CATALYTIC UPGRADING

TECHNOLOGY AREA

CONTENTS

INTRODUCTION

The Catalytic Upgrading Technology Area is one of 12 technology areas reviewed during the 2023 Bioenergy Technologies Office (BETO) Project Peer Review, which took place April 3–7, 2023, in Denver, Colorado. A total of 19 presentations were reviewed in the Catalytic Upgrading session by five external reviewers. For information about the structure, strategy, and implementation of the technology area and its relation to BETO's overall mission, please refer the corresponding Program and Technology Area Overview presentation slide decks, which can be accessed at the Peer Review website: www.energy.gov/eere/bioenergy/2023-project-peer-review.

This review addressed a total U.S. Department of Energy (DOE) investment value of approximately $16 million, which represents approximately 3% of the BETO portfolio reviewed during the 2023 Peer Review. During the Project Peer Review meeting, the presenter for each project was given 20–90 minutes to deliver a presentation and respond to questions from the review panel.

Projects were evaluated and scored based on their approach, impact, 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 Review, including scoring information for each project, comments from each reviewer, and the response provided by the project team.

BETO designated Sonia Hammache as the Catalytic Upgrading Technology Area review lead, with contractor support from Umakanta Jena of Boston Government Services. In this capacity, Sonia Hammache was responsible for all aspects of review planning and implementation.

CATALYTIC UPGRADING REVIEW PANEL

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Dr. Cory Phillips*	Director of Engineering Development, Air Company
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CATALYTIC UPGRADING REVIEW PANEL SUMMARY REPORT

Prepared by the Catalytic Upgrading Review Panel

INTRODUCTION

For the 2023 cycle in the Catalytic Upgrading Technology Area, the review panel evaluated a portfolio of 16 projects. Most (15) of these were housed within the national-laboratory-led (National Renewable Energy Laboratory [NREL], Pacific Northwest National Laboratory [PNNL], Los Alamos National Laboratory [LANL], Oak Ridge National Laboratory [ORNL], and Argonne National Laboratory), annual operating plan (AOP)-based Chemical Catalysis for Bioenergy Consortium (ChemCatBio). The remaining project was a funding opportunity announcement (FOA)-based project led by the University of South Florida. The overall quality of the presentations was excellent, and the session was completed in just 2 days, remaining on schedule, with adequate Q&A following each talk. Frequently, there was ample time for the audience to offer some technical inquiry as well. The high-level themes remained the same: (1) core technology—catalytic upgrading of C1, C2, and biochemical intermediates and catalytic fast pyrolysis (CFP)—and (2) crosscutting and enabling tools—catalyst synthesis, characterization, deactivation, multiscale, computational modeling, and data hub. However, in this cycle, the conceptual process designs and objectives pivoted and focused mainly on sustainable aviation fuels (SAFs) and chemicals as key products to align with the overall BETO objectives.

Because ChemCatBio was already focused on pathways to produce bio-derived hydrocarbons and oxygenates as fuels for internal combustion applications over the last few review cycles, the switch to SAFs and chemicals seemed like a natural progression. For the *core technology* thrust, the C1 team successfully converted CO_2-rich syngas into precursors for SAF using the syngas-to-hydrocarbons (STH) method developed through insights gained from high-octane gasoline (HOG) production over copper (Cu)/beta zeolite (BEA). The team also initiated a proof of concept for isoalkane dehydrocoupling. The C2 team focused on directly converting ethanol to mixed C4 olefins in one step, bypassing the dehydration step over a tunable dealuminated beta zeolite and M/SiO_2 (M = Ag/Zr) materials, followed by oligomerization to SAF-range material. The CFP team developed a regenerative fluidized-bed system capable of CFP followed by upgrading to SAF using traditional hydrotreating approaches. The Catalytic Upgrading of Biochemical Intermediates (CUBI) team worked on four approaches to SAF based on catalytically upgrading biomass-derived feedstocks such as organic acids (volatile fatty acids [VFAs], butyric acid), furan, and butanediol (BDO). The upgrading was achieved by incorporating a variety of catalyst-driven synthesis steps to accomplish C-C bond formation and deoxygenation, such as condensation, ketonization, hydrodeoxygenation (HDO), dehydration, and methyl ethyl ketone (MEK) deoxygenation. From the *enabling tools* thrust, the Advanced Catalyst Synthesis and Characterization (ACSC) team accelerated the development of next-generation M/BEA zeolites and collaborated with the deactivation team to understand the degradation in activity for the Pt/TiO_2 system during CFP. The Consortium for Computational Physics and Chemistry (CCPC) team showed good agreement between density functional theory (DFT) predictions and characterization experiments for the VFA upgrading work, as well as a number of studies in support of the C2 upgrading work on Cu/BEA and M/SiO_2 systems covering deactivation and regeneration mechanisms. Further advanced material characterization tools and analysis were provided in the biogas conversion project, where the team did an excellent job of understanding the surface and bulk behavior of Zinc using isotopic transient kinetic analysis, *in situ* X-ray photoelectron spectroscopy, diffuse reflectance infrared Fourier-transform spectroscopy, extended X-ray absorption fine structure, and X-ray absorption near edge structure.

The principal investigators (PIs) provided copies of the presentations prior to the in-person session. This allowed each peer reviewer to make preliminary comments and compile a short list of key urgent questions. Most of the presenters were able to answer any concerns and provide additional context. There seemed to be an adequate number of breaks throughout the day, and presenters were able to engage with the review panel easily for any additional knowledge exchange. The organization of the sessions allowed for seamless transitions between speakers. For example, the CUBI team presented an overview talk on Day 1, along with several subtopic presentations related to each of the biochemical intermediate upgrading pathways, that was well received by the review panel. An informal debriefing between the Catalytic Upgrading program leadership and the review panel occurred at the end of each day to share thoughts and comments on the presentations.

The review panel was asked to evaluate each project using straightforward criteria based on the three elements of (1) research approach, (2) impact, and (3) results and progress, providing scores from 1 (unsatisfactory) to 5 (outstanding). The entire session scored well on the research approach element. Projects that received high scores tended to have early feasibility and techno-economic analysis (TEA) guidance, a clear understanding of the current state-of-the-art competing catalyst/process technology, a variety of strong collaborations across ChemCatBio, results with real feeds and engineered formed catalysts, inclusion of experiments and multiscale modeling, strong project management organization, effective external collaborations that included industry, a track record of publishing articles and patents on similar topics, tools to accelerate R&D, use of bifunctional catalysis to invoke process intensity, effective use of advanced catalyst characterization tools, significant time-on-stream (TOS) testing to understand catalyst deactivation, realistic and clear risk management, demonstrated ability to pivot and be flexible based on unforeseen bottlenecks, use of high-throughput synthesis and screening methods, and an effective ongoing diversity, equity, and inclusion (DEI) plan. Projects that that scored well in the impact category had features such as effective and actionable go/no-go stage gates, publicly available tools and knowledge, a significant number of articles in high-impact catalysis journals (impact factor >10), technology licensors, viable new pathways for underutilized bio-feedstocks to hydrocarbon fuels, conference presentations, webinars, analytical method development, enablement of other projects, direct connections to DOE/Office of Energy Efficiency and Renewable Energy (EERE)/BETO goals and metrics (e.g., greenhouse gas [GHG], minimum fuel selling price [MFSP], carbon utilization, carbon efficiency), reduction of capital expenditure (CapEx) and operating expenditure (OpEx) relative to the state of the art, commercial analogs, reduction of catalyst synthesis cost, improvements to catalyst lifetime (mitigating deactivation), a considerable amount of close industry collaboration at the business unit level, and experience with novel tools and techniques. Finally, the projects that scored above average in the results category had the following qualities: technical breadth and SAF pathway diversity; attainment of key milestones; experimental and modeling/simulation results with excellent agreement; TEA optimization via experimental work; molecular class level understanding; elucidation of structure-property relationships for catalysts, intermediates, and fuels; multiscale data and analysis from active site to engineered formed catalysts; tangible and clear evidence of catalyst development acceleration; examples that demonstrate the elucidation of selectivity, stability, and deactivation mechanisms; introduction of novel tools and methods for catalyst synthesis and characterization; and tangible, actionable DEI outcomes.

STRATEGY

Goal Alignment

The mission and goals of the Catalytic Upgrading portfolio are well aligned with those set at the BETO, EERE, and DOE level. Specifically, two of the three proposed 2030 BETO goals were clearly targeted in this cycle:

- Support scale-up of SAFs and other biofuels with >70% GHG emissions reduction.
- Enable 10+ renewable chemicals and materials with >70% GHG emissions reduction.

There was also clear alignment and support for other initiatives and goals as outlined in the SAF Grand Challenge, U.S. Blueprint for Decarbonization, Inflation Reduction Act, and Multi-Year Program Plan (MYPP). The mission is highly aligned with the MYPP decarbonization objectives, where there is a clear shift away from specific biofuel molecules, blend compositions, and corresponding pathways. There is a focus on climate process technology that can reduce carbon emissions. The Catalytic Upgrading thrust toward using more engineered catalysts across the portfolio aligns with the MYPP goal to demonstrate four integrated biorefineries by 2030 with SAF capability. Several of the Catalytic Upgrading projects address the goals of decarbonizing the chemical industry and using waste streams to further decarbonization efforts. In terms of the latter, the benefits to disadvantaged communities must be realized and measured. With respect to the Catalytic Upgrading portfolio, this objective commences with the DEI activities, which were available to most projects. A high degree of R&D acceleration will be required to meet many of these aforementioned goals and objectives, which have deadlines less than a decade away. The Catalytic Upgrading portfolio goals are well defined, with a flexible mission and clear technical targets that are being implemented through a very successful consortium-based research program. This is why the goals of the program focus on acceleration of the catalyst design cycle, improvement of catalyst performance, process intensification via catalyst surface engineering, and production of high-value chemical byproducts through selective catalytic processes. These activities support future commercialization and technology transfer milestones. It should be noted that all of the goals, objectives, and targets were covered by the Catalytic Upgrading portfolio management using a variety of methods: peer reviewer training presentation, plenary lecture, and the session introduction/background presentation.

Stakeholder Impact

Most of the projects reviewed in this cycle adequately addressed the 2021 peer reviewer commentary and recommendations, which also seemed to have impacted the goal development for the session—in particular, (1) the need for high-value coproducts and chemicals, (2) bolstered effort on catalyst deactivation, and (3) the use of engineered forms of catalysts (e.g., extrudates, pellets). The 2030 BETO goals of developing processes to produce renewable chemicals and scale up align well with this stakeholder input. In particular, ChemCatBio has shown considerable success with industry stakeholder engagement via industry advisory board (IAB) meetings, work within cooperative research and development agreements (CRADAs), and support across multiple directed funding awards (DFAs). These industry interactions continue to influence the language and objectives within FOAs and national lab calls. The technology licensing activities in collaboration with key industrial partners demonstrate that the work done in ChemCatBio is being noticed and leveraged appropriately. Due to the tight presentation schedule and agenda during the Peer Review, it is difficult to see how the Catalytic Upgrading program participants interact with other BETO programs. For example, the Catalytic Upgrading team should consider including an update on these kinds of activities as part of the introduction presentation given on the first day of the session. Topics like the collaboration between ChemCatBio (CUBI) and the Bioprocessing Separations Consortium (SepCon) would be an example of the cross-consortia interactions that could be highlighted in such a discussion. BETO also has an opportunity to engage airline original equipment manufacturers (OEMs) at a deeper level, as well as wholesale fuel blenders and manufacturers for SAF. The IAB composition should reflect this new strategic direction.

Funding for Major Gaps

Overall, the review panel was in consensus that no major, unfunded technical gaps were identified across the Catalytic Upgrading portfolio. The program supports the most critical technologies using various funding mechanisms properly. Certain projects remain below desired carbon efficiencies and GHG reduction levels, but these projects are tied to other factors (renewable hydrogen) and have strong research trajectories within the budgeting limits to close these gaps. The gaps in the technologies available to achieve the MYPP objectives must be identified further and built out to pivot the technology area quickly. For instance, ChemCatBio has done an excellent job of isolating the key mechanistic events contributing to deactivation on several classes of catalysts. There is still more research to be conducted in the area of active site stability and selectivity, as well as liquid-phase catalysis. Although these aren’t major technical gaps, there is an opportunity to bolster the funding resources on these topics. Many of these same gaps exist for the new SAF-focused pathways as well. From a nontechnical standpoint, there was a lack of consistency in DEI reporting and efforts across the projects. The review panel understands that this initiative is still new and evolving. The deliberate high-level planning and recent hiring of DEI professionals in this area is a positive step forward. The review panel looks forward to seeing the results of the implementation phase by the next review with the expectation of being on par with ChemCatBio technical efforts in terms of focus and quality. The technology area managers and coordinators are actively involved in managing the projects and are keenly aware of the limiting factors, gaps, and de-bottlenecking efforts that need to be resolved in order to achieve success.

Funding Relevance

In this review cycle, there were 16 projects funded: 15 from ChemCatBio and one from a university awardee. The ChemCatBio projects were awarded through the AOP funding vehicle, which is appropriate given the high degree of interlaboratory collaboration and support across the consortium. Obviously, the Catalytic Upgrading program managers will continue to attempt to balance the funding sources across the portfolio in the future, but this cycle happened to be more heavily skewed toward ChemCatBio work. The one university-led project came from a Fiscal Year (FY) 2018 FOA: BioEnergy Engineering for Products Synthesis, which seemed to be appropriate and adequate funding based on the solid results presented. The data hub and catalyst deactivation projects have the potential to contribute even more to the Catalytic Upgrading program if they receive more funding. However, it is understandable that the program must be very careful to distribute the funds across a variety of projects in the most effective way. The management team has indeed done an impressive job of trying to keep this financial balance. With the push toward SAF, there may be an opportunity to partner with ASTM International and provide support through the DFA funding vehicle for novel pathways. As the project portfolio evolves to the next cycle, the review panel would like the Catalytic Upgrading team to consider including projects that address other chemical driving forces beyond thermochemical, such as electrochemical, photochemical, and hybrid approaches. For example, organic electrosynthesis has made significant strides in technology readiness over the past decade. The Catalytic Upgrading team should monitor and leverage opportunities to connect these advances to the catalysis and engineering expertise across the portfolio. DFA projects might provide one such outlet to pursue these topics without significant risk to the core areas. It is recommended that the DFA funding vehicle be continued. This funding strategy successfully connected industry projects to the enabling technologies across ChemCatBio.

STRATEGY IMPLEMENTATION AND PROGRESS

Support for Catalytic Upgrading Strategy

The overall aligned BETO and Catalytic Upgrading strategy centers on catalyst development, specifically (1) improvements in selectivity, (2) determination of impurity impact, (3) elucidation of deactivation mechanisms, and (4) early use of engineered catalyst forms in the material development cycle. The program is funding an excellent range of projects that are very closely tied to the BETO and program strategic direction mentioned above, especially across ChemCatBio. For instance, all of the enabling projects (e.g., ACSC, CCPC, Deactivation) have tasks that tie into one or more of the catalyst development strategic elements mentioned above. ChemCatBio is central to the catalytic upgrading component of the BETO portfolio. The effort melds catalysis and applied engineering in a unique way, allowing for intermediate technology readiness level (TRL) process technology integration to happen. It is clear that ChemCatBio plays a critical role in accelerating catalyst and process development associated with bioenergy-derived conversions. The continued push toward the study of engineered and more industrially relevant catalyst formulations is justified given the evolving nature of ChemCatBio along the catalyst development cycle. This strategic direction helps to accelerate catalytic process technology development and deployment, especially the experimental testing component required to scale up design. There also appears to be significant collaboration between the national labs and universities across the portfolio, which could be critical in fulfilling DOE’s commitment to workforce development and DEI.

Leading-Edge Industrial Catalysis

As far as decarbonization is concerned, many of the projects have found themselves on the leading edge by developing industrially relevant catalytic materials capable of converting oxygenates, such as alcohols, to jet-range hydrocarbons for SAF blending. Additionally, at the leading edge appear liquid-phase catalytic transformations for key intermediates, such as the promising work of the CUBI team, as well as electrochemical transformations, like the work in collaboration with a leading carbon transformation startup company. Other notable work with industrial partners can be considered leading edge because their deliverables could have a significant impact on the first-generation bioethanol industry. These projects show their potential to be scaled up and commercialized into industrial-scale processes. The catalyst and process technologies used in these projects are on the leading edge considering their potential to be industrialized. If successful, these projects will most likely meet the BETO goals concerning SAFs and GHG emission reduction. Other evidence of many projects in the Catalytic Upgrading portfolio being on the leading edge relates to the quality of the partnerships and the level of industrial participation. Collaboration across ChemCatBio consortia with industrial partners—such as the data hub project's engagement of a leading multinational computing corporation along with the numerous projects that enlist catalyst OEMs as scale-up partners—drives technology development and transition. It is clear that many of the projects in this area are indeed leading the field, creating benchmarks and serving as repositories for relevant process technology. The DFA projects are great examples of how the ChemCatBio teams are adapting and maturing their research for industry applications by quickly incorporating new results into their business partners' workflows. The general record of publications and intellectual property (IP) generated across the portfolio of projects is strong (140 papers and 29 patents), with a significant percentage appearing in high-impact, high-visibility journals that ensure dissemination of new knowledge to the broader catalysis community. This level of scientific productivity as an aggregate metric is just another indicator of the leading-edge contributions from the Catalytic Upgrading program. For example, ChemCatBio continues to shed light on the research premise that C-C bond formation via oligomerization in the vapor phase or carbonyl coupling chemistry in the vapor and/or liquid phase will be increasingly important in order to upgrade the biogenic carbon routes sponsored through BETO. One DFA project clearly demonstrated how additive manufacturing can offer a novel and unique set of potential opportunities within the areas of reactor design, process intensity, and material synthesis. The Catalytic Upgrading team is encouraged to look for new ways to leverage these advances, particularly in the areas of catalyst synthesis and performance testing. For example, the strong additive manufacturing expertise at ORNL could be leveraged and partnered with the strong material synthesis and characterization acumen of the ACSC and funded under ChemCatBio.

Catalytic Upgrading Portfolio Viability

The targets in the Catalytic Upgrading program seem quite achievable and fit well within previous MYPP elements. The BioEnergy Engineering for Products Synthesis FOA responded to the final strategic goal related to decarbonization by using waste streams. In general, projects tend to be near or exceed GHG targets at or before go/no-go deadlines. The Catalytic Upgrading Technology Area has been very deliberate on the strategy to enable higher TRL and focus on decarbonization with a product emphasis on SAF. This appears to be very aligned with the overall DOE/EERE/BETO direction. In general, this review cycle dealt with all pathways to SAF focused on understanding catalyst stability, deactivation, and progressing the TRL (>2 or 3). In previous cycles, there was ample discussion dedicated to MFSP estimates for every project. Here, the TEA project consolidated all of this information, and more emphasis was placed on catalyst development activities. The state-of-technology (SOT) TEA estimate for the CFP route had the modeled SAF MFSP at less than $3 per gallon gasoline equivalent (GGE), which is well on par with petroleum-based commercial Jet A. In the same way, single-step syngas conversion to SAF also gave a preliminary MFSP of $2.61/GGE. These were significant results, because many novel SAF routes can be as much as 2–3 times higher in MFSP than the commercial baseline. The Catalytic Upgrading portfolio's focus on accelerating catalyst development was apparent, as less emphasis was placed on formulation discovery and more was placed on the art of engineering robust, stable industrial materials with respect to process synthesis and product design. This was exemplified in the meso- and reactor-scale work of the CCPC on (1) engineering catalyst modeling using X-ray reconstruction tools, (2) coking kinetic modeling for CFP regeneration cycles, and (3) reaction network modeling for the ethanol to jet route. It should be noted that most presentations included backup materials that included "responses to previous reviewer comments" and addressed any previous concerns of relevance.

Catalytic Upgrading Portfolio Management

The review panel was given an opportunity to discuss the Catalytic Upgrading portfolio management approach in more detail during the debriefing sessions after each day of presentations. The Catalytic Upgrading program's overall success is a reflection of the active, engaged management style of leadership, who have stayed fully committed to the critical success factors and use their expertise across the portfolio to assist in closing technical gaps where possible. Effective industry engagement, along with continuous, actionable program cycle-to-cycle improvement based on recommendations and feedback, have proven to be credible success factors in many projects. Both the Catalytic Upgrading and ChemCatBio management teams have made a concerted effort to respond to the concerns raised in prior review cycles, and the consortium continues to evolve based on changing BETO directives. The consortium has continued to foster industry collaborations, the majority of which are successful endeavors that have positively impacted all the companies involved as well as the ChemCatBio. There are other examples of successful projects linked to the Catalytic Upgrading/ChemCatBio management style and oversight: (1) the three DFA projects completed in 2022, (2) the industry-led CRADAs, and (3) the C2 upgrading work.

RECOMMENDATIONS

Based on the comments and conclusions discussed above in this summary report, the 2023 review panel submits the following recommendations:

1. ***Portfolio Balance and Budget:*** For the next program cycle, the Catalytic Upgrading team should consider diversifying and rebalancing the project portfolio funding among AOP, FOA, and DFA, but not from a budget neutrality standpoint. It is recommended that additional funding be pursued in parallel with this endeavor. The current $32-million budget should be increased by a factor of two to deal with the acceleration needed for decarbonization, especially when most climate technology development starts with catalyst and material development. A strategic cross-office partnership with the Office of Clean Energy Demonstrations—maybe even publishing joint AOP calls and FOAs—could be effective here.

2. ***Renewable Chemicals and Coproducts:*** Prioritization on high-margin chemicals continues to be a promising and refreshing direction for the office from both a scale feasibility and de-risking standpoint. This trajectory should be sustained with additional TEA optimization iterations guiding the process feasibility options. Furthermore, coproduct development continues to be a space where the Catalytic Upgrading team has even more opportunity. One approach could be to look at higher-risk feedstocks and/or investigate alternative energy inputs to drive selectivity to new products. The goal is not to place too much risk on the portfolio, so just a single project investigating this at a lower TRL could suffice here.

3. ***DEI Reporting:*** There appears to be a lack of consistency in how DEI and environmental justice (EJ) efforts are reported across the projects. It is recommended that a common reporting format with a more prescribed granularity be considered here. This will be critical for evaluating the impact in this area. The leadership on DEI and EJ has been genuine, deliberate, and tangible. Although dedicated professionals have been hired as resources to help guide the cohort in DEI, it is increasingly important that each scientist, engineer, technician, operator, and manager can connect their work to some type of benefit to the community.

4. ***Artificial Intelligence (AI):*** At this point, it is unclear how AI technology will impact the catalyst manufacturing, bioenergy, chemical processing, hydrocarbon processing, and biochemical industries of the future, but its presence as a tool utilized daily by professional scientists and engineers around the globe is imminent. It is highly recommended that the Catalytic Upgrading team make room in the portfolio for this disruptive technology by coordinating, monitoring, and partnering with other programs across DOE that are already positioned to take advantage of these next-level algorithms. The development of technologies such as digital twins; fully automated, large-scale, high-throughput catalyst discovery processes; and detailed, machine-learning (ML)-based process design and development may eventually factor into the scale-up activities required for bioenergy processes. The Catalytic Upgrading team should be prepared for this seismic shift in workstreams, as most process design activities begin with catalyst development. This work could be led by the CCPC, and it is strongly recommended that funding levels increase for that consortium within ChemCatBio.

CATALYTIC UPGRADING PROGRAMMATIC RESPONSE

INTRODUCTION

The Conversion R&D Program would like to thank the five Catalytic Upgrading session reviewers for their time and effort in reviewing the 16 projects presented in this session. The time and effort contributed by each reviewer to review the projects before the meeting, attend the meeting, provide their insight, and prepare their review is greatly appreciated. Their substantial contribution made this Peer Review meeting a success.

The review panel recognized the high quality of the presentations and was largely impressed with the ability of the presenters to answer their concerns with added context. The panel was particularly impressed with the research approach of the projects, scoring this criterion highly in every project. The high-scoring projects were noted to have strong collaborations across ChemCatBio and with industry, to involve real feeds and engineered catalysts, and to have flexibility in the face of unforeseen bottlenecks. In addition to direct improvements in process performance, projects with high scores for the impact criterion displayed effective and actionable go/no-go gates and released knowledge and tools to the public through scientific articles, presentations, and patents. The final formal criterion, results and progress, was found in high-scoring projects with wide technical breadth that attained their key milestones. Special mention was made of aspects that demonstrated good understanding of the factors that affect process performance, including agreement between experimental work and modeling and elucidation of catalyst structure-property relationships. Tangible and actionable outcomes were characteristic of high impact in this year's new criterion, DEI.

BETO was gratified to see that the reviewers noted that the Catalytic Upgrading mission is well aligned with BETO's 2023 goals to support scale-up of biofuels with greater than 70% GHG emissions reduction, and to enable 10+ renewable chemicals and materials with greater than 70% GHG emissions reduction. The use of engineered catalysts was also identified as a strength of the Catalytic Upgrading activity, specifically of ChemCatBio.

The reviewers suggested that BETO consider projects that use electrochemical, photochemical, and hybrid approaches in addition to the existing portfolio of thermochemical processes, noting that these technologies have made strides in recent years. BETO has an interest in these technologies and is currently supporting the electrochemical process by creating a \$10-million CO_2 utilization consortium that focuses mainly on CO_2 conversion through electrocatalysis. BETO has been following the advances in the field of organic electrosynthesis closely and is poised to support this technology when its maturity allows it to support BETO's goals and mission.

Recommendation 1: Portfolio Balance and Budget

The role catalysis can play in the effort toward decarbonization is well understood by BETO. Catalytic Upgrading of bio-based feedstocks can provide sustainable, economically viable sources of biofuels and other valuable bio-based chemicals. In the last 2 years, the BETO portfolio has included several projects focused on catalytic upgrading and is continuing to develop in this area. Communication with other offices, including the Office of Clean Energy Demonstrations, remains strong, although the difference in the TRL of the portfolio of each program creates barriers to increased cooperation.

BETO's strategy includes utilizing a variety of funding strategies, including AOPs, FOAs, and DFAs. In the last 2 years, the BETO portfolio has included several projects focused on catalytic upgrading and is continuing to develop in this area.

Although the session included 16 catalysis projects, other projects involving catalysis were assigned for review to other sessions and were therefore not reviewed in this session. As an example, many of the electrocatalysis and renewable natural gas catalytic upgrading projects from the FY 2021 FOA were presented/reviewed in the CO_2 Utilization and Organic Waste Conversion sessions, respectively.

Recommendation 2: Renewable Chemicals and Coproducts

BETO continues to pursue multiple pathways to the upgrading of biomass to fuel and chemicals. Our main emphasis remains upgrading biomass to fuel. This includes the major focus of the Catalytic Upgrading portfolio, generation of SAF. However—and as noted in the recently published MYPP—chemicals/products can also make significant contributions to decarbonization goals, and BETO has goals to contribute to a minimum of 10 molecules and at least 1 million metric tons per year of carbon-dioxide-equivalent reductions. BETO recognizes that several conversion and feedstock processes can be de-risked by recognizing the economic potential of valuable chemical coproducts or intermediates that can be upgraded to fuel or higher-value chemicals. Favorable routes will be shaped by TEA and life cycle analysis (LCA) results. The Catalytic Upgrading portfolio includes two recently completed directed funding opportunity (DFO) projects (Sironix and Visolis), which are continuing to develop processes to produce bio-based chemicals, and we expect that the formation of high-value chemicals will remain a project de-risking strategy for future BETO projects.

Recommendation 3: DEI Reporting

DEI and EJ efforts are a priority in the BETO portfolio. Although DEI reporting has only been recently implemented and is still developing, it is expected that with experience in reporting, it will become more expressive and more effective in its goal of improving the BETO portfolio. As projects include more diversity, BETO expects that reporting of DEI will naturally improve. Although assistance from DEI and EJ experts continues to be important, project officers are becoming increasingly adept at both developing DEI and EJ plans and reporting on their performance. To aid in this, BETO has distributed new guidance ahead of this year's lab call with suggestions on milestones and activities that can support these DEI and EJ priorities. These include suggestions that can be incorporated into research plans at any TRL and opportunities to collaborate with broader DEI initiatives.

Recommendation 4: AI

BETO agrees that AI can be a very powerful tool in designing catalysts. However, AI is still in its infancy for catalysis design. It can be a strong tool for determining reaction mechanisms and predicting and tweaking the best catalysts. This type of work is currently facilitated by the Office of Science. Even so, BETO is always looking for opportunities to improve catalyst design using new techniques, including AI and related computational techniques, that can provide a clear and reasonable path to serve office goals. At present, BETO's major focus is scaling up the catalysts developed in the last 3+ years. Consequently, most of the work will be on developing the engineered form of the catalysts.

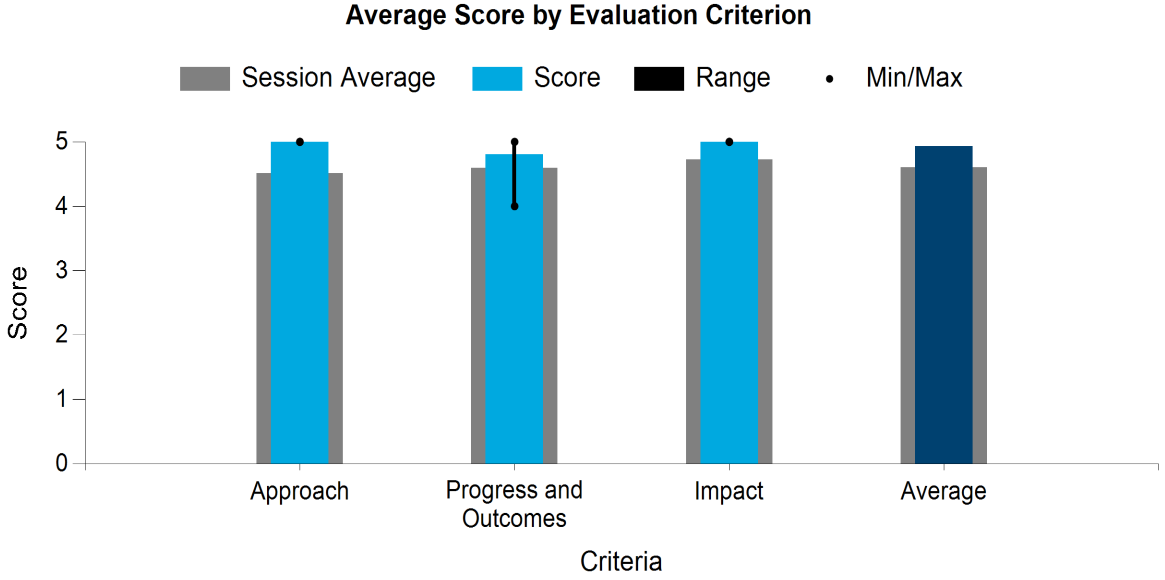
CHEMCATBIO LEAD TEAM SUPPORT

National Renewable Energy Laboratory

PROJECT DESCRIPTION

Work Breakdown Structure (WBS):	2.6.3.500
Presenter(s):	Dan Ruddy
Project Start Date:	10/01/2017
Planned Project End Date:	09/30/2025
Total Funding:	$96,000.00

The goal of this project is to enable ChemCatBio to achieve its mission by providing leadership for the consortium, managing the R&D portfolio and DEI activities, serving as single point of contact for potential partners, pursuing action items identified from the IAB, and developing strategic initiatives to position the consortium for the future. In addition to the director, deputy director, and steering committee, the consortium structure includes an IAB, DEI lead team, and all contributing researchers. To facilitate internal coordination, this project organizes recurring ChemCatBio all-hands meetings (every 2 weeks) and biannual face-to-face meetings, coordinates quarterly IAB meetings, and engages with other consortia. Further, to enable effective management of ChemCatBio and to facilitate engagement from all national labs, critical steering committee roles were enacted in FY 2018 that included face-to-face meeting coordinators, conference outreach, industry outreach, website point of contact, capabilities point of contact, consortia liaisons (Feedstock-Conversion Interface Consortium [FCIC], SepCon), data hub point of contact, and media development. By the end of FY 2025, this project will support ChemCatBio as a central hub of knowledge, methods, and tools for catalytic bioenergy applications by (1) supporting the development of the Catalyst Design Engine; (2) publishing our biannual newsletter, *The Accelerator*; (3) maintaining and expanding the capabilities of the CatCost™ and Catalyst Property Database (CPD) tools; (4) developing and sharing content on our website about mitigation of catalyst deactivation and advancements in state-of-the-art technology for conversion pathways; and (5) leading consortium-level DEI activities.



COMMENTS

- I am extremely impressed with the dual-cycle approach for the catalyst and process development cycle. This research team has very cleverly designed a process that allows for the concurrent development of novel catalytic materials (synthesis/computational modeling) and processes (TEA and LCA/process scaling), with bench testing being the link between them. This scheme allows for concurrent work, tied by validation, and no doubt considerably accelerates the overall catalyst and process development timeline. Additionally, the approach to considering both fuel and chemical products that can be produced by the various feedstock and process combinations allows for the creation of a wealth of data that can be leveraged as market factors change. The management plan is being well implemented, with more than 130 researchers participating in the projects across eight national labs. This plan has resulted in an impressive amount of scientific impact, demonstrated by the number of publications/citations, patents, follow-on projects, and community resources it has spawned. This could only have been accomplished if there was substantial communication between the researchers and the 14 members of the IAB. In addition, this project is clearly a leader in the DEI space, having established the diversity, equity, inclusion, and accessibility (DEIA) lead team, along with an impressive collection of resources and trainings.

- First, I have to give kudos to the DEIA efforts of this project, which have already created a wealth of resources. Ditto for community engagement, which is a closely tied effort. I really appreciate the effort to lead on best practices in heterogeneous catalysis to improve the rigor and reproducibility of the work published in the literature. Next, the demonstration of a fourfold time reduction for the development of a next-generation catalyst while substantially improving its performance is an unprecedented feat that demonstrates the advantage of leveraging the work across this exceptional, collaborative research team. The work with Pyran and Catalyxx exemplifies this process. It is clear that risk mitigation strategies have been successfully implemented to address the issue of catalyst deactivation.

- This project has demonstrated significant impact at a bargain price—in the development time of next-generation catalysts, in the development of the chemical property database, in the work with Pyran and Catalyxx, in the DEIA efforts and community engagement, and in addressing critical challenges to the production of SAF.

- ChemCatBio is central to the catalytic upgrading component of the BETO portfolio. The intro presentation did an excellent job of framing and justifying the role of ChemCatBio in accelerating the catalyst and process development associated with bioenergy-derived conversions. The effort melds catalysis and applied engineering in a very suitable way to connect intermediate-TRL technologies to a transition phase to industrial adoption. The continued push toward study of engineered and more industrially relevant catalyst formulations is justified given the evolving nature of ChemCatBio. The current focus areas align with the BETO goals laid out in the SAF Grand Challenge and also represent an effort to evolve, as a multicycle center should, by building on the most impactful portions of prior work while also incorporating new elements with an opportunity to enhance the effort. The shift to carbon efficiency and GHG reduction metrics is appropriate given the cross-agency mandate to focus primarily on decarbonization efforts. The consortium has the difficult task of threading the needle of having suitable diversity in approaches and inputs while not being spread too thin across exploratory topics. By and large, the effort succeeds. There is diversity in the inputs considered across the portfolio—ranging from biogas to syngas to ethanol and others—but there is still a general focus on pathways and intermediates to SAF that link the efforts. Collaboration across BETO consortia and with industrial partners is important for an effort that sits in this technology development and transition arena. The ChemCatBio partnerships with IBM and other catalyst partners is a highlight in this space, along with many individual examples in the specific projects. Cross-consortia interactions exist—such as CUBI with SepCon—but these could be highlighted more effectively in future cycles. Project management is strong, with well-established mechanisms at this point for in-person and virtual meetings. The established synergies of the enabling capabilities continue to allow the individual projects to thrive. This reviewer sees no major gaps across the ChemCatBio portfolio. One could perhaps note that certain projects remain below desired carbon efficiencies and GHG reduction levels, but these projects are tied to other factors (renewable hydrogen) and do have potential trajectories to achieve the desired metrics. Some points for consideration as ChemCatBio evolves in the next cycle:

  - ChemCatBio should begin to consider how nonthermal inputs (electro, photo) may begin to impact the conversion landscape. For example, organic electrosynthesis has made significant strides in the past decade, which will begin to transition to the technology space. The consortium should monitor these advances and leverage opportunities to connect these advances to the catalysis and engineering expertise in ChemCatBio. DFA projects may provide one such outlet to pursue these or related areas outside of core AOPs, expanding expertise without significant risk to core areas.
  - The additive manufacturing space also offers some similar, evolving opportunities; consortium members are aware of many of these. I would encourage the group to continue to look for opportunities to exploit advances in this space to enhance catalyst synthesis and performance testing when possible.
  - Although coproduct integration was included in strategic instances, I believe this is a space where ChemCatBio can continue to look for ways to be more ambitious. This may result from examining higher-risk feedstocks in a single project, alternative energy inputs to drive selectivity to new products, etc. I do not see this as a theme that must be incorporated in the majority of projects, but ChemCatBio should look to take advantage of opportunities when they present themselves in this space.
  - In general, there was a lack of consistency in DEI reporting and efforts across the projects. The reviewer understands that this space is evolving and does note that the high-level planning and recent hiring in this space is a positive. I look forward to seeing the plans for this area and the activities implemented by the next review, with the expectation that they will be on par with all other ChemCatBio efforts. I do feel strongly that establishing a common reporting format for the presentations and regular reporting for individual projects will be critical to assessing the impact in this area in subsequent review cycles.

- Progress: BETO directions. Particular highlights from this reviewer’s perspective include the CCPC multiscale modeling efforts, the general transition of the portfolio to robust and non-platinum-group-metal (non-PGM) catalysts, and the ability of all projects to access alkane fractions suitable for fuel testing. In general, projects tend to be near or exceeding GHG targets at or before go/no-go dates. It is clear that ChemCatBio has made a concerted effort to respond to concerns raised in prior review cycles, and that the consortium continues to evolve based on BETO directives. The consortium has continued to foster industry collaborations, the majority of which are successful endeavors that have impact for the company and ChemCatBio. The consortium-wide accelerator generates strategic ChemCatBio-wide partnerships in the areas of computing, catalyst evolution, and benchmarking, which have the potential to make a significant impact on the effort. For general management, the nine presentations at national and international venues are a good mechanism to spread the word about the activities and impact of ChemCatBio. The technical briefs are another vehicle to interact with the community in a separate but important way. I do appreciate the attempt to engage the catalysis community across all levels—from students (with the American Chemical Society travel award) all the way to the researcher level. One additional comment: Given the strong connection to industry partners, ChemCatBio could consider expanding its outreach efforts by having panels/webinars on career development topics that involve both ChemCatBio PIs and the partners. One could imagine a range of topics (general experiences and tips for startups, large industry, etc.; how to prepare for pursuing jobs in those areas; how technology transfer really works) that a spectrum of researchers would be interested in. I recognize that this isn’t a highest-priority activity, but it is one that could have an outsized impact on increasing awareness about ChemCatBio.
- The ChemCatBio project continues to be the hub for catalysis research in BETO by serving as an umbrella resource provider and setting the vision for the entire consortium. The approach to accelerating bioenergy catalysis that can also assist in decarbonization is quite timely and relevant. The team should

continue to work out the decarbonization emphasis and harmonize it into the overall strategy, so it doesn't appear to be a parallel effort. The partnerships, collaborations, and industrial advisors are strong and are enabling the consortium to make an impressive impact in both peer-reviewed literature and published IP.

- The revised ChemCatBio mission, which is focused on rapid decarbonization, is a very timely and appropriate R&D direction that is responsive to public, private, and governmental interests. At the core of this mission is advanced catalytic material development for utilization pathways in support of the sustainable circular economy. There is an opportunity for the existing petroleum-rich carbon inventory to be addressed to a certain extent with new projects similar to hydrotreating coprocessing to assist the energy transition for existing refineries. ChemCatBio really tries to reduce the threshold of technical barriers throughout the project. It seems like there could be an opportunity to accelerate the process synthesis step in the applied process model. ChemCatBio has put together a DEI team to deal with the issues across the entire consortium, and they bring up a DEI conversation at every meeting. This is quite progressive. ChemCatBio should be benchmarked quantitatively in comparison to other consortia within BETO and DOE, using a set of metrics to evaluate the state of the art in scientific consortia.

- The ChemCatBio team has clearly shown how the project can accelerate catalyst development to the point of technology licensing. The team has learned from the C1 catalyst development cycle and has applied those learnings to the ethanol conversion development cycle. This is a successful technical story. The progress with modifying the effectiveness factor was a great contribution. The team developed an understanding of the effect of trace inorganic salts on the environment and the intrinsic activity of the active site for several catalyst systems to the level of publishing several articles. More insight should be provided into understanding inorganic precursor type and various synthesis methods. Several tools are available for public use, including the CPD and Catalyst Cost Model. The Option 3 approach to developing engineered forms for catalysts will benefit the entire catalyst community. The IAB should be leveraged even further to assist in this work. Any preliminary look at the effectiveness of the predictive ML methods being considered for the data hub catalyst development initiatives would be interesting. The team is working with a large, respected information/data science OEM to develop in-house tools with ML and AI. This is very promising.

- The impact that ChemCatBio has on the bioenergy community is undeniable; this impact includes several open-source web-based catalysis tools, webinars, technology licenses, patents, awards, and papers. The consortium has been very successful. The team should continue to educate the broader community about their contributions and resources.

- ChemCatBio provides a general framework for accelerating catalyst design, synthesis, understanding, and deployment. The team is focusing on the SAF Grand Challenge and provides versatile toolkits to accelerate the catalyst development and deployment for this challenge.

- The team focuses on developing tools to lower the barriers between the different development stages of catalysts. They integrate synthesis, computation, and testing to accelerate the research on catalyst science. They also integrate TEA/LCA, scaling, and testing for applying developed catalysts in real applications. These two integrations provide a unique way to connect foundational research and applied engineering. The team also conducted efforts in developing databases and tools to embrace new technologies such as ML and AI. It would be more beneficial if the team could leverage the potential of ML, AI, data-driven discovery, and high-throughput experiments.

- The team has achieved significant progress in catalyst development and deployment to help address DOE's SAF Grand Challenge. The related research has resulted in >100 publications, three technology licenses, six software packages, 29 patents, and 12 awards with industrial partners. These numbers illustrate the progress of the team. Meanwhile, the team also provides three tools, 11 webinars, and two technical briefs. These materials show the commitment of the team to engaging the community. It would be more beneficial if the team would work more actively to reach out to the communities that are not likely involved in BETO research, like some underserved communities. The team also shows a commitment to DEI efforts.

- The ChemCatBio lead team illustrates its impact by integrating a wide variety of efforts that aim to accelerate the development and deployment of catalysts for the SAF Grand Challenge. They build a robust mechanism to connect foundational catalyst research with applied engineering of catalysts to scale up processes. This connection will be critical to enhancing the commercialization of the catalysts developed under the Catalytic Upgrading program.

- ChemCatBio's platform is driving the advancement of catalytic processes to convert biomass into sustainable fuel and other value-added products, utilizing effective accelerating and prioritizing strategies. Collaborations among national laboratories, academia, and industry have led to impressive accomplishments in fundamental science, computation, economics, and engineering. These high-quality works not only promote sustainable energy, but also benefit the community by expanding knowledge and education and upholding high ethical standards. ChemCatBio's approach is outstanding, as it integrates aspects from both the micro level (atomic-level fundamental understanding) and macro level (market), which is not easily achieved by academia or industry alone. Such an approach requires significant project management skills. The ChemCatBio management team and PIs have done an excellent job ensuring that almost all projects progress on track at a fast pace, achieving a fourfold reduction in catalyst development time. The focus on deactivation, catalyst engineering, TEA, and kinetics, in addition to fundamental understanding, is a step in the right direction for scaling up. The successful approach has resulted in impressive outcomes, including high-quality publications, licenses, patents, and tools (e.g., CatCost), with numerous potential opportunities for industry to explore. The inclusion of DEI in project plans is also impressive. BETO sets a standard for others to follow to create a more equitable society, fostering innovation and creativity. It is encouraging to see that DEI is incorporated into every project, and I look forward to seeing its implementation. Overall, the impact of these projects will last for generations, as renewable energy utilization and decarbonization are essential for our only home, the Earth. The contributions from these projects also promote DEI and community engagement, which are equally important.

- Some suggestions for most projects under this program:

    - Providing a more detailed breakdown of budget allocation and timelines would enhance the reviewer's/reader's understanding of the project management. Many projects lack a breakdown of budget over the years, and some do not have clearly defined milestones or timelines.

    - To garner more support from the catalysis society, consider implementing additional promotional efforts, such as exhibiting booths, sending group emails, putting on webinars, and encouraging PIs to include promotional slides during their conference presentations.

    - To generate greater interest from industry stakeholders and increase their investment intentions, various uncertainties should be considered in TEA, instead of just presenting the best-case scenario.

    - To broaden the DEI efforts, consider creating visually appealing promotional materials with scientific content related to SAF. These materials can be developed for younger audiences, including middle and high school students, to promote and support STEM education.

PI RESPONSE TO REVIEWER COMMENTS

- The lead team appreciates the many positive comments about our consortium-level goals, approach, DEIA strategy, progress to date, and future plan. We appreciate the note on highlighting cross-consortia interactions in this overview presentation. We will take this action through FY 2025, especially highlighting existing partnerships with SepCon, FCIC, and the CO_2 Reduction and Upgrading for e-Fuels Consortium, as well as partnerships currently in development with other BETO consortia. Related, we appreciate the comment to stay abreast of advancements in electrochemical and photochemical conversion technologies, as they relate to both fuels and value-added chemical production that could intersect with the catalytic technologies being developed in ChemCatBio. Our collaboration with the CO_2 consortium is one way we currently do this. Participation at conferences is another way our PIs engage with emerging technologies. We will consider a consortium-level milestone by FY 2025 that assesses these topics and how they could integrate with ChemCatBio research. Similarly, advancements in additive manufacturing have been integrated into the ChemCatBio R&D portfolio through our newly added engineered catalyst development effort within the ACSC project. This effort builds on the preliminary success highlighted in one of our DFO presentations, where millifluidic reactors were designed and printed to enable high-throughput nanoparticle catalyst synthesis. We are seeking to expand additive manufacturing to access improved catalyst architectures in the ACSC project, but this effort may require additional funding support. Related to the engineered catalyst effort, our IAB has been instrumental in guiding our initial efforts. One of our IAB members from a major catalyst production company worked with our team to prepare and present an overview of industry standard practices for us. This presentation will be the basis of our next webinar, expected in the summer of 2023. We appreciate the note to standardize the reporting structure from our DEIA activities. As noted, this is a new effort for us, and it is still evolving, but the note is well taken and will be put into our immediate consortium-level plan that will be finalized by the end of this FY. The comment to participate in career development efforts is an excellent suggestion. Although noted as a lower priority within our consortium, it is an excellent complementary effort that will be implemented in our workforce development plan.

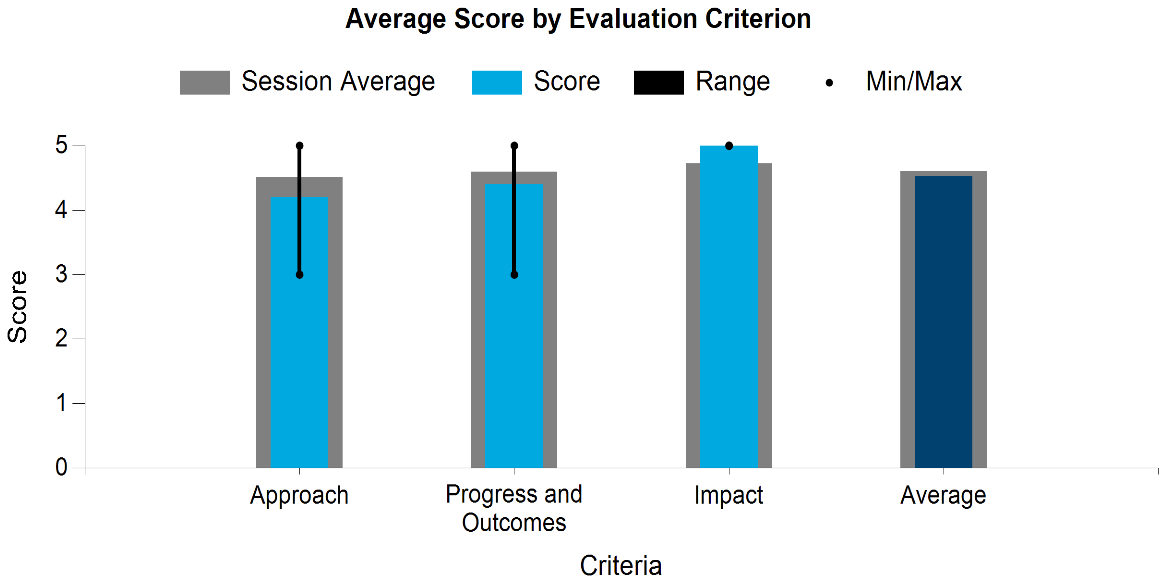
THERMOCHEMICAL PLATFORM ANALYSIS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.1.0.302
Presenter(s):	Abhijit Dutta
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$784,128.00

This Thermochemical Platform Analysis project serves to guide biomass thermocatalytic conversion research for significant-volume feedstocks toward higher-impact outcomes through TEA. Outputs include the quantification of associated sustainability metrics and environmental benefits. The key contribution of this project is to analyze ongoing and new research, as well as to explore new and hybrid conversion pathways for biomass and wastes, thus playing a key role in providing actionable metrics for BETO-funded research efforts. Our analyses have shown that thermocatalytic biofuels pathways, with associated coproducts (providing significant sustainability and cost benefits), have the potential to enable the achievement of BETO's ambitious SAF production goals while meeting GHG and cost reduction targets. Although the analysis of new conversion approaches will continue to be a primary thrust of this project, our efforts also emphasize industrial engagement and support partnership projects toward the successful deployment of biorefineries by leveraging our analysis knowledge and tools. Another key area of analysis under this project is facilitating integration with existing facilities and infrastructure, including at petroleum refineries, to enable lower production costs of liquid transportation fuels.



COMMENTS

- This project is focused on TEA and evaluation of process sustainability. It ties to the other projects in this area through experimental results from the other projects. The feedback loop from this project to the experimental work is through information on industrial context and risk. This process seems well poised to make sure that the laboratory developments stay relevant to things that can be industrially scaled. There is strong evidence of interlaboratory collaboration. The new approach, focused more on TEA and LCA, is the next logical step after the SOT report created in previous years. The focus on SAFs makes sense in light of the administration's goals; however, I believe that it would be a misstep to completely stop work on sustainable gasoline- and diesel-type fuels. The diversity, equity, and inclusion plan (DEIP) includes publication with a minority-serving institution (MSI), which seems like a reasonable goal, but I would like to see more substantive involvement—perhaps summer internships for the MSI students.

- The progress since the last review is significant. Although the 2022 CFP pilot scale did not proceed, that is actually a resounding success for the project based on the risk assessment. I can only imagine how much money and effort was saved by this analysis. The resultant analysis provides a framework for future consideration of the process as factors and technology change. Additionally, this analysis identifies the sources of risk, GHG emissions, production costs, etc.

- The project demonstrates clear impact—saving resources (money and time) by not scaling up the CFP process—and is able to narrow the expansive parameter space for investigation, as well as quantify the influence of various aspects of the project on risk, emissions, production costs, and other factors. In addition, this work and the learnings from it can be leveraged across multiple projects and processes.

- This project enables TEA and modeling across projects. It is critical to have this type of effort integrated with consortium projects to have any hope of transitioning technology as desired to the appropriate scale for industrial implementation and to ensure that the right perspectives on cost and other target metrics are represented accurately. It is clear that the project collaborators cover the needed areas and tap the spectrum of approaches necessary for success. At the same time, the presentation provided nice context for the entire analysis portfolio and where this piece fits within the broader national lab complex. The feedback loop established with experts in feedstocks, catalyst formulation, and fuels is absolutely essential to ensure that the right parameters and assumptions go into the modeling efforts. The use of modeling tools (Aspen Plus for process models; Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies [GREET] for LCA) is appropriate and standard practice for the field. The organization regarding the tiering of analyses performed is logical and prioritized to ensure that time-consuming, highest-level analyses are only performed as needed. The priorities of the modeling group are important to understand. In particular, the goals of SAF/heavy fuels and repurposing of existing refinery infrastructure are logical and aligned with current BETO directions. Moreover, the shift away from SOT reports and the focus on SAF, de-risking elements of technology, etc. seem to further align with current BETO priorities. The DEI plans are manageable and contain a quantifiable metric that seems potentially achievable and a realistic goal to work toward. As an enabling project, specific metrics are less critical than the examples presented in how the interaction with other upgrading activities has been influenced by the modeling analysis. It is clear that thermochemical platform analysis helps inform milestones and whether technologies should move forward as is or have some type of remaining barrier. The examples presented in the presentation highlighted the flexibility in the group in the types of analysis performed on a diverse range of systems. The ability to incorporate SAF specs into process models seems very important. Examples that both support changes in systems—from multistep to single-step processes, reactor engineering modifications, etc.—and flag critical issues were presented. Both types of scenarios highlight the key role thermochemical platform analysis plays. Moreover, the group consistently demonstrated the need for holistic considerations of system design and the need for this to occur with a group of experts outside those performing the upgrading technology directly. In general, I was also impressed with the diversity of feedback provided to the modeling team and how it was integrated into the effort. Broadly, the mechanisms—engaged experts, consultants, or advisors, as topics warrant—seem appropriate to ensure that expert opinions on rapidly changing areas are incorporated to develop the best analyses possible. The shift in this year and subsequent years to focus on SAF seems clearly aligned with ChemCatBio and broader BETO directions. Two broader comments:
    - In general, sensitivity/error analyses could be better represented to a larger degree in most project presentations. I have no doubt about the technical capabilities of the team; it was just a consistent issue that arose.

  - Some deeper general discussion of the differences/challenges in analysis involving powder versus scaled/engineered catalysts would be desirable, as this matches the direction of BETO and most of the projects. Specifically, I am thinking of ways to integrate transition into these formulations in early-stage analysis to serve as a tool to flag potential issues as early in the development process as possible.

- Impact: The pervasive impact thermochemical platform analysis has within the broader upgrading portfolio is clear. When projects attempt to radically change processing (moving to different reactors, different catalysts, etc.), risk assessments, emissions reduction estimates, coproduct values, etc. are needed to evaluate viability. Thermochemical platform analysis is a vital part of these efforts given the metric-driven nature of the projects—identifying the key choke points/bottlenecks beyond the science limitations is absolutely essential. Additionally, thermochemical platform analysis has broader impacts for the community, demonstrating the power of economic modeling to drive potential demonstration and ultimate deployment. The group has been productive in terms of outputs to the community, with several publications in a variety of field-relevant journals. I have no doubt that these reports will be viewed and picked up by the community. However, the group could look to expand presentations or perhaps participate in combined webinars with the projects they support to further articulate the value of the integrated approach and the critical need for this type of modeling within projects. Recording these presentations could provide a living reference for the community to access.

- Overall, the thermochemical platform analysis project team has made good progress since the last Peer Review, publishing several peer-reviewed articles and running meaningful targeted simulation cases, including GHG and cost/gallon impacts. The team avoided advancing pathways that were too risky and continued to drive the focus toward SAF pathways. This is a good pivot for the team, with research efforts adapting and moving forward in this new direction. The continued interest in working with existing refinery partners is a solid strategy, and the team should continue to drive those relationships.

- The current state of the art is to first compile experimental lab-scale and/or pilot-scale data from the published literature and/or in-house-run campaigns, then build process simulation models. The team should clarify which process scale is being used in these calculations, as well as the quality of the data. The two routes being considered are (1) catalytic pyrolysis product upgrading to SAF and (2) syngas to SAF via C4 oligomerization. Here, a simple statement of the design basis being considered should be provided for both routes. Any process design feasibility endeavor requires input from key stakeholders, in particular experimentalists. This approach appears to be no different, but incorporates additional LCA constraints and feedback from Argonne National Laboratory, as well as feedstock cost/specs from Idaho National Laboratory, which provides an opportunity for innovative solutions to optimize the TEA for SAF production. The risks were not clearly identified as compiled by the industry expert panels. It appears that hydrotreating coprocessing is one de-risking strategy. The beneficial cyclic and isoalkane components in CFP to SAF should be separated before any coprocessing step. The schedule and plan were not adequately addressed. The DEIP needs measurable goals and an action plan to track progress, as well as a community impact assessment from an EJ perspective.

- The team demonstrated the importance of TEA for making multiscale go/no-go decisions by placing the CFP on the shelf. The key specific risks associated with hydrogen introduction that halted the progress of the work should be highlighted here as a lesson learned for the BETO community; these can serve as a seed for future R&D efforts. It appears that downstream processing of coproducts was challenging and that finding a commercial partner for the coprocessing option was a hindrance.

- The thermal analysis team deploys developed tools such as Aspen Plus, Excel, and GREET to provide TEA/LCA to the other projects. This is an enabling project. They calculate TEA/LCA based on the data provided by the other projects and provide feedback about the projects based on their calculations. It would be more beneficial if the calculations involved uncertainty quantification because some data used in the TEA/LCA are based on estimation or present certain variations. It could provide more guidance if the TEA/LCA showed the confidence level in some way.

- The team provides three types of analysis: quick-turnaround analysis, more detailed analysis, and detailed design report. The three types of analysis cover the wide spectrum of needs of different projects well.

- The team also shows a commitment to DEI. They plan to develop work with identified MSI(s) to help develop the capacity of TEA/LCA. It is not very clear which MSIs the team is referring to or what stage the plan is at now. It would also be more beneficial if they could work with DOE/BETO to develop a plan for how to involve these MSIs in the project after they develop such capacity.

- The project presented impressive progress since the 2021 review. They conducted TEA for fixed-bed *ex situ* CFP and concluded the key closeout. This example indeed shows the importance of TEA/LCA in guiding the direction of an applied R&D project. They also presented progress in refinery integration and SAF.

- The impact of this enabling project is illustrated in driving the transition to a one-step hydrocarbon process. Because of its impactful role, it would be beneficial to evaluate how the uncertainty in the data may influence the TEA/LCA outcomes.

- The TEA project plays a critical role in assessing and guiding all projects toward commercialization. The outcomes generated from this project are of great interest to industry stakeholders and the general public. The project management approach, which allocates more resources to core projects and promotes close collaboration, is in the right direction, and a great effort has been put into this project.

- The TEA has covered almost all aspects of scaling up, including modeling, economic calculations, and LCA, showing good project management. It is impressive to see that almost all projects under this program have undergone TEA, and transparent data sharing among different projects has made the process more efficient, avoiding duplicated efforts. Partnerships with KBR and collecting feedback from industry reviewers have helped improve accuracy and reliability.

- The impact of this work is significant, as the estimations generated by the TEA work have not only been used by BETO to accelerate processes, but also serve as trustworthy references for researchers worldwide. However, carrying out TEA at a relatively early stage of the development cycle for a catalytic process is still challenging. In many cases, TOS longer than 1,000 hours is still considered short term for the industry, not to mention that most of these processes used model feedstocks.

- To avoid misleading information, TEA should consider adding uncertainties and should have a confidence factor or risk factor. This way, when comparing the likelihood of commercialization, entities can consider not only the projected cost, but also the challenges. For instance, TEA carried out at an earlier stage should have a lower confidence factor. If a process requires any modification of the current setup, the risk should be much more significant, regardless of the magnitude of the modification. Recent challenges facing the industry, including supply chain issues, labor shortages, and uncertainties in policy, should be part of the risk factor.

PI RESPONSE TO REVIEWER COMMENTS

- Thank you for your review highlighting the strengths of this project, as well as the constructive feedback regarding areas where changes can be made. Our responses below focus on how we plan to address or may already have considered addressing the suggestions made by the reviewers.

- Comment: I believe that it would be a misstep to completely stop work on sustainable gasoline- and diesel-type fuels.

- Response: While SAF will be our focus based on BETO priorities, we cannot achieve 100% selectivity to SAF in most processes. In our analysis, the remainder of the products will continue to be evaluated for use as blendstocks for other fuels, including gasoline and diesel.
- Comment: The DEIP includes publication with an MSI, which seems like a reasonable goal, but I would like to see more substantive involvement—perhaps summer internships for the MSI students.
- Response: Our plan, as shown in the diagram on Slides 14 and 24, includes internships. We did not present further specifics within the presentation because we are still in discussions with faculty to finalize the process.
- Comment: In general, sensitivity/error analyses could be better represented to a larger degree in most project presentations. I have no doubt about the technical capabilities of the team; it was just a consistent issue that arose.
- Response: We prominently highlight sensitivity analysis presented in tornado plots with most of our analysis. However, an example of a tornado plot was not included in this year's presentation. We will include an example with a tornado plot/sensitivity analysis in future Peer Review presentations to convey this emphasis in our work.
- Comment: Some deeper general discussion of the differences/challenges in analysis involving powder versus scaled/engineered catalysts would be desirable, as this matches the direction of BETO and most of the projects.
- Response: Thank you for this comment. We will work with the experimental research teams to incorporate this aspect in the future.
- Comment: The group could look to expand presentations or perhaps participate in combined webinars with the projects they support to further articulate the value of the integrated approach and the critical need for this type of modeling within projects. Recording these presentations could provide a living reference for the community to access.
- Response: Thank you for this comment. We will organize webinars/presentations with corresponding experimental teams in the future to address this.
- Comment: The current state of the art is to first compile experimental lab-scale and/or pilot-scale data from the published literature and/or in-house-run campaigns, then build process simulation models. The team should clarify which process scale is being used in these calculations, as well as the quality of the data.
- Response: We do highlight the source of our data (usually bench scale) in our analysis and highlight the assumption that we are scaling up bench-scale performance to a 2,000-dry-metric-tonne/day (typical) biomass conversion plant in our conceptual process models. The consistent plant scale helps to compare different conversion pathways on the basis of economic and carbon intensity performance. We will continue to highlight this aspect and assumption in our future work.
- Comment: The two routes being considered are (1) catalytic pyrolysis product upgrading to SAF and (2) syngas to SAF via C4 oligomerization. Here, a simple statement of the design basis being considered should be provided for both routes.
- Response: We tried to convey the design basis for (1) CFP oil upgrading to SAF on Slide 19, and (2) syngas to SAF with the simple diagram on the bottom left of Slide 23. In addition, process basis details are provided for each pathway in the "Additional Slides" section. We will continue to convey this via statements, tabulated summaries, and associated graphics in future presentations.

- Comment: The risks were not clearly identified as compiled by the industry expert panels. It appears that hydrotreating coprocessing is one de-risking strategy. The beneficial cyclic and isoalkane components in CFP to SAF should be separated before any coprocessing step. The schedule and plan were not adequately addressed.

- Response: This aspect is covered under the experimental research project and its associated milestones (linked to this project). Multiple experimental approaches are being assessed within the constraints of available resources. This analysis project uses experimental data (and engineering judgement, where appropriate) to assess the feasibility and impact of the various approaches. We have two joint milestones during this FY (in Q3 and Q4) documented in our AOP to explore various hydroprocessing strategies, and we will continue to include milestones in future years.

- Comment: The entire status of the current SAF material's ability to meet the entire spec should be provided, so the gaps are understood.

- Response: We will continue to emphasize this aspect, building on current efforts described on Slide 20 (right-hand side). The experimental team has included multiple property measurements covering major properties associated with SAF specifications. This TEA project is working with experimental projects to include property prediction capabilities within our process models.

- Comment: It would be more beneficial if the calculations involved uncertainty quantification because some data used in the TEA/LCA are based on estimation or present certain variations. It could provide more guidance if the TEA/LCAs showed the confidence level in some way.

- Response: We will continue to include and highlight uncertainties in our analysis and include this aspect wherever appropriate. For example, we highlighted key uncertainties/sensitivity analysis in the Executive Summary (page viii) of the 2020 *ex situ* catalytic fast pyrolysis SOT report (www.nrel.gov/docs/fy21osti/80291.pdf).

- Comment: It is not very clear which MSIs the team is referring to or what stage the plan is at now. It would also be more beneficial if they could work with DOE/BETO to develop a plan for how to involve these MSIs in the project after they develop such capacity.

- Response: We started our 3-year project cycle in October 2022, with a plan to execute the DEIP presented within the 3-year period. We did not publicly disclose the names of the MSIs with whom we are in ongoing discussions. Because our plans have not been finalized, mentioning names of MSIs would be premature. We plan to have deep and ongoing relationships that will include continued involvement of MSI partners in the future. We will publicly disclose the MSI(s) once we have agreements in place.

- Comment: The impact of this enabling project is illustrated in driving the transition to a one-step hydrocarbon process. Because of its impactful role, it would be beneficial to evaluate how the uncertainty in the data may influence the TEA/LCA outcomes.

- Response: Thank you for the comment. We will include sensitivity to uncertainties in forthcoming work and associated publications.

- Comment: In many cases, TOS >1,000 hours is still considered short term for the industry, not to mention that most of these processes used model feedstocks. To avoid misleading information, TEA should consider adding uncertainties and have a confidence factor or risk factor. This way, when comparing the likelihood of commercialization, entities can consider not only the projected cost, but also the challenges. For instance, TEA carried out at an earlier stage should have a lower confidence factor.

- Response: As mentioned above (in response to another comment), we will continue to include uncertainties, risks, and associated sensitivity analysis in our work.

- Comment: Recent challenges facing the industry, including supply chain issues, labor shortages, and uncertainties in policy, should be part of the risk factor.
- Response: While some of the cost escalations associated with the problems mentioned above get captured through our cost indices, we will include additional associated risk factors if these problems persist and require further highlighting beyond the cost escalations estimated by the indices.

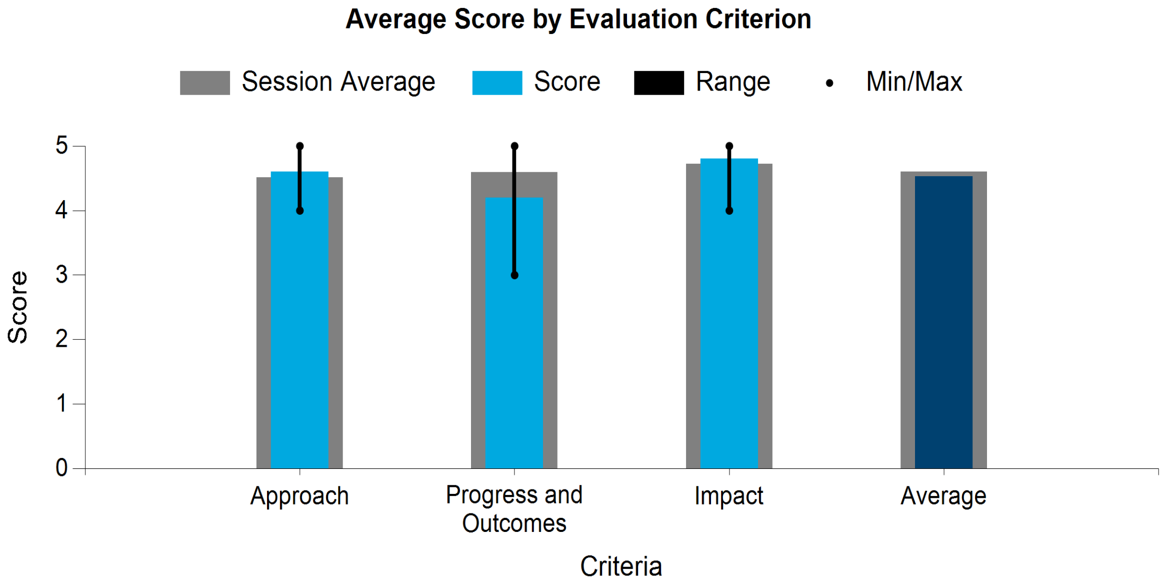
UPGRADING OF C1 BUILDING BLOCKS

National Renewable Energy Laboratory

WBS:	2.3.1.305
Presenter(s):	Dan Ruddy
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$2,190,407.00

PROJECT DESCRIPTION

This project is developing the centerpiece technology for an integrated biorefinery concept based on the conversion of renewable and waste sources of C1 intermediates (e.g., syngas, CO_2, methanol) to produce SAF with improved carbon efficiency and reduced CapEx and OpEx compared to traditional gas-to-liquids processes. Advanced syngas upgrading technologies are critical for the successful commercialization of fuel production at a scale relevant for biomass gasification. Research tasks within this project leverage complementary catalyst and process design for (1) the direct conversion of CO_2-rich syngas (15%–20% CO_2 in syngas) to achieve high carbon yields of C4+ hydrocarbons in a single reactor, termed STH, and (2) the subsequent conversion of these hydrocarbons to SAF. Research progress is compared to the Mobil olefins to gasoline and distillate process and the three-step STH process through dimethyl ether previously explored in this project. This research effort supports BETO and ChemCatBio goals, using catalyst and process R&D as a foundation to address risks for process integration and commercialization. The STH pathway generates high-quality SAF precursors with a >70% reduction in GHG emissions compared to petroleum jet fuel. This project assesses catalyst/process durability using real bio-/waste-derived feedstocks in practical reactor configurations with engineered catalyst forms.



COMMENTS

- The goal of this project is to use the conversion of renewable and waste sources of C1 intermediates to produce SAF with improved carbon efficiency and reduced CapEx and OpEx compared to traditional processes.
- The goals of this project are sound, and the scattershot approach (simultaneously investigating multiple processes) makes sense at lower TRLs for similar process conditions. There are clearly identified research challenges: carbon efficiency improvement, regeneration procedures for multicomponent catalyst mixtures, extended operating times, and improved yields. The task management is integrated

across the entire ChemCatBio Consortium and incorporates technical capabilities, TEA, and DEI (at least in theory, as the DEI milestones are not yet determined for this project).

- Progress seems steady, but at a slower rate than projected by modeling. Carbon efficiency is at ~30% (which was the FY 2021 go/no-go) and hasn't progressed further. A regeneration protocol has been established, but the process has not yet been run. Plots lack error analysis, making it difficult to assess the results.
- The impact is strong. This project was about to accomplish technology transfer with the bioenergy industry (research license with Enerkem), as well as publish ~10 papers in top journals and generate patents.
- Approach: The project is focused on C1 feeds (syngas, methanol inputs) to intermediates to ultimately generate SAF. The approach is differentiated from the state of the art in syngas conversion with a focus on funneling chemical intermediates through a methanol/dimethyl ether pathway. A stacked-bed reactor allowed for direct STH conversion. The isoalkane products can then be dehydrocoupled to access SAF. The catalyst design and engineering components that work in concert and reinforce one another to enhance improvements to the overall technology are a highlight of the work. The overarching topics of the project—involving tandem reactions, process intensification, etc.—are recurring themes in the upgrading activities and are viewed as needed strategies to transition the reactions to viable technologies. The presentation could have focused more on the specific management of this project. I don't have any doubts regarding this aspect, but it was not as strong a component relative to other topics. This could be a function of the lead PI having discussed management in the overarching ChemCatBio presentation. I would note that PI Bhan is a great partner for kinetic studies of zeolite catalysts. A forward-looking comment: Given the ability to perform tandem thermal catalysis, in the longer term, this (and other projects) may well consider alternative energy inputs (electro/photo processes) in cases where the economics can work. Given the modularity of these systems, one could imagine funneling intermediates from a thermal reaction to an electro-driven process (as one example). While this is certainly not always feasible, the expanding area of electro-organic synthesis suggests that longer-term opportunities may exist in this space. Perhaps this is more suited for coproduct generation, but it is something worth long-term consideration. The move to more realistic feedstocks is notable and necessary. One question not clear from the presentation is: How does biomass syngas differ from the current feedstock mixtures? Will this be expected to create significant issues? For this reviewer, it was not clear from the slides or presentation. The collaboration with one of the other BETO consortia to obtain the biomass-derived syngas is notable and another sign of cross-talk among consortia. Progress: The outcomes extend beyond prior studies in related HOG systems to include the impact of CO_2 feed stream ratios, optimum regen protocols, catalyst synthesis treatment studies to achieve optimum conversion, and prolonged TOS. These logical investigations generate data to inform further catalyst evolution for a system that can be regenerated to full activity and is robust over long time periods. Progress on all fronts seems promising, as the isoalkane coupling is at the proof-of-concept stage with a similar mixed-bed system. Other goals, such as further studying deactivation and movement toward engineered catalysts, are in line with other efforts in ChemCatBio and can leverage the existing capabilities within the consortium. The goal of moving to biomass-derived syngas to SAF in an integrated process seems at least possible from the results gained from the project to date. Impact: Ten publications is good to strong productivity, with many in high-impact-factor journals (impact factor >10). One patent and numerous presentations by project PIs also suggest successful IP development and dissemination of results to the broader catalysis community. If progress toward goals and milestones continues, the target of direct syngas to SAF, or at least precursors to fuels, will be achievable. Economic modeling suggests that these pathways are certainly worth exploring in an intermediate-TRL effort such as this. Given the group's success with the HOG technology, I'm convinced that the evolved technology developed in this project will have significant impact and will be seen as a commercialization opportunity for the sustainable fuel industry.

- Overall, this project team has made significant progress since the last Peer Review, giving new prospective routes for C1 conversion with high selectivity to either HOG or SAF. They have created materials that have tunable properties and have begun a good approach toward scale-up by establishing good internal and external partnerships.

- This team did an excellent job of centering the audience on the bottlenecks associated with the state of the art in syngas to SAF technology, namely product selectivity, number of unit operations (complexity), aromatics, and monomers as desired products. The team is focused on reducing complexity by converting syngas-type feedstocks directly (in one step) into SAF. This lab-scale work has been published in peer-reviewed journal articles and has resulted in a patent highlighting stacked-bed reactor configurations. The relative size of the stacked packed beds should be disclosed due to CapEx implications. The dual R&D cycle strategy for designing novel catalysts continues to be a progressive approach in process technology development. The technical approach here is to investigate the impact of CO_2 composition in the feed on the STH process to make paraffins; then, once those paraffins are created, they are dehydrogenated and coupled in a single step to SAF-range hydrocarbons. This is a new process-intense route for the team and seems quite interesting. Some key risks were identified: loss of carbon to CO_2, catalyst regeneration challenges, and TOS product yields. Mitigation actions should be provided for each of these. DEIP or EJ strategy was not necessarily provided in detail. It appears that the ChemCatBio DEI resources are being leveraged here.

- The review of the 2021 baseline was good for the audience. The R&D focus from that review dealt with increasing carbon efficiency and reducing CapEx via process intensity. The decrease in CO_2 selectivity and the C efficiency of 32%, as predicted by conceptual modeling, should be validated experimentally. In 2021, the team was able to publish the types of aromatic coke species on the surface of Cu/BEA and develop a regen schedule that enabled complete recovery for over 2 days. This was a major accomplishment. The team also figured out that forming extrudates from the powder catalyst versus depositing copper after the material-forming event results in higher C4 selectivity. The team should report the size of the extrudates and the tube diameters used in the analysis. Some of the work involved collaborations with the thermochemical platform analysis and ACSC projects, leveraging modeling and characterization tools. The direct STH route should still include MFSP estimates (using literature) for the dehydro-oligomerization step, even though the work is at the proof-of-concept stage.

- The C1 team has had major successes and impact in both the journal and patent literature, with a Technology Commercialization Fund being awarded for commercialization of the HOG technology with Enerkem. This technology can also be tweaked to make some kerosene-range molecules. Further, SAF-range material has been demonstrated in the laboratory, passing several key jet fuel specs.

- The project aims to develop engineered Cu/BEA catalysts for direct CO_2-rich STH. They also initiated the effort for isoalkane dehydrocoupling. This project creates a unique approach that integrates foundational catalyst research and applied catalyst engineering. Currently, more information flows from the foundational catalyst research to the applied engineering. It would be more beneficial if applied engineering could generate critical questions that drive the foundational research.

- The project has met its goals and is ready for the next stage of R&D. It would be more beneficial if the team had articulated their R&D plan in the event that the engineered catalysts cannot meet the setup goals, or which avenue they plan to pursue to optimize the engineered catalysts.

- The team already showed that their product could satisfy the criteria for being SAF. The success of this project will help fulfill DOE's SAF Grand Challenge if their R&D activities lead to the scaling up of the process.

- The overall outcome of this project is highly encouraging, as the team has successfully converted CO_2-rich syngas into precursors for SAF using the STH method developed through insights gained from

HOG. The dual-cycle approach, which integrates fundamental studies with the development of engineering catalysts, has proven to be very effective, allowing the team to keep pace with the fuel market shift. The past 2 years of work have yielded impressive results, producing a cost-effective catalytic process with great promise. Moving forward, the team may consider studying reaction kinetics, mass and heat transfer, and the impact of catalyst forming on performance for scaling up.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the many positive reviewer comments about this project's goal, approach, progress, and future plan. We appreciate the note about including error bars and error analysis in our data. Detailed error analysis was omitted here for clarity of the plots, but it is included in our published reports and papers. To the question about how biomass syngas differs from other feedstocks, this project partnered with the FCIC in 2018 and 2019 to assess variability in syngas composition and yield from five top biomass feedstocks. That report was published in the journal *Applied Energy* in 2019. The H_2:CO ratio from biomass is approximately 2.6, which is higher than coal-based syngas (approximately 1.0) and comparable to that produced from steam methane reforming (theoretical value of 3.0). Impurities in the biomass-derived syngas are important considerations, and there are both existing and emerging technologies to remove those impurities for downstream processing. To date, no significant issues with biomass syngas compositions have been identified that cannot be handled with cleanup technologies. This project works closely with the FCIC to stay at the forefront of syngas cleanup technologies to reduce that risk to commercialization for the catalysts and processes being developed in this project. The comment to include MFSP estimates for the early-stage dehydrocoupling step is appreciated, and this is a priority in working with the Thermochemical Analysis project through FY 2025. Relatedly, we appreciate the comment to highlight how information from the applied engineering cycle flows back through catalyst testing. Perhaps not emphasized in the presentation was the direction from the Thermochemical Analysis team to test the STH catalyst system at higher temperatures and pressures (up to 300°C and 5 MPa) than originally targeted (220°C and 0.75–1 MPa) to improve product separation efficiency. This will be emphasized in future reports. The comment to study kinetics, mass transfer, and the effect of catalyst forming was not highlighted in this presentation due to time constraints, but this is an ongoing effort with the CCPC team, with a deliverable at the end of FY 2023 and continuing work through FY 2025. Lastly, with respect to DEIA and EJ, this project supports the overarching ChemCatBio goals, and one project-specific activity was participation in the development of the Justice Underpinning Science and Technology Research (JUST-R) framework, which is an approach to assessing EJ in early-stage research that was recently published in the high-impact journal *Joule*.

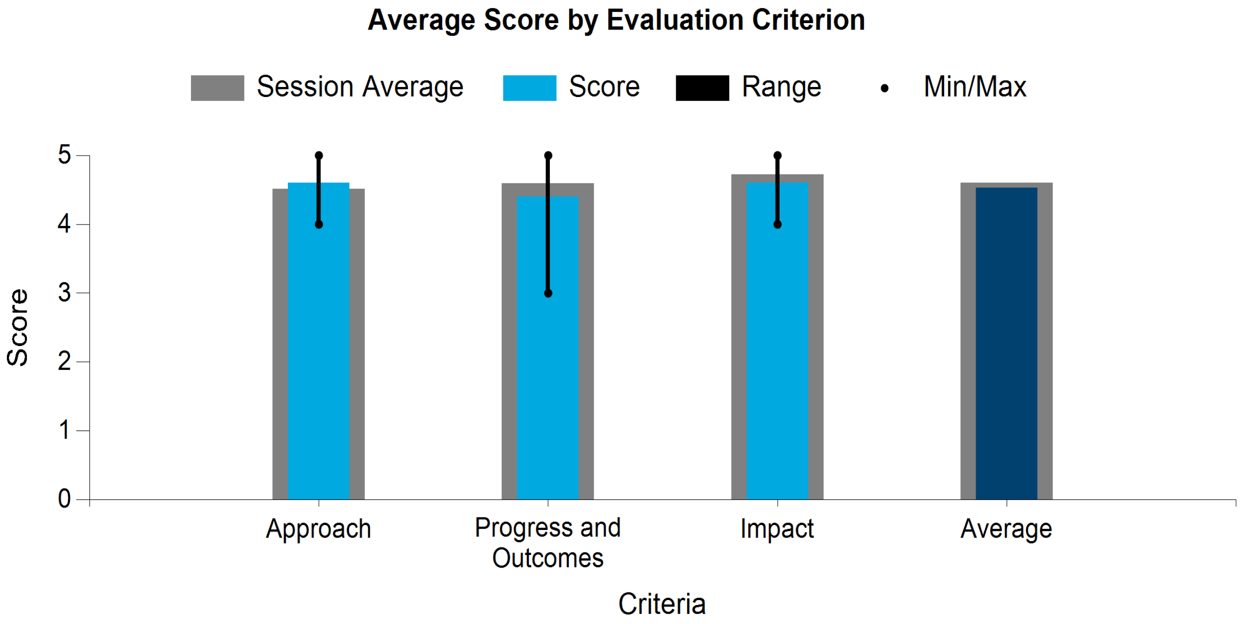
CATALYTIC UPGRADING OF PYROLYSIS PRODUCTS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.314
Presenter(s):	Mike Griffin
Project Start Date:	10/01/2021
Planned Project End Date:	09/30/2024
Total Funding:	$1,950,000.00

The objective of this project is to advance the state-of-the-art technology for a CFP + hydrotreating process to produce SAF and other biogenic products. Our approach focuses on performing integrated experiments using realistic biomass feedstocks and non-noble metal technical catalyst formulations. CFP is performed in an *ex situ* configuration using a fluidized-bed reactor without co-fed hydrogen. Research advancements over the past 2 years include establishing benchmark yield structures and compositional data for each step of the biomass-to-SAF process, demonstrating the ability to produce a cycloalkane-rich SAF product that meets key ASTM 4054 guidelines, generating benchmark characterization data for technical catalyst formulations with an emphasis on determining the unique composition and combustion properties of biogenic coke, and establishing bio-oil critical material attributes (CMAs) to mitigate the risk of plugging during downstream hydroprocessing. Other impacts from this project include generation of broadly enabling scientific knowledge (12 publications and 12 presentations since 2021), engagement with industry partners (Johnson Matthey, ExxonMobil, and Phillips 66), and identification of a promising pathway to market that addresses emerging demands for biogenic refinery feedstocks.



COMMENTS

- This project aims to develop a pathway to convert woody biomass into SAF and other products by CFP and hydrotreating.
    - Made a pivot in 2021 from fixed-bed to fluidized-bed fast pyrolysis in response to challenges. The jury is still out on hydrotreating, and fraction testing looks good so far but is still an unknown.

  - Integrated experimental campaigns with supporting analysis of continuous CFP experiments without co-fed H_2 or noble metal catalysts.
  - High O_2 content is difficult to deal with—perhaps coprocessing or a refinery pilot scale?
  - Use of realistic biomass feedstocks.
  - Technical catalyst formulations.
  - Strong management plan for tasks and communication leads to strong collaboration, as shown by publications.
  - Included DEI, though weak room for improvement here.
  - Progress:
    - Good industrial engagement.
    - Good carbon balances (though no error analysis in tables on Slides 8 and 9).
    - No error analysis on plots.
    - Benchmark yield structures and compositional data for three levels of CFP upgrading.
    - Evaluation of SAF properties.
    - Identification of opportunities to produce a cycloalkane-rich product stream.
    - Characterization data for technical zeolite catalysts.
    - Bio-oil CMAs to mitigate the risk of plugging during downstream hydroprocessing.
    - Defined pathway to market via existing refineries and integration points, which leverages existing infrastructure and workforce.
    - Twelve publications, 12 presentations, two issued patents, and six patent applications.
    - Generated a spinoff project.

- This project was focused on CFP conversion of biomass to bio-oil and subsequent hydroprocessing for SAF applications. The project is commended for the pivot from fixed-bed to fluidized-bed reactors in the past cycle, in part due to the inherent challenges with that set of reactor conditions. The benefits are already evident in the switch, with the ability to perform CFP without co-fed hydrogen and to do the transformation without precious metals. Movement toward use of more realistic biomass feedstocks is another strength of the effort. The project is also involved with multiple collaborations with ChemCatBio partners (Catalyst Deactivation Mitigation for Biomass Conversion [CDM], ACSC, and CCPC). The catalyst characterization work is a particular highlight in the view of this reviewer. The strong connection with various industrial partners is also a positive. Regarding DEI efforts, most aspects seemed pretty standard, and it seems as though the project is waiting on ChemCatBio direction for significant engagement. The energy-justice-related publication is one exception and a clear indication of their efforts in this space. The planned science and experiments are well put together and seek to explore rational structure-property relationship development. Studies of inorganic dopants will certainly impact further catalyst development. The dopant probe students are a specific highlight of the work, which has identified aldehydes as a functionality to monitor in the reactions. Another key aspect of the work is the development of benchmark data for CFP in these new reactor systems, as well as catalytic data for zeolite catalysts. Given the heavy focus in other projects on related zeolitic materials, these specific studies can have an impact on studies across the whole upgrading consortium. In general, promising results from the 2021 pivot were obtained from the CFP, hydrotreating, and fraction testing. The general milestone targets seem achievable, particularly with current results demonstrating good carbon efficiencies, significant GHG reductions, and a promising ability to remove the oxygen content to below detectable limits. Other targets—involving improving catalyst durability and more modest increases in efficiency—seem attainable. The access to predominantly cycloalkane fractions was promising and somewhat unique relative other technologies in the upgrading area, which generally gave isoalkane products. The CMA experiments, designed to determine the effect of contaminants on the fuel fraction properties, were important control experiments. With this information on hand, mitigation methods to circumvent issues with reactive carbonyls in fuel fractions can be pursued. The project, with 12 publications (many in high-impact catalysis journals) and two patents (and six additional patent applications), was very productive. The energy-justice-related publication is another highlight and added dimension of impact. The existing connections with industry are another avenue through which to establish impact with proposed studies. In terms of the technology, there are several advantages to CFP, including the ability to plug and play, unlike other systems. For example, CFP allows distributed pyrolysis to stable bio-oil conversion, which can then be transported to centralized hydrotreating. This modularity is a strength of the effort and is unique relative to some other upgrading projects, which must rely primarily on economies of scale. The direct refinery repurposing connection is another strength, reducing capital costs and also potentially repurposing existing workforces. As such, it is an important technology to investigate at these intermediate TRLs, given the many potential advantages of a viable process in this area.

- The team has done a good job of using a variety of tools to develop a regenerative fluidized-bed system capable of CFP followed by upgrading to SAF. The approach is reasonable, focusing on integrating the CFP and the hydrotreating units while characterizing the CFP oil as a key intermediate. The partnerships are strong, involving major oil and gas companies, catalyst manufacturers, and industry advisors. This work will have a major impact on the industry, allowing existing operating assets of oil and gas companies to be considered for future scale-up and integration for SAF production.

- The team gave a good overview of the 2021 baseline and the research pivot to SAF via catalyst and reactor configuration major changes. The current state of the art suffers from catalyst deactivation, excess hydrogen consumption, and difficult thermal management. The comprehensive approach is to establish a process technology performance baseline, initiate a CFP oil spec sheet, characterize catalytic materials, and investigate refinery economics with strong industry advisory support/CRADAs from the oil and gas and catalyst manufacturing communities, as well as ChemCatBio engagement, which promotes new R&D opportunities. The use of sulfided hydroprocessing catalysts aligns well with existing oil and gas downstream assets. This approach limits the opportunity to develop new materials for this application to some extent. The risks associated with establishing the new baseline using fluidized-bed arrangements were not outlined with any contingency. A DEI lead was mentioned along with several activities.

- The team has made significant progress by designing, constructing, commissioning, and starting up a fluidized-bed-based CFP system. The regeneration cycle was optimized using thermogravimetric analysis/infrared spectroscopy and nuclear magnetic resonance (NMR) to characterize coke type and combustion characteristics for complete restoration of the surface area and total acidity. The team should have provided some insight into the residence times associated with the active riser section and the regeneration side. On the trickle-bed hydrotreating unit, the team should specify any sulfur co-reactants, how the temperature in the reactor is measured, and the amount of carbon going into the gas phase for hydrogen recovery. The final SAF product looks promising with the high amount of cycloalkanes. The identification of the 20 wt % oxygen as the sweet spot in the CFP feed is a good specification based on quality experimental data. The high-throughput CMA spiking experiments appear to be a reasonable approach and tool. More data science (e.g., quantity and processing) discussions were expected here.

- This project opens new opportunities for pyrolysis product upgrading pathways by focusing on the SAF commodity as the end goal. The notion of de-risking downstream hydroprocessing should be clarified relative to early-generation pyrolysis oils. The estimated MFSP and overall process carbon efficiency looks competitive relative to other routes.

- This project focuses on developing a fluidized-bed CFP process. This process utilizes a zeolite catalyst and helps remove co-fed hydrogen, which will have a significant impact on process TEA/LCA and safety.

- The project has an illustration of the production of SAF that meets the ASTM D4054 guidelines for density, viscosity, boiling point, heating value, flash point, freeze point, and volatility. They also establish three CMAs for CFP bio-oil. It would be more beneficial if the team could address how the feedstock varies based on their source and how the variation in feedstock may affect the quality of their final products or the process operating parameters. An omics analysis may be beneficial to enlist the compounds in bio-oil qualitatively or semi-quantitatively. This omics information may help develop a framework to determine the operating parameters of the process based on the feedstock.

- The project has made impressive progress toward the goal.

- The project has developed knowledge and technologies that can benefit the development of fast pyrolysis processes. If successful, this project will help achieve the SAF Grand Challenge. The R&D activities of the team have also led to the development of two other research projects focusing broadly on sustainability. The team has shown commitment to the DEI effort by initiating various activities.

- The progress of this project in producing SAF through pyrolysis of biomass is promising. The use of realistic biomass and fluidized-bed reactors is a significant step closer to achieving success. Collaborating closely with industry and adopting a multitask strategy to address challenges at various stages has helped maintain balanced progress. Over the past 2 years, substantial outcomes have been achieved, including commissioning a reaction system and conducting a relatively long deactivation study, among other scientific achievements.

- The production of SAF from pyrolysis of biomass still appears challenging due to poor miscibility, poor thermostability, and high oxygen content of pyrolysis oils. Coprocessing is a reasonable technical choice to address these challenges after pyrolysis oils have been treated. Collaborating with industry partners to leverage their existing laboratory- or pilot-plant-scale cracking units for coprocessing is recommended. Additionally, modifying the fluid catalytic cracking catalysts or developing new additives could be another approach to improving the utilization of pyrolysis oils.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their excellent feedback and appreciate the positive comments related to our project's approach, progress, and impact. As highlighted by the reviewers, research from this project has led to the development of yield structures and compositional data for an integrated biomass-to-SAF process, demonstrated the ability to produce a high-quality cycloalkane-rich SAF product, and identified CMAs for bio-oil to mitigate the risk of plugging during downstream hydroprocessing. These achievements are a result of a coordinated research effort with ChemCatBio enabling projects and industrial partners, and we would like to acknowledge our collaborators for their contributions. We also appreciate the reviewers' helpful suggestions for improvement and offer the following responses to clarify certain details and outline our plans for future work. Fluidized-bed reactor system: We are pleased to hear the support for our pivot toward utilizing a fluidized-bed reactor system. As highlighted, fluidized-bed CFP can be performed without co-fed hydrogen, utilizes non-noble metal catalysts, and provides greater flexibility in managing catalyst deactivation. It is also true that there are unique risks to this approach. Of primary concern is the comparatively low carbon efficiency of bio-oil versus fixed-bed hydrodeoxygenation. In this project, we plan to address this risk through the development of modified zeolite catalysts that increase carbon efficiency by reducing coking rates and coupling light end molecules into fuel-range products. We are also working closely with collaborating projects to identify opportunities for effective utilization of all byproduct streams (e.g., char). Another important risk is associated with catalyst deactivation, attrition, and regeneration. We are addressing this risk both within the CFP project and through collaborative research with the ChemCatBio enabling projects. This ongoing work focuses on identifying deactivation mechanisms by characterizing pre- and post-reaction catalysts (ACSC), evaluating the unique combustion kinetics of biogenic coke (CDM), and developing regeneration models for riser-type reactor systems (CCPC). Thermal stability experiments: The project team appreciates the positive feedback related to the bio-oil thermal stability experiments and agrees that this approach will provide an excellent opportunity to utilize data science and statistical analysis techniques. Currently, the application of these techniques is precluded by the limited number of experiments. However, ongoing work is focused on expanding the dataset, and we plan to utilize sensitivity analysis and multiple linear regression to identify and predict correlations between bio-oil chemical composition, physical properties, and thermal stability. The reviewers are also correct in pointing out the importance of understanding how feedstock variability impacts bio-oil properties. This represents a central goal within the FCIC, and we coordinate closely with our collaborators to support these efforts. Collectively, the development of feedstock CMAs for biomass pyrolysis (FCIC) and bio-oil CMAs for hydrotreating (this project) will provide a framework to inform quality specifications for the end-to-end process. DEI: Our project's DEIP has three main components: (1) foster an inclusive environment within the project team, (2) promote DEI through research implementation, and (3) benefit underrepresented and underserved communities. Toward these goals, we have encouraged feedback, including conducting anonymous surveys, and have adjusted our meeting structure to make it more inclusive in response to feedback received. We have also developed workshops and "DEI minutes" to raise awareness about citation bias, stereotype threat, and the model minority myth, among other topics. Additionally, members of our project team (including the PI and DEI lead) were collaborators on a recently published manuscript focused on identifying metrics and methods to incorporate energy justice concepts into early-stage research and development (doi.org/10.1016/j.joule.2023.01.007). Later, the input/output method was applied to our project specifically. We have also been fortunate to host two student interns from MSIs as part of the Student Training in Applied Research and Growth Sector STEM Core programs. While we believe these efforts represent strong steps in the right direction, we also recognize that there is room for further improvement and look forward to working across ChemCatBio to ensure that our collective research promotes an energy transition in which benefits are equitably distributed and ideas are widely sourced. Hydrotreating methods: We are happy to provide additional details about the hydrotreating experimental methods. The catalyst is presulfided *in situ* with di-tert-butyl disulfide using industrially established protocols. To maintain the catalyst in a sulfided form during hydroprocessing, hydrogen sulfide is included in the hydrogen gas at a concentration of 60 ppm. The temperature inside the bed is measured by a six-point thermocouple placed along the centerline of the reactor. Carbon losses in the exit gas represent 3%–6% of carbon in the CFP oil and comprise primarily C1–C5 hydrocarbons. Error analysis: Data quality and experimental reproducibility are priorities in our research, and we appreciate the opportunity to provide additional detail on this important point. After commissioning a new vapor-phase catalytic upgrading reactor for CFP, we successfully completed a milestone to demonstrate mass and carbon balance closures of 100% ± 5% and data reproducibility with relative standard deviation of <10% on key metrics. Typical mass and carbon balance closures for the hydrotreating system are 96% ± 2%, and the relative standard deviation on product composition is <2%.

UPGRADING OF C2 INTERMEDIATES

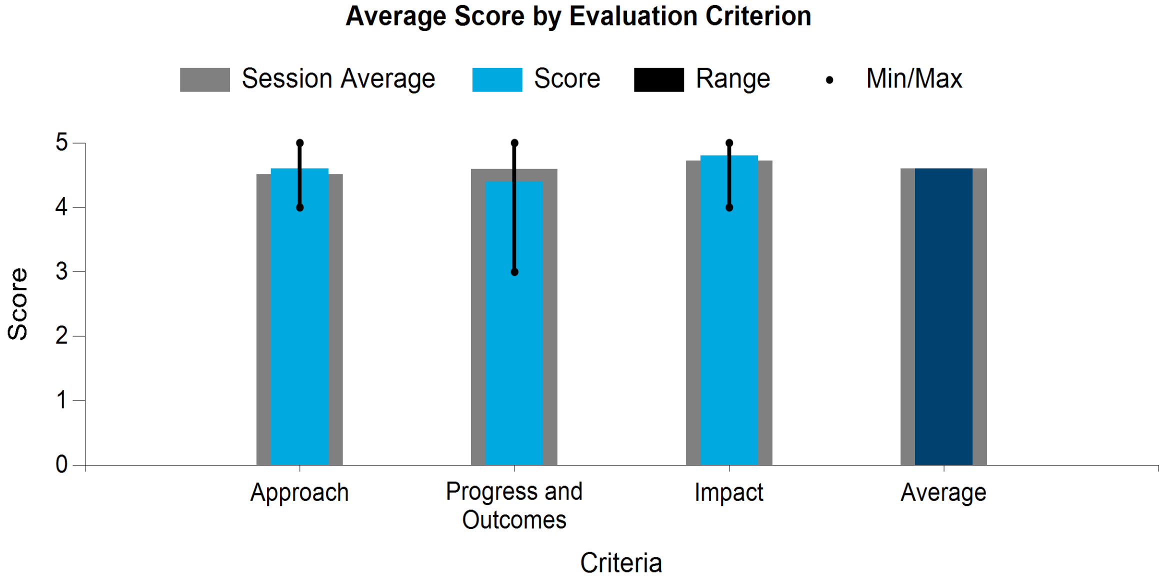
Oak Ridge National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.100
Presenter(s):	Andrew Sutton
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2025
Total Funding:	$1,680,834.00

This project is focused on the conversion of intermediate ethanol to jet-range hydrocarbons with integrated routes to coproducts. Ethanol is an attractive feedstock for the production of fuels and chemicals, as it is already produced at commercial scale and can be produced from a variety of renewable biomass and waste sources. In addition, the ethanol "blend wall," coupled with advances in production efficiency and feedstock diversification, is expected to lead to excess ethanol at competitive prices. Initiated in FY 2017, ORNL has performed proof-of-concept and applied R&D, utilized advanced characterization tools to understand key catalytic mechanistic steps and catalyst active site structure-function relationships, and obtained experimental data using scalable fixed-bed reactors to inform models for TEA and LCA.

Efforts at ORNL have culminated in the development of a new biomass upgrading pathway for the direct conversion of ethanol to C4-rich olefins. This pathway provides a more economic route to jet-range hydrocarbons than current technology. The current state of the art for the ethanol-to-distillates process requires four catalytic steps: (1) ethanol to ethylene, (2) oligomerization of ethylene to C4-rich olefins, (3) oligomerization of C4-rich olefins to distillate-range hydrocarbons, and finally, (4) hydrotreating to saturate olefins. Producing C4-rich olefins directly from ethanol with high yield is new and impactful because the produced C4-rich olefins can be selectively oligomerized to distillate-range hydrocarbons, thus eliminating one step. This reduces capital cost requirements, while simultaneously providing energy savings realized by coupling endothermic and exothermic reactions. Further, this project is also evaluating new, promising coproduct options that hold promise in further reducing fuel production costs through the sale of value-added coproducts.



COMMENTS

- Generally, progress has been good. The project has been able to reduce the number of unit operations and demonstrate tuning of the products through catalyst use, and the technology has been licensed by the team's collaborator, Prometheus. It is very interesting to note that the use of miscanthus gets the process to be CO_2 negative. I'm interested to see more details with respect to this. Additionally, the project has demonstrated an excellent C balance of 80%, and more importantly, believes that 100% is possible with recycle. There are remaining issues that have been identified:
    - Deactivation conditions may be too mild to draw conclusions right now—more work is necessary.
    - Nitric acid use and wastewater generation are issues of concern, and should be minimized.
    - Tax credits have a disproportionately large impact on cost (2x in some cases).
- The project has already demonstrated strong commercialization potential, and there is room for further improvement.
- This project is focused on ethanol to higher olefin conversion, using a Cu/La zeolite catalyst, with the lanthanide allowing tuning of the product distribution. The flexibility to dial in distributions suitable for aviation or diesel fuels is impressive. The effort also clearly benefits from a variety of collaborations throughout ChemCatBio; these were also articulated well in the presentation. The work also presented the state of the art and challenges in the space effectively. Also, the push toward engineered catalysts is commendable and in line with evolution of most projects in the upgrading area toward more commercially relevant systems. The mechanistic and contaminant studies are first rate and hopefully provide key insights into the design of next-generation catalysts. While the current catalyst formulation seems very tolerant, I would be curious to know the effects of additional impurities—e.g., trace sulfur. The project management seems well in order and particularly synergistic with the related PNNL efforts with ethanol to olefins. There is clear delineation of projects regarding systems and approaches, meaning knowledge transfer between groups should be relatively seamless. One point for consideration: I think further comment on lanthanide availability might be in order moving forward. Although I realize that this is built into economic modeling, critical element availability and supply chain variability are something gaining scrutiny. Ability to recycle the catalyst or lanthanide might be something to comment on further in future review cycles. Milestones in the project seem to have been achieved or are on a trajectory for success. The current Cu/La catalyst has been demonstrated as scalable, able to be oxidatively regenerated, and tolerant of various feed streams of ethanol. The movement toward engineered catalysts during the next funding period is logical and aligned with most projects in the upgrading section. The versatility and tunability of the catalyst system is impressive and is something I highlight as a true differentiator of the project. The economic modeling as part of ChemCatBio informs knowledge of the system to be cost-effective (e.g., high concentrations of ethanol are required to be economically competitive) while at the same time suggesting significant GHG emission reductions with the system. Fuel testing of the mainly isoalkane products derived from the olefin coupling also appear promising. Here again, the ability to leverage collaborations with ChemCatBio members is key to the timely completion of the fuel analysis and understanding of the system economics. The impact to the broader community is clear, based on the four publications (many in high-impact catalysis-centric journals) and three patents during the prior funding cycle. The licensed tech is also an indication of successful technology development and commercialization potential. If the goals of the project are fully realized, this would certainly have significant impact in the ethanol to fuels/feedstocks space, at least on par with other licensed technologies in the alcohol to jet (ATJ) space.
- As a strategic approach, the project team has been able to forge effective collaborations across ChemCatBio to help elucidate the critical elementary steps in converting ethanol to higher olefins. These

collaborations have led to creating catalyst surfaces that can be tuned to influence overall product distributions.

- The focus is the ethanol to olefins step. The current SOT in the literature is dehydration followed by dimerization. Their sound process-intensity-based approach is to bypass the dehydration step and go straight to butadiene or mixed olefins. It is based on a dealuminated BEA. There are quite a few olefins and oxygenates in the product stream, so the team's approach is to collaborate with the crosscutting enabling technology groups to elucidate the reaction network. The team should spend more time identifying the risks associated with product selectivity control and other potential bottlenecks. The team should be clearer about the DEIP activities and future EJ directions.

- The team showed interesting results on tuning the olefin distribution with lanthanum composition. The connection between structure and activity as characterized by microscopy and X-ray analysis would be useful to show based on the conclusions, as well as surface titration with basic probes to show shifts in total acidity. TOS data showing the impact of regeneration cycles would also be useful. Hydrothermal aging had little effect on product distribution after only 24 hours. With the tools available at ORNL for monitoring material quality, the team should target catalyst synthesis scale-up on the order of kilogram batches. The team is publishing a paper that shows how copper is redispersed when the oxidative regeneration is conducted.

- The original license was with Vertimass, and a licensing negotiation with Prometheus is ongoing. These are clear commercial pathways that the team should be excited about supporting. Further, the impact of this route on the entire bioenergy industry and Gen I ethanol facilities will be quite significant.

- This project is developing catalytic upgrading technologies that enable cost-competitive conversion of cellulosic ethanol to SAF. The project focuses on upgrading zeolite-supported catalysts that enable the direct conversion of ethanol to C3 olefin, which could be used to eventually convert to SAF. The same procedure could be tuned to product chemicals as alternative products.

- The project deploys a collaborative workflow to accelerate the R&D activities. They collaborate with the three enabling teams in the program, as well as the TEA/LCA team, using the results to determine the direction of the R&D activities. They also collaborate with the other C2 project in the program. This collaborative workflow helps advance the research, with significant innovation in both foundational work and technologies. It would be more beneficial if the team could be more proactive in DEI.

- The project developed and tested engineered catalysts, improved catalyst selectivity and stability for C4-rich olefin streams, and conducted calculations for reactor-scale modeling and kinetics for future scale-up. This progress was achieved with a close collaboration with the enabling teams. These efforts successfully demonstrate integrated processing of ethanol to SAF with at least 80% carbon efficiency. There is a clear connection between the deployed approach and the outcomes. The deployment of engineered catalysts and the modeling of reactors illustrate the potential of the processes to be commercialized. The success of this project will help achieve DOE's SAF goal as well as the GHG emission reduction.

- This project has generated several patents that are either in the negotiation process of being licensed to a company or on that track. This record illustrates the impact of the project on industrializing the biomass-based conversion for SAF.

- The project presents a promising new strategy for meeting the shifting market demand for different product distributions from bioethanol by bypassing the ethylene step using tunable catalysts. This approach significantly reduces unit operations and energy consumption. Collaborative efforts with ACSC, CCPC, and industrial partners have led to impressive progress in understanding deactivation mechanisms, scaling up catalyst synthesis, achieving high conversion and selectivity, and meeting GHG reduction goals.

- However, the high water content in the feedstock still poses a significant challenge to this process. Further research is needed to investigate the impact of water on catalyst stability. It is also important to examine the impact of other impurities, such as dimethyl sulfide and dimethyl sulfoxide, on catalyst performance before scaling up. Overall, the outcomes of this project are encouraging, with high conversion, high selectivity, and competitive GGE. With continued research and development, this innovative approach has the potential to make a significant contribution to sustainable energy production.

PI RESPONSE TO REVIEWER COMMENTS

- We would like to thank the reviewers for the time and thoughtfulness in the feedback they have provided as part of the Peer Review process. We are encouraged by the positive feedback and the appreciation of our work thus far, and we appreciate the opportunity to address some of the points that have been raised. A general point was that DEI progress and EJ involvement was lacking. We agree that this was not mentioned explicitly in the review material, but we are fully engaged with the ChemCatBio DEI team, and a member of our team is a member of that team. We view DEI as very important, and we are continuing to learn ways we can progress. We highly value the information shared from the ChemCatBio DEI team in our consortium meetings. At ORNL, we have been committed to STEM outreach to underserved schools and communities for several years, and we are developing further strategies to remove internal biases, including in hiring, collaborations, and publication citations. In response to the negative CO_2 balance using miscanthus, this takes advantage of the production of dedicated energy crops. This has been published recently, and more details can be found at doi.org/10.1039/D1GC02854E. We also reported MFSPs in this publication and reported updated numbers, taking into account the current blenders tax credit, which offers incentives for producing fuel with a certain GHG reduction relative to petroleum fuels. Even though the TEA in this publication was very competitive, it was provided to show the potential that these tax credits and incentives could have on the SAF industry. In response to the nitric acid and wastewater generation, we agree; it is an important consideration when thinking about scale-up of the catalyst production and an aspect that is rarely considered in explorative research. To use extrudates for our work, we had to scale up the catalyst synthesis, and during this process, we reduced water usage by a factor of 10 and reduced the nitric acid by a factor of 5. This is a significant improvement, and we aim to work with catalyst manufacturers to gain insight into further process improvements as we aim to de-risk this technology for industry adoption. In terms of catalyst lifetime, regeneration, and deactivation, we have an upcoming manuscript discussing the mechanism of deactivation and regeneration, which includes data that we had reported at the previous Peer Review and so did not include it in this review cycle. We do have data for more than 100 hours TOS with multiple regenerations that completely recover the initial catalyst activity. We are excited to scale up this process with engineered catalyst pellets and perform longer TOS experiments that will provide much more relevant data for this system. In combination with this, we have screened multiple typical contaminants that are present in current ethanol production, including methanol, acetic acid, isopropanol, and acetaldehyde, at levels higher than those found in commercial ethanol, with no deleterious effects on yield, conversion, or selectivity. We also have ethanol from a commercial producer that we will screen. The reviewers also mentioned dimethyl sulfide and dimethyl sulfoxide. We have been planning to test for sulfur impurities and will be performing these trials in FY 2024.

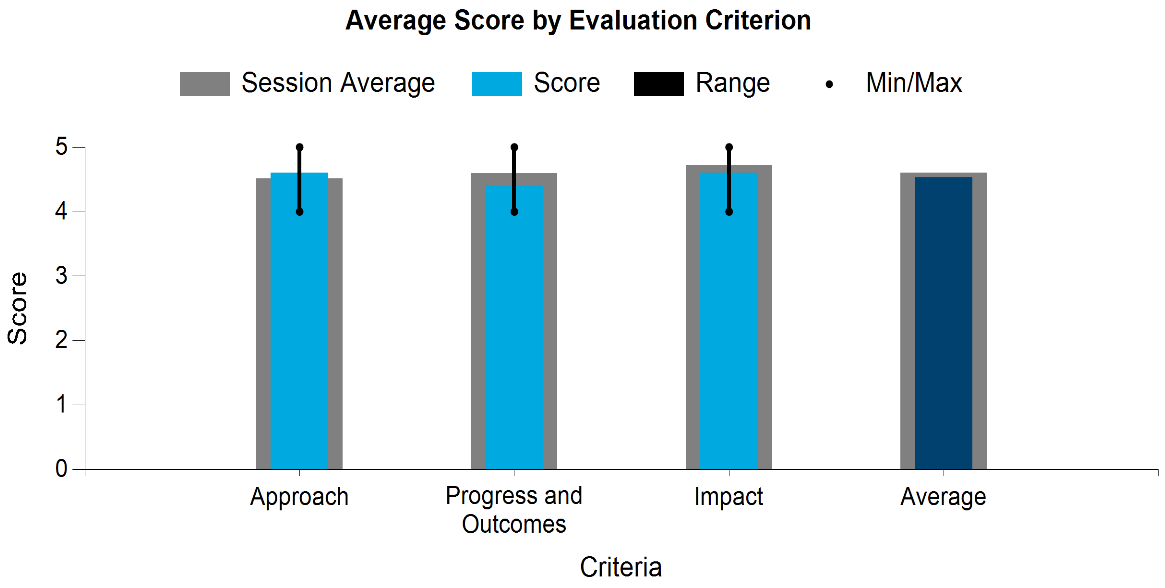
UPGRADING OF C2 INTERMEDIATES

Pacific Northwest National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.304
Presenter(s):	Rob Dagle
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$751,940.00

This project is focused on the development of a new, cost-effective route to jet- and diesel-range hydrocarbons from ethanol, with integrated routes to coproducts. Ethanol is an attractive feedstock to produce fuels and chemicals, as it is already produced at commercial scale and can be produced from a variety of renewable biomass and waste sources. In addition, the ethanol "blend wall," coupled with advances in production efficiency and feedstock diversification, is expected to lead to excess ethanol at competitive prices. This technology provides an advantage over the current state-of-the-art ATJ technology, with elimination of a unit operation and energy savings realized by coupling exothermic and endothermic reactions. Efforts here have culminated in the development of a new, multifunctional catalyst system for the direct conversion of ethanol to n-butene-rich olefins. Additionally, a second multifunctional catalyst has been developed for the single-step oligomerization of produced olefins to jet-range hydrocarbons. An integrated process demonstration was performed, resulting in the production of a liquid product meeting ASTM specifications for jet blendstock. Ongoing efforts are aimed at further improvements to overall carbon efficiency, as well as engineered catalyst development, using conventional extrudates and kinetic and reactor modeling to accelerate reactor scale-up efforts. The project team is currently engaged in scaling up the catalyst technology developed on this project, employing modular, microchannel reactors. This separate effort leverages recent reactor fabrication advances made using additive manufacturing, teaming with LanzaTech and Oregon State University to take this new process technology one step closer to commercialization.



COMMENTS

- This project is developing a catalytic pathway for direct conversion of ethanol to butene-rich olefin intermediates. The team is moving toward an integrated process demonstration with engineered catalyst development to accelerate the process scale-up effort.

- The project explores two different catalyst systems to convert ethanol to C3 olefins and produce distillate fuels from olefin intermediates and produced fuels with the desired properties meeting target economics. It is a good collaborative effort—both within and outside of ChemCatBio. DEI approach and efforts are conducted via collaboration with the University of New Mexico (UNM). The project risk is addressed in collaboration with partners, with defined mitigation strategies.

- Carbon efficiency and ethanol cost are key cost drivers for improvements in carbon efficiency. The team developed a one-step oligomerization process that incorporates all olefinic intermediates. The team demonstrated integrated processing of ethanol to SAF with a high carbon efficiency of >80%. There is a question about the steady-state performance of catalysts with respect to water. The water content is of concern. More work is needed here—perhaps there could be more interaction with the deactivation project. The process was demonstrated with partial success, but further improvements are required for oligomerization processing: >95% ethanol conversion, 92% C2 olefin selectivity, and 75% C3 olefin selectivity.

- This could enable existing ethanol producers to pivot their product streams toward middle-distillate fuels and renewable chemicals. LanzaTech is commercializing the ATJ process for scaled SAF production developed previously (but this seems to not be from this project). Microchannel reactors enable process intensification and modularity, which is useful for distributed feedstocks.

- The project—focused primarily on ethanol conversion to higher alkenes for conversion to fuels or as valuable coproducts—clearly aligns with broader BETO goals to focus on SAF. It also builds logically from prior efforts by the group in the design of catalysts for ethanol upgrading. This reviewer was particularly impressed with both project collaborations (CCPC, Washington State University [WSU] for fuel testing, and UNM experts in related emission control catalysis) as well as the industrial links, which are established for both the fuel and coproduct components of the work. Extension of the work to greater process integration of the complete process and use of engineered catalysts in the upcoming cycle are warranted and aligned with prior review comments and the natural evolution of the work. Some DEI component exists with the MSI/Established Program to Stimulate Competitive Research (EPSCoR) institution PI, but the project is encouraged in subsequent cycles to provide some additional specifics regarding the interactions to demonstrate tangible connections in this space. The modeling and NMR characterization studies are another highlight. They complement one another, give a better-defined picture of the system, and will hopefully lead to improvements in catalysis design. The additive manufacturing component was brief but is something that should be considered moving forward as an opportunity area, particularly when a DFA/CRADA could arise. There are many directions this area can move—printing catalysts, reactor design (in some cases), etc. Also, given Rapid Advancement in Process Intensification Deployment (RAPID) Institute capabilities and PNNL's role there, the project should look to leverage available capabilities when it is appropriate. The metrics presented were clear. The expanded goals to determine kinetics for reactor modeling and the move to engineered catalysts are consistent with the general shift to these topics in the upgrading portfolio. I view the milestones as a bit aggressive for one project cycle, but they are potentially achievable. The state of the art was summarized well. The presentation also laid out well the progression within the catalyst systems to base metals, understanding of contaminant effects (specifically the role of water in deactivation), and promoter effects on performance. The careful understanding of the effects on the current processes provides pathways for improvement. I also appreciate the transparency about some areas that still need improvement. With this stage of TRL development, it is critical to identify these issues so they can be probed as soon as possible if they end up being a red flag point for the technology. Milestones generally seem on track, as modeling has established the pathway as a viable route to the desired cost metrics. Current targets for FY 2024 and FY 2025 extend to the areas necessary to achieve overall project goals. In particular, it can be highlighted that the results with the single-step catalyst look promising—I look forward to seeing the progression of research and development of this system in a subsequent review cycle. The six publications (the majority of which are in catalysis-focused journals) and the three patents are solid output. The commercial engagement is also a highlight, with partners in both the fuels (LanzaTech) and coproducts (Bridgestone) spaces. It is very rational to pursue alternatives to the ATJ process for the reasons highlighted in the presentation (more versatility, diversity of products/coproducts, etc.). Having scalable alternatives would have clear potential for a commercialization path, much as ATJ is progressing.

- The C2 upgrading team continues to make strides in the area of direct ethanol conversion to C4 olefins for continued oligomerization to SAF. The surface chemistry from a yield perspective remains challenging.
- The team aims to have a bench-scale demonstration of two pathways for converting biogenic ethanol directly to C4 olefins that can eventually oligomerize further to SAF. The approach is to continue developing the catalysts, then provide a process integration proof of concept at the bench scale. The state-of-the-art single-step technology involves catalysts that produce mostly aromatics from alcohols. Here, the team's approach is to design a material that can be highly selective to butenes, as published in a peer-reviewed article in 2020. Several key risks were identified, only for the catalysts, selectivity, durability, and engineered structure performance. The mitigation strategy is to partner with crosscutting functions across ChemCatBio for characterization and insight, which is a great approach. The collaborations include university, national lab, and industry partners. More risks on the integrated process development side should be identified moving forward. The DEIP or EJ plan was not strongly highlighted, except for UNM being an MSI. UNM recently won an award where PNNL helped on the proposal.
- The identification of the butyraldehyde surface intermediates within the reaction pathway as more favorable (in terms of promoting better catalyst performance) was a major accomplishment. The team was able to show how certain promoters mitigate sintering events out to 200 hours on stream. The negative impact of feed water on Cu sintering was experimentally determined. The team was able to demonstrate the entire integrated two-step conversion to SAF, showing 300 hours on stream for single-step ethanol conversion to olefins and several 100-hour regeneration cycles for the oligomerization step. The team disclosed some of the key risks/gaps with the oligomerization step, namely, C2 olefin conversion, regeneration effectiveness, and integration of separation strategies between reaction unit ops. By working to solve the C2 olefin conversion gap, the team developed a multifunctional material capable of handling mixed olefinic feeds for converting to SAF-range material. A patent was filed for this work.
- Based on the most recent progress, the MFSP projection is only slightly above the \$3/GGE target, which makes this pathway quite attractive and industrially relevant. Ethanol will continue to be a strong building block in the biochemical/bioenergy industry, with opportunities to valorize into both the fuels and chemical commodity markets. This technology pathway will become more important within the next decade as the ethanol supply becomes challenged, opening up new opportunities for the Gen I ethanol facilities.
- This is one of the two projects focused on developing processes that convert C2 to SAF. This project focuses on the M/SiO_2 (M = Ag/Zr, X) process. The objective is to develop new upgrading technologies that enable the cost-competitive conversion of C2 oxygenated intermediates to distillate fuels and valuable coproducts.
- The team is focusing on ethanol-to-butene-rich olefin catalyst development, olefin oligomerization catalyst development, and the integrated process demonstration. They also plan to conduct TEA/LCA and develop engineered catalysts as their next step in their R&D activities. They have developed a clear plan for risk analysis and mitigation and have shown a commitment to DEI by reaching out to MSIs. They have also developed a framework to collaborate with the enabling teams and the other C2 project.
- The team has illustrated that they are progressing toward new R&D activities. By collaborating with CCPC, they have discovered that proximity of small Cu nanoparticles and ZrO_2 interfaces facilitates the

desired route via a butyraldehyde intermediate. In collaboration with the CDM team, multiple catalyst design strategies were investigated, leading to catalysts providing >95% ethanol conversion, 92% C2 olefin selectivity, and 75% C3 olefin selectivity. They also analyzed the impact of real feedstock on catalytic performance. This progress is appropriate and will help achieve the goal of this project, as well as DOE's goal for SAF and GHG emission reduction.

- Ethanol is a large amount of biomass raw chemicals. This project aims to develop processes that can convert ethanol to SAF. The progress of the project has illustrated its potential to be commercialized. More efforts will be needed to analyze the impact of real feedstock on the catalyst performance and duration.
- This project has made significant progress in exploring a new route to directly produce C3 olefins from ethanol. A good risk and mitigation approach was employed, with close collaboration within ChemCatBio and academia. This has resulted in a promising catalyst system developed through rational catalyst design based on mechanistic studies using state-of-the-art techniques.
- Although the addition of dopants has improved the stability of the olefin catalyst, further enhancements are necessary, particularly in the presence of water in real feedstock. Using accelerated deactivation as a pretreatment step for catalysts before activity screening is recommended to identify catalysts with higher potential for commercialization.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the positive comments from the reviewers highlighting the following: our innovation approach over current ATJ processing; the use of ethanol as a strong building block for renewable fuels and chemicals; strong collaborations both within and outside ChemCatBio, which includes industrial links; our DEI approach via collaboration with UNM; the use of partnering to mitigate technical risks; the use of modeling and NMR characterization to identify the favorable surface intermediate (butyraldehyde) within the reaction mechanism; the discovery of how the catalytic properties can be tuned to facilitate the favored pathway, with CCPC collaboration; the use of multiple catalyst design strategies to improve performance; our progress toward reducing Cu metal sintering; the evaluation of real feedstock on performance; our determination of water having a negative impact on catalyst performance; our transparency about some areas that still need improvement, including better separation between reaction units; the extension to include process integration, including a 300-hour two-step conversion demonstration; the future development of engineered catalysts and kinetic and reactor modeling; the development of a new, patent-pending, multifunctional oligomerization catalyst; the potential for commercialization; our solid publication and patent outputs; clear metrics; and our well-laid-out presentation. Regarding reporting more details about our collaboration with UNM: Here, we are focused on new catalyst concepts for improving catalyst durability, leveraging UNM's unique synthesis and characterization capabilities. UNM's expertise in designing thermally stable single-atom catalysts can be extended to metal clusters relevant to our catalyst system. By providing suitable support structures, it is possible to make these catalysts more thermally stable and regenerable. UNM will prepare new formulations that PNNL will test for reactivity. UNM's unique microscopy capabilities will also be leveraged to characterize spent samples. With this collaboration having just kicked off in April 2023, we will share progress in the next review. Regarding the comment that more work is needed to mitigate catalyst deactivation, particularly in the presence of water that is present in real feedstocks, we agree. Improving catalyst durability is certainly a key part of this research. Water in the feed has been identified as having a negative influence on catalyst durability. We note that water in the feed can be removed prior to conversion, if necessary, as commercially practiced. Thus, water removal is a risk mitigation to the overall processing. However, a significant amount of water is also produced during the reaction. Thus, we will continue to develop a more water-tolerant catalyst. Further, we will work with the CDM and use accelerated deactivation as a pretreatment for catalysts before activity screening (as one reviewer suggested). Regarding the comment that more risks should be added for the integrated process development side: Indeed, these risks were not highlighted in the risk table. However, when discussing results for the two-step processing, we highlighted key challenges that remain. These include (1) better interstage separation, and (2) improved oligomerization processing to incorporate the smaller amount of ethylene produced, along with butylene, into jet-range hydrocarbons in one step. These are what we consider to be the key risks to the integrated processing. That is why we worked to develop a patent-pending oligomerization catalyst. In subsequent work, we will work to improve interstage separation, and then demonstrate improved integrated processing. Regarding the expanded goals for kinetics for reactor modeling and the move to engineered catalysts being “a bit aggressive” for one project cycle, we agree that the broadened scope is challenging. This will be alleviated in part through partnering with the CCPC for kinetics and reactor modeling, where this scope will largely lie. The engineered catalyst development will be a key portion of the scope for this project. The reviewer was correct to point out that these expanded goals are consistent with the general shift to these topics in the ChemCatBio portfolio.

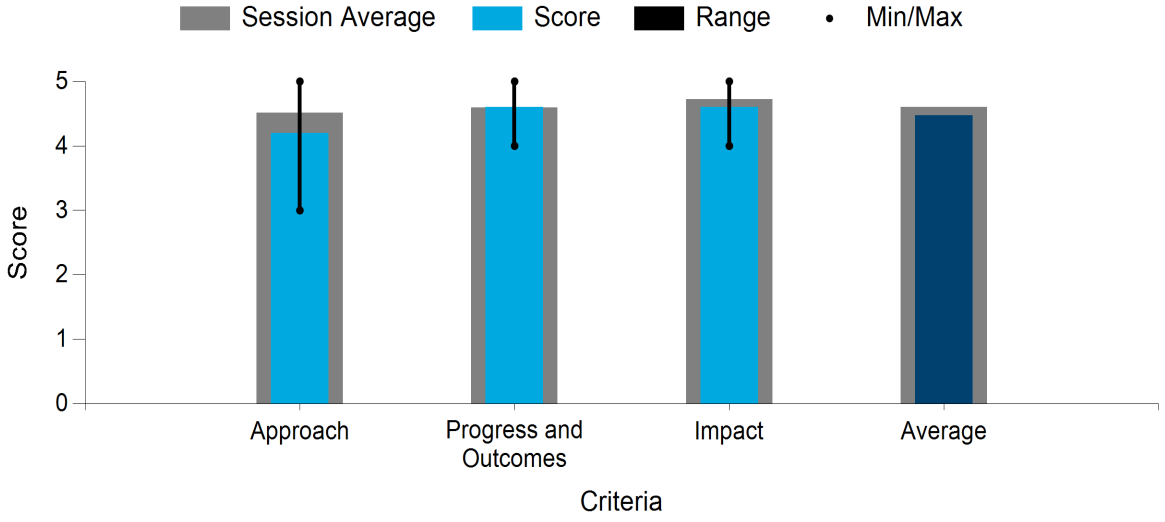
CATALYTIC UPGRADING OF BIOCHEMICAL INTERMEDIATES

National Renewable Energy Laboratory, Pacific Northwest National Laboratory, Oak Ridge National Laboratory, Los Alamos National Laboratory

PROJECT DESCRIPTION

The biochemical conversion of biomass via sugars and related intermediates to fuels is a primary conversion pathway within the BETO program. This CUBI project addresses critical barriers to the catalytic conversion of sugars and sugar-derived intermediates into SAFs and coproducts. Specifically, efforts are focused on key fuel intermediates that are identified in the 2018 BETO biochemical conversion design report, namely biomass-derived sugars/furans that do not require a biological conversion step, along with carboxylic acids and fermentation-derived 2,3-BDO. First, we are developing a pathway that upgrades biomass-derived sugars directly through dehydration to furans, followed by condensation and HDO. Complementary pathways upgrade platform molecules (carboxylic acids, BDO) derived from biomass-derived sugar fermentation. For the carboxylic acids project, we focus primarily on ketonization, HDO, and cyclization for the production of SAF. Regarding BDO upgrading, CUBI has two complementary research tracks: BDO upgrading (1) via methyl ethyl ketones and (2) through reactive extraction via dioxolanes. In this presentation, we will highlight these routes toward SAF from a technical perspective as well as through a summary of TEA and LCA. By pursuing coordinated and independent research directions and collaborating with complementary projects, the CUBI project strives to develop viable routes toward SAF production.

Average Score by Evaluation Criterion



COMMENTS

- Common comments for all projects:
    - One thing that was rather challenging about reviewing this project, which was split across multiple labs, who each gave their one presentation as a part of a large block, was keeping everything straight, as we went all the way through and did questions at the end. Additionally, the lack of a consistent format across the component presentations made it difficult to follow a cohesive story.
    - TEA and LCA: Overall, it was difficult to separate out approach, progress, and impact for each pathway.

- As the name implies, this project is focused on upgrading intermediates derived from biochemical pathways. The potential diversity of products used as intermediates to access SAF is greater than in other projects, which also adds a layer of complexity to the catalytic methods employed. Issues with contaminants for real broth-derived products or waste streams is another issue that ultimately must be addressed. The attempt to use such realistic streams and the handling of mixed feedstocks in some cases is noteworthy. It would likely only be pursued in the context of a national lab project like this one for de-risking to the point that it could be of interest as a viable technology to industry. Given the many layers of scientific diversity in the project, economic modeling provides another key pillar to the effort. Furfural, carboxylic acids, and BDO are major platform molecules of focus, with each lab concentrating on a particular substrate or reaction pathway. General comments here precede specific lab-by-lab notes. With the spectrum of reactions involved in CUBI, the need for collaborations across ChemCatBio is clear. In general, these connections are evident and well utilized across other BETO consortia (SepCon) and within ChemCatBio. The breadth of these interactions is what one would expect for an effort spanning biochemical inputs and chemical upgrading. I would also note that the many industrial interactions are vital to the project and provide some indicator of potential for transfer of successful technologies. The initial DEI statement is broad and not really descriptive as to specific actions taken within the project. While individual labs sometimes included information with specific actions (ORNL), the unevenness of this in the presentation is something to remedy in a future cycle.

- Discrete overall milestones of CUBI involved developing a viable butyric acid in FY 2023 and the BDO pathway in FY 2024, along with an end-to-end pathway that met discrete fuel and efficiency/GHG metrics. The goals are in line with moving from concept to demonstration and, ultimately, further down the technology development slope. Overall, viability seems present in all pathways. In general, all aspects of CUBI demonstrate a reasonable degree of productivity in the publication and IP spaces, with a distribution of 1–2 publications per topic and one patent during the evaluation cycle. The ORNL aspects are one area I would specifically highlight, as the VFA ketonization is being scaled/licensed by Alder, and output in the dioxolane area is significant, particularly on the IP generation side. I also commend the NREL component that examines the paper sludge as a feedstock—this has some loose connection to the topic of a prior university project in ChemCatBio. It is gratifying to see that prior knowledge is being leveraged (when appropriate) within the consortium to advance technology development. I believe it is a great sign when companies want to continue working with their partners past the funding phase of a given project. This, combined with CUBI's many industry interactions, bodes well for the ultimate integration of technologies developed within the project. In general, I think that many of the pathways are reaching a critical juncture to begin the process of exploring scaling, shifting to realistic feeds, etc. I look forward to seeing the results of the next funding cycle and how these processes translate through the next phase of development.

- The CUBI team has improved in communicating the approach and benefits of this project at a high level to the public and peer review community since its inception. The presenters were able to keep the audience centered on which part of the SAF pathway involves the CUBI research focus. The opportunity to cyclize ketones to aromatics without the use of hydrogen for use in SAF blends should be impactful and industrially important, as realized by the industrial fuels startup partner licensing the patent. The project has always been challenged by its tendency to take on too many pathways at once, with those pathways having significant CapEx. The team did an excellent job of organizing quite a bit of research work and science. They should continue to prioritize the resources allocated to various pathways as ranked based on factors such as technical/business risks, TEA (CapEx, OpEx), LCA (% GHG reduction), etc.

- The approach of upgrading sugars either biologically or thermochemically to SAF-range products is very clear and succinct. This project continues to have a strong technical approach of increasing the molecular weight of biochemical intermediates using a combination of aqueous transformations and traditional thermochemical deoxygenation where necessary. The state of the art was difficult to determine across all the projects. The partnerships and collaborators are strong and promising, covering a comprehensive approach to developing the technology that includes TEA, LCA, multiscale modeling, separations, feedstock optimization, etc., as well as leveraging ChemCatBio's crosscutting services. The team should not lose focus on generating the spec sheets for key biochemical intermediates and their corresponding pathways, as this has always been the underpinning of the project. The project has always been challenged by its tendency to be too expensive and take on too many pathways at once. The increased emphasis on project planning and organization is apparent. An external collaboration should be prioritized to enable a pathway's potential of success to be ranked based on factors such as technical/business risks, TEA (CapEx, OpEx), LCA (% GHG reduction), etc. The current state of the art of producing biochemical intermediates and/or their corresponding SAF pathways was not presented. For the quantity of research conducted, the number of risks/gaps was not clearly identified, and mitigation actions were not stated. A small table was presented in the appendix dealing with research interests for catalyst performance and reactor parametric studies. A good effort to hire interns and co-ops was mentioned.

- Generally, it looks like steady improvements in the economics continue across the various pathways explored. Additional cost reductions were identified in most pathways, with most hovering in the \$2.5–\$3 range. Some pathways incur minor to moderate cost increases (dioxolane pathways), but reap the benefit of significant (10%) GHG reductions. Because the individual pathways are intimately tied to the economic modeling throughout the development process, I have little doubt that the feedback loop between the modeling and the science will result in progress in the technology and economic viability.

PI RESPONSE TO REVIEWER COMMENTS

- General responses: Given that the CUBI projects (2.3.1.101, 2.3.1.102, 2.3.1.103, and 2.3.1.104) presented together, and that many of the reviewer responses addressed the project at large, we will provide a single, collective response to the reviewers' general comments, followed by task-specific responses in the appropriate sections. First, we would like to thank the reviewer panel for taking the time to provide their valuable feedback, thoughtful comments, and suggestions on our project. We appreciate the review panel's generally positive assessment of this project and the research activities occurring at each laboratory. Although presentation time constraints can make balancing all aspects, such as a comprehensive background for each section, challenging, future presentations will aim to outline the current state of the art. Along with this, we will place a greater emphasis on the potential risks and gaps in future presentations. We will work on improving the consistency of our presentation format and will aim to provide more detail to help reviewers understand the overall approach, progress, and impact for each pathway. The responses below generally follow the format of a reviewer comment in quotations followed by a brief response.

- "The attempt to use such realistic streams and the handling of mixed feedstocks in some cases is noteworthy. It would likely only be pursued in the context of a national lab project like this one for de-risking to the point that it could be of interest as a viable technology to industry." We thank the reviewer for pointing this out and agree that integration with upstream projects and the use of real streams is of critical importance to the industry at large.

- "The CUBI team has improved in communicating the approach and benefits of this project at a high level to the public and peer review community since its inception. The presenters were able to keep the audience centered on which part of the SAF pathway involves the CUBI research focus." As this is a large and complex project, we will continue to work to harmonize our communications moving forward. Although in some ways, it may seem that CUBI is five independent projects that simply share a project title, in reality, we find great synergies within this group of researchers and collection of projects. We strive to ensure that this synergy comes through in our presentations.

- “The initial DEI statement is broad and not really descriptive as to specific actions taken within the project. While individual labs sometimes included information with specific actions (ORNL), the unevenness of this in the presentation is something to remedy in a future cycle.” We agree. While DEI initiatives are formally managed at the consortium level, we would like to emphasize that each lab participating in this project incorporates DEI principles into its strategies, policies, practices, and decision-making processes. This commitment helps create a more inclusive and equitable research environment, leading to better science, increased collaboration, and positive societal impact. We agree that in the Peer Review presentation, some individual labs included information on specific actions regarding DEI strategy, but there was unevenness in the overall presentation. To address this concern, we will emphasize and improve communication on the DEI aspect in future CUBI presentations and include specific actions, initiatives, and strategies implemented to promote diversity, ensure equity, and foster inclusion within the project.
- “The current state of the art of producing biochemical intermediates and/or their corresponding SAF pathways was not presented.” We agree with the reviewer that this will be an important component to expand upon in future presentations. We opted to leave out a detailed discussion of upstream pathways because they were covered in other projects during Peer Review. Although these upstream research activities fall outside of the research purview of CUBI, with highly integrated projects like this, we understand the value of discussing the pathway as a whole as opposed to compartmentally.

CATALYTIC UPGRADING OF BIOCHEMICAL INTERMEDIATES

National Renewable Energy Laboratory

WBS:	2.3.1.101
Presenter(s):	Jeffrey Linger; Jacob Miller; Ashutosh Mittal
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$1,350,000.00

COMMENTS

- This part of CUBI is focused on the conversion of VFAs to SAF through ketonization followed by HDO to create fuel molecules or SAF precursors. The background makes a clear case for the opportunity to pursue wet waste fractions beyond the oil phase that is currently utilized. The current cycle goals revolve around scale-up of prior demonstrated reactions and transition to flow conditions. Both are necessary for a viable process to be developed and are the right targets to pursue at this stage. The role of water in deactivation of the catalyst was an important (while perhaps negative) result. Follow-up studies do indicate one can accept deactivation if a sufficiently economical catalyst is used. The concept demonstration of HDO to an arene fraction is significant and establishes the complete pathway. The next cycle will be critical for determining whether the process can be transitioned to a scalable and economical system.

- The VFAs project is one area I would specifically highlight, as the VFA ketonization is being scaled/licensed by Alder, and output by the dioxolane area is significant, particularly on the IP generation side. I also commend the NREL component that examines the paper sludge as a feedstock—this has some loose connection to the topic of a prior university project in ChemCatBio. It is gratifying to see that prior knowledge is leveraged (when appropriate) within the consortium to advance technology development. I believe it is a great sign when companies want to continue working with their partners past the funding phase of a given project. This, combined with the many industry interactions for CUBI, bodes well for the ultimate integration of technologies developed within the project.

- Mixed sugars to SAF: This portion of CUBI is focused on sugar dehydration, condensation, and HDO to access SAF. Current efforts involve exploring the parameter space of these steps (solvent/reagent use in particular) to reduce cost metrics. The parameters selected to explore—a new solvent, use of a base catalyst that favors mono-adduct formation, understanding deactivation in conditions that mimic broth-derived intermediates, and optimized catalysts for HDO—seem logical and like good target spaces to explore. In general, I think that the division of pathways is very logical, and the projects are pursuing rational parameter optimization for the stage each technology is at. Although some of these are at an earlier stage of scaling relative to other ChemCatBio projects, it is important to have the diversity seen here in a portfolio of projects with the breadth of the consortium, particularly when you hope to use the true spectrum of platform molecules that can be provided by biomass-derived sources.

- Mixed sugars to SAF: This activity exceeded cost-driven metrics, with paper-derived waste sources looking promising. The move toward cyclic hydrocarbons is more exploratory, but is warranted from the perspective of an improved property of the fuel product.

- The TEA improvements were clearly identified, with significant improvements in $/GGE for (1) the furan path, due to condensation reactor optimizations; (2) the VFA path, due to ketone recovery upstream HDO; (3) the BDO/MEK path, due to improved MEK separation; and (4) the BDO/butene path, due to dioxolane phase separation efficiency. The replacement of the precious metal catalysts for VFA HDO seems like it should have resulted in a lower $/GGE reduction than 1 cent/GGE. There was a slight increase in the MFSP, even with the dioxolane recovery improvement. The stability of the solid base catalyst and adduct yields was quite impressive for furfural conversion. The platinum-supported HDO catalyst with >20 wt % loading of precious metal showed high yields. More R&D on reduced or zero precious metal loaded supported catalysts is necessary and should be a collaboration with the ChemCatBio ACSC team. The peer-reviewed published article highlighting the modeling efforts on ketonization was insightful regarding water inhibition and the interstage design implications of a commercial reactor. There is still much more to complete in order to de-risk such design configurations with no pilot-scale experimental validation for the reaction rate effectiveness factor. Operating the ketonization plugged-flow powder bed reactor for up to 70 hours on stream was a reasonable start to understanding the long-term stability risks. The MFSP estimate before the stabilized rate for ZrO_x catalyst deactivation should be higher than 4 cents/gallon, especially because the ketonization catalyst lost 80% of its initial activity. The proton Zeolite Socony Mobil–5 (ZSM-5) ketone upgrading experiments were promising. The progress is at an early stage, with low conversion, short TOS, and small reactor beds. The proof of concept has been completed at the bench and prototype lab scale.

- There was a significant shift (>$5 GGE) in the MFSP estimate when using BDO feedstocks in 2021 versus the dioxolane pathway in 2023, which should be explained by the catalyst performance being comparable.

- The presentation was very comprehensive and organized. This was greatly appreciated given the number of R&D activities within this project. This project could almost be its own consortium focused on various upgrading, solvent recovery, and catalyst regeneration strategies.

- This project was reported under the umbrella of CUBI. It focuses on R&D activities to enable industrialization of VFA-SAF processes. The team conducted an in-depth, scale-up-oriented study of the ketonization step, mainly in two directions: (1) reactor design and (2) catalyst deactivation. They discovered water as the main factor that inhibits the desired reactions in a process using engineered catalysts and developed an industrial-scale reactor model with the integration of a multistage reactor and interstage water removal via separation. Their R&D activities led to the development of a flow reactor process for light ketone upgrading to replace the condensation step. Aligning with their research activity, they have shown their commitment to DEI by recruiting researchers from underrepresented groups. It will be beneficial if further R&D activities can reduce the complexity of the reactor model. For instance, would a reactive membrane concept work for this process? It may also be beneficial if future R&D activities can understand the heat/mass transport in this reactor model, which may help develop principles for scale-up. Overall, the project has illustrated the appropriate progress that can help achieve its goal. The project has also demonstrated its impact by (1) developing a new reactor that can help achieve DOE's SAF Grand Challenge, if it can scale up and industrialize, and (2) illustrating its commitment to DEI.

- The CUBI projects demonstrate excellent teamwork and numerous promising processes. All of the processes have successfully met their targets and have become increasingly eco-friendly and efficient compared to 2 years ago. TEA/LCA plays an important supporting role in evaluating both the technical and economic aspects of the projects to make go/no-go decisions. The furfural upgrading project has made significant advancements by utilizing non-azeotropic solvents and heterogeneous basic catalysts and achieving a 31% reduction in GGE. The VFA to SAF project has progressed even further with industrial-scale reactor modeling, utilizing the equilibrium activity of the catalyst, and working with an industry partner to build a 1-gallon/day demo unit. These are all very encouraging outcomes. Further research is recommended to gain a better understanding of the processes, such as studying the deactivation mechanism to assist with rational catalyst design. For example, in the case of furfural upgrading, a common issue associated with solid base catalysts is leaching. Thus, multiple cycle runs are necessary to assess the stability of the catalysts.

PI RESPONSE TO REVIEWER COMMENTS

- “The platinum-supported HDO catalyst with >20 wt % loading of precious metal showed high yields. More R&D on reduced or zero precious metal loaded supported catalysts is necessary and should be a collaboration with the ChemCatBio ACSC team.” We agree with the reviewer panel’s assessment that the current platinum-supported HDO catalyst with a high loading of precious metal has shown promising results, but further research and development are needed to explore the potential of reduced or zero precious metal loaded supported catalysts. Based on reviewer recommendations, collaborating with the ChemCatBio ACSC team will be pursued. By leveraging their expertise, we will be able to identify ways to improve the performance of the catalyst while reducing the use of precious metals, thus making the process more cost-effective and sustainable in the long run. Moreover, we have been working to develop effective and robust non-precious-metal catalysis for HDO, and we believe that the impact of this advance would be more easily recognized in comparison with the current state of the art, which is the use of expensive precious metal catalysts.

- Regarding de-risking VFA ketonization: We appreciate the reviewer’s comment regarding the status of de-risking the VFA ketonization step, particularly with regard to pilot-scale experimental validation of the catalyst effectiveness factor. Luckily, our upcoming FOA with Alder Fuels will allow us to perform this work.

- “The team should not lose focus on generating the spec sheets for key biochemical intermediates and their corresponding pathways, as this has always been the underpinning of the project.” We agree with the reviewer that specification sheets of CMAs for our biochemical intermediates are crucial to generate. Currently, the still-evolving nature of the biochemical processes supplying our intermediates complicates the process of making spec sheets. However, as these processes become optimized, we can perform targeted studies to determine allowable concentrations of contaminants, etc. in each intermediate upgrading progress.

- “It will be beneficial if further R&D activities can reduce the complexity of the reactor model. For instance, would a reactive membrane concept work for this process? It may also be beneficial if future R&D activities can understand the heat/mass transport in this reactor model, which may help develop principles for scale-up.” We appreciate the reviewer’s comment about reactor heat and mass transport and model complexity. There was not time in our presentation to specify, but our model does capture heat and mass transport phenomena on the particle and reactor scales. Luckily, ketonization reactions are roughly thermoneutral (ca. 0 to +15 kJ mol^{-1}, depending on acid reactant identity); this prevents major thermal gradients on the particle scale and results in a net temperature decrease of ca. 10°C across the length of an adiabatic reactor running at 100% conversion. Our model also captures the effects of internal and external mass transfer on the pellet scale. The internal mass transfer limitations were discussed in the presentation (effectiveness factors can be as low as ~0.5), but there are negligible external mass transfer limitations, provided that flows are close to the turbulent regime. We will consider alternative reactor designs such as membrane reactors in the future.

CATALYTIC UPGRADING OF BIOCHEMICAL INTERMEDIATES

Pacific Northwest National Laboratory

WBS:	2.3.1.102
Presenter(s):	Vanessa Dagle
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$449,614.00

COMMENTS

- The R&D is focused on three pathways: dehydration, aldol condensation, and HDO. This aspect of CUBI involves BDO dehydration to MEK, MEK to olefins, and subsequent oligomerization/hydrogenation to produce SAF. Major areas explored in this cycle include understanding contaminant impact on conversion, adjusting the economics to changes in process, and demonstrating the pathway to obtain adequate samples for fuel testing properties. The need to study contaminants is clear with the switch to realistic feedstocks. Subdividing the role of organics versus inorganics is important, as mitigation may proceed differently for each category of impurities. Here, collaboration with other ChemCatBio-wide effects (catalyst deactivation) is critical.

- Progress: Discrete overall milestones of CUBI involved developing a viable butyric acid in FY 2023 and the BDO pathway in FY 2024, along with an end-to-end pathway that met discrete fuel and efficiency/GHG metrics. The goals are in line with moving from concept to demonstration and, ultimately, further down the technology development slope. Overall, viability seems present in all pathways. The activity demonstrated full pathway progression to access fuel fractions with reasonable to promising properties. The next cycle will be key to translating the knowledge gained on contaminants to determine the ability to circumvent any issues related to the real feedstock.

- The team did an excellent job of experimentally demonstrating the negative effect on catalyst stability of processing real BDO feedstock versus surrogate. There was a significant decrease (>30%) in the MFSP 2030 progression due to improvements in per-pass conversion for MEK upgrading and alkene oligomerization. Key oxygenated and metal feed impurities were well characterized in collaboration with the ACSC team. The proof of concept for the liquid-phase conversion of 2,3-BDO is an important result. The team should discuss how trace oligomers in Step 2 for the BDO/MEK route go into the water phase and what the future concept is for water treatment. For liquid-phase BDO chemistry, the time of the regeneration cycles and whether vaporization is required should be explained.

- The 2,3-BDO/MEK pathway has good promise, even with the risks associated with feed impurities. This route could use more industrial engagement and support to enhance commercial interests. The presentation was very comprehensive and organized. This was greatly appreciated given the number of R&D activities within this project. This project could almost be its own consortium focused on various upgrading, solvent recovery, and catalyst regeneration strategies.

- This project was reported under the umbrella of CUBI. It focuses on a BDO-MEK-SAF process. This project focuses on the impact of the impurity of the feedstock on catalyst stability, particularly the impact of potassium. The conversion from a model feedstock to a real feedstock is a key step to determining the potential of a process to be industrialized. The project has shown the change in the catalyst performance due to this change and has identified the impact of the feedstock impurity. It would be beneficial to collaborate with enabling projects like CCPC or catalyst synthesis to reversely develop catalysts that can endure this impurity, or to collaborate with upstream or separation teams to either tune the feedstock or develop a cost-effective process for pretreatment. The project shows that some progress has already been made in this direction. The project also shows an updated TEA and has initiated the LCA. The TEA/LCA will play an important role in determining the potential of industrialization for this process. The coproducts play a role in reducing the overall cost. It would be beneficial to evaluate whether the coproducts and SAF have a similar market size. The team also shows a liquid-phase upgrading of BDO to MEK. They have tested three catalysts under various conditions. This exploration has illustrated that the liquid-phase conversion may be a viable path. Overall, this project has illustrated appropriate progress to achieve its goal. The detailed R&D on the effect of feedstock impurity on process performance and catalyst stability will play a critical role in the industrialization of this process. The knowledge and technology may be transferrable to the other projects within the Catalytic Upgrading program. The new liquid-phase process opens another possible way to industrialize the BDO-MEK-SAF process. This project has illustrated its impact by (1) developing a BDO-MEK-SAF process that can help accomplish the SAF Grand Challenge if successful, and (2) conducting R&D activities on feedstock impurity, which will be a big roadblock for commercializing biomass-based chemical conversion processes.

- The progress made in upgrading 2,3-BDO to SAF via MEK has been significant, using feedstock that contains impurities. The systemic study in collaboration with ACSC on the impact of organic and inorganic impurities with TOS was impressive. This study is crucial, as it provides guidance for feedstock specification and catalyst design. It is also encouraging to see that the feasibility of this route has been demonstrated by this project.

PI RESPONSE TO REVIEWER COMMENTS

- PNNL (2.3.1.102): We thank the reviewers for their time and feedback. We appreciate that the reviewers understand the value of the BDO/MEK pathway to SAF, that they highlight the relevance of the work from this pathway, and that they acknowledge the progress made.

- “The team should discuss how trace oligomers in Step 2 for the BDO/MEK route go into the water phase and what the future concept is for water treatment.” Water is removed from the process prior to Step 2 as opposed to after Step 2. Indeed, MEK can be easily separated from water using conventional distillation. The MEK solution contains trace amounts of some compounds, but traces of olefin oligomers were neither detected nor expected. The main trace compounds detected include iso-butyraldehyde, iso-butanol, and butadiene. The catalyst for Step 2 is a $ZnZrO_x$-based catalyst with unique redox and acid properties that allow for hydrogenation/dehydration and aldol condensation, which lead to the desired olefins. Traces of alcohols, aldehydes, ketones, and acids are converted into olefins over the $ZnZrO_x$ catalyst. Traces of butadiene are expected to be converted into butenes due to the presence of hydrogen and the mild hydrogenation properties offered by the catalyst.

- “For liquid-phase BDO chemistry, the time of the regeneration cycles and whether vaporization is required should be explained.” The team recently started liquid-phase upgrading and presented the results obtained for 40 consecutive cycles in a batch reactor. The catalyst was not regenerated between cycles. Catalyst durability and potential regeneration needs will be investigated in future work conducted in a fixed-bed reactor.

- “To further reduce the energy cost of the process, in addition to the use of renewable natural gas, it is recommended to consider the use of waste heat from other processes.” We agree with the reviewer that other sources of renewable energy could be used to reduce the energy cost in addition to the use of renewable natural gas. For this preliminary life cycle assessment, renewable natural gas and renewable H_2 were considered because we already had access to the associated costs.

- “It would be beneficial to collaborate with enabling projects like CCPC or catalyst synthesis to reversely develop catalysts that can endure this impurity, or to collaborate with upstream or separation teams to either tune the feedstock or develop a cost-effective process for pretreatment.” The team is already collaborating with ACSC and CDM, and it interacts with the upstream biological team. In fact, the results for the organic and inorganic impurity studies have already been shared with the biological team producing the fermentation broth, which has been investigating and has already identified solutions for some of the impurities.

- "The coproducts play a role in reducing the overall cost. It would be beneficial to evaluate whether the coproducts and SAF have a similar market size." All the pathways under CUBI involve adipic acid coproduct from lignin upgrading, and it is reducing the cost. The BDO pathway has also been investigated for the possibility of diverting some of the MEK from SAF production to the coproduct market to investigate the potential for decreasing the need for lignin upgrading. The SAF market is much bigger than the MEK coproduct market, and only a small fraction of MEK should be diverted to the coproduct market if this is the chosen pathway in order to avoid saturating that coproduct market.

CATALYTIC UPGRADING OF BIOCHEMICAL INTERMEDIATES

Los Alamos National Laboratory

WBS:	2.3.1.103
Presenter(s):	Claire Yang
Project Start Date:	10/01/2015
Planned Project End Date:	09/30/2025
Total Funding:	$250,000.00

COMMENTS

- This project aims to convert fermentation-derived 2,3-BDO into SAF with a distillate MFSP of $2.50/GGE at maximum and a GHG emissions reduction of 70%. Conversion of BDO to a protected dioxolane has advantages in processing through a straightforward separation, if the dioxolane can be upgraded economically and the aldehyde used can be recovered. This half of the dioxolane project is centered on exploring the dioxolane structure space by varying the aldehyde to understand the impact on separations and upgrading. A range of dioxolanes were prepared, with linear/branched structures, on scales that were amenable to subsequent upgrading studies. The ability to deal with materials derived from realistic fermentation broths is another goal—even if the majority of impurities stay in the broth, there may be impacts to the chemistry you are unaware of until working under those conditions.

- Improvements in the acid catalyst allow for a significant reduction of the excess aldehyde used to form the dioxolane and improve process economics. At the same time, the family of desired structures was prepared and scaled for further upgrading. The modeling is promising, suggesting that the pathway could approach or exceed desired GHG reduction goals.

- The industrial version of the dioxolane production process could resemble traditional alkylation units if the mineral acid technique is favored. An entire section was dedicated to discussing the formation of alkenes from dioxolanes. This was a good way to organize this part of the content. Dioxolane is really a BDO carrier, which is fascinating. The team should disclose the extent to which metal ions penetrate the dioxolane phase.

- The CUBI team has provided a promising pathway for sugars to SAF with immediate commercialization potential, as evidenced by a published paper and design report. The team should mention any efforts engaging ASTM at this early stage. The dioxolane intermediates research still has progress to make in terms of raising more technical awareness of the opportunity.

- This project was reported under the umbrella of CUBI with several other experimental projects that focus on developing processes to produce SAF using intermediates from biomass conversion. This project focuses on 2,3-BDO upgrading via dioxolane intermediates. The team reports a very promising reactive extraction process. This reactive extraction process was developed using normal acid catalysts and liquid-liquid phase separation with the dioxolane products with high purity. The team then used this dioxolane as the platform chemical to develop SAF products. The reactive extraction process has potential because it does not require expensive noble metal catalysts. The reduction of the cost and GHG emissions for the production of dioxolane will help make the SAF production more competitive in terms of price and will reduce the overall GHG emissions for the final SAF products. This process is based on a liquid-phase process. The recycling, storage, or remediation of the liquid phase may influence the commercialization potential. It would be beneficial for commercialization for the team to conduct NMR or another analysis to identify side products in this process and discuss with other consortia, like SepCon, to develop related processes. It is also interesting to note that the dioxolane derivatives produced in this process may have some potential electrochemical applications. 1,3-dioxolane is one of the most commonly used electrolytes for lithium-ion batteries. Although the market for electrochemical applications is smaller than the SAF market, the ability to produce such compounds from biomass could be interesting. The ability to tune the structure of dioxolane derivatives by adding different chemicals may pave the way for producing electrolytes with specific conductivity. It may also have some potential applications in the electrochemical conversion of CO_2 and the production of H_2. Overall, this project has illustrated suitable progress in producing various dioxolane derivatives via the developed reactive extraction processes. The team also presented significant progress. The team showed process integration under the guidance of TEA, examined the catalyst stability, and developed a pretreatment that can enhance catalyst stability. It has been observed that catalyst stability is an overarching challenge over the whole Catalytic Upgrading program. It would be beneficial if the program could develop general principles or guidance that would help mitigate catalyst deactivation. This project has demonstrated its impacts by (1) developing a process that can help address DOE's SAF Grand Challenge, and (2) inventing a likely biomass-based process to produce electrolyte products for electrochemical applications.

- BDO upgrading via dioxolane intermediates could be a game-changing process toward the formation of SAF via BDO. The formation of dioxolane is an important step, as a significant drop of GGE has been achieved downstream using dioxolane as feed. The progress that has been made in the development of dioxolane since 2021, including the identification of feasible precursors and catalyst development, is promising.

- Further research is needed to study the deactivation mechanism of resin-based catalysts. Leaching of the acidic group is a common cause for deactivation of those catalysts in liquid-phase reactions. In searching for alternate acid catalysts, liquid acids may raise concerns regarding corrosion and environmental impact. Alternative non-resin solid acids, such as sulfonic silica/zeolite or carbon-based acids, may provide better stability. Has any research been conducted to evaluate their effectiveness in this process?

PI RESPONSE TO REVIEWER COMMENTS

- LANL (2.3.1.103) responses: "Improvements in the acid catalyst allow for a significant reduction of the excess aldehyde used to form the dioxolane and improve process economics. At the same time, the family of desired structures was prepared and scaled for further upgrading. The modeling is promising, suggesting that the pathway could approach or exceed desired GHG reduction goals." We greatly appreciate the acknowledgment of the process' potential and successes to date. Issues related to contaminants and other such factors when using real fermentation broth, as the reviewer raises, are absolutely a key factor moving forward and the major point of focus. Isolation of dioxolane directly from the broth has already been and will continue to be carried out for downstream processing in the LANL BDO upgrading approach. Both organic and inorganic contaminants/impurities have been analyzed by high-performance liquid chromatography and inductively coupled plasma mass spectrometry. Further testing is also underway with real fermentation broth to establish what effect this has on reaction parameters, such as the acid strengths and required loading amounts, as well as the resulting conversion and dioxolane yield. This testing also ties into broader investigations into different types of acids, which will be essential for further process analysis and modeling to help de-risk potential future process scale-up in industry. Additional work is underway to look at the effect of different acids on the minor organic components that remain in the fermentation broth as well.

- With regards to metal ions penetrating the dioxolane phase, this is a good point the reviewer raises, but it will potentially be affected by the reaction systems used (such as the acid and its quantity). As such, this has not currently been determined, but it is certainly something to be established in our next step once the acid type is determined. We appreciate the reviewer's comments on leveraging traditional alkylation units in the industrial version of the dioxolane production process if the mineral acid technique is favored based on TEA and LCA.

- We appreciate the reviewer's comment regarding raising more technical awareness of this promising dioxolane pathway opportunity for industry engagement. We are currently planning on working with the

BDO fermentation team at NREL and the dioxolane upgrading team at ORNL to package this technology with IPs and bring it to potential industry partners.

- "The recycling, storage, or remediation of the liquid phase may influence the commercialization potential. It would be beneficial for commercialization for the team to conduct NMR or another analysis to identify side products in this process and discuss with other consortia, like SepCon, to develop related processes. It is also interesting to note that the dioxolane derivatives produced in this process may have some potential electrochemical applications. 1,3-dioxolane is one of the most commonly used electrolytes for lithium-ion batteries. Although the market for electrochemical applications is smaller than the SAF market, the ability to produce such compounds from biomass could be interesting." The reviewer raises a good and key point with regard to future commercialization—namely, that the contents of the residual aqueous phase (post dioxolane isolation) are important to understand and consider. Current work using actual fermentation broth is indeed aimed at looking into the residual organics within the aqueous phase both before and after reaction with different acids, to determine how the choice of acid may affect this aspect. We appreciate the reviewer's suggestion of connecting with the Separations Consortium. This dioxolane technology has indeed been brought to Separations Consortium, and the process was examined by the SepCon team. One manuscript (doi.org/10.1021/acs.iecr.2c04307) has been published based on this reactive extraction process for separating 2,3-BDO from fermentation broth. We will continue working closely with the Separations Consortium to further address some aspects of acid type selection and potential pretreatment options.
- We thank the reviewer for acknowledging the progress made but also for raising the potential of the formed dioxolanes as solvents in electrochemical applications. This is something we haven't explored yet. This could indeed add further value and could be another avenue of contribution to the process. While perhaps outside the scope of the current work, it is definitely an avenue the authors are keen to explore further and hopefully pursue in the future.

CATALYTIC UPGRADING OF BIOCHEMICAL INTERMEDIATES

Oak Ridge National Laboratory

WBS:	2.3.1.104
Presenter(s):	Andrew Sutton
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2025
Total Funding:	$1,227,920.00

COMMENTS

- This project aims to adapt a BDO conversion approach to utilize dioxolanes as a BDO synthon.

- The second half of the project, which is focused on dioxolane, involves its conversion to olefins and ultimately to SAF. Given the PI's other ChemCatBio project, this coupling to the related technology makes complete sense. The project is exploring optimization of reaction conditions, including temperature, the viability of various dioxolane intermediates, and demonstration of aldehyde recovery. These are all logical to explore at this stage before attempting to move forward with further scaling of a potential process. Progress: Discrete overall milestones of CUBI involved developing a viable butyric acid in FY 2023 and the BDO pathway in FY 2024, along with an end-to-end pathway that met discrete fuel and efficiency/GHG metrics. The goals are in line with moving from concept to demonstration and, ultimately, further down the technology development slope. Overall, viability seems present in all pathways.

- It is reassuring that the various cyclic intermediates are effectively interchangeable with BDO in upgrading, and the renewably sourced aldehydes might be used at some stage. Optimization of reaction conditions—temperature, demonstration of aldehyde recovery, etc.—are logical and move in the right direction. The next key steps of moving to fermentation-derived intermediates, shifting to longer TOS, and understanding ways to improve the economics of aldehyde recovery are logical and necessary. The fuel properties of the upgraded products also appear promising.

- The team should provide a little insight into or hypothesis on the increased MEK formation over Cu-ZSM-5 with branched versus unbranched dioxolane feeds. The nature of the protons left on the zeolite and their ability to acidify dioxolanes back to BDO should be explained. An explanation of MEK as an intermediate for enhanced paraffin formation in the reaction network could be helpful as well. The olefin product yields (X, S) were impressive for the data presented, regardless of dioxolane precursor. The team should report the TOS information as well.

- The CUBI team has provided a promising pathway for sugars to SAF with immediate commercialization potential, as evidenced by a published paper and design report. The team should mention any efforts engaging ASTM at this early stage. The dioxolane intermediates research still has progress to make in terms of raising more technical awareness of the opportunity. The SAF analytical data seems very believable with the challenge on flash point, which can be overcome easily. There is a clear advantage of being able to process hydrous BDO as a feedstock. The presentation was very comprehensive and organized. This was greatly appreciated given the number of R&D activities within this project. This project could almost be its own consortium focused on various upgrading, solvent recovery, and catalyst regeneration strategies.

- This project was reported under the umbrella of CUBI. It focuses on de-risking the process of converting 2,3-BDO to SAF via the dioxolane derivatives developed in another project under the same umbrella. This project focuses on examining how the quality of the final SAF products relates to the various conditions of the dioxolane feedstock produced in the other project (like BDO versus dioxolane) and the process operation parameters, such as temperature. Such correlation will be important for determining which technology to focus on when conducting the R&D activity for scale-up. It would be beneficial if the team could show how the selection of catalysts could affect the SAF products from various dioxolane feedstocks. It may also be beneficial to collaborate more closely with the teams focused on separation and recycling to develop a viable process under the guidance of TEA/LCA. The team already illustrates this direction by investigating the recycling of aldehyde. Overall, this project has illustrated appropriate progress to develop a BDO-dioxolane-SAF process that has the potential to be industrialized. The success of this project will help meet the SAF Grand Challenge for DOE.

- The project to upgrade BDO via dioxolane intermediates has made significant progress in its second phase, building on lessons learned from earlier work. The project benefits from well-structured project management and planning. Most importantly, the results have been very promising, with high conversion and selectivity toward olefins using a Cu/ZSM-5 catalyst without any evidence of coke formation.

- How to integrate this process with the synthesis of dioxolane is not clear at this point. I look forward to more progress in the overall process design.

PI RESPONSE TO REVIEWER COMMENTS

- We would like to thank the reviewers for their time and all the positive feedback on our project. The questions they raised have been very useful as we plan the next stage of this work and have already stimulated thoughts on improvements to our approach and aspects where we need to focus more attention. In this regard, there are specific points raised that we would like to expand upon.

- “The team should provide a little insight into or hypothesis on the increased MEK formation over Cu-ZSM-5 with branched versus unbranched dioxolane feeds.” The reviewers raise a very interesting point from a fundamental standpoint. MEK generally increases with increasing size of the aldehyde used in dioxolane formation, although a direct correlation between branching and MEK formation is not evident. A potential hypothesis for this is that, due to the size of the aldehyde, this exhibits a longer time in the zeolite framework due to confinement effects, leading to increased coke formation and partial catalyst deactivation for MEK reduction to the alcohol. This is just a hypothesis, and we aim to elucidate this in more detail.

- “An explanation of MEK as an intermediate for enhanced paraffin formation in the reaction network could be helpful as well.” Alkanes are present in negligible amounts unless the temperature is increased, which drives the alkane reduction to alkenes. This over reduction results from the formation of alkenes from either the aldehyde or the BDO/MEK intermediate, which are indistinguishable from each other in this process.

- “The dioxolane intermediates research still has progress to make in terms of raising more technical awareness of the opportunity.” We have a set of publications on this process ready to submit that will allow us to present a complete portfolio of this technology from fermentation to SAF, including newly updated TEA and LCA. We also continue to work with the separations and fermentation teams to present a comprehensive vision for this application.

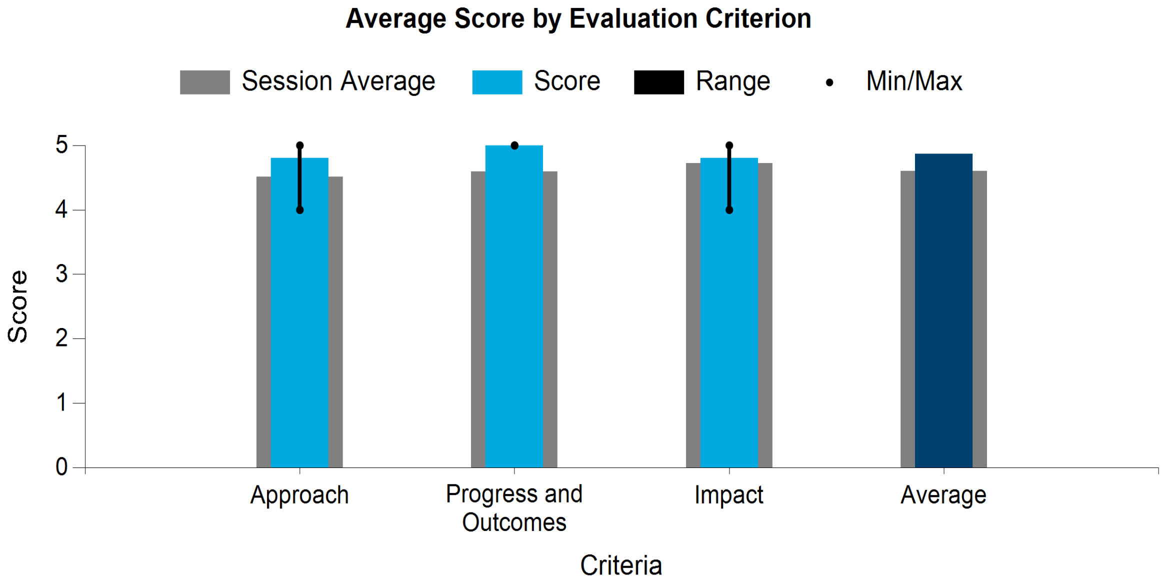
CONSORTIUM FOR COMPUTATIONAL PHYSICS AND CHEMISTRY – CHEMCATBIO

Oak Ridge National Laboratory

WBS:	2.5.1.301
Presenter(s):	Jim Parks
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$2,021,157.00

PROJECT DESCRIPTION

The CCPC is an enabling consortium of BETO that utilizes computational modeling to support the achievement of goals in ChemCatBio and other consortia such as the FCIC and SepCon. It comprises six national laboratories (ORNL, Argonne National Laboratory, Idaho National Laboratory, National Energy Technology Laboratory, NREL, and PNNL).



COMMENTS

- The CCPC is a BETO consortium made up of six national labs that applies multiscale computational science to enable bioenergy successes in other BETO consortia. The consortium's primary goal is to develop and apply a fundamental-science-based computational tool set that enables and accelerates the discovery and optimization of cost-effective catalyst materials for bioenergy applications, the translation of catalyst discoveries to higher TRLs, and the cost-effective scale-up of bioenergy technologies relevant to industry. The CCPC Tool Set Applied includes atomistic scale modeling (periodic DFT) for elucidating reaction mechanisms, theory and experimental characterization for identifying key reaction intermediates, DFT calculations, grand canonical free energy minimization, chemical bonding analysis to investigate structural and chemical changes during reaction over both catalysts, and *ab initio* molecular dynamics simulations plus enhanced free energy sampling to ascertain the mechanism and thermodynamics of deactivation. The impact and relevance of the CCPC Tool Set Applied include the determination of optimal reaction conditions for enhanced catalytic activity and selectivity, elucidation of reaction mechanisms of reductive etherification of n-butanol and 4-heptanone on Pd/$NbOPO_4$ catalyst, catalyst optimization for SAF production via CUBI, and a first-of-its-kind set of contaminants/poisons database for bioenergy applications. In addition, a full mechanism for deactivation and regeneration of ORNL's catalyst reveals strategies for preventing deactivation and/or accelerating regeneration, and new open-source code enables high-fidelity mesoscale simulations to optimize catalyst architecture for reactor configuration commercial performance targets. The CCPC also developed modeling tools to screen potential catalyst architectures before synthesis, and 3D X-ray reconstructions of commercial catalysts can also be directly imported for detailed performance simulations. Additionally, COMSOL bed models were developed for deconvolution of combustion kinetics and mass/heat transport effects from temperature programmed oxidation data complemented by spent and partially regenerated particle/coke characterization. Impact: CCPC models enable industry partners to advance bioenergy via CCPC's DFO program.

- CCPC is another enabling project, spanning five labs, that brings the power of multiscale modeling to ChemCatBio and other BETO consortia. The ambitious scales of the effort are impressive, as is the incorporation of the power of high-performance computing (HPC) into the effort. For such a broad but core enabling capability, it is critical that the effort evolves to meet the needs of ChemCatBio. It is clear in many ways that this is the case, based on adjustments from cycle to cycle on funding allocations to various computing scales. While this is a work in progress, this reviewer does strongly advise continued assessment of these levels to ensure that the signature aspect of CCPC (the significant investment in cross-scale modeling) is not lost. One piece missing from the presentation was a high-level description of the management of CCPC. Particularly given the scope and size of the effort, some details regarding how day-to-day management of the group occurs was a missed opportunity. In addition, I think that prior review questions regarding the ability to provide some type of metric for the degree of catalyst acceleration should not be lost to the wind. While I would agree that it is not easy, efforts to do so (even if difficult or unsuccessful) should at least be documented and disseminated. Regarding progress, let me be clear that CCPC checks all the boxes to me—the collaborations are tangible and varied across ChemCatBio projects, the funding allocation shifts to account for evolution in consortium project needs, advanced computing methods are being implemented (AI/ML/data science), and interactions with the data hub are vibrant and robust. The diversity of examples highlighted across ChemCatBio efforts was impressive, particularly the crossing of atomic, meso, and reactor scales. While the distribution of highlights will likely evolve in future cycles with the greater focus on reactor modeling, it is clear that a strength and signature of the effort its diversity and ability to walk between scales. I encourage CCPC not to lose this focus despite the heavier emphasis on the larger length scales. One question that could have been better articulated in the presentation involves allocation of time between consortia within CCPC. Some comments on this topic could provide broader context for reviewers. I think it is a legitimate question to discuss more broadly, as CCPC is a support engine for so many other BETO efforts. The HPC discussions were enlightening, and the focus on lessons learned was excellent, as it provides a starting point for productive use of new resources. The anticipated strategies for effective HPC use seem like the right ones. In particular, the Advanced Scientific Computing Research/Basic Energy Sciences collaborations on code development and leveraging the basic science programs' expertise with HPC (in theory) seem like clear wins for CCPC in advancing the HPC components of the project. One opportunity area mentioned in other review comments relates to modeling associated with additive manufacturing. As there are opportunities on the experimental side in this space, some of which were demonstrated by DFA projects reviewed this cycle, I believe there are opportunities connecting theory to these systems, whether they involve catalyst synthesis or reactor design. In particular, developing real-time AI/ML responsive systems is something that should at least be considered. Perhaps this is still at more of a fundamental phase, but I do believe this type of real-time feedback between theory and experiment is not far off and can have an impact in many arenas, one being the manufacturing space. The 35 total publications are quite impressive. In the future, a high-level breakdown of the percent of these reports that are collaborative with PIs in CCPC projects versus stand-alone reports would be valuable. I don't doubt the collaborative nature of the effort, but it provides a simple quantifier for evaluation. It is good to see review comments from past cycles being implemented, especially regarding working more with industrial partners. From the vignettes presented, the impact these collaborations have on the companies was clear (the Pyran 1,000x scale-up comes to mind as one signature example). The somewhat flexible degree of tech transfer and the experience of working with both large and small industrial entities was a nuance that came out clearly in the presentation and Q&A; I had underappreciated this. One point to consider: Given the now extensive pivot to reactor modeling, is there some way to develop tools in this space that could be combined with other data hub efforts accessible to the broader catalysis/engineering community? Currently, this seems like a potential gap in the suite of tools offered by that project and one that could be incredibly impactful. As a whole, it is clear that CCPC is having a significant impact on ChemCatBio, the greater BETO consortium portfolio, and its industrial partners.

- The team has done a great job of developing DFO projects and moving the HPC initiatives forward. More atomistic studies have been conducted, providing key insight into C=0 and C-C bond activation and most probable surface structures.

- The fact that the CCPC is able to stitch the modeling across multiple scales, coupled with experimental validation, makes this team very unique. They have a strong collaborative approach where they are doing work with several consortia. They are the oldest consortium in the BETO portfolio and can be considered state of the art. Their strength is how they adapt and collaborate with others. This flexibility enables them to stay on the leading edge of technology and solve important problems creatively. The team continues to stay flexible, working with more industry partners while solving problems at the atomistic level. More emphasis on the goals and objectives within the project plan over the next few years can be bolstered with additional commentary on DEIP and EJ activities.

- CCPC continues to bring major value across all of ChemCatBio, working a variety of projects across multiple scales using different *ab initio* and modeling tools. The agreement between the DFT predictions and the characterization experiments for the VFA work could be interesting. CCPC has been involved in several successful DFO funded collaborations. The structure-activity relationship between palladium and etherification rates was simulated along with surface mechanistic detail. Similarly, the overlay of experiments and modeling calculations would be useful for that discussion. Spillover surface calculations for unsaturated bond activation provided good insight and should be connected back to the key synthesis parameters responsible for controlling it. The formation of CuH active sites as migrating from silanol nests is an important observation and result. The oxidation mechanism for regenerating the proper Cu-Si distance should be explored further. The Guerbet reaction kinetic modeling will be useful for the community when published eventually. The reaction network selected should be verified and justified. Catalyst deactivation simulations using HPC matched experimental images very well. The modeling work with Pyran seems to be helpful for scale-up and should include a few experimental data points. The scale-up modeling with Catalyxx appears to be proceeding well. The larger 5-ton reactor radial temperature profile should be provided along with the axial analysis.

- The Johnson Matthey partnership for creating and modeling extrudates appears to be promising. CCPC continues to demonstrate successful DFO projects, as indicated by collaborations with Forest Concepts, Pyran, and Catalyxx. All of these projects have a clear path to contributing deeply to commercial technology development. The team should consider how to collaborate with the data hub project as well as an industrial partner to provide multiscale modeling software tools at the commercial level. By leveraging HPC capabilities to engage the external bioenergy community, the team will establish a lasting impact and legacy.

- CCPC develops and applies a computational tool set to support catalyst design and deployment, as well as process scale-up.

- CCPC is a consortium composed of six national labs. They provide computational support ranging from DFT for catalyst design to mesoscale modeling for reactor design. They provide unique enabling technologies to accelerate the development and deployment of catalysts for bioenergy-related conversion. Their role in this program is unique, especially in an era in which computation is playing a more and more important role in the R&D activities. CCPC has shown a successful way to manage the diverse efforts in the team. It would be beneficial to be more creative in developing activities that contribute to DEI and workforce development.

- CCPC has illustrated impressive progress from all scopes. One note is that the effort of CCPC is shifting from catalyst design to reactor process modeling. This shift is reflected by the funding allocation and the ongoing projects. At the DFT for the catalyst design aspect, CCPC has illustrated the success of several projects, including revealing the deactivation mechanism of catalysts and the mechanism for reductive etherification on Pd/$NbOPO_4$ catalysts. On the mesoscale modeling, CCPC has also illustrated their outstanding abilities, including analyzing the effect of particle size, shape, and porosity on the performance of engineered catalysts. These accomplishments, which have been achieved by closely collaborating with the other forces in the program, are accelerating the development and deployment of catalysts and help fulfill DOE's goals for SAF and GHG emission reduction. It would be more beneficial if CCPC could be more proactive or take a more leading role in the catalyst design and development efforts. It would also be beneficial if CCPC could adapt more advanced computational technologies, such as deep learning, to enhance their R&D outcomes.

- The computation-based design of catalysts and the reaction process demonstrates a clear connection between CCPC's effort and DOE's goals for SAF and GHG emission reduction. The approaches used by CCPC establish a clear connection with their outcome. CCPC may not generate any products that can be commercialized immediately or directly. However, such efforts play a role that cannot be replaced in this era, when we are witnessing the growth of computation.

- CCPC has been a leading force in computational catalysis, providing critical support to accelerate biomass conversion projects through long-term investment and support from BETO. The collaboration between national labs and computational experts with strong bioenergy backgrounds, who have shifted resources toward scaling up, has proven to be highly effective in supporting biomass conversion projects. Cosponsoring computational projects with industry has also been an excellent approach to optimize resource utilization. CCPC's numerous contributions and impressive achievements are commendable. The scaling up assistance provided by CCPC to Pyran is an excellent showcase.

- Moving forward, in addition to continuing its current efforts, such as mechanistic studies, upgrading data hub, and realistic catalyst structure, CCPC should pursue research in both fundamental and applied directions. It is essential to maintain a balance between these two research directions, as a lack of fundamental understanding could hinder progress in applied research. Thus, it is vital to continue funding fundamental studies, especially those that incorporate AI and ML techniques.

PI RESPONSE TO REVIEWER COMMENTS

- The CCPC team thanks the reviewers for their comments. Notable positive comments from the reviewers include compliments on the number and variety of collaborations and related successful outcomes, including collaborations that extend beyond BETO (e.g., the Basic Energy Sciences program), the unique and important role that the CCPC serves in the BETO program, and the multiscale modeling approach of the CCPC. The CCPC is encouraged to maintain our approaches in these areas based on the positive feedback. The reviewers offered a number of guiding comments that the CCPC values as constructive feedback. While complimentary of the multiscale approach of the CCPC, reviewers advised actively balancing the research across the multiple scales to maintain both fundamental discovery science and scale-up efforts. The CCPC shares the concerns of potential misbalance across the scales of research, and in particular, the current risk to underserving the atomic-scale catalysis research that is critical to the ChemCatBio catalyst discovery cycle. Reviewers also encouraged more emphasis on AI/ML approaches. Again, the CCPC agrees with this feedback and seeks to advance further on the successes utilizing AI/ML to date, and to do so by further leveraging the unique HPC resources in the national lab system. The reviewers also suggested further collaboration with the data hub project or industrial partners to make multiscale modeling tools available to the community. The CCPC has made available to the public open-source code of models developed previously in the spirit of this feedback, and the CCPC will consider what more can be done in this area with the data hub project and industry partners. Additional suggestions from the reviewers related to outreach and impact included recommendations to outline more specific goals and objectives for DEI and workforce development. Again, the CCPC appreciates this feedback and will look to define, incorporate, and achieve such objectives. Overall, the CCPC appreciates the constructive remarks and guidance from the review panel, as the recommendations are in line with the CCPC's own vision and priorities moving forward. Any additional resources provided to the CCPC will be utilized to strengthen the balance of multiscale research, advance CCPC tool sets with AI/ML and HPC, extend the impact to the broader bioenergy community, and advance DEI and workforce development activities.

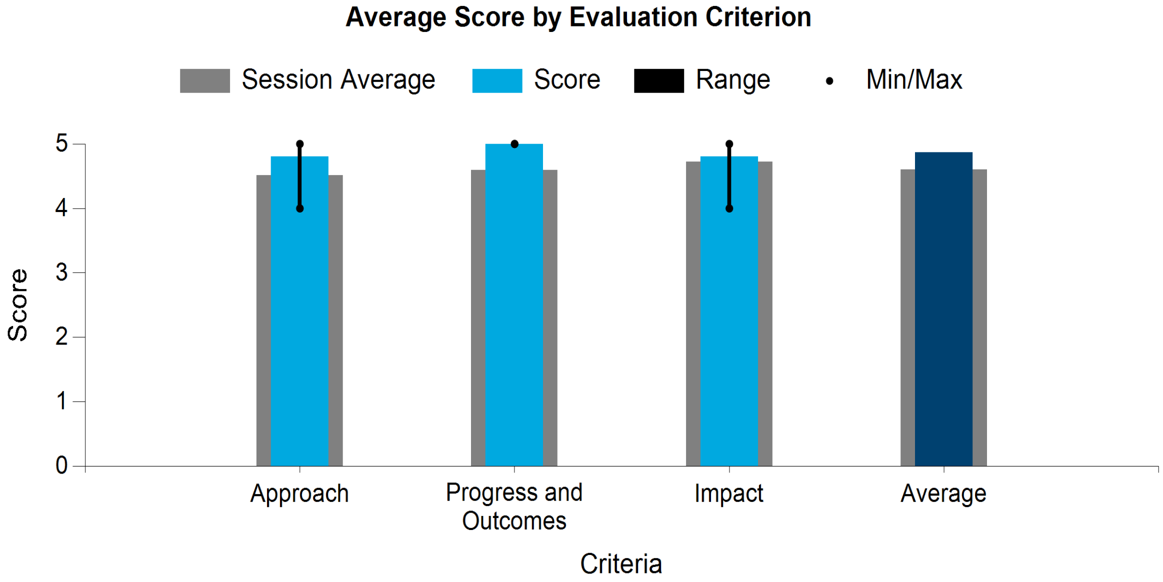
ADVANCED CATALYST SYNTHESIS AND CHARACTERIZATION

National Renewable Energy Laboratory

WBS:	2.5.4.304
Presenter(s):	Susan Habas
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$581,473.00

PROJECT DESCRIPTION

The ACSC project, in close collaboration with the ChemCatBio enabling capabilities, (1) provides actionable insight into catalysts under realistic process conditions for each of the Catalytic Technology projects, (2) addresses overarching catalyst durability challenges central to ChemCatBio, and (3) adapts and applies new synthesis methodologies and *in situ*/*operando* characterization capabilities to meet the needs of the Catalytic Technology projects. The outcome is a reduction in the time required for the Catalytic Technology projects to meet transportation decarbonization targets. The ACSC project contributed to the demonstration of a fourfold acceleration in the catalyst and process development cycle for the ethanol to olefins process within the Upgrading of C2 Intermediates project. It did so by leveraging the knowledge, capabilities, and expertise developed within ChemCatBio for the Upgrading of C1 Building Blocks project. The outcome was a threefold acceleration in the time leading up to licensing of the technology, highlighting the impact of the collaborative and integrated resources of ChemCatBio on technology maturation. The enabling capabilities will leverage the capabilities and expertise developed in these efforts to provide similar insight into engineered catalysts, accelerating the catalyst and process development cycle and reducing commercialization risks for catalytic technologies.



COMMENTS

- The synthesis and characterization work was excellent. This is a key enabling technology/project for the success of ChemCatBio.
- This project had strong support of ChemCatBio, direct engagement with all projects, and joint milestones with all catalysis projects.

- This project enables evaluation of catalytic performance for engineered catalysts and develops structure-property relationships. Clear benefits to the catalyst development cycle can be seen.

- The synthesis and characterization are world-class. There is evidence of direct industry interactions. Outputs included 18 publications, eight external presentations, five direct-funded industrial engagements, webinars for community outreach, and novel characterization techniques.

- This enabling project is focused on accelerating catalyst and process development through contributions in synthesis, advanced characterization, and microscopy. The effort spans three lab partners with expertise ranging from a variety of synthetic methods to X-ray methods to multimodal microscopy. Discrete examples from multiple projects demonstrate the critical role of ACSC in its enabling capacity. The project overview in the presentation highlights the feedback loop between all capabilities. Even though this effort involves lab groups, this reviewer is impressed at the clear signs of integration across ACSC and the interactions with other upgrading projects. Part of this may involve the management and project structure, where joint milestones with individual projects create a level of dual ownership. Regardless, the synergy is a clear strength of ACSC. In prior review cycles, ACSC was challenged to quantify their ability to accelerate technology development. They answered this call, showing a fourfold reduction in development time. This demonstrates their responsiveness to reviewers and paints a clear picture of the project's value to the consortium. Furthermore, the group is attempting to be responsive to ChemCatBio's evolution and other review comments, with a movement toward more industrially relevant catalyst formulations. The current partnerships cultivated with catalyst providers should help make this transition a smooth one. The types of advanced tools that may be needed could evolve, particularly the analysis of spatial resolution as one moves to extrudates. There are many impressive things to note about ACSC, but I would particularly highlight the following. The first is their expertise in the synthesis and characterization of a broad range of materials—from Cu zeolite to carbide/nitride supported materials. This suggests that, as ChemCatBio interests continue to shift, there is complete flexibility in the catalysts accessible to the group. The second strength is the range of scales characterized—from individual active sites to bulk materials. This is a significant challenge but is critical to accomplishing consortium goals. ACSC, with access to a broad swath of advanced tools within the national lab complex, clearly meets this need. Finally, the annual reevaluation cycle to reinvigorate the methods used is another key strength. This is a great general operating procedure and has recently led the synthetic push to advanced engineered forms of catalysts as well as the micro-X-ray absorption spectroscopy technique. A few areas of consideration include the following. First, there is potential for greater interaction with the RAPID Institute/incorporation of advanced additive manufacturing techniques. Although the consortium has implemented such methods in specific projects, this group is poised to leverage this area in unique ways. I understand that specific systems are more amenable than others, but I encourage the group to look to exploit this area given the opportunities provided to synthesis and reactor design. Second, while electrocatalysis was mentioned somewhat in passing, long-term evolution could involve hybrid thermal/electro or fully electro technologies. I would encourage ACSC to remain agile in the types of materials studies (revisiting carbide/nitride materials at some stage, perhaps) and characterization methods employed so that opportunities in the space of nonthermal energy inputs can be fully realized by the group when they present themselves. No significant DEI component was articulated, but it was communicated that the ChemCatBio-wide strategy will be implemented. I don't have doubts that the next cycle will show increased focus on this area. The specific examples provided in the presentation highlight the defined contributions of ACSC to other ChemCatBio efforts. I would highlight one, the University of Southern California/ACSC collaboration, which altered cost/energy inputs in the synthesis of MoC catalysts, resulting in a 50x increase in throughput, which is quite impressive. I would also note that external partners, like this one, are well chosen based on area of expertise, which likely results in the interactions being so fruitful. The significant enabling highlights provided for each of the major task areas were impressive. They provide a comprehensive picture of the acceleration of a suite of technologies across ChemCatBio and establish ACSC as a signature crosscutting effort for ChemCatBio. Evolution from prior cycles is also evident. Time to development with collaborative projects can now be quantified. Also, the pivot from certain techniques—neutron vibrational spectroscopy as one example—is well justified based on the evolving needs of the consortium and is responsive to the science and technology required in individual projects. In addition, the data and catalyst tools being developed in ChemCatBio are integrated into ChemCatBio efforts, as the CatCost tool was highlighted as a value add for Ni nanoparticle synthesis. I have mentioned the acceleration charts elsewhere, but the level of detail is impressive and provides unequivocal evidence of the value ACSC provides to the consortium. Although these charts are timely to prepare, I think continuing to evolve the current example or also expanding on another system in future cycles would continue to demonstrate the unique value the project provides to the broader portfolio. The 18 collaborative publications—the majority if not all of which are with other consortium project PIs—is a testament to the project's role in the broader effort. Prior reviews indicated that interaction with the industrial partners in DFAs was a missed opportunity, and in this cycle, five such projects involved ACSC collaborations. The responsiveness to review and BETO directions is clear. Two patents also resulted from the work directly in ACSC. The ability to develop separate IP from the other projects is impressive given the prescribed role of ACSC as such a collaborative endeavor, which indicates a level of independent technology development within the project. The impact in all facets—when measured by output, level of collaboration with other projects, or connection with industrial partners—is excellent.

- The ACSC project continues to be one of the most successful endeavors within the BETO portfolio, focusing on the problems that enable catalysis R&D to accelerate and using tools that help elucidate the critical mechanisms and root causes behind the bottlenecks in material synthesis. The core of the success of this project partly stems from choosing the right collaborators and problems to pursue, thus allowing for actionable deliverables to emerge in a timely manner.

- ACSC continues to be a strong project with a solid approach, supporting all aspects of ChemCatBio with advanced synthesis, *in operando*, imaging, and spectroscopic tools. The team's work is the heart of the catalytic upgrading effort. They work directly with ChemCatBio projects and try to respond to urgent requests as well. The use of micro-X-ray absorption spectroscopy for studying engineered forms is a next-level approach and tool for ACSC. The project team clearly understands how to plan and accelerate catalytic material research. More discussion around the instrument reliability program for these indispensable resources should be offered, as well as the DEIP and EJ commitments.

- The team continues to use advanced characterization tools to provide critical insight into the development of heterogeneous catalytic materials across the entire ChemCatBio Consortium. An excellent, detailed, and thorough chronology was provided, highlighting the impact the ACSC project had on normal catalyst development cycles from formulation inception to material technology licensing. A normal cycle could range from 7–10 years, as in the case of the Cu/BEA system, versus 3–5 years for the Cu-Zn-Hf/BEA system. This is a major accomplishment, and fundamental research questions were also answered along the way. Another key accomplishment was using *in situ* Fourier-transform infrared spectroscopy to identify a low-temperature oxidative regeneration cycle for the STH materials. It was interesting to observe how a small degree of sintering creep tends to help the C4= selectivity with each regeneration cycle. The team should explore this phenomenon more and collaborate across ChemCatBio to enhance understanding. There was excellent characterization work provided for the Pt/TiO_2 deactivation during pointing to metal poisoning and surface instability during CFP upgrading. The team should be clear regarding the re-dispersion aspects of the regeneration protocol allowing for full recovery and should show the changes in exposed surface area. The role of fully reduced metallic copper on diol deoxygenation chemistry should be clarified a little further and is quite interesting. The team should further explore how to use the non-carbidic coke to their advantage during the metal carbide regeneration cycle.

- Significant and important peer-reviewed journal articles and project reports have been generated from this project. There have been 18 peer-reviewed publications since the last Peer Review. Fifty percent of the industry projects in ChemCatBio utilize the ACSC. The IAB gave excellent feedback. They are currently helping BETO reach its goals by characterizing catalysts for key routes. They are also helping with the SAF Grand Challenge, as well as the CO_2 electrochemical reduction techniques.

- ACSC is an enabling project in the Catalytic Upgrading program. The goal of this project is to provide actionable insights into catalyst development challenges under realistic process conditions by leveraging world-class synthesis and characterization capabilities across multiple DOE national laboratories. This is an unreplaceable asset in the whole program.
- The project's R&D activities focus on two directions: direct engagement with specific projects to assist the synthesis and characterization of catalysts and overarching challenges in catalyst synthesis and characterization. Both directions are important to the success of this project as well as the whole program. The team has illustrated their ability to balance the two directions well. They also developed three modes for the experiment projects to collaborate with ACSC, casting their different needs. However, keeping the balance between the two directions is an important factor and needs careful management in the future. With more research activity extending to engineered catalysts, it is critical to still build a close connection between the efforts addressing the direct engagement and those addressing overarching challenges. The team has illustrated their commitment to DEI. It would be beneficial if they could be more proactive in workforce development.
- They have successfully improved the synthesis of several catalysts for several C1 and C2 projects. They also collaborate with the other enabling team to analyze the catalyst deactivation mechanism and develop actionable technologies to mitigate the deactivation. This progress is appropriate and helps achieve the SAF and GHG emission reduction goals set by DOE. They have shown a clear risk analysis and mitigation plan to help seize the success of their project. It would be beneficial if the team would address more overarching challenges in catalyst synthesis via these direct engagements. It would also be beneficial if the team could consider deploying additive manufacturing, high-throughput technologies, or even AI to help accelerate the design of synthesis pathways for catalysts.
- The ACSC project enables the other projects to possess catalysts with the desired properties. This is the enabling technology that makes the other experimental R&D activities possible. It also provides a crucial technology to lower the cost of catalyst preparation and extend catalyst lifetime, making commercialization possible.
- The ACSC platform leverages expertise to expedite the development of catalytic processes through synthesis and characterization. It combines cutting-edge *in situ* techniques for both bulk and surface analysis with computational modeling to identify active sites and deactivation mechanisms, along with throughput and statistical tools, resulting in a powerful approach for catalyst development. The platform's project management is exceptional in supporting multiple projects with rapid response times, and the outcomes have been remarkable, reducing catalyst development time by a factor of four.
- This platform should continue to serve as a driving force for new projects. Bottlenecks in resources should be identified, and additional funding should be allocated if necessary to ensure that critical resources have backups, especially during unprecedented challenges like supply chain disruptions during the pandemic.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their thoughtful insight and constructive feedback. Notable positive comments included (1) the critically important role of the ACSC project as an enabling capability within ChemCatBio for accelerating the catalyst and process development cycle as well as tackling overarching catalysis research challenges, (2) the successful management of the ACSC project and its integration with the Catalytic Technology projects and industrial partners, and (3) the responsiveness of the team to the evolution of consortium and previous reviews, with a transition toward more industrially relevant engineered catalyst formulations. We also appreciate the enthusiastic responses regarding quantification of the catalyst and process development cycle. This effort, in collaboration with other enabling capabilities and Catalytic Technology projects, enabled us to set a baseline for the time required to develop next-generation catalysts that meet target metrics, and then to exceed this time by a factor of four for a related catalyst system by leveraging the knowledge, capabilities, and expertise within the consortium. Going forward, this same approach will be applied to engineered catalyst formulations. Success in this next development cycle will require, as the reviewers have noted, continued adaptation and demonstration of characterization techniques with spatial resolution across multiple length scales and cost-effective, scalable synthesis methods informed by industry partners that provide targeted catalytic performance while reducing risks associated with commercialization. In addition to continuing to develop *operando* characterization capabilities and expertise that keep pace with the evolving needs of ChemCatBio, the reviewers highlighted synthesis expertise for a broad range of materials as a strength. The reviewers advised addressing overarching catalyst synthesis challenges in conjunction with relevant characterization to flexibly respond to new catalytic technologies. As suggested, we will continue to explore new catalyst materials such as transition metal carbides and their utilization and incorporate additive manufacturing or high-throughput technologies in conjunction with AI/ML techniques to help accelerate the design of synthesis pathways for catalysts. This is an ongoing goal of the collaboration with the University of Southern California, which was noted by reviewers as a strength, and we will continue to foster this partnership. Further, our partnerships will be leveraged to develop project-specific goals and objectives for DEIA and workforce development, as suggested by the reviewers, in addition to targets that will be implemented consortium-wide. For example, providing training in catalyst characterization for students has been highlighted as a need by current and prospective partner institutions and can provide a framework for broader outreach. Overall, we appreciate the positive feedback and constructive guidance from the reviewers and will seek to continue balancing our commitment to direct engagement with the Catalytic Technology projects to answer pathway-specific questions with our efforts to tackle overarching catalysis challenges that can provide broad value to the bioenergy community.

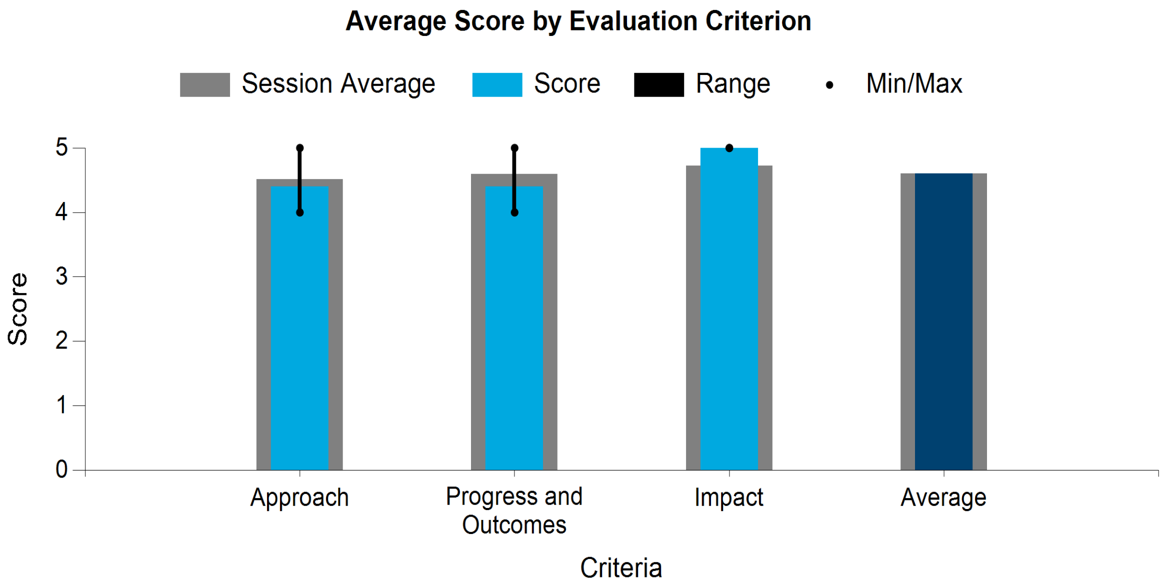
CATALYST DEACTIVATION MITIGATION FOR BIOMASS CONVERSION

Pacific Northwest National Laboratory

PROJECT DESCRIPTION

WBS:	2.5.4.501
Presenter(s):	Huamin Wang; Karthikeyan Ramasamy; Katarina Younkin; Michele R. Jensen
Project Start Date:	10/01/2022
Planned Project End Date:	09/30/2025
Total Funding:	$332,910.00

Catalyst Deactivation Mitigation for Biomass Conversion will enable the accelerated development of commercially viable catalytic processes for biomass conversion to SAF technologies by tackling catalyst deactivation issues that have the potential to impact multiple BETO-funded programs. Significant challenges exist for developing catalysts with long lifetimes for bioenergy applications due to some unique problematic properties of biomass-derived feedstocks. This project, an enabling capability of ChemCatBio, serves as an R&D team specialized in identifying catalyst deactivation mechanisms and developing solutions for improving catalyst lifetime. We coordinated and worked collaboratively with various projects to address some overarching catalyst deactivation challenges and to support specific technologies in expanding catalyst lifetime. Examples include (1) a comprehensive study on the impact of water on different types of catalyst active sites and mitigation strategies, and (2) enhanced understanding of the deactivation mechanisms leading to new catalysts with improved stability for ethanol and butanediol conversion. We provide fundamental insights into catalyst longevity to guide the rational design of robust and industry-relevant catalysts. We directly address catalysis barriers to improve catalyst lifetime and achieve ChemCatBio's goal of accelerating catalyst development and technology readiness for industrial application.



COMMENTS

- The ChemCatBio project aims to provide foundational insights and actionable recommendations for extending catalyst lifetime in biomass catalytic conversion, enabling cost and risk reductions of catalytic processes for BETO conversion technologies. The project's relevance lies in addressing the critical need for catalyst stability in catalysis and biomass conversion R&D and avoiding pitfalls during technology maturation. The goal is to increase awareness of catalyst deactivation issues and focus on catalyst stability within ChemCatBio through a collective and collaborative effort. The approach involves a systematic study of catalyst deactivation, including multiple approaches to understanding the deactivation mechanism, providing actionable recommendations, and developing regeneration methods to address deactivation. Progress has been made in addressing overarching catalyst deactivation challenges, such as the impact of water on multiple catalysts, regeneration methods for coke removal, and the impact of catalyst scale-up on stability. The project has improved catalyst lifetime for specific ChemCatBio catalysis technologies, such as C1 upgrading, C2 upgrading, CUBI, and CFP. The impact of the project is significant in terms of improving catalyst lifetimes, achieving cost and risk reductions for conversion technologies, filling gaps, and providing a knowledge base for rational design of more stable catalysts. Ultimately, this project will lead to accelerated catalyst and process development, a better understanding of catalyst deactivation issues, and the development of tools and methods to evaluate stability more quickly.

- Studying targeted catalyst deactivation across consortium projects is a critical need, particularly given the inherent challenges of biomass use as a feedstock (mixed and variable feed, water content, etc.). The specific emphasis of the effort on characterization/advanced tools to understand structure and induced changes in catalyst composition is a sound approach and aligns well with the existing strengths of the national-laboratory-led consortium. While deactivation studies have ties to basic understanding of catalyst function, they also have direct cost benefits. I would specifically highlight the strong focus on stability, which is key for scalable/deployable technologies. The approach is well aligned with an effort that seeks not to duplicate industry/field practices (with more focus on activity and selectivity), but to lay the foundation for reducing the catalyst development and deployment cycle by focusing on a gap between the research and development/deployment spaces that is sorely in need of being addressed. The major areas of focus—coking, contaminants, and water—are logical. At the same time, the overview did a good job connecting the broader areas to science questions that must be studied to gain the type of knowledge that can impact catalyst design and optimization. The deactivation pathways of a process influence all aspects of the system—whether it be feedstock inputs or the catalyst itself, along with reactor engineering. As the consortium continues to evolve and the types of problems examined increase in complexity, this project is encouraged to continue to think beyond just improvements in the catalyst piece, and to also consider feedstock and reactor improvements to performance. The pivot toward the study of primarily copper zeolite catalysts and engineered systems is appropriate given prior review feedback and the heavy reliance on these systems by ChemCatBio. The upcoming cycle seems focused on the study of more realistic catalysts, greater collaboration with theory, and perhaps exploring reactor advances. These all seem like reasonable directions to pursue. In particular, the nature of specific catalyst formulation will add a layer of complexity beyond prior studies of powder-based systems. One aspect that can perhaps be further explored as complexity builds is the nature of feedstock streams and the impact on catalyst performance. This is perhaps addressed to a degree with the contaminants theme, but I believe there could be valuable studies that explore the impacts of feed mixtures on catalyst behavior beyond what is currently done. Additionally, more time could have been spent with a forward-looking lens, specifically on the changes and challenges anticipated in moving to a heavier emphasis on the study of engineered catalysts. The management plan is suitable and connects, as it should, with broader consortium themes while also being integrated with key aspects of individual projects. Sufficient details were provided on more community-facing activities (perspective on deactivation, etc.) and contributions to individual consortium projects during the last project cycle. Looking forward, the project should also be thinking about moving beyond deactivation in zeolites, especially with some focus on the use of non-PGM systems necessitating exploring other catalyst/support systems. Being ready to enable study of deactivation involving alternative energy inputs (nonthermal) and new catalyst systems will be important to advancing the broader goals of ChemCatBio. DEI efforts were mentioned in passing. There is an opportunity to have some impact in this space, given the collaboration with an MSI/EPSCoR institution. The project would benefit from further fleshing out the details of the interactions and outcomes in a subsequent review cycle. The track record in prior cycles of identifying discrete topics (inorganics impact as one example) and making measurable progress improvements on specific consortium projects is notable. As an enabling capability of ChemCatBio, the synergy of the deactivation effort appears to be increasing, and future plans would continue to strengthen these ties. The specific examples presented reinforce interaction with other projects in the consortium, as one would expect. The well-organized vignettes demonstrate clear value across various projects in the consortium. What could be better delineated in the slides is a discrete degree metric of improvement in some of the catalyst systems. It is not clear in most cases how new, improved catalyst formulations impacted the stability, conversion, etc. Scaling factors (double lifetime, etc.) would be a rough way to disclose the impacts, and project members are encouraged to state these in future cycles. The science focus of the work is strong, but some type of metric of improvement, even if crude, is desirable. The publication of five papers, all in high-impact-factor journals, is commendable. The review article in particular, along with the blog, provides ways to extend project impact beyond just specific ChemCatBio projects. Furthermore, the inclusion of contaminants in the property database is notable and provides a broader resource to the catalysis community. Development of standard deactivation protocols could also be incredibly impactful. As a suggestion, the project could look to expand awareness of the effort through regular webinars as a visual complement to the blog. For the level of support of the activity, the work has an outsized impact on both the ChemCatBio projects and the broader catalysis community that should be commended.

- The team has provided a very focused approach for dealing with the key catalyst deactivation technical gaps facing the ChemCatBio community, with an emphasis on coke, water, and feed contamination in both powder and engineered forms. Much progress has been made with developing regeneration techniques and understanding reactor loading profiles.

- The project has a very clear and methodological approach to studying and understanding deactivation. This is a well-designed project. The team is working across ChemCatBio in a close manner, making sure the work is relevant to the deactivation concerns. The technical approach is to first identify the deactivation problem, determine the mechanism, develop a mitigation approach, and then verify the solution. The interwoven challenge of contaminants, water, and coke is a good way to simplify the mission. The team will also get more involved in the engineered structure stability efforts moving forward. Unfortunately, the state-of-the-art deactivation programs are often proprietary to commercial catalyst manufacturers. The team can either engage the IAB further or collaborate openly with catalyst suppliers on targeted initiatives. The project plan appears to be clear and focused with reasonable objectives. The team should continue to highlight the DEIP and EJ efforts, as PNNL is known to be highly active in this area.

- The project has informed ChemCatBio about key modes of deactivation and solutions to rectify and regenerate the catalyst. The use of model catalysts to understand real catalysts under real reaction conditions is often very tricky. The team was able to pull it off for the Pt/TiO_2 system, developing a regeneration method that involves removing potassium impurities. It is good to see the collaboration with CUBI start to define the 2,3-BDO feed spec sheet with respect to sugar, potassium, and water levels, using deactivation severity as the standard. The concept of an axial deactivation reactor profile is an effective analysis with important unit configuration implications. The team should disclose the coprocessing feed content level with an acceptable impact on the diesel hydrotreater performance. The dependence of Cu dispersion on the water content in ethanol was a good observation, and the results of improved stability should be shared if available. The situation with water and surface modification should be a high priority for this project, with an emphasis on stabilization solutions. For the Pt/TiO_2 system, they identified five modes of deactivation contributors: poisoning, sintering, coke, bulk crystalline phase change of the support, and attrition. The team learned that water must be managed in the ethanol feed to mitigate the Cu sintering.

- The deactivation project expands beyond ChemCatBio and will provide key information for the entire global catalyst community, as indicated in the high-impact publications released. The review article recently published on deactivation due to the conversion of biomass was an excellent contribution to the research community. By gaining more fundamental, root-cause, mechanistic information, the team should continue to pursue opportunities to bolster the predictive power of models in short time scales.

- This enabling project targets an overarching challenge for realizing bioenergy: catalyst deactivation. The goal of the project is to provide foundational insights and actionable recommendations for extending catalyst lifetime in biomass conversion.

- This project deploys an integrated and collaborative effort to address the catalyst deactivation issue. They work closely with ChemCatBio projects for specific catalysts. They also collaborate with other enabling projects, including CCPC, ACSC and Data Hub. They have also built close communication with stakeholders, developed joint milestones, and set up go/no-go decisions to help manage the projects. Their research targets specific catalysts such as $Cu/ZrO_2/SiO_2$ and Y/Beta for ethanol to butenes or zeolite catalysts for CFP. Meanwhile, they address overarching stability challenges when studying those specific catalysts. They focused on three interwoven challenges: contamination, water, and fast coke formation. They started to shift from model catalysts to engineered catalysis due to the need of the program. Overall, this project has deployed appropriate approaches to conduct their R&D activities. They showed clear management and an efficient way of communicating with the other groups. It would be beneficial if they could be more proactive in their DEI efforts.

- The project has illustrated impressive progress in supporting ChemCatBio efforts and addressing the overarching challenges related to catalyst deactivation. The team has helped identify potassium as an important feature to reduce catalyst lifetime, as well as revealing the mechanism and developing actionable methods to mitigate the deactivation. It would be beneficial if the enabling projects could be tied together more closely and build a cross-process platform or knowledge base that can address some overarching challenges that are common in multiple processes.

- Catalyst deactivation is one roadblock to commercializing the biomass conversion process. This project utilized an integrated and collaborative approach to address the deactivation challenges with the aim of extending catalyst lifetime. These R&D activities have shown a clear impact on enabling commercialization of the biomass conversion process and helping DOE achieve its goals in SAF and GHG emissions. Although most of the R&D activities focus on specific catalysts, the overall goal focuses on several overarching challenges. Resolving these challenges will help improve the design and deployment of the catalysts. It would be more beneficial if the project would prepare the harvested knowledge and data in a digital format that could be used for the AI design of catalysts.

- Developing a project that specifically addresses the deactivation challenges in catalytic upgrading during biomass conversions is a strategic approach to promoting both fundamental understanding and commercialization. Although complicated, with many variables, the deactivation mechanisms share common features for heterogeneous catalysts. The outcomes of this project are impressive, not only in terms of the progress in identifying the deactivation mechanisms, but also in terms of the fruitful regeneration efforts. The learnings from this project will not only accelerate the biomass conversion projects, but also benefit the entire catalysis society. However, one challenge with the deactivation study at the benchtop scale is developing lab deactivation protocols that can predict the performance and lifetime of a catalyst in commercial units. Typical deactivation protocols for automobile emission control catalysts and fluid catalytic cracking catalysts could be used as references. Cyclic reactions at low and high temperatures can be conducted without modifying the reaction systems to quickly assess the sintering or coking issues of catalysts. For future investigations, it should be useful to invest in a fixed-bed steamer with a horizontal tube furnace. Such equipment requires minimal capital investment and enables efficient deactivation under high temperatures, high steam, and other poison gases for multiple samples. Furthermore, collaborating with industry partners can assist in developing deactivation protocols.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their support for the project, their thoughtful insight, and their constructive feedback. We agree on the importance of addressing catalyst deactivation, a key roadblock in commercializing the biomass conversion process. The central goal of this project is to overcome these challenges, aiming to enhance the design and deployment of the biomass conversion process. By doing so, we can contribute to DOE's goals in SAF production and GHG reduction. We are grateful for the positive comments regarding the impact of our work on the ChemCatBio projects and the broader catalysis community, the outcomes of this project related to identifying in-depth deactivation mechanisms and fruitful regeneration methods, and our collective and collaborative effort to address the overarching deactivation challenges. We will continue to work closely with other enabling projects to utilize diverse tools, tackle the most impactful catalyst stability challenges, and balance overarching challenges with the specific needs of catalysis projects. We agree with the reviewers that this project should continue to provide specific metrics of improvement in certain catalyst systems, and we are looking forward to working closely with catalysis project teams to quantify these aspects. We agree with the reviewers about the importance of engaging with industry to access existing state-of-the-art deactivation programs. We are actively interacting with our IAB and industrial partners, including a catalyst company through our accelerator partnership, to facilitate industry engagement. Developing standard deactivation protocols is another valuable suggestion from the reviewers, and we are actively exploring this possibility. We are committed to sharing our generated knowledge with industry and catalysis R&D communities through various channels, including publications, workshops, webinars, ChemCatBio technology briefs, and Data Hub. To support DEIP initiatives, we will maintain our collaboration with the MSI institution and actively engage in our consortium-level efforts.

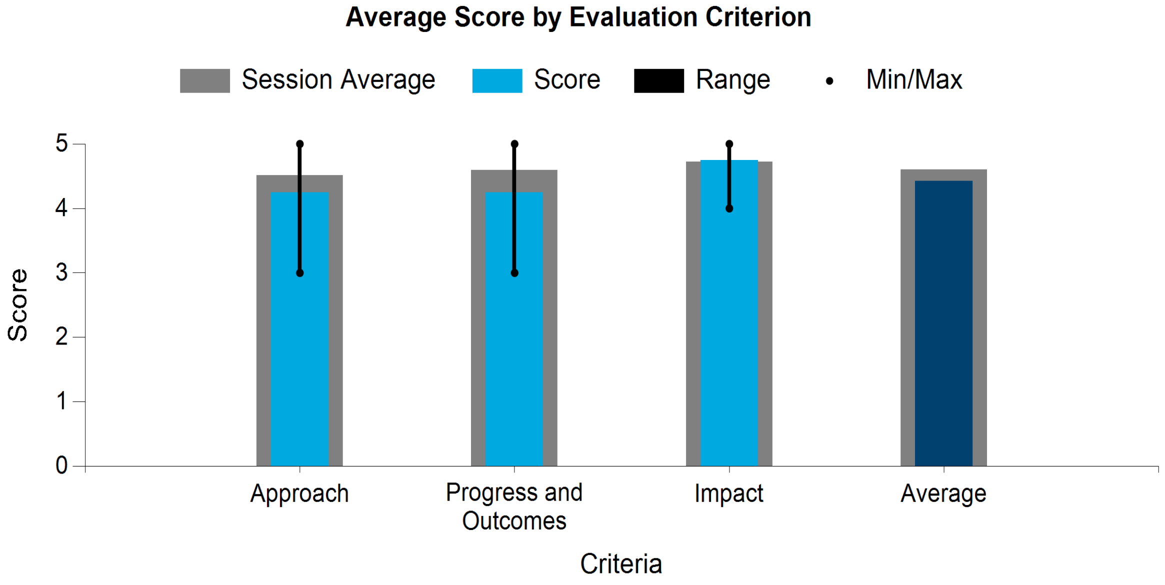
CHEMCATBIO DATA HUB

National Renewable Energy Laboratory

WBS:	2.6.2.500
Presenter(s):	Frederick Baddour; Carrie Farberow
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2025
Total Funding:	$150,000.00

PROJECT DESCRIPTION

The ChemCatBio Data Hub project accelerates the catalyst and process development cycle by providing (1) a secure repository and plug-ins for centralized data storage and sharing and (2) advanced analytics tools to provide predictive capabilities for research and development. In FY 2020–2022, the project was focused on the development of a Catalyst Design Engine, a pathway-independent tool that evaluates the trade-off between the predicted performance and material cost of catalysts for producing a diversity of end products from biomass and waste resources. Realizing this vision requires that the building blocks of the Catalyst Design Engine, namely CatCost and the CPD, are powerful, intuitive, expert-vetted tools with substantial buy-in from the research community. Toward this goal, the CPD has added a user guide, opened to community uploads, upgraded the user interface, and progressed the development of a unique “reference species interconversion” feature that enables comparison and pooling of broad adsorption energy data. A new dataset containing binding of contaminants relevant to catalyst deactivation has been generated through collaboration with CCPC and will be made publicly accessible in the CPD. During the next 3-year project cycle, efforts will focus on the development of transformational tools, expansion of the database, and integration with AI/ML methods for predictive applications.



COMMENTS

- The goal of this project is to accelerate the catalyst and process development cycle through development of analytics tools and to harness and curate catalyst data.
- This project takes the approach of integrating technology data (performance and properties), catalyst cost estimation, and ML to create a database that can be used to accelerate future catalyst design and process development. The data hub is intended as a data sharing tool and a framework for collaboration, in addition to serving as a repository for data that can be used for research beyond the scope of this project.

The project has a strong, logical approach, starting with intra-consortium data sharing, then opening up the database and analysis tools to the public, and finally, allowing public user interaction—all while handling the administration and software development for the code base and tools for the data hub. There is a diverse project team that brings significant and curated experience. The management plan for accomplishing the work and the communication between team members seem strong and include agile methods. Additionally, having routine interactions with the user community means the tool is being developed in response to how it will be used.

- Exceptional progress has been made on this project. The CPD exists as a free and public R&D resource. The initial release contains DFT-computed data plans that include allowing for user uploads (subject to quality control) in a future iteration. To date, 10 experts have been interviewed for feedback on the database. This is a good start, but additional interviews at additional experience levels are still necessary. The researchers have created a public Wiki-style documentation website that details how to use and search the CPD and a public webinar to engage the research community. Additionally, they are working to develop a data curation plan. This is very exciting, as I see great potential for this database.

- This project has already demonstrated impact and has great potential for further impact. The ability to compare data in the published literature or enable a comparison of experimental data to DFT calculations is huge. There is so much potential to save duplication of efforts (and the associated money) as well as to aid the catalyst community in faster and cheaper catalyst discovery. Additionally, this data hub should make it easy to identify outlier datasets and help the catalyst community converge.

- The team has a solid approach that focuses in the near term on optimizing the application programming interface development process to enhance user query experiences as the property database expands. This work will impact the catalyst development community as more reference data is uploaded along with the user training documentation.

- The team spent a good amount of time walking the audience through the risks associated with the project. The team should continue to coordinate and collaborate with larger industrial information technology organizations to leverage the capability and accelerate the work. In terms of data curation and quality, partnering with organizations like the National Association of Manufacturers could be an important relationship if not already explored. This project will always enable more innovation in the field of catalyst development using automated computer science. There was no mention of DEIP or EJ standards related to this project. There is a huge opportunity here due to the coding and information technology gap across the United States for disadvantaged communities.

- Effective user guide documentation takes a significant number of man-hours to properly prepare for public consumption. The data hub team was able to pull together a web-based user guide with searchability. The team should expound more on the data quality and verification aspects of the curation plan and even consider automation for this part of the process. It is probably a good idea to include usage analytics for the tools that are released. The reference species interconversion tool continues to be a very strategic feature for the project. The team did an excellent job of walking the audience through a species interconversion activity. More examples like this would allow progress to be evaluated more easily in the future.

- The data hub, when finally executed with fully functional tools and algorithms, will have a significant impact on the scientific community, as catalysis is at the core of process technology development. The team should continue to raise awareness of BETO's commitment to this technology development and continue to engage the power user community.

- This project provides a unique asset to the Catalytic Upgrading program. It will build a cyber-infrastructure that could be used for future ML research of catalyst design and deployment or for enabling the search of existing catalysts. This cyber-infrastructure is expected to change the paradigm of catalyst R&D. This specific project indeed has a limited budget, which may impact its progress. With this limited budget, it would be more beneficial for the project to engage the AI community and to leverage the existing capacity of the community. Some open competitions on Kaggle or the other platform may help identify suitable ML models. It would also be beneficial to develop a concrete plan for data integrity and safety when reaching out to the community.

- The ChemCatBio Data Hub is a highly valuable platform for the catalysis society, and it is vital that this effort continues to expand. The approach and project management of the data hub are fantastic, with a very clear development plan that includes risk management strategies to reduce data gaps. The breakdown of the budget is helpful for reviewers, making it easier to evaluate the project's progress and resource allocation. I strongly recommend providing more funding to support the growth and expansion of the data hub. With the assistance of AI, the data hub could become an even more comprehensive resource for the catalysis society, including more digested information such as safety data sheets and U.S. Environmental Protection Agency and U.S. Department of Transportation regulations related to raw materials and products. More promotion of the platform will attract more users and partners, leading to increased collaboration and innovation in the field of catalysis. This approach will not only help avoid duplicated work but will also ensure that the platform remains a relevant and effective resource for the community. Overall, the ChemCatBio Data Hub is a critical asset for the catalysis society, and it deserves continued support and investment.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their thoughtful comments on our project management and approach. The reviewers were optimistic about the value of the ChemCatBio Data Hub as a resource for the catalysis community. In particular, the reviewers noted the benefit of reducing redundancy in catalysis research, the ability of the data hub to serve as a collaborative framework that supports accelerated catalyst discovery, and its utility in helping the community reach consensus. They noted the continued strategic importance of unique features like the reference species interconversion tool for the CPD. The reviewers further highlighted the importance of engaging with industry experts both in the information technology industry and in catalysis communities to accelerate development and remain responsive to the needs of catalyst researchers. We were glad to hear the broad support for these areas, which have been a major focus of the project, and we will continue to keep these engagements as priorities to provide guidance to the project. The reviewers also provided a number of helpful suggestions to guide the project. They highlighted the importance of leveraging existing tools and capabilities within the AI/ML community, which aligns with the FY 2023 Q4 milestone for this project, "Define scope and conduct gap analysis to advance toward the Catalyst Design Engine Vision," which will establish the road map for utilizing AI/ML features within the CPD. Toward the goal of data growth and quality, the reviewers suggested exploring relationships with catalysis organizations like the National Association of Manufacturers and highlighted the importance of the data curation plan under development within the project. The reviewers suggested including usage analytics for the tools developed within the project. We agree with the reviewers that usage analytics will be increasingly valuable as the database becomes more integrated with the catalysis community and may offer a source of additional development guidance. We are continuing to evaluate these approaches and agree that they are promising avenues for accelerating data growth while maintaining data integrity. In conclusion, the reviewers highlighted that the project has advanced substantially since the 2021 Peer Review and has demonstrated significant impact. They reiterated the value of continued development of the data hub platform and emphasized the importance of sustained community engagement. We appreciate this assessment and the reviewers' numerous helpful comments, which we will integrate into project plans as we continue the development of data tools to accelerate catalysis research.

LOW-PRESSURE HYDROGENOLYSIS CATALYSTS FOR BYPRODUCT UPGRADING WITH VISOLIS

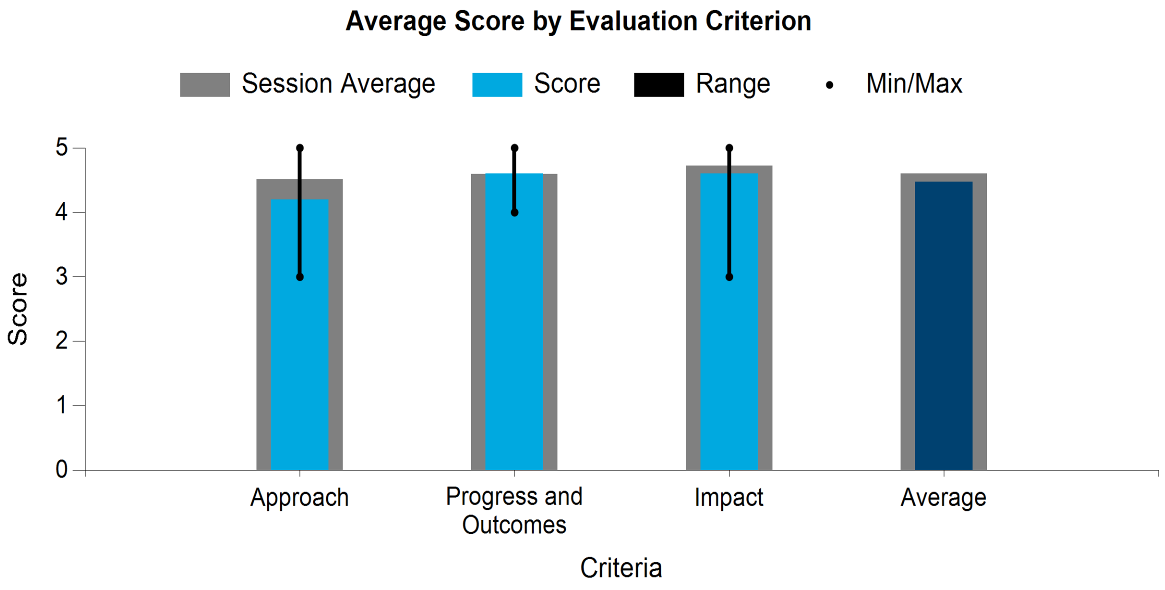
Pacific Northwest National Laboratory, Visolis

WBS:	2.3.1.700
Presenter(s):	Karthikeyan Ramasamy
Project Start Date:	10/01/2020
Planned Project End Date:	09/30/2022
Total Funding:	$205,000.00

PROJECT DESCRIPTION

In late 2017, ChemCatBio invited industry to partner with national laboratories and leverage ChemCatBio capabilities. Visolis, a small company coupling bioengineering with chemical processing, answered the charge with a hybrid process to produce high-value monomers at near-theoretic yields. Visolis has previously demonstrated demo-scale (6,000 L) fermentation to produce an intermediate with low projected costs at a commercial scale. The development of hydrogenolysis to convert the bio-derived intermediate to the desired monomer was proposed to ChemCatBio. A major production cost in hydrogenolysis is the requirement for very high pressures—typical pressures for hydrogenolysis exceed 25 MPa. In earlier work, Visolis and PNNL demonstrated complete conversion of the fermentation-derived intermediate with a selectivity of over 90% at 200°C and 12.5 MPa, but facilities capable of operating at such high pressures are expensive. Lower hydrogenolysis pressures improve capital and operating costs.

The Phase I objectives were met by demonstrating a stable and robust hydrogenolysis catalyst in FY 2020 for the conversion of the fermentation-derived intermediate to a high-value monomer at >80% selectivity under 5 MPa pressure. Objectives of the Phase II effort are to understand and develop mitigation strategies for the feedstock impurities on the catalyst stability and engineer the catalyst to the extruded form for scale-up studies. The team will also provide TEA for a pilot-plant design using Aspen Plus process models and discounted cash flow analysis.



COMMENTS

- Supporting a biotech startup by developing a hydrogenolysis catalyst is a very interesting demonstration of catalyst development for a private commercial entity. Not a lot of detail was given on the approach. Progress and impact are excellent based on the corporate partner being pleased with the final product.

- The approach is as follows: This DFA project with Visolis seeks to develop low-pressure hydrogenolysis catalysts to convert a small molecule intermediate derived from fermentation to a value-added monomer. Within the work plan, the roles of PNNL/the company are clearly delineated in the presentation, with PNNL handling synthesis, combinatorial screening, and attempts to convert to a flow process. Phase II seeks to move to engineered catalysts, which aligns well with prior review suggestions to move to more realistic systems. While generally lacking any details, the presentation did highlight nicely the power of throughput screening methods, which were well suited for this project. The slides and presentation lacked a degree of detail that was desirable as a reviewer. In particular, some specifics regarding the rationale behind results would have demonstrated fundamental understanding of the systems and ability to perhaps apply knowledge to other systems. As an example, regarding the role of water in promoting increased selectivity—positing some rationale for the observation would provide a better-developed picture of the work without compromising IP. This was a moderate weakness of the project. In terms of progress, the project has met milestones in both phases—developing a successful low-pressure catalyst with at least reasonable durability in Phase I and seeking lower PGM content, understanding containment tolerance, and developing mitigation routes in Phase II. These goals were achieved with the discovery of a system that had excellent water/acid tolerance, a demonstrated ability to scale catalyst synthesis, and robust catalyst stability. The lack of details makes some aspects of evaluation difficult. For example, the need for the key synergistic promotor and the lack of any idea of the general elements involved might mitigate PGM loading savings. The projected cost reductions mitigate this concern, but some level of detail could be provided. The impact for Visolis is clear, given that their expertise is more in the fermentation area. The benefit to experts in catalyst synthesis and high-throughput discovery was crucial. However, it was less clear what the benefit was to the PNNL researchers. Some further comments on the experience and how it benefits future research projects would enhance the presentation. The connection to engineered catalysts could also be in line with evolution of the broader upgrading portfolio, but this was generally inferred and not expanded on in any significant detail.

- As a catalyst development and testing community needing acceleration in R&D, more projects should embrace combinatorial catalysis. This project team did a great job of using these tools.

- Combinatorial catalysis is an excellent approach for this project and will always open new opportunities for discovery and innovation with heterogenous catalyst design. The team did not mention the need for data science and data management that truly accompanies any combinatorial program. There appears to be a significant breakdown of scale-up development work that is missing in the approach from catalyst discovery to testing catalyst stability. The state-of-the art hydrogenolysis catalyst for C6 upgrading was not mentioned. The industrial partner originally started with $CuCrO_x$, and the national lab discovered the current catalyst platform. The project plan in Phase II was completed and was aggressive in moving from reduced PGM loading in engineered formed catalysts. The team should outline the real technical risks and gaps associated with making this work viable. There was no mention of a DEIP or EJ perspective with this work, especially from the industrial partner perspective.

- The project team demonstrated how an effective industry collaboration with an appropriate and effective tool in combinatorial testing accelerated the catalyst development. This was done in a batch combinatorial system at PNNL. The lowering of the platinum group promoter loading should have gone through a maxima in product selectivity. The TOS for this TRL level seemed appropriate, approaching 500 hours with a stable selectivity. The catalyst seems to be stable in the presence of two organic acid contaminants. It is difficult to determine what a surrogate feed and real feed is for the project to evaluate the impurity study. Lactone appears to be an important intermediate side product. The point at which water is not helpful to the product distribution should be determined. The 50-cm^3 reactor with extrudates was deemed a scaled-up unit at a 25x factor. The dehydration-based undesired side product rate appears to rise and ultimately decrease over time. There seems to be a period under 200 hours where the surface is unstable. An overlay of the carbon balance would be useful here.

- The team mentioned that the project has moved on, and there is an ongoing collaboration with a scale-up partner. There was no data or design information shared on this activity. There should be some type of resource benefit to ChemCatBio in this combinatorial approach that covered formulations in extrudate structures. This project has a very clear commercialization pathway as the TRL matures. This route provides a solid addition to BETO's chemical process technology portfolio.

- This project serves as an example of successful translational research. The team successfully converts a catalyst discovered in foundational research to a viable catalyst for real industrial applications. The team has deployed various methods, such as combinational methods, to help accelerate the deployment of catalysts for industrial applications. This project has met all its goals and is ready to be completed with success. Due to the lack of detail, it is challenging to address whether this project will help achieve DOE's SAF Grand Challenge. However, based on the information shared by the presenter, this project is ready to enter the next level by scaling up with an industrial partner. This R&D activity illustrates the potential benefit of this project in enhancing the sustainability of the energy or chemical supplies.

- This project serves as an excellent example of successful collaboration between BETO and industry for the commercialization of bioproduct upgrading. The approach and outcomes are highly impressive, with the development of a cost-effective catalytic process for hydrogenolysis, and the proven stability of the engineered catalyst is very encouraging. The R&D support from BETO highlights the potential of this program to serve as an incubator for many startups in industry. Although the project has been completed, following up on the progress at Visolis to validate the technology would be beneficial to finalize the TEA. In case Visolis is unable to scale up the process for any reason, it is important to ensure that the learnings from this project are available to other interested entities.

PI RESPONSE TO REVIEWER COMMENTS

- The project team would like to express our gratitude for the insightful comments provided by the reviewers. We sincerely apologize for the lack of detailed information related to the product streams, the role of water in promoting increased selectivity, and the breakdown in scale-up development work from catalyst discovery to testing catalyst stability during the Peer Review presentation. This limitation is primarily due to the constraints of confidentiality imposed by our industrial partner. However, once the novelty of the project is protected by a patent, our objective is to make the information accessible to the public and document all relevant details in the data management hub operated by ChemCatBio. We acknowledge the impact of high-throughput screening methods in this project. Combinatorial catalysis has proven to be an excellent approach, accelerating catalyst development and creating opportunities for innovation. We agree that incorporating data science and data management into our combinatorial program is crucial, and we will ensure we address these aspects in our future work. We appreciate the reviewer's recognition of the direct funding opportunities from BETO to support the industry in the commercialization of bioproduct upgrading. The development of a cost-effective catalytic process for hydrogenolysis and the proven stability of the engineered catalyst are encouraging outcomes from this project. We agree on the importance of following up on the progress at Visolis to validate the technology and share project learnings with other interested entities for the TEA. We will ensure that we provide updates and share relevant information on this ongoing activity. Thank you for suggesting that we outline the benefit to the PNNL researchers and explain how the experience gained from this project benefits future research projects. We will incorporate this information in our future presentations to provide a comprehensive view of the project's impact on our team and its relevance to future opportunities. We would like to express our gratitude for your comments regarding the importance of DEI and EJ perspectives. It is important to note that this project was funded prior to the implementation of the DEI programs in BETO, and as such, it did not have a direct milestone specifically dedicated to DEI and EJ aspects. However, we fully recognize the significance of these perspectives and are committed to integrating them into our projects to ensure a more inclusive and equitable approach.

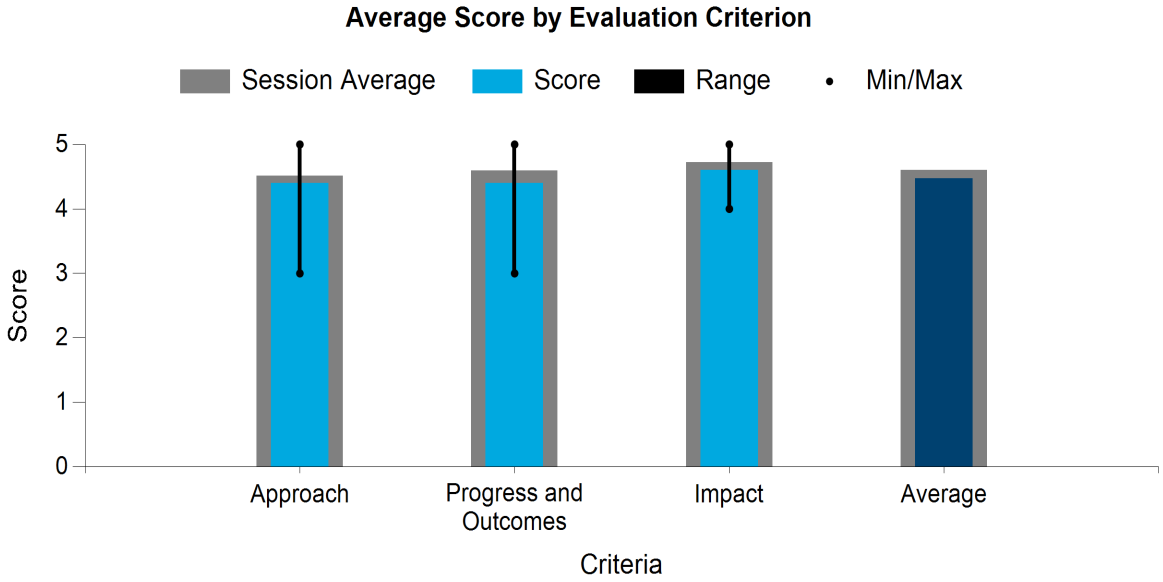
CATALYTIC PROCESS INTENSIFICATION OF BIO-RENEWABLE SURFACTANTS PLATFORM WITH SIRONIX

Los Alamos National Laboratory, Sironix

WBS:	2.3.1.704
Presenter(s):	Claire Yang
Project Start Date:	07/01/2017
Planned Project End Date:	09/30/2023
Total Funding:	$282,000.00

PROJECT DESCRIPTION

The size of the global surfactants market is projected to reach $52.4 billion (U.S. dollars) by 2025. Surfactants are the key active ingredient in cleaning and personal care products and are one of many petrochemical products that could be supplemented with biomass-derived materials. Sironix Renewables LLC has invented a new class of surfactants, called oleo-furan surfactants (OFSs), which utilize the unique properties of biomass by linking the function of bio-based furan building blocks with natural oils to provide 100% bio-based multifunctional and eco-friendly cleaning and personal care products. This project is helping Sironix Renewables de-risk their process scale-up for new product development and maturation. The Phase II joint research project with Sironix Renewables is designed to leverage the catalyst development resources and catalytic reaction engineering of ChemCatBio with the surfactant's platform of Sironix Renewables to accelerate the DOE-invented and DOE Small Business Innovation Research-funded technology toward market commercialization. Technical goals accomplished include the development of new catalysts and reaction pathways of various furan-based structures to lower production costs with environmentally benign materials, process improvements to achieve the efficient scale-up strategy of existing surfactants, and detailed TEAs to guide experimental efforts and measure market potential.



COMMENTS

- This is an interesting project, as it seems to consist of the development of a catalyst to enable a process for private industry company Sironix. In terms of the project goal, "reducing barriers to scaling up Sironix technology by addressing catalytic upgrading and process intensification challenges," it would be interesting to know the value of this work beyond this specific instance. The project scores very well in progress and impact. The development work is complete and the technology has been transferred to the company such that development of detergent formulations is currently underway; in addition, a laundry product partnership has been achieved.

- This DFA project, on a no-cost time extension, leverages LANL and ChemCatBio capabilities to further guide Sironix as they develop oleo-furan-derived surfactants and value-added chemical intermediates. The choice to pursue bio-based surfactants certainly aligns with BETO goals of exploiting bio-derived molecules for use in products. The focus in this phase on scaling the technologies is consistent with consortium efforts focused on more downstream aspects of technology development and deployment. The capabilities at LANL provide an obvious value add for Sironix, given the combination of reactor capabilities, catalyst synthesis, and TEA. It does seem like this project could have benefited from an even tighter collaboration with the consortium, specifically regarding the characterization capabilities of other parts of ChemCatBio. However, at this later stage, the synergy shown between catalyst development and economic modeling is a key element of the work that is vital for success of the project. In particular, it appears that prior review critiques of using economic modeling to guide decision-making were heard and implemented in this subsequent cycle. Aspects of project management appear well in order and were articulated clearly in the timeline/milestone slide. Further evidence that the project is effective stems from the desire to submit a no-cost time extension to continue the fruitful collaboration. No DEI efforts were specifically called out. Provided that this is an existing project that is sunsetting, the lesser emphasis on this area might be the direct result of the current ramp down of the work.

- Improvements across the various phases of the project are clear. These improvements include moving from batch to flow synthesis, developing new reactions informed by TEA, and exploring new processes that access novel chemical building blocks of potential interest. While the catalysis has clearly evolved to be enabling for chemical formation, it is also promising to see that the target products show utility for the desired applications. The economic modeling was clearly instrumental in identifying areas for improvement on the catalyst synthesis and process sides. The issue of feedstock variability is an interesting and critical one for this particular space. The ability to recognize the opportunity to prepare a former costly reagent as a valuable coproduct is clever while also making the entire process more economically viable. Stressing flexibility in processes and products increases the likelihood of a sustainable and successful business model.

- As mentioned above, Sironix benefits from the project in critical and unique ways. The business is continuing to make inroads because of the ability to be flexible in the intermediates produced and the routes used to access OFSs. The proposed pivot toward high-end markets makes sense and is likely necessary to compete (at least perhaps in the short term) economically with well-established companies in the surfactant space. Less clear are some of the benefits to LANL. While the presentation brought out this impact to some degree, more commentary on transferrable insights that LANL gained in the catalyst synthesis, testing, and modeling arenas—even if statements are general due to the nature of the project—would more effectively demonstrate knowledge gains for both partners.

- The iterative design approach for the project has been an effective R&D strategy enabling a new class of furan-tail intermediates to be synthesized. Small batches have been transferred in the industrial collaboration, suggesting a process with viable economics.

- The project appears to have a successful approach that involves close collaboration between the laboratory and industry partners, where frequent design and material synthesis iterations at small scales are critical. The state-of-the-art OFS catalysts need improvements in lifetime, cost, and yields, and the corresponding process design CapEx needs a reduction, which is the core of the goals in this project. The process intensity approach was explained in this work switching from batch to flow reactors. A new process design based on new chemistry was launched in 2023, and it seems like this would introduce a few new risks in the project. There were no critical risks identified for moving the project forward to the next level. No comments were made concerning DEI or EJ.

- The project team made good progress on finding a fatty alcohol feedstock replacement for reacting with furans along with a new catalyst and a patent to cover it all. An additional patent was filed that looked at using furfural, furfural alcohol, and furoic acid as precursors, along with a new catalyst. The team should look at scaling up and delivering intermediates in the 100 gram to 1 kilogram range now. This will require the use of additional quality control R&D tools.
- The project team already has a good industrial partner with a product with decent margins. The project is closely tied to the business objectives and has a great opportunity for success. This pathway offers the BETO community a new route into existing niche chemical production markets. Once the volumes are scaled, the economics will improve dramatically.
- This project reports an effort to develop and commercialize bio-based surfactants. It is currently under non-cost extension.
- The project uses an iterative design cycle to meet the project goals. The cycle includes TEA-based process viability determination, tail options and chemistry definition, catalyst synthesis, characterization and evaluation, and surfactant production and testing. This iterative cycle turns out to be a practical and efficient approach to evolving the products.
- The project has patented catalysts for Phases 1–3 and has developed new OFS platform chemicals. They also delivered 10 grams of new materials to the industrial partner.
- If successful, the project will enable the company to enter a $12-billion U.S. market. The R&D activities have led to three patent applications, several awards for green technology, and partnership with several top players in the field. The surfactant market is a highly divided and competitive market. It will be critical for the company to produce the first profitable production.
- This project is a great example of the successful partnership between ChemCatBio and industry, resulting in remarkable outcomes in the conversion of biomass into value-added products. The project management has been exceptional, with a well-defined timeline and a comprehensive approach to risk mitigation. The progress made over the past 2 years in catalyst upgrading and process optimization is impressive. The successful advancement of this project also serves as an excellent case study for fine-tuning the TEA model to more accurately predict the costs of a process.
- The story of this successful project should be included in promotional materials to raise public awareness and support for this kind of collaboration.

PI RESPONSE TO REVIEWER COMMENTS

- First, we appreciate the review panel's overall positive assessment of this project with the progress and impact we made in supporting bio-advantaged product development with Sironix. Here, we will provide some insights on the higher-level question from the reviewers: Why were DOE funds used to develop a key technology for private industry? This is a great opportunity called a DFO that is designed specifically for industry and academic partners to utilize ChemCatBio's capabilities. This funding opportunity provides resources for partners to collaborate with ChemCatBio's investigators for developing novel catalysis processes and creating new capabilities and approaches to improve the lab's capabilities in the catalysis and conversion portfolio. This DFA project sits in the industry partnership portion of the consortium. This project with Sironix serves as a successful example in this regard by leveraging LANL's capabilities in catalyst development and TEA-guided reaction process improvement and intensification to help address key challenges and reduce barriers to accelerated commercialization for performance-advantaged bioproduct industry partners. We understand the reviewer's concern that the technology being demonstrated appears specific to Sironix. While this research has clear benefits to the commercialization of Sironix's OFSs, the development of alternative feedstocks to provide a domestic source of renewable furan, furfural, and furfural alcohol has applications across a wide variety of bio-advantaged products. The key building block of OFSs is furan or 2-methylfuran. Furan is produced by the decarbonylation of furfural. 2-methylfuran is a byproduct of the hydrogenation process for producing furfuryl alcohol. The major use of furfural is the production of furfuryl alcohol, which is used as a binder for foundry sands. In 1991, the United States produced 49,000 tonnes of furfural and 25,000 tonnes of furfuryl alcohol per year, accounting for 36% and 23% of world production. By 2001, domestic furfural production dropped to 8,000 tonnes/year, or 4% of the world market, and domestic furfuryl alcohol production dropped to 5,000 tonnes/year, or 4% of the world market. Today, the United States produces no significant quantities of furfural or furfuryl alcohol. China processes 80% of the world's installed furfural capacity, and they produce 70% of the world's furfural. Both the United States and the European Union have issued dumping findings against Chinese furfuryl alcohol production. LANL has developed a new process for converting corn bran, which is a byproduct of corn ethanol production, into furfural. This work was part of a BETO-funded project to develop a sustainable source of JP-10. Our TEA for this process indicates that it is competitive with Chinese-produced furfural. Sironix is one of several companies interested in a reliable domestic source of furfural. Helping Sironix develop a new market for furfural-derived chemicals may help revive a domestic furfural industry, which will also benefit domestic ethanol producers. Each year, multiple consortia within BETO provide DFOs for industry and academic partners to utilize their capabilities. Proposals will leverage the consortium's world-class capabilities to address challenges as identified by successful applicants from industry and academia. The DFOs have been demonstrated as a good strategy to accelerate technology maturation and commercialization to benefit the community with new inventions; in this project are surfactants, which are one type of bio-advantaged product. At LANL, we are planning to propose more projects with Sironix and other industry partners in the coming years to meet their needs with the capabilities we have developed and are developing in the lab. In addition, ChemCatBio DFOs are open to all U.S. companies and universities. We appreciate the reviewer's acknowledgment of our efforts in catalyst development and TEA-guided process improvement, and the priority of better serving Sironix's needs and key challenges to commercialization. More proposals have been submitted looking for funding support and collaboration opportunities on process development and scale-up for newly invented surfactant production. Due to time constraints, we didn't get a chance to present our DEI efforts along with our technical progress in this project. The project brings together a diverse team in terms of gender identity, racial and ethnic background, and career stages. The LANL PI has been working closely with the LANL workforce and pipeline program on hiring postdocs and student interns from MSIs to help with surfactant platform molecule synthesis. As part of efforts to reduce hiring and workplace bias, Sironix has developed hiring practices targeting the recruitment of a diverse set of STEM professionals through a series of proactive practices involving equitable job advertising, bias reduction in hiring material review, interviewing practices, and candidate pool selection guidelines. As part of this project work, Sironix will continue to refine policies for hiring, work, promotion, and pay, as well as employee protections that ensure confidential reporting and zero tolerance for all forms of abuse. In addition, Sironix will be implementing new initiatives for the development of equitable and inclusive business practices, including improving their outreach to and representation of underserved communities. This will entail increasing minority representation on the company's board of directors by hiring one additional member and providing at minimum one additional language translation for Sironix's website, newsletter, and other public-facing materials originating internally from Sironix. We agree with the reviewer that additional comments on the knowledge gains yielded for LANL over the course of this project would be helpful. To this end, LANL is benefiting from this project not only by expanding capabilities in catalyst design and increasing the TRL of catalytic conversions and surfactant development, but also by widely opening the door to developing other performance-based bioproducts. For example, the patented chemical reaction and process we developed during this project can also be applied to produce chemical herders to help prevent petroleum oil spills, to produce pesticides that can help address global security challenges, etc., which align well with our mission at LANL. This project is undoubtedly a win-win for both parties. A systematic risk assessment of OFSs has not been performed. This task was beyond the scope of the current CRADA. However, the process engineering done in support of the TEA has provided insights into potential problem areas. The overall process involves a combination of standard unit operations and processes that are well understood and not of particular concern. Sulfur trioxide production for sulfonation is an example of such a process. Other parts of the process are new and pose risks to the project. Our current work helps mitigate the risks associated with producing the backbone molecules. Key reactions in the process are very exothermic. Heat removal from these reactions at a commercial scale is a concern, as is the thermal stability of the reaction products. Other areas of concern include the following: (1) two separation processes key to purifying the product have not been tested at scale, and (2) sulfonation of the furan with sulfur trioxide has not been tested. Producing kilogram quantities of the oleo-furan intermediate would need more funding support. At the end of this project, we will provide Sironix with our recommendations concerning scaling the production and purification of the intermediate to kilogram quantities. The focus of our recommendations will be on the processing steps involving new chemistry. We also submitted new proposals seeking to address the scale-up challenges of the newly developed technologies. The TEA has provided a good understanding of which areas of the process have the greatest impact on capital investment. Our current work in developing alternative chemistry and exploring alternative tails to attach to furan and furfural derivatives is an effort to reduce capital investment. Some of the alternatives that we are currently considering will simplify the process, and the simplifications have the potential to reduce capital investment by 50%. We agree with the reviewer that the 100 gram to 1 kilogram scale is the primary target for intermediates, as well as for surfactants and formulations to facilitate application testing. Sironix's assessments during this project provided proof of concept for the commercial viability of the newly invented surfactants. In our new proposed project, LANL and Sironix are aiming to work cooperatively to increase the scale of intermediate and surfactant production to meet these volume targets. Sironix has access to the quality control and R&D tools required for this product, either in-house or with the use of available facilities at Washington Clean Energy Testbeds. We thank the reviewer for the recognition of our useful and effective iterative design cycle and for providing positive feedback. We are also expecting to see Sironix and its partner manufacturers produce the first profitable production in the near future, and we would be happy to provide more technical support along the way. We appreciate the positive feedback from the reviewer. The laboratory produced materials as part of the R&D 100 submission for this work. These materials included written materials as well as a video. The suggestion to raise public awareness of this work is appreciated, but it needs to be subject to Sironix's business strategy. We should review and update the materials generated for the R&D 100 award if appropriate. A good first step would be an article in the laboratory's magazine, *Los Alamos Science*, and visibility for the work on the laboratory's external website. We will also try to submit this success story to an outlet targeting trade and professional publications, such as *Chemical Engineering Progress* and *Chemical & Engineering News*.

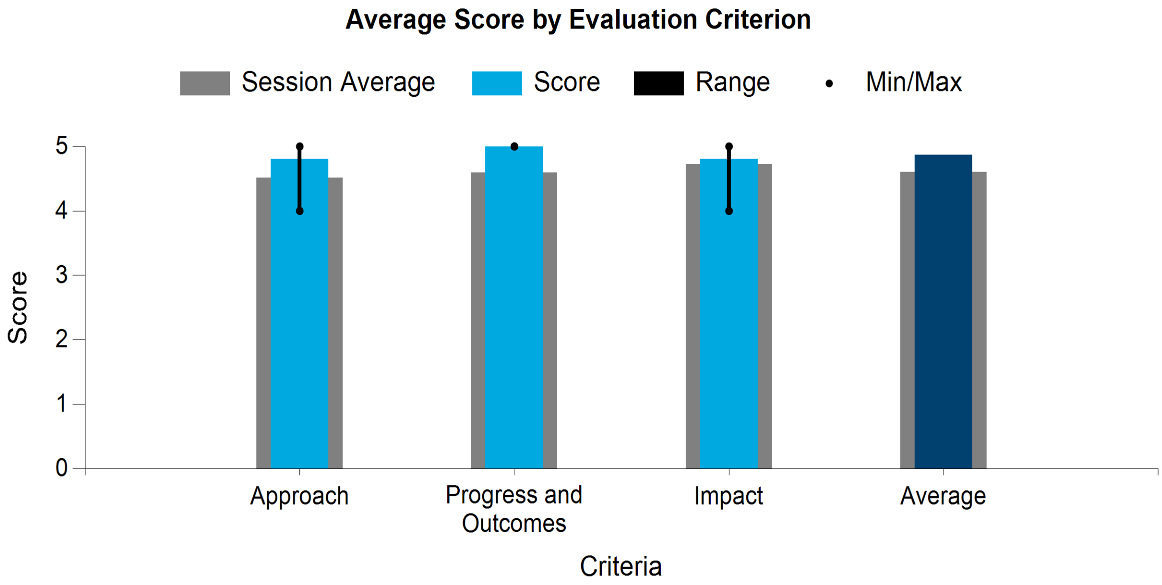
CATALYST DEVELOPMENT FOR SELECTIVE ELECTROCHEMICAL REDUCTION OF CO_2 TO HIGH-VALUE CHEMICAL PRECURSORS WITH OPUS 12

National Renewable Energy Laboratory, Opus 12

WBS:	2.5.4.707
Presenter(s):	Frederick Baddour
Project Start Date:	10/01/2020
Planned Project End Date:	09/30/2022

PROJECT DESCRIPTION

Cost-effective electrochemical CO_2 reduction (ECO_2R) is considered one of the holy grails of green chemistry. However, widespread commercial fuel and chemical production via ECO_2R is limited due to the lack of a suitable reactor design and catalysts with high selectivity to the desired products. This technology has the potential to convert CO_2 into a range of molecules that would benefit the biofuels and bioproducts industry. Within the bioenergy industry, more than 45 million metric tons per year of CO_2 are generated from existing domestic biorefineries. With projections of abundant and inexpensive renewable electricity, utilization of this domestically produced CO_2 to make fuels and chemical products has the potential to significantly enhance the economic viability of these operations. Twelve's core innovation is a reactor design that enables ECO_2R in a polymer electrolyte membrane (PEM) electrolyzer. A novel polymer blend and transition metal nanoparticle catalysts on carbon in the cathode layer transform a PEM water electrolyzer into a PEM CO_2 electrolyzer. The goal of this project as a follow-on Phase II DFO is to implement stereolithographic 3D printing to rapidly prototype advanced millifluidic elements to develop a versatile platform for the preparation of nanostructured CO_2 electroreduction catalysts at throughputs >10 g per day. This production capability will enable the systematic evaluation of catalyst properties and ink preparations for membrane electrode assemblies (MEAs) >600 cm^2.



COMMENTS

- This DFA project seeks to advance high-throughput synthetic methods to permit scaling of MEAs for electrolyzer synthesis. With the expertise at NREL in catalyst synthesis and characterization, this project seems a natural partner with ACSC PIs and their capabilities. The electrolyzer target of CO_2 to CO is a strong near-term goal to advance CO_2 conversion to viable fuels and chemical feedstocks. The potential versatility of the process and plug and play in biorefineries and standard refineries is another clear strength. Given that this is in Phase 2 with the same parties, it is no surprise that the communication lines seem appropriate. Use of the data hub for collaboration provides another value add to the database, given that it allows secure communication channels for data exchange between the lab and industrial participants. The use of CatCost further highlights the integration of the tools developed by ChemCatBio into the ethos of all research the consortium performs. Furthermore, the slides clearly delineated the roles of Twelve and NREL. It was also evident that there was mutual benefit from the interaction, as Twelve scaled catalyst synthesis while NREL was able to hone microfluidic synthesis, which may well impact non-DFA funded projects. *In situ* analysis to understand catalyst synthesis is another highlight of the work and something that can be done in a multimodal fashion, as NREL can, in a select number of organizations. The additive manufacturing component of the work was a highlight and hopefully something the consortium can continue to leverage in this and other projects. Given the success here, exploring and integrating 3D reactor printing and reactor design may be worth additional consideration in certain instances with other consortium efforts. The direct connection with theory in reactor design further highlights the utilization of the consortium's full suite of capabilities in DFA projects and is a resounding response to prior review comments. In the long term, opportunities may exist to connect such synthetic methods as described here to high throughput, or to couple data science with responsive reactors to further decrease the time needed to optimize the systems. The consortium is encouraged to push current capabilities in this space when the opportunity arises with potential future DFA projects that align with these areas. DEI was not explicitly called out from broader consortium interests in the space. For an existing project with an external partner focus, this is perhaps not too surprising relative to some of the continuing efforts that rely heavily on national laboratory or university leadership. For new DFAs, some level of effort to disseminate DEIPs would be expected.

- The project results clearly speak for themselves—the flow system has been demonstrated with good to great results. The catalyst and MEA can be scaled and shown to maintain comparable reactivity. While Phase I focused more heavily on identifying potential catalyst improvements and provided the basis for targeting a specific catalyst, Phase 2 moves toward scaling. This is very much consistent with prior review suggestions to move in the direction of advanced catalyst synthesis with an aim toward technology development and deployment. The choice to explore microfluidics was a sound and well-rationalized one for nanocatalyst synthesis. The results demonstrate not only successful synthesis on the desired scales, but also decreased throughput time and time needed for grafting. As performance was not impacted, the project is considered a resounding success.

- The Phase I and Phase II collaborations were critical to the development of a viable catalyst for the assembly, while also providing a path to the needed scaling to continue to pursue the electrolyzer technology. The project also has clear benefits for the consortium, providing experience with additive manufacturing and microfluidics that can be leveraged in other nanocatalyst synthetic schemes. Experience with the full cycle of catalyst development and scale with these systems could prove invaluable if/when new catalyst architectures are explored for AOP projects. Also, the DFA project enables the pursuit of methods and capabilities that are not mature enough for AOP-type projects but could complement work in these major areas in future cycles. The products stemming from the work (one paper accepted in a solid-impact-factor journal, one paper in preparation, and two patents) represent a solid output, given the IP considerations and ultimate desire to develop the technology. The project is also clearly evolving consortium interests, moving from batch-type synthesis to reactions in flow. The increasing comfort level with such systems can only reap benefits in general for DFA and AOP projects alike. Furthermore, this reviewer was unaware of the robustness of the 3D printed resins and reactors—this versatility should be exploited (when feasible) in other synthetic examples that could further benefit consortium efforts in other areas.

- Here, the work was focused on the Phase II objectives, which were to create catalyst synthesis methods that can be scaled. NREL provides the catalyst and reactor design, characterization, and modeling, while the industrial partner performs the assembly and performance testing activities across multiple scales. To accelerate the research, NREL takes an innovative approach of fast-prototyping continuous flow material synthesis reactors for nanoparticle production. These nanoparticles make up the ink used in MEA fabrication, and the material synthesis microreactors can provide a way to scale up. The team did not provide a clear comparison with the current commercial synthesis method for the same type of nanoparticles to show all the technical benefits. There is no question that this approach opens up a variety of innovation pathways for material design and modeling. The only key risk mentioned was the inability to create a material synthesis scale-up process. The project plan appears to be reasonable with the close collaboration and iterative technical feedback between the teams. No DEIP or EJ discussion was provided by the lab or industrial partner with relevant goals within this project.

- The team did an outstanding job of using the 3D printing and additive manufacturing tools, as well as the computational design tools, to fabricate microfluidic elements. The microchannel design features of these elements were selected through literature research, COMSOL analysis, and interactions with CCPC. All these activities are great examples of using advanced tools and collaboration to complete critical tasks and advance the work. In the last 2 years, by using this method, the MEA geometric surface area was able to be scaled by 30x and the nanoparticle production rate increased by 7x. Further, the technique was a clear way of adopting process intensity batch-to-continuous strategies successfully. The results were compelling, showing no difference in performance between batch and continuous methods.

- This project clearly shows how a close collaboration between labs and industry can be advanced using innovative approaches with direct application to the final process technology. This route has significant promise for both BETO and the decarbonization climate technology community. The work went directly into the business strategy, impacting the scaling objectives, which are at the core of technology development for high-tech startup organizations. The team was able to include material quality features in the synthesis process by using spectroscopic property correlation techniques that are very common to industrial processes. The team should discuss more of what it would take to put together a real material synthesis process design for this micro-fab approach based on 90-degree micromixers.

- This project reports aim to de-risk the commercialization of CO_2 electrolysis by developing high-throughput synthesis methods for high-performance nanocatalyst production. This project is with Opus 12 (Twelve).

- The project has two phases of R&D activities. The Phase 1 activities developed a better catalyst and effective supporting methodologies to retain particle size and morphology at increased loadings. The Phase 2 activities involved designing and fabricating millifluidic reactors using additive manufacturing techniques, evaluating the impact of millifluidic reactors on catalytic properties, demonstrating an end-to-end process for nanoparticle catalyst synthesis, and supporting MEA fabrication and performance evaluation. This innovative approach has illustrated that it could be used to accelerate the industrialization of catalyst deployment. Such an approach may also be used to accelerate catalyst selection and upscaling in the other projects.

- The project has made appropriate progress toward addressing its goal and has accomplished the setup tasks properly.

- Electrochemical conversion would be an exciting direction to develop a sustainable process with GHG emission reduction. This project has illustrated its close ties with DOE's targets of reducing GHG emissions. The development of a millifluidic-based high-throughput approach could have a significant impact on catalyst design and deployment. It could be beneficial for ACSC to see this technology, and it could be leveraged to accelerate catalyst synthesis and characterization in a broader spectrum.

- The design and implementation of a high-throughput millifluidic system in this project demonstrates the exciting potential for future labs. The combination of high-throughput stereolithographic 3D printing, online spectroscopy monitoring, computational modeling in reactor design, and integrated processes is an impressive approach. The results, including a 6.6-fold increase in throughput and 40x scale-up, are convincing.

- Although the cost-effectiveness of further scaling up these techniques is unclear without a cost breakdown, the insights gained from this project can be leveraged in future projects. For example, the project team could collaborate with CCPC to design and fabricate novel catalysts using the techniques developed in this project.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their thoughtful comments on our project management, communication, and industrial engagement. The reviewers were positive about this project's demonstration of accelerated technology development through close collaboration between labs and industry. They also noted the clear linkages between this project and DOE's decarbonization and GHG emission reduction targets. Further, the reviewers highlighted the benefits of the crosscutting capabilities that were developed within the project and their interest in seeing these technologies leveraged within AOP projects to the benefit of ChemCatBio. Notably, the developed expertise in the additive manufacturing of reactors and millifluidic synthesis were encouraging outcomes of the project and were indicated as valuable capabilities that could benefit the consortium more broadly. We share the reviewers' optimism and excitement about the potential impact these developed capabilities could have on ongoing work in the consortium and will continue to seek opportunities to leverage them to address targeted catalyst deployment challenges. In conclusion, the reviewers highlighted that the project has advanced substantially since the 2021 Peer Review and demonstrated significant impact. We appreciate this assessment and the reviewers' numerous helpful comments.

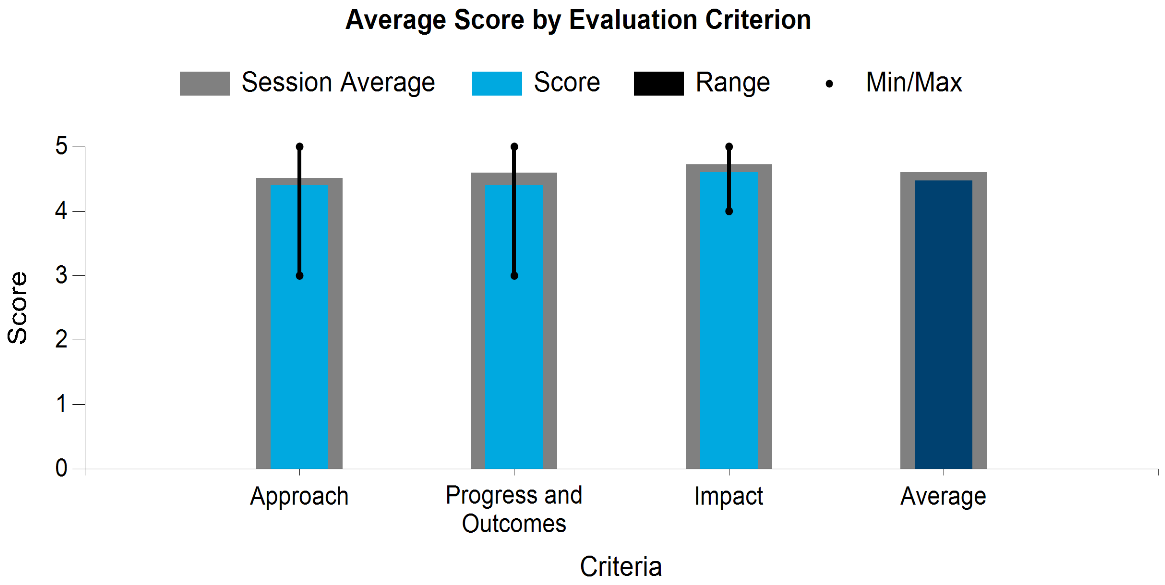
SYNGAS-DERIVED MIXED OLEFIN OLIGOMERIZATION FOR SUSTAINABLE AVIATION FUEL

Pacific Northwest National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.318
Presenter(s):	Karthikeyan Ramasamy; Katarina Younkin; Michele Jensen
Project Start Date:	10/01/2021
Planned Project End Date:	09/30/2024
Total Funding:	$472,139.00

To meet the immediate need for decarbonization of the aviation industry, leveraging existing commercial processes and feedstocks will be the most efficient path toward producing SAF in the near term. Syngas is one of the most attractive feed sources because it can be derived from a broad range of renewable and waste feedstocks via gasification while benefiting from existing infrastructure throughout the petrochemical industry. Of the existing industrial processes for transforming syngas to synthetic fuels, none produce aviation fuel efficiently. However, methanol synthesis followed by methanol-to-olefin processing offers an already established and active commercialized pathway to produce mixed light olefins, primarily ethylene and propylene. This mixture can potentially be directly oligomerized to jet-range products in a single reaction step. If demonstrated with high yield and selectivity, elevating this single operation unit to industrial scale would complete an end-to-end commercial pathway for producing SAF from syngas derived from various ecologically disadvantaged feedstocks. To achieve this goal, this project will develop a C2–C5 co-oligomerization catalyst and demonstrate an efficient path to generating SAF from syngas via a mixed olefin intermediate.



COMMENTS

- This project develops a process to produce SAF from syngas-derived mixed olefins, demonstrating a commercially viable path to achieve a 70% reduction in GHG emissions.

- The project aim is to design/develop a catalyst that enables integration of metal and acid catalysis pathways for co-oligomerization of C2 and C3 to produce SAF. The highly collaborative research team includes PNNL, WSU (fuel property analysis), and Haldor Topsoe (catalyst development). The DEIP is to “hire at least one student from groups underrepresented in STEM,” which I find to be a pretty weak plan. First, it really has to be more than one student, as the data clearly shows that hiring just one of any minority group puts an undue amount of pressure on them, and keeps them in a high-pressure “spotlight” situation. Ideally, the group would be on the order of at least three. This also gives them some ability to form a support community and not feel isolated. Second, just hiring them without a clear mentoring plan or programming in place to support them is not a great way to set them up for success.

- The project has had solid progress so far. The first milestone (September 2022) was met, and the September 2023 milestone is on track. The team developed the hybrid catalyst system and optimized reaction conditions to achieve C2–C5 co-oligomerization with more than 75% selectivity to jet-range products. The team still needs to demonstrate the durability of the catalyst, and is planning to test for ~500 hours.
- This project demonstrated a co-oligomerization process with mixed olefin (C2–C5) feedstock to produce hydrocarbons in the jet fuel range. This meets the standard at = 50% blend level.
- The approach is as follows: This project is focused primarily on one step of the syngas-to-fuels conversion chain—co-oligomerization of the olefins generated in the process—while also attempting to demonstrate linkage of all associated reactions to provide significant quantities of hydrocarbon fractions for further testing. The focus on mixed streams of olefins makes complete sense to mimic the potential feeds from methanol to olefins (MTO). The same can be said of a strategy focused on the need for multifunctionality in catalyst design, given the mechanisms that will be accessed in the oligomerization process. Furthermore, the reactor/bed engineering focus of the work is appropriate given the collected data. The roles were clearly defined in the presentation. The WSU connection for fuel testing is a vital component, given their expertise in fuel testing, and the project’s milestones heavily focused on obtaining adequate amounts of hydrocarbons for blend testing. In the proposed cycle, the move toward an integrated sequential process and the use of engineered catalysts are logical and align with increasing the complexity of the consortium projects. Understanding deactivation in these systems is critical to sort out, given that the process may be very different in the sequential versus hybrid bed catalysts. This project represents a clear opportunity to interact with the deactivation project to advance understanding of the reaction system and continue to increase the efficacy of the transformation. The DEI component—support of a summer college research student from an underrepresented STEM background—is commendable. Hopefully the student can link to the broader opportunities provided to Science Undergraduate Laboratory Internship and other summer research students at PNNL. In terms of progress, the results are primarily a function of reactor bed manipulation, as the mixed catalyst in a single bed is less effective than a sequential approach. It is gratifying to see that the mixed streams behave much as the lighter olefin feedstocks do. The initial milestone of providing the needed quantity of the mixture for blend testing was achieved. The reviewer also acknowledges that the setup used to provide the mixed olefin feeds is an impressive tool in this work and one that took nontrivial effort to establish. The property testing also yields some promising initial results, and provides the ability to tune properties to the desired ranges with some modifications to the system. The challenge now is to integrate all parts of the syngas-to-fuels pathway to provide the desired product and to do so at longer times. Economic modeling will also be explored further to guide subsequent cycles. Given the progress to date, moving to these more ambitious milestones is appropriate. In terms of impact, the desired move of the technology from TRL level 2 to 4 seems like a manageable yet impactful step in moving from development toward scalability during the project timeline. If all milestones are achieved, the syngas-to-fuels pathway will be demonstrated and a better understanding of the economics of the process will be achieved. For one cycle of a project, this would provide a strong basis for potentially continuing the work or pursuing a handoff/collaboration with an interested industrial partner. While the impact can clearly be inferred from the slides, it was surprising to see no reference to outputs (potential publications or patents) as seen with

all other projects. The lack of details in this space—even if the outputs were provisional, in progress, or anticipated—was disappointing.

- The project team has a good collaboration strategy with a reputable catalyst manufacturer, enabling the metal/acid bifunctional catalyst design to be realized in an engineered form. The project has provided good insight into the impact of various reactor loading strategies and the associated modeling for it.
- The approach here is to take the mixed olefin stream out of MTO and to oligomerize that further into SAF-range material, eventually followed by a hydrogenation stabilizing/polishing step. This approach is a generally accepted pathway for methanol-to-jet technology, looking at a supported metal on an acidic surface. The bulk of the work on this project will take place at the national lab. The approach is to do fuel property testing at the university and develop the engineered form of the catalyst along with scale-up manufacturing. A third-party inspection lab verification could also be useful on this project. There was no mention of aromatics potentially showing up in the product stream. The state-of-the-art material and how materials on this project differ were not discussed in any detail. One risk—catalytic deactivation due to the impurities present in the real feed—was mentioned, but no mitigation strategy was proposed to address it. The plan to connect the MTO and oligomerization reactors together should be able to happen in a year. The plan to hire one intern from an underrepresented minority group is a notable goal for 2023 because it is directly related to the project. Additional milestones/goals for DEIP should be included along with a vision for EJ with this technology. They have students from underrepresented minority groups. They hired a student from the Energy and Environment Diversity Internship Program (EEDIP). This is a good outcome.
- The team should highlight any special features of the testing apparatus for carrying out the oligomerization reaction. The co-dimerization C5 product offers interesting opportunities for SAF-range material. The carbon number of the sequential versus hybrid study should be disclosed. Olefins are no good for SAF. The team should recommend the appropriate reactor configuration strategies for the 75% loss of activity within one day on stream. The team should define moderate acidity outside of just numbers and show amine titration results by temperature programmed desorption to understand strength (via surface energy). The sequential reactor gave high yields of SAF-range material for a day on stream. The team should carry out the reactions on much longer time scales and work more closely with the catalyst deactivation team out of ChemCatBio. The project yielded material that demonstrated good SAF properties after hydrogenating the mixed olefin product. There were no details on the hydrogenation step, and there was no insight on the possibility of cofeeding hydrogen into the sequential reactor.
- Renewable methanol from biogenic syngas will continue to be a strong path for the bioenergy industry. The opportunity to upgrade this methanol to a premium fuel commodity such as SAF could have a huge impact. A robust catalyst system capable of performing oligomerization on stream in a stable manner for thousands of hours would also resonate across the industry. The team was able to get a reputable catalyst manufacturer as a collaborator on the project, which points to the significant business potential as a result of this work. In terms of benchmarking, this project has significant kerosene yields relative to other well-known routes (e.g., Fischer–Tropsch [FT], Mobil olefins to gasoline and distillate, Shell middle distillate synthesis), which opens up an opportunity for significant R&D in this pathway moving forward.
- This project aims to develop C2–C5 co-oligomerization catalysts and demonstrate an efficient path to generating SAF from syngas via a mixed olefin intermediate.
- This project targets a low-TRL step in the process of converting syngas to SAF. The R&D activities include the catalyst development, evaluation, and characterization. It has tested two kinds of catalysts and discovered their different ability to catalyze the co-oligomerization of olefin. The team also integrates the R&D activities with DEI activities by recruiting summer interns through PNNL's diversity

internship program. The team also combines catalyst development with TEA/LCA to analyze the viability of the process in terms of scale-up and commercialization.

- Despite the short period, the project has illustrated impressive progress that can help achieve the project goal and DOE's mission for SAF and GHG emission reduction. The project has delivered 100 milliliters of finished jet fuel sample from the representative methanol-to-olefin feedstock. It would be very interesting to observe how the process might work with real feedstock. The team is also constructing a new reactor that can handle multiple olefin feeds. The construction of this reactor can help accelerate the R&D, focusing on the scale-up. The team also discovered the distinct performance of metal and zeolite catalysts in oligomerization. I encourage the team to reach out to CCPC to further analyze the science behind this difference. It may lead to a foundation for developing catalysts that can selectively catalyze the co-oligomerization reactions.

- The project is targeting the step with the lowest TRL in a multistep syngas-SAF process. Its success will improve the TRL of the whole process and could lead to a complete syngas-SAF process that has commercialization capacity.

- The olefin oligomerization project is progressing well, with the development of a dual-catalyst system in sequential configuration and commissioning of a new reactor system for performance evaluation. The catalyst system has shown promising activity and stability, which is an important step toward producing SAF from bio-syngas via the MTO route with higher jet fuel yield than other routes. However, further investigation is required to determine the root cause of the hybrid catalyst's quick deactivation. Using a different kind of zeolite could potentially lead to better results.

- Moving forward, it is critical to determine whether this catalyst system can still function as an engineered catalyst under commercial operation conditions. Computational modeling and fundamental understanding of active sites and kinetics should aid in rational catalyst design. The two-catalyst zone design may require dealing with different mass and heat transfer requirements and different deactivation mechanisms. Therefore, hybrid catalysts may still be an option.

PI RESPONSE TO REVIEWER COMMENTS

- Thank you for your valuable feedback on the "Syngas-Derived Mixed Olefin Oligomerization for Sustainable Aviation Fuel" project. We appreciate your positive remarks about the progress made and the potential impact of our work in achieving the project's goal of reducing GHG emissions and aligning with DOE's mission for SAF. We are glad to hear that you recognize the collaborative efforts of our research team, which includes PNNL, WSU (fuel property analysis), and Topsoe (engineered catalyst development). The expertise and contributions of WSU in fuel testing have been instrumental in the project's milestones at the end of Year 1 of this project. The development of a catalyst system and the optimization of reaction conditions to achieve C2–C5 co-oligomerization with over 75% selectivity to jet-range products are significant accomplishments. We acknowledge the durability of the catalyst as a key aspect, and we plan to conduct testing for approximately 500 hours to demonstrate its long-term stability by the end of this 3-year project. This project will demonstrate the syngas-to-fuels pathway and provide a better understanding of the process economics by successfully achieving milestone goals set by this project. Moreover, our project is specifically targeting the unit operation with the lowest TRL in a multistep syngas-SAF (via methanol) process. Its success would not only improve the TRL of the whole process, but also pave the way for a complete syngas-SAF process with commercialization capacity. We highly value the reviewers' feedback regarding diversity and inclusion, as well as the significance of establishing a support community to foster collaboration and alleviate individual pressure. Our team shares the same recognition and is actively implementing measures to address these aspects. We have successfully hired a student through the EEDIP, which has allowed us to bring in multiple students to work on various projects within the energy and environment program areas. Furthermore, EEDIP includes a comprehensive mentoring plan and programming to provide dedicated support to these interns, ensuring their success and facilitating their growth throughout the project. We appreciate your emphasis on collaboration and interaction with the deactivation project in ChemCatBio and CCPC. Understanding deactivation mechanisms in the sequential versus hybrid bed catalysts is indeed critical, and we will actively engage with the deactivation project to advance our understanding of the reaction system and increase its efficacy. We apologize for the oversight of not providing sufficient details about potential outputs, such as publications or patents, in our presentation. As this project is in its early stages, having commenced in FY 2023, we currently have limited published journal articles or patents. However, we are actively working on completing two journal articles based on the experimental outcomes of this project, and we anticipate their publication prior to the next Peer Review. Additionally, our project team has already submitted a patent application for the mixed olefin co-oligomerization process derived from our research. We recognize the importance of sharing these outputs and will ensure that we provide updates on publications and patents as they become available. We acknowledge the concerns raised regarding the presence of aromatics in the product stream and the potential catalytic deactivation due to impurities in the real feed. To address these challenges, our Year 3 project plan incorporates longer-time-scale experiments, allowing us to study and mitigate these issues effectively. Furthermore, we are committed to investigating the root cause of the hybrid catalyst's quick deactivation and gaining a deeper understanding of the associated deactivation mechanisms. This knowledge will enable us to refine and optimize the hybrid catalyst system, ensuring enhanced stability and performance. We appreciate your comment regarding the hydrogenation step and the possibility of cofeeding hydrogen into the sequential reactor. In our process, we opted for a commercially available hydrogenation catalyst for this well-studied unit operation. However, we did not consider cofeeding hydrogen to eliminate the hydrogenation of small olefins (feedstock) to maintain process carbon efficiency. Thank you once again for your valuable feedback and suggestions. Your input will help us improve our project and address the mentioned areas of concern. We remain dedicated to the successful implementation of our project and the advancement of SAF technologies.

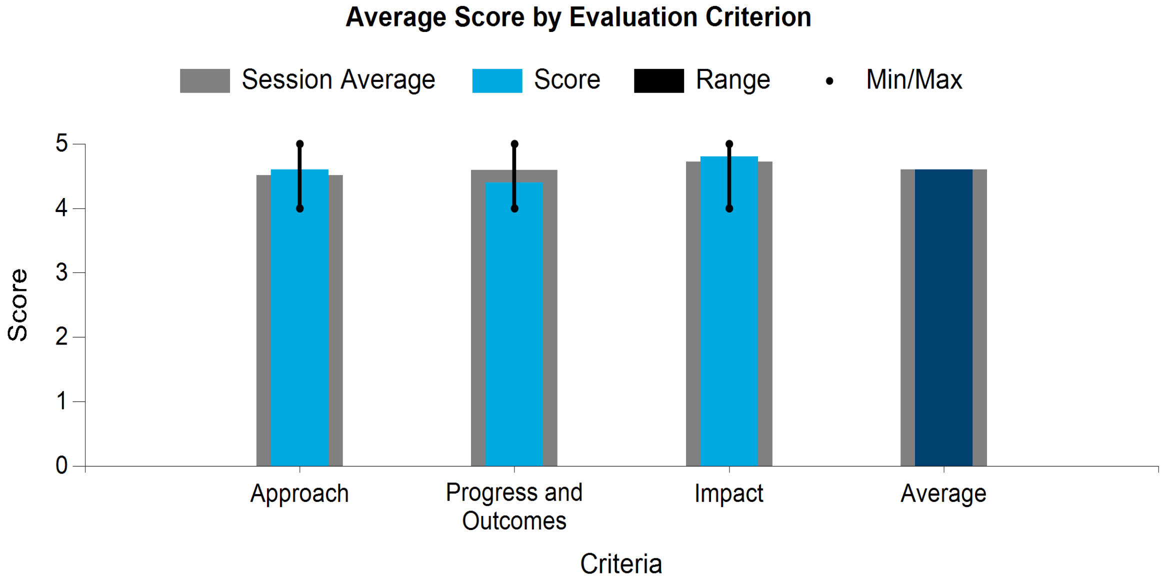
INTENSIFIED BIOGAS CONVERSION TO VALUE-ADDED FUELS AND CHEMICALS

University of South Florida

PROJECT DESCRIPTION

WBS:	2.3.1.414
Presenter(s):	John Kuhn
Project Start Date:	10/01/2018
Planned Project End Date:	04/30/2023
Total Funding:	$2,296,756.00

The overarching goal of this project is to convert biogas obtained from landfills, wastewater treatment plants, or anaerobic digesters to hydrocarbon fuels and chemicals. The specific goal is to develop an intensified process to reduce CapEx and enable a 15% reduction in MFSP relative to SOT. This project also aims to diversify products from biogas conversion and minimize flaring. The project management plan allows each organization to focus on its core capabilities to enable rapid catalyst and process development. The project leverages DOE resources, including ChemCatBio. Development is accelerated by an iterative, multifaceted approach to R&D challenges. Activities focus on critical success factors by addressing the go/no-go criteria and reducing project risks, which has included scale-up and use of real biogas. The approach is to integrate catalysts tuned to specific reactions into the same reactor bed. The project so far has more than tripled the single-pass production nonmethane hydrocarbon products compared to the SOT. Gains are obtained via catalyst development, concurrently to minimize the use of precious metals, and tuning of process conditions. It is anticipated that the inherently improved heat and mass transfer will lower costs, as well as reduce fossil GHG emissions compared to alternatives. The project addresses several BETO barriers, such as increasing yields from catalytic processes, decreasing the time and cost to develop novel industrially relevant catalysts, and improving catalyst lifetime.



COMMENTS

- This project is an excellent fit within the portfolio, and the catalyst characterization work is excellent. This is an amazing pivot. I think this was one of my favorite projects to review.

- The project develops biogas obtained from landfills or anaerobic digesters into liquid hydrocarbon fuels by developing an intensified process with conversion in a single reactor operating at mild conditions to reduce the capital expenses and enable small, modular reactors for distributed production. Currently, the conventional process uses three reactors, operates at high pressure, and has significant methane loss in the reformer. This project had to make an amazing pivot when they lost their original partner (Big Ox Energy), who was supposed to supply their biogas. They were instead able to partner with a local landfill and compress landfill gas (which is really impressive). This project aims to avoid carbon loss and undesirable products as they convert the biogas to chemicals, in line with BETO goals. To do this, they will need to create tailored catalysts with a range of functionality—all while combining process steps into a single reactor. The approach is collaborative; there is a great industry/lab/university partnership.

- This team blew away their 10% target of C_2 hydrocarbons—by achieving 16% hydrocarbon yield on the lab scale using real biogas. That is truly impressive. They have achieved improved catalyst activity by lowering the C-H activation temperature, reduced (maybe eliminated?) platinum with ruthenium and zinc (major cost driver), and demonstrated 100 hours of operation with high carbon efficiency. The characterization work to help determine mechanisms is really impressive. The economic and environmental assessments demonstrated that the capital and operating expenses can be made lower than comparable techniques—and that using landfill gas resulted in net NEGATIVE GHG emissions (huge win!).

- This project demonstrated a new pathway for biofuel production with an underused feedstock and developed a process intensification strategy that creates a low-cost pathway for production. This project is extremely industrially relevant, as it creates a diverse portfolio of products, and the interest from both upstream and downstream companies demonstrates this. This project demonstrates that there are truly cost-competitive pathways to produce valuable products from waste gases that would otherwise simply add to the GHG inventory. This is exceptional work.

- This project is focused on the conversion of biogas to liquid fuels under mild conditions and high carbon efficiency. The project has elements involving both catalyst and process intensification/reactor design. The general topic has a unique niche in the space of projects in the consortium and is clearly a need area for some level of investment. Although mixed hydrocarbon/CO_2 streams may contain less energy content, the opportunity to take such biogas mixtures and leverage them for production of fuels/chemicals of value should certainly be pursued to some degree in parallel with other biomass-to-chemicals platforms. The presentation identifies the challenges in this space well. Moreover, the project brings interesting aspects to the broader portfolio, including considerations of catalyst bed configuration and a separation component relative to catalyst construction and reactor design. There are unique features in these spaces that can add value to the broader ChemCatBio Consortium. Furthermore, the project has forward-looking goals—particularly in developing low-PGM to PGM-free catalysts—that align well with broader consortium efforts. Project roles are generally outlined in the presentation, with one exception. The reactor modeling portions could more clearly be delineated in the slides. The project benefits significantly from ChemCatBio ACSC and thermochemical platform analysis enabling projects. Given the potential complexity involved with overcoat catalysts, it seems that ACSC might offer additional opportunities beyond advanced characterization for the project and should be pursued where appropriate. Risk mitigation was also well identified, with sufficient strategies in place if particular scenarios play out. The go/no-go milestones were clearly achieved, and bifunctional catalysts were prepared with activity, selectivity, and stability profiles that appear promising. The further movement toward non-PGM catalysts and more realistic biogas streams is also notable. The use of precision synthesis in preparation of coated catalysts seems like a real game-changer in the removal of PGMs. The role of ACSC in the project is critical, particularly when it comes to characterization of the mixed metal systems. Reactor-scale modeling, assumed to occur within CCPC, is also a highlight of collaborations across the consortium. The Fe-In catalysts appear promising, given good selectivity despite somewhat reduced activity—however, the lack of atomistic modeling to elucidate what is happening at the active site is a potential missed opportunity and is something that should be considered in the future. This may be an example where a beefed-up emphasis on larger-scale modeling may come at the expense of a better handle on catalyst behavior. The reviewer does recognize that finite resources force these types of prioritization. The process intensification/reactor bed configuration studies also appear to be promising for ensuring that the overall process maximizes efficiency. Furthermore, various components of the system—potential contaminants, promoters—are studied in the context of the system, as one would expect. The move toward realistic feed gas mixtures is commendable and indicates that the technology is moving closer to viability. The economic modeling highlights a strong selling point of the project with potential for a negative carbon footprint. At the same time, coproduct formation and high alkane yield will likely drive economic viability. Continued modeling refinement will be needed to really determine system feasibility. This is a minor note, but more details about the reaction scale would be valuable in framing the current status of the technology for the reviewer. Later slides mention lab-scale studies, but some bars on this magnitude would be useful for the evaluation. Accomplishing the milestone for the formation of C_2 products is a notable outcome that is attracting interest from both downstream and upstream groups associated with biogas utilization. The publication and patent output (five papers and one patent) is also solid.

- The team made great use of characterization tools to help design the encapsulated catalyst concept, as well as supporting Fe-based FT materials. The modeling approaches seem interesting and should continue on the path of verification with experimental data.
- This approach of designing and encapsulating material has always been interesting and promising from a surface reaction engineering standpoint. The team should address the concept of pore restrictions from the external surface. The entire approach is very organized and understood by the team. The state-of-the-art technology is not modular for small-scale processing, needs additional units (e.g., water-gas shift, heat exchangers), and requires more severe conditions (>pressure), and this project solves all of these issues by invoking process intensification within the catalyst pellet. This approach allows for more innovation opportunities at the engineering reactor design scale, which is clear from the loading strategies investigated between the FT synthesis and reforming catalysts. The major tasks outlined for the project appear to be reasonable, with much of the work falling on the university partner. The durations of the tasks weren't mentioned. A project such as this could use a catalyst synthesis scale-up partner or leverage NREL's capability in this area. The actual contributions of the university to the technology readiness task should be explained. The team highlighted a couple of notable risks, namely, a real feed gas contaminant causing catalyst and product issues (solved by treating all gases) and equipment failure threatening process operation uptime (solved by purchasing spare parts and equipment). The DEIP should have been comprehensive because the project is university-led, as should the EJ commentary because landfills have a long history of being near disadvantaged communities. There were no comments on either issue.
- Modeling information was published in 2022 on designing outer core thickness along the axial profile of the reactor. The team made a good case for the impact on training students, releasing information to the public (via presentations and publications), and forming local industrial partnerships. There is an interest in knowing whether larger multinational process technology licensing organizations have inquired about this work yet. This pathway provides a sustainable route to transportation fuels using wasted biogenic carbon, which is worth highlighting.
- The team did an excellent job of characterizing the positive impact of incorporating zinc to a certain level on turnover frequency. The catalysis was clear, confirming the presence of zinc in the bulk crystalline and surface moieties. The TOS for data using dry reforming went out over 150 hours. The dynamic catalysis work using isotopic transient kinetics analysis, *in situ* X-ray photoelectron spectroscopy, and diffuse reflectance infrared Fourier-transform spectroscopy was impressive, as was the work using extended X-ray absorption fine structure and X-ray absorption near edge structure. The

conclusions from this work should be clarified a little further, as it looks like different experiments were being presented across a variety of objectives. For the pore restriction work, the team should present the entire product distribution rates, including any wax formation. The effect of indium promotion of iron FT materials was interesting. The dispersion count data seemed to show only up to a certain level of indium concentration. The team was able to show in a compelling way how activated CH_4 spent three times longer on the surface of the indium promoted, supported, dispersed iron surface. The materials spent >70 hours TOS. The team should define the selectivity and if normalized to 100%. Potassium-on-iron materials had a significant effect on C-C bond forming transformations. The team should report where the rest of the mass yield is going for combined bed testing. It looks like an online analyzer output. This project aims to develop an intensified process to reduce CapEx and enable a 15% reduction in MFSP relative to SOT. This is a project led by a university and participated in by the national lab.

- The team focused on tailoring the catalyst activities, designing bed configurations, and developing a zeolite coating that enables an *in situ* separation for reactions. The various R&D activities include catalyst synthesis, validation and reaction testing, materials characterization, design, TEA/LCA, and commercialization exploration with industrial partners. They also set go/no-go objectives to help evaluate the progress of the project. It could be beneficial if they reached out to ACSC to discuss the optimization of their zeolite-coated catalyst preparation and characterization. It could also be beneficial if they reached out to CCPC to analyze how the zeolite coatings may impact the heat and mass transfer.

- The R&D activities have illustrated appropriate progress that helps achieve the project goals. For instance, the team illustrated that their R&D has helped reduce the cost of catalysts by 40% and increase the catalytic activity at low temperatures significantly. It would be beneficial if the team could introduce TEA/LCA efforts into the R&D activities and use them as a tool to help determine the viability of technologies and processes.

- This project demonstrates a new pathway for biofuel production to BETO. If successful, it will enable the industrialization of a process that converts the underused feedstock—biogas—to valuable fuel products. The R&D activities have shown the potential of this process to be commercialized via intensification. The team also leveraged the R&D activities to connect academia, a national lab, and industry. It would be beneficial if the project could leverage the R&D activities more to enhance the DEI and workforce development.

- This study investigated intensified catalytic synthesis for the conversion of biogas into liquid fuels on a small scale to meet the requirements for landfill waste treatment. The research was a significant challenge, but its potential impacts are enormous. The study employed remarkable approaches, such as the tailoring of catalysts, close collaboration, and simulation/computation work. Both mechanistic understanding with many *in situ* techniques and the efforts toward commercialization with real gases and stability testing with impurities are very impressive, leading to numerous outstanding achievements, including satisfactory C_2 hydrocarbons yield and GGE. The stability of reforming/FT catalysts is a crucial factor to consider, as they are expected to operate for several years. Most zeolites exhibit coking and structural stability issues under hydrothermal conditions, despite having good initial activity. Additionally, metal migration from other catalysts could adversely affect zeolites. Therefore, further deactivation studies are recommended.

PI RESPONSE TO REVIEWER COMMENTS

- In addition to the many positive comments, our team appreciates the time and effort of the reviewers. We would like to note that many literature contributions are still in progress. As three Ph.D. students are wrapping up their respective dissertations on these topics, there are a handful of additional papers in the pipeline. Thus, we anticipate further contributions in the literature within the next year. We agree that the doped (e.g., indium) iron carbide catalysts are a great opportunity to delve deeper into structure-functional relationships and mechanisms. A subsequent proposal was written in collaboration with

NREL. The reviewer comments were positive, but the proposal was not awarded. We will look for other opportunities to dive deeper into this topic. We also agree with the reviews that additional examinations of deactivation would be great next steps in this effort. We apologize that at least one reviewer noted a lack clarity in the reactor modeling. We were limited due to time/space limitations. We also note that the collaboration with CPPC is in an early stage. We agree that such a collaboration, especially to leverage expertise in heat transfer effects, would be a great direction. There were some uncertainties about the overall mass balance. Carbon dioxide, carbon monoxide, methane, and condensables, including heavier hydrocarbons, oxygenates, and water, are the primary species in the effluent that are not reported with the TOS gas-phase gas chromatography analysis. For the hydrocarbons, the cutoff point for gas or liquid phase is ~C6/C7, based on the operation of the condenser. Those that are lighter than the cutoff chain length are included in the TOS data for C_{2+} and C_{5+}. The condensable hydrocarbons typically add ~4 mass % to the TOS mass yield. In a hypothetical case of 1:1 methane:carbon dioxide in the feed, ~53% of the feed mass is oxygen atoms, which does not result in the hydrocarbon products. Moreover, only one molecule of CO_2 is reacted per three molecules of methane ($3\ CH_4 + 2\ H_2O + 1\ CO_2 \Rightarrow 8\ H_2 + 4\ CO$) to achieve a hydrogen to CO ratio of 2:1, which is the molecular ratio in targeted hydrocarbons. Thus, there is a substantial amount of CO_2 in the effluent. The experimental studies were on a single pass. In our process simulations, we modeled recycling to increase the overall conversion to C_{2+}. With recycling, the non-condensables (CO_2, CO, and light hydrocarbons) can be used to boost the higher hydrocarbons. However, in any scenario, CO_2 and water will be formed to allow escape of oxygen atoms, which are not desired in the final product. We note that the project was funded under a FOA in which a DEIP was not required. We acknowledge that there are many potential benefits of new processes being applied to the waste industry.