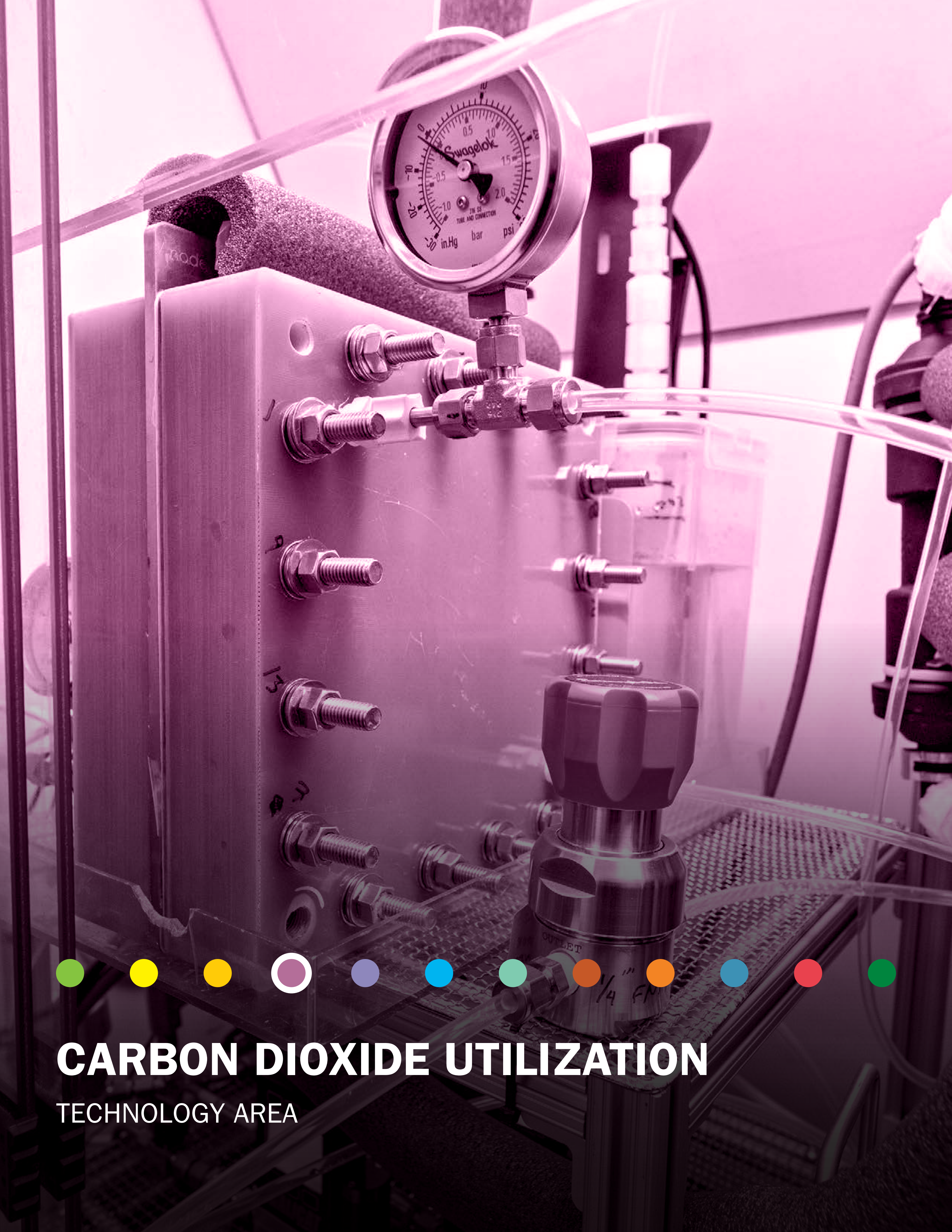

CARBON DIOXIDE UTILIZATION

TECHNOLOGY AREA

CONTENTS

INTRODUCTION

The CO_2 Utilization Technology Area is one of 12 technology areas that were reviewed during the 2023 Bioenergy Technologies Office (BETO) Project Peer Review, which took place April 3–7, 2023, in Denver, Colorado. A total of 18 presentations were reviewed in the CO_2 Utilization session by six external experts from industry, academia, and other government agencies. For information about the structure, strategy, and implementation of the technology area and its relation to BETO's overall mission, please refer to the corresponding Program and Technology Area Overview presentation slide decks (https://www.energy.gov/eere/bioenergy/carbon-dioxide-utilization).

This review addressed a total U.S. Department of Energy (DOE) investment value of approximately $18,026,188, which represents approximately 3% of the BETO portfolio reviewed during the 2023 Project Peer Review. During the Project Peer Review meeting, the presenter for each project was given 30 minutes to deliver a presentation and respond to questions from the review panel.

Projects were evaluated and scored for their project management, approach, impact, and progress and outcomes. This section of the report contains the Review Panel Summary Report, the Technology Area Programmatic Response, and the full results of the Project Peer Review, including scoring information for each project, comments from each reviewer, and the response provided by the project team.

BETO designated Ian Rowe as the CO_2 Utilization Technology Area review lead, with contractor support from Anthony Sorbera. In this capacity, Ian Rowe was responsible for all aspects of review planning and implementation.

CO_2 UTILIZATION REVIEW PANEL

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CO_2 UTILIZATION REVIEW PANEL SUMMARY REPORT

Prepared by the CO_2 Review Panel

INTRODUCTION

The CO_2 Utilization program was established by BETO in Fiscal Year (FY) 2017 with the goal of developing new biological and artificial strategies for upgrading waste CO_2 into value-added chemicals and fuels using renewable energy and CO_2 and water (H_2O) as feedstocks. The unique aspect of the CO_2 Utilization program's approach to CO_2 upgrading is the integration of electrocatalytic CO_2 reduction and biocatalytic upgrading to convert CO_2 into highly reduced, valuable chemicals and fuels. The review panel agrees that the CO_2 Utilization program is a crucial component of the DOE mission to decarbonize hard-to-electrify sectors, such as sustainable aviation fuel (SAF), and the production of commodity chemicals.

The review panel reviewed 17 projects in total: 11 were conducted at national labs, three were conducted at academic institutions, and three were conducted in industry labs. The review panel also reviewed a presentation overview of the management strategy for the CO_2 Reduction and Upgrading for e-Fuels Consortium (CO_2RUe), a group of 11 projects within the program led by national labs that regularly meet to synergize research approaches. The panelists engaged in rigorous discussions with project presenters, principal investigators (PIs), BETO program managers, and other participants. Overall, the review panel was impressed with the breadth and depth of research within the program and felt that the programmatic goals are likely to be met with the project portfolio. The projects within the program have generated important knowledge toward scaling and implementing CO_2 utilization technologies. Although the review panel's overall impressions of the program were very positive, the panel recommends improving focus within the center by tailoring research milestones to individual projects and improving communication between projects, especially those that are not part of the CO_2RUe. In this report, the review panel provides summarized review comments and recommendations on program development.

STRATEGY

Impact

To mitigate the worst effects of climate change, governments throughout the world, including the United States, have pledged to reduce carbon emissions in the coming decades and achieve net-zero emissions by 2050. This commitment has been mirrored by numerous companies in the manufacturing, technology, transportation, and energy sectors. The production of renewable carbon is a crucial component of the decarbonization strategy for hard-to-electrify sectors, including air transportation, long-distance shipping, and commodity chemical production. In particular, converting CO_2 into value-added chemicals and fuels is a particularly useful mechanism to recycle waste carbon into renewable carbon to help decarbonize these sectors; however, CO_2 conversion technologies still remain at middle to low technology readiness levels (TRLs). There have been some moderate-scale demonstrations of CO_2 conversion to one-carbon (C1) products, such as carbon monoxide and formic acid, but not for the production of large concentrations of other two-carbon-plus (C2+) products.

The BETO CO_2 Utilization program is well poised to facilitate the discovery and implementation of scalable, practical CO_2 conversion technologies for the production of high-value and high-energy chemicals, such as SAF. The strategy of the CO_2 Utilization program combines electrochemical CO_2 conversion to intermediate C1 feedstocks with downstream biological upgrading into C2+ fuels and commodity chemicals. This program fits well within the broader BETO funding portfolio, and it is unique compared to the other programs under the BETO umbrella. Moreover, this strategy is well considered for eventual practical CO_2 conversion to high-value and high-energy chemicals, such as SAF. By coupling these C1 conversion products to biological upgrading, the projects in this technology area have the potential to lead the world in developing technology for the conversion of CO_2 to fuels and commodity chemicals through sustainable, non-hydrogenation pathways.

The projects within the CO_2 Utilization program are well aligned with the broader BETO mission, and they are responsive to its strategic priorities, especially decarbonizing transportation and decarbonizing industry. The projects are all at approximate TRLs from 2–5, which well matches the target TRL for BETO-supported applied research. Many of the teams in the program are part of the larger CO_2RUe, which involves the National Renewable Energy Laboratory (NREL), Argonne National Laboratory (ANL), and Lawrence Berkeley National Laboratory (LBNL). The projects outside the consortium included projects led by a combination of academic institutions, including Montana State University (MSU), Johns Hopkins University, and the University of Delaware; and industry teams from LanzaTech, Dioxide Materials, and Twelve.

Overall, six projects focused on developing and scaling CO_2 electrolyzer technology. These projects covered a broad spectrum of approaches—from early-stage projects focused on validating novel CO_2 electrolyzer technologies at a small scale to projects focused on scaling more well-established CO_2 electrolyzer technology for CO or formic acid production. The review panel felt that the projects in this section were on the cutting edge of research within their respective fields. Three projects in this topic area specifically focused on scaling CO_2-to-CO electrolysis using membrane electrode assembly (MEA) electrolyzers: one from NREL, one from Dioxide Materials, and one from Twelve. Electrochemical CO_2 reduction (ECO_2R) to CO or $CO:H_2$ blends is a rapidly maturing field, but the review panel felt that these projects successfully differentiated themselves from other work by specifically focusing on durability, degradation, scalability, and integration rather than fundamental technology development. The review panel identified the work by Dioxide Materials focusing on degradation mechanisms and mitigation strategies in CO_2 electrolyzers as particularly impactful and highlighted that funding projects looking into these types of failure processes is critical for scaling processes that are vital to the success of the CO_2 Utilization program. Another project, from NREL, focused on scaling MEA electrolyzers for formic acid production to the 25-mA cm^{-2} scale. The remaining two projects in this topic area were early-stage projects focused on developing novel electrolyzer technology and included the development of a solid-state electrolyzer for formic acid production, led by the University of Delaware, and new catalyst designs for CO_2 electrolysis to methanol, led by ANL. The review panel considered these projects important areas of research that are breaking new ground in their topics and was supportive of their inclusion in the broader CO_2 utilization research portfolio.

An additional eight projects focused on biologically upgrading CO_2-derived intermediates into valuable chemicals and fuels. Two of these projects focused on engineering microbial systems for the biocatalytic conversion of pure input streams. An additional project focused on scaling bioreactor designs to enable large-scale fermentation for biofuel production from gaseous $CO_2:CO:H_2$ streams. The final five projects in this topic area focused on integrating CO_2 electrolysis and biocatalytic processes. These projects focused on engineering biocatalytic processes to be specifically compatible with inputs from CO_2 electrolysis and on integrating the CO_2 electrolysis directly with the biocatalytic reactors. Overall, the review panel was supportive of the research in this topic area and felt that the projects in this topic area were making good progress. The review panel recommends that each bioconversion project provides a more comprehensive justification of their choice of the starting microbe for engineering and their choice of production target. For example, in the project from NREL focused on engineering acetogens for conversion of $CO:H_2$ syngas into 3-hydroxybutyric acid, the review panel suggests the researchers better justify why they are focusing on acetogen as the target microbe rather than engineering native strains that already produce the target. In another example, in the project from NREL focused on biological conversion of formic acid to fatty acids, the review panel was unclear how the target fatty acids could be converted downstream into sustainable fuels. In some cases, the review panel was also concerned about the feasibility of scaling some biological conversion processes to meet midterm targets. For example, in the case of the project led by MSU focused on integrating CO_2 electrolysis to formic acid with the bioconversion of formic acid to ethylene glycol, the project was able to achieve midterm production goals only by adding high concentrations of reducing equivalents and coenzyme A (CoA) donors into the system, limiting the scalability of the approach. In general, the review panel recommends the use of techno-economic analysis (TEA) and life cycle analysis (LCA) to justify the use of co-additives in microbial metabolism where applicable and to justify target products at target performance metrics; however, the review panel recognizes that TEA and LCA tied to current production values are not useful for some lower-TRL projects until they can convert C1 inputs into the desired products at fast production rates and high titer. The review panel commends the focus on integrating electrolysis and bioconversion into many projects and notes that this renewed focus on integration is responsive to the recommendations from the 2021 Project Peer Review.

The remaining three projects in the program focus on developing TEAs and LCAs to help guide research directions and inform production targets. Although each individual project within the CO_2 Utilization program had some level of TEA and LCA, the three projects in this topic area focus instead on program-level goals. For example, one project from NREL focuses on combining TEA and LCA in feasibility studies of current and emerging CO_2-to-fuel technologies to identify knowledge gaps and future technological targets. A second project from NREL focuses on using location-specific resource availability to determine viable markets for implementing CO_2-to-fuels conversion technologies. A third project from the portfolio compares the TEA and LCA of different CO_2 utilization pathways for SAF production. The projects in this topic area were seen as a strength of the CO_2 Utilization program. One suggestion of the review panel was to encourage greater collaboration between the analysis groups and the researchers in the first two topic areas. This could help standardize the TEA and LCA modeling and facilitate participation by experimental groups that do not have experience in TEA and LCA.

Innovation

The review panel was impressed with the research output and directions of the projects within the CO_2 Utilization program. Overall, the projects are tied to the strategic direction of the program and are at the forefront of their fields. The projects regarding CO_2 electrolysis were mostly focused on scaling and durability and have identified key technology gaps and possible solutions regarding membrane durability, degradation mechanism, reactant transport, and product crossover upon scaling. A small subset of projects in this area are early-stage projects focused on validating novel electrolyzer technology at a very small scale, but that could eventually lead to important new research directions. The projects regarding biological conversion included two projects focused on developing new strains for CO and formic acid conversion, five projects focused on integrating electrolysis and biocatalytic reactors, and one project focused on scaling continuous stirred-tank reactors (CSTRs). The projects focused on integration highlighted numerous important knowledge gaps, most of which were not present in the individual electrolysis and biocatalytic processes and only presented when the processes were integrated. The projects focused on TEA, LCA, and feasibility analysis set important and realistic performance targets and provided important insights into the technological and economic viability of the eventual implementation of CO_2 utilization technologies.

STRATEGY IMPLEMENTATION AND PROGRESS

Synergies

In response to a specific recommendation in the 2021 Project Peer Review to improve communication between projects in different research areas, the CO_2 Utilization program created the CO_2RUe in 2022. Eleven projects within the CO_2 Utilization program (~65%) are part of the CO_2RUe, with researchers in five national labs. As discussed in the first presentation of the review, the CO_2RUe has a formal leadership structure, with a consortium lead that is advised by the program and both an internal advisory board and an external advisory board of leading researchers in academia and industry. The consortium hosts regular meetings between PIs, regularly interacts with the advisory boards, and works to establish research pathways to achieve the broader programmatic targets of the CO_2 Utilization program.

The review panel saw the creation of the CO_2RUe as a game-changing strategic advance that strengthens the overall CO_2 Utilization program by dramatically increasing communication between projects, leading to increased synergy and better integration of project goals. Collecting projects from all topic areas within one consortium has increased the likelihood that the projects will address important challenges unique to the CO_2 Utilization program.

Despite the success of the CO_2RUe, there is still room to improve communication across the different projects within the program to ensure beneficial outcomes for the performer and the government. For example, there was substantive overlap across projects focused on electrolyzer development that would have benefited from cross-pollination. Specific examples are the distinct projects led by ANL and Johns Hopkins University that both focused on integrating molecular catalysts into electrolyzers for CO_2 electrolysis. It was clear that the two projects were developing very similar technology but had not met to discuss challenges and generate solutions. To further improve synergy within the program, the review panel suggests that other projects not within the consortium be invited and encouraged to participate in regular discussions with the CO_2RUe.

Focus

The review panel was impressed by the diverse and ambitious research portfolio within the CO_2 Utilization program. Research being conducted in the program fits well into BETO's strategic plan to decarbonize industrial and transportation sectors through targeted, applied research focused on recycling waste CO_2 into value-added chemicals and fuels through a combination of electrocatalytic and biocatalytic processes. Technical targets were well defined, and projects are responsive to these targets.

Projects funded in this program fell into three broad topic areas: (1) developing and scaling electrolyzer technology for CO_2 reduction to C1+ intermediates, (2) biocatalytic upgrading CO_2-derived intermediates to valuable products, and (3) developing TEAs and LCAs to inform research goals and product targets.

In the first topic area, four of the six projects specifically focused on scaling electrolyzer technologies to the necessary output rate and product concentrations for downstream biological upgrading and on determining their durability under practical operational conditions. This focus on electrolyzer scaling and durability testing is directly responsive to the recommendations from the 2021 Project Peer Review, and it allowed the project teams to determine the knowledge gaps that are being bridged through targeted, applied research. The remaining two projects in this topic area focused on developing new electrolyzer technologies. The inclusion of these more exploratory, lower-TRL projects was seen as a promising addition to the program that, if successful, could provide additional research avenues in the coming years; however, the review panel felt that the target metrics should be de-emphasized for these early-stage, high-risk/high-reward projects to allow the project teams to focus on technology development rather than scaling and integration. The balance of the research portfolio seemed about right to the review panel, with most projects focused on the scaling and durability of higher-TRL technologies for nearer-term progress and a smaller contingent focused on lower-TRL research that has the potential to advance in the future.

In the second topic area, most projects focused on integrating electrolyzer and biocatalytic processes. The focus on integration in the current funding portfolio was directly responsive to the 2021 Project Peer Review recommendation that the program focus on integrated scale-up approaches that more fully combine electrocatalytic and biocatalytic processes. This topic area also included a project focused on scaling CSTRs, which was another recommendation from the 2021 Project Peer Review. Overall, the review panel felt that the shift in this topic area toward the integration and scaling of biological conversion with real, intermediate feeds from electrolyzers was appropriate and aligns with the goals of the CO_2 Utilization program.

In the third topic area, the projects focused on program-level LCA and TEA for CO_2 upgrading using the combined electrochemical and biocatalytic strategy supported by the CO_2 Utilization program. This program was part of the CO_2RUe, and as such, it was well aligned with the goals of the consortium and the individual projects. This close alignment of the analysis with the experimental research is responsive to the 2021 Project Peer Review feedback and is seen as a success of the program by the review panel. The analysis projects are able to assess the feasibility of implementing the technologies being developed within the program and provide important feedback to the research projects regarding target inputs, products, and performance metrics. The review panel suggests maintaining a focus on these types of program-level analysis projects within the broader program research portfolio.

Overall, the review panel felt that the projects within the CO_2 Utilization program aligned with programmatic strategy and goals. The implementation of the CO_2RUe dramatically enhanced communication between projects within the consortium, which has helped focus research directions. Improving communication between CO_2RUe projects and those outside the consortium, especially regarding feasibility assessment, could further enhance research focus toward the most promising technologies and reduce research overlaps. Another concern of the review panel is that sometimes projects spend effort and resources on unproductive research directions simply to meet short-term and midterm milestones, even if these research directions are not important for the success of the project. For instance, some projects used recirculation to meet CO_2 conversion efficiency milestones or introduced co-additives into biocatalytic reactors to improve yields and titer milestones, even if these additions are not scalable. The review panel felt that the milestone target goals might be more effective if they were tailored to the needs of each individual project, or the program should more effectively communicate to the projects that it is okay to miss some performance milestones as long as the projects are making progress and increasing knowledge.

RECOMMENDATIONS

Recommendation 1: Improve communication between projects to prevent overlap of effort.

The creation and implementation of the CO_2RUe has dramatically enhanced communication and synergy for projects within the consortium; however, this improved communication has not benefited projects outside the CO_2RUe but rather those that are still within the CO_2 Utilization program's research portfolio. To further improve synergy with the program, the review panel suggests that projects outside the consortium be invited and encouraged to participate in regular meetings with CO_2RUe projects. Taking this step will help improve communication among all projects within the program and will help ensure that projects are collectively working to achieve the broader program goals.

Recommendation 2: Tailor project milestones to each project.

The CO_2 Utilization program has set uniform performance milestones for projects operating in the various technology areas. In some cases, projects have spent time and effort to develop unscalable approaches or otherwise unproductive research paths for the sole purpose of meeting these milestones. The program should work with the projects to develop specific performance milestones tailored to each individual project. The program should also clearly communicate that although it is important to strive toward performance milestones, the overall purpose of each project is knowledge generation, and it is okay to occasionally miss performance milestones as long as the project is making research progress and generating important knowledge in its field.

Recommendation 3: Develop a facility to help test CO_2 electrolysis under "real-world" conditions.

A common roadblock to testing ECO_2R is the inability to run and do onstream testing and analysis for long durations of time with the full system. A facility for CO_2 electrolysis scaling could help mitigate risks by discovering challenges that are difficult to see in conventional bench-scale setups and experimental time frames. Such a facility could help normalize long-duration, "real-world" stress tests and degradation studies for the different electrolyzer technologies being developed within the program.

CO_2 UTILIZATION PROGRAMMATIC RESPONSE

INTRODUCTION

The Conversion Research and Development (R&D) Program Area is quite thankful for the valuable insights and engaging discussion on this subject provided by the CO_2 Utilization review panel. This type of critical assessment continues to be a driving force in the development of this portfolio. As stated by the Review Panel Summary Report, this portfolio has significantly grown since its inception, and it would not have been possible without such expert involvement from the private and academic sectors. BETO is indebted to the reviewers, both new and returning members.

The panel agrees that a program such as this—that focuses on leveraging CO_2 as a feedstock for fuels and chemicals—is a "crucial component of the DOE mission to decarbonize hard-to-electrify sectors" of the economy. As with all R&D endeavors, striking the right balance between the quantity of areas explored and the depth within specific topics is difficult. The review panel stated that the CO_2 Utilization portfolio achieves an impressive breadth and depth of research.

The areas being researched by BETO were generally seen as appropriate for the challenge of enabling CO_2 conversion, which generally remain at low to middle TRLs today. The panel described the portfolio as consisting of three broad areas: electrolyzer technology, biocatalytic conversion of intermediates, and TEA and LCA. The review panel spoke highly of the newly formed CO_2 consortium and saw it as the appropriate way to increase communication among these efforts and allow for integration where needed. Establishing this consortium was a major accomplishment of the CO_2 Utilization portfolio during the past 2 years, and it was influenced by feedback from the 2021 Project Peer Review.

The electrocatalytic applied R&D work occurring in the portfolio, a combination of national lab projects within the consortium as well as those occurring externally, were seen as cutting-edge efforts that are helping to advance the start of technology in this area. The biocatalytic work was also assessed to be making good progress in the field; however, projects could benefit from additional justification for the choice of host organisms and the production target as well as deeper investigation into whether they could scale to hit ambitious climate targets within a reasonable time. Last, the analysis projects in the portfolio were also seen as a strength that can inform program-level goals and identify technical gaps, though they could be better leveraged to inform the researchers on the electrocatalytic and biocatalytic projects.

The reviewers pointed out the synergistic opportunity for combining researchers who work on catalyst development with their counterparts who 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. Overall, the reviewers saw room to improve communication across the portfolio, both within the consortium and with other projects in industry and academia. The following section specifically addresses the three major recommendations from the review panel.

Recommendation 1: Improve communication between projects to prevent overlap of effort.

BETO agrees with the panel on the importance of communication across the portfolio. Although the consortium has been successfully established and readily communicates among relevant projects across the national labs, it has minimal interaction with projects that are not within this group, such as funding opportunity announcement (FOA) awardees at companies and universities. This blind spot misses an opportunity to allow learnings to filter into the public. Per the review panel's recommendation, BETO and the CO_2 consortium are exploring mechanisms to allow and encourage external awardees to participate in consortium activities and share their work with that group.

Recommendation 2: Tailor project milestones to each project.

The program appreciates and agrees with this recommendation. Milestones should be tailored to the specific project work, and there is room for improvement in the BETO CO_2 Utilization portfolio on this front. Specifically, certain projects selected from an earlier FOA have goals and milestones that adhere to specific targets that were outlined in the initial FOA language, but some of those milestones proved not to be very relevant once the projects were underway. To meet the review panel recommendations, BETO will set more flexible targets in future FOAs and, through active project management, will ensure that awardees work toward answering important scientific questions related to the spirit of the project, not simply hitting arbitrary metrics to technically meet the stated requirements within the financial agreement.

Recommendation 3: Develop a facility to help test CO_2 electrolysis under "real-world" conditions.

BETO agrees with this assessment and is actively exploring the subject. As stated by the reviewers, the lack of access to long-duration electrocatalytic testing is a major hurdle in the field. There is an opportunity to help advance the field by providing a mechanism for stakeholders to address things like catalyst durability, accelerated testing, protocol standardizing, and electrolyzer scale-up. Although such an effort is difficult to establish under current BETO funding, some future efforts within the consortium could be dedicated to answering some of these questions. In addition, BETO will explore collaborations on this subject with other applied R&D offices across DOE that are interested in CO_2 conversion.

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

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.1.0.304
Presenter(s):	Gary Grim
Project Start Date:	11/01/2020
Planned Project End Date:	09/30/2023
Total Funding:	$400,000

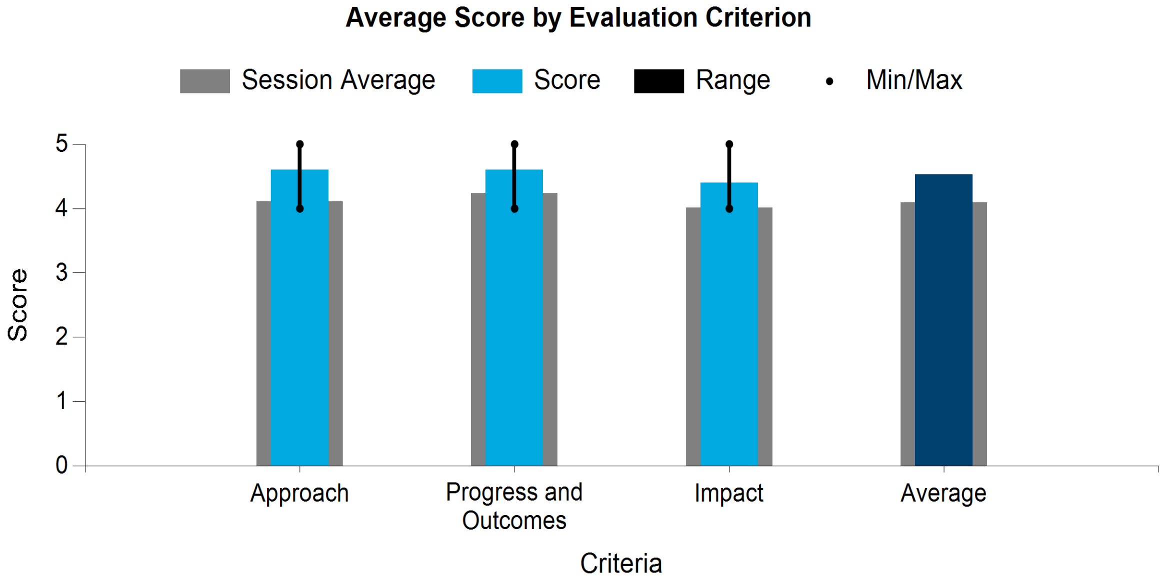
The increasing availability of renewable electricity at costs competitive with, and even lower than, electricity from fossil fuel sources, along with increasing interest and recent technological advancements in reducing carbon emissions through CO_2 capture (whether from point sources or the air), is challenging the status quo in the way that we produce and consume energy and products. Renewable electricity can be leveraged to produce fuels and chemicals from CO_2 via CO_2 reduction, offering sustainable routes to reduce the carbon intensity of our energy and products-driven economy. It has been estimated that the annual market opportunity for CO_2 utilization (all products and pathways, not only electricity-driven CO_2 reduction) is on the order of $1 trillion. More specific to CO_2 reduction, a recent study from 2019 estimated that producing chemicals such as methanol, polyolefins, and aromatics from CO_2 and renewable electricity instead of fossil fuel-based resources could reduce annual greenhouse gas (GHG) emissions by up to 3.5 gigatons of CO_2-equivalents in 2030, albeit at a cost of hundreds of billions of U.S. dollars per year. In most existing biorefineries in the United States and in BETO's conceptual biorefinery designs, CO_2 is released to the atmosphere either as a concentrated stream (i.e., ethanol fermentation) or as a component of flue gas (e.g., gasification and pyrolysis). As of 2018, the 216 existing biorefineries in the United States emit 45 million tons of CO_2 annually. Capturing and converting this CO_2 into valuable products, leveraging renewable electricity as the primary energy input, could increase overall biorefinery CO_2 utilization by as much as 40%; however, due to the diversity of CO_2 capture and conversion technologies (many of which are at low TRLs) and the trade-off between improved biogenic carbon yield at the expense of additional energy input, considerable uncertainty exists around the impact of these electron-driven CO_2 utilization strategies on the minimum fuel selling price (MFSP) and the overall carbon intensity of the process.

This project combines TEA and risk evaluation to address this uncertainty. More specifically, this project evaluates the conceptual stand-alone, electricity-driven CO_2 utilization technologies (i.e., CO_2 reduction strategies) and their integration into existing biorefinery designs to quantify the impact on the MFSP. The key differentiators of this project are as follows: (1) We take a holistic approach to addressing this uncertainty (most studies in the literature focus on a single technology, e.g., thermochemical hydrogenation of CO_2, whereas our study spans existing technologies and evaluates the integration of these technologies into existing biorefinery designs), (2) we maintain a strict focus on the intersection of electricity and biorefinery streams (CO_2), (3) we have a world-class analysis team with deep expertise in modeling emerging technologies (low TRL) with complex chemistry, and (4) we leverage in-house chemical and biological conversion experts.

Our FY 2021–FY 2023 scope focused on (1) specific CO_2 reduction technologies that represent the greatest potential to reduce the MFSP for SAF and generating out-year technical targets and comprehensive reports, and (2) providing crosscutting, technology-agnostic guidance to the field of CO_2 reduction. Further, we aim to address key feedback from the 2019 Peer Review regarding process parameters that need more in-depth assessment of carbon intensity and process risk. The key innovations of this project include (1) establishing state-of-technology (SOT) and waterfall projections based on ongoing BETO-supported experimental work, (2) integrating with LCA to assess carbon intensity, (3) evaluating technological risk (especially for low TRLs) via a node-by-node and complex systems-level approach, and (4) evaluating opportunities for process intensification (combining CO_2 capture and conversion) and coupling CO_2 with other biorefinery streams. Our project will extensively collaborate with other ongoing and proposed new-start projects supported by BETO, including the newly formed CO_2RUe.

The key outcome of this work is to inform and guide stakeholders toward the effective utilization of electricity to improve biorefinery CO_2 utilization. The specific stakeholders for this work are (1) researchers, (2) technology developers, and (3) biorefinery owners/operators. For researchers, this project identifies opportunities for transformational research, i.e., research that will result in significant reductions in cost and/or risk, and it guides R&D efforts by setting future targets for key technical metrics. Integration of this project with experimental teams working on CO_2 utilization technologies will result in tangible technological advancements and cost reductions through analysis-guided R&D. For technology developers, this project identifies and assesses technological barriers and risks that are limiting the commercial viability of these CO_2 utilization processes. For biorefinery owners/operators, this project helps them understand the trade-offs of implementing these CO_2 utilization technologies (i.e., energy requirements, capital costs, and product yield and quality captured in comprehensive design reports) so that they can assess the value proposition based on their specific needs.

Since the 2021 Project Peer Review, this project has directly authored or contributed to five peer-reviewed journal publications: (1) https://doi.org/10.1021/acsenergylett.0c02692, (2) https://doi.org/10.1039/D0EE03525D, (3) https://doi.org/10.1039/D2EE02439J, (4) https://doi.org/10.1016/j.apenergy.2021.117637, and (5) https://doi.org/10.1002/9783527833634.ch3.



COMMENTS

- The information gained from this complex project—pulling multiple key aspects of technology, economics, modeling, and LCA—is key to guiding research efforts. Analyzing information from current projects can help mitigate risk and increase the chances of successful scaling and implementation. The online tool that was developed can increase awareness in a broader audience.

  Potential impact:

  - More outreach to industry with the knowledge gained from their research and the online tool could help normalize the LCA/TEA in this field
  - Increased communication with specific projects within the CO_2RUe could assist with guiding the target goals of each project—e.g., additional guidance on the effect of the per-pass CO_2 conversion

on the TEA versus recycle loop, limits to venting the recycle loop, tuning the conditions in the reactor affects the major cost drivers, target products, scenarios where the focus should be on formate versus MeOH versus CO/H_2.

- This project aims to combine TEA and LCA to provide technological guidance for CO_2-to-SAF technologies. It evaluates the production cost and carbon intensity of various CO_2-to-SAF processes based on the SOT performance and highlights key cost drivers of these processes. Overall, the project has a significant impact and offers key insights to move CO_2-to-SAF forward. The project has been managed well, with interactions/contributions from all key parties. The progress and outcomes are excellent, as demonstrated by multiple publications and the launch of an interactive website. It is not clear how various steps in the CO_2-to-SAF processes are integrated. The level of integration between various steps (e.g., ECO_2R, fermentation of syngas, catalytic ethanol upgrading) would significantly influence both production cost and carbon intensity. It is also not clear how the target performance values for each individual step are determined based on the target value of the final SAF product.

- This project is well executed and an important component of the CO_2RUe. The goal of the project is to use the TEA and LCA of current and emerging technologies to identify existing technology gaps and future technical targets for CO_2 utilization. Assumptions used in the models were largely pulled from the literature, but crucially, the project also leveraged key industry partners to provide validation for key assumptions. A significant strength of the project is its integration of emerging technologies within the CO_2RUe into its TEA/LCA to help ensure that the project's analyses are responsive to the changing landscape of CO_2 utilization. The integrated TEA/LCA approach is an important and unique component of the project that allows for simultaneous optimization for price and environmental parameters. This integrated TEA/LCA approach is a strength of the project that helps identify economic and environmental trade-offs, although it would be useful for the project to provide more guidance on how LCA and TEA should be weighted in these analyses to help define the technical targets for research components. Overall, this is a successful project that has already demonstrated significant impact through peer-reviewed publications, the launch of an interactive website, and engagement both within and external to the CO_2RUe.

- The project goal of the integration of TEA and LCA models is very important because it will guide the development of different technologies and will allow for excluding non-promising products from consideration at early stages. Strangely, in some examples, future and theoretical costs are about the same, which assumes (highly unlikely) zero losses. A cost analysis was performed on a \$/kg basis, though for energy purposes it would be useful to also represent this in \$/kWh (\$/Btu) units. The performed Monte Carlo analysis is definitely a plus of this project; however, some used parameters are questionable—e.g., capacity factor (should go as low as 25%) and electrolyzer cost (it is better to present this in \$/kW units). It is not clear how the team plans to perform the optimization of the integrated TEA/LCA model: What will the optimization target be—cost, carbon intensity, etc.? What weight for different factors will be used? Setting future targets is undoubtedly a plus, but the analysis of current trajectories for the most important products would be useful.

- This was an excellent presentation that gave a clear, tangible sense of the progress and outcomes. The work is a critical component of the CO_2 utilization consortia because it informs the group of the current pain points and therefore where to focus the research. The durability, cost, efficiency, and lifetime of electrolyzer units were highlighted as important variables affecting the success of a CO_2-derived product. This was good to see because the clear majority of projects funded in the CO_2 utilization consortia focused on electrolyzer development. The authors have also published four peer-reviewed articles and generated an interactive website to help communicate their work. One important consideration for the group and BETO as a whole is how to ensure that this sort of analysis and *in silico* tools live on. Are there plans to diversify the products analyzed using similar analysis pipelines?

PI RESPONSE TO REVIEWER COMMENTS

- We thank the subject matter expert panel for taking the time to review this project and provide thoughtful and constructive feedback. Moving forward, we will apply this feedback to (1) continue to guide and inform our partner programs within the CO_2RUe, (2) provide transparent and actionable information on CO_2 conversion through peer-reviewed publications and online tool kits, (3) provide multicriteria decision analysis as a means to weigh the outcomes of our integrated TEA/LCA, and (4) balance our approach between the production of intermediate products and fully integrated pathways to fuels.

MARKETS, RESOURCES, AND ENVIRONMENTAL AND ENERGY JUSTICE OF CO_2-TO-FUELS TECHNOLOGIES

National Renewable Energy Laboratory

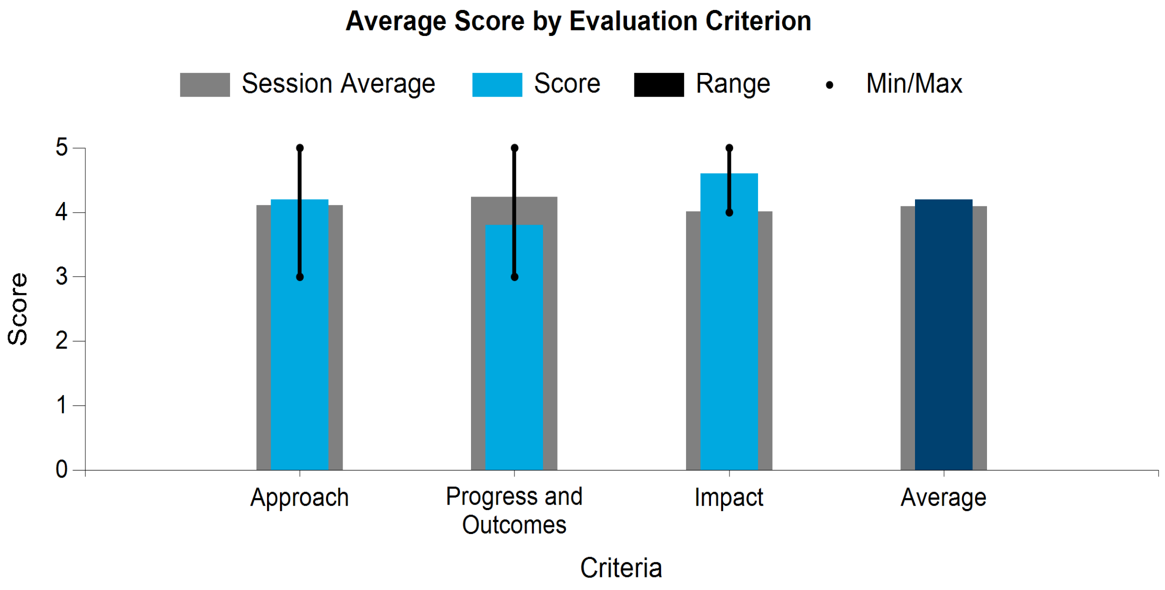
PROJECT DESCRIPTION

WBS:	2.1.0.504
Presenter(s):	Ella Zhou; Jiazi Zhang
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$950,000

Today's production and market locations for fuels and chemicals are largely determined by fossil fuel resources and existing infrastructure (e.g., natural gas and petroleum oil).

To achieve DOE's decarbonization and energy justice objectives, at-scale investment in CO_2 utilization technologies needs to be informed by detailed analyses of CO_2 and H_2 resources and costs, non-fossil fuel electricity availability and prices, air emissions, job and gross domestic product impacts, and other factors.

This project informs the development of the CO_2 utilization industry by (1) assessing the resource potential, market potential, and infrastructure requirements for the near-term (2030) and long-term (2050) deployment of CO_2 utilization technologies; and (2) evaluating the energy equity and environmental justice (EEEJ) implications. The insights can be used across a large portfolio of CO_2 utilization technologies so that stakeholders can make decisions according to both economic and societal factors.



COMMENTS

- This project shows impactful research on resource availability, CO_2 markets, and EEEJ analysis. Their research is key to strategically scale CO_2 technology and identify focus areas while addressing EEEJ. Can they communicate their work to a broader audience? Additional information/questions for further assessment include:

  Risk management:

  - Additional information regarding how they are measuring health impacts and exposure disparity

  - Additional information regarding the scenarios they chose to focus on.

  Potential impact:

  - Additional information regarding other potential unforeseen consequences and mitigation strategies.

- The project aims to quantify the effect of carbon sources (capture cost and transportation) and energy sources (cost and carbon footprint) on CO_2-to-SAF conversion. The goal is to identify possible locations for CO_2-to-SAF based on two key paths: (1) low-temperature electrolysis to produce syngas followed by fermentation and (2) water-gas shift followed by the Fischer-Tropsch process. Progress has been made in identifying CO_2 and energy sources at different locations. It is unclear how the final goal can be achieved within the timeline of the project. It is also unclear how societal impacts are evaluated. Some aspects that may affect the overall process, including CO_2 purity and product distribution, have not been considered/discussed.

- The project uses a cross-sector modeling framework assessing location-specific resource availability to determine viable markets for CO_2 utilization technologies for SAF production. A key strength of this project is the close collaboration with other projects in the CO_2RUe, especially the other modeling and analysis groups, which provided the 2233 TEA/LCA metrics used in the cross-sector modeling. The project has already made significant progress, identifying three preliminary sites for CO_2 utilization with the correct balance of grid electricity capacity and cost, proximity to CO_2 resources, and proximity to jet fuel refineries. Future immediate plans appropriately focus on expanding the model to include emissions inventory analysis and estimated delivery and storage costs for hydrogen and reduced CO_2 intermediates. It remains unclear how the EEEJ component will be integrated into the cross-sector modeling. The timeline for onboarding this component is not until Year 3 of the project, but no approach was discussed as to how this would be integrated and weighted into the current cost-based models. Although pilot-scale implementation of CO_2 utilization is not part of the CO_2RUe portfolio, this project nonetheless provides an important and impactful contribution to the consortium by assessing the feasibility of implementing CO_2 utilization technologies at scale in optimal location-specific markets based on technology performance targets.

- Quantification of resource (feedstock and renewable electricity) availability and costs for CO_2 conversion to fuels is extremely important to guide development and deployment, and the project is moving in the right direction. A couple of comments are as follows: The team showed the advantages of the preferred pathway (LTE – syngas fermentation – EtOH to SAF) with the pathway based on reverse water-gas shift reaction. It seems that another pathway (LTE – CO_2 H_2 – MeOH) may be more cost-competitive and should be used as a base case. Second, localization of the distributed SAF production (close proximity to major airports, delivery infrastructure) should be analyzed. I also recommend considering water resources.

- The specific goals of this project were not clearly communicated. Slide 9 sets the stage at a very high level, but beyond that, the reviewers need to go to the quad chart to see the goals. Because this project followed WBS 2.1.0.304, it would have been useful to hear more about how this project differed from the previous one. I was left wondering if the work was significantly distinct or simply looking at the same issue in a slightly different way. More collaboration and communication between these two projects would have helped highlight and differentiate their added value to the program. I see that mentioned on Slide 20, but it was not clear from the presentation.

  In regard to progress and outcomes, I've given this project a three because although they have made good progress toward their goals, little mention was made of risk mitigation and challenges. This left me with the impression that the work could have been more challenging.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the valuable feedback provided by the reviewers and their insightful comments. We are grateful for their contribution to the refinement of our methodology. In the following sections, we break down the questions and provide detailed answers.

  Comments 1: Impactful research on resource availability, CO_2 markets, and EEEJ analysis. Their research is key to strategically scale CO_2 technology and identify focus areas while addressing EEEJ. Can they communicate their work to a broader audience? Additional information/questions for further assessment: risk management—additional information regarding how they are measuring health impacts and exposure disparity, additional information regarding the scenarios they chose to focus on; potential impact—additional information regarding other potential unforeseen consequences and mitigation strategies.

  Answers:

  - 1.1 Communicate our work to a broader audience. We will continue to present and publish the key findings in conferences, peer-reviewed journals, and reports to inform stakeholders, industry partners, and the public.

  - 1.2 Risk management. Insufficient transmission capacity to meet the increasing electrolyzer demand resulting from SAF targets is a potential risk. This risk can be managed by investigating other future capacity and transmission expansion scenarios that consider new technologies, such as long-duration energy storage build-out and high-voltage direct current. Decreasing the CO_2 available from sources by industrial decarbonation is a potential risk. The risk can be managed by including additional potential CO_2 from direct air capture (DAC) or bioenergy production that may replace petroleum fuels. In particular, DAC provides a direct way to decrease CO_2 concentration from atmosphere. Green hydrogen shortage due to the low-carbon electricity supply shortage is another potential risk. NREL is addressing this risk through the electricity market analysis. Hydrogen production by polymer electrolyte membrane (PEM) electrolysis may face material supply barriers, such as for platinum or iridium. This is investigated by a separate supply chain study. CO_2 pipeline construction might be a bottleneck due to the permit application/approval and construction hurdles. This will not be a risk if DAC is used for CO_2 source.

  - 1.3 Additional information regarding how they are measuring health impacts and exposure disparity. The NREL team will estimate the EEEJ factors, including impacts on human health and job distribution, using the results from the TEA/LCA project. To estimate high-spatial-resolution human health impacts of air emissions, the Intervention Model for Air Pollution (InMAP) will be used. Its results will be combined with demographic data to evaluate the impacts to specific communities. Outputs include changes in the annual average concentration of particulate matter (PM) 2.5 (particulate matter with diameter 2.5 µm or smaller) and avoided (or additional) annual average mortality by demographic. Socioeconomic impacts, including regional wealth and job distribution, will be estimated using the Bio-based circular carbon economy Environmentally-extended Input-Output Model (BEIOM) with regional supply and demand conditions and electricity generation mix developed in this project and process-level TEA and LCA data provided by the TEA/LCA project team.

  - 1.4 Additional information regarding the scenarios they chose to focus on. We have analyzed high- and medium-purity process CO_2 sources from six industries (ethanol, ammonia, natural gas processing, steam methane reforming [SMR] hydrogen, cement, and iron and steel). For these potential CO_2 sources in the future, we have two scenarios: one in the near future, i.e., 2030, and another longer term, in 2050. The 2030 CO_2 scenario is based on available data obtained from the Annual Energy Outlook by the U.S. Energy Information Administration. The 2022 Annual Energy

Outlook projected an amount of CO_2 emissions in 2030 similar to that in 2022 from the six selected industries. For the considered 2050 CO_2 sources, we adopted a scenario in which the considered industries would achieve the net-zero CO_2 emissions target; thus, we assumed that ammonia, hydrogen, and iron and steel will be decarbonized via clean hydrogen production and use in current and emerging technologies, such as Haber-Bosch and direct reduction of iron. We assumed reduced CO_2 emissions from the cement industry due to switching from fossil fuels to alternative low-carbon fuels for combustion. We also assumed reduced CO_2 emissions from natural gas processing because less natural gas will be used by 2050 (especially in residential and commercial sectors). The grid-mix simulation with additional electricity demand for CO_2 utilization is based on the available CO_2 sources in 2030 and 2050 as well as the corresponding SAF production potentials via selected CO_2 utilization pathways. The NREL team has used the Regional Energy Deployment System (ReEDS™) model to conduct capacity expansion modeling and outline the U.S. power sector planning from the present day to 2050. A standard power grid capacity expansion scenario with a high energy demand growth projection has been chosen as the baseline scenario, and a net-zero CO_2 emissions target for 2035 has been enforced. The SAF Pathway 1 facilities in each balancing area, accounting for 27% of the SAF target in 2050 as provided by the ANL team, have been converted to the energy demand for SAF fuel production and incorporated into ReEDS. Additionally, a sensitivity analysis has been conducted considering SAF targets of 10%, 15%, and 20% in 2050 to compare the power grid impacts of different SAF targets. The outputs of power system capacity and transmission expansion, along with the identified SAF demands, have been passed to the power system production cost model for daily grid operation analysis. The resulting electricity costs, locational marginal prices, and marginal generation mix will be provided to the TEA/LCA project to adjust the TEA and LCA factors. Further, the SAF facility siting constraints identified through the grid analysis will be provided to the ANL team to optimize the selection of the SAF facility siting.

- 1.5 Potential impact. This study quantifies the potential CO_2 reductions in the aviation sector by producing low-carbon SAF. Such a methodology can be adopted to decarbonization scenarios of other fuels and chemical markets. This study will provide information on key external factors that will impact the market potential for CO_2 utilization technologies. The project's outcomes, in conjunction with the TEA/LCA project's outcomes, will provide understanding of the market potential of a CO_2 utilization industry, the associated costs and environmental implications, and the potential technical and market barriers to inform future R&D decisions. This project's outcomes will also provide DOE and other stakeholders with an understanding of CO_2 sources; impacts on the grid by increasing loads; and the trade-offs between transporting CO_2, electricity, possible intermediates (e.g., H_2), and CO_2 utilization products that are necessary for siting. It will quantify regional and national environmental benefits and trade-offs as well as potential impacts on human health, gross domestic product, and job distribution. All these factors provide the essential information necessary to determine the priority for future CO_2 utilization research, development, and demonstration projects, whether funded by the government or private industry. Because this project is analyzing both mid- and long-term time frames, the information will be useful in considering the evolution of a CO_2 utilization industry over the next 30 years.

- 1.6 Additional information regarding other potential unforeseen consequences and mitigation strategies. A significant amount of clean electricity demand may increase the electricity cost. This is a major cost driver for CO_2 utilization products. This is being investigated by NREL as part of grid simulations.

Comments 2: The project aims to quantify the effect of carbon sources (capture cost and transportation) and energy sources (cost and carbon footprint) on CO_2 to SAF conversion. The goal is to identify possible locations for CO_2-to-SAF based on two key paths: (1) low-temperature electrolysis to produce syngas followed by fermentation and (2) water-gas shift followed by the Fischer-Tropsch process.

Progress has been made in identifying CO_2 and energy sources at different locations. It is unclear how the final goal can be achieved within the timeline of the project. It is also unclear how societal impacts are evaluated. Some aspects that may affect the overall process, including CO_2 purity and product distribution, have not been considered/discussed.

Answers:

- 2.1 It is unclear how the final goal can be achieved within the timeline of the project. The project team is on track to complete tasks according to the project timeline. The project completion date is the end of September 2024. The team has already identified 2050 potential CO_2 sources and is currently modeling the additional electricity demand for the 2050 SAF production scenario. Our target is to complete the 2050 CO_2 utilization SAF production scenario (including electricity costs, marginal generation mix, CO_2 sources, and SAF production potential by CO_2 utilization) by the end of this year. The evaluation of the EEEJ implications of deploying CO_2 utilization technologies is scheduled to start in July 2023 because it requires information from the 2050 modeled scenario.

- 2.2 It is also not clear how societal impacts are evaluated. We appreciate the reviewer for raising this valuable question. In fact, the societal impact assessment can be divided into our proposed Task 5, the assessment of air quality impact and public health impacts, and Task 6, the assessment of socioeconomic impact. These tasks will be addressed in Budget Period 3; however, we are pleased to provide the proposed assessment method here. For Task 5, the focus is on assessing the regional air quality and public health impacts associated with long-term exposure to PM 2.5 emissions from various sources related to CO_2 utilization pathways. This is achieved using the InMAP air quality model. The model provides fine-resolution and demographic-specific estimates of air quality impacts, which are important for EEEJ analysis. The analysis incorporates criteria air pollutant emissions and siting information to create location-specific inputs for InMAP. The concentration-response function is used to estimate health impacts considering changes in PM 2.5 concentration. The output metrics include changes in population-weighted exposure to PM 2.5, net health impacts, and corresponding economic valuations by different demographics and income levels. For Task 6, the socioeconomic impact assessment focuses on evaluating the economywide impacts of industry-scale deployment of preselected CO_2 utilization technologies. This is done using a regional version of the BEIOM macroeconomic model, which considers supply chain interactions and estimates socioeconomic and environmental impacts. Demographic and economic data from official sources are collected and modeled to forecast the baseline U.S. economy. The preselected CO_2 utilization technologies are specified in BEIOM using process-level data from the TEA/LCA project. Additional data collection is conducted to detail the primary supply chain industries and perform sensitivities to scenarios and electricity generation mixes.

- 2.3 Some aspects that may affect the overall process, including CO_2 purity and product distribution, have not been considered/discussed. We have considered the impacts of CO_2 purity and transportation to the CO_2 utilization site as follows. CO_2 purity: CO_2 purity from different industries was considered and reflected by the difference/variation in CO_2 capture costs (i.e., low CO_2 capture cost for high-purity CO_2 and high CO_2 capture cost for medium-purity CO_2). In addition, we considered CO_2 transportation cost with different scales and distances. We analyzed the cost of CO_2 capture, compression, and transportation for various CO_2 sources in the 2030 CO_2 utilization scenario. We are currently analyzing these costs for the 2050 scenario. Product (SAF) distribution: We have selected the potential SAF production locations considering three criteria: (1) electricity cost, (2) proximity to CO_2 sources, and (3) proximity to the jet fuel production in refineries. Criteria (1) and (2) are related to SAF production cost, and criteria (3) considers SAF markets. We can use the current blending facilities and jet fuel pipeline network in the United States by locating SAF facilities near the current refineries producing jet fuel.

Comments 3: The project uses a cross-sector modeling framework assessing location-specific resource availability to determine viable markets for CO_2 utilization technologies for SAF production. A key strength of this project is the close collaboration with other projects in the CO_2RUe, especially the other modeling and analysis groups, which provided the 2233 TEA/LCA metrics used in the cross-sector modeling. The project has already made significant progress, identifying three preliminary sites for CO_2 utilization with the correct balance of grid electricity capacity and cost, proximity to CO_2 resources, and proximity to jet fuel refineries. Future immediate plans appropriately focus on expanding the model to include emissions inventory analysis and estimated delivery and storage costs for hydrogen and reduced CO_2 intermediates. It remains unclear how the EEEJ component will be integrated into the cross-sector modeling. The timeline for onboarding this component is not until Year 3 of the project, but no approach was discussed as to how this would be integrated and weighted into the current cost-based models. Although pilot-scale implementation of CO_2 utilization is not part of the CO_2RUe portfolio, this project nonetheless provides an important and impactful contribution to the consortium by assessing the feasibility of implementing CO_2 utilization technologies at scale in optimal location-specific markets based on technology performance targets.

Answers:

- 3.1 It remains unclear how the E component will be integrated into the cross-sector modeling. The timeline for onboarding this component is not until Year 3 of the project, but there was no approach discussed as to how this would be integrated and weighted into the current cost-based models. We thank the reviewers for raising this question. The integration of the EEEJ components into the cross-sector modeling will be addressed in our proposed Task 5 and Task 6, which will be delivered in Budget Period 3. In Task 5, the focus is on assessing the regional air quality and public health impacts associated with long-term exposure to PM 2.5 emissions from various sources related to CO_2 utilization pathways. This is achieved using the InMAP air quality model. The model provides fine-resolution and demographic-specific estimates of air quality impacts, which are important for EEEJ analysis. The analysis incorporates criteria air pollutant emissions and siting information to create location-specific inputs for InMAP. The concentration-response function is used to estimate health impacts considering changes in PM 2.5 concentration. The output metrics include changes in population-weighted exposure to PM 2.5, net health impacts, and corresponding economic valuations by different demographics and income levels. In Task 6, the socioeconomic impact assessment focuses on evaluating the economywide impacts of the industry-scale deployment of preselected CO_2 utilization technologies. This is done using a regional version of the BEIOM macroeconomic model, which considers supply chain interactions and estimates socioeconomic and environmental impacts. Demographic and economic data from official sources are collected and modeled to forecast the baseline U.S. economy. The preselected CO_2 utilization technologies are specified in BEIOM using process-level data from the TEA/LCA project. Additional data collection is conducted to detail the primary supply chain industries and perform sensitivities to scenarios and electricity generation mixes.

Comments 4: Quantification of resource (feedstock and renewable electricity) availability and costs for CO_2 conversion to fuels is extremely important to guide development and deployment, and the project is moving in the right direction. Following are a couple of comments: The team shows the advantages of the preferred pathway (LTE – syngas fermentation – EtOH to SAF) with the pathway based on reverse water-gas shift reaction. It seems that another pathway (LTE – CO_2 H_2 – MeOH) may be more cost-competitive and should be used as a base case. Second, localization of the distributed SAF production (close proximity to major airports, delivery infrastructure) should be analyzed. I also recommend considering water resources.

Answers:

- 4.1 The team shows the advantages of the preferred pathway (LTE – syngas fermentation – EtOH to SAF) with the pathway based on reverse water-gas shift reaction. It seems that another pathway (LTE – CO_2 H_2 – MeOH) may be more cost-competitive and should be used as a base case. The project is currently scoped to SAF production due to the large size of its market. In the future, we will evaluate CO_2 utilization for chemical production such as methanol because it is an important intermediate with broad applications and also a potential marine fuel decarbonization application.
- 4.2 Second, localization of the distributed SAF production (close proximity to major airports, delivery infrastructure) should be analyzed. We analyzed the SAF markets and infrastructure in our research. In particular, we considered (1) proximity to the current jet fuel distribution infrastructure and (2) proximity to the end users (i.e., blending facilities connected to infrastructure). Because the jet fuel pipeline is already well distributed from the jet fuel refineries to the airports, we assumed that the current jet fuel pipeline network in the United States will be used for SAF transportation to various markets, and hence we located CO_2 utilization SAF facilities near the current jet fuel refineries, where SAF will be replacing or blended with the petroleum jet fuel.
- 4.3 I also recommend considering water resources. Water resources are analyzed in parallel in the other project (WBS 2.1.0.506 and WBS 2.1.0.507) that we are closely working with.

Comments 5: The specific goals of this project were not clearly communicated. Slide 9 sets the stage at a very high level, but beyond that, the reviewers need to go to the quad chart to see the goals. Because this project followed WBS 2.1.0.304, it would have been useful to hear more about how this project differed from the previous one. I was left wondering if the work was significantly distinct or simply looking at the same issue in a slightly different way. More collaboration and communication between these two projects would have helped highlight and differentiate their added value to the program. I see that mentioned on Slide 20, but it was not clear from the presentation. In regard to progress and outcomes, I’ve given this project a three because although they have made good progress toward their goals, little mention was made of risk mitigation and challenges. This left me with the impression that the work could have been more challenging.

Answers:

- Three projects (WBS 2.1.0.504 and WBS 2.1.0.505, WBS 2.1.0.506 and WBS 2.1.0.507, and WBS 2.1.0.304) are closely coordinated to align and interface their different scopes and system boundaries. This project (WBS 2.1.0.504 and WBS 2.1.0.505) focuses on potential CO_2 and clean power for SAF production, the cost of their supply to SAF production facilities, and SAF market size and distribution to end users. WBS 2.1.0.506 and WBS 2.1.0.507 use the cost of power and CO_2 supply to the SAF facility from the first project and evaluate SAF production cost, water use, and GHG emissions throughout the SAF value chain using a bottom-up TEA, LCA, and water analysis approach. The feasibility study project (WBS 2.1.0.304) evaluates the feasibility of the entire CO_2 utilization landscape by considering the competition among multiple products and using information from the other two projects to complement the development of a comprehensive CO_2 utilization analysis portfolio.

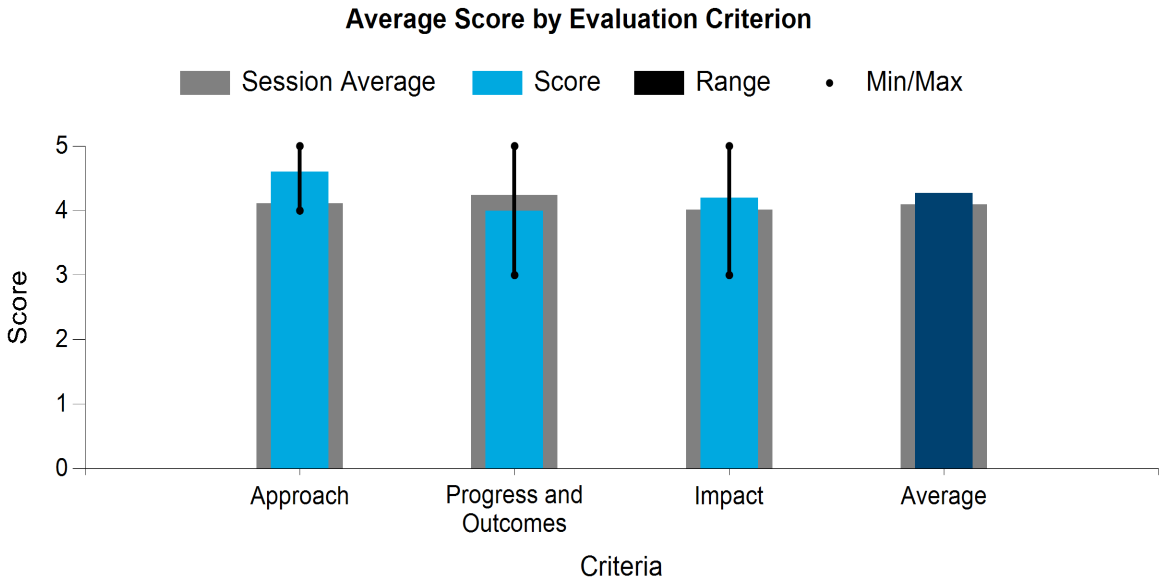
ECONOMICS AND SUSTAINABILITY OF CO_2 UTILIZATION TECHNOLOGIES WITH TEA AND LCA - NREL

Argonne National Laboratory

PROJECT DESCRIPTION

WBS:	2.1.0.507
Presenter(s):	Michael Wang
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$700,000

This project performs TEA, LCA, and water analysis of CO_2 utilization technologies to address their costs and sustainability implications. The project leverages TEA capabilities at NREL; the Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET) LCA capabilities at ANL; and water modeling capabilities at ANL to develop analytic capabilities of TEA, LCA, and water for the CO_2RUe. The team incorporates the data sets from other projects of the CO_2RUe to produce the cost and energy/environmental results of CO_2 utilization technologies. The outputs of this project have been used by the other two analysis teams and the R&D teams of the CO_2RUe for improving cost and sustainability performance. Specific outcomes include: (1) TEA results with key cost drivers for CO_2 utilization technologies; (2) LCA results with an expanded, updated GREET CO_2 utilization LCA module for relevant CO_2 utilization technologies covering electricity generation, hydrogen production, and CO_2 sourcing; and (3) a compilation of analyses addressing regional water resource availability and stress for CO_2 utilization facilities using the water models. With the results from this project, BETO, CO_2RUe teams, other agencies, and industry will be able to present the value proposition of CO_2 utilization technologies and identify bottlenecks/hot spots of costs and the sustainability of CO_2 utilization technologies for improvements.



COMMENTS

- The approach of incorporating water analysis into the investigation of CO_2 utilization technologies will provide key information to the community. Expanding and updating GREET is extremely important and will make a wide impact. More communication between the groups in the CO_2 consortium could be fruitful. Additional information/questions for further assessment:

Risk management:

- Additional information regarding how the individual unit operations are designed and modeled
- Additional information regarding the analysis of this group and how it guides and communicates with the CO_2 consortium and industry partners regarding their target products, reactor configurations, and operating conditions.

Potential impact:

- More information regarding the analysis of CO_2 electrolysis versus other methods to produce target products
- More information regarding the analysis of CO_2 electrolysis versus other methods to produce SAF.

- This project aims to perform TEA, LCA, and water analysis to analyze CO_2 utilization technologies. Several pathways for CO_2 conversion have been considered. Results for energy inputs and carbon footprint have been discussed; however, the connection between the energy input and carbon footprint with key performance metrics has not been discussed. Therefore, it is unclear how the TEA/LCA can help direct the research direction. It is unclear if the carbon footprint for CO_2 capture is considered. It is also unclear how the performance for each individual step is considered.

- This project represents the third portion of the TEA/LCA component of the CO_2RUe. This project specifically focuses on the TEA and LCA of different CO_2 utilization pathways to SAF. The goal of the project is to address the cost and environmental impacts of the proposed technologies within the CO_2RUe for CO_2 utilization. A specific strength of the project is the close collaboration with the analysis and research teams within the CO_2RUe in defining conversion processes and performance metrics for consortium-relevant modeling. The incorporation of water stress analysis is another key strength of this project and highlights the close collaborations with the other analysis projects in the CO_2RUe, especially with WBS 2.1.0.504. This project is an important component of the CO_2RUe, with significant impact in validating the feasibility of and informing research priorities for proposed CO_2 utilization technologies and processes.

- The team is doing a good job modifying the GREET model to additional conversion pathways. Will this model be available to the public (it was stated only for the consortium teams)? It is good that water availability is included in the analysis, but competition for the resources should be included. It is not clear which capacity factor is included in the cases with \$0.02/kWh electricity cost. Negative CO_2 emissions should be taken with a grain of salt because this loophole could be closed in the future. Carbon emissions of renewable natural gas (RNG) are probably underestimated (high fugitive methane leakage due to distributed and poor technology). It is strange that the cost of pathways using renewable H_2 is lower than the baseline. I recommend putting more effort into analyzing Pathway 5 as the most probable promising alternative.

- This project has a very strong plan, with talented researchers invested in addressing questions on which factors impact the competitiveness of CO_2-based SAF production. The analysis is detailed and thorough, leaving little question of the results or their significance. The part where this project suffers is the same as WBS 2.1.0.504: uniqueness. How different is this work from that project? It seems as though the three analysis projects have shared interests (as expected), but more energy spent on differentiating each project would be helpful in assessing how much value the three projects yield for BETO and the public as a whole and individually.

PI RESPONSE TO REVIEWER COMMENTS

- Comments: The approach of incorporating water analysis into the investigation of CO_2 utilization technologies will provide key information to the community. Expanding and updating GREET is extremely important and will make a wide impact. More communication between the groups in the CO_2 consortium could be fruitful. Additional information/questions for further assessment: risk management—additional information regarding how the individual unit operations are designed and modeled, additional information regarding the analysis of this group and how it guides and communicates with the CO_2 consortium and industry partners regarding their target products, reactor configurations, and operating conditions; potential impact—more information regarding the analysis of CO_2 electrolysis versus other methods to produce target products, more information regarding the analysis of CO_2 electrolysis versus other methods to produce SAF.

  Responses: The project encompasses key metrics, including economic feasibility and environmental impacts, such as life cycle GHG emissions and water consumption/stress. We aim to develop an extended version of GREET that includes all significant CO_2 utilization pathways with all relevant CO_2 utilization technologies. We will maintain active communication within the consortium and engage with external stakeholders to enhance the value and applicability of our analysis results. When it comes to risk management, a critical issue is associated with data availability. Because CO_2 utilization technologies are still in the early stages of R&D, our analysis heavily relies on process modeling and/or limited experimental data in the literature and as provided by R&D teams. To mitigate this risk, we plan to actively engage with the R&D teams within the consortium. Through the engagement, we will gain deeper insights into conceptual process designs, access timely developed data, refine our parameters, and improve the representation of our analysis. Individual unit operation design is based on both active collaborations between the R&D teams and process engineers and engineering judgment from the TEA team. Additionally, we recognize the importance of engaging with external industry stakeholders who can provide valuable input, expertise, and reality checks. Their inputs will further enhance the quality and reliability of our analysis by validating and enriching the data and process-related knowledge upon which we rely. We follow an iterative process throughout the project with the consortium. Once we generate analysis results for a technology, we inform the corresponding R&D team and engage in discussions to identify opportunities for improving the economic and environmental metrics. These discussions help us refine parameters, update processes, and improve configuration to reflect R&D efforts. Given that the project includes all major CO_2 utilization pathways, this allows us to evaluate and compare their respective benefits, challenges, and opportunities for improvements. The iterative process enables us to continuously refine our methods and results, leading to more informed R&D decision-making and ultimately maximizing the consortium's impact on both economic and environmental fronts.

  Comments: This project aims to perform TEA, LCA, and water analysis to analyze CO_2 utilization technologies. Several pathways for CO_2 conversion have been considered. Results for energy inputs and carbon footprint have been discussed; however, the connection between energy input and carbon footprint with key performance metrics has not been discussed. Therefore, it is unclear how the TEA/LCA can help direct the research direction. It is unclear if the carbon footprint for CO_2 capture is considered. It is also unclear how the performance for each individual step is considered.

  Responses: Our team has been conducting comprehensive analyses of the economic and environmental impacts associated with CO_2 utilization pathways, employing TEA and LCA methodologies. As highlighted by the reviewer, the carbon footprint (life cycle GHG emissions) of these pathways significantly varies based on the type and amount of energy used. As we mentioned in the approach section of our presentation, this is an iterative process, and the TEA/LCA is directly linked with R&D to help guide the research direction. Because of the presentation time limitation, we did not present the details of the TEA and LCA. For instance, key cost drivers and key carbon reduction strategies were analyzed in detail for each selected pathway and have been communicated with the R&D teams to provide specific guidance on cost reduction or sustainability improvement strategies. This communication enables us to identify R&D activities on the major cost and emissions contributors for each pathway and guide discussions on potential strategies for further reducing these key performance metrics. In our LCA, the energy use and associated emissions of CO_2 capture and transportation are included. Note that we used a consistent LCA system boundary and methodology as used in other BETO-funded projects, ensuring comparability and consistency across studies. By employing rigorous analysis methodologies, collaborating with the consortium R&D teams, and using consistent LCA practices, we aim to provide robust and reliable results that will inform R&D decision-making to maximize the effectiveness of CO_2 utilization pathways in reducing emissions and advancing sustainability goals.

Comments: This project represents the third portion of the TEA/LCA component of the CO_2RUe. This project specifically focuses on the TEA and LCA of different CO_2 utilization pathways to SAF. The goal of the project is to address the cost and environmental impacts of the proposed technologies within the CO_2RUe for CO_2 utilization. A specific strength of the project is the close collaboration with the analysis and research teams within the CO_2RUe in defining conversion processes and performance metrics for consortium-relevant modeling. The incorporation of water stress analysis is another key strength of this project and highlights the close collaborations with the other analysis projects in the CO_2RUe, especially with WBS 2.1.0.504. This project is an important component of the CO_2RUe, with significant impact in validating the feasibility of and informing research priorities for proposed CO_2 utilization technologies and processes.

Response: Thank you for your positive comment.

Comments: The team is doing a good job modifying the GREET model to additional conversion pathways. Will this model be available to the public (it was stated only for the consortium teams)? It is good that water availability is included in the analysis, but competition for the resources should be included. It is not clear which capacity factor is included in the cases with $0.02/kWh electricity cost. Negative CO_2 emissions should be taken with a grain of salt because this loophole could be closed in the future. Carbon emissions of RNG are probably underestimated (high fugitive methane leakage due to distributed and poor technology). It is strange that the cost of pathways using renewable H_2 is lower than the baseline. I recommend putting more effort into analyzing Pathway 5 as the most probable promising alternative.

Responses: The main objective of incorporating the CO_2RUe pathways into the GREET model is to assess and enhance the environmental metrics of the CO_2 utilization conversion technologies under consideration by the consortium; however, our team also has plans to include these pathways in the public version of the GREET model, subject to the decision of the consortium and BETO. Thus, these CO_2 utilization pathways will be available to others via public release of the GREET model. We agree that water is a critical component of the sustainable implementation of CO_2 utilization technologies. In response to the reviewer’s comments on the competition for water, we agree that the competing water use from all sectors is a key issue. In fact, water tools used in this project are capable of assessing the impact. The Available Water Remaining for the United States model is indeed intended to address the impact on regional water supply and demand by different competing water uses in specific regions; the WATER estimates changes in freshwater available to other economic sectors after meeting water demand from CO_2 utilization technologies at a local level. Further analysis of reclaimed water use by CO_2 utilization technologies represents the degree to which the competing demand can be reduced. Regarding the avoided GHG emissions credits of RNG, we plan to conduct a thorough review of the conditions and parameters to affect the so-called counterfactual scenario emissions of waste management practices. This will help revise RNG avoided emissions credits. As the comment correctly points out, it is essential to prevent overestimating the emissions credits attributed to the production of RNG and to fully account for the methane leakage of the RNG supply chain. The cost of $0.02/kWh for renewable electricity is from the estimated cost of renewable electricity in the next 10 years. The capacity factor is assumed to be 90% onstream. While the cost or the capacity factor for renewable electricity is optimistic, we used it in our TEA as a case of continuing success of renewable power deployment as observed in the past 10 years globally and domestically. In addition, variations of these parameters were included in the sensitivity analysis to address the uncertainty, which is part of the project efforts but was not included in the presentation because of time constraints. Similarly, our use of low-cost renewable hydrogen is based on the premise of low-cost renewable power and significant cost reduction in hydrogen electrolysis that reflect the success of DOE and the federal government's significant R&D investment in renewable hydrogen in the next 10 years. Our FY 2023 analysis has been centric on Pathway 5 and cross-comparing direct or indirect CO_2-to-methanol pathways using a consistent analysis basis. We sincerely appreciate the comment and will definitely put more emphasis on analyzing this pathway.

Comments: This project has a very strong plan, with talented researchers invested in addressing questions on which factors impact the competitiveness of CO_2-based SAF production. The analysis is detailed and thorough, leaving little question of the results or their significance. The part where this project suffers is the same as WBS 2.1.0.504: uniqueness. How different is this work from that project? It seems as though the three analysis projects have shared interests (as expected), but more energy spent on differentiating each project would be helpful in assessing how much value the three projects yield for BETO and the public as a whole and individually.

Responses: The consortium leadership has defined the scope, the boundary, and the interrelationships among the three analysis projects to ensure coordinated efforts and to avoid potential duplication among them. This project covers the TEA, LCA, and water analysis (WBS 2.1.0.506 and WBS 2.1.0.507) with a bottom-up approach, starting with process-level modeling that encompasses CO_2 utilization conversion technologies and other relevant life cycle stages, such as CO_2 capture and transportation. Thus, detailed TEA and LCA are performed to provide guidance to the R&D teams for cost reduction and sustainability improvement strategies. Our goal is to provide information to and incorporate R&D progress data from the R&D teams of the consortium. Also, we aim to bridge data gaps in TEA/LCA with relevant data from industry experts and stakeholders in addition to the data from the consortium's R&D teams. We strive to make the TEA/LCA/water analysis an integral part of the consortium's efforts to develop credible, relevant cost and sustainability results to rally policy and public support of CO_2 utilization technology deployment. The TEA/LCA data from this project are fed to the market/resources assessment project (WBS 2.1.0.504 and WBS 2.1.0.505) to (1) analyze how much renewable power and CO_2 resources would be needed for CO_2 utilization plants to meet BETO's SAF production goal; (2) determine the optimal regional locations of CO_2 utilization plants and potential transportation of CO_2, renewable electricity, and/or renewable hydrogen; and (3) address potential constraints of regional availability for all major resources. Additionally, the feasibility study team (WBS 2.1.0.304) takes a more holistic approach to evaluate the technology feasibility of the entire CO_2 utilization landscape by considering the competition among multiple products, which contributes to the development of a comprehensive portfolio. Detailed TEA/LCA data from this project are also fed to the feasibility study team (WBS 2.1.0.304) so that more holistic conclusions can be distilled for providing road-mapping strategies for major CO_2 utilization potentials.

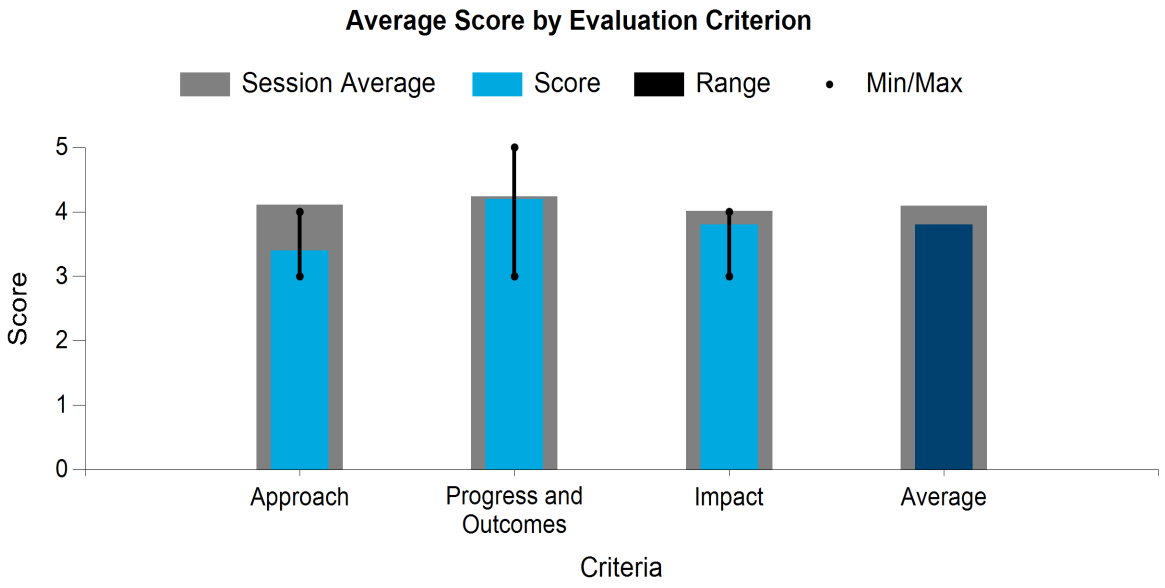
CO_2 UTILIZATION: THERMO- AND ELECTROCATALYTIC ROUTES TO FUELS AND CHEMICALS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.316
Presenter(s):	Jack Ferrell
Project Start Date:	11/01/2020
Planned Project End Date:	09/30/2023
Total Funding:	$300,000

Existing biomass conversion processes, such as fermentation to produce ethanol, produce very pure industrial sources of CO_2. In fact, domestic ethanol biorefineries are the largest single-sector supplier of CO_2 to the merchant gas markets. This provides a unique opportunity for the bioenergy industry: to reduce the cost (MFSP) of the primary product (ethanol) by valorization of this large CO_2 waste stream. In this project, first, we work closely with TEA/LCA projects to identify/quantify the largest risks for the commercialization of low-temperature CO_2 electrolyzers. Next, we perform targeted experimental work to address the identified risks. While there has been significant recent interest in this field, challenges remain before this process can be performed industrially. The goal of this project is ultimately to enable long-term and stable operation at high current densities for low-temperature CO_2 electrolysis. During the past 2 years, we have helped identify risks, incorporated these risks into TEA/LCA, and published this work in *Energy & Environmental Science*; these risks have also been incorporated into the strategic plan for the CO_2RUe. We have also performed research on cathode electrocatalyst degradation and carbon corrosion. Moving forward, we plan to focus on catalyst degradation. By addressing the persistent issues facing these technologies, we aim to enable the economic electrochemical conversion of CO_2.



COMMENTS

- The approach of doing experimental research guided by TEA is important for risk mitigation, and focusing on various key real-world drivers is valuable. Their work on testing MEAs with online gas chromatography units will provide key information regarding the conversion and migration of CO_2 and the mass balance of the reaction. I would like to see more communication with the other projects that are working on the increased stability of ECO_2R. Additional information/questions for further assessment:

Risk management:

- Additional information on testing and methods to test the system in real-world conditions; R&D road map to achieve their goals
- More information regarding other cost drivers and other target goals used in other groups within the consortium.

Potential impact:

- More information regarding the justification of research on carbon paper and the translatability of their findings to other catalysts.

- The goal of the project is to identify and de-risk low-temperature electrocatalytic CO_2 reduction to CO. Efforts have been made to understand the corrosion of carbon at the anode side. The project also aims to understand the degradation of the catalyst at the anode side using *ex situ* characterization. Carbon corrosion is quite common, and often titanium porous transport has been used to overcome this problem. Would it be more efficient to consider using titanium instead of porous carbon support for the anode? A lifetime of more than 4 years would be challenging for evaluation; would you consider any accelerated testing to understand the catalyst degradation? Catalyst degradation can come from the failure of other parts in the electrolyzer, such as the membrane, or leaching of anode, or salt formation. It would be more impactful if catalyst degradation was studied in parallel with other components.

- The approach of this project is to closely collaborate with the analysis teams in the CO_2RUe to identify key risks in CO_2 electrolysis commercialization and then to conduct targeted experiments to address those risks. Initial studies have focused on MEA durability testing, which has been identified as a key technology gap in CO_2 utilization. To assess durability, the project has developed an MEA testing system with online detection at both the anode and cathode for full mass balance and *ex situ* microscopic and spectroscopic analysis of component degradation. Key findings of the project include 100-hour durability of the catalyst materials during operation within the MEA testing system but appreciable degradation of the carbon support used in the gas diffusion electrode (GDE). One concern with the project approach lays with the scale of the MEAs tested. It is unclear if issues determined at the 5-cm^2 scale are translatable to larger-scale, 100–1,000-cm^2 systems. For example, many (but not all) larger-scale electrolyzers eschew the use of carbon supports in favor of tin, possibly limiting the impact of the initial studies. Another concern is that the timescale of the degradation measurements, 100 hours, is small on the scale of the proposed electrolyzer lifetime needs, meaning that some degradation pathways may be missed due to the short durability testing time. The short testing timeline highlights the need for developing accelerated lifetime testing protocols in the CO_2 electrolysis field, although such work is likely outside the scope of this project. Overall, this project plays an important role in the CO_2RUe of quantifying risks in emerging electrochemical CO_2 utilization pathways being explored within the consortium and in performing important studies to help mitigate these risks.

- Using CO_2 waste from biorefineries may indeed provide early opportunity for the deployment of CO_2 utilization due to the low-cost available feedstock and the possibility of having the single product stream (if the product is ethanol); however, high capital expenditures (CapEx) may be a showstopper for owners (payback period?). The proposed external testing of materials could potentially accelerate the development of durable MEAs; however, the results of the CO_2 electrolyzer generally showed much better durability than can be calculated from the reported *ex situ* tests, which demonstrated extremely fast degradation. So, it is unclear how relevant these results are to real-life electrolyzer durability, and the final milestone though this method could be possibly used for comparison of different materials. It is absolutely necessary to identify key degradation factors and establish a transfer function between *ex situ* and *in situ* testing, especially for commercially meaningful current densities. In addition, the duration of tests (100 hours) is clearly insufficient to identify the root causes of degradation. The demonstrated potential cost-competitiveness is based on not yet demonstrated current densities, so it is useful to monitor the current cost of SAFs using experimental performance and durability parameters. It is also unclear how the team is going to quantify technology risks.

- This is an important study looking into key factors that influence MEA degradation and performance during runs. To that end, the researchers have developed an *ex situ* carbon corrosion test relevant to their anodes. Unfortunately, significant mass loss and carbon corrosion were observed in only 24 hours. The project proposes testing lower voltages for longer periods of time. Although understanding the correlation between the demand on the cell and degradation is important, we need to be going up in voltage over time to achieve economic feasibility.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their time and feedback. We agree that increasing the durability of low-temperature CO_2 electrolysis systems is critical for moving this technology forward, and our close collaboration with TEA/LCA projects has highlighted the importance of achieving increased electrolyzer lifetime. Beyond lifetime, recent TEA/LCA (which has been incorporated into the strategic plan for the CO_2RUe) also shows that performance increases are needed, such as increasing current and single-pass conversion and decreasing voltage and electrolyzer cost. Regarding the carbon corrosion work, the high mass loss presented was collected at a high anode voltage of 2 V, which is an accelerated condition leading to higher corrosion rates. We have used higher voltages for the development of the *ex situ* carbon corrosion test and are currently exploring longer experiments (>1 month) at realistic anode voltages (~1 V). We also agree that it is likely that a metal-based anode (e.g., porous transport layer) will be needed to achieve sufficient lifetime in commercial electrolyzer devices; however, the majority of the field is currently using carbon-based GDEs on the anode. Our goal with the carbon corrosion work is to highlight that carbon corrosion is an issue under CO_2 electrolysis conditions and ultimately to provide recommendations on the types of experiments where carbon should be avoided on the anode. We hope that this work will encourage the community to switch to non-carbon materials on the anode, because moving toward commercially relevant MEA architectures sooner will accelerate the path toward commercialization. We also agree that the development of accelerated durability tests remains a large gap for CO_2 electrolysis. This will require a large, dedicated effort to be successful, and we agree that multiple degradation routes should be studied in parallel during longer-duration durability testing. Further, different routes to accelerating different degradation pathways (e.g., voltage cycling, increased molarity of solutions, increased temperature, increased voltage) will need to be probed to arrive at accelerated durability tests.

ELECTROLYZERS FOR CO_2 CONVERSION FROM BIOSOURCES

Dioxide Materials

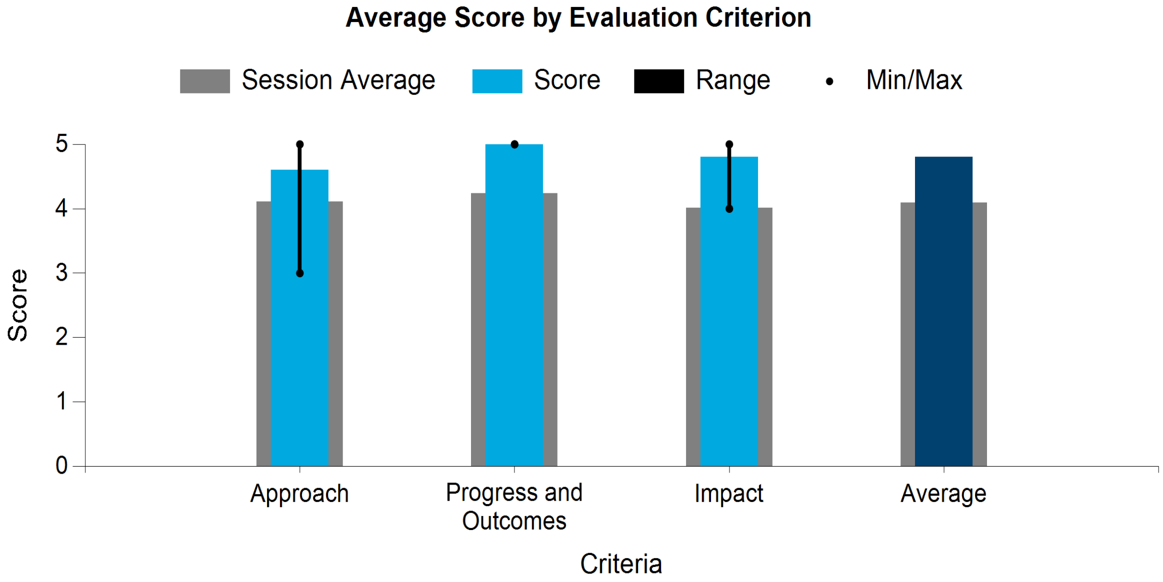
PROJECT DESCRIPTION

WBS:	2.3.1.418
Presenter(s):	Rich Masel
Project Start Date:	10/01/2020
Planned Project End Date:	02/28/2024
Total Funding:	$3,125,000

Dioxide Materials' anion exchange membrane electrolyzers for CO_2 reduction to CO have demonstrated the highest Faradaic efficiency and stability of any CO_2 electrolyzer reported in the literature. To interface with an industrial-scale biorefinery, the surface area must be increased to at least 1 m^2 and scaled to tens of megawatts. The performance is also reduced due to components in fermentation flue gas. In the proposed work, we will:

- Create electrolyzer designs that are scalable to the megawatt scale.
- Develop improved catalyst/ionomer layers that are robust to changes in flue gas composition.
- Integrate the improved electrolyzer with a CO fermenting microbe.

If successful, this project will create scalable electrolyzers that can be combined with bioreactors to convert biorefinery CO_2 into biofuels and products, thereby achieving BETO's goals of producing fuel.



COMMENTS

- Investigating the effects of scaling ECO_2R is as important as studying the individual processes, such as detailed catalyst degradation. The information they have gained from their approach of scaling a CO_2 electrolysis reactor and testing the performance and failure mechanisms in a larger system is valuable to the CO_2 utilization field. They are addressing effects such as humidity in the system, which will be able to be applied to other projects scaling ECO_2R.

  It would be great to see increased outreach and knowledge exchange of their investigations and results. Additionally, contributing to a facility where their system could be used by different groups to quickly gain initial insights into challenges associated with scaling may be helpful. Additional information/questions for further assessment:

Risk management:

- Additional information regarding the system; current and target flow rates of CO_2, mass balance calculations; additional information regarding CO_2 crossover, impurity management at scale, and analysis of the active catalyst (STY)
- Additional information regarding the target product—a performance comparison of when the system is optimized for production of CO versus a specific ratio of H_2:CO
- Additional information regarding experiments, the reproducibility of the system, and the duration and number of experiments with the 1,000-cm^2 electrolyzer
- Detailed plans for temperature management and further elaboration on the plans for redesigning flow and how it will scale.

Potential impact:

- Additional analysis regarding the use of specialized GDE in this system.

- The project aims to develop electrolyzers for CO_2 conversion to CO using bio-derived CO_2. Overall, very impressive progress in scaling up the electrolyzer has been achieved (stability of over 100 hours with 1,000-cm^2 electrolyzer). A critical challenge in scaling up this technology has been identified. The integration of the CO_2 electrolyzer with the biological reactor has been demonstrated. While most key performance metrics have been demonstrated, CO_2 crossover has not been quantified and addressed.
- This project focuses on scaling electrolyzer cells from the 250-cm^2 active area size commercially available today to a 1,000-cm^2 active area, which has been identified as the appropriate size for deployable cell stacks to convert CO_2 from biorefineries to CO for downstream bioconversion. A key part of the project approach is performing deconstructive tests in which failing components from the 1,000-cm^2 active area electrolyzers are removed and loaded into small test cells to determine failure mechanisms. The project makes use of the NREL process development unit for the large cell testing. The project team has designed eight 1,000-cm^2 cells and built three. All three met the milestone goals of >200-mA cm^2 for 100 hours with >90% selectivity. The project team observed failure at a longer time, however, and was able to identify several failure modes due to thermal hot spots in the membrane, mechanical failures of the cathode gas diffusion layer, and membrane ruptures. The project team has been able to address many of these failures with changes to the electrolyzer cell design or through modifications to the gas diffusion layer and membranes, including manufacturing stronger membranes. The project approach also examines which parameters influence product selectivity by running the electrolyzers with CO, CO_2, and H_2 gas mixtures from initial performance tests and tuning selectivity by modifying electrolyzer components such as humidity and catalysts. Through this process, the project team has identified that humidity plays a crucial role in catalyst utilization and electrolyzer performance. Immediate future goals of scaling to 1,000 hours of performance for the large cells are appropriate. This project has made excellent progress on an important topic of scaling electrolyzers, and it will have significant impact in practical CO_2 conversion and utilization.
- The team successfully built and tested a commercial-scale, 1,000-cm^2 cell in CO_2 reduction to CO with high Faradaic efficiency. An anion exchange membrane with increased strength has been developed. The durability milestone (100 hours at 200 mA/cm^2) has been met; however, the cell voltage was steadily growing, and the cell failed after 200 hours due to a cracked gas diffusion layer. This and other pathways of the electrochemical cell failure were established and studied, which is very important for commercial

deployment. Reaction selectivity was studied using a differential cell, and factors controlling the selectivity (e.g., relative humidity) were established. A major focus for future work should be on MEA quality control and durability (cell voltage and Faradaic efficiency).

- This was easily the most impactful presentation of those reviewed. It was refreshing to see a team invested in “breaking things and figuring out what went wrong.” Top marks for progress and innovation. I was also very pleased to see open communication from an industry partner like this.

PI RESPONSE TO REVIEWER COMMENTS

- I want to thank the reviewers for taking the time to review our program and for their constructive comments. The reviewers raised valuable points, and I do not disagree with anything they said. We have taken the reviewers’ suggestions. The major focus for future work will be on MEA quality control and durability (cell voltage and Faradaic efficiency). We are sending the system shown on slide 22 to NREL, as the first reviewer suggested.

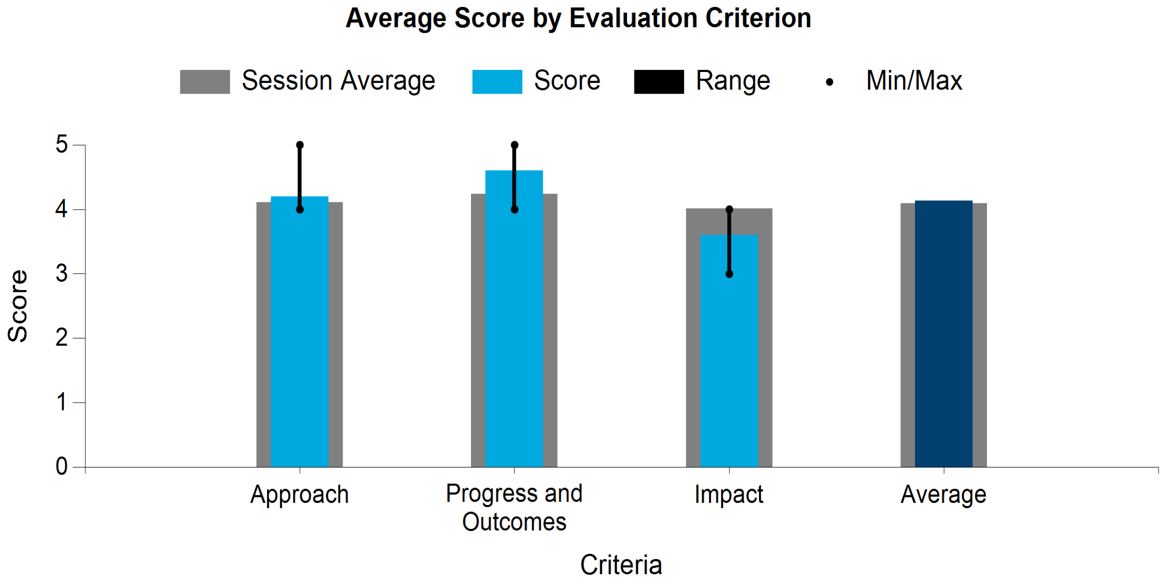
ELECTROCHEMICAL PRODUCTION OF FORMIC ACID FROM CARBON DIOXIDE IN SOLID ELECTROLYTES

University of Delaware

PROJECT DESCRIPTION

WBS:	2.3.1.421
Presenter(s):	Feng Jiao
Project Start Date:	10/01/2020
Planned Project End Date:	08/31/2024
Total Funding:	$3,135,186

The proposed work is divided into three distinct R&D phases, with clear milestones needed to progress the state of the art (SOA) for CO_2 electrolysis to formic acid. In particular, the work scope is directed at improving the activity, selectivity, and durability of individual components and a large-scale (>750-cm^2) electrolyzer. In Phase I, we will focus on the initial verification of the results from the team that stand out as the SOA in ECO_2R to formic acid. Here, we will use the bismuth catalysts, which have been able to show high selectivity (90% Faradaic efficiency to formic acid) at current densities of 100 mA/ cm^2 while also showing long-term stability (100 hours, continuous or noncontinuous interval operation) at an applied current density of 30 mA/cm^2. This phase is expected to be complete upon meeting the performance in a 5-cm^2 electrolyzer, as previously published. Phase II will focus on maintaining the high selectivity toward formic acid (90% Faradaic efficiency) while doubling the current density to 200 mA/cm^2 in a cell that is >100 cm^2. The stability of the system will also begin to be assessed at >200 hours (continuous or noncontinuous with interval system regeneration) to record potential degradation in terms of increased cell voltage and decreased Faradaic efficiency toward formic acid. The main goal is to achieve all these metrics in one cell, but individual performance metrics will be assessed to gain insights into which operating conditions lead to overall cell degradation (increasing voltage and decreasing selectivity to formic acid). The final phase of the project, Phase III, will translate the catalytic performance of the bismuth catalysts to an industrial electrolyzer. Here, the selectivity and activity (Faradaic efficiency and current density) of the previous phases will be maintained while focusing on translating this performance to a large (>750-cm^2) cell and operating for >1,000 hours (continuous or noncontinuous with interval system regeneration).



COMMENTS

- Approaching the design of a reactor that considers the energy intensity of electrolyte processing and greatly minimizes it is important to developing a commercial system. Testing has been done in larger electrodes (25 cm^2 and 100 cm^2), which increases the number of challenges; however, the information gained will help guide the R&D to investigate scaled systems. Additional information/questions for further assessment:

  Risk management:

  - More information regarding the amount and rate of formate oxidation in these systems compared to liquid electrolytes
  - More information regarding any other byproducts formed on the catalyst and their interaction with the solid electrolyte
  - More information regarding impurity management in the electrolyte and the interactions with the catalyst
  - More information regarding any temperature change within the catalyst/solid electrolyte.

  Potential impact:

  - Further information and analysis regarding the justification of using this approach over liquid electrolytes
  - Further details on the stability of the selectivity and carbon conversion percentage
  - Further details on the analysis of formate as an H_2 carrier.

- The proposed project focuses on producing formic acid from CO_2 reduction using solid electrolytes. Significant progress has been made in the area of catalyst development and TEA. Excellent publication outcome. The PIs have identified challenges with scaling up the solid-electrolyte layer. Several strategies have been tried and proposed. While impressive progress has been made, it is still unclear how the final milestone (demonstrate formic production with cell size >750 cm^2) can be achieved. A key challenge with using the solid-electrolyte layer is the high cell resistance. Together with current density, Faradaic efficiency, and stability, it is also important to set the target for cell voltage.

- The aim of this project is to scale electrolyzers using solid electrolytes for formic acid production to the >750-cm^2 sizes with stable 100-hour performance at >200 mA/cm^2 with 90% current density. This project approach builds from previous demonstrations of selective formic acid production by solid-electrolyte electrolyzers at the lab scale. The approach is well structured, with eight specific tasks divided into three phases: initial verification, catalyst and reactor scaling, and performance and durability testing at scale. The project team has made substantive progress, although they have run into significant technical challenges in the scale-up of solid-state interlayers and catalyst scale-up. The catalyst challenge has been overcome due to changes in synthesis routes, but challenges with scaling the solid-electrolyte interlayers have required a complete redesign of the interlayer structure. Still, the project team has managed to produce 100–250-cm^2 reactors with 15-hour stability for formate production at >90% initial Faradaic efficiency. Overall, the project has made good progress, especially given the low TRL level of the novel solid-electrolyte CO_2 electrolyzers compared to other electrolyzer technologies. If successful, this technology would have enormous impact. The solid-electrolyte CO_2 electrolyzers produce formic acid directly, which eliminates the need for downstream acidification and salt removal needed by the more conventional CO_2 electrolyzers that produce formate. It remains to be seen whether this technology can scale to the 750-cm^2 electrolyzer size with the necessary 100-hour performance stability, but the project has made promising initial progress in this direction.

- The team proposed a novel electrochemical cell structure with the incorporation of a porous layer, which allows for direct production of formic acid with high Faradaic efficiency at reasonable current density, albeit at high cell potential; however, this approach requires application of the IrO_2 anode catalyst, which may be an issue due to low iridium availability and competition with PEM water electrolyzers. The high variability of performance with time and the decrease of Faradaic efficiency should be greatly improved. The proposed novel operando diagnostic tool for overpotential breakdown is useful for electrolyzer development. The TEA shows some promise for this electrochemical method to be on par with conventional formic acid cost if all design parameters are achieved. Note that the prospective of using formic acid as a hydrogen carrier is overestimated, and the projected transportation cost is clearly wrong.
- This project is another example of an early-stage effort to explore novel electrolyzer technologies. As such, it is an important part of the consortia's portfolio as long as expectations are tempered around how much risk is baked into the proposal and the TRL of the technology being pursued. It was clear from the presentation that many challenges have been faced along the way but that measurable progress was being made despite those challenges.

PI RESPONSE TO REVIEWER COMMENTS

- Dear reviewers, thank you so much for your constructive comments. Below is a point-by-point response to all comments. We hope that your concerns are fully addressed.

  Comments: Approaching the design of a reactor that considers the energy intensity of electrolyte processing and greatly minimizes it is important to developing a commercial system. Testing has been done in larger electrodes (25 cm^2 and 100 cm^2), which increases the number of challenges; however, the information gained will help guide the R&D to investigate scaled systems. Additional information/questions for further assessment—risk management: more information regarding the amount and rate of formate oxidation in these systems compared to liquid electrolytes, more information regarding any other byproducts formed on the catalyst and their interaction with the solid electrolyte, more information regarding impurity management in the electrolyte and the interactions with the catalyst, more information regarding any temperature change within the catalyst/solid electrolyte; potential impact—further information and analysis regarding the justification of using this approach over liquid electrolytes, further details into the stability of the selectivity and carbon conversion percentage, and further details into the analysis of formate as an H_2 carrier.

  Reply: We appreciate the feedback provided by the reviewer. For clarity, we have separated and answered the concerns in the following list:

  - Formate oxidation has the potential to create significant losses in energetic efficiency. We plan to quantify this effect in future experiments by measuring CO_2 produced on the anode.
  - The only other possible byproducts formed are hydrogen and carbon monoxide. We quantify both products using gas chromatography. A typical working electrolyzer at the beginning of the test using bismuth catalyst will typically have <10% hydrogen Faradaic efficiency and <5% CO Faradaic efficiency. Both products are gaseous and do not cross over an intact polymer membrane; therefore, they cannot affect the solid electrolyte.
  - We have specific elemental characterization capabilities, such as X-ray fluorescence and inductively coupled plasma mass spectroscopy, to assay potential impurities in the product stream. Details regarding operating conditions and the performance stability of the system will become available as tests are completed.

- Temperature change is negligible at the laboratory-scale testing but will become more significant at the larger scales. The temperature increase is related to the overpotential, which can fluctuate during a long-term test. We find that the 100-cm^2 reactor can reach up to 35°C, but we have not yet tested the impacts. Further experimentation is needed. If detrimental, the interlayer deionized water flow can potentially also act as a cooling channel to keep temperatures homogenous.

- Our preliminary TEA shows a clear advantage in our novel design versus using a liquid electrolyte due to downstream separations cost. Further in-depth comparisons will be made in the comprehensive TEA and LCA.

- From our long-term testing at 25 cm^2, the Faradaic efficiency toward formate does decrease with respect to time. Further analysis will be performed to see if the stability of the selectivity can be improved or recovered through different methods. Because our current goal is to achieve high selectivity, we have not experimented with improving conversion. The current carbon conversion is ~2%. Analysis on an economically appropriate conversion will be performed in our comprehensive TEA.

- Thank you for the additional comments and feedback on using formic acid as a hydrogen carrier. This study was an interesting tangent our team analyzed. In relation to the project, note that our main project outcome is coupling formic acid to a bioreactor, not using it as a hydrogen carrier; thus, this project should only be judged based on the current market for formic acid and will be the focus of our comprehensive TEA in Task 8.

Comments: The proposed project focuses on producing formic acid from CO_2 reduction using solid electrolytes. Significant progress has been made in the area of catalyst development and TEA. Excellent publication outcome. The PIs have identified challenges with scaling up the solid-electrolyte layer. Several strategies have been tried and proposed. While impressive progress has been made, it is still unclear how the final milestone (demonstrate formic production with cell size of >750 cm^2) can be achieved. One key challenge with using the solid-electrolyte layer is the high cell resistance. Together with current density, Faradaic efficiency, and stability, it is also important to set the target for cell voltage.

Reply: We thank the reviewer for the comments. The identification of reliable methods to scale up the size of individual reactor components is critical for the success of this project in achieving large cell sizes, and therefore we have developed several different solid-electrolyte layer designs as a risk mitigation strategy. Activities in the upcoming quarters to reproduce the developed interlayer designs with suitable properties at the final cell size area will provide key information for the down-selection and optimization of the solid electrolyte. Further planned activities to refine the solid-electrolyte layer by manipulation of material properties—such as conductivity and porosity by choice of initial resin, binder, or substrates—will inform achievable cell resistances using a porous solid electrolyte.

Comments: The aim of this project is to scale electrolyzers using solid electrolytes for formic acid production to the >750-cm^2 sizes with stable 100-hour performance at >200 mA/cm^2 with 90% current density. This project approach builds from previous demonstrations of selective formic acid production by solid-electrolyte electrolyzers at lab scale. The approach is well structured, with eight specific tasks divided into three phases: initial verification, catalyst and reactor scaling, and performance and durability testing at scale. The project team has made substantive progress, although they have run into significant technical challenges in the scale-up of solid-state interlayers and catalyst scale-up. The catalyst challenge has been overcome due to changes in synthesis routes, but challenges with scaling the solid-electrolyte interlayers have required a complete redesign of the interlayer structure. Still, the project team has managed to produce 100–250-cm^2 reactors with 15-hour stability for formate production at >90% initial Faradaic efficiency. Overall, the project has made good progress, especially given the low TRL level of the novel solid-electrolyte CO_2 electrolyzers compared to other electrolyzer technologies. If successful, this technology would have enormous impact. The solid-electrolyte CO_2 electrolyzers produce formic acid directly, which eliminates the need for downstream acidification and salt removal needed by the more conventional CO_2 electrolyzers that produce formate. It remains to be seen whether this technology can scale to the 750-cm^2 electrolyzer size with the necessary 100-hour performance stability, but the project has made promising initial progress in this direction.

Reply: We thank the reviewer for your kind comments. Scaling up the porous solid-electrolyte layer is a new challenge being addressed by ongoing and proposed activities for this project. If successful, these activities will provide transferable knowledge regarding the design of materials for other electrochemical reactors and devices, such as electrodialysis cells, that use porous solid-electrolyte materials. To ensure the greatest chance of success, we have identified and explored multiple working solutions for preparing solid-electrolyte material that will be screened at the final electrolyzer size for the final deliverable.

Comments: The team proposed a novel electrochemical cell structure with the incorporation of a porous layer, which allows for direct production of formic acid with high Faradaic efficiency at reasonable current density, albeit at high cell potential; however, this approach requires application of the IrO_2 anode catalyst, which may be an issue due to low iridium availability and competition with PEM water electrolyzers. The high variability of performance with time and the decrease of Faradaic efficiency should be greatly improved. The proposed novel operando diagnostic tool for overpotential breakdown is useful for electrolyzer development. The TEA shows some promise for this electrochemical method to be on par with conventional formic acid cost if all design parameters are achieved. Note that the prospective of using formic acid as a hydrogen carrier is overestimated, and the projected transportation cost is clearly wrong.

Reply: We thank the reviewer for the comment. Note that comparing hydrogen carriers was an interesting tangent that our team explored and is not related to the outcome of this project. Our goal is to directly couple a bioreactor with a CO_2 electrolyzer for formic acid production. The comprehensive TEA in Task 8 will focus on analyzing a bioreactor coupled with a CO_2 electrolyzer for the current formic acid market.

Comments: This project is another example of an early-stage effort to explore novel electrolyzer technologies. As such, it is an important part of the consortia's portfolio as long as expectations are tempered around how much risk is baked into the proposal and the TRL of the technology being pursued. It was clear from the presentation that many challenges have been faced along the way but that measurable progress was being made despite those challenges.

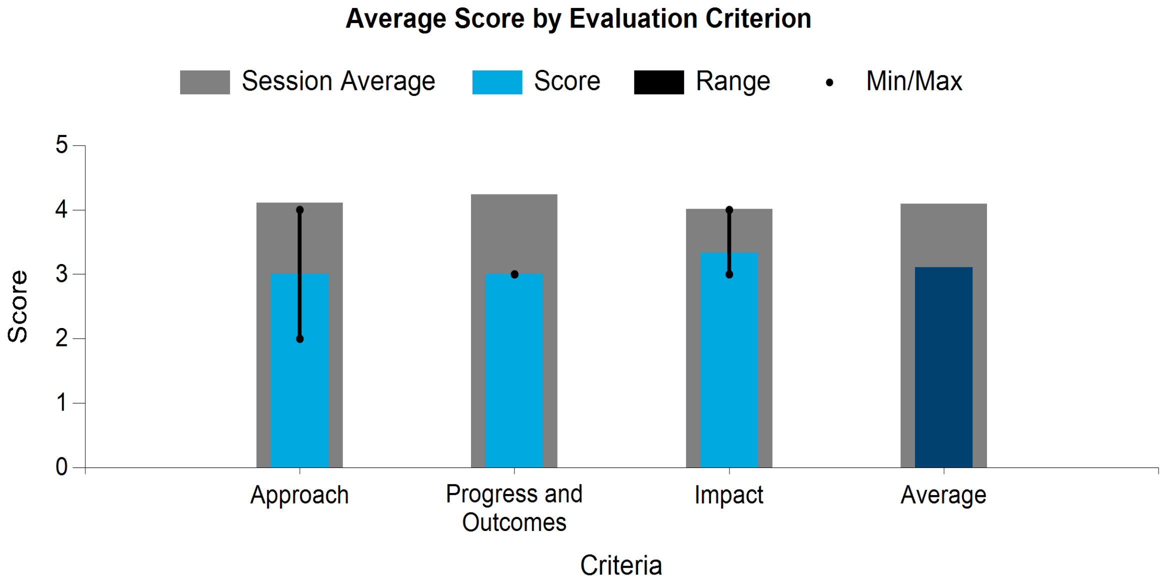
Reply: We thank the reviewer for acknowledging the progress made by the team.

PEM CO_2 ELECTROLYZER SCALE-UP TO ENABLE MEGAWATT-SCALE ELECTROCHEMICAL MODULES

Twelve

WBS:	2.3.1.423
Presenter(s):	Kendra Kuhl; Sadia Kabir
Project Start Date:	10/01/2020
Planned Project End Date:	02/28/2024
Total Funding:	$3,125,000

The objective of this project is to accelerate the development and deployment of our commercial-scale membrane electrode assemblies, which are the core component of our novel carbon dioxide electrolyzers. Specifically, this project seeks to validate the design, fabrication, electrochemical performance, and characterization processes for large-format membrane electrode assemblies. Key challenges include: optimizing across a complex parameter space and coordinating with partners from across the value chain (universities, national labs, vendors, etc.).



COMMENTS

- The project aims to develop electrolyzers for CO_2 conversion to CO. It appears that good progress has been made and some key milestones have been achieved; however, it is difficult to evaluate the overall progress of the project due to the lack of details. The level of collaboration is strong, with contribution from both academic and other industry partners. The final milestone seems attainable. Two key performance metrics in CO_2 conversion to CO are cell voltage and CO_2 crossover; however, they were not discussed in the presentation.

- The presentation mostly focused on the selling points, was overly sanitized, and lacked the experimental data. All reported parameters, including TEA, are vague or relative to an unknown baseline; therefore, although the milestone was met, it was very difficult to evaluate the team's progress toward the project and FOA goals without performance data.

- Threes for progress and impact here because the data were so sanitized that it was difficult to get a sense of how well the project was structured, how much progress they had actually made, and how impactful their results might be. I encourage BETO to push industry partners to agree to being more open about their progress and results in the future. This is a major concern because it is a publicly funded project. I gave this project a two for approach because I feel as though they did not appear to have any interest in collaboration or sharing their results with the group.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their thoughtful comments and feedback. We particularly appreciate their recognition of our milestone progress and collaborative approach with academic and national laboratory partners. Collaboration is one of Twelve's core values, and BETO offers a facile platform for working with leading researchers and organizations. The reviewers' feedback largely focused on the availability of data, which made it difficult for them to evaluate the overall project progress. In general, Twelve defaults to not sharing business-sensitive information to avoid enabling competitors or complicating customer negotiations; however, we acknowledge the validity of the reviewers' criticism and the necessity of being transparent with taxpayer-funded work. As such, we have added an additional slide showing additional lifetime data (Slide 22). Further, we have added numbers to our cell performance plots as well as throughout the deck, and we have highlighted the differences between Twelve's performance targets and the targets of the FOA.

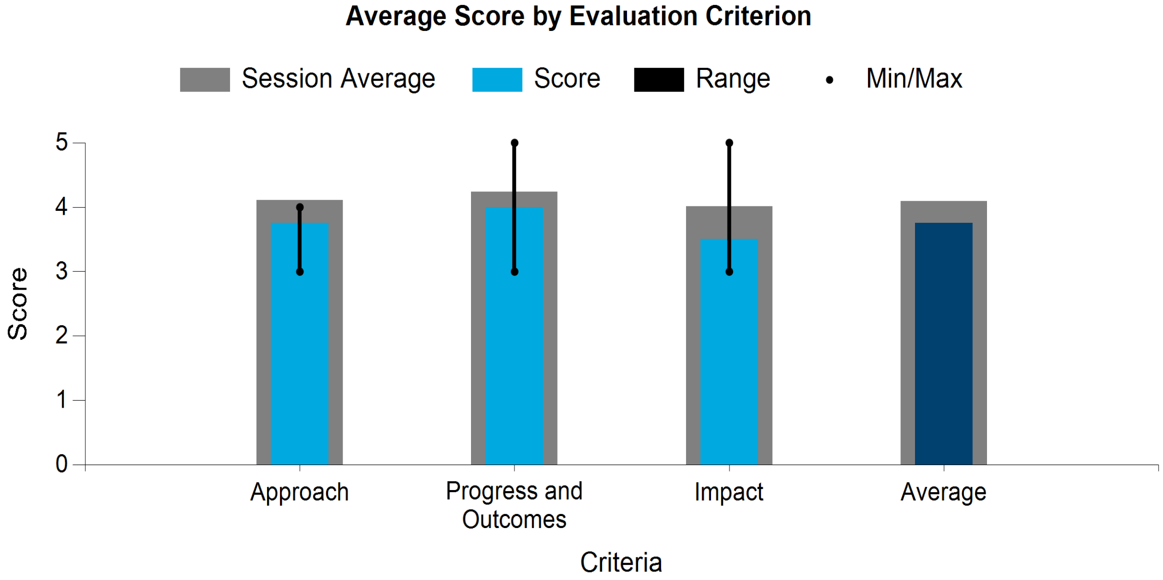
CO$_2$ VALORIZATION VIA REWIRING CARBON METABOLIC NETWORK

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.2.106
Presenter(s):	Wei Xiong
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$275,000

Energizing the world sustainably requires revolutionizing the way we harness natural resources. New renewable technologies include the microbiological upgrading of CO$_2$, the primary GHG that causes climate change. This project aims to develop a new bioeconomy by taking up CO$_2$ and converting it into high-value products using an autotrophic microbe. Specifically, the team constructed an acetogenic bacterium, *Clostridium ljungdahlii*, and developed gas fermentation processes that convert syngas (CO$_2$/H$_2$/CO) to the platform compound 3-hydroxybutyrate (3HB). The project has achieved several key successes, including the design and construction of 3HB genes in the gas-fermenting bacterium, the identification of a native 3HB pathway, the conversion of syngas to 3HB through strain engineering, and the improvement of the conversion through rational and iterative strain development. The optimized strain has achieved industry-relevant production rates (0.1 g/L/h) and titers (9.2 g/L), and it has sustained continuous gas fermentation for 3HB production for >50 days in a benchtop gas bioreactor. The project has both industry and scientific implications, including the exploitation of host microbes and processes to improve industrial-scale production of value-added compounds from CO$_2$ and the promotion of gas fermentation technology. The team is also strengthening R&D synergies with other teams and industry partners in the CO$_2$ consortium, developing cutting-edge approaches for the rapid and rational engineering of gas-fermenting hosts and dissecting the thermodynamics and kinetics of processes for biological syngas valorization. So far, one patent application and one research article have resulted from this work, and the team anticipates additional significant outcomes from this project.



COMMENTS

- Developing methods to rapidly engineer robust microorganisms to consume relevant intermediates to produce valuable products with high productivity is an important aspect of these integrated systems. This project seems to have a good method to achieve this and further test the system. Additional information, including the LCA and TEA regarding their target product 3HB, would be helpful in evaluating the potential impact of this project.

- The project aims to upgrade syngas to liquid fuels using metabolic engineering approaches. Progress has been made, but the carbon conversion efficiency for ethanol and 3HB seems quite low compared to that of acetate. It would be interesting to develop strains that are capable of converting acetate and ethanol to 3HB.
- This project aims to use strain engineering and adaptive laboratory evolution to modify acetogen anaerobes to convert syngas into 3HB, a useful chemical precursor to plastics and hydrocarbon fuels. As part of the project approach, the project team designed a lab-scale syngas fermenter, one of the few available in the United States that can safely handle syngas mixtures at this scale. This fermenter is a unique capability of the project. The project team has successfully engineered acetogens for 3HB production through genetic engineering that produce decent titers >9 g/L of 3HB and that can operate for up to 50 days of continuous 3HB production. Future work is focused on further engineering the microbes to achieve >12 g/L of 3HB titers. Overall, this project has made appropriate progress in its aims. The choice of acetophens as the host organisms for genetic modification instead of rewiring native strains that already produce 3HB remains an unanswered question for the project. The project has demonstrated good impact in the development of new gas fermentation technology and new strategies for the rapid genetic engineering of acetophen hosts. The project team has one publication and one patent, and it has engaged with key companies regarding integrating fermentation technology.
- This project presents a fairly straightforward approach for upcycling syngas to value-added compounds, specifically 3HB. That said, I have several concerns about the approach and presentation of the results that need to be addressed.

    1. Why were the same strains not tested on fructose and syngas on Slide 10? Each of the modifications made have the potential to affect both pathways to 3HB.
    2. Slide 10: 3-hydroxybutyryl-CoA dehydrogenase from *Clostridium ljungdahlii* and *Clostridium kluyveri* improved 3HB production, not *Clostridium ljungdahlii* alone, as stated.
    3. Slide 12: This is not a continuous run and should not be claimed as such. There were significant changes in the gas regime that resulted in changes in the optical density and therefore could impact production metrics. Also, it seems as though the feed rate was very influential for 3HB production, but this was never discussed. At 0.6 mL/min, 3HB production spikes and then falls off. Interestingly, a feed rate of 1.2 mL/min produced the same spike in optical density but not in 3HB. It would be useful to further explore the 70/20/10 CO/CO_2/H_2 gas regime with a 0.6-mL/min feed rate because the data in the first ~350 hours look very promising.
    4. Slide 15: "CRISPRi targeting the pta gene (encoding phosphate acetyltransferase) has increased 3HB titer as well as decreased acetate titer from a competing pathway." It would have been useful to describe what "T0" and "Mid" are, because it is unclear to the reader. Also, some statistics would be helpful for the interpretation of the titer data. While 3HB might be slightly increased, I'm not sure how significant the decrease in acetate titer is.
    5. Downstream processing: This is a significant concern. The fermentation will yield acetate, EtOH, and 3HB, which are all largely miscible in water, and no explanation was given for how to deal with purifying the 3HB away from the other products.
    6. The project goals were not clearly covered. This should be included for those who are not intimately familiar with them.

7. ALE goals on Slide 13: The criteria are not very specific ("Isolate adapted acetogen strains."). What are they adapted for? A numeric metric should be added to this goal.
8. The maximum 3HB titer is claimed to be 9.15g/L (Slide 11), but the data are not shown. Also, under what conditions was that titer achieved, and how long was it maintained? This should be included because it is an important data point linked to project milestones.

PI RESPONSE TO REVIEWER COMMENTS

- Comments: Developing methods to rapidly engineer robust microorganisms to consume relevant intermediates to produce valuable products with high productivity is an important aspect of these integrated systems. This project seems to have a good method to achieve this and further test the system. Additional information, including the LCA and TEA regarding their target product 3HB, would be helpful in evaluating the potential impact of this project.

  Reply: We have indeed conducted preliminary TEA back in 2020. This preliminary work was instrumental in setting our industrial benchmarks and initial laboratory research objectives. This project has met the TEA metrics of 0.1 g/L/h for commercial viability. We absolutely concur with the reviewer that updated TEA along with additional LCA would enhance our evaluation process. We are currently in conversation with BETO to shape our next phase of research.

  Comments: The project aims to upgrade syngas to liquid fuels using metabolic engineering approaches. Progress has been made, but the carbon conversion efficiency for ethanol and 3HB seems quite low compared to that of acetate. It would be interesting to develop strains that are capable of converting acetate and ethanol to 3HB.

  Reply: The reviewer rightly pointed out the significance of acetate in the role of acetogenic hosts. Bioenergetics of acetogens indicate that acetate production is integral to adenosine triphosphate (ATP) generation, a critical factor that is particularly important in a syngas fermentation process where the thermodynamic driving force would be constrained. We are actively working on a metabolic engineering approach to reduce acetate production by modifying relevant genes and pathways. We are also interested in a potential strategy involving a helper microbe that can recycle acetate and redirect the carbon flux toward our target compounds. Our preliminary findings are promising, and we are optimistic about the potential benefits these strategies could bring to the syngas fermentation process.

  Comments: This project aims to use strain engineering and adaptive laboratory evolution to modify acetogen anaerobes to convert syngas into 3HB, a useful chemical precursor to plastics and hydrocarbon fuels. As part of the project approach, the project team designed a lab-scale syngas fermenter, one of the few available in the United States that can safely handle syngas mixtures at this scale. This fermenter is a unique capability of the project. The project team has successfully engineered acetogens for 3HB production through genetic engineering that produce decent titers >9 g/L of 3HB and that can operate for up to 50 days of continuous 3HB production. Future work is focused on further engineering the microbes to achieve >12 g/L of 3HB titers. Overall, this project has made appropriate progress in its aims. The choice of acetophens as the host organisms for genetic modification instead of rewiring native strains that already produce 3HB remains an unanswered question for the project. The project has demonstrated good impact in the development of new gas fermentation technology and new strategies for the rapid genetic engineering of acetophen hosts. The project team has one publication and one patent, and it has engaged with key companies regarding integrating fermentation technology.

  Reply: Thanks! Regarding the use of native strains for the production of 3HB, these strains, to our knowledge, typically generate the polymer form (polyhydroxybutyrate [PHB]), not the monomer. Extracting PHB requires breaking (kill) the cells and extracting the polymer from the cells, which we understand to be an inefficient process; hence, our focus is on producing the monomer, which can be excreted from the microbial hosts, thus facilitating downstream processing.

Comments: This project presents a fairly straightforward approach for upcycling syngas to value-added compounds, specifically 3HB. That said, I have several concerns about the approach and presentation of the results that need to be addressed.

1. Why were the same strains not tested on fructose and syngas on Slide 10? Each of the modifications made have the potential to affect both pathways to 3HB.
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5. Downstream processing: This is a significant concern. The fermentation will yield acetate, EtOH, and 3HB, which are all largely miscible in water, and no explanation was given for how to deal with purifying the 3HB away from the other products.
6. The project goals were not clearly covered. This should be included for those who are not intimately familiar with them.
7. ALE goals on Slide 13: The criteria are not very specific (“Isolate adapted acetogen strains.”). What are they adapted for? A numeric metric should be added to this goal.
8. The maximum 3HB titer is claimed to be 9.15g/L (Slide 11), but the data are not shown. Also, under what conditions was that titer achieved, and how long was it maintained? This should be included because it is an important data point linked to project milestones.

Reply: I appreciate the detailed feedback and constructive suggestions. Allow me to address them in order:

1. All our strains were indeed tested on fructose as a primary step. The best-performing strains under fructose conditions were subsequently tested on syngas. More details can be found in our publication (https://doi.org/10.3389/fmicb.2022.948369).
2. Yes, we concur that 3-hydroxybutyryl-CoA dehydrogenase plays a pivotal role, regardless of its origin.
3. The experiment was conducted under continuous-feed conditions. The objective was to assess the impact of different gas ratios on 3HB production. We are open to exploring other conditions to further optimize 3HB production.

4. In our experiment, “T0” represents the point when the inducer of Cas9, anhydrous tetracycline (aTc), was initially added, and “Mid” represents when aTc was added during growth.
5. We agree that downstream processing is a critical factor, and we aim to focus more on this aspect as we advance toward achieving viable titers.
6. The project’s main goal, as stated in Slide 2, is to “develop a carbon-negative biorefinery with gas-fermenting bacteria.” Our current focus is on developing an engineered *C. ljungdahlii* for 3HB production as a model system.
7. Our aim is to improve H_2 utilization in gas fermentation. Because H_2 is a cleaner electron source than carbon monoxide, which has to produce CO_2 as a byproduct when providing electrons, we are striving to enhance hydrogen usage in our fermentation process.
8. On Slide 11, we provided the maximum 3HB titer in millimolar (mM), which equates to 9.15 g/L. We apologize for any confusion caused by not presenting this directly in grams per liter. The conditions under which this titer was achieved involved a gas mix of 70% CO, 20% CO_2, and 10% H_2, at pH 5.2, grown in YT media. We thank you for pointing out this crucial data point’s relevance, and we will be sure to include such details for a more precise understanding in the future. All thoughtful feedback and suggestions are invaluable to us and will certainly guide us in our ongoing research endeavors. We will strive to address all these points and improve our project for better outcomes. We look forward to further discussions and insights from reviewers.

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

National Renewable Energy Laboratory

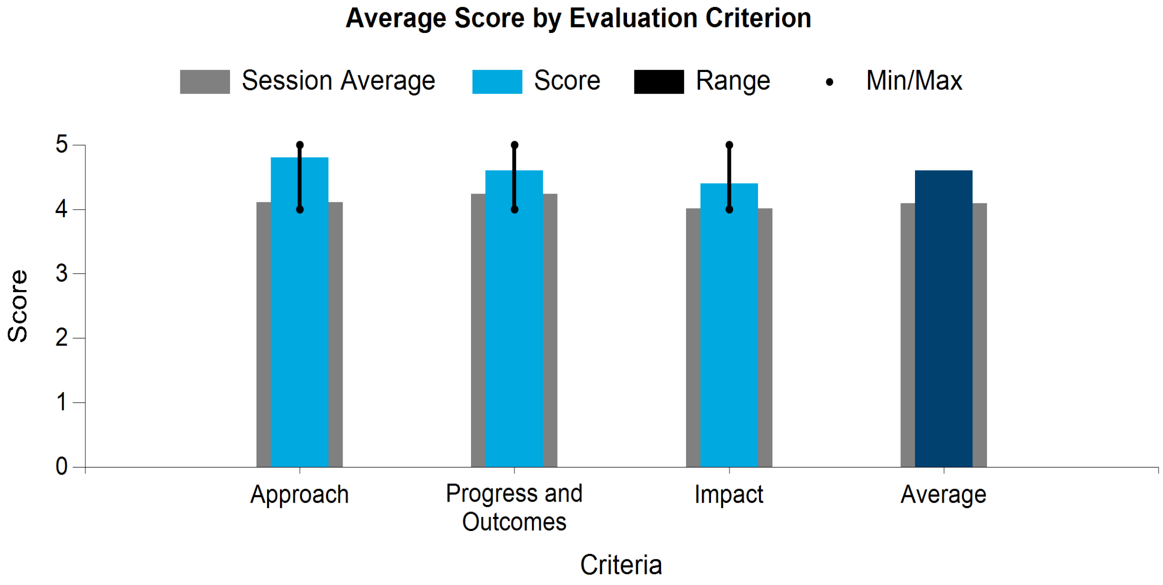
PROJECT DESCRIPTION

WBS:	2.3.2.116
Presenter(s):	Michael Resch
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$1,750,000

The production of valuable products from flue gas-derived CO_2 could incentivize conventional carbon capture technologies, leading to a more economically favorable and sustainable process. This project is a member of the CO_2RUe, focusing on integrating electrochemistry with gas fermentation, with ongoing unique modeling efforts. 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, and it can increase the carbon conversion efficiencies of biorefineries.

We are actively working with our industry cost-share partners LanzaTech and Dioxide Materials to identify integration hurdles for the scale-up of the conversion of biorefinery flue gas mixtures. At scale, we envision that this type of system would be collocated at an industrial source for the direct conversion of concentrated or dilute sources of CO_2.

Presently, we are focusing on understanding the effects of sulfur on CO_2 electrolyzers' ability to reduce CO_2 into CO, to improve the carbon conversion efficiency of gas-fermenting microbes, and to develop transformation tools for *Clostridium autoethanogenum*. We are also analyzing renewable electricity requirements and cost implications in utilizing biorefinery CO_2 waste streams at scales of up to 14 T/h.



COMMENTS

- The approach is well thought out, and pulling together the expertise of industry players to tackle key aspects of these bio-integrated systems is advantageous. Their approach of utilizing the larger CO_2 electrolyzers from Dioxide Materials and the knowledge from LanzaTech has the potential of filling knowledge gaps, which some of the more detailed studies do not fill at this time. In addition, testing and optimizing the CO_2 electrolysis process with the contaminants from flue gas is an important challenge to tackle. Additional information/questions for further assessment:

Risk management:

- Additional information or tests regarding using the recycle loop with flue gas
- Additional information on potential methods to mitigate the contaminants on the catalyst or catalyst regeneration methods.

Potential impact:

- Additional information regarding the comparison of CO_2 to liquid intermediates versus CO_2 to gaseous intermediates
- Additional information on the TEA and cost drivers of these systems and the numbers they need to reach to make it cost-competitive
- Additional information on the baseline TEA calculations and how sustainable and saleable are the SOA numbers from Dioxide Materials
- Additional information regarding the TEA of storing the produced CO or using batteries to store electricity.

- The project focuses on combining CO_2 conversion to CO and microbial syngas upgrading. Overall, great progress on the stability of the CO_2 conversion system in the presence of H_2S. The integration of CO_2 conversion and the CSTR bioreactor has been demonstrated. One milestone of the project is to reduce CO_2 crossover, but this has not been discussed/demonstrated. It seems that the path toward this goal is also unclear. The LCA shows the significant effect of the single-pass conversion. It would be important to study the effect of the single-pass conversion on the durability of the CO_2 conversion system. While the CO_2 conversion system is not affected by low H_2S concentration, it would be impactful if strategies for addressing high H_2S concentration were discussed/studied.

- This project uses a multifaceted approach to explore the durability and carbon conversion efficiency of both electrochemical and biocatalytic CO_2 upgrading technologies using realistic feedstocks. The research directions are focused on closing technology gaps that address key cost drivers identified by the analysis teams of the CO_2RUe. The close collaboration between this project and the analysis teams at the CO_2RUe is a significant strength of the project. To date, much of the progress has focused on testing the effect of the flue gas contaminant H_2S on electrolyzer performance and adapting *C. autoethanogenum* to produce acetate from low- and high-CO gas outputs from electrolyzers. The project team has demonstrated 3,000 hours of operation of a 250-cm^2 CO_2 electrolyzer at 100 mA cm^2 with H_2S-contaminated CO_2 feedstocks, although they identified Ag and S accumulation in the membrane after operation. This is an important finding for eventual integration of electrolyzers using S-contaminated CO_2 streams from biorefineries, because such electrolyzers may need sulfur purging built in to prevent catalyst degradation and accumulation, especially if recycling is used to increase the carbon conversion efficiency. The project team has successfully integrated an electrolyzer with a gas fermenter for 120-hour operation. Overall, this project is an important part of the CO_2RUe, with significant impact in guiding future research directions by identifying integration challenges related to key cost drivers for CO_2 utilization technologies.

- The project has a clear technical path forward and has demonstrated progress toward the project goals. The integration of a 250-cm^2 CO_2 electrolyzer with the CSTR was demonstrated. Preliminary data on H_2S tolerance are encouraging but only for low current densities. Reasonable coordination between partners can be seen. Milestones have been met; however, one of the stated goals is the reduction of CO_2 membrane crossover by 20%, but no work has been started yet. The idea of using CO_2 feedstock from ethanol refineries is good but is not analyzed in depth. For example, requirements as to the source of renewable electricity (wind)—such as placement, capital investment, availability, and the business model—are not developed. The performed TEA points to the CO_2 single-pass conversion as a major cost factor. In other processes, its importance is very low, because the addition of an inexpensive CO_2 separation and recycling loop eliminates this issue.

- It's very exciting to see a project integrating electrolyzer technology with a proven, industrial microbe to produce SAF precursors. The approach here is solid, and the team has made good progress toward their goals. In regard to the mevalonate pathway introduction, the product is a good choice, provides a great deal of flexibility for further refinement, and has been proven out by industry (albeit in yeast). Generating some detectable level of mevalonate should be straightforward, but going beyond that might prove difficult as the team tries to shift flux away from acetate. Some flux balance modeling specifically looking at redox equivalents and energy consumption might help mitigate risks.

PI RESPONSE TO REVIEWER COMMENTS

- Risk management:
    - Additional information or tests regarding using the recycle loop with flue gas. We have examined recycling the CO_2 from the electrolyzer and fermenter to optimize carbon conversion efficiency. There are benefits to the overall system carbon conversion efficiency and considerations for removing contaminants such as sulfur compounds from the fermenter and oxygen from the electrolyzer. The process engineering of designing a recycle loop is of interest but outside the scope of our current project.
    - Additional information on potential methods to mitigate the contaminants on the catalyst or catalyst regeneration methods. The current results showed that H_2S induced the carbon corrosion in the anode. We proposed to use titanium-based substrate to replace carbon fiber paper used in the anode and to refresh anolyte every 200 hours. If these two strategies do not mitigate the effects of sulfur on the electrolyzer, we will know the maximum sulfur amounts allowable to the system and use a SulfaTrap to remove sulfur and other contaminants before introduction to the cell.

  Potential impact:
    - Additional information regarding the comparison of CO_2 to liquid intermediates versus CO_2 to gaseous intermediates. Work focusing on key trade-offs between liquid and gaseous intermediates has informed the project scope (https://doi.org/10.1039/C9EE02410G). We build on this work by focusing on CO_2 converted to gaseous CO via low-temperature electrolysis because it represents one of the more near-term pathways for electrochemical CO_2 conversion. We acknowledge that this is an extremely active research space, with the SOA subject to change in the future as the performance and cost of these electrolyzers progresses. We intend to continue TEA to inform and guide these research efforts.
    - Additional information into the TEA and cost drivers of these systems and the numbers they need to reach to make it cost-competitive. The identification and analysis of key process-level parameters is the subject of ongoing work in the TEA tasks in this project. We intend to publish an exhaustive report outlining these considerations prior to the end of this project. Initial results indicate that the levelized cost of carbon monoxide produced via low-temperature CO_2 electrolysis is primarily driven by the cost of supplying low-carbon electricity to the electrolyzer. As such, TEA activities have focused on relationships between the variable supply of low-carbon electricity and possible gas or energy storage to act as a buffer to manage temporal variability.

  - Additional information on the baseline TEA calculations and how sustainable and saleable are the SOA numbers from Dioxide Materials. There are ongoing CO_2RUe analysis projects looking into the economics and life cycle of liquid versus gaseous intermediates.
  - Additional information regarding the TEA of storing the produced CO or using batteries to store electricity. This is a topic of interest to us, and we hope to have a report or paper to compare these process parameters to take advantage of low-cost, low-carbon electricity and CO_2 feedstocks. In the case of either storing electrolysis feedstocks and products versus storing energy to supply the electrolyzer, the added capital cost of storage systems must be contrasted with the cost savings from supporting the variable operation of the electrolyzer. In other words, the cost of purchasing and operating a battery energy storage system must be less than the cost savings from the ability to selectively purchase surplus grid electricity. Ongoing TEA tasks are focusing on addressing these questions, and we intend to publish a document addressing the results of these analyses in the near term. The reduction of CO_2 crossover was scheduled to start on October 1, 2023, and meet the milestone by December 31, 2024. We propose to recapture CO_2 from anode exhaust. First, we will determine the acceptable oxygen level in the CO_2 stream, and then we will design a membrane separation system to separate CO_2 from the CO_2/O_2 mixture. We agree with the reviewer. We have demonstrated thousands of hours of stability of CO_2 electrolyzer with single pass at a stoichiometry of 3–4. We have investigated the effect of concentration of H_2S up to 25 ppm. The CO_2 electrolyzer was able to run over 1,000 hours at 25 ppm of H_2S. It seems that H_2S in CO_2 induced the corrosion of carbon substrate used in the anode, leading to the loss of IrO_2 and the increase in the cell voltage. We propose to use titanium-based substrate to replace carbon fiber paper or refresh anolyte every 200 hours or so. The detailed degradation mechanism is under investigation. We also proposed to use SulfaTrap to remove sulfur before the cell if these strategies do not work. We agree with the reviewer that questions regarding business models and risk management considerations for such conversion pathways are not proven at scale yet. We hope that ongoing TEA work within this project will help inform and support the community, identifying key R&D pathways as well as economic drivers to support de-risking and proving these technologies at scale.

The performed TEA points to the CO_2 single-pass conversion as a major cost factor. In other processes, its importance is very low, because the addition of an inexpensive CO_2 separation and recycling loop eliminates this issue. Initial results indicate that the levelized cost of carbon monoxide produced via low-temperature CO_2 electrolysis is primarily driven by the cost of supplying electricity to the electrolyzer. As such, TEA activities have focused on relationships between the variable supply of electricity and possible feedstock or energy storage to act as a buffer to manage temporal variability. These findings do vary from one case to another, depending on project location and process design. This is a very good point, and we will monitor the flux balance and redox requirements necessary to maintain energy for cellular metabolism and maximize product formation.

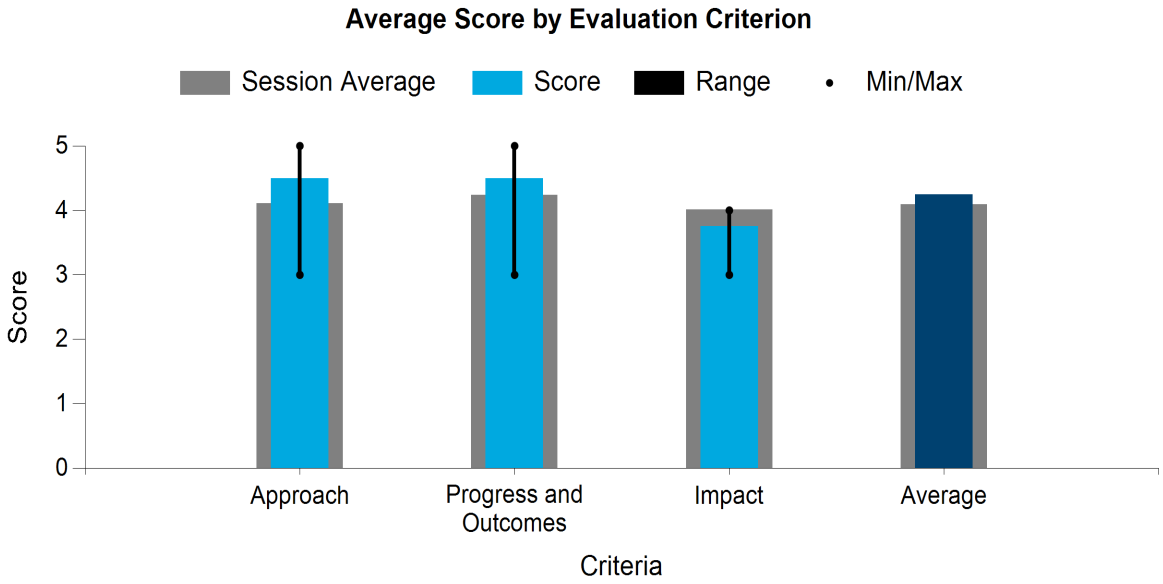
BIOCONVERSION OF SYNGAS FROM ELECTROCHEMICAL CO_2 REDUCTION TO SUSTAINABLE AVIATION FUELS—LBNL

Lawrence Berkeley National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.2.118
Presenter(s):	Eric Sundstrom
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$1,000,000

The economic conversion of CO_2 and renewable electricity to fuels and chemicals is a critical technological component of deep decarbonization. This project couples electrochemical syngas generation with aerobic carbon monoxide bioconversion to generate SAF directly from CO_2. Electrolyzer technology development focuses on efficient single-stage generation of tunable CO:H_2 blends from influent CO_2 and water, with an emphasis on computational modeling to drive quantitative improvements in the efficiency, longevity, and scalability of the electrolyzer assembly. Bioconversion technology development relies on metabolic engineering of the aerobic carboxydotroph *Hydrogenophaga pseudoflava* for heterologous expression of the isoprenoids epi-isozizaene and isoprenol, both promising intermediates for high-energy-density SAF. Experimental results to date have validated the tunability of syngas composition, and they have demonstrated high Faradaic efficiency over operating times exceeding 10 hours. In addition, we have developed inducible promoter and DNA methylation systems for *H. pseudoflava*, and we have commissioned a gas fermentation bioreactor system for high-density cultivation at dry cell weights exceeding 8 g/L. If successful, this project will develop an efficient and flexible platform for the direct synthesis of highly reduced and long-chain molecules from CO_2, overcoming a significant drawback associated with incumbent anaerobic syngas conversion technologies. The project team is well positioned to disseminate these learnings via inter-consortium collaboration, via collaborations with other BETO programs, and via new and existing connections to a variety of industry partners.



COMMENTS

- I believe their approach of combining modeling, system design, and experimental tests to guide research to enable scale-up is very valuable. Their specially designed electrochemical cells enable a high level of control of the conditions in the reactor, which increases our understanding of the ECO_2R process. Their use of modeling can further increase our understanding of these systems, help design optimal reactors, discover optimal conditions, and increase the chances of successful scaling of the technology. The approach of focusing on using microorganisms that can produce a diverse array of products is advantageous due to increasing the potential flexibility of these integrated systems. Additional information/questions for further assessment:

Risk management:

- o Further information regarding the stability of the electrolyzer after longer durations and simulated scaled conditions or stress testing.

Potential impact:

- o Additional information regarding the comparison of CO_2 to liquid intermediates versus CO_2 to gaseous intermediates
- o Additional information regarding the system; TEA including various components, such as electrolyte and pH management, recycle-loop operations, carbon selectivity, CO_2 flow rate, CO_2 crossover, the effect of the ratio of $CO:H_2$, what is necessary to achieve to make this a cost-competitive technology, and how they plan to achieve their necessary targets
- o Additional information regarding the higher-density fuels and how they will be used as SAF
- o Additional information regarding how this method compares to other methods to make SAF.

- The project focuses on developing an electrolyzer for CO_2 conversion to syngas with a tunable $CO:H_2$ ratio. The syngas is then upgraded via biological process. Although progress has been made in electrochemical CO_2 conversion to CO, its performance is much lower compared to other projects focusing on electrolyzer development. It is unclear why the $CO:H_2$ ratio should be controlled with the CO_2 electrolyzer. It would be easier (and more economic) to achieve the goal by simply combining CO_2 and water electrolyzers. Stable operation of around 10 hours has been demonstrated, but it is unclear what would make the system unstable and how the target of 100 hours can be achieved.
- The team selected aerobic bioconversion of syngas to cyclic hydrocarbons with high energy density, which could be important for the implementation of this pathway for the production of mixed SAFs. The application of an adaptive oxygen supply allowed for optimizing isoprenoid formation. The team demonstrated that increasing the back pressure may be an effective tool for the reduction of the cell voltage and changing $H_2:CO$ ratio. The one-dimensional model showed good correlation with experimental data, but a model for the membrane crossovers was not as accurate. The electrochemical longevity tests (tens of hours) are clearly not sufficient. It is unclear if the benefits of the proposed pulsed-current approach outweigh the increased complexity. Unfortunately, TEA was not discussed, and the projected costs of cyclic SAFs (below Jet A) and fuel savings look unlikely.
- This is a very interesting and unique project in the CO_2 utilization portfolio. *H. pseudoflava* is an interesting organism that should provide a robust platform to build off of. I have given the impact section a score of three because I found little discussion or consideration of a few important risks with the proposed approach.

    1. One issue with producing more complex products is cellular toxicity. The project has a goal of bioreactor isoprenoid titers >1g/L over 24 hours, but it is unclear which isoprenoid compound(s) are being pursued. This is important because many isoprenoids are very toxic to microbial hosts, and achieving titers of 1g/L might be very challenging. I suggest the authors look at the toxicity of different isoprenoids to *H. pseudoflava*.

2. Related to the first point, defining a product (or a few products) now will save a great deal of time later.
3. There was no mention of what would be done with the excess CO_2 that will (assumedly) be produced in this aerobic fermentation. Most organisms produce vast quantities of CO_2 under aerobic growth conditions, and that risk should be incorporated into the vision for this project. You could likely recycle that gas stream into the electrolyzer.
4. I suggest switching everything from plasmids to chromosomal integrations as soon as possible. Several critical variables related to flux and performance will likely be significantly different, and working with plasmids is inherently prone to genetic escapees and is unscalable.

PI RESPONSE TO REVIEWER COMMENTS

- We would like to thank the reviewers for their thoughtful comments and guidance. We share their enthusiasm for this product and the impact it can provide as a unique synthesis of electrochemical syngas generation and aerobic syngas conversion. We look forward to presenting our continued progress at the next BETO Project Peer Review. The two target molecules for our biological production system (isoprenol and epi-isozizaene) were chosen based on previous experience engineering expression in heterotrophic hosts and on commercialization interest from biofuel producers, industry end users, and the U.S. Navy. The production of these molecules is already characterized in heterotrophic host organisms, mitigating risk associated with pathway expression. Chemical and fuel properties are also well characterized, mitigating downstream risks, including purification, catalytic upgrading, and the suitability of the resulting fuels as SAF blendstocks. In-depth TEA of the integrated system is scheduled for FY 2024 within the CO_2RUe analysis and modeling working group. Key considerations for TEA and LCA include: (1) comparison of integrated versus separated CO_2 and water electrolysis and (2) comparison of direct aerobic synthesis of high-energy-density molecules with a higher-TRL alternative: anaerobic syngas fermentation coupled to catalytic upgrading. This work is planned for FY 2024 and will be heavily informed by our research results, projections of optimal system performance, and outcomes of related analysis efforts within the consortium.

  A dual system featuring both CO_2 and water electrolyzers would certainly exhibit preferable economics at the current SOT development; however, we believe that with further development, a single electrolyzer producing the desired ratios of syngas directly from CO_2 and H_2O could significantly simplify the system design, enabling the reductions in manufacturing cost and reductions in infrastructure required to support the process. While water electrolyzers are currently a much more mature technology with superior operating expenditures (OpEx) and energy efficiency, there are no thermodynamic barriers suggesting that a single electrolyzer could not reach the same energy efficiencies with equivalent investment in technology development. We note that the CO_2RUe is taking a portfolio approach by exploring both combined and integrated approaches for electrochemical syngas generation, and we emphasize that the single electrolyzer approach is a lower-TRL (2–3) R&D project that is less demonstration oriented. Within this portfolio approach, our research efforts will be heavily influenced by the CO_2RUe analysis and modeling working group, as they quantitatively compare the economics and emissions impacts of both system designs.

  We fully agree with the observation that 10 hours of electrolyzer operation is insufficient. Unfortunately, due to the timing and brief format of the presentation, we were unable to incorporate our most recent electrolyzer stability results into the official slides. With automated salt dosing and pulsed-current protocols, we have now been able to achieve >130 hours of stable operation, with voltage decay indicating potential for significantly longer operation barring a sudden failure, such as a membrane rupture. Given the lower TRL (2–3) of this project, we are currently focused on optimization at +100 hours of operation to provide stress-testing feedback to our component R&D efforts. The development of accelerated stress-testing protocols for CO_2 electrolysis and evaluation of system performance over longer timescales (+1,000 hours) would be compelling topics for follow-on research efforts at a higher TRL. Because our pulsed-current approach has relatively long time constants—on the order of tens of minutes to hours—we do not see any barriers to implementing a pulsed-current approach in an industrial setting. In fact, our industry partners are leveraging similar pulsed-current protocols to achieve thousands of hours of stability in their CO_2 electrolyzer stacks.

We agree that there is room to improve the agreement between the experimental and simulated CO_2 crossover measurements. We will continue incorporating relevant physics into the model by gathering additional polarization data to reduce parameter uncertainty and by modifying the model equations to correctly account for salting-out effects and the electroosmotic drag of water. Experiments will also be performed to track the pH of the electrolyte over time and validate boundary conditions used in the model. Note that there is little precedent for modeling CO_2 crossover in the literature, particularly at high current densities. The validated experimental model we are developing is therefore an important contribution to the overall development of CO_2 electrolyzers.

When comparing our electrochemical system performance to other efforts, we note that our single-cell performance indicators are comparable to those of similar geometric surface area units from Dioxide Materials, a CO_2RUe member. Because our project is at a lower TRL (2–3), we are still conducting R&D on components such as the catalyst layer and flow fields to further advance these metrics, particularly for tunable syngas production at low cell potentials. Product toxicity for our chosen molecules (isoprenol and epi-isozizaene) is absolutely a critical factor for project success. Our data indicate isoprenol tolerance above 5 g/L without prior adaptation, well above the 1-g/L productivity target and aligns with alternative hosts previously engineered for isoprenol. While epi-isozizaene standards are not available for toxicity evaluation, we plan to use an extractive fermentation approach for this hydrophobic molecule to mitigate toxicity at higher titers, aligning with current industry standards for large-scale sesquiterpene production. Single-pass consumption of CO_2 is a key factor in our process design; under optimal gas transfer conditions, we anticipate higher CO_2 emissions at high $CO:H_2$ ratios, with minimal CO_2 emitted at stoichiometric $CO:H_2$ ratios. The interplay between electrochemical $CO:H_2$ ratios, single-pass gas uptake in the bioreactor, and overall process economics will be a key focus of analysis efforts in the coming years. If higher CO concentrations are superior economically, excess CO_2 could indeed be purified and routed back to the electrolyzer. Concerning the use of plasmids versus chromosomal integration for genetic engineering of *H. pseudoflava*, we appreciate this comment, and we agree completely. Genetic tools for *H. pseudoflava* are currently rudimentary, and Oak Ridge National Laboratory is therefore developing a suite of easy-to-use tools for chromosomal engineering. While the plasmid-based system is providing critical early data, we anticipate transitioning to chromosomal-based engineering later this year.

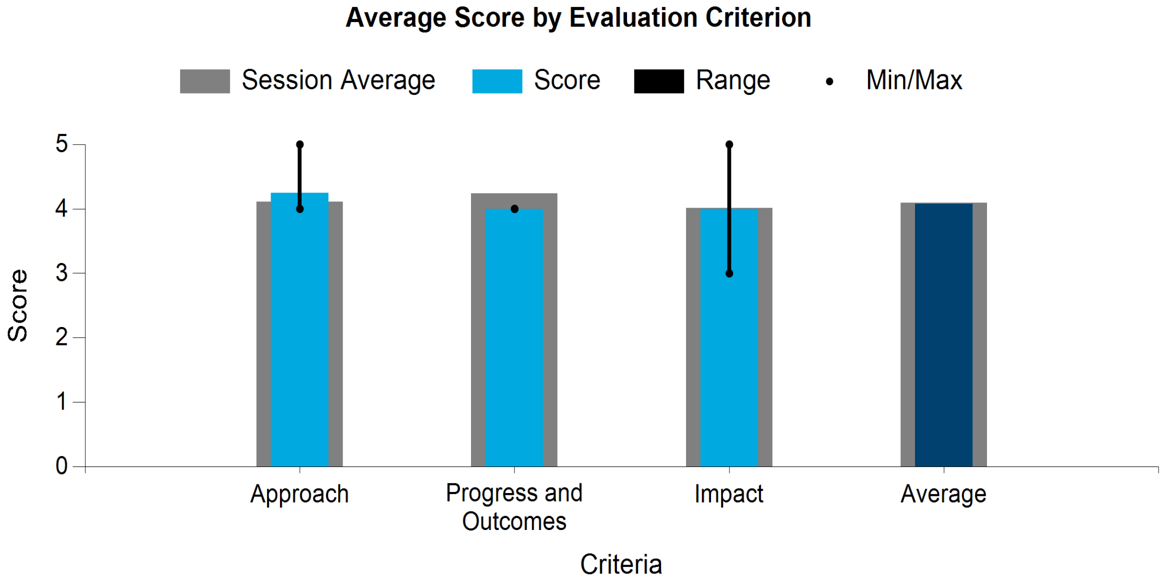
BIOLOGICAL CONVERSION OF FORMIC ACID FOR CO_2-TO-FUELS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.2.121
Presenter(s):	Christopher Johnson; Violeta Sanchez i Nogue
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$1,100,000

Increasing demand for energy and natural resources is causing a rise in the atmospheric concentration of GHG, including CO_2. The conversion of CO_2 to value-added products represents a key opportunity for the development of disruptive technologies to reduce GHG emissions and generate economic revenue. Formate/formic acid can be generated by electrocatalytic reduction of CO_2 and has been proposed as a soluble intermediate for the storage of carbon and energy. Biological systems capable of assimilating formic acid could enable the conversion of formic acid generated from low-cost renewable energy and waste CO_2 to myriad fuels and chemicals. To that end, the goal of this project is to develop the natural formatotroph *Cupriavidus necator* as a robust microbial chassis for the efficient conversion of formic acid to value-added products, in this case fatty acids, which can be readily converted to fuels using established methods. By introducing an acyl-CoA thioesterase to produce free fatty acids and attenuating the organism's ability to degrade them, we are engineering *C. necator* strains that produce fatty acids from formic acid in a pH-stat method of cultivation being concurrently developed. Toward an integrated process, we have also demonstrated the ability of this organism to convert a raw formic acid generated by electrocatalytic reduction of CO_2.



COMMENTS

- Engineering microorganisms to convert formic acid to fatty acids is important to the CO_2 utilization and SAF landscape. The approach of integrating these systems as they are being developed improves risk mitigation. I also appreciate the approach of both microbial engineering as well as developing scalable methods for the bioprocessing inoculation, feeding rate, and aeration. Further stress tests simulating real-world electrolyzer conditions and using the raw formic acid solution from these experiments could help determine if there are additional purification steps between feeding the raw formic acid to the bioreactor. Additional information/questions for further assessment:

Risk management:

- Additional information regarding the production of fatty acids; limits to the concentration of fatty acids in the system and separation costs and carbon intensity (of the fatty acid from the culture)
- Additional information regarding impurities in the electrolyte and the potential effect on microorganisms in real-word testing scenarios
- Additional analysis of how the concentration of the raw formic acid in the electrolyte will affect the system.

Potential impact:

- Analysis and comparison of integration projects using formic acid as an intermediate versus gaseous intermediates
- Additional information regarding how this method compares with other methods for producing SAF, such as reverse water-gas shift with Fischer-Tropsch and direct CO_2 to hydrocarbons
- Additional information and analysis regarding the type of SAF and blending requirements
- Additional information regarding the product production rate they need to reach to be cost-competitive with other methods
- More information about the bioreactor and culture, durability of the microorganisms, and sensitivity of the microbes to changes in the environment
- Additional information regarding carbon conversion to biomass versus product
- Additional information regarding the recycle loop, amount of CO_2 generated, and effect on recycling on the system and energy intensity.

- The project focuses on upgrading formic to fuels. CO_2-derived formic was used to demonstrate the potential of an integrated system. Good progress on biological growth on formic has been demonstrated. Does formic acid need to be concentrated for the integration? It seems that the concentration of formic in the bioreactor is not that high. It is unclear how the fatty acid can be effectively converted to SAF. Perhaps it is not a problem from a technical point of view, but TEA is needed to evaluate the economic aspect of the process.
- This project focuses on the bioconversion of formic acid to fatty acids that could then be converted to SAF via other downstream processes. *C. necator* was chosen as the microbial host organism due to its metabolic versatility, high cell density, and proven affinity for the production of polyhydroxyalkanoates (PHA). The main project approach focuses on using known genome modification methods to engineer *C. necator* to enhance free fatty acid formation and delete competing pathways for undesired products and on evolving *C. necator* to improve assimilation and the conversion of formic acid. To date, the project has met all performance milestones, and it has collaborated with WBS 2.3.2.121 to feed CO_2-derived formic acid from electrolysis directly to their bioreactor, leading to formic acid upgrading to 2-hydroxymucoante semialdehyde. The significant progress to date and close collaboration with other projects within the CO_2RUe are strengths of the project that highlight the impact of the project within the consortium; however, one significant limitation is the low relative yield of fatty acids from formic acid (~1.3%) compared to the maximum theoretical yield of ~20%. Also, the coproduction of biomass in the

bioreactors may lead to downstream separation challenges, depending on where the fatty acids accumulate. The initial results and the potential scalability of the process due to the high cell density of *C. necator* make this a promising direction with significant potential impact.

- This project is a great example of using an industrially relevant production strain with great potential for pushing a lot of flux toward value-added compounds. A couple of comments/risks worth mentioning:
    - The CoA synthetases are obviously a big concern. As discussed at the 2023 Project Peer Review, it could be just one, it could be two, or it could be any combination of 49 of the 50 that are required to knock out beta oxidation. Anything that can be done to expedite that workflow would be worthwhile to pursue immediately. Also, if the solution is indeed a combination of a few or more of these genes, it will be nearly impossible to determine the correct combination required within the timeline of this grant. It might also be worthwhile to do some sequence-based flux analysis or obtain omics data from the literature to determine which copies are functional and maybe even which are influential for flux to beta oxidation.
    - Longer term, CO_2 evolution during this fermentation will be significant and therefore will need to be addressed.

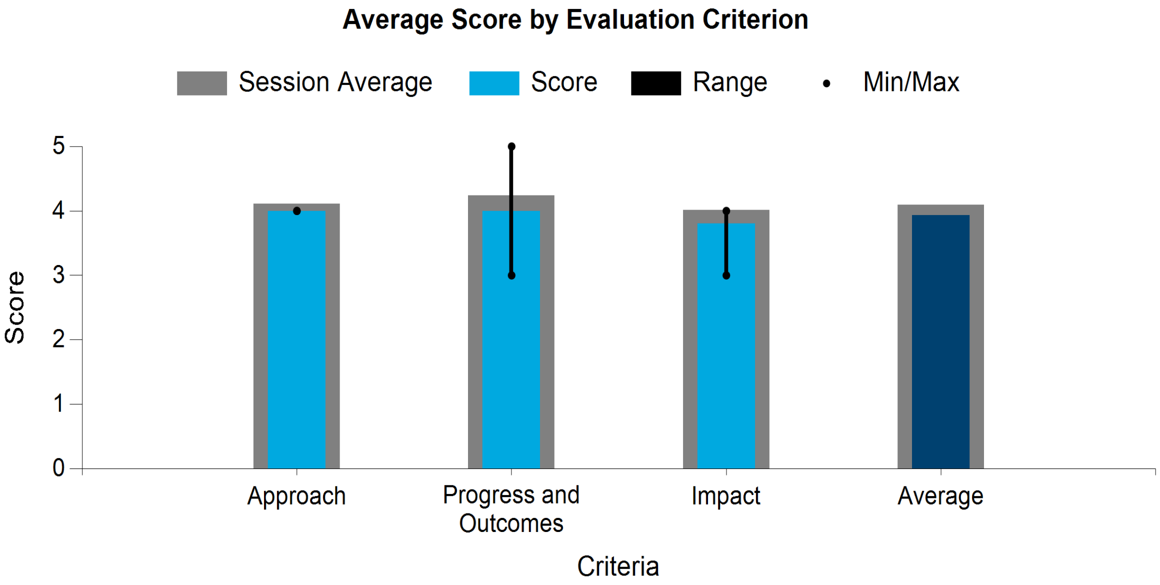
PI RESPONSE TO REVIEWER COMMENTS

- We are grateful to the reviewers for their careful evaluation of this project and thoughtful comments and suggestions. The goal of this project is to develop the soil bacterium *C. necator* as a host for the conversion of CO_2-dervied formic acid using fatty acids as an exemplary product. While it is outside the scope of this project, we recognize that the integration of our project with the upstream process of reducing CO_2 to formic acid, the downstream processing of fatty acids to fuels, and the TEA and LCA of the entire system will be critical to the development of this technology. These aspects are being addressed by other projects within the CO_2RUe (i.e., electrocatalytic reduction of CO_2 to generate formic acid, TEA, and LCA), outside the consortium (i.e., conversion of fatty acids to fuels), or will be incorporated into the project at a later stage (i.e., integration with upstream and downstream processes). With respect to what is within the scope of this project, we agree that a 1.3% carbon yield for the conversion of formic acid to fatty acids is low relative to the maximum theoretical yield of 20.5%, but we expect low yields at this point considering we have not yet deleted enough acyl-CoA synthetase genes to prevent these fatty acids from being degraded and re-assimilated. We presented the hypothesis that we may need to delete as many as 50 acyl-CoA synthetase genes, but it is very possible we may not need to delete all of them to prevent degradation of the C14–C18 fatty acids we are producing. And while we did not have the data at the time of the presentation, we are using omics to help prioritize these knockouts and could use tools being developed in other projects to further refine the list if necessary.

AN EFFICIENT, SCALABLE PROCESS FOR THE ELECTROCHEMICAL REDUCTION OF CO_2 TO FORMATE—NREL

National Renewable Energy Laboratory

WBS:	2.3.4.301
Presenter(s):	K. C. Neyerlin
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$1,400,000



COMMENTS

- The approach of developing a reactor with guidance from the TEA and using off-the-shelf components is mitigating risk and complications with scaling novel reactor materials. In addition, the information gained by investigating effects at a scale of 25-cm^2 and higher current densities also provides necessary information for scaling this technology and can be applied to other systems. Additional information/questions for further assessment:

  Risk management:

  - More information regarding the perforated membrane; durability, effects on the catalyst, and any effects on the integrated system
  - More information regarding key areas of failure in a scaled-up system and methods to mitigate them. For example, R&D plans regarding how they will mitigate the voltage increase over time.

  Potential impact:

  - More information regarding the sensitivity of the amount of formate oxidation and how it affects CapEx

  - More information regarding the specialized anode catalyst, durability, CapEx/OpEx, scalability, etc.
  - Additional information regarding the H_2 generation and how it affects the TEA in various scenarios.

- The project aims to develop a scalable electrolyzer for CO_2 conversion to formate/formic. Membrane development is the main strategy used in the project. A relatively stable system (over 100 hours) for formic production has been demonstrated using perforated membrane and hydrogen oxidation in the anode. One key question is whether hydrogen oxidation in the anode would be economically competitive compared to water oxidation. This is an important question because it governs the selection of anodic catalyst. With the current cell configuration, it would be expected that membrane delamination occurs due to the CO_2 bubble formation between the two layers of the membrane. It is unclear how the target of 500 hours will be achieved. Single-pass conversion of over 30% is a milestone, but strategies to achieve it are not clear.

- This project sets an ambitious goal of scaling CO_2 reduction to formic acid, an important feedstock for downstream bioconversion to SAF. It leverages existing capabilities developed at NREL for the roll-to-roll production of MEA components using automatic film applicators for catalyst loading. The key innovation of the project to date is the development of a perforated membrane MEA configuration, in which formate produced at an alkaline cathode is purposely allowed to migrate through perforation in a bipolar membrane (BPM) to the anode side, where it is pronated to formic acid from protons produced from hydrogen oxidation at the anode. Immediate future work will focus on suppressing formic acid oxidation at the anode by using encased Pt catalysts developed at ANL. This innovation directly addresses the need for product acidification of formate to formic acid for integration with bioconversion systems. From a fundamental science and engineering standpoint, using a perforated membrane is a clever strategy that leads to the production of the desired formic acid product; however, the project has not yet performed the crucial TEA and LCA to determine if the use of H_2 for proton production in the perforated membrane configuration is competitive with other conversion technologies using H_2, such as direct CO_2 hydrogenation or CO_2-to-CO electrolysis followed by CO hydrogenation. Such TEA and LCA are crucial to determine the practical viability of this otherwise interesting approach. Importantly, the project has successfully collaborated with project WBS 2.3.2.121 to feed their CO_2-derived formate directly into a bioconversion reactor for further upgrading, demonstrating the potential impact their approach to formic acid production may have on the process of CO_2 conversion to SAF pending TEA and LCA validation.

- The team showed a certain progress in scaling up electrodes to fit a 25-cm^2 cell. Faradaic efficiency is low, with substantial losses due to the crossover/back-diffusion that must be (but is hard) suppressed. The proposed increase of membrane thickness will reduce crossover but increase the cell resistivity (increase CapEx). This and high cell voltage led to low energy efficiency. The major reaction product in the conventional process is formate, which must be converted to formic acid. The proposed perforated BPM configuration allowed for the production of formic acid directly, which is encouraging, but the noticeable decrease (probably due to the catalyst ripening) in Faradaic efficiency with time is worrisome. It would be interesting to evaluate the pressure effect on the cell performance. In addition, for this method, it is necessary to use expensive hydrogen instead of inexpensive (but still costly) neutralization, and the effluent distillation of the diluted stream is still needed. A thorough TEA is necessary to compare these options.

- Formic acid oxidation seems to be a major limitation of this technology, and it should be recognized as a significant risk to mitigate against going forward. Second, the approach requires the electrolyzer to be split into two parts. This seems like an important variable considering that the electrolyzer CapEx is the top cost driver. Given that, is it worthwhile to invest in this approach given the other electrolyzer technologies available?

Are platinum catalysts an economically feasible option for this technology? No discussion was provided on this front, and I would caution against employing unscalable methods to meet a near-term goal.

PI RESPONSE TO REVIEWER COMMENTS

- Comments: The approach of developing a reactor with guidance from the TEA and using off-the-shelf components is mitigating risk and complications with scaling novel reactor materials. In addition, the information gained by investigating effects at a scale of 25-cm^2 and higher current densities also provides necessary information for scaling this technology and can be applied to other systems. Additional information/questions for further assessment:

1. Risk management—more information regarding the perforated membrane; durability, effects on the catalyst, and any effects on the integrated system.

   Reply: This is a newly developed system, and we are doing our best to provide more fundamental information while scaling.

2. More information regarding key areas of failure in a scaled-up system and methods to mitigate them. For example, R&D plans regarding how they will mitigate the voltage increase over time.

   Reply: First, we need to elucidate the mechanism of failure, which remains unclear at present. We have developed some studies to try to isolate the effect of increasing formic acid concentration on anode performance and also isolate catalyst degradation as a function of operating potential.

3. Potential impact—more information regarding the sensitivity of the amount of formate oxidation and how it affects CapEx.

   Reply: We are in the process of gathering initial TEA data to this point. In short, there is little sensitivity to formate oxidation and cell voltage relative to effluent formic acid concentration. The subsequent distillation costs dominate the process. We have identified that if we are able to produce 1.3M formic acid, then we can come close to the current market price of $0.66/kg formic acid using our approach.

4. More information regarding the specialized anode catalyst, durability, CapEx/OpEx, scalability, etc.

   Reply: This is ongoing, and a significant part of future work will be on durability (see above) and identifying solutions to mitigate formic acid oxidation and improve formic acid effluent concentration at scale.

5. Additional information regarding the H_2 generation and how it affects the TEA in various scenarios.

   Reply: With an intermediate estimate of $0.3.2/kWh electricity and $2.3/kg H_2, we are able to meet the current market price of 85 wt % formic acid if we produce 1.3M formic acid effluent. This is from a preliminary TEA that has just been completed.

6. The project aims to develop a scalable electrolyzer for CO2 conversion to formate/formic. Membrane development is the main strategy used in the project. A relatively stable system (over 100 hours) for formic production has been demonstrated using perforated membrane and hydrogen oxidation in the anode. One key question is whether hydrogen oxidation in the anode would be economically competitive compared to water oxidation. This is an important question because it governs the selection of anodic catalyst.

Reply: Currently, the most stable water oxidation catalyst is unsupported Ir or IrOx, which must be coated at a significantly higher loading (0.2 to 0.4 mg/cm^2) to obtain a uniform coating than the Pt-supported carbon catalyst, where we are currently using 0.05 mg Pt/cm^2 at the anode. Coupled with the fact that Ir is 4.5 times the cost of Pt and requires 4–8 times the loading, the Pt cost is a minimal contribution (approximately 1/16 to 1/32 of the Ir cost) to the overall device. This will be showcased in a TEA.

7. With the current cell configuration, it would be expected that membrane delamination occurs due to the CO_2 bubble formation between the two layers of the membrane. It is unclear how the target of 500 hours will be achieved.

   Reply: The approach using a perforated membrane prevents bubble formation within the membrane. The perforations allow CO_2 to escape from the anode. We showed a postmortem membrane cross-section image from an optical microscope for both the nonperforated and perforated BPMs. The nonperforated BPM had delamination, but the perforated BPM remained laminated and intact.

8. Single-pass conversion of over 30% is a milestone, but strategies to achieve it are not clear.

   Reply: This will come down to flow-field optimization during the scale-up process. Additionally, recent literature argues that single-pass conversion may not be relevant to reduce cost.

9. The team showed a certain progress in scaling up electrodes to fit a 25-cm^2 cell. Faradaic efficiency is low, with substantial losses due to the crossover/back-diffusion that must be (but is hard) suppressed. The proposed increase of membrane thickness will reduce crossover but increase the cell resistivity (increase CapEx). This and high cell voltage led to low energy efficiency. The major reaction product in conventional process is formate, which must be converted to formic acid. The proposed perforated BPM configuration allowed for the production of formic acid directly, which is encouraging, but the noticeable decrease (probably due to the catalyst ripening) in Faradaic efficiency with time is worrisome. It would be interesting to evaluate the pressure effect on the cell performance. In addition, for this method, it is necessary to use expensive hydrogen instead of inexpensive (but still costly) neutralization, and the effluent distillation of the diluted stream is still needed. A thorough TEA is necessary to compare these options.

   Reply: This is underway, and we have preliminary results (see responses to 3 and 5).

10. Formic acid oxidation seems to be a major limitation of this technology, and it should be recognized as a significant risk to mitigate against going forward.

    Reply: See responses to 3.

11. Second, the approach requires the electrolyzer to be split into two parts. This seems like an important variable considering that the electrolyzer CapEx is the top cost driver. Given that, is it worthwhile to invest in this approach given the other electrolyzer technologies available? Are platinum catalysts an economically feasible option for this technology? No discussion was provided on this front, and I would caution against employing unscalable methods to meet a near-term goal.

    Reply: Please see responses to 3, 5, and 6.

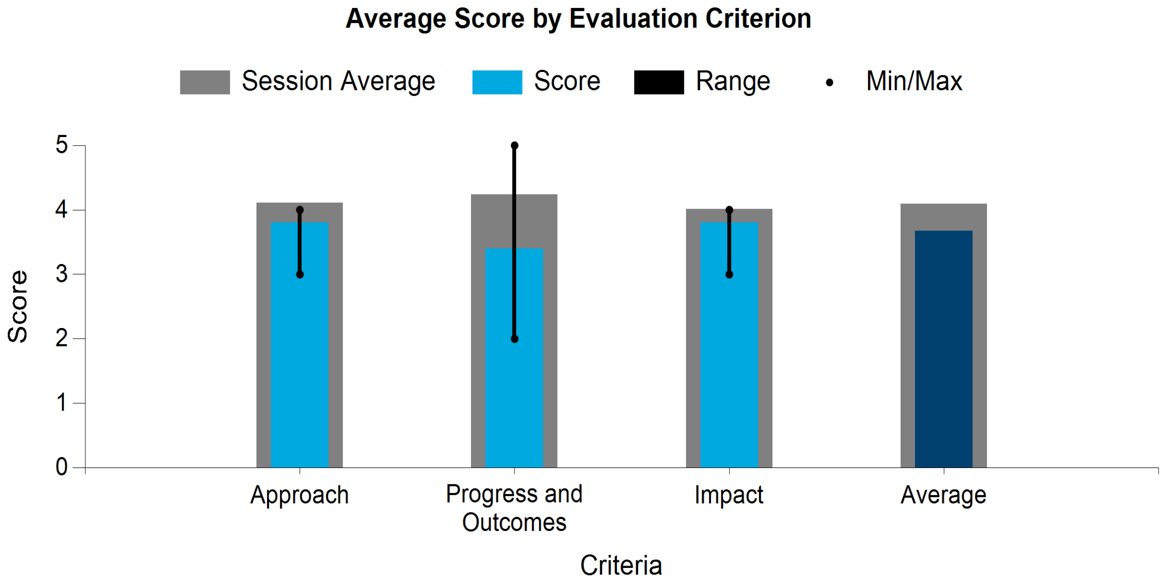
ELECTRODE AND MEMBRANE MATERIALS FOR CO_2 ELECTROLYZERS: A MOLECULAR APPROACH—ANL

Argonne National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.4.304
Presenter(s):	Ksenija Glusac; Meltem Urgun Demirtas
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$800,000

Electrocatalytic CO_2 reduction to fuels and value-added chemicals is an important process in carbon recycling. A main challenge associated with CO_2 reduction is the product selectivity: Myriad reduced products—such as CO, H_2, formate, methanol, ethanol, and oxalate—are formed at similar thermodynamic driving forces, making it difficult to selectively generate the target product. Here, we investigate molecule/electrode hybrid materials for the selective and efficient electrochemical production of methanol from CO_2. Methanol was selected as a desired product because it can be used as a fuel to generate electricity (in methanol fuel cells) or heat (in methanol boilers) or in transportation (in road and marine engines). Further, methanol is an important chemical industry feedstock for the synthesis of formaldehyde, acetic acid, and other important products. Methanol is also a feedstock for the biosynthesis of amino acids and other products by methylotrophic microorganisms. Electrochemical methanol production is advantageous over the competing thermocatalytic CO_2 hydrogenation process because the energy input to drive the electrochemical process can, in principle, be powered using CO_2-free energy, leading to a net reduction of CO_2. Further, ECO_2R methods, unlike thermocatalytic CO_2 hydrogenation, can act as stabilizers of the electric grid by consuming the excess electricity generated by renewables.



COMMENTS

- Molecular catalysts for ECO_2R have the potential to be highly tailorable and efficient catalysts, which has potential to make an impact in the field of ECO_2R, despite currently being at a lower TRL. I appreciate their approach with using molecular catalysts immobilized on carbon nanotube. Focusing on converting CO_2 to MeOH, with high selectivity and in one step (eliminating the need for $H2_2$), could provide an efficient path for CO_2 utilization. I look forward to seeing more testing in real-word reactors and conditions as well as collaboration with industry partners as this project matures. It would be nice to see more communication/collaboration with the Betenbaugh group. Additional information/questions for further assessment:

Risk management:

- Address selectivity risk: Provide a road map for improving the MeOH selectivity in addition to pH effects.
- Address durability risk: Provide a road map for increasing durability.
- Assess the trade-offs in process stability and energy intensity between using a BPM versus pH control during continuous runs in a scaled-up system.
- Address the risk of the catalyst: Provide more information regarding the computational work on the catalysts, synthesis of the catalyst, and related experimental data.

Potential impact:

- Explain how your experimental targets (carbon selectivity, cell voltage, current density) relate to projected system performance (yield, product cost, energy efficiency).
- Demonstrate through analysis the advantage of using carbon nanotube supports over other supports with similar characteristics (e.g., why should carbon nanotubes be pursued?).
- Demonstrate through analysis the advantage of the one-step pathway: Compare the one-step pathway to pathways that leverage green H_2 using high/medium/low scenarios for the efficiency of the one-step pathway and high/medium/low scenarios for technology advancements involving green H_2.

- This project focuses on developing catalysts and electrochemical systems for CO_2 conversion to methanol. Molecular catalysts were selected and electrolyzers were developed based on BPM. A methanol Faradic efficiency of around 10% has been achieved. It is unclear how the target of 60% can be achieved by the end of the project. The catalysts are not so stable. It would be very challenging to achieve stability of over 100 hours at a current over 200 mA/cm^2. While the project focuses on CO_2 conversion, it would be interesting to see how the catalyst would perform if CO was used as the reactant. It is also important to compare e-methanol versus methanol produced via thermal catalysis. It is unclear how methanol produced directly from CO_2 electrolysis would be greener than the one produced from CO_2 and green H_2.

- The goal of this project is to enable the direct electrochemical conversion of CO_2 to methanol with high selectivity and energy efficiency. CO_2-generated methanol could be used directly as a fuel, a commodity chemical, or a feedstock for bioconversion to SAF, and thus the potential impact of this project is substantial; however, this project has the lowest TRL of all those in the CO_2RUe. The project's approach is to develop cobalt-based macrocycles, incorporate them onto carbon supports, and explore them for methanol production in a CO_2 electrolyzer. Progress to date has focused on exploring cobalt phthalocyanine (CoPc), a complex that has been previously shown to be effective for moderate methanol production in an electrochemical batch reactor. The project has confirmed low-single-pass Faradaic efficiencies.

- The team made some progress achieving a methanol Faradaic efficiency of 11% at the total current density of 100 mA/cm^2 and demonstrating a pH effect; however, substantial decline of Faradaic efficiency was observed at more practical higher current densities. The water dissociation BPM transmembrane potential (go/no-go milestone) was not even discussed during the presentation. The team clearly has a reproducibility issue, and more replicates are recommended. The selected catalyst, CoPc, demonstrated very low stability and, surprisingly, no methanol formation below 50 mA/cm^2. The methanol crossover through a BPM is noticeable. More mechanistic studies are required to understand the conditions and catalyst requirements for the preferential electrosynthesis of methanol.

- This project is at an earlier TRL stage than many of the other projects but provides important, foundational work on electrolyzer R&D. Projects like this are (in my opinion) an important part of BETO's investments as long as they are tethered to more mature parts of the consortia. One common challenge with this project and WBS 2.3.4.603 seems to be the specificity of methanol production by the electrolyzer. Significant investment will be needed to address this issue. One idea that was proposed was to increase the concentration of CO in the electrolyzer's microenvironment to promote the formation of methanol.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for taking the time to evaluate this project and provide useful feedback. We are quite excited to see that the reviewers recognized the significance of electrochemical methanol production and appreciated the challenges associated with the catalyst selectivity and stability. Addressing methanol selectivity is the main goal of this 3-year project. As the reviewers recognized, the methanol selectivity demonstrated so far by our team is 30% (in a three-electrode cell) and 10% (in an electrolyzer). Our synthetic and computational efforts are focused on increasing this value, and we look forward to reporting our progress in this direction next year. The reviewers' suggestion to use carbon monoxide as an initial feedstock for reduction is excellent, and we will follow up on this in the upcoming months. The reviewers' suggestion to perform the cost analysis of our one-step pathway for e-methanol and compare it to the existing two-step approaches is excellent. We are currently collaborating with Ling Tao on this project, and we anticipate that this analysis will provide us with information regarding the target performance characteristics of the one-step approach needed to ensure economic competitiveness relative to the two-step methods. While we recognize the catalyst durability challenge, our plan is to devote this initial 3-year funding period to the study of catalyst selectivity. Our catalysts are currently not tested for durability, and all our electrolyzers are evaluated during 1 hour of operation. The literature reports have shown that the durability of similar catalysts can be improved through molecular functionalization that prevents hydrogenation of the molecular macrocycle, and we anticipate that this approach will be applicable to our systems as well. Our plan is to address this issue in the next funding cycle. Our go/no-go work associated with BPMs has been terminated because we wanted to devote our full attention to the work associated with the catalyst design. We plan to redirect the resources planned for the BPM work toward the studies of selective methanol production with molecule/electrode hybrid catalysts. The reviewers' suggestion to increase communication with Dr. Michael Betenbaugh and their team (WBS 2.3.4.603) is excellent. We will follow up on this.

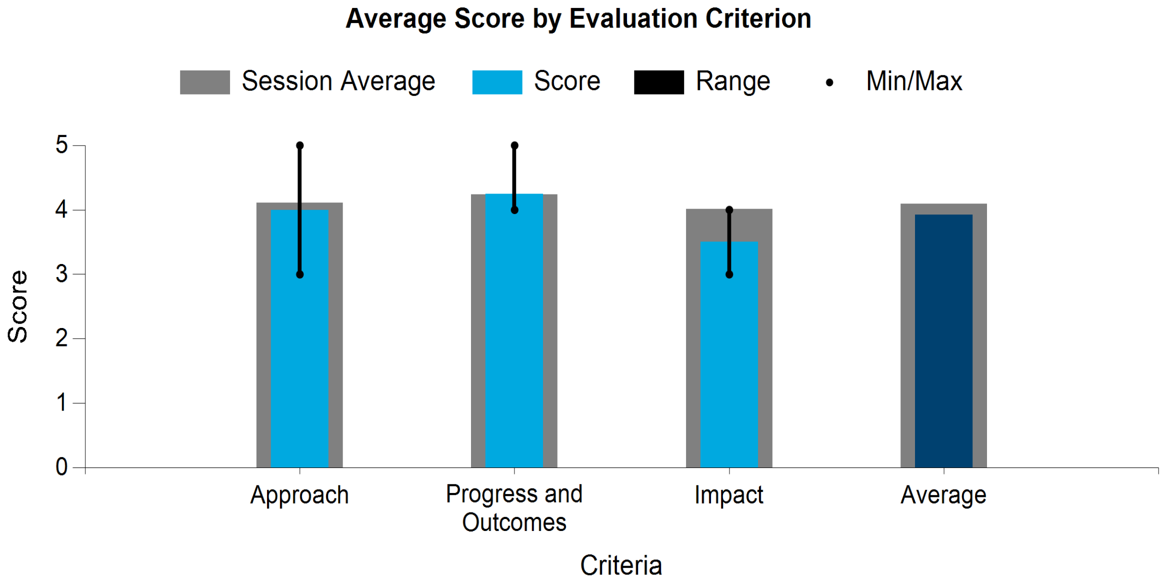
DEVELOPMENT OF A SCALABLE, ROBUST ELECTROCATALYTIC TECHNOLOGY FOR CONVERSION OF CO_2 TO FORMIC ACID VIA MICROSTRUCTURED MATERIALS

Montana State University

PROJECT DESCRIPTION

WBS:	2.3.4.600
Presenter(s):	Lee Spangler
Project Start Date:	10/01/2018
Planned Project End Date:	07/31/2022
Total Funding:	$1,862,958

The goal of this project is to develop an economically feasible pathway to convert CO_2 into higher-value chemical products. This project focusses on improving the efficiency of two key steps: (1) converting CO_2 to a formate salt intermediate by improving gas diffusion layers in a proven electrochemical reactor and (2) biologically upgrading the formate-to-ethylene glycol, a two-carbon compound using a new enzyme-catalyzed, carbon–carbon bond-forming reaction that uses single carbon inputs.



COMMENTS

- The project focuses on making ethylene glycol from CO_2 via a two-step pathway: ECO_2R to formate, followed by biological upgrading to ethylene glycol. The electrolyzer for formate production was developed based on a flow cell configuration where the flooding of the electrode is quite common. A relatively stable system (over 150 hours) has been demonstrated, with a formate Faradaic efficiency of over 85%. This was achieved by optimizing the composition of the gas diffusion layer. Self-supporting GDEs have been developed using a freeze tape casting (FTC) approach. Overall, good progress has been achieved in the part of electrochemical CO_2 conversion; however, it is unclear if the demonstrated system represents significant progress in the field. The operating cell voltage of 4.2–4.5 V at a current density of 125 mA/cm^2 is relatively high. With the flow cell configuration, it is unclear how the system will be scaled up. While the self-supporting electrode is interesting, it is unclear if it can be useful for a practical system. First, the cost of the electrode would be significantly increased. Second, its advantage over traditional carbon electrode is unclear.

- This project aims to enable CO_2 conversion to ethylene glycol by integrating CO_2 electrolyzers for formate production with a bioreactor for formate up-conversion. The overall project is divided into three distinct aims: (1) scaling CO_2 electrolyzers for formate production to >100-cm^2 sizes, (2) developing an FTC procedure for the preparation of gas diffusion membranes with lateral and vertical grading that will enhance electrolyzer stability and performance, and (3) engineering microbial systems to enhance formate conversion to ethylene glycol. The project team has made significant progress in each aim, but the research in each aim is siloed. While there is some evidence of communication between the different aims—such as testing the bioconversion process for compatibility with the potassium chloride electrolyte used in the electrolyzer—overall there has been almost no work on the integration of the work in the different aims. Some of this lack of integration may be due to travel and shipping difficulties during the COVID-19 pandemic. Another weakness of this project is the lack of a TEA-proposed CO_2 conversion process to ethylene glycol compared to conventional ethylene glycol production. The project has far-reaching potential scientific impact, especially the new FTC process for gas diffusion membranes and the biological up-conversion process.

- The team met most milestones, including relatively stable performance at 125 mA/cm^2 with an approximate 90% Faradaic efficiency for over 150 hours, but the cell voltage is higher than the target, and, more worrisome, a slight current increase to 150 mA/cm^2 resulted in fast performance decline. In addition, catholyte and anolyte have different pH values, which, without the appropriate membrane, would require some method of pH control and would increase material consumption. Unfortunately, there is no discussion of TEA and mass balance for bioconversion to support the selection of ethylene glycol as a target material. The cost of formate conversion to formaldehyde and the target product separation from the very dilute stream should be accounted for.

- This project seems to be progressing well. The electrolyzer work illustrates some very interesting and novel techniques for casting gas-permeable membranes. “Industrially relevant titer (>5 g/L), rate (>0.2 g/L/h), and yield (>90%), and remarkable scalability across different formats was demonstrated for the core condensation pathway, which can be further extended for formate-to-ethylene glycol conversion.” I find the wording of this statement misleading. It would be more accurate to say that “work will now focus on integrating parts of the pathway and testing for complete conversion from formate-to-ethylene glycol.” This is the most challenging aspect of the engineering portion of this project. Working with individual reactions is much simpler. Considering the confidence of the authors around the robustness of this system, I would suggest modifying Milestone 15.2 to include a metric around titer. The presenter mentioned that this is an aerobic process, and, as with other projects, this should be a concern for BETO because it undermines the vision of CO_2 utilization. *E. coli* grown under aerobic conditions produces *a lot* of CO_2. What is the plan for dealing with that?

PI RESPONSE TO REVIEWER COMMENTS

- Comments: The project focuses on making ethylene glycol from CO_2 via a two-step pathway: ECO_2R to formate, followed by biological upgrading to ethylene glycol. The electrolyzer for formate production was developed based on a flow cell configuration where the flooding of the electrode is quite common. A relatively stable system (over 150 hours) has been demonstrated, with formate Faradaic efficiency over 85%. This was achieved by optimizing the composition of the gas diffusion layer. Self-supporting GDEs have been developed using an FTC approach. Overall, good progress has been achieved in the part of electrochemical CO_2 conversion; however, it is unclear if the demonstrated system represents significant progress in the field. The operating cell voltage of 4.2–4.5 V at a current density of 125 mA/cm^2 is relatively high. With the flow cell configuration, it is unclear how the system will be scaled up. While the self-supporting electrode is interesting, it is unclear if it can be useful for a practical system. First, the cost of the electrode would be significantly increased. Second, its advantage over a traditional carbon electrode is unclear.

Response: Effectively scaling CO_2-formate membranes is a confluence of fluid hydrodynamics and electrochemistry. Carbon papers are a common baseline given their usability across multiple electrochemical platforms, but they do not necessarily represent specific system optimums, particularly related to scale and degradation. The research of novel freeze-processed, porous tin-based membranes has numerous potential advantages over carbon paper; however, direct comparison with simple empirical tests is challenging given the multifunctionality of the FTC TiN, and it requires an iterative approach with real electrochemical testing. The TiN membranes have already been tested by the OCOchem company, demonstrating that they can be deployed in electrochemical systems. The MSU technology eliminates multiple layers because the FTC TiN serves as the GDE and catalyst support where the underlying TiN membrane is also selectively catalytic for CO_2 to formate. In this manner, multiple laminated planar layers are eliminated into a single multifunctional membrane, where interfaces always represent bottlenecks and degradation points in electrochemical systems. The electrical conductivity of the FTC TiN is shown to be nearly three orders of magnitude improved over the carbon paper, where current collection in larger-scaled systems can be particularly influenced when the length scales of the electron current pathways are expanded. Carbon can also catalyze the production of hydrogen, where TiN is selective to formate, also potentially improving yield. The cost of TiN has been in decline, and current prices of $25/kg represent a very low cost for metals. Further, the MSU processing is done at less than 200°C, requiring low-energy and low-cost ovens for processing in lieu of higher-performance furnaces.

Comments: This project aims to enable CO_2 conversion to ethylene glycol by integrating CO_2 electrolyzers for formate production with a bioreactor for formate up-conversion. The overall project is divided into three distinct aims: (1) scaling CO_2 electrolyzers for formate production to >100-cm^2 sizes, (2) developing an FTC procedure for the preparation of gas diffusion membranes with lateral and vertical grading that will enhance electrolyzer stability and performance, and (3) engineering microbial systems to enhance formate conversion to ethylene glycol. The project team has made significant progress in each aim, but the research in each aim is siloed. While there is some evidence of communication between the different aims—such as testing the bioconversion process for compatibility with the potassium chloride electrolyte used in the electrolyzer—overall there has been almost no work on the integration of the work in the different aims. Some of this lack of integration may be due to travel and shipping difficulties during the COVID-19 pandemic. Another weakness of this project is the lack of a TEA-proposed CO_2 conversion process to ethylene glycol compared to conventional ethylene glycol production. The project has far-reaching potential scientific impact, especially the new FTC process for gas diffusion membranes and the biological up-conversion process.

Response: The price of ethylene glycol made via conventional means is the basis for comparing the proposed process and TEA. Currently, mono-ethylene glycol is made from ethylene ($500/ton), with a higher CapEx, or ethylene oxide ($1,200/ton), with a lower CapEx. The mono-ethylene glycol market price has averaged $1,250/ton in the United States over the last year. Based on final experimental results, a TEA will determine the market price that is achievable based on the OpEx and CapEx cost profile of using the proposed process.

Comments: The team met most milestones, including relatively stable performance at 125 mA/cm^2 with an approximate 90% Faradaic efficiency for over 150 hours, but the cell voltage is higher than the target, and more worrisome, a slight current increase to 150 cm^2 resulted in fast performance decline. In addition, catholyte and anolyte have different pH values, which, without the appropriate membrane, would require some method of pH control and increase material consumption. Unfortunately, there is no discussion of TEA and mass balance for bioconversion to support the selection of ethylene glycol as a target material. The cost of formate conversion to formaldehyde and the target product separation from the very dilute stream should be accounted for.

Response: Yes, we agree that there is a few percentages higher voltage requirement in the demonstrated scale-up reactor performance. A further rigorous reactor design with optimization of the electrode-membrane gaps, which is out of the scope of the current project, will be needed, and it can be planned into the next project specifically looking at a scaled-up, industry-size reactor with optimal design to provide the desired electrochemical performance. The current density could be increased by further tuning the GDE, but was not done in this work because we were meeting our target current densities. The cation exchange membrane, under proper application of the voltage that then creates the electromigration impact opposite to the diffusive impact, should help maintain the reaction rate despite the different pH values on the two sides of the membrane, as evidenced by the >120-hour test performances demonstrated.

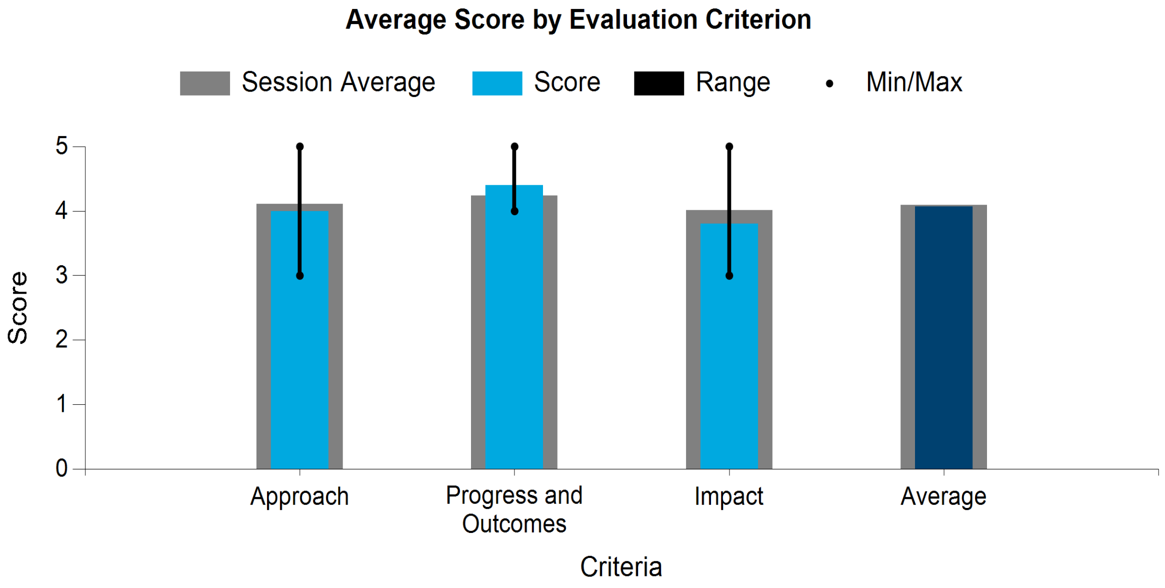
Comments: This project seems to be progressing well. The electrolyzer work illustrates some very interesting and novel techniques for casting gas-permeable membranes. "Industrially relevant titer (>5 g/L), rate (>0.2 g/L/h), and yield (>90%), and remarkable scalability across different formats was demonstrated for the core condensation pathway, which can be further extended for formate-to-ethylene glycol conversion." I find the wording of this statement misleading. It would be more accurate to say that "work will now focus on integrating parts of the pathway and testing for complete conversion from formate-to-ethylene glycol." This is the most challenging aspect of the engineering portion of this project. Working with individual reactions is much simpler. Considering the confidence of the authors around the robustness of this system, I would suggest modifying Milestone 15.2 to include a metric around titer. The presenter mentioned that this is an aerobic process, and, as with other projects, this should be a concern for BETO because it undermines the vision of CO_2 utilization. *E. coli* grown under aerobic conditions produces *a lot* of CO_2. What is the plan for dealing with that?

Response: The University of South Florida appreciates the comment and agrees that the statement should be reworded as suggested. The University of South Florida also agrees that Milestone 15.2 should be modified to include a metric around titer. With regard to CO_2 generation, we can distinguish CO_2 generation during the growth phase and bioconversion phase. For the growth phase, we solely focus on the biomass production with minimum time and resource input to obtain the required biomass and bioconversion rate. Our goal is to reduce the growth phase and extend the bioconversion phase to limit the resource input for biomass production (growth phase) below 10% (in carbon basis) of the amount of the substrate utilization in the bioconversion phase. While capturing CO_2 from this process would be challenging due to the presence of oxygen under aerobic conditions, as noted in the comment, we envision that the amount of CO_2 generation from the growth phase would be substantially smaller than the amount generated during the bioconversion phase, which we plan to capture and recycle. For the bioconversion phase, the generation of CO_2 is inevitable considering formate as the only source for the generation of ethylene glycol, a significantly more reduced product. We plan to use formate dehydrogenase to compensate the requirement for reducing power by oxidizing a fraction of formate to CO_2. The CO_2 generated from this process can be captured and recycled to the upstream CO_2 electrolyzer.

PRODUCTION OF BIOPRODUCTS FROM ELECTROCHEMICALLY GENERATED C1 INTERMEDIATES

LanzaTech, Inc.

WBS:	2.3.4.601
Presenter(s):	Jason Bromley
Project Start Date:	10/01/2018
Planned Project End Date:	07/31/2022
Total Funding:	$1,734,576



COMMENTS

- The information gained by their integration test setup can help advance the field of integrated bio-electrochemical systems. The recycle loop and other controls will provide valuable information regarding the integrated system and the mass balance. The test station setup (recycle loop, pressure control, gas chromatography analyzers, etc.) could be valuable to the other projects converting CO_2 to $CO:H_2$, so it may be beneficial to have more collaboration with the other projects. Additional information/questions for further assessment:

  Risk management:

  - I look forward to seeing the results when the recycle loop is continuously operational and a mass balance can be obtained, along with further insight into the efficiency losses.
  - Additional information regarding the potential toxicity of isopropyl alcohol (IPA), and how does this factor into operations and the energy intensity of the process?

  Potential impact:

  - Additional information regarding the target product (IPA), what numbers their processes need to reach to be cost-competitive, and a road map as to how they aim to achieve their targets
  - Additional information regarding the additional cost of generating hydrogen
  - Additional information regarding the effect of the CO_2 conversion percentage on the TEA.

- The project focuses on integrating electrochemical CO_2 conversion and biological reactors at a relatively large scale. Great effort on demonstrating an integrated system, overcoming several obstacles. Carbon crossover in an MEA cell would limit the overall carbon conversion efficiency. It is important to evaluate the energy cost and carbon footprint for CO_2 separation (in the anode side) step. Combining the CO_2 electrolyzer and water electrolyzer to tune the CO_2:CO:H_2 ratio and achieve 100% carbon efficiency would have a significant impact.

- This project by LanzaTech focuses on integrating CO_2 electrolysis with gas fermentation to convert CO_2 to isopropanol with performance targets of 0.65 g/L/h isopropanol production with >37% carbon efficiency. The project uses a 250-cm^2 electrolyzer from Dioxide Materials for the CO_2 conversion to CO, followed by the integration of the output stream with their own biofermentation CSTR. All target performance metrics were achieved and exceeded, although circulation was required to achieve the carbon-efficiency targets. Recirculation did cause unforeseen issues in the system design due to the buildup of inert salts and sulfur impurities in the recycled CO_2 streams. The choice of the project to de-emphasize integration and focus on performance enhancement was well considered, as it is unclear that prioritizing integration is needed at such small production scales. This project achieved its stated objectives and is an important proof of concept that integrated electrolyzer and fermentation technologies can convert CO_2 to useful products.

- The team made substantial progress in the integration of Dioxide Materials' electrolyzer with the bioconversion of CO to IPA, including the energy consumption target. It would be interesting to evaluate the effect of temperature and back pressure on electrolyzer performance. The increase of the H_2:CO ratio may increase the CO_2 utilization, but this is not good for bacteria, so further microbial optimization is desirable; however, optimistic projections of IPA cost are based on the assumption of very low electricity and arginine prices that should be dropped five times. It is not clear what capacity factor for renewable electricity is used and how the arginine price could be reduced so much (unfortunately, attempts to replace it with inexpensive ammonia were unsuccessful). Based on experimental data, the separation of IPA from biomass and ethanol should be included in the cost structure (so far not included in the flow diagram). The IPA market is noticeably smaller than that of ethanol, so it is desirable to add the market analysis to the project scope to estimate commercialization prospectives in this approach.

- This project seems to be progressing well, and I have little concern about the overall approach, results, or impact. The goals involving arginine should be modified, as it appears that despite the modeling, no benefit was seen when using arginine instead of ammonia.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate all the reviewers' comments and suggestions, including the acknowledgement of the progress made in integrating biologic and electrochemical systems and understanding the reasons for shifting the project focus to performance once initial integration data were generated. Some additional points to address questions and comments raised:
  - The test station setup has already been used to provide a sample of potable alcohol from biogenic CO_2.
  - We have reached the end of the project budget, and one main conclusion is to recommend larger piloting reactors (10–100 times this size) to make more accurate assessments of performance,

including the closure of mass and carbon and energy balances, which is a big challenge at this stage when including a recycle loop.

- IPA has similar physical properties to ethanol, whose toxicity is known to a greater degree on similar acetogens, but detailed toxicity data of IPA on the LanzaTech strain are unable to be shared publicly.
- TEA is part of the project, but unfortunately most details are unable to be shared publicly. The TEA model relies on data generated from lab experiments and are updated at each billing period.
- Additional hydrogen will consume CO_2 to the following stoichiometric ratio to produce IPA: $9H_2 + 3CO_2 \rightarrow C_3H_8O + 5H_2O$. The cost of green hydrogen is steadily decreasing based on improvements to sustainable electricity generation and water electrolysis.
- While this project has completed operations, the reviewer feedback on back pressure and temperature will be considered as avenues for future work involving electrolyzer integration.
- The project successfully demonstrated the production of IPA using an engineered strain from gases. The use of arginine as a nitrogen source to boost production was muted.

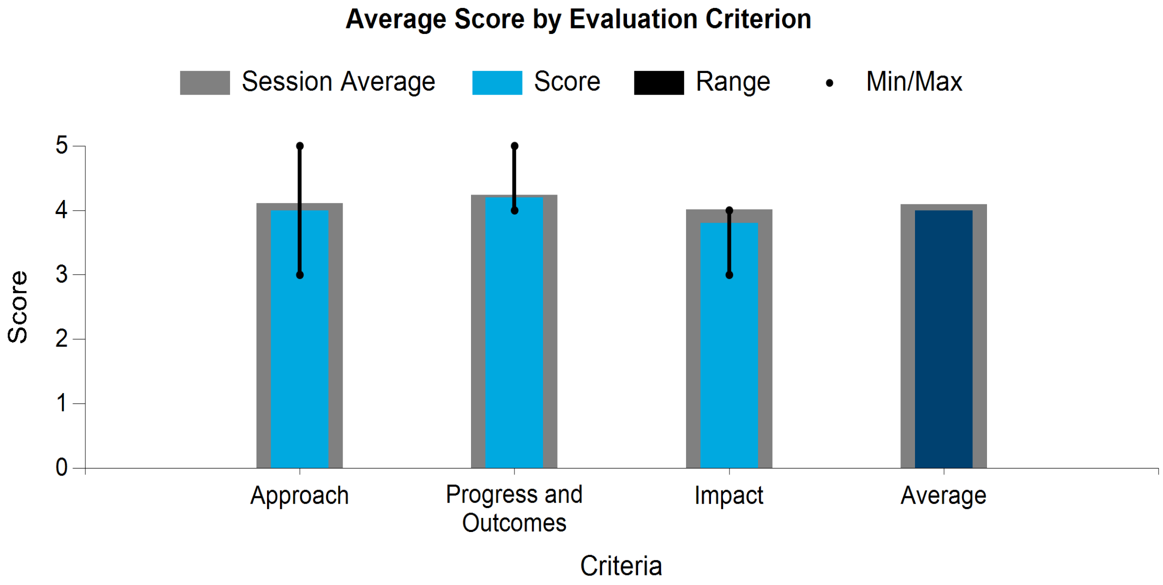
INTEGRATING CHEMICAL CATALYSIS AND BIOLOGICAL CONVERSION OF CARBON INTERMEDIATES FOR DERIVING VALUE-ADDED PRODUCTS FROM CARBON DIOXIDE

Johns Hopkins University

PROJECT DESCRIPTION

WBS:	2.3.4.603
Presenter(s):	Michael Betenbaugh
Project Start Date:	10/01/2018
Planned Project End Date:	07/31/2022
Total Funding:	$1,951,339

Capturing and upgrading point-source CO_2 represents a desirable technological goal to achieve sustainability targets. Electrocatalytic processes excel at reducing CO_2 into simple carbon compounds. Conversely, biocatalysts excel at upgrading reduced carbon compounds. In this project, we are developing a two-stage integrated platform that leverages the advantages of both electrocatalytic and biocatalytic systems: CO_2 is converted into methanol and hydrogen via electrocatalysis and is subsequently valorized using a methanotrophic bacteria. The electrocatalytic reduction of CO_2 uses an advanced catalyst that achieves a high carbon conversion efficiency into methanol. Cell line development to optimize the bioconversion of methanol by *Methylotuvimicrobium alcaliphilum* 20ZR incorporates metabolic engineering to channel the electrocatalytic product into PHA and biomass. Cell line adaptation is used to adjust to the high-saline electrocatalytic conditions entering the bioreactor, and transcriptomics analysis is applied to determine regulatory mechanisms for optimal cell line performance. A TEA and LCA of the complete process further investigate commercial feasibility and opportunities for future process development. In total, this technology represents a potentially transformative platform combining electrocatalytic and biological conversion steps into an integrated approach for the bioproduction of commercial products.



COMMENTS

- This approach to this project is novel, both in catalyst and biological upgrading, and well thought through. I appreciate the adjustments of the intermediate products made to determine an efficient path forward demonstrating continued communication, analysis, and risk mitigation. Targeting MeOH as an intermediate is an important path to explore regarding CO_2 utilization. I suggest more communication with other groups researching similar pathways, such as Glusac. I felt that the information shared regarding their electrolyzer was insufficient to make a good judgment; however, I understand there was not enough time to address everything during this review. Additional information/questions for further assessment:

Risk management:

- Additional information regarding the statement stable electrocatalysts for continuous operation. Details regarding the conditions, stability, and scalability (including pH, temperature, current density, voltage, etc.)
- Additional information regarding the covalent organic framework (COF)-CoPc catalyst; stability and scalability
- Additional information regarding the gas and liquid recycle loops; accuracy of the mass balance calculations, conditions in the liquid recycle loops, further analysis of the scaled-up version, TEA sensitivity regarding per-pass conversion of CO_2 and operation of the recycle loop, production of trace byproducts
- Additional information regarding their high conversion rate: stability and scalability.

Impact

- Additional information regarding the current and future target of the space time yield of MeOH/formate.

- This project focuses on converting CO_2 to bioproducts via methanol. The team has diverse and complementary expertise. Some progress on CO_2-to-methanol conversion has been achieved, especially the carbon efficiency; however, the selectivity of the process (Faradaic efficiency) has not been discussed. There seems to be some overlap with other projects (converting CO_2 to CO using molecular catalysts). It is unclear what the requirement for CO_2 to methanol would be based on TEA. In addition, CO_2 conversion to methanol via thermal catalysis has been quite advanced. It is unclear if the electrocatalysis process would have advantages compared to thermal catalysis. Comparisons of the two pathways using TEA/LCA would be helpful.
- This project aims to integrate a CO_2-to-methanol electrolyzer with engineered biocatalysts to convert methanol to PHA. The project is divided into three main tasks: electrocatalysis, biosynthesis, and integration. Each task has made significant progress during the project period. In electrocatalysis, the project team uses CoPc to convert CO_2 to methanol. CoPc is one of the few catalysts previously reported to produce methanol with up to 44% Faradaic efficiency in highly optimized batch reactors through a cascade catalysis process in which CoPc first converts CO_2 to CO and then CO to methanol; however, single-pass flow electrolyzers incorporating CoPc typically produce CO, not methanol, likely because the local concentration of CO is not allowed to build up in these traditional electrolyzer setups. The project team uses a recirculating electrolysis system and a COF support for the CoPc that has enabled them to achieve 90% carbon conversion efficiency with 40% Faradaic efficiency for methanol production. This is an important achievement and validation of CoPc as a CO_2-to-methanol catalyst; however, more comprehensive TEA and LCA are required to determine whether this approach could be economically viable due to the relatively low Faradaic efficiency for methanol. In the biosynthesis task, the project team has engineered microbes to convert methanol to PHA and biomass with a high carbon conversion efficiency, >50%, and good yields. In both the electrolyzer and biosynthesis tasks, the project team has met or exceeded milestone goals. In integration, the project team has also made progress, but

perhaps less than the other tasks. They are able to perform 50-mL-scale bioconversions using mock electrocatalysis products and meet their carbon conversion efficiency and process yield target milestones, but they have not yet scaled the process to the target 1-L scale or used real electrocatalysis projects. Still, there is evidence of close communication between the scientists in each task and clear demonstration of how integration challenges have led to new optimizations in the electrocatalysis and biosynthesis tasks. This is a well-executed project that has already made significant impact in electrocatalysis and biosynthesis, and it has a good chance of meeting its final integration milestone goal. This project would likely benefit from increased discussion and collaboration with members of the CO_2RUe, especially WBS 2.3.4.304, which aims to design new catalysts for electrochemical CO_2-to-methanol conversion.

- The project pivot from formate to methanol looks justified, and the team demonstrated noticeable progress in the conversion of CO_2 to methanol. Carbon conversion efficiency was close to the target (32% versus 37%); however, it was not quite clear what changes have been made (in addition to recirculation of the gas stream) to switch the reaction mechanism from CO to MeOH as a major product with the same catalyst. The methanol current density and Faradaic efficiency (~27%) are still too low to be practical. The stability of the single-atom cobalt catalyst was not presented. There are some questions about the performed TEA. The cost baseline was not defined, and the proposed credit for the hydrogen sell ($5–$6/kg) seems to be high in light of the current DOE target ($1–$2/kg). The energy balance for the two-step process (CO_2-MeOH-PHA) was not presented, and the process of PHA separation (6%) from biomass was not discussed.

- The project seems to be going well and is supported by a talented group of investigators. The strain engineering side seems particularly strong with the support of Dr. Marina Kalyuzhnaya. In regard to communication, I was surprised to hear that this team had not (apparently) heard of the work being conducted by Dr. Glusac in WBS 2.3.4.304 (hence the three on approach). I would encourage the two teams to meet and discuss their findings because that would likely benefit both groups.

PI RESPONSE TO REVIEWER COMMENTS

- In our study, we achieved a Faradaic efficiency of 40% for the conversion of CO_2 to methanol using our CoPc-COF electrocatalysts. This high efficiency was made possible by the CoPc active center, which has been established as a leading catalyst for methanol production, as reported in https://doi.org/10.1038/s41586-019-1760-8. Note that the byproducts of this conversion process were hydrogen and CO. Additionally, we observed a slightly lower Faradaic efficiency of 20%–25% for the conversion of CO to methanol on the CoPc-COF catalyst, without the presence of other carbon byproducts. Consequently, the overall carbon conversion efficiency in our electrocatalysis system exceeds 90%; therefore, our findings demonstrate the feasibility of achieving high methanol production rates while maintaining a significant carbon conversion efficiency. In terms of scalability, we used a 5-cm^2 flow cell electrolyzer, which has proven capable of producing approximately 1 gram of methanol/day. This was achieved by operating at a current density of 100 mA/cm^2 with a 40% Faradaic efficiency. Further, it is worth clarifying that our CO_2-to-methanol conversion process does not involve an intermediate step through formate. We have distinct electrocatalytic processes for CO_2-to-methanol and CO_2-to-formate conversions, each utilizing different catalysts. The CO_2-to-methanol conversion is facilitated by our synthesized CoPc-COF catalysts, while commercially available TiN oxide powder serves as the catalyst for CO_2-to-formate conversion. Regarding the stability of our system, we have identified catalyst deactivation as the primary failure mechanism for CO_2-to-methanol conversion. The reduction potential applied during the electrocatalysis process chemically reduces the CoPc catalyst, leading to deactivation; however, based on the findings presented in the aforementioned paper, the stability of CoPc can be enhanced by introducing amine groups to the aromatic rings. Our CoPc-COF catalyst incorporates tetraamine-substituted CoPc, which has demonstrated stability over 100 hours of continuous operation. While the failure mechanisms related to COF formation require further investigation, our current study focuses on the stability and efficiency of the electrocatalytic process for CO_2-to-methanol conversion.

There are two groups of PHAs according to the number of carbon atoms in the monomer units: short-chain-length PHAs (scl-PHAs) with 3–5 carbon monomers (most common, polylhydroxybutyrate, PHB), and medium-chain-length PHAs (mcl-PHAs) with 6–14 carbon monomers. While most bacteria produce PHB, the polymer is not "ready-to-go" plastic because it has low thermal stability and is brittle (not elastic). Contrary to PHB, mcl-PHAs are thermoplastic with attractive properties for biomedical applications (according to https://doi.org/10.1002/app.34772). As a result, mcl-PHAs have a higher price. We used two standard protocols for PHA separation at the lab scale: (1) chloroform extractions followed by cold acetone precipitation. The chloroform solubilization/precipitation step was repeated two to three times to achieve high purity of preparations for nuclear magnetic resonance studies (https://doi.org/10.1007/BF00500854). (2) Bleach extractions were used for quick culture screens (adapted from protocol provided by Dr. Averesch, Stanford University). Briefly, cell cultures (25–50-mg dry cell weight) were harvested by centrifugation and lyophilized overnight. Freeze-dried pellets are weighed for dry cell weight. PHA is released with 10% NaClO (0.2-mL/mg dry cell weight). Vortex vigorously until all biomass is dispersed. After no more than 1 hour, dH_2O is added 2:1 to allow precipitation of PHA by centrifugation (10 min, 4,800 g). The raw polymer is washed twice with dH_2O, washed once with methanol (or ethanol, or not at all), and freeze-dried. Dry PHA samples were weighed to determine the yield. If needed, the samples were further purified using the chloroform extraction method. Assessment of the scaled-up, integrated system is currently underway and is a primary focus for the remainder of the project. Previous experiments have shown that the mock electrocatalysis products used are comparable to the real electrocatalysis products produced in this project, although these data were not presented during the presentation due to time constraints. We intend to use the actual electrocatalysis products in the next tests of the integrated system. Preliminary testing has also shown comparable performance at larger (>1-L) scales, although final testing is still in progress.

As this project nears completion, we look forward to the opportunity to potentially collaborate with the other groups (Dr. Glusac, CO_2RUe) mentioned by the reviewers in the future. The previous TEA performed as part of this project confirmed that a formate product is preferred to methanol for the electrolyzer due to superior Faradaic efficiency and economic incentives. The production of methanol required a distillation column to separate the produced methanol from the electrolyte, resulting in significant operating costs; however, the production of methanol is found to achieve higher carbon conversion efficiency, and experimental work has been done to adapt the bioreactor system to higher concentrations of sodium bicarbonate electrolyte. This allows us to possibly bypass the distillation column, prevent significant utility costs, and achieve more favorable economics.

Regarding electrolyzer performance, the single-pass and overall conversion of CO_2 is 98% and 96%, respectively, according to the current technological benchmarks. In comparing between the choice to recycle CO_2 or not, there are slight differences in the net present value due to the reduced amount of mcl-PHA produced. Recycling CO_2 is preferred, and the implementation of a recycle stream is also important for preventing CO_2 emissions from the plant. A possible comparison of the use of thermal catalysts instead of electrocatalysis can be performed using reference data from other sources of literature. https://doi.org/10.3389/fenrg.2020.621119 provides a detailed analysis of thermocatalytic methanol synthesis and can be used for comparison in terms of both TEA and LCA. For the downstream processing of biomass and mcl-PHA, the process is based on work developed by from the patent "Process for the solvent-based extraction of polyhydroxyalkanoates from biomass" by Narasimhan et al. and from https://doi.org/10.1016/j.jece.2016.07.033, with guidance from industry experts. Bioreactor effluent is sent to a gravity belt thickener where the liquid is thickened to 8 wt % solids content. The thickened sludge is fed to a decanter centrifuge, where it is further dewatered to 35 wt % solids. The wet solids are then sent to a horizontal belt dryer to be dried further to 90 wt % solids. A pressurized solvent extraction vessel is used to extract the mcl-PHA from the biomass where acetone is used as the solvent.

The mcl-PHA is dissolved in the acetone phase using a mixer and heater. A disk stack centrifuge is used to separate the biomass from the hot liquid to 20 wt % solids. Any mcl-PHA lost in the wet biomass effluent needs to be recovered using a rotary drum pressure filter. This produces a solid biomass product for sale. The mcl-PHA liquid stream is cooled and sent to a stirrer where it is combined with water at a predetermined ratio to precipitate the mcl-PHA. A gravity belt thickener and a rotary vacuum drum filter is used to dewater the mcl-PHA to 65 wt % solids. It is then washed with acetone to remove extra lipids and then sent to a final horizontal belt dryer to evaporate off solvents and produce a dried mcl-PHA product at 99.5 wt % solids. For the improved technological scenario without the use of a distillation column, we currently have calculated a cost baseline of $968.61 million for total capital costs and operating expenses of $748 million/year. Note, however, that this baseline assumes an H_2 sale price of $5.75/kg. This estimate was originally chosen based on a 2020 report from NREL; however, it is understandable that this baseline sale cost is still considered high and can be reduced to the target sale price of $1–$2/kg for the final analysis.

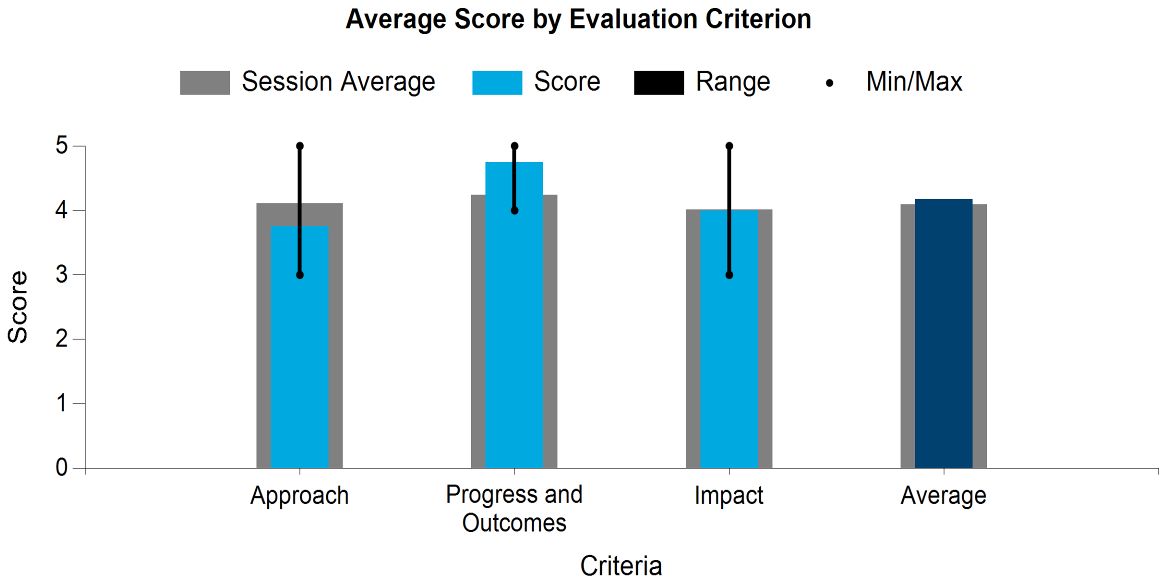
MULTIPHYSICS CFD FOR DESIGN AND SCALE-UP OF GAS BIOREACTORS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.4.1.102
Presenter(s):	Hari Sitaraman
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024
Total Funding:	$250,000

Gas fermentation technology offers sustainable and high-carbon-efficiency routes to fuels and chemicals; however, efficiently delivering low-solubility substrate gases to production-scale bioreactors is a significant technical challenge that could limit productivity. We perform fundamental and applied multiphysics computational fluid dynamics (CFD) research targeting specific challenges of gas delivery in fermentation systems that used varied gas compositions—e.g., CO_2/CO/CH_4/H_2 substrates: bubble dynamics, coupled mass transfer and reaction—that can lead to optimal reactor designs at scale. This work will support BETO goals toward GHG reduction, de-risking technologies toward commercialization/deployment and SAF synthesis targets.



COMMENTS

- The knowledge gained from this project has the potential to improve the efficiency of bioreactors across the field. It is not clear to me how much of an impact this project can have without further information regarding the range of improvements in TEA, LCA, productivity, etc., that can come from the findings of this project.

- The project focuses on modeling bioreactors for scaling up. There are several experimental projects on biological upgrading that could be beneficial from this project. Progress has been made on the effect of gas mixture (H_2:CO_2:CO) on the mass transport in the bioreactor; however, experimental design to validate the model is needed. I am not sure if mass transport is the limitation factor in this type of reaction or the rate of the bioreaction. Also, products from biological reaction (e.g., fatty acid) can act as bubble stabilizing agents and affect bubble size and the mass transport.

- This project plays an important role in the CO_2RUe by modeling the performance of different bioreactors as they translate from the lab scale to the industrial scale. Understanding the challenges and limitations to scaling bioreactors to relevant industrial production scales is crucial for the eventual implementation of CO_2 utilization technologies for SAF, so this project has high potential impact. The project has mostly focused on bubble reactor designs for the current funded work, but the project team has previously considered other reactor designs. A key strength of this project is the close interactions with stakeholders, including industry partners who provide experimental data and advice on scale-up. Much of the future immediate work will focus on simulation validation and expanding the simulations to new reactor designs. The project would be strengthened through closer interactions with the consortium analysis teams who could provide TEA and LCA to help down-select reactor designs. Overall, this is an impactful project that should continue to make important contributions to scaling biofermentation processes.

- Developing and validating novel reactor designs is critical to the success of gas utilization platforms, and this project provides excellent insight into how different reactors influence performance metrics. The only concern I have regarding this project is really a hope that this work will translate into tangible improvements in reactors that can be validated in the real world. I understand that is out of scope for this project.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their comments and constructive feedback that will strengthen the impact of this project. Our efforts in the past year (during early stages of the project) have been working toward developing a validated and predictive computational model for bioreactors that use CO_2. The real impact on TEA/LCA improvements will be achieved through the final phase of our project on novel reactor designs at scale that can improve CO_2/syngas conversion. Our models can predict theoretically possible bioreactor yields and efficiencies through more accurate, three-dimensional, multiphase simulations compared to zero- and one-dimensional models used in current TEA software. As improvements in microbial bioreactions are being pushed to the limits, mass transfer and mixing limitations at scale are going to drive the overall productivity, thus emphasizing the need for accurate and predictive multiphase flow models for reactor optimization and scale-up. We agree with the reviewers regarding the effect of surfactants on bubble size distributions, which is being added to our model for the validation work planned in our second year. Our current efforts on model validation have been through experiments from literature that are idealized (pure CO_2, constant bubble size), which will be improved for achieving the go/no-go milestone in September 2023. We agree with the reviewer on tightening collaborations with analysis efforts within the consortium, which is planned in the final phase of this project where we simulate large-scale reactors. We are also working closely with industry partners such as LanzaTech to enable the widespread usage of our modeling tools and provide tangible improvements in reactor designs.

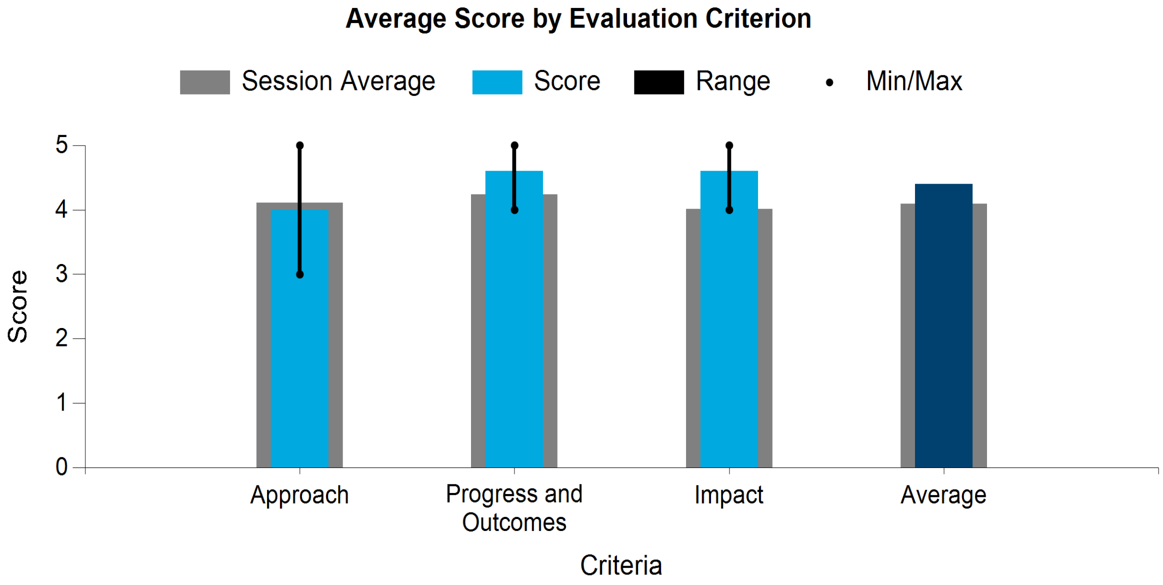
CO_2 CONSORTIUM PROJECT MANAGEMENT

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.6.3.502
Presenter(s):	Michael Resch
Project Start Date:	01/01/2022
Planned Project End Date:	12/31/2024

This project funds the management activities of the CO_2RUe. The PI and project manager coordinate the analysis, electrolysis, and biological working groups focusing on the integration process to convert CO_2 into SAF and high-value products supporting BETO's goal of decarbonizing energy-intensive industries. This project will directly support BETO's CO_2 Utilization program goals under "Decarbonizing energy-intensive industries" by providing project management support and oversight to BETO's CO_2RUe and ensuring that BETO has a robust plan and well-run consortium to develop technologies to upgrade CO_2 to fuels and chemicals to reduce GHG emissions, decrease land and water use, and incentivize decarbonization. The project will support the PI and project manager at NREL. The PI will provide scientific direction and leadership, assist BETO with technical management and organization of all consortium projects, integrate the scope and effort of individual projects into a cohesive consortium, promote the consortium to external stakeholders, and maintain a positive relationship with internal and external advisory boards, BETO, and the PIs of individual projects. The project manager will maintain documentation and outreach materials; curate information management; manage communication; develop and revise processes; launch the consortium website; and craft and implement a diversity, equity, and inclusion (DEI) plan. This project directly supports BETO's DEI goals by making resources available on the consortium website for students and teachers to learn about BETO technologies in a free and accessible environment.



COMMENTS

- The CO_2 utilization consortium has done an amazing job with overviewing and managing complex interconnected projects. The CO_2 utilization consortium project leaders have the potential to guide the direction of the consortium as well as the individual research projects in a unique way with a broad perspective.

Risk management:

- Increased communication between the groups and further collaboration and synchronization between each research effort
- More connection between the LCA/TEA groups and the experimental research projects would guide research efforts and synchronize target outcomes.
- More information and effort on outreach to industry and widespread knowledge exchange
- Plans to prioritize DEI. As leaders of the CO_2 consortium, there is an opportunity to make an impact regarding DEI.

Approaching the complex challenge of scaling ECO_2R from multiple angles is key to determining the most viable route to scaling this technology; however, more clarity and focus on which topics to address may help limit R&D overlap between the groups, e.g., designing and testing larger electrodes. Increased synchronization between the groups focusing on scaling the reactor and system setup (recycle loop, humidity control, pressure regulation, etc.) could prove to be more efficient. Some of these experiments get hampered by operability and equipment, and with further collaboration, more real-world testing could be done faster from an equipment, analysis, and operability standpoint.

Another example is with the research on bio-electrochemical systems. There is emphasis on proving that the integrated system can work, and this can lead the integrated systems to function for a short amount of time in an unsustainable way. The separate systems need to reach a higher level of maturity, particularly electrochemical CO_2 reduction, before focusing on their integration; however, I believe the information gained from integrating the systems is critical. Perhaps having fewer groups focusing on designing test stations to integrate the system could help improve efficiency while not losing the valuable information gained from the integration early on in R&D.

- This is a great initiative with combined expertise and technical capability. There seem to be multiple TEA and LCA projects looking at the integration of different processes. Many projects focus on the conversion of CO_2 to CO and formic as intermediates for further fermentation. Each project seems to focus on different parts or performance metrics for CO_2 conversion; perhaps it would be more impactful if there was a unified effort on advancing the electrolysis part that can be combined with subsequent upgrading processes.
- The focus of the CO_2RUe is to facilitate collaboration between research groups working on the CO_2 conversion to SAF. The CO_2RUe divides its projects into three working groups: CO_2 electrolysis, biological upgrading, and analysis and modeling. To foster collaboration, CO_2RUe members participate in regular working group meetings and larger consortium meetings and have collaborative milestones built into their individual projects. This collaborative approach is well considered and effective, and it has led to substantive collaborations between the individual CO_2RUe projects. The consortium structure is reasonable and consists of a central lead advised by internal and external advisory boards. The consortium lead's role is to help coordinate project goals, facilitate collaborations, set overarching research directions, and meet biweekly with BETO program managers. The consortium uses a bottom-up leadership approach rather than top-down mandates, so the project lead has no direct control over project funding or research directions. This is a strength in terms of engagement and project buy-in, but it may provide future complications if a project is underperforming or not effectively engaging within the consortium portfolio. A strength of the CO_2RUe is that it magnifies the impact of the individual consortium projects. For instance, the CO_2RUe hopes to set near-term technical targets for the entire community in terms of electrochemical and biological CO_2 upgrading and help de-risk technologies by evaluating location-specific feedstock and output markets. These efforts require communication between several projects in each working group, and they can only be achieved through a coordinated

multiproject effort. The CO_2RUe appears to be a well-run consortium with a reasonable management structure that has the potential to have appreciable impacts on CO_2 upgrading to SAF.

- The project has a clear technical path forward and has demonstrated progress toward the project goals. The integration of a 250-cm^2 CO_2 electrolyzer with CSTR was demonstrated. Preliminary data on H_2S tolerance are encouraging, but only for low current densities. Reasonable coordination between partners can be seen. Milestones have been met; however, one stated goal is the reduction of the CO_2 membrane crossover by 20%, but no work has been started yet. The idea of using CO_2 feedstock from ethanol refineries is good but is not analyzed in depth. For example, requirements to the source of renewable electricity (wind)—such as placement, capital investment, and availability—as well as the business model are not developed. The performed TEA points to the CO_2 single-pass conversion as a major cost factor. In other processes, its importance is very low because the addition of an inexpensive CO_2 separation and recycling loop eliminates this issue.

- The organization around the CO_2 Utilization consortium is clearly adding a lot of value. The project seems well integrated with BETO's higher-level strategy and is generally managed effectively. Some feedback worth considering for future iterations of this consortium:

    - Improve communication between research groups. It was clear during the review that many of the groups had not interacted with each other that much or at all. This is a clear area for improvement that should be led by the group's leadership.

    - Balance lower- and higher-TRL projects. There is a need to continue investment in lower-TRL projects, but that obviously comes with some risk. BETO is encouraged to ensure that these projects are anchored to well-established aspects of the consortium to promote engagement and success. I would also encourage BETO to calibrate their investment for these projects based on the balance between risk and reward.

    - Continue engagement with industry, with some prerequisites. Industry partners have a unique opportunity to add value to this program and should be included in future iterations. That said, BETO is encouraged to set some expectations regarding communication around results to ensure that there is a sufficient level of openness around these data.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the supportive comments, and we will address the listed concerns.

  To increase communication between the groups and further collaboration and synchronization between each research effort, we will have our second annual all-hands meeting in June 2023. The intent of this consortium meeting is to discuss progress and plan for future work. The majority of the participants will be able to attend in person, and we believe this will be an important opportunity to build relationships and collaborations between projects and working groups. Additionally, this will be an opportunity to identify research gaps and identify ways to improve our collaborations as a consortium. To enable more connections between the LCA/TEA groups and the experimental research projects to guide research efforts and synchronize target outcomes, the all-hands meeting will be an opportunity for cross collaborations between working groups with a focus on future planning. There has been expressed interest in more collaborations between the analysis group and the other two working groups, so this is something that will be explored further. Our project management effort on outreach to industry and widespread knowledge exchange will be expanded. We are in the process of communicating with other CO_2 upgrading research consortia in Europe to collaborate and exchange ideas and find ways our projects synergize. Our external advisory board was selected from industry and academic members with backgrounds across the value chain. We are also attending international scientific meetings to present the ongoing work in the consortium.

We agree that DEI is an important priority for the consortium. We recently hired a project manager with experience in DEI and community development, and she will work with the consortium to improve DEI and community benefit plans in current and future projects. We are also employing GEM fellows on two research projects. The mission of The National GEM Consortium is to enhance the value of the nation's human capital by increasing the participation of underrepresented groups (African Americans, American Indians, and Hispanic Americans) at the master's and doctoral levels in engineering and science.

At NREL, we have been working with the recently formed design-build team, who have experience in building CO_2 electrolyzer test stands in coordination with industry and environment, safety, health, and quality. We hope that these efforts can be standardized to safely build and install test stands across the national labs.

To synergize the electrolyzer efforts, we have the electrolyzer CO_2 working group (e-COWG). This group collectively focuses on key aspects of electrolyzer conversion efficiency, durability, and cell hardware designs.

Although we prioritize a bottom-up leadership approach, the leaders of the consortium work to find solutions with projects that are underperforming or not engaging. We have bimonthly individual meetings with each project team to discuss project progress and any challenges the PI or project may be facing.