NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Advanced Combustion and Fuels

P.I.: Bradley T. Zigler
Collaborating Researchers:
Jon Luecke, Matt Ratcliff, Greg Bogin, Eric Osecky, Jon Burton, Petr Sindler, and Drew Cameron

June 11, 2015

Project ID # FT002

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline

Project Start Date: October 2014
Project End Date: September 2015
Percent Complete: 66%
Program funded one year at a time.

Budget

Funding Received in FY14: $835K

Funding for FY15: $680K

Partners

- Colorado School of Mines (CSM)
- 15 industry, 6 university, and 6 national lab partners via Advanced Engine Combustion (AEC) – Memorandum of Understanding (MOU)
- Project Lead: National Renewable Energy Laboratory (NREL).

Barriers

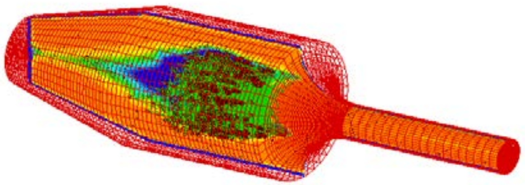
From DOE/VTO 2011–2015 Multi-Year Program Plan

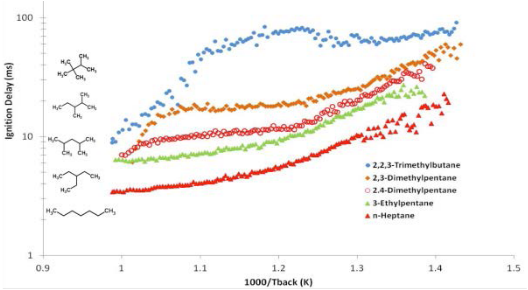
- Inadequate data and predictive tools for fuel property effects on combustion and engine efficiency optimization (Fuels & Lubricants Technologies)
- Lack of modeling capability for combustion and emission control (Advanced Combustion Engine R&D)
- Inadequate data on long-term impact of fuel and lubricants on engines and emission control systems (Fuels & Lubricants Technologies).

Relevance

Objective: Address technical barriers of inadequate data and predictive tools for fuel and lubricant effects on advanced combustion engines.

- Develop experimental techniques to address data voids for ignition performance where other methods are challenged:
  - Low volatility fuels
  - Surrogate fuel blends
  - Prototype compounds where only small quantities (~25 mL) are available
  - Lubricating oil/high boiling point fractions (to address low speed pre-ignition [LSPI]).
- Provide development feedback and validation of kinetic mechanisms through coupled simulation of experiments.
- Conduct complementary engine-based studies focusing on quantifying fuel physico-chemical effects not fully captured by other means (octane number).





NREL 23595
Credit: Dennis Schroeder / NREL

Milestones

Month/ Year	Milestone or Go/No-Go Decision	Description	Status
Sep 2014	Milestone	Deliverable – Project status summary to DOE Program Manager.	Completed
Dec 2014	Milestone	Deliverable – Submit updated task summary table with supporting documentation.	Completed
Mar 2015	Milestone	Deliverable – Submit updated task summary table with supporting documentation.	Completed
Jun 2015	Milestone	Deliverable – Submit updated task summary table with supporting documentation.	On schedule
Sep 2015	Milestone	Deliverable – Draft report with results of single cylinder research engine studies to quantify fuel chemistry impacts on the efficiency potential for gasoline direct injection (GDI) engines.	On schedule
Sep 2015	Milestone	Deliverable – Draft report or journal article documenting chemical effects of lubricants and lubricant fuel blends on autoignition.	On schedule

Approach/Strategy

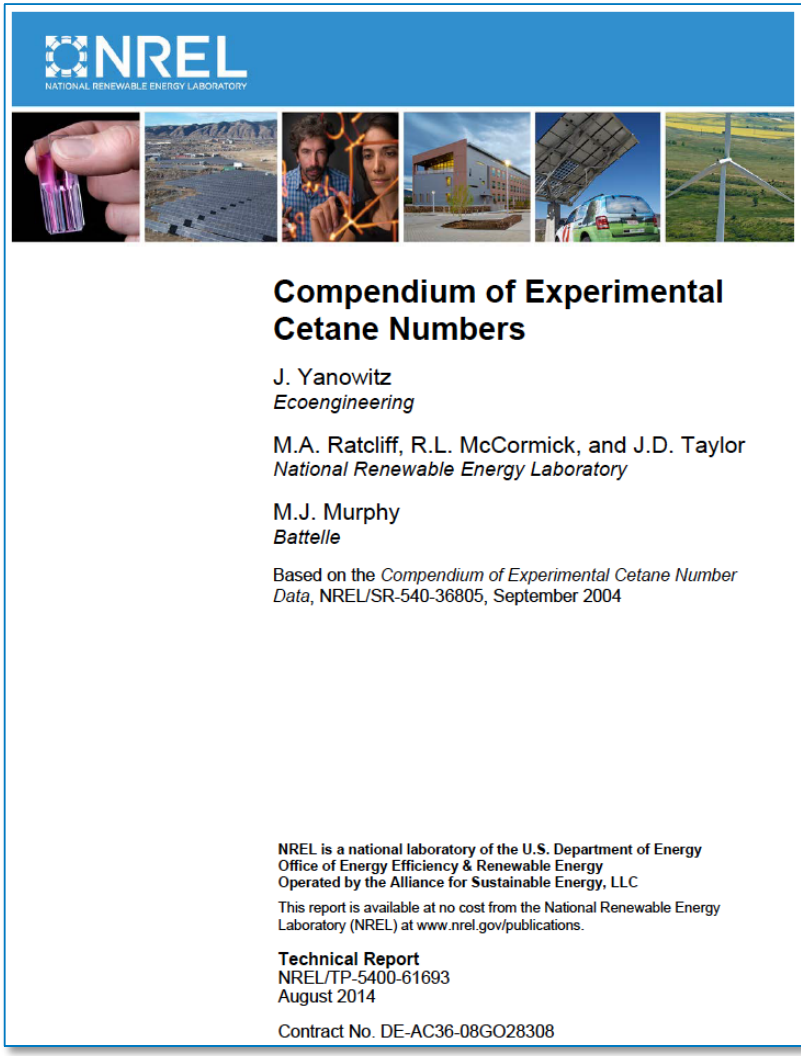
Through collaboration, develop techniques, tools, and data to quantify critical fuel physico-chemical effects to enable development of advanced combustion engines that use alternative fuels.

- Address technical barriers of inadequate *data and predictive tools* for fuel effects, including biofuels, on advanced combustion engines.
- *Collaborate* with other laboratories, universities, and industry to *develop accurate, computationally efficient kinetic mechanisms* and models necessary for coupled computational fluid dynamics (CFD) simulation.
- Develop unique capability to *experimentally test and validate simulations* for ignition performance of compounds, blends, and surrogates at engine-relevant conditions, addressing data voids and complementing other methods.
- *Adapt tools to study novel problems*, like lubricant impacts on LSPI.
- *Share information* through publication, direct collaboration, and forums like the Advanced Engine Combustion – MOU.
- *Contribute to the "portfolio"* of tools and technologies necessary to increase engine efficiency and renewable fuel use, reducing greenhouse gas impacts.

Technical Accomplishments: DCN Measurements of Small Quantities

	ASTM Method D613 (CFR)	ASTM Method D6890 (IQT)	ASTM Method D7170 (FIT)	Other Ignition Delay Method	Blend	Unknown Method	Total
Measurements in 2004 compendium	3	16	0	76	85	142	322 measurements, 296 different compounds
Total measurements in this compendium	58	128	4	70	135	189	584 measurements, 387 different compounds

- Update of 2004 *Cetane Number Compendium*
- Cetane values for 388 pure compounds, including 187 hydrocarbons and 201 oxygenates
- Update includes more than 250 new measurements, including 112 with the IQT
- 82 of the IQT measurements were conducted at NREL over the past several years, often with very limited quantities of compounds with no prior known measurements.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Compendium of Experimental Cetane Numbers

J. Yanowitz
Ecoengineering

M.A. Ratcliff, R.L. McCormick, and J.D. Taylor
National Renewable Energy Laboratory

M.J. Murphy
Battelle

Based on the *Compendium of Experimental Cetane Number Data*, NREL/SR-540-36805, September 2004

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC

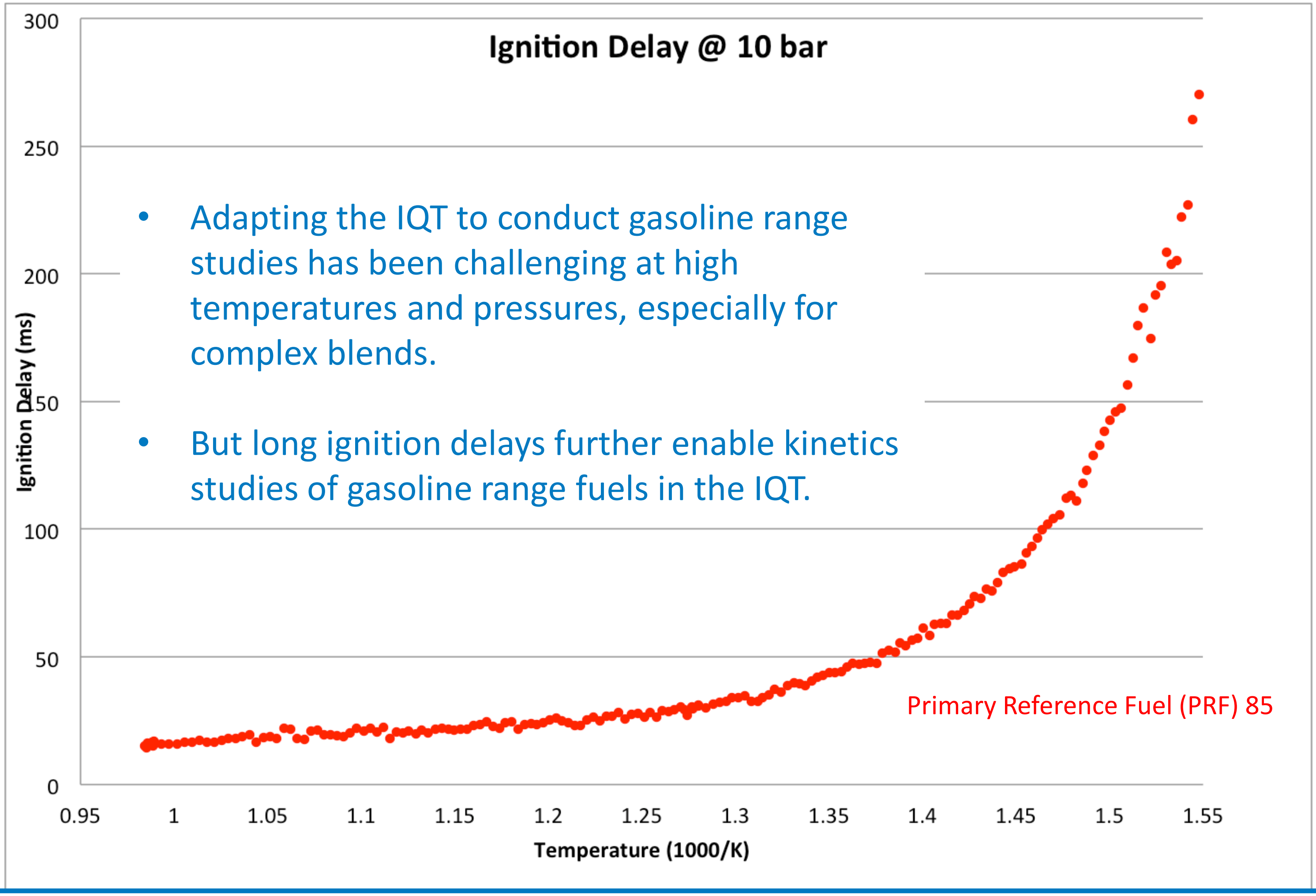
This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Technical Report
NREL/TP-5400-61693
August 2014

Contract No. DE-AC36-08GO28308

CFR = Cooperative Fuel Research
DCN = derived cetane number
FIT = fuel ignition tester
IQT = Ignition Quality Tester

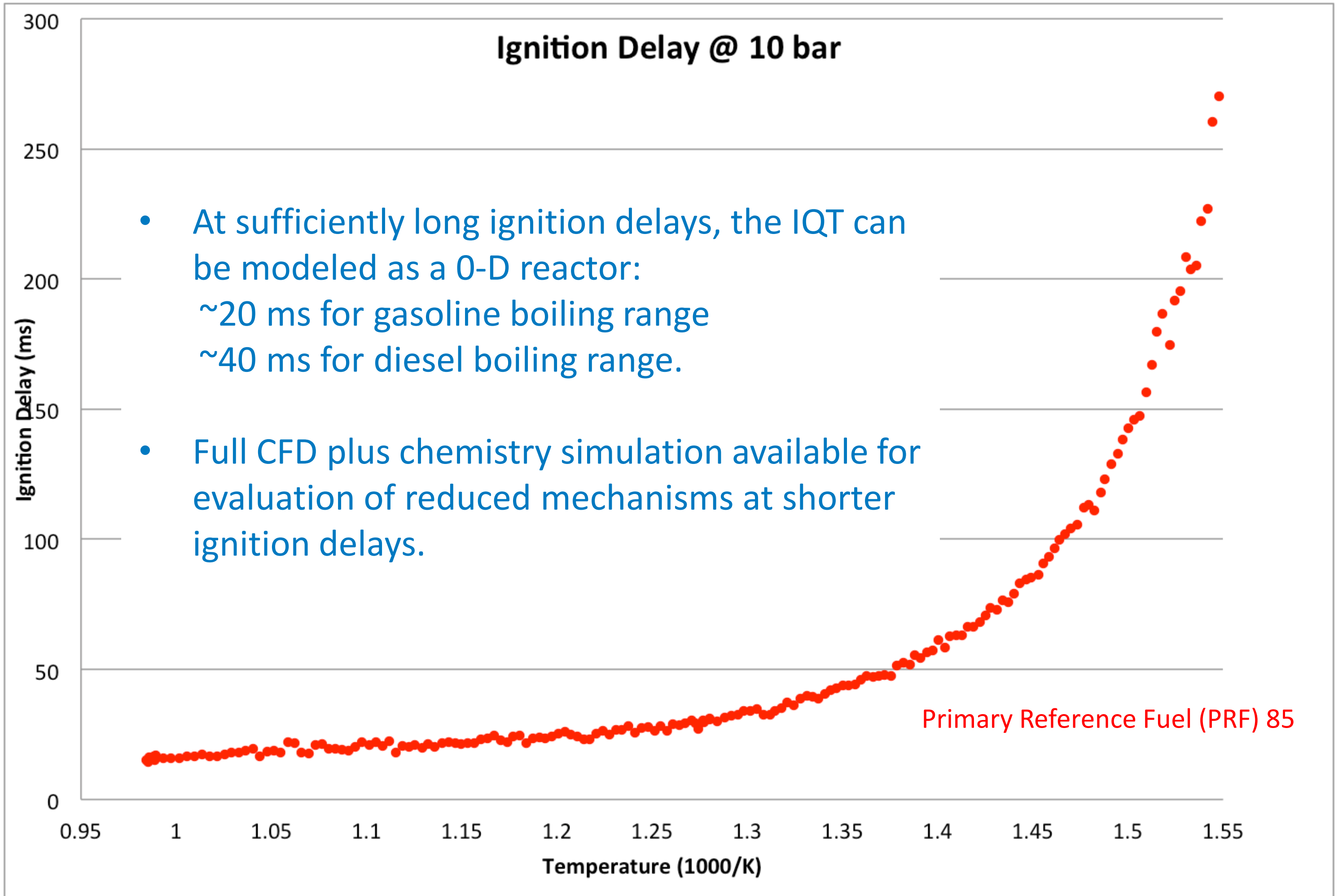
Technical Accomplishments: Kinetic Studies of Octane References



- Adapting the IQT to conduct gasoline range studies has been challenging at high temperatures and pressures, especially for complex blends.
- But long ignition delays further enable kinetics studies of gasoline range fuels in the IQT.

- Provide broad data for kinetic mechanism development.
- Complement research or motor octane numbers (RON, MON) with insight relevant to advanced spark ignition (SI) or low-temperature combustion (LTC) strategies.

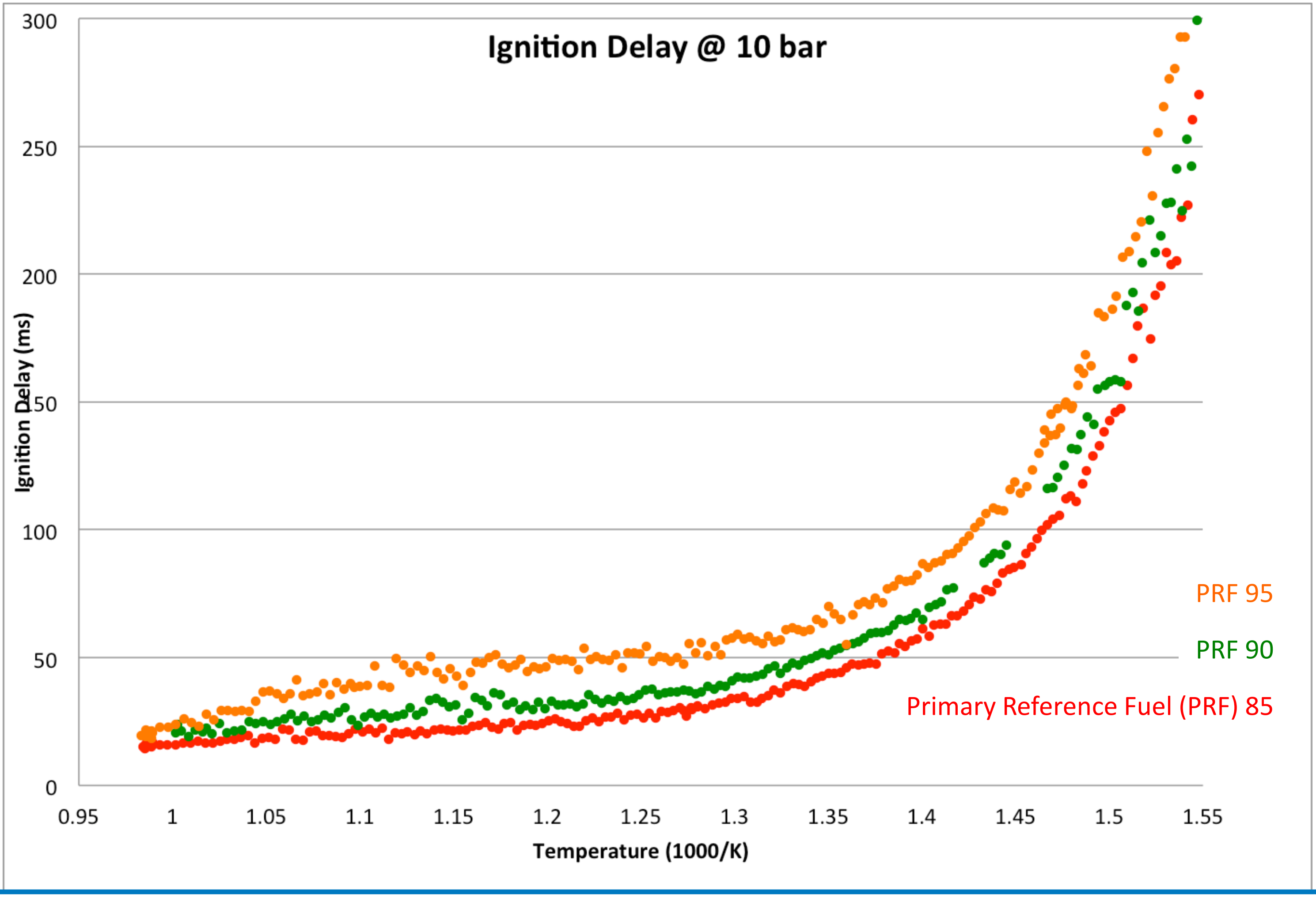
Technical Accomplishments: Kinetic Studies of Octane References



- At sufficiently long ignition delays, the IQT can be modeled as a 0-D reactor:
  ~20 ms for gasoline boiling range
  ~40 ms for diesel boiling range.
- Full CFD plus chemistry simulation available for evaluation of reduced mechanisms at shorter ignition delays.

- Provide broad data for kinetic mechanism development.
- Complement research or motor octane numbers (RON, MON) with insight relevant to advanced spark ignition (SI) or low-temperature combustion (LTC) strategies.

Technical Accomplishments:
Kinetic Studies of Octane References



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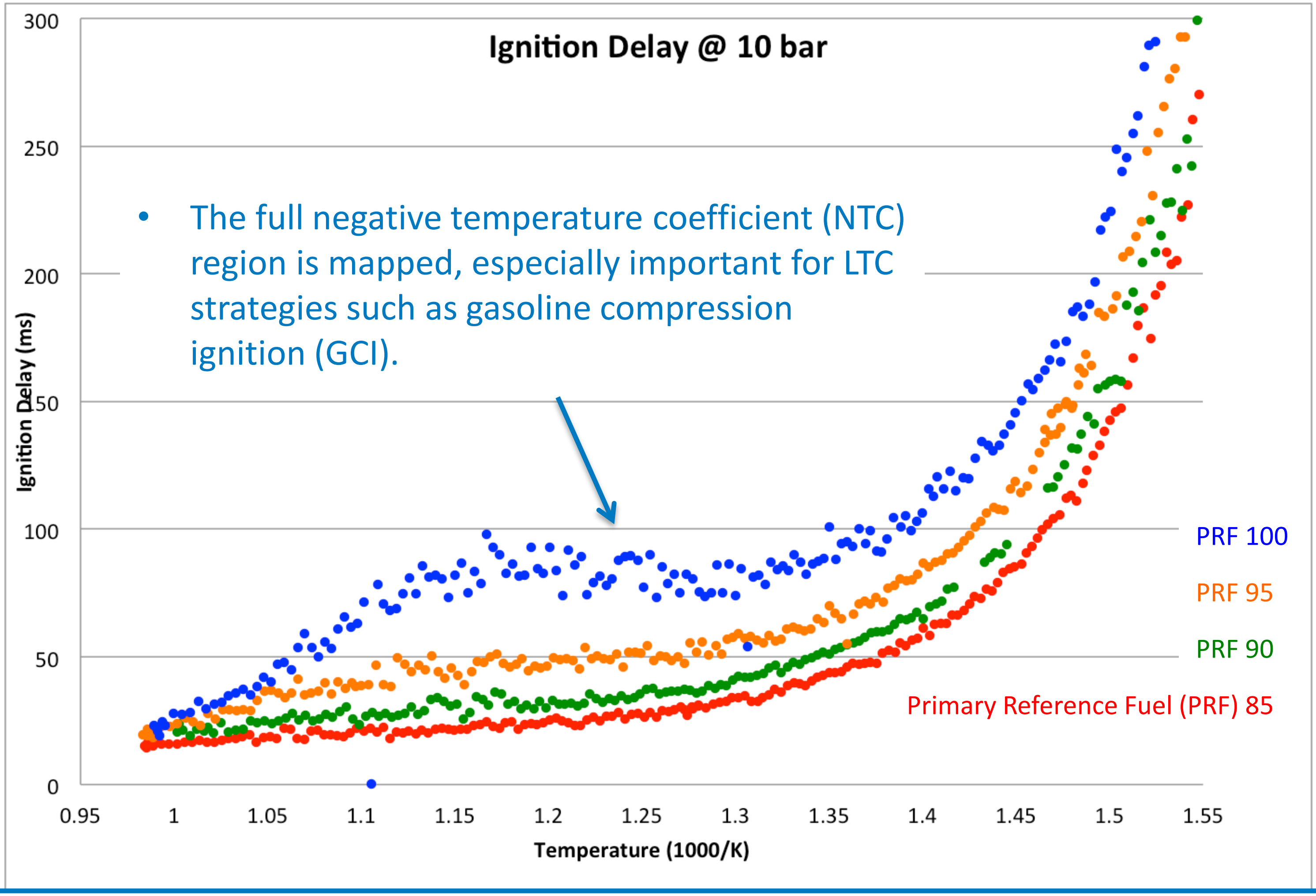

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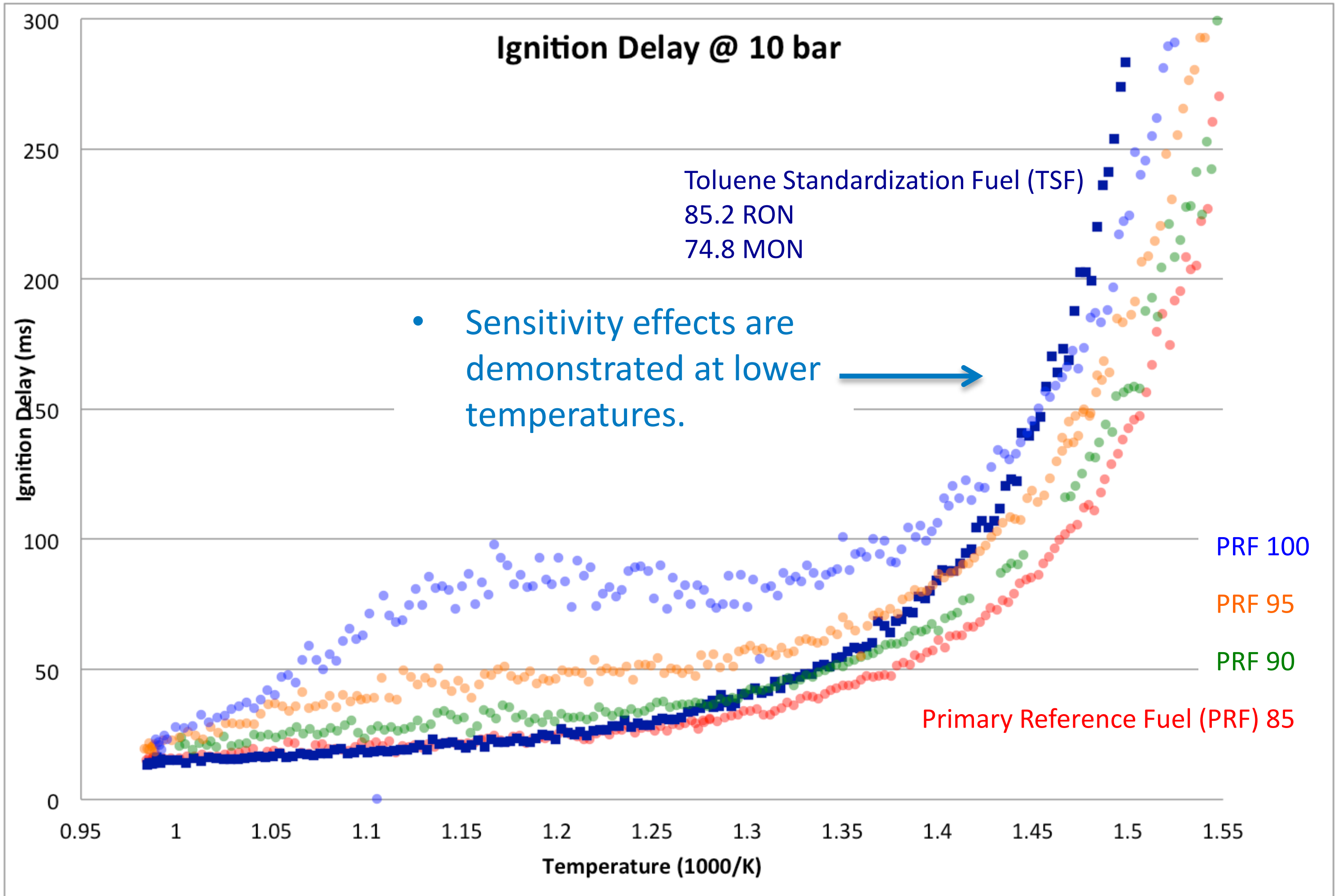

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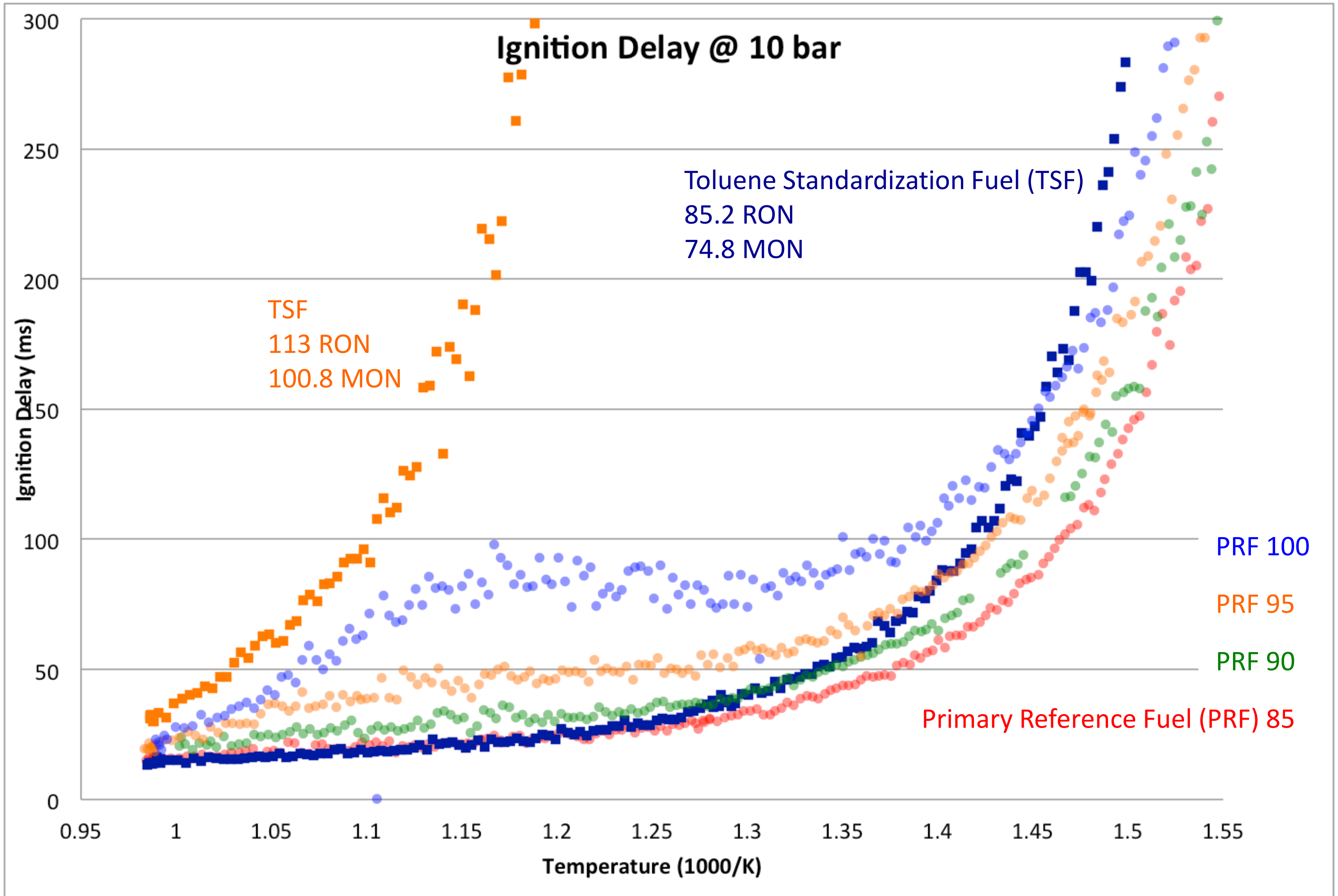

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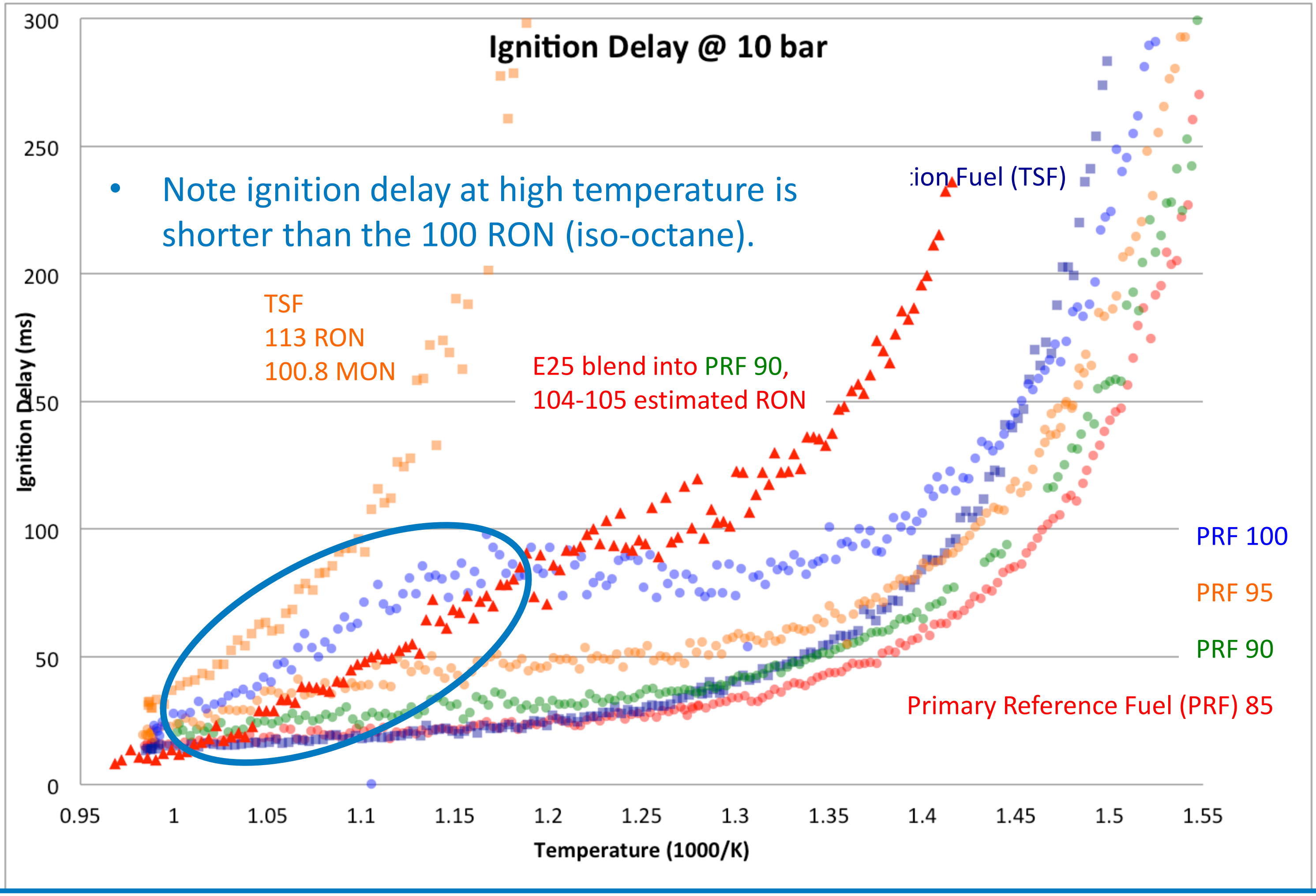

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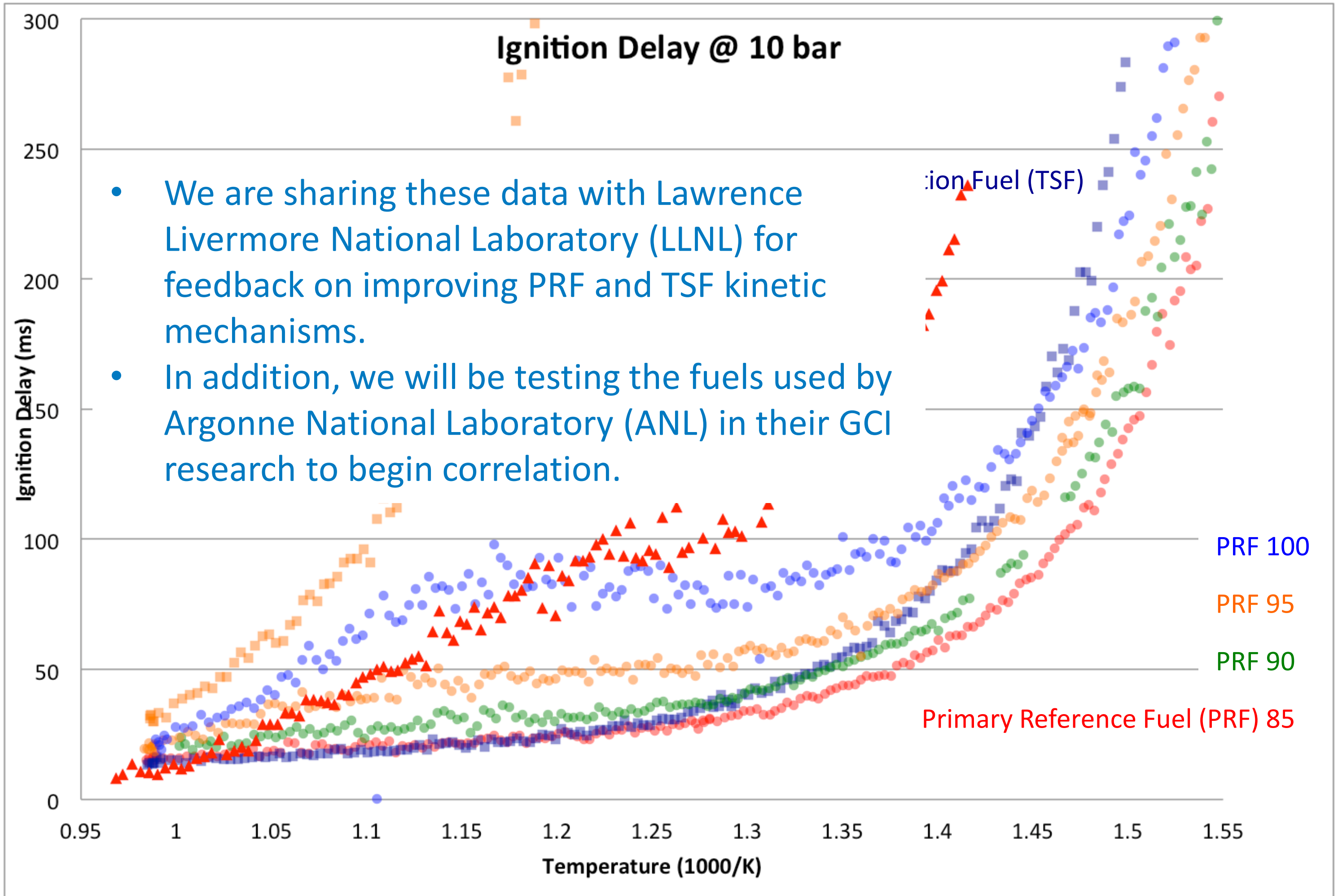
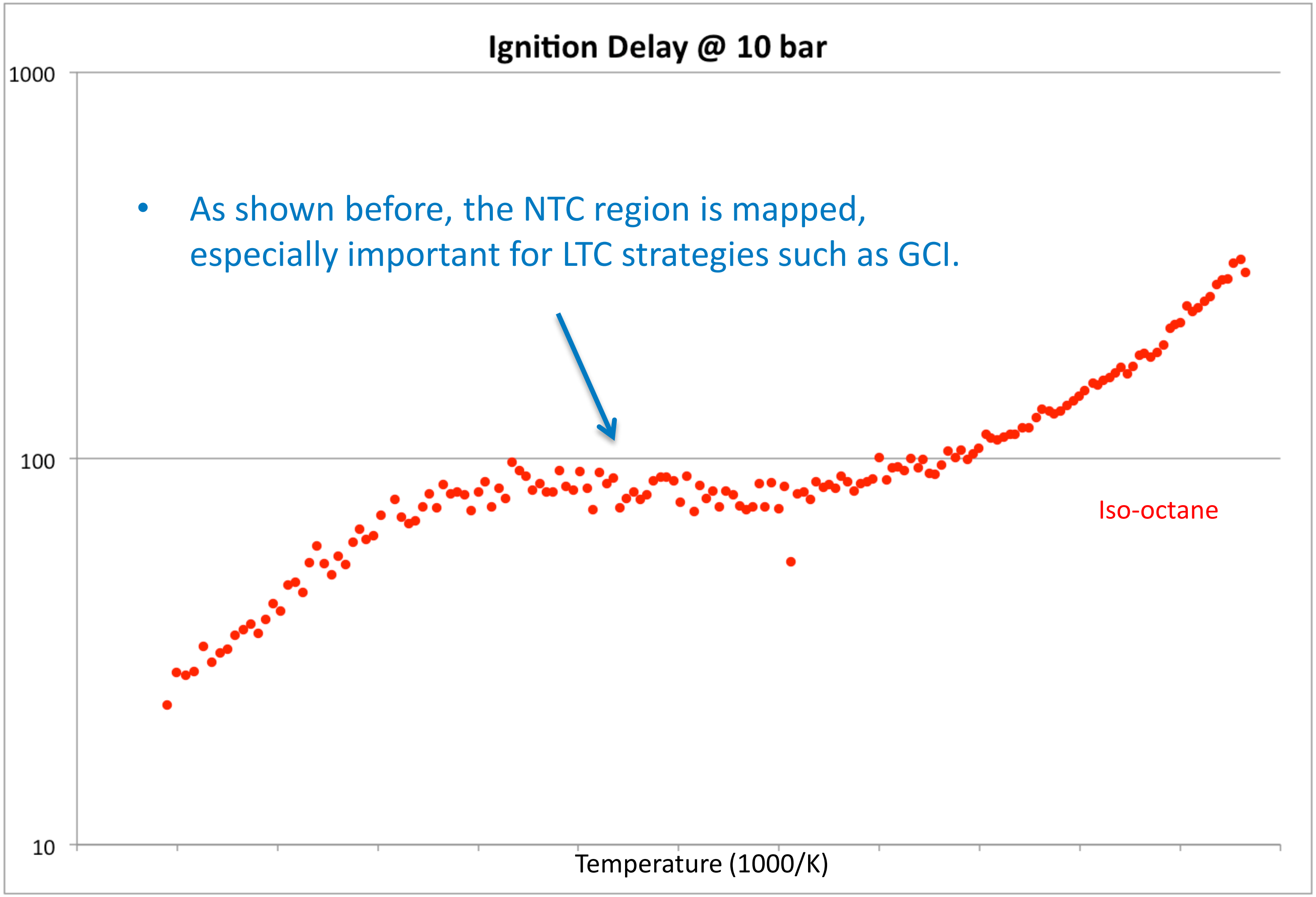


- We are sharing these data with Lawrence Livermore National Laboratory (LLNL) for feedback on improving PRF and TSF kinetic mechanisms.
- In addition, we will be testing the fuels used by Argonne National Laboratory (ANL) in their GCI research to begin correlation.

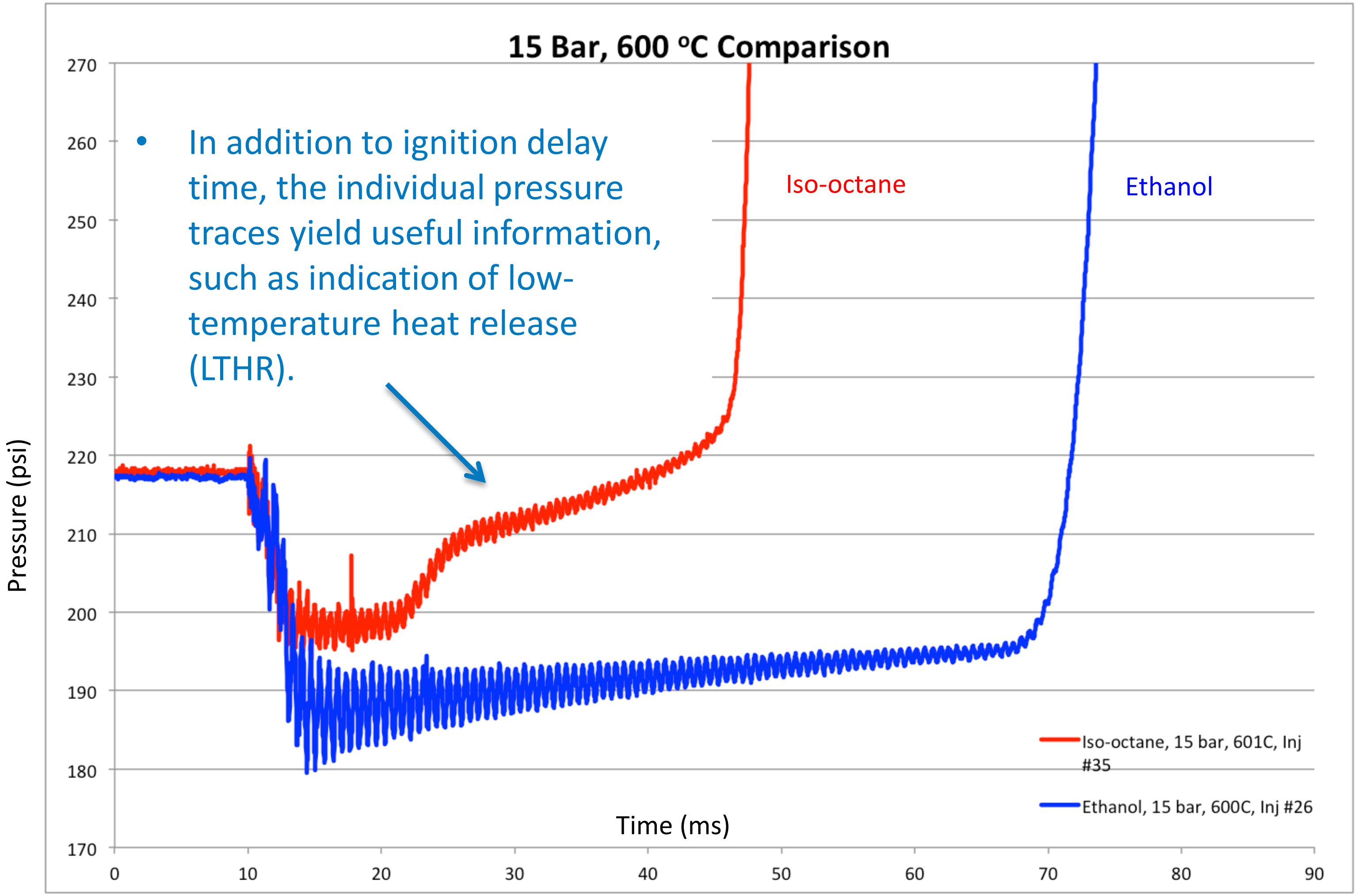
- Provide broad data for kinetic mechanism development.
- Complement research or motor octane numbers (RON, MON) with insight relevant to advanced spark ignition (SI) or low-temperature combustion (LTC) strategies.

Technical Accomplishments: Kinetic Studies of Ethanol Blends



- Provide broad data for kinetic mechanism development.
- Complement RON and MON with insight relevant to advanced SI or LTC strategies.

Technical Accomplishments:
Kinetic Studies of Ethanol Blends



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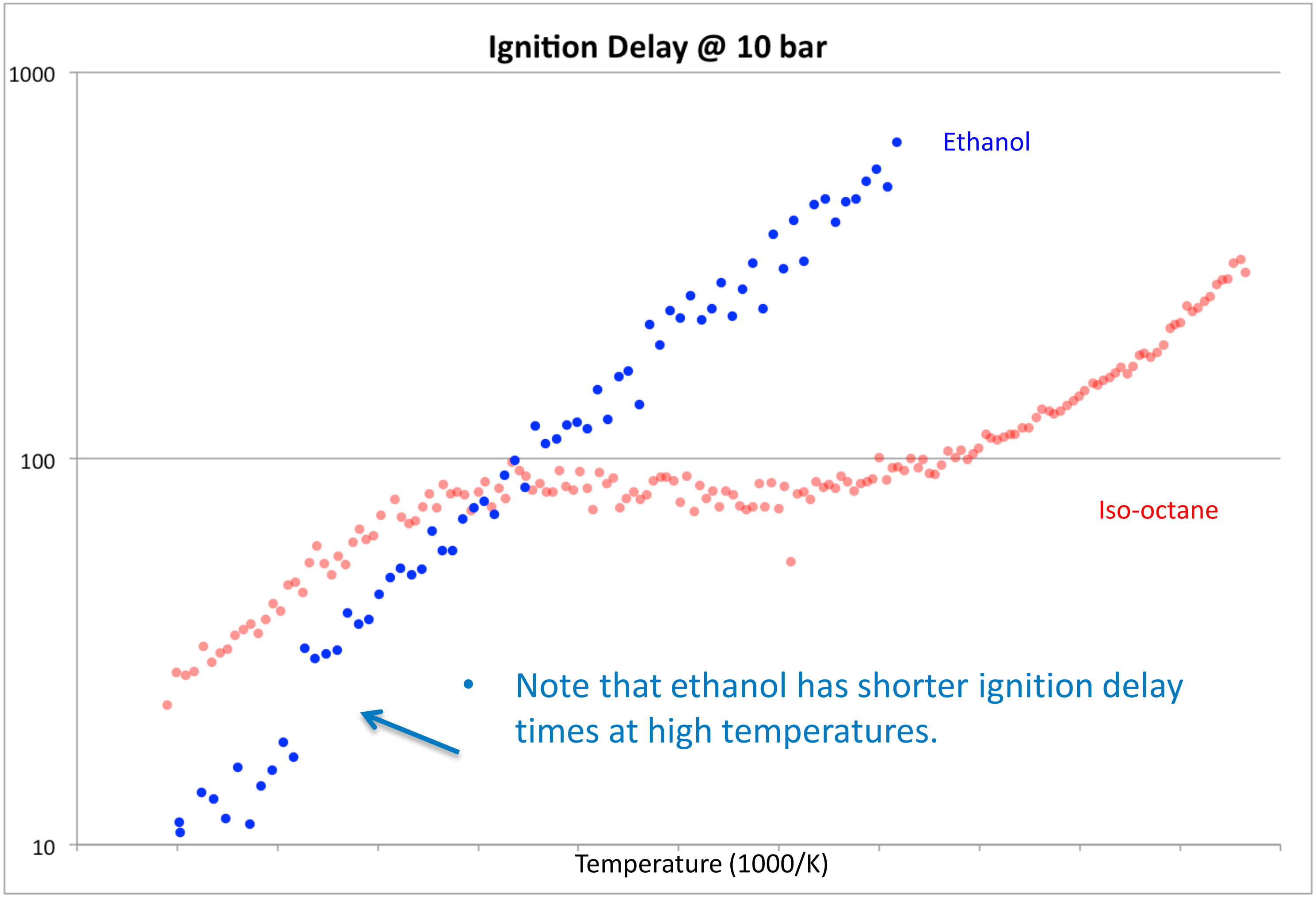
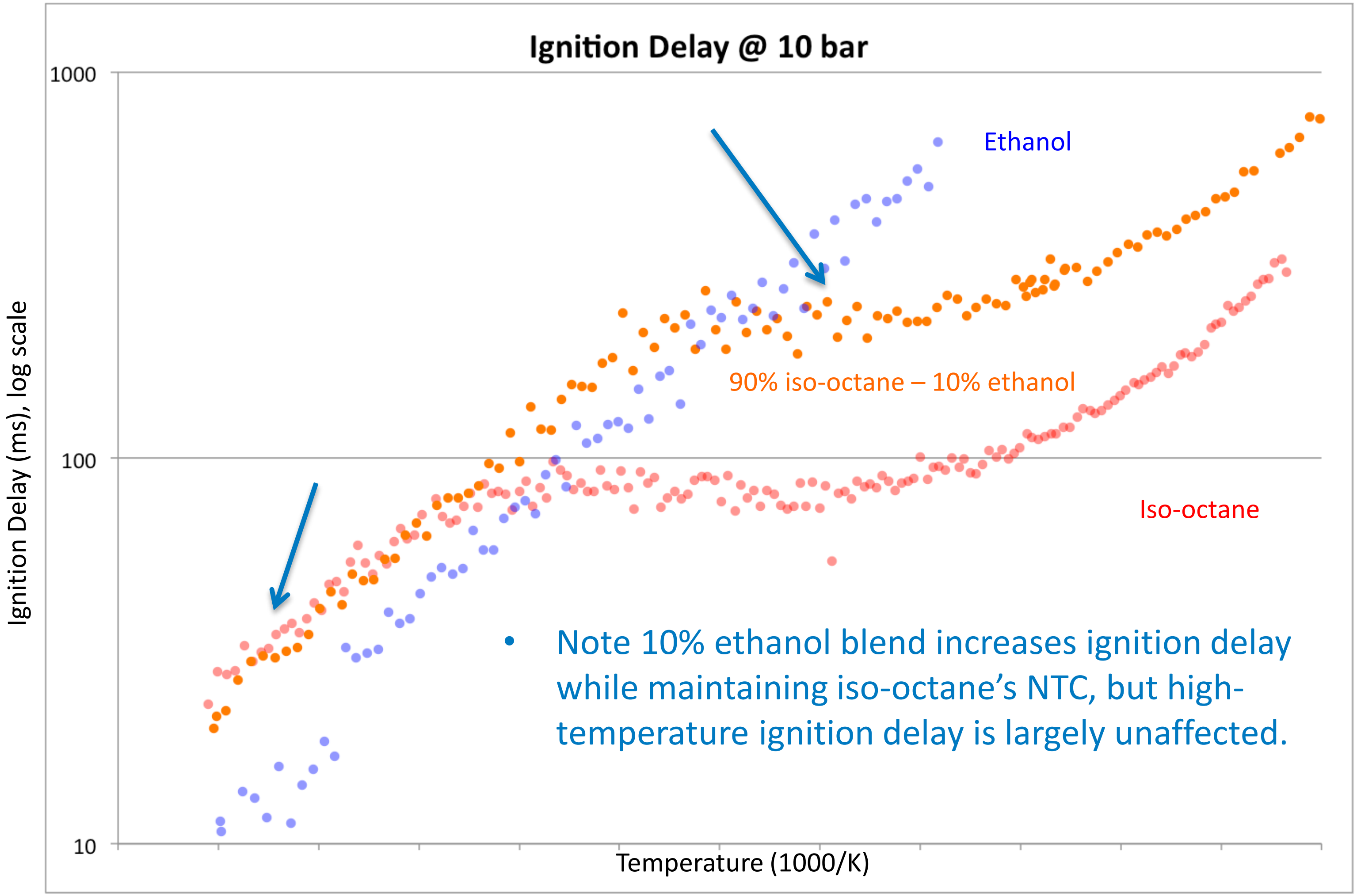


- Note that ethanol has shorter ignition delay times at high temperatures.

- Provide broad data for kinetic mechanism development.
- Complement RON and MON with insight relevant to advanced SI or LTC strategies.

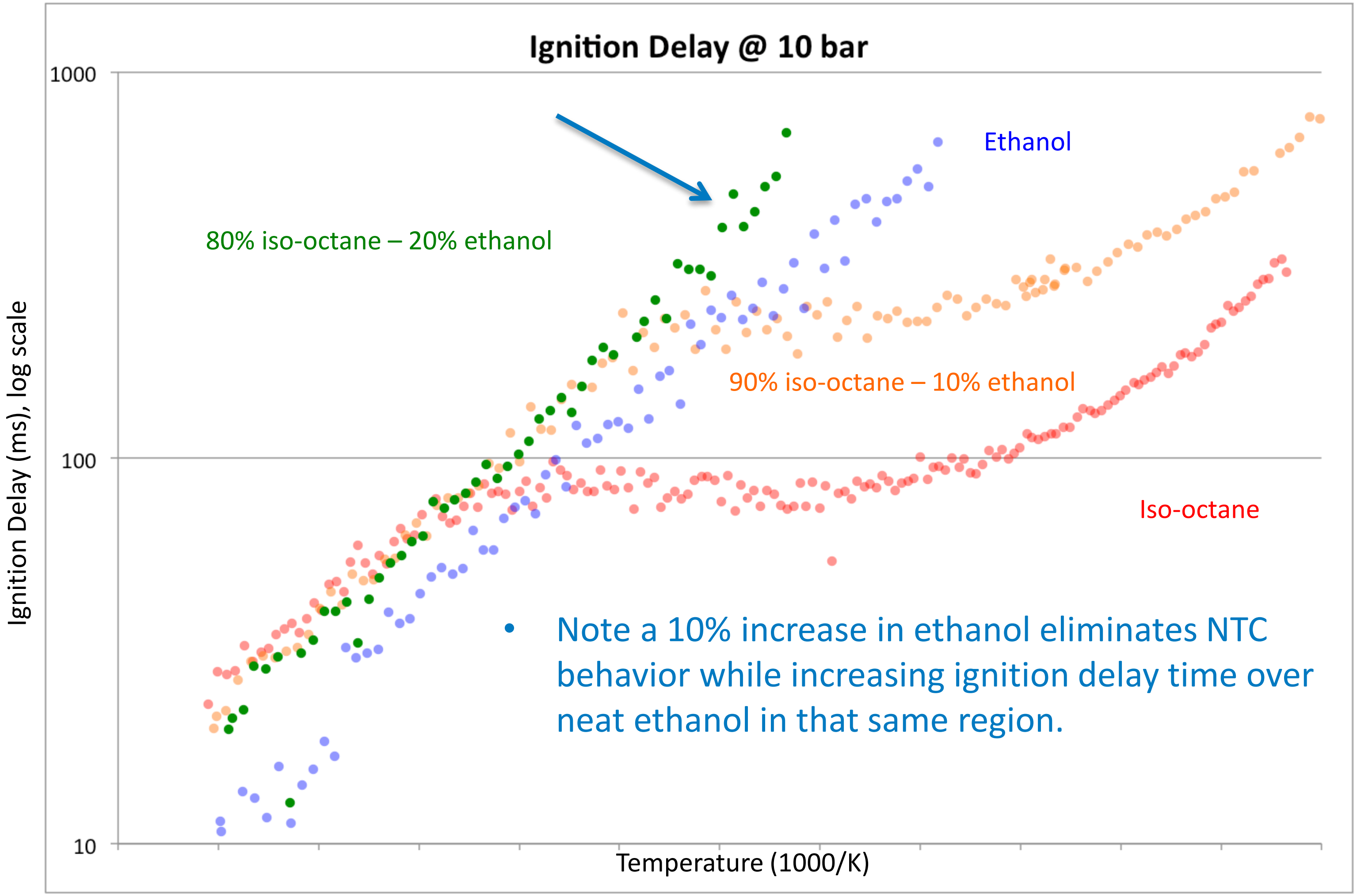
Technical Accomplishments:
Kinetic Studies of Ethanol Blends



- Note 10% ethanol blend increases ignition delay while maintaining iso-octane's NTC, but high-temperature ignition delay is largely unaffected.

- Provide broad data for kinetic mechanism development.
- Complement RON and MON with insight relevant to advanced SI or LTC strategies.

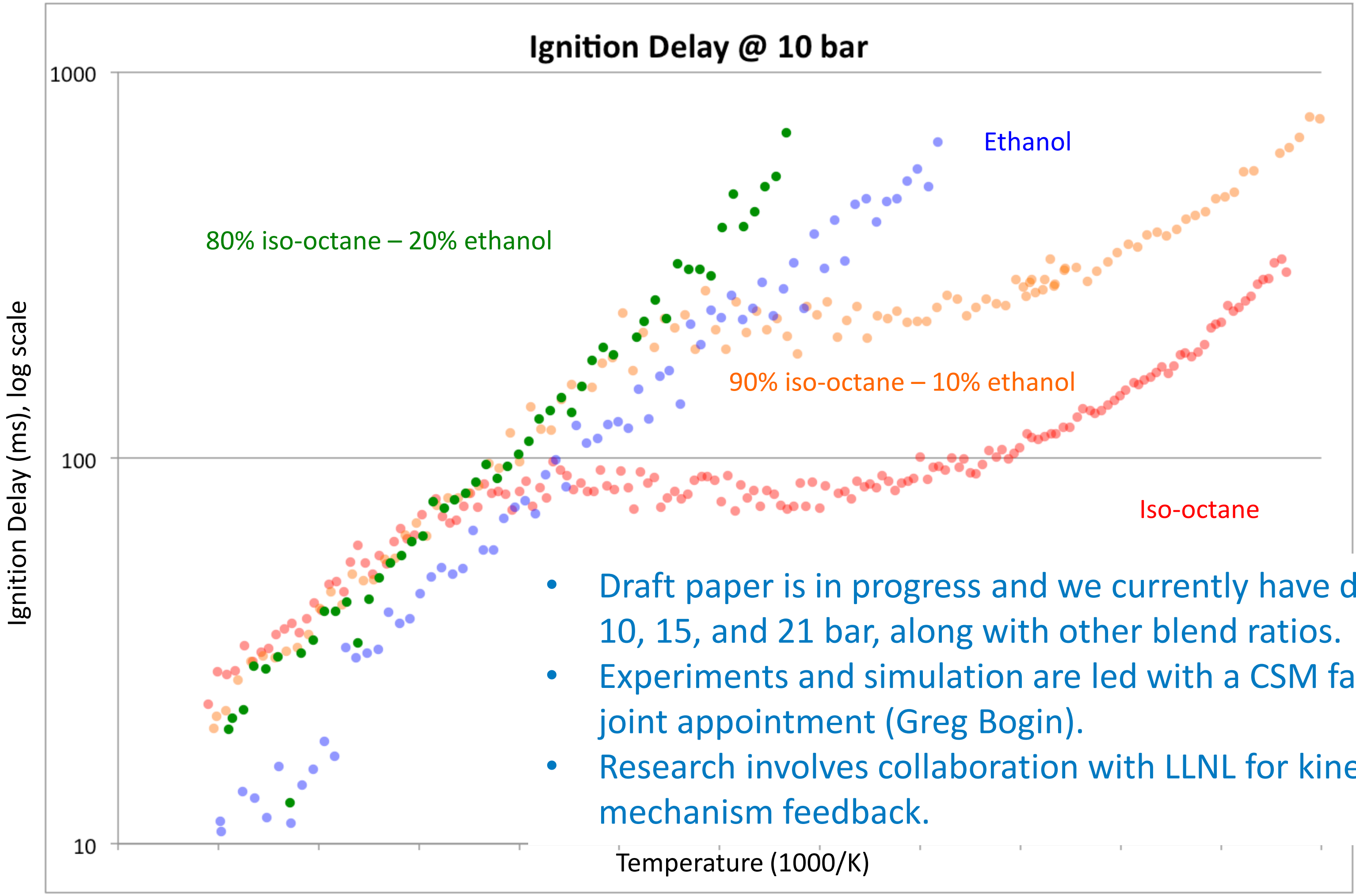
Technical Accomplishments: Kinetic Studies of Ethanol Blends



- Note a 10% increase in ethanol eliminates NTC behavior while increasing ignition delay time over neat ethanol in that same region.

- Provide broad data for kinetic mechanism development.
- Complement RON and MON with insight relevant to advanced SI or LTC strategies.

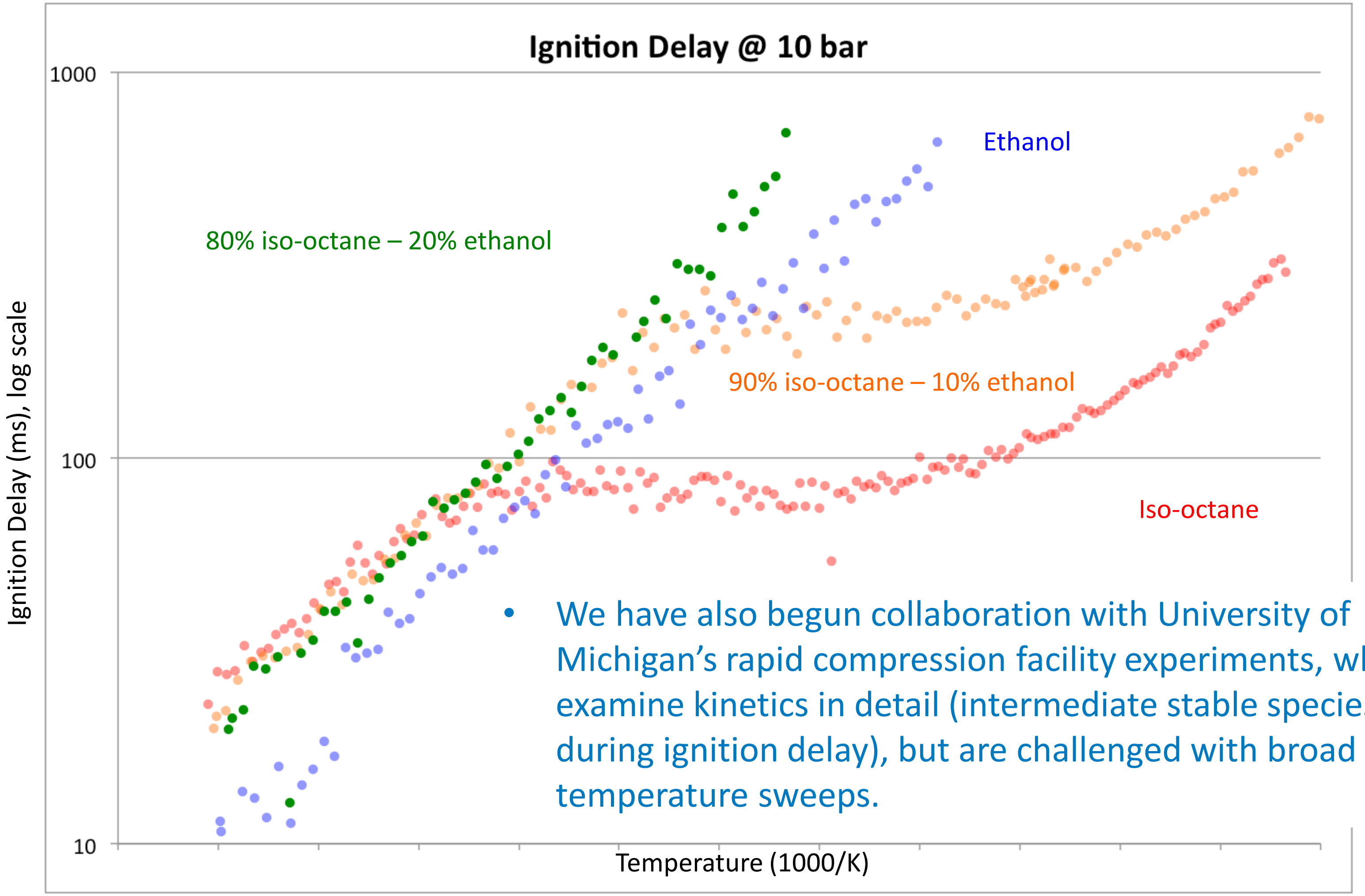
Technical Accomplishments:
Kinetic Studies of Ethanol Blends



- Draft paper is in progress and we currently have data for 5, 10, 15, and 21 bar, along with other blend ratios.
- Experiments and simulation are led with a CSM faculty joint appointment (Greg Bogin).
- Research involves collaboration with LLNL for kinetic mechanism feedback.

- Provide broad data for kinetic mechanism development.
- Complement RON and MON with insight relevant to advanced SI or LTC strategies.

Technical Accomplishments: Kinetic Studies of Ethanol Blends



- We have also begun collaboration with University of Michigan's rapid compression facility experiments, which examine kinetics in detail (intermediate stable species during ignition delay), but are challenged with broad temperature sweeps.

- Provide broad data for kinetic mechanism development.
- Complement RON and MON with insight relevant to advanced SI or LTC strategies.

Technical Accomplishments: Engine Studies for High Octane Fuels

- Single cylinder engine based on production General Motors 2.0L Ecotec turbo GDI "LNF" engine, which is also used in other DOE labs.
- Fuel injection system has upstream injection (UI) added that is temperature compensated to provide same inlet temperature conditions as direct injection (DI) operation, cancelling heat of vaporization (HoV) effects (like prior AVL and Ford research).

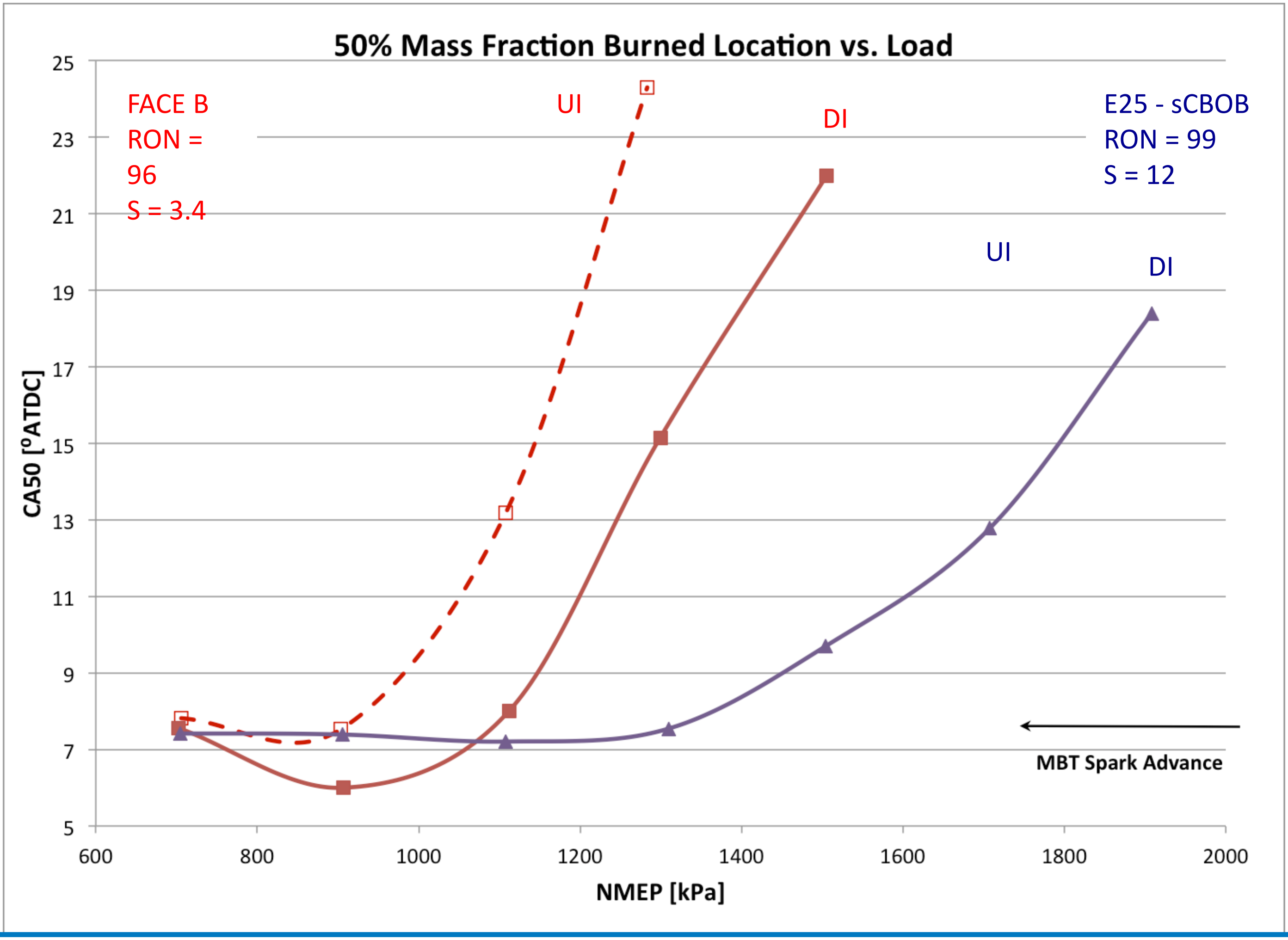
NREL photo 23595.jpg
Credit: Dennis Schroeder / NREL

NREL photo 22767.jpg
Credit: Dennis Schroeder / NREL

Technical Accomplishments: Engine Studies for High Octane Fuels

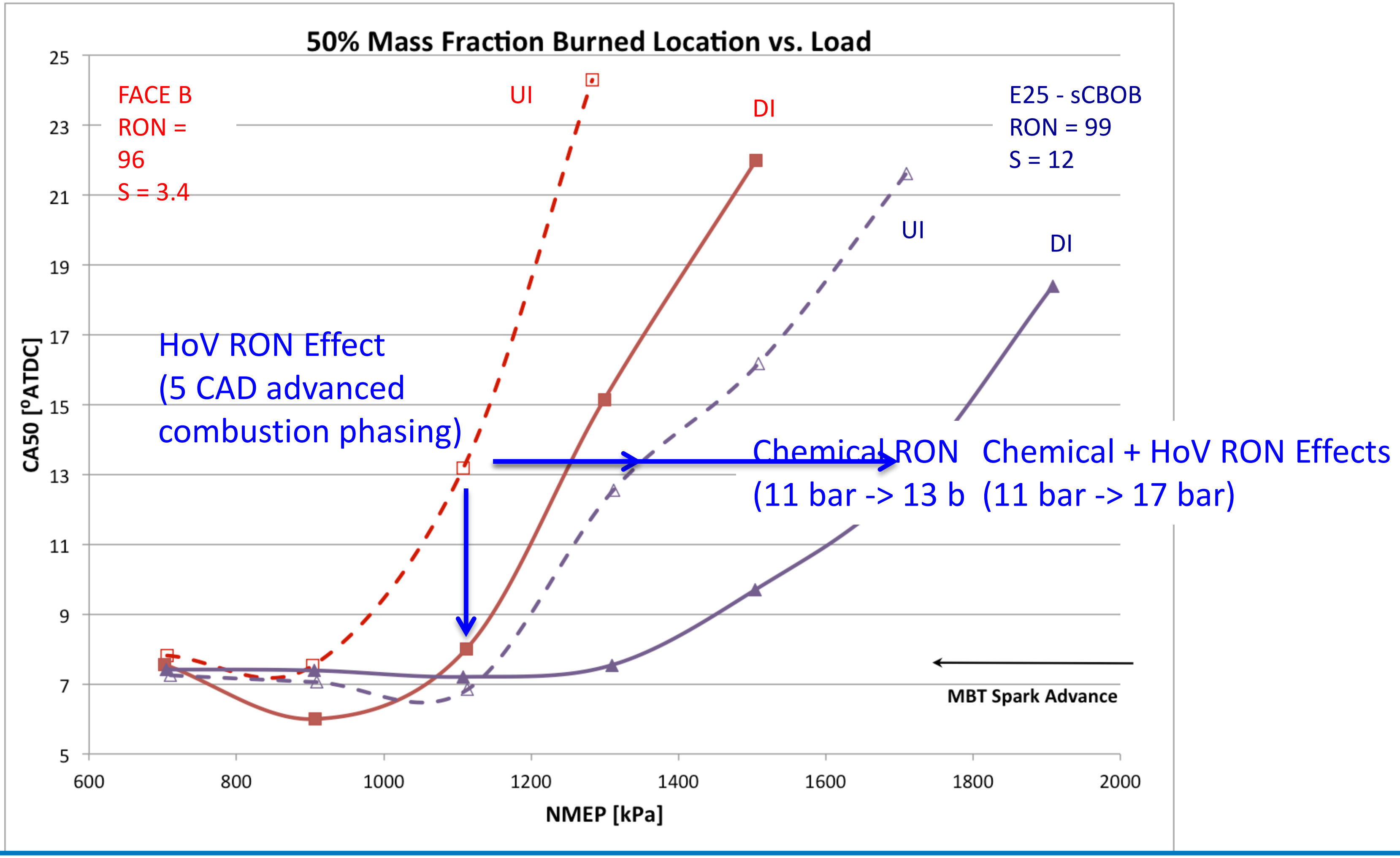
- Studying effects of the following fuel blending variables on load, combustion phasing, and efficiency:
  - RON
  - Sensitivity
  - HoV.
- Definitions for following slides:
  - ATDC = after top dead center
  - CA = crank angle
  - CAD = crank angle degree
  - DI = direct injection
  - FACE B = Fuels for Advanced Combustion Engines research gasoline “B”
  - MBT = minimum spark advance for best torque
  - NMEP = net mean effective pressure
  - S = sensitivity (RON-MON)
  - sCBOB = summertime conventional blendstock for oxygenated blending
  - UI = upstream injection.

Technical Accomplishments:
Engine Studies for High Octane Fuels



- Single cylinder engine fuel studies separate HoV and chemical octane effects, and indicate relative efficiency potential for alternative fuel blends.
- Links will be established with HoV measurements of blends and IQT-based studies.

Technical Accomplishments: Engine Studies for High Octane Fuels



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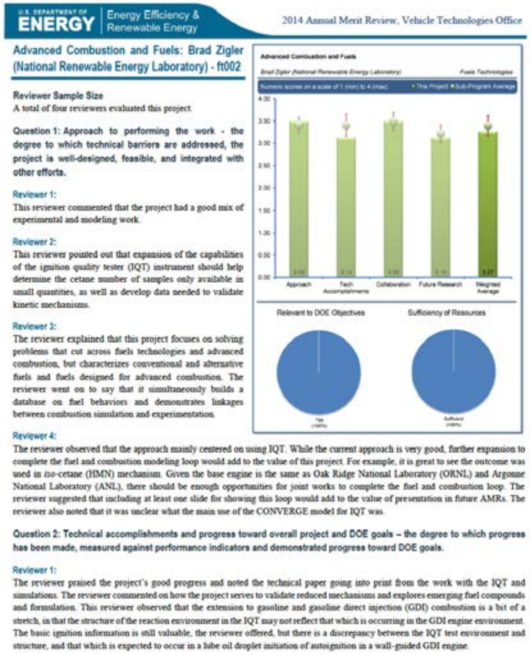
Responses to Previous Year Reviewers' Comments



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

2014 Annual Merit Review, Vehicle Technologies Office

Advanced Combustion and Fuels: Brad Zigler (National Renewable Energy Laboratory) - ft002

Reviewer Sample Size

A total of four reviewers evaluated this project.

Question 1: Approach to performing the work - the degree to which technical barriers are addressed, the project is well-designed, feasible, and integrated with other efforts.

Reviewer 1:

This reviewer commented that the project had a good mix of experimental and modeling work.

Reviewer 2:

This reviewer pointed out that expansion of the capabilities of the ignition quality tester (IQT) instrument should help determine the cetane number of samples only available in small quantities, as well as develop data needed to validate kinetic mechanisms.

Reviewer 3:

The reviewer explained that this project focuses on solving problems that cut across fuels technologies and advanced combustion, but characterizes conventional and alternative fuels and fuels designed for advanced combustion. The reviewer went on to say that it simultaneously builds a database on fuel behaviors and demonstrates linkages between combustion simulation and experimentation.

Reviewer 4:

The reviewer observed that the approach mainly centered on using IQT. While the current approach is very good, further expansion to complete the fuel and combustion modeling loop would add to the value of this project. For example, it is great to see the outcome was used in *iso*-cetane (HMN) mechanism. Given the base engine is the same as Oak Ridge National Laboratory (ORNL) and Argonne National Laboratory (ANL), there should be enough opportunities for joint works to complete the fuel and combustion loop. The reviewer suggested that including at least one slide for showing this loop would add to the value of presentation in future AMRs. The reviewer also noted that it was unclear what the main use of the CONVERGE model for IQT was.

Question 2: Technical accomplishments and progress toward overall project and DOE goals – the degree to which progress has been made, measured against performance indicators and demonstrated progress toward DOE goals.

Reviewer 1:

The reviewer praised the project's good progress and noted the technical paper going into print from the work with the IQT and simulations. The reviewer commented on how the project serves to validate reduced mechanisms and explores emerging fuel compounds and formulation. This reviewer observed that the extension to gasoline and gasoline direct injection (GDI) combustion is a bit of a stretch, in that the structure of the reaction environment in the IQT may not reflect that which is occurring in the GDI engine environment. The basic ignition information is still valuable, the reviewer offered, but there is a discrepancy between the IQT test environment and structure, and that which is expected to occur in a lube oil droplet initiation of autoignition in a wall-guided GDI engine.

The "reviewer observed that the extension to gasoline and gasoline direct injection (GDI) combustion is a bit of a stretch, in that the structure of the reaction environment in the IQT may not reflect that which is occurring in the GDI engine environment." *– We agree that adapting the IQT to study gasoline range has been challenging. But as the conditions become more homogeneous with long ignition delay times, the IQT has produced unique data for kinetic mechanism development. And these complementary data may provide significantly more insight than octane numbers alone.*

The reviewer stated: "results from this project help to develop reduced order chemical kinetic mechanisms and also develop low-order models of ignition delay for combustion control applications. Given that the current focus of internal combustion engine (ICE) program on low-temperature combustion (LTC) engines, it is necessary to ensure that IQT testing covers all the fuels which have been exploited in LTC engine studies." *– We have met with Steve Ciatti and planned IQT testing of fuels used in ANL's GCI research. This early stage correlation of our IQT data to LTC engine data, as well as our own GDI engine data, will direct how the IQT data may serve in predictive modeling. These efforts will involve collaboration with ANL and LLNL, and industry collaboration is welcome.*

Collaboration and Coordination with Other Institutions

- **Colorado School of Mines**
  - Sponsorship of Professor Greg Bogin's joint appointment at NREL supporting fuel ignition research
  - Sponsorship of Eric Osecky's post-doctoral research supporting IQT-based simulation and kinetic mechanism development
  - Sponsorship of Research Professor Stephanie Villano's joint appointment at NREL supporting *ab initio* kinetic mechanism development.
- **University of California–Berkeley**
  - Collaboration with Professor J. Y. Chen on IQT-based simulation, experiments, and validation of reduced hexadecane mechanism.
- **Lawrence Livermore National Laboratory**
  - Collaboration with Bill Pitz, Marco Mehl, and Charlie Westbrook on important surrogates and compounds, including ethanol blends in primary reference fuels.
- **Argonne National Laboratory**
  - Collaboration with Sibendu Som on experiments and simulation of biodiesel surrogate blends
  - New collaboration with Steve Ciatti on fuel studies complementing GCI research.
- **University of Michigan**
  - New collaboration with Margaret Wooldridge and Cesar Barraza-Botet on ethanol kinetics experiments.

Collaboration and Coordination with Other Institutions

- **Coordinating Research Council**
  - Co-development of advanced diesel surrogates with accurate compositional, ignition-quality, and volatility characteristics (AVFL-18a project, see Mueller, Project # FT004).
- **Advanced Engine Combustion – MOU**
  - Ten engine original equipment manufacturers (OEMs)
  - Five energy companies
  - Six DOE national laboratories
  - DOE-funded universities also participate by invitation.
- **DOE Office of Science – Science Undergraduate Laboratory Internship (SULI) Program**
  - Hosting of Drew Cameron (Seattle University) for IQT-based ignition studies.

Remaining Challenges and Barriers

- **Fuels and lubes ignition studies**
  - The IQT "ignition delay" incorporates both spray physics and ignition kinetics. Operating in regimes where the physical delay fraction is only a small portion of the ignition delay time has been a challenge. This bounds experimental space where IQT data are of value. A new fuel injection system (or other device, such as the Fuel Ignition Tester) may help.
  - How can we provide ignition performance screening feedback with even smaller quantities, becoming part of a transformative feedback loop to biofuel development?
  - Correlating the IQT data to GDI and LTC (including GCI) engine data is challenging, but offers unique, complementary insight.
- **Single-cylinder GDI engine studies on advanced biofuels**
  - The studies underway must complement past AVL/Ford work on ethanol as well as Oak Ridge National Laboratory (ORNL) studies, but expand to other advanced biofuels.
  - Can we provide enough guidance for potential efficiency gains with load and spark timing sweeps with the current production compression ratio?
  - How do we correlate complementary IQT data in a meaningful way?

Proposed Future Work

- **Fuels and lubes ignition studies**
  - Provide additional data and feedback for key gasoline range surrogates, octane references, oxygenates, and blends to refine kinetic mechanisms.
  - Propose parametric bench-scale "ratings" to complement RON and MON.
  - Develop capability to measure relevant ignition properties of novel compounds with extremely small samples (on the µL scale).
  - Use IQT-based fuel effects studies to complement ANL's GCI research.
  - Use IQT as complementary tool to provide guidance for lubricant formulations and high boiling point fractions to suppress LSPI.
- **Single-cylinder GDI engine studies on advanced biofuels**
  - Build on knowledge gained for key compounds from Bob McCormick's Advanced Biofuels research area.
  - Coordinate research with ORNL to ensure projects are complementary.
  - Continue focus on physico-chemical effects that may be leveraged to increase efficiency.
  - Identify and quantify effects not captured with current methods, specifically due to heat of vaporization.
  - Tie together with IQT-based studies.

Summary

Objective: Address technical barriers of inadequate data and predictive tools for fuel and lubricant effects on advanced combustion engines.

- Guidance from past Annual Merit Reviews (AMRs) and other forums (AEC – MOU) has improved quality and guided focus for this research activity.
- IQT-based research involves several collaborations to address data voids, provide feedback for mechanism development, and enable simultaneous development of advanced fuels and advanced engine combustion.
- Engine-based research complements industry and other DOE labs, with focus on fuel effects versus engine combustion process development.
- Linking of IQT- and engine-based research is in progress to yield additional insights.

Through collaboration, develop techniques, tools, and data to quantify critical fuel chemistry effects to enable development of advanced combustion engines that use alternative fuels.

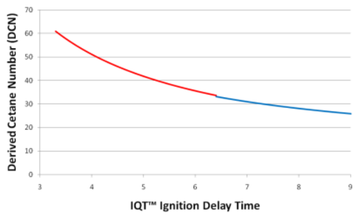
Acknowledgements

- Kevin Stork – DOE Vehicle Technologies Office
- Jon Luecke, Matt Ratcliff, Jon Burton, and Petr Sindler – NREL
- Greg Bogin and Eric Osecky – Colorado School of Mines
- Drew Cameron – Seattle University
- DOE lab colleagues and other collaborators

Technical Back-Up Slides

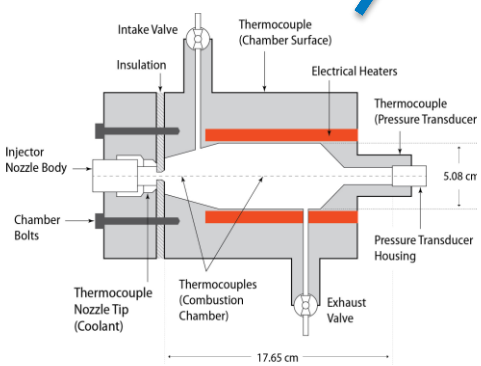
Past Technical Accomplishments and Progress

DCN

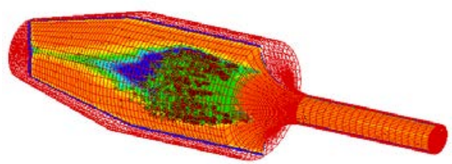


8-point parametric studies

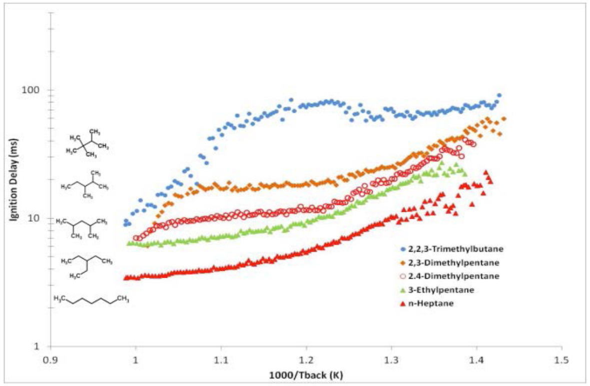
$$Rate = \frac{1}{\text{ignition delay}} = A \cdot \exp\left[\frac{E_a}{RT}\right] \cdot [O_2]^{b}$$



Simulation



Temperature sweeps



IQT has been developed as a research tool to:

- Determine DCN given very limited volumes (~25 mL) of new fuel components or complex blends for early-stage fuel screening feedback.
- Determine Arrhenius parameters given small volumes for initial simulation work.
- Complement rapid compression machine (RCM) and shock tube data voids.
- Provide valuable data/feedback loop to assist kinetic mechanism development.