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Advanced Petroleum Based Fuels Research at NREL

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Overview of APBF Research at NREL

- **Fuel impacts on advanced combustion engines**
  - Advanced ignition characterization using IQT
    - FACE standardized set of research diesel fuels
    - Collaborative diesel LTC/HCCI projects
  - Installation of a single cylinder research engine
- **Advanced fuel & lubricant impacts on current and emerging engines**
  - Fuel impacts on toxic/unregulated emissions (w/ NPBF)
  - Impact of biodiesel on advanced emission control systems (NPBF)
  - Lube oil impact on PM emissions (Health Effects)
  - Impact of GTL diesel fuel on fleets

Fuel Impacts on Advanced Combustion Engines

- **Technical Barrier**
  - Inadequate data and predictive tools for fuel property effects on combustion and engine optimization
- **Accomplishments**
  - Improved understanding of biodiesel ignition chemistry
  - Differentiation of ignition properties in diesel fuels
  - Established collaborations to relate our ignition metrics to advanced combustion engines

Goals and Objectives

- ***OVTP Task 2: Fuel property effects on advanced combustion engines***
  - Develop fundamental understanding of fuel effects on in-cylinder combustion and emission formation in advanced combustion regimes
- ***NREL Objective: Develop improved tools to quantify fuel effects on advanced combustion engines***
  - Improved metrics for characterizing fuel ignition
  - Correlate ignition metrics with advanced combustion engine studies
  - Investigate fuel structure effects on emissions

Feedback from 2007 Merit Review

- General appreciation of our approach to improving ignition property metrics for advance combustion engines
- IQT™ apparatus for measurements
  - Positive feedback on simplicity and availability
  - Lack of differentiation among surveyed commercial fuels
- Need to correlate results with advanced combustion engine studies
  - Preliminary results from FACE diesel fuels are available
  - Beginning collaborative engine projects with NRC-Canada and CRC

Advanced Ignition Characterization

Background:

- Cetane number alone is insufficient to characterize fuel ignition properties for advanced combustion engines

Approach:

- Develop a more comprehensive characterization of fuel ignition properties using the Ignition Quality Tester (IQT ™)
  - Measure ignition delay over range of conditions
  - Fit model with 3 parameters
    - Derived cetane number (DCN)
    - E_a = sensitivity of ignition to temperature
    - b = sensitivity of ignition to pressure/composition

$$Rate = \frac{1}{\text{ignition delay}} = A \cdot \exp\left[\frac{E_a}{RT}\right] \cdot [O_2]^b$$

Model Compound Preliminary Results

Contributions of primary C-H_3

Secondary C-H_2 chemistry

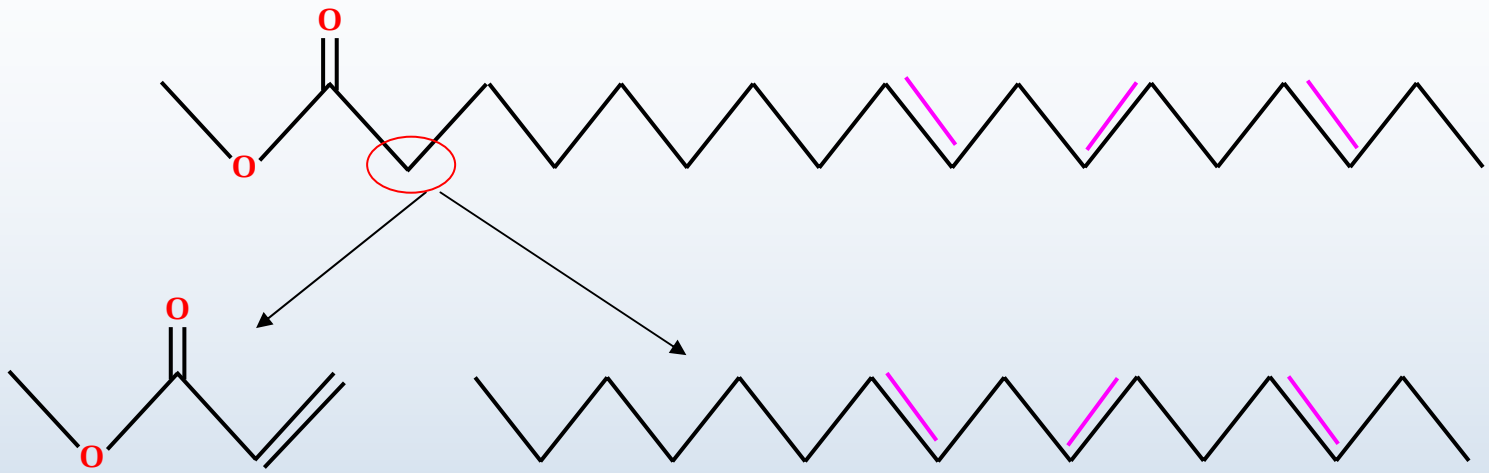
Contributions of double bonds

Compound	DCN	E_a kJ/mol
Hexane	47	53
Heptane	53	51
Octane	57	49
Hexadecane	100	49

Compound	DCN	E_a
Methyl Stearate (18:0)	96	49
Methyl Oleate (18:1)	59	57
Methyl Linoleate (18:2)	43	63
Methyl Linolenate (18:3)	36	61

Biodiesel ignition chemistry dominated by hydrocarbon chain

Mechanistic Insights for Biodiesel Ignition



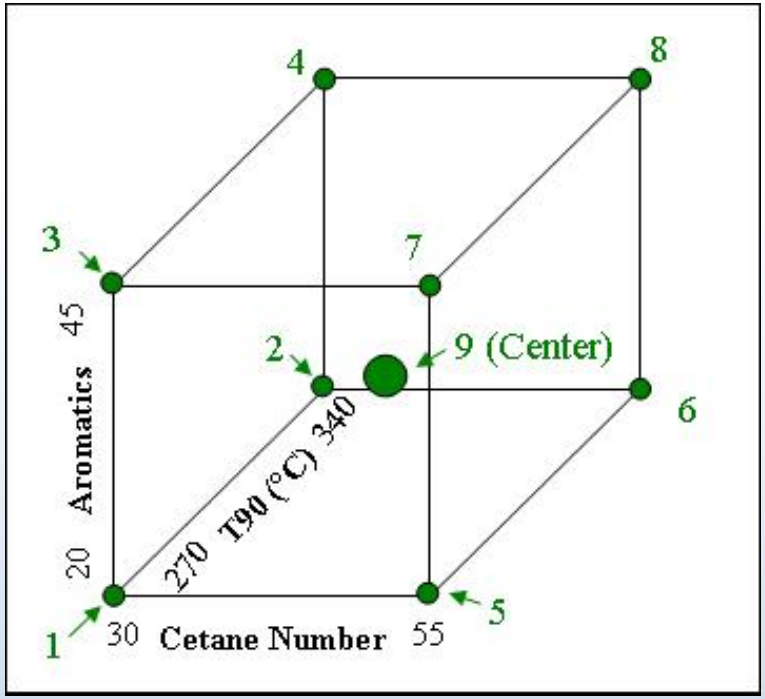
- **Proposed mechanism**
  - Biodiesel molecules cleave via β-scission, forming methyl acrylate and hydrocarbon radicals
  - Oxidation of hydrocarbon radicals then proceeds as expected
- **Supporting Evidence**
  - Methyl acrylate detected in both engine and IQT exhausts
  - Ignition properties (Ea) similar to a comparable hydrocarbon

FACE Fuels

Large Industry and National Lab Consortium

- **Approach:** Develop matrices of standardized test fuels for advanced combustion engine research
- **Status:** Diesel fuels available and being tested
  - NREL has characterized ignition properties of FACE diesel fuels received to date (#3, 4, 6, 9)
  - Remaining fuels blended and scheduled to be tested
  - Gasoline matrix is being reformulated

FACE Diesel Fuel Matrix



Preliminary IQT Results

Fuel #	CN (COA)	DCN (IQT)	Ea (kJ/mol)	b
3	32.0	32.9	52.2	0.86
4	28.4	32.9	48.1	1.02
6	53.3	53.6	54.0	0.85
9	45.0	44.6	55.8	0.88

Collaborative Diesel HCCI Projects

- **MOU with NRC-Canada**
  - Modified CFR engine capable of diesel HCCI experiments
  - Test plan agreed upon, allows correlation with IQT results
    - Have begun testing a set of research fuels already tested at NREL
    - Will purchase and test all FACE diesel fuels
- **Joint project with CRC Advanced Vehicle Fuels and Lubes (AVFL) committee**
  - Will test FACE fuels in advanced combustion engine
  - Scope of tests includes HCCI operation

Advanced Fuel Impacts on Current and Emerging Engines

- **Technical Barrier**
  - Inadequate data and predictive tools for fuel effects on emissions and emission control system impacts
- **Accomplishments**
  - Identified ethyl nitrite emission from ethanol combustion

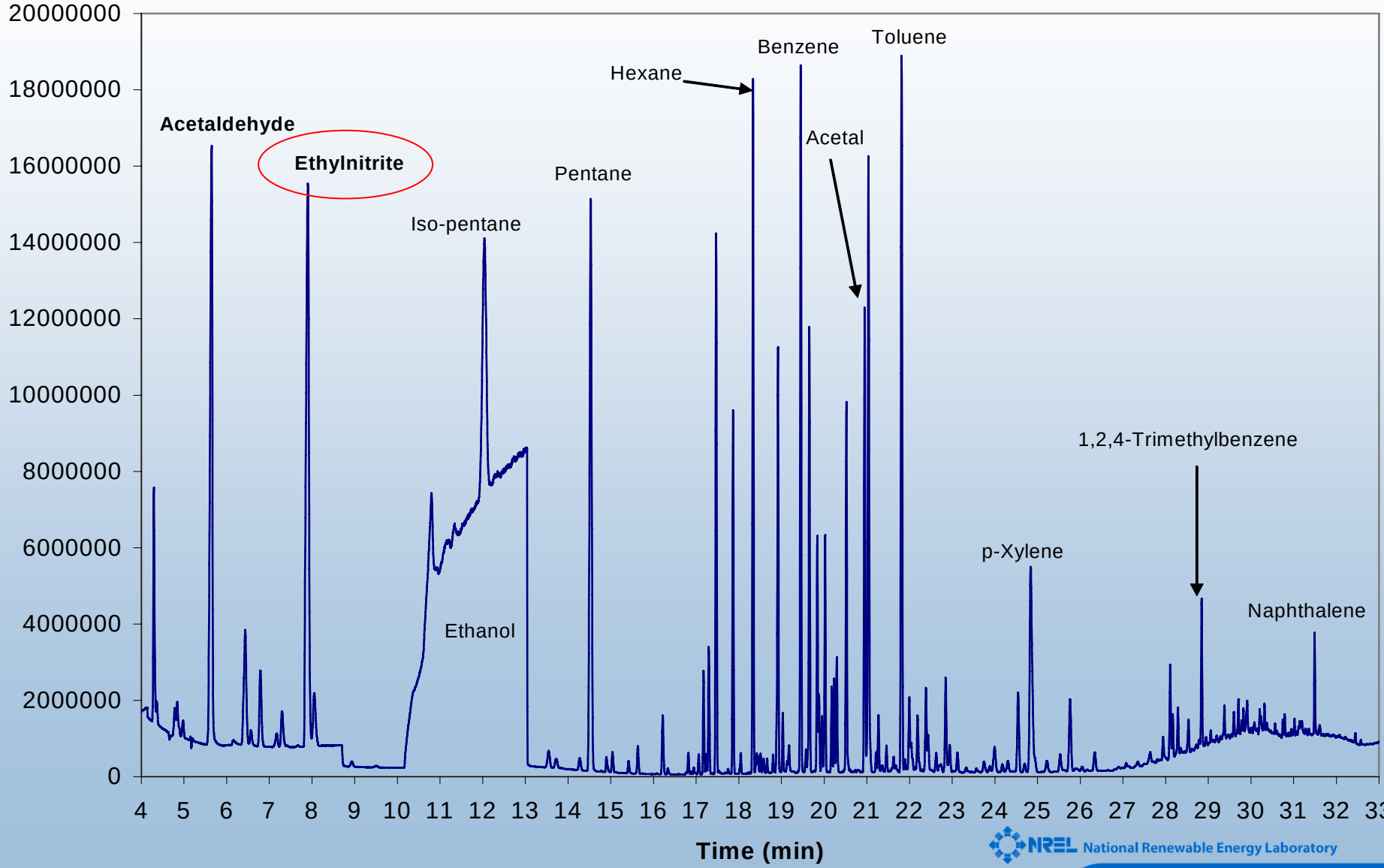
Goals and Objectives

- ***VTP Task 3: Petroleum displacing fuels and fuel blending components***
  - Study combustion and emissions formation processes of non-petroleum based fuels
  - Identify renewable and synthetic fuel blending components that provide enhanced efficiency, performance and emissions
- ***NREL Objective: Quantify unregulated emissions from emerging fuels and fuel components***
  - In-use E85 vehicles
  - Intermediate ethanol blends in non-FFVs

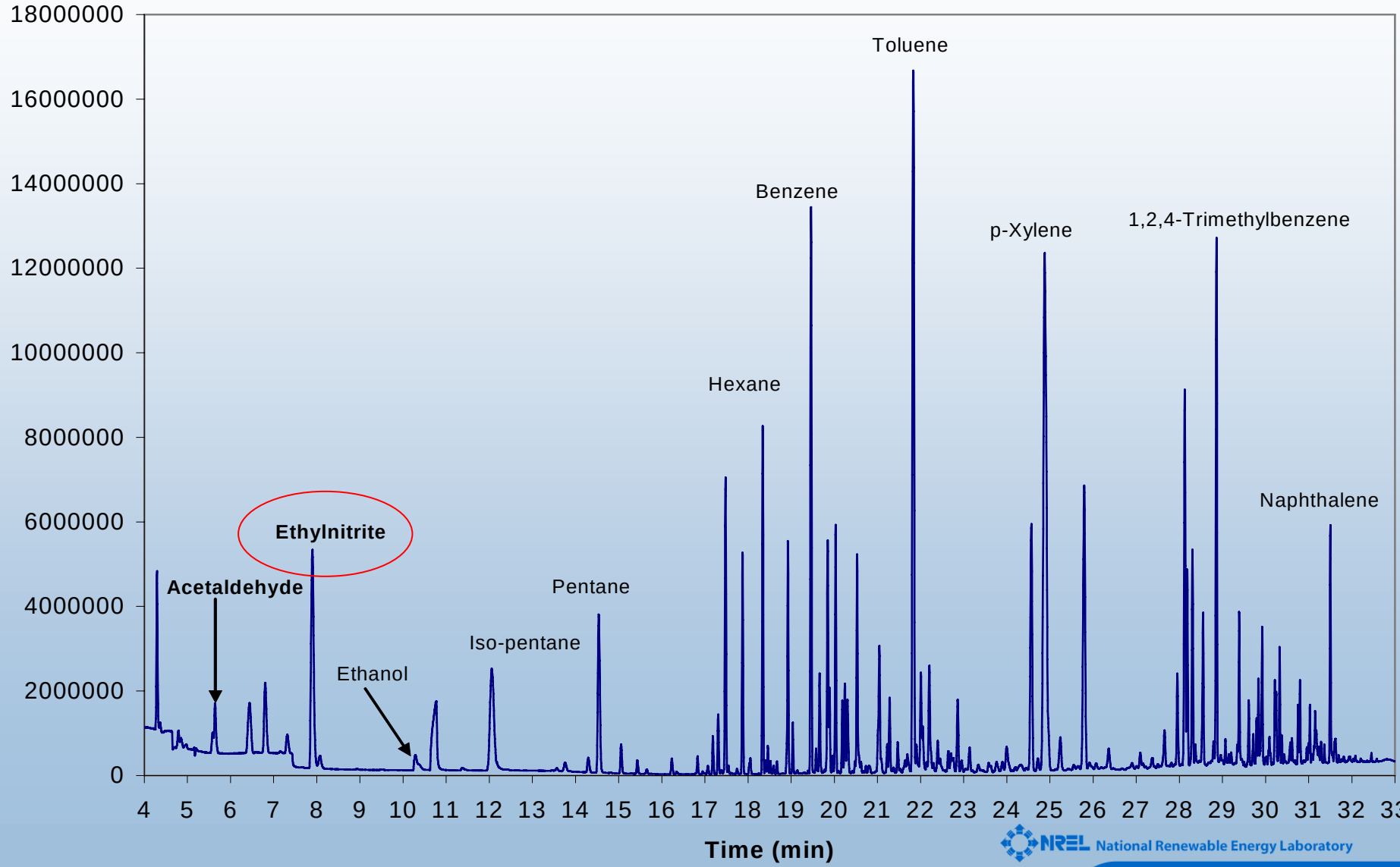
Speciated Emissions from In-Use FFVs

- **Approach:** Evaluate impacts of alternative fuel use on exhaust emissions
  - Quantify carbonyls and speciated hydrocarbons down to ppb levels
  - Identified ethyl nitrite in Bag 1 samples
- In-use vehicle testing on ethanol blends
  - Sub-ambient cold start
  - Various drive cycles
  - Summer and winter blends
  - Flex-fuel vehicles
  - Low and high mileage, plus high emitter

Bag 1 NMOG from 2003 Dodge Caravan, 55K miles, E85, 20ºF



Bag 1 NMOG from 2003 Dodge Caravan, 55K miles, E10, 20ºF



Reducing Emissions from Transport Refrigeration Units (TRUs) with GTL Diesel

Approach: Use GTL diesel to reduce emissions, especially PM

Status:

- Baseline emissions testing complete (GTL vs. ULSD), CARB collating data
- 2 of 6 months in-use data collected, final emissions testing June 2008

- NREL/DOE – SCAQMD CRADA (CARB cash and in-kind)
- MOUs established with project partners:
  - Thermo King: TRU, Emissions Control OEM
  - Sasol Chevron: GTL provider
  - Rockview Farms: Host fleet

Industry Collaboration

- FACE working group
  - Energy companies, LD and HD OEMs, and other national labs
- Project with Coordinating Research Council
  - Diesel fuel effects on HCCI
- Memorandum of Understanding with National Research Council-Canada
  - CFR single cylinder HCCI engine
- Other national labs and universities
  - Joint work on fuel measurements with ORNL, PNNL
  - Participation with NCUT
  - Developing collaboration with Colo. School Mines and LLNL
- Colorado Department of Health's light-duty emission lab
  - Emissions from intermediate ethanol blends and in-use FFVs

Future Work

- Correlate chemical structure with NOx formation: IQT study of pure compound combustion
- Correlate IQT and HCCI results using FACE fuels
- Report on emissions and operability of GTL fueled TRUs
- Complete speciation for intermediate ethanol blends study
- Complete speciation for in-use FFV study
- Develop experiment validated-modeling study on biodiesel ignition mechanisms with Tony Dean at CSM and Bill Pitz at LLNL
- Installation of single cylinder research engine

Single Cylinder Research Engine

- **Focus:** Investigate fuel effects in a stratified charge gasoline direct injection engine
  - Study impact of fuel chemistry and properties on emissions and efficiency
    - Range of conventional fuels
    - Intermediate and higher blends of ethanol
    - Butanol and mixed alcohols
- Operation in LTC regimes
  - With or without spark assist
- **Status:** Ordering equipment

Summary

- **Accomplishments:** 1) New information on biodiesel ignition 2) Ignition characterization of FACE diesel fuels, 3) Collaborations relating IQT ignition metrics to advanced combustion engines, 4) Identified ethyl nitrite emission from ethanol fueled vehicles.
- **Relevance:**
  - Better characterization of ignition properties enables optimization of advanced combustion engines
  - Improved understanding of unregulated emissions from advanced fuels
- **Approach:**
  - Use IQT to quantify ignition properties and correlate results with advanced combustion engine testing
  - Use GCMS and HPLC to quantify unregulated emissions from vehicle, engine and IQT tests
- **Collaborations:** Active joint programs with CRC, FACE working group, NRC-Canada, and other national labs
- **Future Plans:** Integrate combustion and analytical capabilities, and expand collaborations