Co-Optimization of Fuels & Engines

# Naphthenic Biofuel-Diesel Blend for Optimizing Mixing Controlled Compression Ignition Combustion


Dimitris Assanis, SUNY - *Stony Brook* (PI)

Ofei Mante, *RTI International*



Award Number: DE-EE0008481

(WBS 3.5.1.18)


## DOE Bioenergy Technology Office (BETO) 2021 Project Peer Review

**March 16th, 2021**

Co-Optimization of Fuels & Engines Technology Area

better fuels | better vehicles | sooner

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

Stony Brook University

RTI INTERNATIONAL

# Project Overview

**Project Overview**

Bio-blendstock oils rich in naphthenes will be produced using the catalytic fast pyrolysis (CFP) + hydrotreating pathway and evaluated *for the first time* as a blendstock fuel for MD/HD MCCI engines currently operating on No.2 Diesel fossil fuel.


## Goals

- Demonstrate that the naphthenic bio-blendstock can be blended with diesel fuel and the mixture meets ASTMD975 specifications
- Investigate the effects of using blended fuel in diesel engine efficiency and emissions
- Show lifecycle GHG emissions reduction of 50% compared to petroleum diesel

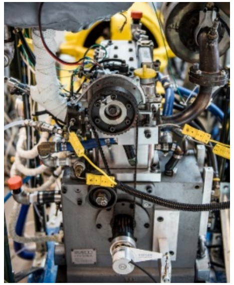
# 1 - Management

- **PI Dimitris Assanis** is responsible for technical progress including engine experimental testing, project management and reporting

- **Co-PI Ofei Mante** is responsible for guiding surrogate fuel formulation, bio-blendstock production and distillation at RTI, and managing RTI's tasks

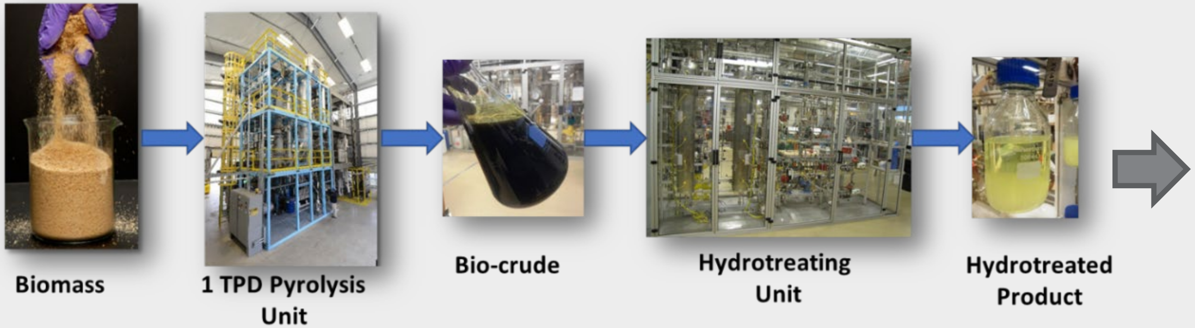
- **Gina Fioroni**, National Renewable Energy Laboratory - project team interfaces with an advisor from the national laboratory Co-Optima team

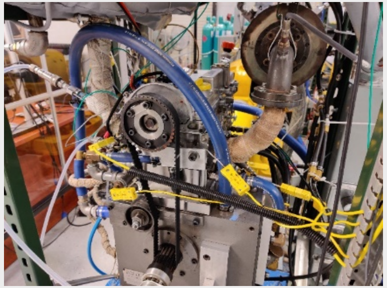
| Task | Description | Entity |
|---|---|---|
| 1 | Evaluation of Napthenic Bio-blendstock from Hydrotreated Products | RTI |
| 2 | Investigation of Surrogate Fuel Properties and Effects on Combustion | SBU |
| 3 | Production, Qualification, and Verification of the Bio-blendstocks | SBU/ RTI |
| 4 | Production of Napthenic Bio-blendstock | RTI |
| 5 | Detailed Engine Testing of Blended Fuels | SBU |
| 6 | Techno-Economic Analysis and Life Cycle Assessment | RTI |
| 7 | Technology Transfer and Outreach | SBU/ RTI |



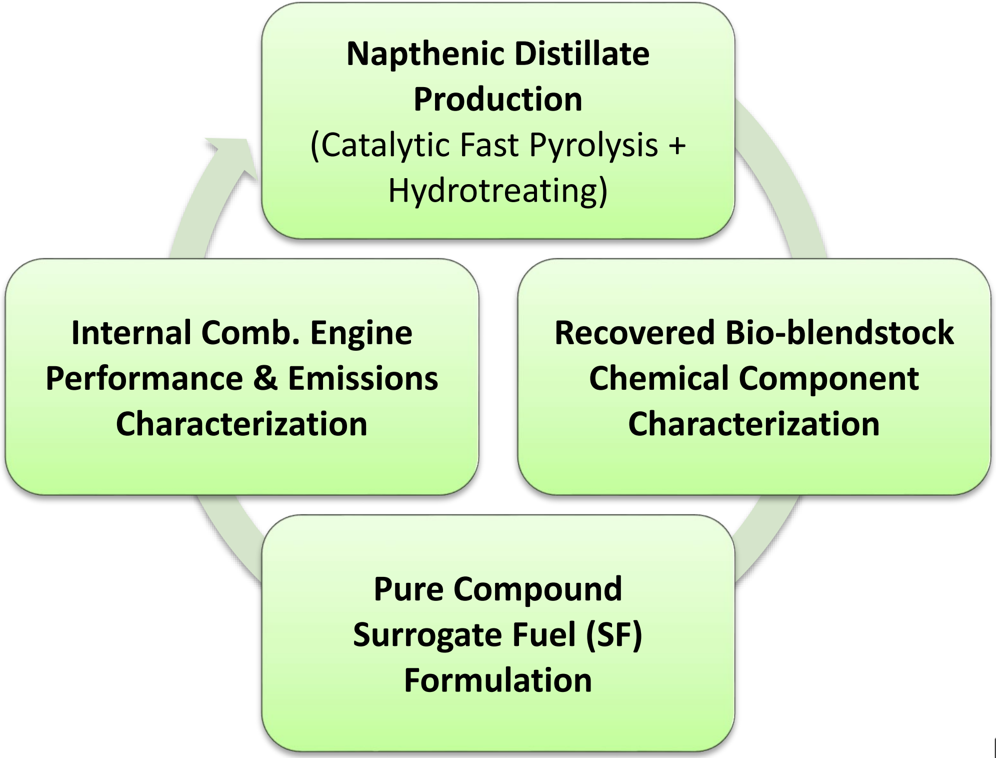
# 2 – Approach: Technical Approach

- Leverage ongoing process development of the catalytic pyrolysis technology and hydroprocessing at RTI to produce a naphthenic fuel that meets ASTM D975 to improve cold weather properties and sooting propensity of diesel fuels.
- Characterize the bio-blendstock and use surrogate fuels to understand the impact of major functional groups of compounds on diesel fuel properties engine combustion when blended up to 50% by volume.
- Perform experimental testing on a research diesel engine to evaluate the blending effects on MCCI combustion.
- Perform Techno-Economic Analysis (TEA) and Life-Cycle Assessment (LCA) of the biofuel production to demonstrate the ability of the proposed bio-blendstock to reduce GHG emissions by at least 50% compared to conventional petroleum-derived diesel.



# 2 – Approach: Project Overview




## Challenges

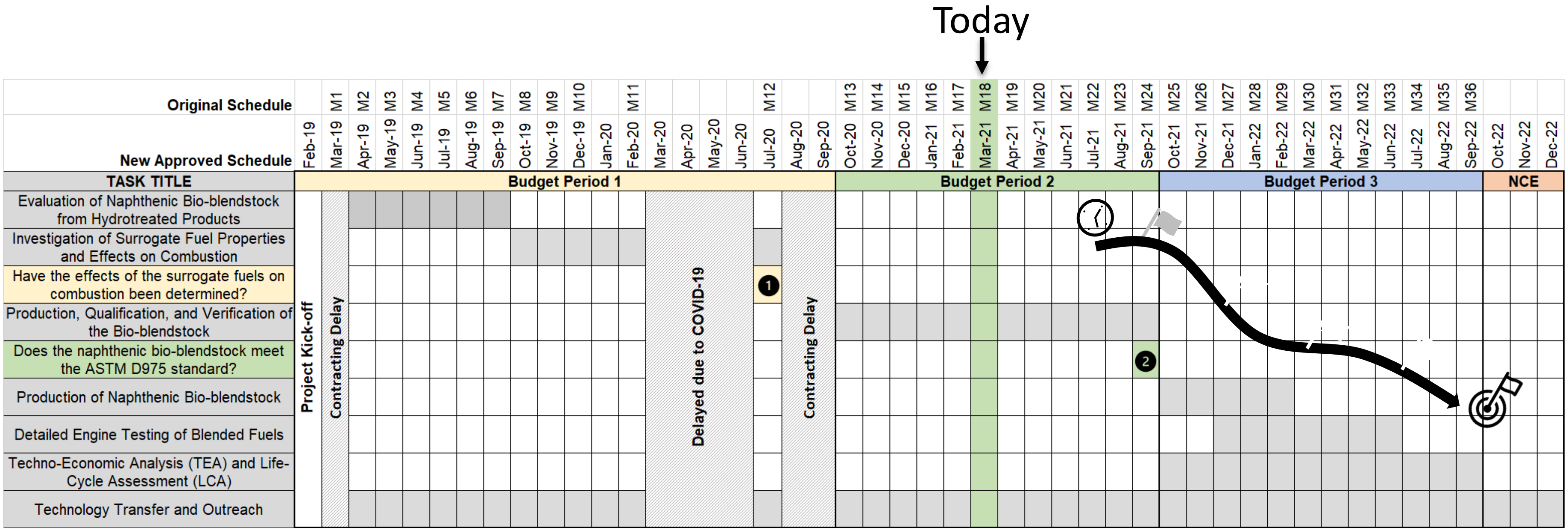
1. Lack of fundamental understanding of the influence of different chemical specifies in bio-blendstocks on diesel fuel performance, MCCI combustion and emissions
2. Ensure that the produced bio-blendstock quality meets ASTM specifications
3. Upscaling bio-blendstock production capacity (surrogate fuel approach required)
4. Demonstrating emissions reduction in MCCI combustion at similar thermal efficiency

# 3 - Impact

- Development of an advanced biofuel that can be sustainably produced domestically **(improved energy security)**
- Naphthenic rich bio-blendstocks can yield energy content parity fuel relevant to long-haul trucking **(drop-in replacement)**
- Acceleration of advanced biofuels deployment
- Reduction of fossil fuel consumption **(blends up to 50%)**
- Decrease in transportation GHG emissions **(up to 50%)**
- Cleaner air quality from decreased sooting propensity of fuel

***The successful demonstration of this research project will develop a biofuel-based pathway to reduce the use of fossil-derived diesel fuel in transportation today and promote co-optimized high efficiency engines that achieves cleaner vehicles sooner.***

# 4 – Progress and Outcomes

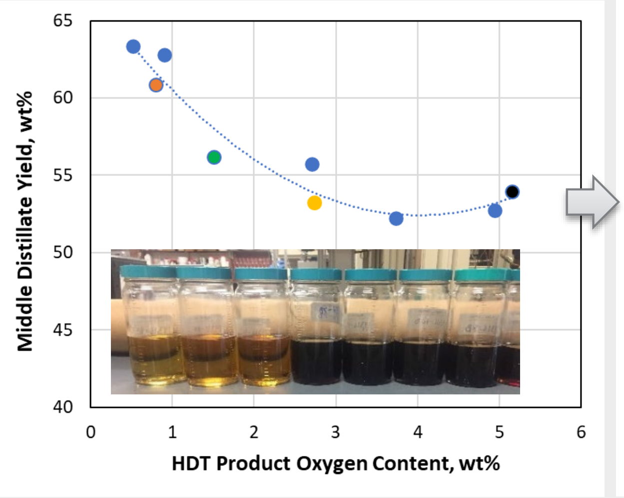


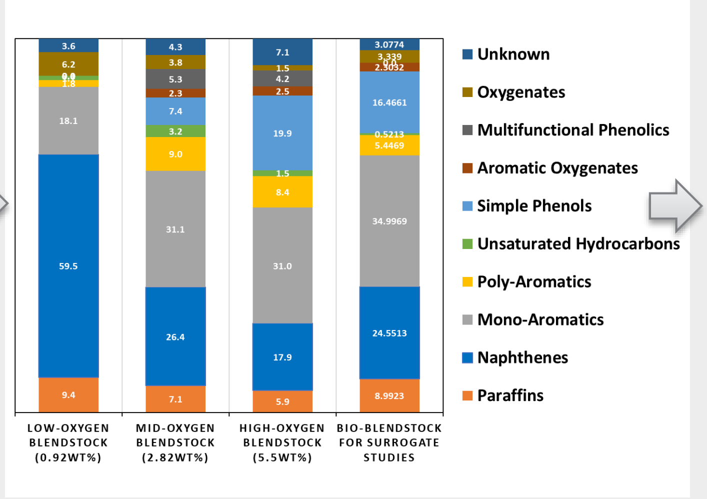

| Go / No-Go Decision Description | Date |
|---|---|
| Validate the potential of the naphthenic bio-blendstock to improve the cold weather behavior (pourpoint, cloudpoint) and decrease the sooting propensity of No.2 diesel based on fuel characterizations and physical property measurements. | 7/09/2020 |
| Verification that the naphthenic bio-blendstock meets ASTM D975 specification and improves the cold weather behavior (pourpoint, cloudpoint) and decreases the sooting propensity of No.2 diesel. | Anticipated July 2021 |

# 4 – Progress:
# Naphthenic Bio-blendstock from Hydrotreated Products

**Objective:** Production and characterization of bio-blendstock oils of varying oxygen content to understand the compositional species make-up.

1. **Accomplishments:** Bio-blendstocks were recovered from 9 hydrotreated oils with oxygen contents varying between 0.5 wt% and 6 wt% from a bench-scale PILODIST laboratory distillation unit.
2. GC-MS compositional analysis of bio-blendstocks was performed.
3. Selected pure compounds to represent the different classes of chemical components.




| Naphthenic hydrocarbons | Paraffins | Mono-Aromatics |
|---|---|---|
| Propyl Cyclohexane | Octadecane | Indane |
| Ethyl Cyclohexane | Decane | Propyl Benzene |
| Butyl Cyclohexane | Nonane | Tetralin, |
| Pentyl Cyclohexane | Dodecane | 1-methyl-4-(1-methylethyl) Benzene |
| Hexyl Cyclohexane | Hexadecane | 2-cyclohexylethyl Benzene |
| Decalin | | 1-(3-Methylbutyl)-2,3,5-trimethyl Benzene |
| 1,1'-(1,2-ethanediyl) bis Cyclohexane | | |
| cis-octahydro-1h-indene | | |
| **Di-Aromatics** | **Poly-Aromatics** | **Simple Phenols** |
| 1,7-dimethyl Naphthalene | 1-methyl-7-(1-methylethyl) Phenanthrene | 4-methyl Phenol |
| 1-methyl-7-(1-methylethyl) Naphthalene | | 2-propyl Phenol |
| | | 2-(1-methylpropyl) Phenol |
| | | 3,5-dimethyl Phenol |
| **Multifunctional Phenolics** | **Oxygenated Aromatics** | **Other oxygenates** |
| 2-methoxy-4-propyl Phenol | 3,5-di-tert-butyl-4-hydroxyanisole | 2-Oxabicyclo [4.4.0] Decane |
| 2-methoxy-4-metyl Phenol | 2,3-dihydro-2-methyl Benzofuran | |
| | 4-methoxy-1-ethyl Benzene | |
| | 2-ethyl Benzaldehyde, | |
| | 4-Chromanol | |

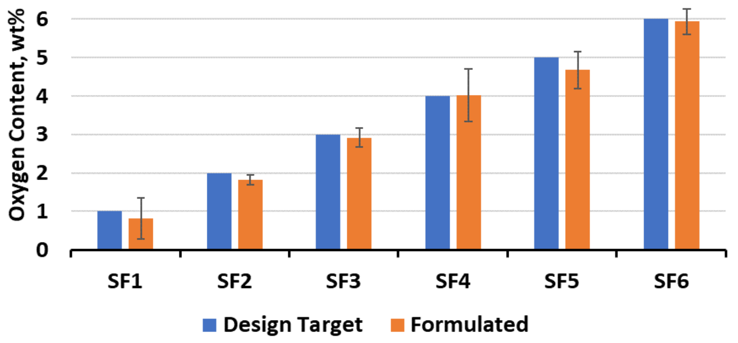
# 4 – Progress: Surrogate Fuel Studies

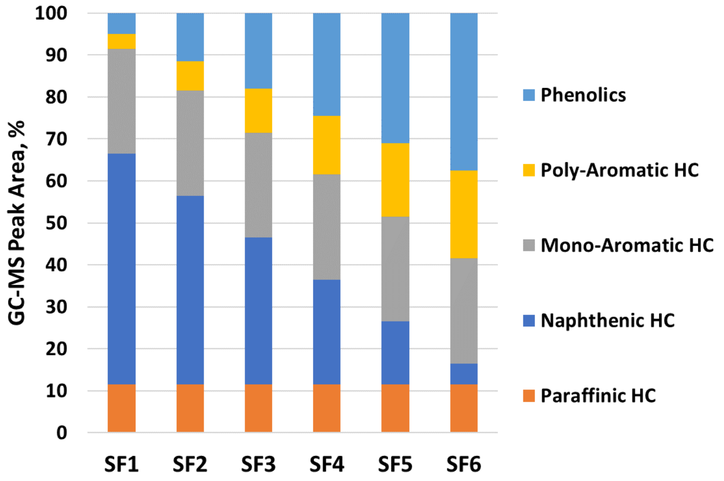
**Objective:** Design Surrogate fuels using pure components to match the various compound class distribution found in the bio-blendstock. The design property target used for the formulation were oxygen content and the C/H ratio.

**Accomplishments:** Six surrogate fuels (SF) were formulated with oxygen contents varying from 1 to 6 wt%.

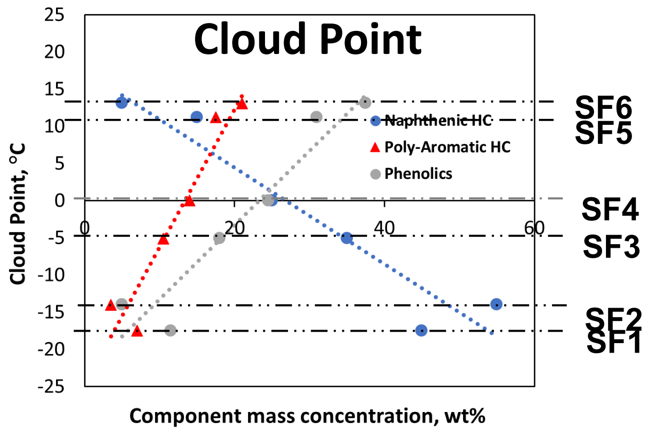
| Chemical Compound | Wt.% | | | | | |
|---|---|---|---|---|---|---|
| | SF1 | SF2 | SF3 | SF4 | SF5 | SF6 |
| 4-Methylphenol | 5.0 | 11.5 | 18.0 | 24.5 | 31.0 | 37.5 |
| Phenanthrene | 3.5 | 7.0 | 10.5 | 14.0 | 17.5 | 21.0 |
| Tetralin | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 |
| Decalin | 55.0 | 45.0 | 35.0 | 25.0 | 15.0 | 5.0 |
| Octadecane | 7.0 | 6.0 | 5.0 | 4.0 | 3.0 | 2.0 |
| Decane | 4.5 | 5.5 | 6.5 | 7.5 | 8.5 | 9.5 |

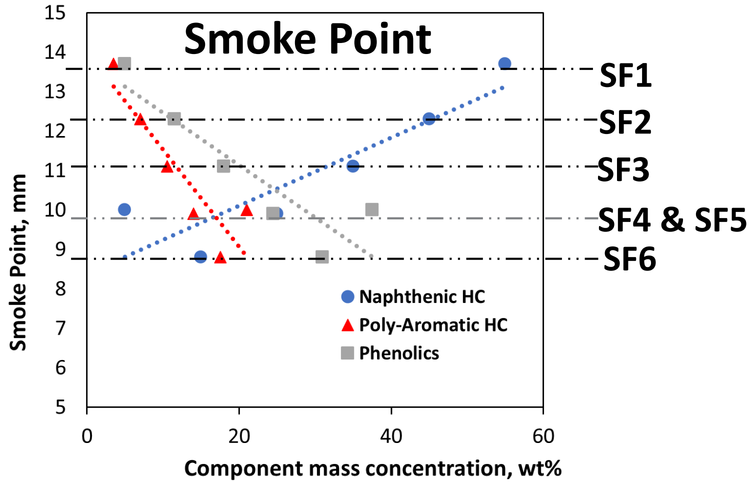
Oxygen contents (1, 2, 3, 4, 5, and 6 wt%) of the six surrogate fuels formulated.



# 4 – Progress: SF Fuel Chemistry Relations on Cloud Point (CP) and Smoke Point (SP)




**Objective:** To understand chemical component effect on fuel properties

**Naphthenic HC:**

- Cloud Point ↓ (Cold-weather properties ↑)
- Smoke Point ↑ (Sooting propensity ↓)

**Phenolics:**

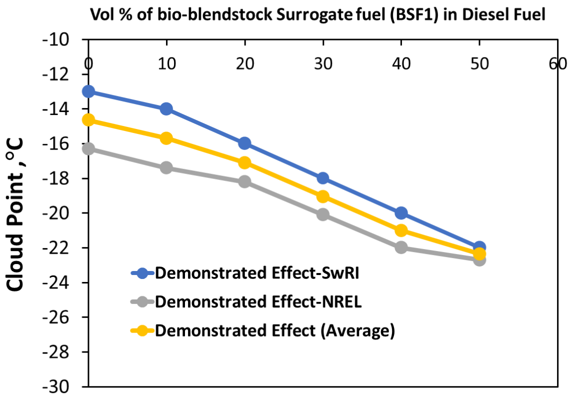
- Cloud Point ↑ (Cold-weather properties ↓)
- Smoke Point ↓ (Sooting propensity ↑)

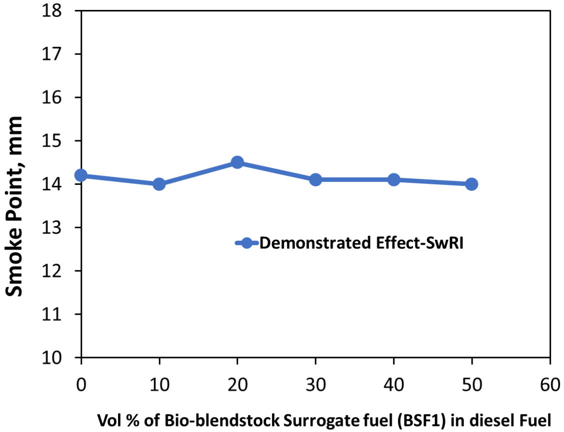
**Poly-Aromatic HC:**

- Cloud Point ↑ (Cold-weather properties ↓)
- Smoke Point ↓ (Sooting propensity ↑)

**Comments:** The concentration of paraffinic HC and mono-aromatics were kept constant across the surrogate fuels as observed with bio-blendstocks with different oxygen contents.

# 4 – Progress: SF1 / No.2 Diesel Blend Effects on Cloud Point (CP) and Smoke Point (SP)




**Objective:** To understand blend ratio effects on fuel properties

**Cloud Point:**
The prepared bio-blendstock surrogate fuel demonstrated the proposed effect by reducing the cloud point of the No.2 research diesel fuel by up to 8 °C when blended up to 50% by volume

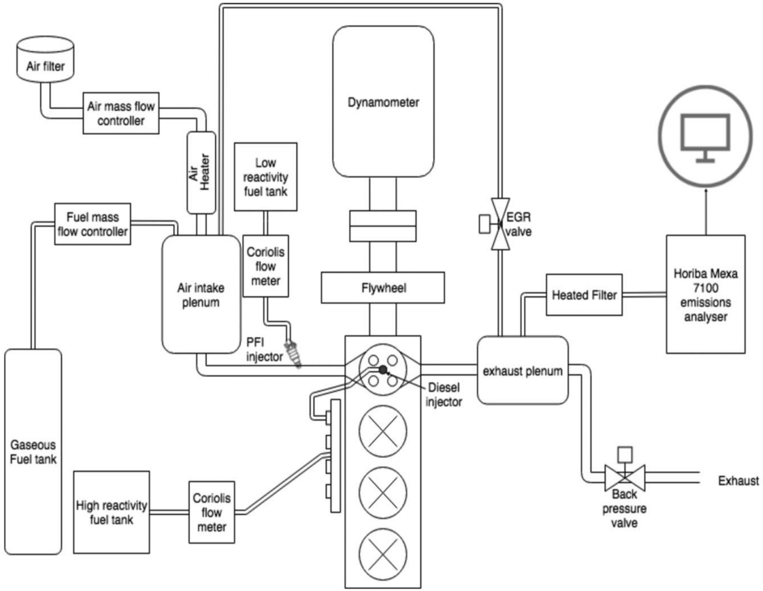
**Smoke Point:**
The prepared bio-blendstock surrogate fuel did not increase the spoke point of No.2 diesel by up to 7 mm points when blended up to 50% by volume.

*Mitigation:* Lower sooting propensity pure compounds selected for BP2. Aromatic HC content ↓ & ↑ Napthenic content decalin→butylcyclohexane & propylcyclohexane).

# Preliminary Engine Testing Methodology

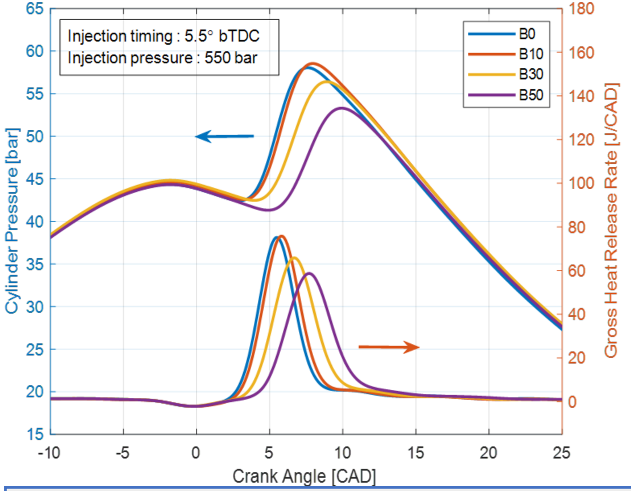
**Approach:**

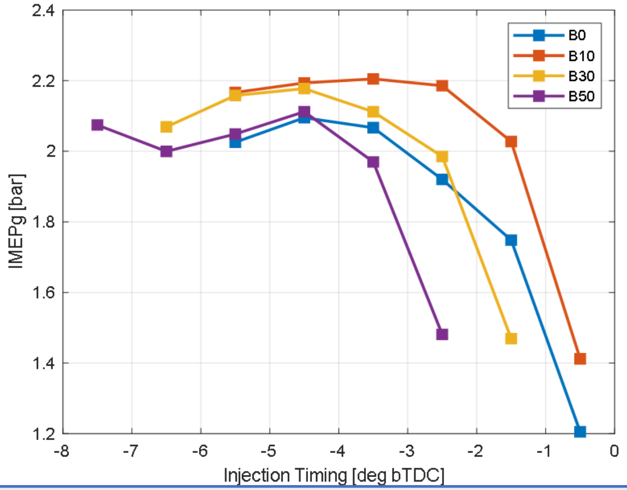
- Preliminary experimental studies were conducted on the Ricardo Hydra diesel engine
- Intake pressure and temperature were kept at ambient with fixed engine speed of 1200 RPM
- Injection pressure fixed at 550 bar
- Injection timing sweep performed until combustion was either knock-limited or misfire occurred

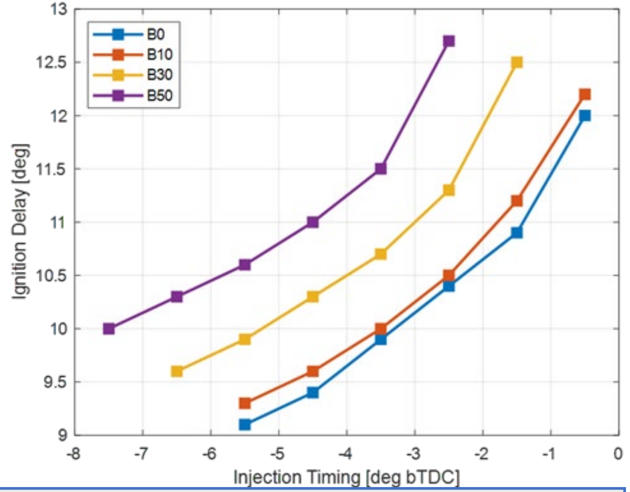



Hydra Diesel Engine Schematic

# 4 – Progress: Effects of Fuel Inj. Timing on Cyl P., HRR, Load & Ign. Delay



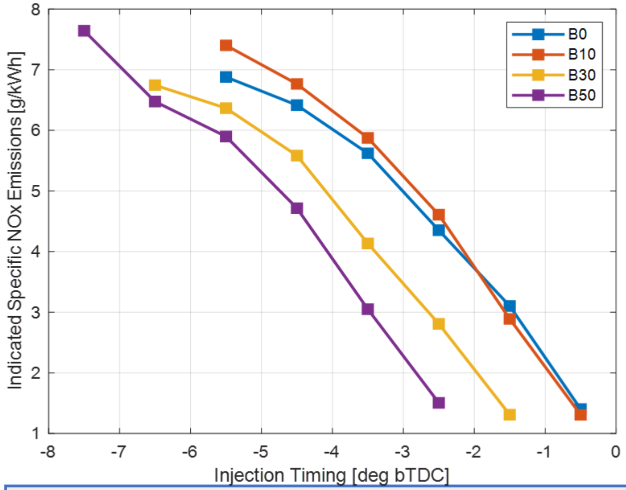



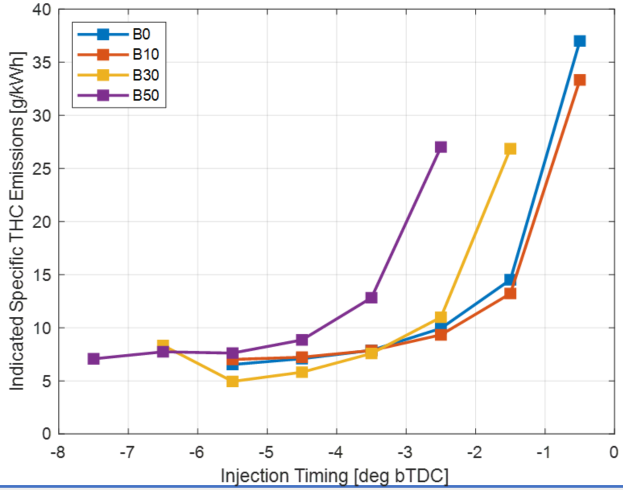



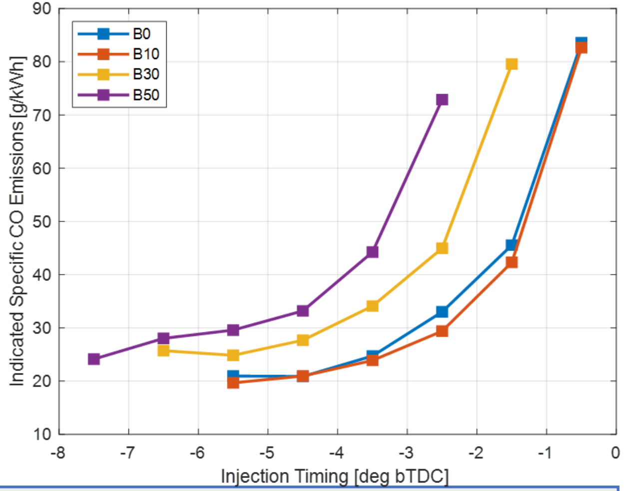

**Results:**

- Combustion B10 (10% blend) yields highest overall pressure trace and heat release profile.
- Combustion B50 yields the lowest pressure trace and smallest heat release profile.
- B10 and B30 resulted in overall higher load than B0.
- Ignition delay decreases with advancing fuel injection timing and increases with blend ratio. Mixing vs. kinetic effect? The longer ignition delay of surrogate fuel blends could be a result from the higher viscosity (mixing effect).

# 4- Progress: Effects of Fuel Inj. Timing on NOx, THC, & CO Emissions




**Results:**

- NOx emissions increased as the fuel injection timing is advanced from TDC due to higher peak temperatures in the combustion chamber.
- THC emissions decreases as the fuel injection timing is advanced from TDC.
- CO emissions decrease as fuel injection timing advances (and inversely proportional to combustion efficiency)
- B0 & B10 resulted in overall similar emissions levels.

# Summary / Lessons Learned

1. **Three naphthenic blendstocks** boiling within mid-distillate (diesel) fuel range (160-360°C) from hydrotreated products containing oxygen contents <1%, 3%, and 6% were recovered for characterization.
2. The results show that the low-oxygen bio-blendstock has the potential of **meeting ASTM D975 specification** for diesel.
3. Surrogate studies show that **aromatic hydrocarbons** and **phenolics** have **negative impact** on **sooting** propensity and **cold weather** properties of diesel fuel.
4. The prepared bio-blendstock surrogate fuels demonstrated a **reduction in cloud point by up to 8 °C** when blended up to 50% by volume in No.2 research diesel .
5. Blending of the prepared bio-blendstock surrogate fuel with No.2 research diesel up to 50% by volume did not enhance the sooting propensity. However, the surrogate studies show that reducing the concentration of aromatics to less than 10 wt% has the potential of improving the sooting propensity.
6. Bio-blendstock with **high concentration** (at least 70wt%) of **naphthenic hydrocarbons** can be used to **improve both sooting propensity and cold weather properties** of diesel fuel.
7. There is also opportunity to take advantage of certain oxygenated aromatics such as methoxyphenols and simple phenols to improve sooting propensity as predicted by NREL YSI estimator model.
8. **Preliminary engine testing was successfully performed** to characterize the combustion performance and emissions generated using bio-blendstock surrogate / No.2 research diesel fuel blends (up to 50% by vol).

# Quad Chart

## Timeline

- Project Start: 02/01/2019
- Project End: 12/31/2022

| | Budget Period 1 | Budget Period 2 | Budget Period 3 | Total Funding |
|---|---|---|---|---|
| **DOE Funding** | $397,658 | $445,930 | $643,524 | $1,487,112 |
| **Project Cost Share** | $193,317 | $140,880 | $141,343 | $475,540 |

## Project Partner:

- RTI International

## Project Goal

- To investigate and demonstrate the use of a naphthenic bio-blendstock as a fuel for MD/HD MCCI engines.

## End of Project Milestone

- Demonstrate that the naphthenic bio-blendstock can be blended with diesel fuel and the mixture meets ASTMD975 specifications
- Show lifecycle GHG emissions reduction of 50% compared to petroleum diesel

## Funding Mechanism

- Fiscal Year 2018 Funding Opportunity Announcement (FOA) Number DE-FOA-0001919
- Area of Interest 5-b: Co-Optimization of Engines & Fuels – Bio-blendstocks to Optimize Mixing Controlled Compression Ignition Engines

# Additional Slides

# Publications, Patents, Presentations, Awards and Commercialization

## Presentations

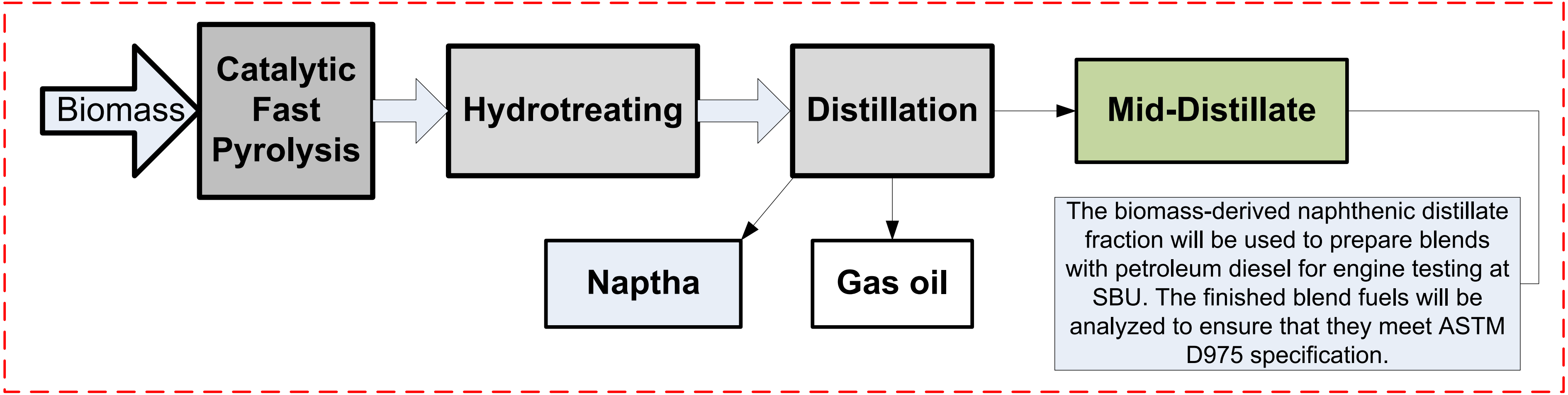
- Co-Optima All Hands Annual Meeting, Virtual, July 28th, 2020

## Publications

- 1 journal manuscript submitted/in-review from BP1 activities
    - 1 additional manuscript with expected submission by May 2021

- >2 journal manuscripts expected for BP2 & BP3 activities

# Bio-blendstock Production Pathway




- Biocrude is produced by catalytic fast pyrolysis at 475-525 °C using a non-zeolite alumina in RTI's 1TPD unit.
- The biocrude is hydrotreated over a sulfided catalyst at 2000 psig and at 300 °C in RTI's hydroprocessing unit into a biofuel product.
- The biofuel is distilled to recover naphtha (< 160 °C); mid-distillate range (160-360°C), and gas oil (>160 °C) fractions.
- The mid-distillate fraction is referred as the naphthenic bio-blendstock in the project.

# BP1 Milestones Completed

| Recipient Name: SUNY - Stony Brook University | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project Title: Naphthenic Biofuel-Diesel Blend for Optimizing Mixing Controlled Compression Ignition Combustion** | | | | | | | |
| **Task Number** | **Task Title or Subtask Title (If Applicable)** | **Milestone (Go/No-Go Decision Point)** | | **Milestone Description (Go/No-Go Decision Criteria)** | **Milestone Verification Process (What, How, Who, Where)** | **Anticipated Date from Project Start** | |
| | | **Type** | **Number** | | | **Months** | **Quarters** |
| 1.0 | Evaluation of Naphthenic Bio-blendstock from Hydrotreated Products | | | | | | |
| 1.1 | Distillation of Hydrotreated Products | Milestone | 1.1 | Complete preparation of three naphthenic bio-blendstocks | Report from RTI documenting the preparation of three naphthenic bio-blendstocks from hydrotreated products of <1%, 3%, and 6% oxygen contents | 3 | 1 |
| 1.2 | Characterization of naphthenic bio-blendstocks | Milestone | 1.2 | Complete chemical and physical analysis of naphthenic bio-blendstocks | Analysis report from RTI showing the chemical composition and physical properties of the three naphthenic bio-blendstocks. | 6 | 2 |
| 2.0 | Investigation of Surrogate Fuel Properties and Effects on Combustion | | | | | | |
| 2.1 | Preparation of naphthenic surrogate fuels | Milestone | 2.1 | Prepare surrogate fuels with key molecules prepared for experimental testing | SBU will prepare surrogate fuels for characterization and engine testing | 9 | 3 |
| 2.2 | Fuel property characterization of naphthenic surrogate fuels | Milestone | 2.2 | Establish molecular structure-fuel property relationships | Report from SBU showing molecular structure-fuel property relationships. Documentation of surrogate fuels that meets ASTM specification and when blended up to 50% by volume into No.2 diesel can potentially lower the cloud/point by at least 8 °C and improve soot propensity by increasing the spoke point by at least 7 mm points. | 12 | 4 |
| 2.3 | Preliminary engine testing of surrogate fuels | Milestone | 2.3 | Complete preliminary engine testing of surrogate fuels. | Report from SBU showing quantified effects of fuel composition on heat release profile and emissions formation. | 12 | 4 |

# BP2 Milestones & Go/No-Go Decision 2

| **Recipient Name: SUNY - Stony Brook University** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project Title: Naphthenic Biofuel-Diesel Blend for Optimizing Mixing Controlled Compression Ignition Combustion** | | | | | | | |
| **Task Number** | **Task Title or Subtask Title (If Applicable)** | **Milestone (Go/No-Go Decision Point)** | | **Milestone Description (Go/No-Go Decision Criteria)** | **Milestone Verification Process (What, How, Who, Where)** | **Anticipated Date from Project Start** | |
| | | **Type** | **Number** | | | **Months** | **Quarters** |
| 3.0 | Production, Qualification, and Verification of the Bio-blendstocks | | | | | | |
| 3.1 | Production of naphthenic bio-blendstock | Milestone | 3.1 | Complete production of at least 1 gallon of naphthenic bio-blendstock | Minimum of 1 gallon of naphthenic bio-blendstock produced by RTI | 15 | 5 |
| 3.2 | Detailed Engine Testing of Surrogate Fuels | Milestone | 3.2 | Complete experimental testing of the three best surrogate fuels. | Determination of the effects of surrogates on MCCI combustion quantified by analyzing engine experimental data. | 18 | 6 |
| 3.3 | Full fuel characterization and analysis | Milestone | 3.3 | Complete fuel compositional analysis for the naphthenic | Report from a selected commercial lab showing that completion of fuel characterization and that the naphthenic fuel meets the ASTM D975 specification | 21 | 7 |
| 3.4 | Independent verification of fuel properties and performance | Milestone | 3.4 | Submission of a minimum of 500 mL of naphthenic bio-blendstock to the national laboratory Co-Optima team. | Report from the national laboratory Co-Optima team showing receipt and verification of the naphthenic bio-blendstock | 24 | 8 |
| [redacted] | | Go/No Go Decision Point | GNG2 | Verification that the naphthenic bio-blendstock meets ASTM D975 specification and improves the cold weather behavior (pour point, cloud point) and decrease the sooting propensity of No.2 diesel.<br>• Fuel properties of the naphthenic bio-blendstock verified by the national laboratory Co-Optima to meet ASTM D975 standards.<br>• Blending of 50% of the naphthenic bio-blendstock by volume lowers the cloud point/pour point of No.2 diesel by at least 8 °C and improves soot propensity by increasing the spoke point of No.2 diesel by at least 7 mm points.<br>• Completion of detailed engine experimental testing. | | 24 | 8 |

# BP3 Milestones

| Recipient Name: SUNY - Stony Brook University | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Project Title: Naphthenic Biofuel-Diesel Blend for Optimizing Mixing Controlled Compression Ignition Combustion** | | | | | | | |
| **Task Number** | **Task Title or Subtask Title (If Applicable)** | **Milestone (Go/No-Go Decision Point)** | | **Milestone Description (Go/No-Go Decision Criteria)** | **Milestone Verification Process (What, How, Who, Where)** | **Anticipated Date from Project Start** | |
| | | **Type** | **Number** | | | **Months** | **Quarters** |
| 4.0 | Production of Naphthenic Bio-blendstock | Milestone | 4.1 | Complete production of naphthenic bio-blendstock | Minimum of 10 gallons of naphthenic bio-blendstock produced by RTI | 27 | 9 |
| 5.0 | Detailed Engine Testing of blended Fuels | Milestone | 5.1 | Complete detailed engine experimental testing of blended fuels | Report from SBU documenting experimental data showing effects on engine efficiency and emissions | 30 | 10 |
| 5.0 | Detailed Engine Testing of blended Fuels | Milestone | 5.2 | Demonstrate effects of using the naphthenic fuel on MCCI combustion. | Report from SBU showing changes in engine efficiency and emissions formation due to the naphthenic fuel. | 33 | 11 |
| 6.0 | Techno-Economic Analysis and Life Cycle Assessment | | | | | | |
| 6.1 | TEA | Milestone | 6.1 | Complete TEA | Report from RTI on the TEA of the production of the bio-blendstock will be provided to SBU | 36 | 12 |
| 6.2 | LCA | Milestone | 6.2 | Complete LCA | Report from RTI on the LCA production of the bio-blendstock and engine end-use will be provided to SBU | 36 | 12 |