DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

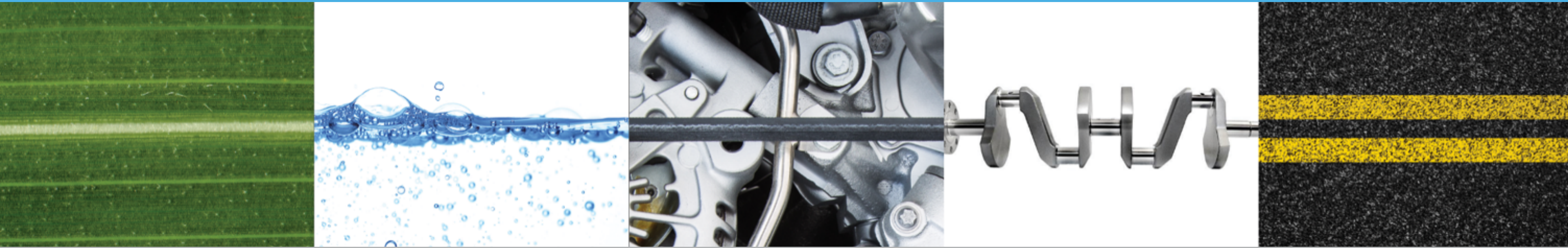
Bioblendstock Generation and Testing

March 15, 2021

Derek Vardon
National Renewable Energy Laboratory

CO-OPTIMIZATION OF FUELS & ENGINES

better fuels | better vehicles | sooner



Project Overview

What we do in Co-Optima for Bioblendstock Generation & Testing

Goal

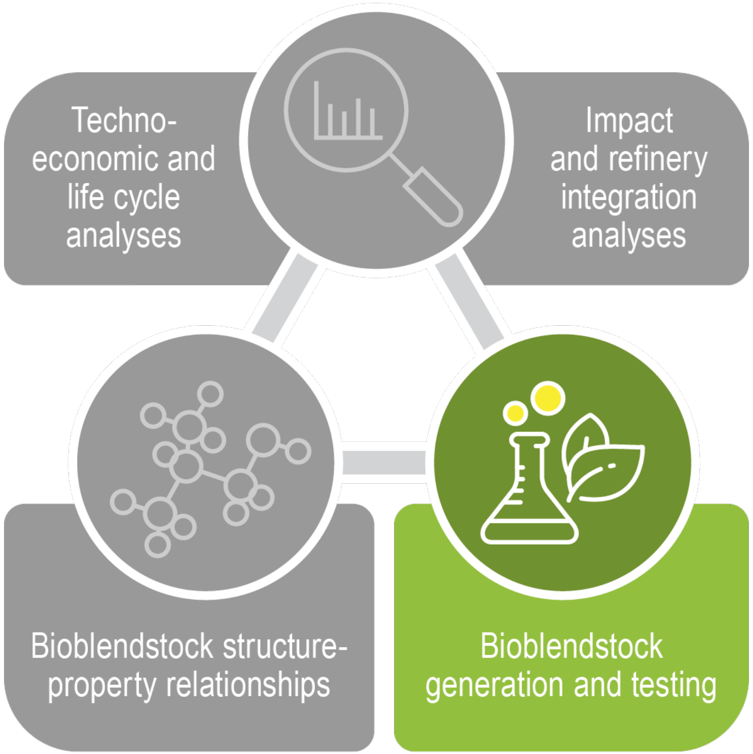
- Generate new bioblendstocks for light-duty and heavy-duty to validate their fuel properties and production viability

Approach

- Receive input from Structure Property Relationships on which bioblendstocks to generate and test. Provide conversion data to Analysis for TEA/LCA. Scale select bioblendstocks for handoff to engine team.

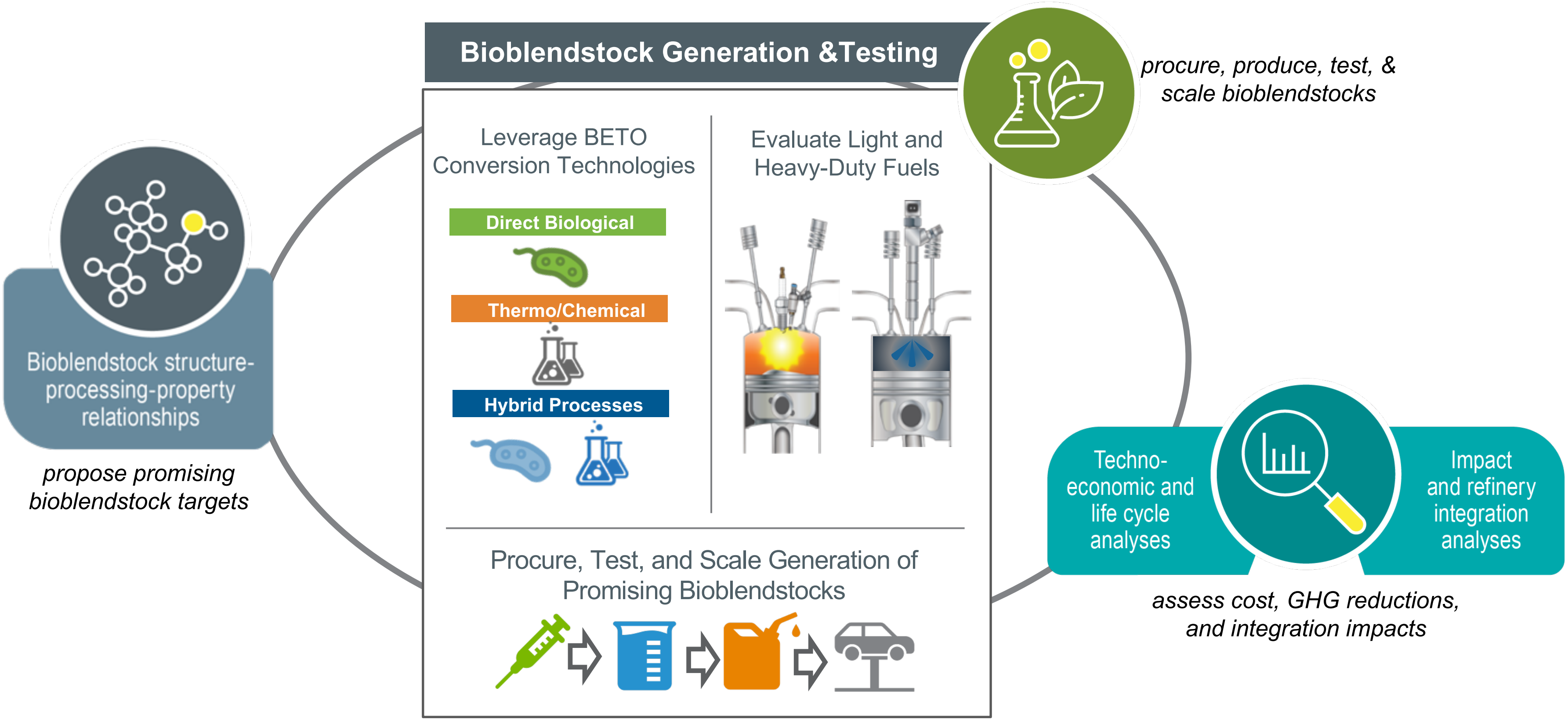
Relevance

- Supports BETO's goals to derisk new bioblendstocks that meet fuel properties, infrastructure compatibility, TEA/LCA targets, and engine performance



1. Management

BBG&T interfaces with the other Co-Optima teams to advance bioblendstocks



1. Management

BBG&T works in collaboration with 7 National Labs and 7 Universities

National Lab High Performance Fuels Teams and Task Leads

HPF Team Lead: Derek Vardon (NREL) HPF Deputy: Vanessa Dagle (PNNL)

Lab	Task Leads
Idaho National Laboratory	Magdalena Ramirez
Los Alamos National Laboratory	Cameron Moore, Andrew Sutton, Troy Semelsberger
Berkeley Lab	Eric Sundstrum, Blake Simmons, Jay Keasling, Taek Soon Lee
NREL National Renewable Energy Laboratory	Tom Foust, Dan Ruddy, Derek Vardon, Teresa Alleman
Oak Ridge National Laboratory	Todd Toops, Mike Kass
Pacific Northwest National Laboratory	Evgueni Polikaprov, Lelia Cosimbescu, Tim Bays, Vanessa Dagle, Karthi Ramasamy, Mike Thorson, Dan Gaspar
Sandia National Laboratories	Eric Monroe, Ryan Davis, John Gladden, Corey Hudson, Anthe George, Alex Landera, Joey Carlson, Bernard Nguyen

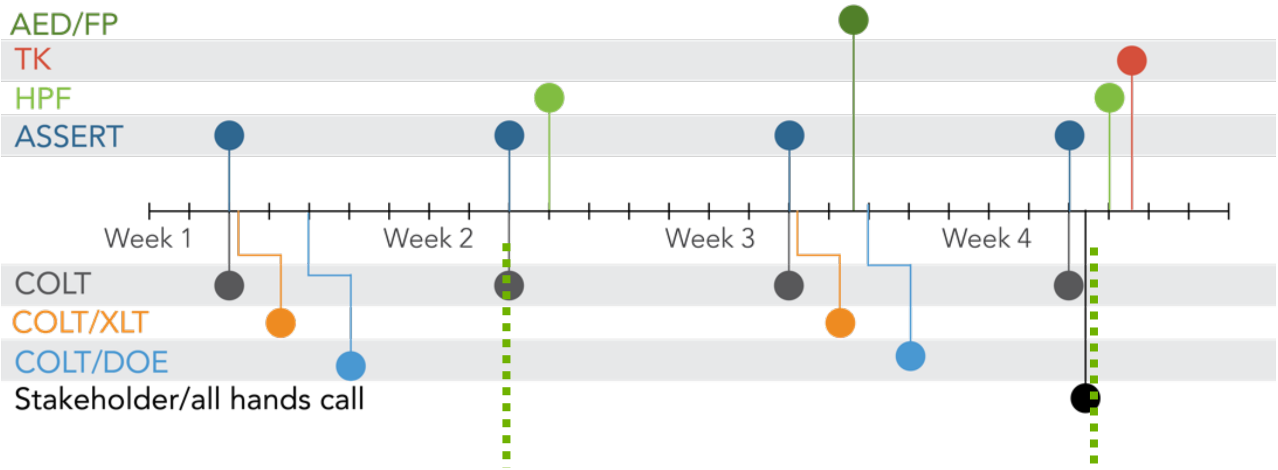
University Project Collaborators

University	Collaborator
Yale	C. McEnally
University of Central Florida	K. Ahmed
Cornell University	C. Thomas Avdisian
Alabama	A. Agrawal
University of Michigan	J. Martz
MIT	W. Green
LSU	I. Schoegl

1. Management

BBG&T participates in technical and Co-Optima wide coordination meetings

Co-Optima regularly scheduled meetings



Coordination & update meeting during "Lightning Round"

In-depth technical & industry talks during "Deep Dive"

External Stakeholders

Biannual External Advisory Board Meeting

Biannual ACS National Conference

Upcoming Co-Optima Capstone Webinars

1. Management

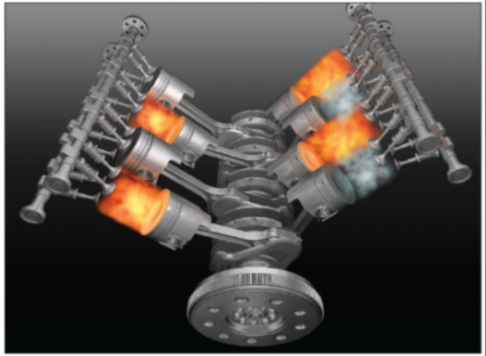
BBG&T mitigates risk when developing new bioblendstocks

BBG&T Major Risk Factors	Risk Mitigation Strategy
BBG&T confirms favorable fuel properties of model compounds and simple mixtures that do not translate to complex biomass	BBG&T work scope includes testing complex biomass-derived fuels from core BETO program and vetted Co-Optima pathways
BBG&T tests bioblendstocks that pass fuel property screening, but they are too costly, polluting, or poor-performing in engines	BBG&T supplies Analysis with conversion data to ensure cost and GHG criteria met, and sends fuels to Engine Testing team for performance validation

2. Approach

BBG&T addresses two foundational questions for Co-Optima

What fuels do engines *really* want?



What fuel options work best?

What will work in the real world?

2. Approach

BBG&T advances light and heavy-duty fuels with tiered screening and scaling

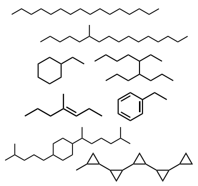
Biomass & Waste Carbon

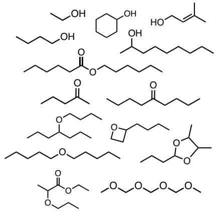
Direct Biological

Thermo/Chemical

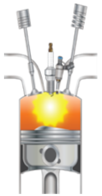
Hybrid Processes

Hydrocarbons & Oxygenates

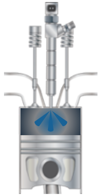




Light & Heavy-Duty Fuels



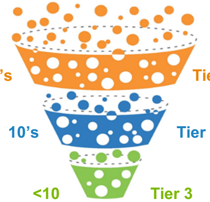
Light Duty
RON / MON / S
Energy Density
Flash / Boil / Freeze
RVP / HOV
Sooting



Heavy Duty
Cetane
Energy Density
Flash / Boil / Freeze
Water Sol
Sooting

Tiered Testing & Analysis

Biofuel Candidates | Tier Screen Level



100's — Tier 1
10's — Tier 2
<10 — Tier 3

Techno-Economic & Lifecycle Analysis

Scale from mL to multi-L

10 mL Fuel Property Screen

100 mL Tiered Screening Tests

1 Liter Polymer & Single Cylinder

Multi-Liter Engine Testing

2. Approach

BBG&T designs tasks and milestones to span chemical families and production levels

BBG&T Light Duty and Heavy-Duty Research Tasks

Select Light-Duty BBG&T Research Tasks – FY19 to Current

Alkenes	**PNNL** Iso-olefin phi sensitivity	**NREL** Auto-ignition micro kinetics	Esters	**LBNL** High sensitivity bio-esters	**SNL** Cyclic carboxylic bio-esters
Alkenols	**LBNL** Prenol hyperboosting	**LBNL** Unsaturated bio-alcohols	Mixed Oxygenates	**NREL** Lignin First Oxygenates	**SNL** Electrochemical Oxygenates
Alcohols	**PNNL** EtOH derived short chain R-OH	**NREL** Synergistic alcohol blends			

Select Heavy-Duty BBG&T Research Tasks – FY19 to Current

Alkanes	**LANL** Myrcene derivatives	**PNNL** Cylopentadiene derivatives	**SNL** Cyclopropane bioengineering	Esters	**SNL** Lactate ester derivatives
Alcohols	**PNNL** EtOH derived long chain R-OH	**LBNL** Bioderived long chain R-OH		Bio-Oils	**PNNL** HTL bio-oils for engine testing
Ethers	**LANL** Dioxolanes from BDO	**NREL** POME end group exchange	**NREL** Ethers from short acids	Scale-up	**SNL** Cyclopropane scale-up

X-Cutting

- **NREL** Toxicology and biodegrade
- **SNL** Retrosynthetic analysis
- **INL** Blendstock optimization
- **PNNL** Lubricants and oxygenates
- **ORNL** Polymer compatibility
- **PNNL** Impurities and stability impacts

Select Milestones

FY19 Q4 –Generate 100 mL of cyclopropanes via fermentation and validate fuel property predictions for cetane number

FY20 Q2 – Produce 1 gallon of upgraded HTL bio-oil and deliver to Advanced Engine team for emissions testing

FY20 Q3 – Scale production of 2 dioxolanes that meet MCCI Tier criteria and deliver 1 liter for polymer compatibility testing

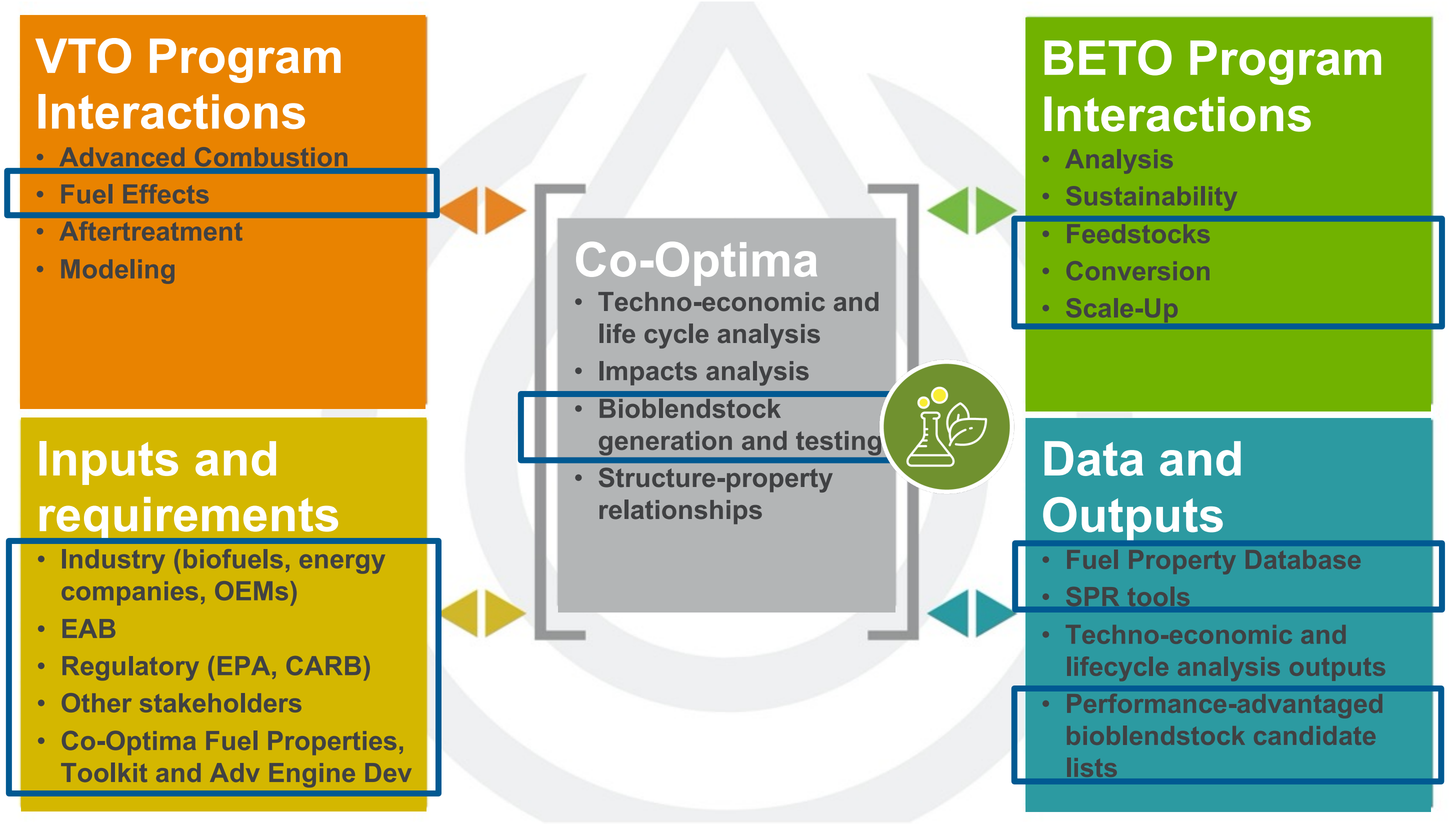
2. Approach

BBG&T employs success metrics and Go/No-Go's to measure and ensure progress

Success Metrics for Barrier	Go/No-Go Decision Points
Light-duty and heavy-duty Tiered screening criteria are used by **BBG&T** to vet current and novel bioblendstocks	Bioblendstocks that do not meet fuel property criteria are no longer pursued for further development
After screening, bioblendstocks evaluated for their potential to meet <$5.50/gge and 60% lower GHGs targets by **Analysis**	Bioblendstocks that do not meet **Analysis** TEA/LCA criteria are not pursued for multi-liter production for handoff to **Engine Team**

1. Management

BBG&T connects with the broader BETO conversion program



3. Impact

BBG&T advances emerging bioblendstocks and disseminates results

BBG&T Derisks & Validates New Biofuels

Advance public knowledge sharing fuel properties in public database and conversion results in external deliverables

Inform **BETO program** of promising bioblendstocks, scalable production methods, and low cost/GHG routes

Prioritize viable bioblendstocks for **industry** and community through fuel property data, conversion cost/GHG metrics, and joint **DFO projects**

BBG&T Shares Findings with Community

Inform public and key stakeholders in peer-reviewed journals, Co-Optima reports, public databases, conferences, and industry engagement

3. Impact

BBG&T impacts community with technical handoffs, engagement, and deliverables

University and Industry

- ✓ Measured >50 fuels saved in public database so **University Partners** could develop new fuel property prediction tools
- ✓ Handed off dioxolanes and branched ethers to **BETO Conversion Program** for further pathway R&D
- ✓ Partnered with **>5 Companies** for Co-Optima DFO call on bioblendstock development with 2 existing CRADAs

Stakeholder Engagement

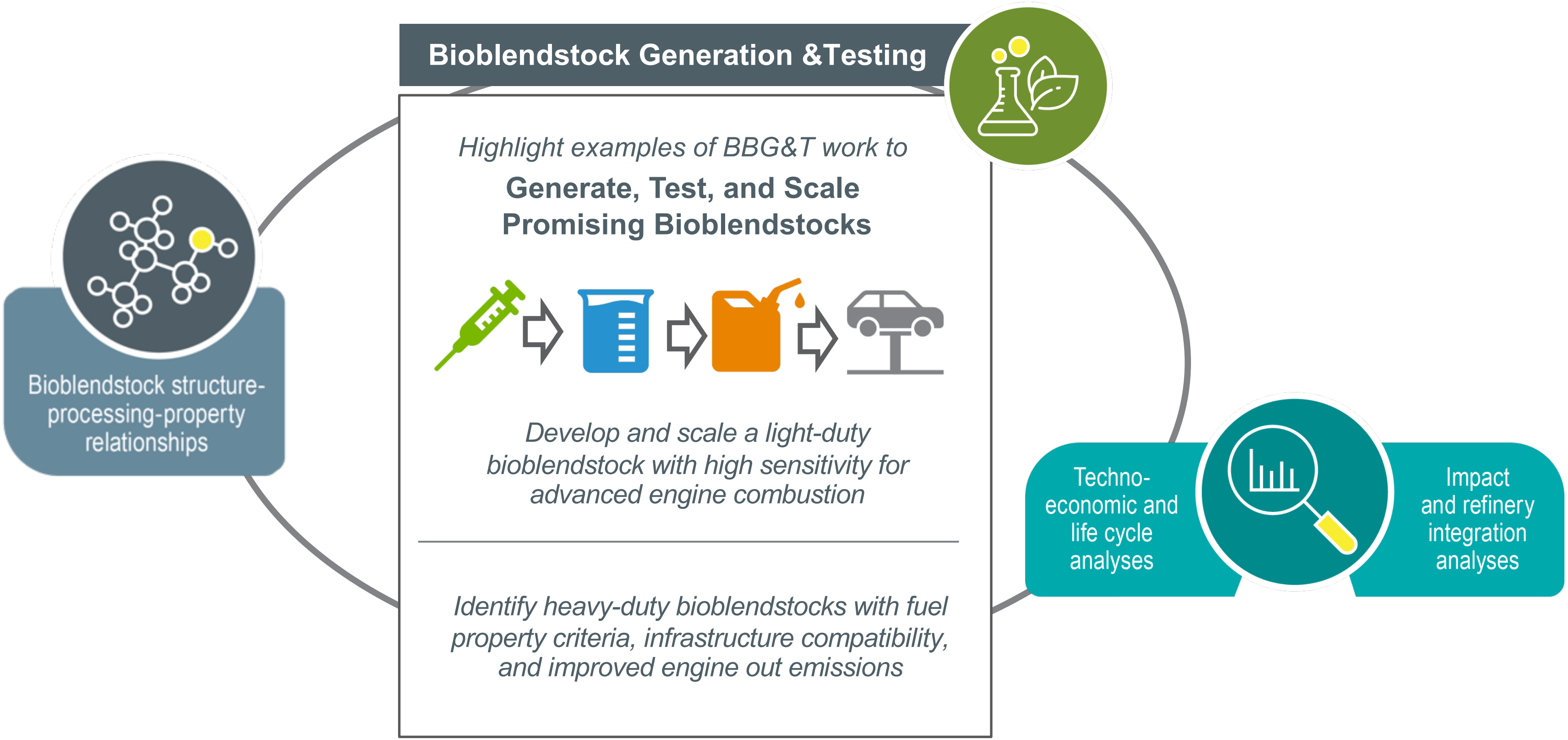
- ✓ Attend Co-Optima quarterly External Advisory Board meetings for feedback
- ✓ Conduct quarterly industry meetings (Cummins) for latest fuel and engine market trends
- ✓ Engage industry experts (Virent) and BBG&T task leads through technical panel presentations

Public Facing Deliverables

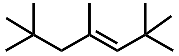
- ✓ Published **19 papers**, filed **7 patents**, and delivered numerous presentations
- ✓ Released annual Co-Optima Year in Review and “Top 10 Boosted SI Bioblendstock” reports with major findings
- ✓ Scheduled Co-Optima Capstone webinars and ACS Conference symposium to engage with community

4. Progress and Outcomes

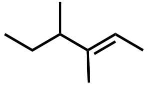
Recent BBG&T work to derisk bioblendstocks and scale for engine testing



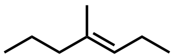
Scaled mixture of high sensitivity iso-olefins to validate engine autoignition gains



Olefin Sample A
Highly Branched (51 wt%)

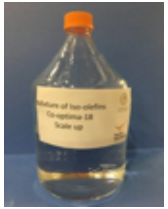


Olefin Sample B
Dimethyl Hexenes (87 wt%)



Olefin Sample C
Methyl Heptenes (74 wt%)

Co-Optima Bioblendstock Engine Testing



Light Duty	RON	MON	AKI	S
Base Fuel	86.1	83.1	84.6	3.0
100% Iso-Olefins	94.0	80.5	87.3	13.5
20 vol% Blend	89.5	83.1	86.3	6.4

Structure-Property Relationships

Determine bioderived iso-olefins can provide high octane sensitivity (RON minus MON) and phi-sensitivity (fuel-air equivalence ratio)

Bioblendstock Generation

Developed conditions and catalysts for bio-butene oligomerization to vary branching and produce gallons to validate predicted autoignition improvements

Fuel Property Testing

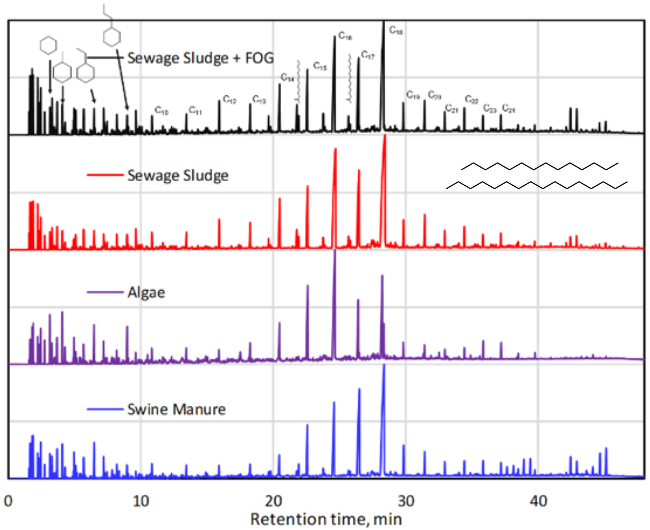
Performed engine testing with neat and 20 vol% blend of iso-olefin to confirm autoignition improvements in RON, MON, AKI, and S

Lead: Dagle, PNNL

Dagle et al. (2020) Fuel. 277, 118147

4. Progress and Outcomes

Determined which HTL bio-oil waste feedstocks meet heavy-duty fuel criteria



MCCI Bioblendstock	DCN	LHV (MJ/kg)	Flash Pt (°C)	Cloud Pt (°C)
Tier 1	**> 40**	**> 25**	**> 52**	**< 0**
HTL sludge	55 to 68	43 to 44	>55	-10 to 20
HTL algae	55 to 68	44	62	< -60
HTL wood	30	42	56	--25

Previous BETO Work

Advanced hydrothermal liquefaction (HTL) and bio-oil upgrading technology with a variety of wet waste feedstocks with low GHG

Fuel Property Testing

Confirmed upgraded HTL bio-oil fuels produced from sludge and algae meet Tier 1 criteria due to high normal paraffin content, while cycloalkanes in wood do not meet cetane cutoff

Bioblendstock Generation

Scaled production of upgraded HTL bio-oil to gallons for blending and handoff to engine testing for sooting and NOx reduction potential

Lead: Thorson, PNNL

4. Progress and Outcomes

Produced food waste mixed isoalkanes to advance previous single compound work

Previous Co-Optima Work

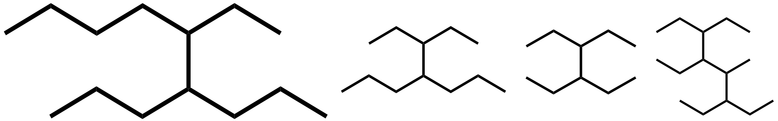
Early work produced 4-ethyl-5-propylnonane from butyric acid and confirmed single isoalkane meets MCCI Tier 1 and Tier 2 criteria

Bioblendstock Generation

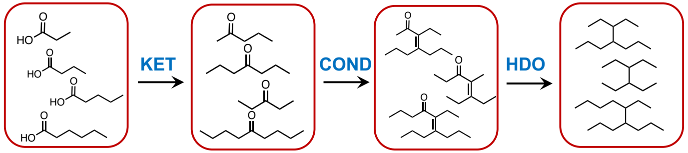
Expanded fuel production to include mixed volatile fatty acids derived from food waste with data provided to Analysis for TEA/LCA

Fuel Property Testing

Confirmed food waste-derived mixed isoalkanes also meet MCCI Tier 1 criteria with high cetane and flash point, despite varying chain lengths, with exceptional freezing point from branching



4-ethly-5-propylnonane *mixed isoalkane analogues*



Waste Derived C3-C6 VFAs → **Mixed Ketones** → **Enone Dimers** → **Mixed Isoalkanes**

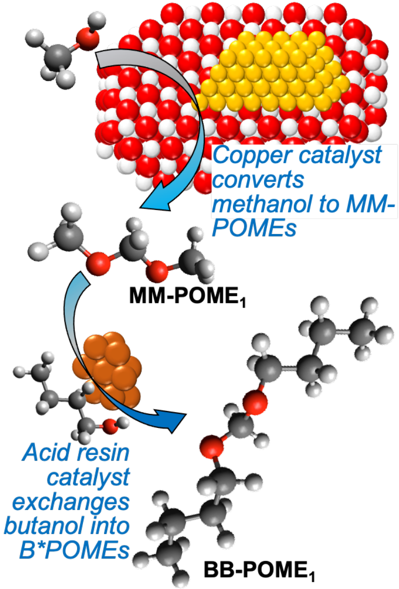
MCCI Bioblendstock	DCN	LHV (MJ/kg)	Flash Pt (° C)	YSI	Melting Pt (° C)	Boiling Pt (° C)
Tier 1	**> 40**	**> 25**	**> 52**	**< 200***	**< 0**	**< 338**
4E5PN	45	44.0	74	98	< -80	230
VFA Mix	73	44.4	62	NA	< -53	268

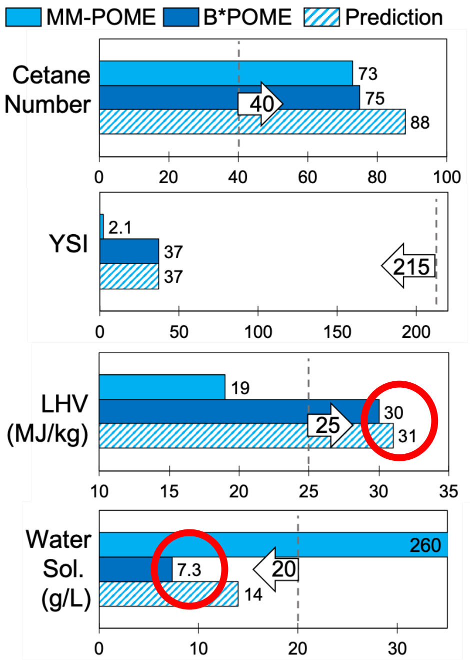
*Measured values. Fossil diesel YSI typically above 200**

Lead: Vardon, NREL *Huo et al. (2019) Green Chem. 21, 5813-5827* *Huq et al. (2021) PNAS. Accepted.*

4. Progress and Outcomes

Developed scalable end-group exchange method to improve water solubility and LHV





*B*POME = butyl-end group exchanged POME*

Structure-Property Relationships

Determined butyl-termination can address methyl-terminated POME issues of low energy density and high water solubility

Bioblendstock Generation

Developed liter-scale method for butyl end-group exchange at mild conditions with commercial catalysts to enable handoff for testing

Fuel Property Testing

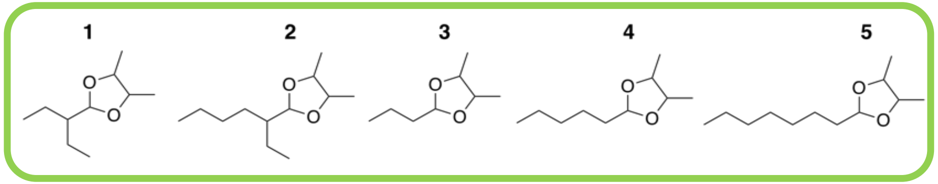
Confirmed butyl-exchanged POMEs addresses energy density and water solubility limitations, while retaining benefits of high cetane and low yield sooting index (YSI)

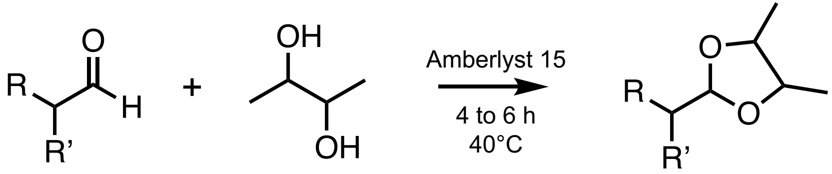
Lead: Foust & Ruddy, NREL

Arellano-Trevino et al. (2020) ACS SusChemEng. Submitted *Bartholet et al. (2020) Fuel. Submitted*

4. Progress and Outcomes

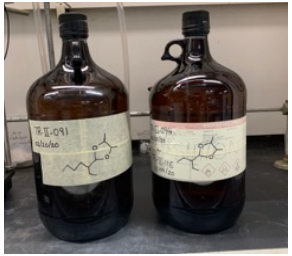
Validated polymer compatibility for dioxolanes as a new class of heavy-duty oxygenate





Compound	DCN	LHV (MJ/kg)	Flash Pt (° C)	YSI	M.P. (° C)	B.P. (° C)
Tier 1	**> 40**	**> 25**	**> 52**	**< 200***	**< 0**	**< 338**
1	45	33	54	58	< -100	174
2	64	34	58	69	< -100	184
3	33	31	43	37	< -100	161
4	48	33	70	49	< -100	177
5	69	34	80	63	< -100	188

*Measured values. Fossil diesel YSI typically above 200**



Previous Co-Optima Work

Earlier work confirmed dioxolane structures meet Tier 1 MCCI fuel property criteria

Bioblendstock Generation

Developed scalable production method to generate 4 liters each of two dioxolanes for polymer compatibility testing, with conversion data provided to Analysis for TEA/LCA

Fuel Property Testing

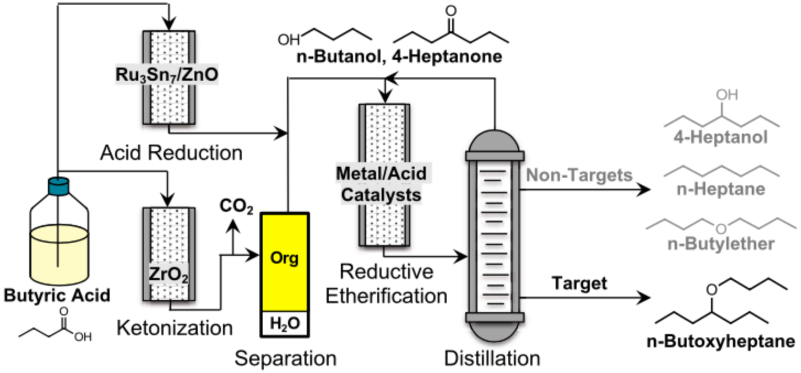
Polymer compatibility testing confirmed no issues with dioxolanes as a new class of heavy-duty oxygenate, with oxidation storage stability testing underway using additives

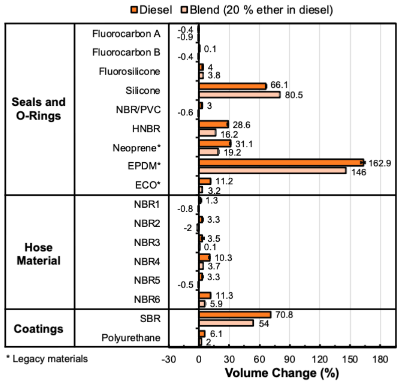
Lead: Sutton & Moore, LANL

Staples et al. (2018) Sust. Energy & Fuels. 2, 2742-2476

4. Progress and Outcomes

Confirmed polymer compatibility, blend performance, & storage stability of novel ether





4-Butoxy Heptane	DCN	LHV (MJ/kg)	Flash Pt (° C)	YSI
Tier 1	**> 40**	**> 25**	**> 52**	**< 200***
Neat	80	40	64	58
Tier 2	**> 40**	**NA**	**> 52**	**NA**
20 vol%	49	40	62	173

*Measured values. Fossil diesel YSI typically >200**

Structure-Property Relationships

Screened >40 oxygenates from C2/C4 acids that can be produced from biomass and wet waste to identify 4-butoxyheptane as a promising ether

Fuel Property Testing

Validated favorable fuel properties retained after 20 vol% blending in diesel with excellent polymer compatibility and sufficient storage stability using commercial additives

Bioblendstock Generation

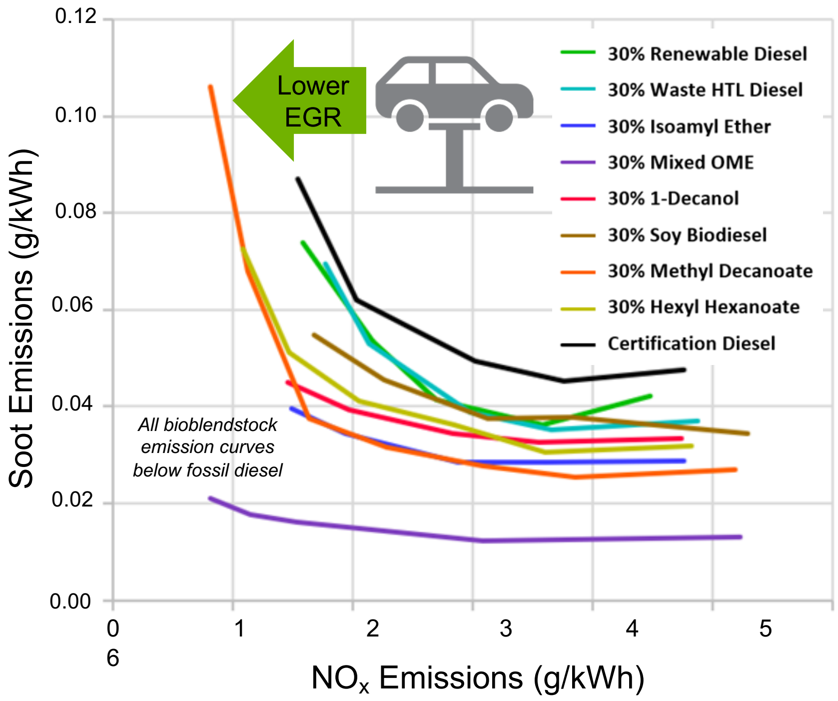
Advanced from batch to continuous liter-scale to enable Tier 1 and Tier 2 testing; provided data to Analysis for TEA/LCA and handed ethers off for combustion kinetic testing and modeling

Lead: Vardon, NREL

Huq et al. (2019) PNAS. 52, 26421-26430 *Hafenstine et al. (2020) Green Chem. 22, 4463-4472*

4. Progress and Outcomes

Quantified engine-out NO_x and soot emission reduction for heavy-duty bioblendstocks



Bioblendstock Generation

Delivered gallons of 8 heavy-duty bioblendstocks for engine testing that included biodiesel, renewable diesel, heavy-duty oxygenates (mixed OME, 1-decanol, iso-amyl ether, esters) and HTL bio-oil

Co-Optima Engine Testing

Quantified bioblendstock improvements to the soot-NOx emission trade-off curve with engine testing of novel low GHG bioblendstocks that stand to benefit emission control systems at low-load operation

Lead: Burton, NREL

4. Progress and Outcomes

BBG&T contributed to achievements of Co-Optima goals

Medium- and Heavy-Duty

Lower-cost path to reduced engine-out criteria emissions

- Procured or scaled production of 8 heavy-duty bioblendstocks to validate reduced engine-out emissions
- Provided bioblendstock conversion data to analysis for techno-economic analysis

Biofuels

Diversify resource base and increase market opportunities for biofuels

- Expanded base & validated fuel properties for waste-derived biofuels (sludge HTL, food waste VFAs)
- Partnered with industry on DFO calls and CRADAs to advance new bioblendstock routes

Crosscutting Goals

Decrease greenhouse gas emissions by at least 20% for 30% blendstock fraction

- Provided bioblendstock conversion data to for lifecycle analysis for promising light and heavy-duty fuels

5. Summary

BBG&T management, approach, impact, progress and outcomes

1. Management	• Goal to generate new bioblendstocks to validate their fuel properties and production viability • Work with Co-Optima teams for Structure Property Relationships, Analysis, & Engine Testing • Coordinate efforts for 7 National Laboratories and 7 universities
2. Approach	• Generate bioblendstocks based on Structure Property Relationships and latest conversion R&D • Test fuel properties and infrastructure compatibility with Tiered screening approach • Provide conversion data to Analysis for cost & GHG analysis, with sample handoffs to Engines Team
3. Impact	• Advance public knowledge through fuel property database and external deliverables • Inform BETO of promising bioblendstocks and generation methods for further R&D • Partnered with >6 industry members for Co-Optima DOF call to advance bioblendstocks • Engage stakeholders through reports, publications, presentations, webinars, and advisory meetings
4. Progress & Outcomes	• Confirmed favorable auto-ignition properties of biobased olefins through engine testing • Validated favorable fuel properties of waste-derived heavy-duty bioblendstocks • Demonstrated ethers show favorable fuel properties, polymer compatibility, & storage stability • Delivered gallons of 8 bioblendstocks to quantify engine emission improvements over fossil diesel

Acronyms: Bioblendstock Generation & Testing

CO-OPTIMA OVERVIEW

- **BBG&T** – Bioblendstock Generation and Testing is a research thrust within Co-Optima High Performance Fuels team
- **SPPR** – Structure Property Process Relationships is a research thrust within Co-Optima High Performance Fuels team
- **Analysis** – ASSERT team within Co-Optima handles analysis for sustainability, scale, economics, risk, and trade
- **COLT** – Co-Optima Leadership Team
- **TEA / LCA / GHG** – Techno-economic analysis / lifecycle analysis / greenhouse gas
- **GGE** – Gallon of gasoline equivalent based on energy density
- **LD / HD Bioblendstocks** – Light-duty gasoline bioblendstocks / heavy-duty diesel bioblendstocks

TECHNICAL HIGHLIGHTS

- **Boosted SI** – Boosted spark ignition for light-duty vehicles
- **MM** – Multi-mode ignition for light-duty vehicles
- **RON / MON**– Research octane number / motor octane number
- **AKI / S** – Octane sensitivity (RON minus MON) / anti-knock index (average of RON and MON)
- **HOV / RPV** – Heat of Vaporization / Reid Vapor Pressure
- **MCCI** – Mixing controlled compression ignition for heavy-duty vehicles
- **CN / DCN** – Cetane number / derived cetane number from auto-ignition measurements
- **LHV** – Lower heating value
- **YSI** – Yield sooting index
- **M.P. / B.P** – Melting point / boiling point
- **MM-POME / B-POME** – Methyl terminated polyoxymethylene dimethyl ether / butyl-exchanged POME

Quad Chart Overview – Bioblendstock Generation & Testing

Timeline

- Phase 1: October 1, 2015 to September 30, 2018
- Phase 2: October 1, 2019 to September 30, 2021

	FY20	Active Project
DOE Funding	$2,890,000	$9,430,000

Partner Labs

- INL, LANL, LBNL, NREL, ORNL, PNNL, SNL

Barriers addressed

19ADO-E: Co-development of Fuels and Engines

19At-D: Identifying New Market Opportunities for Bioenergy and Bioproducts

Project Goal

Generate new bioblendstocks for light-duty and heavy-duty to validate their fuel properties and production viability

End of Project Milestone

Identify low carbon fuel-engine combinations that increase fuel economy by 35% (light duty) or 4% (heavy duty) over a 2015 baseline, with reduced emissions

Funding Mechanism

AOP

Responses to Previous Reviewers' Comments – Bioblendstock Generation & Testing

Comment: BBG is in discovery mode now and this is the most exciting place to be as a scientist. There are many practical issues that must be addressed as pathways are suggested and in which the TEA effort must now develop accelerated assessment tools with BBG to suggest the key screening work for these showstoppers.

Response: We appreciate the reviewer's feedback. As highlighted in this talk, in this latest phase of Co-Optima we have emphasized the following:

- Show-stopper screening that includes toxicology and biodegradability with Structure Property Relationships, as well BBG&T heavy-duty oxygenated bioblendstock infrastructure compatibility assays for water solubility, flash point, polymer compatibility, and oxidative storage stability

- Close interface with BETO Conversion and Co-Optima Analysis team to ensure the latest conversion pathways are leverage that have low-cost potential, with metrics applied early in the Tiered screening process. In addition, we evaluated waste-derived bioblendstocks to help address feedstock costs.

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Heilmeier Catechism for BBG&T

What are we trying to do? We derisk new bioblendstocks by i) screening with the latest computational and experimental tools, ii) procuring/producing novel bioblendstocks, iii) providing conversion data for TEA/LCA to assess cost and GHG footprint viability, and iv) scaling production for handoff to engine and fuel property testing.

How is it done today? What are the limits? The design of new pathways to produce bioblendstocks often waits until the end of the development cycle to validate fuel properties and infrastructure compatibility. This Edisonian approach can result in undesirable fuel properties, require new costly infrastructure, and delay deployment.

What is new in our approach? Why will we be successful? We leverage the latest fuel property prediction and screening tools to ensure new bioblendstocks meet safety, performance, and operability in less R&D time and cost. We also provide data to develop TEA/LCA at an early stage to provide guidance based on fuel cost and GHG criteria.

Why is it important? We reduce the technical barriers for the design and selection of new bioblendstocks of relevance to the academia and industry. This work is needed to reduce the cost and carbon footprint of ground transportation.

What are the risks? Major risks include poor fuel property prediction tools, lack of knowledge for new oxygenates, and selection of bioblendstocks that are too costly or GHG intensive. We mitigate these risks in through coordinating Co-Optima work in Structure-Property Relationships, Bioblendstock Generation and Testing, and Analysis.

How long will it take to be relevant? The fuel property screening tools, bioblendstock fuel property data, and conversion pathway analysis results are released live as they are developed for use by academia and industry.