



DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Multitude Characterization and Prediction of DOE Advanced Biofuels Properties

03/07/2019

Advanced Development and Optimization

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The Center for Advanced Turbomachinery
& Energy Research

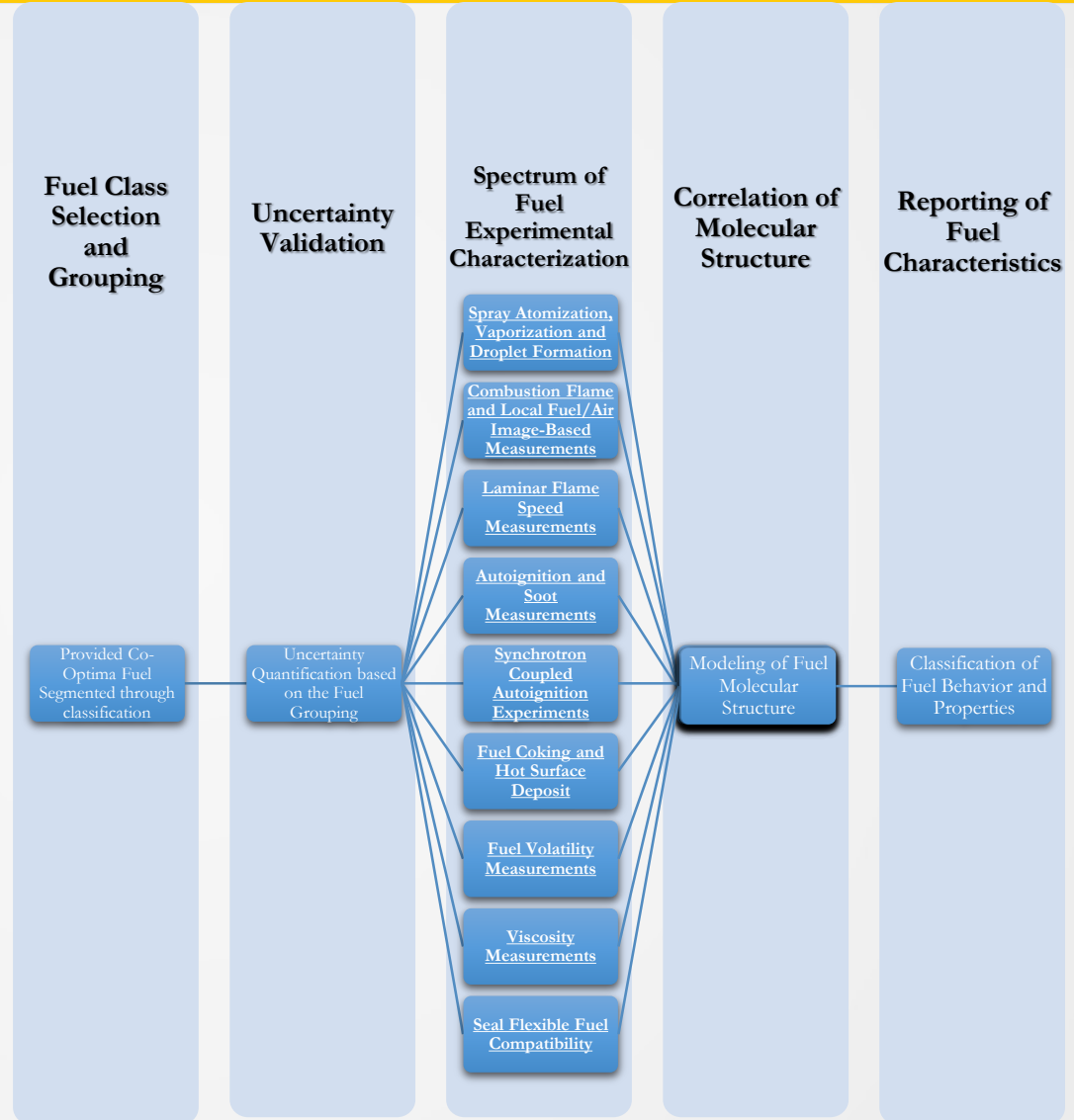


Co-Optimization of Fuels & Engines

Goal Statement

The goal of this project is to provide a detailed data set of multiple combustion experiments relevant to engine combustion of Co-Optima fuels. The data and information for the fuel behavior will mitigate the potential for combustion operability issues due to the particular fuel being used.

The research project accelerates the introduction of affordable, scalable, and sustainable high performance bio-based fuels for use in high-efficiency, low emission engines thereby achieving the Co-Optima and BETO outcomes.





Quad Chart Overview

Timeline

- Project start date: 1/15/2017 (work began: 9/1/2017)
- Project end date: 08/31/2020
- 50% complete

	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	\$0	\$468k	\$426k
Project Cost Share*	\$38k	\$12k	\$50k

•Partners:

- Robert L. McCormick, Fuels Performance Group, National Renewable Energy Laboratory (NREL)
- William J. Pitz, Lawrence Livermore National Laboratory

Barriers addressed

- ADO-E. Co-Development of Fuels and Engines

Objective

The goal of this project is to provide a detailed data set of multiple combustion experiments relevant to engine combustion of Co-Optima fuels.

End of Project Goal

Validated fuel characteristics and properties and quantified uncertainty levels that can be applied to select and optimize fuels. In addition to physical designs and test data, we expect to have easy-to-apply performance correlations that will aid designers in the application and operation of the Co-Optima fuels.



1 - Project Overview

Focused on characterization of Co-Optima fuels: (incoordination with National Labs)

I. Fuel selection and grouping

- *Two groups - each with five promising fuels.*

II. Execution of a spectrum of fuel characterization experiments with validated uncertainty (fluid-to-combustion)

Spray Atomization, Vaporization and Droplet Formation (cone angle, droplet)	Combustion Flame and Local Fuel/Air Image-Based Measurements (Optical fuel/air measurement in optical constant volume combustion chamber)	Laminar Flame Speed Measurements (S_L)
Soot Volume Fraction and Induction Time Measurements (Soot induction times and soot volume fraction)	Synchrotron Coupled Fundamental auto-ignition Experiments (auto-ignition chemistry)	Fuel Coking and Hot Surface Deposit Exposure (coking volume fraction and thermal stability)
Fuel Volatility Measurements (volatility fraction)	Viscosity Measurements (quartz crystal microbalance viscosity)	Seal Flexible Fuel Compatibility (degradation of these polymers)

III. Correlation of molecular structure



2 – Approach (Management)

- ❑ This project is actively coordinated and collaborated with the DOE National Laboratories and Co-Optima Consortium including:
 - Data sharing
 - Participation and attendance in regular project and annual meetings (Co-Optima and AEC meetings)
 - Communicating regularly with National Laboratory expert researcher (Dr. Robert L. McCormick)

❑ Go/No-Go Decision Points:

In order to mitigate risk associated with the project, several go/no-go decision points corresponding to SMART project milestones and their respective success criteria have been defined:

Go/No Go	Milestone	Description	Success criteria
GNG1	M1	Group Fuel	Successfully obtain fuel grouping
GNG2	M2	Fuel characteristics	Successfully obtain Fuel characteristics
GNG3	M3	Correlation of molecular structure	structure

❑ Project Plan:

Task 1. Grouping the Co-Optima fuels based on fuel class

Task 2. Execution of experiments (*fluid-to-combustion*)

- Task 2.1 Spray Atomization, Vaporization and Droplet Formation
- Task 2.2 Combustion Flame and Local Fuel/Air Image-Based Measurements
- Task 2.3 Laminar Flame Speed Measurements
- Task 2.4 Autoignition and Soot Measurements
- Task 2.5 Synchrotron Coupled Fundamental Autoignition Experiments
- Task 2.6 Fuel Coking and Hot Surface Deposit
- Task 2.7 Fuel Volatility Measurements
- Task 2.8 Viscosity Measurements
- Task 2.9 Seal Flexible Fuel Compatibility

Task 3. Correlation of molecular structure

Task 4. Manage and Report

❑ Team:

- Kareem Ahmed, Ph.D., Principal Investigator, University of Central Florida
Role: Overall project lead and data analysis from spray and combustion testing.
- Subith Vasu, Ph.D., Co-Principal Investigator, University of Central Florida
Role: Autoignition, flame speed characterization, and fuel structure modeling
- Jayanta Kapat, Sc.D., Co-Principal Investigator, University of Central Florida
Role: Fuel viscosity and seal compatibility.
- Richard Blair, Ph.D., Co-Principal Investigator, University of Central Florida
Role: Fuel volatility and soot/coking.



2 – Approach (Management)

❑ **Project Risks:**

- Securing beam time at the Advanced Light Source - Lawrence Berkeley National Laboratory
- Compatibility of the fuels with the experiments explored (e.g. neat vs. blended)
- Limits with measurement techniques for explored fuels

❑ **Critical Success Factors**

- Fuel group based on fuel class and coordination with National Laboratory expert researcher (Dr. Robert L. McCormick)
- Investigators previous experience in exploring bio-fuels under previous Air Force program
- Uncertainty quantification for each experiment and measurement technique to define the limit of the testing
- Communicating with Program Officer Dr. Alicia Lindauer (Co-Optima Lead for BETO) facilitated securing beam time.

❑ **Key Challenges:**

- Scheduling experimental tests at the Advanced Light Source - Lawrence Berkeley National Laboratory
- Measuring carbon surface deposit thickness established through Raman
- Viscosity measurements with QCM required fine control of temperature



2 – Approach (Technical)

The project is focused on providing experimental fuel characterization and property prediction for Co-Optima biofuels and blends. A series of targeted experiments will characterize and predict Co-Optima fuel spray atomization, flame topology, flame speed, soot induction time, volatility, viscosity, soot/coking, and compatibility. Fuels will be selected and prioritized based on input from national lab members.

The technical approach includes :

1. Fuel test matrix development based on known fuel properties and with the objective of optimizing the experimental plan to reduce experimental uncertainty
2. Execution of a spectrum of fuel characterization experiments from fluid-to-combustion
3. Correlation of molecular structure with fuel properties derived from the experimental data.



Technical Accomplishments/ Progress/Results



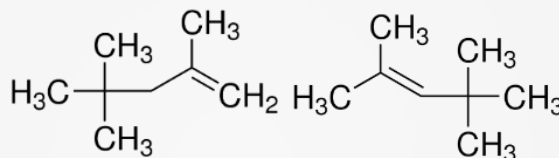
Task 1. Fuel Matrix Development

Select fuels for each of the detailed characterization experiments (task 2) in consultation with the National Labs

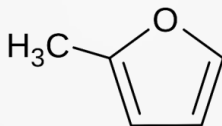
Fuel Matrix 1- ICE Fuels

1. Ethanol (alcohol)

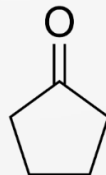
2. Diisobutylene (alkene)



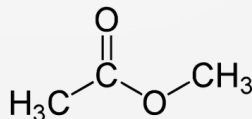
3. Methyl furan (furan)



4. Cyclopentanone (ketone)

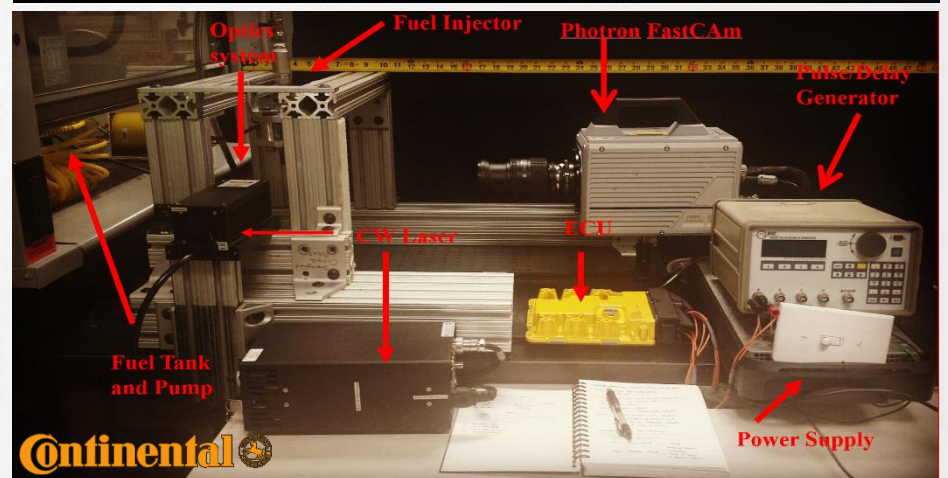
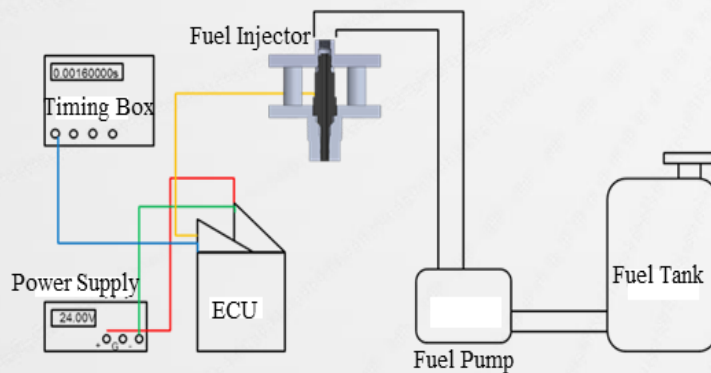
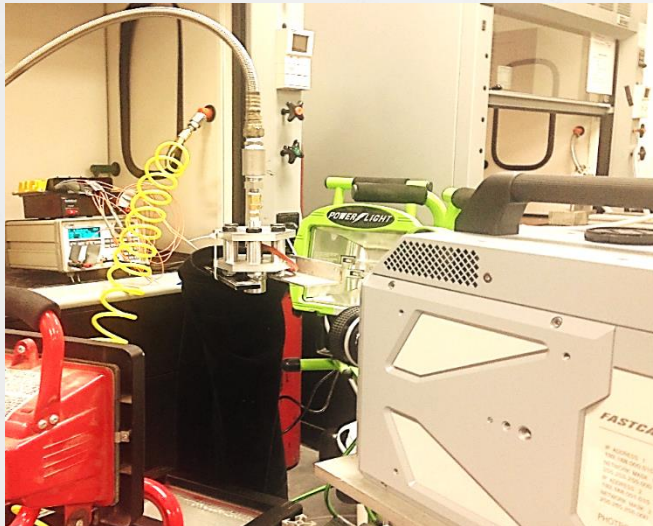


5. Methyl acetate (ester)



Spray Atomization, Vaporization and Droplet Formation (cone angle, diameter)

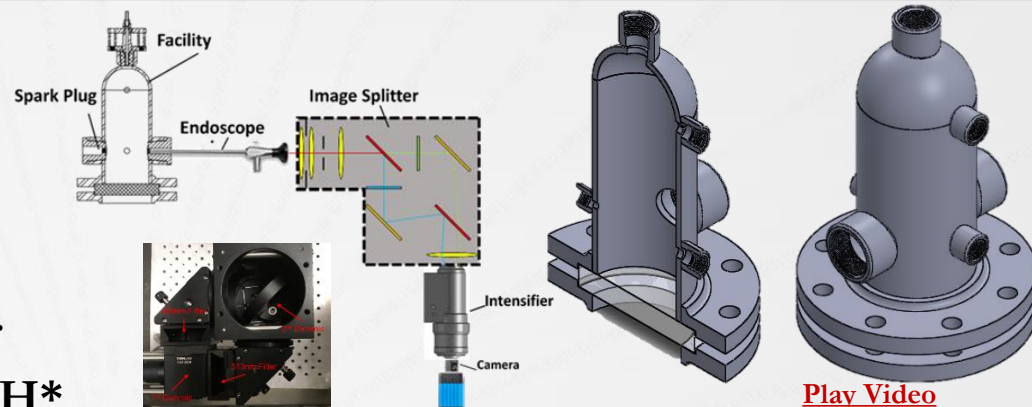
Characterize spray injection, atomization, and mixing. Detailed imaging of dense biofuel core spray jet dynamics in an extreme, high optical density biofuel spray. Furthermore, droplet size from the spray will be simultaneously measured.



Capability:

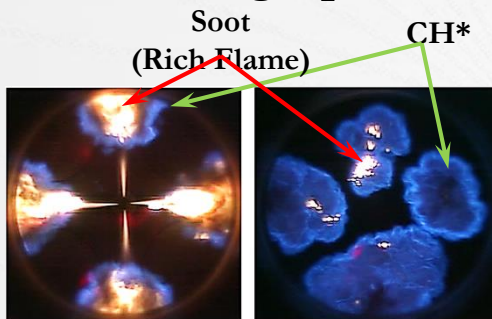
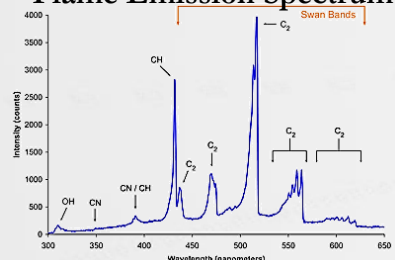
- Charge Pressure: 1 - 20 bar
- Combustion Pressure: 1 - 130 bar
- Gaseous and Liquid Fuels
- Pre-heating Temp: 30 - 130°C
- Fuel Injection Pressure: Up to 103 bar

Fuel-air measurements of using C_2^*/CH^*

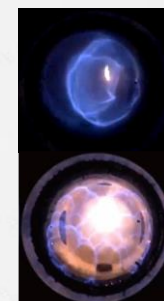


[Play Video](#)

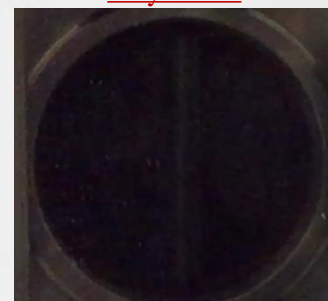
Flame Emission Spectrum



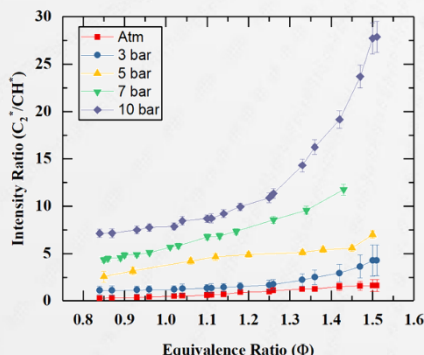
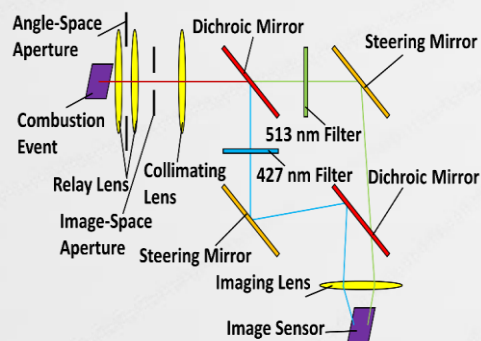
Reacting Mixture



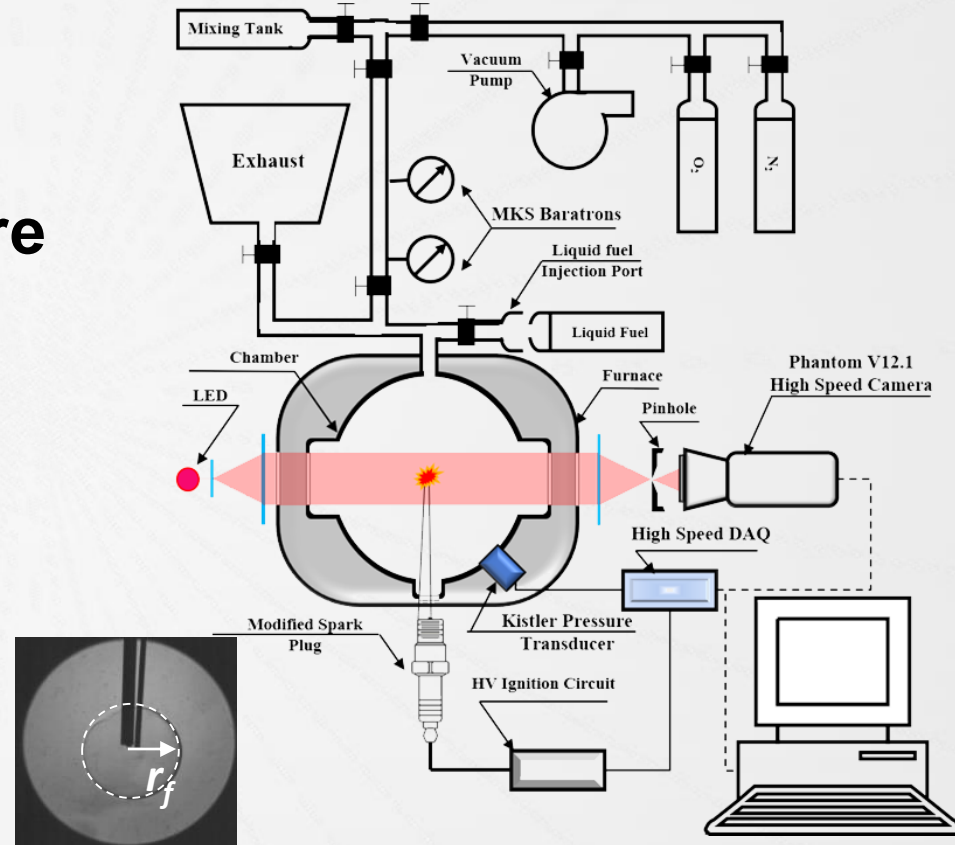
CH* Production



C₂* Production



- ❖ Initial T & P 428K & 1 atm
- ❖ $0.7 \leq \phi \leq 1.5$ for all fuels
- ❖ Schlieren Imaging to capture flame
- ❖ Staged fill control
 - ❖ Oxidizer/diluent pumped into mixing tank (synthetic air)
 - ❖ Liquid fuels injected at port



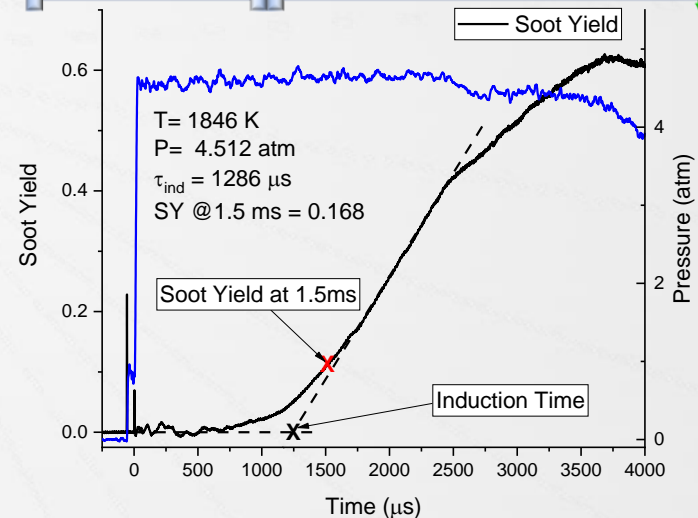
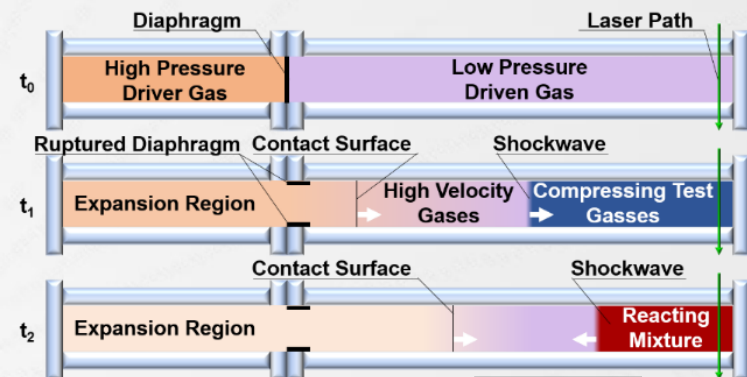
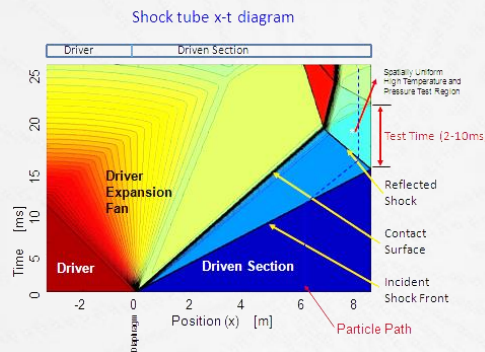
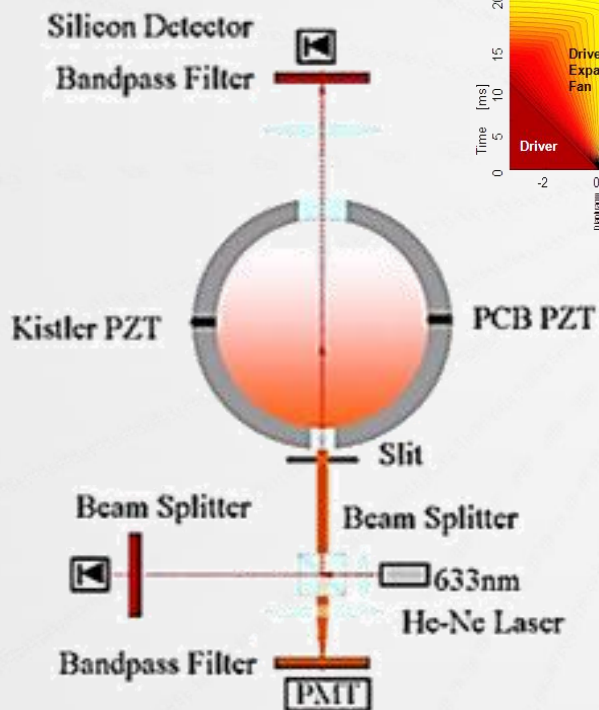


Soot Volume Fraction and Induction Time Measurements (Soot induction times and soot volume fraction)

UCF's shock tube and laser based soot extinction measurements.

- Soot extinction was measured using a HeNe laser at 632.8 nm.
- Soot Yield for all experiments were taken at 1.5ms = "[C]exp" / "[C]total"

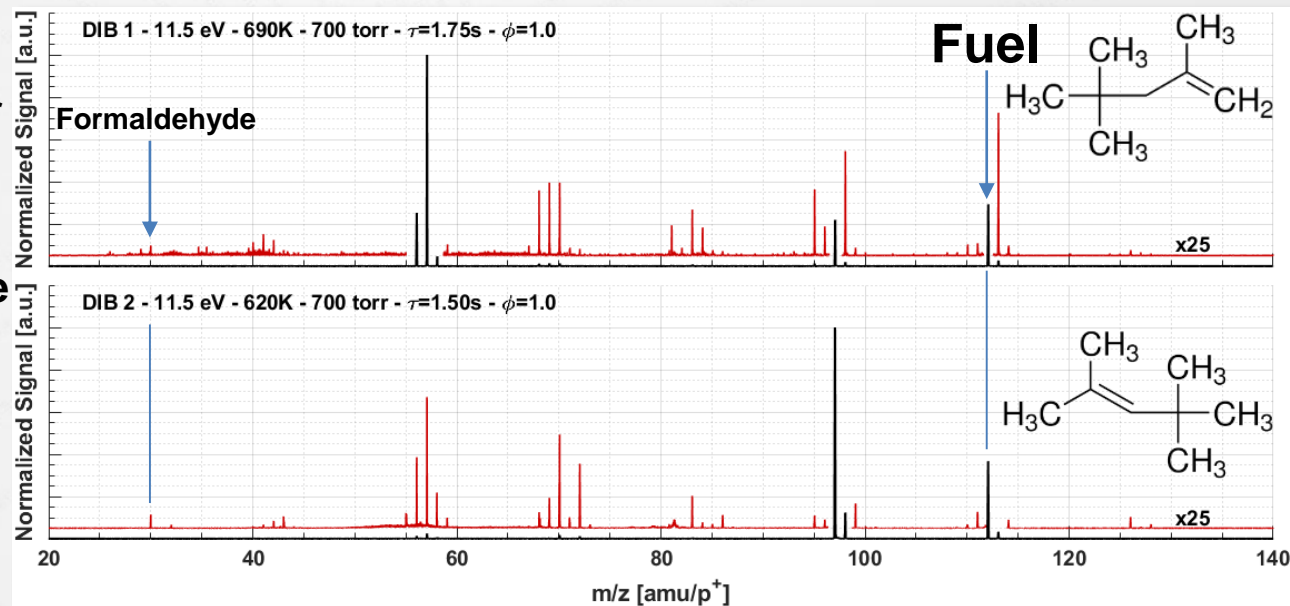
Soot diagnostics





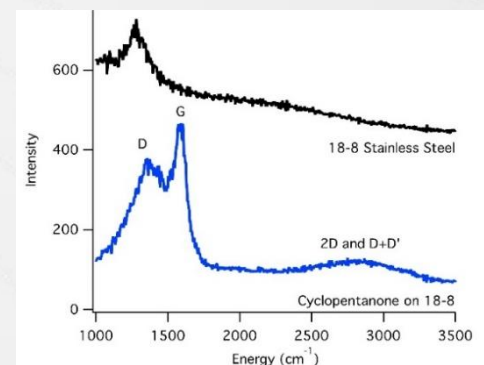
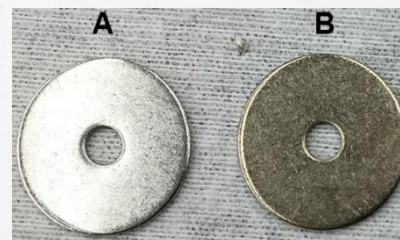
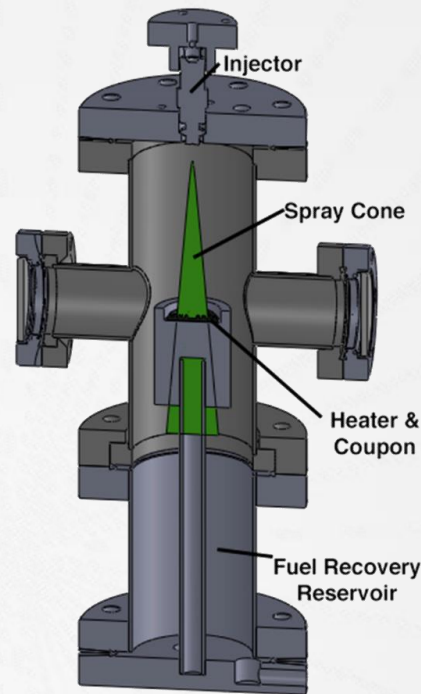
Synchrotron Coupled Fundamental auto-ignition Experiments (auto-ignition chemistry)

- ❖ ALS at Berkeley Natl Lab used for Diisobutylene synchrotron photoionization studies
 - ❖ Dilution used to control residence time τ
 - ❖ Externally heated to lowest ignition temperature
- ❖ DIB 2 Ignites 70K lower
 - ❖ C=C bond location is assumed dictating behavior
- ❖ Formation of Formaldehyde in both tests
- ❖ Radicals heavier than the fuel species
- ❖ DIB1 more intermediate species <45 amu at T_{ig}
- ❖ DIB2 produces similar ratios of species at 55 amu in lower quantities



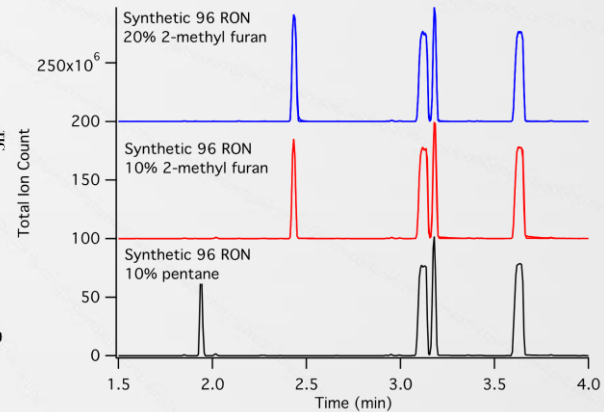
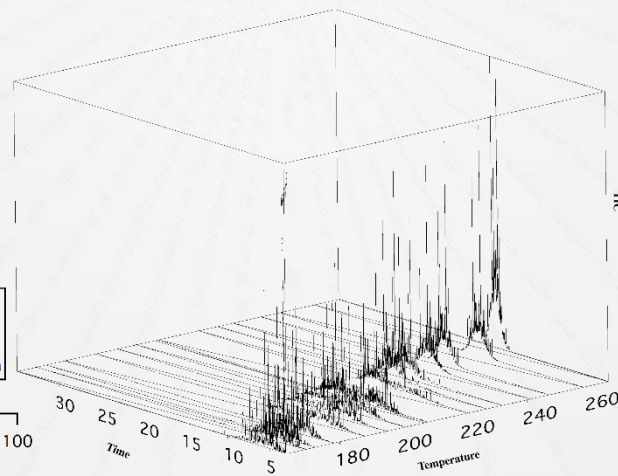
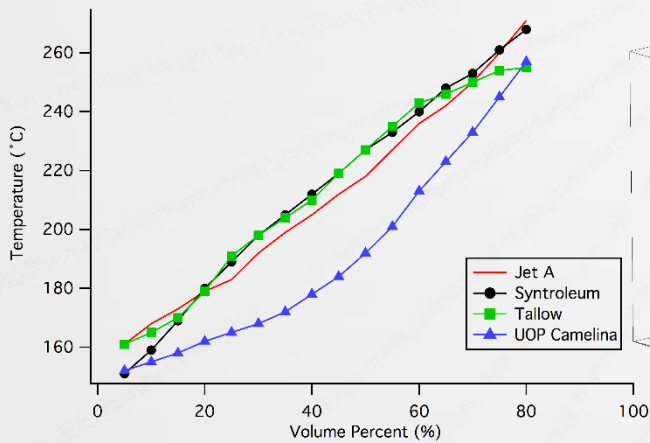
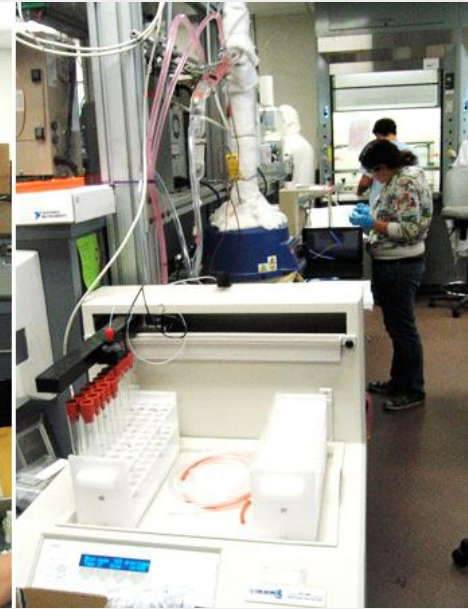
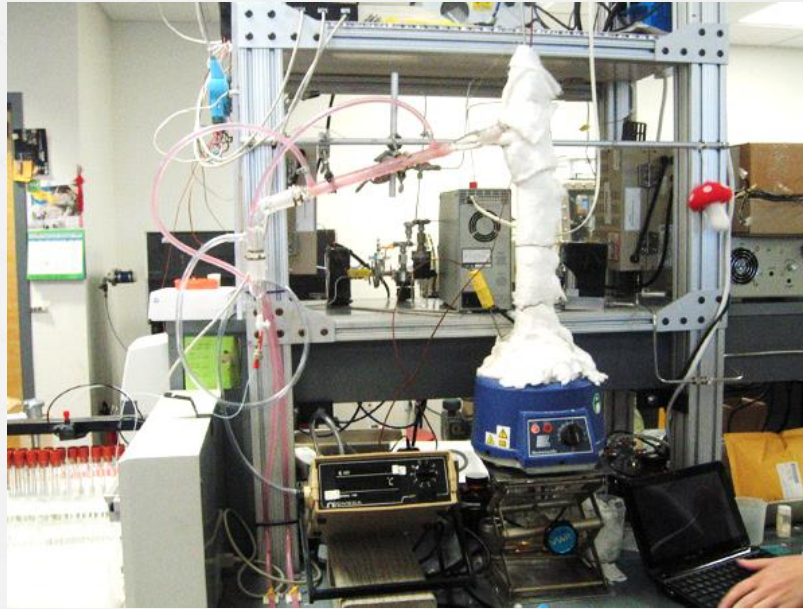
Fuel Coking and Hot Surface Deposit Exposure (coking volume fraction and thermal stability)

- ❖ Fuel sprayed onto a steel washer inside apparatus
 - ❖ Coupon is heated to $350 \pm 2^\circ\text{C}$
- ❖ Test rig is has an Ar atmosphere
 - ❖ 174.31 ± 2 kPa
 - ❖ Ar flow of 1 scfh
- ❖ Bosch EV14 Injector
 - ❖ 200 fuel pulses, of 10 ms
- ❖ Vapor is carried out with Ar, condensate collected on sample
- ❖ Carbon can be seen
 - ❖ A – clean surface
 - ❖ B – following fuel spray
- ❖ Raman G and D bands used to characterize carbon at 1300 and 1600 cm^{-1} correspond to sp^2 and sp^3 c-c bonding
- ❖ Higher D:G ratio indicates larger graphitic sheets



Fuel Volatility Measurements (volatility fraction)

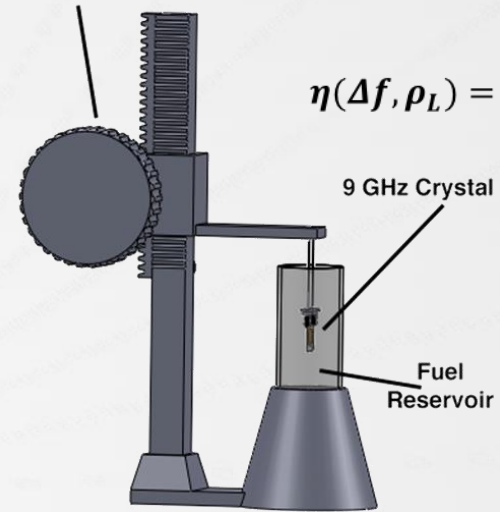
ASTM methods for fractional distillation of fuels. By fractionating the fuels we will thoroughly understand the volatility of a give fuel. In addition, each fraction will be analyzed by gas-chromatograph mass-spec (GC-MS) to correlate it chemical composition to the volatility data.



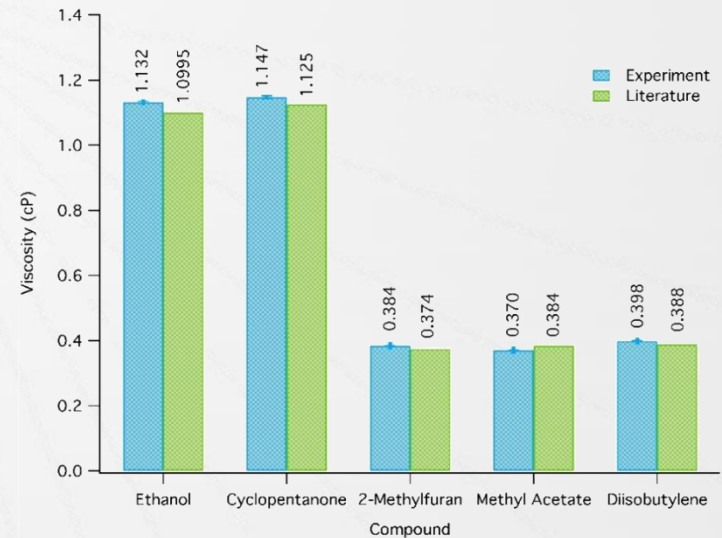
Viscosity Measurements (quartz crystal microbalance viscosity)

- ❖ Viscosity is obtained by measuring QCM oscillation frequency when immersed in a fluid compared to air
- ❖ A beaker containing fuel is held isothermally (25 ± 0.05 °C)
- ❖ 10 minute relaxation period allowed for equilibrium determination

Height Adjustment



$$\eta(\Delta f, \rho_L) = \frac{\Delta f^2}{k} / \rho_L$$





Seal Flexible Fuel Compatibility (degradation of these polymers)

- ❖ O-rings, Tested with ASTM specification
- ❖ Viton durometer 75A
 - ❖ Initially 2 mm thick, 3 mm outer diameter
- ❖ 10 o-rings per fuel, suspended in the fuel in a insulated container and separated by microcrystalline quartz spheres
- ❖ Properties measured daily for first 5 days, then every 3 days.
 - ❖ Mass (nearest 1×10^{-5} gram)
 - ❖ Volume (nearest 1×10^{-4} g)
 - ❖ Dimensions (nearest 1×10^{-4} mm)
- ❖ Largest gain observed after 1 day

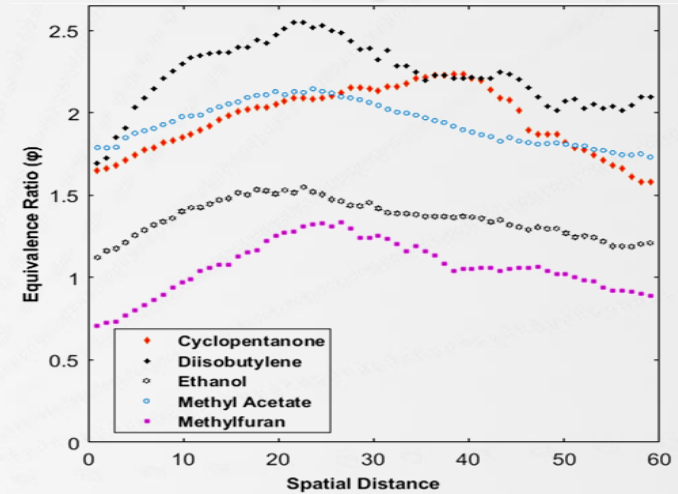


Results of Investigations

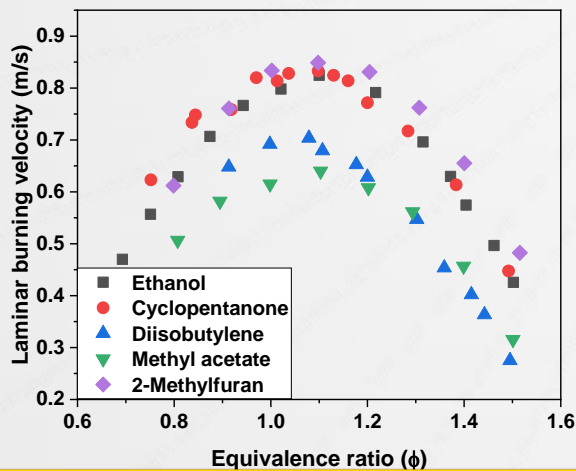
Spray Cone Angles

Blend %	30%-vol
Methyl Acetate	$5.79 \pm 0.10^\circ$
Diisobutylene	$6.71 \pm 0.05^\circ$
Cyclopentanone	$6.97 \pm 0.09^\circ$
Methyl Furan	$8.08 \pm 0.04^\circ$
Ethyl Alcohol	$6.28 \pm 0.04^\circ$

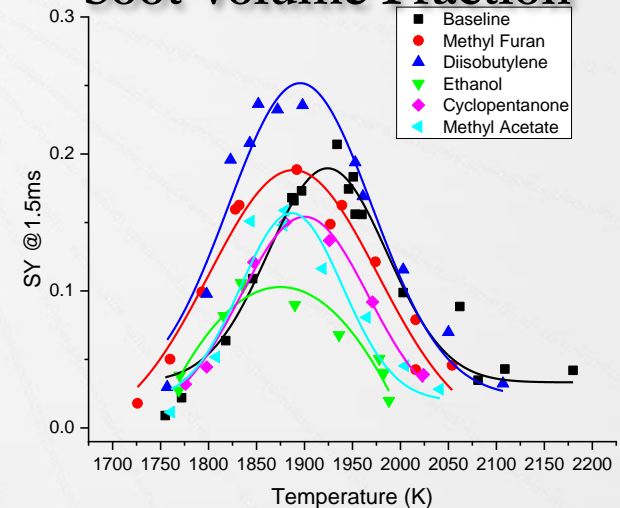
Local Fuel-Air (Equivalence Ratio)



Laminar Flame Speed



Soot Volume Fraction





Results of Investigations

Carbon Deposit

Compound	Size (μm)
methyl acetate	$5.19 \pm 6.2\%$
2-methylfuran	$1.78 \pm 2.7\%$
cyclopentanone	$2.33 \pm 5.8\%$
diisobutylene	$2.52 \pm 9.9\%$
ethanol	$2.22 \pm 8.6\%$

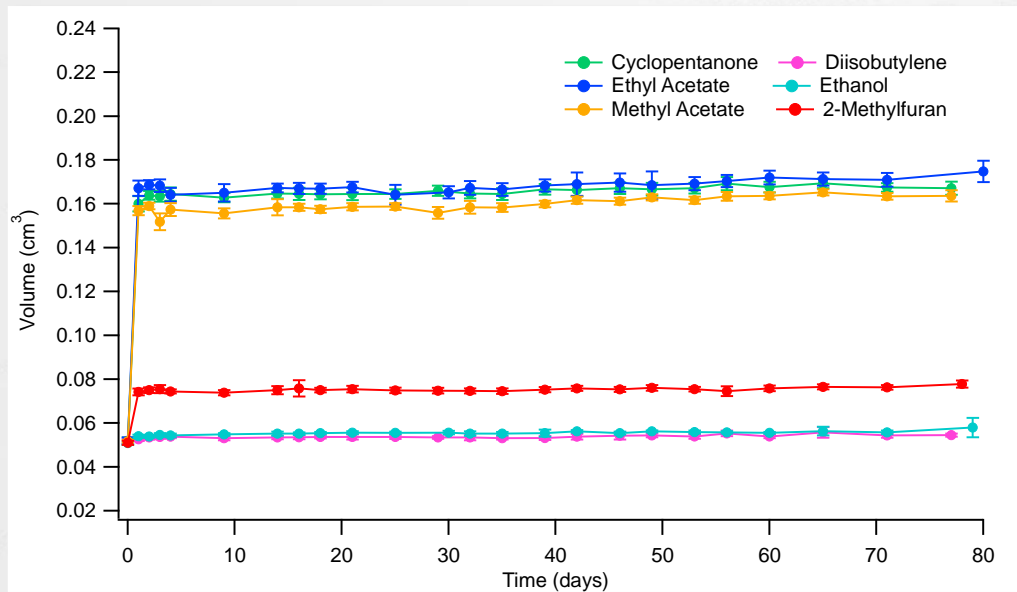
Viscosity & Density

Compound	Density (g/cm^3)	Viscosity (cP)
3:7 Ethyl Alcohol	0.750	0.487
3:7 Cyclopentanone	0.791	0.545
3:7 Methyl Acetate	0.783	0.367
3:7 Ethyl Acetate	0.778	0.380
3:7 Diisobutylene	0.724	0.389
3:7 Methyl Furan	0.778	0.366

Spray Cone Angles

	Fraction (v%)	Boiling Point ($^{\circ}\text{C}$)
96RON		
Iso-Octane	56.7	98
Heptane	10.0	98.4
Toluene	33.3	111
10% Ethanol in 96RON		
Ethanol	10	78
Iso-Octane	51.0	98
Heptane	9.0	98.4
Toluene	30.0	111
20% Diisobutylene in 96RON		
Iso-Octane	45.3	98
Heptane	8	98.4
2,4,4-trimethyl-1-pentene	7.5	101
2,4,4-trimethyl-2-pentene	2.5	104
Toluene	26.7	111
20% Methyl Acetate in 96RON		
Methyl Acetate	20.0	57.4
Iso-Octane	45.3	98
Heptane	8.0	98.4
Toluene	26.7	111
20% 2-Methylfuran in 96RON		
2-Methylfuran	20.0	64
Iso-Octane	45.3	98
Heptane	8.0	98.4
Toluene	26.7	111

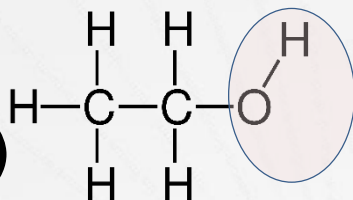
Seal Swell



Task 3- Correlation of molecular structure

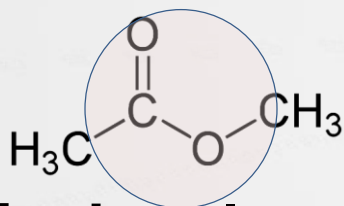
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❖ Ethanol (alcohol)

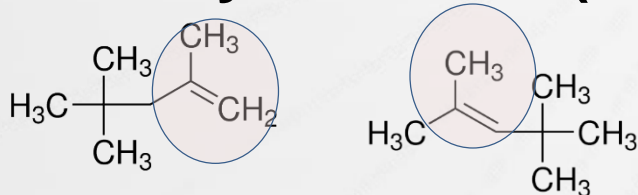


- ❖ Selected as a baseline comparison of existing biofuels

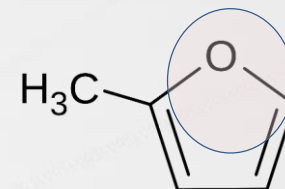
❖ Methyl Acetate (ester)



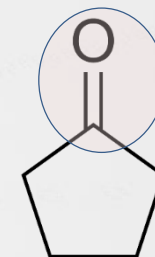
❖ Diisobutylene 1 & 2 (alkenes)



❖ Methyl Furan



❖ Cyclopentanone (ketone)



- ❖ The 5 candidates were chosen for their specific functional groups as highlighted in the figures. The correlation of the molecular structures will be beneficial to identify fuel similarities. The goal is to examine the relationship between the experimental results from task 2 and the fuel molecular structure. This information will be useful for the Co-Optima effort for predicting new fuels (outside of the selected ones) and their behavior.



Effects of Molecular Structure on Properties

❖ Spray Cone Angles and Droplet

- ❖ Increases in the inertial moment of the fuel molecule trend with larger spray cone angles. Furthermore, blending multiple fuels compounds, increases the number of small particles.

❖ Fuel-Air Flame Measurements

- ❖ Alcohols and furans have lower fuel-air equivalence ratio (close to stoichiometric) under comparable conditions than esters, ketones, and alkenes. Thus for SI engines, optimal burning could be achieved with alcohols and furans.
- ❖ No remarkable differences between alcohols, and furans when it comes to fuel-air flame burning.

❖ Carbon Deposition

- ❖ Prevalence of C-C and C=C, versus C-O or C=O bonds increases the quantity of soot deposited.

❖ Viscosity & Density

- ❖ The existence of a C=C bond exhibits a shorter bond length than a C-C bond, thus the orbital dipole nature of this compound is decreased resulting in reduced viscosity.
- ❖ Density is dependent on both molecular weight and dipole characteristics of molecular structure.

❖ Laminar Burning Velocity

- ❖ Alcohols, ketones, and furans have higher laminar burning velocities under comparable conditions than esters and alkenes. Thus for SI engines, where flame speeds are a design parameter, alkenes and esters may not be a good choice.
- ❖ No remarkable differences between alcohols, ketones, and furans when it comes to flame speeds.



Effects of Molecular Structure on Properties

❖ Synchrotron Photoionization

- ❖ Position of a C=C double bond can greatly impact the ability of a fuel to ignite. As it can be seen the ignition temperature of DIB2 which has a C=C bond on the backbone, is significantly below that of DIB1 which has a C=C bond on a side chain.

❖ Distillation

- ❖ The larger the hydrocarbon chain backbone, or the existence of a ring structure, increases retention time.
- ❖ The addition of functional groups lowers the retention time of a fuel.

❖ Fuel Swell

- ❖ The addition of non-alcohol functional groups and ring chemistry greatly enhance the ability of Viton to uptake compounds.
- ❖ Compatibility best for alcohols and alkenes, worst for ketones and acetates
- ❖ Straight chain hydrocarbons exhibit the least amount of swelling in seals.

❖ Soot Formation

- ❖ Ethanol which has the shortest carbon chain of any species tested and is oxygenated produces the least amount of soot at the highest sooting condition tested.
- ❖ Subsequent lowest sooting species: cyclopentanone and methyl acetate are both oxygenated hydrocarbons which do not feature a C=C bond.
- ❖ Methyl furan, and DIB produced the most soot of all fuels tested. Both compounds are unsaturated (have the C=C structure) and thus such compounds will make more soot. However, the fact that methyl furan produces less soot compared to DIB is due to the presence of an oxygen within the parent fuel (greatly inhibits soot formation.)



Conclusions

- ❖ **5 fuels selected for study**
 - ❖ Ethyl Alcohol, Diisobutylene, Cyclopentanone
 - ❖ Methyl Methyl Acetate, Furan,
- ❖ **Spray cone angle for fuel mixtures was determined using image recognition**
- ❖ **Droplet breakup information was obtained**
- ❖ **Fuel-air measurements were conducted**
- ❖ **Coking deposits were identified from fuel sprays using Raman Spectroscopy**
- ❖ **Density and Viscosity of test fuels were identified at room temperature**
- ❖ **Cyclopentanone & Methyl furan exhibit similar LBV to ethanol**
- ❖ **Synchrotron studies show different ignition characteristics of DIB1 & DIB2**
- ❖ **20vol-% Methyl acetate distills in fastest of fuels tested**
- ❖ **Volume change with seals happens rapidly 95% change in 24 hours for all items tested**
 - ❖ Ethanol & diisobutylene swells Viton minimally
 - ❖ Other tested fuels cause significantly more swelling
- ❖ **Tested fuels have significantly higher soot yield compared to ethanol**



4 – Relevance

- Technology developed under this program has significant impact through accelerating the process of screening potential fuels to find the optimal fuel-engine combinations
- The project provides validated fuel characteristics and properties data with quantified uncertainty levels applied to Co-Optima and BETO biofuels
- In addition to physical designs and test data, we provide easy-to-apply performance correlations that will aid designers in the application and operation of the Co-Optima fuels
- The product that will result from this project is data and information for the fuel behavior that mitigates the sensitivity of the alternative fuels enabling sustainable, nationwide production of advanced biofuels that can reduce greenhouse gas emissions

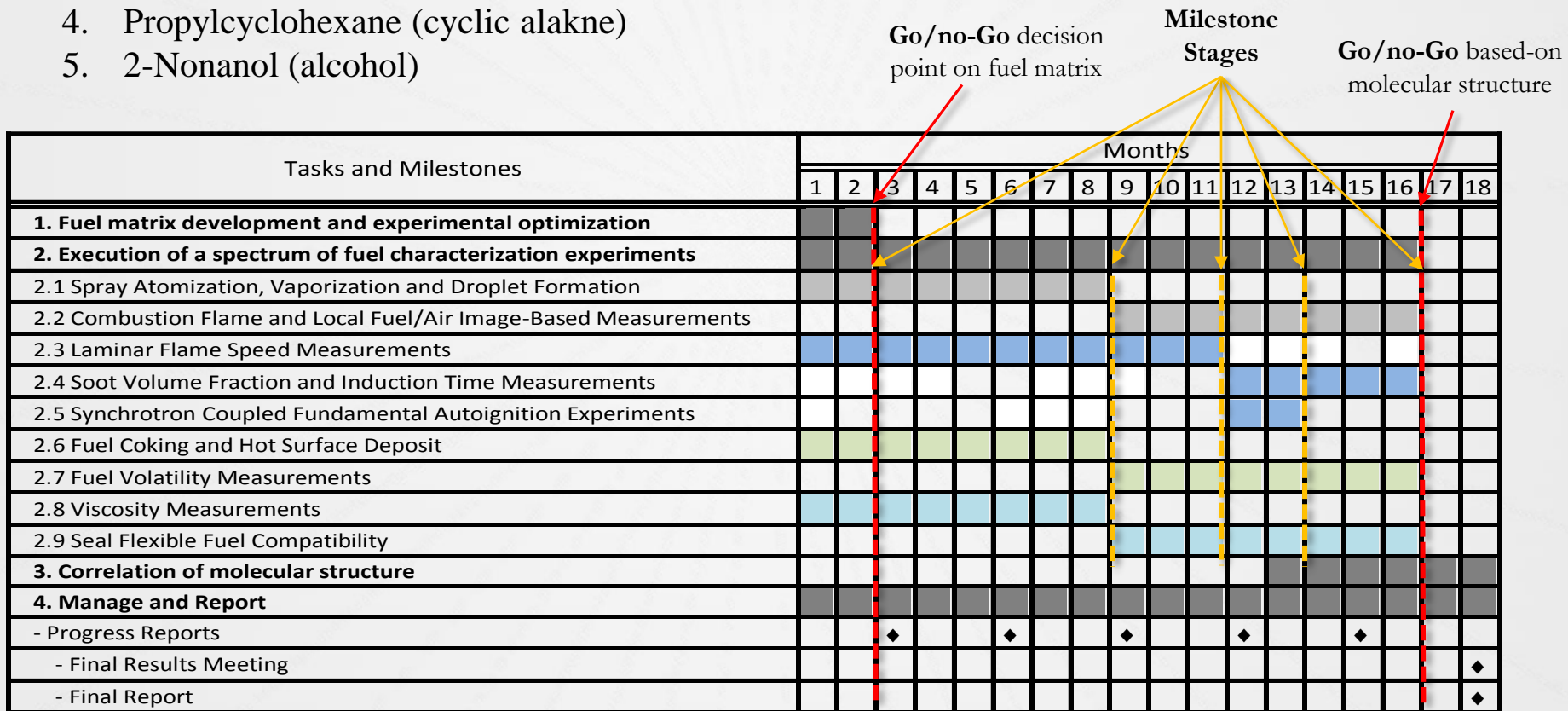


5 – Future Work

Heavy Fuels Matrix Development: (in consultation with the National Labs and DOE)

Fuel Matrix 2- Heavy Fuels

1. 1,1'-oxybis-butane (ether)
2. Nonane (normal alkane)
3. 2,3,6-Trimethylheptane (branched alkane)
4. Propylcyclohexane (cyclic alkane)
5. 2-Nonanol (alcohol)





Summary

1. Overview:

The goal of this project is to provide a detailed data set of multiple combustion experiments relevant to engine combustion of Co-Optima fuels. The product that will result from this project is data and information for the fuel behavior that mitigates the sensitivity of the alternative fuels.

2. Approach:

A series of targeted experiments characterize and predict Co-Optima fuel spray atomization, flame topology, flame speed, soot induction time, volatility, viscosity, soot/coking, and compatibility.

3. Technical Accomplishments/Progress/Results:

The three tasks has been completed on fuel group 1 and the data has been shared with DOE and the National labs. Presentations and publications are underway with presentation scheduled for the all-hands meeting and AEC meeting.

4. Relevance:

Validated fuel characteristics and properties and quantified uncertainty levels that can be applied to select and optimize fuels. Easy-to-apply performance correlations that will aid designers in the application and operation of the Co-Optima fuels.

5. Future work:

The three tasks will be completed on heavy fuels group 2.