Co-Optimization of Fuels & Engines

DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Bioblendstock Generation

Co-Optima Review Session

Derek Vardon, NREL

March 7th 2019

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Bioblendstock Generation (BBG)

Goal, Outcome, and Relevance

Co-Optima works to identify blendstocks derived from biomass providing critical fuel properties, and assess benefits of and barriers to adoption

❖ BBG Goal

The goal of BBG is to address gaps in fuel property and conversion knowledge for non-commercial bioblendstocks by generating samples for fuel property characterization and supplying preliminary conversion data.

❖ BBG Outcome

The BBG effort will generate bioblendstock samples and conversion data to (i) span both hydrocarbon and oxygenate production pathways, and (ii) address fuels for both light-duty and heavy-duty vehicles.

❖ Relevance to Bioenergy Industry

In concert with the other Co-Optima teams, BBG will (i) provide a framework to derisk and evaluate novel bioblendstocks, (ii) develop production pathway assessment tools, and (iii) inform future conversion targets within the BETO Core program.

Quad Chart Overview

Timeline

- **Start: FY2016**
- **Merit review cycle: FY2019-2021**
- **58% complete of review cycle**

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	$4,993	$4,290	$3,515	$11,025

DOE Labs part of Bioblendstock Generation Effort (BBG):
LANL, LBNL, NREL, PNNL, SNL

Barriers Addressed

- **ADO-E. Co-Development of Fuels & Engines**
- **Ot-B. Cost of Production**

Objective

Address gaps in fuel & conversion knowledge for promising bioblendstocks by (i) generating samples for fuel property testing and (ii) supplying preliminary conversion data for ASSERT feasibility

End of Project Goal

Identify, procure, and produce promising bioblendstocks for light-duty and heavy-duty vehicle applications that address:

(i) major blendstock chemical families (e.g., alcohols, ethers, alkanes, etc.)
(ii) existing and future modes of combustion (e.g., boosted spark, multi-mode, mixing controlled compression, kinetically controlled)

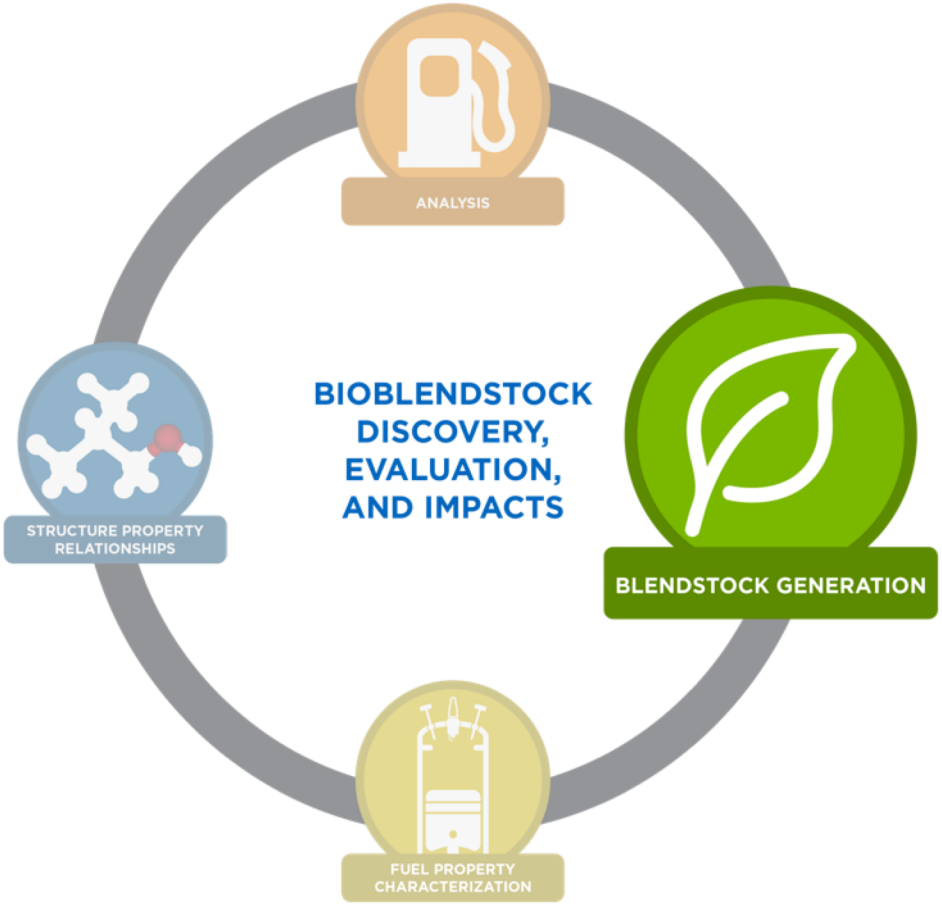
1 - Project Overview

Bioblendstock generation objective within Co-Optima

Integrated Team Effort

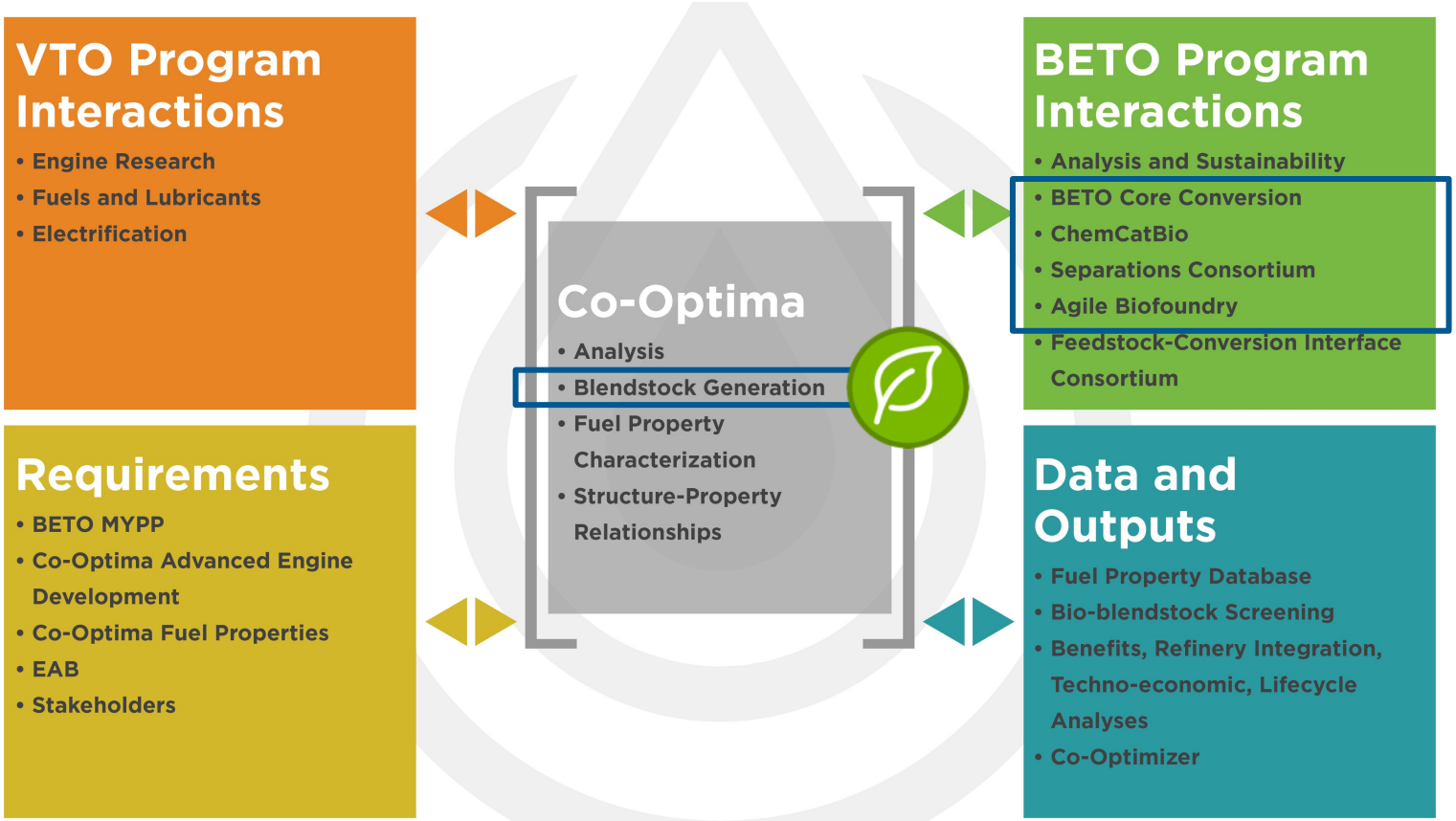
Bioblendstock Generation is part of a multi-thrust Co-Optima team that interacts through the following:

- ***Structure Property Relationships*** inform which bioblendstocks are promising for BBG to target
- ***Fuel Property Characterization*** evaluates samples provided by BBG for tiered screening
- ***Analysis Team*** provides initial feasibility assessment based on BBG pathway mapping and preliminary conversion data



1 - Project Overview

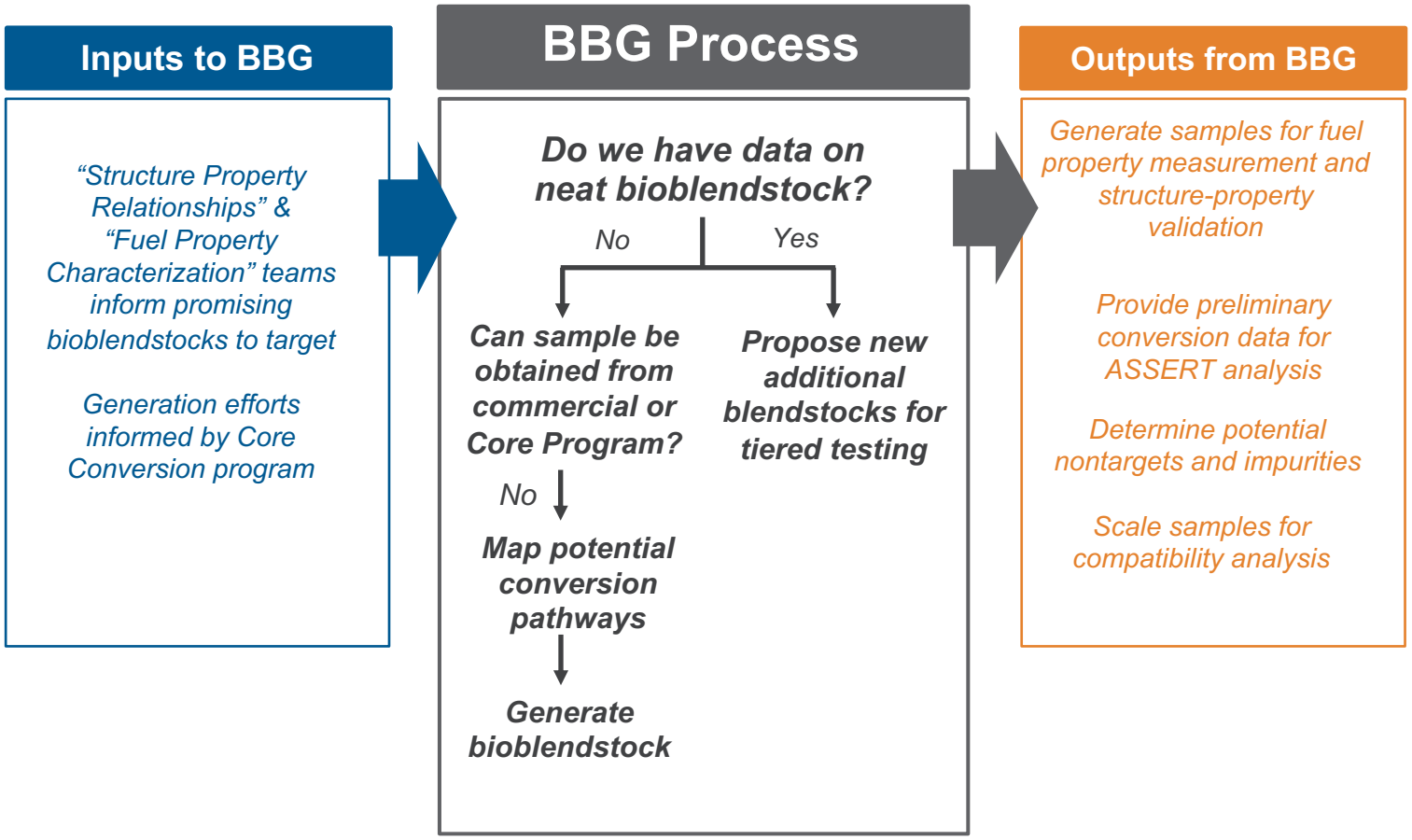
How BBG efforts fit into and connect with the BETO program



BBG works with other BETO programs to (i) select novel targets and pathways not being addressed, (ii) and leverage latest conversion tools and knowledge

2 - Approach (Management)

BBG decision criteria for generating bioblendstocks



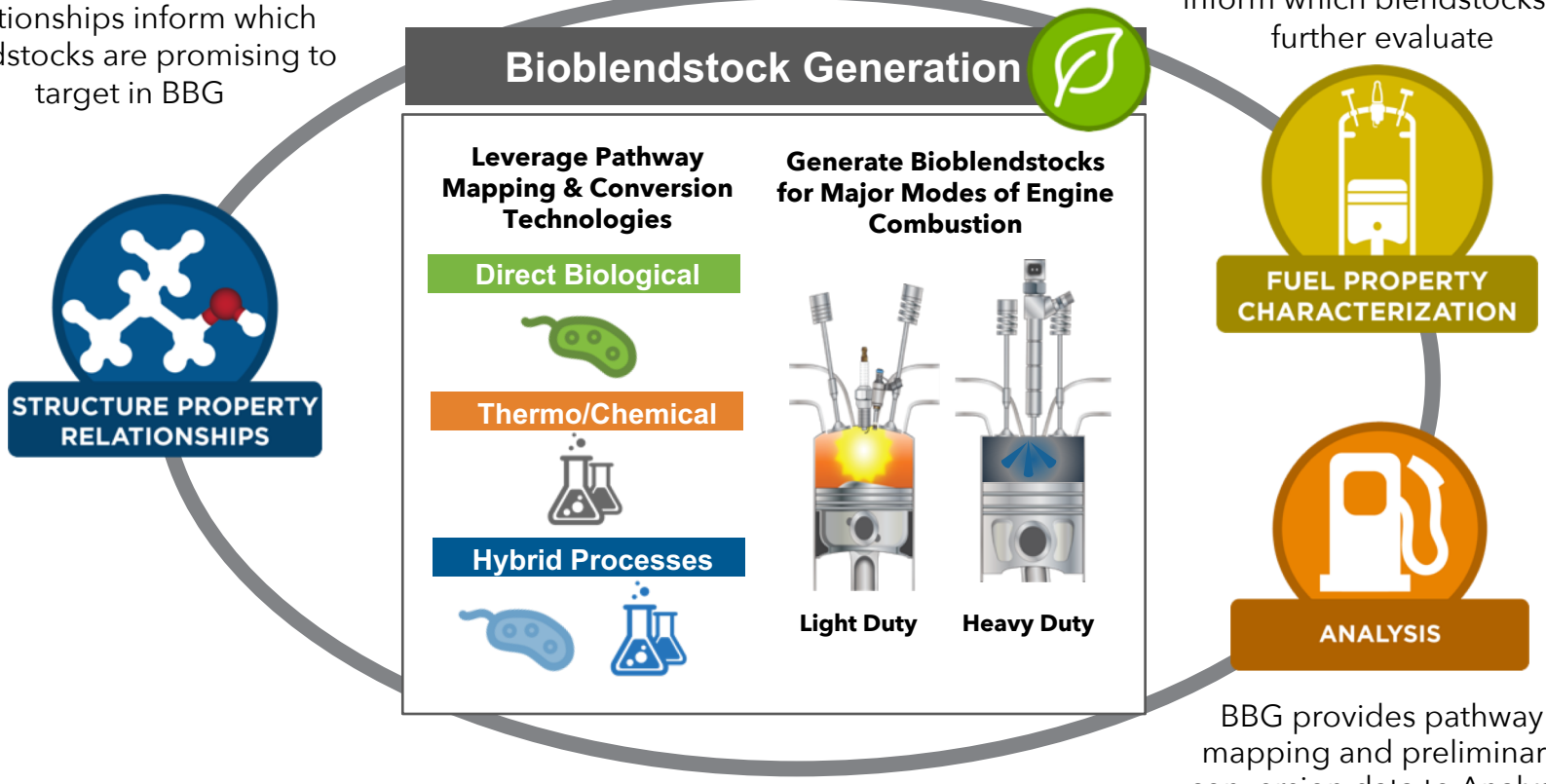
Rational approach to bioblendstock generation and evaluation

2 - Approach (Management)

BBG research approach interfaces with Co-Optima teams

Structure property relationships inform which blendstocks are promising to target in BBG

BBG provides samples for characterization and testing to inform which blendstocks to further evaluate



BBG provides pathway mapping and preliminary conversion data to Analysis

Input guides BBG efforts and output informs other team activities

2 - Approach (Management)

Team member roles clearly defined within Co-Optima

National Labs & Principal Investigators

HPF Team Lead: Anthe George (SNL) HPF Deputy: Derek Vardon (NREL)

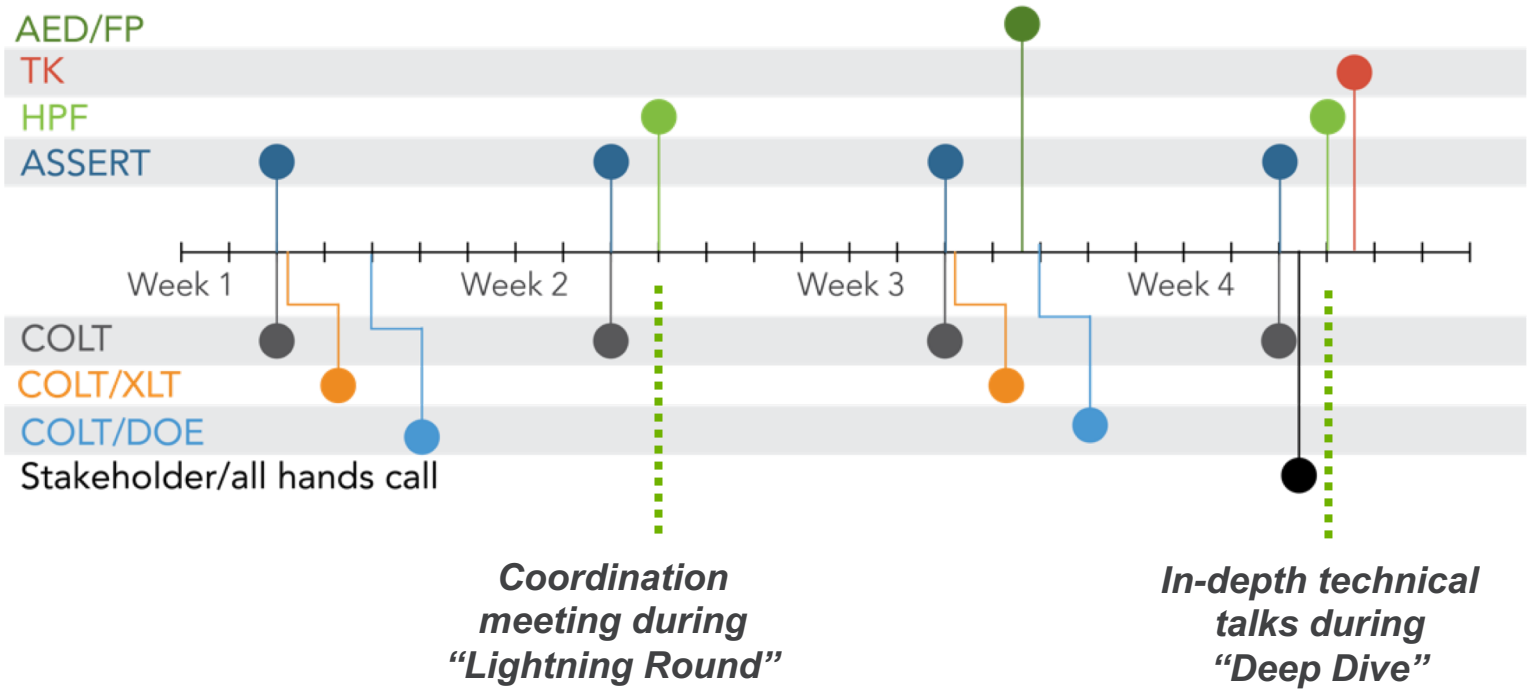
Los Alamos NATIONAL LABORATORY EST. 1943	**Andrew Sutton,** Cameron Moore, Troy Semelsberger
BERKELEY LAB	**Todd Pray,** Blake Simmons, Jay Keasling, Eric Sundstrom
NREL NATIONAL RENEWABLE ENERGY LABORATORY	**Tom Foust,** Dan Ruddy, Nabila Huq, Trenton Wilke, Glenn Hafenstine, Gregg Beckham, Derek Vardon
Pacific Northwest NATIONAL LABORATORY	**Evguini Polikaprov,** Lelia Cosimbescu, Karl Albrecht, Vanessa Dagle, Karthi Ramasamy
Sandia National Laboratories	**Anthe George,** Ryan Davis, Eric Monroe, John Gladden, Corey Hudson

Experienced team knowledgeable in biomass-to-biofuel conversion

2 - Approach (Management)

Communication and coordination essential to success

Co-Optima regularly scheduled meetings



Coordination within High Performance Fuels team and broader Co-Optima

2 - Approach (Technical)

Tasks address combustion modes across chemical families

FY17/18 - Boosted SI for Light Duty

Alcohols	LANL - Chem Acetone Derivatives	LBNL - Bio Polyketide Synthase	NREL – Hybrid Anaerobic Acid Derived	SNL – Bio Fusel Alcohols
Alkanes	LBNL - Bio Mono & Sesquiterpenes	NREL – Thermo Catalytic Fast Pyrolysis	PNNL - Thermo Iso-olefins via Oxygenates	
Ketones	LANL - Chem Acetone Derivatives	LBNL - Bio Polyketide Synthase	NREL - Hybrid Anaerobic Acid Derived	PNNL - Thermo Et-OH Derived Ketones

FY18/19 - Mixing Controlled Compression Ignition

Alcohols	LBNL – Bio Branched Long-chain	PNNL – Thermo Et-OH Derived Branched		
Alkanes	LBNL - Chem Energy Dense Oxetanes	LBNL - Bio Energy Dense Ladderanes	PNNL - Thermo Dicylcopentane Derivatives	NREL – Hybrid Anaerobic Acid Derived
Ethers	NREL - Thermo Mixed Alcohol Poly-ether	NREL - Hybrid Anaerobic Acid Derived	SNL - Hybrid Fusel Alcohol Derived	SNL- Hybrid Fatty Acid Derived

Cross Cutting

SNL Retrosynthetic Analysis

PNNL Impurity & Hydrolysis Study

BBG maps conversion pathways and generates bioblendstock samples

2 - Approach (Technical)

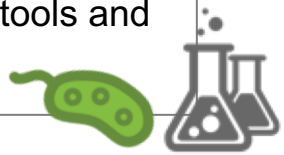
Well-defined milestones and strategies to address risk

BBG Potential Risks

- ✓ Mismatch with fuel property prediction and experimental values
- ✓ No known routes to produce promising bioblendstocks

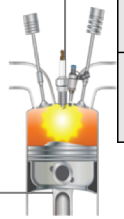
BBG Risk Mitigation Strategy

- ✓ Procure or produce samples to validate structure-property relationships
- ✓ Leverage pathway analysis tools and latest conversion strategies



HPF Milestones for BBG

- ✓ HPF complete >20 milestones in FY18 related to “Structure Property” and “Bioblendstock Generation”
- ✓ Planned >20 milestones in FY19 for Heavy Duty MCCI and Light Duty MM bioblendstocks



Combustion	BBG-HPF Select FY19 Milestones	Quarter
Heavy Duty MCCI	Complete synthesis of FAME-derived ethers and collect DCN, YSI, oxidative stability, and cold-flow data for comparison to esters (SNL).	Q2
Heavy Duty MCCI	Develop atom efficient (>80% C-balance) chemical routes to produce 150 mL of four oxetanes using simple to perform CN, LHV, YSI, and cold flow testing (LBNL).	Q4
Light Duty Multi-Mode	Develop production proof-of-concept data along with fuel property verification for short-chain unsaturated alcohol. Prepare report and provide data to other teams (LBNL).	Q2
Light Duty Multi-Mode	Generate >20 mL of iso-olefins from alcohol pathways and predict fuel properties using NMR model. Determine composition by GC-MS and boiling range by Sim-Dist (PNNL).	Q4

Progress measurable with risk mitigation strategies and Milestones in place

2 - Approach (Technical)

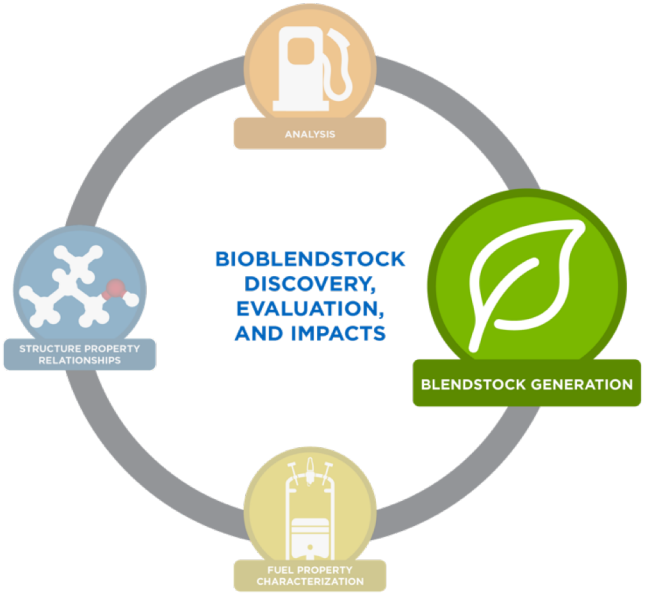
Critical success factors, challenges, and key activities

BBG Success Factors	Barriers to Overcome	BBG Key Activities
Assess preliminary feasibility for generating novel bioblendstocks and provide follow-on handoff to Core Conversion Program	Lack of pathway and production data for novel bioblendstocks that result in significant unknowns and risk during handoff	Utilize retrosynthetic analysis to map possible pathways Conduct initial assessment of production pathways Work with Analysis team to evaluate initial bioblendstock feasibility
		

Project activities designed to address major barriers to success

2 - Approach (Technical)

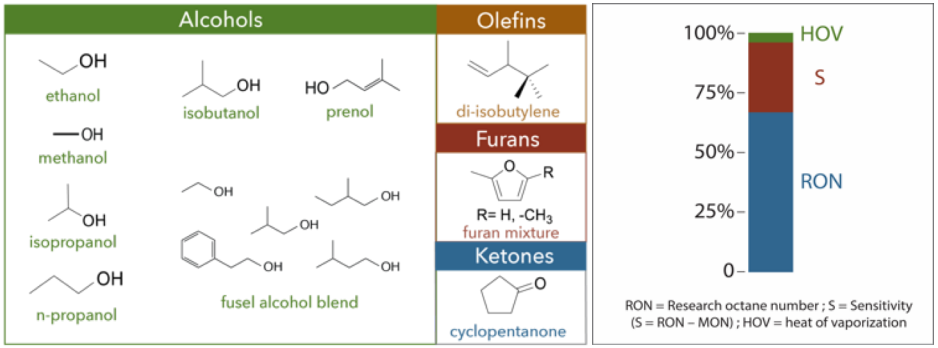
Demonstrated results needed to meet targets



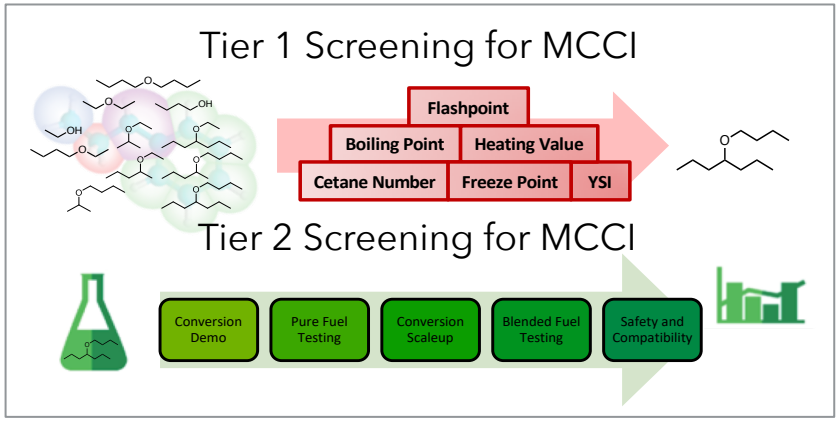
BBG Specific Role

BBG supports major Co-Optima deliverables by (i) procuring and generating bioblendstock samples for tiered screening, and (ii) providing preliminary conversion data for initial feasibility analysis

Inform "Top 10" Bioblendstocks for Boosted SI



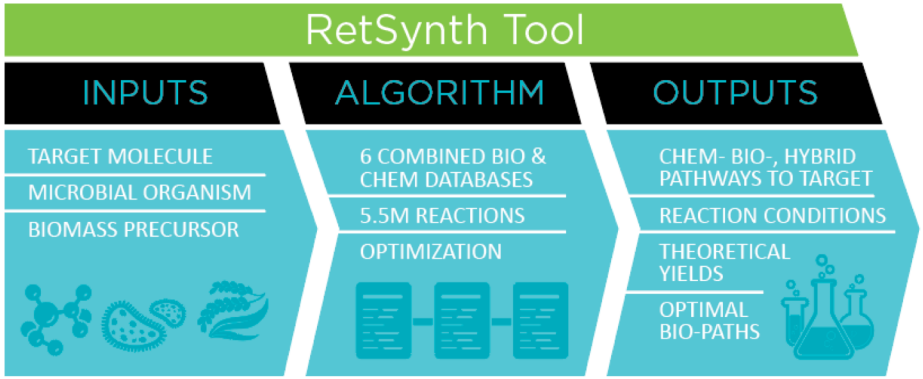
Ongoing Support for MCCI Tiered Screening



3 - Progress *Retrosynthetic analysis of production pathways to promising bioblendstocks from biomass*

Developed scalable algorithm for predicting biological, chemical and hybrid paths to production

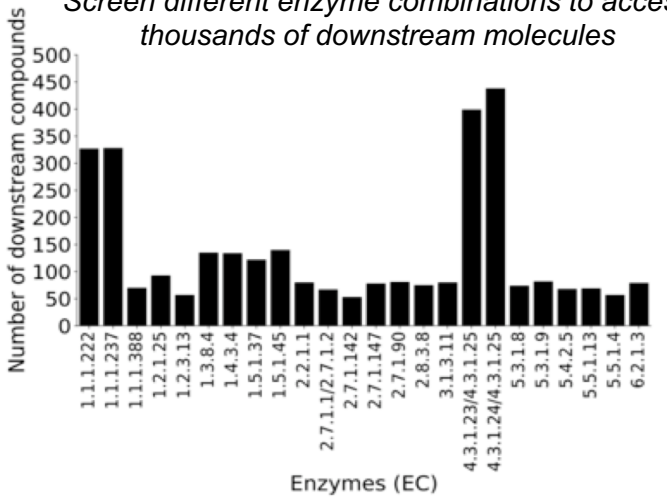
- Collected six biological and chemical databases (5.5 million reactions)
- Provided capacity for 10s of thousands of chassis organism for biological routes
- Incorporated multiple pathways and theoretical yields



Tested a large number of gasoline and diesel-like compounds

- Included biological pathways for 3462 compounds in Metacyc database
- Analysis of asymmetric ethers, methyl ketones and cyclopropenated fatty acid methyl esters
- Results distributed via Open Source at https://www.github.com/sandialabs/RetSynth

Screen different enzyme combinations to access thousands of downstream molecules



Lab PI: George & Hudson SNL

- Developed retrosynthetic analysis tools to help determine available conversion routes to pursue for promising bioblendstocks

3 - Progress *Direct biological production of fusel alcohols from waste streams to produce "Top 10" light duty bioblendstock*

Fusel alcohol mixtures shown to have high octane & energy density

- Energy density 33% higher than ethanol
- Nonlinear octane enhancement demonstrated in blends with gasoline (bRON)

Demonstrated that blendstock can be produced from waste streams

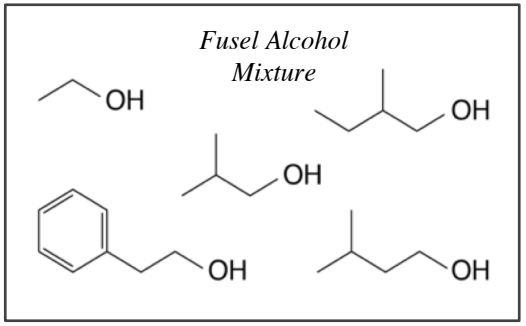
- Fusel alcohol production demonstrated by Liu et al 2018 with waste feedstocks
- Waste feedstocks included algae grown on wastewater and waste distillers grains

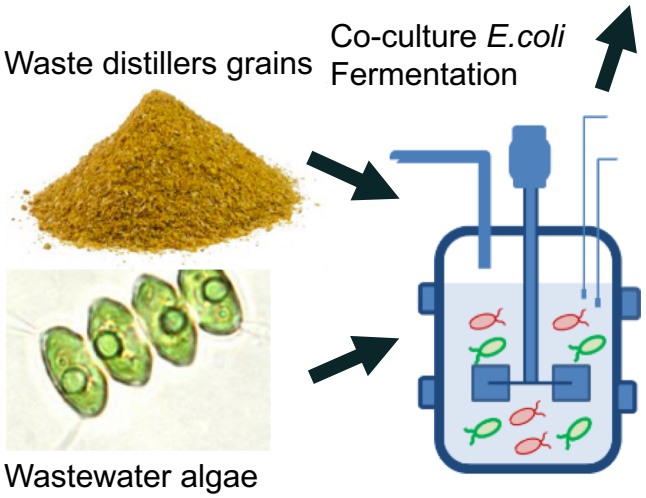
Ability to tailor composition for improved fuel properties

- Relative abundance of C4 and C5 alcohols shown to be feedstock sensitive, which can be used to target fuel properties

Liu et al (2018) Biodiesel and Biofuels

Property	Fusel Alcohols
RON/MON	110/98
Sensitivity	12
bRON at 20%	115
HOV (kJ/kg)	637
LHV (MJ/L)	26.8





SNL team: George, Davis, Liu & Monroe

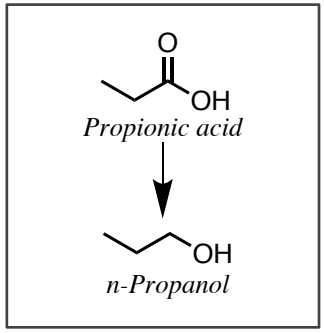
- Determined fusel alcohol mixtures show greater energy density than ethanol
- Demonstrated their production from waste feedstocks

3 - Progress *Derisk the hybrid production of 1-propanol for generating "Top 10" light duty bioblendstock*

1-Propanol identified as promising light duty blendstock, with limited work to date on conversion viability

- 1-Propanol has good overall combustion properties with no major compatibility issues
- Barriers for 1-propanol include (i) limited data for feasibility assessment, (ii) lack of economical production routes

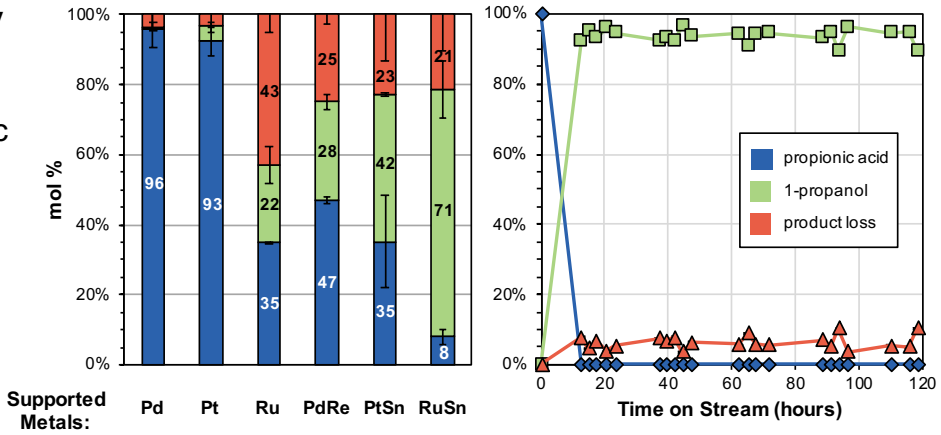
Vorotnikov et al. (2019) Submitted



Property	1-Propanol
RON/MON	104/89
Sensitivity	15
bRON at 20%	121
HOV (kJ/kg)	789
LHV (MJ/L)	24.7

Efforts helped derisk 1-propanol by demonstrating high-yield process

- Utilized anaerobic biological route to propionic acid, followed by chemo-catalytic processing
- Identified high yielding catalyst (>94% molar) for 1-propanol production that was stable for >100 hours of time-on-stream
- Preliminary conversion data provided to ASSERT team for feasibility evaluation



Lab PI: Vardon & Beckham NREL

- Identified 1-propanol as a promising yet under explored light duty blendstock
- Helped derisk production route from microbial acids for feasibility assessment

3 - Progress *Polyketide synthesis pathway for the biological production of short-chain ketones for light duty bioblendstock*

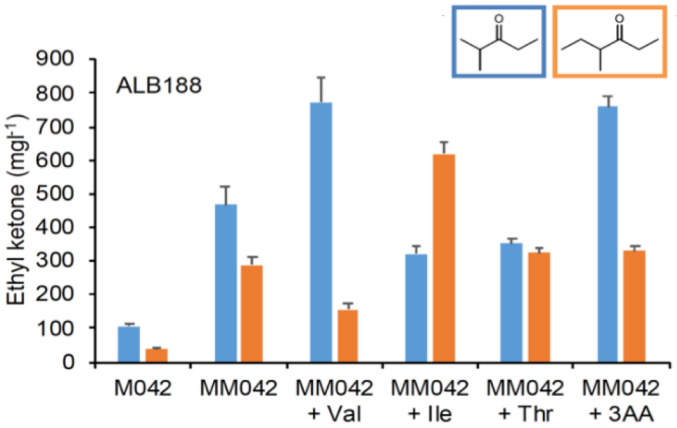
Developed tunable biological synthesis pathway to short branched ketones that provide octane boosting

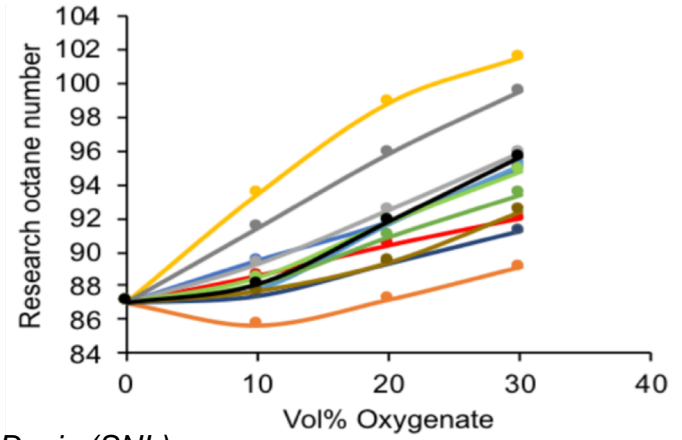
- Modular enzyme system can incorporate different metabolic intermediates for structural diversity
- Octane boosting shown for a variety of short-chain ketones, with several comparable octane enhancement to ethanol, with greater energy density and lower water solubility

Intrinsic production of mixed ketones can enable tailored fuel properties

- Mixtures can help balance fuel properties of individual molecules for improved performance
- Ongoing work to understand ketone material combability constraints
- Potential to further expand fuel molecules by converting ketones to alcohols

Yuzawa et al. (2018) Nature Communications





Lab PI: Pray, Keasling, Sundstrom (LBNL), George, Gladden, Davis (SNL)

- Developed new biochemical route to short-chain branched ketones that boosts octane and offers tunable mixture with tailorable fuel properties

3 - Progress *Single-step thermochemical production of low sooting polyethers for heavy duty bioblendstock*

Oxymethylene ethers (OME) offer dramatic soot reduction with high-cetane behavior

- OMEs show 50% soot reduction at 20% blend
- OMEs not readily available for purchase and have known water solubility challenge

Established single-step route from methanol to greatly simplify process

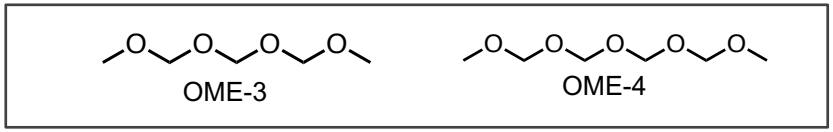
- Multifunctional catalyst enables key rxn steps from MeOH with decreased by-products
- Ongoing work to address water solubility by end-group modification with longer alcohols

Initial economic estimates suggest minimum fuel selling price of $3.50/gal

- In comparison, multi-step routes at $6-8/gal
- Opportunities to reduce price to $1.88/gal with catalyst and process development

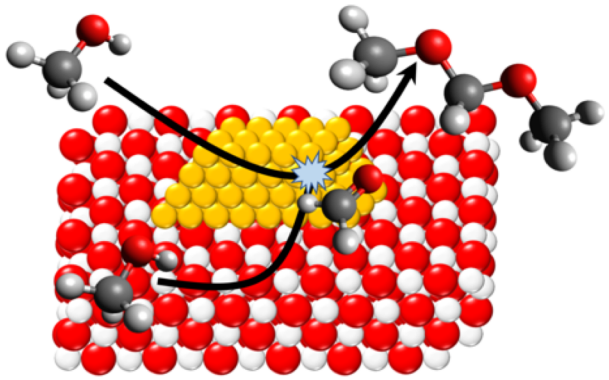
Lab PI: Foust & Ruddy, NREL

To et al. (2018) Submitted



Compound	DCN	LHV (MJ/kg)	Flash Pt (° C)	YSI	M.P. (° C)	B.P. (° C)
Tier 1	**> 40**	**> 25**	**> 52**	**< 200***	**< 0**	**< 338**
OME-3	70	20	54	13	< -43	156
OME-4	90	19	88	16	< -10	201

Metal-acid bifunctionality enables dehydrogenative coupling



- Established novel single-step route to OME polyethers from methanol
- Ongoing work to modify chemical structure to address water solubility limitation

3 - Progress *Chemical production of dioxolanes from small alcohols for water insoluble heavy duty bioblendstock*

Pathway to upgrade ethanol and butanediol to water insoluble heavy duty blendstocks

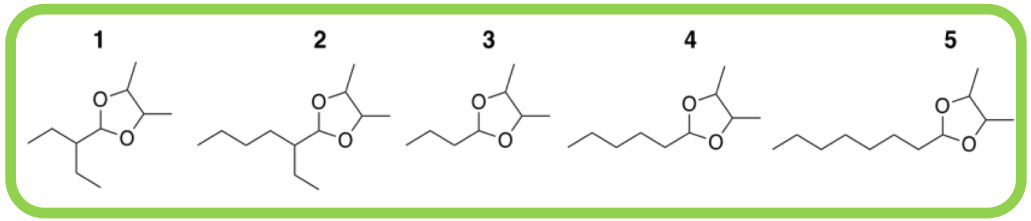
- Low temperature approach to produce diesel grade fuels from small alcohols
- Work leveraged structure property relationships to further improve cetane and reduce sooting
- Bioblendstock water insoluble and readily phase separates after conversion

Multiple dioxolanes meet heavy-duty Tier 1 criteria

- Dioxolanes maintain or improve all diesel fuel properties while drastically reducing sooting index
- Only one dioxolane molecule screens out
- Extended fuel property and infrastructure compatibility testing underway

Staples et al. (2018) Sustainable Energy & Fuels

Example Dioxolanes accessible from Ethanol and Butanediol



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

*All measured values. Diesel YSI typically above 200**

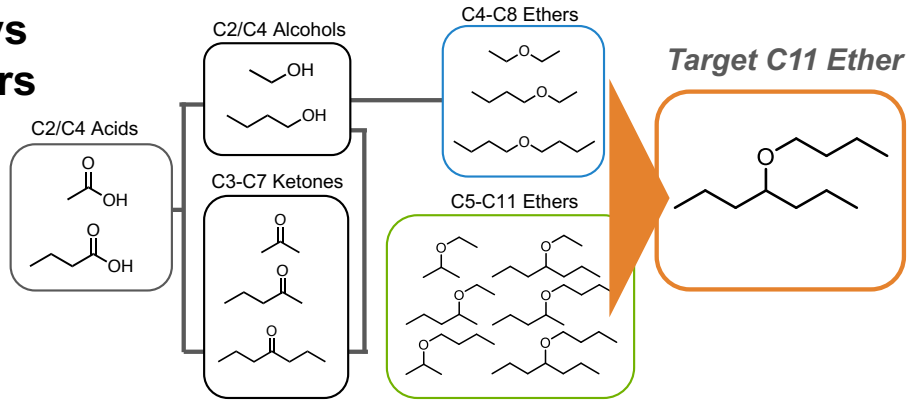
Lab PI: Sutton & Moore, LANL

- Rationally developed blendstock from small alcohols that is water insoluble
- Dioxolanes shown to have cetane and sooting advantage over conventional diesel

3 - Progress *Hybrid production of energy dense mono-ethers from short chain microbial acids for heavy duty bioblendstock*

Identified catalytic coupling pathways to produce energy dense mono-ethers from C2/C4 microbial acids

- Fuel property prediction tools were leveraged to to rapidly screened promising heavy duty fuel target molecule
- Flash point determined to be key criteria that required extending ether chain length



Scaled continuous production routes to meet Tier 1 and Tier 2 fuel criteria

- Transitioned conversion chemistry from batch to continuous production to facilitate scale-up
- Demonstrated that predicted and measured fuel properties agree well for mono-ethers
- Confirmed C11 ether is energy dense with high cetane, low sooting, and low water solubility
- Blend tests with diesel meet Tier 2 criteria with promising stability and combability

Tier 1 Properties of Neat C11 Ether Bioblendstock

Compound	DCN	LHV (MJ/kg)	Flash Pt (° C)	YSI	M.P. (° C)	B.P. (° C)
Tier 1	**> 40**	**> 25**	**> 52**	**< 200***	**< 0**	**< 338**
Predicted	76	43	60	55	-53	194
Measured	80	39	64	58	-80	198

Select Tier 2 Properties of 20% C11 Ether Blend

Compound	Blend CN	T90. (° C)	Flash Pt (° C)	Cloud (°C)	Visc (cSt)
Tier 2	**> 40**	**< 338**	**> 52**	**< 0**	**1.9 - 4.1**
Blend	50	198	62	-11	2.1

Lab PI: Vardon, NREL

- Leveraged fuel property prediction to identify routes to ethers from microbial acids
- Produced energy dense mono-ether that meets Tier 1 and Tier 2 criteria

3 - Progress *Pursuing a step-wise approach for using iso-olefins as a feedstock for light duty multi-mode bioblendstock*

1st step

Screened potential iso-olefins candidates

- Leveraged structure-property fuel relationships to assess targets

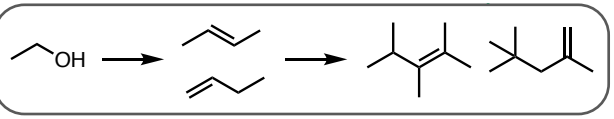
2nd step

Identified promising biobased iso-olefin pathways

- Tuning process conditions to target specific iso-olefins
- Measuring fuel properties by experimental and modeling approaches
- Providing conversion parameters to ASSERT team for analysis

ethanol→ butenes → $C_{4\text{-}16}$ olefins
2,3-butanediol → $C_{3\text{-}6}$ alkenes → $C_{4\text{-}16}$ olefins

Example Ethanol to Iso-Olefin Pathway



3rd step

Produce iso-olefins for multi-mode evaluation

- Generated >400 mL for fuel property tests to date
- Focus on phi sensitivity structure-property relationships
- Results feedback and inform bioblendstock generation in Step 2

Lab PI: Dagel, PNNL

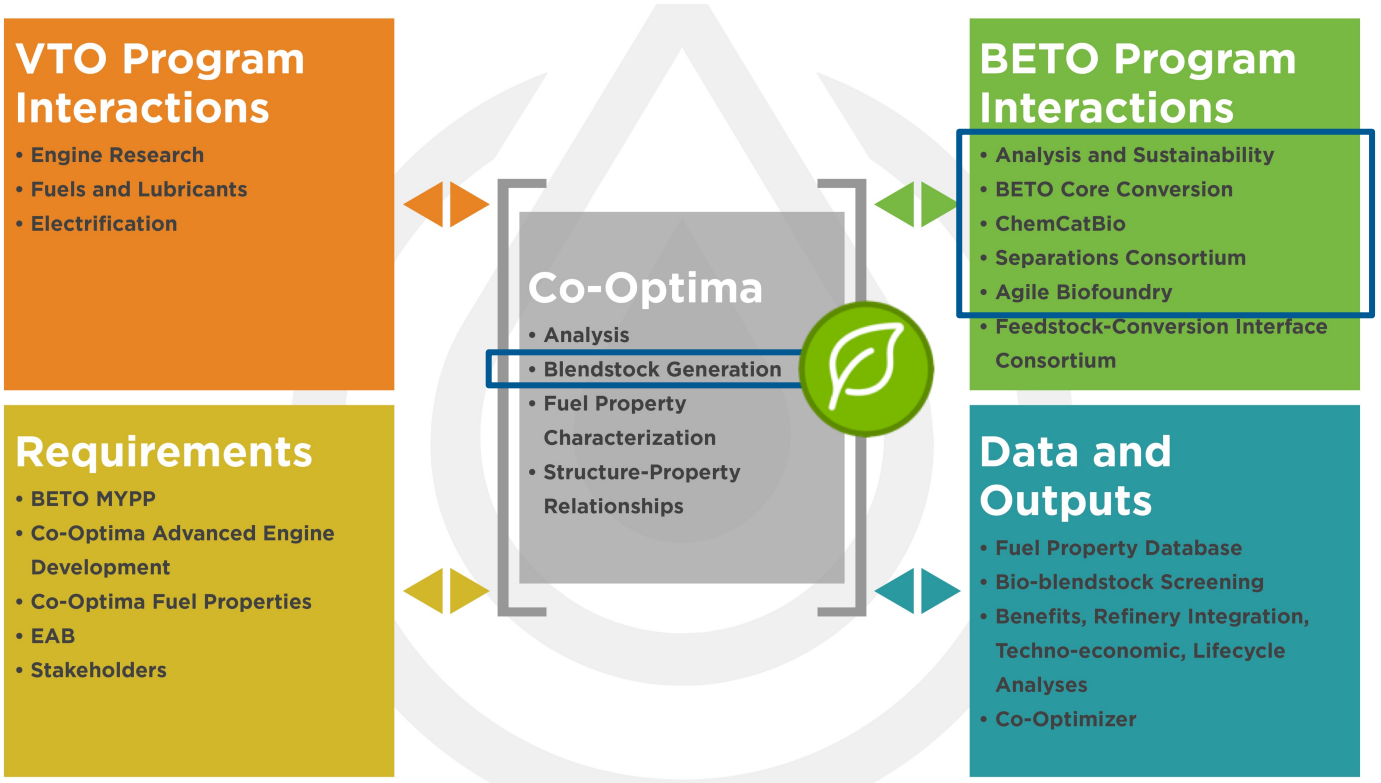
- Identified pathway to convert biobased iso-olefins to light duty multi-mode blendstock
- Ongoing work to generate sample for phi sensitivity structure-property relationships

4 - Relevance

How BBG efforts impact BETO goals and objectives

Specific MYP Barriers addressed by BBG

- ADO-E. Co-Development of Fuels & Engines
- Ot-B. Cost of Production

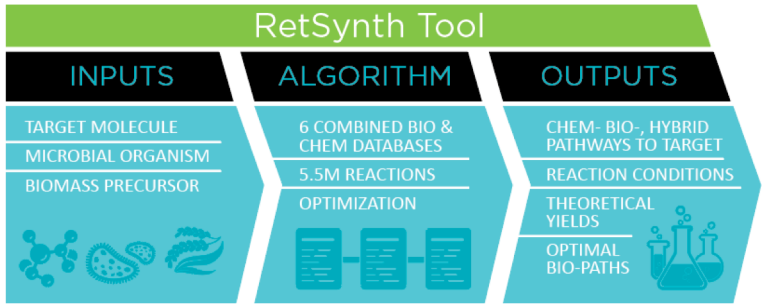


Output 1. Evaluate new pathways and fuel targets not addressed within BETO portfolio
Output 2. Inform future targets and metrics in handoff to BETO Core Conversion

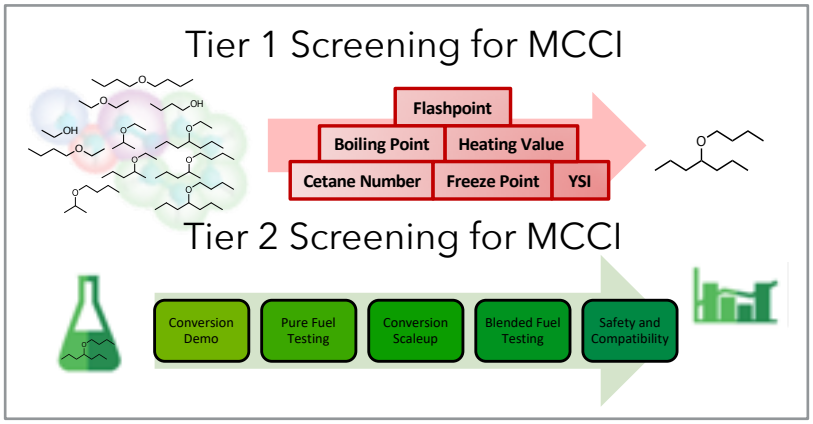
4 - Relevance

How BBG efforts impact bioeconomy stakeholders

Supply New Online Tools for Public



Support Framework for Assessing Bioblendstocks



Document Findings for Stakeholders in Public and Peer Reviewed Literature

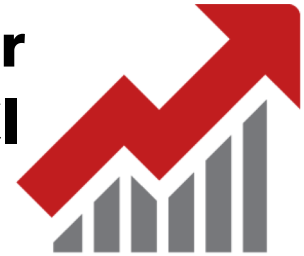
Output 3. Supply new tools & support framework to derisk promising bioblendstocks

Output 4. Support major deliverables on fuel properties and conversion feasibility

5 - Future work

Select future milestones and upcoming decision points

Scale-up for Tier 2 MCCI Testing



Impact of Impurities & Non-targets

Combustion	BBG Select FY19 Milestones	Quarter
Heavy Duty MCCI	Synthesize 100 mL of alcohol mixture (C5-C13) from ethanol with yields >70% and CN>40. Measure fuel properties of resultant product mix (PNNL).	Q4
Heavy Duty MCCI	Develop atom efficient (>80% C-balance) chemical routes to produce 150 mL of four oxetanes using simple to perform CN, LHV, YSI, and cold flow testing (LBNL).	Q4
Fuel Impurity Impacts	Quantify the upper limit of moisture tolerance of BOB/ester blends towards hydrolysis of esters by analysis of carboxylic acids in the aged fuel samples (PNNL).	Q4

- FY19 will scale production for Tier 2 testing of select heavy duty MCCI blendstocks
- FY19 will also look to address impact of impurities on advantaged fuel properties

5 - Future work

Upcoming decision points and remaining issues

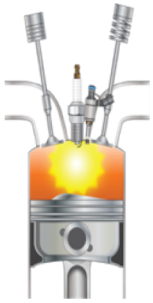
FY19 **FY20** **FY21**

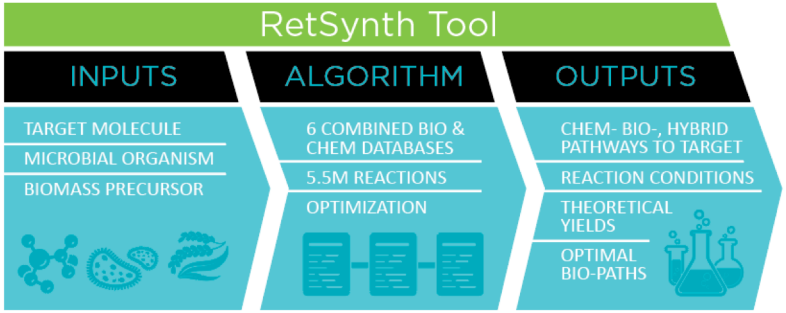
FY19: Identify "Top 10" Bioblendstocks for MCCI and assess their advantages and current limitations

BBG Remaining Issue: *Each bioblendstock will present its own impurity profile. BBG will look to address common impurity and stability issues and communicate remaining challenges to stakeholders.*

FY19 to FY21: Shift focus towards multi-mode and kinetically controlled modes of combustion that require unique fuel properties

BBG Decision Point: *Success will require a coordinated effort within Co-Optima. BBG will map and select promising production pathways for bioblendstocks well suited to these new modes of combustion.*





Summary for BBG Effort

Overview	**Generate bioblendstocks and conversion pathway data to: (i) validate structure property relationships, (ii) assess fuel properties, and (iii) initially inform conversion pathway feasibility**
Approach	• Identify promising bioblendstocks and conversion pathways based on fuel properties • Purchase or produce bioblendstocks for major chemical functional families and map potential conversion pathways • Coordinate with Co-Optima efforts in Structure Properties, Fuel Properties, and ASSERT team for integrated bioblendstock assessment
Technical Progress	• **Pathway Assessment -** Developed retrosynthetic analysis tool to help determine efficient routes for producing light duty and heavy duty bioblendstocks • **Light Duty Boosted SI -** Developed novel routes to "Top 10" candidates and generated conversion data to initially assess conversion feasibility • **Heavy Duty MCCI -** Leveraging fuel property screening tools to rapidly screen and select novel bioblendstocks for production and fuel property validation
Relevance	**Enhance bioenergy value proposition by identifying bioblendstocks that maximize engine performance and energy efficiency, & minimize environmental impacts**
Future Work	• Generate bioblendstocks to help complete Tier 1 and Tier 2 screening across chemical families and facilitate selection of "Top 10" for Heavy Duty MCCI • Transition bioblendstock targets for advanced modes combustion for light duty (multi-mode) and heavy duty (kinetically controlled) engines • Assess impact of impurities on fuel properties with promising bioblendstocks

List of Acronyms

CO-OPTIMA TEAMS & RESEARCH THRUSTS

- **ASSERT –** The ASSERT research team within Co-Optima that handles analysis for sustainability, scale, economics, risk, and trade
- **BBG** – Bioblendstock Generation is a research thrust within Co-Optima

ENGINE COMBUSTION MODES

- **Boosted SI** – Boosted spark ignition for light-duty vehicles
- **MM** – Multi-mode ignition for light-duty vehicles
- **MCCI** – Mixing controlled compression ignition for heavy-duty vehicles
- **KC** – Kinetically controlled ignition for heavy-duty vehicles

FUEL PROPERTY MEASUREMENTS

- **B.P.** – Boiling point
- **M.P.** – Melting point
- **HoV** – Heat of vaporization
- **LHV** – Lower heating value
- **CN** – Cetane number
- **DCN** – Derived cetane number based on ignition delay measurements
- **MON** – Motor octane number
- **RON** – Research octane number
- **bRON –** Research octane number for a blend of gasoline and bioblendstock
- **S** – Octane sensitivity, defined as RON minus MON
- **YSI** – Yield sooting index

Thank you for your time!
Let’s discuss

Pubs, Presentations, and Patents

FY18 Publications and Presentations

- **A Simple, Solvent Free Method for Transforming Bio-Derived Aldehydes into Cyclic Acetals for Renewable Diesel Fuels –** O. Staples, C.M. Moore, T.A. Semelsberger, J.H. Leal, C.S. McEnally, L. Pfefferle and A.D. Sutton. Sustainable Energy Fuels, 2018. https://doi.org/10.1039/C8SE00371H
- **Annual Merit Review and Peer Review Evaluation Presentations –** 12 presentations: A. Agrawal, S. Curran, J. Farrell, G. Fioroni, C. Kolodziej, G. Lavoie, C. McEnally, M. McNenly, C. Mueller, J. Pihl, I. Schoegl, and S. Sluder. https://www.energy.gov/eere/vehicles/annual-merit-review-presentations
- **Bio-derived Building Blocks for Various Drop in Fuels and Value Added Chemicals** – O. Staples. Presented at the 255th American Chemical Society National Meeting, New Orleans, LA, March 18 -22, 2018.
- **Catalytic coupling of short chain microbial acids to biofuel precursors.** Invited Presentation. D.R. Vardon. ACS Catalysis Division, Spring 2018 American Chemical Society Meeting, New Orleans, LA. March 2018.
- **Co-Optimization of Fuels & Engines: Fuel Blendstocks with the Potential to Optimize Future Gasoline Engine Performance; Identification of Five Chemical Families for Detailed Evaluation –** J.T. Farrell, J.E. Holladay, and R. Wagner. Technical Report, 1434413, April 2018. https://dx.doi.org/10.2172/1434413
- **Demonstration of Fusel Alcohols as a Platform for a Tunable Suite of High Performance Biofuel Compounds for Advance Combustion Strategies –** E. Monroe, F. Liu, M. Tran-Gyamfi, A. George, and R. Davis. Oral presentation and Abstracts of Papers of The American Chemical Society, March 18, 2018.
- **Discovery and Synthetic Demonstration of High-Performance Fuel via Solvent-Free Etherification –** N. Huq, X. Huo, J. Stunkel, P.C. St. John, S. Kim, R.L. McCormick, D.R. Vardon. ACS National Fall Conference, Boston, Massachusetts, August 2018.

Pubs, Presentations, and Patents

FY18 Publications and Presentations

- **Engineering β-oxidation in Yarrowia Lipolytica for Methyl Ketone Production –** E. Hanko, C. Denby, V. Sànchez i Nogué, W. Lin, K. Ramirez, C. Singer, G. Beckham, and J. Keasling. Metabolic Engineering, 48:52-62, 2018. https://doi.org/10.1016/j.ymben.2018.05.018
- **Exploring Bio-Derived Building Blocks For The Simultaneous Production of Fuels and Chemicals** – O. Staples. Presented at the 22nd American Chemical Society Green Chemistry & Engineering Conference in Portland, OR, June 18-20, 2018.
- **Fungal Metabolites as Precursors to Renewable Transportation Fuels –** M.G. Butcher, P.A. Meyer, et al. Fuel, 215:123-141, March 2018. https://doi.org/10.1016/j.fuel.2017.10.052
- **Next Generation Biofuel Production –** C.M. Moore, Invited presentation, Department of Chemistry and Biochemistry, University of San Diego, San Diego, CA, July 18, 2018.
- **Optimizing Genetic Manipulation of Microbial Organisms for Production of Multiple Target Chemical Compounds –** L. Whitmore. ACS National Fall Conference, Boston, Massachusetts, August 2018.
- **Performance advantaged fuel synthesis and fuel property work –** C. Moore presented at the American Chemical Society Green Chemistry Conference in Portland, Oregon, June 18-20, 2018.
- **Renewable diesel fuel via catalytic upgrading of anaerobic acids.** Invited Presentation. D.R. Vardon. Invited Presentation. 22nd Annual Green Chemistry & Engineering Conference, Portland, OR. June 2018.
- **Polyketide Synthases as a Platform for Chemical Product Design –** A. Zargar, J.F. Barajas, R. Lal, and J.D. Keasling. AIChE Journal 64(12):4201-4207, 2018. https://doi.org/10.1002/aic.16351
- **Probing the Flexibility of an Iterative Modular Polyketide Synthase with Non-Native Substrates in Vitro –** S.C. Curran, A. Hagen, S. Poust, L.J.G. Chan, B.M. Garabedian, T. de Rond, M. Baluyot, J.T. Vu, A.K. Lau, S. Yuzawa, C.J. Petzold, L. Katz, and J.D. Keasling. ACS Chemical Biology, 13(8):2261–2268, 2018. https://pubs.acs.org/doi/10.1021/acschembio.8b00422

Pubs, Presentations, and Patents

FY18 Publications and Presentations

- **Production and Upgrading of Fusel Alcohols as High Performance Fuels from Whole Algae Bioconversion** – Monroe et al. ABO Summit – Oral Presentation, October 2017. http://thealgaefoundation.org/upload/Eric_Monroe_ABO_Poster_2017.pdf
- **Production, Blending, and Upgrading of Advanced Renewable Fuels for the Co-Optimazation of Fuels and Engines** – E. Monroe, F. Liu, M. Tran, A. George, J. Gladden, R.W. Davis. Presented as a Poster at ACS 2018, San Francisco, California.
- **Replacing Non-Renewable Carbon with Bio-Derived Alternatives –** A.D. Sutton. Presented at Yale University, invited, Chemical and Environmental Engineering Seminar, October 19th, 2018.
- **Retrosynthetic Analysis of Bio-Derived Fuels, and the Identification of Commodity Feedstocks Critical to Potential Commercialization –** J. Page, P. Koech, D. Malhotra, K. Albrecht, D. Gaspar, L. Whitmore, C. Hudson, A. George, C. Moore, R. Wu, L. Silks, A. Sutton, C. Bailey, A. Zargar, and L. Katz. Presentation and Abstracts of Papers of The American Chemical Society, March 18, 2018.
- **Simultaneously Producing Fuels and Chemicals From Bio-Derived Molecular Building Blocks** – A.D. Sutton. Presented at the 255th American Chemical Society National Meeting, New Orleans, LA, March 18 - 22, 2018.
- **Synthesis of a Biofuel Target through Conventional Organic Chemistry –** J.P. Page, J.W. Robinson, K.O. Albrecht, and L. Cosimbescu. Tetrahedron Letters, 59(14):1421-1423, 2018. http://dx.doi.org/10.1016/j.tetlet.2018.02.073
- **Targeting Petroleum Replacements Using Bio-Derived Feedstocks –** C. M. Moore presented at the 22nd American Chemical Society Green Chemistry & Engineering Conference in Portland, Oregon, June 18-20, 2018.

Pubs, Patents, Presentations, Awards

FY18 Publications and Presentations

- **Catalytic upgrading of short chain acids to renewable diesel fuel.** X. Huo, N.A. Huq, J. Stunkel, N.S. Cleveland, A.K. Starace, A.E. Settle, A.M. York, R. Nelson, D.G. Brandner, L. Fouts, P.C. St. John, E.D. Christensen, J.H. Mack, C.S. McEnally, P.A. Cherry, L.D. Pfefferle, T.J. Strathmann, D.Salvachúa, S. Kim, R.L. McCormick, G.T. Beckham, D.R. Vardon. Poster presented at Frontiers in Biorefining, St. Simons Island, GA. November 2018.
- **Bioconversion of Distillers' Grains Hydrolysates to Advanced Biofuels by an Escherichia Coli Co-Culture–** F. Liu, R.W. Davis, et al. Microbial Cell Factories, 16:192, 2017. https://doi.org/10.1186/s12934-017-0804-8

FY18 Patent Application

- **Solid catalysts for producing alcohols and methods of making the same.** D.R. Vardon, T.R. Eaton, A.E. Settle. U.S. non-provisional patent application No. 15/828,658 filed on December 1, 2017

Pubs, Presentations, and Patents

FY17 Publications and Presentations

- **2017 Project Peer Review Presentations** – 4 Presentations: M. Biddy, J. Dunn, J. Farrell, D. Gaspar, J. Holladay, and D. Longman. Bioenergy Technologies Office 2017 Project Peer Review, Denver, Colorado, March 6-9, 2017. https://energy.gov/eere/bioenergy/ downloads/2017-project-peer-review-co-optimization-fuels-and-engines
- **Acetaldehyde as an Ethanol-Derived Bio-Building Block: An Alternative to Guerbet Chemistry** – C.M. Moore, O. Staples, R.W. Jenkins, T.J. Brooks, T.A. Semelsberger, and A.D. Sutton. Green Chemistry 19:169-174, 2017. http://pubs.rsc.org/en/content/articlepdf/2014/GC/C6GC02507B?page=search
- **Bioeconomy 2017 Presentations –** 5 presentations: D. Brooks, J. Eichenberger, J. Farrell, L. Harmon, and A. Lindauer. Bioenergy Technologies Office Bioeconomy 2017, Arlington, Virginia, July 11-12, 2017. https://energy.gov/eere/bioenergy/bioeconomy2017-presentations-and-agenda
- **Co-Optimization of Fuels & Engines –** A. Lindauer. Transportation Research Board 96th Annual Meeting, Washington, DC, January 8-12, 2017.
- **Co-Optimization of Fuels & Engines: FY16 Year in Review –** January 2017. https:// www.nrel.gov/docs/fy17osti/67595.pdf
- **Co-Optimization of Fuels & Engines (Co-Optima) Initiative –** J. Farrell. SAE 13th International Conference on Engines and Vehicles, Capri, Italy, September 13, 2017. https://www.nrel.gov/docs/fy18osti/70200.pdf
- **Heterogeneous Ketone Hydrodeoxygenation for the Production of Fuels and Feedstocks from Biomass –** R.W. Jenkins, C.M. Moore, T.A. Semelsberger, and A.D. Sutton. ChemCatChem, 9:2807-2815, 2017. http://onlinelibrary.wiley.com/doi/10.1002/ cctc.201601678/full
- **Leveraging Microbial Biosynthetic Pathways for the Generation of "Drop-in" Biofuels –** A. Zargar, C.B. Bailey, R.W. Haushalter, C.B. Eiben, L. Katz, and J.D. Keasling. Current Opinion in Biotechnology, 45:156-163, 2017. https://doi.org/10.1016/j. copbio.2017.03.004

Pubs, Presentations, and Patents

FY16 Publications and Presentations

- **The Effect of Functional Groups in Bio-Derived Fuel Candidates —** R.W. Jenkins, C.D. Moore, T.A. Semelsberger, D.J. Chuck, J.C. Gordon, and A.D. Sutton. ChemSusChem, 9: 922, 2016. onlinelibrary.wiley.com/doi/10.1002/cssc.201600552/full

Past Reviewer Comment

Comment: I like the fuel property based approach, its rational and upstream process agnostic so could be widely used. I do not like the portion of identify candidates where the labs are producing the biofuels for mixing. Due to the volumes involved for engine testing, it may be better for the labs to procure the chemicals from private parties pilot or demo plants. The quality may be better than what can be obtained in a lab as well. It would be helpful to determine what data that the EPA will ask for to qualify the fuels so that the project can generate data usable by a third party for fuels qualification.

Response: We appreciate the reviewer's agreement with the fuel property based approach applied in Co-Optima. In regards to the labs identifying candidates and the concern of production volumes, we agree and therefore look to procure commercially available candidates whenever possible, as well as leverage the BETO Core conversion program efforts. For promising candidates that are not commercially available, we utilize prediction tools and a Tiered approach to bioblendstock generation and evaluation (Tier 1 tests ~100 mL, Tier 2 tests ~1 L). Further, we look to provide handoffs to the Core conversion program for further conversion development of promising bioblendstocks.