new syngas source. This work is very relevant to BETO's mission and displays a great example of industry/government collaboration. The performers are encouraged to list clear goals of what titer/productivity they hope to achieve using the new syngas stream.
- The system under investigation is potentially a promising strategy to valorize fermentation flue gas. It is not clear, however, how the system would make biopower plants more impactful or economic because the energy demand of converting the emissions to fuel is greater than the output of the biopower plant. The team is likely to generate sufficient data to address the project goals.
- The project demonstrates clear goals and technical approaches to integrate CO_2 electrolysis with microbial syngas upgrading to ethanol. It contributes to BETO objectives, and the partnership with industry improves the potential of applicability. The project can be improved with more quantitative milestone measures, such as product yields, rates, and conversion efficiencies. The low-value products can be better justified. TEA and LCA should be done very carefully to justify why this approach is advantageous compared to mature alternatives such as fermentation. The novelty of the approach is not clear, as the industry partners have already demonstrated similar systems and published results.

- This project aims to capture CO_2 from a biopower plant and convert that into value-added products via the combination of electrolysis and gas fermentation. Two already proven technologies are being integrated and the main findings will be focused around the process integration. It is not clear whether this technology is best suited for CO_2 capture and conversion for biopower plants, but the combination of two technologies does have a great potential for a wide range of CO_2 sources.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- If successful, we feel that this system will be able to utilize a variety of CO_2 feedstocks and renewable energy sources.

- We appreciate the reviewers' supportive comments on how this meets BETO objectives and industrial partnerships. We agree that the milestones could be more quantitative. We are using the native product(s) as a proxy for diverse microbial syngas conversion product suites. A variety of biocatalysts from our industrial partner, LanzaTech, can be substituted and produce a variety of fuels and high-value chemicals. However, the primary goal of this project is to evaluate the potential impact of flue toxins to the electrocatalysts and the biocatalysts. Notably, previous work by our partners has exclusively evaluated pure CO_2. We will determine how the flue gas components effect selectivity when low concentrations of impure CO_2 are utilized, and how do these varied gas streams propagate downstream to effect fermentation. There is a need for catalysts that are more tolerant of lower-quality feedstocks. Ultimately, what methods might be used for mitigation (filtration or other)—this project will lead to understanding of what is tolerable and not—and costs associated with cleaning gases can be determined. This should have been made clearer in the presentation. We have worked with our industrial partners on building the detailed (although preliminary) TEA models, as some of their data came from vendors' quotations or previous demonstrations. We agree that TEA and LCA should be done very carefully, as this process is much different from terrestrial lignocellulose conversion or water-splitting H_2 electrolysis. We have a Q3 FY 2019 milestone to update the TEA metrics needed for TEA under varying electricity availability and potential CO storage and gas cleanup.

NOVEL CELL-FREE ENZYMATIC SYSTEMS FOR CO_2 CAPTURE AND UTILIZATION: BIOENERGY-BASED BIOLOGICAL CARBON CAPTURE AND VALORIZATION (BECC&V)

National Renewable Energy Laboratory

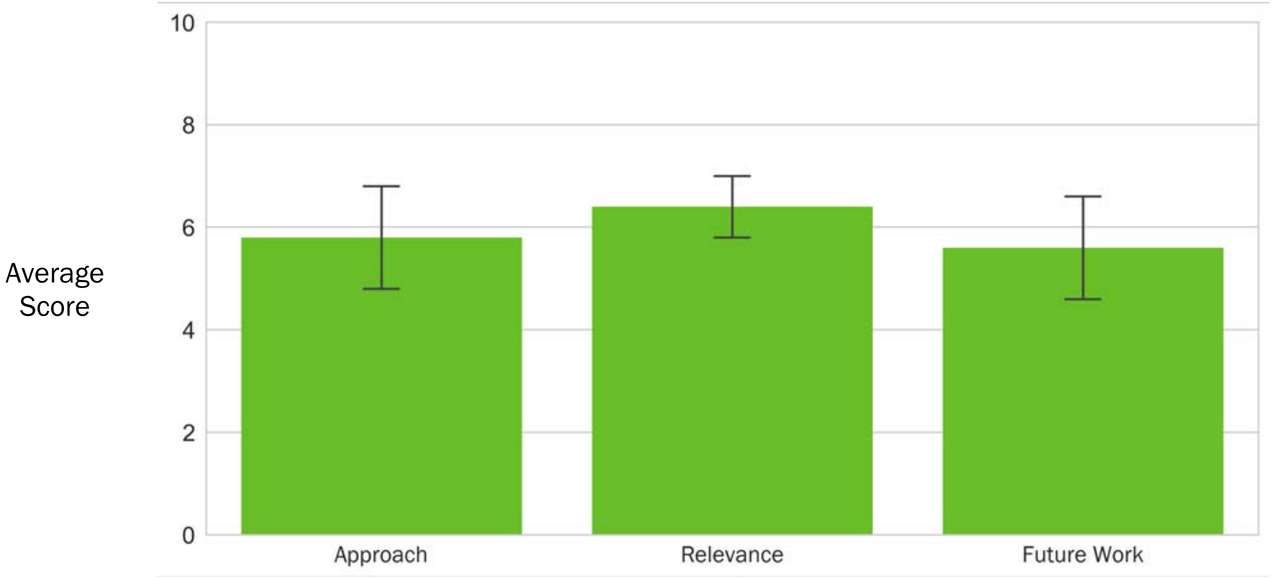
PROJECT DESCRIPTION

WBS:	5.1.3.103
CID:	NL0034006
Principal Investigator:	Dr. Min Zhang
Period of Performance:	5/1/2018–4/30/2021
Total DOE Funding:	$1,500,000
DOE Funding FY16:	$0
DOE Funding FY17:	$0
DOE Funding FY18:	$1,500,000
DOE Funding FY19:	$0
Project Status:	New

The goal of this project is to develop a novel biological, sustainable, and low-energy CO_2 waste gas scrubbing technology applicable to waste gases using enzyme-accelerated solvents with low regeneration energy. Fast-reacting CO_2 absorption solvents such as monoethanolamine (MEA) require high regeneration energy due to high heats of absorption. Alternatively, more benign and sustainable solvents have lower heats of absorption but react more slowly. Bench-scale and pilot testing has proven the ability of carbonic anhydrase to accelerate CO_2 absorption in alternative solvents in both dissolved-enzyme and immobilized-enzyme forms. However, process improvements are still needed to achieve energy reduction versus benchmark MEA. We aim to develop a low-energy CO_2 waste gas scrubbing technology using improved, immobilized thermotolerant carbonic anhydrases and enzyme-accelerated solvents operating at low-regeneration energy. This project will demonstrate a new technology at bench scale that supports TEA and LCA enabling 20% energy reduction compared to the MEA reference case (~90% CO_2 capture). Our process also generates a favorable sustainability profile and potential for capital savings due to

Weighted Project Score: 5.8

Weighting for New Projects: Approach - 25%; Relevance - 25%; Future Work - 50%



I One standard deviation of reviewers' scores

use of benign solvents. This technology can be deployed to many industries that generate waste gases to capture CO_2 from biopower, fossil-based power plants, and biogas productions, thus upgrading natural gas, biogas, and CO_2 for revenues.

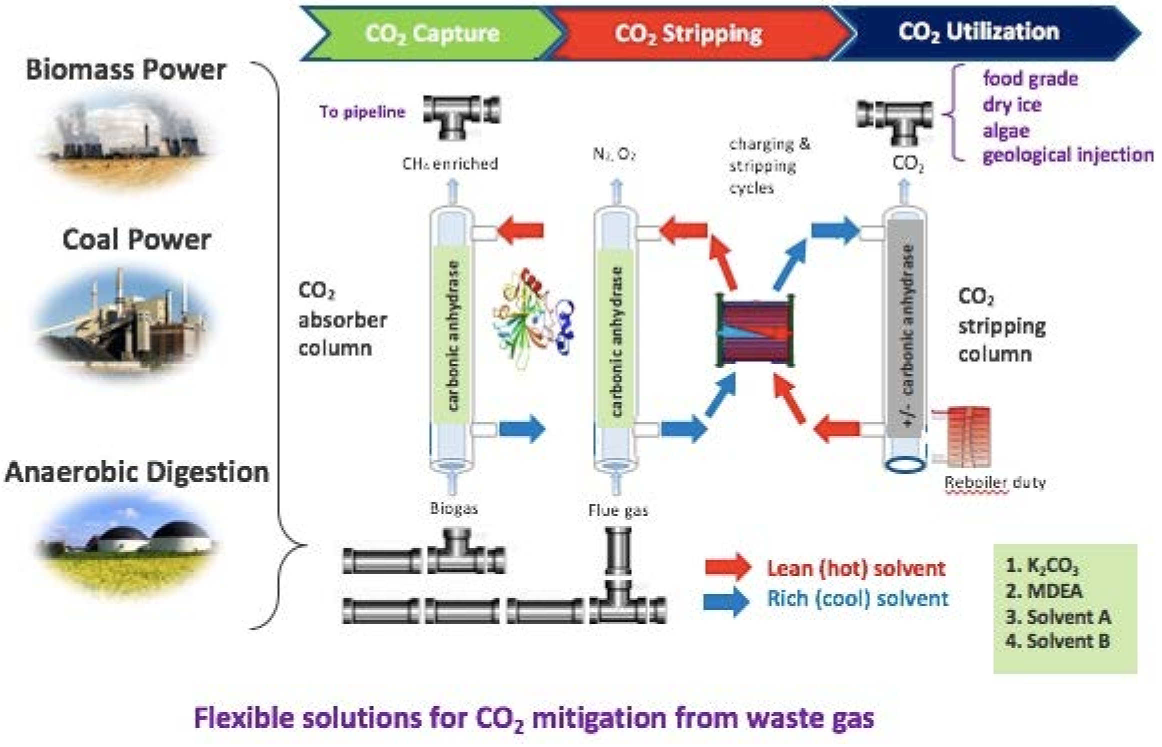


Photo courtesy of National Renewable Energy Laboratory

OVERALL IMPRESSIONS

- This project aims to use carbonic anhydrase enzymes to create a bio-inspired carbon-capture system for point sources.

- The performers propose to replace the current CO_2-scrubbing solvent MEA with another nontoxic solvent that works with an engineering carbonic anhydrase. The goal of the overall process is to reduce energy requirement compared to the MEA case. The performers will need to ensure that their enzyme is cheap, highly active in the new solvent conditions, and scalable. Though this project does not strictly upgrade CO_2 to another product, reducing the energy footprint of CO_2 scrubbing is still of importance to the DOE. The performers are encouraged to describe in more detail how they plan to perform the enzyme engineering, what their screening capacity is, and what the basal level of activity is of various enzymes in the solvents of interest. More focus on TEA should be placed early in the program to ensure that this technology, if successful, will outcompete the MEA process.

- The researchers have crafted a thoughtful plan based on good preliminary results to advance the performance of an interesting technological concept for CO_2 capture. More analysis of the cost of enzyme production is needed to determine feasibility.

- This project aims at using carbonic anhydrase to accelerate CO_2 capture by solvents with lower regeneration energies. Carbonic anhydrase is immobilized to improve its long-term stability. The overall approach is interesting, and the team is well equipped to carry out this study.

- While the project has scientific merit in terms of enzyme development, the focus of using expensive and delicate enzymes to scrub CO_2 from high-temperature and often toxic biogas/flue gas with the goal of reducing 20% energy consumption requires serious evaluations and justification. The commercialization pathway can be better justified. The team could have provided better state of the art, as there have been similar products on the market.

RECIPIENT RESPONSE TO REVIEWER COMMENTS

- We thank the review panel for their positive comments and helpful critiques. Our goal is to develop a high-performance, robust, scalable, economical, enzyme-catalyzed, solvent-based CO_2 scrubbing system with low energy penalty and low Environment, Health, and Safety (EHS) impacts as an alternative to MEA. Uniquely, in this project we will start by comparing top carbonic anhydrases from published sources and private industry in selected solvents to verify the state of the art and guide our engineering of new, more active, and highly stable enzymes through structure analysis and targeted mutations. These improvements, together with a novel immobilization strategy, will enhance enzyme longevity in desirable solvents at relevant process conditions. High enzyme longevity is a key strategy to minimize enzyme cost. TEA analysis is planned both in early and late stages of the project.

- A previous National Energy Technology Laboratory (NETL) project, led by Novozymes together with the University of Kentucky, Pacific Northwest National Laboratory, and Doosan, reported that improving enzyme longevity is a critical element in reducing operating costs. Thus, by achieving sufficiently high enzyme longevity, concerns around enzyme production cost can be overcome.

- We are excited to move this technology forward with new aspects that build on important previous work.

- Enzyme-based CO_2-scrubbing technology has been actively developing over time. Supported by federal funding (NETL, ARPA-E), initial promising field tests and feasibility assessments were reported by Akermin (NCCC), Codexis (NCCC) and CO_2 Solutions (with Husky Energy). Additional federally funded projects led by Akermin, Codexis, University of Illinois Urbana-Champaign, Novozymes, and others have outlined the opportunities and challenges of the technology. Building on these prior works, the current project aims to close gaps in enzyme catalyst longevity and improve understanding of enzyme-solvent interactions that will lead to more robust, cost-effective, lower-energy CO_2-scrubbing process options for the research and industrial community.