Co-Optimization of Fuels & Engines

High Performance Fuels

Dan Gaspar, PNNL

8 March 2017

Goals

Co-Optima Goal

Determine key fuel properties that enable improved engine efficiency

Provide key science to enable high efficiency combustion modes

Capitalize on unique properties available from bio-blendstocks

Use stakeholder input to guide analysis

Accelerate market penetration of both engines and fuels.

HPF Goals

Develop fuel chemistry-fuel property-engine performance relationships

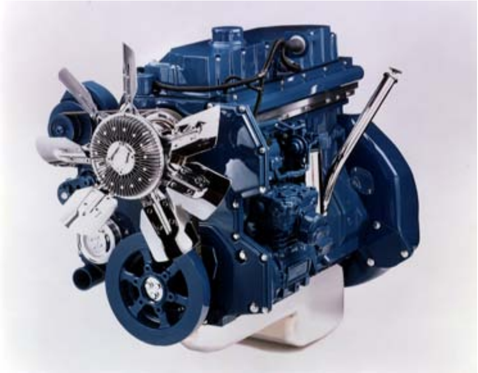
Determine new fuel options afforded by bio-derived fuels, including conversion pathways, for more efficient engines with lower harmful emissions

Generate market pull for biofuels through co-optimization

Governing Hypotheses

Central Engine Hypothesis

There are engine architectures and strategies that provide higher thermodynamic efficiencies than are available from modern internal combustion engines; new fuels are required to maximize efficiency and operability across a wide speed / load range.



Central Fuel Hypothesis

If we identify target values for the critical fuel properties that maximize efficiency and emissions performance for a given engine architecture, then fuels that have properties with those values (regardless of chemical composition) will provide comparable performance.

The governing hypotheses provide a framework to pursue engine and fuel development research simultaneously.

HPF Quad Chart Overview

Timeline

Project Start Date:	Oct. 1, 2015
Project End Date:	Sept. 30, 2018
Percent complete:	42%

Partners

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

Budget

	FY 16 Costs	FY 17 Costs	FY18 Budget
DOE Funded	$9,510	$7,147	$7,147

Barriers and Actions

It-D: Engines not optimized for biofuels: Identify bio-blendstocks with required fuel properties for combustion approaches optimized for efficiency and emissions

Ct-N: Product finishing acceptability and performance: Determine and meet fuel property requirements, incl. blending behavior. Conduct retrosynthetic analyses and pathway development to determine conversion pathways to bio-blendstocks with desired fuel properties

Im-H: Lack of awareness and acceptance of biofuels as alternative: Provide fuel property basis for win-win value propositions

At-C: Data availability across the supply chain: Providing pathway data to enable determination of benefits and impacts

1 – Project Overview

HPF Project Overview

Strategy

Develop fundamental biomass conversion/bio-blendstock chemistry/engine performance relationships	Identify new fuel options for more efficient engines	Measure blended fuel performance and provide data for technical analyses

Approach	Outcome	Relevance
• First systematic fuel property-based approach for biofuels	• Establish chemical structure–fuel property relationships • Merit function • Blended fuel properties • Basis for future fuel improvements	• Relate bio-blendstock chemistry to engine performance • Understanding of real-world fuel • Opportunity for future fuels offering improvements in sustainability, energy density, performance, efficiency, etc.
• Tiered screening	• Efficient evaluation of high potential blendstocks • Identification of high-potential bio-blendstocks	• Combines market & science based approaches • Enables science-based approach with limited resources

HPF Project Overview (cont.)

Strategy

Develop fundamental biomass conversion/bio-blendstock chemistry/engine performance relationships	Identify new fuel options for more efficient engines	Measure blended fuel performance and provide data for technical analyses

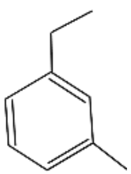
Approach	Outcome	Relevance
• Co-optimization	• Fuels enable expansion of optimally efficient engine operating conditions	• Meet Co-Optima engine efficiency targets (9-14% improvement)
• Informed by stakeholders	• HPF selection criteria based on stakeholder needs	• Provide market acceptable options

HPF Project Overview (cont.)

Fuel property-based approach

Establish fuel criteria

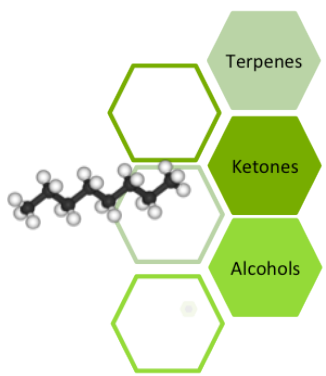
Rigorous candidate screening process



Procure and test blendstocks

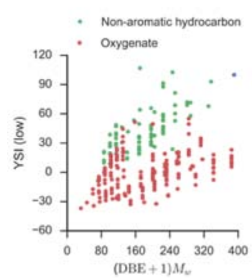
Purchase or produce candidates for evaluation

Create database, generate property relationships



Validate and understand

Determine blend properties, model fuel properties



Establish pathway data

Target fuel properties to generate key data

Retrosynthetic analysis

Feedback to ASSERT & MT

Compatibility, performance, and production data

2 – Approach (Management)

HPF Responsible for Identifying and Characterizing Candidate Bio-blendstocks

Survey potential high-performance, low-GHG blendstock options available from biomass and petroleum sources, including pathway development and sample generation for mixtures and materials not available elsewhere

Evaluate their fuel characteristics

Measure and/or simulate their engine performance

Assess their sustainability, scalability, and affordability metrics

Evaluate infrastructure / retail barriers to their use

Share this information broadly with stakeholders and scientific community

FY17 Team Lab Leads and PIs

INL: ***Erin Searcy***

Berkeley Lab: ***Blake Simmons,*** Todd Pray, Jay Keasling, Leonard Katz

Los Alamos: ***Andrew Sutton***

NREL: ***Tom Foust,*** Amie Sluiter, Mark Nimlos, Seonah Kim, Bob McCormick, Gregg Beckham

Oak Ridge: ***Brian West,*** Mike Kass, Chaitanya Narula

Pacific Northwest: ***Karl Albrecht,*** Dan Gaspar, Tim Bays, Phillip Koech

Sandia: ***Anthe George,*** Ryan Davis, John Gladden, Corey Hudson, Oliver Kilian

Team Lead: Dan Gaspar (PNNL)

Co-Lead: Anthe George (SNL)

Integrated Team Leverages Strengths of Members

	INL	LBNL	LANL	NREL	ORNL	PNNL	SNL
Establish fuel property criteria				Core effort		Core effort	Core effort
Obtain candidate blendstocks		Core effort	Core effort	Core effort	Effort complete	Core effort	Core effort
Measure & validate properties		Executed via commercial vendor	Executed via commercial vendor	Core effort	Core effort	Core effort	Core effort
Establish pathway data	Effort complete	Core effort	Core effort	Core effort		Core effort	Core effort

Effort complete

Core effort

Executed via commercial vendor

Communication Strategies

- Biweekly technical teleconferences for all HPF members; COLT and BETO invited (along with any interested Co-Optima members)
  - 2nd Wednesday – Lightning round (all PIs briefly describe progress)
  - 4th Wednesday – Technical presentation and program update
- Biweekly management teleconferences for HPF leadership, COLT, Tom Foust, Blake Simmons
  - 1st Wednesday – HPF opportunities and issues
  - 3rd Wednesday – invite leadership of another team
- Annual HPF PI meeting (early in FY)
- **Annual Co-Optima meeting (winter)**

- HPF lead and co-lead engagement with other teams' meetings

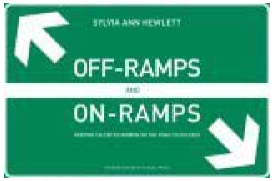
Large, complex HPF team coordinates and communicates to maximize collaboration

Connections to BETO Core Programs and Industry

- Leveraged work from core programs
  - Historical knowledge
  - Samples
- Achieved feed forward and feed backward with core BETO programs
  - Information
  - New discoveries
- Established easy conduit for information exchange
  - Exchanges of information not historically fluid
  - Crossover research prevents duplication of effort
  - Input from multiple platforms shifts ideas and research in core programs
- Establishing routes for transfer of work
  - Back to BETO core programs
  - External partnerships or agreements (FOAs, CRADAs, etc.)

Historical Knowledge → Samples → New Discoveries → Advanced Development → Increased TRL

BETO Core Programs ↔ Co-Optima



Transfer to:
BETO Core
Industry
Academia

Go/No-go Milestone (3/31/2017)

Milestone

1. Identify at least three bio-blendstocks that have passed Tier 2 screening as a Thrust I blend component
2. Demonstrate in an engine that a fuel blended with one of these components provides matching engine performance to a petroleum-derived fuel

Criteria

1. Demonstrate sufficient progress on Thrust I R&D to justify continued funding
2. Establish validity of the research approach
3. Determine if the project scope needs to be redefined

Decision Point (March 2017)

Purpose: Define relative Thrust I and Thrust II research priorities

Timing coincides with end of Thrust I fuel discovery (candidate identification) and preliminary evaluation

Key questions: What essential fuel R&D is needed in Thrust I and are there candidates ready for further scale-up R&D?

The team will have:

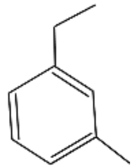
- **Surveyed the potential low-GHG blendstock options available from biomass and petroleum sources**
- **Evaluated their physical / chemical properties**
- **Measured and/or predicted their engine performance**
- Assessed their sustainability, scalability, and affordability metrics
- Evaluated infrastructure / retail barriers to their use
- Shared this information broadly with stakeholders / scientific community

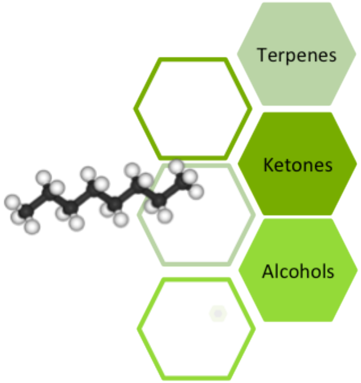
2 – Approach (Technical)

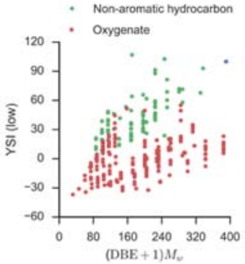
Technical Approach is Fuel Property-Based

Aimed at establishing critical relationships

Establish fuel criteria	Procure and test blendstocks	Validate and understand	Establish pathway data	Feedback to ASSERT & MT
Rigorous candidate screening process	Purchase or produce candidates for evaluation Create database, generate property relationships	Determine blend properties, model fuel properties	Target fuel properties to generate key data	Compatibility, performance, and production data







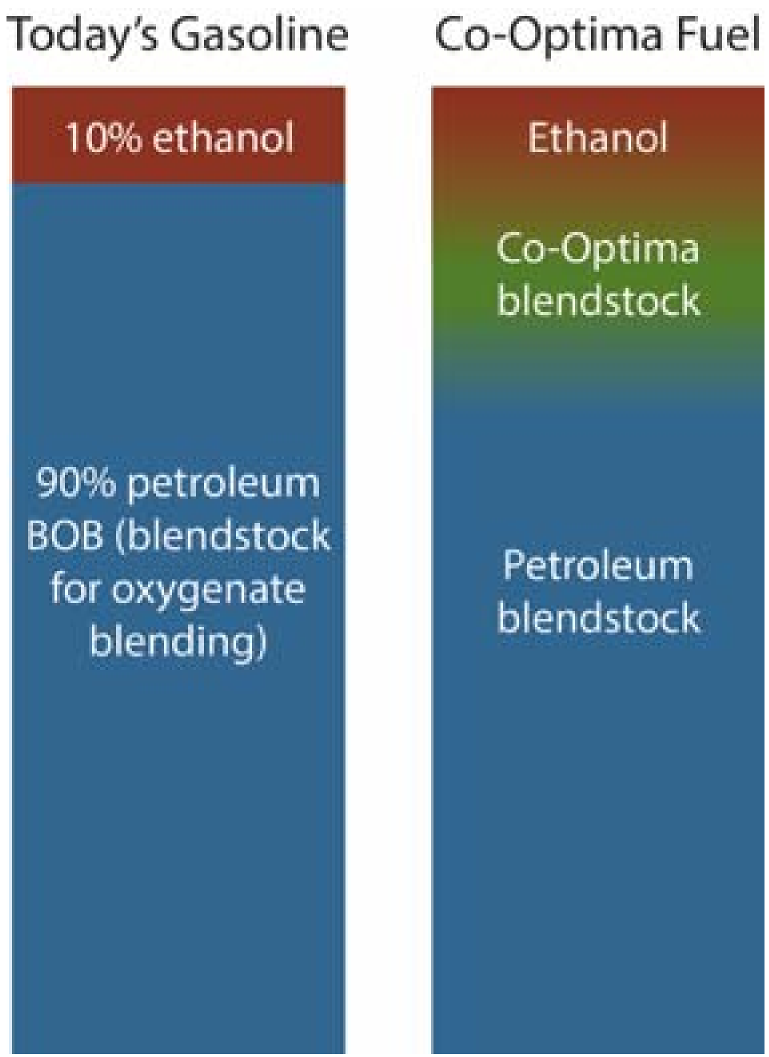
BC

TC

Retrosynthetic analysis

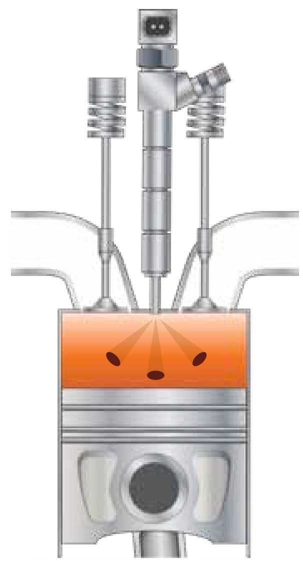
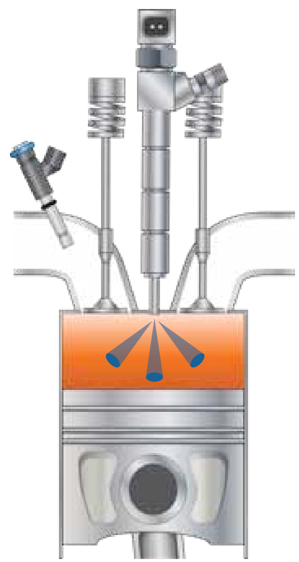
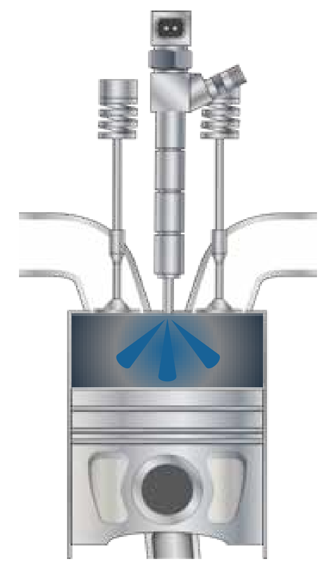
Three Critical Relationships

- **Identifying relationship between molecular structure and fuel properties**
- **Identifying relationship between fuel properties and engine performance**
- **Understanding the (nonlinear) blending behavior of bio-blendstocks in petroleum blendstocks**

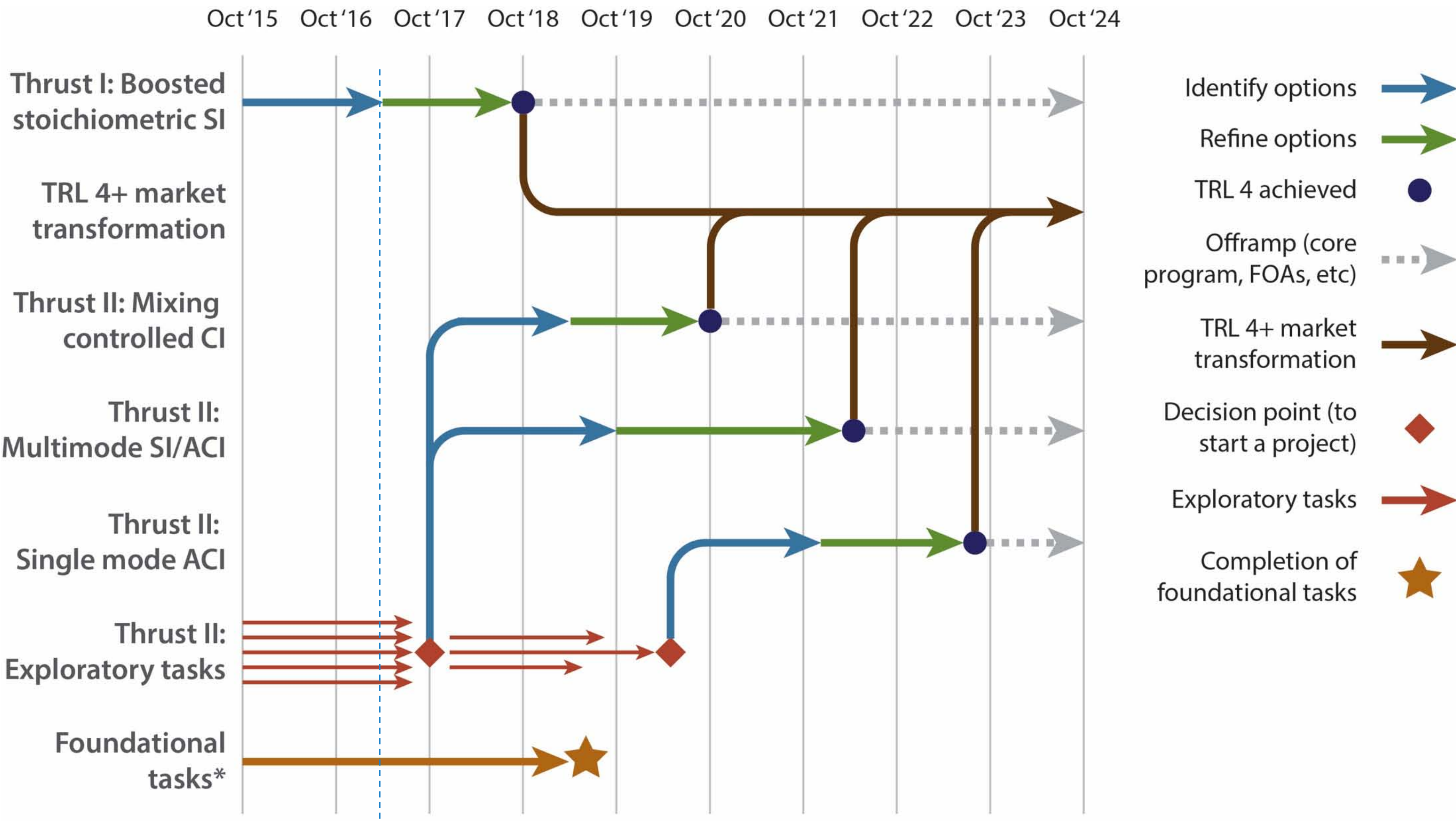


Staged Approach: Two Research Thrusts

Thrusts are distinguished by **fuel properties** required for performance using different combustion approaches

Thrust I: Spark Ignition (SI)	Thrust II: Advanced Compression Ignition (ACI) kinetically-controlled and compression-ignition combustion		
			
Low reactivity fuel	Range of fuel properties TBD		High reactivity fuel

Staged Approach: Timeline



* Development of fuel property database, analysis framework, fuel blending models, etc.

Co-Optima HPF Technical Challenges

- Bio-blendstock **chemistry-fuel property relationships require refining** to identify best chemistries to optimize engine efficiency and emissions performance via merit function
- Some fuel property tests require **large volumes** by research standards (~500 mL each). Generating enough material is difficult for low technology readiness level (TRL) pathways, especially mixtures and new chemistries
- Production **pathway information is not well defined** for many materials which have promising properties, making market and technical evaluation difficult
- **Blending fuel properties are often nonlinear** and not well understood for new bio-blendstock chemistries and mixtures

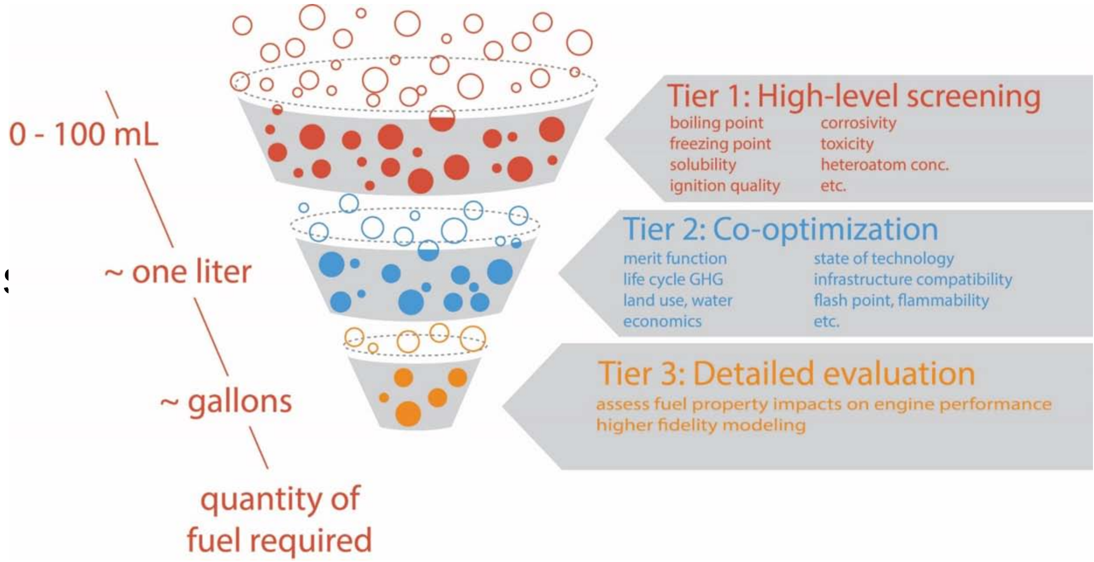
RON
Octane Sensitivity
HOV

$$\text{Merit} = \alpha \bullet [RON - 92] - \beta \bullet K \bullet [S - 10] + \gamma \bullet ON \bullet [HOV - 415] + \delta \bullet [HOV - 415] + \varepsilon \bullet [S_L - 46] - LFV_{150} - H(PMI - 2.0)[\zeta + 0.5(PMI - 2.0)]$$

Flame Speed
Distillation
Particulate Emissions

HPF Critical Success Factors: What Fuels Should We Make?

- Rigorous fuel property screening criteria that successfully relate fuel properties to engine performance provide basis
- Multiple candidates identified that pass each stage of tiered screening process



- Viable conversion pathways identified for each high-potential candidate
  - Viability determined by ASSERT analysis
- Finished fuels show improved performance vs. current fuels
  - Improve performance (emissions, efficiency)
  - Exhibit no show-stopping performance characteristics (compatibility, emissions, blending)

Approach – HPF Technical Tasks

FY16 → FY17

FY16

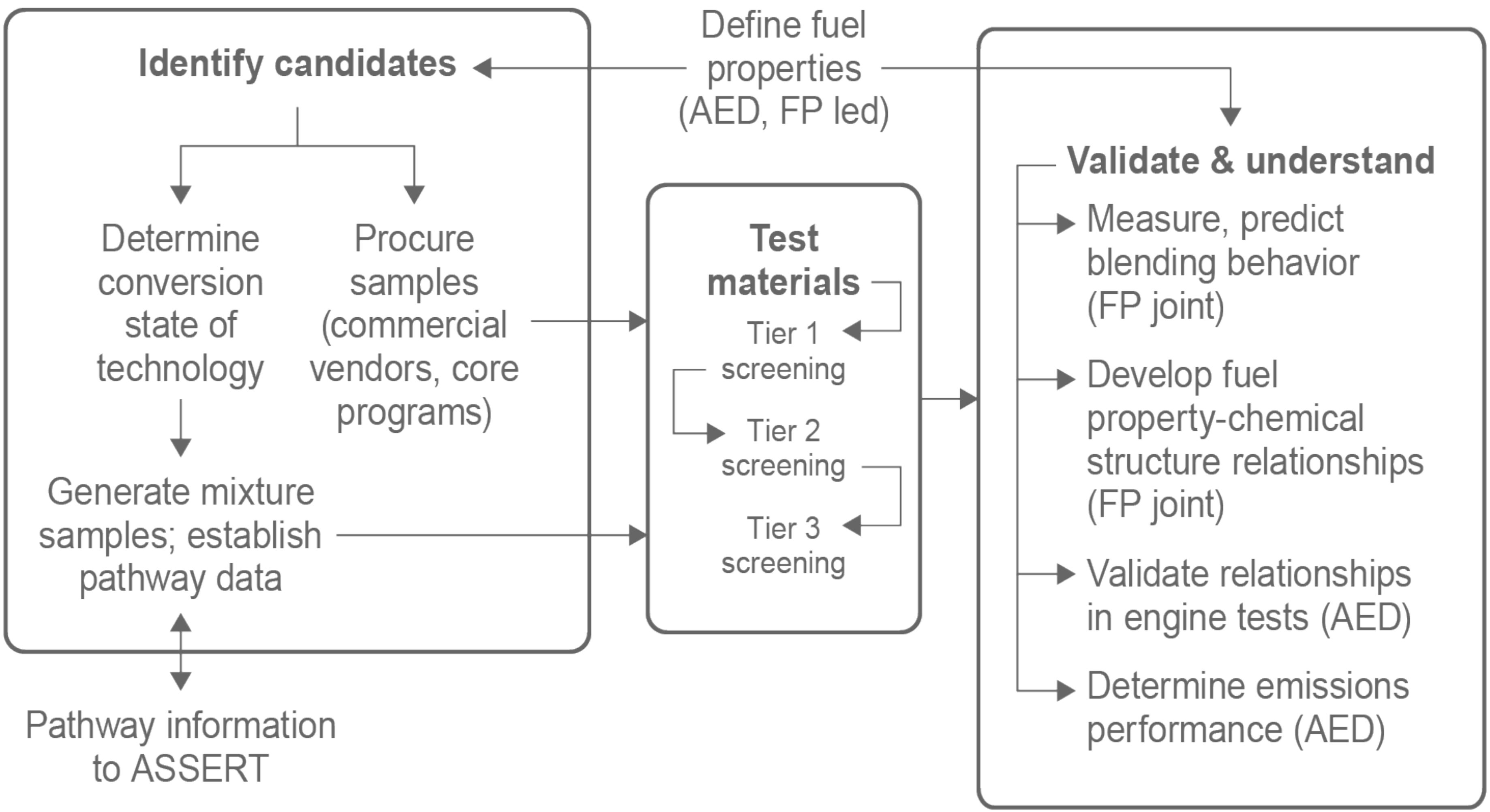
- Develop Thrust I selection criteria
- Thrust I chemical-fuel property correlation
- Survey Thrust I candidates
- Determine Thrust I blending properties

- Identified, evaluated >370 candidate bio-blendstocks
- Identified nearly 40 high-potential materials meeting Tier 1 screening criteria
- Measured blending behavior of nearly 40 materials
- Assisted ASSERT selection of 20 materials for technical analysis

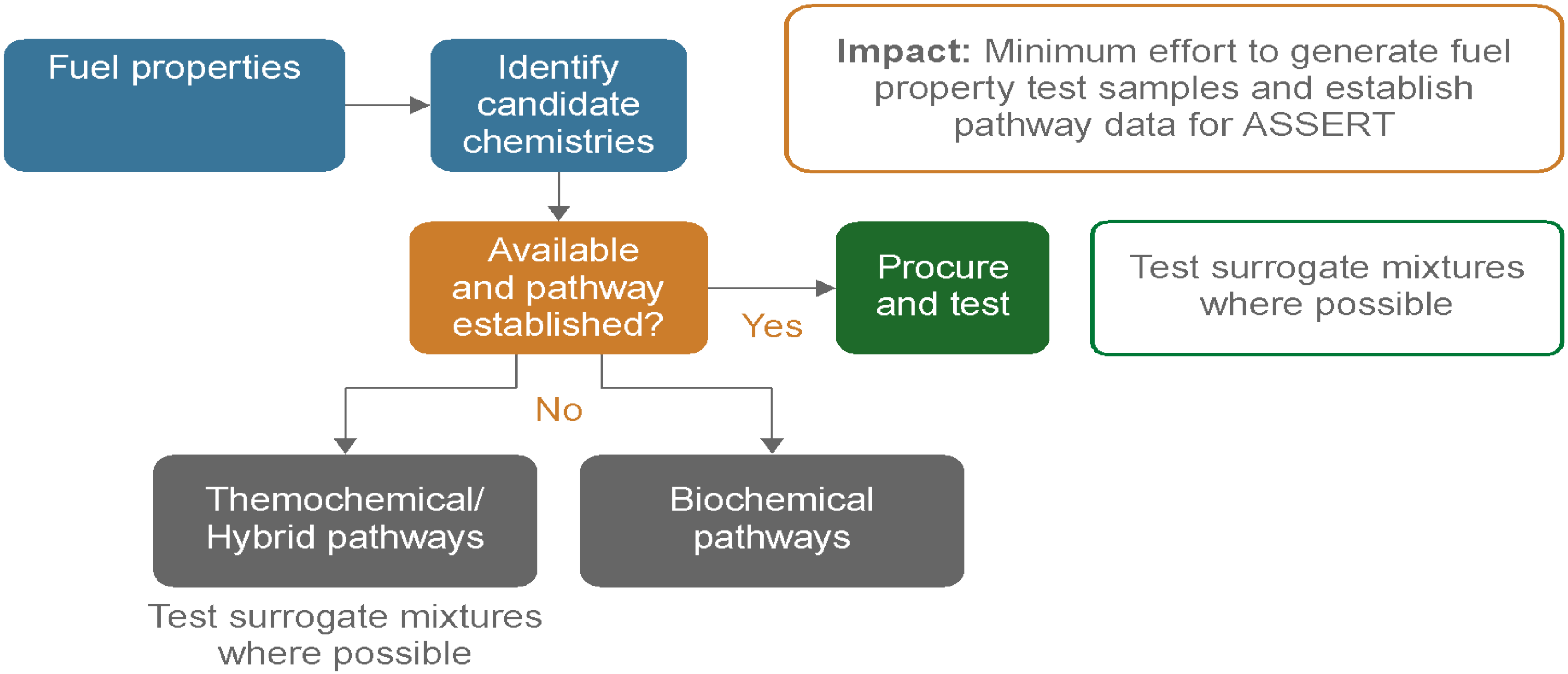
FY17

- Generate Thrust I pathway data and produce mixtures
- Determine Thrust I fuel and blending properties
- Develop Thrust II selection criteria
- Generate Thrust II pathway data and produce mixtures
- Survey diesel-like Thrust II candidates

Integrated Approach to Address Technical Challenges & Testing of Hypotheses

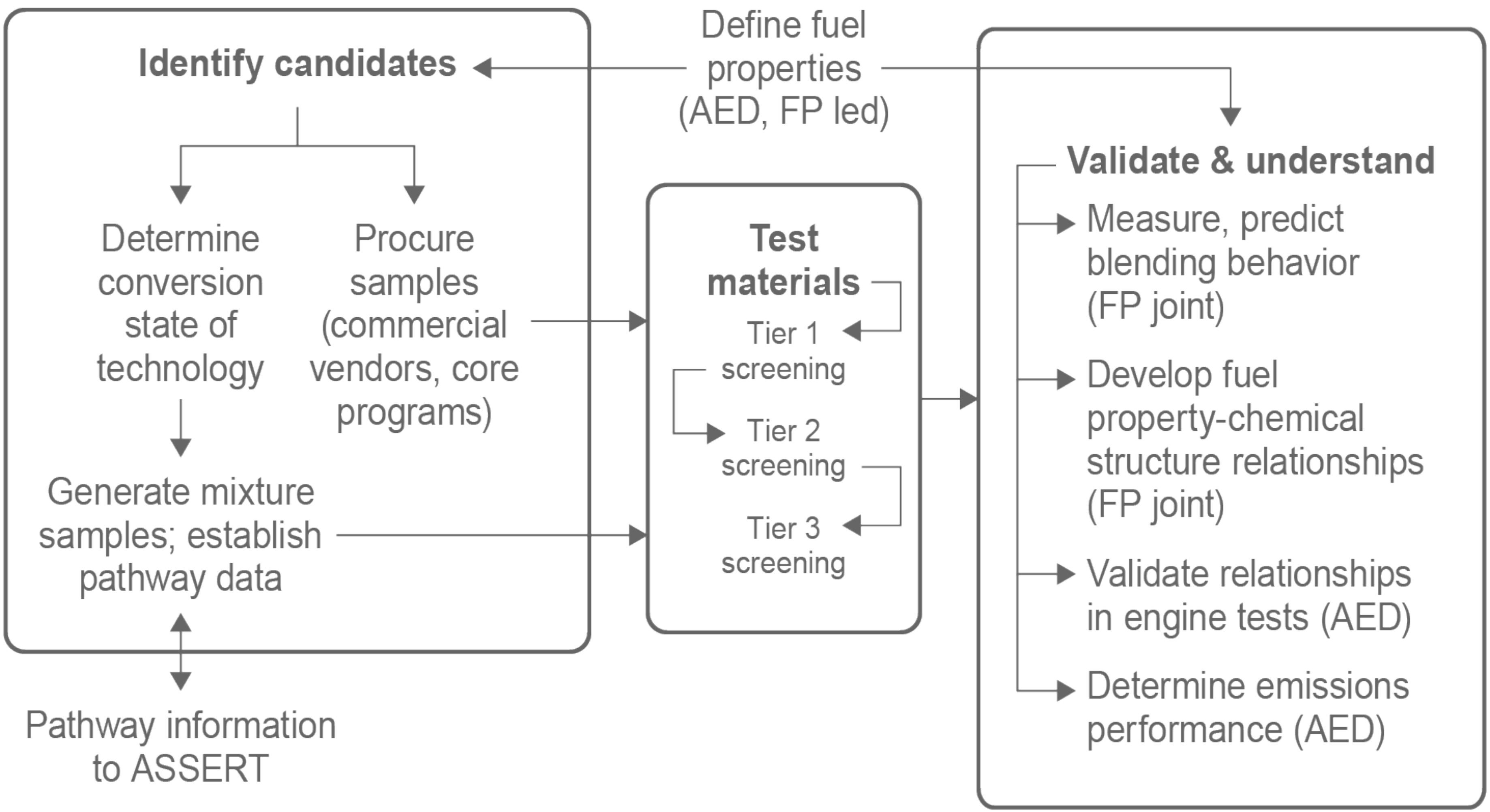


Coordinated Effort to Generate Fuel Property Test Samples and Establish Pathways



3 – Technical Accomplishments

Integrated Approach to Address Technical Challenges & Testing of Hypotheses

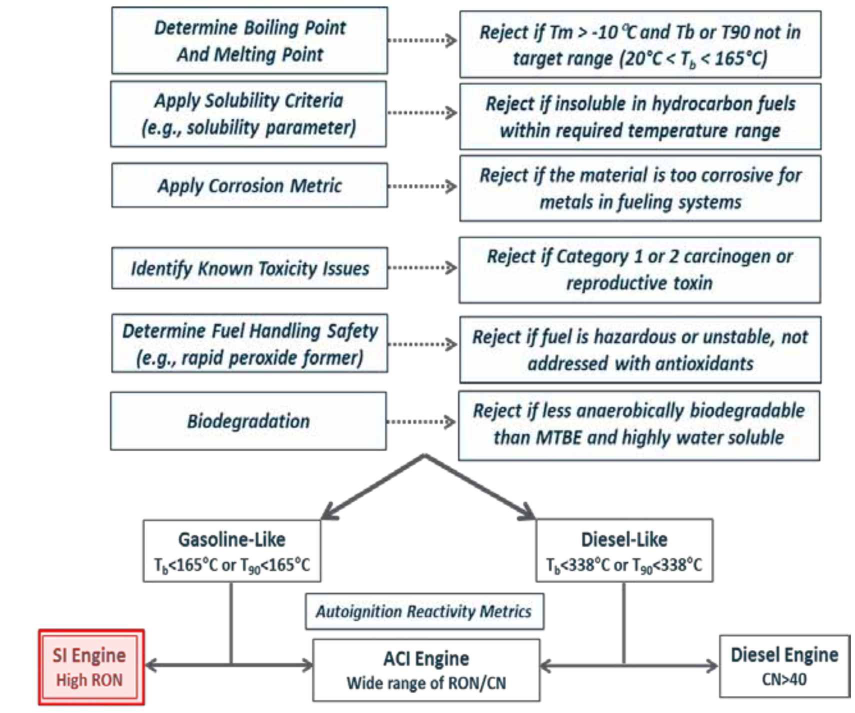


TA: Established Screening Criteria and Tiered Screening Process

Goal / HPF Task: Establish Thrust I screening criteria

- Fuel property-based approach bridges biofuel and engine communities
- Combination of considerations
  - Safety
  - Physical properties
  - Chemical properties
  - Autoignition characteristics
- Toxicity basis is “no more toxic than existing fuels”

Tier 1 Screening



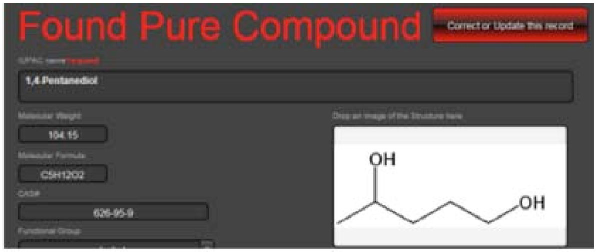
Contributing Labs: NREL, SNL, ORNL

First systematic fuel property-based approach to biofuels eliminating those with low potential

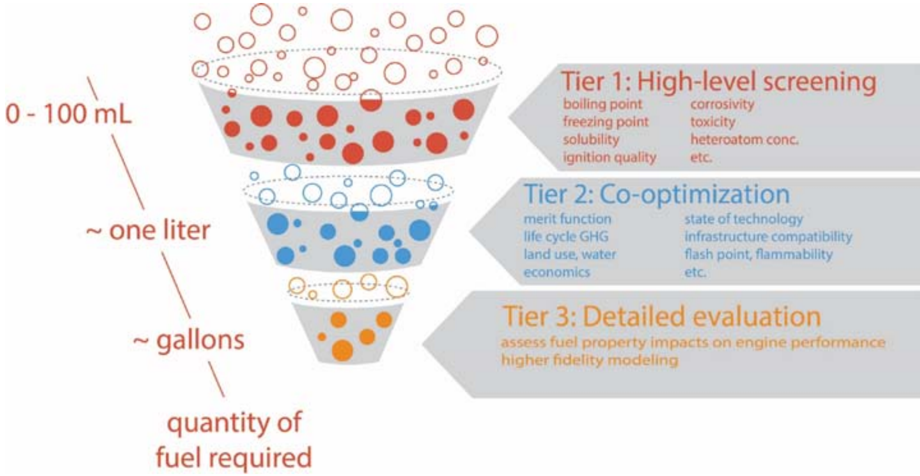
TA: Developed Fuel Property Database

Goal / HPF Task: Develop and populate fuel property database

- Produced on-line fuel property database
  - Includes 370 bio-blendstocks
  - Includes 130+ finished fuel blends
  - Continually updated to reflect new research and information
- Screening criteria developed for advanced SI engine fuels
- Tier 1 – bio-blendstock properties
- Tier 2 – finished fuel blend properties
  - Blending behavior critical to real-world performance
  - RVP, distillation curve, stability, HoV, particulate matter index (PMI), flame speed
  - Blending RON and MON



Publicly available: https://fuelsdb.nrel.gov/



Contributing Labs: NREL, SNL, ORNL, PNNL, LANL, LBNL

Provides data in public, accessible format which can be used by all stakeholders

TA: 40 High-Potential Thrust I Bio-Blendstocks Identified

Goal / HPF Task: Gather baseline evaluation data for Thrust I fuel property / chemical structure relationships

- Evaluated more than 300 molecules and mixtures
- Concluded 40 Thrust I bio-blendstocks met Tier 1 screening criteria
- Investigated high octane bio-blendstocks to improve engine performance
- Represents significant effort to identify, procure, test, and screen
- Enabled evaluation by ASSERT and MT teams

Alcohols	
1	Methanol
2	Ethanol
3	n-propanol
4	2-propanol
5	1-butanol
6	2-butanol
7	2-Methylpropan-1-ol
8	2-Methyl-1-butanol
9	2-Pentanol

Alkanes	
10	2,2,3-trimethylbutane

Alkenes	
12	Di-isobutylene

Furans	
13	2,5-dimethylfuran/ 2-methylfuran mixture

Esters	
14	Methyl acetate
15	Methyl butanoate
16	Methyl pentanoate
17	Methyl isobutanoate
18	Methyl-2-methylbutanoate
19	Ethyl acetate
20	Ethyl butanoate
21	Ethyl isobutyrate
22	Isopropyl acetate
23	Butyl acetate
24	2-methylpropylacetate
25	3-methylpropylacetate

Ethers	
26	Methoxybenzene (anisole)

Ketones	
27	2-butanone
28	2-pentanone
29	3-pentanone
30	Cyclopentanone
31	3-hexanone
32	4-Methyl-2-pentanone
33	2,4-dimethyl-3-pentanone
34	3-Methyl-2-butanone
35	Ketone mixture

Multifunctional mixtures	
36	Vertifuel (60% aromatics)
37	Catalytic conversion of sugars
38	Methanol to gasoline
39	Bioreformate
40	Catalytic fast pyrolysis
41	Sugar upgrading

Contributing Labs: NREL, SNL, ORNL, PNNL, LANL, LBNL

Application of first systematic fuel property-based screening approach allows determination of high-potential molecules and mixtures whose properties can improve engine performance

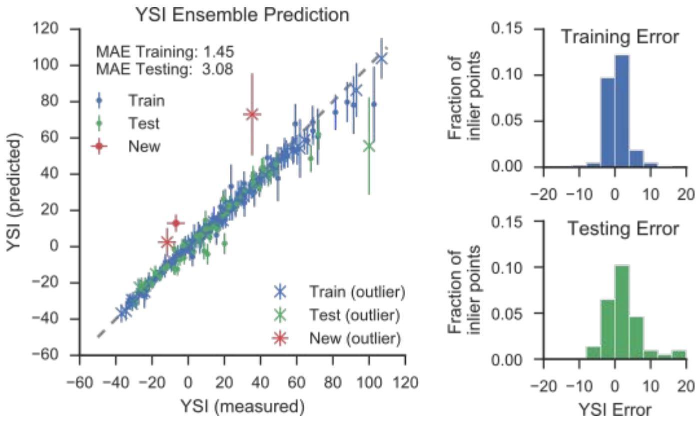
TA: Powerful Fuel Properties Prediction Tools Developed

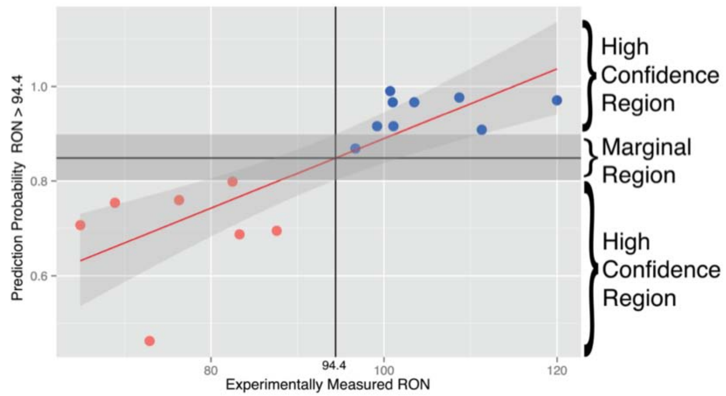
Goal / HPF Task: Develop fuel property-chemical structure relationships

- Prediction of yield sooting index (YSI) using a quantitative model
  - Finalized model shows good predictive accuracy to both test-set newly-measured compounds

- Developed general-purpose fuel property tool, using machine learning, applied to RON, threshold sooting index (TSI), melting point (MP)

Lab – PIs: NREL – Kim, St. John
SNL – Hudson, Whitmore, George





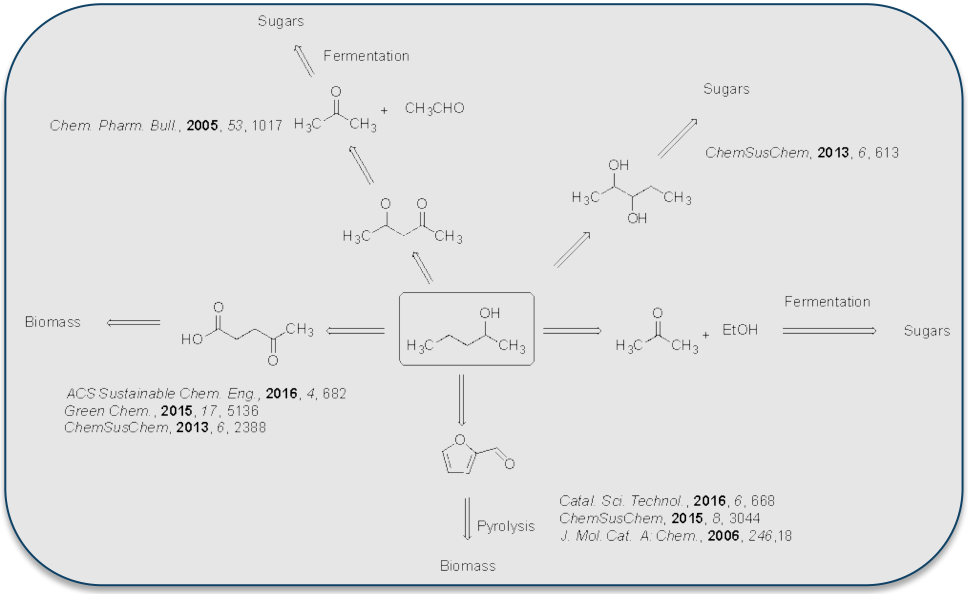
Modeling fuel properties based on chemical structures decreases need for testing and increases screening rate of new molecules

TA: First Combined Biochemical and Chemical Retrosynthetic Analysis

Goal / HPF Task: Determine conversion state of technology

- Retrosynthetic analysis: reverse engineering process to synthesize a desired product
    - First systematic fuel property-based approach
- Identified one or more biochemical and thermochemical pathways for all 40 high-potential blendstocks (except biochem approach for 2-methylfuran)
- Provides basis to evaluate conversion pathways, identify gaps, and inform ASSERT analyses

2-Pentanol RSA



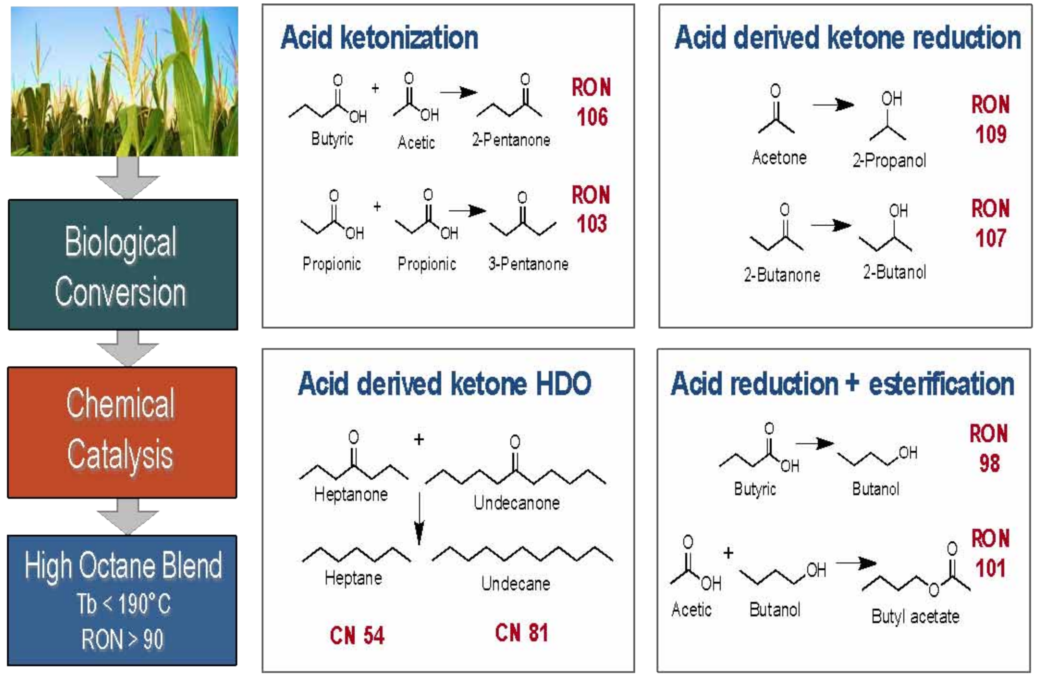
Contributing Labs: SNL, PNNL, LANL, LBNL

Provides pathways for evaluation, and basis for determining whether additional pathway development is necessary

TA: Established Biochem/Chemo-catalytic Routes to Esters, Alcohols, Ketones

Goal / HPF Task: Thrust I baseline synthesis data and generate mixtures for analysis

- Designed optimal hybrid biochem/chemo-catalytic target oxygenated fuels including esters, alcohols, and ketones
- Produced non-commercially available aerobically derived bio-blendstocks (e.g., MKs)
- Platform development for production of other short- and medium-chain ketones and alcohols



Lab - PI: NREL - Beckham

Hybrid biochemistry/chemistry platform used to target development of molecules and mixtures exhibiting Thrust I fuel properties

TA: Demonstrated High-Titer, High Volume Production Mono- and Sesquiterpenes

Goal / HPF Task: Thrust I and Thrust II baseline synthesis data and generate mixtures for analysis

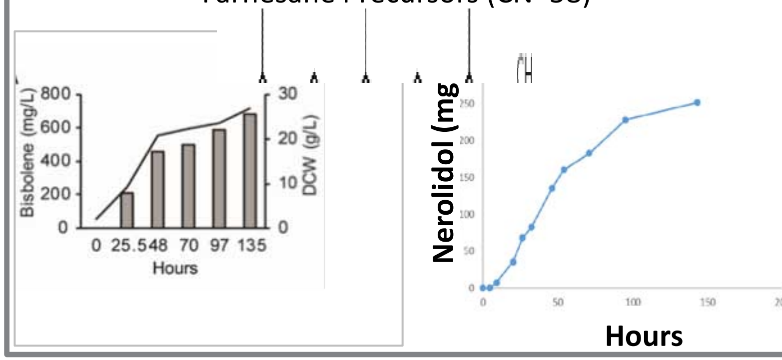
- Mono- and sesquiterpenes represent rich source of Thrust I and Thrust II fuels
  - Terpenoid family comprises >50,000 compounds
- Established protocols by producing 6 members: 1,8-cineole, carene, limonene, ocimene, pinene, and sabinene
- Demonstrated production on alkaline hydrolysate at 2-L batch fermentation:
  - High RON (99.2) 1,8-cineole (eucalyptol)
  - Improved bisabolene titers from 300mg/L to 700mg/L
  - Nerolidol at titer of 260mg/L

Lab – PIs: SNL – Kilian, Gladden, George
LBL – Simmons, Pray, Katz

Rhodosporidium IFO0880 x EC17-3

Eucalyptol

Farnesane Precursors (CN=58)



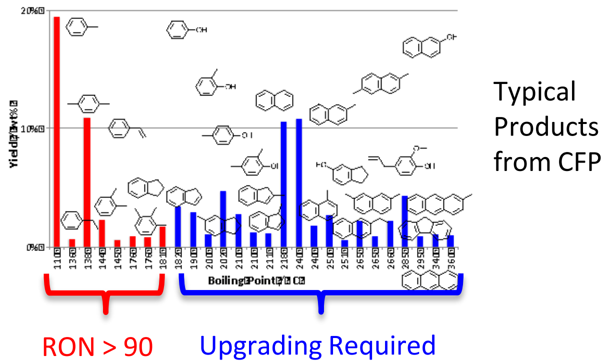
Biochemistry platform used to target development of molecules and mixtures exhibiting Thrust I and II fuel properties not available from other sources

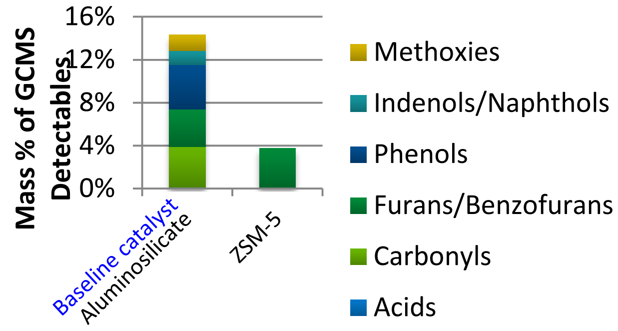
TA: Catalytic Fast Pyrolysis (CFP) Oil Production and Catalyst Development

Goal / HPF Task: Thrust I and Thrust II baseline synthesis data and generate mixtures for analysis

- Collected 500 mL of CFP oil
  - Demonstrated distillation into light and heavy fractions
  - Light fraction has high RON – well suited for Thrust I fuel
  - Heavy fraction requires hydrotreating
- Tested dozens of catalysts at micro scale
  - Down-selected catalyst for oxygenate production
  - Demonstrated oxygenate enhancement at bench scale
  - Closed mass balance and measure composition of oil

Lab – PI: NREL – Nimlos





Thermochemical approach modified to target hydrocarbon and oxygenate mixtures expected to meet Thrust I fuel property targets

TA: New High-Octane Mixtures Designed From Alcohols and Light Oxygenates

Goal / HPF Task: Thrust I baseline synthesis data and generate mixtures for analysis

Mixed Ketones or Alcohols

- Original Guerbet alcohols did not meet 98 RON requirement
- Alternative approach generates ketone mixture from ethanol or acid mixtures meeting 98 RON target with 30% greater energy density

Iso-olefins from Oxygenates

- Use light oxygenates not meeting fuel property requirements with no separation
- Single catalytic step to produce isobutene followed by oligomerization
- Product meets targeted RON>99 with high energy density

Lab – PI: PNNL – Albrecht

Thermochemical approaches were modified to target mixtures expected to meet Thrust I fuel property targets

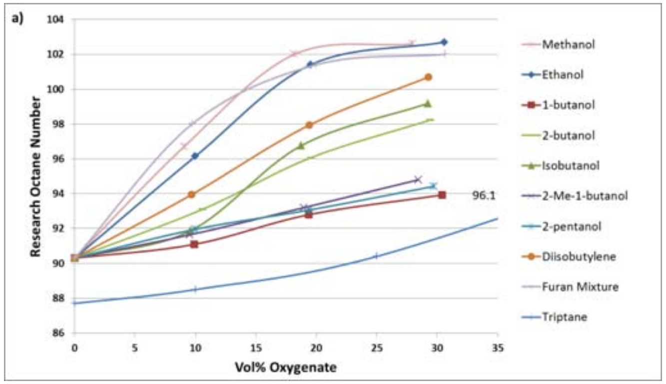
TA: Blend Property Testing (1)

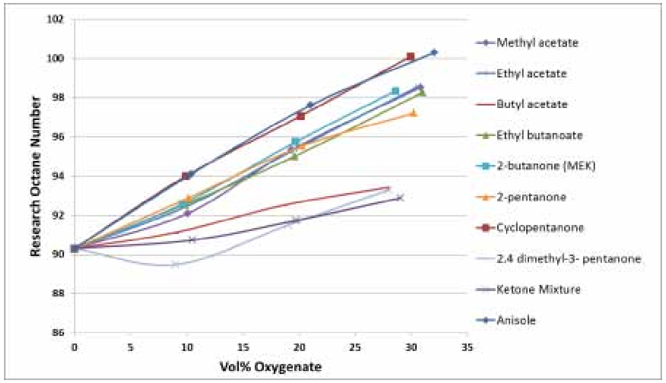
Goal / HPF Task: Measure blend properties to predict engine performance

- Octane Number
- Measured as blends into 4-component surrogate

Property	Result
Isooctane, vol%	55
n-Heptane, vol%	15
Toluene, vol%	25
1-Hexene, vol%	5
RON	90.3
MON	84.7
AKI	87.5

- 98 RON threshold was achieved by all but seven of the 20 blendstocks tested
- Triptane, with a pure component RON of 112, did not attain the 98 RON level at 25 vol%





Lab – PI: NREL – McCormick

Blend properties relate bio-blendstock properties to engine performance, focusing future engine research on most promising candidates

TA: Blend Property Testing (2)

Goal / HPF Task: Measure blend properties to predict engine performance

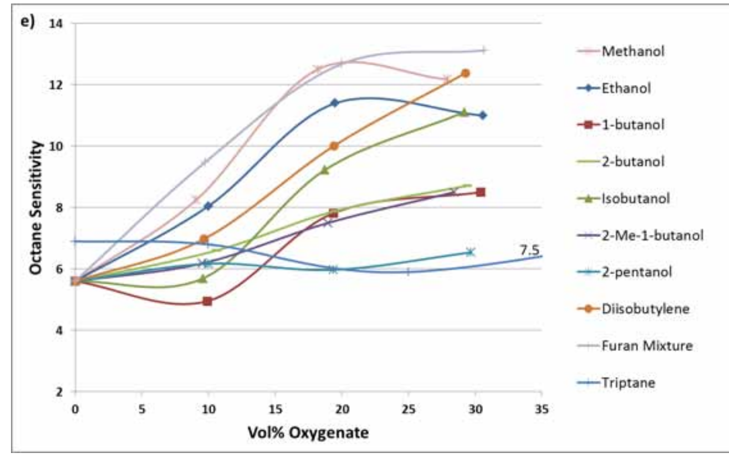
Octane Sensitivity, S (RON – MON)

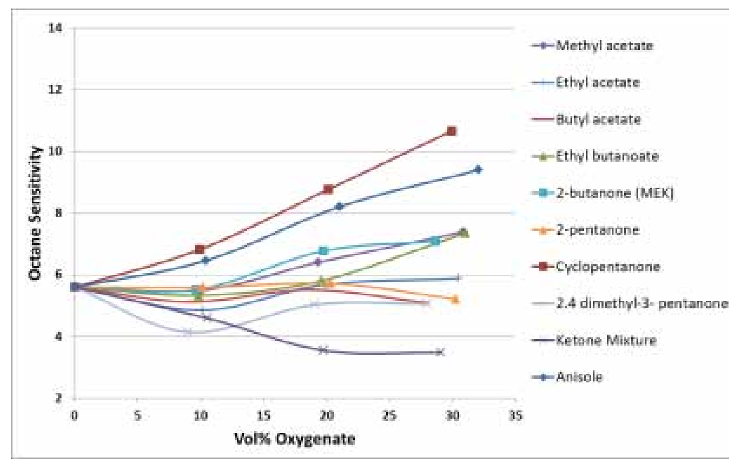
- Alcohols (except 2-pentanol), di-isobutylene, furans, cyclopentanone, and anisole all achieve S > 8
- Esters and ketones fail to do so

Tier 2 Results – Other Properties

- Blends into a commercial RBOB
- Methanol and methyl acetate increase RVP more than ethanol
- Anisole and methyl acetate have large effects on distillation
- Cyclopentanone and furan blends fail oxidation stability

Lab – PI: NREL – McCormick



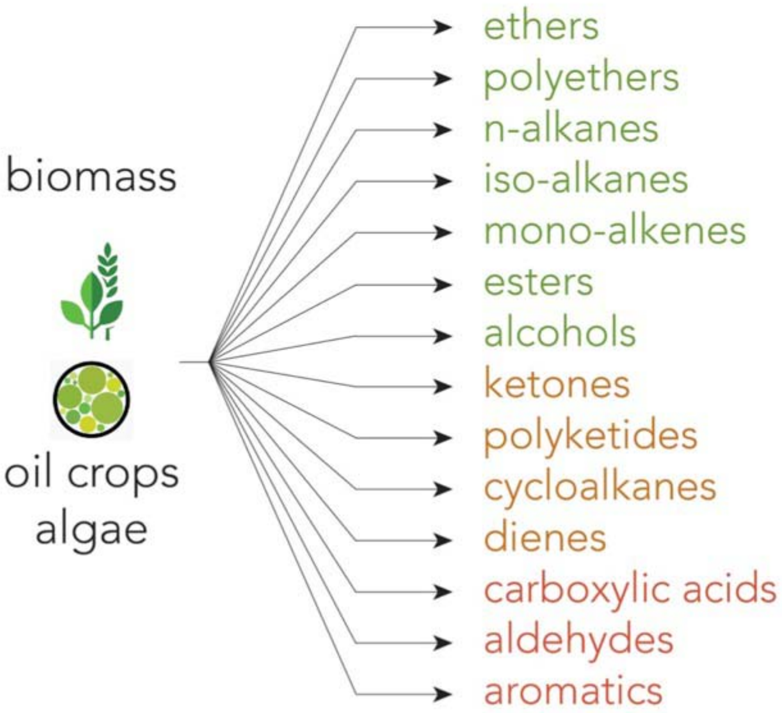


Blend properties relate bio-blendstock properties to engine performance, focusing future engine research on most promising candidates

TA: Thrust II Functional Group Analysis

Goal / HPF Task**:** Determine what chemistries have potential as diesel-like Thrust II bio-blendstocks based on preliminary selection criteria

- Determined several of hydrocarbon and oxygenate functional groups are (green) or may be (orange) suitable for use as diesel-like bio-blendstocks
- Screening functional groups based on fuel properties:
  - Autoignition (cetane number)
  - Boiling point
  - Flashpoint
  - Kinematic viscosity
  - Freezing point
  - Biodegradability and toxicity
- Analysis based on literature



Labs – PI: PNNL – Gaspar, NREL – McCormick

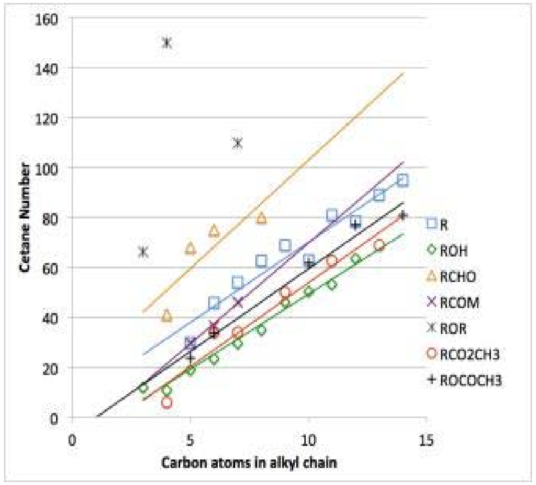
First systematic application of the fuel property-based approach to diesel-like bio-blendstocks

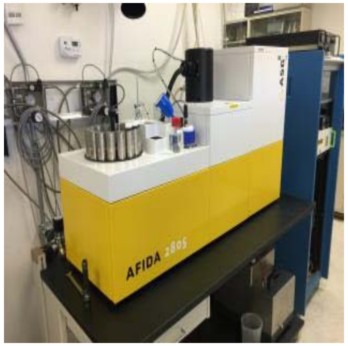
TA: Thrust II Diesel-like Bio-blendstock Screening Criteria Established

Goal / HPF Task: Develop screening criteria for diesel-like Thrust II bio-blendstocks

- Developed critical screening properties
  - Cetane number > 45
  - Boiling point or T90 < 300°C
  - Flashpoint > 52°C
  - Kinematic viscosity > 1.9 mm^2/s and < 4.1 mm^2/s
  - Freezing / cloud point < -10°C
  - Biodegradability and toxicity no worse than current fuels
  - Potential to reduce particulate emissions
- FP database populated with data for diesel boiling range components
- High throughput cetane number measurement system established

Lab – PI: NREL – McCormick



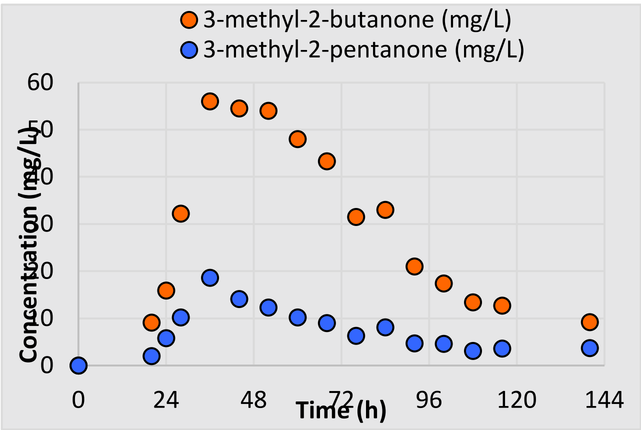


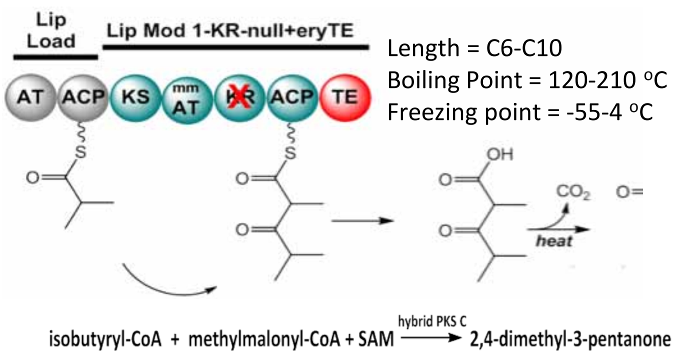
Biochemistry platform used to target development of molecules and mixtures exhibiting Thrust II fuel properties not available from other sources

TA: Optimal Polyketide Synthases Designed to Make Mixed Methyl Ketones

Goal / HPF Task: Thrust II baseline synthesis data and generate mixtures for analysis

- Fermentation process development for *S. venezuelae* and *S. albus* in fed-batch fermentation
- Platform development for production of short- and medium-chain ketones and alcohols
  - Demonstrated production of short-chain two-ketone mixture up to 80 mg/L
  - High volatility implies actual production above this titer
- Design optimal polyketide synthases in biological hosts for the production of medium-chain mixed methyl ketones
  - Identified as promising for Thrust II
  - Good properties for diesel-like fuels





Lab - PIs: LBL - Simmons, Pray, Keasling, Katz

Biochemical platform used to target development of molecules and mixtures expected to exhibit Thrust I and II fuel properties

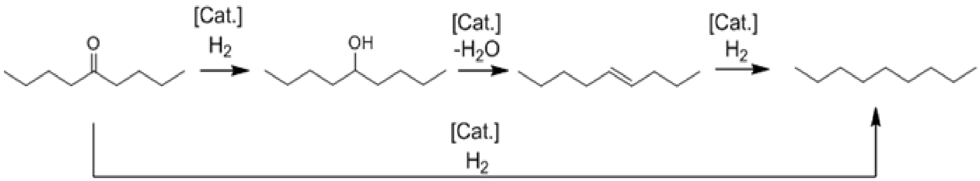
TA: Simple Catalytic Approaches Can Build Carbon Scaffolds of Required Chain Length

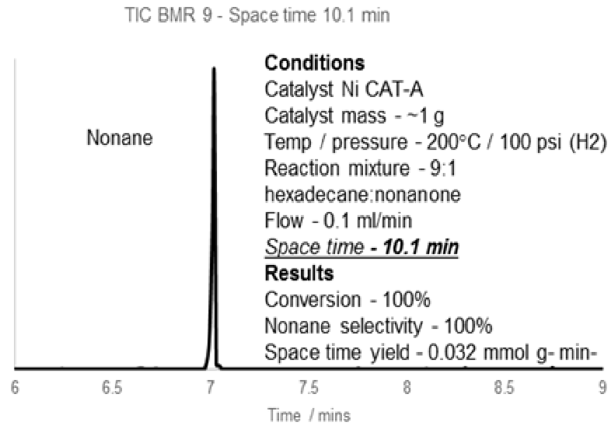
Goal / HPF Task: Thrust II baseline synthesis data and generate mixtures for analysis

- Developed simple routes using cheap robust catalysts for the conversion of functional groups to support Thrust II production

- One reactor conversion with low temperature and no additional catalyst required

- Space time of only 10 minutes and batch residence time of 14 hours





Lab – PI: LANL – Sutton

Catalytic platform used to target development of molecules and mixtures exhibiting Thrust II fuel properties

Technical Accomplishment Summary

Thrust I Accomplishments

- Developed criteria, screened and evaluated broad range of bio-blendstock chemistries
- Identified chemistries with potential to improve spark ignition engine performance
- Developed baseline understanding to address key barriers
- Provided key data to ASSERT, FP, and AED

Thrust II Accomplishments

- Initial steps complete: Developed criteria for diesel-like Thrust II and initiated candidate identification and testing
- Initial results suggest bio-blendstocks can offer performance improvements over current fuels

4 – Relevance

Goals

Co-Optima Goal

Determine key fuel properties that enable improved engine efficiency

Provide key science to enable high efficiency combustion modes

Capitalize on unique properties available from bio-blendstocks

Use stakeholder input to guide analysis

Accelerate market penetration of both engines and fuels.

HPF Goals

Develop fuel chemistry-fuel property-engine performance relationships

Determine new fuel options afforded by bio-derived fuels, including conversion pathways, for more efficient engines with lower harmful emissions

Generate market pull for biofuels through co-optimization

Relevance: Why Co-Optima, and Why High-Performance Fuels?

From the MYPP: "**Co-development of fuels and engines** has proved successful for **controlling** criteria **pollutants** and has the potential to drive increased vehicle **engine efficiency** and **reduced** GHG **emissions**."

HPF Goals…

Develop biomass conversion-fuel chemistry-engine performance relationships

Provide new fuel options for more efficient engines with lower harmful emissions

Generate market pull for biofuels through co-optimization

…can help achieve these aims by providing **data and new options** for **decision makers** with an **enhanced value proposition** for bioenergy via improved engine performance

Relevance: BETO Strategy

Strategy

Develop fundamental biomass conversion/bio-blendstock chemistry/engine performance relationships	Identify new fuel options for more efficient engines	Measure blended fuel performance and provide data for technical analyses

Co-Optima specifically addresses the BETO Strategic Plan:

"…including co-designing next-generation engines and biofuels through a collaboration with Vehicle Technologies Office. Co-optimization of fuels and engines offers the potential to significantly improve vehicle engine efficiency, maximize engine performance and carbon efficiency, and reduce harmful emissions through accelerating the widespread deployment of improved fuels and engines. BETO will work with the national laboratories and stakeholders to address technical barriers and facilitate eventual market entry of co-optimized fuels and engines."

Impact: Co-Optima approach links BETO and VTO strategies

Relevance: BETO Program Goals

Strategy

Develop fundamental biomass conversion/bio-blendstock chemistry/engine performance relationships	Identify new fuel options for more efficient engines	Measure blended fuel performance and provide data for technical analyses

Enhance bioenergy value proposition per BETO MYPP

- Database and understanding provide options to improve engine performance with fuels that do not behave like petroleum-based fuels

Improve knowledge of biofuels emissions compared with conventional fuel emissions

- HPF provides candidate materials for testing by engine experts, including in innovative new engine technologies and operating approaches
- HPF has developed new tools to predict and understand sooting from fuels with bio-blendstocks and petroleum fuels

Impact: Co-Optima approach enhances bioenergy value proposition and advances BETO emissions reduction goals

Relevance: BETO Program Goals (cont.)

Strategy

Develop fundamental biomass conversion/bio-blendstock chemistry/engine performance relationships	Identify new fuel options for more efficient engines	Measure blended fuel performance and provide data for technical analyses

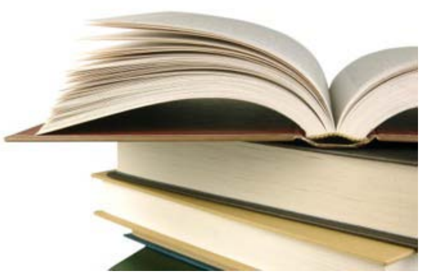
Validate Technology and Reduce Risk

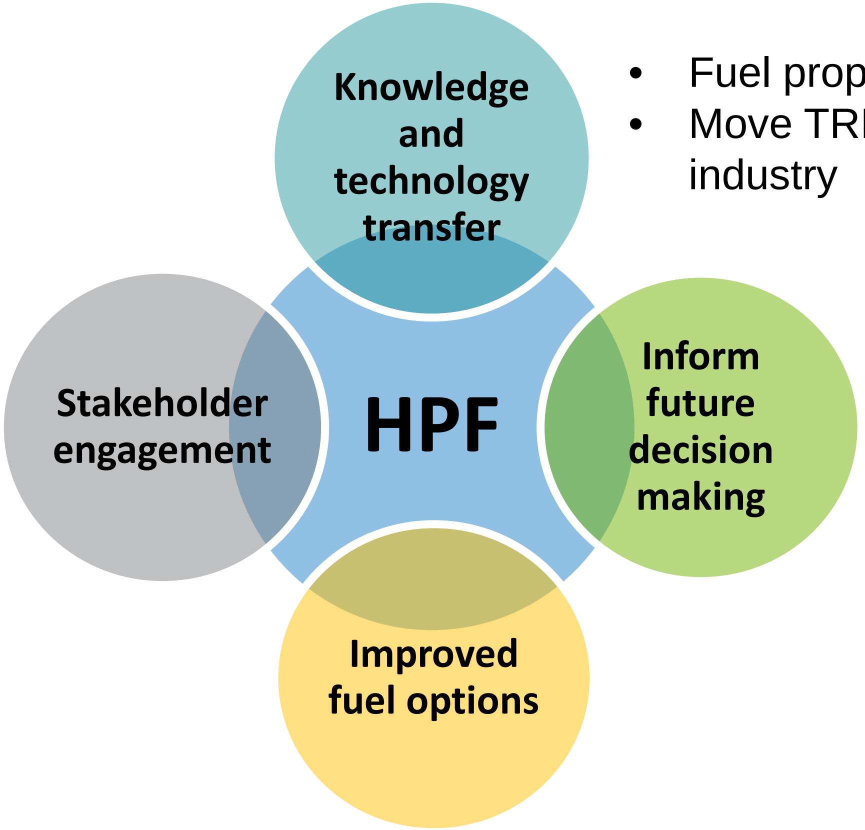
- Verification of bioenergy-conversion pathways underpins BETO's production cost and emissions-reduction estimates
- BETO uses techno-economic and emissions-reduction models based on pathway verification to focus its R&D
- Co-Optima fuel property-based approach couples technical performance basis to TEA and LCA
- Leveraging BETO core activities focused on process improvements through "Improved Catalysts and Separations" and "Engineering Biology" to generate target molecules and mixtures identified through screening for testing, when necessary
- HPF pathway development data directly informs technical analyses (ASSERT, MT)

Impact: HPF enables rapid assessment of candidates' potential benefits by ASSERT, MT

Relevance: Bioenergy Industry

- Meetings
- Informational webinars
- Reports
- Journal articles





- Fuel property data
- Move TRL ready science to industry

- Fuel property database

- Light duty
- Medium duty
- Heavy duty

Relevance: Impact on Commercial Viability of Biofuels

Change the value proposition

- Provide technical basis for engines optimized for biofuels
- Create win–win opportunities

Change the approach from formulation to fuel property specifications

- Grease the skids for future biofuel innovations

Increase bio-blendstock options for biofuels companies

- Provide technical basis to take advantage of bio-blendstock properties to enhance engine performance

5 – Future Work

Future Work: Summary

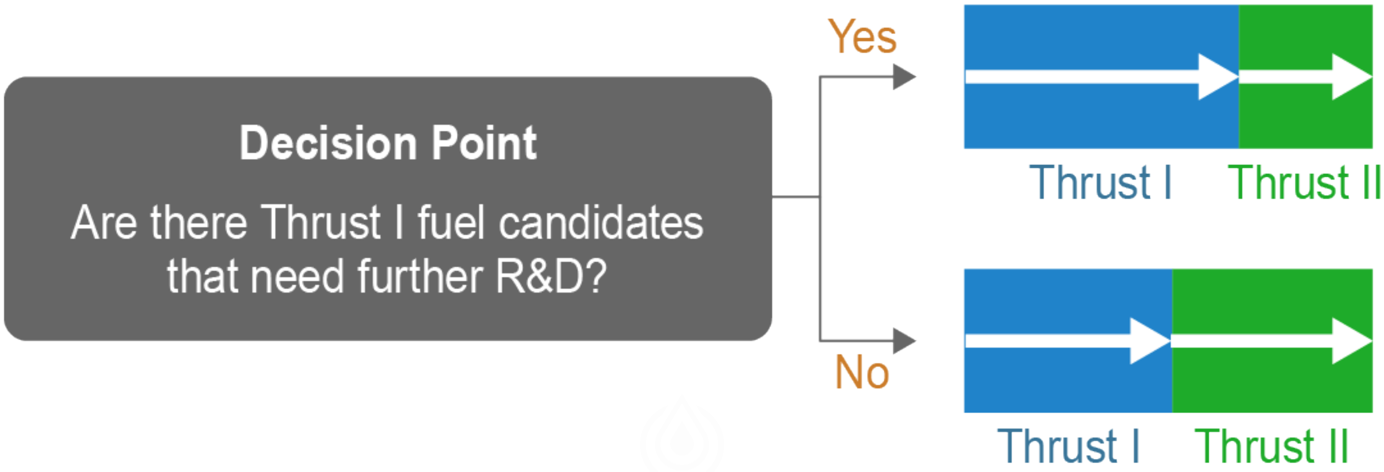
Decision Point will determine relative additional effort on Thrust I

Thrust I

- Finish screening, including validation in engine tests
- Obtain final pathway data
- Finalize understanding of blending behavior and compatibility

Thrust II

- Execute candidate identification and screening process to generate options
- Enable TEA and LCA analyses
- Determine blend behavior and compatibility



Decision Point (March 2017)

Purpose: Define relative Thrust I vs. Thrust II research priorities

Timing coincides with end of Thrust I fuel discovery (candidate identification) and preliminary evaluation

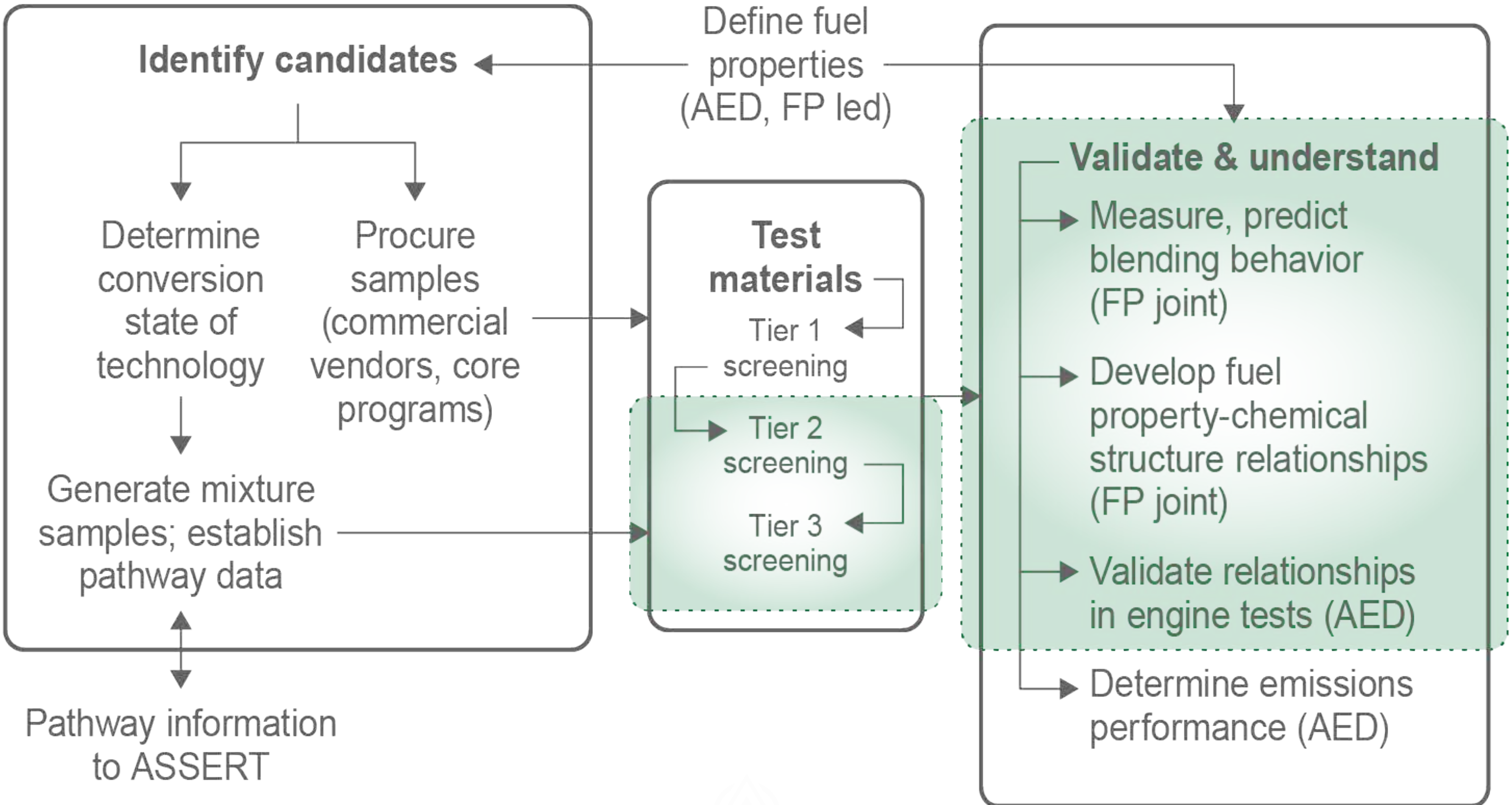
Key questions: What essential fuel R&D is needed in Thrust I, and are there candidates ready for further scale-up R&D?

The Co-Optima team will have:

- Surveyed the potential low-GHG blendstock options available from biomass and petroleum sources
- Evaluated their physical / chemical properties
- Measured and/or predicted their engine performance
- Assessed their sustainability, scalability, and affordability metrics
- Evaluated infrastructure / retail barriers to their use
- Shared this information broadly with stakeholders / scientific community

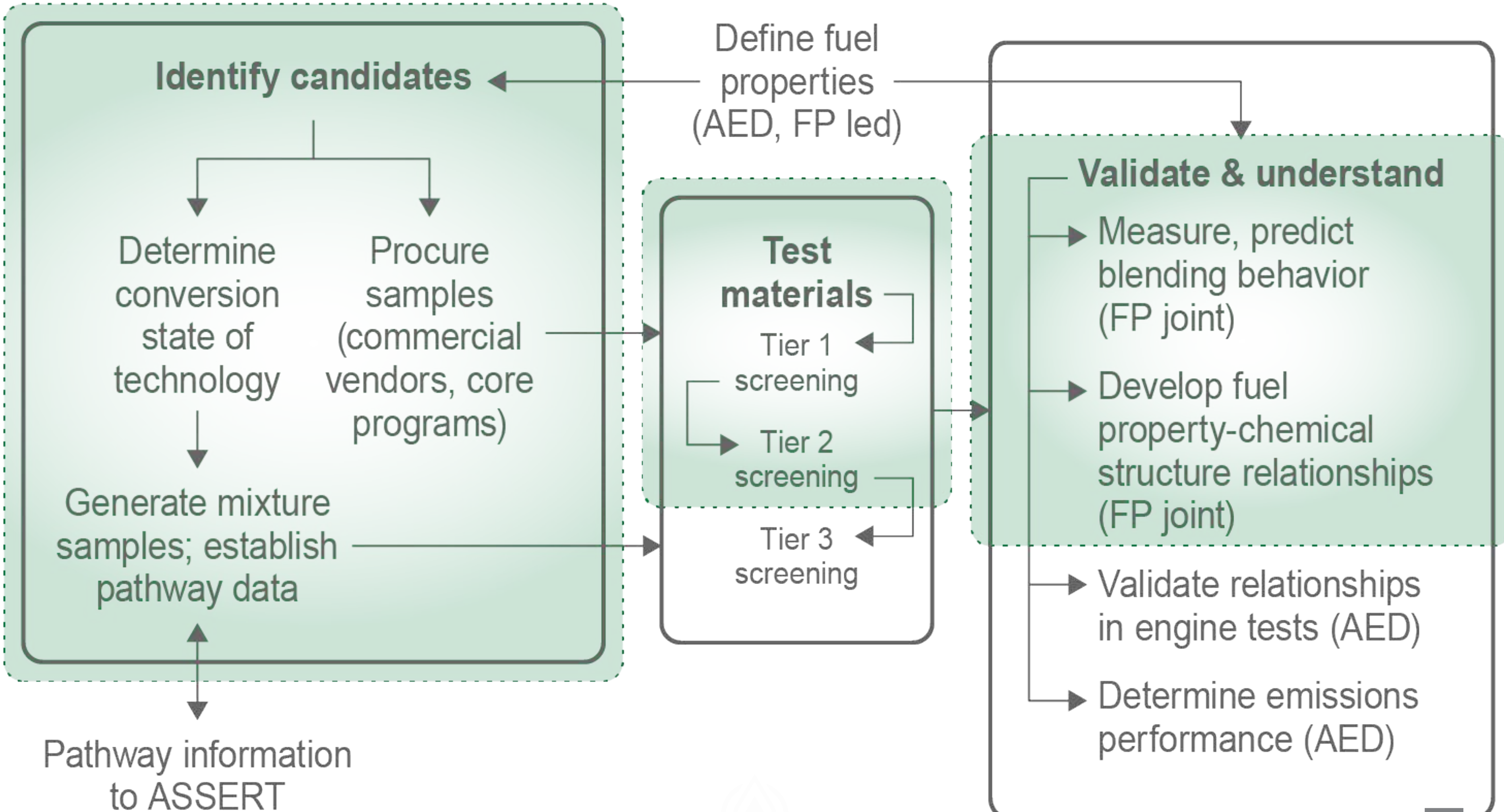
Future Work: Thrust I

HPF will complete Thrust I screening, measuring blending behavior, and development of fuel property-chemical structure relationships



Future Work: Thrust II

Future Work: Complete Thrust II candidate identification, screening, measure blending behavior, and initiate development of fuel property-chemical structure relationships



Thrust I Scope After Decision Point

High Thrust I Scenario

Establish fuel criteria → Procure and test blendstocks → Measure and validate → Establish pathway data → Feedback to ASSERT &

Blending performance and engine tests in realistic range of real BOBs and fuels validates performance (high aromatic, low aromatic, high olefin, E10, etc.)

Final pathway information for 5 highest potential bio-blendstocks to enable in depth TEA and LCA

Comprehensive infrastructure and fuel system compatibility testing mitigates market risk

Low Thrust I Scenario

Establish fuel criteria → Procure and test blendstocks → Measure and validate → Establish pathway data → Feedback to ASSERT &

Determine blending performance in finished fuels; Tier 3 testing

Limited infrastructure and fuel system compatibility testing identifies potential risks

Final pathway information to enable TEA, LCA

Future FY17 Thrust I Example: Compatibility Analysis Identifies Fuel System Risk

Approach

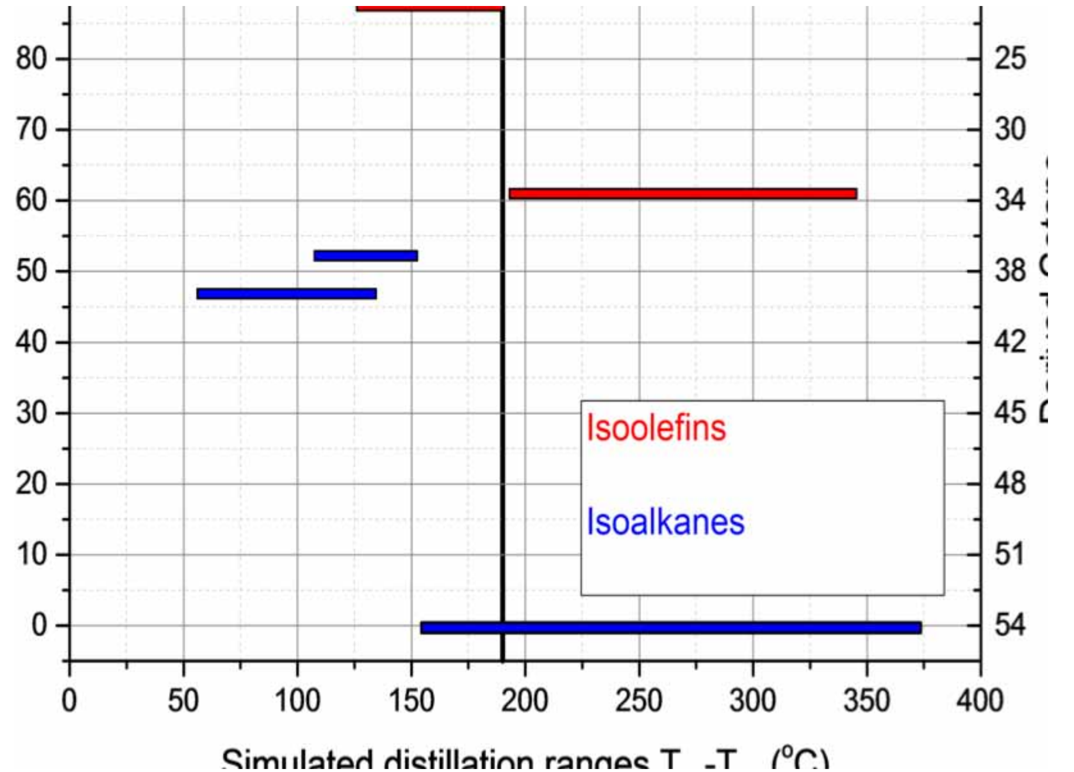
- Two follow-on activities are planned for FY2017
  - Solubility analysis for infrastructure plastics
  - Exposure studies
- Hansen solubility study will be performed on key infrastructure plastics and elastomers (nylons, polyethylene, Teflon, etc.) ubiquitous in fueling systems
- Limited exposure studies on elastomers and plastics
  - Volume and hardness change measurements will be used to validate or adjust solubility assessment
  - 5+ each Thrust I and II candidates

Thermoplastics	Application
Polyphenylene sulfide (PPS)	Permeation barrier
Polyethylene terephthalate (PET)	
Polytetrafluoroethylene (PTFE)	
Polyvinylidene fluoride (PVDF)	
Nylon 11, Nylon 6, Nylon 6/6 and Nylon 12	Flexible piping wall material
High density polyethylene (HDPE)	
Acetals: Polyoxymethylene (POM)	Other common plastics
Polyesters: Polybutylene terephthalate (PBT) and PETG	
Polypropylene (PP)	
Thermosets	
Polyester resin	Fiber-reinforced plastic piping and storage tanks
Novolac vinyl ester resin	

Future FY17 Thrust II Example: Thermochemical Conversion of EtOH to Diesel

Approach

- Leverage PNNL/LanzaTech ATJ (alcohol-to-jet) technology to make improved diesel from alcohols
- Generate test materials with highest diesel yield and DCN
- Can tune olefin content by varying space velocity
- First attempt to maximize diesel fraction yield



Expected Impact: Pathway data for high-potential diesel bio-blendstock; results for fuel property database

Future Work Example: Address Unexpected Challenges

Challenge

- Enhanced sooting for some EtOH-containing fuels

Crucial experiment

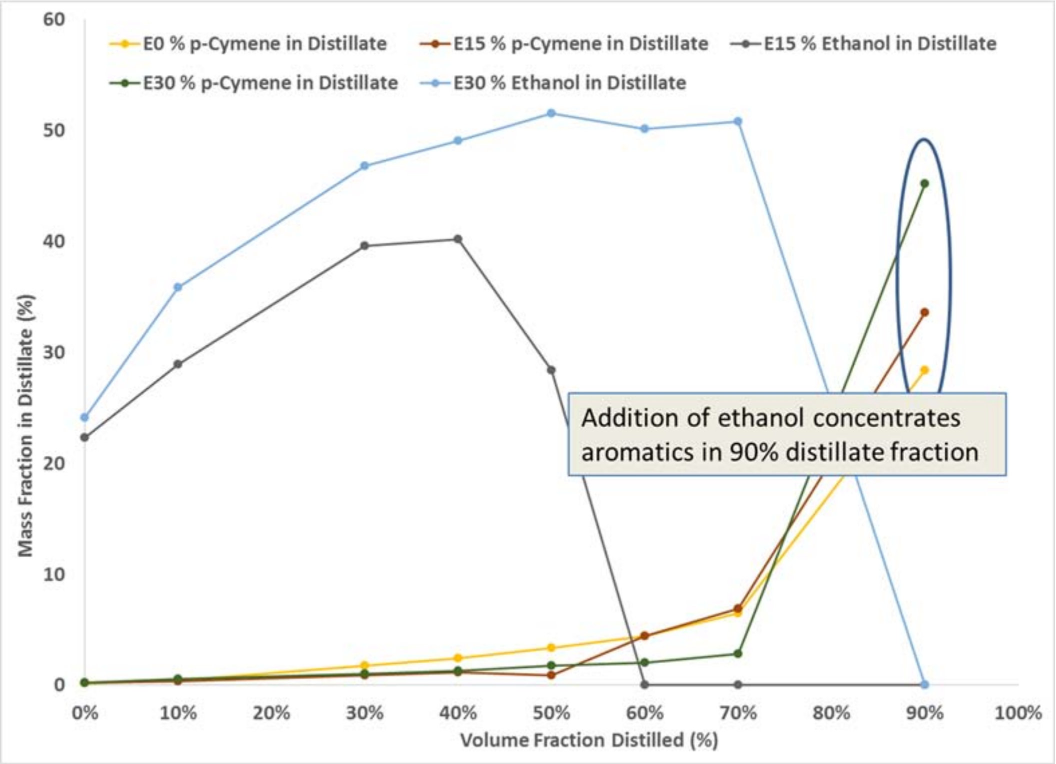
- Measured distillation properties for EtOH blends

Results

- EtOH changes distillation properties under some conditions
- Possible cause of increased sooting observed in some studies

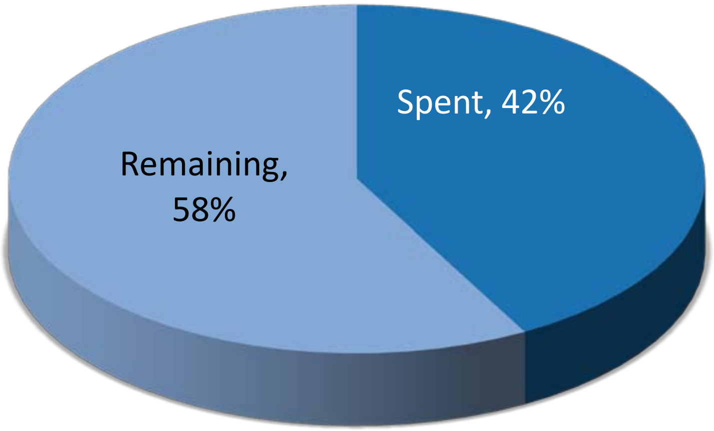
Impact

- Implications for fuel formulations



Future Work: Budget

- Decision Point at 18 months determines relative Thrust I/Thrust II effort levels
- Budget is sufficient to complete Thrust I work
- Budget is sufficient to reach current Thrust I status for diesel-like Thrust II
  - Additional progress may be possible depending upon resources



Future Work: Key Milestones

	FY17		FY18
Establish fuel criteria	Complete series of blend measurements and include in FPD		
Procure and test blendstocks		Screen >200 candidate diesel-like Thrust II materials	Measure blending behavior of 10 promising candidates in diesel
Measure and validate	Retrosynthetic toolkit for all compounds	Establish engine emissions & efficiency for top 2 candidates	Determine blending behavior in range of BOBs
Establish pathway data	Determine missing pathway data	Establish pathways	
Feedback to ASSERT & MT			Determine infrastructure & fuel system compatibility for highest potential blendstocks

Thrust I

Thrust II

Summary

- Goal: Develop biomass conversion-fuel chemistry-engine performance relationships, so we can provide new fuel options for more efficient engines with lower harmful emissions, resulting in market pull for biofuels.

Approach	Accomplishments	Relevance	Future Work
Coordinate across teams and Labs, and leverage existing program outputs (BETO and VTO), while providing feedback to programs Hypothesis-driven fuel property-based Output informs analysis, fuel and engine teams, as well as industry stakeholders	Developed and applied rigorous fuel property selection process, identifying high-potential Thrust I candidates Measured blending behavior of chemically diverse bio-blendstocks in two base fuels Established candidate pathway data enabling technical analyses	Providing technical basis for evaluating bio-blendstocks Identifying bio-blendstocks that enable co-optimization with engines to improve efficiency and reduce emissions Developing performance and pathway data to enable technical analyses	Establish performance improvements offered by high-potential Thrust I candidates Identify high-potential diesel-like Thrust II bio-blendstocks Improved technical analyses that point the way to most suitable candidates and production barriers to address

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

1. Kass, Michael D, and Brian West, "Compatibility of Fuel System Elastomers with Bio-blendstock Fuel Candidates Using Hansen Solubility Analysis," SAE Technical Paper No. 2017-01-0802 (2017).
2. Moore, Cameron M., Orion Staples, Rhodri W. Jenkins, Ty J. Brooks, Troy A. Semelsberger, and Andrew D. Sutton, "Acetaldehyde as an ethanol derived bio-building block: an alternative to Guerbet chemistry," Green Chemistry, November 15, 2016, DOI: 10.1039/c6gc02507b.http://pubs.rsc.org/en/content/articlepdf/2014/GC/C6GC02507B?page=search
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4. Whitmore, L.S., R.W. Davis, R.L. McCormick, J.M. Gladden, B.A. Simmons, A. George, and C.M. Hudson, BioCompoundML: A General Biofuel Property Screening Tool for Biological Molecules using Random Forest Classifiers. Energy & Fuels 30: 8410-8418, 2016. http://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels.6b01952
5. L.S. Whitmore, A. George, and C.M. Hudson (2016) Mapping chemical performance on molecular structures using locally interpretable explanations. *Presented at NIPS Workshop on Interpretable Machine Learning for Complex Systems.* Presented in Barcelona, Spain, Dec 7, 2016. (*Peer Reviewed Paper on ArXiv Preprint Server:* https://arxiv.org/abs/1611.07443).
6. L.S. Whitmore, A. George, and C.M. Hudson (2017) Developing a high- and low-cetane classifier for biologically produced chemicals using variable quality training data. *Accepted at 253rd ACS National Meeting* in San Francisco, California, April 2-6, 2017.
7. McCormick, R.L., Fioroni, G.M., Fouts, L., Yanowitz, J., Polikarpov, E., Albrecht, K., Gaspar, D.J., Gladden, J., George, A. "Selection Criteria and Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Advanced Spark-Ignition Engines" SAE Technical Paper No. 2017-01-0868 (2017).

Publications, Patents, Presentations, Awards, and Commercialization

8. Burke, S., Ratcliff, M., McCormick, R.L., Rhoads, R., and Windom, B., "Distillation-based Droplet Modeling of Non-Ideal Oxygenated Gasoline Blends: Investigating the Role of Droplet Evaporation on PM Emissions," SAE Technical Paper No. 2017-01-0581 (2017).
9. McCormick, R.L., "Co-Optimization of Fuels and Engines," Presented at Biodiesel Technical Workshop, Kansas City, November 8, 2016.
10. McCormick, R.L., Fioroni, G.M., Ratcliff, M.A., Zigler, B.T., Farrell, J. "Bioblendstocks that Enable High Efficiency Engine Designs," Presented at CRC Advanced Fuels and Engine Efficiency Workshop, Livermore, CA, November 3, 2016.
11. McCormick, R.L., "Co-Optimization of Fuels and Engines," Presented at Auto/Ag/Ethanol Workgroup Annual Meeting, Detroit, October 5, 2016.
12. Sluder, C.S., Szybist, J.P., Ratliff, M., McCormick, R.L., and Zigler, B.T., "Exploring the Relationship between Fuel Heat-of-Vaporization and Sensitivity," *SAE Int. J. Fuels Lubr.* 9(1):80–90, 2016, doi:10.4271/2016-01-0836.
13. McCormick, R.L., "Co-Optimization of Spark-Ignition Engines and Biofuels," Presented at Colorado State University, April 19, 2016.
14. McCormick, R.L., "High Octane Fuels: Benefits and Challenges," Presented at Clean Cities Coordinator Webinar, March 17, 2016.
15. McCormick, R.L., "Co-Optimization of Internal Combustion Engines and Biofuels," Presented at Future Fuels Workshop, King Abdullah University of Science and Technology, Saudi Arabia, March 8, 2016.
16. McCormick, R.L., "High Octane Fuels: Benefits and Challenges," Presented at National Ethanol Conference, New Orleans, LA, February 17, 2016.

Publications, Patents, Presentations, Awards, and Commercialization

17. Gaspar, D.J., "Flexibility in Biofuel Manufacturing," Presented at Sustainable Transportation Summit, Washington DC, on July 14, 2016.
18. Gaspar, D.J., "Co-Optima: Low Greenhouse Gas Fuels and Properties." Presented at Bioenergy 2016, District of Columbia, Wash DC, on July 14, 2016.
19. Gaspar, D.J., "Getting to 20: Selection of Co-Optima Thrust 1 bio-blendstock candidates for analysis." Presented to American Petroleum Institute by webinar, October 12, 2016.
20. Gaspar, D.J., "Co-Optimization of Fuels and Engines: High Performance Fuels," Presented by Dan Gaspar at Advanced Engine Crosscut Webinar, January 12, 2017.
21. St John, Peter, Carie Farberow, Dhrubjyoti D. Das, Charels S. McEnally, Lisa D. Pfefferle, Bradley T. Zigler, Robert McCormick, Mark R. Nimlos, Thomas Foust, Yannick J. Bomble, and Seonah Kim, "Prediction of Yield Sooting Index (YSI) from Chemical Structure using a Feed Forward Artificial Neural Network," 36th International Symposium on Combustion, July 31 – Aug. 5, 2016, Seoul, Korea.
22. St. John, Peter, Drubajyoti Das, Charles S. McEnally, Lisa D. Pfefferle, Yannick J. Bomble, and S. Kim, "Prediction of the Sooting Tendencies of Candidate Biofuels from Molecular Structure Via an Artificial Neural Network," 2016 AlChE Annual Meeting, Nov. 13-18, 2016 (San Francisco, CA).
23. St John, Peter C., Paul M. Kairys, Dhrubajyoti D. Das, Charles S. McEnally, Lisa D. Pfefferle, David J. Robichaud, Mark R. Nimlos, Bradley T. Zigler, Robert L. McCormick, Thomas D. Foust, Yannick Bomble, and Seonah Kim, "A quantitative model for the prediction of sooting tendency from molecular structure," submitted to Environmental Science & Technology (2016, under review).

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24. Whitmore, L.S., George, A., and Hudson, C.M., “BioCompoundML: A General Biofuel Property Screening Tool for Biological Molecules using Random Forest Classifiers”, Tailor made fuels from biomass, 4th International Conference, Aachen, June 2016
25. George, A., “Co-optima: co-optimization of fuels and engines”, Low carbon fuels workshop, Imperial College London, June 2016
26. George, A., “Co-optima: Biofuel production and design predicated upon engine performance criteria”, Bio4fuels Kickoff meeting, Norway, February 10, 2017
27. Zhuang, X. Kilian, O., Davis, R., Gladden, J., George, A., “High performance terpenoid biofuel production by oleaginous yeast *Rhodosporidium toruloides*” 253rd ACS National Meeting symposium Advances in Chemistry of Energy & Fuels., Poster, April 2017
28. Zhuang, X. Kilian, O., Davis, R., Gladden, J., George, A.,. “High performance terpenoid biofuel production by oleaginous yeast *Rhodosporidium toruloides*” SIMB 39th Symposium on Biotechnology for Fuels and Chemicals, Oral, May 2017
29. Whitmore, L.S., George, A., and Hudson, C.M , “RetroSynth: A tool for identifying best metabolic routes for production of a target compound,“ SIMB 39th Symposium on Biotechnology for Fuels and Chemicals, Oral, May 2017
30. Whitmore, L.S., George, A., and Hudson, C.M. ,“BioCompoundML: A General Biofuel Property Screening Tool for Biological Molecules using Random Forest Classifiers”, Open Source BSD 2-clause License. https://www.github.com/sandialabs/BioCompoundML
31. Whitmore, L.S., George, A., and Hudson, C.M “RetroSynth: A tool for identifying best metabolic routes for production of a target compound”, Open Source BSD 2-clause License

Publications, Patents, Presentations, Awards, and Commercialization

32. Davis, R.W., Monroe, E., Liu, F., Gladden, J.M., George, A. "Production, Blending, and Upgrading of Advanced Renewable Fuels for Co-Optimization of Fuels and Engines" 253rd American Chemical Society National Meeting and Expo, San Francisco, CA April 2-6, 2017

33. Monroe, E., Davis, R.W., Liu, F., Gladden, J.M., George, A. "Production, Blending, and Upgrading of Advanced Renewable Fuels for Co-Optimization of Fuels and Engines" Symposium on Biotechnology for Fuels and Chemicals, San Francisco, CA, May 1-4 2017

Acronym List

HPF – Co-Optima High Performance Fuels Team

COLT – Co-Optima Leadership Team

ASSERT – Co-Optima Analysis of Sustainability, Scale, Economics, Risk and Trade Team

MT – Co-Optima Market Transformation Team

FP – Co-Optima Fuel Properties Team

AED – Co-Optima Advanced Engine Development Team

AKI – anti-knock index [(RON+MON)/2]

BOB – blendstock for oxygenate blending

CARBOB – California reformulated blendstock for oxygenate blending (more stringent limits on some components)

CN – cetane number

DCN – derived cetane number

FPD – fuel property database

GHG – greenhouse gas

HOV – heat of vaporization

IQT – ignition quality tester (an auto-ignition test device which determines DCN)

LCA – lifecycle analysis

MON – motor octane number

PMI – particle mass index

RBOB – reformulated blendstock for oxygenate blending

RON – research octane number

RVP – Reid vapor pressure

S – octane sensitivity (RON-MON)

TEA – techno-economic analysis

Approach – Definitions

- **bio-blendstock:** biomass-derived molecule or mixture being evaluated by Co-Optima for use as a blending component in a finished fuel.
- **octane number:** ON; metric indicating resistance to autoignition (100 = high; 0 = low); measured in a standard “octane rating” engine and used for gasoline.
- **research octane number:** RON; ON measured under specific set of conditions
- **cetane number:** CN; metric indicating ease of autoignition (0 = low; 45 = high); measured using rating engine or ignition quality tester to determine derived cetane number (DCN)
- **retrosynthetic analysis:** an organic chemistry technique for determining production pathways by transforming a target molecule into simpler precursor structures without assumptions regarding starting materials. Each precursor material is examined using the same method. We have modified the standard process to specify that ultimate precursors must be biomass-derived.

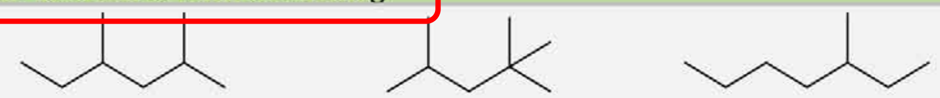
Additional Technical Accomplishments

Technical Accomplishment: Determined Guidelines for Chemical Functional Groups

Goal / HPF Task: Thrust I Chemical-fuel property correlation

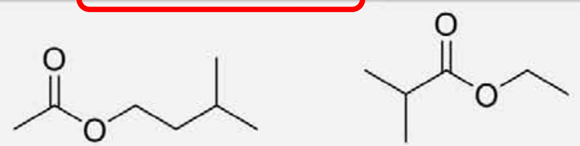
Examples of Thrust I Chemistry Analysis

Isoparaffins RON increases with branching



2,4-dimethylhexane | 2,2,4-Trimethylpentane (iso-octane) | 3-methylheptane

Esters Good physical properties volatility uncertain (produced from volatile fatty acids)



Isoamyl acetate | ethyl isobutyrate

Thrust I Efficiency Merit Function

RON | Octane Sensitivity | HOV

$$\text{Merit} = \alpha \bullet [\text{RON} - 92] - \beta \bullet K \bullet [S - 10] + \gamma \bullet \text{ON} \bullet [\text{HOV} - 415] + \delta \bullet [\text{HOV} - 415]$$
$$+ \varepsilon \bullet [S_L - 46] - \text{LFV}_{150} - H(\text{PMI} - 2.0)[\zeta + 0.5(\text{PMI} - 2.0)]$$

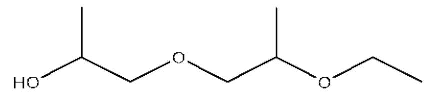
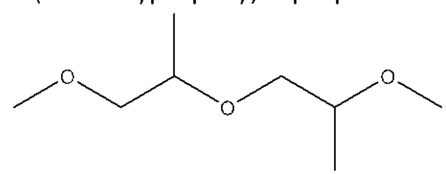
Flame Speed | Distillation | Particulate Emissions

Analysis reduces search space for Thrust I candidate bio-blendstocks

Technical Accomplishment: Determined Guidelines for Chemical Functional Groups

Goal / HPF Task: Thrust II Chemical-fuel property correlation

Examples of Thrust II Chemistry Analysis

polyethers, including acetals and glymes R-(O-R')n-R''	Very good	Pros: Very high autoignition propensity. Potential for reduced emissions. CN depends upon branching. Cons: Possible hydrolysis under mild aqueous acid conditions. Cost. Glymes from ethylene glycol are toxic.	 1-(2-ethoxypropoxy)-2-propanol  2-methoxy-1-(2-methoxy-1-methylethoxy)propane
cyclic alkanes/ naphthenes C_nH_{2n} (saturated); C_nH_{2n}-2 (unsaturated)	Fair	Pros: Substituted napthenes may exhibit good CN (1-methyl-3-dodecylcyclohexane ~70) Cons: Low CN for unsubstituted naphthenes (decalin ~36). Increased sooting tendencies.	decalin (bicyclohexane); 1-methyl-3-dodecylcyclohexane

Analysis reduces search space for Thrust II candidate bio-blendstocks

Technical Accomplishment: Facile Interconversion of Functional Groups Depending on Required Properties

Goal / HPF Task: Thrust I baseline synthesis data and generate mixtures for analysis

- Specifically evaluate fuel properties for non-AOP funded work for $C_6/C_9/C_{12}$ ketone mixtures from acetone condensation reactions and $C_8/C_{10}/C_{12}/C_{14}$ esters/acetals from non-Guerbet ethanol chemistry

- We can readily interconvert functional groups from ketone → alcohol → alkene → alkane for further functionalization to enhance properties

Lab – PI: LANL – Sutton

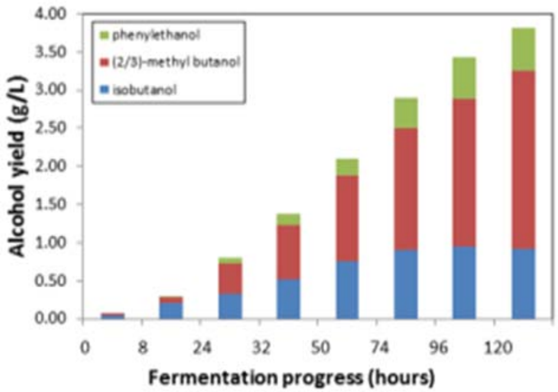
Methodology developed allows us to chose process routes based on fuel properties required

Technical Accomplishment: Demonstrated Versatility of Fusel Alcohols as Thrust I or Thrust II Fuels

Goal / HPF Task: Thrust II baseline synthesis data and generate mixtures for analysis

- Produced fusel alcohols as Thrust I fuel molecules at very high titers
- Minimal inhibition of engineered strain in 50% v/v deacetylation and mechanical refining feedstock and fusel alcohol products up to 10 g/L
- Upgraded fusel alcohols to esters and ethers for Thrust II fuels
- Upgrading achieved with, e.g., acetate, ethanol, or by ether formation with other fusel alcohols

A



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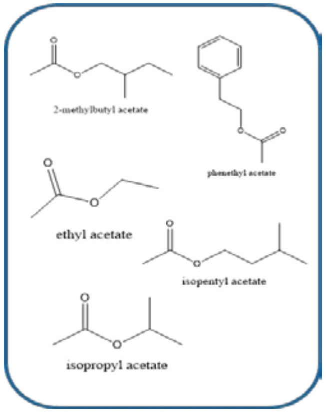


A: Production of fusel alcohols phenylethanol, methylbutanol and isobutanol in robust industrial host, *Corynebacterium glutamicum*.
B: Examples for fusel alcohol upgrading with acetate.

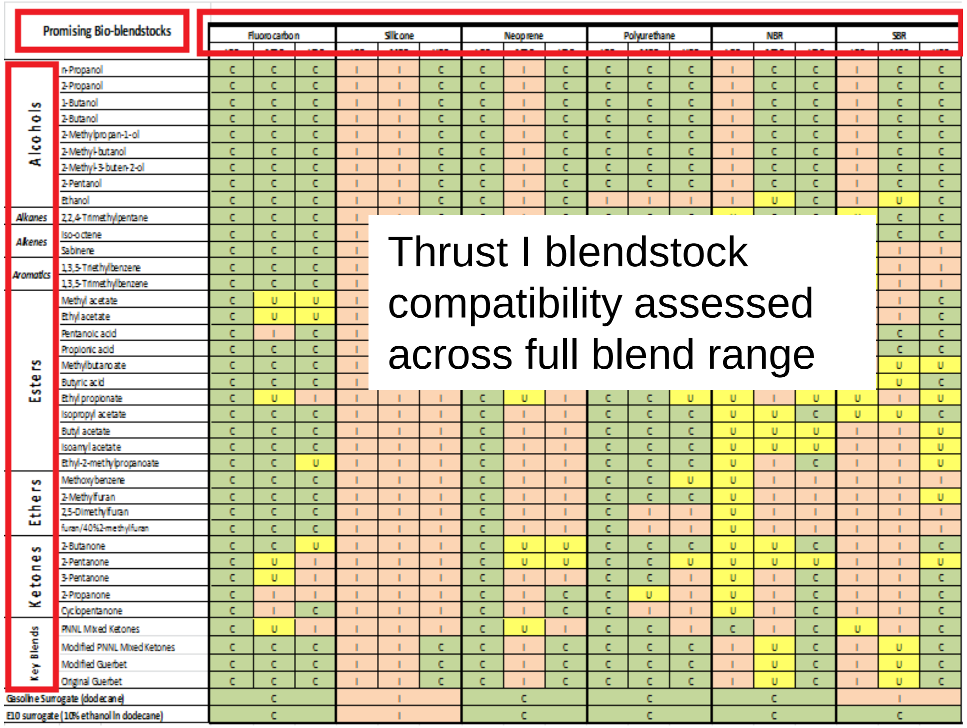
Lab – PIs: SNL – Davis, Gladden, George

Demonstration of production of Thrust I fuels at very high titers and simple chemical upgrading to Thrust II fuels

Technical Accomplishment: Hansen Solubility Analysis

Goal / HPF Task: Thrust I compatibility analysis

- Assessed Thrust I blendstocks' compatibility with key elastomers and fuel system plastics
- Hansen solubility analysis indicates good compatibility for most bio-blendstocks with key elastomers, including fluorocarbons, polyurethane, neoprene
- Found ketones and some esters are likely to have more limited compatibility with fluorocarbons and others



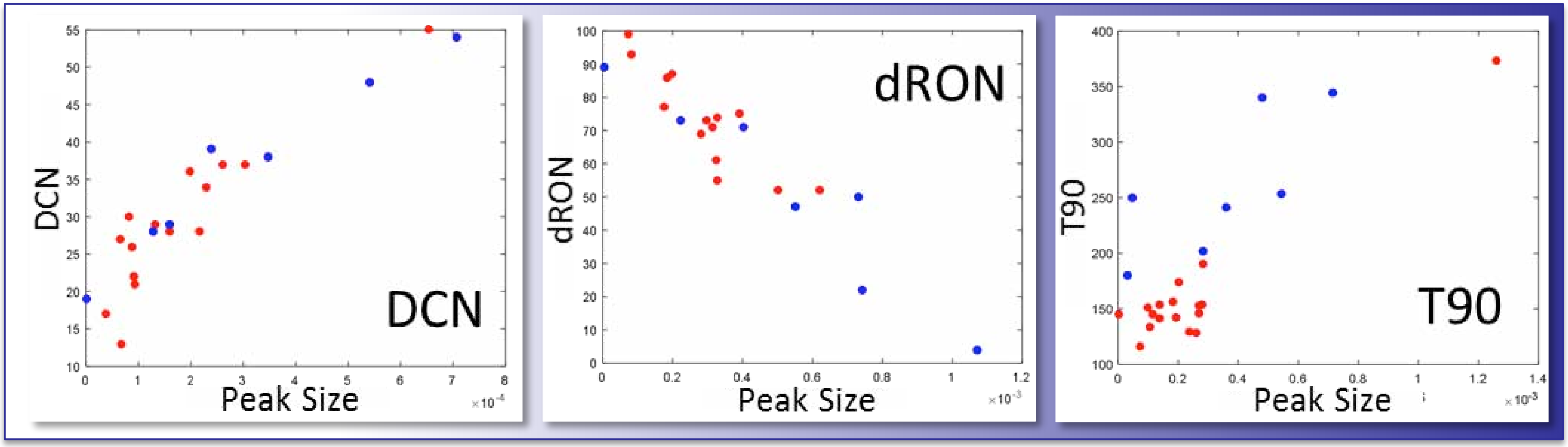
Thrust I blendstock compatibility assessed across full blend range

Understanding compatibility of blendstocks with elastomers and fuel system plastics is critical for adoption into existing vehicles and infrastructure, or to inform retrofits

Technical Accomplishment: Fuel Blend Spectroscopy

Goal / HPF Task: Develop fuel property-chemical structure relationships

- Completed 2D-NMR measurements for 30 complex bio-derived mixtures
- Fuel property-feature correlations demonstrate ability to generate useful blend model from ~200-mL samples



Small-volume analysis to estimate blend and mixture properties provides rapid screening capability

FY16 Milestones Achieved and Technical Progress Made

Task	Title	Milestone	Lead Lab	Date	Key Accomplishment(s)
A.1.1	Selection Criteria	Complete definition for criteria desired in RON-enhancing molecules	SNL	12/31/15	FP and AED developed merit function, fulfilling this milestone
		Identify 20 bio-derived blendstocks for evaluation as Thrust I blend components (Dashboard)	PNNL	12/31/15	Identified hundreds of candidate bio-blendstocks
A.1.2	Chemical-Fuel Property Correlation	Complete analysis of up to 20 molecules or mixtures that can be used in spark ignition engines	NREL	3/31/16	Evaluated more than 300 candidates
A.1.3	Survey Candidates	Briefing document on complete set of properties for 20 high-potential Thrust I bio-blendstocks	PNNL	6/30/16	Identified nearly 40 high-potential materials meeting Tier 1 screening criteria
A.1.4	Determine blending properties	Determine blending behavior of 5 high-priority blendstocks	NREL	9/30/16	Measured blending behavior of nearly 40 materials

FY17 HPF Milestones (1 of 3)

Task #	Milestone	Lead Lab	Due Date
A.1.5.1	Report detailing retrosynthetic analysis of high-priority Thrust I bio-blendstocks	PNNL	Q1 ✓
A.1.5.1	Retrosynthetic toolkit for all compounds	SNL	Q4
A.1.5.2	Generate fusel alcohol production data for ASSERT	SNL	Q2
A.1.5.2	ID specific bio-blendstocks requiring additional information	LBNL	Q3
A.1.5.3	Ignition delay predictive model for C5 oxygenates	NREL	Q2
A.1.5.3	Prepare branched interior alcohols for RON and MON testing	PNNL	Q4
A.1.5.4	Convert functional groups of alcohols from A.1.5.2 and A.1.5.3 and test via IQT	LANL	Q3

FY17 HPF Milestones (2 of 3)

Task #	Milestone	Lead Lab	Due Date
A.1.6.1	Complete T1 FPD with 20 additional compounds	PNNL	Q1 ✓
A.1.6.2	Report describing compatibility of 5+ T1 bio-blendstocks with 10+ infrastructure mtls	ORNL	Q2
A.1.6.3	Develop blend model to predict physical properties relevant to merit function for base fuel or surrogate	SNL	Q3
A.1.7.1	Complete blend measurements and include in FPD	NREL	Q1
A.1.7.2	Report detailing NMR correlations with measured FPs for T1 bio-blendstocks	PNNL	Q4

FY17 HPF Milestones (3 of 3)

Task #	Milestone	Lead Lab	Due Date
A.2.1.1	Report detailing functional groups analysis, incl. their suitability as diesel-like fuel	PNNL	Q1 ✓
A.2.1.2	Report describing retrosynthetic analysis of Thrust II candidate blendstocks	SNL	Q2
A.2.1.3	Prepare mixture in diesel boiling range for IQT	SNL	Q2
A.2.1.3	Report recommending additional T2 materials for development	SNL	Q4
A.2.1.4	Prepare aryl ether mixture in diesel boiling range for IQT	PNNL	Q2
A.2.1.5	Prepare and test mixtures of diesel-like molecules from acetone condensation and non-Guerbet pathways	LANL	Q3
A.2.1.6	Identify at least 20 compounds spanning >4 functional groups and submit to DCN analysis via IQT	NREL	Q4