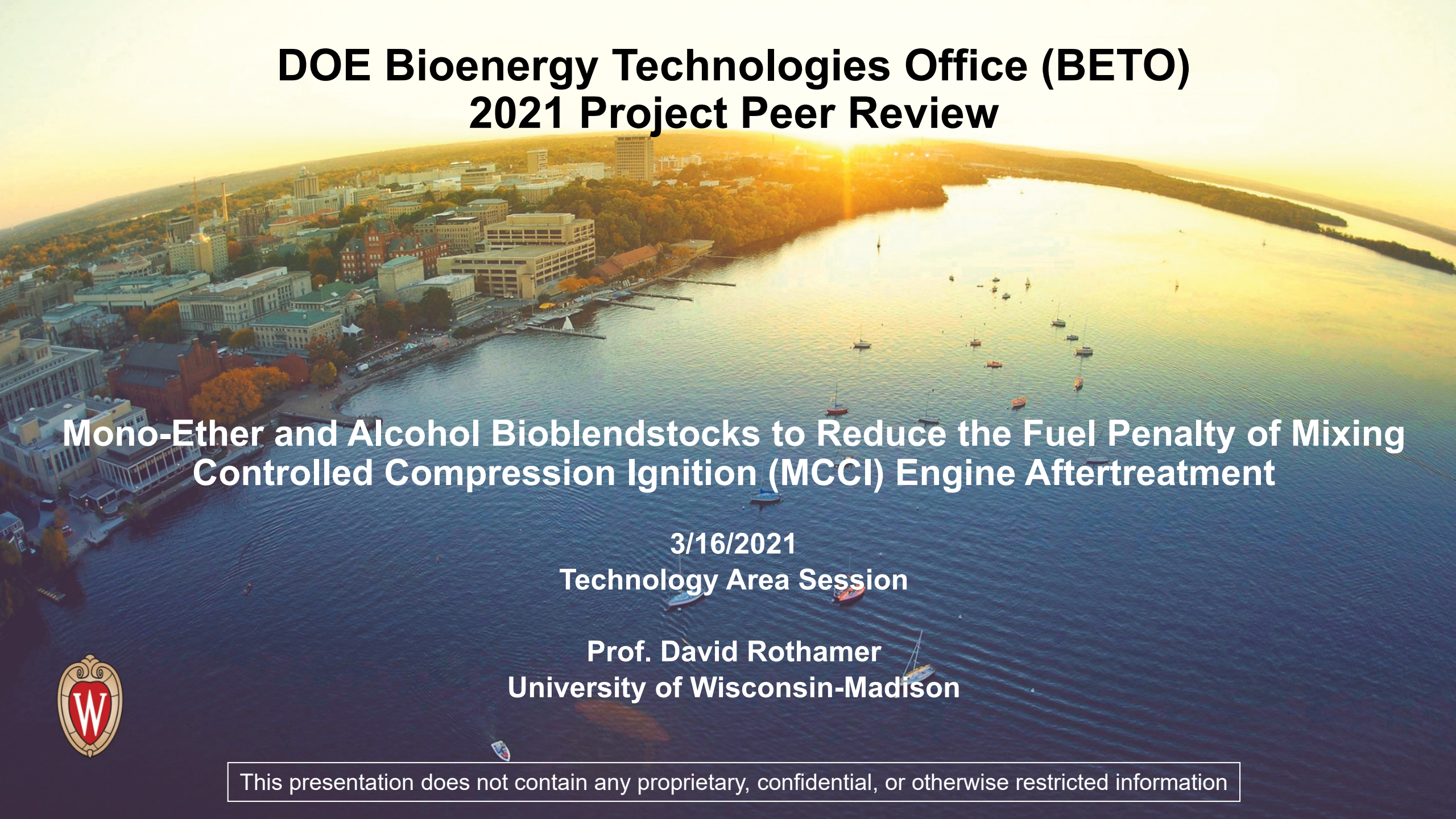
DOE Bioenergy Technologies Office (BETO)
2021 Project Peer Review



Mono-Ether and Alcohol Bioblendstocks to Reduce the Fuel Penalty of Mixing Controlled Compression Ignition (MCCI) Engine Aftertreatment

3/16/2021
Technology Area Session

Prof. David Rothamer
University of Wisconsin-Madison

Project Overview - Background

Project resulted from FY 2018 Adv. Vehicle Technologies Research FOA (DE-FOA-0001919), AOI 5b:

Bioblendstocks to Optimize Mixing Controlled Compression Ignition (MCCI) Engines

Goals and objectives of the FOA area of interest (AOI) 5b

- Develop and demonstrate liquid bioblendstocks for medium and heavy-duty MCCI blended into diesel base fuel at no less than 5% by volume
- Achieve at least 50% reduction in greenhouse gas emission relative to conventional diesel fuel
- Improve at least two of following fuel properties: energy density, sooting, cetane #, cold weather behavior

Project Overview - Background

Project start date: May 2019

- BP 1 completed Dec. 2020, just started BP2 for the award
- This is the first peer review for this project

Project Focus:

- Develop a diesel bioblendstock catalytically produced from cellulosic ethanol to improve engine operation and reduce greenhouse gas emission
  - Two step catalytic process to produce blendstock rich in monoethers
  - Project tasks focus on catalysis, process, engine, and life-cycle optimization

Multi-disciplinary team

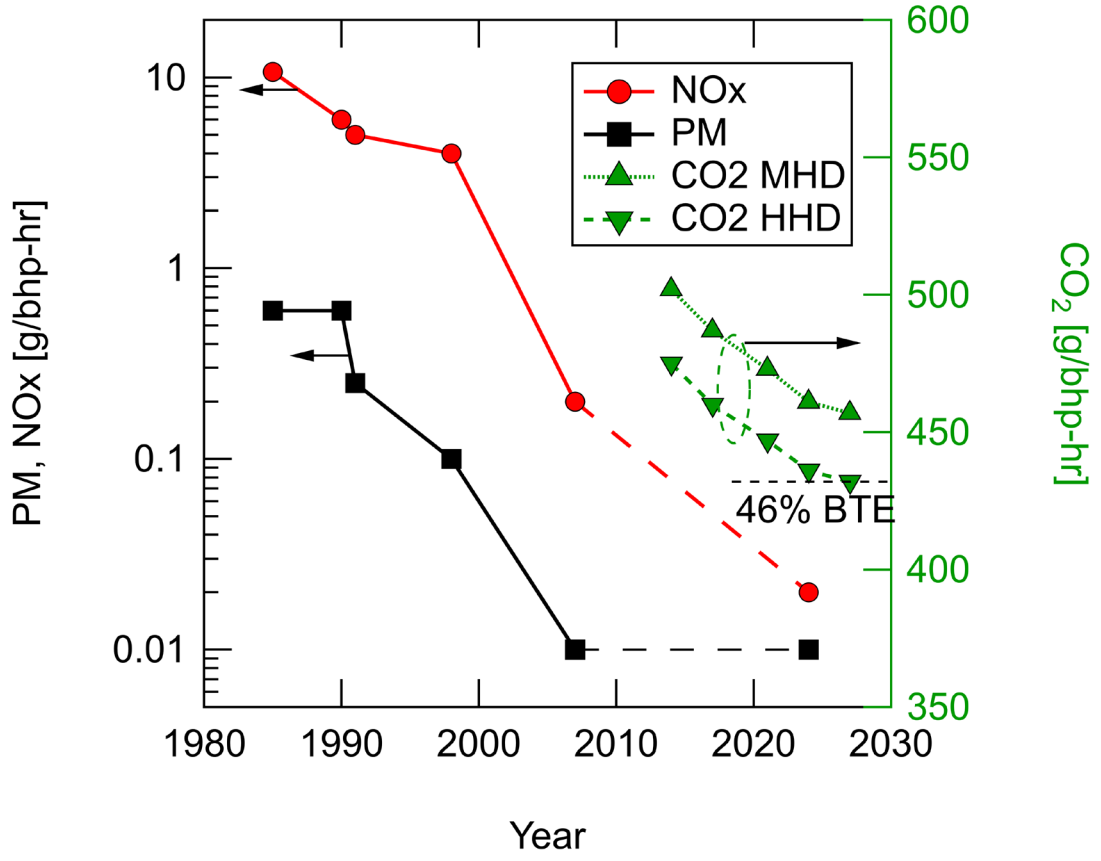
- ***Catalysis*** – Prof. George Huber, Chemical and Biological Engineering
- ***Technoeconomic and lifecycle analysis*** – Prof. Christos Maravelias, Chemical and Biological Engineering
- ***Engine system analysis*** – Prof. Sage Kokjohn
- ***Fuel property engine impacts*** – Prof. David Rothamer

Project Overview - Motivation

Challenge

- Heavy-duty engine emission regulations require simultaneous decrease in NOx and CO2
- Difficult to achieve with current fuel and engine technologies

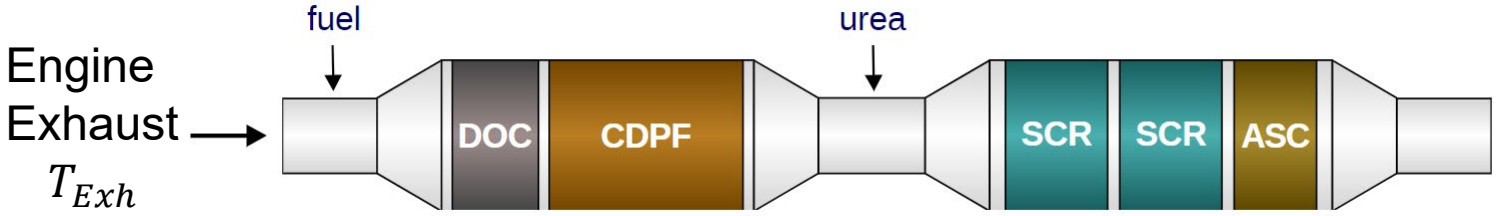
Solution- Diesel bioblendstocks that reduce net CO_2 emissions and enable reduced NOx emissions



US EPA heavy-duty engine emissions regulations versus time

NO_x = Nitrogen oxides, CO_2 = carbon dioxide, PM = Particulate Matter (soot)

Project Overview – Research Hypothesis



Typical layout of diesel engine aftertreament

Image source: https://dieselnet.com/tech/engine_heavy-duty_aftertreatment.php

- Efficient aftertreament requires operation above light-off temperature
- Engines operate in catalyst heating mode with late injection (post)
  - Used at engine startup and at light load to maintain catalyst temperatures
  - Once DOC is lit off oxidation of unburnt fuel in exhaust can be used for heating
- Operation below catalyst light-off temperature results in bulk of emissions

Research Hypothesis

Co-optimization of bioblendstock production, fuel properties, and engine operation will enable greatest reductions in emissions at the lowest cost

DOC = Diesel oxidation catalyst, CDPF = Catalyzed diesel particulate filter, SCR = Selective catalytic reduction, ASC = ammonia slip catalyst

Project Overview - Goal and Objectives

Overall goal: Co-optimization of catalytic production and engine operation for a diesel bioblendstock produced from cellulosic ethanol to produce ***economically viable*** product that reduces emissions

Develop diesel bioblendstock* to:

Improve fuel properties

- reduce pour point and cloud point temperatures
- increase cetane number
- meet ASTM D975 specifications

Improve engine performance and emissions

- reduce soot mass emissions by > 25%
- reduce the fuel energy penalty of MCCI engine aftertreatment
- reduce greenhouse gas emissions by > 50% relative to #2 diesel

*when blended with #2 diesel fuel at >5 vol. %

1-Management – Project Team

Project is divided into 4 main task areas

(Overall project lead: Prof. David Rothamer)

Task 1: Catalytic production – Prof. George Huber (Co-PI)

- **Role:** Identify catalysts, develop kinetic models, optimize reaction conditions

Task 2: Process Synthesis – Prof. Christos Maravelias (Co-PI) and Prof. Sage Kokjohn (Co-PI)

- **Role:** Perform plant process design, TEA, LCA (Maravelias), engine system modeling (Kokjohn)

Task 3: Engine Performance – Prof. David Rothamer (PI) and Prof. Sage Kokjohn (Co-PI)

- **Role:** Single-cylinder, optical (Rothamer), and multi-cylinder (Kokjohn) engine fuel performance characterization

Task 4: Fuel Property Testing and Modeling – Prof. David Rothamer (PI)

- Role: Property measurements, property modeling, and fuel surrogate formulation

1-Management – Project Risks and Mitigation

Projects Risks

1. Bioblendstock process design, TEA, and LCA optimizations cannot be completed until catalysis and engine studies are completed
2. Representative bioblendstock surrogate components are expensive and limited variety is available
   - Limited quantities of bioblendstock will be produced in project (~liters) so a surrogate bioblendstock will be formulated for multi-cylinder engine testing

Risk Mitigation Strategies

1. Develop and implement process design, TEA, and LCA optimizations with preliminary data and continuously update during project
   - Ensure close collaboration and data sharing between task areas with regular research meetings
2. Develop understanding of fuel property impacts through engine experiments and apply weighting to those most important for combustion and emissions performance during surrogate formulation

1-Management– Collaboration and Feedback

Internal Collaboration

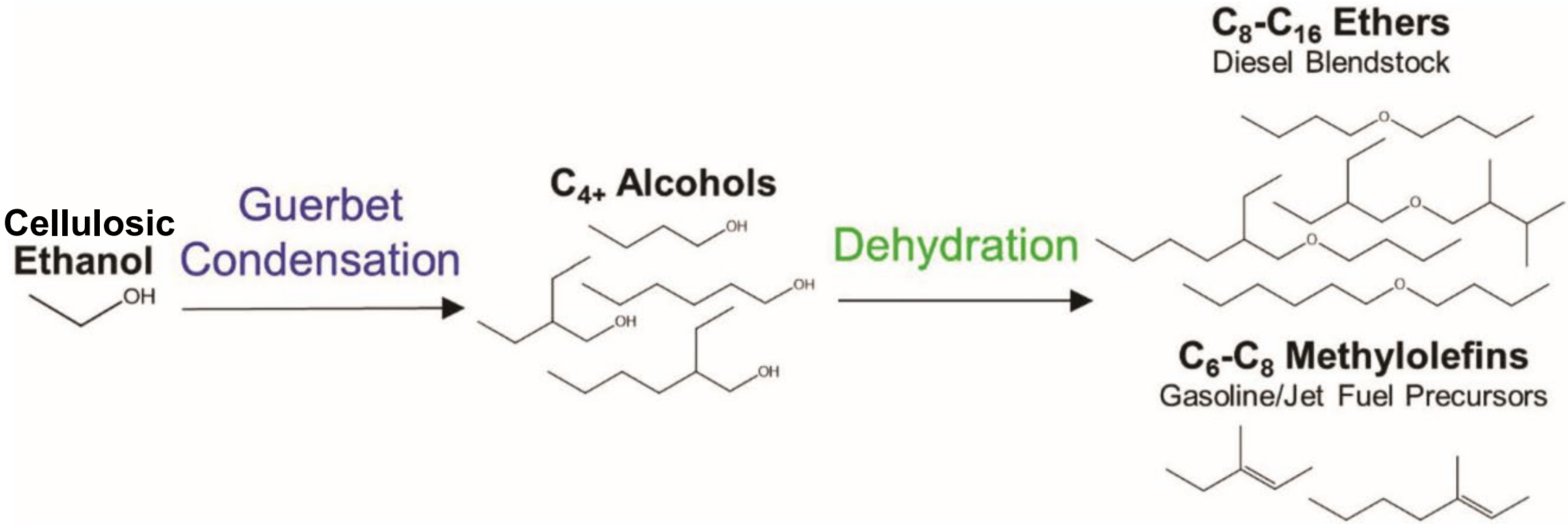
- Monthly all hands meeting to review research progress and promote coordination across task areas
- Higher frequency (weekly) task and inter-task meetings

Project Feedback Mechanisms

- Engine Research Center Direct Injection Engine Research Consortium
- Industry research sponsors
- Participation and attendance at regular Co-Optima meetings

2-Approach - Diesel Range Ethers from Ethanol

Good properties for blending with diesel fuel



Two step approach for conversion of ethanol into diesel fuel ethers

Eagan, N. M.; Moore, B. M.; McCelland, D. J.; Wittrig, A. M.; Canales, E.; Lanci, M. P.; Huber, G. W. Catalytic Synthesis of Distillate-Range Ethers and Olefins from Ethanol through Guerbet Coupling and Etherification. *Green Chem.* **2019**, *21* (12), 3300–3318. https://doi.org/10.1039/c9gc01290g.

2-Approach – Task Area Descriptions

Task 1 Catalytic Production of Bioblendstocks – Optimization of processing conditions and provide inputs to process system engineering.

Task 2 Process Systems Engineering – Synthesize process and analyze techno-economics and life-cycle impacts for bio-refinery/engine system.

Task 3 Engine Testing - Identify property constraints needed to meet the engine/aftertreatment system performance targets, validate performance of produced bioblendstocks.

Task 4 Testing and Modeling of Fuel Properties – Establish range of fuel properties available and develop suitable surrogate for bioblendstocks for engine testing.

Tasks involve true co-optimization of fuel properties and engine operation

- Fuel property modeling and engine-system modeling used in conjunction with the process systems engineering TEA and LCA analysis to determine the best bioblendstock and optimal blend percentage with #2 diesel fuel that simultaneously enables engine operation optimization and minimizes cost.

2-Approach – Task Integration

Fuel Property Testing and Modeling

Prof. David Rothamer

Fuel Properties Measure/Model for Mixtures

1. Flash point – ASTM D93
2. Distillation temperature – ASTM D86
3. Kinematic viscosity (40 C) – ASTM D445
4. Cetane number – ASTM D613
5. Cloud point – ASTM D2500

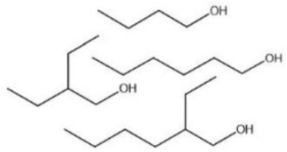
Catalytic Production

Prof. George Huber

Cellulosic Ethanol

Guerbet Condensation

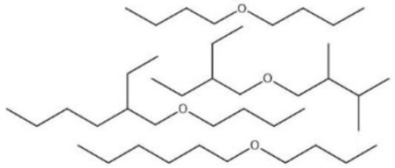
C_{4+} Alcohols

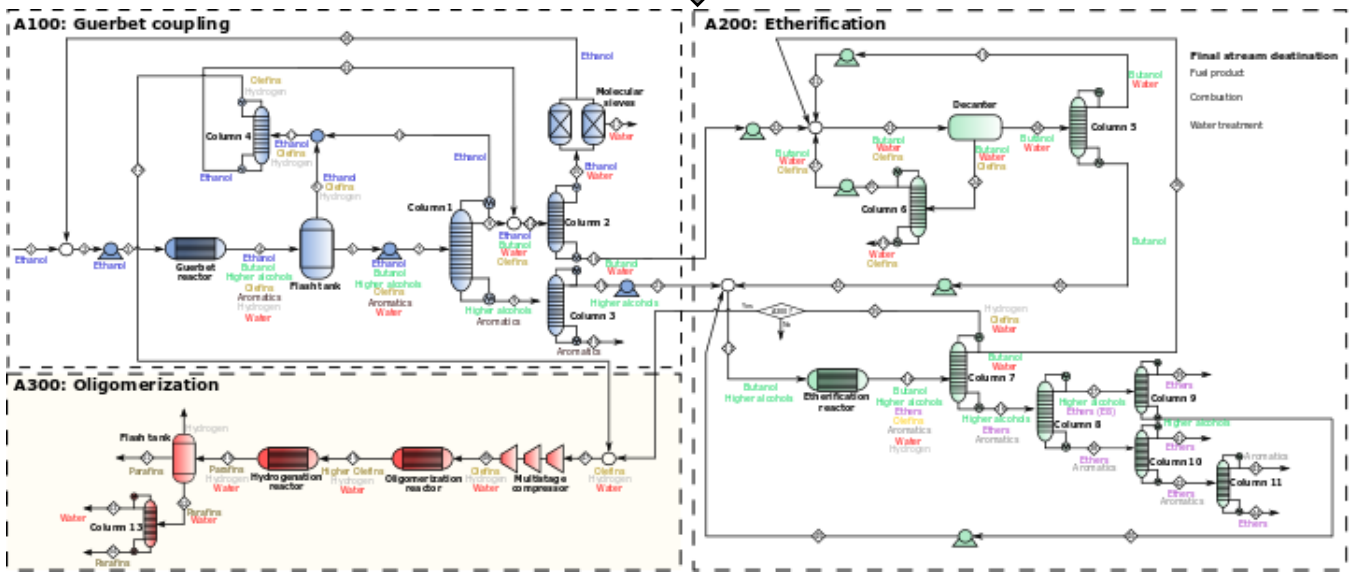


Etherification

C_8-C_{16} Ethers

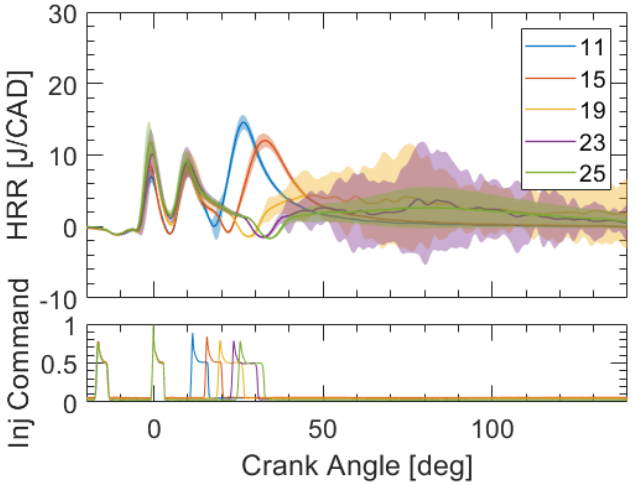
Diesel Blendstock





Engine Performance

Profs. Sage Kokjohn and David Rothamer



Process Synthesis, TEA, LCA, and Engine System Modeling

Prof. Christos Maravelias, Prof. Sage Kokjohn

2-Approach – Technical Risks

Risks

1. Catalytic processes produce range of components some with undesirable properties
   - Separations to remove components adds additional cost
   - Want to maximize carbon efficiency and energy efficiency
2. Influence of fuel properties on catalyst heating operation performance is currently not well known
   - Magnitude of fuel property benefits was unknown at project start

Mitigation approaches

1. TEA, LCA, and engine system model used to optimize production process
   - Perform optimization for overall lifecycle and cost including engine operation
2. Utilize optical and metal engine experiments to establish fuel property impacts and use data in engine system simulations
   - Results from simulations provide inputs to TEA and LCA to optimize process

TEA = Technoeconomic analysis, LCA = Lifecycle analysis

2-Approach – GO/NO-GOs

Go/No-Go #1 (Complete) – Guerbet coupling catalyst stability for 300+hour on stream with 85% selectivity and 45% conversion to bioblendstock precursors at a scale of 40 mL ethanol per week.

- Demonstrates the industrial relevance of guerbet coupling step

Go/No-Go #2 - Select bioblendstock composition with predicted > 50% reduction in lifecycle GHG emissions relative to conventional petroleum-derived diesel fuel and predicted >1% combined MCCI engine/aftertreatment system efficiency improvement which minimizes bioblendstock cost.

- Demonstrates the potential of the designed bioblendstock to meet primary end of project goals (pending experimental validation)

3-Impact

Impact on state-of-technology and/or industry

- Provide path for current and future ethanol production to help meet CO_2 reduction goals as light-duty vehicles become electric and light-duty ethanol demand decreases
- Enable engines to meet needed CO_2 and NO_x emissions reductions for heavy-duty applications at modest cost

Dissemination of results

- Journal Publications
  - Restrepo-Flórez JM, Maravelias CT. Advanced fuels from ethanol–a superstructure optimization approach. *Energy & Environmental Science.* https://doi.org/10.1039/D0EE02447C
- Direct-Injection Engine Research Consortium
  - Consortium with ~25 member copies
  - Presentations at last two annual meetings
- Industry and National Labs

4 – Progress and Outcomes

4 – Progress and Outcomes

Status of key Milestones (all are on schedule)

Task 1

- BP1 Go/No-Go – Guerbet coupling catalyst stability (complete)
- Milestone 1.2.1 – 1.2.3 – Etherification catalyst identification, etherification of ethanol guerbet production, and etherification of C8+ linear alcohols (complete)

Task 2

- Milestone 2.1.1 -2.1.2 Process simulation model and TEA of alternative biorefineries (complete), simulation of target biorefinery (In progress)
- Milestone 2.1.3 – Initial LCA of biorefinery-engine system (prelim. LCA performed)

Task 3

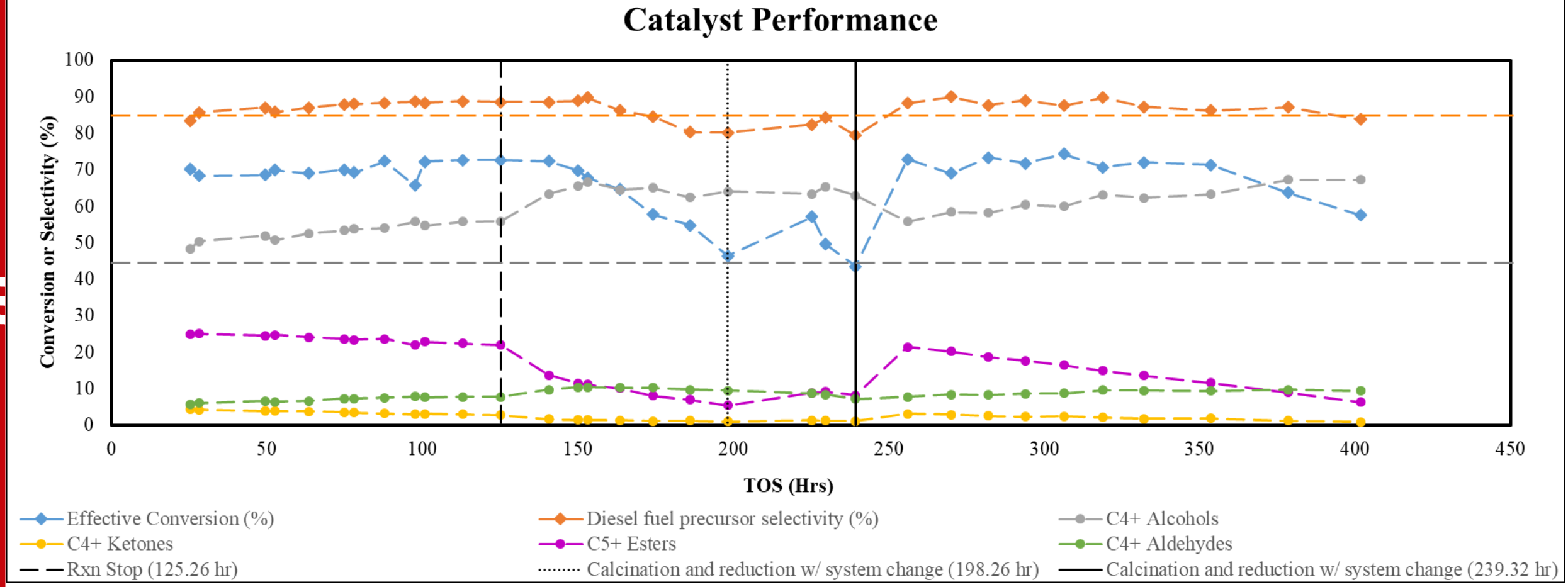
- Milestones 3.1.1 and 3.2.1 – Baseline SCME and SCOE operation (complete)
- Milestone 3.3.1 and 3.4.1 – SCME and SCOE studies of fuel component for catalyst heating operation (SCME complete, SCOE in progress)

Task 4

- Task 4.1 Property testing for model components (complete)
- Milestones 4.2.4 and 4.3.2 – Diesel fuel surrogate (complete) and bioblendstock surrogate (just starting)

SCME =Single-cylinder metal engine SCOE =Single-cylinder optical engine

Task 1.1 - Guerbet Coupling of Alcohols Go/No-Go BP1



Effective ethanol conversion and selectivity to diesel bioblendstock precusors vs. time. Cu/Mg_xAlO_y catalyst, reaction Conditions: 325 °C , 300 psig H_2, 2.6 ml/min H_2, ~0.017 ml/min EtOH, WHSV = 0.39 h^{-1}.

- Catalyst was regenerated three times, indicating that activity can be fully recovered
- Diesel fuel precursors made up of mainly C4+ alcohols and C5+ esters
- Composition output from Guerbet coupling will affect etherification step (impact on etherification currently being studied)

Task 1.1 - Guerbet coupling of alcohols Go/No-Go BP1

Average effective ethanol conversion

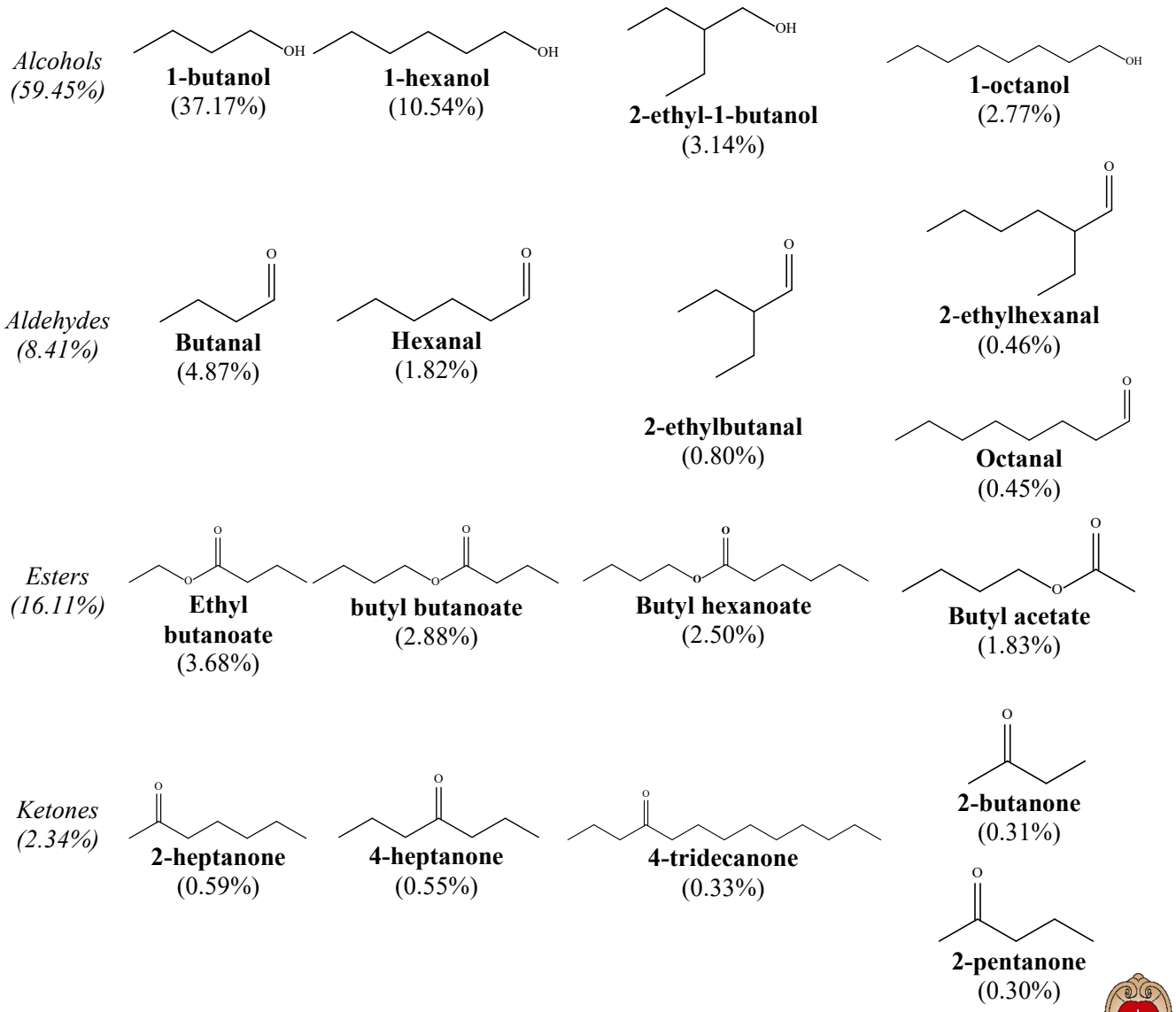
=65.7% > 45% for Go/No-Go

Average diesel precursor selectivity

= 86.3% > 85% for Go/No-Go

Diesel precursor composition

- Four classes of components
  - Alcohols, aldehydes, esters, ketones
- 4 to 5 most abundant molecules shown for each class

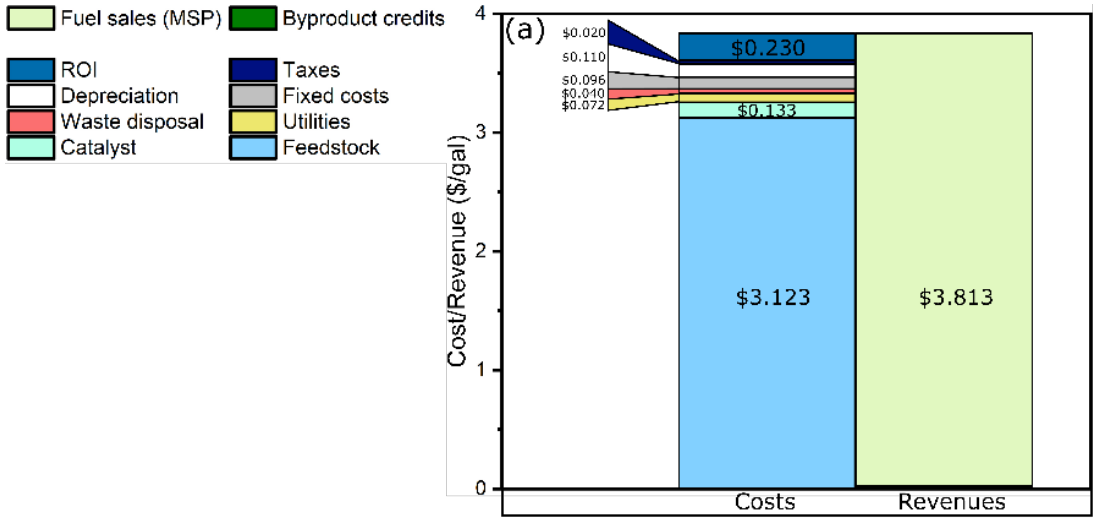


Average-product distribution from Guerbet coupling and side reactions over Cu/Mg_xAlO_y catalyst for 425 TOS.

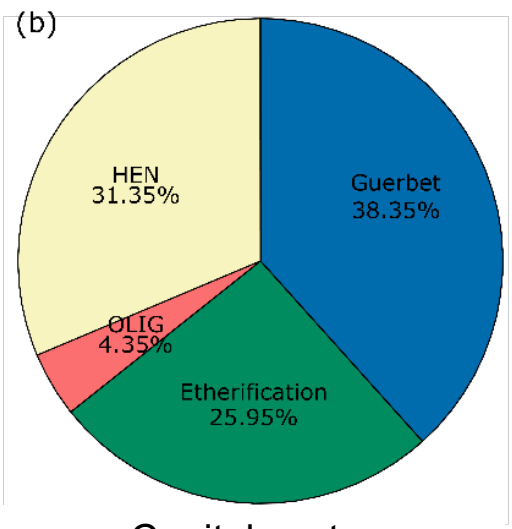
Task 2 - Process Systems Engineering

Process synthesis, technoeconomic analysis (TEA), and life cycle assessment (LCA)

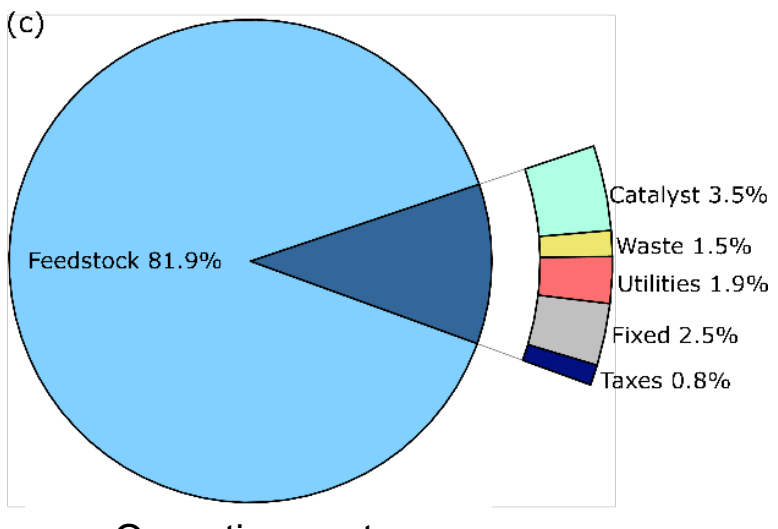
- We have synthesized a biorefinery for the production of a diesel bioblendstock based on Guerbet coupling and etherification. The feedstock used is lignocellulosic ethanol.
- Preliminary TEA shows minimum fuel selling price (MFSP) of $3.8/gal in $2007
- Preliminary LCA reveals a potential reduction in CO_2 emissions of more than 50%



Cost breakdown
MFSP 3.8/gal



Capital costs
$145MM



Operating costs
$141MM/a

Cost distribution for the biorefineries synthesized

Task 2 - Process Systems Engineering

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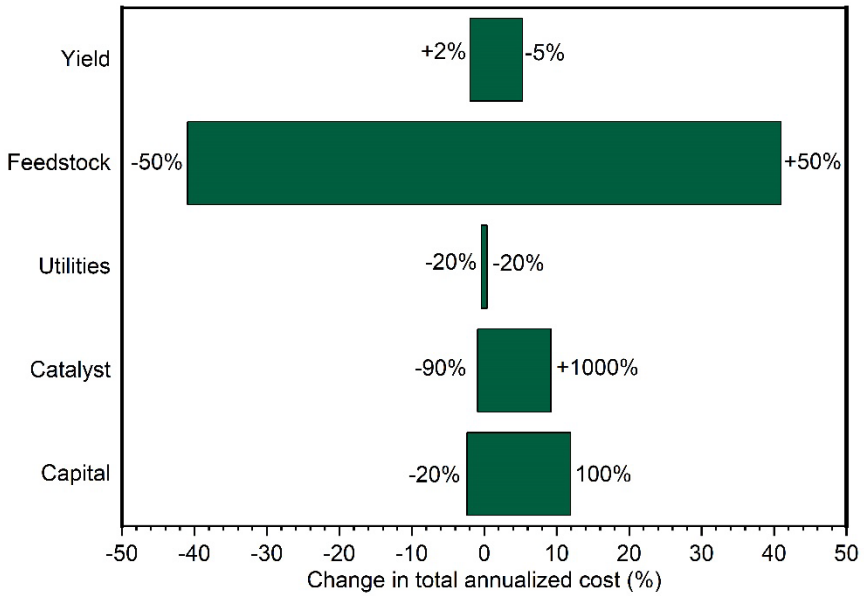
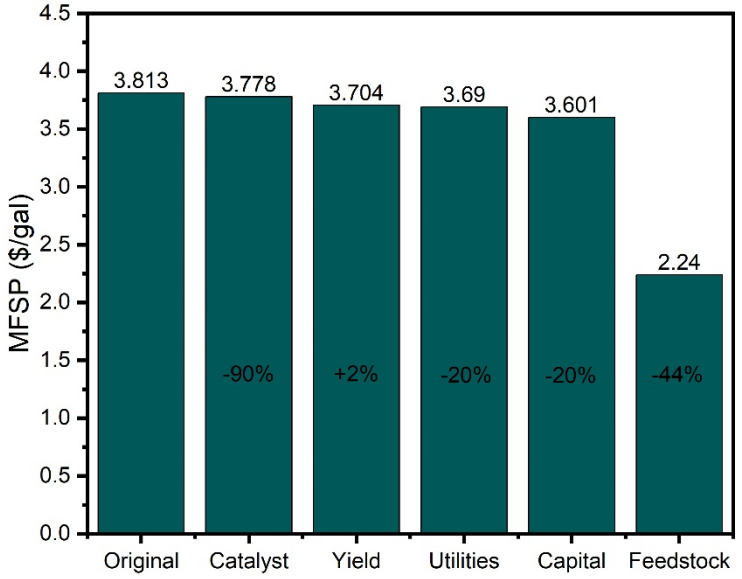


Tornado plot showing sensitivity analysis



Minimum selling price under different scenarios

The major cost driver is the feedstock cost. Improving the total yield or using a cheaper feedstock are the main strategies to reduce the cost

Task 2 - Process Systems Engineering

Process synthesis, technoeconomic analysis (TEA), and life cycle assessment (LCA)

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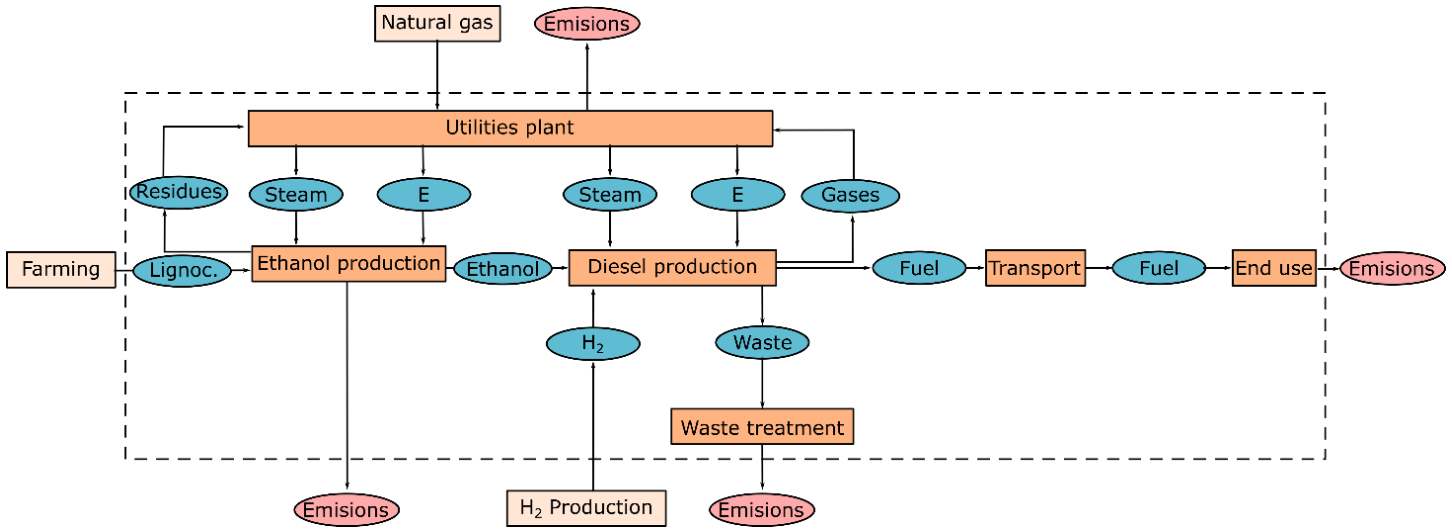
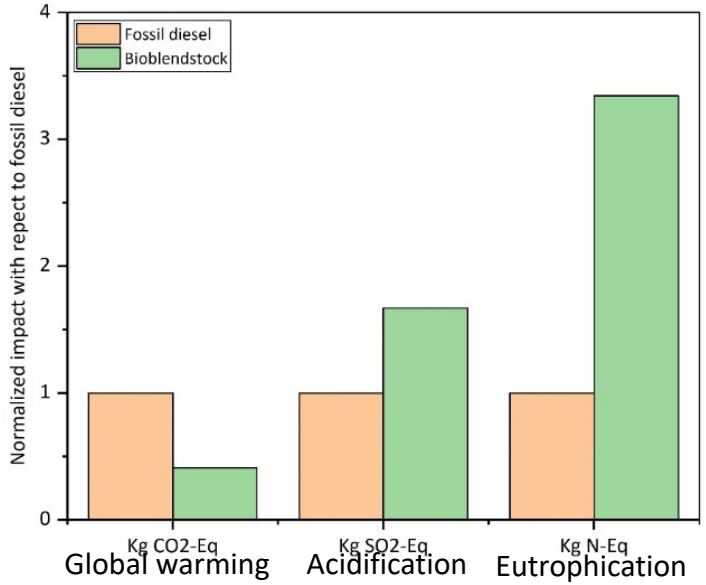


Schematic diagram used in LCA showing the main flows



Initial assessment of environmental impacts

CO_2 emissions of the bio-blendstock are less than 50% of fossil diesel throughout the entire life cycle. Acidification, and eutrophication impacts increase as a consequence of farming and ethanol production (ethanol feedstock used was switchgrass).

Task 3.3 - SCME Studies of Fuel Components

Milestone 3.3.1 and 3.4.1 are essential to understanding impacts of fuel properties

Milestone 3.3.1: Single-cylinder metal engine (SCME) testing of fuel components at catalyst warmup conditions

- Triple injection strategy to increase exhaust temperature to reduce warmup time
- Investigation of fuel properties impacting combustion and emissions performance
- 10 fuel blends investigated to study impacts of three fuel properties:
  - Cetane number (CN), defines reactivity of a fuel
  - Volatility, as measured by distillation curve
  - Energy entrainment requirement, a derived property to define energy required by fuel spray to reach autoignition temperature
- Conceptualized bioblendstock blended with diesel also investigated to study:
  - Effects of residual alcohol
  - Benefits/drawbacks on emissions and combustion performance from blending bioblendtock with diesel

- **Next Milestone 3.4.1:** Optical investigation of fuel components at catalyst warmup conditions
  - To better understand emission trends by imaging spray development and combustion event

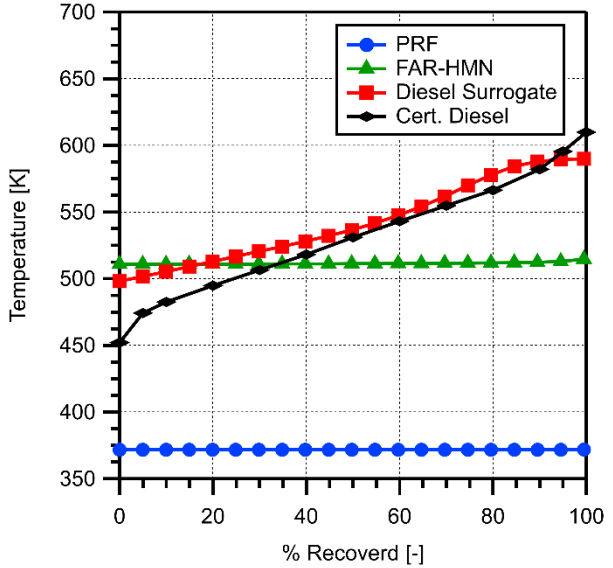
Task 3.3 – SCME Studies of Fuel components

- **Fuel properties of interest:**
  - Cetane number (CN)
  - Entrainment requirement of fuel spray
  - Volatility (distillation curve)

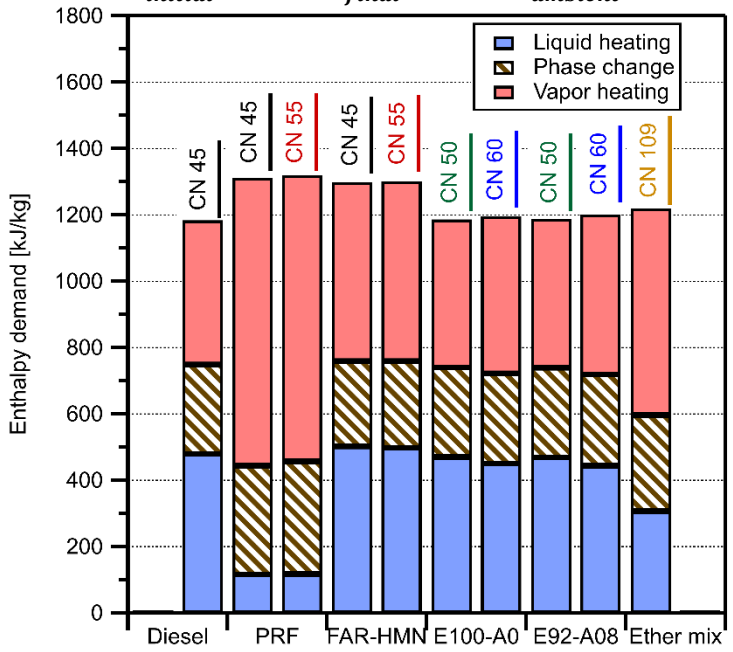
- **Fuel blends (total 10) under consideration:**
  - Primary reference fuel (PRF)
  - Farnesane-Heptamethylnonane (FAR-HMN)
  - Ether*-Alcohol^ mixture
  - Ether* mixture

- **Fuel blends designed to isolate impacts of all three fuel properties**

* → *dibutyl ether, dihexyl ether & diisoamyl ether*
^ → *butanol & hexanol*



$T_{initial}$=323 K, T_{final}=700 K, $T_{ambient}$=1000 K



(Bottom) ASTM D86 distillation curves
(Top) Entrainment requirement for fuel blends.
E#A#: Ether & alcohol mixture volume %.

Task 3.3 - Engine Testing – SCME Results

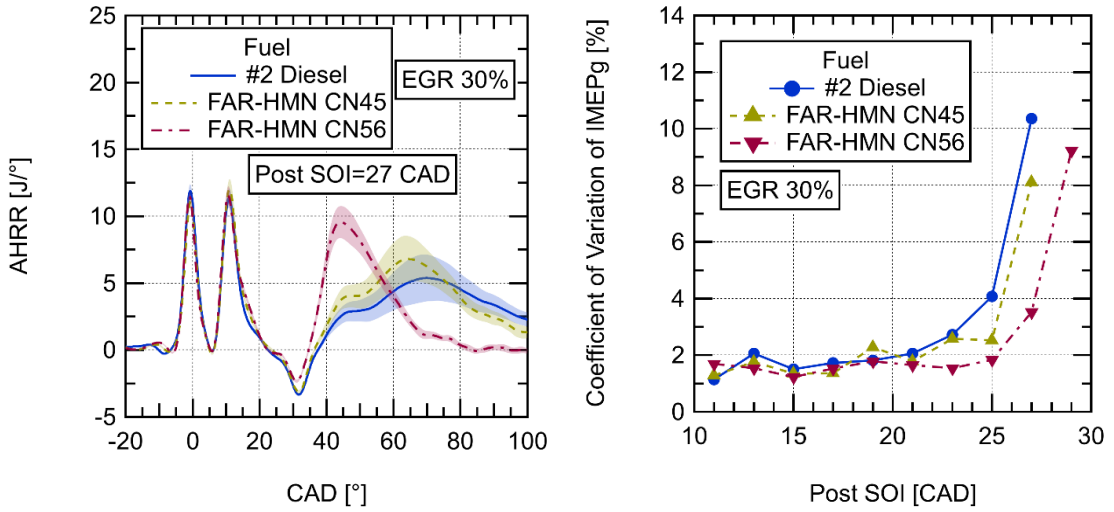
Influence of fuel properties on catalyst heating operation

Increasing CN:

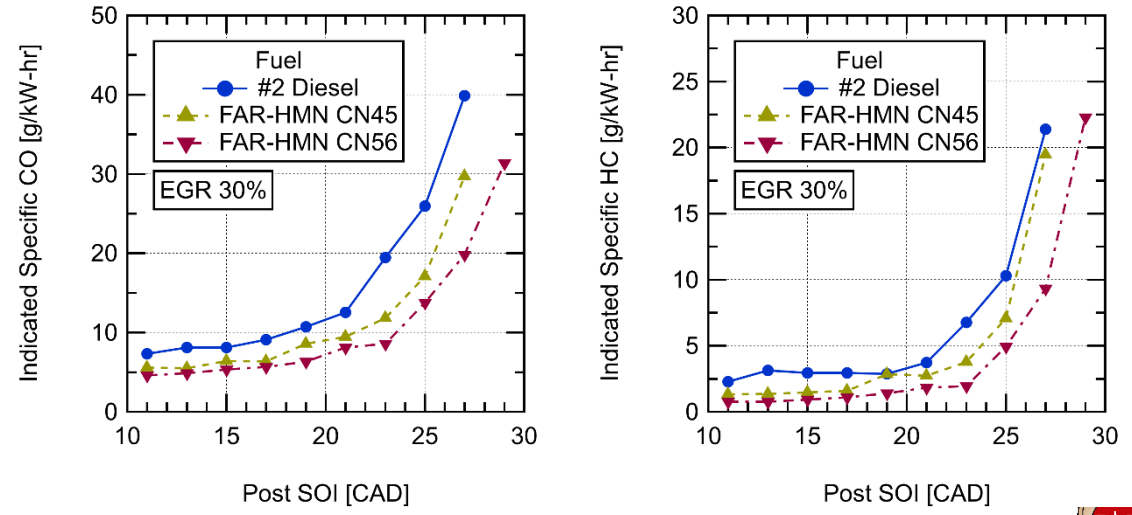
- Allows the post injection to be retarded further into expansion stroke
- Higher combustion stability achieved
- Reduction of engine-out HC and CO emissions

Volatility impact:

- Minimal impact of volatility on emissions and combustion (not shown here)
  - Suggests overmixing is the primary cause of HC emissions



Left: HRR curves; **Right**: COV of IMEP for Diesel and Farnesane-Heptamethylnonane at CN 45 and 56



Engine-out emissions **Left:** CO and **Right:** HC for Diesel and Farnesane-Heptamethylnonane at CN 45 and 56

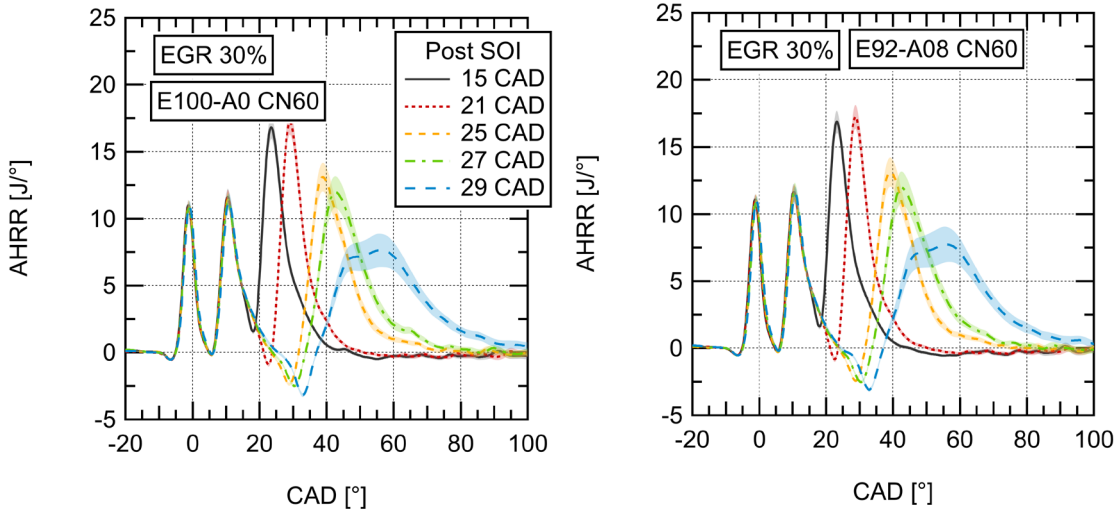
Task 3.3 - Engine Testing – SCME Results

Results with preliminary bioblendstock surrogates

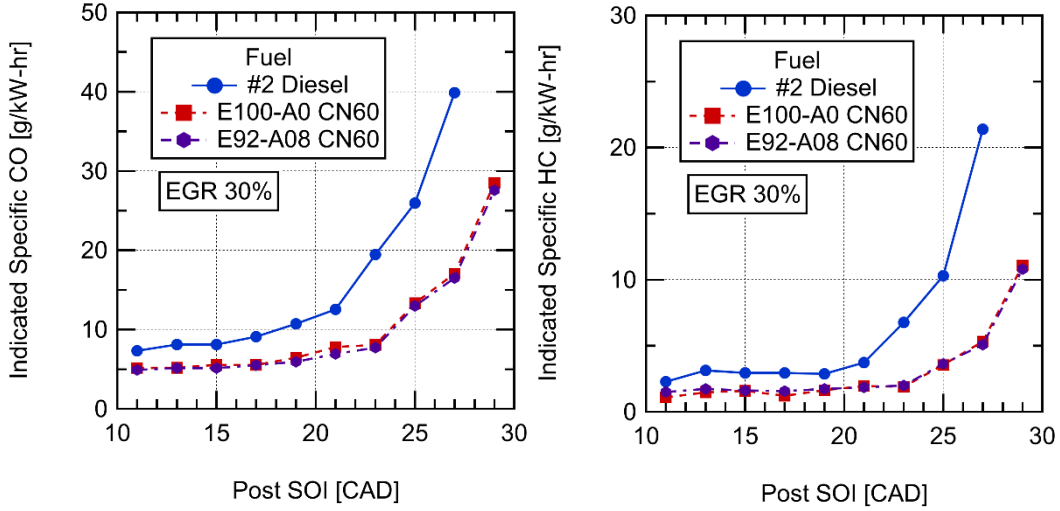
- Bioblendtock blending results in:
  - Better combustion stability
  - Lower CO and HC emissions at similar soot level as diesel fuel
  - Results due to increased CN

Residual alcohol in bioblendstock (up to 8% by vol.) has little to no effect on combustion and emissions at matched CN

E#: Ether blend vol. %; A#: Alcohol blend vol. %
Ether composition: dibutyl, dihexyl & diisoamyl ether
Alcohol composition: Hexanol & butanol



HRR curves for **Left**: E100-A0 CN60; **Right**: E92-A08 CN60



Left: CO; **Right**: HC emissions for bioblendstock blends and Diesel fuel (CN 45)

Task 4.2 - Fuel Property Modeling – Blendstocks

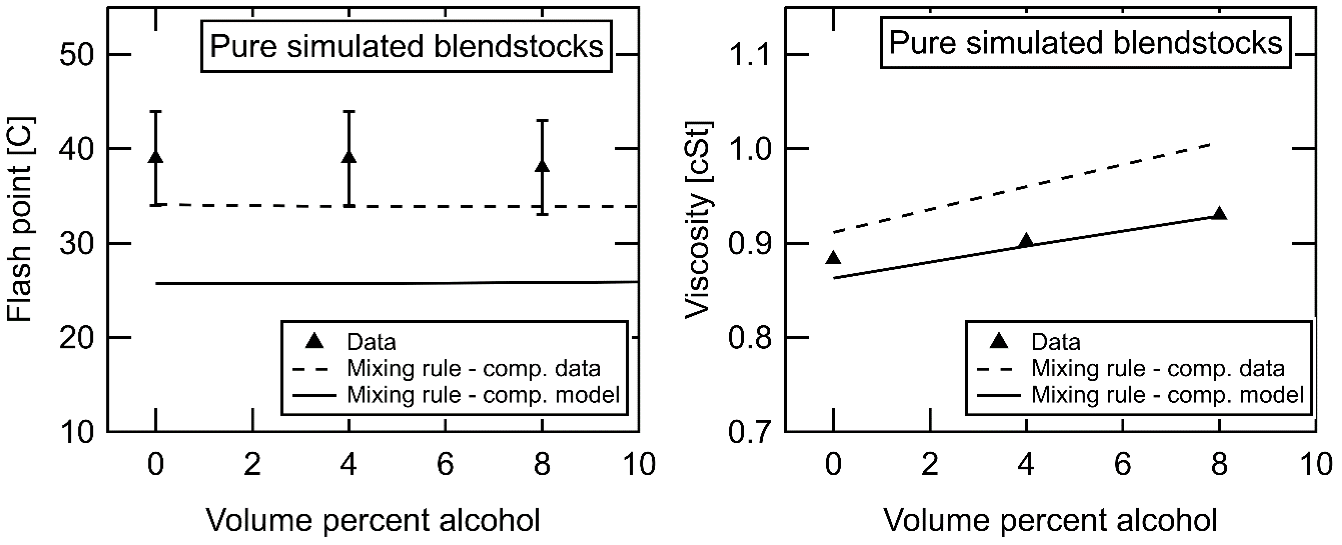
- Goal is to implement / validate models for bioblendstock and blends with #2 diesel fuel
  - 3 representative blendstocks prepared with guidance from process synthesis
  - ASTM tests include distillation, density, flash point, viscosity and cetane

Alcohol in bioblendstock added up to 8 vol. % results in minimal impact on properties

  - Mixing models used to interpret data [1,2] reproduce muted impact observed experimentally
  - Effect is due to non-ideal mixing behavior in alcohols

Composition of representative blendstock products from Guerbet coupling process

	Di-n-butyl ether %[vol]	Di-isopentyl ether %[vol]	Di-n-hexyl ether %[vol]	N-butanol %[vol]	N-hexanol %[vol]
BLEND1	65	2	33	0	0
BLEND 2	62	2	32	1	3
BLEND 3	60	2	30	2	6



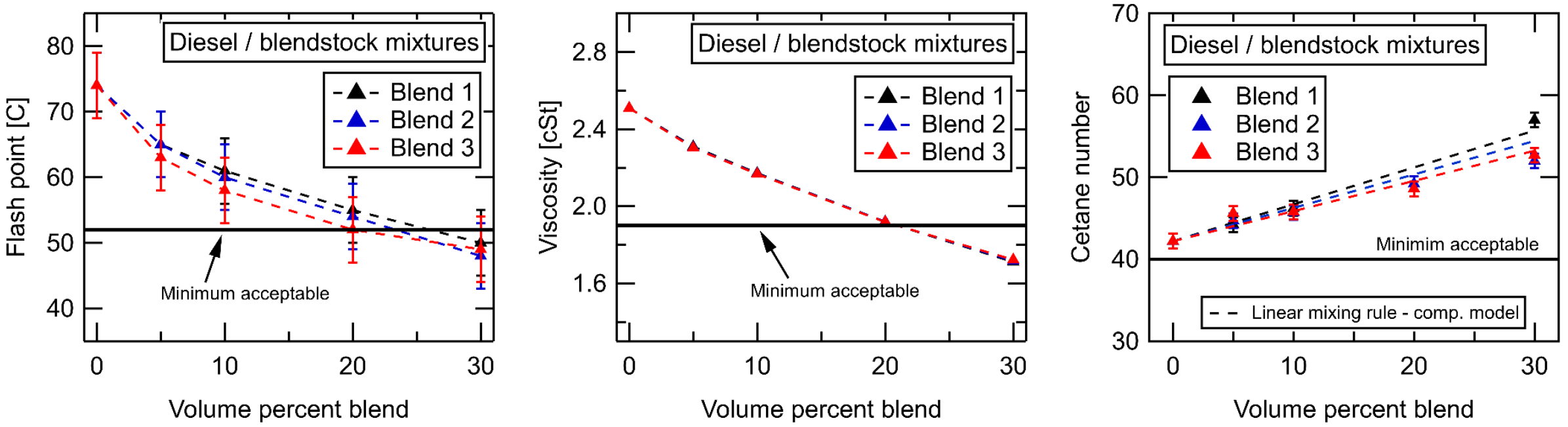
(Left) Flash point and (right) viscosity of simulated blendstocks as a function of alcohol concentration

Task 4.2 Fuel Property Modeling–Diesel/Bioblendstock Mixtures

Surrogate bioblendstocks were mixed from 5 – 30 % by volume with #2 diesel

- Effect of alcohol again minimal on properties → May allow for less intensive separations during fuel production

Need accurate diesel physical property computational surrogate to predict and optimize mixtures of #2 diesel and the bioblendstock (information on surrogate in backup slides)



(Left) Flash point, (middle) viscosity and (right) cetane number of blendstock/diesel mixtures as a function of blendstock concentration

Summary

- Project features integrated approach of catalysis, process systems engineering analysis, engine testing, and fuel property modeling and testing
- **Overall goal:** Co-optimize catalytic production and engine operation for a diesel bioblendstock produced from cellulosic ethanol to produce economically viable product that reduces emissions
- Good progress made to date and project is on schedule following completion of BP1 Go/No-Go
- **Preliminary analysis indicates >50% reduction in GHG emissions and good potential for fuel properties to benefit engine operation via optimization of engine operation**

Quad Chart Overview

Timeline

- Project Start Date: May 14, 2019
- Project End Date: December 31, 2022

	FY20 Costed	Total Award
DOE Funding	$428,703	$1,499,894
Project Cost Share	$69,856	$383,793

Project Partners*

Project Goal

Optimize catalytic production and engine operation for a diesel bioblendstock produced from cellulosic ethanol to produce economically viable product that reduces emissions

End of Project Milestone

Bioblendstock with

- > 50% reduction in lifecycle greenhouse gas emissions relative to conventional petroleum-derived diesel fuel
- >1% combined MCCI engine/aftertreatment system efficiency improvement
- optimized blend percentage (>5 vol.%) with #2 diesel fuel that meets all ASTM D975 specification

Improved catalytic process with

- >85% conversion of ethanol into diesel fuel bioblendstock precursors.
- > 90% conversion of C4+ alcohols into C8+ ethers.

1 L sample of bioblendstock provided to National Laboratory Co-Optima Team.

Funding Mechanism

FY 2018 Adv. Vehicle Technologies Research FOA (DE-FOA-0001919), AOI 5b: Bioblendstocks to Optimize Mixing Controlled Compression Ignition Engines

Additional Slides

Task 1.2 – Etherification of Guerbet coupling products

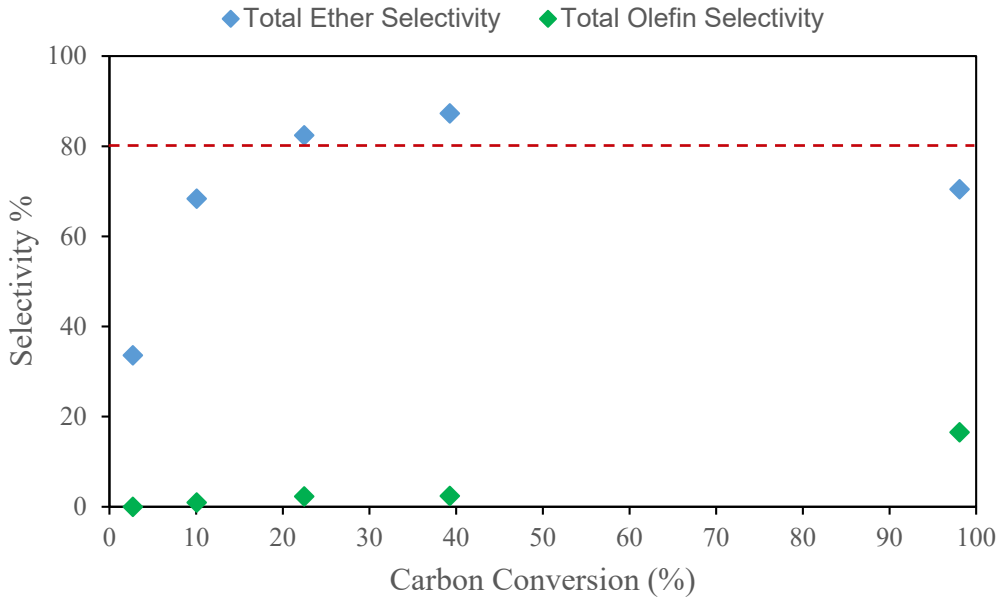


Figure 2. Selectivities of di-n-hexyl ether and olefins (Hexenes) vs conversion in parr reactor; 2M hexanol (C6 Alcohol) in n-decane, 0.4 g H-Y, 500 psi (Ar).

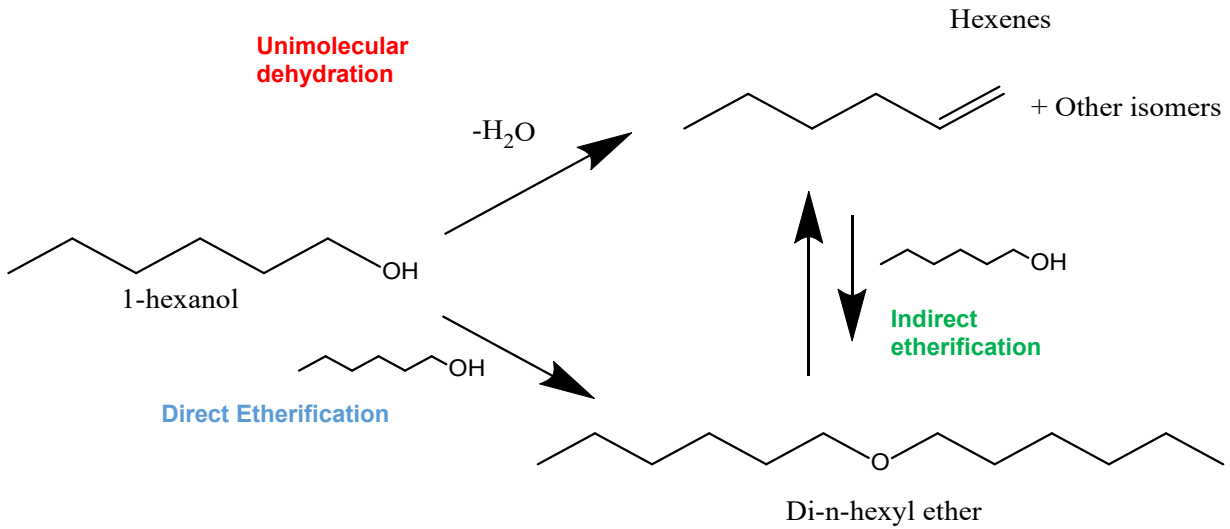


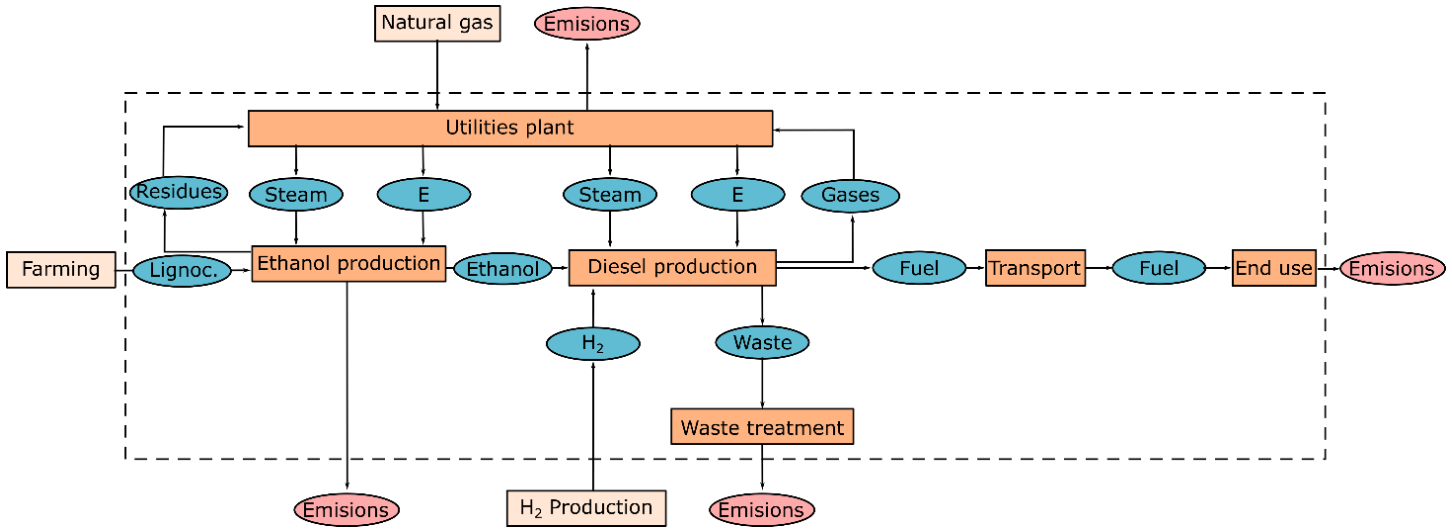
Figure 3. Reaction pathway for etherification of 1-hexanol.

- Selectivity of 80% to C8+ ethers achievable over H-Y catalyst ***(Meeting Milestone 1.2.1 and 1.2.2)***
- Current progress is to use 1-octanol (C8 alcohol) to produce C16 ethers ***(Milestone 1.2.3)***
- BP2 will involve etherification in a continuous reactor
- Model feeds will contain esters to study effects on etherification

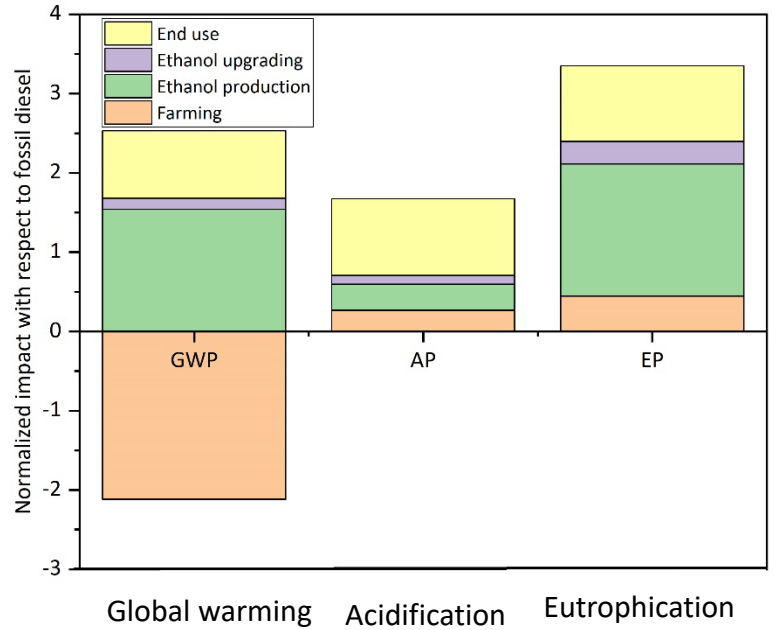
Task 2 - Process Systems Engineering

Process synthesis, technoeconomic analysis (TEA), and life cycle assessment (LCA)

- We have synthesized a biorefinery for the production of a diesel bioblendstock based on Guerbet coupling and etherification. The feedstock used is lignocellulosic ethanol.
- Preliminary TEA shows minimum fuel selling price (MFSP) of $3.8/gal in $2007
- Preliminary LCA reveals a potential reduction in CO_2 emissions of more than 50%



Schematic diagram used in LCA showing the main flows



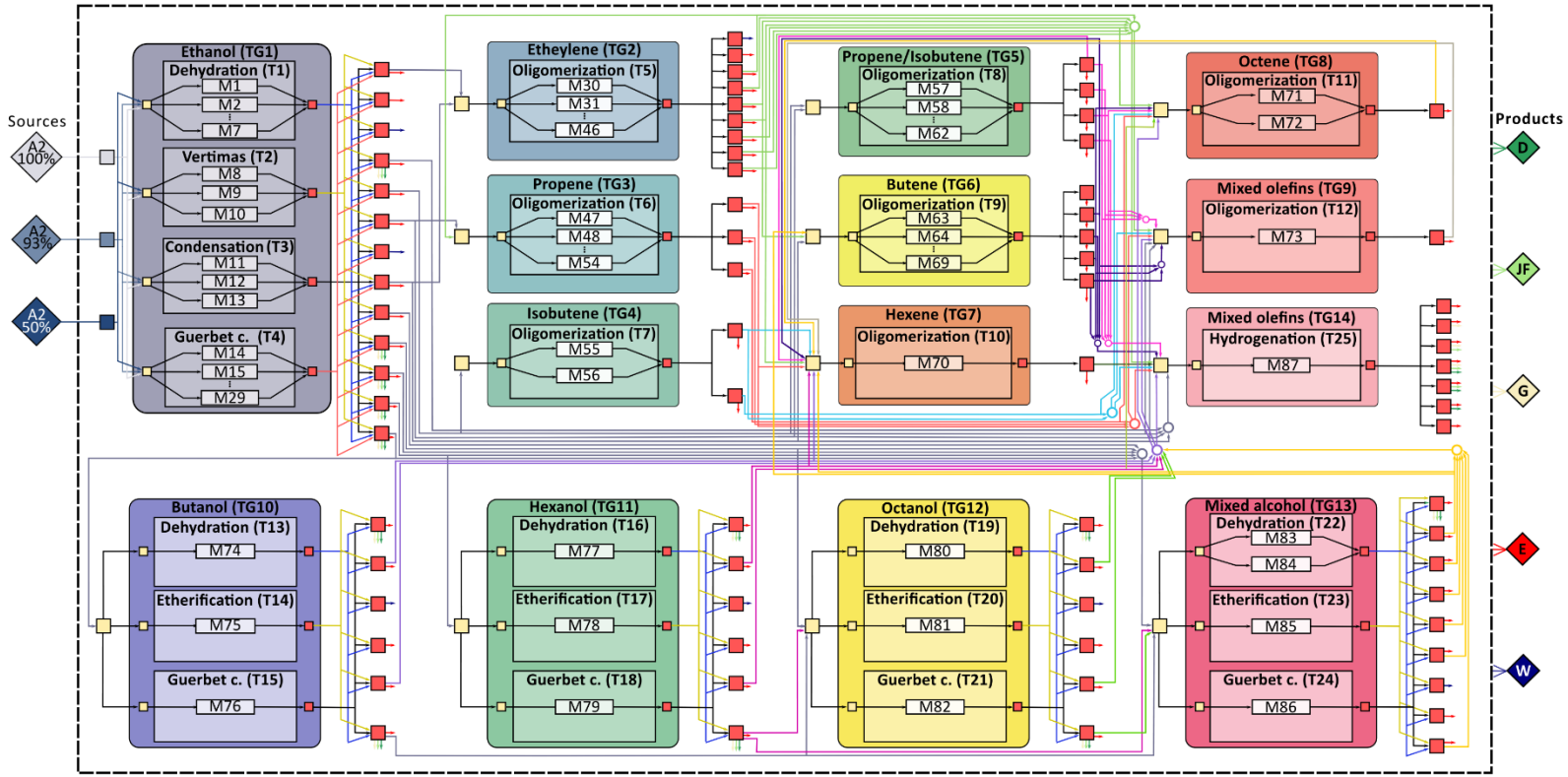
Breakdown of environmental impacts

CO_2 emissions of the bio-blendstock are less than 50% of fossil diesel throughout the entire life cycle. Acidification, and eutrophication impacts increase as a consequence of farming and ethanol production (ethanol feedstock used was switchgrass).

Task 2 - Process Systems Engineering

Development of optimization framework for the synthesis of biorefineries

- We have developed a superstructure optimization framework for the automatic design of ethanol upgrading biorefineries. This framework selects the chemistries and processes required to upgrade ethanol while simultaneously considering:
  - Capital and operating costs associated with the biorefinery
  - Properties of the fuel products obtained (Gasoline, diesel, and/or Jet fuel)



Superstructure with different chemistries, processes, and possible connections

Task 2 - Process Systems Engineering

Development of optimization framework for the synthesis of biorefineries

- We have developed a superstructure optimization framework for the automatic design of ethanol upgrading biorefineries. This framework selects the chemistries and processes required to upgrade ethanol while simultaneously considering:
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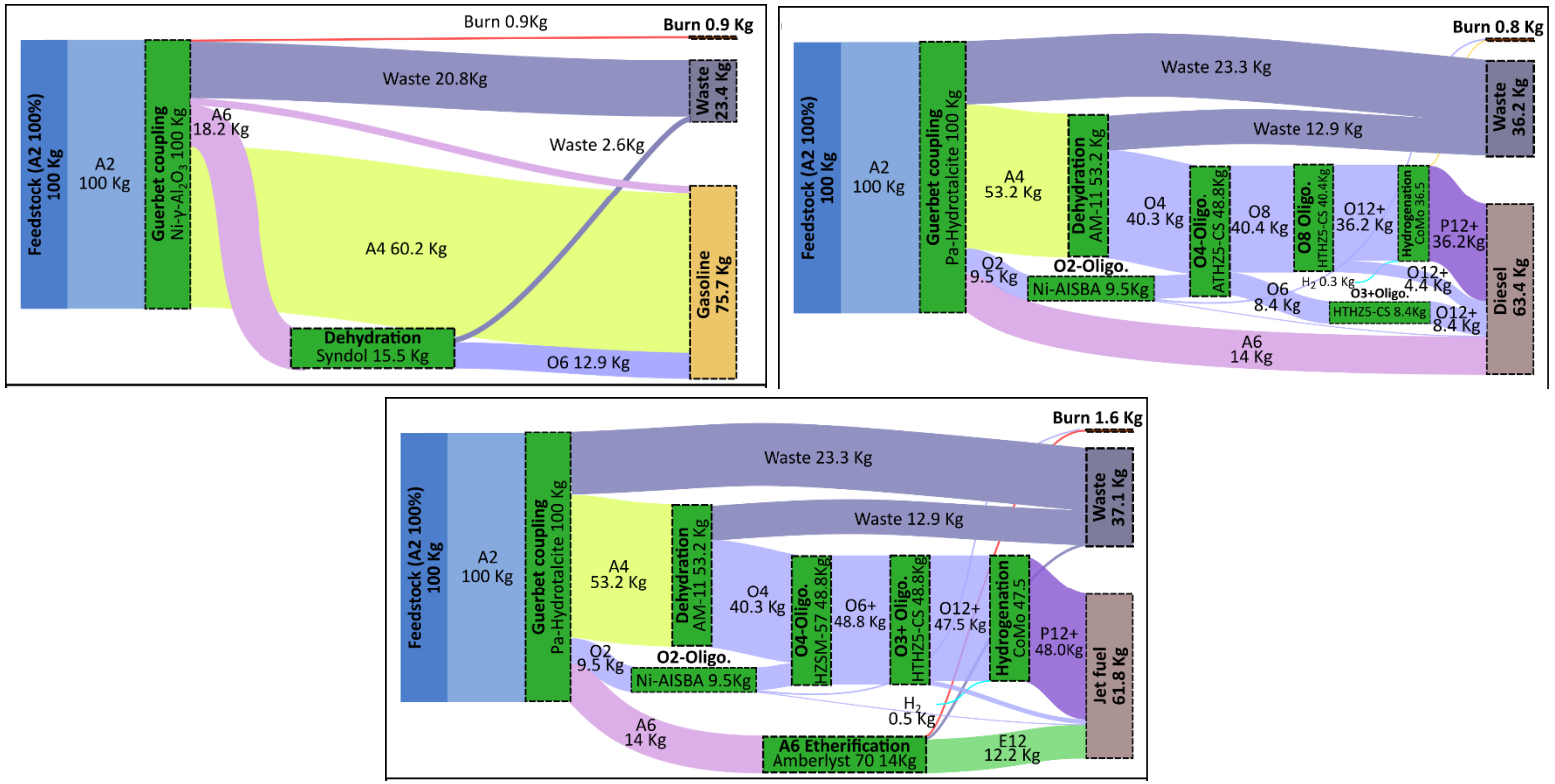
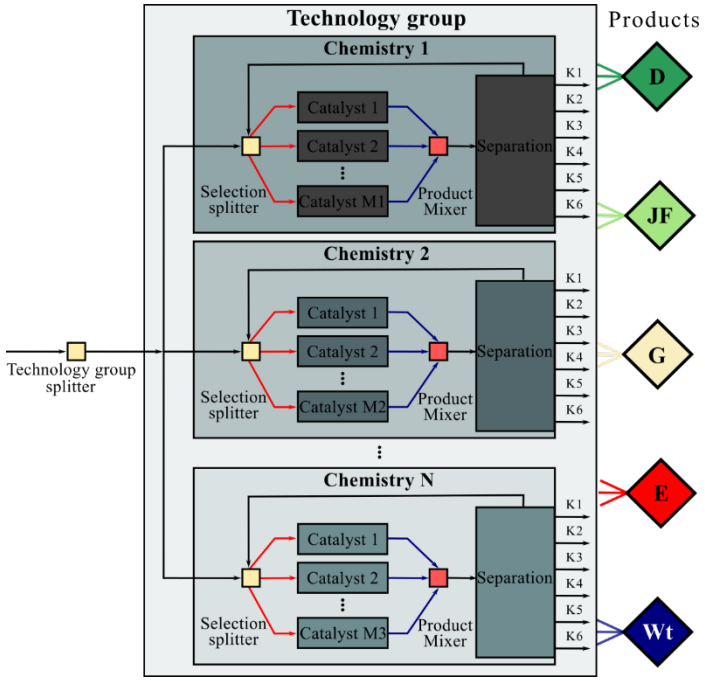


Biorefineries obtained for the production of gasoline, jet fuel, and diesel

Task 2 - Process Systems Engineering

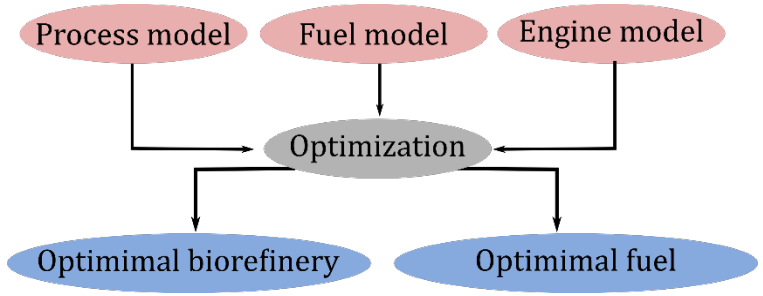
Future and ongoing work

1. We are developing a superstructure optimization framework for early design of biorefineries that does not require external information for capital cost, operating cost or energy requirements.

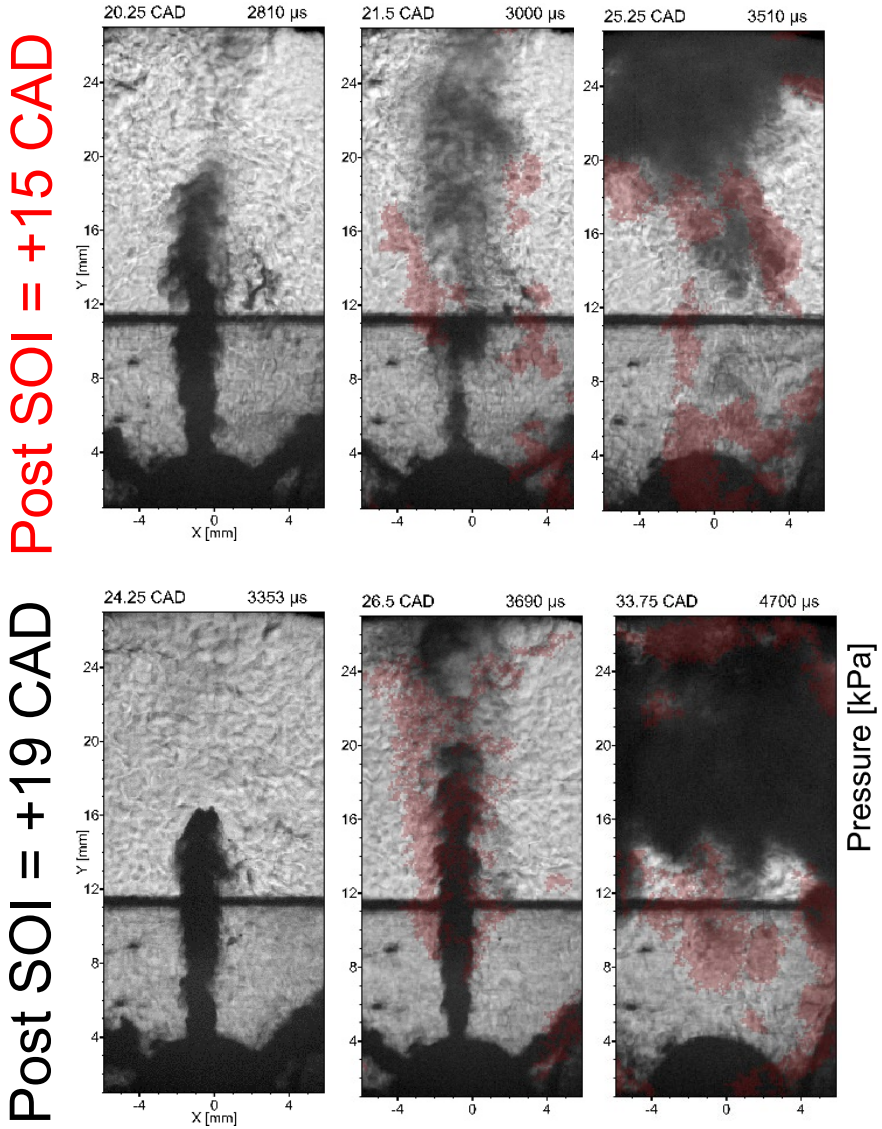


Architecture of the designed superstructure

2. We are working to incorporate engine emissions information into our optimization models such that an integrated approach for the design of fuels and processes can be implemented

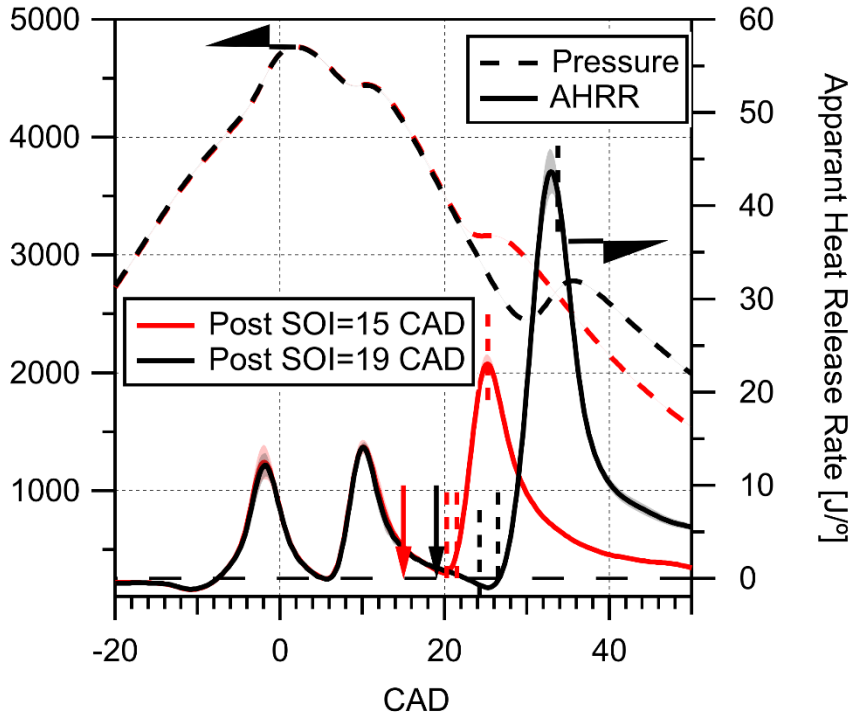


Task 3.2 – Baseline single-cylinder optical-engine operation



Baseline #2 diesel optical engine results (Milestone 3.3.1

- As post injection is retarded:
  - Longer liquid penetration & lower vaporization of jet
  - Significant soot formation
- Fuel volatility may be important to limit/avoid liquid fuel impingement at late injection times



(Left) Simultaneous schlieren and OH chemiluminescence imaging (OH overlaid in red)

(Right) Pressure and apparent heat release for post SOIs of +15 and +19 CAD. Post SOI denoted by vertical arrows, timing denoted by vertical dashed lines.

Task 4 - Diesel surrogate formulation

- 8 model components from literature [3] were used to construct diesel surrogate palette
  - Diesel surrogate composition chosen by minimizing error for Cetane, Flashpoint, Viscosity, distillation curve and H/C (see additional slides)
  - Distillation and cetane surrogate model validated against previous EXPERIMENTAL diesel surrogate data [3] with the same chemical palette as used here (see additional slides)
    - Agreement between simulated and measured distillation curve < 1% over entire range
    - Agreement between simulated and measured cetane number < 4%
    - Future work should additionally validate viscosity and flash point models

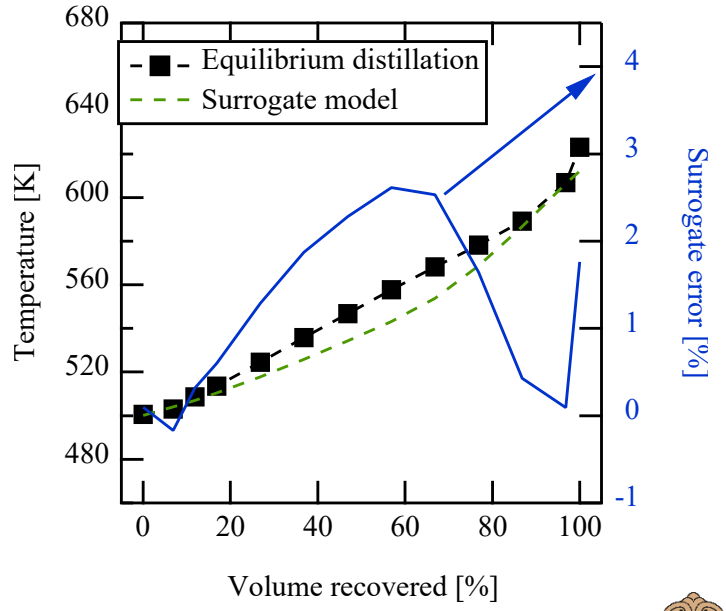
All computed surrogate properties matched within target specifications

NAME	**SURROGATE MOLE FRACTION**
Transdecalin	***0.279***
Heptamethylnonane	***0.512***
1-methylnaphthalene	***<0.01***
N-hexadecane	***0.013***
1,2,4-trimethylbenzene	***<0.01***
Tetrahydronaphthalene	***<0.01***
N-octadecane	***0.126***
N-eicosane	***0.071***

Composition of selected diesel surrogate

Property	**Surrogate**	**Diesel**	**Error**	**Target**
T10 [K]	506	508	0.4%	5%
T50 [K]	537	550	2.4%	5%
T90 [K]	592	595	0.5%	5%
Cetane [-]	44.7	42.2	6%	10%
Viscosity [cP]	2.39	2.14	12%	20%
H/C [-]	2.06	1.84	12%	N/A
Flash point [C]	79	74	7%	N/A
Density [g/ml]	0.802	0.854	6%	N/A

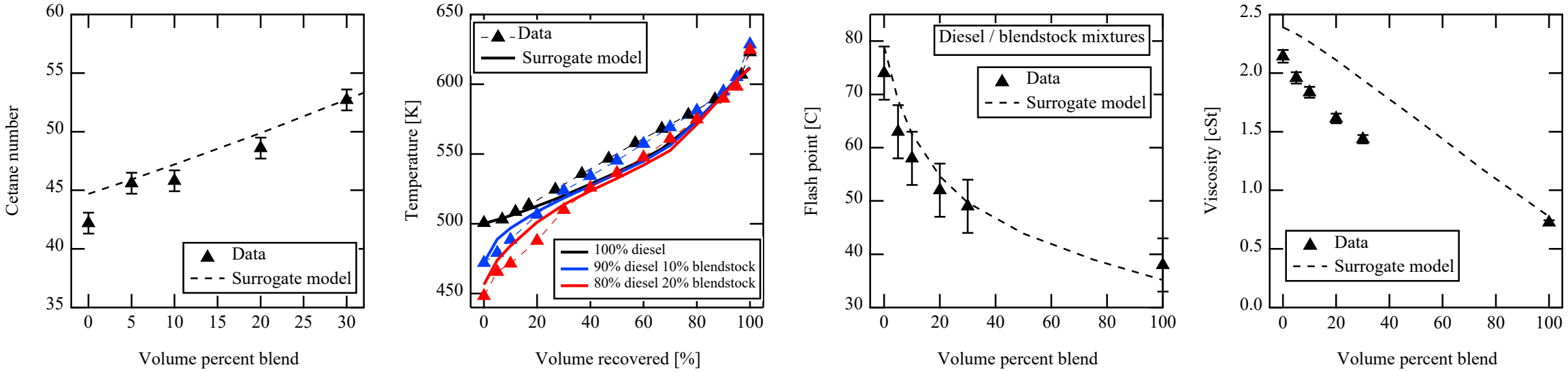
Comparison between diesel and surrogate physical properties



Comparison between diesel equilibrium distillation curve [4] and surrogate simulation

Task 4 - Diesel/ blend 3 mixture comparison

- Diesel surrogate model used to predict impact of diesel mixed with “BLEND 3” (92% ether, 8% alcohol)
- Cetane, distillation and flash point behavior all well captured by mixing models
  - Worst agreement is for viscosity (avg. error 21%, max error 35%)
- Potential future work – Determine maximum allowable alcohol for a given diesel/blendstock mixture fraction



Comparison between experimental and simulated (Left) Cetane number, (left-middle) distillation, (right-middle) flash point and (right) viscosity of blend 3 / diesel mixtures as a function of blendstock concentration

Task 4 - Diesel Surrogate Palette

- 8 model components from literature [1] added to the fuel database for constructing diesel surrogate
- Diesel surrogate composition chosen by minimizing error for Cetane, Flashpoint, Viscosity, distillation curve and H/C through objective function (E) using an in-house developed Matlab code.

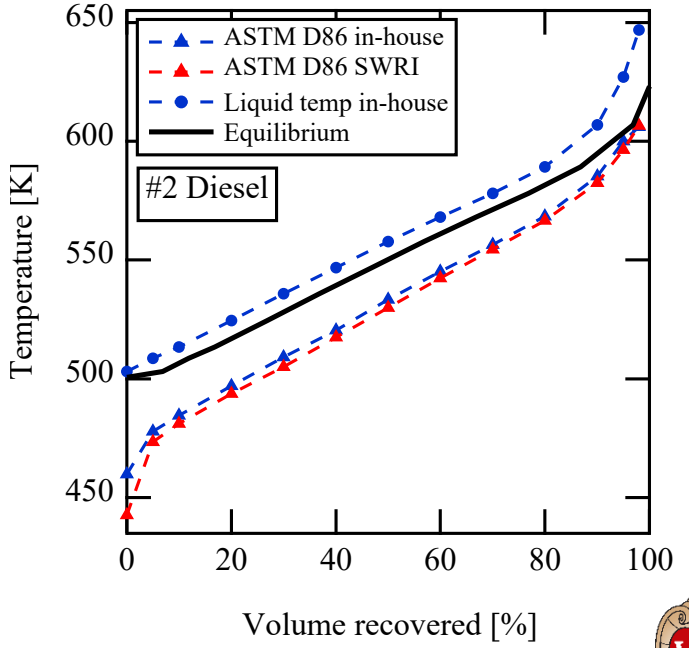
$$E = \sqrt{\frac{1}{\sum w_i}\sum_i w_i \epsilon_i^2} \qquad \epsilon_i^2 = \left(\frac{X_{i,calc} - X_{i,meas}}{X_{i,meas}}\right)^2$$

w_i - Weighting for property i , $X_{i,calc}$ - Calculated value fro property I, $X_{i,meas}$ - Experimental value of property i

- Equilibrium distillation curve was measured for target diesel using the method of Ferris and Rothamer [4]

NAME	*DENSITY [g/ml]*	*FLASH POINT [C]*	*VISCOSITY [Pa-s]*	*CETANE [-]*	*BOILING TEMP [C]*	**SURROGATE MOLE FRACTION**
Transdecalin	0.874	57	0.0015	45	187.3	***0.279***
Heptamethylnonane	0.787	95	0.0024	15	246.4	***0.512***
1-methylnaphthalene	1.01	82	0.0021	0	244.8	***<0.01***
N-hexadecane	0.773	135	0.0023	100	286.8	***0.013***
1,2,4-trimethylbenzene	0.880	44	0.00066	9	169.4	***<0.01***
Tetrahydronaphthalene	0.970	78	0.0015	13	207.7	***<0.01***
N-octadecane	0.785	165	0.0031	106	316.8	***0.126***
N-eicosane	0.791	176	0.0041	110	343.8	***0.071***
#2 Diesel	***0.854***	***74***	***0.0021***	***42.2***		

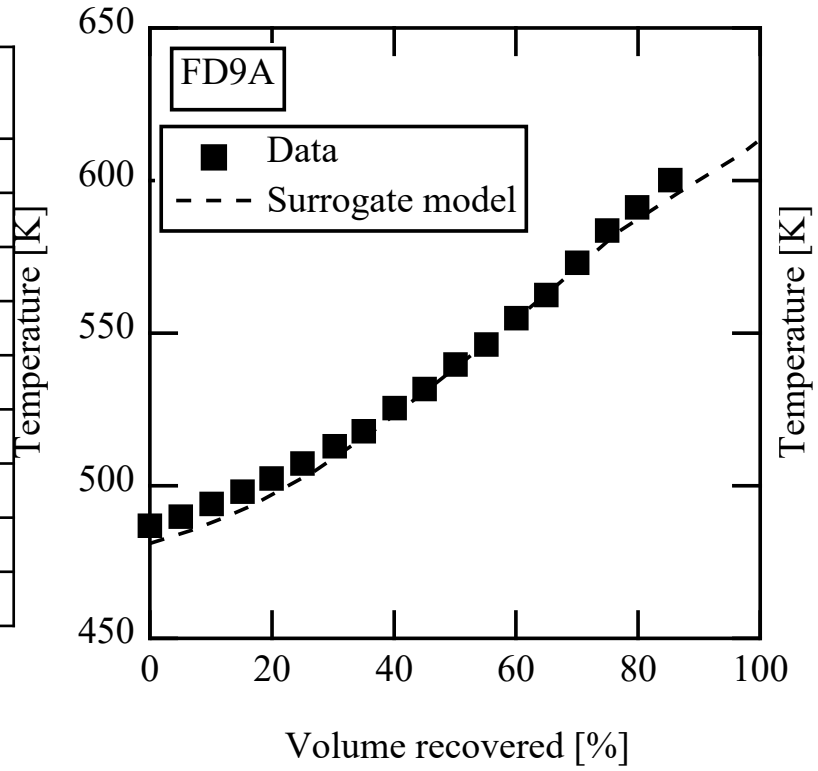
Experimental properties of target diesel and surrogate palette

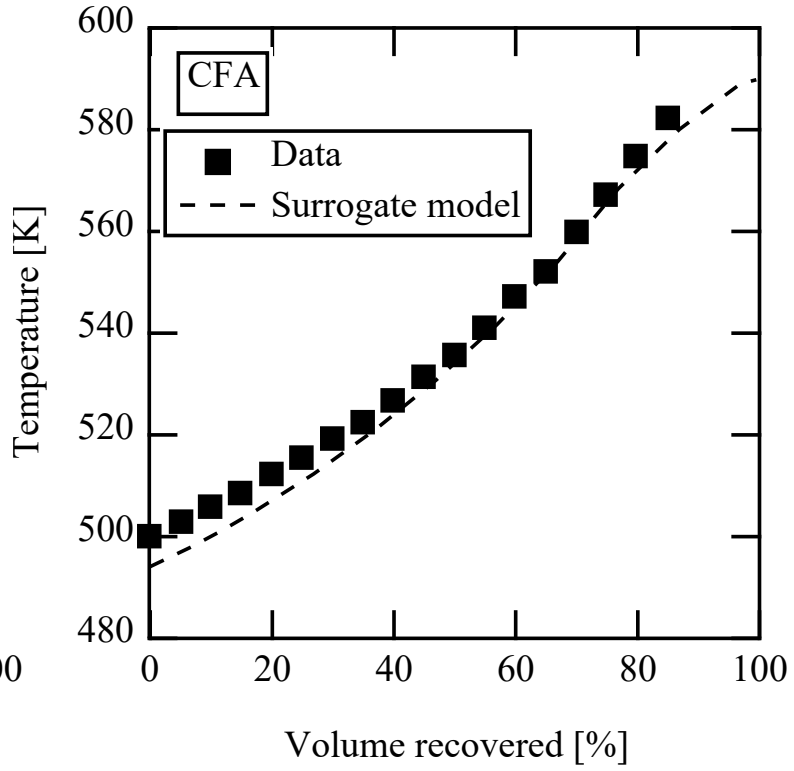


Task 4 - Surrogate model validation

- Distillation surrogate model validated against previous EXPERIMENTAL data [1] that tested 2 diesel surrogates (FD9A, CFA) using the same chemical palette as used here
  - Differences between our surrogate distillation model and experimental data 1% or less over the entire distillation range
  - Volumetric DCN blending rule used in [1] (and here) matched experimental data within <4% for both surrogates as well

NAME	**FD9A MOLE FRACTION**	**CFA MOLE FRACTION**
Hexadecane	***0***	***0.027***
Octadecane	***0.131***	***0.202***
Eicosane	***0.078***	***0***
Heptamethylnonane	***0.282***	***0.292***
Butylcyclohexane	***0.05***	***0.051***
Transdecalin	***0.10***	***0.055***
Trimethylbenzene	***0.188***	***0.075***
Tetrahydronaphthalene	***0.113***	***0.154***
methylnaphthalene	***0.058***	***0.144***





References

1. Gaston-Bonhomme, Y., P. Petrino, and J. L. Chevalier. "UNIFAC—VISCO group contribution method for predicting kinematic viscosity: extension and temperature dependence." *Chemical engineering science* 49.11 (1994): 1799-1806.
2. H.-J. Liaw and Y.-Y. Chiu, "A general model for predicting the flash point of miscible mixtures," Journal of Hazardous Materials, vol. 137, pp. 38-46, 2006/09/01/ 2006.
3. Pitz, William J., and Charles J. Mueller. "Recent progress in the development of diesel surrogate fuels." *Progress in Energy and Combustion Science* 37.3 (2011): 330-350.
4. Ferris, Alison M., and David A. Rothamer. "Methodology for the experimental measurement of vapor–liquid equilibrium distillation curves using a modified ASTM D86 setup." *Fuel* 182 (2016): 467-479.

Links to all experimental property data for diesel surrogate palette

1. Density and viscosity of tetralin and trans -decalin | SpringerLink
2. Decahydronaphthalene | C10H18 - PubChem (nih.gov)
3. Mass Density of 2,2,4,4,6,8,8-Heptamethylnonane (pure) – SpringerMaterials
4. Dynamic Viscosity of 2,2,4,4,6,8,8-Heptamethylnonane (pure) – SpringerMaterials
5. 2,2,4,4,6,8,8-Heptamethylnonane, 98%, ACROS Organics | Fisher Scientific
6. 1-Methylnaphthalene | C11H10 - PubChem (nih.gov)
7. Density and Viscosity of the 1-Methylnaphthalene+2,2,4,4,6,8,8-Heptamethylnonane System from 293.15 to 353.15 K at Pressures up to 100 MPa | SpringerLink
8. Hexadecane | C16H34 - PubChem (nih.gov)
9. accepted manusript C16 viscosity JPCRD 2018.pdf (imperial.ac.uk)
10. n-Hexadecane CAS 544-76-3 | 820633 (emdmillipore.com)
11. 1,2,4-Trimethylbenzene | C9H12 - PubChem (nih.gov)
12. Mass Density of 1,2,4-Trimethylbenzene (pure) - SpringerMaterials
13. Dynamic Viscosity of 1,2,4-Trimethylbenzene (pure) – SpringerMaterials
14. 1,2,3,4-Tetrahydronaphthalene | C10H12 - PubChem (nih.gov)
15. Mass Density of 1,2,3,4-Tetrahydronaphthalene (pure) – SpringerMaterials
16. Dynamic Viscosity of 1,2,3,4-Tetrahydronaphthalene (pure) – SpringerMaterials
17. Mass Density of Octadecane (pure) – SpringerMaterials
18. Dynamic Viscosity of Octadecane (pure) – SpringerMaterials
19. Octadecane | 593-45-3 (chemicalbook.com)
20. n-Eicosane for synthesis | 112-95-8 | Sigma-Aldrich
21. * Estimated eicosane viscosity based on agreement between model and experiment for n-hexadecane and n-octadecane