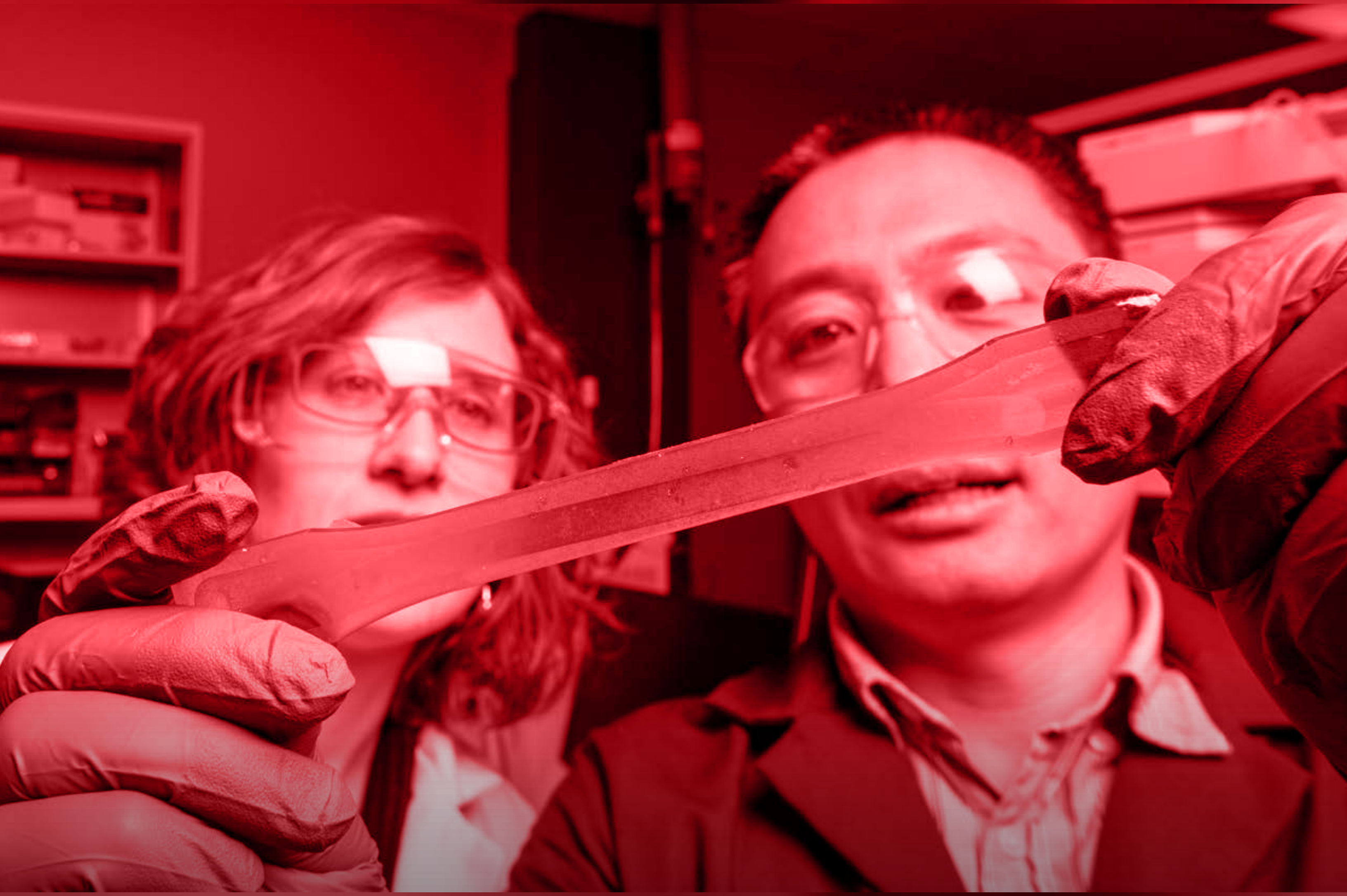


PERFORMANCE-ADVANTAGED BIOPRODUCTS, BIOPROCESSING SEPARATIONS, AND PLASTICS

TECHNOLOGY AREA

CONTENTS

INTRODUCTION

The Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics Technology Area is one of 12 technology areas that were reviewed during the 2021 Bioenergy Technologies Office (BETO) Project Peer Review, which took place virtually March 8–12, March 15–16, and March 22–26, 2021. A total of 20 presentations were reviewed in the Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics session by seven external experts from industry, academia, and other government agencies. For information about the structure, strategy, and implementation of the technology area and its relation to BETO's overall mission, please refer the corresponding Program and Technology Area Overview presentation slide decks, which can be accessed here: https://www.energy.gov/eere/bioenergy/2021-project-peer-review-performance-advantaged-bioproducts-bioprocessing.

This review addressed a total U.S. Department of Energy (DOE) investment value of $40.9 million, which represents approximately 6% of the BETO portfolio reviewed during the 2021 Peer Review. During the Project Peer Review meeting, the presenter for each project was given 30 minutes to deliver a presentation and respond to questions from the Review Panel.

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

BETO designated Gayle Bentley as the Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics Technology Area Review Lead, with contractor support from Ben Simon (Boston Government Services). In this capacity, Gayle Bentley was responsible for all aspects of review planning and implementation.

PERFORMANCE-ADVANTAGED BIOPRODUCTS, BIOPROCESSING SEPARATIONS, AND PLASTICS REVIEW PANEL

Name	Affiliation
Matt Tobin*	Independent consultant—Formerly: Lygos, Amyris, and Codexis
Peter Keeling	Iowa State University
Karen Draths	Michigan State University
Ray Miller	Independent consultant—Formerly: DuPont
Bill Orts	U.S. Department of Agriculture
Sharon Haynie	Independent consultant—Formerly: DuPont and University of Delaware
Paul Bryan	Independent consultant—Formerly BETO, Sandia National Laboratories, and Chevron

* Lead Reviewer

PERFORMANCE-ADVANTAGED BIOPRODUCTS, BIOPROCESSING SEPARATIONS, AND PLASTICS REVIEW PANEL SUMMARY REPORT

Prepared by the Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics Review Panel

INTRODUCTION

The Review Panel was impressed with the overall strategy, technical quality, implementation, and progress on projects presented at the Peer Review. This is a wide-ranging technology area with appropriate breadth and strong science evident across the three programs. In the words of one reviewer, "There is a lot to like here."

The review process was coordinated effectively by the technology manager, especially given the first-time virtual setting. Presenters were provided with a master slide deck, aiding presentation quality. Suggested upgrades would be to include technology readiness levels (TRLs) at the project start, present, and finish on quad charts, and more use of process diagrams. Use of the Heilmeier Catechism was effective in the project framing. For question-and-answer (Q&A) sessions, the panel and presenters engaged in productive discussions. The Review Panel used a separate communication channel during the review process, which was especially helpful in coordinating Q&A sessions. Suggestions from previous feedback appeared to be incorporated, most notably the addition of a plastics consortium and improved management practices.

The Review Panel members represented a range of backgrounds to cover the broad scope of the technology area, each panelist bringing their own lens to the review (science and technology, process and separations, commercialization, project management expertise). Despite different backgrounds, individual reviewers were often aligned on relative ratings, with some variation and exceptions that are detailed in the report. In addition to sound science and technology, Review Panel members were aligned on the importance of the ability to scale and economic advantage. Considerable weight was placed on engagement of industrial advisors; projects with appropriate industrial inputs tended to be strongest.

This technology area summary provides only a high-level view. More detailed individual reviewer feedback can be found in the project reviews that follow. Principal investigator (PI) responses to reviewer comments are equally important, providing clarifications and information that may not have been anticipated or selected for inclusion in the original presentations, where strict time limitations were applied.

STRATEGY

Overall Strategy

The overarching goal of BETO is to dramatically reduce carbon emissions that affect climate change. Burning fossil carbon for transportation, energy generation, and in chemical manufacture produces significant point sources of those emissions. Reducing fossil carbon utilization in plastics, chemical products, and in separations can also contribute meaningful reductions to the overall carbon emissions, which is in line with the strategy. The three component programs within the technology area contribute to the strategy by discovering and developing potential replacement performance-advantaged bioproducts (PABPs), plastics, and processes. Funding opportunity announcement (FOA)- and annual operating plan (AOP)-funded projects are represented, each with control mechanisms appropriate for their charter. For example, the AOP funding has some autonomy in their verifications; the three-step verifications for FOA projects apply a "stress" test in the very beginning to ensure good probability of success and can identify issues at an early stage.

Performance-Advantaged Bioproducts Strategy

The PABP program is identifying and producing a sensible variety of higher-value, performance-advantaged bioproducts. These may be integrated with biofuels production in a biorefinery, where the valorization of feedstock components that are otherwise underutilized or discarded is an opportunity to improve economics. Industry tends to favor tried-and-true incumbent products to limit risk, so new products and processes with performance and economic advantages are best positioned to compete. Funding is well balanced between AOP and FOA mechanisms, and the use of consortia that bring together a range of expertise and capabilities is an excellent use of funds. Most projects have utilized industrial input, but the strategy involved in prioritizing targets might further benefit by involving materials experts/advisors early on in the process. Utilization of business metrics in prioritization—return on investment, net present value, along with more rigorous techno-economic analysis (TEA)—earlier in the process would help to focus investment on the best opportunities. A prototyping philosophy would be useful to develop minimum viable products, which would be early-stage prototypes with some basic features that can be provided for external validation and feedback for improvement (or redesign).

Bioprocessing Separations Strategy

Separations can account for 50% or more of the capital and energy consumption in process operations, often rendering processes and biorefineries unprofitable. This provides a clear mandate for the program: identify and develop separations technologies that can be scaled economically, ideally applicable across products (crosscutting). Separations that cover diverse needs are in scope—upstream (feedstock) and downstream recovery (product). These technologies are also useful for prototyping. A TEA/life cycle assessment (LCA) component is being used to quantify potential impacts. AOP funding is appropriate because shared resources would be difficult to duplicate under the FOA structure. The program solicits industry input, but the Separations program has gaps that would benefit from upgraded consultation from commercially experienced parties. These are discussed more thoroughly in the project reviews that follow.

Plastics Strategy

Based on the draft Plastics Innovation Challenge Roadmap, program objectives address the end-of-life fate of most plastics, achieve >75% carbon utilization from plastic waste, develop cost-competitive recyclable-by-design plastics, and reduce energy consumption by 50% relative to virgin material production. A metric for greenhouse gas (GHG) reduction is also being developed. These are ambitious targets, but they inform program mission, goals, and targets. To achieve strategic outcomes, the program addresses the minimization of nonrecyclable plastic waste by developing technologies to deconstruct plastic waste streams and recover reusable material, identifying new circular-use plastics and developing energy-efficient production, including bio-based approaches. The panel was enthusiastic about the plastics program strategy overall, with some different opinions on scope and potential gaps. For example, although they represent a major part of the waste stream, polyethylene terephthalate (PET)-containing fabrics are not included in the feedstock strategy. Chemical or thermochemical recycle of waste plastics to manufacture monomers and fuel precursors is also a potential technology gap. The panel expressed considerable concern that plastic waste recycle is not addressed. Success of programs with waste recycle inputs will depend on vastly improved mixed plastic waste recovery and sorting (ideally not only from land but also oceans). It is debatable if this belongs within the program; what is not debatable is that the environmental impact of waste plastics is a severe problem in need of immediate mitigation. Ultimately, policy that drives industry and public behavior is needed to achieve widespread commercial adoption. Breakthroughs achieved within the plastics program could provide considerable "technology push" to catalyze policy development. The overall level of funding is appropriate for such a large mission, with funding mechanisms split between the BOTTLE™ (Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment) Consortium and FOAs. Current funding leans toward BOTTLE, appropriate at this stage to best leverage national laboratory expertise to build a technology foundation. Industry and stakeholder inputs are generally solicited to develop strategy. Ideally, stakeholders should include not only new entrants trying to replace incumbent technology but also incumbents themselves who have technical, scale-up, and market expertise.

STRATEGY IMPLEMENTATION AND PROGRESS

Overall Implementation and Progress

The range of projects in this technology area is impressive. Projects are tied to its strategic direction, and many are at the technological leading edge in their fields. Projects themselves have clear goals to develop robust technologies and processes, and they track progress with defined decision points. Projects are generally on track in their progress, and the likelihood of achieving near- to mid-term goals is broadly favorable. Most feedstocks under consideration are derived from land-based sources. Consideration of ocean-derived plants would offer more diversification—for example, kelp or related large seaweed sources, which have the added benefit of not using land, fertilizer, or fresh water to grow, therefore conserving those resources for food production. These types of plants offer both lignocellulose and alginate polysaccharide sources.

The technology area is well managed; the director has good working relationships with the PIs and an understanding of the progresses and challenges of each project. The creation of consortia in each program was very well received by the Review Panel. In every program area, there are appropriate mechanisms to leverage cross-laboratory resources and knowledge. In general, project management practices have improved and even excelled in some projects. Effective project coordination is reflected by clear management structures and communication plans, especially benefiting multi-institutional and geographically dispersed projects. This has been particularly important because in-person exchanges have been affected by the COVID-19 pandemic restrictions. Concerning risk management, although risk identification was satisfactory, risk rating, ranking, and mitigation are improvement opportunities for some projects. Stakeholder input from industrial or other appropriate advisors has been key to develop technologies with the potential for commercial impact and industry engagement. The strongest projects tend to have stakeholder input from the outset and on a continuing basis relative to those with less (or delayed) input.

The panel would like to emphasize the importance of active management in making timely difficult go/no-go decisions so that efforts can be directed to the most impactful areas. Overreliance on a favorite tool should be on management's radar; there is some precedent for this in the national laboratories and elsewhere. There may be opportunities for improvement in the portfolio selection and management process by employing more of a business lens—for example, developing metrics such as return on investment and net present value to select and rank opportunities.

Performance-Advantaged Bioproducts—Strategy Implementation and Progress

The Review Panel reacted favorably to the funding of a wide range of innovative projects at different stages of development, including cutting-edge predictive technologies, such as machine learning to identify a variety of PABPs, biosynthetic routes, materials discovery and synthesis, and pilot scale-up. Much of the program is focused on the identification of multiple PABPs, several of which could spin out into future projects. The approach, when fully developed, could open up many renewable and sustainable replacements for polymers, plasticizers, and additives. Highly targeted projects are included in the portfolio (the pilot-scale development of polyacrylonitrile and the Tulipalin A enzymatic pathway project). FOA-funded projects are nicely diversified: designing bio-advantaged vitrimers as closed-loop bioproducts, the "bioprivileged" molecule discovery project, the Tulipalin A project, and the cellulose-chitin composite project for barrier packaging applications.

Diverse feedstocks are represented, including lignin, cellulose, fermentable sugars, and chitin. The latter is unique within the program, being the only non-land feedstock (mainly derived from shellfish exoskeletons, which are a significant volume waste product). Lignin-based projects, which include lignin-derived thermoplastics and bioinsecticides, are attempting to address the challenges associated with complex mixtures of molecules by avoiding the need to separate each component. This could be an exciting development if successful because it would decrease the operations and costs of purifying more specific lignin streams; however, the availability and variability of lignin streams presents a significant risk to lignin programs.

Progress across the PABP program was generally viewed as on track by the panel, with a good probability of short- and medium-term success. Projects receiving the highest overall scores were Synthesis and Analysis of Performance-Advantaged Bioproducts, the Renewable Carbon Fibers Consortium, and the Inverse Biopolymer Design Through Machine Learning and Molecular Simulation projects. All projects in the area received overall favorable ratings, with some differences in panel feedback. Projects with the largest rating variances were the Melt-Stable Engineered Lignin Thermoplastic and the Bioinsecticides projects. Deeper insight into reviewer feedback is available in the individual project reviews.

In the long term, new PABPs will face commercial adoption hurdles, particularly in applications where high-performance materials and/or purity specifications are essential. Key questions remain regarding scale-up and how PABPs match up with biorefinery scale and location.

Bioprocessing Separations Implementation and Progress

A broad mix of technologies for solid, liquid, and vapor phase separations are represented in the program. The Separations Consortium is proving to be a great way to leverage the cutting-edge expertise of the national laboratories. Due to its management effectiveness, approach, progress, and potential for impact, it received the highest combined score in the technology area review. Progress on near- to mid-term goals is generally on track. Although industry engagement appeared reasonably well represented, some gaps were highlighted. Notably, members of the Review Panel were not in agreement with the 2,3-Butanediol Separations project TEA. This highlights an opportunity to improve industry engagement at early project stages to obtain critical feedback and a reality check on what is scalable. The Review Panel suggested adding other technologies to the list under consideration, including reactive distillation, centrifugal enhanced heat transfer and extraction, and flash recovery from volatile pressurized extraction media.

Plastics Strategy Implementation and Progress

The plastics program includes a broad basket of projects at different levels of development (many at very early-stage TRL). Analyses of different plastics across performance and TEA/LCA metrics are being performed, with several targeted within the program for recycle and/or replacement. The portfolio includes projects using diverse feedstocks (recovered plastics, carbon fiber reinforced epoxy composite [CFRP], and biomass components such as lignin). The portfolio is aligned with the strategic direction, is actively managed, and is making good progress. The formation and progress of the BOTTLE Consortium was particularly well received by the Review Panel. This consortium is making significant progress and is capable of high impact across a large spectrum of plastics, although with its complex array of targets, active management decisions are likely to be needed. The Responsible Innovation for Highly Recyclable Plastics (ResIn) project is also rated highly, with very promising progress using a computational approach to discover pathways to biomanufacture biodegradable polyurethanes (PU).

As with other programs, market size and relative valuations of products were at the forefront of reviewer scrutiny, as was availability of the required feedstock for each process. For example, polyester polyurethanes may offer higher-value outlets and be more recycle-friendly than replacements for isocyanate polyurethanes; market size of thermosets (and carbon fiber reinforced thermoset plastics) appear relatively small in the total reinforced engineering plastics markets today. Regarding feedstocks, attaining efficient recovery of waste feedstocks at scale (including lignin, mixed wastes, and dispersed waste in oceans) is a necessary precondition to enable the commercial adoption of those projects requiring them.

There were some differences of opinion from the Review Panel. For example, some reviewers were impressed by the innovative science and potential of the biological PET degradation efforts, whereas others were doubtful that the enzymatic approach to depolymerize mixed wastes into useful monomers could be competitive with existing chemical recycle processes. An apparent duplication of effort was also noted on this approach between BOTTLE and the Bioconversion of Heterogenous Polymer Waste project. A concern over polyhydroxyalkanoates (PHAs) as part of the plastics program was flagged due to their current performance and commercial shortcomings, although developing performance-advantaged PHAs appears to be under consideration.

Overall, the plastics program is viewed as a solid effort to address key challenges that are barriers for transformative breakthroughs to achieve a low-carbon circular plastics economy. Given its complexity and size, a disciplined active management approach is required to focus on the most promising areas, including early-stage TRL projects to supply a pipeline of promising technologies, and sunsetting those that may not fulfill expectations.

RECOMMENDATIONS

What are the top three most important recommendations that would *strengthen* the portfolio in the *near to medium* term?

- The availability of feedstocks from plastic waste recycle/recovery is particularly uncertain, so it is worth considering how the technology area can influence this. Coordination and collaboration across government funding agencies (e.g., National Science Foundation/DOE Office of Energy Efficiency and Renewable Energy) and R&D development arms of agencies (e.g., U.S. Department of Transportation, U.S. Environmental Protection Agency) would be an efficient use of taxpayer dollars.
- Ensure the best use of industry/commercial/subject matter experts and robust industry advisory boards (IABs) from the onset of projects and throughout. This has improved over previous years but continues to vary, so there is room for upgrading and universal best practices. There were examples where this would have meaningfully improved project/product selection and design. It is not enough that appropriate advisors are involved; the communication process must be optimized to make the most of their expertise. Materials experts are a specific area to consider.
- Introduce the concept of prototyping. Aim to identify products and technologies that can be put into the hands of "customers," where appropriate, to test at early and regular time points. This would also be helpful in identifying meaningful decision points.

PERFORMANCE-ADVANTAGED BIOPRODUCTS, BIOPROCESSING SEPARATIONS, AND PLASTICS PROGRAMMATIC RESPONSE

INTRODUCTION

The program thanks the reviewers for their dedication and thoughtful review of this diverse portfolio. BETO appreciates the reviewers' efforts and expert recommendations. The program agrees with reviewers that the Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics portfolio can collectively advance the deployment of technologies critical to decarbonizing industry through discovering and developing potential replacement PABPs, plastics, and processes, as stated by the reviewers. BETO also agrees that continued industry engagement and the adoption of industry terminology may help further accelerate the deployment of BETO technologies. Specific recommendations and feedback will be discussed and considered when working on future project selection and program design, as future appropriations allow. For each recommendation, BETO provided a general response, followed by some specific examples of how they will be integrated into the two technology areas covered in the session.

Recommendation 1: Address availability of feedstocks from plastic waste recycle/recovery.

The program thanks the reviewers for raising this concern. It will be critical to the success of BETO and DOE plastics efforts to enable the efficient conversion of waste plastic into value-added materials, or even fuels. There is an enormous reservoir of plastic waste that could be potentially converted into higher-value products in a market-driven manner. Even with increased recycling and reduced plastic use, the rate of plastic waste production is anticipated to grow at a dramatic rate. New technologies to address existing plastic waste and to preventing new waste from accumulating will be critical.

As the reviewers highlighted, plastic waste is a challenging feedstock. One of the first steps in addressing this challenge is developing a baseline understanding of the scale and characteristics of plastic waste as a potential feedstock. BETO, in coordination with other DOE offices, including the Advanced Manufacturing Office and Water Power Technologies Office, has already begun a resource characterization of plastic waste. One study is evaluating the geographic distribution of plastic waste to better understand where plastic waste is produced, in what quantity, and where it is processed. Another study is focused on characterizing plastic entry into waterways. Additionally, a recent study published by members of the BOTTLE Consortium calculated the GHG and energy demands of plastic production across the plastic life cycle. This study clearly outlined the potential opportunity to reduce the GHG emissions associated with plastics use. Additional studies will further characterize the opportunity and challenges associated with plastic waste. These studies will be leveraged heavily in determining BETO's strategic direction in this area to ensure that federal funds are used to tackle the most pressing issues.

Beyond these DOE efforts, BETO is actively coordinating with representatives from the U.S. Environmental Protection Agency, the U.S. Department of State, the National Science Foundation, and the National Institute of Standards and Technology to ensure our efforts are complementary to other agencies. BETO plans to continue coordination with these agencies as well as expand coordination to other agencies and organizations.

Recommendation 2: More integration of industry engagement.

BETO thanks the reviewers for recognizing improvements in industry engagement and involvement in recent years. BETO has encouraged increased industry engagement and will continue to ensure our research activities are informed by industry stakeholders.

BETO employs two primary mechanisms to ensure direct collaboration and investment from industry: cost share and directed funding opportunities (DFOs). BETO requires all FOA recipients to contribute cost share. By requiring cost share, applicants must identify an industry partner willing to contribute their own funds or efforts to the proposed project. As a result, our FOA recipients in recent years have increasingly developed meaningful collaborations with industry, providing a shorter path to commercializing new technologies and integrating industry perspectives into the core project design.

DFOs provide an opportunity for industry to engage directly with BETO's core AOP projects. In this panel, the Bioprocessing Separations Consortium has hosted DFOs in order to leverage the consortium's capabilities to solve pressing challenges facing industry. The successes from this effort were highlighted in the Bioprocessing Separations Consortium's overview presentation. For example, the consortium developed various separations approaches for glucaric acid purification from fermentation broth for the industry partner Kalion. The consortium's expertise was able to solve a real problem facing this company, integrally connecting industry needs with the consortium's activities.

Beyond these project-level mechanisms, BETO also regularly solicits feedback from relevant stakeholders by hosting requests for information (RFIs) and workshops/listening days. An RFI was released in 2020 to solicit feedback from relevant stakeholders on the key priority areas facing bioprocessing separations. A total of 13 responses were submitted, 6 from industry. Information from this RFI was used to shape BETO's Fiscal Year

2021 FOA, to ensure that industry feedback informs BETO's funding solicitations. Another RFI was released in 2021 to solicit feedback on DOE's strategy for plastics, as detailed in the draft Plastics Innovation Challenge Roadmap. This RFI received 43 responses, with 15 from industry. Responses from this RFI were used to inform DOE's (and BETO's) *Plastics Innovation Challenge R&D Strategy*.

Workshops and listening days are one other mechanism that BETO uses to engage industry. The Bioprocessing Separations Consortium hosted an Industry Listening Day in July 2021. This event brought stakeholders from academia, industry, and national laboratories together to identify key opportunities for separations research. Prior to the official launch of the BOTTLE Consortium, BETO and the Advanced Manufacturing Office hosted a workshop in 2019, *Plastics for the Circular Economy Workshop,* focused on soliciting feedback from stakeholders on the key challenges and opportunities facing plastics research. The feedback from that workshop was published in a report and has provided key information to BETO during strategic planning efforts.

Although BETO has worked to improve industry involvement, BETO appreciates the constructive feedback that these efforts have further room for improvement. BETO agrees that beyond involving advisors, clear communication channels must be established to fully leverage the expertise of the advisors. Reviewers also highlighted the need for materials experts, in particular. This is a helpful perspective, and BETO will ensure a range of advisor expertise is represented in any advisory group. One point BETO would like to highlight that was not addressed by reviewers is diversity and inclusion. BETO has made it a priority to improve diversity, equity, and inclusion in all efforts. BETO will encourage consortia and FOA applicants to consider diversity and inclusion in industry engagement. Inclusion, beyond diversity, may be one effective mechanism to ensure that all perspectives are reflected.

Recommendation 3: Introduce prototyping.

BETO thanks the reviewers for this suggestion. Several BETO technologies have shown substantial commercial interest and promise, including renewable acrylonitrile and performance-advantaged nylon. As part of the project scope, when appropriate, projects are encouraged to produce a demonstration-scale quantity of the product of interest. This recommendation complements these existing activities. BETO may consider incorporating a more formal prototyping pathway for the more applied projects.

Related to prototyping, BETO supports the Energy I-Corps program, part of the Office of Technology Transitions. This program teams researchers with industry mentors for two months of training to develop technology transition skills, including defining value propositions, conducting customer interviews, and developing viable market pathways for the researchers' own technologies.

UPCYCLING OF CFRP WASTE: VIABLE ECO-FRIENDLY CHEMICAL RECYCLING AND MANUFACTURING OF NOVEL REPAIRABLE AND RECYCLABLE COMPOSITES

Washington State University

PROJECT DESCRIPTION

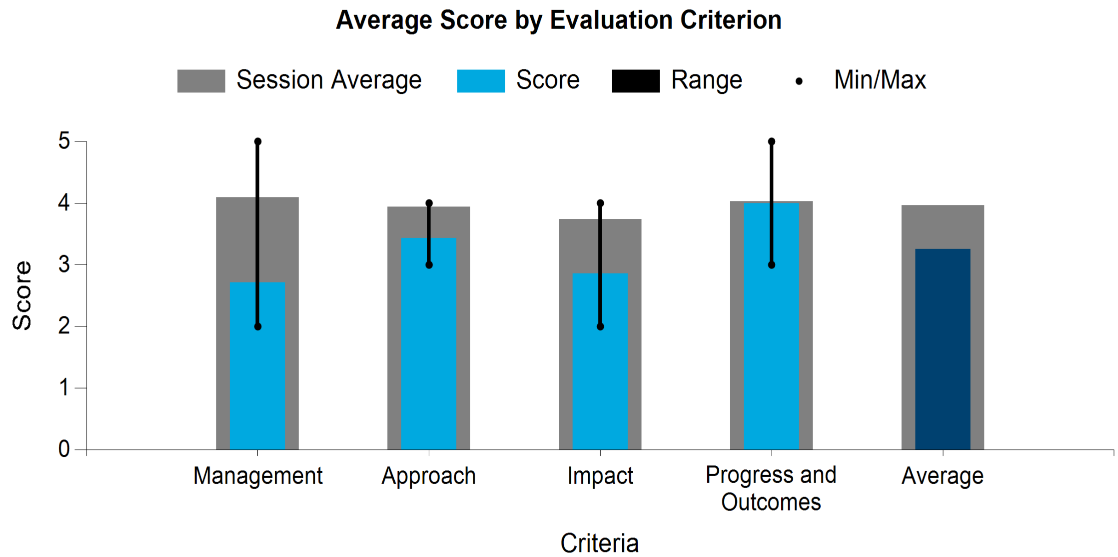
WBS:	2.2.3.400
Presenter(s):	Jinwen Zhang
Project Start Date:	10/01/2019
Planned Project End Date:	12/31/2022
Total DOE Funding:	$1,609,883

The rapid growth of the polymer composite market also propels researchers to find value-added applications for the out-of-date prepregs, manufacturing scraps, and end-of-life components. At present, most polymer composite wastes are disposed by burning or landfill. To make use of the residual value and reduce the burden to the environment, various mechanical, thermal, and chemical approaches have been attempted to recover fiber, matrix, or both; however, these current practices are disadvantageous due to low cost-effectiveness, energy inefficiency, generating secondary waste, and bringing new pollution problems.

In this project, the researchers aim to develop a viable chemical recycling technology for carbon fiber reinforced epoxy composite (CFEP) wastes, which is eco-friendly, energy-efficient, and cost-effective in the breakdown of the matrix polymer structure and makes use of both recovered carbon fiber and decomposed matrix polymer in new advanced composite manufacturing. The key innovation resides in the integration of the mild chemical recycling of CFEP and the preparation of new composites.

The success of this project will address the most significant cost/technology barriers for thermosetting composite recycling. With this technical research success, the developed technology will move from the lab scale to the small pilot scale in collaboration with commercial partners. We expect to advance the technology from current TRL 2–3 to TRL 5–6 by the end of this project.

The project is led by Washington State University professor Jinwen Zhang, and the major team members include Tuan Liu, Michael Wolcott, both from Washington State University; Long Jiang, of North Dakota State University; and Kevin Simmons, of the Pacific Northwest National Laboratory (PNNL).



COMMENTS

- The research teams have adequate connections to each other and to the BETO project management, but they do not seem to be connected to other teams doing work in this area. It is not apparent how industry is connected to this research to guide the approach and transfer the results to future users. The risks—such as supply, costs, and disposal of treatment materials—are not clearly identified, and their mitigation strategies are not adequately addressed. The collection and recovery of useful carbon fibers from CFRP is not adequately explained. The form of final recovered carbon fiber seems inconsistent with the recycling approach of compounding it with nylon 6. The performance and cost of new nylon 6 resins containing recovered carbon fiber is not compared to the performance of new materials to show incentive to collect, process, and recycle CFRP. Carbon fiber plastics is today a relatively small component in the total reinforced engineering plastics markets. A TEA is not presented to understand the relative competitiveness of this approach to recycling carbon fiber thermosets versus other options. They have made good progress in demonstrating the technical feasibility of the proposed approach for the stated objectives.

- Management: The presentation covered the bare minimum about the makeup of the team. No information is provided about how this team communicates with each other, decides future steps, or adjust plans when contingencies are required. Some mention of specific corporate partners would strengthen this section. Approach: The experimental methods are appropriate, describing the basic technology. The flowchart is appreciated. Questions arise about where the water goes during the drying step (after decomposition) and how salty this water would be. This may be significant. Impact: In the project overview, citing an old forecast from 2014 to describe future demand for carbon fiber does not inspire confidence in the current relevance of this work. How much carbon fiber actually goes to landfills? Many larger pieces—including automobiles, boats, and airplanes—would likely not go to landfills. The presentation could have used some careful editing and/or a clear glossary to clarify things. As written, it is confusing and distracting. Some mention of how the substrates were obtained and/or a projection of how they would be recycled so that they arrive at some processing plant would be appreciated. Modeling of that step could show the expected cost points for making this process economical. Progress and outcomes: It is commendable that milestones 1.1–1.4 include the preparation of nylon 6 composites with the recyclates and preparation of new epoxy using decomposed polymer as reactive ingredient. This is good progress. Completion of the other milestones is on schedule as well. Patents and publications outline a good start to the work.

- Management: The management plan and implementation appear to be high level, and there is a well-organized consortium (Washington State University, North Dakota State University, PNNL) and cooperation with an IAB. The team is showing good progress and appears to be well organized with clear management organization. Approach: There is substantial merit and significant potential in this approach of developing an eco-friendly, cost-efficient chemical recycling of carbon fiber composites. The aim is to develop a viable chemical recycling technology of CFEP wastes with reuse of the recyclates in new composites. Specifically, the plan is to integrate mild chemical recycling of CFEP by preswelling and delamination in order to prepare new composites. Impact: The project impact appears to be headed toward promising outcomes, with thorough review processes and deliverables in place. The chemical recycling, recovery, and reduced carbon footprint toward reuse all appear to be on track. A key future deliverable will be to identify significant cost/technology barriers for thermosetting composite recycling. Progress and outcomes: Results are showing great promise relative to milestones (effective degradation and delamination and partial milestone completion for reclaimed carbon fiber). The project appears to have coped well despite the COVID-19 impact, and progress and outcomes look promising. Critical future efforts will include the reuse of recyclate and economics. Partnering with companies would seem like a good addition for this project in order to focus on the kinds of metrics they would demand for recycling CFEP and the reuse of the nylons or fibers.

- The management plan is only a rudimentary organizational chart. There is no risk mitigation plan. Approach: Not much is said about the choice of zinc acetate. Reusing the “catalyst” solution at least three times … what then? Disposal costs? There are some energy-intensive steps involved, and acetic acid has some MoC issues. The process diagram seems to show only one product, not two. Are the polymer and fiber recycled together? The impact would be substantial if beneficial use can be made of both carbon fiber and polymer matrix from recycled materials (assume costs, wastes, etc., are acceptable). The team has made good progress given the time, percentage costed, and challenging situation during the past year.

- The project team provides a good general overview of carbon fiber recycling technology and a helpful pie chart displaying carbon fiber demand versus application. The project applies a team member’s proven zinc catalyst system to induce a mild chemical degradation that delaminates and degrades the thermoset without disrupting the carbon fiber’s structure, thus preserving its high value. This milder treatment will overcome deficits inherent in the incumbent approaches (thermal, mechanical, strong acid). The project status report could be significantly strengthened by: (1) providing at the outset a list of all the milestones with projected timing over the multiyear funding cycle; and (2) including more data details in their milestone progress summaries and frame completion or partially completed status in a more meaningful and measurable context (e.g., Milestone 2.1 and Milestone 3.1 have conditions described, but one is marked completed and the other partially completed). Generally, without the context, it is difficult to assess the significance of the milestones met. Finally, the team did not address the potential challenges and risk mitigation strategies.

- The use of mild conditions to pretreat and depolymerize CFEP seems a marked improvement over more severe processes described in the literature, and it is innovative (patented). Inclusion of a process diagram is very helpful in understanding the project. The impact of a mild process is clear, as is its reuse of carbon fiber and matrix polymer. The project has made good progress on milestones and appears to be on track to date, with pretreatments demonstrated on automotive and aerospace CFEP degradation. It will be interesting to see how this material can be reused and how the process can scale to meet economic targets. The project has a clear management team and communication plan. Industry input was noted although not detailed; risk identification/mitigation planning was not detailed.

- This project aims to provide energy-efficient, cost-effective recycling technology for CFRP and to recover and reuse the carbon fiber and matrix polymer in composite manufacturing. Tasks have been assigned to project participants, but inadequate information is provided regarding sharing of data. No risk assessment or mitigation plan is outlined, and no go/no-go decision points are included. A patent describing the technology has been issued, but industrial partners are not identified, jeopardizing the impact. Decomposition studies are reported, although it is not clear if conditions have been optimized. Characterization of recycled materials was not reported. Process flow diagrams indicate recycling of zinc acetate catalyst approximately 10 times; however, recycling experiments are not reported.

RECYCLABLE THERMOSET POLYMERS FROM LIGNIN-DERIVED PHENOLS

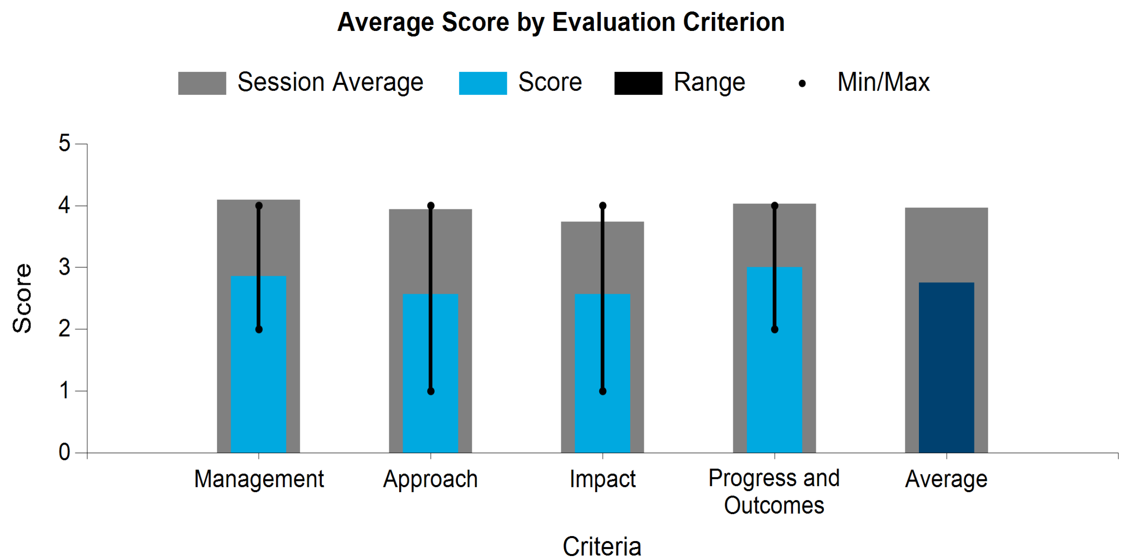
Spero Renewables, LLC

PROJECT DESCRIPTION

WBS:	2.3.1.416
Presenter(s):	Ian Klein
Project Start Date:	10/01/2019
Planned Project End Date:	08/31/2022
Total DOE Funding:	$2,000,000

Recent innovations at Spero Renewables have resulted in a proprietary technology for producing decomposable and recyclable thermoset polymers. Thermosets are a class of polymers that are irreversibly cured from soft solids or liquid prepolymer, with the aid of heat or other action of energy. Because of the permanent cross-links, thermosets generally possess outstanding mechanical properties, chemical and thermal resistance, and excellent insulation. Thermosets are now commonly used as the plastic matrix in performance composites, also known as carbon fiber reinforced composites. Despite the outstanding material properties of carbon fiber reinforced composites, the non-decomposable and nonrecyclable nature of thermosets has limited the widespread application of thermoset composites. It is estimated that hundreds of millions of dollars are lost each year from the landfilling of thermoset composite wastes.

Spero Renewables' recyclable thermosets incorporate bio-based feedstocks derived from lignin, which can be incorporated at more than 50% of the mass of the polymer. Through this project, the technology is being refined to produce thermosets that can be decomposed under mild conditions yet possess comparable thermomechanical properties to conventional bisphenol A-based thermosets. Spero's thermosets can be chemically recycled, with the thermomechanical properties of recycled thermosets comparable to virgin thermosets. Through collaboration with Argonne National Laboratory (ANL), a comprehensive LCA of the synthesis and recycling of Spero's thermosets and carbon fiber reinforced composites is underway. TEA is being used to validate the commercial potential of Spero's technology. At the conclusion of this project, Spero expects to have sufficient data to enter large-scale pilot production ahead of commercialization.



Recyclable Thermoset Polymers from Lignin Derived Phenols

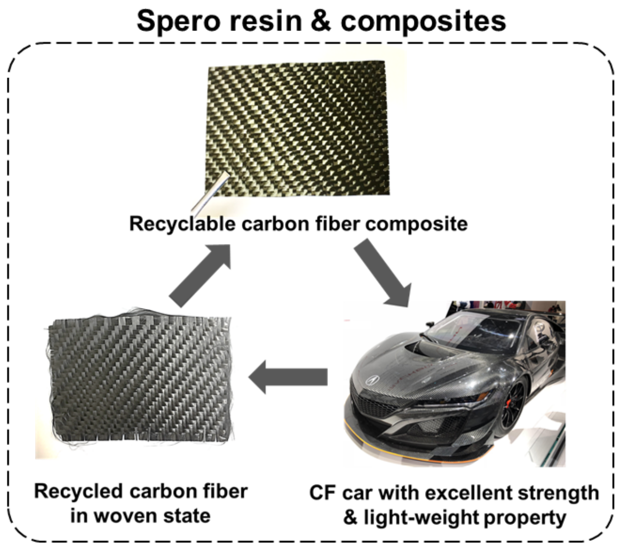


Photo courtesy of Spero Renewables, LLC

COMMENTS

- Specific industrial participants not identified in the project write-up should clearly indicate how they are influencing the goals, risk mitigation, and route to markets. I can't tell if there are connections to other BETO projects dealing with developing thermosets. The TEA's links to goals and risk mitigation are not shown. Need to show how the recovered carbon fiber will be utilized in representative reinforced lignin thermosets, and show the performance comparison with those types of commercial products. The project relies on the availability of sufficient lignin of the right composition to manufacture recyclable thermosets. I would like to see how the infrastructure for producing new resins and recycling used resins is being addressed in the plan to commercialize. Thermosets are a small part of the market, and lignin availability is currently limited. Critical demonstrations of decomposition and water resistance remain to be completed. TEA needs to be completed to determine if the approach being developed will lead to cost-competitive thermosets.

- Management: The team appears to have experience and appropriate expertise. The management structure was only broadly outlined, with no real specifics, so it is not clear how this team is organized under this program. How does it work with partners? A communication plan was not described. Nothing was presented on how the team will deal with any feedback or changes in plans. Everything in this report was minimal, requiring imagination on the reviewers part.

  Approach: The approach was so broadly outlined that it did not describe anything but a general approach to creating general lignin-based resins. The publication listed at the end of the presentation is only a review, so it provides little specific detail on how this team will proceed. Nothing in this presentation made their approach specific to lignin nor was anything presented that appeared particularly novel. This write-up required a leap of faith by the reviewers to believe that progress was as described. The technical approach was too broadly written to provide much to review.

  Impact: The biggest question in this field is to ascertain how this project is different from lignin programs that have been undertaken during the past decades. Why will this project succeed when others with similar approaches have not? The source of lignin is critical for the cost-effectiveness of any lignin-related program (i.e., there are significant differences between Kraft, sulfite, or organosolv lignins). None of this was outlined in detail, making it difficult to review. The end value of any resin must be justifiable, considering that many paper companies use lignin as their hog fuel to run their plants; thus, the end value of any lignin product must not only compete with alternative fuel sources such as diesel but also justify the costs of changing the process, which may require significant capital investment for a paper mill. The presentation outlined success through industry engagement. This would have been strengthened by listing partners, potential partners, or at least types of industrial partners that they are approaching. A significant advantage of this process is that it results in composites that can be recycled. How? What infrastructure is needed to recycle these composites versus any other composite, and how are these materials better than other natural composites?

Progress and outcomes: The results on hardeners are very promising but require some context even if it is an allusion to the type of hardeners used. Even some description of the general materials used would strengthen these data. The pictures of prototypes are useful and imply that these composites are promising.

- Management: The management plan and implementation appear to be organized. The management and implementation of technical work is conducted by Spero and LCA by ANL. Based on the presentation provided, there is a clear management team defined. Unfortunately, the management and implementation process are not described, and therefore it is not possible to determine how well this is run and organized. There is no description of risk mitigation. Overall, based on the rather generalized presentation, it is very difficult to assess routes for communication and collaboration with related projects and/or advisory boards.

  Approach: The approach describes using a “network structure of Spero lignin-based resin.” There is a graphic showing a network with “reversible bonds,” but none of this describes any kind of chemical basis of this resin or reversible bonds. It is, of course, understandable that confidentiality might be paramount, but it would have been helpful to see non-enabling information of some form. Overall, because of the level of restricted information that had been determined by the management team, it is not possible to evaluate the approach used in this project in terms of potential or see opportunities for further innovation. More specifically, it is not possible to understand whether there is substantial merit to advance the state of the art (SOA0, as relevant to the defined BETO Program and Technology Area goals. Further, it is also not possible to determine whether the project performers have developed an approach with significant potential.

  Impact: The project impact appears to be headed toward good outcomes; however, the absence of any technical information makes it impossible to evaluate this impact. Of course, one understands the needs for confidentiality with Spero technology, but this degree of restricted information is problematic to this review process, in my opinion. The project performers should consider how to share some levels of non-enabling information so that an adequate review of impacts could be accomplished.

  Progress and outcomes: Results are presented as accomplishments against milestones but with little to no supporting data. The work looks like it might be innovative, but the absence of details makes it impossible to assess this in any meaningful way; therefore, it is difficult/impossible to properly quantify progress and outcomes and conclude (or otherwise) that this work is promising. Again, the lack of details and technical information is problematic, in my opinion, to this review process. Without supporting technical details, it becomes easy to conclude that this may be too naive or that progress is a wish list rather than concrete. It is simply not possible to determine if this is a worthy investment.

- Demonstration of leisure/sports prototypes makes project proposition credible using lignin from in-house Spero technology. The project has defined the technical approach for each critical task, and the team has nearly completed all of the milestones outlaid for this phase and is taking approaches to improve the thermoset water resistance post-recycling. Generally, the absence of detail—in particular around the business case—makes the project challenging to evaluate. With an industrial-led project, we are sympathetic with Spero's need to protect proprietary technology; however, a more transparent business proposition would be helpful, especially if the project leader states that the next step is piloting through a joint development agreement.

- The approach of using lignin-derived molecules to develop novel thermosets and CFRP that are decomposable and recyclable while retaining the desired performance characteristics ticks several boxes for this area. The impact on composite waste and the potential economic benefit to biorefineries by lignin valorization are positives; however, it is not clear what lignin fractions (narrow or broad) are useful. A narrow fraction might be especially challenging to attain attractive economics. It is not clear how the project views commercialization and logistics, such as CFRP waste collection, transport, and processing sites. Project participants, management structure, and assignments are described generally, and the work appears to have industry relevant advisors, although not identified. The method and frequency of communications across organizations as well as risk identification and management are not clear. The project appears to be on time in achieving its progress and milestones, although it is difficult to assess given that insufficient data are available, perhaps due to proprietary status. It seems possible that more data could be presented in a sanitized way. It is suggested that the program be active in capturing novel innovations (e.g., intellectual property filings), which, when completed, would also allow for better transparency. I look forward to seeing more results in the future, including how TEA and LCA analyses contribute to the ultimate feasibility of the work.

- This project seeks to produce thermoset polymer coatings for carbon fiber using lignin-derived monomers. Thermosets should decompose (>90%); however, no time frame is provided for the degradation process. The corporate management team is provided, but it is not indicated which members are actively participating in the project or their contribution of expertise. The impact of the project is potentially significant, with reductions in carbon fiber waste and downgrading; Spero is interacting with unnamed industrial partners at multiple levels. Components of the prepolymer are being optimized; lab-scale synthesis of 1 kg of prepolymer daily is reported, although it is not clear if the most advanced formulation has been synthesized on this scale. Multiple unspecified hardeners have been tested; to date, however, no hardener has afforded the same level of hydrophobicity as the control. Currently, the company is able to decompose up to 50% of the thermoset.

- Too much was withheld for confidentiality reasons, apparently, making any judgment at all fairly difficult. Scoring likely would be higher if more information was available. The management plan is okay but not very detailed. There is no real risk management plan. The goal of recyclable thermosets is challenging enough, but to make them from lignin adds tremendous additional complexity. Lignin is famous for resisting more than a century and thousands of man-years of effort to make useful commercial products, and without more detail about the methods being employed here, it is hard to form a positive impression about prospects for success. It was unclear the extent to which fiber composite components would fully retain their strength and other properties upon recycling. Synthesis and test efforts appear thorough. Progress is good in light of the brief and challenging project period so far and the low percentage costed to date.

PI RESPONSE TO REVIEWER COMMENTS

- Spero thanks the reviewers for their time in reviewing this project. We understand that further technical details would be useful for review of the project, but, unfortunately, we cannot disclose confidential information in a public meeting. Note that all project milestones are on track for timely completion per the schedule in the Statement of Project Objectives. The management team shown in the presentation is actively participating in the project management. Spero's chief technology officer, Dr. Ian Klein, oversees and coordinates the project with Spero's senior materials engineer, Dr. Shou Zhao, managing experimental design. Direct communication with subcontractors (ANL) is facilitated through monthly meetings. Lignin of sufficient volume and purity is commercially available today and will be further reduced in cost as Spero's in-house technology for producing clean chemical feeds from lignin becomes available.

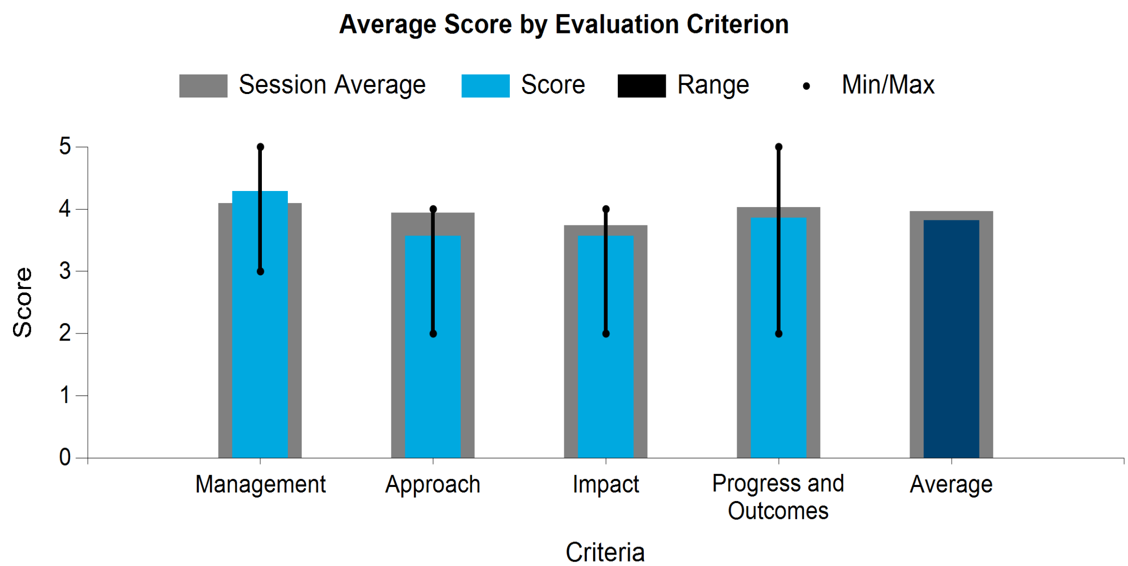
BIOINSECTICIDES FROM THERMOCHEMICAL BIOMASS CONVERSION

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.705
Presenter(s):	Nolan Wilson
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$632,000

This work is developing a sustainable and inexpensive bioinsecticide that leverages the inherent chemical functionality created from thermochemical biomass conversion. The impact of this project lies at the intersection of energy and agricultural sustainability. Thermochemical conversion of biomass to fuels remains an attractive pathway, and bioinsecticides, isolated from a fraction of upgraded bio-oils, are a high-value coproduct that can increase biorefinery profitability. Existing insecticide products are facing significant pressure from regulators and consumers due to negative health and environmental impacts. Bioinsecticides, produced through the deconstruction of biomass, can offer a safer, more environmentally benign alternative due to the chemical homology with biologically degraded lignin. To enable the thermochemical coproduction of bioinsecticides, insecticidal activity must be competitive with existing products, separations of the bioinsecticide must be technically viable, and the overall process economics must be improved. Using vacuum distillation, we have separated a bioinsecticide active ingredient that has similar activity to current commercial products, and techno-economic modeling has shown it can be produced at market competitive prices. This work has established a bioinsecticide fraction that is ready for further, more resource-intensive development by addressing early technical, economic, and toxicological risks.



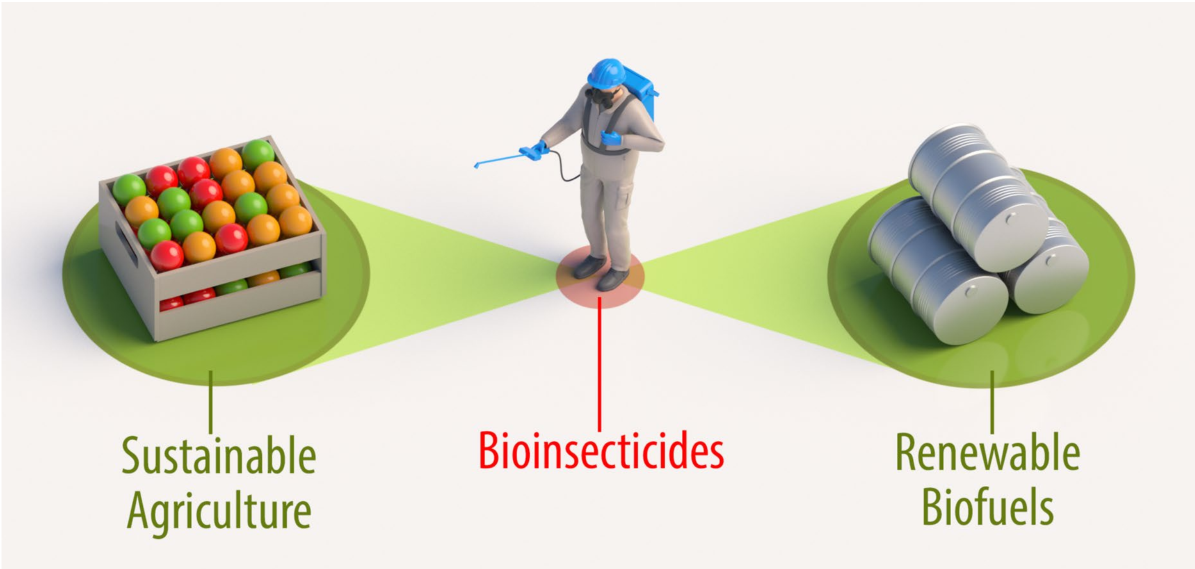


Photo courtesy of NREL

COMMENTS

- Management: The management plan and implementation appear to be at a relatively early stage, which is probably commensurate with the funding. The consortium of entities involved (NREL, U.S. Department of Agriculture, Michigan State University, and Marrone) is good and probably sufficient to make some progress.

  Approach: It is difficult to assess the merit and potential of the approach in this work. There are insufficient details provided to see how biopesticides will be screened, and there is no evidence presented to show that something in the pyrolysis stream is biocidal. A patent is cited (PCT/US20/66306), but it was not available upon searching patent databases. Not sure what the waste stream will look like? Separations can be very challenging.

  Impact: The project might have potential to make an impact (if a chemical of sufficient efficacy and value is found), but at the current stage of the project, it is difficult/impossible to assess or project any real potential impact. Biocides have very exacting specifications for use as well as safety and environmental impact.

  Progress and outcomes: Results are relatively light (screened 14 fractions from two bio-oils against seven insect models, two application spaces, and three assay modalities), and it remains unknown whether biocidal activity is due to a single molecule or multiple chemical interactions. At this stage, the progress and outcomes appear to be highly unpredictable, and the challenge of finding an effective biopesticide that passes through so many giant technical and regulatory hurdles toward commercial application is daunting. Recognizing the size of the budget and technical challenges ahead, this project needs a partnering entity to step up and set clear benchmarks and deliverables and perhaps consider additional funding.

- The management plan, partners, and outreach all look good. Risks are briefly listed; taken as a whole, though, they are rather daunting. The connection with Ensyn and Marrone seems promising, but if they are already partnered on this, what are the other participants bringing to the project? The variability of catalytic fast pyrolysis (CFP) oil is going to be an issue. Has the team considered how this will fit in with the transportation and processing of the whole CFP oil? It may only be practical in a refinery setting, and there it might not be convenient in light of logistical and processing/storage requirements. It is not made clear why there was reason to believe that components of CFP oils might be good insecticides. This is a small market compared to fuels, but it seems amenable to a "skimming" approach rather than full-fledged integration at the biorefinery level, so it should be viable. Active compounds clearly arise from lignin, not from (hemi-)cellulose—has consideration been given to starting with lignin pyrolysis oil rather than that from whole biomass? Progress seems very good in light of time, funds costed, and difficult conditions during the past year.

- Management: The team is strong, with specific expertise that can lead to success. Industrial and agricultural partners are included, and their roles are well defined. The team leverages other DOE and BETO projects. Slide 7, for example, shows other synergies and important commercial relationships. The potential path to commercialization is in place.

  Approach: The presentation of the approach is clear, although this reviewer would have preferred more details. Implications from results show that their approach to GHG reduction has value. Testing of toxicity and environmental impact and then showing that 0/50 compounds were hazardous is an important component of their approach.

  Impact: This project only aims to reach a relatively modest goal to identify and characterize one active biocide derived from thermochemically modified biomass sources and prepare that ingredient for field trials. It will very likely reach that relatively modest goal. Their tie-in to bioenergy is a stretch if the argument is put forward that the thermochemical conversion of biomass to create insecticide will improve biofuel economics. Even if this team succeeds completely, it is hard to argue that success will significantly change biomass-to-bioenergy economics. The market volumes for insecticides are small, so its processing will operate on a completely different scale from bioenergy development. Insecticides are used sparingly, with small quantities required to meet all of the markets needs, so it is hard to imagine it changing the economics of a commodity-level processing plant. But safer, more sustainable insecticides are still an important part of the bioeconomy, and it would be nice to have an array of high-value chemicals derived from thermochemical biorefineries. CFP is a low-cost process with flexible feedstock, so bioinsecticide production can occur regionally, independent of petroleum supply, thus lowering supply chain emissions and transportation costs. This part of the energy equation is noteworthy. The team might benefit from picking a target pest and then target crops that would benefit from their bioinsecticide. Agriculture-based stakeholders (such as a growers group) could help this team take it to the next level, which will be the relatively expensive step of government trials/approval.

  Progress and outcomes: Slide 12 is promising, showing that biocide effectiveness has improved >40% since the start of the study and that their bioinsecticide competes well against a commercial product. The cost analysis (slide 13) shows that the breakeven price of the active ingredients from their thermochemical conversion makes this process cost competitive. This would be a significant result, showing that sustainable does not need to be more expensive.

- Participants cover the major risks and mitigation strategies well. The inclusion of the feedstock producer (Ensyn) and the route to market for bioinsecticides (Marrone) improve the probability of commercial success. The mitigation plans are well thought out. There is a systematic approach to identifying candidates for the screening of efficacy. Removing phenols from the bio-oil increases the probability of adoption of CFP for fuels while adding a high-value coproduct. Additional toxicity analysis resources would improve the probability of success, especially with regulators. There is potential impact in both the big commodity market (fuels from bio-oil) and in agriculture (bio-based insecticides). The value proposition has a good upside potential for phenol feedstocks. I would like to understand how when insects develop resistance to these products, like they do to current insecticides, what are the mitigation plans beyond rotation. It is dependent on the adoption of CTP, which is the major risk. Candidates to date appear to have reasonable efficacy as insecticides. The plan to screen for plant and pollinator toxicity is a plus. Explain how a small insecticide player will be able to address the larger global markets.

- Project participants have screened multiple fractions from two CFP bio-oils for insecticidal activity. Participants have leveraged separations expertise to increase the mass balance from 39% to 99% of distillate fractions. Compound identification is critical if these materials are to be used as pest control agents. Participants have also identified strong partners for commercialization. My concern lies in obtaining U.S. Environmental Protection Agency approval to utilize mixtures containing numerous active and inactive ingredients as bioinsecticides. How much additional time and financial resources will be required for toxicity, soil persistence validations? I also recommend that preparation of multiple identical samples to determine reproducibility in content and bioactivity.
- The approach of producing a bioinsecticide from CFP-derived lignin is appealing, with potential beneficial impact to biofuels/bioproducts as well as to the agricultural sector. Incumbent insecticides are often undesirable in their persistence and impact on nontarget organisms (including pollinator and humans), and the emergence of pesticide resistance is a problem, so there is a clear need for alternative products that are both effective and safe. The premise here is that lignin-derived compounds can meet these criteria. A significant difficulty may be that the process may produce a mix of compounds, and consistency may be compounded by source lignin variability. Because of this, the product may require additional separations (and costs) to meet agricultural and safety specifications (including content consistency). The program is innovative, with one patent application filed to date. The project management plan, communications, risks, and mitigations are well addressed. The team includes an industrial/commercialization/license partner who should be helpful on the agricultural/pesticide issues. Project results are satisfactory to date, with several thermochemical treated fractions exhibiting insecticidal activity on various target species, apparently due to alkylated phenols and methoxyphenols.
- The project has assembled a sound management plan and partners to develop environmentally friendly pesticides from biomass. For program dollars invested, this project has made great progress in its critical tasks: identified a blend of phenolic molecules that show promising insecticidal activity; closed mass balance by separations and characterization of the aromatic stream; developed an economic model that identifies a profitable window of opportunity; and engaged an industrial partner that brings regulatory/registration experience to mitigate commercialization risks associated with the project. Major questions that emerge: whether the active phenolic mixture will meet the toxicity goals; is DiPel(R) the appropriate benchmark for activity studies? DiPel is an entirely different molecule class, a blend of protein toxins with a distinct mode of action. The investigators may want to consider a mechanism-of-action work stream in the second year to acquire data if they anticipate a product regulatory strategy that proposes low resistance potential. A major strength of this project is the knowledge depth brought by various members of the team in understanding approaches to pest management; finally, a successful product would be very compatible with the portfolio and niche market approach of Marrone, the potential licensee.

PI RESPONSE TO REVIEWER COMMENTS

- We would like to thank the reviews for their insightful and constructive feedback. We agree that the identification, purification, and consistent production of a high-quality active ingredient from thermochemical streams will be key to the success of the bioinsecticide. The team has pursued single-component model compound studies (e.g., 3-ethylphenol, 4-ethylguaiacol) to verify that the activity is derived from alkyl phenols and methoxyphenols found within the bioinsecticide fractions. Significantly more work—especially related to mode-of-action, efficacy, safety, and environment impact—will be required to meet the necessary regulatory requirements. We fully agree with the need to align market volumes of chemical products and fuels. The team appreciates the recommendation of identifying and pursuing a target pest and crops, which will improve the likelihood of achieving initial market adoption, and we will consider this as part of future development work.

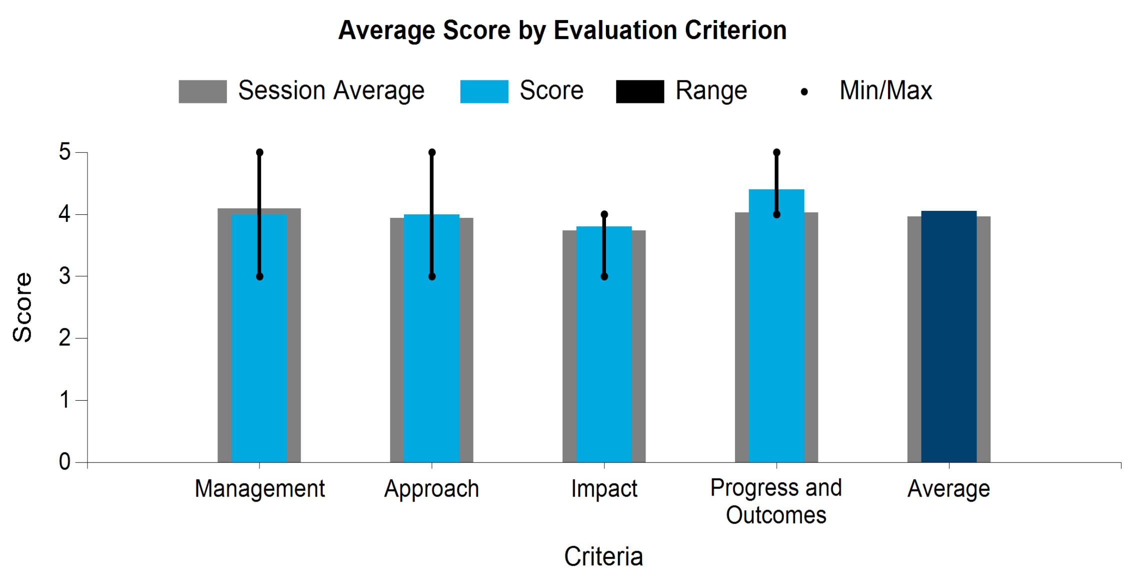
DESIGN AND DEVELOPMENT OF BIO-ADVANTAGED VITRIMERS AS CLOSED-LOOP BIOPRODUCTS

University of California, Berkeley

PROJECT DESCRIPTION

WBS:	2.3.2.219
Presenter(s):	Jay Keasling
Project Start Date:	10/01/2018
Planned Project End Date:	03/31/2023
Total DOE Funding:	$1,997,861

Plastics in use today are predominantly single-use and are rarely recycled. The linearity of their life cycles is not only wasteful from a resource and energy perspective—it has also resulted in environmental stresses, with >6 billion metric tons of plastic waste. The goal of this project is to elucidate design rules by which life cycles for plastics become circular and therefore sustainable. We focus our efforts on a new class of dynamic covalent polymer networks, known as vitrimers, which combine the processing and recycling ease of thermoplastics with the performance advantages of thermosets. Regarding circularity, most vitrimers are differentiated from classical thermosets in that they can be chemically de-polymerized, typically into small molecules or short oligomers, including dimedone, ß-keto-d-lactone (BKDLs), and diacids in this project. For decades, microbial production of commodity chemicals has been limited in the diversity of the molecules produced by natural or modified enzymes. Our technology of recombining the Type I polyketide synthases demonstrates a promising strategy for the synthesis of diverse molecules, including BKDLs and diacids. With computational materials genomics of vitrimers and TEA/LCA for bioproducts, we can design and develop infinitely recyclable and therefore closed-loop polymeric bio-based materials for potential commercialization.



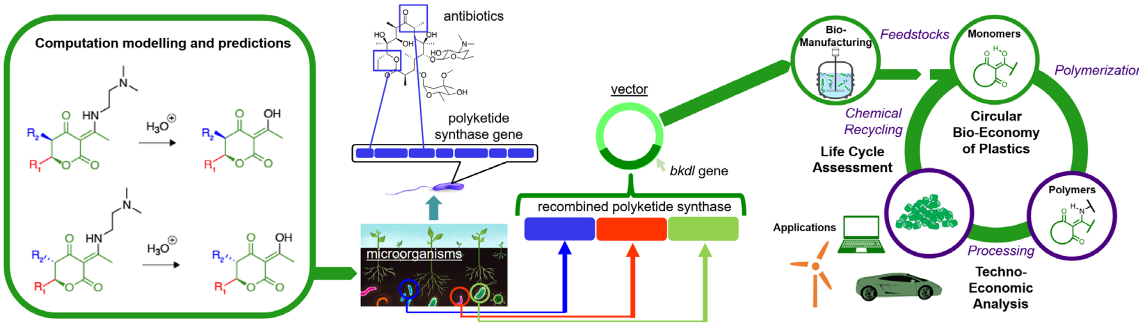


Photo courtesy of University of California, Berkeley

COMMENTS

- Management: The management plan and implementation appear to be high level and well organized. There is a good collaboration between the University of California, Berkeley and Lawrence Berkeley National Laboratory (LBNL), showing good progress and organization. At present, there are no industry-focused entities involved, and there is not much description of risk assessment. Of course, this is envisioned down the road, but I think an IAB would help to set targets, identify risks, and push the project in practical directions.

  Approach: There is substantial merit and significant potential in this approach toward a vitrimer based on diketoenamine hydrolysis in acid. Nevertheless, concerns remain on whether all components are infinitely recyclable with little loss and no decay in the recycle process over time. Multiple engineered organisms is a plus. The overall concept of elucidating design rules for recyclable plastics is intriguing.

  Impact: The project impact appears to be solid and headed toward promising outcomes, with thorough review processes and deliverables in place. At the present time, there appear to be no connections to industry advisors, and yet this will be required to deliver an impact with clear commercialization potential. It will be challenging to identify good thermoplastics with the performance advantages of thermosets.

  Progress and outcomes: Results are showing great promise relative to the metrics set in what is a very novel and promising area of recycling. Appears to have coped well despite the COVID-19 impact. The project as a whole is still relatively early stage, although progress and outcomes look promising. There are several key steps where progress is being made, but many challenges lie ahead if this is to make it to the market.

- The project research teams are well coordinated and have clear goals. They would likely benefit from the inclusion of industrial partners with routes to markets to challenge cost/benefit assumptions and facilitate technology transfer. Developing an entirely new polymer system from carbohydrates to monomers, polymers, applications, and then recovery and recycling is a daunting goal. Would benefit from better understanding of the property set that these polymers would offer over incumbent polymers. TEA earlier in the development path would help identify cost/benefit risks and needed mitigation plans. Without significant improvements in material properties, the potential market penetration of circular poly(diketoenamine) (PDK) polymers likely will be limited versus low-cost and well-known properties of high-density polyethylene and PET in major markets. A target of 4 gm/L in fermentation is quite low. Commercial viability may need 25 times that goal unless high-value properties are identified. A commercial route to market players is needed to guide target goal setting, especially because they are counting on a high level of recycle. The technical program progress is on track. Commercial target risks and mitigation plans are needed.

- The approach of identifying, synthesizing, and testing bio-produced molecules such as BKDLs and diacids has substantial merit to produce potentially infinitely recyclable vitrimers. Polyketide synthases genes provide a great platform for novel enzymes to be created and produced in various hosts to make target molecules. The impact of a successful project toward a circular economy for more environmentally benign formulations in these applications, as well as a bio-based economy, is clear. Project management, responsibilities, and high-level risks are addressed, and excellent progress is evident on several fronts: engineering of polyketide synthases to produce numerous BKDLs, high bio-content vitrimer production and recovery, engineering of various production organisms (which may be needed to produce different molecules optimally), and predictive polymerization/depolymerization models. Future progress on performance and prioritization of targets and process (e.g., titer, rate, and yield fermentation targets) will inform the scale-up feasibility of the approach.

- This is a well-coordinated team of participants that spans biology, chemistry, computation, and environmental/energy spaces. Additional information, including how the groups interact to move forward, would be beneficial. Recyclability and recovery data are impressive, as is the number of enzymes created and screened. The degree of productivity is without question. My concern lies in the area of application and interaction with industrial partners. Given the number of enzymes screened, it might be time to select several of the most promising candidates to determine the scalability of the biological monomer production. Reviewers are uncertain how bioproduction and the circularity of vitrimer mitigates the risk of commercialization, as indicated in the presentation.

- This is an early-stage project; thus, no detail is provided for developing a handoff for industrial development and validation. The project, which leverages the well-established polyketide platform, expands the BETO platform and has potential synergies with other projects. The project team has a clear timeline layout to manage all of the critical tasks—the chart on page 4 is a great visual aid to see the tasks per budget period. (This could be a model template for all portfolio projects because it is easy to see at a glance the task sequence paired with timing with the visual color link to the project leader.) Judicious selection of targets using economic analyses and criteria of monomer recovery; product value; energy inputs, etc. The project team has made good progress on key milestones: (1) the exploration of the structure space and the analyses of and understanding of differing influences of R1 and R2 substituents in model Beta-diketolactides on the depolymerization recycling rates model; (2) host comparison and strain development; (3) robustness of synthesis with delivery of 50-g batch triketone biomonomer; and (4) TEA and LCA analyses on bio-vitrimer recycling. Can they clarify whether they will narrow the number of candidates for microbial host strain development?

PI RESPONSE TO REVIEWER COMMENTS

- Reviewer 1: It might be time to select several of the most promising candidates to determine the scalability of biological monomer production. Reponses: In the next stage of the project, we will screen alternative BKDLs that can be produced from different hosts. Thereafter, we can optimize the production of those most promising candidates to reach a higher titer. We will also take the specific property of the BKDLs into consideration before scaling up the production.

- Reviewer 2: Uncertain how bioproduction and circularity of vitrimer mitigates the risk of commercialization. Reponses: Bio-based polymers that are conducive to increased recycling rates by closing the loop in their life cycles reduce petroleum demand, decrease the volume of plastics sent to landfills, and mitigate emissions associated with any plastics still combusted (and, in the case of landfilling, sequester biogenic carbon). Circular plastics are a market-disrupting counterpoint to single-use plastics, which are increasingly regulated, if not outright banned, due to their negative impact on the environment.

- Reviewer 3: No connections to industry advisors. Reponses: We have deeply developed a network of industry advisors, including C-level executives of major chemical companies (Jean Sentenac, CEO, Axens; Hartwig Michels, President, Petrochemicals, BASF; etc.). We also have nondisclosure agreements and material transfer agreements with BASF, Arkema, Proctor and Gamble, Clorox, Ford, and others. We were not asked to provide this information in the 15-minute talk, but we have done this. We are also pursuing funded collaborations with these partners to scale up the research products from this BETO project.

- Reviewer 4: A commercial route to market players is needed to guide target goal setting, especially because they are counting on a high level of recycle.

- Reviewer 5: No detail for developing a handoff for industrial development and validation. Reponses: This project falls into the FOA Topic Area: 3a: Performance-Advantaged Bioproduct Identification, which explicitly required projects at TRL 2. Many of the comments touch on the need for industry advisors, assessing scalability, arranging for handoff to industry, and the development of a plan for commercialization. Although the project team is in active discussions with industry partners in anticipation of follow-on research at a higher TRL, the biopolymers being developed and evaluated as part of this project will require further exploration and optimization prior to commercialization. The fact that these biopolymers can be tailored to achieve different product specifications and tuned to depolymerize under mild conditions will make them attractive to companies aiming to reduce their plastic waste footprint.

- Reviewer 6: Without significant improvements in material properties, the potential market penetration of circular PDK polymers likely will be limited versus low-cost and well-known properties of high-density polyethylene and PET in major markets. Reponses: The reviewer misunderstood our directions; we are not expecting to displace PET or high-density polyethylene. We are expecting to displace nonrecyclable polyamides and polyurethanes. We have substantially demonstrated performance improvements over those materials in bio-based formulations and have maintained lossless circularity in recycling outcomes. We have further carried out detailed analysis of the economics and pricing to assess potential roadblocks to commercialization. In our most recent paper (by Vora et al., published in *Science Advances* earlier this year) we calculated the cost of virgin PDK production and waste PDK recycling. The cost of recycling is well below that of virgin polyurethane, which is our initial target market. High-density polyethylene and PET are not our immediate targets because those are the two plastics that are most frequently recycled in the United States today.

- Reviewer 7: The target of 4 gm/L in fermentation is quite low. Commercial viability may need 25 times that goal unless high-value properties are identified. Reponses: We understand that the current titer of 4 g/L is not high for the commercial viability. Different fermentation conditions will be optimized to reach higher titers for future commercialization. Additionally, we may perform more engineering of the host to reach a better production of BKDLs.

- Reviewer 8: Clarify whether they will narrow the number of candidates for microbial host strain development. Reponses: Regarding the host development, we will focus on one or two hosts that are good for the BKDL production. The hosts working well with polyketide synthases genes and supplying a rich amount of necessary CoA esters will be preferred. The future strain engineering will focus on these aspects.

BIOCONVERSION OF HETEROGENEOUS POLYESTER WASTES TO HIGH-VALUE CHEMICAL PRODUCTS

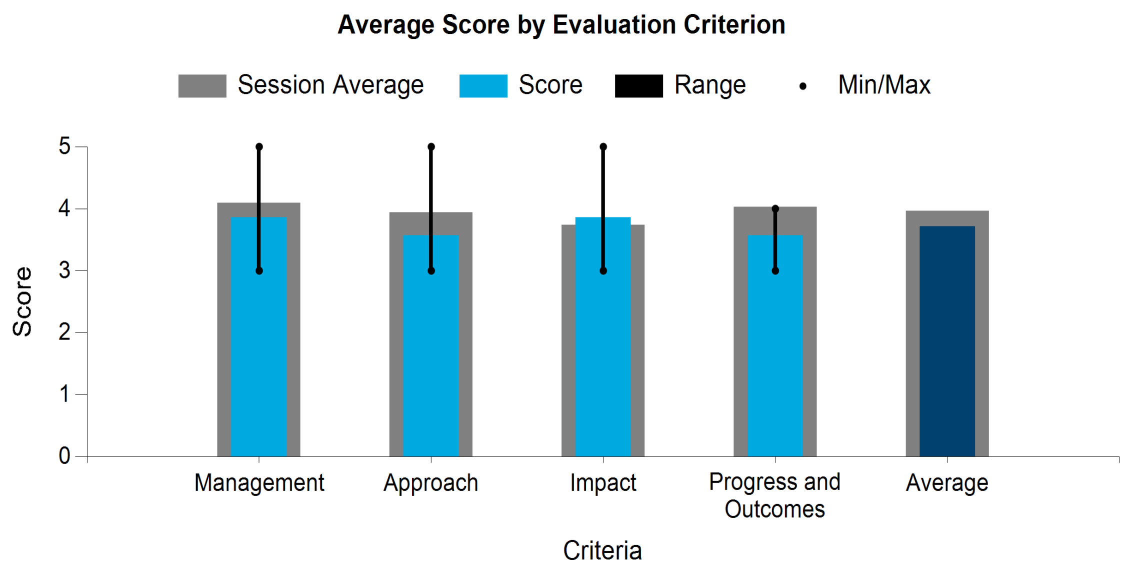
University of Massachusetts Lowell

PROJECT DESCRIPTION

WBS:	2.3.2.224
Presenter(s):	Margaret Sobkowicz-Kline
Project Start Date:	10/01/2019
Planned Project End Date:	06/30/2023
Total DOE Funding:	$1,500,814

The University of Massachusetts Lowell, in collaboration with NREL, aims to discover, evaluate, and develop pathways for the economical biochemical recycling of waste polyesters into small molecule products with added value in the chemicals and materials industries. The overall plastics recycling rate in the United States has stagnated at around only 9%, with the remainder ending up in landfills or leaking to the environment (e.g., oceans). Most successful recycling processes rely on mechanical shredding of the plastics to form new products; however, this approach results in inferior secondary feedstocks only suitable for less valuable applications due to degradation, contamination, and other technical factors. Chemical recycling schemes have the potential to provide better long-term solutions because pure monomers or high-value chemicals can be recovered and recycled in a closed loop; however, typical thermochemical recycling methods are energy intensive and reduce the embodied energy in the plastics.

This project will explore energy-efficient biochemical means to deconstruct and convert the heterogeneous polyester waste stream into high-value chemical intermediates suitable for a wide range of applications. The planned three-step recycling process involves mechanical pretreatment, enzymatic polymer deconstruction with integrated ball-milling, and microbial bioconversion to address critical bottlenecks in current SOA processes. This 3-year effort will result in demonstration of a >1-L reactor design that can produce 70% conversion of heterogeneous PET waste streams to monomer. The project will enable industry to demonstrate and deploy high-performing drop-in chemicals as an alternative to conventional unsustainable sources.



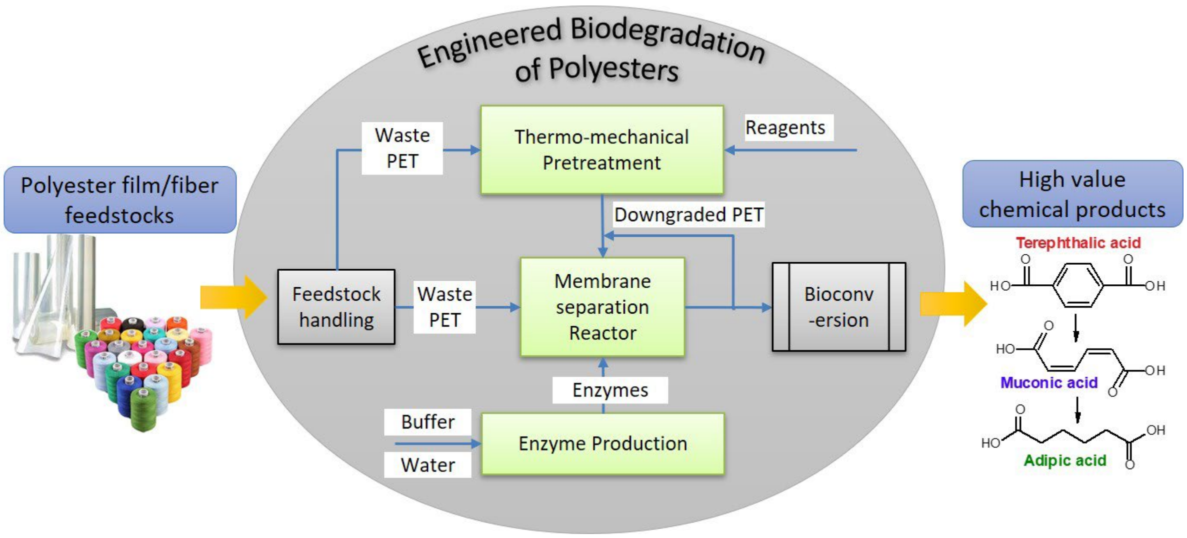


Photo courtesy of University of Massachusetts Lowell

COMMENTS

- Management: The management plan and implementation appear to be high level and well organized with the University of Massachusetts Lowell and NREL. This includes regular management meetings and risk mitigation. There is an impressive consortium of entities involved, it shows good progress, and it is very well organized. I think additional landfill-based entities might be worth adding as an advisory board.

  Approach: There is substantial merit and significant potential in this approach of thermomechanical pretreatment, enzymatic hydrolysis, and bioconversion to recycle polyester waste to high-value chemicals. The initial focus is on PET, looking for high-efficiency PET hydrolase or enzyme recipe and recover terephthalic acid (TPA) product. The approach does not (yet) incorporate how this would be used to impact landfills, and I think this remaining macro challenge should begin to be addressed.

  Impact: The project impact appears to be headed toward good outcomes with thorough review processes and deliverables in place. There is potential for significant impact and outcomes, although exactly how these efforts will be implemented in landfills to deliver meaningful change is not so clear. The project is early stage and currently not engaging with industry partners, yet that would help to refine this major challenge. It is not clear how the energy impacts will be realized.

  Progress and outcomes: Results are showing great promise relative to the metrics set and noted that the project started in April 2020. It appears to have coped well despite the COVID-19 impact, and progress and outcomes look promising. It is early stage for milestones, but they appear to be on track to assess PET sources with modest progress with various tasks: e.g., #2 evaluate waste streams and characteristics for degradation showing PET sources vary, #3 hydrolase expression system working, #4 less active PET hydrolase modified with binding protein, #5 started pretreatment strategies, #6 assay tests operational, and #7 designed reactor system using smaller particles better. The investigators might consider: (1) the composition of the remaining waste that is leftover after processing and recovering what is possible from the technology and (2) the fate of the remaining waste at a holistic process level with a process design flow diagram. I am concerned that this waste stream could become a very challenging concern. I think this is an example of where company advisors could get involved to identify and address challenges.

- Management: This is a strong management team. The University of Massachusetts Lowell maintains a strong expertise in sustainable polymers, which results in synergies between team members. The communication plan appears consistent and appropriate.

Approach: The expression of leaf compost cutinase in *E. coli* is commendable, and the continued research to express leaf compost cutinase in *B. subtilis* is also promising. Perhaps the team could explore cutinase expression in fungal hosts. Many industrial enzymes are pumped out in the highest volumes using fungal systems. Pretreatment (slide 13): How clean does rPET need to be to be enzymatically degraded? Some discussion on the effect of contaminants may improve this section. Preliminary results presented here are likely on very clean rPET samples, which raises the question whether it is more cost-effective to recycle the material versus degradation if significant pretreatment is required. Results outlined from the ball-mill reactor are promising (slide 16). It raises questions about the size/scope of this reactor. Discussions about residence time and/or the size of the reactor (per kg of substrate treated) could strengthen this section. Scale is a question.

Impact: The impact of this project represents a significant breakthrough and describes how this is an energy issue as well as one with social impact (slide 7 is a nice summary). Questions about the size of a scaled-up, optimal version of this process have implications on its scope. It would be interesting to discuss where such a reactor facility would be located within the waste-treatment infrastructure. Is this a facility akin to wastewater treatment?

Progress and outcomes: Perhaps the first objective is misstated and/or progress has not been rapid. The first goal is to determine the most prevalent forms of PET film and fibers in post-consumer and industrial waste streams; classify their physical characteristics before and during biodegradation. Yet only a single recycled (rPET) substrate is described (slide 8) without describing its cost or background. That is not comprehensive. More information is needed on how they arrived at that particular rPeT. If this result is to be universal, more detail is needed on how other forms of recycled materials are to be collected, compared, assayed, and then utilized. Otherwise, they are overstating their statement of characterizing different recycled streams. Progress on enzymatic improvement appears to be moving along well.

- The focus on PET fiber degradation has merit and is worthy of investigation. This project aims to combine mechanical pretreatment with enzymatic degradation to ultimately produce terephthalic acid and other value-added chemicals. Task assignments to project personnel are defined, and file and data-sharing are described. It is early in the project timeline, but it appears each task is being addressed independently. It would be helpful if the investigators described a cohesive plan to integrate task-specific advances. With respect to the approach, it is not clear if an enzymatic degradation system has been settled upon given that both leaf compost cutinase and PETase-MHETase are included. Is the plan to ultimately use isolated enzymes for PET degradation or whole cells that are exporting enzyme? A go/no-go decision point for Q4 2021 requires a percentage of PET degradation; it would be helpful if a ratio of PET to enzyme or a quantity of initial PET was specified to meet the milestone. It also is not clear why or how terephthalic acid produced from PET degradation would be upcycled to muconic acid or adipic acid. Is the difference in selling price between muconic acid/adipic acid and terephthalic acid high enough to justify the additional cost for biological upcycling?

- The management plan is a bit superficial; the risk mitigation a bit generic. The latter should not be just, "We'll keep a careful eye on things," but more specific thoughts about specific obstacles that might be encountered, things that could turn out unexpectedly in the course of the research, etc. The approach appears sound and well thought out. The list of tasks 2–12 does suggest some risks that ought to have been folded into the risk mitigation plan, for example. Impacts can potentially be significant. The approach seems especially appropriate for PET not recovered/recycled as whole bottles. Progress is a bit hard to judge based on the style of the presentation. "Progress Task X" on each slide reiterates the task, sometimes explains the task, and may or may not present some data, but it's not 100% clear the data are from THIS project, if they are ALL of the data taken so far, etc. It would be helpful to enumerate to actions that have been completed as part of this project. Given the constraints we've all faced since April 1, 2020, and the <10% costing, progress seems more than reasonable.

- The project team does not seem to include industrial representation for mixed waste feedstocks, PET manufacture, and end users. Including these representatives in the team will likely lead to the identification of additional technical and commercial risks, better targets set for research efforts, and intermediate go/no-go decisions. A successful plastic waste recovery and recycle strategy must be able to start with mixed plastic wastes. Utilizing enzymes to economically depolymerize PET containing mixed wastes and recovering useful quality monomers is a very heavy lift compared to existing chemical recycle processes, especially considering the economic targets that must be achieved for commercial adoption. It would help to see the final envisioned process (including organism, if appropriate) with expected steps. I would like to see PET-containing fabrics included in the scope because they represent a major part of the potential waste stream. If this approach were to be successful, it would have a large impact on the PET markets, but a TPA cost target of $2/kg is 10 times higher than today's cost from petrochemical routes. Progress has been made toward finding enzymes that have some performance potential, but the targets for titers, rates, and efficacy seem unrealistically low to be a commercially successful way to deal with mixed plastic wastes otherwise going into landfills.

- The project approach of acquiring PET feedstocks, enzyme development and expression, biodegradative pretreatment development, reactor design, TEA, and scale-up appears sensible and has technical merit. The project is relevant to BETO program and technology goals. The potential for innovation potential is high, and the identification of enzymatic and biochemical routes is particularly interesting albeit challenging. The management structure, plan, and communication are clear; risks/mitigations are addressed. Industrial advisors are not mentioned. The impact of a successful project is potentially high: the development of economic, integrated, and scalable biochemical processes to harvest plastic feedstocks for use in the production of chemical products could provide significant reductions in energy and reduce waste streams. PET-hydrolyzing enzymes and expression systems are being designed and improved for *E. coli* and *B. subtilis*. Progress across tasks appears on track, with the first go/no-go decision point achieved. There is much work to do here; for example, enzyme secretion levels are very low and require improvement. It was not clear whether these enzymes are secreted naturally; it can be challenging to secrete high levels of enzymes that are not naturally secreted. Reaching a decision point on which organism/expression system to move forward is desirable to focus efforts. The envisioned process is somewhat unclear, so it is hard to predict how much enzyme/organism improvement may be needed or methods to improve intrinsic enzyme properties.

- This project underwent an initial verification step with critical input—and redesigned and changed goals. The project leaders clearly enumerate the daunting hurdles and risks it faces to achieve its objectives. Made good progress in installing analysis methods to characterize feedstock and to monitor PET degradation. Hard to assess likelihood of success—in particular, it would be helpful to see a high-level reactor design scheme with all inputs and perform crude TEA modeling in the current budget cycle. In particular, apply enzyme catalytic parameters, if known—to estimate quantities required for end-of-project demonstration milestone: 70% TPA conversion yield in 24 hours. If this analysis reveals unfavorable quantities, it could define the need for and guide future production strain and enzyme engineering work so that a more desirable outcome is achieved.

PI RESPONSE TO REVIEWER COMMENTS

- Thanks to the Peer Review team for the very helpful questions and suggestions. We would like to respond to the Peer Review comments, addressing the following points.

- Involvement of industry partners: We are working with recycled PET fiber manufacturer Unifi to understand the utility of the pretreatment and bioconversion process on textile PET. We have received materials for testing from Unifi but have not yet worked with these materials. We appreciate the suggestion to work with waste management companies and will seek partners in this area. We also appreciate the suggestion to work with PET producers; we have had conversations with Eastman Chemical in the past and will attempt to reengage with them.

- Addressing impacts on landfills: The team plans to work with the TEA team from NREL to discuss these issues for the current enzymatic deconstruction process. It is not anticipated that the byproducts and residuals would be different than for the existing iterations of biochemical recycling.
- Process flow diagram: In response to comments about the entire process flow, we have included the process flow diagram in this response. We are currently evaluating the *B. subtilis* expression system and plan to finalize the organism of choice in the next quarter.
- Enzyme secretion levels low: Despite our attempts to incorporate a secretion module, we acknowledge lower extracellular enzyme production; thus, we plan to evaluate the potential of using unpurified enzyme directly after fermentation and cell lysis as a more economical way to obtain a large amount of hydrolytic enzyme for the degradation.
- Low target titers, rates, efficacy: The titer of 5 g/L from glucose within 36 hours, 70% conversion in 1 day, and $2/kg TPA are targets set based on the SOA bioconversion of PET and agreed upon with the BETO project administration team. It is the belief of the team that attaining these milestones in a scaled-up reactor dealing with contaminated PET wastes would be a significant achievement in the field.
- Cleanliness of PET: To date, the project team has investigated the enzymatic degradation of at least three forms of PET with different characteristics. In order to understand in greater depth the influence of pretreatments and enzyme design changes, we have focused most work on a prewashed recycled PET bottle flake as a substrate. We agree that working with fiber forms of PET and other contaminated forms will be important for proving the scalability and industrial relevance, but at this stage in the program, we are still working to understand the fundamentals of the system. We will move to other PET forms in subsequent work.
- Risk mitigation: As the team gets up to speed on each other's fields of expertise, we are starting to be able to identify risks in each other's research: waste characterization and pretreatment, enzyme production and relative performance, reactor design, and *in situ* product removal/purification. Team members have suggested alternative approaches such as micronization direct from melt and degradation using nonpurified enzymes, and these conversations are turning into a more robust risk mitigation strategy. In addition, we see results from the recently completed TEA out of NREL helping to direct the research to the most effective strategies to realize an efficient and effective process.

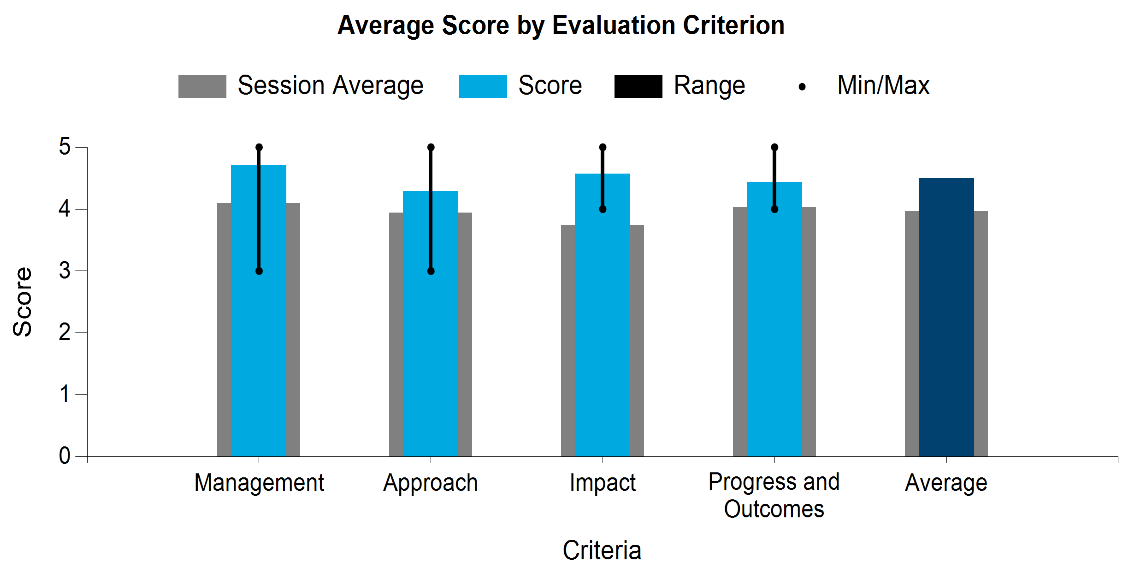
RENEWABLE CARBON FIBERS CONSORTIUM

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.4.102
Presenter(s):	Adam Bratis
Project Start Date:	01/01/2018
Planned Project End Date:	09/30/2021
Total DOE Funding:	$3,805,600

The primary objective of the Renewable Carbon Fibers project is to demonstrate the cost-effective production of renewable carbon fibers. To achieve this goal, this project brings together world-class research professionals to address all aspects of R&D on renewable carbon fibers along the entire value chain, from feedstock to finished composite material. Acrylonitrile, currently made from petroleum, is the primary chemical building block of high-quality carbon fibers. Making acrylonitrile from biomass (bio-acrylonitrile, bio-ACN) cost-effectively could help to displace petroleum consumption and buffer against carbon fiber price volatility by providing a renewable drop-in feedstock. Through bench-scale R&D, the Renewable Carbon Fibers project has identified a promising hybrid (biology/catalysis) path to bio-ACN. This next phase of the project, in partnership with key industrial entities, will entail a single scaled-up production run of 50 kg of bio-ACN with subsequent carbon fiber and composite production and testing.



COMMENTS

- Management: The management plan and implementation appear to be high level and well organized. There is an impressive consortium of large entities and industry partners (NREL, ORNL, Cargill, Johnson Matthey, MATRIC, SGL Carbon, Ford) involved, and all components are showing good progress. Management appears to be very well organized, with a highly commendable team of people.

  Approach: There is substantial merit and significant potential in this approach. The production of 3-hydroxypropionaldehyde (3-HPA) is going well, and its conversion to bio-can looks very promising. The catalyst supply looks robust to produce polyacrylonitrile, and carbon fiber production is set to start in readiness for composite testing.

Impact: The project impact appears to be headed toward good outcomes, with thorough review processes in place, with specifications well defined for deliverables. The cost of bio-ACN is also at a good price point. Key is scale-up, which so far appears to be progressing well with go/no-go decision points. Polymerization work is planned and pending pilot scale production of intermediates.

Progress and outcomes: Results are showing great promise relative to the metrics set. The project appears to have coped well despite the COVID-19 impact, and progress and outcomes look promising alongside a timeline that looks highly feasible. As with all projects, there is risk of failure to deliver against challenging technical targets, but current indicators are promising. It is not yet clear if the project will meet commercial metrics for catalyst stability and GHG reductions. It is impressive to see this moving toward scaled-up production (single run of 50 kg of bio-ACN) with subsequent carbon fiber and composite production and testing.

- Management: Very strong relationships with industrial partners, which adds to the impact of this continuing project. The role of each partner (slide 6) is well defined and makes sense. The strategic collaboration between these specific partners will result in a near-complete “supply chain” toward commercial adoption. Managing expectations is nice to see in a project (slide 6). The communication schedule and feedback loop with DOE is outlined.

  Approach: Previous work was spelled out nicely to provide context and outline next steps toward success. The ester nitrilation that has been discovered via background work merits further research, as is being researched here. The advantages are outlined nicely in slide 4: simpler catalyst (TiO_2), good yields (~95%), easier to control endothermic reaction, and relatively safe byproducts. The MATRIC analysis is important to verify whether this process is ready for scale-up to pilot-scale production.

  Impact: Scaling up the production of acrylonitrile (ACN) via the sustainable production of 3-HPA is needed. This project should provide critical information toward commercialization realization. Slide 5 is a clear outline of the project direction, all of it positive. Ford is an ideal partner to leverage conventional carbon fiber production from bio-derived ACN. Deriving 3-HPA from sugars is not necessarily via the most cost-effective carbon source. Alternative routes to 3-HPA could have been mentioned to provide broader context, but it is understandable here as the route used by their critical industrial partner.

  Progress and outcomes: The milestones are noted, and the specific status of each one needed for go/no-go is specifically noted. Most milestones are very close to being met. A pilot-scale amount (40 kg) of 3-HPA fermentation broth has been delivered to MATRIC (NREL), and stage 2, delivering 400 kg, is reportedly on schedule, which is very good. NREL’s recent work on improving catalysts is noteworthy and points to changing from TiO_2 to aluminum-based catalysts due to regeneration. This makes sense. This research is hypothesis-driven, which is commendable.

- Excellent, well-connected team delivering great results. Good coverage by partners from feedstock to end users. The bio-based route to 3-HPA catalytic conversion to ACN is a good example of a drop-in renewable technology. Would like to see details of the TEA versus conventional propylene ammoxidation to ACN, with sensitivities relative to the cost of propylene and ammonia given the large supply of low-cost natural gas liquids, and also rate, titer, and yield of the fermentation. The key catalyst life obstacle is being addressed aggressively. The impact is dependent on a step change in the cost of carbon fiber in order to accelerate the adoption of carbon fiber reinforced plastics. Unfortunately, there are no remaining polyacrylonitrile fiber producers in the United States, so sourcing of polyacrylonitrile carbon fiber will not be domestic. Matches up nicely to programs for the recovery and recycle of carbon fiber thermosets and other plastics. A lower-cost route to 3-HPA could enable many other bio-based intermediates. Making excellent progress toward the goals. Greater that 80 gm/L is a good start for the fermentation. Would like to see closer to 125 gm/L and TEA benchmarks for rate and yield.

- Great demonstration of a process vision that capitalizes on the strengths of biology/biochemistry (upstream production of the feed 3-HPA) with an efficient chemical catalytic dehydration followed by nitrilation. This project team has a clear, mature management plan: For each process step, there is a partner who is assigned responsibility for executing milestone tasks; the milestone deliverables have well-defined performance and quality specifications. This is a well-managed project that at the outset created a map for success, and the team has steered the project team steadily on course toward the goal of demonstrating an economically viable hybrid bio/chemical process to carbon fiber. Excellent progress to date. Cargill and MATRIC are on schedule to hand off bio-acrylonitrile to the partner SGL for spinning into carbon fiber after polyacrylonitrile preparation. Project leaders pursued the 2019 Peer Review recommendation to screen for a more stable catalyst and identified a much-improved catalyst with longer lifetime. In addition, the team having a proposition for mechanism for catalyst deactivation and how to retard it is a valuable asset for a potential commercial process, so there is a possible handle to troubleshoot future problems if they emerge. Given the awareness that polyacrylonitrile carbon fiber is not currently produced in the United States, is this an opportunity for U.S. manufacturing or an obstacle? The project team should evaluate hypothetical scenarios and requirements.

- It is exciting to see the demonstration and scale-up of a bioproduct-derived process from the laboratory scale to the pilot scale, and this multipartner project is not an exception. The coordination between partners appears seamless, and good progress is being made even with COVID-19 restrictions. Project success may be jeopardized by the lifetime of the current catalyst. A preliminary investigation has identified a superior catalyst, but the project is proceeding with the initial catalyst. Whether it is a good idea to proceed with a problematic catalyst is uncertain.

- The Renewable Carbon Fibers Consortium is an outstanding example of commercial relevance in the development of a novel, bio-based route to replace a dirty, inefficient, and dangerous chemical route. The project team is well described and includes a suite of industrial partners who are experts in their specific part of the program. Most of this team has worked together on an earlier project, where the technology was developed, so the likelihood of successful interactions seems favorable. In addition to using bio-based starting materials, the impact of a technically, economically, and environmentally successful scale-up would be transformational to the production of ACN, polyacrylonitrile, and composites. If more economical, it may broaden carbon fiber market penetration, allowing lightweighting of more products (e.g., in transportation) with concomitant energy savings. Progress is promising across the project and appears on time (understandably, the project timetable has been adjusted to accommodate COVID-19-related delays). A specific concern continues to be catalyst lifetime, although progress has been made (10-fold improvement in regeneration interval); this work continues.

- This is a very solid consortium, with lots of positive features. The fossil-based route is neither clean nor efficient, so it should be both an easy target and a process well worth replacing for multiple reasons. The merger of biotechnology, catalysis, and thermal processing is an innovative combination. It is also something not frequently mentioned, but the fossil route uses propylene, and bio routes to propylene are not very efficient, so we’re better off going to 3-HPA directly rather than trying to replace the fossil propylene source with a bio-based equivalent. Strong partner group. The management plan is superficial, and there is no risk mitigation plan. The approach seems appropriate, though there is not a lot of depth in the explanation. Progress is good given timing, costing to date, and COVID-19 impacts.

FERMENTATIVE PRODUCTION OF TULIPALIN A: A NEXT-GENERATION, SUSTAINABLE MONOMER THAT DRASTICALLY IMPROVES THE PERFORMANCE OF PMMA

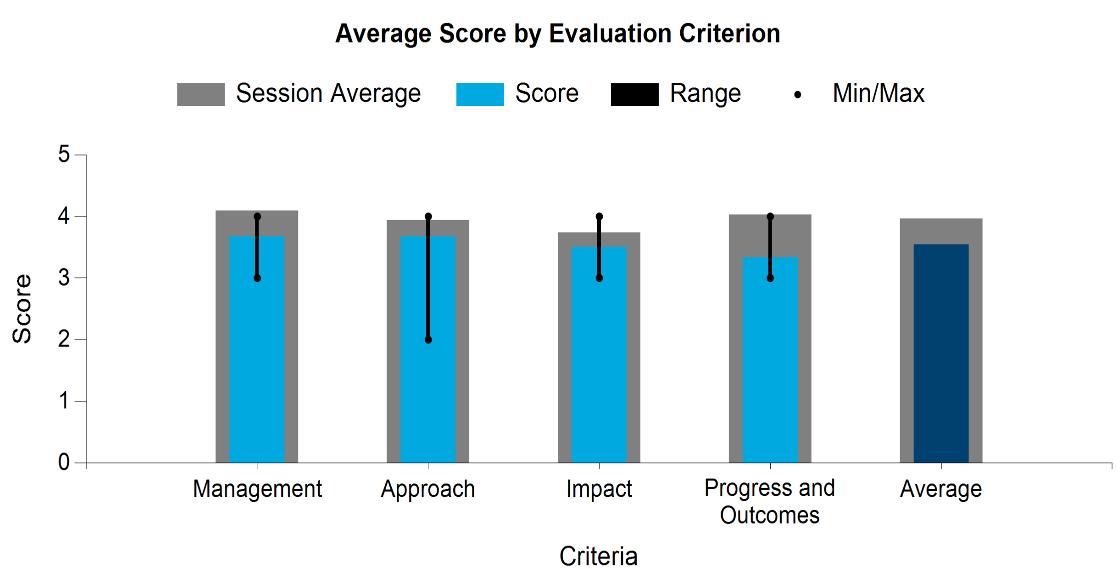
Arzeda

PROJECT DESCRIPTION

WBS:	2.3.4.208
Presenter(s):	Alex Zanghellini
Project Start Date:	10/01/2018
Planned Project End Date:	03/31/2021
Total DOE Funding:	$1,997,854

Methylmethacrylate (MMA) is a large-volume petrochemical monomer with a $6 billion/year global market. Its homopolymer, polymethacrylic acid (pMMA) is a transparent plastic with applications in surface coatings, automotive and aerospace casts/sheets, and optical devices. Tulipalin A (alpha-methylene butyrolactone, MBL) is a sustainable monomer that as a homo-polymer or copolymer with MMA yields materials with similar properties as pMMA but significantly higher Tg (105°C for pMMA, 195°C pMBL), improved scratch and mar resistance, improved weatherability, as well improved birefringence in optical applications. Although MBL occurs naturally in small amounts in tulips, the metabolic pathway is only partially known, and the molecule is not produced by any microorganism. Chemical routes are too expensive to reach target prices, so today there are no scalable, cost-effective production routes.

Using proprietary computational pathway and enzyme design techniques, Arzeda has developed an MBL catalytic route. Implementation into a fermentation host has already produced titers in the g/L from sustainable lignocellulosic material. Arzeda has developed a downstream process for the extraction and purification of MBL monomer from fermentation broth at high purity and yield and has demonstrated the ability to polymerize monomer into the clear plastic pMBL. Desirable thermal, mechanical, and optical properties that rival those of its competitor pMMA have been confirmed in collaboration with PNNL.



COMMENTS

- Management: The management plan and implementation appear to be high level and well organized. There is a clear list of risks (project challenges) that were identified. There is a small consortium of Arzeda and PNNL involved and appropriate organization for management. There are no downstream polymer processing companies involved, but this could be an opportunity for improvement later.

  Approach: There appears to be merit and potential in this approach to utilize Tulipalin A (alpha-methylene butyrolactone, MBL) as a sustainable monomer. MBL can be used as a homo-polymer or copolymer with MMA; however, delivering an organism that can produce a lactone (MBP) at scale is a considerable challenge. Also, it is plausible but very challenging to deliver a novel polymer into the marketplace. Although it is not clear whether Arzeda has freedom to operate due to related prior patents from DuPont (WO2002101013), for the purpose of this review, it is assumed that this is not a concern.

  Impact: The project impact appears to have potential to head toward good outcomes as a polymer improvement. The authors describe having go/no-go goals and deliverables. The value proposition as a performance improving monomer/additive for polymers looks challenging but intriguing.

  Progress and outcomes: Current status includes a "proof of concept" strain producing detectable MBL product from two distinct pathways and early evidence that the polymer from MBP has "desirable properties" relative to MMA. The next steps of delivering iterative improvements in enzyme and strain appear to be making some progress, but with titers in the range of ~0.25 g/L from sustainable lignocellulosic material, there is still a long way to go. It is not clear if the product from "mock fermentation broth" involved fermentation or was simply extraction processing. Also, it is not clear how this work differs relative to citations described in the mini review by Kollar et al. (published in 2019 in *Frontiers in Chemistry*). The project describes polymer testing by outside labs, including improvements in properties (like glass transition point, modulus of elasticity, tensile strength, elongation at break and light transmission), which is promising. The information provided describes clear strain engineering targets, with the intermediate production milestone 1 g/L within sight and an initial market viability goal of 20 g/L titer. Progress toward these later viability goals will become critical.

- The technical team has correctly identified key risks as low-cost production of Tulipalin, acceptable cost of MBL, and superior properties. The adoption of a not-in-kind plastic versus pMMA and polycarbonate would benefit from early engagement of plastic users to help determine incentives for switching and mitigate risks. A TEA earlier in the development timeline would be useful to guide targets for fermentative rate/titer/yield and cost to be competitive with current pMMA and polycarbonate. There is DuPont literature and patents in this area from 2002. Suggest looking at algal options in addition to other bacterial and fungal routes for establishing a scale-able and productive metabolic pathway to Tulipalin. A conventional sugar approach could improve potential for low-cost fermentation versus uncertain cellulosic sugar sources. Potential for a substantial reduction in GHG and energy is significant, but totally new polymers represent a challenging path to success. The current supply chain for pMMA and polycarbonates is well established, so replacing it with a not-in-kind MBL will likely require very differentiated performance and cost. Current organism performance of 0.25 gm/L is quite far from a potentially competitive fermentation platform.

- The project proposes to identify a novel fermentative route to Tulipalin A (MBL) that can be scaled to enable MBL-based polymer to compete with pMMA. Although there is precedent for a bio-based Tulipalin A route (DuPont), MBL is not currently available except in relatively small quantities synthesized chemically. A successful program could ultimately lead to the production of a bio-based polymer at scale, providing positive impact to biomanufacturing and competing with incumbent petro-based processes. Project management and high-level risks along the development pathway were generally identified. More data would have helped to clarify the route and progress and connect the different parts of the project. For example, it was not completely clear whether the end product (MBL) was being (and is to be) produced in the fermentation strain or whether an intermediate in the pathway is produced fermentatively, with MBL made in a final (extracellular) reaction. Good progress has been made in identifying novel bioroutes to MBL. A strain was constructed and produces low titers when grown at the lab scale. An MBL-based polymer was made from sourced nonbiological MBL and exhibits some property improvements over pMMA. An initial downstream process has been developed to separate MBL from fermentation. The next stages of the program will be critical to determine the viability of the process and product. The titer, rate, and yield performance of the fermentation will need significant improvement (cells and enzyme performance), and the separations process will need to be scalable, maintaining yields and purity to enable economics.

- This is a project with a great target molecule, MBL. They have expertly anticipated and navigated several technical and marketing uncertainties: demonstrated MBL production strain tolerance to high [Tulipalin] in media without the need for continuous product removal; simulated product isolation in high purity from a mock fermentation stream; and submitted bio-MBL to potential commercial partners to validate the performance of bio-pMBL. Pathway and enzyme engineering is a core strength of the investigators, but the basic science, the metabolic intermediate, and the three productive pathways to bio-MBL are not revealed. When the patent applications publish, it will be interesting to see what pathways achieved *in vitro* production titers of 0.25 g/L. Can the authors describe productivity in the Tulipalin A bioprocess? What improvements are necessary to hit targets: strain improvements and/or enzyme(s) engineering? What is the anticipated timeline to improve production titer to 8 g/L to produce the requisite kg of bio-pMBL for the end-of-project milestone (when is project funding end)? Is the Tulipalin A pathway in the plant genus Alstroemeria revealed in PCT/US02/18230; WO2002101013A2 relevant to this work? MBL production follows the action of four key enzymes (glutamate decarboxylase, gamma-aminobutyrate aminotransferase, gamma-hydroxybutyrate dehydrogenase and UDP-glucosyltransferase) on product intermediate of pyruvate and aspartate condensation.

- This project seeks to create a biological process for Tulipalin A, an alternative to MMA with improved polymer characteristics. My impressions are related to the ability of the participants to obtain Tulipalin A, and not on the merits of Tulipalin A as a sustainable replacement for MMA. Project-related tasks are outlined in a general sense, but no information is provided relative to personnel, interaction/communication between various tasks, or data management. Qualitative milestones would facilitate progress evaluation. Two reasons for optimism: a product isolation protocol has been developed that provides high-quality polymerized product an unidentified, necessary intermediate can be produced at concentrations of 80 g L-1. Unfortunately, it is not possible to determine the likelihood of success for evolving the necessary enzyme(s) for conversion of 0.25 g L-1 material to the required concentration to reach the next stage of development.

- Unclear how it was concluded *a priori* that Tulipalin A is: "Price competitive to MMA." What does slide 7 tell us? Isn't that the same plot for every substance whose production we might want to scale up? Reasonable enumeration of potential R&D/scale-up risks. Reasonable management plans. The approach appears to be sound, mostly familiar steps and methods. Assuming that some reasonable price target can be met, the impact would be large. But it is not clear that is possible based on a fermentable sugar feedstock. What is the theoretical yield? At that yield, what is a likely minimum selling price based on a rough estimate of fermentation costs? There should be at least a preliminary block flow diagram/process flow diagram (BFD/PFD) and "back-of-the-envelope" economics. It is not clear from the quad chart how much was costed when, and how that relates to the work presented, so progress is difficult to assess.

PI RESPONSE TO REVIEWER COMMENTS

- The reviewers comment on the lack of TEA data in our public release. Arzeda enzyme performance, fermentation, and separation goals have been guided for this project using Arzeda TEA models since inception (2017). We calibrate our TEA using industrial fermentation benchmarks. These models are periodically reviewed and updated. The most recent detailed review was August 2020, where we examine manufacturing at 1,000 te/yr and 60,000 te/yr scales at specific sites in the United States. Process water recovery costs are included in the Arzeda TEA for bio-based MBL. This includes capital equipment and operating costs (primarily energy) for the recovery of most process water, following the precedent for typical existing fermentation sites in locations such as Iowa, Nebraska, and Illinois. Separation costs for the DSP including three orthogonal separation steps are included in the Arzeda TEA for bio-based MBL. We elected to design this way to ensure exceptional purity and robust quality for customers, even upon transition to industrial operation in tanks of 250,000-liter scale and larger. There are higher initial capital costs and operating costs for this choice; however, these costs are offset at the project level by the reduction of market risk. Note that Arzeda BioMBL will be used as a performance acrylate in the MMA space.

- The reviewers requested more details on our fermentation targets and the likelihood of success in improving fermentation titers. Theoretical molar yield is 1 mole MBL per mole glucose fermentation or 54.4 gram MBL per 100 gram glucose. The fermentation is microaerobic, in the limiting case with ½ mole oxygen utilization per mole glucose. Arzeda has four performance targets. Each successive target has higher rate, titer, and yield. Our initial commercial goal ("target 4") performance target represents 36% of known related pathway flux; 75% approach to theoretical yield; 15% of known specific rate gram product/gram cell-hour; and economic titer goal. This was used to define our first milestone of 8g/L titer and ultimate DOE project target of 20g/L titer. At the time of our presentation, we had reached a titer of 0.25g/L. In the last 3 months, the incorporation of our latest generation of enzymes yielded a titer of around 2.5g/L in 4 days of fermentation (a 10-fold improvement). With additional rounds of computational enzyme design, metabolic engineering, and fermentation process optimization, we are very confident in our ability to reach titers in excess of 20g/L within the end of this project (in 12 months). Regarding feedstocks and hosts, the bulk of our work is dedicated to converting DE95 to Tulipalin A (MBL), but we have demonstrated that we can utilize C5 and C6 sugars from lignocellulosics. We anticipate initial commercial applications might be using commercial DE95 but would like to ultimately transition to lignocellulosics based on feedstock availability and economics.

- The reviewers rightly emphasize the consideration to be given to the difficulty and long timeline associated with commercializing a new monomer. We agree and are well aware of such challenges, but we have incorporated this in our Tulipalin A commercialization plan. As pointed out by one of the reviewers, we engaged from the inception of the project in business development and customer application testing of Tulipalin A (MBL) and uncovered that MBL can be used either as high-performance additive and copolymer as well as a monomer for new polymer (pMBL). This means that we have the opportunity to first enter the market as a high-value, low-volume additive, which lowers the scale-up barriers as well as the adoption time compared to an entirely new monomer. Instead of immediately attempting to transform the MMA value chain, we will initially introduce MBL as a new additive to the existing value chain for performance applications. As we complete this, get market traction, and continue to improve our fermentation process economics, we will then be able to expand the market to introduce MBL as a pure play MMA replacement over the typical 5- to 10-year period needed to ensure market adoption of new polymer while having generated recurring revenues to sustain the effort.

SYNTHESIS AND ANALYSIS OF PERFORMANCE-ADVANTAGED BIOPRODUCTS

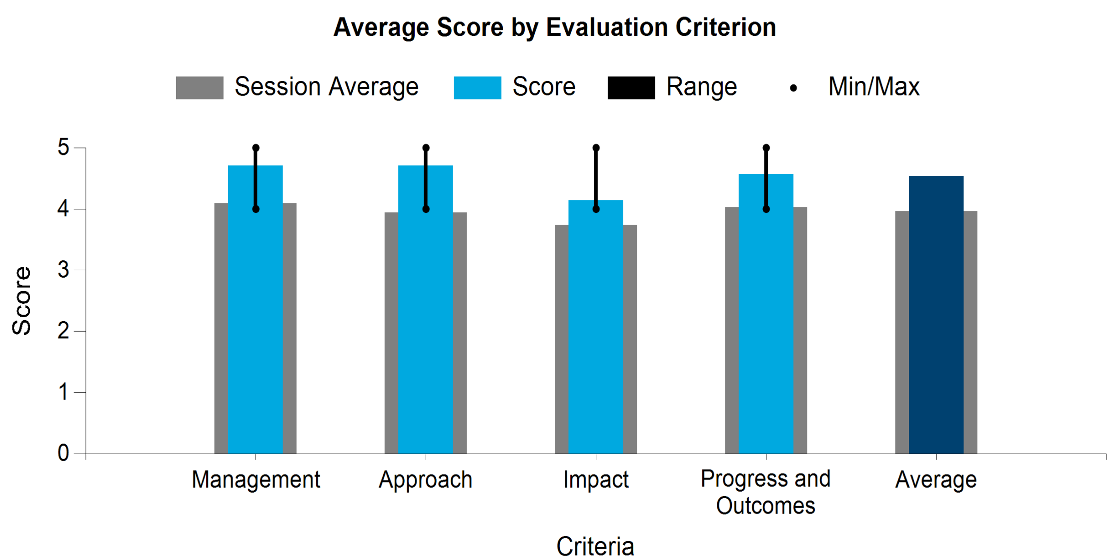
National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.4.501
Presenter(s):	Gregg Beckham
Project Start Date:	10/01/2020
Planned Project End Date:	09/30/2023
Total DOE Funding:	$920,000

PABPs are "novel products where the bio-based … product does not resemble an existing petroleum-derived molecule … but offers a performance advantage over existing products" (Fitzgerald, Bailey 2018). PABPs are an exciting area with near-term potential to accelerate the bioeconomy. We focus on synthesis, characterization, and economic and sustainability analyses for PABPs, aiming to leverage the inherent chemical functionality of molecules from carbohydrates and lignin via chemical and biological transformations. We collaborate with other BETO projects to source new molecules. Our work is integrated with the Inverse Design project, which provides computational predictions for PABPs and first principles-based results to explain observed properties.

Primary outcomes include (1) a *Nature Reviews Materials* paper that establishes PABP design principles, (2) performance-advantaged nylons from beta-ketoadipic acid, (3) new recyclable thermosets from bio-aromatic amines, (4) new performance-advantaged plasticizers that are less toxic, and (5) the experimental validation of a machine learning tool, PolyML, from the Inverse Design project. Going forward, we are working toward an integrated framework to dramatically narrow PABP design space and a material flow analysis of commodity chemicals as a benchmark for PABPs. Our main challenges are in the sourcing of new molecules that are not commercially available and the need for comprehensive characterizations and scale-up for technology transfer.



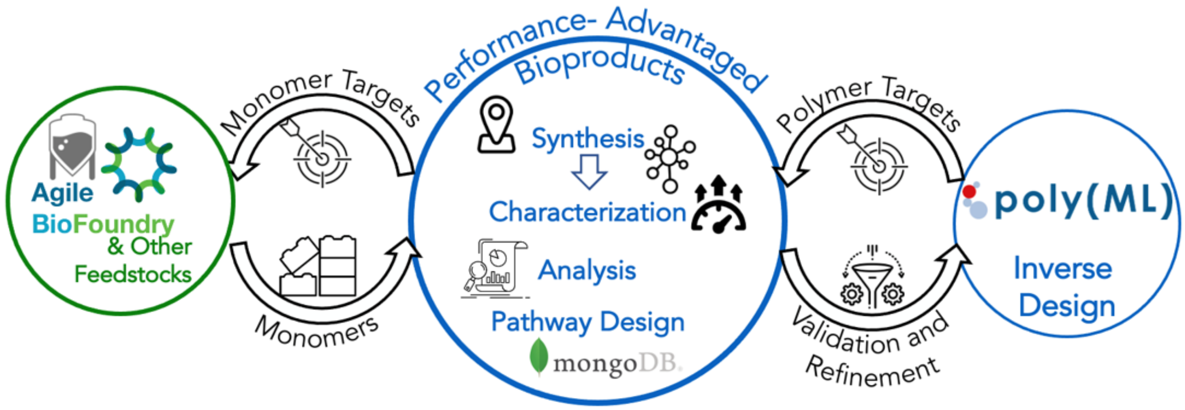


Photo courtesy of NREL

COMMENTS

- Management: The management plan and implementation appear to be well organized and high level. Risks are identified. There is an impressive team of contributors from NREL as well as ongoing collaborations with multiple universities through the collection of BETO projects in the portfolio. There are regular meetings, and the program is showing good progress and appears to be very well organized.

  Approach: There are multiple parallel projects embedded in this overarching team of efforts "at the nexus of multiple projects." Overall, there appears to be substantial merit and significant potential in these efforts. The goal is to identify sustainable PABPs through synthesis, characterization, and economic analysis. The organizational/management aspect of this project is commendable and keeps everyone focused on deliverables and making progress. With a broad array of efforts, this has significant potential for innovation and looks promising.

  Impact: The project impact has the potential to deliver good outcomes with thorough oversight and review processes and deliverables in place. It is not clear at this time which subproject will be the lead. The most promising areas are: (1) PABP design principles, (2) performance-advantaged nylons, (3) new recyclable thermosets, (4) new performance-advantaged plasticizers, and (5) the machine learning tool, PolyML. It will be good to see how well this can deliver against end-of-project milestones and how this might enable future focus toward identifying lead topic/targets and honing in on the most promising.

  Progress and outcomes: Results are showing excellent promise relative to the metrics set. Impressive set of publications. The project appears to have coped well despite the COVID-19 impact, and progress and outcomes look promising. Overall, the project has made good progress toward addressing the project goals.

- Management: Strong management team, with synergies between partners. Communication protocols are outlined well. Risks are conveyed, with contingencies considered. Slides 3–4 are clear and strong. This section is excellent.

  Approach: Combining PolyML with directed polymer synthesis is clever and should result in useful biomaterials. It is clear that this project is closely tied in with project 2.3.4.500, which strengthens the breadth of this approach. Together, they provide excellent synergy (it raises the question as to why they are separate projects).

  Impact: Agreed (slide 7), experimental R&D coupled with PolyML analysis can de-risk technology prior to industry scale-up of polymer production. It is appreciated that amines are derived from biomass and that methyl muconates are sourced via the thermochemical conversion of biological materials. Having said that, biomass represents a broad swath of materials, and describing bio-based amines is equally broad. For the uninitiated, this section may have been made stronger by briefly describing the sorts of substrates that are imagined to be used for these end products. The front end of this argument (i.e., substrate pretreatment, availability and broad costs, even conveyed broadly) would improve context. Even saying products from lignin is very broad.

Progress and outcomes: Excellent progress to date on multiple fronts, including the beto-keto acids and plasticizers. Great progress shown in slide 18, whereby 8 polyesters and 12 polyamides are synthesized to validate PolyML predictions.

- Excellent team composition for defining potential pathways to PABPs from inherent bio-based sources. Developing performance targets would benefit from additional participation of materials companies early in the design process. Additional access to prototyping candidates will accelerate go/no-go decisions. Focusing on molecular structure/property relationships is paying big dividends by helping screen thousands of candidates to a promising few. TEA and routes to market analysis re needed to further refine the selection of candidates for scale-up. Would like to see replacements for currently expensive hexamethylenediamine for polyamide monomers, potentially over adipic acid replacements. This approach, when fully developed, will open up many renewable and sustainable replacements for polymers, plasticizers, and additives. Potentially exciting game-changers. Despite limitations on prototyping, the candidates identified so far have great potential. Low productivity of beta-ketoadipate production is a concern. The polyamide polymer has promising properties, but cost may be a potential showstopper.

- The project linkages are excellent, including ABF and BioSeparations. As with some other similar projects, there should be more recognition that this is not just "to make fuel production more economical." Biofuels can be displaced by alternatives, either now or eventually. The key is that where we need chemicals and materials, we need to find ways to get them without maintaining access to an extensive petroleum and natural gas liquids supply line. Otherwise, we never get to 100% renewable. The management and risk mitigation plan are a little light, but okay. The scope, approach, and subprojects/themes are a little confusing. Exposition could use some work. The Van Krevelen diagram is useful, although for non-polymers or low-polymers, matching C-numbers would be another obvious criterion. There are so many high-value functional molecules and formulations, how to cast the net even more widely? Progress appears very good for the time and money spent and with the difficulties of the past year.

- This program is outstanding and well-rounded, working hand in glove with the Inverse Design project (reviewed separately). The project team, communication plan, risks/mitigations, and commercialization path are well described. The approach uses computational-experimental interplay to navigate the biodesign space to identify possible PABPs, and experiments focus on PABP syntheses and characterization. This project focuses on the synthesis and characterization of bio-derived PABP candidates and feedback into the design loop to the Industrial Design project. The approach has a high potential for innovation and novelty, including the development of tools to design, produce, and analyze PABPs. The team is actively engaged with industry to determine customer needs and value propositions. Progress has been excellent, with the number of new formulations exceeding the project target; several of these are PABPs. Examples (improved nylon enabled with bio-based beta-keto diacid; bio-derived amines for thermosets; methyl-muconates as PVC plasticizer) illustrate the potential for PA as well as manufacturing/environmental benefits.

- This project has multiple BETO project connections (from conversion to separations) and is on course to develop a powerful and enabling platform technology. Very energized by the diacid work (beta-keto adipic acid) and the bio-amines (4-aminophenyl ethylamine): the former when incorporated into nylon polymers, which had a significantly higher glass transition (Tg) while significant lowering of water permeability; the latter when incorporated into epoxy thermosets creates a triazine, which provides a degradable site target end-of-life recycling. The focus is on performance-advantaged nylons (with BKA) and thermosets from the bio-derived amines and potential future plasticizers (near and longer-term project), but there may be great value looming in the additives space; a small quantity can make a high impact in a formulation. Given the increasing regulation and scrutiny of some incumbent additives (as preservatives, plasticizers, stabilizers), it is a space to continue exploring for more benign molecules that provide a performance benefit. I appreciate the inclusion of meaningful metrics (e.g., yield expressed on a mol/mol basis and productivity). The charts on pages 12 and 14 provided excellent clarity of the impact on GHG emissions by the parsing processes based on feedstock.

- This project utilizes the expertise that resides in the national labs—extending from bioproduct acquisition to formulation, characterization, and TEA/GHG analysis—to identify performance-advantaged biomaterials. An impressive array of targets and formulations have been examined and multiple PABPs identified and communicated in publications. Several polymers are being scaled up for testing by industrial partners. This reviewer is left with the following questions: When is the right time to shift focus away from identifying additional PABPs to pushing several PABPs to the point necessary to garner significant industrial investment? Alternatively, would it make sense to spin a small number of PABPs off into separate projects for more focused efforts on pathway engineering, materials validation, and applications?

PI RESPONSE TO REVIEWER COMMENTS

- We thank the Review Panel for the positive comments and constructive inputs. We are very excited about the continued success of this project, in collaboration with the Inverse Design efforts, to provide a generalizable framework for the identification, optimal production, synthesis, and characterization of PABPs. We fully agree that performance targets for new PABPs cannot be fully defined by our project's efforts alone and that industry collaboration to that end will be critical. Our focus is thus on synthesizing new PABPs, determining their baseline properties, reporting them in the patent and peer-reviewed literature, and then working with industrial partners who can help us define additional performance criteria that must be met. As described in the presentation, this project has spawned multiple Energy I-Corps teams, active technology transfer, and active partnering efforts with the industrial community—all toward exactly what the reviewer suggests: namely, that we need industry collaboration and input to make any of these PABPs ultimately successful in the marketplace. In terms of the need for TEA, we have this effort embedded in this project, as described during the presentation, and we are using TEA and Materials Flows through Industry as key tools to identify opportunities for scale-up activities. In terms of hexamethylenediamine, this is an excellent suggestion, and as discussed during the Q&A session, we have several strategies to make this molecule (and related molecules) now, which we will test when bandwidth allows. For the concern regarding the low productivity of beta-ketoadipate, we note that from lignin-derived aromatics in the Biological Lignin Valorization project, we are currently able to achieve 0.9 g/L/hr, and we are actively working to improve the productivity from sugars in the Agile BioFoundry project beyond the current level of ~0.2 g/L/hr. Regarding substrates, we fully agree with the reviewer that there are many potential substrates that could be leveraged for PABP syntheses. We are excited to have onboarded Northwestern University (Linda Broadbelt) and Iowa State University (Brent Shanks) as academic partners exactly to this end. Using chemical operator tools that Professor Broadbelt is a world leader in the development of, we will be able to identify the most atom and energy-efficient routes from waste biomass (and other waste) feedstocks to PABPs. Moreover, as identified by the reviewer, this project aims to source molecules from the entirety of the BETO portfolio. The reviewer brings up an excellent point related to spin-off into separate projects for individual PABPs. Our current mechanisms are to leverage other projects (e.g., the Agile BioFoundry, Biological Lignin Valorization, Lignin Utilization) for the pathway engineering and catalysis development (to make the necessary molecules in a cost-effective manner) and to collaborate with industry via Technology

Commercialization Fund projects, Small Business Innovation Research, FOAs, and other mechanisms that DOE has established to aid in viable technology transfer. Certainly, we fully realize, as the reviewer does, that this project alone will not be able to wholly develop the full potential of some of the promising PABPs developed herein, but there are mechanisms in place that DOE has enabled to aid in this transition. In addition to leveraging DOE mechanisms, we are continuously investigating methods to enable a single molecule to be used in multiple applications that can further de-risk technology development and enable a more facile pathway to market. To cast a wider net, we are targeting more PABP product classes in the current 3-year AOP cycle. This includes additives, such as our PVC plasticizer example, that command large market sizes and can exhibit have a shorter path to market than new polymer formulations because small molecules can be used in many formulated products. Last, we fully agree that bio-based chemicals and materials are critical to displace our collective dependence on fossil carbon-based inputs used for today's chemicals and materials.

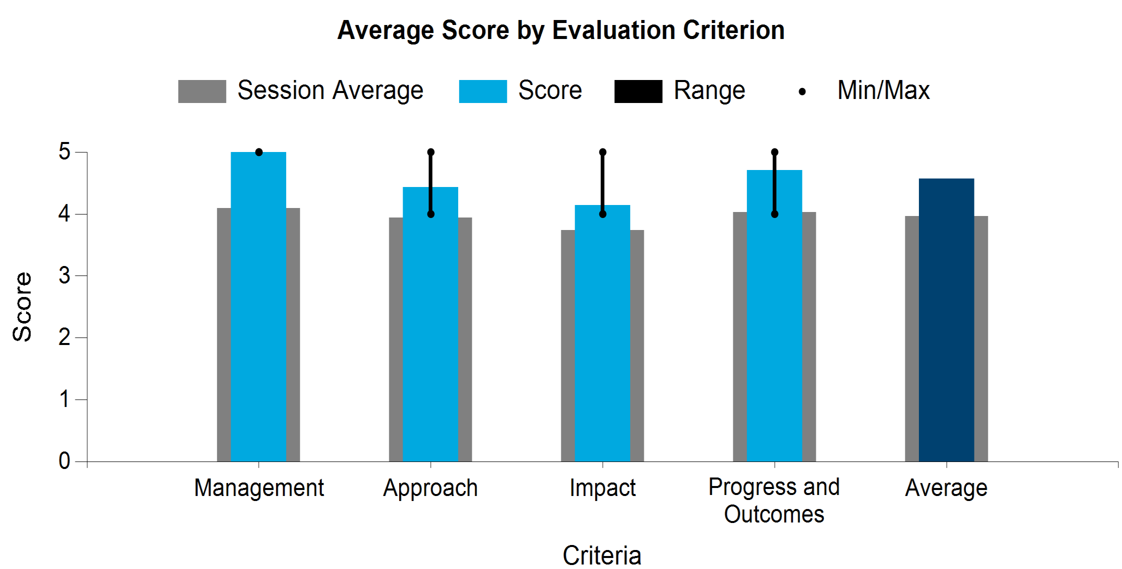
BIO-OPTIMIZED TECHNOLOGIES TO KEEP THERMOPLASTICS OUT OF LANDFILLS AND THE ENVIRONMENT (BOTTLE)

BOTTLE

PROJECT DESCRIPTION

WBS:	2.3.4.504
Presenter(s):	Gregg Beckham
Project Start Date:	10/01/2020
Planned Project End Date:	09/30/2023
Total DOE Funding:	$10,125,000

Plastics have revolutionized modern life, but reliance on these fossil-based materials that persist for centuries is causing a pollution crisis and contributing to GHG emissions. To develop new technologies to address this problem, the BOTTLE Consortium will deliver selective, scalable technologies to enable cost-effective recycling, upcycling, and increased energy efficiency. BOTTLE is an interdisciplinary team of experts that aim to develop selective, scalable processes to deconstruct and upcycle today's plastics and thermosets; redesign tomorrow's plastics to be recyclable-by-design and derived from both bio-based and plastic waste-based feedstocks; work with industrial partners across the value chain to catalyze the circular economy for plastics; and leverage the Advanced Manufacturing Office and BETO investments in analysis-guided R&D, integrated process development, chemical and biological catalysis, materials characterization, modeling, and data science. BOTTLE is guided by TEA and supply chain-based LCA. BOTTLE comprises members from 10 partner institutions. Primary outcomes to date include the establishment of a full consortium; impactful, benchmarking analyses that will be important for the plastics recycling and upcycling community; and multiple impactful, high-impact publications across the breadth of our research portfolio.



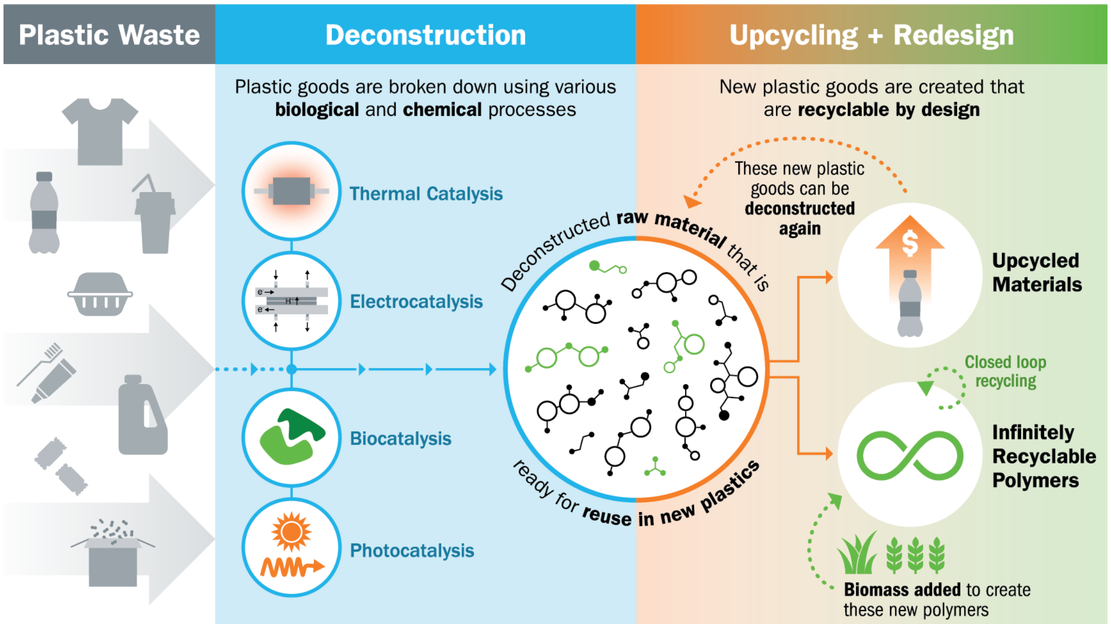


Photo courtesy of BOTTLE

COMMENTS

- Management: This is a remarkably diverse program. It includes thermal and biochemical routes toward deconstruction, upcycling, designed recycling, scale-up, and deployment. This presents an unwieldy team, by definition. Their management proposal is very good and well-presented—considering their breadth and diversity. Slides 10–15 (part 1) in the presentation are strong, showing a wide array of partners, specific roles, the advisory board, etc. Individually, team members are strong leaders within their respective fields, starting with Gregg Beckham, which, accordingly, implies strong leadership across individual projects across this broad program. The communication chain is described (slides 19–21, part 1), which is not always the case. This is a strong discussion. The role of industrial partners will be important and provides confidence that this project will have impact beyond publications.

  Approach: BOTTLE is aimed to be complementary to other DOE activities in this space: REMADE, Energy Frontier Research Centers, etc., and the machine learning, modeling work (described here and elsewhere) is strong. The case for analysis-guided R&D is clear and strong. It is clear that TEA, LCA, Materials Flows through Industry, and environmentally extended input-output will be used widely for decision making, which is commendable. This should broaden the impact beyond basic science.

  Feedstocks: A significant shortcoming of the discussion was the lack of detail on how real-world substrates (from our current material-handling infrastructure) will be utilized within the relatively clean science described throughout. Slide 27, which mentions a Substrate Csar and use of model substrates, is a good start, but it does not really address real-world substrates. There’s a gap here. Accordingly, the project missed a chance to address how we are going to get from here to there. Plastic recyclers have very dirty feedstocks with little incentive to clean them and few market outlets. So, even if this project succeeds completely, it did not describe how relatively diverse and dirty plastics coming from a recycling plant will be characterized and utilized. The broad swath of programs that are at differing TRLs but under “one roof” allows for synergies that might not occur among individual projects. For example, if biological conversion of PET falls short, the team can transfer priorities toward chemo-catalytic approaches, and so forth.

  Impact: The team provided an excellent context to the problem, outlining clearly why plastics is an energy issue. Specifically, 6% of the worlds fossil fuel consumption goes into making polymers, which is to expand toward 20% in the next decades. The potential impact is outlined well. Industry engagement is strong. Presumably through this engagement, the impact will go well beyond academic channels (beyond basic research toward commercialization). PET upcycling is definitely still in its very early stages; it represents basic research that will likely require a long time period toward impact, likely well beyond the scope of this project. Universal adoption of PolyML in and of itself is a potentially strong impact from this research. It holds promise well beyond the scope outlined here, but the BOTTLE project can give PolyML visibility and range.

Progress and outcomes: The PET projects are particularly promising. This team includes some of the world's leading proponents of catalytic conversion of PET to reusable chemicals as well as enzymatic deconstruction/conversion. The research on alkane hydrogenolysis of polyethylene (PE) (slides 21–23, part 2) is solid research and very promising. Similarly, the polystyrene chemo-catalytic deconstruction research (slide 24) is appreciated, but harping back to comments about substrate infrastructure, it is not clear what streams of polystyrene this will address. Polystyrene has proven very elusive to recover within our present infrastructure. The research is elegant, but its impact is debatable (context is needed here). The polyhydroxyalkanoate (PHA) research was presented broadly, raising the direct question: What is new here that has not been tried for the past 30 years? A little more detail would help provide more context and/or scope of impact. The team has already made progress (despite the pandemic) and is on or ahead of some schedules. This is a strong project with a very positive future.

- This is a very comprehensive approach based on sound analysis and extensive use of supporting areas of science and engineering. Strong connections to the plastic industry to provide constructive input. Looking at the volume of individual classes of plastics is an excellent way to prioritize efforts. A broad selection of mitigation options, from deconstruction to recycling, upcycling, and developing renewable alternatives to the design of products that can be more easily recycled. I'm concerned that there is a heavy reliance on PHA, which has current property deficiencies and significant risks to successful scale-up and commercialization. I would like to see mitigation of landfill disposal with improved mixed plastic waste recovery, sorting, and chemical or thermochemical recycle to monomers and fuel precursors. I suggest benchmarking of end of life to see if more robust but ultimately biodegradable polymers could significantly improve the overall LCA. This broad yet deep approach has the potential to significantly reduce the impact of current products as well as guide the development of attractive and more sustainable alternatives for the future. Although it is still early in the plan, good progress has been made in identifying ways to mitigate impacts via recycle, upcycle, and alternative design of products. I would encourage additional emphasis on systems that rely on renewable sources and offer ultimate biodegradability because landfills and the environment will remain a significant end of life for plastics.

- Management: The management plan and implementation appear to be high level and well organized with many outstanding organizations (NREL, LANL, ORNL, SLAC, ANL, Northwestern University, Colorado State University, Montana State University, University of Portsmouth, Massachusetts Institute of Technology). This is an impressive consortium of entities and showing good progress and appears to be very well organized with a governing board and strong leadership team; plus, there is a technical advisory board and commercialization council.

  Approach: There is substantial societal and technical merit and significant potential in these approaches of "deconstructing and upcycling plastics" as well as "recyclable-by-design." On the plus side are opportunities that do not involve consumers, such as windmill blade recycling, etc., so I wonder about some kind of targeting exercise to identify those things that could be targeted to become the best fit; however, I am very concerned that much of this technology will amount to naught because (1) there is insufficient value in the downstream value chain, and (2) consumers do not recycle because so many different plastics cause confusion, and there is little incentive. Nevertheless, I recognize that this investment in deconstruction and recycling is not aiming to solve the societal challenge, and therefore I am not negatively evaluating the project.

Impact: The project impact appears to be headed toward good outcomes with thorough review processes and deliverables in place. The project is relatively early stage to define clear commercialization potential, so real impacts are hoped for in the future.

Progress and outcomes: It is too early to comment on progress except in the context of the team and how well it is getting started. BOTTLE is clearly highly functional and working hard and appears to be poised to start making progress toward future outcomes. Being led solely by TEA and LCA is a potential flaw because societal impact might identify what would actually be more likely to work well. It would be interesting to know if there might be an intermediate goal of zero ocean waste, as opposed to reducing incineration. I wondered if there be value in a focus on PET—something like focusing solely on that value chain and trying to make it work and then using that as the learning for a future effort on other targets.

- BOTTLE is extremely well managed and carefully oriented toward the appropriate issues. The direct energy consumption issue is important, of course, as is the environmental impact, but a third key issue is the importance of plastics and their reliance on fossil energy. We need to replace them with recycled plastics or with renewable-based plastics to eliminate a need for the fossil industry in that context. All uses of energy as such can, in theory at least, be replaced by renewable sources other than biomass (e.g., electricity, hydrogen), but organic "stuff" requires a source of carbon, and the only practical source in the foreseeable future is renewable biomass. Another key aspect of BOTTLE, though noted in the slide deck, could do with some emphasis. The United States is responsible for a disproportionate share of the world's waste plastic. Further, as is now well documented, the winds and waves and tides ensure that U.S.-derived waste shows up on the world's beaches, in the world's oceans, and, most recently, in snowfall in the remote Siberian Arctic. Part of the job of maintaining (repairing?) our standing on the world stage is to take responsibility to clean up the messes we make, and waste plastics are a mess for which we are responsible to a very large extent. There are so many elements to the BOTTLE program that it would be impossible to comment on the "approach" for each. It is clear that the selection of topics and the approaches being taken are both being done thoughtfully and effectively. The recycle/upcycle work is especially good. The "recyclable-by-design" elements are a bit naive in some cases. They need to pay more attention to a range of practical issues, and perhaps a more robust industry advisory program would help. The potential for impact is clear, but most of it has yet to be achieved. There should be something included in future Peer Reviews to track outcomes longer term. It is much easier to *project* a successful outcome than to *achieve* one, and we've all become very skilled at doing so. And even applied R&D takes time to achieve real-world impact, so during the course of 3 or 5 years of funding, often all we have is projections. Progress to date is excellent. As is often the case, there are a few sub-elements that have been less successful but that generally seem to be due to the unpredictable obstacles that can crop up in R&D, not to any shortcomings in the researchers or their plans.

- Impressive presentation: Sufficient details were supplied; the content was organized and easy to comprehend. The BOTTLE Consortium has a well-designed organization structure and communication plan that should mitigate risks inherent in managing a large, multi-institutional program and achieve desirable participant communication and collaboration with appropriate external feedback. The consortium engages multiple advisory groups so that its internal communities are linked. Developing and deploying a common set of logos/taglines is a valuable strategy to create uniform messages and strengthen cohesiveness within BOTTLE but also a useful tool for outreach and marketing to external audiences. A clear vision of what success looks like for the BOTTLE projects is well articulated, with specific metrics in energy, carbon, and economics. The initial work has resulted in an attractive patent and publication portfolio. Aggressive outreach to 80 companies has resulted in identifying five companies that may bring earnest investment to the table and provide credible and critical input. This is timely because several BOTTLE projects will transition from ideal samples to confront the challenges of deconstruction on real-world materials. There has been significant progress in the proof-of-concept work since the 3Q20 inception of consortium; BOTTLE appears to be on track with meeting milestones.

- The BOTTLE Consortium presents a strong rationale for taking a go-big-or-go-home approach to the significant challenge of solving plastic pollution and waste. This is a large and diverse effort requiring superior governance to keep it on track, data-transparent, and, at the same time, nimble. The management plan, implementation strategy, risk identification/mitigation, and communication plans are detailed and appear to position the consortium for success. A balance will need to be struck to not overburden the teams with administration. Industry engagement is built into the governance structure and demonstrates a commercial mindset for project outcomes. The well-planned approach addresses the plastic waste crisis by developing and applying a wide set of technologies. This has substantial merit and is consistent with BETO Program and Technology Area goals. Significant innovation will result from many of the technical work streams. This program, if successful, has the capability of providing momentum for more collaborations and industrial adoption. The portfolio appears to be on track: Progress has been significant, with several patent applications and publications to date. Achieving all of the energy, carbon, and economic metrics will ultimately determine the commercial impact. One issue central to commercialization lies upstream, where effective collection of mixed waste and variable substrates in sufficient quantities are prerequisites to commercial success. This will be true for current waste streams and future circular-life polymer designs. Another challenge to the introduction of new polymer designs is slow industrial acceptance. New products will need to exhibit superiority in product performance, economics, as well as environmental footprint. It will be valuable to see how the consortium progresses and adjusts to upselect or downselect specific parts of the portfolio as it matures.
- The strategic planning and organization invested in the BOTTLE Consortium is impressive. With metrics defined around energy reduction, carbon utilization, and improved economics for reclaimed materials, some portions of the consortium (redesign, upcycling) fit better in the BETO portfolio than others (deconstruction); however, a collaborative, multidisciplinary approach is necessary to address the ambitious goals that have been laid out. Based on the pillars of deconstruction, upcycling, and redesign, the consortium seeks to reduce accumulating polymer waste, utilize deconstructed carbon, and, most significantly, lead an effort for the discovery and validation of new polymeric materials. The management structure is clearly defined; however, inclusion of individuals serving on the technical advisory board would be beneficial. Significant progress has been made in establishing foundational documents, which facilitates engaging with industrial partners, and establishing a polished communication platform. The newly established website simultaneously targets technical and nontechnical audiences. There is already strong industrial engagement, and it is appropriate that a government-funded consortium take a leadership role in such a significant global, societal problem. On the technical front, the program is still very new for significant impact or progress. The strength of the program is in the number of approaches that are already under examination. I optimistically look forward to the technological developments to come from this consortium.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the Review Panel for their overall positive comments and constructive inputs on the BOTTLE Consortium. We are incredibly excited about the potential for the consortium to be successful in the coming years as activities ramp up. In terms of the technical advisory board, we are finalizing the composition of this body now, and we did not have full commitments from the board members by the time of the Peer Review presentation, given that BOTTLE is a new consortium. We will be excited to share this information in the next BETO Peer Review. The comment regarding the non-consumer opportunities is excellent and warranted—indeed, we fully agree that there are industrial (non-consumer) plastic wastes that could serve as excellent "point sources" and opportunities for BOTTLE R&D efforts.

Although not discussed in great detail, we have engaged with an outside consulting firm to conduct an industry landscape analysis exactly to this end already. They have identified multiple application areas that we are targeting directly now through our robust industry engagement activities.

- Regarding the comment about much of this technology not coming to fruition because of insufficient value in the downstream value chain—this is exactly the intention of the upcycling efforts in BOTTLE. We are aiming to develop technology that will incentivize the recycling of waste plastics, not only from consumers but from all sectors of the economy. Regarding the comment about the lack of societal impacts in the project evaluation criteria, this is an excellent comment, and something that we are attempting to address as we move forward. Work to this end is emerging now in the analysis literature from leading groups in this space, and we are establishing collaborations to this end to help us quantify the societal impacts outside of what TEA, LCA, and environmentally extended input-output modeling frameworks already provide. In terms of an initial focus on PET, we agree with the reviewer that there is value in developing a technology portfolio focused on a single polymer, then expanding beyond that. For PET in particular, we are indeed already developing a strong R&D portfolio focused on this polymer via enzymatic hydrolysis, glycolysis, and hydrolysis. These technologies are being actively compared now with TEA and LCA.

- In terms of not overburdening the team with administration—we could not agree more. To this end, we have established a centralized management structure with a CEO, COO, and project manager who can handle most of the administrative duties of the consortium leadership, operation, and management, with the intention to enable the BOTTLE team to focus on impactful R&D. Regarding the need for upstream collection, we fully agree with the reviewer that many technologies we are developing will require sufficient substrate of the right quality (which will depend on the conversion technology being employed). Although R&D in the collection and sorting of plastics is outside the BOTTLE scope, we are actively engaged with both R&D activities in this space (e.g., with REMADE) and with industry on this front as well. We are also leveraging efforts in feedstock collection and sorting for plastics ongoing in the Advanced Manufacturing Office and BETO portfolios. We fully agree with the reviewer that new polymers will take many years to come to market in a meaningful way. Because BOTTLE is guided by TEA, Materials Flows through Industry, and other analysis approaches, and because we have the necessary expertise in the consortium to fully develop new polymer synthesis pathways, we are confident that we can rapidly advance new polymer designs to the point that industry engagement will become necessary to implement them at scale. We have a robust industry engagement model as well to ensure early feedback and industry collaboration into the polymer development efforts. Ensuring economics, sustainability, and performance metrics are met are key criteria that BOTTLE is pursuing in the redesign efforts.

- Regarding the comment on PHAs, this was discussed at length during the Q&A session, and we hope that these concerns were mostly addressed there. We stress that we are not developing standard PHB or medium-chain-length PHAs, or even relying on microbial production of PHAs, which has been the traditional path for PHAs taken industrially for many decades. Instead, BOTTLE is relying on the world-class expertise of Professor Eugene Chen (who leads the redesign component of BOTTLE) to chemically synthesize novel PHAs that are not biologically accessible. As shown in Professor Chen's work presented during the redesign component of the presentation, we are able to chemically synthesize novel PHA materials chemo-catalytically that can be tuned to exhibit PE or PP-like properties. We are excited for the paradigm-changing PHA chemical syntheses that Professor Chen brings to the BOTTLE Consortium, which we believe will fully alleviate the justified concerns of the reviewer regarding traditional, biosourced PHA materials. In terms of mixed plastics recovery, this was not covered in detail in the presentation, but we have several ongoing projects that will be reported in future publications and patent applications regarding the deconstruction and upcycling of mixed plastics streams.

- In terms of the comment regarding fuel production, as noted in the overview section of the presentation, BOTTLE focuses on high-value end products, and we are not conducting R&D into plastics-to-fuels. This latter area is well served now by industry in the pyrolysis and gasification of waste plastics. We are conducting benchmark TEA and LCA now to understand the economics and environmental impacts of fuels production from waste plastics but primarily as another benchmark for our more selective approaches in the BOTTLE Consortium. Regarding the comment on biodegradable polymers, we fully agree that this is a rich area. We are actively developing the analysis framework to understand the economics, energy, and environmental impacts of this approach relative to recyclable-by-design polymers. We appreciate the comments regarding the strong leadership of BOTTLE. Regarding the comment about an unwieldy team, we built the BOTTLE Consortium team with complementarity as a key criterion from the start. Accordingly, though we have multiple, parallel activities ongoing, there are defined "lanes" of efforts with cross talk between them enabled by fortnightly R&D meetings that are focusing on impactful, industrially relevant research. The reviewer brings up a fair point that real-world feedstocks were not discussed at sufficient length during the presentation. Although not described thoroughly in the presentation, the BOTTLE Consortium is sourcing waste plastics from both industrial partners and ocean cleanup activities, exactly to this end, such that technologies that work on clean feedstocks can be evaluated rigorously on real-world feedstocks.

- In terms of polystyrene as a substrate, the reviewer brings up an excellent point at the heart of the BOTTLE Consortium deconstruction and upcycling activities—namely, that we are working to develop technologies that will enable the upcycling of plastics that today are not collected in large quantities because mechanical recycling is not adequate for those materials. Not all of the technologies BOTTLE is developing today must be bounded by existing collection infrastructure, but, instead, we are attempting to develop technologies that will lead to the creation of new collection systems toward a more circular economy for plastics. Regarding the PHA research in terms of "what is new"—as described above, we have a wholly new approach to make a much broader range of PHAs use chemical catalysis; thus, we have a clear path that leverages the relatively straightforward depolymerization of PHA materials with the ability to tune the side chains to make completely new polymers, to gain control over the molecular weight and dispersity, and to avoid costly and limited biological production of PHAs that has been researched for many decades. We fully agree with the reviewer that biomass can offer a viable source of carbon for displacing fossil fuels. This is why the redesign component of BOTTLE focuses on the use of bio-based and waste-based feedstocks. In terms of the redesign approach needing a robust industry advisory program, we emphasize that the BOTTLE Consortium technical advisory board consists of representatives with expertise in this space, such that we will have direct advisors aimed at enabling success in redesign. It is also worth mentioning in this context that the BOTTLE Consortium industry engagement team has talked with more than 100 companies to date, and polymer redesign is by far the most common topic in these conversations; in other words, many industries realize that redesign for recyclability is a key component of a circular economy, and they are asking the BOTTLE Consortium and other research projects for new materials to this end.

RESIN: RESPONSIBLE INNOVATION FOR HIGHLY RECYCLABLE PLASTICS

Northwestern University

PROJECT DESCRIPTION

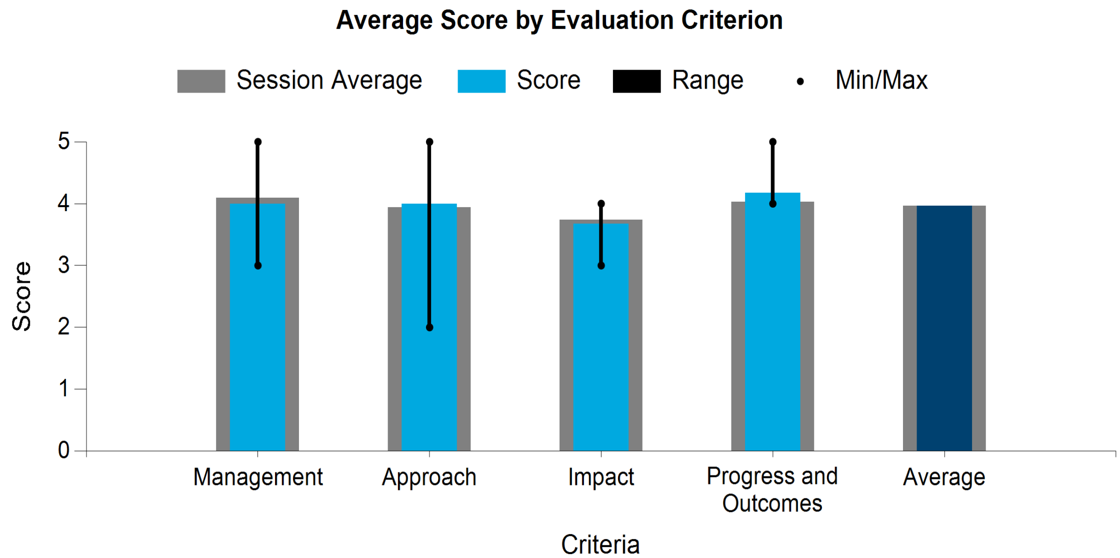
WBS:	2.3.4.607
Presenter(s):	Linda Broadbelt
Project Start Date:	10/01/2019
Planned Project End Date:	12/31/2022
Total DOE Funding:	$2,499,999

We are developing a responsible innovation approach that marries computational-based approaches with experiments to design materials that achieve high polymer recyclability and benign degradation products at end of life. We target the polyurethane family of polymers, which ranks sixth in worldwide production, at 36 billion pounds produced in 2016 and a 6% annual growth rate. Polyurethane is not recycled at any significant level when made of linear chains (thermoplastics) or cross-linked networks (thermosets). The SOA is 0% recovered monomers for polyurethane.

The Northwestern University-ANL team, in collaboration with its industrial partners, focuses its efforts on the responsible recycling of bio-based polyurethane-like materials, namely bio-based polyhydroxyurethanes (PHUs) and polythiourethanes (PTUs), which offer the possibility of recovering value and improving sustainability in two ways: (1) recovery of monomer from spent materials, whether thermoplastics or thermosets; and (2) reprocessability of spent networks with full recovery of cross-link density and associated properties after reprocessing. Our approach is designed to meet the monomer recovery challenge as well as put thermosets on par with thermoplastics, where melt-state reprocessing of spent polymer into recycled high-value products that meet original use guidelines is the most energy-efficient and responsible method of recycling.

Approach: The overall design framework begins with biomass-derived intermediates as starting molecules, to which a computational framework for reaction pathway design is applied to generate potential monomers. These monomers will be used to synthesize PHU and PTU that can be reversibly thermally reprocessed (chemical recycling) for their original use. Experimental studies and kinetic Monte Carlo simulations are used to design conditions for optimal chemical recycling and assess the extent of degradation of properties upon repeated chemical recycling. Experimental design and kinetic Monte Carlo simulations of monomer recovery for PHU and PTU are also done, exploring conditions for high monomer yield. Environmental and economic analyses are being conducted in concert with these studies. Risk assessment for environmental performance is used to understand the potential impacts of disposal pathways of the plastics and exposure analysis of the polymers and their monomers. Testing for end-of-life properties involves both engineered and natural environments. Finally, LCA and TEA are done to assess alternatives, explore economic feasibility, and evaluate sustainability.

Impact: The project will have impact on multiple fronts. We will achieve chemical recyclability of 25% monomer recovery from PHUs and PTUs. We will develop modeling and analysis tools to guide the production and recycling of PHUs and PTUs that are at least 50% biomass-derived; benign at end of life; are cost-effective; and are less energy-, GHG, and water-intensive than baseline polyurethanes. An additional focus is to develop PHUs and PTUs that exhibit equivalent or improved properties compared to conventional polyurethanes. Further outcomes of the project are publicly available tools for PHU and PTU design for recyclability, performance, and benignity that can be evolved to cover other types of polymers and publicly available cost and environmental assessment tools for recyclable bio-based polymers. A critical outcome is the demonstration of successful design of a market-relevant polymer while incorporating key performance requirements and end-of-life considerations that can be replicated for other polymer types.



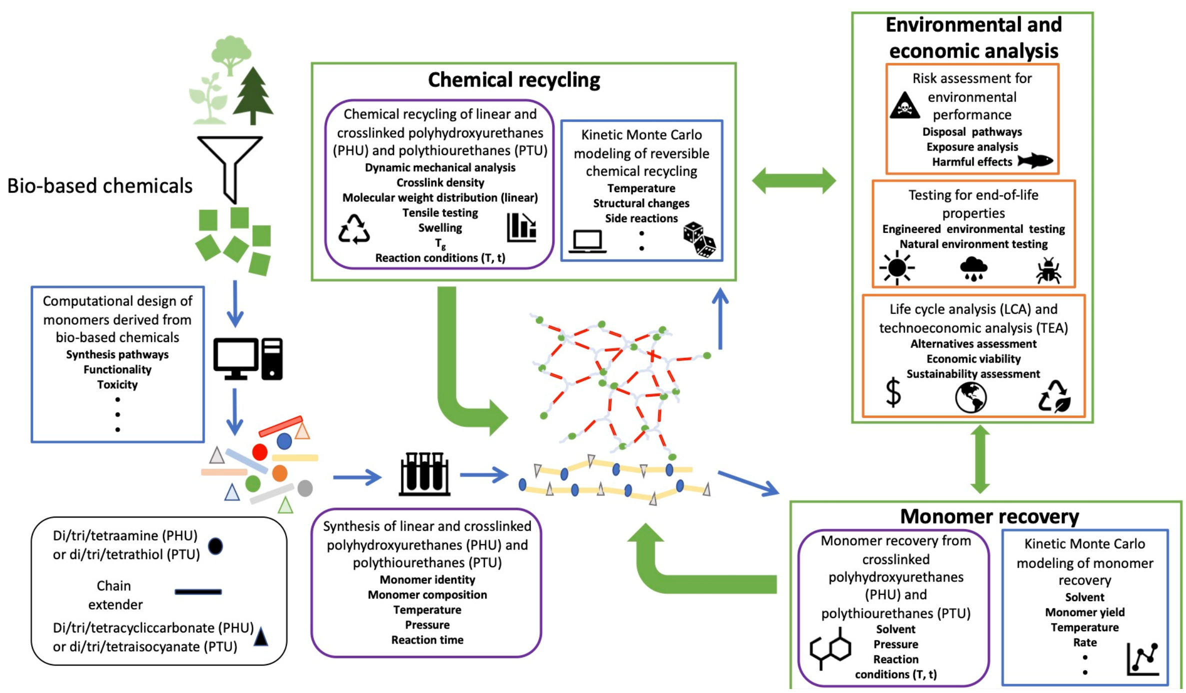


Photo courtesy of Northwestern University

COMMENTS

- The team has excellent breadth and depth. Current industrial advisors well represent the value chain. The use of Monte Carlo screening tools is a definite plus. Including both supply chain and end-of-life benchmarking helps identify key approaches to target development efforts. Having both recycle and biodegradability options in the plan is a plus. Polyester polyurethanes may offer higher-value outlets and be more recyclable. Polyurethanes are a significant market, and lack of recyclability is a major problem. I would like to see higher-value thermoplastic polyester polyurethanes in the plan as well. Monomer recovery from recycle approaches is lagging in this plan, so that is an area needing additional emphasis. There is good progress despite restrictions on mapping out the current state and evaluating on paper the options. There is good progress on the Poly-hydroxyurethane synthesis and characterization. Poly-thiourethane synthesis and characterization is lagging but offers real potential.

- Management: The management team is strong, with expertise across a broad reach of disciplines that are in line with the needs of the project. Corporate partners are strong. Communication strategies are in place. The team addressed the impact of COVID-19 on delays but noted that the computational components of the project had proceeded (which is suitable). The risk assessment framework (slide 15) is well described and looks to be a useful tool to allow stakeholders (corporate partners, presumably) to work closely toward optimal end-use design. As stated, this will make future decision points more meaningful, targeting potential commercial impact.

  Approach: Automated pathway design tools are being utilized, which is a strong starting point and should be encouraged. The modeling approach is described, including TEA and LCA results, Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET), and an evaluation of potential supply chain disruption when polyurethane is designed for 25% monomer recovery (this last piece is unique). Again, the computational design of monomers and PHUs and PTUs for recyclability and functionality is a strong point in this work. Any tool that reduces the amount of trial-and-error chemical synthesis of monomers and polymers is commendable. Flow diagrams are always appreciated, and those on slide 16, for example, are useful guides toward assessing future directions and potential impact.

  Impact: On slide 8, they describe efforts on the responsible recycling of bio-based polyurethane-like materials—namely, bio-based PHUs and PTUs. That seems limiting and difficult. It was not clear how those particular streams would be isolated from post-consumer waste streams. This would have been strengthened by mentioning where and how these bio-based urethanes would be recovered and reused. Specifically, where do the spent materials actually come from? The end-of-life property testing (Task 5) is appropriate and described well, but (to repeat the point), it is not clear how the PHUs and PTUs will be isolated into biodegradation/composting streams. Carpet underlayment was identified as a possibility, but that is a stretch. If the team is depending on consumers, that is also a stretch. The obvious example is polylactic acid, which can degrade in composting facilities, but in today’s infrastructure, polylactic acid becomes a bane to both composters and recyclers. There is no infrastructure to identify and isolate polylactic acid materials (and it piles up, unwanted, at municipal recycling facilities). Will the spent urethanes be separated by consumers or industrial users, and how? It is still not clear enough.

  Progress and outcomes: The project overview (slide 3) is a nice graphic summary of progress and future steps that shows an appropriate level of detail. In computational studies, the team generated >40,000 potential molecules and honed work down to 15 promising bio-based materials. That is good progress. Completing the synthesis of partially bio-based, linear segmented PHUs is a key accomplishment. A lot of work appears to have been accomplished (considering that they stated that the team was slowed by COVID-19). The systems economic and sustainability analysis (slide 21) is promising, outlining that there is potential to recover some polyurethane materials.

- Polyurethanes are the sixth largest class of polymers produced, but there is currently no recycling technology. This project seeks to develop PHUs and PTUs that are recyclable and reprocessable. Each task is assigned to a lead, monthly meetings are scheduled for data sharing, and engagement with industrial partners has been established. The computational framework for the identification of bio-based targets for polymer synthesis has been successfully implemented, and molecules have been identified. The project has may have significant impact associated with identifying biologically derived molecules and performing the initial characterization of the materials and their recyclability. Downstream validation, applications development, and displacement of in-place materials require significant resources; are the current industrial partners committed to serving in this role or are additional partners needed? PHUs that are fully or partially bio-based with tunable characteristics have been synthesized from computationally identified molecules. Whether those characteristics can be tuned for industrial applications is not described. One risk not identified by the project team is the difference between the rate of identifying putative bio-based molecules and the rate of obtaining the molecules and characterizing subsequent polymers. Dissemination of identified molecules to a wider audience might relieve this rate-determining step in the discovery process.

- The approach of discovering biomass-derived pathways to manufacture degradable polyurethane polymers has significant merit. The use of computational approaches is exciting here, potentially enabling the navigation of vast design space to identify the most favorable pathways to be assessed by relevant criteria (including risk assessment and LCA), and, ultimately, wet-lab work. There is significant probability for innovation and invention in this program. Recovery of polyurethane monomer and iterative reuse without loss of desirable properties would have a substantial impact on sustainability, and biomass-derived monomers have a clear positive impact on the bioeconomy. The management plan, structure, communication, and risk identification are well described. Specific industrial entities are mentioned, although their role is not clear. Progress appears on track, including the synthesis and recovery of bio-based PHUs being demonstrated and end-of-life testing.

- The team looks solid, and the management plan is okay. Risk mitigation is generic; it should anticipate likely obstacles to the research itself. With respect to the approach, there are several concerns: How important are PHU and PTU (among all polyurethanes)? Are they “disposable” and do they wind up in the environment? Are they collected/available as such, or must they be recovered by the mechanical deconstruction of complex objects. Recovery of 25% monomer is obviously better than 0%, but what becomes of the other 75%? Is it in a form harder to deal with than before? Can it be disposed of safely? It is not clear that “monomer design” is considering processing or material properties deeply enough. Any communications with the retrosynthesis efforts in the Bio-JET project? Tasks should be unique activities. Three Task 2s and three Task 3s on slide 3 is confusing. Two of the Task 2s seem more suited to conventional computer simulation than to kinetic Monte Carlo simulation. Is this a hammer in search of a nail? Progress is good in light of the constraints we’ve all face during the past year and the percentage costed to date.

- This project is a fitting part of the BETO portfolio because the target polyurethane polymers are widely used but are currently not recycled. To date, the project team has made good progress: completed the syntheses of bio-based and partially bio-based PHU and PTUs (although scale, quantity, and yield data are absent); performed initial material properties characterization; installed end-of-life property test systems; and quickly pivoted to start initial economic analyses. For this reviewer to better assess progress toward anticipated goals, it would be helpful if the five project tasks were transferred to a timeline table in the presentation materials because it allows for better visualization of anticipated start/stop dates in the funding cycle(s). The recovery study achievement seems substantial: demonstrating 10% monomer recovery (40% of milestone target of >25% monomer recovery—but again, lacking details on scale). In notes for systems economic and sustainability analyses, polyester polyols are referenced for clarity; can investigators clearly denote in the body of the presentation whether their base case is based on polyurethane with a polyether polyol segment or with a polyester polyol segment? This may influence the TEA analyses for the baseline polyurethane systems supply chain, and this task is earmarked as the FY 2021 major milestone.

PI RESPONSE TO REVIEWER COMMENTS

- Reviewer comments on the ResIn: Responsible Innovation for Highly Recyclable Plastics project were very helpful and focused on five main points, which are summarized and responded to below.

- Application and adoption of ResIn materials: The reviewers raised important questions about the application areas for the new ResIn materials. Overall, the focus is on developing materials with properties that are comparable to polyurethanes that they would replace, and we have four specific properties on which to evaluate these materials and acceptable ranges: strain at break, Young's modulus, tensile strength, and rubbery-plateau tensile strength modulus. In addition, new applications for ResIn materials have emerged due to properties that were unanticipated at the time of the validation stage of the project; specifically, excellent broad temperature range acoustic noise/vibration damping that is not observed in conventional polyurethane elastomers has been achieved. The industrial partners who are involved in ResIn are indeed providing regular input about the directions that would lead to industrial applications and adoption. Feedback about the desired properties that inform monomer design efforts is in place based on connections between Task 2 and Task 3; in addition, it is anticipated that the PolyML efforts in BOTTLE at NREL may be able to be leveraged for the ResIn project as they continue to develop.

- Development and dissemination of computational platform and results: The dissemination of the results of our molecule discovery efforts is an area where we have put recent attention to ensure that the impact goes beyond our own synthesis activities. As part of the recent publication of our first manuscript in molecule discovery related to polyurethane replacements, we provided supplementary information of all pathways to target molecules, which any reader can download and cultivate to identify molecules that may be of interest to their own development efforts related to polyurethanes or other polymer classes. Although the Bio-JET project mentioned by the reviewers focuses on molecules for different applications those considered in ResIn, there may indeed be some synergies. In our own related work focusing on bioprivileged molecules, we have provided supplementary information to a recently submitted manuscript in the form of a JSON file that can be accessed by readers to explore novel molecule space for their own applications. A MongoDB database as a repository for multiple efforts in molecule discovery is in development.

- Considerations of post-consumer processing and impact: Although the strategies for post-consumer collection, sorting, and processing are beyond the specific scope of ResIn, we acknowledge that these are important considerations and in part depend on the application areas (see above). Using our frameworks for material flow analysis and risk assessment, we will be well positioned to address the other considerations raised, including what happens to mass that is not recovered as monomers, safe disposal routes of materials, and the assessment of the safety of products of biodegradation.

- Management of tasks, risk, and progress: Although COVID-19 presented some challenges toward progress on specific areas of the project, there is a robust risk mitigation strategy in place that is related to other comments that the reviewers raised. In our own anticipation of obstacles to the research itself, the multipronged approach we have adopted with different material classes (i.e., PHUs and PTUs) and balanced efforts on reprocessing and monomer recovery provide opportunities for advances that do not rely on only one project moving forward successfully. The comment about the appearance of distinct multiple threads in two tasks, Task 2 and Task 3, is appreciated. We will focus future communication efforts on the design cycle as the overarching focus of both tasks, which has multiple components, in order to make them successful. Monomer recovery efforts and the synthesis of PTUs will have greater emphasis, now that laboratories have ramped back up more fully and the team is fully staffed, and we will have better metrics of scale and productivity across a broader set of monomer combinations. For the kinetic Monte Carlo simulations that are part of this cycle in Task 2, the ease of formulating models based on this method, as opposed to continuum models in which we have also have expertise, will become more apparent in future communications when we present results on network materials. In addition, we will include the timeline that we have for advancing and measuring progress of the ResIn team as guided by our milestones in future presentations.

- Clarification of systems economic and sustainability analysis: The systems analysis progress presented in the Peer Review presentation was a completed material flow analysis tracking the current production, use, and end of life of today's polyurethanes. The completion of this material flow analysis marked the completion of an FY 2021 milestone. A reviewer requested further information about the treatment of polyester and polyether polyols in this analysis and upcoming TEA within ResIn. The material flow analysis illustrates that as polyether polyols and polymeric methylene diphenyl diisocyanate are currently the most dominant polyurethane starting materials, producing these two compounds from biomass would be the most disruptive to the supply chain, reducing fossil fuel use to the greatest extent. In upcoming TEAs, we will adopt multiple polyurethane products (reaching back to both polyether and polyester polyols) as baselines given the diversity of polyurethane products and uses.

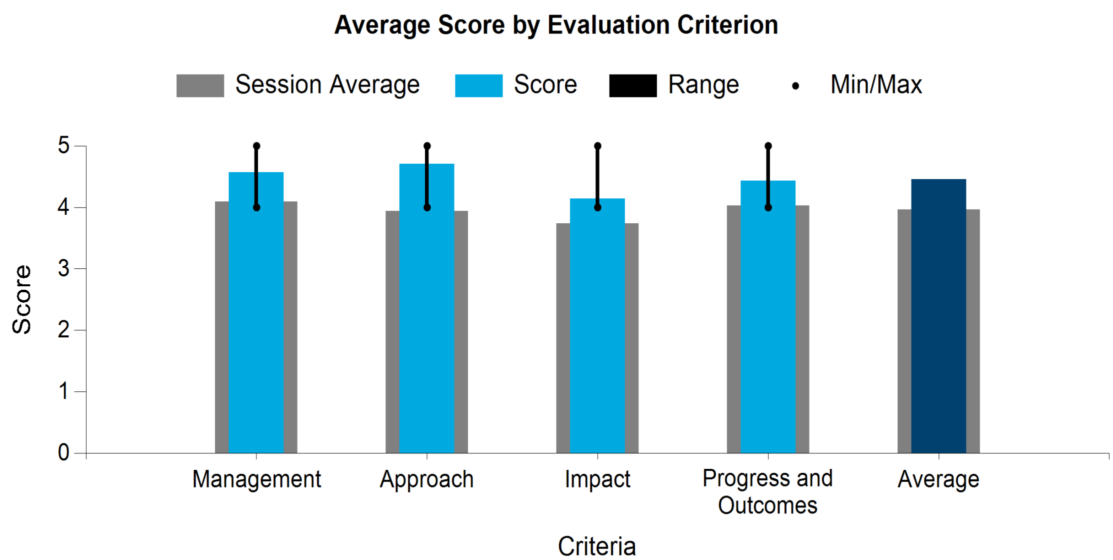
INVERSE BIOPOLYMER DESIGN THROUGH MACHINE LEARNING AND MOLECULAR SIMULATION

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.5.1.500
Presenter(s):	Nolan Wilson
Project Start Date:	10/01/2020
Planned Project End Date:	09/30/2023
Total DOE Funding:	$1,200,000

This work aims to identify PABPs through property prediction, which will guide experimental synthesis. The impact of this work will be faster market adoption of bioproducts with greater performance relative to incumbent products. We have identified >10^6 bioproduct candidates, but only some will have superior performance to create a market pull. High-throughput property prediction, enabled by machine learning, and the elucidation of structure-function relationships, enabled by molecular simulation, provide a hypothesis-driven approach for the downselection of candidate biomolecules to pursue experimentally. To enable machine learning and molecular simulation for bioproduct discovery, automated structure generation and embedding must capture relevant features for prediction, databases must cover domains applicable to bio-based products, and best practices for simulation of polymer systems must be developed. To address these challenges, we have established bioproduct relevant data sets, developed high-throughput polymer structure generation, and built end-to-end neural networks that have predicted eight properties for >1.4x10^6 biopolymers. A molecular simulation pipeline for building, running, and analyzing polymers and polymer additives is being used to predict performance and to develop design principles of bio-based products. In collaboration with the PABP synthesis project, these computational tools are guiding synthesis and informing the design of PABPs.



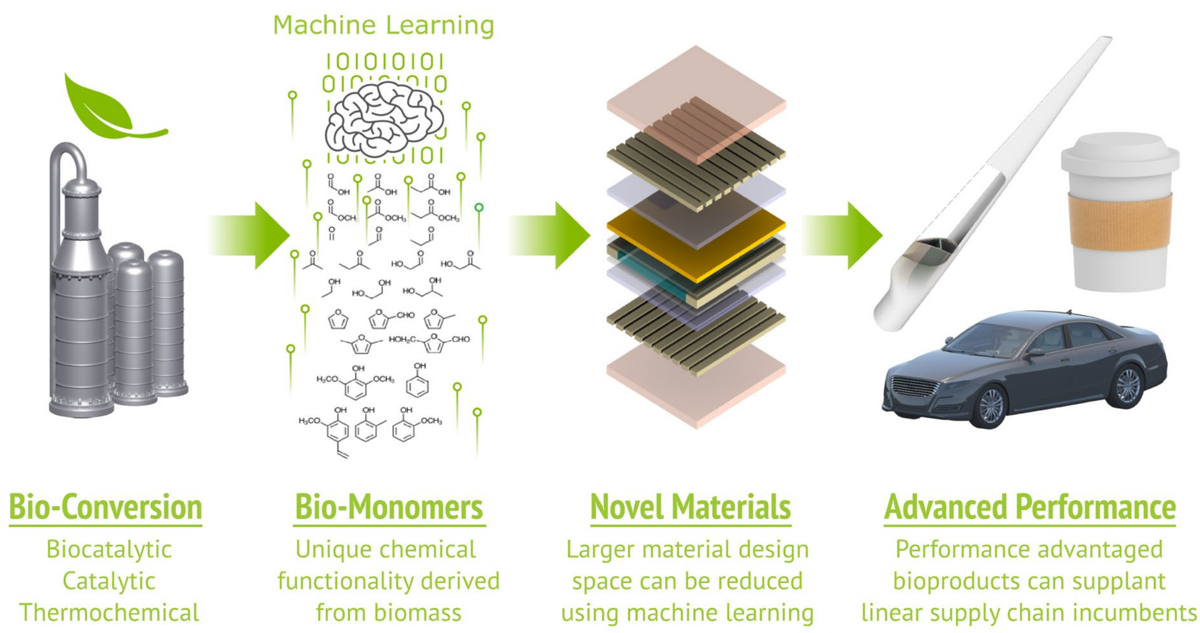


Photo courtesy of NREL

COMMENTS

- Management: The management team is strong, and this section was written very well. Slide 5, outlining how this project fits into other projects, including BOTTLE, was very helpful. Releasing three open-sourced code stacks for nonexperts is commendable, and it should help the greater researcher community toward directed (smart) synthesis.

  Approach: The approach and the justification for the approach is excellent. This is the type of technology that represents the best of national labs, open sources of information that provide important direction to industry, minimizing the need for the Edisonian approach.

  Impact: It is interesting that the team chose to pursue an alternative to PET rather than targeting ways to make PET more sustainable. This team would also have the means to improve PET, producing greener versions of monomers for PET production. They might consider the (often) prohibitively high cost of introducing new polymers versus improving an existing one.

  Progress and outcomes: Slide 15—it is always satisfying when modeling can explain a complicated observable; in this case, how dihedral carbon in nylon 6,ßK6 is locked in contrast to nylon 6,6 and nylon, which increases its glass transition temperature. This is a nice result. It is clear that this project works closely with the other NREL projects on PABD.

- Management: The management plan and implementation appear to be high level and well organized. There is an excellent team involved (NREL), and they are showing good progress and are appropriately organized. More involvement with industry would be a good addition, although it is encouraging to see an exploration of the Commercialization of Fully Renewable Non-Isocyanate Polyurethanes with industry, such as Sealy, Patagonia, and Agilix.

  Approach: The approach of using PolyML as a machine learning web tool to evaluate many chemical options is intriguing. Although this remains partially proven, the project recognizes this with statistical support decision points at FY 2022 Q2 go/no-go. If it works, the web tool has significant potential. It would be very disappointing if it does not work out.

Impact: The project impact appears to be headed toward quantifiable outcomes, with thorough review of processes and deliverables in place. I think that using machine learning like this has fascinating potential, and I really commend the team for tackling this, and I hope it all works out.

Progress and outcomes: Results are indicative of good progress and outcomes. There is emphasis on believing that this is going to work, supported by rigorous statistical input. It is important to bear in mind that a null hypothesis might be that the predictions have potential to deliver a zero outcome. There are clear end-of-project milestones: "Improve the accuracy of machine learning by 50% and identify 10 PABP thermoset materials." Of course, this is extremely challenging, and it is not clear from the data so far how this 50% increase in accuracy will be calculated. It is also not clear (to me) if a 50% increase would be statistically sound. The idea of a molecular simulation pipeline for "building, running, and analyzing polymers and polymer additives" is intriguing. These tools to predict performance and develop design principles of bio-based products seems promising.

- Excellent theoretical versus actual property and molecular structure resources on the team. Very good connectivity to the experimental teams with prototypes under development. Correlating model predictions to actual properties and using machine learning tools is showing increasing success in harnessing computing power to reduce the experimental options and speed prototyping. The key will be to connect to an even greater base of materials experts in industry to tap their insights into structure/property relationships and performance. May want to augment the ability to predict routes to novel and useful materials with the ability to physically prototype and test them. This set of tools can only get better with use. Include comonomers for block and random copolymers in the machine learning tool. Recognize that this is only the front end of a necessary pathway to bring new products with quantifiable merit to market. Prototyping candidates is essential to validate the potential benefits. Already showing great progress in identifying several potentially major material substitutions with greater sustainability and performance profiles than incumbents. Better cost predictions will increase confidence in outcomes.

- The management plan is generally solid. Delegation of risk management to the subtasks is necessary to a degree, but they should still be identified, enumerated, and monitored as part of the overall management plan. It is not clear why machine learning ("black box") is superior to simply using molecular/mechanistic simulation tools. Machine learning could be faster, certainly, but such models are often unreliable upon extrapolation of the training data set. Other than that, the approach looks okay, though the description is rather terse, especially for those not well versed in the principles of machine learning. Is high-throughput property prediction enough, when various combinations of multiple properties may be ideal for various applications? Must one focus on a single application at a time to prevent the search from growing combinatorically? Impact offers a bit of a conundrum. What if I developed a sure-fire method to detect gold ore deposits, then set forth prospecting on a continent where there was no gold? This will surely help us *look* for promising bio-based polymers and additives, but it is hard to say *a priori* how many we will *find*, and how valuable those finds will be. Progress is also a bit difficult to judge based on the lack of clarity about what arose from the 2018–2020 work and what has been done since.

- The project approach is to build and improve machine learning and molecular simulation tools to make predictions on thermosets, thermoplastics, and polymer additives that can be validated experimentally (by the PABP project, reviewed separately) and show that the tools can be improved. Management, processes, communications, and risks/mitigations are well addressed. A project with industry leaders is planned to start in 2021. A successful machine learning and molecular simulations-based approach of predicting properties of bioproducts would greatly accelerate informed discovery, development, and commercial realization. Progress has been excellent: biopolymer accuracy prediction improvement, PABP PET replacement, polymer database development, and molecular simulations expanded to include polymer additives.

- This project is one of several interdependent projects in the BETO portfolio. Machine learning and molecular simulations as enabling technology will direct the synthesis work to a profitable, sustainable, yet functional polymer space. Commendable progress in applying molecular simulations—particularly in understanding and modeling the structure/function impact of the keto-adipate in nylon performance; and in impactful to prediction of small molecule diffusion, a very important consideration for formulation space additive. Results in this year will be crucial to validate the test case and demonstrate hitting predictive O_2 permeability values for the seven PABP-PET replacements. Investigators have upheld the commitment to release simulation tools to nonexperts; the databases are accessible on the web.

- This project represents the future of molecule/materials R&D. With a modest investment of funding, the project team has done an outstanding job combining machine learning and molecular simulation to predict properties of bio-based polymers and additives. This is an excellent use of BETO resources.

PI RESPONSE TO REVIEWER COMMENTS

- The project team appreciates the constructive feedback from the reviewers. The team acknowledges the possibility of the null hypothesis. This would be an unfortunate outcome of the research, and the tools developed within this project will help experimental efforts in identifying both promising candidates as well as candidates that are unlikely to be performance advantaged. We appreciate the costs and challenges in bringing new materials to the market, and we acknowledge that both more sustainable routes to existing materials (e.g., PET) as well as sustainable replacements will likely be needed to realize a fully circular economy. The team does not assert that machine learning ("black box") or molecular simulation is superior because both approaches have their strengths and weaknesses, and leveraging both approaches can provide the greatest outcomes. We are employing machine learning to pare down the immense design space to pass the most promising candidates to our experimental partners. The atomistic simulations are a finer-resolution tool to further pick out promising candidates as well as drive the development of structure-function relationships.

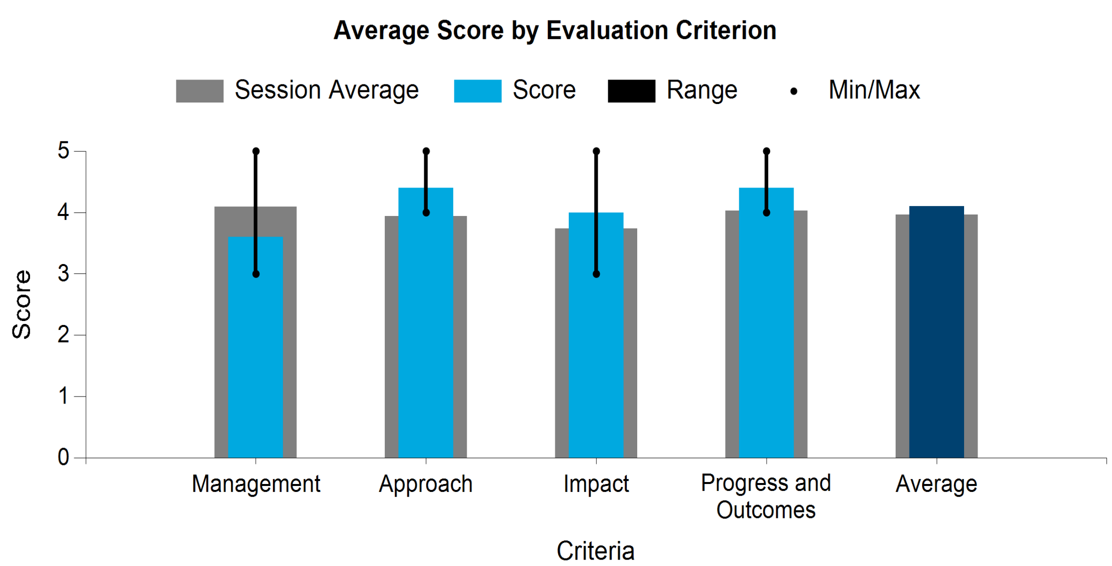
IDENTIFYING PERFORMANCE ADVANTAGED BIO-BASED CHEMICALS UTILIZING BIOPRIVILEGED MOLECULES

Iowa State University

PROJECT DESCRIPTION

WBS:	2.5.1.600
Presenter(s):	Brent Shanks
Project Start Date:	10/01/2018
Planned Project End Date:	12/31/2021
Total DOE Funding:	$2,500,000

This project is focused on developing a systematic process for identifying biomass-derived molecules with improved performance in end-use applications using organic corrosion inhibitors and flame-retardant nylon as the initial test cases. Chemical species performance screening results from the literature are being aggregated through a data mining approach. Then the molecular structures identified from the literature will be used in conjunction with a reaction network generation computational platform to identify key intermediate molecules (i.e., bioprivileged molecules) that could be used to synthesize the literature-identified molecular structures. Importantly, we are identifying bioprivileged molecules that can not only be leveraged for the synthesis of the "identified molecule" but also to provide the basis for generating a library of compounds with similar chemical structure to that of the "identified molecule." Finally, we are screening the libraries to identify novel chemical species specifically for their use as organic corrosion inhibitors and flame-retardant nylon polymers.



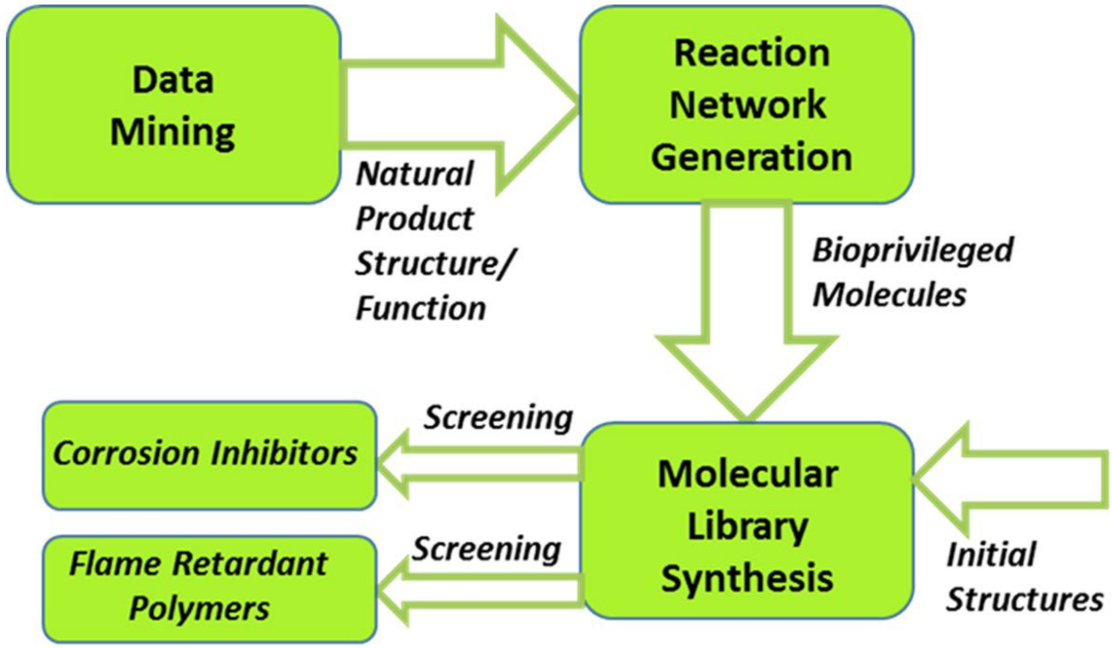


Photo courtesy of Iowa State University

COMMENTS

- This is an interesting approach to connect molecules previously identified with sought-after properties to molecules that could be derived via biological means. Identified tasks are assigned to participants, but there was no discussion of information sharing between participants, which could hamper utilization of the recurrent neural network and reaction network generation-derived information. Identification of candidates from plant secondary metabolism can be risky, given that some metabolites are synthesized in minute quantities. It might be helpful to prioritize the database of metabolites based on carbon flux into the particular pathway.

- The development of a computational approach to identify bioprivileged molecules is a sound idea, taking molecules through screens for desirable properties to identify PABPs with potential. The approach is innovative and could result in novel PABPs for testing. The bio-based approach could benefit the economics of biorefineries, depending on how the economics and scalability play out for different PABPs. The project management team and responsibilities are described. Technology risks and mitigations are broadly addressed. This early TRL project has made good progress, having established their computational networks, identifying more than a dozen high-performing organic corrosion inhibitors from corrosion inhibitor libraries, and progress on flame-retardant nylon 6,6.

- The management plan is a bit light, and there was no real attempt to identify risks or make mitigation plans. The approach is a nice combination of retrosynthesis with a sort of a version of "platform molecules." The potential for speeding up searches for PABPs is obvious. It was very nice that a couple of examples were described, both being targets or real practical interest. Progress is good considering time, budget, and recent complications due to COVID-19.

- This FOA project utilizes multi-institutional computational expertise. The team has delivered viable candidates from its libraries for two test cases: organic corrosion inhibitors and a monomer unit that confers inherent flame-retardant properties to the polymer. Initial data from the work appear promising, but there are several questions/concerns: Has the team acquired insights/input from potential clients? Even though the project is very early stage, the probability of the technology's success is high if grounded in the beginning with a firm understanding of end-user needs and an "insider" view of current material deficiencies. It would be valuable to engage sooner with clients to understand the steps/barriers in the journey to qualify a replacement molecule in a formulation. The flame-retardant nylon case is very interesting and a nice capture of a bioprivileged molecule: With the introduction of the unsaturation functionality, is it reasonable to incorporate into future work tests that characterize the oxidative and UV stability? Are the predictive models sophisticated enough to stack "chemoindicators" and mine for more than one desirable property—e.g., flame retardancy and plasticization?

- The project is well organized and staffed with subject matter experts who understand the bioprivileged molecule approach. It is connected to industrial advisors from key target areas and experts in computational modeling. Having preselected targeted needs from industrial advisors limits the effort to a manageable scope. Screening based on known structure/property relationships and the ability to make from bioprivileged molecules helps contain the possibilities to a manageable level. Having the ability to prototype and test candidates for functional performance helps bridge from theory to practical candidates. The target areas identified appear to have good candidates for moving eventually to commercial applications. Next steps will need to include not only both performance verifications that are in progress but also economic assessment for commercial feasibility in order to quantify the impact. I am looking forward to broader deployment of this approach. Excellent progress in demonstrating, even with this limited scope, the usefulness of this approach and the potential benefits of its solutions.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the positive comments from the reviewers about our project. It is always difficult to determine how much time to invest on each part of the review presentation, and we elected to keep the management plan discussion short because the project has been meeting nearly all milestone and subtask dates despite the complications due to COVID-19 during the past year. The FOA for identifying performance-advantaged bio-based chemicals set the requirement of identifying at least five chemicals with >10% performance improvement over existing molecules. Our project was set up to meet this requirement plus to develop a systematic computational/synthesis process that could be more broadly used for identifying performance-advantaged chemicals. The entire project was set up to mitigate risks by seeding the synthesis work with end-use applications, organic corrosion inhibitors, and flame-retardant nylon 6,6 in which we already had leads. If these original leads were not fruitful, then the computational effort was to suggest other possibilities. Fortunately, our initial synthesis leads were successful, and we have already identified >10 chemicals with >10% performance improvement. We anticipate that these successful results will only be further augmented by the computational discovery portion of the project. We completely agree that engaging with commercial end-use entities is an important step in moving the technology forward. We felt that having preliminary results, which we now have, is a necessary aspect of having fruitful conversations with the potential commercial partners. Engagement with those potential partners has been initiated. Although not within the scope of the current project, we fully believe that the identification process we are developing would ultimately be able to stack "chemoindicators" for polymeric materials.

SEPARATIONS CONSORTIUM

Separations Consortium Steering Committee

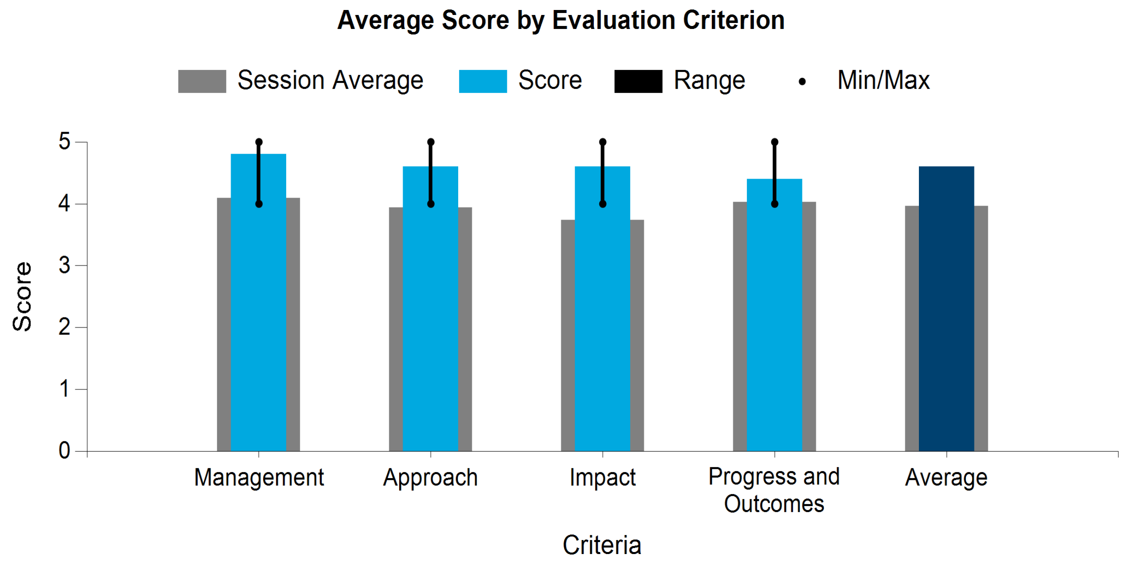
PROJECT DESCRIPTION

WBS:	2.5.5.501
Presenter(s):	Jennifer Dunn
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$7,724,000 *Entire Consortium

Research in the DOE BETO-supported Bioprocessing Separations Consortium is leading to new separation strategies designed specifically to address the challenges and scales of biorefinery technologies. This collaborative project integrates six national laboratories, bringing a broad range of separation techniques to address biorefinery needs. The Steering Committee is responsible for coordinating the research within the consortium, maintaining a dialogue with industry, and guiding research toward impact.

The consortium is organized into three teams. The first is the analysis team, which carries out TEA and LCA analyses that guide research in the consortium toward developing technologies that reduce the minimum selling price of biofuels and bioproducts. Computational efforts yield insights from theory that help improve the design of new materials within the consortium to achieve bioprocessing-specific separations challenges. The second team develops separations solutions that directly address challenges that arise within the broader BETO portfolio. These include fractionating and purifying lignin-rich streams, using redox-based electrochemical separations (RECS) to recover acids, and developing efficient techniques to separate 2,3-butanediol (BDO). The third team develops new capabilities within the consortium. These include developing new materials to capture valuable product in fermentation off-gas streams and evaluating countercurrent chromatography as a separations technique in bioprocessing.

The Separations Consortium Steering Committee has developed collaboration approaches to advance the consortium's research goal—to develop cost-effective, high-performing separations technologies that mitigate risks associated with a decentralized research team. Further, the Steering Committee interfaces with the consortium's 12-member IAB, which provides feedback that keeps the consortium grounded in industry-relevant bioprocessing separations challenges. One pivotal role of the Steering Committee is to shape the consortium's research portfolio, which it does through a process of identifying BETO- and industry-relevant separations challenges. This process involves regular interaction with other BETO consortia and with industry through participation or leading of special conference sessions and through our biannual meetings with the IAB. A set of five projects through a DFO also provided insight into industry-relevant separations challenges. Other factors under consideration in portfolio development include consortium capabilities and the potential for improvements in minimum selling price and sustainability. The Steering Committee also guides the go/no-go decision process and disseminates consortium progress through the website, the release of technical reports, and the chairing of special conference sessions.



COMMENTS

- Separations is often the Achilles heel in many processes. The consortium has been constructed to test separations issues and to exercise new technologies under development. It seems well coordinated, thoughtful, and comprehensive to minimize gaps and enhance relevant problem solving. Very thoughtful analysis plan drawn out. It is essential to have a uniform assessment plan for each technology and to impose consistent TEA/LCA analyses. Impressive diversity of member companies on the IAB representing cross-section interest in chemical and energy industries. The external-facing website is an excellent vehicle to engage with outside stakeholders. The website (bioesep.org) seems lean to capture a viewer/visitor (are there restrictions in posting more content?), particularly in terms of links to critical references (publications, reviews, patents, and talks) or videos demonstrating technology in the five areas (algal bioprocessing, biocatalyst preservation, etc.)?

- The Bioprocess Separations Consortium presented a thoughtful case for why it is a focal point, bringing together diverse separations solutions across the BETO portfolio that individually might not have the horsepower to tackle separations challenges. The consortium is very well organized and managed, has extensive communications to coordinate a diverse and distributed number of participants, and an extensive set of industrial entities providing commercially relevant feedback. Structuring of the consortium into three teams allows focus on techno-economic solutions, generic, and more specific separations. Front-end (biomass) and back-end (product) separations are addressed by the consortium. This is a big de-risking opportunity for smaller entities in particular, which often do not have resources for this expertise, such as DFO projects. Progress has been generally on track, as evidenced by publications, patent applications, DFO results, and industry interactions.

- The Separations Consortium addresses key challenges in the scale-up and commercialization of new bio-based technologies and products. As is amply described in their mission, separation processes are often the dominant capital cost and energy consumer in biotech (as they are in refining and chemicals), and BETO paid too little attention to this area as their interests expanded beyond ethanol, where the separations landscape was already well trodden. Management of the consortium has been active and effective, with outreach and analysis to help target their activities. Impact and progress are in good shape, but it is still early days to assess those with any real accuracy for a relatively young program. One possible area for improvement—and this was perhaps unavoidable for "bootstrapping" a program like this—but there is some flavor of "people with hammers seeing everything as a nail." Some ongoing national lab work has, in this reviewer's opinion, been marginally relevant to what are or should be the top needs for BETO. Not seeing inside the advisory process, perhaps it is a wrong impression, just something to look out for. Perhaps a better survey/outreach to the private sector (and academia) among those providing technical services in separations might encourage a broader set of resources.

- This consortium is well designed, well managed, and well executed. My impression is that the consortium as a whole exceeds the sum of the individual projects due to strong management structure and communication strategy. The consortium has all the marks of a collaborative, unselfish effort to solve problems related to the bioproducts industry. Given the multisite approach, following through with strong information sharing is necessary to mitigate risk and progress. Regularly scheduled, frequent interactions with an extensive industrial advisory committee serves dual functions of assessing industrial needs and the dissemination of advances. Impressive progress in separations, illustrated below by individual projects.

- This project is well organized, with good communications among teams in the consortium. May want to add other equipment manufacturers to the IAB to enable faster adoption in application areas even beyond the biorefinery goals of the consortium. Having the TEA and LCA team involved early on in benchmarking and assessing feasibility for project proposals is an excellent way to guide resource allocation. The targeted solutions team for current separations is an excellent way to focus on key problems needing to be overcome in moving the biorefinery concepts toward reality. Including some new separations approaches in the mix offers the potential for game-changing technologies. Some may be a little esoteric, but thinking outside the box is good, especially including electrical options. Consider adding some other enhanced separations options into the mix, such as reactive distillation, centrifugal enhanced heat transfer and extraction, and flash recovery from volatile pressurized extraction media. As stated, effective and efficient separations are a key enabler of biorefineries. This effort is essential to the adoption of biosolutions for the future. This is a very impressive portfolio of efforts with many good outcomes already. Consider adding some principles of green chemistry into the project selection criteria.

PI RESPONSE TO REVIEWER COMMENTS

- Reviewer comments on the introductory presentation for the consortium were very helpful. In particular, reviewers noted that the consortium is well organized, shares information well internally and externally, and addresses challenges relevant to BETO and industry. They also complemented the analysis-based approach to project selection and management. Finally, they noted that the consortium is important in de-risking separations technologies for small businesses. Reviewers had four main suggestions. First, reviewers stressed that the work in the consortium should be relevant to top BETO and industrial priorities, which should be identified through communications with stakeholders. Beyond activities that we have already completed, discussed in the presentation, we fully agree and aim to gather additional feedback regarding stakeholder priorities through our upcoming special session at the American Chemical Society's Green Chemistry and Engineering Conference and a separate Industrial Listening Day in the summer of 2021. In addition, the Challenge Stream task within the consortium aims to holistically and systematically survey technical challenges in bioprocessing separations. Along with feedback from stakeholder communications, this Challenge Stream effort will help set the consortium's research agenda and, by incorporating LCA, will address many principles of green chemistry (e.g., energy intensity, renewable starting materials), which was suggested as a criterion for project selection by a reviewer. Second, it was suggested that the consortium expand its membership of the IAB to include more equipment manufacturers. We agree that it is essential to have board members who can provide input on a number of topics, including equipment and processes, that may be relevant to addressing challenges in bioprocessing separations. Although most experts on our 12-member board represent companies that produce biofuels or bioproducts and advise us on the main technical challenges they face, we do have equipment and materials developers on the board. As we continue to work with the board, we will take opportunities to add equipment manufacturers. As needed, we can consult with manufacturers on an ad hoc basis. In addition, the reviewers suggested adding capabilities to the consortium, such as reactive distillation, centrifugal-enhanced heat transfer and extraction, and flash recovery from volatile pressurized extraction media. We agree that there are many separations technologies that are not currently in the consortium's research portfolio that could be beneficial. As we work with our stakeholders and leverage the Challenge Stream task, we will identify opportunities to bring in additional technologies for projects that emerge. Finally, it was suggested that links to additional information and resources on bioprocessing separations be added to our website. We are currently in the process of updating our website, including updated capabilities and links to publications, and we will work to expand the resources to which it serves as a gateway.

LIGNIN-RICH STREAM FRACTIONATION AND PURIFICATION

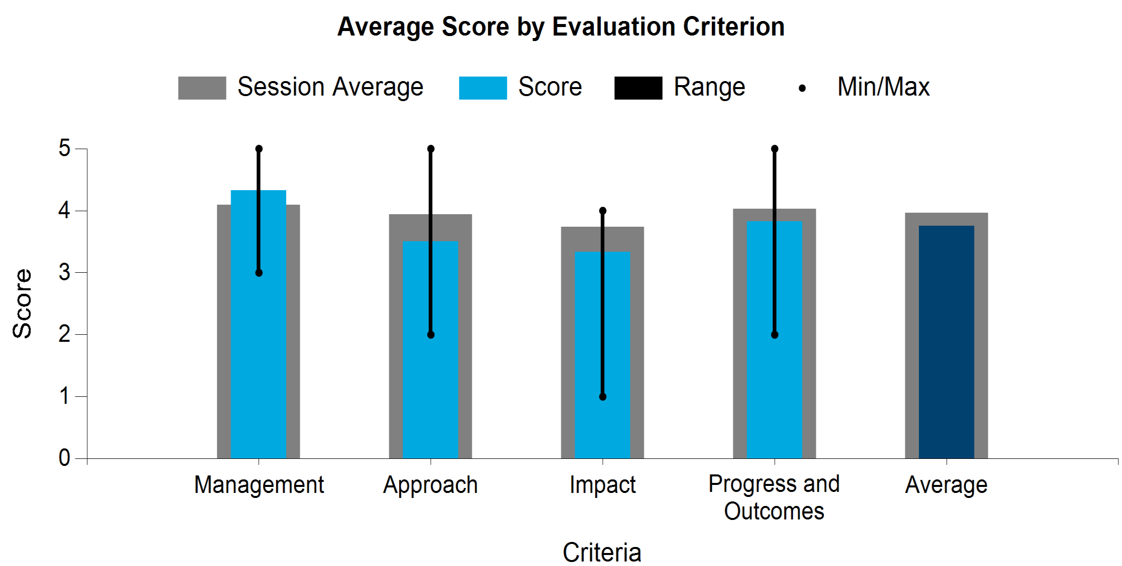
National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.5.5.502
Presenter(s):	Eric Karp
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$7,724,000 *Entire Consortium

In support of BETO in converting lignin to fuels and chemicals, this project develops scalable separations based on membranes and electrodeionization (EDI) to recover low-molecular-weight (LMW) compounds from lignin-rich streams. The project addresses three technology barriers in developing the bioeconomy: (1) cost of production, (2) selective separation of organic acid species, and (3) advanced bioprocess development.

Specifically, membrane cascades using tangential flow filtration (TFF) are investigated for the recovery of LMW lignin compounds from lignin-rich streams, such as alkaline pretreatment liquor, reductive catalytic fractionation oil, and catalytic oxidation oil. Process concepts, including dynamic filtration, are investigated to meet specific performance targets indicated by the consortium's IAB for the membrane filtration, including maintaining permeance >1 LMH/bar and an overall cost target of <$1/kg of LMW lignin. EDI is investigated as an integral part of the membrane cascade to recover LMW aromatic acids and as an alternative to nanofiltration. Economic analysis of the processes is presented with a focus on minimizing energy consumption and capital expenditures (CapEx). Further, a sensitivity analysis is presented to identify key cost drivers and to optimize holistic process operating conditions.



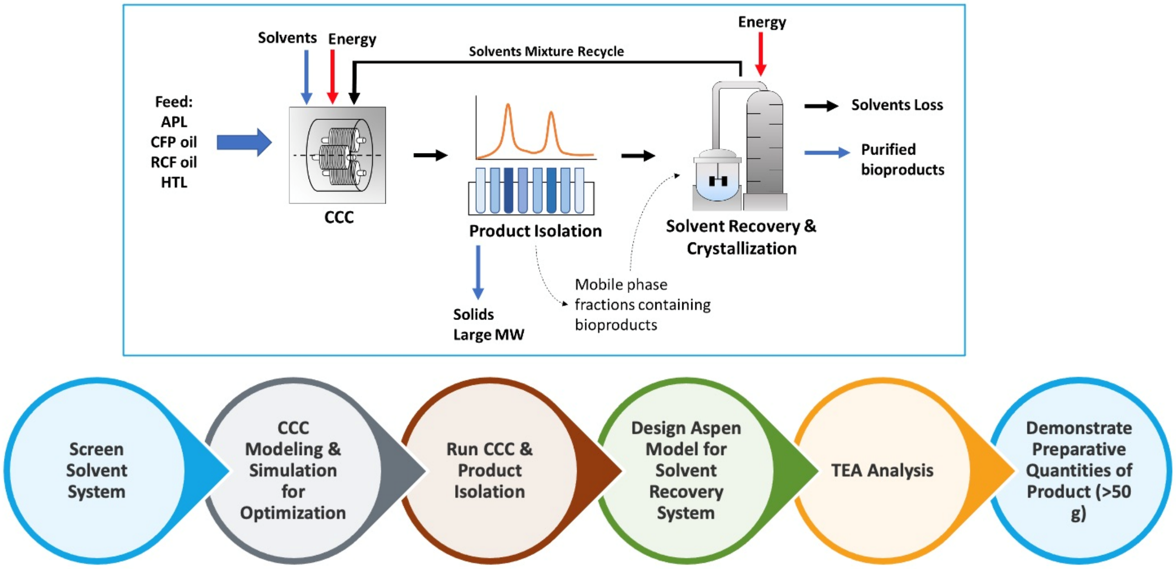


Photo courtesy of NREL

COMMENTS

- Management: The management plan and implementation appear to be adequate for a small consortium of NREL, ANL, and LBNL. Implementation is progressing and well organized. There is an impressive advisory board of separations companies. Risks of low fluxes and fouling are adequately stated and being addressed.

  Approach: There is merit and potential in this approach toward recovering LMW aromatics from lignin-derived process streams. In this project, membrane cascades and EDI and dynamic filtration are explored as they are unproven for lignin streams. Risk mitigation with rotary ceramic disk (RCD) filtration and metrics are described with go/no-go decisions, and TEA targets and processes look scalable. I have concerns that, despite the good work here, the valorization of LMW aromatics from lignin streams may not be able to make it in the real world.

  Impact: The project impact appears to be headed toward measurable outcomes with review processes in place and a consortium of separations companies involved. There is clear commercialization potential with good industry engagement. Key will be achieving necessary flux without much fouling and TEA of the whole process.

  Progress and outcomes: Results are showing some potential of useful separations after moving to dynamic filtration with promising flux (replace TFF where flux too low) and combined with EDI. Fluxes for dynamic filtration look very promising and close to economic viability. Fouling and TEA await further evaluation. Ultimately, the valorization of a holistic process with consistent operating conditions is key and may be challenging as a whole process with waste streams after recovery of LMW aromatics.

- Particle fractionation by membrane filtration is notoriously difficult, and for reasons that are well understood. Protein fractionation is practiced, but typically in very dilute systems and for proteins that are very valuable. It is unlikely that this approach will be justified by any value upgrade resulting from lignin fractionation. Similarly, rotary-disc filters are very expensive on a per-unit-area basis, and though they may partially address the problems of static membrane filters, they will do so at a cost that is, again, very hard to justify when lignin is the product. A more fundamental problem with lignin valorization is that the more valuable the lignin product, the less of it that can be sold before the market is saturated, and therefore the less fuel production it can support. This is similar to the story with biodiesel and glycerol. The latter appeared to be a valuable coproduct when biodiesel was first taking off, but once a few fuel-scale plants were pumping out tons of glycerol, prices crashed, and it was no longer a strong contributor to biodiesel plant economics. The two-stage TFF results were entirely predictable. Rejected solids form a "dynamic filter cake" adjacent to the membrane because they get dragged there by fluid flux and they are limited by how fast they can diffuse away against the net transmembrane flux. They then begin to impede the flux of the smaller particles that are supposed to permeate through the membrane. Only a very high level of surface shear can prevent this. There are a number of ways to achieve this, rotary filters being one, but they are all quite costly. The TFF/RCD results were, again, predictable, at least qualitatively. The problem is that the "economic performance" they are claiming is rule of thumb based on static filters. RCDs are so expensive that and even higher flux would be required for them to be economic. Actually, probably not even the clean-water flux would be economic for lignin with and RCD. Electrochemical deposition is a much more fundamentally sound approach for this application, but it, too, is expensive. Solving this problem economically is unlikely to be done with anything "off the shelf."

- Recovery of low-molecular-weight aromatic compounds from lignin-derived streams is a long-standing goal of the biorefinery industry and within the BETO mission. Project tasks are assigned to participating national labs, and a data sharing plan is in place to coordinate milestones; no details were provided on the decision-making structure in the event of challenges encountered. Multiple experimental approaches are under simultaneous examination; two-stage tangential flow is identified as a baseline. Valorization of lignin-derived aromatic molecules remains an open question, and, in the opinion of this reviewer, a challenge that may never prove to be economically viable. Application of SOA separations technology together with thorough cost and energy optimization and analysis provides the best strategy to get to the answer to this lingering question. A plan is in place for the dissemination of results.

- Targeted goals and close teamwork are evident in the project. Industrial connections are highly relevant to the ultimate applicability and scale-up of the separation methods being evaluated. Separations chosen are limited to EDI and membranes (especially ceramic discs). Might benefit from broadening the candidate separations to include extraction systems. Limited to the types of pretreatments being tested, and their adoption and scale-up. May want to look for other separation needs in the broader efforts for PABPs. Ceramic discs cost, fragility and sealing issues should be addressed versus other sheer enhancement approaches. Subject to further TEA to determine economic potential, the technical outcomes needed for this project are being demonstrated.

- The use of membrane filtration to recover LMW lignin-derived compounds is promising; apparently this type of separation is not currently used for lignin streams. The project uses a TFF base case to compare with other concepts for separations (reductive catalytic fractionation and EDI). The impact on lignin recovery could be substantial for the economics for biorefineries and provide lignin-derived streams for use across projects looking to valorize them. Several such projects are ongoing in the BETO portfolio, so a successful technology would be crosscutting in its value. Project management, assignments, and industrial input (IAB) on the project are appropriate. Progress on this project is moving well by several performance measures. The scalability and operability of processes based on these technologies remains to be proven, such as energy consumption and yields, up-time/low-fouling/corrosion inhibition properties robustness of membranes and equipment, and ultimately, economics.

- This project meets the management metrics. It is particularly notable that the project team at the outset sought guidance from the IAB—specific constraints were used based on that counsel (e.g., not using ceramic filtration at the first stage), which increases the probability of working in commercially relevant space. The investigators are executing a sound comparative study and consistently perform TEA for each process scenario. The most promising case scenario approaches the edges of the desired flux target; however, there still appears to be a significant gap to bridge the flux and fouling challenges.

PI RESPONSE TO REVIEWER COMMENTS

- Regarding the cost and long-term operability and economics of ceramic disks, we note that the RCD unit does not have any rotating seals and, when normalized to needed membrane area, is only ~10% more in cost than a TFF system; however, for a given product flow rate, the TFF system requires 10-fold the membrane area of an RCD system. Taking the increased area into account, the capital cost of the TFF system is ~1.3 times more than the RCD system. This is a result of the 10-fold increase in flux achieved with the RCD unit compared to a TFF unit. Last, RCD is only one form of dynamic filtration; there exist vibrating membranes that use polymeric membrane stacks and achieve high sheer forces through vibration. 100 m^2 vibrating units are available at ~70% less capital cost than RCD units. It is a future area of research to see if these polymeric vibrating units can achieve equal or better lifetime as ceramics in filtering of caustic lignin streams such as alkaline pretreatment liquor. To our knowledge, there is no predictive methodology that would quantitatively describe the performance and TEA of TFF in application to lignin-rich streams (e.g., alkaline pretreatment liquor) because little to no data exist for their filtration. Although many models exist for fouling, they depend on the mechanism that occurs; for example, intermediate pore blocking versus cake formation. Both models are time dependent and assume a filtration resistance due to membrane foulants, with the cake formation model having more severe resistance; thus, our team had to collect data with the TFF system as a baseline to measure the fouling rates and connect that to a fouling mechanism. When alkaline pretreatment liquor is filtered with a nanofiltration membrane, the permeance closely aligns with the cake formation model; however, when microfiltration is used as a stage before nanofiltration, the transient pore blocking model more closely fits. The transition from cake formation to the transient pore blocking model is important because cake formation leads to faster permeance decline and therefore a lower average permeance, leading to more required membrane area and a higher membrane cost.

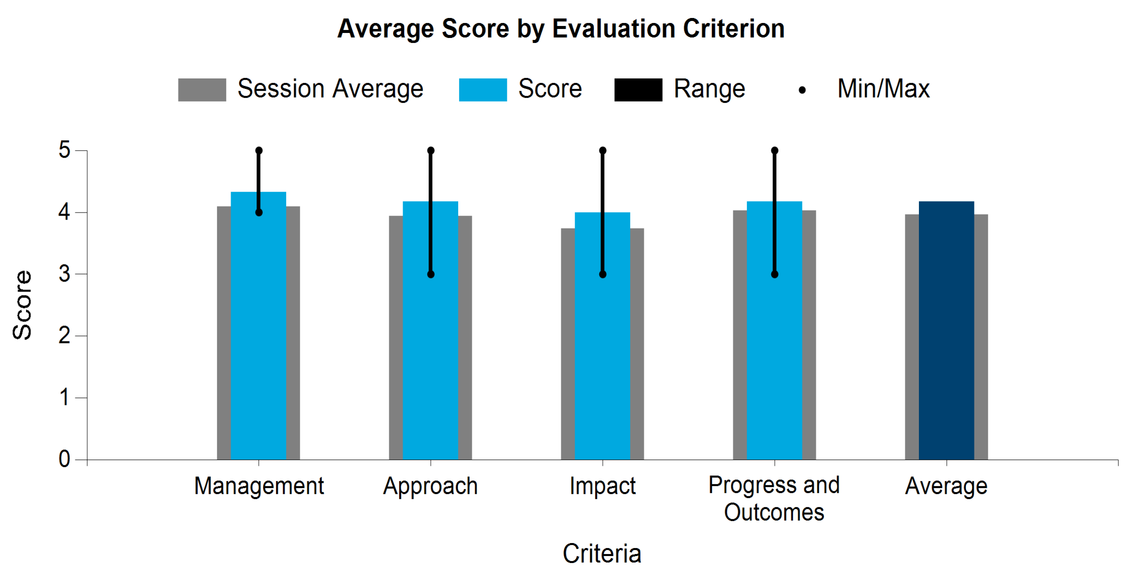
VOLATILE PRODUCTS RECOVERY

Argonne National Laboratory

PROJECT DESCRIPTION

WBS:	2.5.5.503
Presenter(s):	Phil Laible
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$7,724,000 *Entire Consortium

Advances in strain engineering have enabled the biochemical production of a wide array of products. During aerobic fermentation, many of these molecules partition readily to the fermenter off-gas. Several of the products (e.g., 3-methyl anisole, isoprene) are known to volatize fully during fermentation, whereas others (e.g., mid-chain-length alcohols and terpenes) volatilize less—but significantly—under typical conditions. This project utilizes advanced, high-surface-area materials for the recovery of volatile products by adsorption, with specificity achieved through tunable surface chemistries. This strategy thereby eliminates two energy intensive steps (off-gas condensation and a subsequent steam distillation) traditionally required to separate volatile organic products. Scaled adsorbent synthesis has been achieved for the production of xerogel adsorbents, with macroporous structures capable of handling high flow of fermentation off-gases while selectively recovering product from bioreactors (volumes of 10 L or more). Initial tests of performance with limonene have shown integrated recoveries of ~60% of product from the vapor phase (with instantaneous recoveries of ~80%). Desorption of the product from xerogels is through compression with low energy forces (~ 20 psi). Techno-economic evaluation of the baseline condenser/distillation case is complete, and data analyses/cost projections are underway for the new adsorbent technology. Multi-scale modeling is providing mechanistic insights to optimize the volatile product recovery process. Scale validations of the materials approach are underway, and results will be communicated rapidly to key industrial stakeholders.



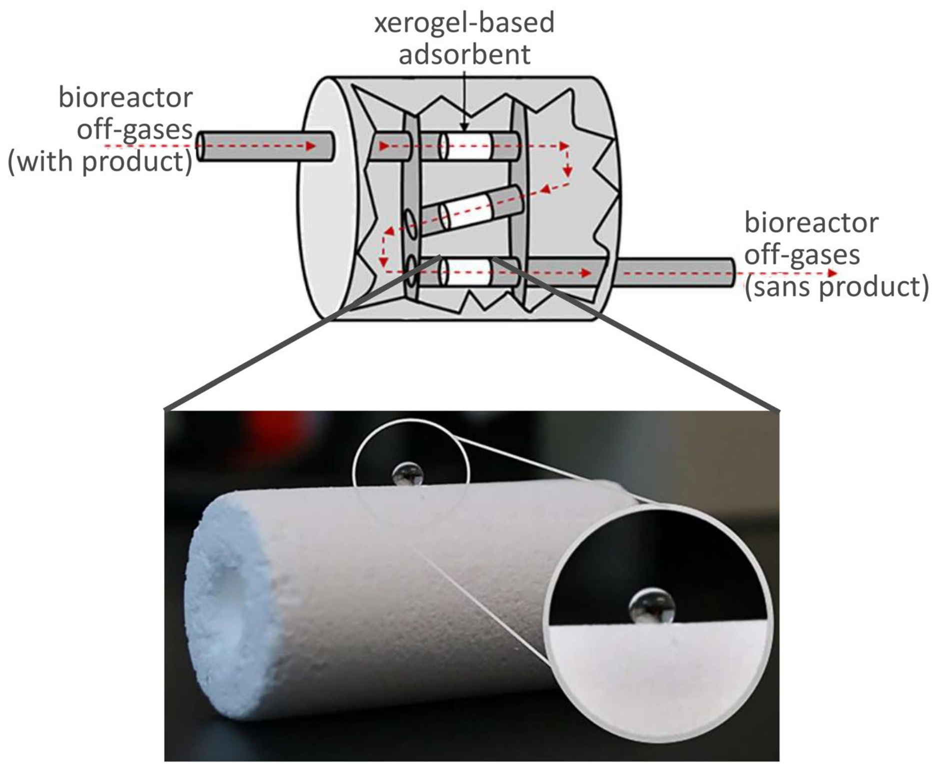


Photo courtesy of ANL

COMMENTS

- Management: The management plan and implementation appear to be high level and well organized with ANL, LBNL, LANL, and PNNL. There are regular meetings among the team and occasional advice from the IAB. I think the project would benefit from industry partners with a real interest in seeing the potential of this new and intriguing technology.

  Approach: There is substantial merit and significant potential in this goal of striving to recover volatiles that are otherwise lost. The approach aims to reduce operating costs and the complexity of volatile product recovery via highly specific and tunable gas-phase adsorbents (high-surface-area materials with high gas flows), with specificity achieved through tunable surface chemistries. The absorbents must outperform condensation approaches.

  Impact: The project impact appears to have the potential to deliver good outcomes with thorough review processes in place. The project is currently early-stage, with downselection from 15 candidate molecules and some progress selecting advanced materials by identifying various macroporous designs. The next stage is to seek next-generation materials using computation-guided design. The recovery metrics must be combined with economics.

  Progress and outcomes: The project appears to have coped well despite the COVID-19 impact. Initial results using limonene and isoprenol are showing promise relative to the metrics set (capture of >50% of volatile products with <20% corecovery of water/impurities and scaled cost $0.39/g xerogel). Economics at scale were viewed as okay after assessing by estimating materials costs plus synthesis costs being amortized over many adsorption/desorption cycles. Much of the current work is computational and based on model predictions, and the work needs to move forward into practical testing and detailed evaluation in a workable lab-scale system. Although this is promising, these metrics are still some way short of the condensation process, which are already achieving <80%–90% recovery. It is stated that the scaled costs are within range, but it is not clear how this conclusion is reached and how this compares with scaled costs of condensation. Overall, it is not clear how risk mitigation strategies might be assessed.

- Clear targets and limited experimental scope facilitate reaching goals more rapidly. Concern that the scope of recovery options may be too limited. May want to include ad/absorbant manufacturers on the advisory team. Considering the limited options being investigated, the approach appears to be sound. Would like to understand other options versus aerogel were considered. Would suggest that the team look at the product recovery conditions to ascertain if the system encounters an unsafe (explosive) regime, especially aerobic fermentations. Suggest that the team also look at emissions post adsorption during the entire loading/unloading cycle. For those fermentations that have volatile components or products, this could be a credible solution versus energy-intensive chillers. Good progress in demonstrating adsorption and recovery at the current scale.

- Conception of the project is in response to the needs of industrial stakeholders and partners. The management is well outlined and focused on risk mitigation. Leads and their responsibilities are identified; a communication strategy is in place. Intriguing approach with significant potential, although reasoning for exclusive focus on xerogel adsorbants was not articulated. Current progress includes admirable results in adsorbant capacity, technical design, and application on bench-scale bioreactors. The adsorbant material cost is high, which will require many cycles of adsorption/desorption. Examination of the recyclability of the adsorbant should be considered in a near time frame. I look forward to increased dissemination of results to industrial partners and the community at large.

- Recovering volatile fermentation products in xerogels is an elegant approach. It could improve process economics and operability by eliminating other intensive steps to recovery as well as address safety issues that might have derailed some processes otherwise, such as those with inflammable products. This technology may have significant impact across a wide variety of volatile products. Management, responsibilities, communications, and risks are all well detailed. Progress is on track for selective product recovery in high yield, and modeling of materials for specific molecules is in progress. Use of xerogels in a cartridge-type design seems highly practical and scalable, assuming it can hit process longevity targets, selectivity, and recovery yields for specific products.

- The issue identified is a real one, and many commercial operations either lose product as a result or use unreasonably expensive methods to avoid doing so. Good target! Xerogels were an interesting choice. Similar streams are routinely treated with various sorts of inorganic and polymeric adsorbents in packed beds or as structured (monolithic) contactors. As is often the case, no clear BFD or PFD was provided of the process approach they intend to use, so it is difficult to assess. Costs on slide 10 seem unrealistic—$0.39/g for an industrial adsorbent is wildly excessive. Industrial equipment vibrates—are xerogels robust in that sort of environment? Performance for intellectual property and limonene look good, although more conventional sorbents also ought to do well, possibly at lower cost. Overall, this is an interesting study for a variant of "extractive fermentation." Economics for preventing modest losses will be different than those for continuous product removal and recovery, but either/both may be practical, depending on the details. A major issue is the (apparently) early fixation on xerogels versus other options. A more through survey/analysis upfront might have identified better options.

- This project utilizes engineered xerogels that can be tailored to capture and desorb versatile volatile product streams from bioprocesses. The simplicity of the concept is highly attractive if the separations process is scalable and hits the necessary flow targets and capture efficiency. Product removal during the process represents de facto *in situ* product removal and could be beneficial in relieving or minimizing the burden of strain engineering if the production strain is susceptible to product inhibition. Under the consortium, the team has access to industry partners—particularly biomanufacturers—and can obtain credible and critical stakeholder inputs. A key challenge is to optimize xerogel chemistry to achieve better selectivity and release in the multiple adsorption/desorption cycles and to manage the durability and lifetime of the xerogel because these articles are the major production cost contributor.

PI RESPONSE TO REVIEWER COMMENTS

- The Volatile Products Recovery team (Task C2) of the Bioenergy Separations Consortium thanks reviewers for their feedback and thoughtful comments. The Volatile Products Recovery approach has been added to ongoing consortium efforts in recent years, based on communications with a number of industry and BETO stakeholders. We agree that the adsorbent-based approach has the potential to be transformative for the low-cost recovery of a broad range of bioproducts, and we will continue to capitalize on its advantages—over baseline approaches—and scalability. The simplicity of the approach does make it an attractive option for both *in situ* product removal and for loss prevention with lower volatility products. The scaled costs of materials for the adsorptive approach were based on preliminary analysis of a contracted firm that specializes in TEA. The emphasis on presenting early estimates of materials costs was to identify sensitivities of the process to materials inputs, utilities, and/or capital expenditures. In this regard, the analyses were highly successful at identifying the largest sensitivity: the expense of monomers used in the xerogel polymerization reaction. This finding allows our team to be selective and discriminatory when choosing surface treatments for new bioproducts and provides a further means of downselection between formulations that provide similar performance. We anticipate that the overall costs of the materials can be dramatically reduced because these initial estimates were based on commercially available prices for silane coupling agents as opposed to bulk chemical prices from higher-volume distributors. Bulk pricing is estimated to reduce syntheses costs twofold to fivefold and will be a focus of interest when comparing to baseline processes. The Volatile Products Recovery team has extensive familiarity with xerogel-based adsorption technology from projects using a similar approach for the recovery of bioproducts directly from fermentation broths (liquid-liquid extraction). We decided to leverage this experience and the patented xerogel platform as the test case for the adsorbent-based recovery of volatile bioproducts while working with industry stakeholders and the Bioenergy Separations Consortium analysis team to develop a systematic understanding of key use cases and alternative technologies for volatile product capture. The xerogel approach takes advantage of the unique properties of xerogel-based adsorbents (adjustable porosity, exceedingly high surface area, flexible solids with tailorable surface chemistries) to build out first-generation process schemes to test out the approach. It is highly likely that other adsorbents (e.g., those based on rigid organic frameworks or resin beads) will work as well, but these technologies would require additional solvents and/or distillation in desorption and recovery processes. Our soft materials offer the means of facile desorption and recovery from the adsorbent materials with simple compression, pressure, and/or temperature swings while allowing recovery of the product in high concentration without the use of additional solvents.

  Recyclability/material longevity: The success of the xerogel-based adsorbent approach will require materials to be used in many cycles of adsorption/desorption to amortize the cost of their syntheses over larger volumes of recovered bioproduct. Although our initial efforts are focused on capture and desorption efficiency, we are confident that our current xerogel-based materials can be cycled tens to hundreds of times based on previous demonstrations with liquid-liquid recovery. As part of the baseline comparison efforts, the longevity of the xerogels in the gas-liquid recovery scenario will be determined and used to better understand trade-offs between synthesis cost and xerogel longevity. These results will inform synthesis formulations, cartridge configurations, and desorption strategies that minimize synthesis cost while maximizing the life span of the adsorbent.

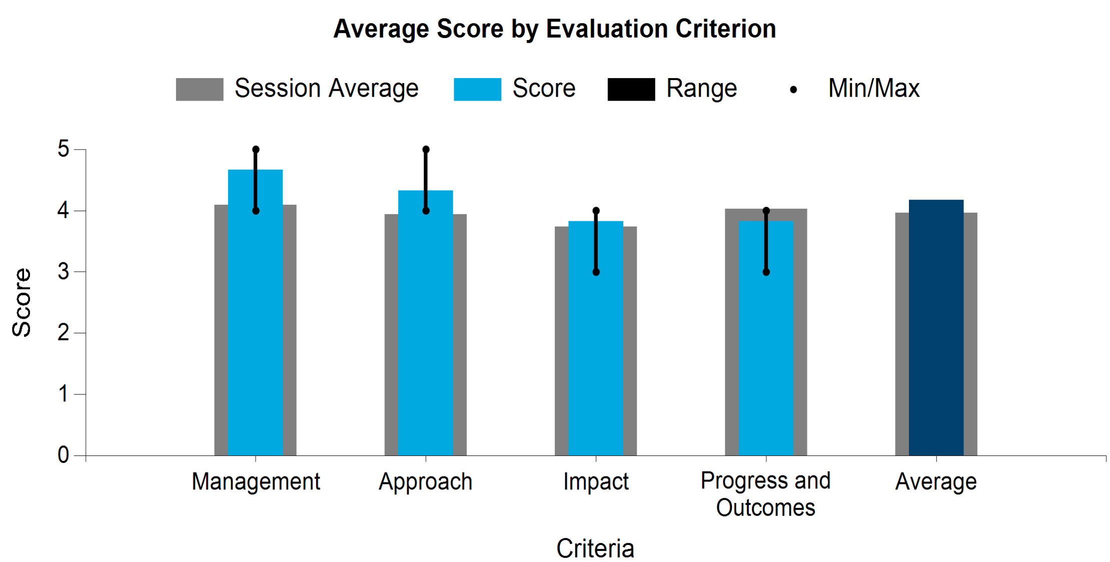
REDOX-BASED ELECTROCHEMICAL SEPARATIONS

Argonne National Laboratory

PROJECT DESCRIPTION

WBS:	2.5.5.505
Presenter(s):	Lauren Valentino
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$7,724,000 *Entire Consortium

Separations play a critical role in the cost-effective manufacturing of biofuel and bioproducts, and a key technical barrier to achieving BETO's 2030 minimum fuel selling price (MFSP) goal of $2.5/gallons gasoline equivalent (GGE) is the separation of organic species for upgrading to final fuel and bioproduct molecules. This project aims to develop cost-effective, electrically driven technologies for selective separation and the recovery of aqueous organic species from fermentation processes with low energy consumption. Specifically, this work is focused on the development of redox-active electrode materials and their implementation into a capacitive deionization (CDI) system for the selective separation and recovery of butyrate. As a result, RECS will be fully integrated and benchmarked against typical CDI. Technical performance, which is measured by energy consumption, recovery, and purity, is compared to consortium-based efforts in EDI and membrane pertraction. This work also targets improvements to process economics and sustainability, estimated through TEA and LCA, respectively. Overall, experimental results of this project along with TEA and LCA will inform the development of a new separations platform that utilizes redox-based electrochemistry for the selective separation of organic species to provide concentrated, clean intermediates from which biofuels and bio-based chemicals can be manufactured.



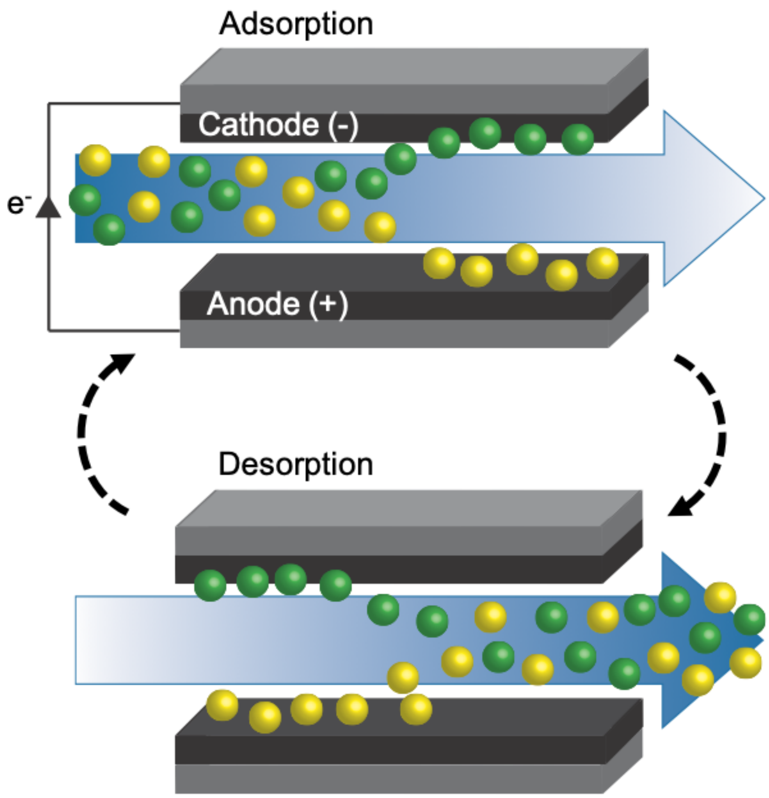


Photo courtesy of ANL

COMMENTS

- Management: The management plan and implementation appear to be high level and well organized with ANL, NREL, and LANL. There is an impressive consortium of entities with some industry partners involved, and the team is showing good progress and is very well organized.

  Approach: There is substantial merit and significant potential in this approach of developing a CDI process in parallel and integration with RECS plus TEA and LCA. The work appears to be SOA, as relevant to the defined BETO Program and Technology Area goals, and the project performers have developed an approach with significant potential.

  Impact: The project impact appears to be headed toward good outcomes with thorough review processes and deliverables in place. The ongoing collaboration with Atlantis Technologies is also good for technology transfer, with clear commercialization potential using industry engagement to guide project deliverables.

  Progress and outcomes: Results are showing great promise relative to the metrics set (determine whether the selectivity, separation, and capture ratio for RECS exceeds metrics). The project appears to have coped well despite the COVID-19 impact. Current progress and outcomes with imminent go/no-go decision look very encouraging. Cost targets with increasing recovery and reducing energy are also positive for an industry partner like Atlantis. This looks on-target to enable the development of a new separations platform. Broadening the potential of all this may be a future challenge. The key lies in the valorization of the whole process with application(s) of clean intermediates to make a biofuel or bio-based chemical products.

- Good participation by other labs. The team explained how oversight by the IAB may lead to faster adoption. Showed evidence of coordination with other separations projects. Scope includes development and testing of membrane options in an effort to increase the recovery efficiency and reduce energy costs. It would be helpful to benchmark to other separations options being explored by other projects. At the current state of development, it appears to be too soon to judge the overall impact of the EDI option. Good potential for broader separations. CDI work looks very promising. This project has yet to complete enough experimental work to conduct a final comparison of EDI to other options being developed in other projects, but it shows promise.

- Ionized species—acids and diacids, in particular—can be challenging to remove from fermentation broths, and a redox-based approach is promising. Good target, good technology choice! The management plan is okay. There is no real effort to identify risks. The approach is sound, and the options examined make sense. Results appear quite promising. Getting into details of electrode fabrication may be a step too far. Once the approach has been shown to work at the proof-of-concept level, it is probably best to engages experts/vendors because the choice of electrode material may have unforeseen effects on cell fabrication, etc. Significant effort may be wasted going down that path. At this point, the motivation may be drifting into "for the science" instead of "to solve the problem." They note that 0.03 kWh/mole is a problem, but that only seems like a few cents per gallon; perhaps my math is wrong.

- Reduction in separations costs would have a positive impact on biofuels and bioproduct costs. This project focuses on exploring CDI in conjunction with functionalized electrodes, using separation of butyrate as the test case. Although the project tasks were not clearly delineated, there appears to be good coordination and discussion of experimental progress and economic and sustainability measures. The project team is utilizing TEA to prioritize and guide experimental work, which is a sensible approach. TEA indicates that electrode capacity and cycle time are the most significant cost drivers, and experimental work is appropriately focused on those elements. The technology has the potential to improve product recovery and decrease energy consumption.

- The approach of developing CDI and redox-active electrode materials to enable a new RECS platform for organics is promising. TEA and LCA are integrated in the project to guide research priorities. A successful project may impact the separation of organics, potentially improving on incumbent technologies, such as simulated moving bed (SMB) and pertraction. Its significance will be determined by several factors, such as selectivity, capacity, need for regeneration, and energy consumption. Project management, communication, and IAB interactions are well described, and good progress has been demonstrated by using CDI to separate sodium butyrate at lab scale.

- The project has a solid management plan with appropriate interdependencies and a collaboration with Atlantis Technologies (an outfit that does custom equipment design and installation). The redox chemical deionization EDI would be an enhanced separations technology offering that could have broad commercial utility because it can manage more complex streams with lower projected GHG emissions and energy consumption. Great deployment of TEA to guide work that has high impact. Success will depend significantly on materials construction for the module, and the achievement of highly selective material with appropriate electrosorptive capacity at economic price point is critical, so alignment and input from a special materials manufacture is essential. The preliminary TEA assessment suggests that the CDI's economic feasibility will be comparable to other technologies, and the graph on chart 17 suggests that it may be unlikely for CDI to hit the desired \$2.50 MFSP. Can the team elaborate on technical concepts to reduce the energy consumption costs (currently at \$0.47/GGE) and by how much?

PI RESPONSE TO REVIEWER COMMENTS

- The RECS team of the Bioprocessing Separations Consortium thanks the reviewers for their feedback and thoughtful comments.

- One reviewer noted that the key to this project lies in the valorization of the whole process and developing clear target(s). This is an important challenge for CDI and RECS particularly because we believe that CDI and specifically RECS can play an important role across a range of product space(s) in biofuels and/or bio-based chemicals. We look forward to the opportunity of demonstrating this, as described by this reviewer.

- One reviewer commented on benchmarking to other separations options. We fully agree that benchmarking other separations options with CDI and RECS is important. We have conducted preliminary TEA, which serves as the basis for LCA, for CDI/RECS in comparison to three technologies: (1) SMB (state of technology), (2) EDI (developed in the Separations Consortium), and pertraction (developed in the Separations Consortium). As experimental work progresses and additional data become available, we will continue to update our TEA and LCA for CDI/RECS for comparison with SMB, EDI, and pertraction technologies. This is aligned with our go/no-go milestone (scheduled for June 2021) to evaluate whether RECS exhibits improvements over EDI and pertraction technologies.

- The reviewers asked for elaboration on technical concepts to reduce the energy consumption costs. The preliminary TEA results indicated a $0.47/GGE gap that encompasses energy costs (electricity and heating) and lower butyric acid recovery (95% vs. ~100% for the target case). A reduction in electricity consumption alone will not help CDI achieve the cost target; however, the 0.03-kWh/mol acid product was estimated based on literature data for conventional CDI using carbon-based electrodes. Unlike conventional CDI processes, we are implementing redox-functionalized electrodes, which modulate surface interactions through the electric potential. The applied voltage also is an order of magnitude lower when redox-based materials are implemented, so we expect energy consumption less than 0.03 kWh/mol for RECS. Although not included in the Peer Review presentation due to time constraints, our preliminary TEA illustrates how key combinations of variables—(1) CDI module cost, (2) butyric acid concentration (BA wt %), (3) the percentage of butyric acid recovery (%BA), and (14) CDI energy consumption—affect the MFSP ($/GGE). In addition to energy consumption, both the concentration of butyric acid and the percentage of butyric acid recovery are critical to MFSP. Higher mass fraction leads to lower downstream CapEx (smaller distillation column) and operating expenditures (reboiler duty). For example, at 25 wt % butyric acid (base case), the energy demands require supplementary energy input from natural gas. At 50 wt % butyric acid, natural gas demand is eliminated. In this way, an increase in the mass fraction of the product stream entering the distillation column will help reduce the MFSP; increasing the butyric acid concentration from 25 wt % (current base case) to 50% alone will improve the MFSP by ~7%. Notably, the TEA results indicate that certain combinations of CDI module cost, butyric acid wt %, % butyric acid recovery, and CDI electricity demand will meet or exceed the cost target.

- One reviewer commented on our identification of risks. Risks and mitigation strategies are described in our AOP, including the risk that the functionalization chemistry is incompatible with the material platform. This particular risk is mitigated by implementing a different material platform, selecting from a range of available foam, xerogel, or networked nanoparticle chemistries. In addition, as noted in the Project Overview slide, another risk associated with this project is that CDI/RECS has not been reported for organic acid separation; therefore, our team identified alternative bioprocesses that could benefit from the use of electrochemical separations technology. High-level TEA of furfural and levulinic acid production processes indicated that electrochemical technology reduces minimum furfural selling price by ~10% and the minimum levulinic acid selling price by a factor of 3. In an effort to focus on the primary conversion pathway (anaerobic production of carboxylic acids and subsequent upgrading to fuels), these alternative applications and high-level TEA results were not included in the Peer Review presentation.

- The same reviewer stressed the need to “engage experts/vendors, especially since the choice of electrode material may have unforeseen effects on cell fabrication.” We completely agree with this and remain determined to do so. This effort will help ensure that we remain committed to solving the problem at hand (cost-effective separations) without drifting too far into the science.

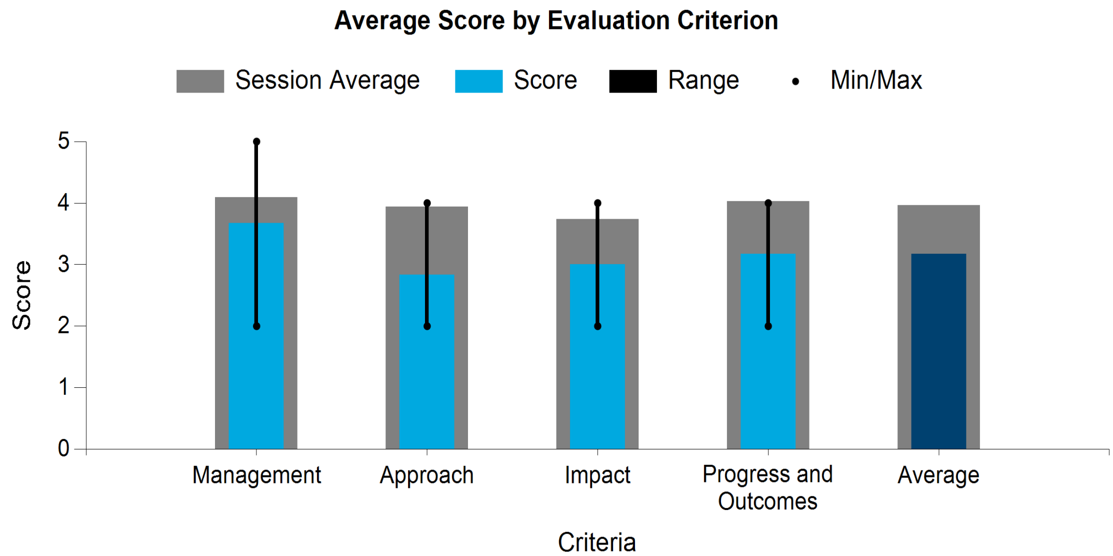
2,3-BUTANEDIOL SEPARATIONS

Oak Ridge National Laboratory

PROJECT DESCRIPTION

WBS:	2.5.5.507
Presenter(s):	Aimee Lu Church
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$7,724,000 *Entire Consortium

The objective of 2,3-Butanediol Separations is to develop low-cost, less-energy-intensive separation technologies for processing dilute fermentation BDO broth generated by the Biochem team (NREL) into suitable feed for BDO upgrading pathways developed by the upgrading team (NREL, ORNL, and PNNL) in aligning with BETO priorities. Specific goals are developing capabilities in (1) BDO enrichment (dewatering) and (2) removal of target molecular/ionic species (proteins, salts/ions, sugars, carboxylic acids) that may negatively impact the downstream BDO upgrading catalyst and reactions.



COMMENTS

- Management: The management plan and implementation appear to be high level and well organized with NREL, ORNL, PNNL, and LANL. There is an impressive consortium of entities involved as well as an industry board (Genomatica, Compact Membrane Systems). Overall, this project is showing good progress and is very well organized.

  Approach: There is substantial merit and significant potential in this approach for recovering BDO using polymer coated porous ceramic membranes. There may be broader implications for other diols, gas separations, and wastewater treatments and even potentially a membrane bioreactor. There was a major issue raised by the review team about the "pervaporation" step, with a recommendation to seek/find an alternative to replace this step (thus, for the purposes of this review, it is assumed that this problem can be fixed).

  Impact: The project impact appears to be headed toward good outcomes with thorough review processes and deliverables in place. Membranes look scalable and economically feasible, replacing energy-intensive distillation. Establishing broad applicability (beyond BDO) of the technology may be a challenging future risk.

Progress and outcomes: Results are showing great promise relative to the metrics set (recovery BDO, scalable, energy consumption, economics). The project appears to have coped well despite the COVID-19 impact, and progress and outcomes look promising. Some initial targets have been met, and others are currently ongoing. The potential challenges with fouling are very problematic although graphene oxide seems to help. Composition of the residue looks like it might be a concern down the road.

- As noted during the discussion, pervaporation is not a viable technology for concentrating from 20% to >50% BDO. Even a very small amount of water vapor removal will rapidly cool the retentate, at which point it must be reheated, and so on, many times, requiring a great many heat exchangers. The process as developed is not viable.

- Concentration of BDO-containing solutions aligns with the BETO mission to transform biomass resources into commercially viable biofuels and bioproducts. Given the project position between BDO fermentation and upgrading, extensive interactions with upstream and downstream project partners are well-defined and articulated. Polymer-coated ceramic membranes are integrated into pervaporation. The milestone of 30% (w/v) BDO enrichment was successfully achieved. Based on comments of reviewers with extensive separation experience, pervaporation not a recommended approach to dewatering BDO fermentation broth; however, the technique may be applicable to other separations within the scope of the BETO mission.

- Narrow scope and limited coordination with other separations projects. The main input is from the IAB, and it is limited to one membrane supplier. The scope is to see if a modified polymer-coated ceramic membrane can be developed to concentrate an aqueous solution of 20% BDO to 30% via pervaporation. The seems like a low hurdle versus the stated goal of 50% BDO. I would like to see alternatives to pervaporation that might be more economical. Membrane modifications via sulfonation and graphene oxide to increase flux, reduce fouling, and maintain adequate separation efficiency versus vacuum distillation seem limited. Suggest examining other options and increasing focus on fouling. Goals are fairly aggressive (up to 50% reduction in energy consumption and reducing losses from 10% to 3%); however, this is a small market for the foreseeable future. Demonstrated only 30% concentration versus 50% target. TEA indicates only a 13% reduction in energy cost without further improvement versus 50% target. Flux is still well below the target.

- Replacing an expensive incumbent process (distillation) with a membrane separations approach is a good idea if it can be implemented effectively on this product stream and enabled at scale. Membrane separation technology can be broadly impactful for bioprocessing. The project TEA appears to be in favor of the process; however, the use of pervaporation on a dilute stream might require numerous heat exchangers, which could be a disabler for process feasibility. Management and communication processes are in place, industrial collaboration is present, and technical risk is discussed. Progress has been on track, with an important milestone for BDO enrichment achieved, and low-temperature BDO recovery demonstrated.

- The program is structured to obtain regular input from the IAB and other experts in their community. The risks and linked mitigation strategies were not described in the project update. The work stream dedicated to developing and characterizing novel polymer-coated ceramic membranes has great merit because it overcomes fouling and flux issues associated with traditional ceramic pervaporation membranes, and creating unique coatings to tailor specific products may be a valuable advancement for this separations technology. The critical question in this work is whether deployment of pervaporation for this process stream is prudent and if the Q2 2021 milestone can be met. It will be helpful if the project team will explore and respond to the concern raised during the review about pervaporation technology viability for a scenario that moves large volumes of water through the member: the energy inputs (heat exchangers needed to drive process due to evaporative cooling).

PI RESPONSE TO REVIEWER COMMENTS

- Thanks for all of the constructive feedback. We appreciate the positive comments. To address the major comment on whether pervaporation is efficient compared to the state of technology, we have updated our TEA results by carefully considering the reviewers' suggestions during the Peer Review meeting. We have updated the process model based on reviewers' comments, including heat exchangers with multiple stages added in the process, and we performed rigorous energy analysis. Our revised TEA results conclude that the use of pervaporation on dilute BDO concentration stream did not show superior energy/cost savings compared to current state-of-technology evaporation/distillation. We have updated the results to the consortium management and recognize the necessity to develop membrane technology but will explore broader applications. We (experimental, analysis team, and consortium management) are in the process of redirecting the project and will finalize it by the end of June. Regarding the next step of membrane materials, the flux of the membrane, it is one of the focuses that we would like to improve by applying higher-surface-area membrane configurations.

COUNTERCURRENT CHROMATOGRAPHY

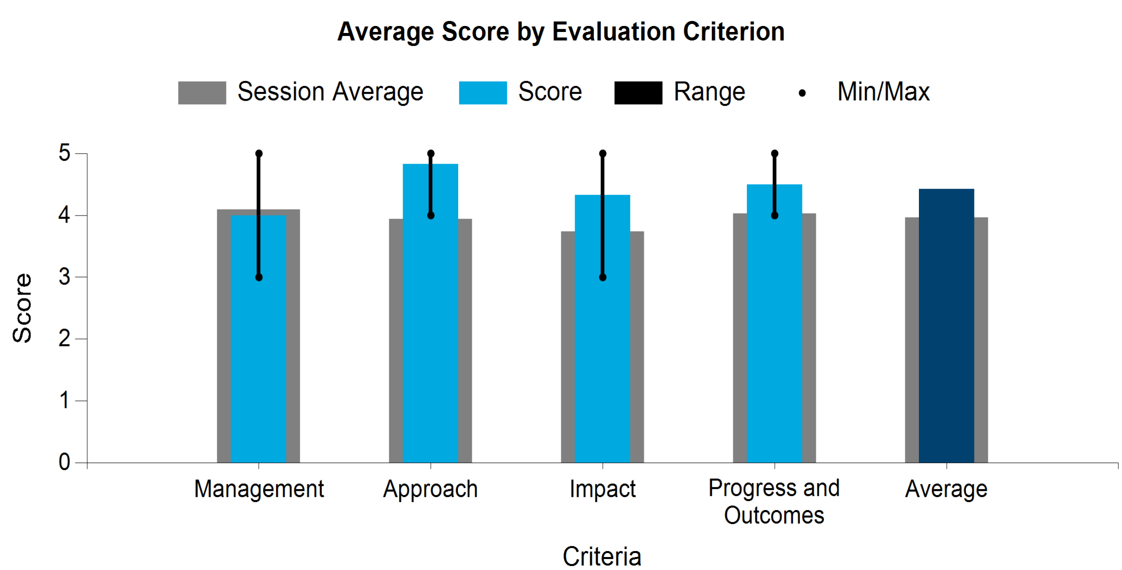
National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.5.5.50x
Presenter(s):	Eric Karp
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$7,724,000 *Entire Consortium

In support of BETO in recovering coproducts in biorefineries, this project evaluates the use of countercurrent chromatography (CCC) in recovering coproducts from reductive catalytic fractionation oil, alkaline pretreatment liquor, aqueous phase hydrothermal liquefaction oil, and catalytic fast pyrolysis (CFP) oil. The project addresses three technology barriers in developing the bioeconomy: (1) cost of production, (2) selective separation of organic acid species, and (3) advanced bioprocess development.

CCC is a unique, scalable, chromatographic technology that operates with two immiscible liquid phases moving countercurrent to one another. Unlike simulated moving bed (SMB) technology, CCC is a true moving bed, and because it uses liquids as both the stationary and mobile phase, it can handle solids directly in the feed. This aspect of CCC allows it to skip the expensive filtration step needed prior to traditional SMB; further, the liquid phases are composed on relatively inexpensive organics (e.g., hexane and ethyl acetate). This project develops CCC methods for direct isolation of coproducts from reductive catalytic fractionation oil, alkaline pretreatment liquor, hydrothermal liquefaction aqueous, and CFP oil. TEA and process modeling are presented to compare CCC to SMB and assess its applicability in a holistic biorefinery. Initial results indicate approximately fourfold reductions in solvent demand and twofold reduction in energy consumption compared to SMB.



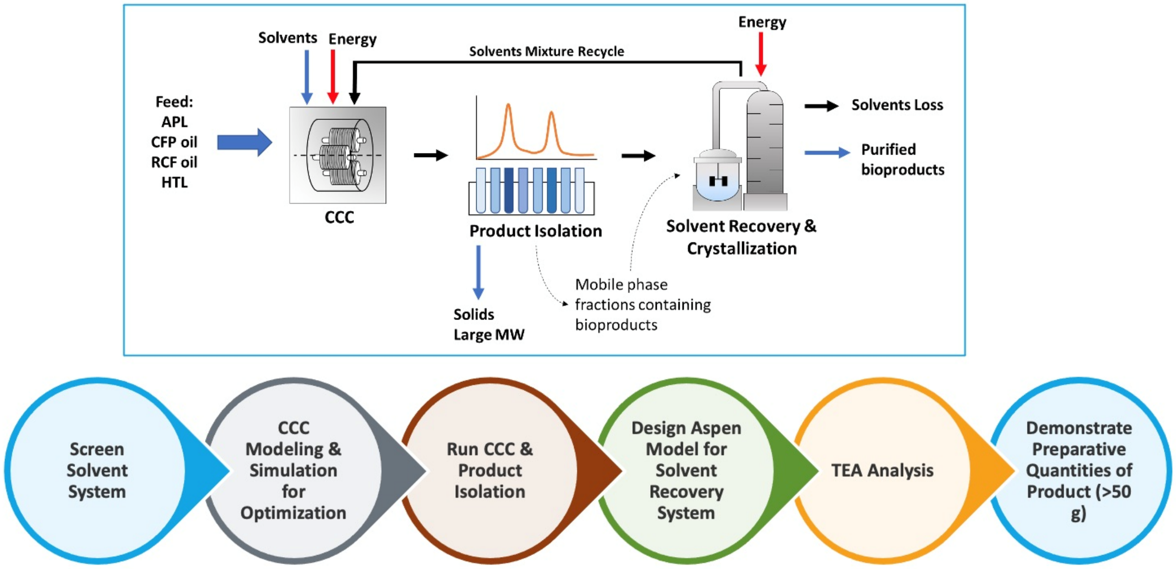


Photo courtesy of NREL

COMMENTS

- Management: The management plan and implementation appear to be adequate for a small consortium of NREL and PNNL. Implementation is progressing and well organized, but it does not show any kind of logical implementation plan with milestones. There is no effort to describe risk identification and mitigation and no advisory boards.

  Approach: There is merit and potential in this approach of multiple coproduct recovery from a lignin source; however, it will be challenging to achieve useful cost-effective separations of multiple components from a complex lignin stream. The work aims to develop CCC methods and mathematical tools for optimizing the purification of the target from reactive catalytic fractionation oil, alkaline pretreatment liquor, and hydrothermal liquefaction streams. This challenge is not addressed in the approach in terms of crucial decision making.

  Impact: The project impact appears to be headed toward measurable outcomes with review processes in place; however, the lack of an overarching project plan makes it difficult to assess where the project is in terms of impact. Much of the results presented appear to be theoretical, using mathematical tools and showing some progress with CCC methods; however, there is no substantial optimization with real-world separations from complex mixtures; thus, the impact is hard to evaluate in terms of moving to higher scale and costs involved. It was noted that industry is using this kind of technology, which is encouraging.

  Progress and outcomes: Results are showing some possibilities of useful separations (1-g scale), but mostly it needs to move to higher amounts and select a key target. Not enough data are provided to assess how much real progress is being made and not enough in terms of critical milestones toward outcomes at larger scale; thus, it is very difficult to conclude how practical CCC might be.

- CCC is being explored for the purification of aromatic coproducts from biorefining streams. The project rates high in significance due to the impact coproducts could have on biorefinery profitability and the high degree of challenge associated with the task. Relative to management, additional information related to decision-making process would be beneficial. CCC is emerging technology and providing resources to remain at the forefront of separations technology is critical. The effective balance of experimental research, mathematical modeling, and TEA constitutes a strong approach. Given the short timeline preceding the review, progress is excellent; significant thought was given to results dissemination via planned publications and patents.

- The technical team has developed and executed a good plan. It is not clear how the industrial partners needed to scale up equipment and drive the utilization of CCC are connected to the development team. There is a very clear plan to evaluate options for the application and small-scale testing of the CCC concept. Analysis of TEA and quantifying competitive advantage to SMB technology is key to future adoption. There may be many more application areas beyond the bio-oil and alkaline pretreatment liquors being tested. Adoption in those applications will be limited primarily by the pace of commercialization in those areas. For the tested areas, good progress and well characterized outcomes. This is a much broader opportunity.

- The possibility of using CCC to handle complex feed streams has significant merit. The approach seems flexible and scalable (initially using deployable skids for batch processing; continuous mode technology under development). Throughput, yield, purity, and energy are identified as important metrics. The impact of a successful project would be an approach that is superior to the incumbent technology (e.g., requiring filtration and SMB) and could lead to broad biorefinery coproduct applications requiring fewer process steps (e.g., filtration). Project management, processes, responsibilities, communication, and industrial partners are in place. Progress is promising at this early stage. The project is identifying products worth recovering and determining/integrating process conditions enabling their recovery. Initial results support lower solvent use and energy costs over the SMB base case.

- This is a truly innovative and highly promising concept. It is the most exciting I've seen in the Separations Consortium (or most anywhere else) for at least a few years. Sherwood plot analysis is a great place to start. It is not perfect, but it gives you a fair idea of the most likely places to start. The management plan is very light; risk mitigation is only a single bullet. It is nice to see some work on thermochem intermediates as well. Modeling effort looks sound as well—useful for screening operating parameters. Some trial and error is probably still necessary, but much less than without a model. Progress is excellent; looking forward to more!

- This robust project appears to be well managed and has the right blend of modeling, source partners for raw materials, separations expertise, energy, and TEA analyses. Great coordination in applying the mathematical modeling along with the Sherwood analyses to mitigate risks. The authors presented a very clear goal statement with measurable targets to measure whether this technology overcomes limitations of the base case SMB chromatography. They made their case with an excellent first-principles description of the technologies for both the base case SMB and the emerging CCC separations strategy. The exciting aspects of the CCC are its flexibility to pick the stream (phase) with lower energy demand, ability to handle solids, high throughput, higher yields, and modeling solvent recovery/reuse as a parameter. Using the Sherwood plot as a tool to define target selections is invaluable and eliminates the need for experimental work because the tool identified hydrothermal liquefaction aqueous streams that are not compatible with CCC for individual compound extraction. This confirms the fact that these are also not high-value targets. They also provided clear and quantitative metrics around the go/no-go decision. The approach of using input streams from different commercial partners is a way to test the versatility of their approach and leaves confidence that they are grounded in developing a realistic and commercially applicable technology. The team has made excellent progress in a brief time period; what has been demonstrated so far shows considerable promise.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the valuable feedback from the reviewers. The implementation plan of the project consists of five systematic steps: (1) prioritizing streams with a Sherwood plot analysis, (2) developing CCC simulations to predict CCC elution and purification profiles, (3) selecting optimal elution solvents, (4) completing CCC experiments with real-world streams, and (5) energy footprint determination through TEA and LCA baselined to traditional SMB chromatography. Detailed milestones and risk mitigation strategies are listed in the AOP and are managed through the consortium-wide Smartsheet tool to coordinate. We apologize if these were not fully covered in the presentation, but limited time may have shortened discussion in this area. The key go/no-go milestone of the project was met last quarter using real reductive catalytic fractionation oil from poplar as the feed. The decision point was "Demonstrates an energy footprint <30% of the heating value of the targeted product and purity level >90% of the recovered products. Demonstrate stationary phase reduction of at least 20%, or eluent load reduction of at least 20% compared to traditional SMB technology as a benchmark." To meet this milestone, the team optimized the CCC method on the real-world reductive catalytic fractionation oil sample through the five-step approach above and achieved separation of the target monomers identified from the Sherwood plot analysis at the 1-g scale. Larger sample separations are to be performed in years 2 and 3 of the project to scale the process to separate >50 g of purified compounds. The COVID-19 pandemic prevented larger-scale experimental runs in year 1, and the modeling tools were instead developed first. Industrial partners listed in the presentation are informal collaborations designed to generate seed data, modeling, and TEA for more specific projects with industrial partners through FOAs to move the technology into existing biorefinery businesses. Scale-up of CCC is an important consideration, especially because it is a newer technology. To help address scale-up, we have a formal collaboration with Brunel University, which is the world expert in CCC. In the last year, brand name companies have released large-scale units capable of processing tons of material per year. Evaluation of these instruments' performance and operating modes at the industrial scale is in the early stages. Future work in the separations consortium may collect full-scale data with these instruments if access to them can be achieved.

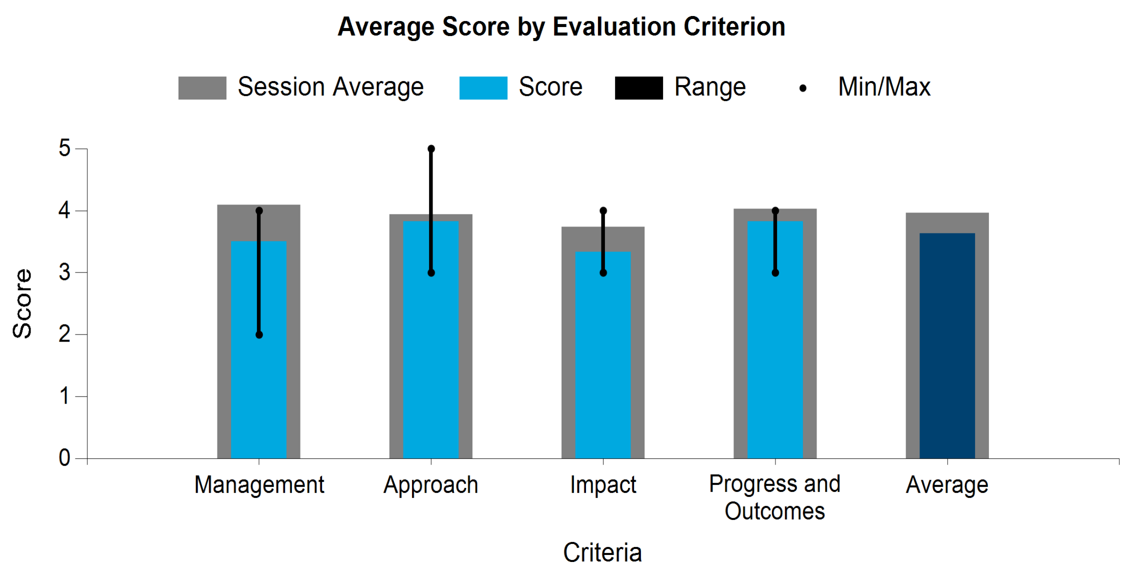
MELT-STABLE ENGINEERED LIGNIN THERMOPLASTIC: A PRINTABLE RESIN

Oak Ridge National Laboratory

PROJECT DESCRIPTION

WBS:	2.5.6.103
Presenter(s):	Amit Naskar
Project Start Date:	10/01/2018
Planned Project End Date:	09/30/2021
Total DOE Funding:	$1,375,000

This work develops a novel family of commercial-ready, lignin-based thermoplastic polymers and polymer composites suitable for high-volume applications. Specifically, lignin derivatives are being produced that are inherently recyclable, rapidly moldable, and 3D printable, while capable of retaining their superior mechanical properties after thermal reprocessing. The objective of this research is to develop and commercialize lignin-derived, industrial-grade polymers and composites with properties, including printability, exceeding current petroleum-derived alternatives. New functionalization chemistry of lignin is introduced in this research that yields reactive lignin capable of synthesizing polymeric products with high lignin contents (50%–70%). Technologies that enable high-value uses of lignin, a biorefinery waste stream, are important to achieve cost-competitive production of biofuels.



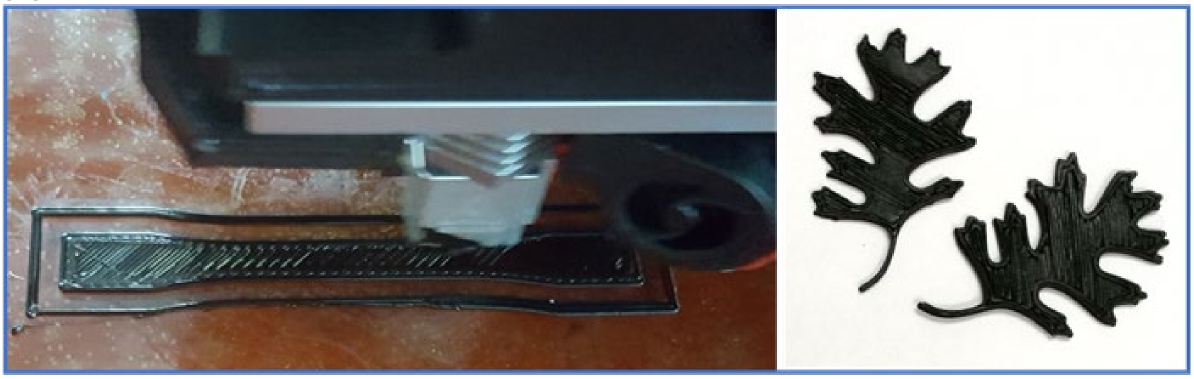


Photo courtesy of ORNL

COMMENTS

- This project brings a compelling vision of applying modeling expertise to design higher-value materials from lignin. The team has made good technical progress and translated that work to an excellent portfolio of several prototype materials, patents, and publications. Good progress in demonstrating a potential use of composite material fabrication for automotive interior parts has led to a rudimentary TEA analysis. The project leaders have engaged with industrial partners (e.g., the R&D license with a renewables company that offers a commercial ABS replacement material is promising). My general concern repeats a theme brought forth in the 2019 Peer Review: management of diverse lignin sources. The team has demonstrated that the functionalization of two different lignin sources results in improved mechanical properties in the acrylonitrile-butadiene-lignin composites; however, the charts on page 12 suggest that differences that reflect the lignin source persist in the final functionalized composites product. Can the project leaders elaborate on their confidence in whether the team can identify an economic and robust process that collapses lignin differences to create a source-neutral starting material? What are the barriers to an opposite approach that capitalizes on unique properties of biosourced materials and can marry with lignin specifications and link to the desired product properties (e.g., in the way that the biosourced alginates or carrageenan gels are managed)?

- Management: A management plan and implementation process appear to be in place; however, this is relatively light in terms of depth because the work is solely at ORNL. There are connections to two industry partners, plus a license with a startup (Prisma Renewables). Commercialization discussions were impacted by COVID-19. There are regular meetings internally and outreach by the PI to industry partners that incorporates risk assessment coordination.

  Approach: The approach of making high-value thermoplastics with functionalized lignin has merit. Although there is value in this approach, there are challenges, risks, and obstacles. Concerns include the consistency and purity of lignins required and the costs associated with the overall process and how this translates to value at the waste stream. It would be useful to see a kind of preliminary scalable process design that could be the basis of detailed TEA evaluation and identification of the challenges. It is not clear how value will be shared with the lignin waste stream.

  Impact: The project shows promising new functionalization chemistry. The high-volume applications are not described but are assumed to be automotive. Commercial readiness is claimed, but full at-scale processes with downstream application targets are lacking. From a fully integrated process-to-application perspective, there is insufficient detail to understand the technical and commercial potential. A process to extract lignin will result in a range of waste products that could be costly to deal with. The investigators state that the product will be high value but omit to make clear how the cost structure of the product will translate across the value chain to become added value of the lignin itself. This premise of high value for the lignin could be invalid, in which case the idea of such high value in a biorefinery waste stream would be false. It is stated that the composite is inherently recyclable without showing studies of this claim.

Progress and outcomes: Some progress has been made with promising outcomes. There is an impressive list of patent applications from 2019/20, most licensed by Prisma. Functionalization improvements are show for new acrylonitrile-butadiene-lignin composites (strain/shear) with potential for automotive applications. A preliminary TEA was conducted, but it lacks rigor. Critical technical and development issues are described superficially and really require a detailed process evaluation and economic analysis and evaluation of the range of different lignins. Such evaluations would have a big impact on the outcomes and ultimate directions of the project.

- Good coordination between national labs. It is not clear what the role of any industrial partners may be in setting the project goals. Reactive extrusion is a reasonable way to produce acrylonitrile-butadiene-lignin resins. There is concern about the variability of sources of lignin based on the feedstock (pine versus poplar on page 12) and the availability of lignin in the future. Cost-competitiveness and performance of resulting acrylonitrile-butadiene-lignin polymers versus other thermoplastics was not addressed. The thermoplastic markets are extremely competitive. It depends on the commercial availability of consistent and good quality lignin. If the lignin value is higher due to this development than the fuel value, it could improve the economics of biorefineries. That benefit needs to be addressed in the TEA. The project has demonstrated the feasibility of making thermoplastics with significant amounts of lignin. The value of this development needs to be ascertained.

- Lignin is a variable and complex biopolymer, with many decades of proving difficult to work with, whereas 3D printing is a demanding application, especially for the high-speed industrial printers that will need to be addressed to make for a significant market. The presenter seemed to make the case of a small market size. So, what is the motivation? The management plan is minimal, and there is no real risk assessment or mitigation plan.

  Approach: Not enough was said about what would be the source of the lignin, how it would be treated, what control there would be over natural variability, etc. The property results for composites were hard to follow. The underlying values/meanings of some of the test methods are not well-known to nonexperts. What is the market size being proposed, given the results obtained? Only 3D printing, or more than that? A value of $2/lb for lignin is excellent, but how much can be sold? Progress is good in light of the time elapsed, the funds costed, and the challenges of the past year.

- The project management structure and communication are in place, although more on risks and risk management would be welcome. The project appears to be coordinating with industry. The goal of producing lignin-derived composites with properties similar to incumbent molecules/technologies is in line with BETO and Technology Area goals. There is a clear end market and application. The successful use of a large percentage of a lignin from a biorefinery has substantial merit and could help economics; however, inconsistency of the input lignin may be a significant issue. It was suggested that the process could tune for this, although it is not clear how practical that may be. The approach is innovative and has already resulted in numerous publications, patent applications, and a license. This is a very promising project, with good accomplishments to date, having met a key go/no-go milestone (and using 70% lignin content).

- This project seeks to develop and commercialize lignin-containing industrial-grade polymers and composites with properties that exceed currently used materials. Nonfederal funds have been raised and a cooperative research and development agreement initiated, but no commercialization partners are identified. Finding partners who will accept variation in material composition may prove challenging. Lignin functionalization that is applicable to all lignins has been developed. It would be helpful to create and test polymer using lignins from various sources to validate this.

PI RESPONSE TO REVIEWER COMMENTS

- Market size and commercial potential: This project has developed three different lignin-based polymer classes: elastomers, thermoplastic, and functional or self-healing composites. Compositions that are 3D printable are easily melt processed; thus, they are compatible with other high-volume processing methods, such as injection molding as well. So, the potential market goes beyond just 3D printed structures. Elastomeric materials are softer and can be processed via resin-transfer molding; thus, all these can find use in automotive composite applications that have a significant market potential. The reviewers are right: It is difficult to penetrate the automotive market. It will certainly need industrial partners.

- Partners: We are working with two startup companies. One of them is working with the world's fourth largest auto parts manufacturer. We have not named all of them in the presentation. We raised nonfederal funds from one of them; thus, the "industrial partner has not been identified" comment was the presenter's failure to communicate that.

- Source of lignin and variation: We have worked with eight different lignin sources and grouped them into three types. Those three types of lignin show three different optimal compositions and materials behavior. These varying optimal conditions make it difficult to formulate a source-neutral starting material. Although we were working on that, the 2019 Peer Review criticized that because it was perceived to be ineffective. We were asked to focus on a certain market. It is indeed a great challenge, and we will address it during our remaining budget period. The claims of recyclability will also be demonstrated in the remaining budget period, but it is expected that they will be fully recyclable based on existing thermal stability data on the composites.

- Fully integrated process to product perspective: Details of the technical aspects associated with sourced lignin to product could not be presented within the given time. Numerous articles published from this work will show the technical merit of the work. We claim solvent-free processing with high bulk material throughput in this integrated process (except lignin isolation). Lignin isolation must happen in a biorefinery.

- TEA and economics that can positively impact the diverse lignin source barrier: We conducted only a preliminary TEA. Though the scalability needs to be demonstrated with an industrial partner, the processing approach is suited to existing banbury-type internal mixing (as well as twin screw extrusion) commonly used in rubber product manufacturing. We have used such processing cost data in our TEA. Instead of using lignin cost from a biorefinery, we estimated what a biorefinery can get as revenue from the lignin stream. We plan to conduct a thorough TEA in our next phase of research in collaboration with our industrial partners.

- Management plan/risk assessment and mitigation: The main risk to commercialization is working with industrial partners and establishing the cost-competitiveness of these materials. This cost risk is mitigated by developing robust polymer compositions within three different polymer classes. Initial market penetration can be targeted in markets with higher end-product price points (e.g., self-healing polymer and 3D printable composites) before competing in the highly competitive commodity polymers market (elastomers for automotive interior).

CELLULOSE-CHITIN COMPOSITES FOR PERFORMANCE ADVANTAGED BARRIER PACKAGING BIOPRODUCTS

Georgia Institute of Technology

PROJECT DESCRIPTION

WBS:	2.5.6.200
Presenter(s):	Carson Meredith
Project Start Date:	10/01/2018
Planned Project End Date:	03/31/2022
Total DOE Funding:	$1,015,501

There is a strong drive to discover and develop alternatives to conventional plastics that offer the ability to be manufactured and used in a circular manner. In a circular economy, as opposed to a linear one, materials are derived from renewable resources or recycled content, and at the end of life, they are able to be circulated back into production via a chemical, physical, or biological pathway. A critical need exists to develop such materials for plastic oxygen barrier packaging, which represents the largest contributor to unrecyclable plastic waste. This project is developing a PABP based on biomass that results in better oxygen permeability than a leading benchmark plastic packaging film, PET. The work innovates by developing a PABP from layers of cellulose and chitin nanofibers coated onto a cellulose acetate substrate. Both the cellulose and chitin layers are deposited simultaneously on a continuous slot-die coating line. To date, the project has succeeded in producing PABPs with oxygen permeabilities that are reduced by 20% to 80% relative to commercial oriented PET film.

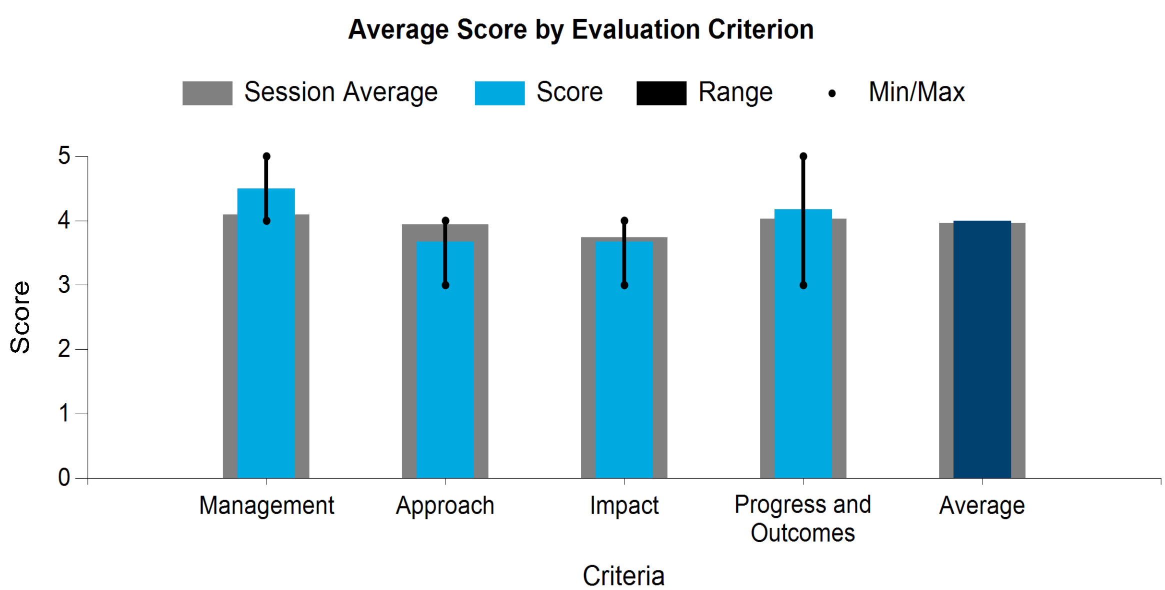


Photo courtesy of Georgia Institute of Technology

COMMENTS

- Management: The management plan and implementation appear to be appropriate and well organized. There is a solid consortium of institutions and industrial partners (academic: Georgia Tech, NREL, UGA; companies: Tidal Vision, Sugino, Winpak, Nestle) involved. There are frequent subteam meetings, showing continuous assessment of progress with bi-/triweekly management meetings.

  Approach: There appears to be merit and potential in this approach. The most critical issues are: (1) technical—the ability to fuse chitin-cellulose nanomaterial bilayers, (2) performance—reduction in oxygen permeability versus best oriented PET on the market, and (3) economic—based on first-pass process design. There were other important criteria, however, such as degradability and carbon reuse. The team appears to have developed various processes to evaluate these various criteria and critical issues. Critical challenges lie ahead with scaling a reliable/consistent source for chitin. There seems to be no effort to determine whether the fused chitin-cellulose nanomaterial bilayers are degradable and reusable.

  Impact: The project impact appears to be headed toward good outcomes with a good review of processes and some technical key deliverables in place. There are promising future opportunities with a U.S. Department of Agriculture proposal and a pilot idea with a major packaging converter.

  Progress and outcomes: Preliminary results are promising relative to the technical performance against intermediate goals. Interesting discoveries, such as the variability of the fiber size being important for performance in a bilayer. Still unknown for economics, but the team is addressing this in the next stage. The project appears to have coped well despite the COVID-19 impact, and progress and current outcomes look okay. Note that considerable technical challenges in perceived applications remain to be evaluated. Also, sourcing a reliable source of inexpensive chitin seems likely to be challenging. It is not clear how this will deliver against the list of "impacts": (1) valuable byproducts from biorefineries, (2) reduced landfill use and ocean leakage, and (3) circular packaging alternative reuse of carbon. Some performance attributes are apparent, but this alone may not be sufficient to carry this chitin-based product to market (degradability might be though). The final goals (optimization of O_2 permeability, effects of humidity, mechanical properties, process design and cost analysis) are likely very challenging.

- This is an interesting idea for waste utilization while also providing 100% biomass-derived alternative to nondegradable single-use packaging with good oxygen barrier properties. Project participants have met timelines for task achievement. Processing costs associated with cellulose and chitin preparation; material formulation is not discussed. Commercial partners have been identified, but it is not clear if this is intended to fill a product niche or is viable for large-scale utilization.

- This is a promising concept. Current composites are fossil based and difficult to recycle or even to dispose other than by landfilling. Chitin is an intriguing choice; not many biopolymers have its favorable oxygen-barrier properties most likely. The management and risk mitigation plans are very good. The impact could be significant, but it was unclear how these composites would biodegrade in the environment. Is any testing planned on that? Progress is excellent based on funds and project duration so far, and on the challenging environment this past year.

- The team was receptive and incorporated suggestions in the 2019 Peer Review. The goals and target are nicely laid out in the presentation, and the team is poised to be on track for the optimization tasks for 2021. The composition optimization study revealed a handle to tune chitin nanofibers/cellulose nanocrystals (ChNF/CNC) bilayers to achieve specific oxygen permeability value. It is great that the program has engaged representative stakeholders along the process chain (raw materials provider/film converter/downstream client). The project goal is to exceed PET oxygen barrier performance in the range of 10% to 500% with input from downstream clients—what are the tangible benefits for flexible food and electronics packaging clients? Is the team confident that PET remains the best film benchmark for oxygen permeability—there are emerging films (e.g., PEF (polyethylenefuranoates))—on the horizon with lower oxygen permeability than PET.

- The potential market size for a better, greener barrier packaging material is enormous, although working out the recycling and recovery of the barrier packaging will be a challenge (outside the scope of this project). The project approach of developing a reusable cellulose-chitin composite for barrier packaging could provide the technology push to help solve the macro issue regarding waste recovery. Chitin nanofibers made from abundant shellfish exoskeleton or from fungi, combined with wood-derived cellulose nanofibers, looks promising from a waste recovery/reuse standpoint. Progress using these bio-derived materials to manufacture layered films with reduced oxygen barriers when compared to PET films has been excellent, supporting this as potentially technically feasible and manufacturable. Project management, assignments, communications are well thought out. Industrial engagement is present, useful from both feedstock and product performance standpoints. The layered structure of the barrier material may, however, prove difficult to deconstruct and recover efficiently. If these issues can be addressed economically, impact on the industrial use of barrier packaging and the replacement of incumbent technologies could be substantial.

- Well-qualified, multifunctional team. Inclusion of key players in the materials supply chain is excellent. Clear goals and milestones. Coating approach prequalified with current packaging suppliers. Coated cellulose film versus PET using oxygen permeability barrier measurements to guide development. TEA of final option for competitive assessment. Would like to see PEF in the competitive offering TEA analysis. Single-use packaging is a major source of plastic waste in the environment. An ultimately biodegradable packaging system would be transformative, provided it meets the performance requirements at a competitive cost. The performance of chitin-coated cellulosic film has exceeded initial targets. Further work is needed to verify TEA and mechanical performance of coated films.

PI RESPONSE TO REVIEWER COMMENTS

- Thanks for a careful and conscientious review. These are helpful as we evaluate the highest priorities in the last year of work. Overall, this project's aim has been to address a prioritized list of risks that affect commercializability. The first of these was the ability to achieve enhanced O_2 barrier properties, and the second was to show that the film structures could be delivered via continuous coating process. We are glad that the reviewers recognized the success of these primary goals. In addition, the reviewers have correctly identified some of the core challenges to progressing to higher TRL/MRL levels. The suggestion to evaluate degradation is a good one. While biodegradation was not in our original project scope, we have initiated a biodegradation assay with collaborators at the University of Georgia, which is presently underway. The last stage of the project, to start in summer 2021, will involve the evaluation of the TEA and major variables influencing the production costs of chitin nanofibers. Along with this aim, we will engage in identifying limits of mechanical property improvement and strategies for improving sensitivity to humidity. The sourcing of large volumes of chitin nanofibers is perhaps the most significant unknown. While the chitin fiber market evolves, one approach we are pursuing is non-chitin sources of cationic polysaccharides. Such materials would function like chitin in our structures but would be sourced from plant carbohydrates.