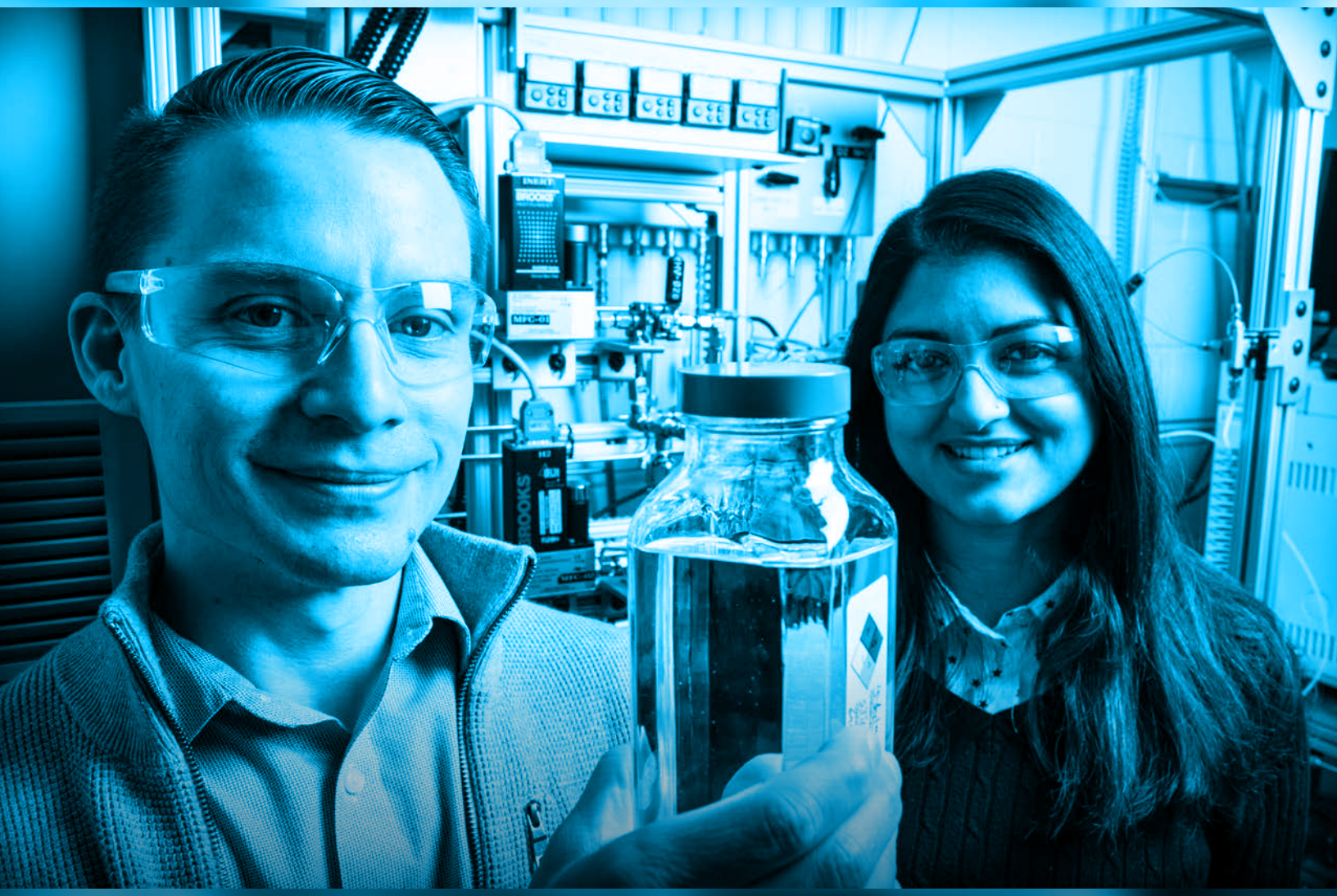

CO-OPTIMIZATION OF FUELS AND ENGINES

TECHNOLOGY AREA

CONTENTS

INTRODUCTION

The Co-Optimization of Fuels & Engines (Co-Optima) 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 11 presentations were reviewed in the Co-Optima session by 7 external experts from industry, academia, nonprofits, and other government agencies. For information about the structure, strategy, and implementation of the technology area and its relation to BETO's overall mission, please refer to the corresponding Program and Technology Area Overview presentation slide decks, which can be accessed here: https://www.energy.gov/eere/bioenergy/2021-project-peer-review-co-optimization-fuels-engines.

This review addressed a total U.S. Department of Energy (DOE) investment value of approximately $43.7 MM, which represents approximately 6.3% 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 Peer Review, including scoring information for each project, comments from each reviewer, and the response provided by the project team.

BETO designated Alicia Lindauer and, later, Trevor Smith as the Co-Optima Technology Area review leads, with contractor support from Robert Natelson (Allegheny Science and Technology). In this capacity, Alicia Lindauer was responsible for all aspects of review planning and implementation. During the post-review report writing period, Trevor Smith took over responsibility.

CO-OPTIMA REVIEW PANEL

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CO-OPTIMA REVIEW PANEL SUMMARY REPORT

Prepared by the Co-Optima Review Panel

INTRODUCTION

The seven members of the 2021 Co-Optima Review Panel appreciate the opportunity to review the management, strategy, approaches, hard work, results, deliverables, and future directions across all of the projects included in this round that essentially build on and represent the numerous research-and-development (R&D) professionals (scientists, engineers, technicians), industry advisors, board members, university partners (professors, staff researchers, students), team leaders, administrators, contractors, bioenergy and vehicle stakeholders, and program and technology managers who have contributed to the success of this technology area during the last half decade. The Review Panel understands the significance and importance of our responses, commentary, and contribution to the overall peer review process. Further, our efforts are not taken lightly, realizing the seriousness of our comments to influence R&D directions within BETO and the DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO). Consequently, we thank all of the DOE, BETO, and VTO technology managers, professionals, and sponsors—in particular, Alicia Lindauer, Gurpreet Singh, Leo Breton, Kevin Stork, Michael Weismiller, Trevor Smith, Jim Spaeth, Colleen Tomaino, and Robert Natelson—for their training, patience, support, and guidance during the years.

The combination of BETO and VTO cooperating on the Co-Optima initiative these past 6 years has greatly improved the state of the art (SOA) in fuel research and helped answered questions surrounding "What fuels should be made?" rather than "What fuels can be made?" The Co-Optima Technology Area is well designed, with both a clear scope of work and quantifiable metrics for success. The portfolio of projects has strong synergy among partners and lab consortium participants with no overlap. The technical links among projects are evident and combine well in pursuit of the technology area's overall goals, which are to (1) identify neat fuel blendstocks with greenhouse gas (GHG) reduction potential greater than 60% relative to petroleum refining, (2) determine fungibility with traditional fuels at blend levels up to or greater than 30 vol %, (3) identify engine-fuel pairs for light-duty vehicle (LDV) fuel economy improvement (FEI) by 10% along with the remaining 25% FEI targeted from other DOE programs, and (4) 4% FEI for heavy-duty vehicle (HDV) applications. The 4% target for improving medium-duty vehicle (MDV)/HDV efficiency continues to be a challenge, with the higher efficiencies inherent to mixing-controlled compression ignition (MCCI) engines.

The Co-Optima Peer Review was conducted remotely via the Zoom virtual meeting application this year due to the COVID-19 pandemic in-person restrictions and guidelines from the Centers for Disease Control and Prevention. Two 3-hour, afternoon sessions were held on 2 days: Monday, March 15, 12:15 p.m.–3:15 p.m., and Tuesday, March 16, 12:15 p.m.–3:45 p.m. Although this virtual format was quite different than the traditional meeting dynamics, the two sessions went very smoothly, and there was enough time for questions and answers (Q&As), and there was ample commentary from the reviewers. The first session highlighted the annual operating plan (AOP)-funded work of the Co-Optima national lab consortium on the following five topics: structure-property-processing relationships (SPPRs), bio-blendstock generation and testing (BBG&T), techno-economic analysis (TEA), life-cycle assessment (LCA), and the potential impact of at-scale deployment. The second session highlighted the funding opportunity announcement (FOA)-funded university-level work on the following six topics: naphthenic biofuels for MCCI (State University of New York [SUNY] at Stony Brook), renewable fuel additives from woody biomass (University of Massachusetts Lowell), tailored bio-blendstocks for MCCI (University of Michigan-Ann Arbor), monomethyl ether and alcohol bio-blendstocks for MCCI (University of Wisconsin-Madison), polyoxymethylene ethers (POMEs) as bio-blendstocks for MCCI (Colorado State University), and renewable butyl acetate as diesel bio-blendstock (Auburn University). From the organization of the sessions mentioned, it is quite evident how well aligned and integrated both the university and national lab projects have become, which was part of the feedback provided from the 2019 Review Panel.

The Co-Optima team successfully completed the Fiscal Year 2020 go/no-go milestone, identifying at least 9 blendstocks for multimode combustion with favorable economics, emissions, and efficiency. The team has identified at least 11 MCCI blendstocks as iso-alkanes, esters, and ethers that also offer similar benefits after *in silico* screening of hundreds of potential mixtures. Every key milestone reached in Co-Optima has resulted in dozens of recommendations for identifying potential blendstocks that ultimately influence the research directions across BETO. An impressive number of capstone reports have been published and are available for public download. From a technology area management point of view, the Co-Optima portfolio is very well run, with excellent oversight and a number of highly visible and high-quality deliverables. The initiative allowed for a good blend of fundamental science, chemistry, and modeling at the molecular structural level, with engine performance evaluation/validation at the application level. Co-Optima has brought together world-class facilities and experts to advance the state of biofuel formulation co-optimized with advanced combustion modes to produce a lot of great science and engineering research direction. Co-Optima's original strategy was born from the observation that certain biofuel properties (e.g., cetane number, octane number, heat of vaporization, soot potential), when tuned properly, could enhance the performance of engines from an efficiency and fuel economy standpoint. As the initiative winds down and commissions the task of handing off the portfolio of work to industry to commercialize, the future success of the co-optimized technology will fall on the private sector decision-makers and economic tides to drive this profound legacy forward.

STRATEGY

Advanced Combustion Mode and Fuel Candidate Pairing

All of the projects appear to be aligned with the mission and objectives of the initiative, which involve identifying optimal fuel-combustion mode pairings that have a realistic chance of penetrating future markets by increasing fuel economy and reducing emissions. The strategy for carrying out this mission resonates clearly throughout the initiative and requires first (1) identifying all of the highly efficient, advanced engine combustion modes most likely to surface in the near term, such as multimode spark ignition and MCCI; (2) downselecting the most critical engine performance and operability parameters for combustion modes of interest (i.e., cetane number, soot index, phi sensitivity, brake thermal efficiency); (3) proposing and experimentally screening at multiple scales (lab, pilot, demonstration) a comprehensive list of fuel candidate molecules/blends derived from renewable processes that meet a tiered property specification; and (4) checking the level of market viability for top fuel blend candidates using stakeholder feedback, TEA, LCA, environmental impact modeling, and industry-accepted refinery planning tools. This well-designed, focused Co-Optima strategy allows for the rapid screening of a very broad range of fuel properties and related pathways while simultaneously reducing risk. Other expected outcomes include tangible benefits in process economics, information sharing, and bioenergy workforce impacts. Relative to traditional fuel development, the downselection of promising fuel candidates was accelerated by Co-Optima; however, the entire commercialization cycle continues to have minor hurdles limiting marketing penetration—namely, from a refinery, vehicle original equipment manufacturer (OEM), and socioeconomic standpoint. Thousands of renewable, neat fuel blendstock candidate molecules were screened by computer simulation techniques, eventually downselecting 9 for multimode LDV and 11 for MCCI HDV applications. The top multimode LDV renewable blendstocks are all oxygenates, primarily alcohols derived from processes with minimum fuel selling price (MFSP) <$5/gallons gasoline equivalent (GGE) and greater than 60% GHG emissions reduction relative to petroleum refining. The top 11 MCCI HDV renewable blendstocks include long-chain straight and branched paraffins (e.g., farnesene) along with widely accepted fatty alkyl esters (e.g., fatty-acid methyl esters). A mismatch in timing may be present with respect to advanced combustion regimes in MDV/HDV and the critical fuel properties needed to enable these regimes. Later projects to evaluate compounds that enable advanced combustion will be appropriate once the fuel properties have more clarity and definition.

Flexibility and Response

The Co-Optima initiative has demonstrated repeatably in both its technical and management flexibility by responding to stakeholder input and shifts in market technology acceptance and trends. The project team has always operated within a defined strategy in terms of technical targets and milestones, which originally

focused on emissions reduction and fuel economy gains for advanced engine combustion technology within both the LDV and MDV/HDV platforms. Recently, however, with the increased industry and consumer momentum toward vehicular electrification, the strategy was modified to reallocate more resources toward HDV applications. Whereas the original focus of Co-Optima was to use the unique properties of biofuels to enable more efficient engine optimization, the initiative has shifted more toward achieving GHG reductions from higher blend percentages of bio-blendstocks into fuels while mitigating any potential trade-offs to low-temperature performance, sooting propensity, and energy density relative to conventional, ultra-low sulfur diesel (ULSD). The 4% target for improving MDV/HDV efficiency is still listed as a goal, but it seems debatable whether that is achievable within the focus of the research being pursued. The co-optimization approach of using fuel properties to truly co-optimize engine performance for MDV/HDV appears to have been de-emphasized, perhaps due to the inherently higher efficiencies of MCCI engines. From the OEM side, there appears to be less excitement about advancing bridging combustion strategies such as MCCI to market for HDV applications, which makes the larger technical leap to homogeneous charge compression ignition a more worthy objective. Regardless, the Review Panel believes this remains a relevant research area in the face of bullish electrification technology investment and policy, especially given the extensive timescale at which the fleet overhaul must transition.

A research initiative such as Co-Optima could not produce such an appreciable number of insightful results and deliverables based solely on one type of funding strategy. The research area management has demonstrated their flexibility in funding by structuring the project portfolio in a well-balanced way that highlights high-risk, very early research, as well as more mature, development-ready efforts. The portfolio provides ample funding with a mix of AOP-, FOA-, and directed funding opportunity (DFO)-funded projects, as well as across the 1–3 technology readiness level (TRL) range. The funding levels have been commensurate to the work output and deliverables. Initially, Co-Optima was conceived as an AOP-funded, well-managed, and coordinated national lab consortium, and that founding premise continues to drive the bulk of the work effort. The diversity of competitive FOA-funded projects at the university level was not redundant or technically overlapping but instead focused on early-stage research, such as butyl acetate production via strain-engineered fermentation and/or the algae biocrude synthesis and upgrading. The modeling and experimental research engine studies using surrogate fuels appear to be reasonable. Co-Optima funded these six targeted and diverse university projects that aligned well with the national lab-led research, which seemed to be a better approach than executing one large FOA with many different projects. Because of time constraints, the Review Panel was unable to hear from the seven DFO-funded project award recipients; however, a few of the highlighted partnerships, such as the one with LanzaTech, appear to be promising, allowing feedstock-type impacts to be examined at a higher TRL.

Stakeholder Engagement

The Co-Optima portfolio is well organized, and the path to full-scale vehicle technology adoption becomes more probable based on the extent of stakeholder engagement across the project teams. The external advisory board (EAB) and steering committee both help to ensure regular feedback to Co-Optima's leaders and ensure course corrections are implemented within a timely fashion. Industry and stakeholder input were used in developing the strategy from the onset, particularly when octane and LDV efficiency were a major push; however, the shift to electrification may have reduced the level of industry engagement on passenger cars. Consequently, there may be a slight shift away or delay on the market transformation and implementation interests, making it less likely for Co-Optima fuels to make a near-term push into the market without significant federal intervention. There remains industry engagement on the HDV side, which was verbally conveyed by the project leaders; however, the details on which Co-Optima HDV research directions drew the most interest from OEM stakeholders and the viable pathways to commercialization from their perspective were not available. Information pertaining to HDV OEM input on short- to near-term, advanced compression ignition investment would be quite useful for the entire portfolio to understand. An example would be determining the techno-economic and volume forecasting impact of hybridization by heavy-duty OEMs and vocational vehicular applications during the next decade.

STRATEGY IMPLEMENTATION AND PROGRESS

Strategic Alignment

The research in the portfolio remains compelling in many ways and not necessarily as tightly tied to the original objectives of simultaneously co-optimizing fuels and engines. The focus appears to be more weighted toward fuel component identification, development, and blend-level maxima. For HDV engines, the reduction of sooting propensity—as demonstrated using single-component, neat mixtures—was promising work and must continue in order to evaluate the impact of these same components within a fungible, blended fuel matrix. Co-Optima's BBG&T and Analysis of Sustainability, Scale, Economics, Risk and Trade (ASSERT) teams work well together by addressing which fuels to produce specifically for a particular combustion regime in mind and, further, how the proposed feedstock and conversion processes will affect TEA and LCA. This should be regarded as a best practice in this research area, especially as calculation methodologies become more standardized. The team should stay accountable to the tiered criteria downselection workflow, eliminating blendstocks that have been tried in the past or may not reasonably fit the application purpose. Some of the proposed ether and alcohol species may fall into this category and could be more suitable as fuel additives rather than high-volume, neat fuel commodities.

Technical Leading Edge

The Co-Optima portfolio showcased a number of results and deliverables that clearly pushed the SOA in the optimization of renewable fuel design for HDV engine applications and was not simply an exercise in repackaging familiar blendstocks to "fit" a combustion regime. The team provided several online tools available for free to the public. The online publication database houses all of the published work relevant to the Co-Optima portfolio along with a search bar to assist the public users. With the ALFABET online application, researchers can enter fuel molecules of interest by using a drawing tool or a SMILES string and bond dissociation energies via machine learning-derived-DFT are provided immediately. A group contribution method-based tool for the yield sooting index (YSI) was also developed. The team continues to attract more users each year to the Retrosynth tool on GitHub: https://sandialabs.github.io/RetSynth/.

The work by the University of Wisconsin-Madison on developing fuel mono-ether and alcohols provided valuable results exploring the potential for upgrading ethanol as a premium MCCI blendstock. The final optimized bio-blendstock composition is designed to be rich in mono-ether compounds with high cetane numbers >90. The ability of these blendstocks to reduce aftertreatment light-off time by up to 15% has already been experimentally validated in single-cylinder engine runs. The team has already worked with hydrocarbon mixtures containing terpene oligomers such as farnesene and branched diesel-range paraffins to assess the impact on autoignition timing. Further, the group understands the importance of structure-performance relationships. The work with oxygenates involves exploiting the elegant Guerbet pathway, followed by dehydration to produce ethers and experimentally establish the kinetics and reactor operating conditions, complete TEA, engine testing, fuel property testing, and then model using fuel surrogates. The uncertainty in catalyst cost for the Guerbet coupling reactor that shows reasonable yields for hundreds of hours on stream was mitigated by using the Chemical Catalysis for Bioenergy Consortium (ChemCatBio) CatCost™ tool. The team understands that this work provides an alternative pathway for EtOH conversion, thus mitigating the future demand destruction related to LDV electrification.

The goal of the Colorado State University project was to synthesize a new group of POMEs with longer terminal alkyloxy groups and perform MCCI engine testing with various blend matrices. These compounds have been previously identified in other BETO research as having viable production pathways from lignocellulosic material. The general approach of the project was to synthesize a family of POMES, develop a combustion kinetic model to help downselect, complete fuel property and engine testing, and provide the TEA/LCA. The team did a commendable job of developing the class of extended terminal alkyl POMEs. Further, the Polanyi-type of structure-property relationships (SPRs) presented were compelling and clear. The team was able to control dibutoxymethane and other targeted oligomer yields by tuning the direct organic synthesis pathway through the formaldehyde-butanol steps, avoiding any need for separation strategies

downstream. The project team meets regularly with NREL to ensure that both POME research efforts remain complementary and synergistic, as reflected in the coauthored journal articles on the subject. The team leverages NREL's facilities for synthesis, separation, ignition, and stability characterization resources. The characterization of these components will be significant to the co-optimized biofuel and engine design communities.

The TEA/LCA collaborative project effort among Argonne National Laboratory (ANL), the National Renewable Energy Laboratory (NREL), and the Pacific Northwest National Laboratory (PNNL) provided a clear framework for analyzing and downselecting biofuel processing pathways with co-optimization potential. The analysis developed through this project fulfills a crucial role for Co-Optima by narrowing the technology area's focus down to only the most cost-effective and climate-friendly blendstocks. The team produced TEA, LCA, and scalability screening results of 13 pathways to produce 9 bio-blendstocks for MCCI and 12 pathways to produce 10 bio-blendstocks for multimode. The team identified 11 blendstock candidates for MCCI, all with cetane numbers >40; GHG emissions reductions >60%; and acceptable cloud point, pour point, and freeze point. The team demonstrated how a variety of environmental and sustainability measures other than carbon intensity can be used effectively to downselect fuel candidates. Further, the team has developed 19 metrics covering costs as well as environmental impact and technology readiness, which aligns well with BETO's goals and missions. The approach has a significant, thorough criteria for fuel candidates to overcome in order to be considered for implementation. The team understands how thorough, challenging decision criteria will help guide R&D decisions and resource management within BETO by identifying low-cost, scalable, implementable fuel candidates. One key project management strategy uses a multilayered quality assurance approach for maintaining high credibility and consistency across results by using proven, widely accepted tools, such as the Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET) model to perform LCA for all pathways or the Global Trade Analysis Project-Bio (GTAP-Bio) model to estimate the impact on land use change (LUC), such as blendstocks derived from soybean and cuphea oil. Several publications dealing with the TEA/LCA for various pathways in the production of both multimode and MCCI blendstocks will emerge soon from the team.

The coupled *in silico* and experimental approaches for accelerating the studies elucidating SPPR across molecular classes of blendstock candidates has been crucial for Co-Optima. This work is a highly effective, multi-lab collaboration among PNNL, NREL, Oak Ridge National Laboratory (ORNL), Sandia National Laboratories (SNL), Lawrence Berkeley National Laboratory (LBNL), Los Alamos National Laboratory (LANL), and Idaho National Laboratory (INL). The publicly available models and information developed by this team are some of Co-Optima's potential longest-lasting impacts to the biofuels community. The team has already proven that their approach can identify viable fuel candidates. One branched long-chain alkane, two ethers, and four dioxolane compounds were identified computationally and verified experimentally for passing Tier 1 property specs. Overall, the work of screening hundreds of species by combined computational and experimental tools and selecting a few with the help of novel approaches is a strong approach that is capable of accessing the impact of slight molecular structure changes on properties such as cetane number, YSI, research octane number (RON), and motor octane number (MON). Twenty compounds with RON >98 and S >8 were identified, and nuclear magnetic resonance (NMR) chemometric models were developed. The rapid compression experiments helped determine lower-branched long-chain alkenes as target molecules for increasing phi sensitivity. This team did impressive work developing high-throughput computational tools for assessing the relationship between phi-sensitivity and functional group structure and in conducting experimental validation of SPRs for >80 blendstocks.

Visualizations were provided illustrating molecular classes broken down into functional group arrays correlated against actual properties, such as cetane number versus POME type or YSI versus alkyl chain length and oxy-alkyl density, thus enabling advanced biofuel design engineering at the molecular structural level. The team has made notable progress toward developing SPPR tools for blends, such as RON and sensitivity correlations with ROH structure for alcohol mixtures, branched alkene structure versus phi-sensitivity for complex olefin mixtures, and olefinic alcohol structural impacts on RON at various blend levels up to 50 vol

%. Additional SPPR tools rooted in NMR are being developed to assist in characterizing complex mixtures. The team has demonstrated with several fuel candidate classes—such as iso-olefins mixtures, the olefinic alcohols, and the POMEs—how to work backward through the process and pathway to inform and make recommendations regarding the optimal biomass feedstock candidates.

The BBG&T team continues to be a key pillar within the Co-Optima management strategy enabling sufficient volumes of high-performing, novel renewable fuel candidates to be produced and evaluated. This successful multi-lab effort is a collaboration among PNNL, NREL, ORNL, SNL, LBNL, LANL, and INL and works closely as an integrated partner in the TEA/LCA and SPPR projects. The team was able to scale up hydrothermal liquefaction (HTL) bio-oil, obtaining gallon quantities from sludge and algae feedstocks that passed Co-Optima Tier 1 specifications. This was a notable achievement, indeed. The project provided important results on polymer compatibility for the dioxolane fuel class. N-butoxyheptane was generated in continuous liter quantities, dramatically improving the scale of material originally produced in the small, batch synthesis runs. Further, storage stability experiments were performed, drastically improving the future marketability. This capability of being able to produce suitable quantities of bio-derived fuels for bench and engine testing is an important aspect of the BBG&T team, particularly given that many of these candidate fuel pathways do not have existing scalable processes to produce or procure fuels. The BBG&T effort worked on a number of different fuel pathways, ranging from iso-olefins for light-duty, HTL bio-oils and iso-alkanes from food waste and dioxolanes, which were a new class of fuel oxygenates. The team generated eight HDV blendstocks that performed better in soot and nitrogen oxides (NO_x) emissions testing relative to a certified diesel. The team deserves recognition on this work and on the polymer compatibility work. In general, high-potential blendstocks—such as POMEs and HTL-derived fatty acids—were chosen based on both SPPR and TEA/LCA inputs exploring water solubility and feedstock cost, respectively. The team has already partnered with at least five private companies to develop new fuels. Although the nature of these relationships and expectation of outcomes were not disclosed, this is an important step in the right direction, along with completing work at the 20%–30% blend levels.

Research Directions and Outlook

Overall, the Co-Optima team should be proud of all the deliverables and accomplishments over the years enabling critical research decisions to be made all the way upstream to the biomass conversion portion of the BETO value chain as well as sparking and inspiring innovation at the engine OEM level, for instance, with the ducted fuel injection (DFI) concept proposed by ORNL. The Co-Optima team has been able to uncover critical molecular SPR and structure-performance relationships for an appreciable number of potential fuel candidates. The major objectives of the initiative have already been reached, and the next stage involves more in-depth, direct communications with vehicle OEMs, particularly focused on the transition, interim period during the LDV fleet electrification overhaul. It is quite evident that the majority of the critical considerations that go into designing new fuels and managing their corresponding molecular profile—both upstream and downstream, all the way to the fuel pump—are well understood by the team. This significantly increases the likelihood of successfully packaging a co-optimized technology ready for adoption and market penetration when coupled with the right external OEM stakeholders and influencers. Despite the need for improved participation with key OEM stakeholders, Co-Optima has a positive, optimistic, post-sunsetting outlook and represents the type of R&D where government support is most effective and needed. In fact, some of the key learnings emerging from the initiative may be applied to marine and locomotive applications. Co-Optima has clear goals, technical targets, and an adequate project structure that empowers team members to continue to explore, expand, and maybe even spin off into new commercial R&D entrepreneurial efforts. The federal funding level and mechanisms were quite adequate to enable the significant achievements reached so far and moving forward. Additional private funding along with the right automotive OEM or consortium of automotive OEMs could take the initiative's mission to new heights, focusing more on the engine technology/tuning side of things. The management team has done a good job assembling a portfolio of cutting-edge project ideas and research personnel across academia and national labs, and as the initiative concludes, the future directions and plans on commercialization and implementation should be laid out with the same rigor and discipline in order to

completely realize the co-optimized engine hardware-fuel pair return on investment for the public at a higher TRL. Most of the investment has already been returned to the public as free online optimization tools/programs/algorithms, publications (>120), presentations, webinars, listening days and patentable concepts such as DFI, and novel fuel blends and biofuel pathways. The consistent modeling approach and extrapolation of TEA and LCA models have allowed many diverse pathways to be assessed on an equal footing. The sum findings of Co-Optima and the publicly available tools developed therein should be utilized for years to come by wise researchers seeking ways to make fuel blendstocks that are attractive across the vehicle OEMs, traditional refining, and bioenergy communities.

For LDVs, the Co-Optima leadership has been quite clear with external stakeholders on how RON, sensitivity, and heat of vaporization are key properties for multimode combustion applications along with alcohols, iso-olefins, and alkyl-furans as the molecular classes with the highest potential. Currently, the team has a major communication campaign ongoing across the United States as well as the international community within Europe, Asia, and Latin America (e.g., the Latin American Energy Organization, or OLADE), informing the public about key research findings.

The team's leadership acknowledges that for HDV vehicle applications, MCCI engines and the required liquid biofuel options will likely be around for a while because electrification will be difficult, so the Co-Optima research premise and direction can still make an impact for the near- and mid-term future. The stated objectives for MDV/HDV have pivoted somewhat away from achieving a 4% efficiency gain and are more focused on emissions reductions, addressing any barriers associated with increased blend levels, and minimizing the trade-off in decreased engine performance, as defined under ASTM D975, for clean distillate. When looking across the key fuel properties, two parameters—sooting propensity and cetane number—appear to be the most promising in terms of proposed co-optimized fuel candidates that bring a technical advantage beyond conventional, clean ULSD. Energy density, though interesting, seems like a much greater challenge to increase beyond traditional petroleum-diesel blends. The whole Co-Optima portfolio showed an impressive level of alignment on the HDV strategy moving forward. The national lab consortium remained on the same page, and the university-funded projects all discussed fuel synthesis strategies for MCCI engine applications. Most of the university projects were looking at various molecular classes and fuel components that are interesting, leading-edge candidates, such as POMEs and esters. The BBG&T project and university FOA recipients proposed new types of compounds and mixtures based on the findings within the Co-Optima community. This demonstrates the benefits of early research already being realized by generating fuel materials that make technical sense and are not just convenient from a commercial supply chain standpoint, which is a good sign for the future direction and outlook. For example, the University of Wisconsin-Madison team will extend the single-cylinder metal engine experiments beyond single-fuel components to multicomponent complex mixtures balanced with ULSD. These complex-blend recipes will also include the mixed-olefin/ether dehydration reactor effluent as well. A similar ULSD blending strategy will be pursued in the near future by the Colorado State University team looking at the impact on YSI, oxidation stability, and autoignition experimentally and through nonlinear modeling techniques. Other university research efforts with accelerating engine testing using mini rapid compression machines will continue to be important for the future outlook of Co-Optima.

For getting impactful research done in this area, independent, isolated work on combustion mode or novel fuels characterization alone would have hindered the effort. It was very important to integrate both the engine and fuel candidates into the same initiative, which Co-Optima has accomplished with a strong management structure. It is almost like having a commercial fuel manufacturer and an automotive OEM housed within the same technical department, which is powerful and unique. The Co-Optima initiative is a very successful endeavor—from the way the projects are managed, to the research topics, results, and deliverables. The project was built from a solid premise rooted in optimization for maximizing engine efficiency and emissions reductions, which is exactly a critical task for powertrain development groups in most vehicle OEMs. The team has managed to propose blends that can achieve >60% reduction in GHG emissions and lower than $5.50/GGE MFSP, which is a remarkable achievement. The outcomes from this work, if implemented properly

in the future, will potentially solve the greater transportation emissions issue. The team continues to broaden its reach across the biofuels industry, sharing results/opportunities/challenges and seeking input and feedback from, and conversation with, various producers of all sizes, maturity, and feedstock diversity.

RECOMMENDATIONS

The Review Panel believes that many project efforts were negatively impacted and hampered due to COVID and, as a result, remains sensitive in our recommendations to this situation with respect to the goals, expectations, outcomes, and progress toward milestones; thus, the following list of recommendations for further improving the exceptionally successful Co-Optima Technology Area were thoughtfully compiled.

Recommendation 1: Continue a small LDV research footprint.

The LDV/multimode research tasks should not be stopped completely without ensuring that proper dissemination of results is accomplished to various regions around the globe where electrification may take longer to take off and where internal combustion engines will remain the dominant on-board power plant. If the anticipated 10% FEI gains across these trailing regional markets around the globe are realized, then the impact will translate to a nontrivial quantity of GHG abatement while the energy transition takes place. When coupled with additional GHG reductions from the biofuel itself, it is still an attractive option for certain markets. The leadership team should firmly identify the markets that companies and fuel producers are still targeting for light-duty engines with downsized boosted, multimode, or advanced compression ignition (ACI) strategies that could take advantage of the Co-Optima research learnings. Once these markets are identified, key information should be shared in partnership to advance the LDV engine technology. In short, the Review Panel agrees that co-optimized fuels still have a place in the LDV electrification future.

Recommendation 2: Go beyond ULSD parity.

The goal is to truly optimize the fuel to the combustion mode and not simply to develop MCCI blendstock candidates that only measure up to traditional reference ULSD, which is really Tier II screening. For instance, in what way can cold-flow properties be optimized for MCCI operation that is beyond ULSD specifications? Although the project teams have done an excellent job of responding to the previous Peer Review Panel recommendation, “Validation work should continue along with benchmarking against traditional hydrocarbons currently being produced in the refinery to establish precision and accuracy metrics,” more work must be done with ULSD blends at appreciable blend levels to continue proving out fungibility, moving past surrogate blends, because cross-interactions are not trivial in complex fuel mixtures. It is expected that these will be common blends because future retail customers will have various types of ULSD mixtures in their fuel tanks. This was also mentioned in a recommendation from the last peer review, “The Bio-Blendstock Generation project team should keep expanding their fuel generation scope within the targeted viable biomass-derived fuel candidate classes by considering blends made up of alcohols, alkanes, and ethers together along with commercial hydrocarbons to form a true fuel matrix. Pure-component data are only good to an extent for extrapolation to the blending values, which is what really matters.” The SPPR and TEA/LCA teams must continue developing predictive tools for blends that incorporate ULSD in the recipe, building off the single-component experimental evaluations. Further, the geographic distribution of the well-characterized, opportunistic feedstocks required to optimize the processing of these complex, co-optimized, ULSD-based MCCI blends must be understood.

Recommendation 3: Enhance BETO/VTO future funding announcements.

The deliverables from the Co-Optima initiative can serve as a prism to include co-optimization-type solicitation criteria elements for future BETO FOAs with fuel deliverables. For example, principal investigators (PIs) could be asked to specifically address how any proposed final liquid fuel blendstock produced will pair with a particular engine combustion mode (e.g., traditional spark ignition, compression ignition, ACI, multimode, MCCI, or homogeneous charge compression ignition) based on predicted properties (e.g., boiling point, cetane number, octane number, freeze point, pour point, viscosity, oxidation stability) and other key engine performance metrics. If the proposed fuel blendstock is completely novel, then fuel property

predictions can be accomplished with the online tools developed by Co-Optima (e.g., Fuel Property Database, Feature Creature), which can be included as part of the standard calculations for submitted proposals along with any tutorials or training webinars available to applicants. This strategy would increase the number of high-quality applications submitted for scalable, fuel blendstock pathways that lead to commercial end use.

Recommendation 4: Renew and maintain the BETO/VTO collaboration and lab consortium relationships.

Because the Co-Optima initiative has proven to be successful, a second-generation collaboration between BETO and VTO may be appropriate in the future. After current advanced combustion regimes in the MDV/HDV space have had time to mature and more of the critical fuel properties that enable MDV/HDV ACI are elucidated and further developed, future interties among fuel properties, engine performance, conversion processes, and their economic and environmental impacts can be considered again simultaneously; thus, maybe a new, rebranded, Co-Optima-like initiative or a program in 3–5 years to address developing metrics needed to co-optimize existing fuels with MDV/HDV ACI engines should be considered. If these metrics were currently well understood, a continuation of Co-Optima today would make sense, but it is time for the engine OEM community to contribute to the optimization work. In the current situation, it makes sense for VTO to focus on deciphering the critical advanced combustion properties/metrics and how to measure them. Meanwhile, it makes sense for BETO to focus on improving the processes for manufacturing high-performing fuel blendstocks using cost-advantaged, available feedstocks. To maintain momentum, an annual or biannual meeting/reunion/special topic (e.g., Society of Automotive Engineers, American Institute of Chemical Engineers, TCBiomass, Biofuels Information Center) for the Co-Optima researcher community should be coordinated to gather and discuss current progress in advanced engines and conversion technologies. It may be possible to spin off an independently funded consortium focused on fuel engine co-optimization.

Recommendation 5: Standardize and publish TEA/LCA methodologies.

One point of concern was the potential for inter-project TEA/LCA inconsistency in the treatment of different bio-blendstocks, particularly with some of the smaller, more focused projects. In the future, it may be helpful to work more closely with project teams to determine the intended final use of a bio-blendstock. Although some products may be well suited to fuels, some may be better used as specialty additives produced in smaller quantities, and thus would have a different small-volume, high-margin value to refiners. In the past, the Co-Optima analysis team has run workshops to help FOA awardees with this expectation, and this practice should continue in support of BETO. Possibly, at the first verification meeting, the TEA/LCA methodology can be confirmed based on a standard design basis (i.e., 200 mtpd or 100 MM gal), including basic bins/categories covering regional incentives, resource availability, scalability, and conversion costs. This is particularly important for molecules identified as additives rather than fuels. For example, a cetane improver may have different LCA implications and economic value when compared to a similar reference fuel. The team must continue to ensure consistent application of assumptions for economics and LCA across a very diverse set of conversion pathways and feedstocks to ensure comparative parity, which is why there must be continued focus on publishing results in peer-reviewed journals and reports while making models available to the biofuels-engine community. The team has done a comprehensive task of evaluating GHG emissions of different blends. There are also opportunities to understand fuel terminal blending optimization versus refinery blending implementation, which may give co-optimized fuel candidates more chances of success, as well as packaging small-volume, niche fuel candidates as novel blend components to existing fuel additive packages.

Recommendation 6: Promote a co-optimized, low-hanging solution to a global, critical combustion problem.

The consortium should consider marketing the solution to one specific combustion problem that can translate into a rapid, viable market adoption response based on market pull at relevant scale (e.g., “ultralow carbon bio-blendstocks that reduce particulate matter through improved sooting performance”). By focusing on one solution to a critical, big problem such as particulate matter along with the corresponding synthesis pathway with cradle-to-grave verification, the right international investors and partners may be attracted to open the

door at the next scale. Unfortunately, the Co-Optima targets are not necessarily set to drive technology adoption in the real world absent other policies, particularly on a relevant time horizon where novel bio-blendstock synthesis pathways become widely available within a potentially heavily electrified future.

Recommendation 7: Prepare strategic scenario plans and publish gaps.

The team should continue to strategize on cradle-to-grave co-optimized solutions that could be robust in the market based on various future scenarios for crude oil and fuel prices. The TEA targets are based on prior BETO targets that may not hold up in the imminent, highly electrified future. Although it may be hard to envision co-optimized solutions at this juncture that have an extremely competitive cost point, at least documenting the gap through this research and publishing to inform policy will be important. The team should consider whether the strategy should be maximizing GHG displacement by increasing blend volumes at potentially uncompetitive prices, producing high-value, neat additives, or co-processing. The scenario modeling should continue to emphasize the positive benefit on job growth and economic development benefits from investing in this technology over the long run.

Recommendation 8: Continue to strengthen stakeholder engagement, feedback, and listening.

It would be helpful to share results from industry engagements in the Co-Optima overviews. The team responded well to the last 2019 Review Panel recommendations on EAB composition: "Better leverage the industry, environmental, and technical expertise of the EAB. Review the composition of the EAB to ensure relevant stakeholder industries and sciences are represented." The 2021 Review Panel recommends that even more visible stakeholder involvement should take place, particularly with engine manufacturers' representation. Further, the fuel producer presence, both bio-based and conventional, was smaller and more marginal than what would have been desirable. This was also stressed by the last Review Panel: "Increase engagement with the fuel additive manufacturers … and other relevant stakeholders (such as potential biofuel producers beyond the existing supply chain of fossil fuels and blenders) for the purposes of resources, perspective, and risk mitigation: To study fuel impact on lubricants, ignition improvers, etc., use the additives companies' engine dynamometer facilities. …" This last round of Co-Optima initiative was heavily weighted on fuel development and less on engine tuning. The Co-Optima initiative can continue to facilitate more coordination between university and national labs, possibly supporting student and postdoc internships and moving this research into a strong workforce development model.

Recommendation 9: Update and maintain public, online modeling tools and resources.

In the future, the team can continue to bolster the computer modeling resources supporting both fuel molecular design and engine design/operation with more emphasis on near-term hardware modifications, possibly inviting more non-U.S. OEM input. The team should continue to define what makes a reasonable MCCI blendstock and suggest a finished mixed-component, complex blend along with a true, published specification in the future. The use of high-throughput screening, predictive computational tools, and machine learning algorithms for developing all of the SPPR tools in Co-Optima were very valuable research deliverables and should continue to be developed and maintained. The researchers should promote the use of more molecular engineering visualizations and diagrams that denote co-optimized "sweet spots" in reference to traditional fuel blends (e.g., hydrocarbons, alcohols, and ethers). Hopefully, the team will continue to develop the computational fluid dynamics (CFD) modeling and finite element analysis tools within Co-Optima because there could be more hidden-property synergy or new combinations of various fuel properties that are even more important descriptors for characterizing MCCI performance than the current set related to ULSD properties.

Recommendation 10: Continue investigations into fuel stability.

Specialized stability tests should also be considered in addition to standard ASTM methods for candidates such as certain functionalized ethers. Although not as scientifically elegant, the ongoing work on polymer compatibility must continue to improve opportunities for market adoption. Issues such as the formation of

peroxides during storage should be considered, and the complex modeling effort should accompany this work. The team may need to develop a special fuel additive with a supplier and/or adjust ASTM criteria accordingly. Practically, the issue of stability can often be solved by working with well-known additive suppliers, but it is quite possible that bio-derived antioxidant could be synthesized or extracted from one of the existing BETO pathways to help stabilize these fuels. Alternatively, the team could develop an oxidation stability analytical standardized method that is more suitable for these types of mixtures. Stability testing will be key to this new class of fuel candidates (e.g., dioxalanes), especially when generating large quantities of material in the future.

CO-OPTIMA PROGRAMMATIC RESPONSE

INTRODUCTION

BETO sincerely thanks the Review Panel for their time, active engagement, and review of the Co-Optima portfolio. As publicly announced in DOE's FY 2022 Budget Request to Congress, FY 2021 is the final year of funding for Co-Optima. Though funding to support Co-Optima work at the national laboratories will end, there will be continuing activities. All the competitive awards will continue as planned, until closeout, using funds appropriated in previous years. Additionally, there are approximately 10 new DFO projects that began in 2021. The DFO projects are led by Co-Optima PIs at the national laboratories who are leveraging the capabilities developed from Co-Optima to work with companies on specific industry needs. The DFO projects will last about 18 months. Nevertheless, the core Co-Optima work at the national laboratories will be ending at the end of FY 2021, after 6 years of tremendous efforts from more than 100 engineers and scientists. So, at this juncture where Co-Optima is sunsetting, BETO will carefully reflect upon the recommendations of the Review Panel on how to best ensure that the outcomes of Co-Optima research have wide impact for the United States.

BETO appreciates that the Review Panel understood the difficulties in BETO's ability to focus on mid-TRL R&D to address rapidly changing trends in the transportation sector, including changes in technology deployment, market acceptance, and policy. A few years ago, stakeholder feedback indicated potential technology deployments in the increased use of turbocharging (which aligned with using fewer cylinders and "lightweighting"). This feedback made the Co-Optima goals for high-octane fuels in LDVs seem reasonable and appropriate. More recent trends, including the increased development of and demand for electric vehicles as well as policy developments in the Renewable Fuel Standard and the Corporate Average Fuel Economy regulations that reduced demand of certain biofuels, have all played roles in how the transportation sector has rapidly evolved. Co-Optima worked to address these trends with its re-scope on more work toward MDV and HDV fuels and vehicles, as opposed to the LDV sector.

BETO agrees with the Review Panel's assessment that the original Co-Optima goal of 4% energy-efficiency improvement for MDV/HDV may be difficult to achieve. Note that the Co-Optima effort still has several quarters of work to complete after the peer review meeting, and much of the work in MDV/HDV energy-efficiency improvement relies on the work of the VTO portion of Co-Optima, which was not presented at this BETO Peer Review. As explored during this BETO Co-Optima session, improving energy density through bio-blendstocks is a difficult task, and it is perhaps more likely that the performance advantage of bio-blendstocks for MDV/HDV will be properties such as reduced sooting propensity and reduced energy penalty of the aftertreatment system. For example, such observations could be seen in the ether-based bio-blendstock work supported by Co-Optima. The ether-based bio-blendstocks tend to have reduced energy density but also reduced sooting propensity. Nevertheless, there may be some opportunities for increasing energy density with bio-blendstocks, particularly in naphthene-rich bio-blendstocks that can be produced by pyrolysis and other conversion pathways. There may even be untapped synergies in bio-based naphthenes that arise through other BETO work. Specifically, a new BETO effort on sustainable aviation fuels (SAFs) has identified naphthenes

as a key component. Work on biobased naphthenes is accelerating across the BETO portfolio to address this demand for SAF. There may be synergies where that SAF work crosscuts into work for improved naphthenes for MDV/HDV fuels. Also, there may be examples where conversion pathways, targeting bio-based naphthenes for SAF, also produce side streams that do not meet the stringent jet fuel requirements but could meet qualifications as MDV/HDV fuels. In summary, biofuel conversion selectivity to SAF is unlikely to be 100%, so BETO and biofuel producers would be smart to continue understanding the market demands in the MDV/HDV ground transportation sector for additional synergies and opportunities.

Recommendation 1: Continue a small LDV research footprint.

As publicly announced in DOE's FY 2022 Budget Request to Congress, DOE EERE is seeking to decarbonize all transportation modes, including road, air, sea, and rail. As such, the DOE strategy for LDV is reliant on VTO to reduce the cost of electric vehicle battery cells to the point where electric vehicles reach cost parity with combustion vehicles by 2030; therefore, BETO is pivoting away from the LDV sector and instead toward other sectors that will be more difficult to decarbonize. Nevertheless, BETO reminds the Review Panel that even as BETO pivots to MDV/HDV, SAF, marine, and rail, conversion processes will inevitability produce side streams of hydrocarbons in the lower boiling range that could find value in the LDV sector. So, it is safe to say that BETO will continue a small LDV research footprint.

Recommendation 2: Go beyond ULSD parity.

BETO agrees in advancing beyond parity with ULSD. To reiterate, the Co-Optima competitive projects presented at the 2021 BETO Project Peer Review were selected from the FY 2018 Advanced Vehicle Technologies Research FOA, Area of Interest 5b: "Bio-Blendstocks to Optimize Mixing Controlled Compression Ignition (MCCI) Engines." These projects were required to focus on researching and developing bio-blendstocks that could improve at least two of four properties of the finished fuel (energy density, sooting propensity, cetane number, and cold weather behavior); therefore, this work is focused on improving the properties of diesel fuel.

BETO takes note of the Review Panel's recommendation to carefully consider blending proposed bio-blendstocks into fuel markets. BETO acknowledges that the FY 2018 FOA required bio-blendstocks that could meet 5% blending levels with petroleum fuels. In order for BETO to meet the new demands to rapidly decarbonize, as addressed in DOE's FY 2022 Budget Request to Congress, BETO will need to strategize not simply on blending but also on biofuels that could be 100% replacements to ULSD in the longer term.

Recommendation 3: Enhance BETO/VTO future funding announcements.

BETO agrees that leveraging Co-Optima learnings could be helpful for future FOAs. At present, BETO typically requires applicants to plan and assess a pathway for ASTM approval of biofuels (e.g., see the FY 2021 BETO Scale-Up and Conversion FOA DE-FOA-0002396, Topic Area 1: Scale-Up of Biotechnologies Overview). The Co-Optima team at BETO will work with BETO and VTO colleagues to seek opportunities in adding more specific language for future funding announcements. This will ensure that the Co-Optima results have a broad impact.

As BETO pivots to an SAF strategy, there will be new opportunities for including fuel approval requirements in funding announcements. For example, ASTM D4054 Standard Practice for Evaluation of New Aviation Turbine Fuels and Fuel Additives now includes fast-track pathways where proposed new SAF candidates can follow a faster approval process requiring less testing if the molecules possess chemistries and properties similar to an approved SAF. As ASTM and the fuel qualification community at large become increasingly familiar with these new biofuels through the SAF fast-track process, there may be synergies where all stakeholders can also rapidly familiarize themselves with new MDV/HDV biofuels.

Recommendation 4: Renew and maintain the BETO/VTO collaboration and lab consortium relationships.

As the transportation sector rapidly electrifies and decarbonizes, the BETO/VTO collaboration will be difficult to maintain within the same structure, but there may be new opportunities for collaboration.

BETO agrees with the Review Panel that advanced combustion technologies need to mature, at which time BETO could possibly renew efforts to evaluate fuels for these combustion technologies. BETO agrees with the Review Panel that the OEMs need to contribute greater efforts on fuel engine co-optimization work to provide market pull. BETO highlights the new publicly announced Co-Optima DFOs where the national laboratories will work with several OEMs; for example, ORNL will be working with Cummins, and ANL will be working with Caterpillar. BETO thanks the OEMs for taking these critical steps in collaboration.

Further, there may be new opportunities for BETO/VTO collaboration. In VTO's section of the FY 2022 Budget Request, VTO mentioned activities for MDV/HDV with integration of hybrids and plug-in hybrid powertrains. There may be opportunities for BETO to explore biofuels best suited to perform in hybrid powertrains in the MDV/HDV sector as these technologies mature.

Recommendation 5: Standardize and publish TEA/LCA methodologies.

The Co-Optima team at BETO will work with BETO's Data, Modeling, and Analysis program to ensure that the Co-Optima results will continue to have an impact. Often, it is difficult to compare technologies across the various TRL ranges, and TEA/LCA methodologies are continually being updated to provide clarity in assumptions, identifying risks and knowledge gaps while providing a measure of progress within the research areas.

BETO would also like to comment that all projects in the FY 2018 FOA on MDV/HDV bio-blendstocks are required to perform TEA/LCA. Because these projects are still in the middle of their schedules, the TEA/LCA is still in progress. Due to the work still being developed and due to time constraints in presenting at the Peer Review, the Review Panel may not have had the opportunity to fully appreciate the TEA/LCA work that is underway. The purpose of this TEA/LCA is not to compare projects against each other; however, one purpose is to provide information to the project itself during the project lifetime to aid the experimentalists' decision-making and then, once the project is complete, to provide information to potential external stakeholders.

Recommendation 6: Promote a co-optimized, low-hanging solution to a global, critical combustion problem.

Solving a global, critical combustion problem requires a tightly focused solution offering single-purpose fuels. For example, the first-generation corn starch ethanol industry came together and offered a high-octane fuel solution to the LDV sector when it was found that methyl tertiary butyl ether and ethyl tertiary butyl ether were environmentally hazardous and needed alternatives. No one company, organization, or stakeholder could solve the global problem. Without a stronger market pull and stronger policies, single-purpose fuels will continue to face challenges in commercialization.

Nevertheless, BETO understands the panel's recommendation on identifying a specific combustion problem and solving it. Sooting would appear to be one critical problem where biofuels can provide a solution. Renewable diesel has illustrated one proven pathway where biofuels can drop in with identical properties to petroleum fuels, but with tuned composition (that is, no aromatics) and thus reduced sooting propensity. Additionally, BETO is a member of the International Energy Agency (IEA) Bioenergy Technology Collaboration Program. BETO will pursue avenues with IEA Bioenergy so that Co-Optima results may be disseminated to the international community.

Recommendation 7: Prepare strategic scenario plans and publish gaps.

BETO agrees that more strategic scenario planning would be useful. Such planning is too complex for BETO to do alone and will require stakeholder support across the renewable power and sustainable transportation

sectors. Nevertheless, BETO agrees that internal planning will be valuable as well. In particular, strategic planning would also align with the needs identified by Recommendation 2 to exceed ULSD parity. That is, BETO agrees that strategic scenarios need to be forecasted such that future demands of specific fuels may be forecasted. By forecasting overall fuel demands, more reasonable forecasts of specific biofuel demands could be predicted. This could then be correlated with biomass resource assessments and conversion pathway TEA/LCA state-of-technology reports and design cases. Such forecasting would help BETO understand where to best support funding along the biomass supply chain. In summary, BETO's Co-Optima team will work more closely with the Data, Modeling, and Analysis team to understand the scenarios where biofuels will play the most impactful role in rapidly decarbonizing the transportation sector. Additionally, BETO will also leverage its collaboration with IEA Bioenergy in understanding global energy forecasting.

Recommendation 8: Continue to strengthen stakeholder engagement, feedback, and listening.

Co-Optima hosted the Capstone webinar series, approximately monthly from March 2021 through September 2021. Co-Optima researchers have presented their key learnings to public stakeholders. Additionally, the university FOA projects and DFO industry partnership projects are required to publish final reports on their findings. Finally, BETO thanks the Co-Optima national laboratories in leading the publishing of the well-designed and engaging annual year-in-review reports.

Recommendation 9: Update and maintain public, online modeling tools and resources.

BETO thanks the panel for the reminder on this important task to keep tools and resources available, even after Co-Optima formally ends after FY 2021. Publications and other wrap-up activities are expected to continue into FY 2022, and the Co-Optima national laboratories are committed to maintaining their existing tools. BETO will seek to work with the Co-Optima national laboratories along with VTO to continue to support Co-Optima developments into the future.

Recommendation 10: Continue investigations into fuel stability.

This recommendation specifically mentioned work in ethers. The Co-Optima project on POMEs, led by Colorado State University, will continue more work in its final budget period on task work studying fuel stability. BETO will also pursue other related avenues to continue this important work on fuel stability and materials compatibility. For example, BETO supports national laboratory work at ORNL that evaluates materials compatibility. Beyond Co-Optima, BETO will also continue including requirements for fuel testing in future funding announcements.

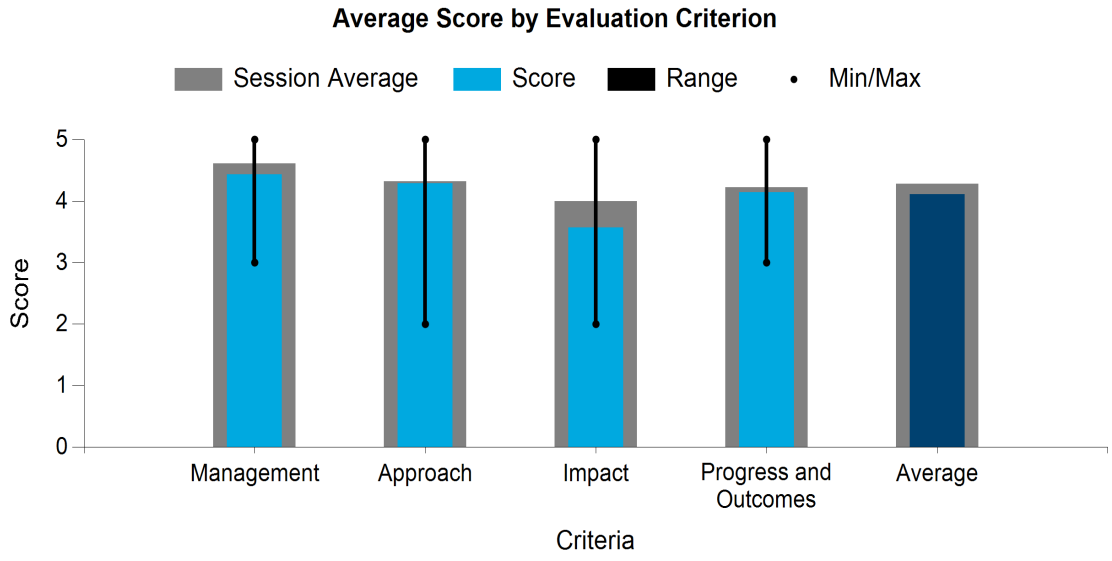
RENEWABLE FUEL ADDITIVES FROM WOODY BIOMASS

University of Massachusetts Lowell

PROJECT DESCRIPTION

WBS:	3.5.1.16
Presenter(s):	Hunter Mack
Project Start Date:	10/01/2018
Planned Project End Date:	05/31/2022
Total DOE Funding:	$1,001,932

The project team proposes a novel, comprehensive approach to the development and production of bio-blendstocks that improve the energy density, sooting propensity, and cetane number of base diesel fuel while maintaining cold weather behavior. The process converts woody biomass into bio-oil through selective fast pyrolysis; the bio-oil is then selectively upgraded to form selectively oxygenated, minimally branched hydrocarbons using non-noble metal catalysts in combination with metal-catalyzed hydrogenation. Advanced predictive models, in conjunction with existing property databases, and experimental testing are used to evaluate overall bio-blendstock properties and their impact on base diesel fuel. An iterative, targeted upgrading approach is implemented to optimize the proposed bio-blendstock's performance. Assessment includes a TEA, an LCA, and engine testing. Identification of a bio-blendstock that can be produced economically at scale while improving the performance and emissions characteristics of internal combustion engines positively affects the economy by boosting domestic fuel production and the environment by decreasing harmful emissions and increasing efficiency. The project team has successfully demonstrated biomass conversion and upgrading, developed numerical tools for fuel property prediction, and integrated the process into the TEA/LCA framework for evaluation and feedback.



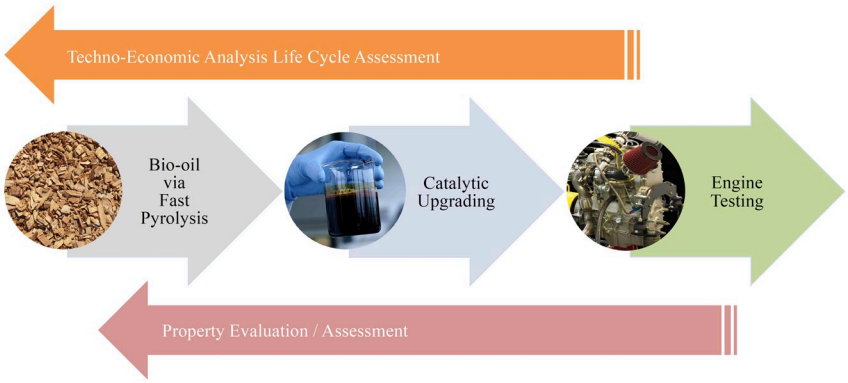


Photo courtesy of University of Massachusetts Lowell

COMMENTS

- In general, I think the project has good merits as pyrolysis oils from woody biomass could, in principle, be a plentiful source of bio-blendstock for transportation fuels. The approach is fascinating and original compared to more traditional hydrotreating methods. It focuses on chemistry and end molecules that exploit the structure of pyrolysis oils rather than force those complex compounds into mimicking conventional fuel molecules. I have concerns about the impact as I would like to understand better how the "micromixing" of the catalysts—and the catalyst type—entails scalability. Also, it appears that some critical milestones to validate the actual suitability of these molecules as bio-blendstocks are still missing. On this matter, however, it appears that a credible case can be made about a positive outcome being plausible.

- This is interesting work in developing computational tools to guide biomass conversion conditions, and it is impressive how COVID-related facility setbacks were turned into useful literature review and model-training project phases. There is important consideration of catalytic esterification side reactions. Overall, this is an excellent analysis of the parameters influencing yield/composition in the conversion of woody biomass to bio-oil while also meeting milestones on LCA and TEA screenings. A potential concern for processes using wood or similar biomass as inputs is the sulfur and ash metal content of the output fuel streams. Diesel exhaust aftertreatment systems are pretty sensitive to these compounds, and it seems like metals cleanup (or avoidance in feed) could add cost when scaling these processes up to use real-world sources. Also, molecules that contain oxygen often attract water from the atmosphere, which can result in materials compatibility challenges in engines and fuel systems.

- Management: Related bodies (BETO; Co-Optima teams; national labs) are identified. Specific risks and mitigation strategies are not presented.

  Approach: The fuel testing plan is robust and satisfactory. It is not clear how much specificity or control may be imparted during fast pyrolysis based on wood particle size outside what is expected from a typical fast pyrolysis product. There are also increased energy requirements with grinding to finer particle size that increase nonlinearly. The catalytic upgrading route is novel and interesting but would seem to be prone to severe coking with hydroxymethylfurfural (HMF) over acid catalysts, thereby diminishing yields and requiring a fluid catalytic cracking-like fluidized bed with oxidative regeneration step or frequent regeneration in a fixed bed. The boiling point of the phenol-ether compounds should be estimated to ensure that they maintain a boiling point below the 338°C distillation point requirement set by Co-Optima screens for MCCI fuels (see presentation on "Structure-Property-Processing Relationships

for Bio-Blendstock Identification"). The boiling point estimate could likely be estimated by the Aspen model used in the TEA under progress and outcomes. The derived cetane number and other fuel properties should be estimated by programs/models developed by Co-Optima, such as Feature Creature or other.

Impact: The project has a clear connection to the project approach. Commercialization will be challenging.

Progress and outcomes: Fast pyrolysis is a commercialized process, and larger-scale units could potentially be utilized to quickly produce material and screen conditions. The upgrading seems to have met challenges with coking via hydrogenation. Hydrogenation prior to etherification may be feasible, but light hydrotreating is difficult because of the exothermic nature of the reaction and a propensity for going overboard into deoxygenation and past stabilization. Ultimately, the palladium catalyst may become a cost driver in the TEA, and feedback on that cost should be implemented in the cost model in the near term.

- The goal of this work is to produce diesel-range fast pyrolysis-derived blendstocks with improved engine performance and physical properties. The roles in the project work breakdown are outlined reasonably well between the University of Massachusetts Lowell, the University of Maine, and Mainstream Engineering, with a dedicated project management function. There appears to be adequate interaction occurring at an unspecified frequency. The most critical risks and mitigation plans were not discussed in the presentation. The conversations were mentioned to take place regularly with the Co-Optima leadership team and other PIs. This type of collaborative behavior should be recognized. The approach here is to couple furans and phenols, followed by hydrogenation step, then blend as branched oxygenates into ULSD. It is not clear how the predictive modeling fits into the approach. Some parity plots were shown for unknown blendstocks to explain this Task 1.2.1. It was not clear how enough blends are going to be prepared with reference values to do the neural network calibrations needed for the modeling or if this is heavily supplemented by literature values. Finally, the engine testing will be completed on a three-cylinder advanced modular diesel research engine that is fully instrumented. TEA will be completed for the project as well. If the goal of the model is to produce pure-component properties, then this must eventually be translated into the cross-interaction terms required in blending models.

  The team understands how the project fits into the Co-Optima mission. The black box artificial neural network (ANN) statistical approach seems appropriate for gaining experimental design vectors. Strong academic groups like this should try to get into the fundamental reaction mechanisms governing pyrolysis, especially for creating new strategies/tools for shaping the product distribution and training students. The first-principle kinetics can be incorporated in the ANN algorithm as relationship validation exercises. For the ANN regression parameters, it may be helpful to put physical meaning behind the weighted coefficients. The team should clarify if removing carbonyl oxygen during the hydrogenation before etherification approach is a minor risk. The team showed that etherification of cresol and HMF could be achieved at high selectivity and conversion with quick deactivation using clean, surrogate feeds. The teams should comment on which side reactions will control the intrinsic kinetics in the real feed because they were expected to have lower turnover frequency. The successful prediction of cetane number, YSI, and lower heating value (LHV) for soy biodiesel and POME did not seem to connect with the blendstock objectives presented in this work. It was not clarified if these blendstocks are serving as fuel additive baseline materials for the project. The team had a successful go/no-go in June 2020, which is a good sign for their future success.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D

versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. For funded university projects, the overall matrixed management framework for the Co-Optima program with liaison to a Co-Optima advisor helps connect the funded projects to the broader Co-Optima initiative and allows for information sharing across the other projects. The approach was to create renewable fuel additive from woody biomass in order to improve cetane number, sooting, and energy density by creating a bio-oil through selective catalytic fast pyrolysis (CFP) using sawmill residues. The approach identified promising molecules using an iterative process starting with 5% blends and working up to higher-blend percentages, and it included predictive efforts on fuel properties. The precise control of fast pyrolysis and resulting oxygen and acidity in order to tailor optimal bio-oil compositions by selectively deoxygenating to reduce reactivity and impose stability was used to demonstrate the ability to produce tunable fuels with desired properties. The approach spanned predictive modeling, tunable fuel synthesis, LCA/TEA, and engine testing. Conversion rates and selectivity to desired molecules was a key metric. The progress to date has generated useful insights into sawdust particle size and resultant distribution of components within bio-oil. The parametric models are able to predict product yields from fast pyrolysis within 10%. The work has demonstrated high conversion and selectivity in the production of desired molecules. Useful blending models have also been developed. The blending models correlated with soy biodiesel and POME were very interesting. Is this getting shared with other groups doing Co-Optima work on single-component or surrogate blends? How extensible are the models to the range of components and blends used across Co-Optima? There is a need for more use of blending models and physical testing of blends at the bench level for Co-Optima. Can you elaborate on how the model uses interaction coefficients on the blend behavior and how that information is updated within the Co-Optima fuel property database? During the presentation discussion, it was mentioned that it can apply up to hundreds of compounds and that you are working with other project teams, such as SUNY-Stony Brook, to share results, which is very positive.

- This project is well designed, considering everything from feedstock selection and conversion facility design through to final use. As such, the GHG and economic impacts of the conversion process are well integrated into the project design alongside the actual work of generating and testing the bio-blendstock of interest. This project is also noteworthy for its consideration of conversion system operating parameters and feedstock pretreatment on the yields and composition of the intended bio-blendstocks; this is a thoughtful project design decision that provides a realistic path forward for feedstock conversion at larger scales.

- This project proposes a new method to produce fuel while evaluating its LCA, GHG emissions, and engine performance. From a management point of view, there is a reasonably good amount of interaction with other, wider Co-Optima teams, which is good for streamlining the process and the overall outcome of the project. Taking the wider Co-Optima approach for LCA and GHG calculations would streamline the overall process. The lower energy density of the fuels being produced can impact the fuel uptake and final outreach. If successful, this project can lead to significant contributions to the overall BETO and Co-Optima goals, though more efforts could be placed in achieving higher energy density.

PI RESPONSE TO REVIEWER COMMENTS

- The project team appreciates the comments, questions, and suggestions put forth by the Review Panel. The positive feedback on our project's directions and results is encouraging, and we look forward to implementing and clarifying our approach with respect to the detailed commentary of the reviewers. We have made great efforts to integrate into the greater Co-Optima framework, and we will continue to do so throughout our development process. This includes aligning our LCA and TEA approaches to those used by other teams in the collaborative effort as well as applying our predictive models for fuel properties to other research efforts. With respect to our approach to predicting fuel properties of neat compounds and

blends, the framework is extremely extensible to other fuels and fuel types; POME and soy biodiesel were used as validation steps because they are well-characterized bio-blendstocks, and early results for the bio-blendstock produced by our process indicate that the suite of blending models remains highly accurate. In terms of the catalytic upgrading of fast pyrolysis products, our preliminary analysis on the pyrolysis product distributions shows that there is a strong effect of the biomass particle size. This suggests that there is a coupling between the pyrolysis chemical kinetics and mass transfer. This phenomenon was also observed in the literature, and the effect appears to be quite tunable. The trade-off between tailoring the product distributions and the additional energy used for the particle reduction process will be investigated and accounted for by the TEA/LCA analysis. Other suggestions, such as the inclusion of boiling point in our evaluation criteria, have already been implemented and serve to strengthen our overall approach.

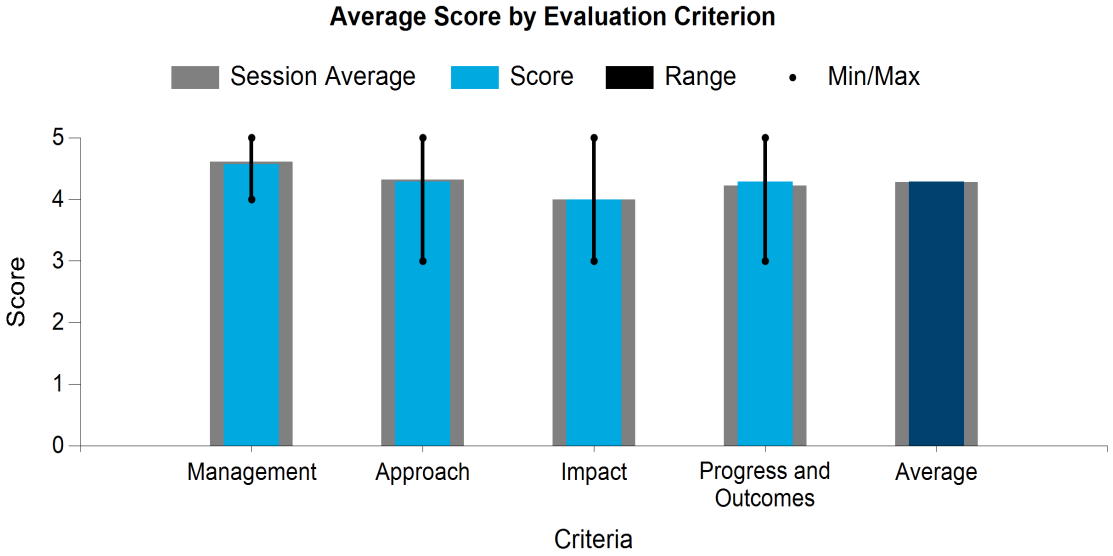
MONO-ETHER AND ALCOHOL BIO-BLENDSTOCKS TO REDUCE THE FUEL PENALTY OF MIXING-CONTROLLED COMPRESSION IGNITION ENGINE AFTERTREATMENT

University of Wisconsin-Madison

PROJECT DESCRIPTION

WBS:	3.5.1.17
Presenter(s):	Dave Rothamer
Project Start Date:	10/01/2018
Planned Project End Date:	12/31/2022
Total DOE Funding:	$1,499,894

Significant research has gone into developing technologies for the fuel production of ethanol from lignocellulosic biomass. These are in the process of being commercialized, with 10 million gallons produced in 2017; however, ethanol produced from lignocellulosic materials cannot be used directly in diesel engines. We have demonstrated a catalytic process for the conversion of ethanol into 8-carbon to 16-carbon (C_8–C_{16}) mono-ether diesel blendstocks at high yields. These mono-ether compounds have desirable properties for blending with No. 2 diesel fuel. This work targets the production of these bio-blendstocks with compositions that improve the properties of diesel fuel and specifically reduce the fuel energy used for the operation of MCCI engine aftertreatment systems. This work combines studies of the catalytic fuel production process, the engine testing to determine the impacts of mono-ether fuel component properties on MCCI engine operation for catalyst heating conditions and for warmed-up operation, and the fuel property testing and modeling. The results of these studies provide inputs to the TEA/LCA and the engine system modeling to optimize the production process and the composition of the bio-blendstock to economically achieve the greatest reduction in GHG emissions while meeting the engine performance targets. The engine performance of the designed bio-blendstock composition blended at an optimized blend percentage with No. 2 diesel fuel will be verified in multicylinder engine tests. The primary objective of the work is to develop a bio-blendstock that improves the properties of diesel fuel and reduces the fuel penalty associated with MCCI engine aftertreatment while simultaneously being economically viable and having at least 50% life-cycle GHG reductions relative to conventional petroleum-derived diesel fuel. In support of this primary objective, the project will identify fuel properties that are most important for reducing the fuel used for the operation of MCCI engine aftertreatment, develop a realistic catalytic fuel production process with conditions tailored to generate the designed bio-blendstock composition, and utilize TEA and LCA combined with engine experiments to verify performance targets. The outcomes of the project will provide the catalytic process and conditions to enable the economic production of the bio-blendstock composition designed in this work. The resulting bio-blendstock is targeted to have a greater than 50% reduction in GHG emissions relative to conventional petroleum-derived diesel fuel and to reduce the fuel energy penalty of aftertreatment system operation, significantly advancing the SOA for the production of bio-blendstocks for No. 2 diesel fuel and the understanding of how to design fuels to minimize the fuel penalty of MCCI engine aftertreatment systems. The project will also produce a 1-L sample of the bio-blendstock for study by the national laboratory Co-Optima team.



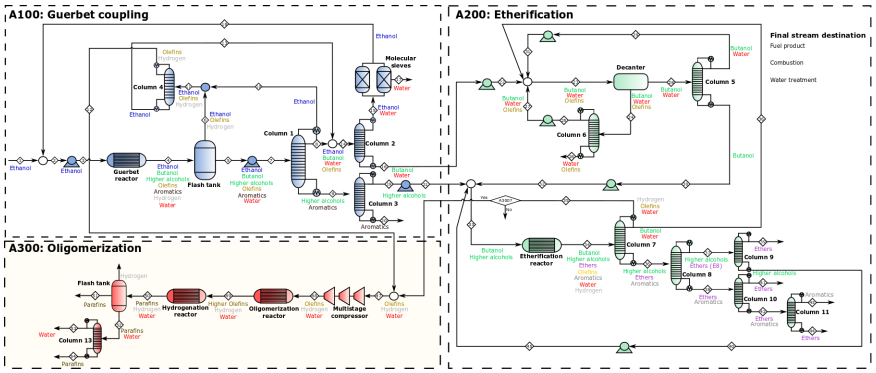


Photo courtesy of University of Wisconsin-Madison

COMMENTS

- I am professionally involved in the renewable diesel market, which is growing very rapidly today. The enthusiasm for hydrotreated vegetable oil fuel tends to hide the fact that the technology is intrinsically limited by the relatively small amount of fats and oil that can be had, especially without clashing with other established supply chains; hence, I found the idea to use ethanol as a precursor molecule—whose feedstock base is substantively larger than fats and vegetable oil, as an intermediate for diesel blendstock—extremely worthwhile. The only significant criticism is that although the investigators show the use of process systems engineering, which I commend, to study at the system level, their approach to some essential data to validate the scalability and possible commercial viability was not present with more detail—particularly related to catalyst performance, expected cost, and life cycle.

- This is interesting work on the production of diesel-range ethers from ethanol using the Guerbet reaction, offering a way to diversify blendstocks that can be produced from standard fermentation processes. It is good to see how aftertreatment light-off was included as a goal and is a potential benefit of the work. Preliminary LCA and TEA results look promising. Of the candidates, cetane is very favorable; and other

parameters, such as flash point and viscosity, are expected to fall within acceptable limits if residual alcohol can be limited. The mitigation of surrogate component costs for small-scale engine testing was accomplished by producing an initial small-volume run of blendstocks within the project. This also allowed some early feedback on the formulation using actual process outputs. Other feedback mechanisms included monthly and weekly internal meetings as well as discussions with industry research sponsors.

- Management: The communication plan with internal teams and meetings are addressed. Risks are identified with mitigation plans throughout the sections. A feedback mechanism with external stakeholders is addressed.

  Approach: The approach is novel and has promise. The researchers are aware of the impacts required to make the process feasible, e.g., working to minimize separation steps to avoid added costs and energy inputs. The stability of the desired ethers should be investigated. Issues such as the formation of peroxides during storage should be considered.

  Impact: Finding alternative uses for ethanol as the light-duty fleet electrifies is a worthwhile endeavor. The $145 MM in capital is significant and presents a challenge to commercialization. This capital cost may be due to the scale of the plants being considered. Opportunities for scaled-down plant sizes and the trade-off on economy of scale may be considered to see if investment could be more palatable in a green field plant scenario.

  Progress and outcome: Given the current scale of the conversion technology, the utilization of model compounds is appropriate. Good progress on rigorous testing of the impact of functional groups is being made with the engine testing. Demonstration of the conversion technology at a larger scale to process 1 L–5 L of ethanol per week would be interesting and would produce larger quantities for small-volume tests, such as an ignition quality tester. Future work/a follow-on project should consider the production of a sufficient quantity blended with No. 2 diesel for an engine test.

- The goal is to create blends using ULSD and mono-ethers produced from cellulosic ethanol for MCCI testing. The team provided some quantitative metrics to this goal relative to ULSD—to create blends at the 5% blending level at a minimum, improving at least two fuel properties (cetane number, pour point, or cloud point), attain 50% reduction in GHG, and reduce soot emissions >25%. The roles and four critical tasks assigned to the University of Wisconsin-Madison team are clearly defined as catalysis, process design, engine, and fuel property testing. There is no task dedicated to generating fuel candidate volume at larger scales, so it is assumed that the catalysis task will take on this role. The team meets both weekly and monthly as well as with the Direct-injection Engine Research Consortium and other undisclosed industry sponsors. Several critical risks were named dealing with delays in TEA/LCA modeling and surrogate component supply position. These risks could be mitigated by establishing regular model updating and developing blends rich in components with an ample, sustainable supply and that dominate fuel performance and properties. The approach is to go through the elegant Guerbet pathway, followed by dehydration, to produce ethers and to experimentally establish the kinetics and reactor operating conditions; complete the TEA, engine testing, and fuel property testing; and then model using fuel surrogates. The excess fuel leftover from lighting off the aftertreatment device should be lower by using this co-optimized fuel. The team understands that this work provides an alternative pathway for ethanol conversion with the pressure on LDVs with electrification as well as the impact on emissions for HDV applications. There is great impact on student and workforce development in this area, especially with shaping technology strategies for existing ethanol biorefineries.

  The team has made excellent progress. Guerbet coupling was achieved, showing several hundred hours on stream, 70% conversion, and >65% to diesel-range alcohol precursors at low weight hourly space velocity. This is a very promising result. TEA revealed lignocellulosic ethanol costs as the key driver to

the overall process economics. The team is encouraged to show a process flow diagram-type of illustration for this biorefinery instead of a simple block flow diagram. The single-cylinder metal engine studies with only 10 surrogate blends and none of the blends containing diesel fuel seem somewhat limiting. The group has already published work on the farnesene-heptamethylnonane effect. There was a promising result regarding the residual alcohol impact being negligible at 8 vol %. The surrogate bio-blendstocks had better combustion stability and showed the anticipated impact from oxygenates by lower carbon monoxide and hydrocarbon emissions. Some property modeling was completed using surrogate Guerbet-derived blendstocks out to 30 vol %. The team should consider spiking the surrogate blend with the full dry product effluent from the dehydration reactor to get the real impact, incremental performance vectors. The Guerbet space velocity is rather low, which is why this may be an effective project mitigation strategy. All key milestones were completed on time, and the first go/no-go was passed with an ethanol feed rate of 44 cubic centimeters per minute.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. For funded university projects, the overall matrixed management framework for the Co-Optima program with liaison to a Co-Optima advisor helps connect the funded projects to the broader Co-Optima initiative and allows for information sharing across the other projects. This project looks at mono-ether compound-rich bio-blendstocks catalytically produced from cellulosic ethanol to improve engine optimization. The approach looks at both the process development of catalysts and engine testing and attempts to span from the catalytic processing of fuels to catalyst aftertreatment with an aim to co-optimize bio-blendstock production, fuel properties, and engine operation in order to achieve the greatest reductions in emissions at the lowest cost. One specific aim was to reduce aftertreatment by changing the fuel properties to improve catalyst light-off and to heat the catalyst as quickly as possible. Pour point, cloud point, cetane, and compliance with ASTM D975 were also targets. The concept of taking a holistic catalyst (process) to catalyst (aftertreatment) approach at co-optimizing the system is interesting, but it requires a bit more explanation on how it all fits together. It was a bit unclear, for example, how the fuel properties would enable lower NO_x. For example, how does higher cetane lead to lower NO_x? It was briefly touched upon that the higher cetane allows for a triple-injection strategy to heat up the exhaust and allows for a delayed third injection that leads to lower NO_x and lower hydrocarbon emissions; however, the explanation was brief, and it was unclear how bio-based fuels enabled that outcome and if it was sufficient, for example, to remove NO_x traps used during the cold start ahead of catalyst light-off. If cetane is a key enabler, is the selected catalytic process and fuel pathway able to create a higher cetane fuel beyond conventional diesel fuels? The progress reporting indicated that much has been completed on Tasks 1–4, but it does not indicate what still remained. The summary also does not bring back to point the key results and the most compelling insights for the research. Bolstering the key takeaways to date and what remains to be complete would be helpful in the presentation.

- The project has a very strong and clear management structure. Overall, the aims and objectives, if successful, would lead to significant contributions to the area of sustainable transportation fuels. Increased interactions with the wider Co-Optima team would further increase the project impact. The team has done well in taking this project further during the current challenging times. The predicted efficiency improvement and reduction in GHG emissions, if achieved, could lead to a route for future transportation fuels. This project aligns well with BETO's goals.

- This research focus is well targeted to mitigate the documented trade-off between reducing NO_x emissions and improving engine efficiency. This project has identified the key conversion step necessary

to generate the intended blendstock, and it has succeeded at generating the necessary conversion rates and precursor selectivities. From there, the project has incorporated that conversion stage into a fairly well-characterized TEA assessment. The results here are very valuable, suggesting the economic potential of upgrading ethanol as a premium blendstock for use in the HDV sector. The primary area of risk here appears to be with generating sufficiently low-carbon intensity ethanol to meet both the GHG reduction threshold and the cost target; the cost analysis implies the purchase of cellulosic ethanol as a feedstock rather than producing it in an integrated process. Although the project team has correctly identified feedstock cost as a key factor in their sensitivity analysis, it would be helpful to expand out the TEA to include more of the assumptions on upstream capital expenditures (CapEx) and costs to provide additional context.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their useful feedback and time spent reviewing the work. We are glad to hear from reviewers that the project aligns well with BETO's goals, and we plan to increase interaction with the broader Co-Optima team during the next year. For clarification, the production of bio-blendstock at larger scales (to produce liters of bio-blendstock) is part of the catalysis task. Also, we have a process flow diagram for the current design of the plant, and we will continue to update this as the project progresses. Current single-cylinder engine experiments were designed to study fundamental property impacts, and future experiments will utilize blends with diesel fuel. We agree that testing the direct output of the dehydration etherification stage as the bio-blendstock may be a promising approach, and we will pursue this testing. The comment on investigating the stability of the desired ethers is well taken. Recent work by Huq et al. demonstrated suitable storage stability for an ether blendstock similar to those targeted here for the neat blendstock and when blended with diesel fuel with the addition of 100 parts per million and 20 parts per million, respectively, of a common antioxidant (butylated hydroxytoluene). This antioxidant approach is also used in our labs when storing ethers.

  We would like to address multiple comments regarding estimates of CapEx and operating expenditures. We agree that it would be desirable to reduce the $145 MM CapEx. We are currently investigating a range of alternatives to reduce the CapEx. They include the study of the effect of conversion on the biorefinery and the simplification of the separation operations. Once we have established these effects, we will be sure to study the effect of changing the biorefinery scale; however, we want to mention that the current size has been established based on the production of the NREL lignocellulosic ethanol production plant, and we believe that, in general, this is a reasonable choice for a base case analysis. We were not able to go into great detail regarding the assumption on upstream CapEx and costs; however, we are considering different scenarios for the production process, including integration with the ethanol production, which has some potential CapEx advantages and potentially life-cycle benefits as well. We also agree that demonstration of the technology at a larger scale would be interesting to enable testing of the produced bio-blendstock blended with No. 2 diesel fuel in multicylinder engines. This would be best suited as a follow-on project, as mentioned, once the current work is completed. Catalyst performance, expected costs, and LCA are considered part of our work, although we did not have sufficient time to present these issues in detail. Here are some additional details on the catalysts used: We have three catalysts involved in the process design (Guerbet, etherification, and oligomerization); both the etherification and oligomerization catalysts are zeolites, and the uncertainty in price estimation for these catalysts is lower considering that they are commercial catalysts, and we have used estimations based on market prices. The main uncertainty comes in the cost of the Guerbet catalyst. In this respect, we can see from the TEA that the catalyst cost is not the main economic driver of the process; however, to mitigate this uncertainty, we will use a tool developed by DOE and the national laboratories called CatCost (https://catcost.chemcatbio.org/). This tool allows for estimating the cost of a catalyst based on the process used in its manufacture as well as its composition. We apologize for not better conveying how the fuel properties of the bio-blendstock will enable lower NO_x emissions. The targeted bio-blendstock composition is rich in mono-ether compounds with very high cetane numbers (>90). Single-cylinder

engine results have demonstrated that fuels with higher cetane numbers allow the third injection (post injection) during catalyst heating operation to be delayed while still achieving stable combustion, increasing the temperature of the exhaust gases. This shortens the time that is needed to get the catalyst to a temperature where urea can be added to allow selective catalytic reduction to be used to reduce NO_x. We see that the light-off time reduces by ~3% per degree of the start of injection timing delay (e.g., enabling a 5-degree delay is expected to reduce the light-off time by ~15%), allowing the engine to switch to more efficient normal operation more quickly, reducing fuel consumption and NO_x emissions.

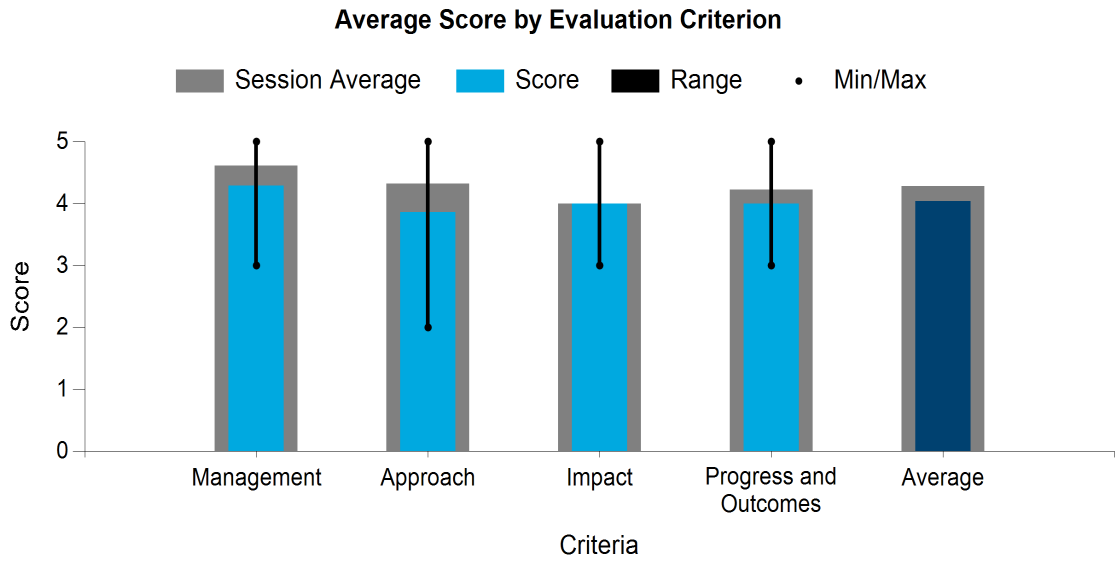
NAPHTHENIC BIOFUEL-DIESEL BLEND FOR OPTIMIZING MIXING-CONTROLLED COMPRESSION IGNITION COMBUSTION

State University of New York at Stony Brook

PROJECT DESCRIPTION

WBS:	3.5.1.18
Presenter(s):	Dimitris Assanis
Project Start Date:	10/01/2018
Planned Project End Date:	12/31/2022
Total DOE Funding:	$1,487,112

The objective of this project is to investigate and demonstrate the use of a naphthenic distillate as a multicomponent liquid bio-blendstock for use in MDV/HDV MCCI engines. The naphthenic bio-blendstock will be produced via CFP and hydroprocessing. Experimental data will be analyzed in order to assess the impact of the bio-blendstock concentration on the mixture preparation, ignition, heat release, and emissions formation processes of the engine. The goals of this project are to (1) demonstrate that the naphthenic bio-blendstock can be blended with diesel fuel and the mixture meets ASTM D975 specifications, (2) investigate the effects of using blended fuel in diesel engine efficiency and emissions, and (3) show life-cycle GHG emissions reduction of 50% compared to petroleum diesel. The successful demonstration of this research project will develop a biofuel-based pathway to reduce the use of fossil-derived diesel fuel in transportation today.



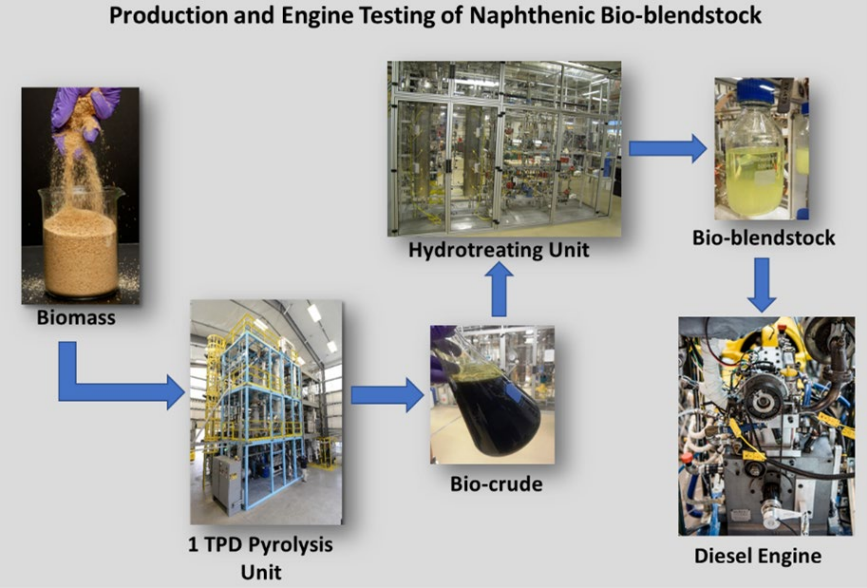


Photo courtesy of SUNY-Stony Brook

COMMENTS

- I found this project to be very interesting and of value, being familiar with fast pyrolysis and its relevance in waste to energy. I gained more insight into the potential value of pyrolysis of waste biomass as I gained a better appreciation of the type of fuel that could be made out of it. Although these fuels are clearly a new class of fuels, which would require a considerable amount of certifications, the results to date seem to justify this effort and, in turn, further justify the effort in fast pyrolysis, a technology that, in my view, has been lagging. Because of that, I wish that there was a bit more of a tie-in with the "upstream"—a common theme across Co-Optima projects—and, in particular, more details about the hydrotreating process. This would have given a complete view of the impact opportunity. The PIs are confident that meeting ASTM D975 is realistic, but I would also argue that the project, particularly with the right potential economics, may deserve to have a follow-up, even if that metric is missed in the last few months of work left.

- This is interesting and impressive work to synthesize and characterize hydrotreated pyrolysis oil blendstocks covering a range of oxygen and naphthene content. The assessments of combustion and emission characteristics of surrogate blends at various levels in petroleum diesel show promising results. There is a very clear project Gantt chart and milestones over time, showing good progress on the goals. One potential concern for processes using wood or similar biomass as inputs is the sulfur and ash metal content of the output fuel streams. Diesel exhaust aftertreatment systems are pretty sensitive to these compounds, and it seems like metals cleanup (or avoidance in feed) could add cost when scaling these processes up to use real-world sources. Also, molecules that contain oxygen often attract water from the atmosphere, which can result in materials compatibility challenges in engines and fuel systems.

- Management: The PIs are well qualified, but interties to other projects; communication within the larger Co-Optima team, stakeholders, etc.; as well as identified risks and mitigation strategies are not addressed. Milestones and go/no-gos are present.

  Approach: The mid-distillate boiling range is appropriate for the distillation properties expected for an MCCI fuel running in today's diesel engines. Previous investigations have looked at higher oxygen

contents for fast pyrolysis oils as direct fuel additives but perhaps not higher-oxygen CFP liquids. Some challenges will remain similar between fast pyrolysis and CFP. For example, the higher oxygen content in the mid- and high-oxygen blendstocks due to phenolics are likely to have acidic properties, which refiners and automobile OEMs may view negatively. (Refer to slide 19 of the "Structure-Property-Processing Relationships for Bio-Blendstock Identification" talk on the first day for a list of MCCI fuel characteristics that may be employed as developed within Co-Optima for screening.) It is possible that only the most deeply hydrotreated samples pass the screening metrics developed in other parts of Co-Optima and called out in ASTM D975, thereby affecting the mixture selected as surrogate as well as the TEA and LCA effects associated with more severe hydrotreating. Even saturated polycyclic compounds, such as decalin, may very well be soot precursors and not have the desired effect in diminishing sooting propensity.

Impact: The project has a clear connection to the project approach. Commercialization will be challenging.

Progress and outcomes: The addition of naphthenic bio-blendstock to diesel fuel does appear to improve cold-flow properties. The improvement of sooting propensity may prove more challenging. Decalin, which is a primary component of the surrogate fuel, will likely quickly convert to naphthalene during combustion (but not necessarily smoke point studies), which, as a polyaromatic, may have a significant sooting propensity. GHG reduction toward the goal of 50% must be tied to the level of hydrotreating required and may be challenging if hydrogen will be made via steam methane reforming. The total acid number and derived cetane number via ignition quality tester should be measured in the immediate term. Neither require significant volumes of material and could be accomplished with the volumes shown on slide 8. Slide 13 suggests a longer ignition delay with increasing blend concentration. The longer ignition delay could be due to higher viscosity but may also be due to a diminished intrinsic cetane number, again suggesting that the bio-blendstocks, surrogate, and mixtures should be subjected soon to low-volume tests such as ignition quality tester. Butylcyclohexane and propylcyclohexane were selected for Budget Period 2 as fuel surrogates in lieu of decalin, but the concentration of these compounds relative to decalin or in the overall fuel mixture of actual bio-derived product is not clear. Whether CFP and/or the subsequent hydrotreating are tunable to the degree to increase alkyl-substituted monocyclic compounds versus polycyclics is a critical question, but appears on the surface to be very challenging. Finally, per slide 15; point 7: Although methoxyphenols may solve the total acid number issue present with simple phenols, methoxyphenols are surprisingly difficult to produce from phenolics, and conversion options should be evaluated prior to employing the strategy of their creation.

- The goal of this project is to show the impact of CFP-derived naphthene/ULSD ASTM D975 blends on engine efficiency and emissions. The PI was able to take over this work midway through, which was impressive, because the predecessor relocated. The approach here is to generate and characterize hydrotreated CFP distillate; synthesize a clean, surrogate version of this mixture; then run engine tests. This will only advance the art to a point because surrogate fuels using pure components are being used. It is quite common in research engine studies to use surrogate blends, so this approach aligns in well within the SOA. Further advancing the SOA should require moving into more complex mixture studies. The team appears to understand how this work connects to the overall goals of Co-Optima. It would be interesting to see how this characterization of hydrotreated oils compares with those reported in the literature or government reports. The merits of the characterization exercise to generate the surrogate molecular classes remain somewhat in question. The team should explain in more compelling detail how these six surrogate compounds captured the most critical blend interaction space, maybe in a statistical experimental design approach. For instance, it appears that the phenolics were used as the only oxygen source. The blend interactions for each compound could be drastically different. There may be an opportunity to conduct spike studies with real hydrotreated product on the clean surrogate to see the effect, such as a 5% blend, which may be more accurate for practical applications. The relationships between napthenic content and smoke and cloud point may be more familiar to the community, although

the literature may not reflect it. The team was able to show the impact of blend composition on ignition delay. With a significant level of aromaticity still present in the surrogate blends, there would be major differences. The impact on ignition delay was not that obvious and may have some degree of stratification present. The team should continue to make sure no moisture is present in the surrogate blends. The team can provide more details on how the B10, B30, and B50 blends were created. Unfortunately, carbon monoxide and total hydrocarbon emissions increased with blend ratio.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. For funded university projects, the overall matrixed management framework for the Co-Optima program with liaison to a Co-Optima advisor helps connect the funded projects to the broader Co-Optima initiative and allows for information sharing across the other projects. The project is interesting and reflects the diversity of scope in the funded Co-Optima efforts.

  I had a question regarding the context for the selection of naphthenic biofuel from CFP and hydrotreating to create a bio-blendstock. It may have been referenced in the earlier Year 1 presentations, but how was the focus on naphthenic compounded selected? Was there any input from the Co-Optima fuel property database or SPR efforts? What makes it a novel pathway or fuel choice? The approach covers the range from fuels characterization, experimental testing on surrogate fuels, and TEA/LCA. It was noted that although cloud point improved in a 50% blend with No. 2 diesel, smoke point did not improve despite its performance as a pure component. It was good that blends were tested as opposed to only single components. Future work was referenced on resolving the smoke point in the blended fuel but was not elaborated as to the intended future approach. Is there some information that can be shared now or insights as to how you would impart the performance via naphthenic fuel design into the blended fuel with diesel? This seems like a big win if there is some fundamental understanding here on improving sooting propensity in a blended fuel. It was discussed during the presentation that on slide 13 the pass/fail line for the 50% blend was not clear. How do we interpret acceptability from an engine performance perspective? During the Q&A discussion, the response was that mean engine performance was a metric. It would help to have a more objective basis defined or to at least know how marginal 40%–50% blend fuels were. The results indicate that naphthenic hydrocarbons can perform better than aromatic hydrocarbons and phenolics at high blend percentages with improved cold weather properties, equivalent energy density, and no impact on sooting propensity. If the soot propensity of the surrogate fuels could be translated to the blended fuel, that would be a big win resulting from this research.

- The work is being managed efficiently with a good management structure, though it could be further improved by more engaged relationship with NREL. The approach of producing and testing bio-blendstocks would deliver one of the solutions to deliver future ground transportation fuels while assisting in achieving BETO's goals. Significant scientific outputs are being developed from the fuel production and testing steps in this study, though the goal of the project also involves achieving ASTM D975 specifications from the viewpoint of considering the produced fuel as a drop-in fuel. In case this is not possible, it might be worth putting the positive outcomes and overall scenario in front of the ASTM committee for any potential addendum to the standards.

- This project has a clear set of goals and a well-designed management approach to evaluate and test the naphthenic bio-blendstock. The approach efficiently utilizes existing resources, particularly the Research Triangle Institute's hydrotreating capacity, to generate the candidate blendstock for further testing. Although this project is relatively early in its cycle, the results so far indicate both success at reducing

soot formation while achieving the ASTM standard for diesel. At this stage of the project, it would be helpful to provide more information on the choice of feedstock and some preliminary results on the emissions necessary to produce the fuel to get a better understanding of the GHG impacts of this pathway.

PI RESPONSE TO REVIEWER COMMENTS

- Production of bio-blendstock: The objective of the project is to investigate and demonstrate the use of a naphthenic distillate produced from biomass CFP and hydrotreating as a multicomponent liquid bio-blendstock to improve cold weather behavior and sooting propensity of diesel fuel for use in MDV/HDV MCCI to ultimately improve combustion performance and reduce emissions. Among the various technologies that are being developed for the production of bio-blendstocks, the biomass CFP and hydrotreating process is relatively more scalable and can make bio-derived fuels widely available in the near term. This is part of the reason the project team selected the pathway. Additionally, the fuel produced from the CFP and hydrotreating process contains a high concentration of naphthenic hydrocarbons (cycloalkanes and alkyl-cycloalkanes). The naphthenes are hydrocarbons between normal paraffins and aromatics; hence, they can be used to tailor the properties of No. 2 diesel fuel by decreasing any negative impact of paraffins and aromatics as needed. Besides, naphthenes have attractive properties, such as a lower freezing point and a higher heat of combustion. The naphthenic distillate bio-blendstock is produced at Research Triangle Institute in a three-step process: (1) Biomass is catalytically converted into biocrude with a non-zeolitic, alumina-based catalyst at pyrolysis temperatures of 475°C–525°C in a 1-ton per day single-loop transport reactor; (2) the biocrude containing between 20 wt %–25 wt % oxygen is hydrotreated over a sulfided catalyst at 2,000 pounds-force per square-inch gauge and 300°C to make a hydrocarbon liquid; and (3) the hydrocarbon liquid is subsequently distilled to obtain a naphthenic distillate boiling between 160°C–360°C. Note that the hydrotreating process conditions (temperature, pressure, space velocity, and hydrogen/oil ratio) can be changed to increase the concentration of naphthenic hydrocarbons and decrease aromatics/phenolic compounds for the bio-blendstock to meet specification. In Budget Period 1, several naphthenic distillates with oxygen contents between <1 wt % and 6 wt % were recovered and characterized. Fuel analysis showed that the less oxygenated bio-blendstock (oxygen <1) has the potential of meeting ASTM D975. The cetane index, boiling distribution (T90), and energy content were comparable to that of No. 2 diesel. Further, the less oxygenated bio-blendstock had better cold weather properties (cloud point and pour point) and lower sooting tendency than No. 2 diesel fuel.

  Surrogate fuels: The surrogate fuels were developed to fundamentally understand how the major chemical compounds in the bio-blendstock influence diesel fuel properties, particularly the cold weather properties and sooting tendency. The surrogate fuel formulation was based on the chemical characterization (gas chromatography-mass spectrometry, detailed hydrocarbon analysis, carbon number distribution, and boiling range distribution) of the bio-blendstocks. The final selection of six major species belonging to chemical classes of naphthenes, paraffins, monoaromatics, polyaromatics, and simple phenol was based on the availability, cost, purity, and safety of pure compounds chosen to represent the class of compounds in the fuel. As a result, some individual major species were not used for most of the studies because of their high cost. An alternative cheaper molecule belonging to the same class of compound in the bio-blendstock was used. For instance, decalin was used in place of propylcyclohexane to represent naphthenes.

  We would like to point out that the project team has been collaborating with NREL and Yale University on the measurement of most of the fuel properties of the surrogate fuels. The blending studies of the surrogate fuels with research-grade No. 2 diesel at 10%, 20%, 30%, 40%, and 50% concentrations by volume have been very useful in understanding how the bio-blendstock could be used to improve the diesel fuel properties. As shown in the Peer Review meeting presentation, the project goal of improving the cold weather properties of diesel fuel by up to 8°C with the bio-blendstock was achieved and

successfully demonstrated at blends up to 50%. In the case of the sooting propensity, the bio-blendstock surrogates prepared did not have an impact. Based on the molecular structure and fuel property relationship established, and the NREL YSI predictive tool, a plan was devised to improve the sooting propensity. The tool suggested that increasing the concentration of the naphthenic hydrocarbon from 55 wt % to 75 wt % and decreasing the aromatic hydrocarbons (tetralin) from 25 wt % to 5 wt % has the potential to decrease the sooting propensity by up to 30%. Also, having a bio-blendstock that contains propylcyclohexane instead of decalin as the naphthenic hydrocarbon component could improve the sooting propensity. We have now experimentally varied the hypothesis, and increasing the naphthenic hydrocarbon to 69 wt % decreased the sooting propensity by more than 50%. Based on this finding, the hydrotreating conditions would be modified to enhance the formation of the alkylcyclohexanes in the bio-blendstock.

Engine testing: Detailed engine testing is presently being performed to evaluate blends up to 50% by volume of the improved surrogate fuel formulation, described above, with research-grade No. 2 diesel. Engine output performance, combustion characteristics, and emissions levels of the blends will be evaluated and compared against pure diesel fuel. Specifically, the effects of fuel injection timing, injection pressure, and exhaust gas recirculation rates will be investigated over a range of operating conditions in the single-cylinder Hydra compression ignition engine. Statistical analysis will be performed to quantify cycle-to-cycle variability, and tolerance/acceptability metrics will be formed to quantitatively qualify the blends.

TEA and LCA: The process requirements for the production of bio-blendstock composition that meets ASTM D975 will be used to perform the TEA and LCA of the proposed biofuel production pathway. Also, the engine-out emissions recorded from experimental testing will be used to demonstrate the potential of the proposed biofuel to reduce the life-cycle GHG by 50% compared to conventional petroleum-derived diesel.

TAILORED BIO-BLENDSTOCKS WITH LOW ENVIRONMENTAL IMPACT TO OPTIMIZE MIXING-CONTROLLED COMPRESSION IGNITION ENGINES

University of Michigan

PROJECT DESCRIPTION

WBS:	3.5.1.19
Presenter(s):	Andre Boehman
Project Start Date:	10/01/2018
Planned Project End Date:	06/30/2022
Total DOE Funding:	$2,000,000

The overall objective of the project is to develop and demonstrate a microalgae bio-blendstock with greater than 60% GHG reduction potential relative to petroleum diesel that can reduce sooting propensity, increase cetane number, and improve engine thermal efficiency relative to a baseline diesel engine operating on conventional fuel. Specific objectives include: (1) development of a new framework for both LCA and TEA that explicitly considers temporal variation in productivity and the frequency of crop loss; (2) determination of how fuel compounds that can be produced from the algal biomass can be "bio-tailored" based on the species composition and biological production process, subsequent processing via HTL to biocrude, and upgrading of the biocrude; (3) execution of a feedback loop (algae production → biocrude refining → combustion optimization → feedback to refining stage) for the optimization of fuels for MCCI combustion; (4) optimization of MCCI combustion and emissions performance, accounting first for the biological processes that dictate the chemical composition of biocrude oil and second for the subsequent chemical processes that comprise MCCI combustion; (6) simulation of MCCI engine combustion processes to demonstrate the incorporation of relevant fuel chemistry that captures the specific impacts of optimized algal fuels.

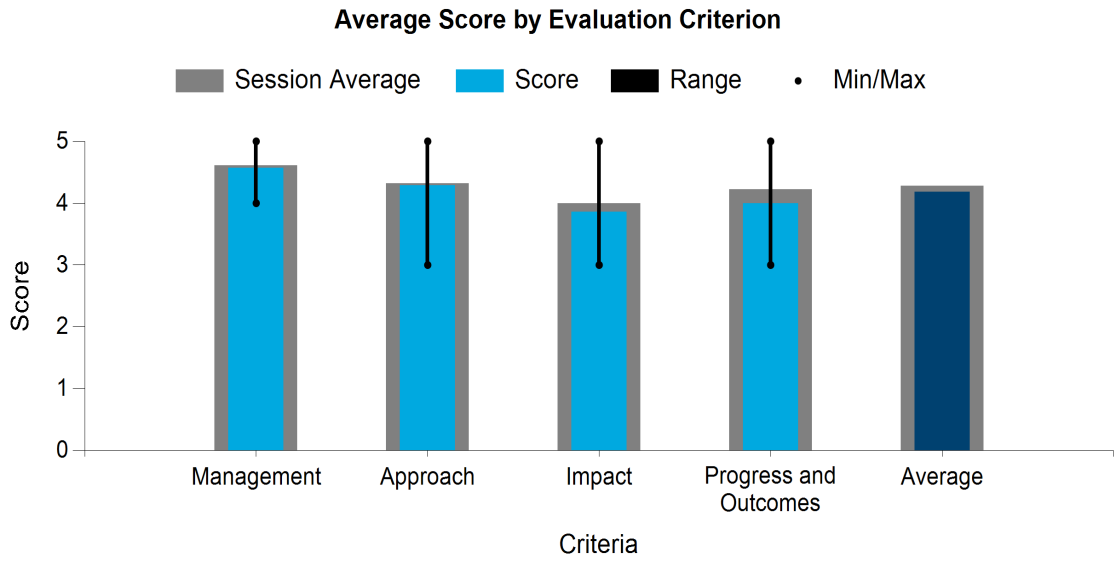


Photo courtesy of University of Michigan

COMMENTS

- There are interesting and important observations from comparing monoculture to polyculture algae systems and the utility of HTL for processing their output. There are notable milestones in the demonstration of catalytic processes to make biocrude and tailored blendstocks as well as collaboration with an energy company to explore the technology transfer possibilities for refinery integration of algae biocrude. The use of algae as input biomass seems to avoid concerns with elemental contaminates (e.g., sulfur, ash metals) that may be an issue with woody biomass sources. Eventually, it will be useful to understand the feasibility and economics of the mass production of algae-based blendstocks.

- Management: The team is well qualified. A few risks around algae cultivation and processing are identified. More information on the communication plan with the Co-Optima teams and external stakeholders would be helpful.

  Approach: The direct recycling of nutrients from HTL back to algae ponds is needed and is wise to include in the plan. HTL is an excellent way to convert algal biomass toward usable fuel. Batch reactors can hide processing challenges relevant for scale-up into continuous reactors, such as the deposition of inorganics in a catalyst bed or long-term (100 hours–1,000 hours) deactivation trends. With HTL and hydrotreating, it is unclear how tailored the fuels produced from algae via HTL and hydrotreating will be because you often get what you put in (i.e., it is more set by biomass properties than processing); however, slight changes in composition affected by processing conditions may be small but possibly meaningful. Certainly, algae could be grown for more lipid content, but this takes more time and often

requires other inputs such as sugar. Such offsets on economics and LCA would be interesting to consider.

Impact: All of the steps in the project will support the commercialization potential. Interactions with an energy company regarding biocrude integration would be very interesting. A refinery may be hesitant to feed biocrude to their refinery hydrotreating unit due to the high concentration of nitrogen and oxygen. Feeding to a fluid catalytic cracker loses many benefits of growing algae, such as the lipids, which would not survive. Alternatives to an over-the-fence arrangement, whereby biocrude is hydrotreated at a separate facility and the hydrocarbons are sold for blending with diesel, are interesting to consider.

Progress and outcomes: Progress and outcomes are progressing well. Good progress appears to have been made even during COVID. The recycling of the nutrients from HTL last year to new ponds this year is good to see.

- The goal of the project is to develop an algae-based diesel fuel blendstock with improved MCCI engine performance, emissions, and physical properties. The tasks and roles were clearly outlined in the work breakdown as growing the algae, performing flow-through HTL, hydrotreating the bio-oil, then testing it in research engines with surrogate blends. In parallel, the modeling—both CFD at the cylinder level and TEA/LCA at the process level—occurs. From a workforce development standpoint, the project does an excellent job of including undergraduate to postdoctoral students. The team also has regular industry interactions with Marathon Petroleum in a consulting role. There was no mention of the meeting frequency. The critical risks and mitigation plans were not mentioned in the presentation. The problem with the contamination of algae cultures was discussed in the Q&A. The approach is to generate enough bio-oil in 2-L continuous stirred-tank reactors to generate enough hydrotreated fuel blendstock to use in MCCI engine and property testing. This testing should inform the algae cultivation and pond operating parameters in the feedback to optimize the entire process. The team works with polycultures to increase the net yield. The team should monitor the hydrogen consumption and carbon dioxide production during the bio-oil upgrading steps and determine what separation steps, if any, are required downstream or can be avoided by proper algae cultivation. The team understands that this work can result in technology transfer opportunities to the energy partner and aligns with Co-Optima's strategy. The team was able to harvest more than 60 kg of algae during six cumulative harvest cycles. There was significant decrease on the 6/25 harvest, and this may have been due to a fungus outbreak, thus demonstrating how difficult this work can be. The team should reveal the rest of the compounds that satisfy the carbon balance for the HTL mass spectrometry results as well as the number of the organic phases that were observed. There was no analysis of the aqueous phase present after HTL. The team should seek to explore the reaction networks that lead to unstable triene diols present in the polyculture. There appears to be an opportunity to minimize the efforts with surrogate hydrocarbon fuel because all of the organic acids can be removed via hydrotreating. These hydrocarbons can then be blended along with hexadecane in diesel and tested in the MCCI environment. More mass spectrometry results from HTL experiments must be disclosed to truly understand the carbon efficiency and how to manage the molecules downstream as well as to identify the biomarkers for these compounds within algae prior to processing. This work must focus on working with real feeds and less surrogate compounds. The team believes that the impurities within the bio-oil should not be an issue. Currently, no OEM partner is participating on the project. Originally, Volvo Trucks served as the OEM partner. The approach toward key milestones could not be determined from the presentation.
- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for

communication and collaboration across related projects. For funded university projects, the overall matrixed management framework for the Co-Optima program with liaison to a Co-Optima advisor helps connect the funded projects to the broader Co-Optima initiative and allows for information sharing across the other projects. The project looks at tailored bio-blendstocks with low environmental impact to optimize MCCI engines using algal-derived fuels for diesel. Sooting and cetane number are key targets as well as engine thermal efficiency. The potential for 60% GHG reduction resulting from the HTL of whole algae into biocrude is explored. Specifically, there is a focus on robustness and stability from polycultures versus highly engineered single strains. Pond crashes in the production of algal-derived fuels contributes materially to the cost and efficiency of producing fuels from algae. The polyculture approach helps create a more tolerant and stable feedstock production source. This project also added to the diversity of funded research in the Co-Optima program.

A key question that I had was whether there was a trade-off from the polyculture versus monocultures. The response during the presentation was that monoculture- or polyculture-to-HTL products are very similar and do not pose a downstream trade-off. A related question is whether the research considered how the properties of the resulting biocrude might be tailored to influence the desired fuel properties or if biocrude upgrading resulted in non-differentiated fuels regardless of the algal feedstock and biocrude characteristics. Hexadecane was selected to represent algal biocrude. Does that lead to a differentiated fuel from conventional diesel? It leaves the question about how the fuel is tailored to meet the desired performance targets if there is no differentiation resulting from the algal feedstock. How do the fuel properties get tailored and passed through to the finished fuel? What is the co-optimization aspect? The approach references a feedback loop in the tailoring of fuel properties. It was unclear if that tailoring stemmed back to the algae itself or just in the upgrading of biocrude. It would be helpful to clarify how this feedback loop for tailoring fuel properties will be implemented in the remaining year of the research program. The results of the engine test to demonstrate sooting propensity and cetane number, with improvement in engine performance and emissions for the algal bio-blendstock, are not yet available. I assume this will be completed in the remaining research period of performance; however, once available, how will that information be used to tailor the fuel properties in the time remaining? It seems likely that with HTL of whole algae a fuel with a higher percentage GHG reduction may be possible. The TEA of achieving the potential MFSP of $3/GGE of fuel seems potentially challenging. What does the current TEA at today's state of development for the HTL of algae say about its cost in terms of $/GGE?

- The project uses a novel approach of exploiting algae for the production of bio-blendstock while taking feedback from the fuel produced and the performance achieved. Overall, the team has strong management skills, and it is clear that the project is being executed well. Interaction with the wider industry could be increased for improved impact of the work being done. The technical approaches being taken in the project are on the track to deliver the objectives of the project. The overall success of the project would lead to a significant contribution to BETO's and Co-Optima's goals. The use of the GREET model for LCA and TEA analysis is aligning well with wider Co-Optima efforts. The team has progressed well in the project, though the timeline is very tight, and efforts need to be optimized to finish the project on time while achieving the full potential of the innovative project being executed. It is expected that the overall work could lead to a significant reduction in GHG emissions.

- There is no doubt in my mind that without HTL, the vision of making algal oil a viable feedstock for fuel production will remain only a mirage hampered by the inescapable reality of thermodynamics and economic constraints. The integration of algal cultivation with HTL is beneficial, and I commend the investigators for dealing with many critical issues, such as the vulnerability of algal monoculture, which at the commercial level has largely dissipated the past interest in algal biofuels. This integration is necessary but not sufficient. I would have liked to see a bit more detail about the steps after HTL—the type of pretreatment of the oils, issues with hydrotreating, and so forth, which are critical to determining the impact. Also, I would have liked to understand more about other scalability issues, such as at what

scale the various steps are executed—for instance, is HTL more distributed than the oil upgrade? And the fate of the water out of the HTL process, and so on.

- This project connects a novel feedstock cultivation and sustainability approach with the Co-Optima goals of producing lower-emitting, optimized fuels. On the LCA and TEA side, this project team has built on promising research linking polycultures of algae that have greater yields than monocultures, and the team has identified a conversion pathway that is well suited to recovering the desired blendstock. These different tasks are well integrated with one another as a feedback loop, allowing for the adjustment of feedstock production and conversion based on the engine testing. Although the initial results are encouraging from a yield and modeled engine performance standpoint, the project success will require (1) additional information on the LCA performance of the polycultured algae in absolute terms rather than compared to the monoculture and (2) an assessment of the techno-economics of scaling up the ponds. (Note to PIs: Reading the linked study, the LCA emissions for the polyculture were still quite high. What is the strategy for reducing the emissions from the algal fuel in order to meet the GHG targets for the technology area? What accounts for the discrepancy in the LCA emissions between the measured values and the literature value you calculate for *Selenastrum capricornutum* of 33 kg carbon dioxide equivalent (CO_2e) per million British thermal units?)

PI RESPONSE TO REVIEWER COMMENTS

- Overall response: We appreciate the supportive comments and constructive criticisms received from the reviewers.

  Response: A reviewer asked about the meeting frequency for the team. The university research team meets monthly via a conference call for updates, planning, and discussion. We have had many informal discussions, roughly bimonthly, and we have had one major meeting with staff from Marathon Petroleum to discuss the project plans and progress and the challenges of integrating algal biocrude into refinery operations. We are planning a second large meeting with Marathon staff this summer. With regard to risks, we mentioned on slide 6 that risks include the challenge of algae instability (crashing of ponds) during cultivation and challenges with processing and upgrading. Risk is mitigated by following a "before, after, control, impact" approach. Risk in processing was mitigated by seeking advice from BETO researchers who are also pursuing HTL processing strategies. Because LCA and TEA are core activities in the project, we are monitoring material and energy inputs through the cultivation and processing tasks, including recycling of nutrients and analyses of byproduct streams. A reviewer mentioned the time history of the algae harvesting, which met our yield goal and exceeded (albeit on one harvest) the areal productivity target. Any decline in the 6/25 harvest was not due to fungal infection because we had yet to add the fungal parasite to the raceway ponds at that point. The lower value of harvest on 6/25 was not "significant." It was a lower mean, but it was not a significant deviation from the overall trend, and it simply represents the natural variation in feedstock biomass due to unknown factors (changes in sunlight, temperature, or some other abiotic or biotic factor we did not measure).

  A reviewer asked that we report our complete chemical analyses during HTL to satisfy the carbon balance and the phase behavior of the HTL products. In general, we observe only two phases (aqueous and biocrude), and though we did not report the chemical analyses of the aqueous phase in our presentation, those analyses will be reported by the team. A reviewer recommended that we explore the reaction networks that lead to unstable triene diols present in the polyculture. We will pursue this in our upcoming efforts, and we appreciate the suggestion.

  A reviewer commented on our approach using a surrogate to represent the algal blendstock. The surrogate approach is necessary to help define the target for the upstream processes of algae species selection, HTL conditions, and upgrading conditions. Our use of n-hexadecane was supplemented and informed not only by analyses of initial HTL biocrude samples but also by studying a full boiling range of renewable diesel fuel and various biodiesel samples. A sample of those results was included in our

supplemental slides. We built into our statement of project objectives the possibility of adjusting the surrogate fuel composition as the algae processing formula is finalized. But to support the numerical simulation of the combustion process to enable engine optimization, we need to represent both the baseline diesel fuel and the algal blendstock in simple terms. A reviewer recommended that more mass spectrometry results from HTL experiments must be disclosed to truly understand the carbon efficiency and how to manage the molecules downstream as well as to identify the biomarkers for these compounds within algae prior to processing. We will include our extensive analytic results in our reporting to DOE and in publications.

Much effort is being devoted to the detailed chemical analysis of the biocrude and upgraded biocrude. A reviewer stated that this work must focus on working with real feeds and less surrogate compounds. The team believes that the impurities within the bio-oil should not be an issue. Currently, no OEM partner is participating on the project. Originally, Volvo Trucks served as the OEM partner. Our algae production was limited in 2019 as a risk mitigation strategy because it was unclear if the successful strains cultivated as monocultures and polycultures in Michigan thrive in Arizona. We believe that HTL is such a robust process that the effect of algae strain will be only a secondary effect, relative to the selection of HTL conditions. HTL can homogenize the results from different algae. We are aware from discussion with our contacts at PNNL that there can be strong effects of minor species in the upgraded algal biocrude, and as we generate sufficient samples, we will be looking for these difficult compounds. Some have been shown by PNNL to impede the effectiveness of cold-flow performance additives. A reviewer commented that the approach toward key milestones could not be determined from the presentation. We have met all milestones throughout the project and both go/no-go decision points. So, we are on schedule based on our current statement of project objectives.

Management: A reviewer commented that more information on the communication plan with Co-Optima teams and external stakeholders would be helpful. A reviewer commented that the direct recycling of nutrients from HTL back to algae ponds is needed and is wise to include in the plan. This is a step that we included in previous bench-scale work, and we did attempt that supplemental experiment in 2019 while we were at the Arizona Center for Algae Technology and Innovation, but the algae failed to grow, even in the controls. We do not know why, but we suspect the lighting conditions in the lab were too intense and the algae were “photo bleached.” Nonetheless, we agree that this is an essential element of a realistic and scalable algae cultivation and processing system.

A reviewer commented that HTL is an excellent way to convert algal biomass toward usable fuel. Batch reactors can hide processing challenges relevant for scale-up into continuous reactors, such as the deposition of inorganics in a catalyst bed or long-term (100 hours–1,000 hours) deactivation trends. Our work will remain as a lab-scale effort, and due to resource and equipment limitations, we must rely on batch reactor processing at this stage of the development of our team’s efforts. We have discussed with our partners at Marathon Petroleum both the need for and challenges that may arise from moving to a continuous process. That is one reason why our partnership with Marathon has been extremely valuable to our team.

A reviewer commented that it is unclear how tailorable the fuels produced from algae via HTL and hydrotreating will be as you often get what you put in (i.e., it is more set by biomass properties than processing); however, slight changes in composition affected by processing conditions may be small but possibly meaningful. This is an aspect with which the team is aware, and our communication with researchers at PNNL has brought some of these challenges to our attention with regard to certain fuel properties. Nonetheless, it is our experience that HTL can serve to homogenize some level of feedstock variation; however, trace constituents can cause problems, and this is why our feedback loop among the major tasks in our project is so important. Moreover, our LCA and TEA studies are being informed by the variations in composition and properties that we observe.

A reviewer commented, in reference to linkage of the cultivation and processes tasks, that the integration is necessary but not sufficient. That reviewer asked to see more detail on the steps after HTL. These steps are evolving as we move from very small bench-scale reactors to larger batch reactors and our largest batch reactors. We are performing separation via centrifugation to obtain a separate aqueous phase that is set aside before the hydro-upgrading. A reviewer commented that the project success will require (1) additional information on the LCA performance of the polycultured algae in absolute terms rather than compared to the monoculture and (2) an assessment of the techno-economics of scaling up the ponds. And that the LCA emissions for the polyculture were still quite high. Our hypothesis in our study is that robustness in cultivation and efficient processing of the algae will yield a successful reduction in the GHG footprint for the algal bio-blendstock. Estimates reported recently by PNNL and the Co-Optima team are >60% renewable content for algal fuels. Relative to diesel fuel, that means approximately 33 kg CO_2e/megajoule (versus diesel fuel's carbon intensity of 95). Working at this small scale reduces GHG footprint reductions and dramatically increases costs. But by enabling robust cultivation, we will make progress on both metrics of performance that can advance the ability to scale up and deploy algal biofuels. In the Carruthers et al. LCA, the main driver of energy return on investment for *S. capricornutum* was phosphate concentrations required to grow the species. *S. capricornutum* requires a lot of phosphorus and is poor at recycling. Because GHGs in the LCA are inversely proportional to the energy return on investment, *S. capricornutum*'s biological need for phosphorus is likely what drives the species GHG. The reason GHGs are higher in our LCA compared to literature values is because we are the first to directly document the species' phosphorus use and recycling inefficiencies (others have ignored it in their LCA). The only way to reduce GHG is to find a polyculture that achieves equal or higher feedstock productivity as *S. capricornutum* but which has a consortium of species that are efficient at using all limited nutrients.

A reviewer asked whether there was a trade-off from the polyculture versus monocultures, whether the research considered how the properties of the resulting biocrude might be tailored to influence the desired fuel properties, and how the fuel properties get tailored and passed through to the finished fuel. What is the co-optimization aspect? The HTL and upgrading conditions allow a powerful lever for controlling the composition of the bio-blendstock. Our upgrading studies, in particular, have shown us that time on stream is a primary control over aliphatic chain length, which exerts a strong effect on sooting tendency and ignition quality. The algae species property that is more important is biochemical content (lipid, protein, polysaccharide), and, in general, that depends more on how the algae grow as opposed to the species being grown. A reviewer mentioned that it was unclear if that tailoring stemmed back to the algae itself or only in the upgrading of biocrude. Algae species selection was driven by concerns over productivity and robustness, of which the processing conditions are most strongly linked to tailoring the fuel properties. The fuel property studies (model compounds, full-boiling-range renewable diesel fuels, model esters, and full-boiling-range biodiesel) informed the targets that we have set for the process design to achieve. This is how our feedback loop is working—by directing the processing based on the composition targets derived from the fuel performance studies at the bench scale. Our ongoing engine work, by necessity, focuses on a surrogate representation of the algal bio-blendstock because the engine requires liter to gallon quantities and the algae production and processing is limited to kilogram and milliliter quantities. But those samples will be studied in bench-scale fuel property instruments (sooting tendency in our smoke point lamp, ignition behavior in our cetane number instrument and modified Cooperative Fuel Research engine, and cold-flow properties in our cloud/pour point test instrument). It is correct that the $3/GGE is a challenge, and at this small laboratory scale, the cost is closer to $50/GGE than $3/GGE. But using our TEA and data from PNNL reports, we estimate that <$3/GGE is achievable at the industrial scale.

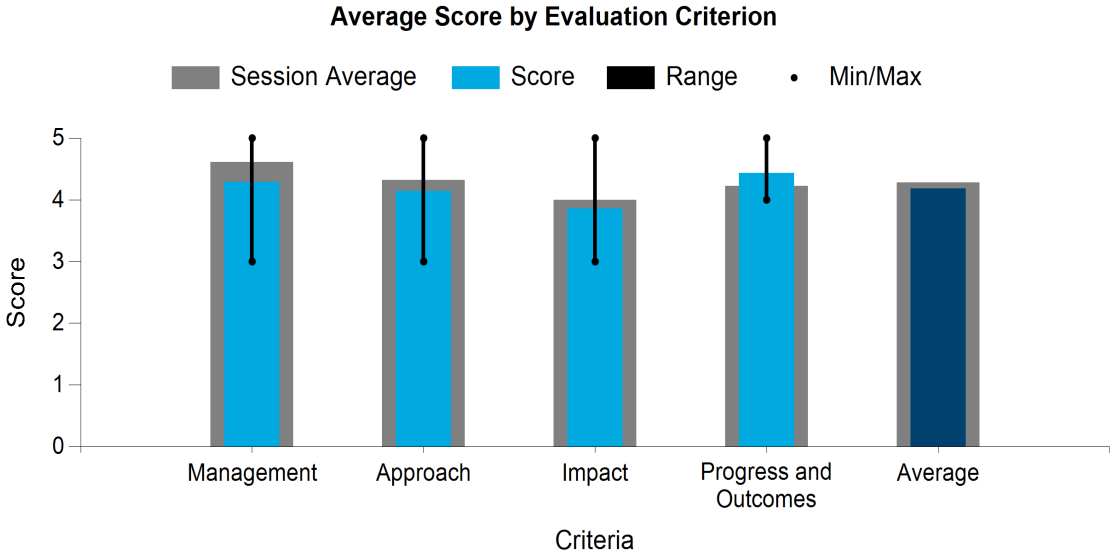
POLYOXYMETHYLENE ETHERS AS A HIGH-CETANE, LOW-SOOTING BIOFUEL BLENDSTOCK FOR USE IN MEDIUM- TO HEAVY-DUTY MIXING-CONTROLLED COMPRESSION IGNITION ENGINES

Colorado State University

PROJECT DESCRIPTION

WBS:	3.5.1.20
Presenter(s):	Bret Windom
Project Start Date:	06/01/2019
Planned Project End Date:	11/30/2022
Total DOE Funding:	$1,972,050

One of the most promising approaches to lower life-cycle GHG, particulate matter, and NO_x emissions from diesel-based internal combustion engines is to use sustainable fuels produced from lignocellulosic biomass either as a direct petroleum-based diesel fuel replacement or as a blendstock. Bio-derived polyoxymethylene dimethyl ethers (POM-DMEs), as a potential carbon-neutral fuel, have previously been shown to be viable diesel fuel blendstocks due to their unique molecular structure leading to high cetane number, excellent compatibility with diesel fuel, and extremely low sooting potential. Although most studies have agreed that POM-DMEs are a promising diesel fuel blendstock, these molecules exhibit undesired physicochemical properties, such as reduced LHV, low flash point, and high water solubility. Based on structure-activity models, many of these properties can be improved by replacing the terminating methyl end group with larger alkyl structures. In this project, we aim to synthesize and characterize a novel group of POMEs with larger hydrocarbon end groups. Fuel properties such as YSI, water solubility, calorific values, and prevaporized ignition delays of the synthesized POMEs were measured for a range of alkyl end group lengths and oligomers, with varying numbers of oxymethylene units. Additionally, microreactor experiments, complemented with kinetic modeling, were used to quantitatively understand and predict the pyrolysis behavior of POMEs. Results from this work conclude that these novel POMEs exhibit favorable physicochemical properties required by a diesel blendstock compared to their methyl-terminated counterparts while still exhibiting remarkable soot reduction potential. Next steps in the project include characterization of diesel/POME blends to understand synergistic/antagonistic blending behaviors on cetane, sooting, oxidative stability, and material compatibility; further POME chemical kinetic mechanism development through additional modeling coupled with microflow reactor pyrolysis and abstraction experiments; fuel performance and emissions assessment in a medium-duty 6.7-L Cummins engine; and sustainability/economics assessment to identify promising synthesis routes and support POME scale-up.



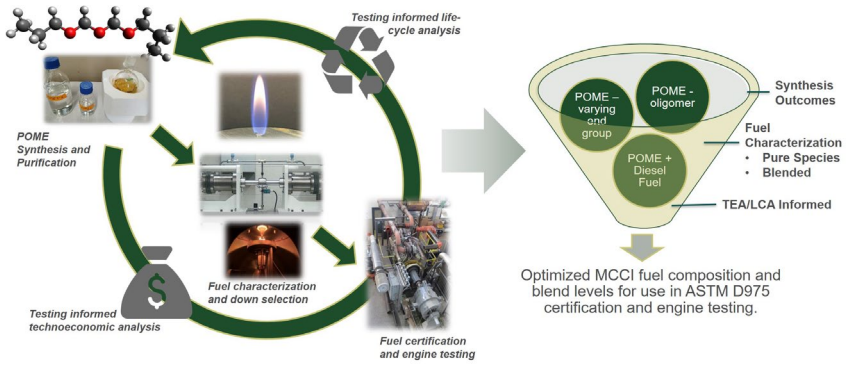


Photo courtesy of Colorado State University

COMMENTS

- I was not familiar with POME before reading the project documentation. Still, in general, the idea of identifying bio-based molecules that can be used to extend and improve the performance of conventional fuels is very appealing to me. Results appear extremely promising, and the investigators provide an excellent rationale for the work carried out thus far. Although I understand that some TEA considerations are very preliminary, I wish the team had provided more detail on the supply's scalability—even if potential—and synthesis pathways from renewable feedstock. These aspects were not very clear to me during the presentation.

- This is interesting work to develop a novel group of POME blendstocks and to characterize their impacts on combustion and emissions. These compounds have previously demonstrated viable production pathways from lignocellulosic material. The team developed important results on the POME reaction pathways and sooting tendencies, which provide structure-property data that feed back into the process.

The team aims to publish results in high-impact journals. The presentation provides clear flowcharts on project management components and risk mitigation strategies.

- Management: The project team is well qualified. The project structure is clearly communicated as well as risks, implications, and mitigation strategies. External communication with stakeholders and tie-ins to Co-Optima are not as clearly defined.

  Approach: The approach to conversion, modeling with YSI, and fuel testing is robust. Questions regarding the conversion process should be addressed. One specific consideration is the selectivity and controllability of the POME process. If produced compounds are found to be unsuitable for fuel (e.g., with a terminal hemiacetal rather than the desired alkoxy group) and the process cannot be tuned to eliminate them, the separation and fate of these compounds and the relevant impact on TEA and LCA will be critical. Improving the conversion without sacrificing product selectivity over those reported in the 2020 American Chemical Society *Sustainable Chemistry & Engineering* paper will be critical, as will demonstration of the suitability for off-path products to be successfully recycled. The water solubility and oxidative stability of the POMEs are slated to be measured by the Marchese group, which is necessary for these compounds and has already begun. Consideration should also be given to the susceptibility of the POMEs to hydrolysis, even at lower water concentration in diesel once blended.

  Impact: Because the POMEs have relatively low energy density, there would likely be an optimal blending level where soot may be mitigated but energy density is not yet dropped to an unacceptable level. A 50% GHG reduction may be difficult due to the limited blending level. The publication record is excellent, but ultimately a commercial process and product would provide the most impact.

  Progress and outcomes: Good progress on developing new end alkoxy terminal groups for the POMEs and associated property and engine testing is evident. LCA and TEA results should be prepared and disseminated within the group soon to guide the most critical (i.e., expensive) aspects for the conversion team on reducing both costs and GHG emissions to provide research focus.

- The goal of this project is to synthesize a new group of POMEs with longer alkyl groups and to perform MCCI engine testing with POMEs containing fuel blends. This goal has at least one quantitative target for reducing GHG by 50% relative to ULSD. Other directional metrics relative to ULSD include reducing YSI and maximizing LHV. The roles between Colorado State University, the University of Colorado-Boulder, and Yale University were clearly explained. The frequency of interactions among team members could not be determined. There are several critical risks—namely, product purity, POME scaling, and bioprocessing impurities. The team suggested a very reasonable list of mitigation actions, which includes partnering with a national lab to leverage separation resources, sourcing commercially available dialkoxy-methane, and obtaining commercial bio-derived alcohols as impurity-free reactants. These commercially sourced materials should serve as baseline testing components in the project regardless. The general approach is to synthesize POMEs, develop combustion kinetic models to help downselect, complete fuel property and engine testing, and provide TEA/LCA. The team did a good job of explaining this approach. Continuous POME synthesis with longer alkyl groups can take place only after the precursors are purified and isolated from the biomass effluent. The connection of the first-principles combustion reaction network modeling to fuel performance should be further clarified because the engine testing task did not involve any validation of these results. It appears that the modeling provides a relative ranking on POME selection. There should be some project feedback to help tweak the modeling parameters or suggest independent experiments that tie/validate photoionization mass spectrometry (PIMS) and MCCI critical kinetic parameters. The team realizes that their work in this area will serve as foundational investigations for C_2–C_4 POMEs as MCCI fuel components. The team has already prepared seven manuscripts they aim to publish in high-impact, peer-reviewed journals. The characterization of these components will be significant to the biofuel design and vehicle engine design communities. More importantly, this class of molecules connects back to several BETO bioprocessing

synthesis pathways for generating feedstock precursors. The team did a commendable job of developing the class of extended alkyl POMEs. Further, the SPRs presented were compelling and clear. These types of Polanyi correlations are always important to science. The team was able to increase the yield of dibutoxymethane and oligomers quite a bit by tuning the direct organic synthesis pathway through the formaldehyde-butanol steps, avoiding any need for separation strategies downstream. The oligomerization is allowed to carry out denoting a product distribution governed via Flory-Schulz without any external control or manipulation strategies. At this stage in the project, the synthesis volumes are small, on the order of a few milliliters. The end group length and density empirical correlation with YSI for oxymethylene molecular substructural units showed excellent agreement. Larger end groups were also shown to decrease the ignition time. The kinetics on slide 28 show a slight change in slope in Arrhenius behavior, so the contribution of diffusion should be addressed. The go/no-go milestones—the YSI <200 and that the ignition delay must be less than the baseline ULSD targets—were reached. The project appears to be on track.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. For funded university projects, the overall matrixed management framework for the Co-Optima program with liaison to a Co-Optima advisor helps connect the funded projects to the broader Co-Optima initiative and allows for information sharing across the other projects. POMEs have the potential for high cetane number and low sooting with the addition of extended alkyl groups; however, POMEs have high oxygen content, low energy density, poor stability, and high water solubility, which are not desirable. The oxygen weight percentage can be reduced by adding alkyl end groups with the aim to improve cetane and reduce soot propensity while maintaining acceptable energy density, water solubility, and stability. POMEs appear to be a promising class of fuel molecules and were referenced in other Co-Optima work. It would be of interest to know the degree of collaboration across projects working with POMEs in Co-Optima.

  Sooting tendency was measured using Yale YSI. It seems that all the Co-Optima projects are using this method but almost none used blended fuels. Is there a reason that blended fuels cannot be used in YSI measurements for comparison to pure-component or surrogate mixtures? As noted in the Q&A portion of the talk, complex sets of reactions happen in combustion with the development of many species. It seems that some properties are inherent within a fuel molecule (e.g., octane) and that its performance will blend somewhat proportionally in a mixture, whereas others are based on chemical or physical interactions in the mixture. Will there be some improved predicative multicomponent blend modeling that comes from this research? The program progress is on track through Task 2.6 approximately halfway through the overall program. The team has produced 10 mL of POMEs with alkyl groups of C2 or greater and has produced YSI measurements, gas phase ignition characterization, oxidative stability, and LHV measurements. Progress includes new approaches to generate greater yield, including larger (n>2) POME oligomers, which addresses the limited POME yield in the original synthesis approach. It has been demonstrated that novel POMEs exhibit favorable physiochemical properties required by diesel blendstocks, which exhibit remarkable soot reduction potential and faster ignition chemistry than diesel. The program appears on track. Future work will investigate sustainability/economics and test the downselected blendstock performance in an MDV diesel engine.

- This project deals with using POMEs to generate bio-blendstock for future transportation fuels. The overall management of the project is being handled well by the right team, which has a strong background in their respective areas. The approach of converting POMEs, measuring their properties, using modeling approaches, calculating GHG emissions, and engine testing is the right one to take for

delivering the goals and objectives of the proposed project and assisting in achieving the Co-Optima goals. The progress to date is good, even after the impact of the current circumstances.

- This project is highly targeted and serves an important purpose in characterizing the properties of POMEs as a bio-blendstock. The progress shared so far illustrates that these compounds have favorable properties. The project team notes that synthesizing the sufficient quantities of POMEs and fuel from biomass could be large risks to the success of the project; this could be mitigated through a more integrated approach, wherein the feedstock and conversion pathways are identified earlier on in the process, to achieve a better understanding of the commercialization and sustainability prospects for the bio-blendstock.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the reviewer's careful consideration of our project. We will look to incorporate much of this valuable feedback in the second half of the project. Please find responses to the questions/concerns from the reviewer's overall impressions. Regarding information sharing, the team has a robust working relationship and meets monthly. Multiple off-cycle meetings occur in weekly and biweekly periods to discuss more specific items, e.g., relating kinetics to global combustion observations (ignition, YSI, oxidative stability) and synthesis outcomes to TEA/LCA process models. In addition, we meet regularly with NREL to discuss our complementary POME research as part of Co-Optima. Although our primary focus to date has been on the characterization of individual POMES, NREL's POME efforts have investigated novel synthesis approaches and blended POMEs (distillation cuts). During our meetings, we ensure that complementary work is being completed and that the two teams are not overlapping efforts. This can be seen by the two co-published journal papers. We have also leveraged NREL's facilities for POME synthesis/separation activities and fuel characterization measurements (ignition and oxidative stability). In the case of the unimolecular decomposition rates, we observe some slight curvature in the kinetics; however, this is due to intramolecular forces rather than diffusion, which is why we plan to use a modified Arrhenius expression to more accurately capture the temperature dependency of the rates. If the reviewer is referencing the low-temperature M2M → CH3 + OCH2OCH2OCH3 plot, there was one point with convergence errors plotted, which has since been taken care of. The property prediction tools used in the early screening of the POME performance were either validated or trained with commercially available POMEs or those that could be easily synthesized.

  We agree with the reviewers—now that we have successfully synthesized a wide matrix of POMEs (with varying end group lengths and oligomers)—that we will want to verify the predictions and update the models accordingly. The focus of the project in Budget Period 2 will have an eye on POME-POME mixtures (with impurities from commercial synthesis/separation) that minimize production costs while meeting performance metrics. Early "fundamental" work wanted to understand the role of POME composition on performance. Upcoming work will leverage the science gained from the first phase of the project with TEA/LCA results to identify subsequent POME blends for scaled-up production and testing. We concur that the TEA/LCA will be critical to guide our future direction, and we are expecting these results to occur early in Budget Period 2. With these results, we will also be able to identify and describe the most promising production pathways. Previous research has shown that YSI of blended fuels can be approximated by mixture averaging the YSI of the individual compounds. Although this has been shown to accurately approximate the YSI of mixtures, our kinetic results indicate that POMEs quickly decompose into aldehydes and alkyl structures, which could subsequently react with compounds in the diesel fuel. Future work to be conducted early in Budget Period 2 will explore possible synergistic/antagonistic effects on the YSI of POMEs when blended with diesel fuel. Similarly, oxidative stability and ignition data will be collected for blended fuels and will be used to identify any nonlinear blending behaviors that occur with POMEs to support improved property prediction models.

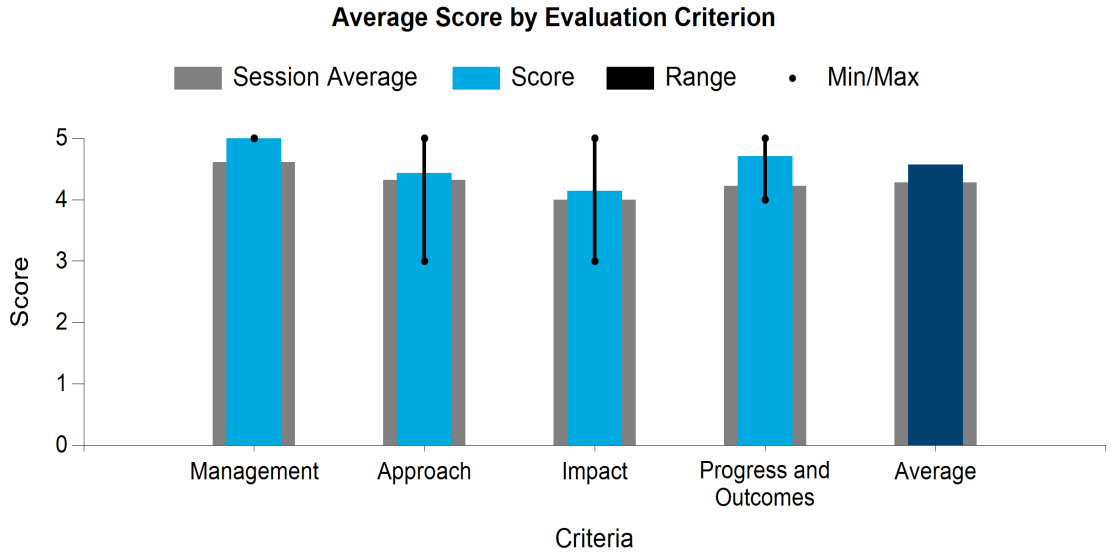
TECHNO-ECONOMIC AND ENVIRONMENTAL LIFE-CYCLE ASSESSMENT

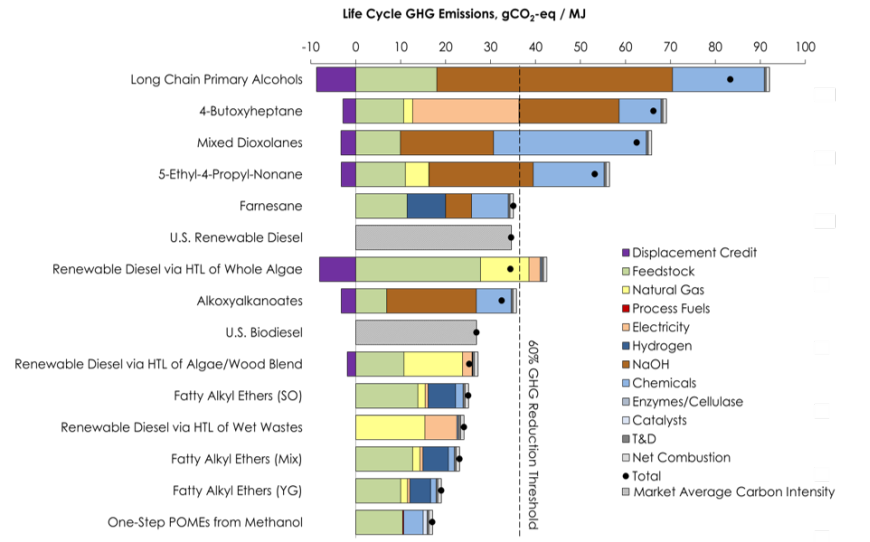
Argonne National Laboratory, National Renewable Energy Laboratory, and Pacific Northwest National Laboratory

PROJECT DESCRIPTION

WBS:	3.5.1.4, 3.5.1.8, 3.5.1.10
Presenter(s):	Troy Hawkins
Project Start Date:	10/01/2018
Planned Project End Date:	09/30/2021
Total DOE Funding:	$1,765,000

The TEA and environmental LCA effort is part of Co-Optima and is working to identify performance-enhancing fuel blendstocks derived from waste and biomass that can provide critical fuel properties and to assess their benefits and potential to scale. The objective of this task is to identify which multimode and MCCI bio-blendstocks may be most viable from an economic, environmental, and scalability perspective and to communicate these results to Co-Optima's stakeholders. We interact closely with other Co-Optima teams to identify candidate bio-blendstocks based on key properties beneficial for boosted spark ignition, multimode, and MCCI engine combustion modes for LDVs, MDVs, and HDVs. The current phase of the project is focused on multimode fuels for LDVs and MCCI fuels for MDVs and HDVs. The task team provides the screening level. During the past 2 years since the last BETO Peer Review, the task team has successfully screened numerous feedstock-conversion pathways for producing multimode and MCCI fuels and deepened the analyses for promising candidates to provide TEA and LCA results for XX (where XX = approximately 10, to be finalized) multimode fuels produced via XX pathways and XX MCCI fuels produced via XX pathways. These results are critical elements in reports on the top multimode and MCCI bio-blendstocks identified by Co-Optima. They are also the basis for peer-reviewed journal articles published and in preparation by the team.





Life cycle GHG emissions for MCCI blendstock candidates by GHG source. Purple bars reflect credits associated with displacing emissions for co-products of bioblendstock production. Two blendstocks already on the market (U.S. Renewable Diesel and U.S. Biodiesel) were compared to nine additional candidates. SO = soybean oil, YG = yellow grease, Mix = 60:40 mix of SO and YG. The results were calculated using Argonne National Laboratory's GREET 2020 model.

Photo courtesy of ANL, NREL, PNNL

COMMENTS

- I really like this project, which provides a common framework for valuation across such a complex undertaking as Co-Optima. I appreciate that a variety of environmental and sustainability measures are considered besides carbon intensity. Relatively minor negative considerations are that I missed a detailed consideration about the scalability of the various pathways.

- Management: Risks are identified and mitigated. The communications plan with clear interties to the rest of Co-Optima and other stakeholders (including BETO) are articulated.

  Approach: The criteria rubric is robust and comprehensive. Significant assumptions must be made, especially with early TRL processes. It may be informative to consider different potential starting feedstocks to compare TEA and LCA results to similar end compounds/mixtures as a function of varying starting points for the most promising blends. The team must continue to ensure consistent application of assumptions for economics and LCA across very diverse conversion pathways to ensure comparisons are apples to apples. Some economic enabling via coproducts may be beneficial to consider. For example, in long-chain primary alcohols, some of these are especially valuable if they can be separated and may support a biofuel economically.

  Impact: Continue to reach out to biofuel producers individually. It may be informative to demonstrate improvements of GHG reductions relative to traditional (e.g., corn sugar-derived) pathways to ethanol or similar products, such as in the case of biochemical pathways that utilize sugar as feedstock.

  Progress and outcomes: There is significant progress on evaluating multiple pathways in a consistent manner. Continue to focus on publishing results in peer-reviewed publications and reports, and make models available for use and review by the biofuels community.

- The goal of this project is to take into account all of the external drivers related to economic/environmental factors and identify the most promising new Co-Optima fuels. The team has dedicated project management roles and team-lead coordination roles as well as emeritus roles, which is a very thoughtful and strategic concept. One of the notable aspects of the management strategy is the multilayered quality analysis approach, which seems to be so critical for any modeling work like this that influences key decisions. One of the key risks named deals with the credibility of results, which can be mitigated by using proven, acceptable modeling tools across BETO and VTO. The management structure is similar to many other Co-Optima team projects, with a significant amount of monthly meetings and interactions. The team meets quarterly with an advisory board, presents at key conferences, and holds individual stakeholder meetings. The list on slide 7 of external stakeholders that provide input is quite impressive, as are all of the other BETO tools that are leveraged. In terms of the SOA for fuel design and downselection heuristics, the Co-Optima TEA/LCA project should advance the approach because the engine performance has already been validated in Tier 2, and the process development provides the mass and energy balances for LCA. Further, the team has developed 19 metrics covering costs, environmental, and scalability. This fits perfectly within BETO's goals and missions. The approach has a significant, thorough criteria for fuel candidates to overcome in order to be considered for implementation. This approach should lead to a handful of promising candidates when completed. The team understands how their work will help guide R&D decisions and resource management in BETO by identifying low-cost, scalable, implementable fuel candidates. The impact also saves time and manpower resources by helping R&D identify risks early.

  The project has great commercial potential. It is expected that some auto OEMs or refiners would already be collaborating with the team at this point. The team should continue to define what makes a reasonable MCCI blendstock and final mixed-component blend, possibly even developing a true specification in the future. The MFSP estimates for the other five paths that were not less than $4/GGE should be disclosed for completeness. The team identified 11 blendstock candidates for MCCI. This was very helpful to the Co-Optima organization in general. The pathways are low TRL at the moment. It may be a better strategy to ensure Tier 2 testing occurs only when pathways are able to make liter quantities. The number of pathways investigated by the team, even at early TRL, is impressive and the correct approach. The renewable diesel costs appear to be in the neutral zone, which the team should clarify are for grassroots, stand-alone units in the analysis. The biochemical pathways continue to struggle with costs. The team should recommend the fundamental risk mitigation science approaches to deal with this gap. There may be an opportunity to explore various scenarios of combining a low-cost, low-carbon feedstock with a high-cost feedstock that is in low volume just to get it into the marketplace. If the biochemical pathways are not ready, the team can still produce them but at high cost and blend volumes <3%. The project may consider using some of the offline, single-batch, commercial blending programs to help generate blending recipe possibilities. The team identified 10 pathways for generating multimode fuel component candidates that have reasonable costs, GHG reduction, and quantity. This provides a clear strategic direction for BETO. This was an extremely successful effort.

- The management structure of the project is strong. The integration of TEA and LCA in the overall Co-Optima program is important. Selected risks and their mitigation methods are appropriate for taking the project forward. The strategy of regular meetings and information dissemination is appropriate because it helps all the stakeholders to give inputs and gain more understanding. Wider outreach activities are appropriate for this stage of the project. The approach of maximum sale price and GHG emissions is leading to the right blends being selected. The team has done a comprehensive task of evaluating GHG emissions of different blends. The work could deliver a different outcome in terms of standard methods for GHG evaluation or something similar, though an analysis on current fuel prices and potential sale of these fuels to public would have helped. The approach of evaluating TEA, LCA, and the scalability matrix is useful, though more options could be added for detailed calculation of GHG. LCA data sets have been made available through GREET, which is good for wider use. For wider impact, it might be

useful to provide LCA detailed methods for general use and iteratively improving them. Overall, the progress has been good and is assisting in achieving BETO's and Co-Optima's goals.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. The approach focused on the foundational question of what will work in the real world and whether TEA of $/GGE fuel prices or LCA of percentage of GHG reduction were below a certain threshold. The threshold for fuel prices, $5.50/GGE, seemed quite high relative to what will work in the real world, but I understand this was potentially reflecting the current state of the fuel pathway maturity and not a final end state.

  The question was also raised by at least one peer reviewer or audience member whether there was use of a standard accepted LCA tool throughout Co-Optima projects. Was the GREET tool considered the accepted standard tool for all Co-Optima projects? If not, what else was used and why? One peer reviewer raised the question of whether LUC was accounted for in the LCA. Can you clarify if the LCA tools take into consideration LUC and are generally accepted by industry?

  A number of pertinent questions related to the cost-effectiveness of potential fuel pathways appear to be assigned to the refinery analysis group and not addressed in the TEA—for example, the potential for aftertreatment emissions cost reduction or relative cost-effectiveness in future high-electrification scenarios where price of crude may fall. Was the focus of the TEA only to calculate the stand-alone fuel cost? It would be helpful to state that certain cost or market analyses were performed in the refinery analysis as a framing for what was in scope and out of scope for this research pillar. The TEA was used to set a threshold for what will work in the real world; however, the Co-Optima targets are not necessarily set at what will drive adoption in the real world, particularly in a relevant time horizon that the fuel pathways become available within a potentially heavily electrified future. So, the targets are not necessarily set at what will drive adoption absent other policy. This often has the discussion shifting to whether higher-value blendstocks and additives should also be a focus alongside deeper GHG reduction from higher-blend content. Should Co-Optima include a focus on higher-value but lower-blend levels for fuel components that might enhance performance for cetane number, YSI, cloud point, etc.? This may help get faster market penetration albeit potentially lower GHG reduction or volumetric uptake of biofuels. The TEA and LCA effort did provide a useful framework for analyzing and downselecting fuel pathways to be considered more closely for LDV and MDV/HDV work. It also highlighted that cost remains an issue; however, in some cases, the TEA highlighted fuels as promising that seemed less scalable, such as HTL of swine manure. It was not clear whether this pathway was, in fact, scalable to commercially relevant volumes.

- The TEAs and LCAs developed through this project fulfill a crucial role for Co-Optima by narrowing the technology area focus to only the most cost-effective and climate-friendly blendstocks. The approach used by this team appears to be well integrated with other projects and utilizes existing resources where possible to reduce redundancy with existing DOE work. The metrics used to assess economics and sustainability appear thorough and are clearly tailored toward the technology area's overall goals. It would be helpful to provide more clarity on the data needs for this team and which data are coming from within BBG&T and which data are coming from outside Co-Optima to develop these assessments. On the LCA and MFSP components of the analysis, it would be helpful to provide more detail on the functional unit for the bio-blendstocks assessed. Is it strictly based on their energetic value for the purposes of assessing LCA emissions and costs? This component of the analysis could be more tightly integrated with the refinery modeling team in order to characterize some products that may be better

suited to be specialized fuel additives based on their value to a refinery rather than to assess them as fuels.

- This team produced TEA, LCA, and scalability screening results of 13 pathways to produce 9 bio-blendstocks for MCCI and 12 pathways to produce 10 bio-blendstocks for LDVs. The work was reviewed through DOE internal as well as external stakeholder advisory panels. In advisory panel discussions, industry regularly expresses strong interest in TEA and LCA to guide decision-making for biofuel investments.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their encouragement and support for this work and the suggestions for taking it further. It is great to hear the reviewers recognize that the TEAs and LCAs developed through this project fulfill a crucial role for Co-Optima. We appreciate the reviewers' concern about using consistent methods for the LCA of bio-blendstock pathways across Co-Optima, and we have done this, consistently using the GREET model to perform the LCAs of all pathways. The question regarding the inclusion of LUC impacts in the LCA results is well received. This is something we include in GREET LCA results for more established pathways using GTAP-Bio through a collaboration with Purdue University. For most of the pathways evaluated for Co-Optima, LUC has not been a factor because the program has focused on waste feedstocks and those grown on marginal land. We have included pathways for fatty alkyl ethers and fatty-acid fusel esters from soybean oil and for short-chain esters from cuphea oil. A challenge with incorporating LUC is that estimates are specific to scenarios for the scale-up of biofuel production and are resource-intensive to execute, and this work has not been part of the Co-Optima scope. For the bio-blendstocks produced from soybean and cuphea oil, we will include LUC as a sensitivity analysis in the publication. We agree with the suggestion to expand the considerations to further address the scalability of the bio-blendstocks, and we have recently added an analysis of the total amount of each Co-Optima bio-blendstock that could be produced given the availability of each feedstock at the price used in the TEA, leveraging the *2016 Billion-Ton Report* (https://doi.org/10.2172/1271651). These results will be included in the publication on the MCCI pathways. The results presented also include consideration of blending behavior with current vehicle fuel and regulatory limitations on blend level as well as competition for the biomass feedstock and sensitivity to feedstock changes. The suggestion to extend the TEA by evaluating the value of the bio-blendstocks based on their beneficial properties beyond their energy value is a good one and is, in fact, addressed in the refinery analysis effort, as the reviewers suggested. We also conducted a study of the potential value of reduced aftertreatment requirements (https://doi.org/10.1021/acs.est.9b03690). This has been an area of focused research, and certain approaches, such as DFI, show promising initial results, which we will consider incorporating in the benefits analysis. Finally, we appreciate the encouragement to continue publishing our results, and we are working to do just that. We are preparing three journal articles on the results of the TEA and LCA of multimode and MCCI bio-blendstocks for submission later this year and the results of the TEA and LCA. Together with these articles, we will be making a version of GREET publicly available with the detailed data for each pathway.

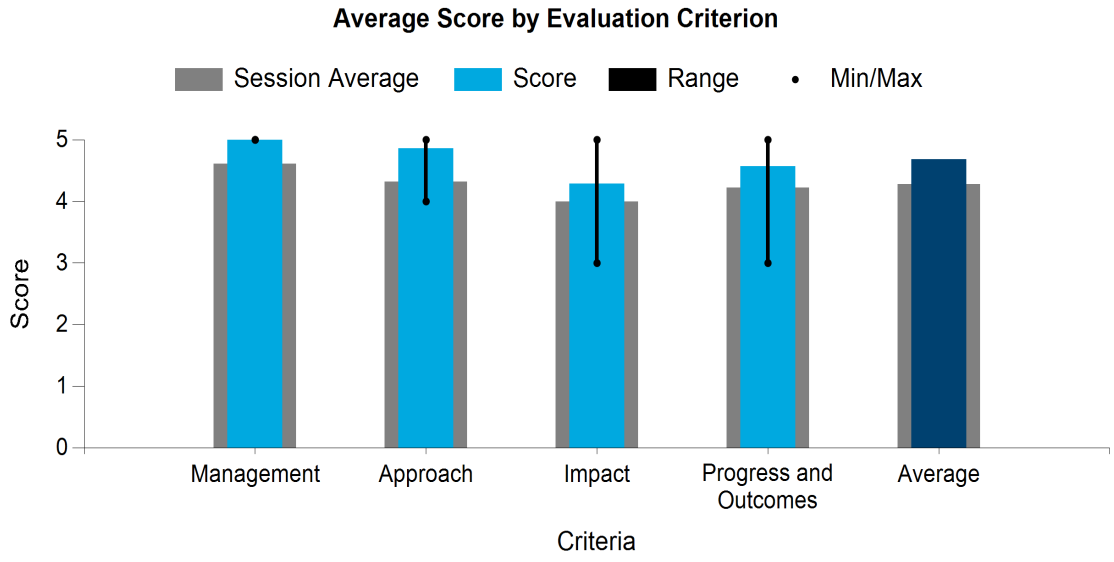
CO-OPTIMA INITIATIVE OVERVIEW

Pacific Northwest National Laboratory, National Renewable Energy Laboratory, Oak Ridge National Laboratory, Sandia National Laboratories, Argonne National Laboratories, Lawrence Berkeley National Laboratory, Los Alamos National Laboratory, and Idaho National Laboratory

PROJECT DESCRIPTION

WBS:	3.5.1.4-11
Presenter(s):	Daniel Gaspar
Project Start Date:	10/01/2018
Planned Project End Date:	09/30/2021
Total DOE Funding:	$33,750,000

The Co-Optima initiative is developing high-performance fuels that can boost engine efficiency and reduce criteria and GHG emissions when combined with diesel and multimode engines. To exploit fuel properties and composition to achieve Co-Optima's goals, Co-Optima researchers have identified blendstocks to improve multimode combustion (using spark ignition combustion under high-load conditions and ACI combustion under part-load conditions). Research octane number, octane sensitivity, and low aromatic content were determined to be the most important properties for multimode engine efficiency. A series of low-molecular-weight alcohols were found to have the highest engine efficiency potential and lowest GHG emissions. Co-Optima is investigating MCCI and advanced combustion modes for MDV and HDV applications. Detailed MCCI fuel property-molecular structure relationships were developed and used to identify hydrocarbon, ester, and ether blendstocks with the potential to reduce sooting tendency, increase cetane number, and improve cold-flow properties and energy density. TEA, LCA, refinery integration analysis, and benefits analysis identified candidates that can be made at scale while reducing GHG emissions by at least 60% with respect to petroleum-derived fuels.



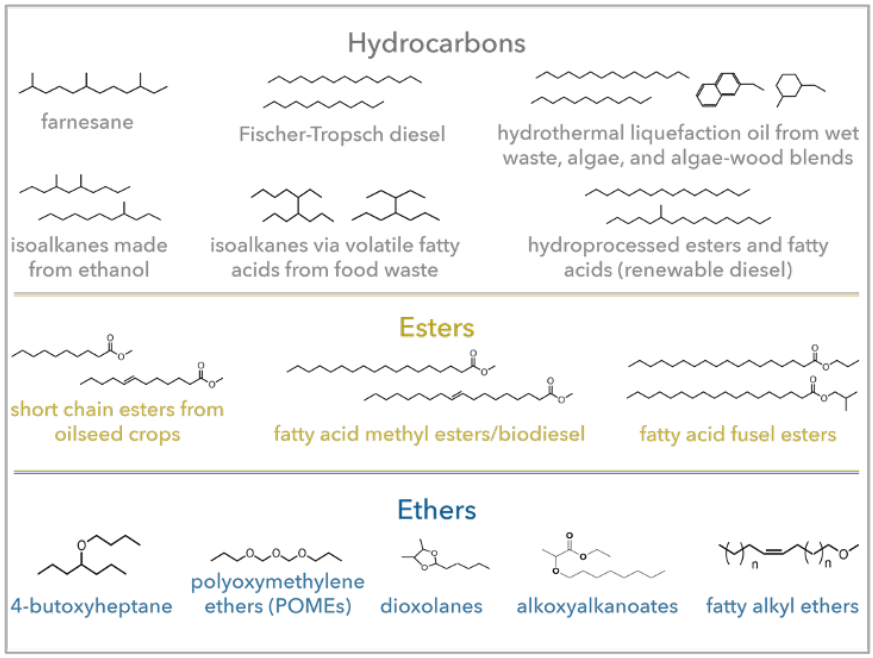


Photo courtesy of PNNL, NREL, ORNL, SNL, ANL, LBNL, LANL, and INL

COMMENTS

- I scored all the projects in management and approach similarly and highly. The Co-Optima leadership implemented a good structure that was well replicated across each project. Such coordination often transpires when looking at individual projects. Nonetheless, I found the link with the biorefinery industry and bio-based feedstock a bit more tenuous than I would have liked, or at least not as explicit for me. This made it difficult for me to understand the potential impact of some of the proposed solutions on the feedstock supply and biorefinery industry; however, I do not consider this a severe deficiency in the development of these projects. The overall screening and ranking of the proposed solutions are excellent. I will comment more in detail in the overall program overview review.

- Management: The organizational structure with feedback from multiple bodies (e.g., EAB, steering committee) is excellent and ensures timely guidance and course corrections from relevant sources. The communications plan is robust. Critical risks are clearly defined with mitigation strategies. Overall, the management plan of this large consortium across the multiple laboratories is clear from the consistent messaging.

  Approach: Shifting to MDV/HDV ACI makes sense given the electrification of the LDV fleet. For MDV/HDV ACI, enough may not currently be known about the given combustion strategies to successfully screen bio-blendstocks for specific chemical properties. Future efforts within VTO and BETO as these properties are determined may make sense.

  Impact: Key to the long-term impact of Co-Optima is informing BETO and the biofuels community at large on what should be made, not only what can be made given a feedstock. Overall, the impact of Co-Optima to guide project development toward new desirable fuels using industry engagement is strong. Continue to seek biofuels producers of all sizes, maturities, and feedstock specialties for their input and to inform them of the progress made by the consortium.

Progress and outcomes: The project has made excellent progress toward addressing the project goals and implementing its specified risk mitigation strategies.

- The Co-Optima initiative is a very successful endeavor—from the way the projects are managed, to the research topics, results, and deliverables. The project was built from a solid premise rooted in optimization for maximizing engine efficiency and emissions reductions, which is exactly a critical task for powertrain development groups in most vehicle OEMs. The work breakdown and team focus areas make sense and have always provided clear objectives and directives. The project really provides the critical downstream considerations for BETO to make more informed pathway decisions. It is almost like having a commercial fuel manufacturer and an automotive OEM housed within the same technical department of the same corporation. This is what makes the initiative so powerful and unique. The teams leverage this close interaction by communicating very clearly and frequently as well as by engaging with an impressive number of university and industry partners. The organization is well structured, with a Board of Directors steering committee, project manager, leadership team, and advisory board. The team does a wonderful job of reaching out to the research community and industry stakeholders with direct visits, webinars, listening days, and forums. The team provided several key risks, in which one included LDV electrification, prompting the mitigation strategy to shift the weight of the research effort to HDV and not expand it into hybrid research. This was quite forward thinking and shows the skill and flexibility of all of the impressive researchers involved in the project. Every project team knows how to communicate the same effective message for their approach by understanding the fuel appetite of advanced engines, looking at the fuel options available, and evaluating the practicality of those options. The leadership team has a consistent message that is concise and clear, noting that the impact of transportation is the largest contributing sector of GHG in the United States and how this project also provides the comprehensive modeling tool suite to evaluate the well-to-wheels impact. Every key milestone has resulted in dozens of blendstock recommendations from Co-Optima that influence the research directions across BETO.

  The team has a significant impact on the internal and external communities, with more than 120 publications, 6 patents, and database contributions. The team has been clear with external stakeholders on how RON, octane sensitivity, and heat of vaporization are key properties and alcohols, and iso-olefins and alkyl-furans are the classes with the highest potential. This important information is assisting the researchers with directional and resource decisions. By focusing on the merit function, the research community can clearly see how critical fuel properties impact engine efficiency. An impressive number of capstone reports have been published and are available for public download. The team successfully completed the FY 2020 go/no-go, identifying at least nine blendstocks for multimode combustion with favorable economics, emissions, and efficiency. The team has identified at least 11 MCCI blendstocks as iso-alkanes, esters, and ethers that also offer similar benefits after computer screening hundreds of potential mixtures. It seems there could be property synergy or new combinations of fuel properties that are even more important descriptors for characterizing MCCI performance. Hopefully, the team will continue to develop the CFD modeling and finite element analysis tools within Co-Optima.

- The Co-Optima overview has been clearly laid out in the presentation. There is a strong management structure and support structure. Appropriate risks have been identified, and mitigation strategies have been presented. The approach of providing ease of access to information and data is useful for the wider community. There has been industry involvement in the project, though it was felt that it could be increased. The project team has managed to propose blends that can achieve >60% reduction in GHG emissions and lower than $5.50/GGE fuel sale price, which is a remarkable achievement. The outcomes from the work have the potential to be implemented to solve the transportation emissions issue. The learnings from the work could also have impact outside ground transportation. The Co-Optima project overall is helping to achieve DOE's and BETO's goals.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies, including the pivot to the MDV/HDV focus based on a shift in LDV focus to electrification. The management structure allows for communication and collaboration across related projects. The Co-Optima program frames its approach with foundational technical questions on: (1) What fuels do engines really want? (2) Which fuel options work best in the real world? and (3) Which fuels will really work in the real world? And then the program aligns research to answer these questions through four pillars of SPR, BBG&T, TEA and LCA, and impact and refinery integration analysis. Each of these interrelated pillars helps the research span from fundamental properties of fuels to how those may translate into scaled-up refineries. The approach has significant potential to identify novel factors that impact engine and emissions performance while also seeing how those fundamental properties may translate to what works in the real world. The focus on both LDV and HDV and different modes of combustion allows more opportunity space to find a novel fit between bio-derived fuel properties and improved engine performance. The high degree of outreach and industry engagement increases the likelihood that the research is guided and has a more direct connection for impact and outcomes.

  The commercialization of any new fuel is challenging even when favorable properties are identified in the lab. Increasing industry engagement is key; however, prior aspects of market transformation or implementation that were part of Co-Optima early on seem to be less emphasized and may hamper how results translate into market impacts. How fuels will eventually get into the market is not well defined.

  Regarding overall goals, there needs to be some clarification. One stated goal was a 35% improvement in LDV fuel economy but was later stated as a 10% goal. Similarly, it is not clear how the goal of 30% renewable blend with 20% GHG aligns with the 60% GHG target, which is also stated as a goal. The LDV results were very promising with regard to Co-Optima's original goals, and while it is understandable that there is the shift to MDV/HDV, it was not clear if efforts were being made to ensure that the LDV results are applied in markets where engines may transition out more slowly. Did the industry take away anything related to LDV that may still be applied in countries with slower electric vehicle adoption? It would be helpful to more clearly state if companies and fuel producers are still targeting LDV engines with downsized, boosted, multimode, or ACI strategies that could take advantage of Co-Optima's learnings in any market. It seems like the light-duty part of the program is being shelved without at least summarizing where results might still be applied and disseminating information. Creating market pull was mentioned as a focus for Co-Optima fuels, but what drives the market pull absent head-to-head cost-competitiveness? It was touched upon but never really delved into how Co-Optima fuels would generate market pull, particularly in the event of falling crude or fuel prices if electrification takes off. Certainly, the GHG benefits will play a role, but will the cost of compliance be enough to span the delta between Co-Optima fuels and forward-looking fossil fuel-based prices? It seems that this will be a major factor in the potential market impact of Co-Optima fuels, and it is not addressed in detail in the program at this stage.

- The team took a multi-office, multidiscipline, hypothesis-driven approach to the evaluation of multimode and mixing-controlled fuel candidates across technical, economic, and environmental factors. There was regular engagement with stakeholders across EAB, OEMs, and fuel producers, as well as the academic community through journal publications and symposia. The project was able to demonstrate high-quality development and performance targets to industry and high potential for improvements in efficiency and criteria pollutant reduction, all delivered within the specified milestone schedule.

- This technology area has a nicely defined scope of work in conjunction with a clear set of goals within the technology area and linked to the rest of BETO. The management plan indicates substantial engagement with industry and stakeholders. The progress and outputs from this technology area are well documented and easily accessible via the Co-Optima portal, which further enhances the impact of the portfolio's projects. Recommendations for this project are similar to those for the overall technology area. As part of the process of identifying candidate blendstocks and/or molecules, an effort should be made to identify and define their functional unit (e.g., cetane improver) in order to tailor the later TEA and LCA analysis and give the team a more accurate comparator for calculating GHG savings and costs. This is particularly important for molecules identified as additives rather than fuels. For example, a cetane improver may have different LCA implications and economic value when compared to a like product than when compared to a reference fuel.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their suggestions and insights, and we appreciate the consistent recognition among reviewers that Co-Optima is well managed and coordinated with a robust communications plan and regular engagement with industry and other stakeholders. We appreciate the reviewers' concurrence that shifting effort to HDV transportation was the correct shift as near-term electrification of LDVs has become more likely. Three reviewers indicated that additional engagement with industry (beyond that noted) would help achieve our desired impacts. We agree, and we are currently making a renewed effort with various parts of the biofuels industry to drive better mutual understanding of opportunities and barriers to impact. One reviewer commented on international impact and wanted to see Co-Optima publicize the LDV results in regions where electrification would be slower. We note that we are currently making a substantial effort to communicate all our key results, including those on LDVs, to industry and other stakeholders in the United States and abroad, including Latin America, Europe, and Asia. For instance, the Co-Optima PI will present the LDV results to the directors of the OLADE in May. One reviewer referenced additives; we apologize for not being clear that all the candidates Co-Optima has examined are intended for blending at 10 vol % or more, even those with a very high cetane number. Another reviewer noted that we expressed the Co-Optima fuel economy and GHG reduction targets in inconsistent ways. To be clear, the blendstock GHG reduction target is 60% at the blendstock level (or >20% for a 30% blend containing a blendstock with 60% reduction). Similarly, the 35% fuel economy improvement includes 10% from Co-Optima efforts in addition to the 25% goal for fuel economy improvements from other DOE programs.

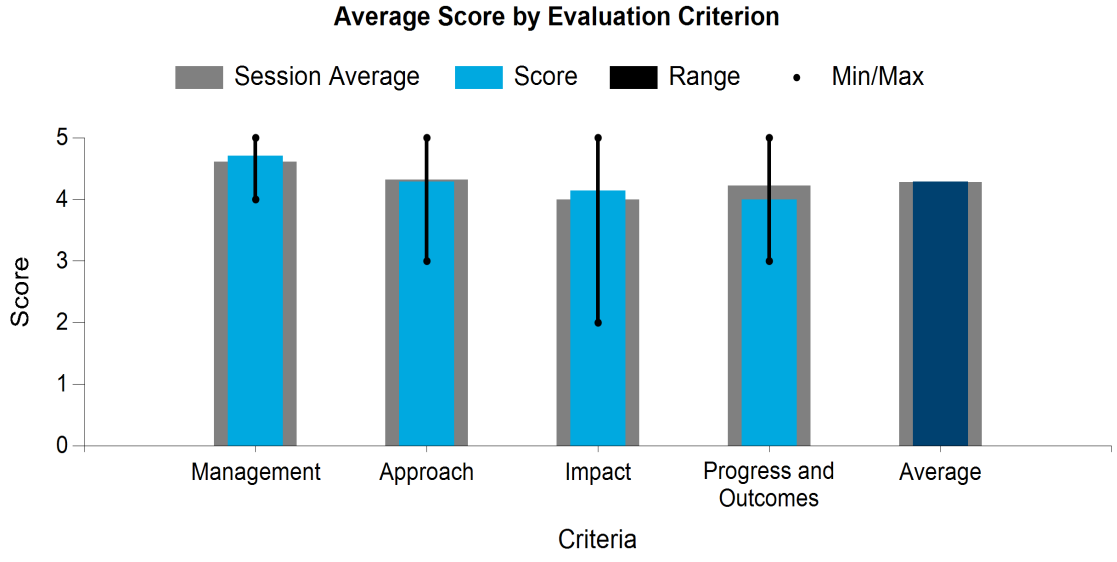
EVALUATING POTENTIAL FOR IMPACT AT SCALE

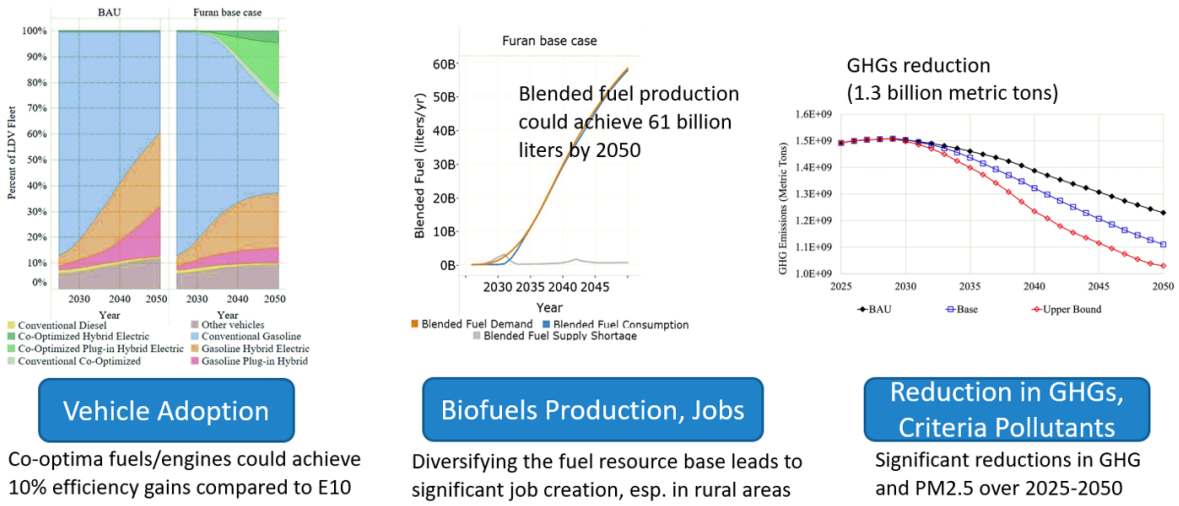
Pacific Northwest National Laboratory, National Renewable Energy Laboratory, Oak Ridge National Laboratory, Sandia National Laboratories, Argonne National Laboratory, and Idaho National Laboratory

PROJECT DESCRIPTION

WBS:	3.5.1.4-5, 3.5.1.8-10
Presenter(s):	Avantika Singh
Project Start Date:	10/01/2018
Planned Project End Date:	09/30/2021
Total DOE Funding:	$6,235,000

"What environmental and economic benefits might be realized by co-optimizing LDV and HDV transportation fuels and engines?" From discussing the selection of top bio-blendstocks that meet the scalability, economic viability, and sustainability criteria, to biofuel properties that potentially enable greater market adoption, we will discuss the integrated modeling tools that were developed to estimate advantages of deploying Co-Optima technology for the LDV and HDV sectors along with their environmental and socioeconomic implications. Key outcomes are: (1) Refinery impact analysis indicates that high-octane, high-sensitivity fuels (boosted spark ignition and multimode bio-blendstocks) and low-sulfur, high-cetane fuels (MCCI) could be valuable to refiners. (2) Coupled LCA model development shows the decrease in refinery emissions and criteria pollutants. (3) The efficiency increase with Co-Optima fuels and engine combination is the largest driver for LDV adoption, and the reduction in aftertreatment costs is the key factor for HDV adoption. (4) Integrated benefits analysis demonstrates better air quality impacts and an increase in domestic job growth. Overall, this project summarizes the potential benefits that can be achieved by the widescale deployment of advancements made in Co-Optima.





Estimating Co-Optima's potential impact at scale using furan as an example of Light-Duty biofuel.

Photo courtesy of PNNL, NREL, ORNL, SNL, ANL, INL

COMMENTS

- Management: Risks are identified and mitigated. A clearer calling out of a feedback loop and type of information from refinery integration to the other teams (especially fuel production teams and SPR investigating desirable fuel properties) would be beneficial, if it is not already ongoing and strong.

  Approach: The approach to assessing the value of biofuels at scale is well implemented. Expanding the consideration to more specifically look at biofuel producers (which may not be the refiners) and not only to the refineries would be helpful. Expanding the consideration from refinery benefits to a hypothetical biofuel producer selling Co-Optima blendstock to a refinery for blending would be worthwhile of the envelope assessing value.

  Impact: Informing BETO of promising bio-blendstocks and their adoption at scale is important to continue to allow funding to be directed toward the most promising options while not stifling early-phase/high-risk projects pointed toward options that would be a good fit for infrastructure if successful.

  Progress and outcomes: Significant progress has been made using several sophisticated models. Additional context around some results would be helpful to understand why certain otherwise seemingly excellent options have slow adoption in the marketplace. For example, if the isobutanol break-even price at a 10% blend is less than ethanol (slide 25), a description of what is holding back the adoption of isobutanol over ethanol would be valuable and could address whether it is a matter of regulatory issues, a cost of entry for adoption, or a lack of supply (or other). Another example regarding vehicle adoption: Descriptions around how the ethanol base case starting in 2030 is different from current ethanol penetration are required. Consider comparisons to the introduction of the ethanol fuel blend of 85% (E85) and vehicles from several years ago and associated vehicle adoption rates as a method to exercise these models to compare against a real case and assess any differences that might arise as an opportunity to refine the models.

- While reviewing some of the projects, I had a common complaint of having only a limited perception of the impact at the scale of the specific technology being reviewed. That was probably not completely fair because each project is carried out under the larger Co-Optima umbrella. The scalability issue can be dealt with in a more general fashion by looking at all the projects comparatively, as was done in this work. The oil refinery industry's impact is well described, and the mitigation of possible hydrogen (H_2) demand is a critical outcome of great relevance. What limits the project from achieving the best scores on impact and progress and outcome is the lack of detail—even if not at the same level—on the other side of the industry, in particular the supply of bio-based feedstock and integration with the biorefining industry.

- The goal of this work is to estimate the benefits of scaling up by using refinery linear programming modeling tools as well as vehicle penetration and scenario models. The team has a strong management approach, with more than 20 researchers spanning the national labs, including a team lead and deputy. The meeting frequency resembles the strong engagement and interaction philosophy permeating throughout the Co-Optima teams. The team has a practical approach looking at optimized refinery models using Aspen PIMS with a variety of reputable inputs—e.g., the U.S. Energy Information Administration, IHS Markit, ASSERT, ASTM, the Automotive Deployment Options Projection Tool (ADOPT), the Petroleum Refinery Life Cycle Inventory Model (PRELIM), GREET, and volatile organic compounds calculations. The Process Industry Model-LCA spreadsheet tool should be published and made available to the public. All of these tools enable the refinery impact to be evaluated. The additional tools available to the Co-Optima team will advance the SOA for refinery long- and short-term operation planning. This team understands how this work will strengthen BETO's pursuit of its goals by providing realistic scenarios that include incremental improvements in engine efficiency, emissions reductions, and jobs. The team continues to release results in reports; peer-reviewed journals; and interactions with the American Petroleum Institute, the U.S. Environmental Protection Agency, and the National Biodiesel Board. Some of the results were not surprising, such as the impact of blending alcohols into gasoline. The sensitivity as a function of blend ratio was interesting. The higher RON still requires more push from the reformer and alkylation units, so the justification of more capacity can become challenging. Reduced aftertreatment was a powerful result for automotive OEMs. This also provides opportunities for new aftertreatment devices that serve other functions. Fuel economy, performance, and reduction in costs should help drive penetration. The impact of electrification is a question remaining in the penetration scenarios. The argument for significant improvements in emissions reduction is a major result for BETO and VTO. The hybrid vehicle scenario seems to be more of a realistic bridging technology scenario, even within the HDV sector. This option could be bolstered in future scenario analysis.

- The management team, management approach, and structure are significantly strong. Major risks have been appropriately addressed. The approach to the assessment of refinery impact, vehicle adoption, and economy-wide impact is important to determine the potential of the overall impact of the Co-Optima work. The analysis of sector-wide economic impact is important to understand, and the wholistic approach being taken to determine this is commendable. It is significant for refineries to know the overall economic impact and optimum blend, and this project has delivered the right information for refineries to make informed decisions. The prediction of market penetration and the reduction in GHG emissions is impressive and shows the impact this project could have in the long term.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. The pillar focus of the potential impact at scale was to answer the foundational question of what will work in the real world with a specific look at

refinery benefits, vehicle adoption, and economy-wide benefits. Initially, it was unclear why some of this was not tied into the TEA work. The presentation references the tools used for the refinery analysis, vehicle adoption, and economy-wide benefits as well as some output from the effort; however, it was not straightforward what pragmatic insights could be derived from the analysis. For example, what do refineries or industry stakeholders say about the modeling results or market acceptability of the Co-Optima solutions? Do they agree that these results will lead to increased market adoption and penetration as the modeling suggests? The biggest hurdle that I see for penetration of Co-Optima fuels into the market is the basic question of how competitive and value-driven they will be in a future electrified transportation system with less demand for crude and potentially lower fuel prices. The impact of future electrification on fuel price was alluded to but not further elaborated. Another pragmatic question is whether any fuel pathways could potentially allow for the removal or reduction of aftertreatment system costs, and if so, would there be enough fuel volume across pathways to create a market fuel specification to allow for a market shift in aftertreatment removal or reduction? There appear to be extensive analytics results from the effort, each of which perhaps contains the details if explored further.

- The presentation did not clearly present the key market takeaways from the viewpoint of the refiners or industry. One example to illustrate this was the reduced need for hydrotreatment due to the lower sulfur content of bio-blendstocks. It was hard to tell the value of that in terms of dollars and cents to the refiner and how impactful this would be. The market acceptability and ability to meet aggregate fuel demand for the MCCI market under a common market fuel performance specification with diverse fuel pathways across the Co-Optima projects were also unclear. Even if one fuel pathway was able to reduce particulate matter, it was unclear whether there would be enough of that specific fuel pathway to satisfy a market or market segment. There will also likely be a comingling of fuels in the market unless the industry adopts a dedicated fuel specification for different vehicles, which seems unlikely given how the market currently operates. From a market viewpoint, equivalent drop-in fuel replacements are needed. This is really a broader thematic question for Co-Optima: How will this ultimately translate to the fuel mixture in the tank of a real-world vehicle? Which benefits from these studies will translate to end use? Can you reduce aftertreatment on all vehicles if only a portion of the fuel pathways supplying the market show a lower sooting propensity?

- The team did interesting and important work to deploy SOA Aspen PIMS and linear programming refinery modeling tools to estimate the potential benefits of Co-Optima technologies if adopted at scale. A review of $/bbl break-even values and optimal blend levels showed that the high RON and cetane number of bio-blendstocks would be key drivers of their value to refiners, along with life-cycle GHG reductions. Risk mitigation strategies included working with the Co-Optima Fuel Property Team for additional measurements and engaging the Advanced Engine Development Team and industry partners to explore a range of key parameters and perform sensitivity analyses.

- This project provides an extremely valuable analytical component to the Co-Optima team. Incorporating a refinery impact analysis provides a more nuanced view of the economic and sustainability implications of various bio-blendstocks. The additional integrated benefits analysis of economy-wide benefits is valuable to assess wider-scale benefits of co-optimization; however, this area of analysis poses a risk of redundancy or inconsistency if it is siloed from the rest of DOE's modeling tools that examine feedstock supply and bioenergy market interactions. Because of the insight provided by the refinery impact analysis, it could be helpful for this team to work more closely with the Co-Optima TEA and LCA team to incorporate their findings on the refinery value and performance of bio-blendstocks with the TEA cost analysis of the products identified. (Note for PIs: This was an excellent presentation. I was concerned about the modeling of large-scale bio-blendstock production and adoption—e.g., the 60 billion-liter assessment for furans. Are these assessments consistent with other feedstock availability and modeling efforts done within DOE? Does this assessment of blended fuels consider feedstock availability and supply costs while still outcompeting other vehicle and fuel technologies?)

PI RESPONSE TO REVIEWER COMMENTS

- We thank the committee for a thorough review and the thoughtful questions and comments. Also, the team is thankful to the reviewers for their recognition of the key achievements of the analysis project, such as the PIMS LCA tool; the refinery benefits in reducing hydrotreatment severity; and the reduced cost of aftertreatment devices in HDV vehicles considering the major industry trends in electrification and decarbonization needs. We address specific comments as follows:

  A. On the comment on linkages with the TEA work, the integrated analysis leverages the information from TEA/LCA (production costs/environmental impacts) of biofuels to evaluate other critical factors that would affect market adoption. These critical factors include refinery blending/value to refineries; vehicle adoption; and sector-wide environmental and socioeconomic benefits, including domestic job growth.

  B. Our modeling tools, particularly the Biomass Scenario Model (BSM) and ADOPT (vehicle adoption) are calibrated and validated frequently—and they are consistently deployed in other DOE efforts.

  C. Related to the pragmatism in the real world, BSM has been calibrated across all feedstock market parameters (feedstock prices, production levels, land allocations) and crops, adjusting the model to approximate the U.S. Department of Agriculture's annual baseline and long-term crop forecasts by tuning the model's internal market signals. ADOPT is the SOA tool for projecting the evolution of the vehicle fleet, and it is used by VTO and the Hydrogen and Fuel Cells Technologies Office. The model matched the real-world vehicle sales data several times in the last decade to predict electric and hybridized trains' sales, which currently comprise less than 5% of the fleet.

  D. Regarding the impact of future electrification, this is being considered in the current modeling scenarios. We have considered the impact on refineries as they adjust product slates to make more diesel fuel in the future (predicted by the U.S. Energy Information Administration and ADOPT) and hybridization and electrification in the vehicle market. The results are being compiled, and the key findings will be explained in upcoming publications.

  E. The comment on quantifying the dollar and cents value of reduced hydrotreatment at a refinery is well taken. One of our approaches measures the break-even value of a biofuel (the maximum price that a refinery would be willing to pay) to quantify the value to a refiner, as shown in the results. Other approaches, such as differences in refinery gross margins, could be alternatively considered by blending biofuels.

  F. The suggestion on the identification of the biofuel supply potential is much appreciated and currently underway based on resource assessment of terrestrial biomass, yellow and brown greases/oils, algae, and waste sludge and manure. This will be discussed in the upcoming TEA/LCA publication for MCCI and multimode bio-blendstocks.

  G. The comment on the potential viability of a Co-Optima fuel mixture in the gas tank of a real-world vehicle is assessed through material compatibility testing (by the Co-Optima Fuel Properties team). Additional infrastructure compatibility studies for biofuels are performed within the BETO Strategic Analysis platform. Co-Optima team members are part of the ASTM committee working on the certification of high-octane, high-sensitivity fuels for market acceptance, and some of the fuels are already eligible for blending into gasoline and diesel.

  H. Biofuel feedstock availability and supply costs analysis currently underway are consistent with other BETO efforts leveraging other resource assessment studies within the BETO portfolio (such as the billion-ton study and the feedstock consortium) Additionally, BSM models consider the

realistic rate of biorefinery construction each year based on the heuristics of the biorefinery construction for cellulosic ethanol, for example.

I. For the broader Co-Optima question, and which benefits will translate to end use, eventually, the market adoption is contingent on the availability of better-performing co-optimized fuels and vehicle engines in the market. This is an overarching assumption in the analysis. Many such options will be offered by biofuel producers, refinery stakeholders, and OEMs; therefore, our goal is to perform a comprehensive analysis to make the benefits and the risks of the Co-Optima technologies well known to all stakeholders.

STRUCTURE-PROPERTY-PROCESSING RELATIONSHIPS FOR BIO-BLENDSTOCK IDENTIFICATION

Pacific Northwest National Laboratory, National Renewable Energy Laboratory, Oak Ridge National Laboratory, Sandia National Laboratories, Lawrence Berkeley National Laboratory, Los Alamos National Laboratory, and Idaho National Laboratory

PROJECT DESCRIPTION

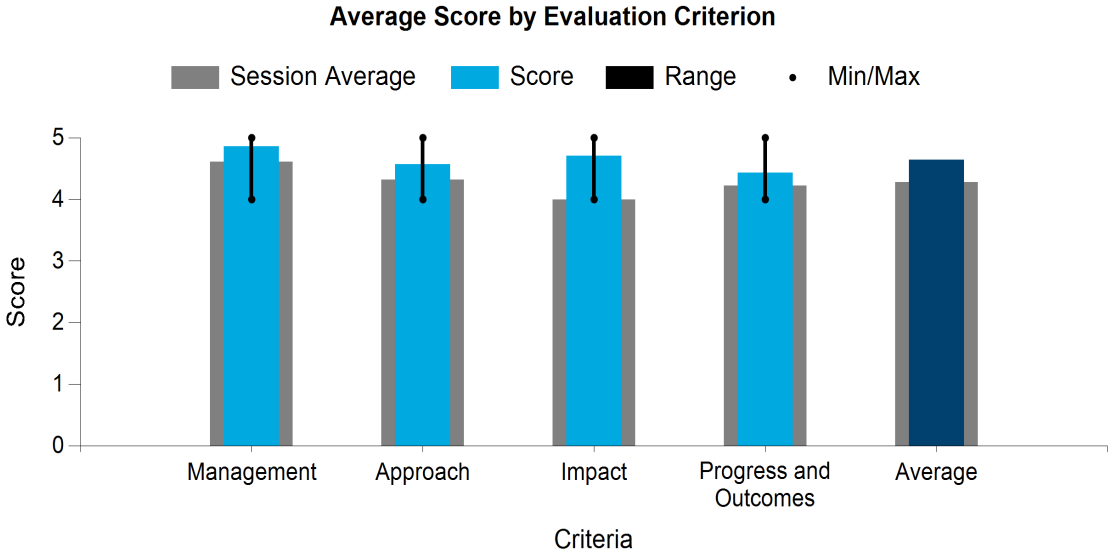
WBS:	3.5.1.5-11
Presenter(s):	Vanessa Dagle
Project Start Date:	10/01/2018
Planned Project End Date:	09/30/2021
Total DOE Funding:	$12,015,000

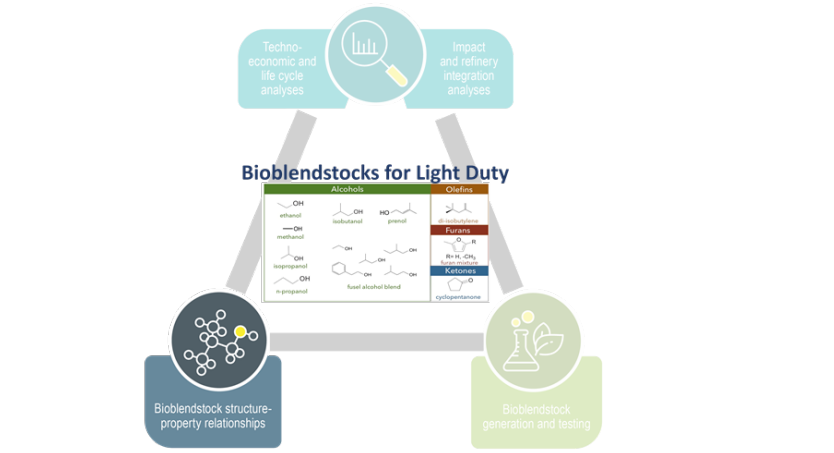
The Co-Optima program uses SPRs to identify candidate bio-blendstocks. We do so by establishing relationships between the chemical structure of bio-blendstocks and the physical properties and combustion behavior that are most important in internal combustion engines. We create these SPRs by (1) evaluating chemical families and a range of structural variants using published data and new and existing predictive tools and (2) determining the relationships that confer certain properties to given structures. We can thereby broadly evaluate whether a chemical family and specific examples are suitable for a given combustion mode. This is done using high-throughput computational tools (theoretical chemistry, machine learning, and mathematical models) complemented by experimental tools for validation.

Key outcomes:

- Established important chemical families, identified multiple bio-blendstocks for both LDV and MDV/HDV engines, and supported the Co-Optima Bio-Blendstock Generation, Characterization, and Analysis efforts
- Expanded the development of SPR tools, methodologies, and understanding of how structure affects properties that can be applied beyond biofuels to better understand how structure impacts thermophysical and combustion properties.

Identifying performance-advantaged biofuel candidates helps increase the bio-blendstock value proposition.





Structure-Property-Relationship tools helped identified bioblendstocks with performance-advantage properties for both light duty and medium/ heavy duty vehicles

Photo courtesy of PNNL, NREL, ORNL, SNL, LBNL, LANL, INL

COMMENTS

- Linking chemical structure to properties is something I have always found extremely useful, even if many times the insight is only directional and qualitative. This project tackles a particularly complex set of performance characteristics, some of which may not be fully understood *a priori*, so I appreciate the complexity and the risks involved. I found the results very compelling and encouraging, and I believe the project has clearly significant technical and scientific impacts. I found the project to be the weakest on the commercialization opportunity and the tie-in with existing or potential bio-feedstock and associated conversion processes. Nonetheless, I rated the project on the previous category because I realize that other projects within Co-Optima have focused on that. I commend the development of tools to allow

third parties to independently evaluate molecules. Although I believe that it is unlikely that we will ever design a fuel molecule *ab initio*, even initial screening of possible bio-based compounds for a subset of critical properties can accelerate the work of researchers investigating new bio-feedstock-based processes.

- Management: The project implementation and strategy plan are defined. Interplays with other portions of Co-Optima are described. Risks are defined with mitigation strategies. Triaging the most important fuel properties as the engine teams decipher critical properties in advanced combustion strategies and how to measure them is a critical step that I well recognized for being called out.

  Approach: The development of computational tools with experimental validation will lead to future breakthroughs when rigorously performed against newly proposed fuels. Test blended mixtures as often as possible with associated computational model development to avoid false positives associated with single compounds or simplified mixtures. I also suggest assessing poorly performing (or anticipated poorly performing) compounds and mixtures to ensure that computational models are robust. In other words, exercise the models with good and bad compounds/mixtures to ensure they can differentiate between good and bad. Ongoing discussions with engine teams are critical, and BETO project interactions with VTO engine teams post-Co-Optima are strongly encouraged.

  Impact: The publicly available models and information developed by this team are potentially some of Co-Optima's longest lasting impacts to the biofuels community. Interties to BETO programs are critical for the success of the office. Continue to employ Co-Optima-developed tools to answer the question of which compounds/mixtures should we be making and to challenge new ideas and PIs to think critically about their proposals to decipher new ways to make desirable fuels, not only fuels that will burn.

  Outcome: There are excellent examples of improving the understanding between the BBG&T team and the SPR teams. Continue to develop characterization methods that can robustly describe complex mixtures.

- The goal here is to identify bio-blendstocks with enhanced fuel properties. The SPR team seeks information from several Co-Optima projects as part of the management strategy (i.e., engine/fuel properties, blendstock generation, analysis) to achieve this goal. The team is organized with two project leads and includes national labs and several universities. Third-party certification labs and well-utilized institutes such as the Southwest Research Institute could be potential collaborators/advisors to this work. Two critical risks were named: schedule delays and the inability to model real fuel blend interactions. The mitigation involved applying more manpower resources to improve the schedule and more experimental validation to capture interaction bonuses. Both mitigation actions are quite acceptable. The key end-of-project milestone is to identify fuel-engine combinations that increase fuel economy by 35% for LDV and 4% for HDV over the 2015 baseline. A clear and comprehensive communication plan was provided on slide 5, with more than 16 formal scheduled meetings occurring every month across the team. This is ample communication. There is no direct industry engagement on this project or industry advisory board at this stage. The SPR project brings more of an advantage than the SOA—which are the classic refinery-based molecular management methods, additive screening methods to generate OEM specifications, or industry consortium methods (i.e., Coordinating Research Council)—because it involves a workflow where most of the coarse candidate screening is done computationally. The fine screening happens experimentally with the validation work to confirm certain properties monitored by standard refereed methods. This approach will potentially lead to new fuel blendstocks because it relies on evaluating properties that are common across many ignition modes. The group has already proven that it can identify fuel candidates.

  The team has made good progress publishing and making tools available to the public (e.g., cetane number, octane number, sooting potential, and NMR). The latter achievement is quite useful to all of the

stakeholders involved in fuel design. There is an opportunity to provide plots/visualizations that show the fundamental functional groups in various combinations and how those combinations impact various properties. Such analysis could denote optimized sweet spots on these diagrams for traditional fuel blends that have worked in the past (e.g., hydrocarbons, alcohols, and ethers). More examples should be shown like those shown on slides 17 (cetane number versus POMEs) and 18 (YSI versus alkyl chain length and oxy-alkyl density) that illustrate classes being broken down into functional group arrays with actual property correlations. This is the heart of the project. New modeling tools were provided correlating flame speed, heat release, and cold-flow properties. The computational tool predicted more than 25 compounds with YSI <100 and more than 37 compounds with cetane number >40. It seems like there is an opportunity for even more fundamental descriptors to increase the granularity of the analysis by incorporating a free energy minimization tool to get the resting geometry. One branched long-chain alkane, two ethers, and four dioxolane compounds were identified computationally and verified experimentally for passing Tier 1 property specifications. This was a good result and another opportunity for third-party inspection labs to verify the slate of distillate property testing. The team should clarify whether ULSD or Tier III gasoline carrier fluids are being used to determine properties in real fungible situations or whether these are neat validation experiments. Twenty compounds with RON >98 and S >8 were identified, and NMR chemometric models were developed. The rapid compression experiments helped determine lower branched long-chain alkenes as target molecules for increasing phi sensitivity. This was an important experimental result as well.

- The management of the program is strong, and assessing the impact of changes in species is the right fit. Overall, the work on screening hundreds of species by combined computational and experimental tools and selecting a few with the help of novel approaches is a strong method. The approach of assessing the impact of a slight structural change on cetane number, YSI, RON, and MON is impactful. The work could lead to faster and cheaper screening of species for the right properties. The impact of this work could be further increased if multispecies are investigated and analyzed. The project is helping to achieve DOE's and BETO's goals.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The structure and property relationship team receives feedback from the other research pillars, such as the blendstock generation and testing activities to experimentally validate results and refine predictive tools. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. The SPR approach focused on the foundational question of which fuel options work best. Their approach of using high-throughput computational predictive tools coupled with experimental methods and machine learning was a significant enabler in the rapid identification of new fuel targets with desired and novel properties. The identification on the LDV side of RON and sensitivity as better determinants of performance in spark-ignition-boosted engines was very interesting. Other novel properties of single-component fuels were assessed; however, they were not assessed with the predicted performance of blended fuels, which would enhance the approach in order to better translate results to finished fuels in engines if tools could be further developed. Still, the SPR approach allowed for rapid learning across a wide array of fuel properties.

  One question I had was whether the SPR effort started with what can be made from biomass or which fuel properties were desired from combustion and then backed into how it can be made from biomass. I believe this was discussed, and it was the latter, but I would like to confirm. The use of high-throughput screening, predictive computational tools, and machine learning and the resulting SPR tools in Co-Optima are a very valuable output of the research and should continue to be developed. The identification of RON and phi sensitivity as an important factor in LDV combustion, which could enable

the use of such fuels in both boosted spark ignition and ACI, was something new that came from Co-Optima. It would be interesting to know if an analog property could be identified for cetane. It seemed that for MDV/HDV performance, there was less opportunity to enhance engine efficiency through structure property relationships; however, the ability to potentially impact sooting propensity remains promising if properties that translate to blended fuels can be identified. The SPR tools and fuel property database were impactful in accelerating the Co-Optima effort and in identifying new performance-advantaged biofuels; however, the predicted performance of certain fuel properties, such as sooting propensity in single-component mixtures, did not seem to translate into later-stage results. The SPR effort does not appear to look in depth at blended fuels with commercial-grade diesel. There was some exploration of this in other pillars of Co-Optima. This question of how blended fuel properties differ from single-component mixtures is a common theme across Co-Optima and should be addressed more directly within the SPR effort. It would be interesting to know if there was an expectation that properties would be identified that could achieve the goal of 4% gains for MDV/HDV efficiency either directly from combustion efficiency or by reduction from downstream aftertreatment penalties. Also, the SPR effort does not specifically look at the commercialization barriers on the components, and it was unclear how that information was fed back and incorporated into the fuel property database.

- This project serves an extremely valuable purpose within the technology area, and it appears to be tightly integrated with other projects and contributes directly to the program's overall strategy. Using a novel software, this team's outputs provide important strategic direction for other projects on which bio-blendstocks may have the most favorable properties.

- This team did impressive work on developing high-throughput computational tools for assessing the relationship between phi sensitivity and functional group structure, and they conducted experimental validation of SPRs for more than 80 blendstocks. Their approach was based on hypotheses related to a defined suite of chemistries and functional groups, and it included collaboration with other Co-Optima teams and universities to reduce scoping and outcome risks. In the end, the team pulled forward seven blendstocks that meet all Tier 1 MCCI criteria, which ensures relevance to OEM R&D and provides key inputs to next steps by the BBG&T team.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their insights and strong endorsement of SPR activities conducted within Co-Optima. We are pleased that the reviewers found that the SPR project contributes directly to the overall program and that the project has clear significant technical and scientific impact. We appreciate the recommendation to further develop SPR tools regarding blends/complex mixtures. Developing SPR tools for single components was a required first step, and we have made progress toward developing SPR tools for blends. A few examples of SPRs established for blends are described as follows: We have demonstrated alcohol structure relationships with RON and sensitivity for mixtures of alcohols. We have established the relationship between phi sensitivity and iso-olefins for on-site-produced complex mixtures of iso-olefins containing approximately 100 compounds. We have determined the olefinic alcohol structure and RON relationship for 0%–50% blends. In addition, we already have begun to develop SPR tools for complex mixtures (e.g., an NMR tool), and we agree that expanding and upgrading the tools to allow further advancement of our understanding of SPRs of blends will enable better translation of data and results to finished fuels. We thank the reviewer for the question about whether we used the SPRs to identify blendstocks with improved properties and then found a way to make them via biomass or vice versa. The answer is that we have done both. We noted several cases in the presentations where we used SPRs to identify new blendstocks and then worked out ways to make them from biomass, including the iso-olefins mixtures, the olefinic alcohols, and the POMEs.

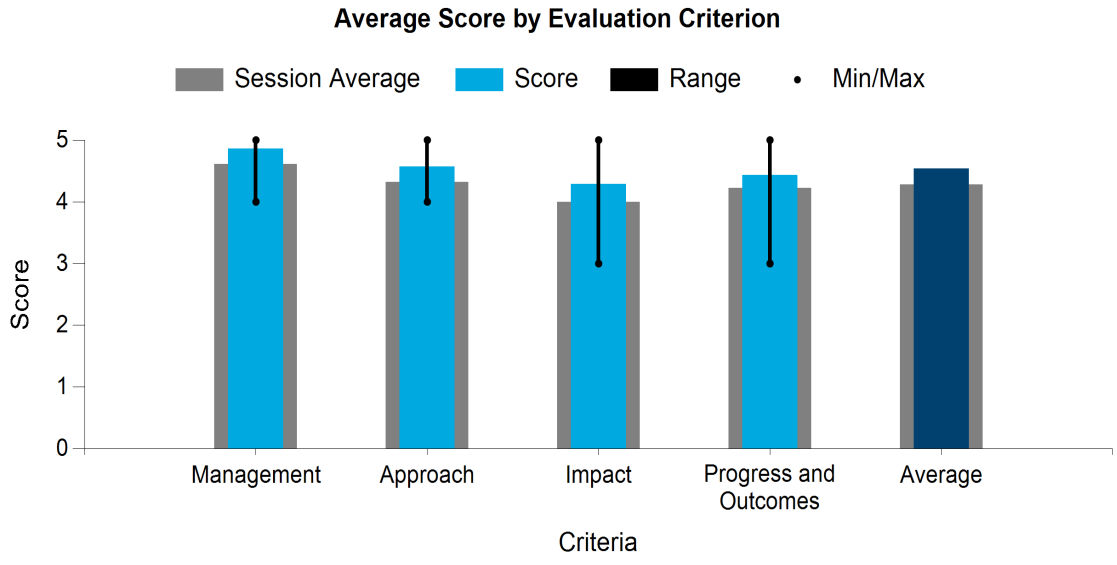
HIGH-PERFORMANCE BIO-BLENDSTOCK GENERATION

Pacific Northwest National Laboratory, National Renewable Energy Laboratory, Oak Ridge National Laboratory, Sandia National Laboratories, Lawrence Berkeley National Laboratory, Los Alamos National Laboratory, and Idaho National Laboratory

PROJECT DESCRIPTION

WBS:	3.5.1.5-11a
Presenter(s):	Derek Vardon
Project Start Date:	10/01/2018
Planned Project End Date:	09/30/2021
Total DOE Funding:	$9,430,000

The BBG&T effort is part of the Co-Optima initiative that is working to identify blendstocks derived from biomass that can provide critical fuel properties and assess their benefits and barriers to adoption. BBG&T develops new bio-blendstocks for LDV and HDV to validate their fuel properties and production viability. We select promising bio-blendstocks based on fuel SPRs, and we provide conversion data for bio-blendstock TEA and LCA. Promising bio-blendstocks that pass our tiered screening process are then scaled for handoff to the Co-Optima engine testing team. Our efforts are coordinated with the BETO Core Conversion program to ensure a focus on production pathways that leverage the latest conversion tools and knowledge base. This project creates impact by de-risking novel bio-blendstocks and advancing public knowledge that informs the biofuel community and BETO program. To date, this multiyear effort has generated novel and promising bio-blendstocks that address both LDV and HDV applications. Key outcomes include (1) confirming the favorable autoignition properties of bio-based olefins with engine testing; (2) validating favorable fuel properties for waste-derived HDV bio-blendstocks, (3) demonstrating ethers that show favorable fuel properties, polymer compatibility, and storage stability; and (4) delivering gallons of bio-blendstocks to quantify engine emissions improvements. Collectively, this project will help ensure the success of Co-Optima's mission for enhancing and understanding the value of blendstocks that can be obtained from biomass.



COMMENTS

- I have no issue with the technical results, which are quite good and show good progress and outcomes. My middle-of-the-range scoring for impact is because I could not sense whether any of the successful molecules have, on the very front end, viable supply chains (bio-based feedstocks) and processes, or if they are not viable today, under which conditions they might be. Incidentally, I believe that successful molecules under this analysis could get a boost in viability. I realize that this is not the primary focus of this project and that those aspects are specifically addressed in other projects under the Co-Optima initiative. Nonetheless, this connection, which is critical to possible commercial impact, is weaker than I would have liked, or at least it is weaker in the way it is presented.

- Management: Communication and planning with other BETO teams are well described. Risks are defined with mitigations. In addition to the risks identified on engine performance and those associated with TEA/LCA modeling, consider risks around compound stability, especially with ethers forming peroxides or hydrolysis. Traditional/standard ASTM fuel stability tests may not always be the most appropriate for those tests.

  Approach: The BBG&T approach to identify and create new compounds and mixtures for testing is innovative and will push the SOA. As expected, many process routes from biomass feedstocks through compounds/mixtures that are desired for fuels may require multiple steps. Breakthroughs are required in feedstock production and/or thermochemistry/biochemistry conversion pathways to consolidate steps and decrease costs. BETO should consider funding these pathways under Conversion in the future.

  Impact: BBG&T projects serve as an excellent example of how the learnings of all of Co-Optima on which fuels engines "want" can be applied to designing and thinking critically toward the production of the "right" compounds and mixtures. Breakthroughs are required for the economic feasibility of several pathways. Specialized stability tests, such as those for peroxides, should also be considered, in addition to the ongoing work on polymer compatibility and standard ASTM tests to improve opportunities for market adoption.

  Progress and outcomes: BBG&T has made excellent progress toward their goals. BETO should consider continued funding of promising technologies under the Conversion or other technology areas as appropriate. As MDV/HDV ACI fuel property requirements continue to develop and gain understanding, a BBG&T-like effort in the future should be considered to address new ways to produce fuels for advanced combustion regimes.

- The goal of the BBG&T project is to generate new bio-blendstock material to complete Tier 2 and Tier 3 property testing at gallon quantities. The team identified a couple risks, mainly around ensuring that blendstocks can be derived from an existing BETO pathway and that no surprises arise later that could derail any candidate blendstock. Both risks can be mitigated by maintaining good communication and engagement along with regular informs among the BETO and Co-Optima teams, in particular analysis. The management structure is similar to the SPR project, with a significant number of monthly meetings and interactions. The team interacts with an industry advisory board, presents at the American Chemical Society, and will participate in the upcoming Co-Optima webinars. The SOA approach for designing new fuel blends at a higher scale will be advanced with the BBG&T project because it covers classes of molecules across several tiers of testing and analysis. This will undoubtedly lead to new fuel compositions that connect back to BETO's 2022 verification pathway objectives. By testing at the Tier 3 level, the project is ensuring that a fuel composition may have commercial potential. This is essentially the end-user application for the new fuel composition. The team understands how the BBG&T project will add value to the public, industrial, and academic communities by establishing cooperative research and development agreements, influencing BETO pathway R&D, expanding the public database,

publishing papers and patents, and making presentations. The project has already partnered with at least five companies to develop new fuels. Although the nature of these relationships and the expectation of outcomes were not disclosed, this is an important step in the right direction.

The team was able to show that combining 10 vol % iso-olefins from bio-derived butene oligomerization with a neat, subgrade fuel could result in improved octane number at minimum commercial grade (87 octane number) and sensitivity. This is not new information for fuel blenders optimizing octane number. The newer information applies mostly to sensitivity. The project was able to scale up HTL bio-oil to gallon quantities from sludge and algae that passed Tier 1 specifications. The project provided important results on polymer compatibility for the dioxolane fuel class. Stability testing will be key to this new class of fuel candidates, especially when generating large quantities of material. It is quite possible that a bio-derived antioxidant could be synthesized or extracted from one of the existing BETO pathways to help stabilize these fuels or the team could develop an oxidation stability analytical method that is more suitable for these types of mixtures. The project generated n-butoxyheptane in continuous liter-scale quantities versus the original, small-batch synthesis techniques. One of the best results showed eight HDV blendstocks undergoing emissions testing for soot and NOx production relative to a certified diesel. The BBG&T blends all performed better than the reference diesel. With this chemistry, the team should continue to monitor any changes in viscosity with butyl functionalization in POMES. This could possibly impact the common rail performance. The team deserves recognition on the polymer compatibility work and emissions work with HDVs. This is very important in the final product development.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. The BBG&T effort bridges two foundational questions of which fuel options work best and which will work in the real world. The BBG&T approach also filters for two risk items. The first is the BBG&T scope, which includes testing complex bio-derived mixtures and not only model fuel components. The second is that it applies an initial threshold on TEA/LCA on fuel pathways that may not be promising from the perspective of cost per GGE or GHG reductions. The $5.50/GGE is still high relative to commercial targets, but I understand this is only an initial threshold for fuel pathways that may not yet be fully costed down but that show a trajectory for achieving BETO targets. Being able to produce suitable quantities of bio-derived fuels for bench and engine testing is an important aspect of the BBG&T team, particularly given that many of these fuel pathways do not have existing scalable processes to produce or procure fuels. The impact of the program has been to advance public knowledge through the fuel property database. The effort has also fed results back into BETO's conversion program. There was industry engagement and dissemination of results to stakeholders through a number of publications and presentations. The BBG&T effort worked on a number of different fuel pathways, ranging from iso-olefins for LDV; to HTL bio-oils; to isoalkanes from food waste and dioxolanes, which were a new class of fuel oxygenate. It was not clear, however, from the presentation how these pathways were settled upon and how results from this were tied specifically into the other pillars. For example, did the SPR effort lead to these specific BBG&T efforts, which, in turn, were scaled up, tested, and fed to the refinery group? Or did the TEA/LCA analysis identify the primary focus of the BBG&T work? The thread on the POME work—from SPR, to bio-blendstock generation, to fuel property testing—was clear. In other cases, the starting point was prior BETO work. If you could clarify how specific fuel pathways of interest were chosen in the BBG&T pillar, that would be helpful.

- The production of bio-blendstock and the validation of their properties is an important step toward achieving the goals of Co-Optima. The point that the team has managed to achieve the gallons production level is remarkable and indirectly indicated the scalability of the work being done. The addition of polymer compatibility testing is good to ensure that the fuel systems' compatibility is maintained. Storage stability will improve the market uptake of the blends, and testing as a 20%–30% blend shows immediate application potential of the bio-blendstocks being proposed in the program. Overall, the approach of ensuring that compatibility and toxicity issues are evaluated would help in ensuring that outcomes are relevant for the industry. The progress and outcomes of the work are impactful and would assist in achieving DOE's and BETO's goals.

- This project fills a critical role in the work stream of the Co-Optima Technology Area and is therefore well integrated into the program's overall goals. This team fills a crucial and necessary niche as the intermediary between the SRP team that identifies molecules of interest and other teams that can then characterize and test bio-blendstocks. This team's screening approach is very useful for the validation of previously modeled bio-blendstock properties; this mitigates overarching technology area risks and helps ensure that research and testing capacity elsewhere in the program is focused on the most promising products. This project has also built up the knowledge base on bio-blendstocks for partners within DOE and outside of it, as evidenced by the high degree of collaboration with BETO, university partners, and industry.

- This team made great progress in assessing the fuel properties of upgraded HTL bio-oils and butyric acid polymers for use in MCCI scenarios. The team also provided important data for the next steps in TEA/LCA work for these blendstocks as well as POMEs and other ethers. Key management, outreach, and de-risking steps included close coordination with other national labs; generation of multiple peer-reviewed publications; and regular engagement with Cummins, Virent, and other industry partners.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their time and effort, and we appreciate the overall comment that the BBG&T effort provides key value to the BETO program by providing samples for novel fuel evaluation, scale-up, and infrastructure testing, as well as handing off conversion data for cost and LCA that can inform ongoing and future efforts. We agree with the reviewer's comment that the front-end feedstock supply chain is a key consideration for any new bio-blendstock. That scope of analysis typically falls within the domain of the Co-Optima ASSERT team, which is why it was not strongly highlighted in this presentation. We agree that future presentations would benefit from further emphasis of this critical linkage for each bio-blendstock. We appreciate the reviewer's comment that each bio-blendstock would benefit from additional background rationale regarding why it was chosen. To the reviewer's comment, blendstocks were chosen based on both SPR and TEA/LCA inputs, depending on the level of background information and fuel chemistry questions of interest that varied for a given pathway. As specific examples, based on SPR, we systemically varied the POME end groups to understand the impact on addressing water solubility limits and cetane number. For TEA/LCA, that motivated our approach to look at wet waste-derived HTL and food waste-derived volatile fatty acids to address feedstock cost and the potential for landfill methane diversion. Multiple reviewers commented on the importance and value of the polymer compatibility and oxidation stability work performed with new bio-blendstocks, which we appreciate. We also take note of the recommendation to consider pathways to biomass-derived antioxidants for future work.

BIOPRODUCTION AND EVALUATION OF RENEWABLE BUTYL ACETATE AS A DESIRABLE BIO-BLENDSTOCK FOR DIESEL FUEL

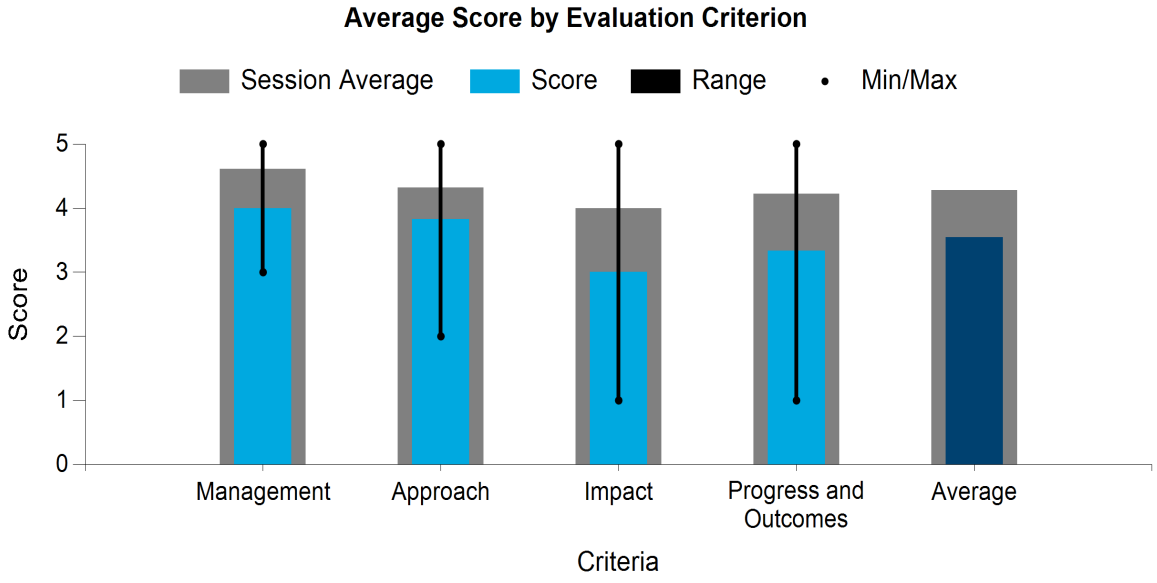
Auburn University

PROJECT DESCRIPTION

WBS:	Auburn
Presenter(s):	Yi Wang
Project Start Date:	10/01/2018
Planned Project End Date:	12/31/2022
Total DOE Funding:	$1,999,990

Butyl acetate has various merits for being used as a bio-blendstock for petroleum fuels, particularly for MCCI applications. Butyl acetate's high flash point makes it safe for operation as a diesel additive, whereas the low freezing point can help improve cold-flow properties of diesel with minimal impact on cetane number and the mixture's heat of combustion. Also, as an oxygenated fuel, butyl acetate may lower the sooting propensity of a butyl acetate/diesel mixture. In this project, we target developing an integrated bioprocess for efficient butyl acetate production through the systematic genome engineering of *Clostridium* and the design of MicroNiche Engineering Technology (MNE)-based cell immobilization process. Meanwhile, we evaluate butyl acetate as a desirable bio-blendstock for diesel through fundamental combustion and full-scale engine testing.

Our engineered strain can produce 24.7 g/L butyl acetate in a batch fermentation process, which is approximately 2,900 times higher than the previously reported butyl acetate production through the biological route. We developed MNE biocatalysts that can provide consistently high butyl acetate yields, enhance toxicity resistance, and offer storage capabilities. The combustion experiments showed favorable impacts on butyl acetate ignition, liftoff length, sooting behavior, and burning rates. TEA and LCA results demonstrated the economic feasibility and environmental sustainability of our bioprocess, even based on the current butyl acetate production level. This project would provide strong evidence for producing bio-based butyl acetate to be used as a desirable blendstock for diesel. The developed technology could lead to an enabling industrial bioprocess in support of the bioeconomy.



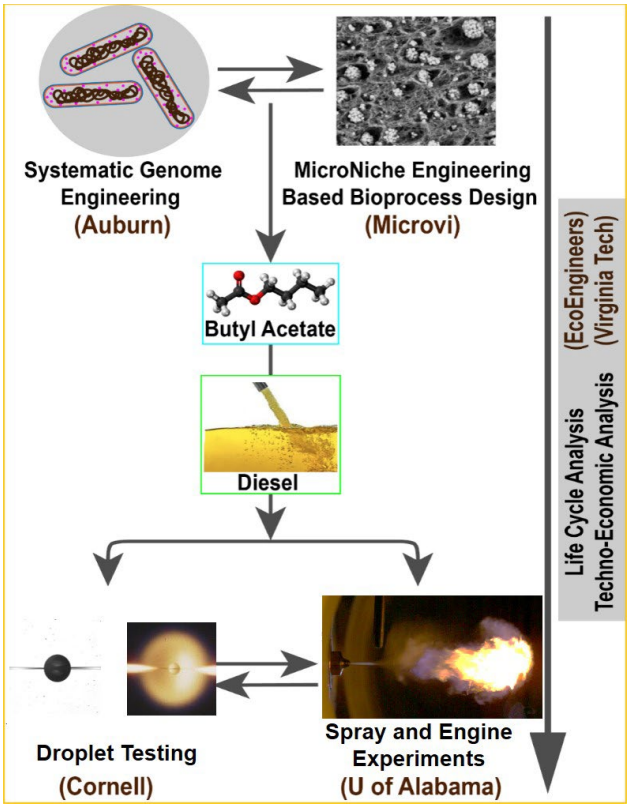


Photo courtesy of Auburn University

COMMENTS

- This team shows impressive work on iterative systematic genome engineering to produce massive improvements in the *Clostridium* yield for butyl acetate. There is a clear description of the management workflow and responsibilities between Co-PIs and other DOE collaborators. There is a clear rationale for the droplet combustion experiments to produce quantitative results when only very small quantities of blendstocks are available. TEA and LCA results have demonstrated that feasibility and environmental targets can be met based on the current butyl acetate yields and corn stover hydrolysate feedstock. The team is pursuing high-impact journal publications as well as patent application and preliminary licensing discussions.

- Management: The outline of the management and tasks are clear. Project risks are mentioned throughout the slides with mitigations. The team ensures clear and consistent progress with subteams and gathers external feedback to stay on track.

  Approach: The strain and process development all appear to be cutting edge; however, butyl acetate would appear to be eliminated as a diesel fuel blendstock by Co-Optima's own criteria. Per the SPRs for the bio-blendstock identification presentation on day 1, slide 19 lists MCCI fuel property criteria, including a flash point >52°C, which precludes butyl acetate's flash point at 22°C. Butyl acetate's autoignition properties were previously investigated by Co-Optima as a spark ignition fuel and published in McCormick et al. (https://doi.org/10.4271/2017-01-0868). The cetane number of butyl acetate is approximately 10, as estimated by RON/cetane number correlation, as found in the SAE paper, and this is significantly less than the threshold of >= 40 criterion developed by Co-Optima for screening diesel

fuels. Regarding engine testing, droplet combustion studies are useful and can extrapolate to engine performance and support kinetic model development, as stated. Engine testing appears to be planned per the supplemental slides. Although ultrapure (>99.9%) butyl acetate may be quite expensive, commercial suppliers online, such as Sigma-Aldrich, list butyl acetate at levels of >99.7% on the order of $100–$150/L. This grade of purity should be a suitable economic alternative for engine blending tests to provide the multi-liter quantities required. These model compound blending tests would supplement any engine testing requirements in anticipation of creating the 10.5 L of 95% butyl acetate for go/no-go No. 2 diesel fuel and are suggested to begin in the near term.

Impact: The development of the strain using SOA tools and dissemination via publications is valuable. Butyl acetate commercialization as a diesel fuel blend will likely be challenging due to the relatively low flash point and low cetane number, as noted.

Progress: Progress toward the project goals of organism development and fuel droplet testing is progressing well, even during COVID. Given the availability of butyl acetate as a model compound, fuel properties (e.g., cetane number, energy density, flash point) and engine tests with butyl acetate blended in a standard No. 2 diesel fuel should commence as soon as feasible to assess the suitability of butyl acetates as a diesel blendstock and any associated blend-level limitations due to diminished properties below those specified in ASTM D975 above certain concentrations.

- The goal of the project is to produce butyl acetate as a 10% treat rate fuel additive by genome engineering of solventogenic *Clostridia*, avoiding self-toxicity using MNE biocatalysts. Further, commercial butyl acetate will be blended with ULSD to study fundamental combustion and engine experiments as well as TEA/LCA. There were no direct quantitative metrics attached to these goals. The roles for the six major project tasks were outlined with dedicated project management responsibilities, monthly conference calls, and interactions with other relevant Co-Optima and BETO teams. There were no discussions regarding risks and mitigation plans. The team has the pioneered development of a subclass of proven clustered regularly interspaced short palindromic repeat techniques (Cas 9) for strain modification and has published their understanding of genetic engineering, which is the dominant technical gap hindering breakthrough rates for butyl acetate. The approach will be to adapt these techniques to solventogenic *Clostridia* for producing butyl acetate directly via batch extractive fermentation; followed by parallel screening for optimizing MNE biocatalyst composition; and, finally, combustion testing at the droplet, spray, and engine scales. The MNE concept and platform integrating materials science as biocatalyst polymer composites seem to be innovative. The droplet experiments allow surrogate butyl acetate blends to be examined at small nanoliter volumes and scales to spray flames. This appears to push the SOA for elucidating combustion kinetic routes from other approaches, such as shock tubes and flow reactors, due to the boundary constraints. The droplet experiments can be further validated through imaging techniques as part of the constant pressure flow rig.

  The team understands that their research allows for a new fuel product opportunity within the fermentative pathways across BETO and informs the strain/metabolic engineering community with important observations. The fuel and engine communities will have fundamental combustion information on the butyl acetate-based fuel blends, and several publications and patents have already been authored. The most significant impact will be the cost-effective purification and scale-up of butyl acetate. The team made significant progress in strain engineering toward the first go/no-go this summer. Metabolic fluxes for acetyl-Coenzyme A were improved, doubling the product alcohol titer in the presence of various promotors. By removing parts of prophage genetic sections and embedding the ATF1 enzyme in the cell walls, organisms could produce butyl acetate in concentrations almost five times higher. It seems like there are some real optimization opportunities with the MNE biocatalyst composite work to tailor and tune product distribution at higher initial titers than 5 g/L. The initial work looks very promising. It will be important to keep the stability and reliability of these systems high; there are already commercial applications and service conditions for MNE-biocatalysts that have demonstrated time on stream over

several years. The droplet combustion experiments could not detect any differences between the commercial and actual genome engineered butyl acetate-derived fuel blends. The team also saw no major difference in the 50% butyl acetate/heptane blends for visual soot formation.

- The matrixed management structure of Co-Optima—which includes a board of directors, leadership team, steering committee, EAB, project manager, and technical team leads—is an effective arrangement to manage such a large and complex program with concurrent but related research happening across different pillars within the Co-Optima lab program and funded projects. It enables simultaneous R&D versus linear and iterative programs, allowing for a more compressed program with faster learning. The program also identifies risks and mitigation strategies. The management structure allows for communication and collaboration across related projects. For funded university projects, the overall matrixed management framework for Co-Optima with liaison to a Co-Optima advisor helps connect the funded projects to the broader Co-Optima initiative and allows for information sharing across the other projects.

  The development of integrated bioprocess for efficient butyl acetate production through strain development by systematic genome engineering and process development using biocatalyst composites (MNE technology or MNE biocatalysts) make this research interesting as a novel strain development and process technology, which leads to ways to mitigate toxicity from butyl acetate and increase yield that, in general, could also be applicable to other biological production processes of fuels and chemicals. So, the impact of the research is potentially multifaceted; however, the motivation for selecting butyl acetate as a fuel pathway to begin with was a bit unclear. It was clear that butyl acetate had certain desirable properties, such as a high flash point, low freezing point, and lower sooting potential based on the molecule; however, the presentation stated that there is a lack of direct evidence concerning the combustion performance of butyl acetate as a bio-blendstock for diesel. Was there any published or prior research on butyl acetate for use in diesel combustion, or was this a first effort? And if this is a first effort, could the research have started first with droplet and spray combustion evaluations of commercially available butyl acetate before any work was done on the biological approach? Some context on why butyl acetate was selected as a diesel fuel substitute would be helpful as well as some clarifications if any combustion work was done in advance with commercial butyl acetate before proceeding with the biological approach. Although the yields on a g/L basis were demonstrated to increase through strain engineering, and the tolerance to butyl acetate toxicity was higher on MNE biocatalysts than suspended cells, relatively speaking, the process streams would be fairly dilute with respect to butyl acetate and may be fairly water intensive and energy intensive from a separations perspective. Were these considerations factored into the TEA and LCA? The bench data suggest that synthetic and commercial butyl acetate perform similarly on droplet combustion testing, and spray combustion work was performed to characterize some fuel performance behavior; however, fuel performance in actual engines using butyl acetate does not appear to be part of the research. It would be helpful to understand how the research will ultimately be used to tie into the acceptability of butyl acetate as a bio-blendstock in commercial diesel.

- This is a well-designed project that tightly integrates a variety of different work streams. The team has done a good job of identifying the biochemical pathway for producing butyl acetate and tailoring the microorganism through genetic engineering to improve the effectiveness of the conversion process. The feedstock selection and conversion process appears to be well integrated with GREET and suggests continued GHG reductions based on the efficiency gains from the choice of microorganism and catalysts. It would be helpful to clarify the intended next steps to improve the yield to reach the intended goal of 0.4 g of butyl acetate per g of sugar necessary to reach the cost and GHG reduction goals for this project. (Note for PI: To what extent is n-butyl acetate constrained by blend limits as with fatty-acid methyl esters? Should blending constraints be noted as a risk factor for the adoption of the bio-blendstock?)

- This project makes a stronger case for bio-based butyl acetate as a chemical commodity than a diesel blendstock. I believe the PIs had some great science; however, the notion of a large amount of butyl acetate as a diesel fuel substitute is not credible. The projected economics indicated a competitive product in the chemical markets, but they are not convincing sustainable economics as a fuel blendstock, especially because the reference was a model fuel rather than actual diesel fuel. The project has merits, and the scientific execution is good, but I feel it is a poor fit for Co-Optima. My poor scoring reflects the latter, not the former.

PI RESPONSE TO REVIEWER COMMENTS

- The reviewer is correct about diesel. Our work is progressing in stages, with the common approach of testing a bio-blendstock mixture with simpler blends (surrogate fuels) before proceeding to the complex petroleum fuel—in this case, diesel. For the droplet and spray experiments, the tasks involve butyl acetate plus heptane as a basic mixture and, finally, butyl acetate plus diesel. We will test blends of butyl acetate with diesel in a later stage in a multicylinder engine. These plans are in progress. Engine studies are part of the project in the later stage. Results of the project will provide the information needed to make such decisions about adopting butyl acetate as a potential commercial additive to diesel. Note that the spray/engine studies are performed at near end-use test conditions, and results from them will determine butyl acetate's acceptability in a commercial context. Regarding the comment that butyl acetate is "a poor fit for Co-Optima," actually, as mentioned by another reviewer's comments, there is *not* a clear demonstration for or against butyl acetate in diesel blend in the literature, which justifies the value of our project. We are unaware of any published research on butyl acetate combustion by itself or blended with any petroleum fuel such as diesel; however, there have been a few studies on butyl acetate in the context of catalytic burning and decomposition. And butyl acetate properties have been considered in the context of a wide range of other potential blendstocks for oxygenate blending (BOBs) (i.e., McCormick et al).

  A reviewer also commented that there were no direct quantitative metrics attached to some of our goals. We have clear metrics for the butyl acetate production tasks. For tasks related to combustion and engine testing, we measure the soot production in the test chamber for different fuels using two-color pyrometry to quantify the effects of butyl acetate blends. We will use the following diagnostics to quantify soot concentration in engine testing, including the AVL Smoke Meter for filter smoke number, the TSI Engine Exhaust Particle Sizer spectrometer for particulate size distribution, and the Sierra system for particulate sampling and weight measurement.

  Risks of the research were inherent in the main tasks: butyl acetate production and at scale, and butyl acetate ignition and burning. Within each of these broad tasks exists a wide range of mitigation strategies. For example, if we were unable to ignite butyl acetate by spark discharge in droplet experiments, we would have explored alternative means, such as autoignition in a high-temperature gas. And our production capabilities have significantly improved during the project, from our initial grade of butyl acetate containing approximately 5% byproducts to our most recent efforts in which the impurity has been reduced to approximately 3%. Regarding the comment that "the cetane number of butyl acetate is approximately 10 estimated by RON/cetane number correlation, as found in the SAE paper, and this is significantly less than the threshold of >= 40 criterion developed by Co-Optima for screening diesel fuel," based on our communication with Co-Optima investigators in national labs, the cetane number of butyl acetate is somewhere closer to 20, but it is not conclusively established. In our initial tests, we are not seeing a significant impact to ignition, which is a metric of initial ignition and may be correlated with cetane number; however, as the flame liftoff length is increased, the mixing-induced soot reduction is likely multiplying the oxygenation effect. It needs to be strongly stated that simple cetane number-based guidance for fuel selection may not be as clear-cut in diesel engines in contrast to RON, MON, Octane Index, etc., criterion for spark ignition engines, where ignition is driven by spark. The work by McCormick does show results of butyl acetate in RON/MON tests and demonstrates minimal increased

sensitivity as a blend compound, but that result is not transferable to MCCI, in our opinion (https://doi.org/10.4271/2017-01-0868). For the target of improving butyl acetate yield to 0.4 g of butyl acetate per g of sugar, we have identified that further improvement of reducing the power availability and enhancement of the precursor availability (especially for butanol) through genome engineering of the strain would have significant contributions to further improving butyl acetate yield to our targeted metrics. In addition, the further optimization of the fermentation condition would help as well.