Co-Optimization of Fuels & Engines

The development of yield-based sooting tendency measurements and modeling to enable advanced combustion fuels (Co-optima)

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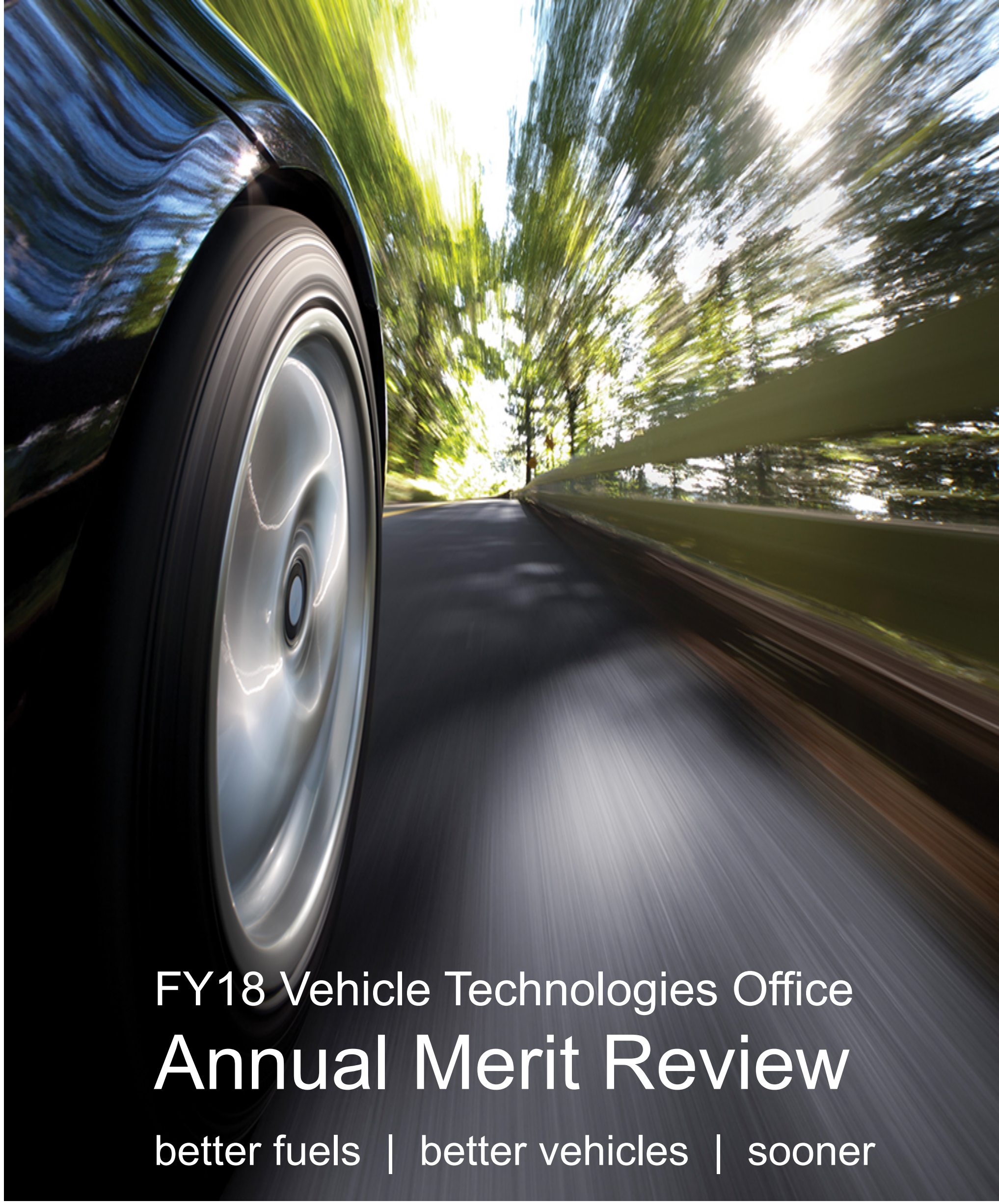


FY18 Vehicle Technologies Office
Annual Merit Review
better fuels | better vehicles | sooner

Overview

Timeline

- Project start date: 1 May 2017
- Project end date: 30 April 2020
- Percent complete: 30%

Barriers

- IC engines must meet particle emissions standards
- Effects of fuel composition on emissions is poorly understood

Budget

- Total project funding: $1,452,787
    - DOE share: $1,307,505
    - Contractor share: $145,282

Partners

- Predictive YSI model – Seonah Kim, Peter St. John (NREL)
- Fuel samples – Magnus Sjöberg (Sandia), Tim Bays (PNNL), Co-optima HPF team
- Kinetic mechanisms – Bill Pitz (LLNL), Bill Green (MIT)

Relevance

- **Project Objective 1** – develop a database of measured sooting tendencies (YSIs) for hydrocarbons identified by Co-optima as promising biomass-derived fuel blendstocks
- ”sooting tendency” = measure of intrinsic propensity of a fuel to form soot due to its chemical structure

Data to support early-stage screening of potential blendstocks – identify the blendstocks that provide the easiest path to meeting particulate emissions standards

Relevance

- **Project Objective 2** – formulate emissions indices that predict particulates output from specific engine types (GDI, MCCI, etc.) based on YSI and other relevant fuel properties (P_v for GDI, CN for MCCI, etc.)

Tool to quantitatively predict emissions reduction benefits of proposed blendstocks

Relevance

- **Project Objective 3** – simulate the measured YSIs using detailed chemical kinetic mechanisms
- Test the ability of mechanisms to predict soot formation and suggest improvements based on reaction pathway analysis

Deliver a set of validated mechanisms that can be used in CFD simulations to optimize engine design for low emissions

Milestones

Month / Year	Description of Milestone or Go/No-Go Decision	Status
July 2017	Second YSI apparatus assembled	Completed
Oct 2017	15+ YSI measurements	Completed
Jan 2018	Initial 2D simulation completed	Completed
April 2018	50+ YSI measurements	Completed

Approach – Yield Sooting Index

Yield Sooting Index (YSI) = novel measure of sooting tendency based on soot production in a fuel-doped methane/air flame

$YSI_i = A*M_i + B$

$YSI_{n\text{-heptane}} = 36.0$ (1)

$YSI_{toluene} = 170.9$ (2)

M_i: Measured maximum concentration of soot in flame doped with species i

A and B: Apparatus-dependent constants chosen to satisfy (1) and (2)

- 100 microliter sample volume
- High measurement throughput
- Measured values can be computationally simulated

Flame Conditions for YSI Measurements

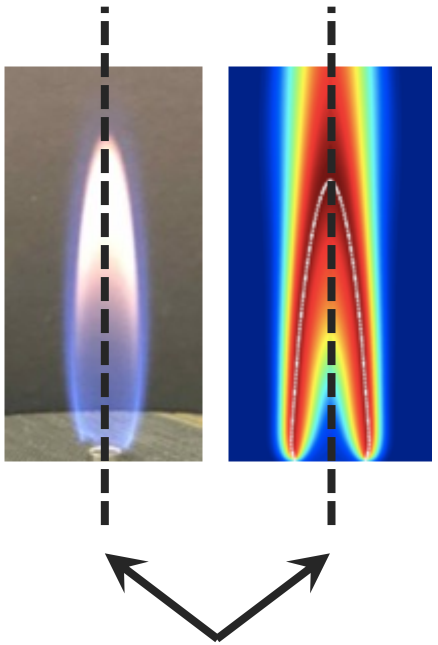
Dopant	1000 ppm
CH_4	~70% by mole
N_2	Balance
Total	~470 cc/min

Approach – Simulations

Measured YSI data can be easily simulated with perturbation approach

- Perform one 2D simulation of the base flame
- 1000 ppm of dopant does not change the overall flame structure
- Use the 2D results to account for the effects of radial transport in the doped flames without explicitly calculating them
- Simulate the doped flames with 1D calculations along the flame centerline

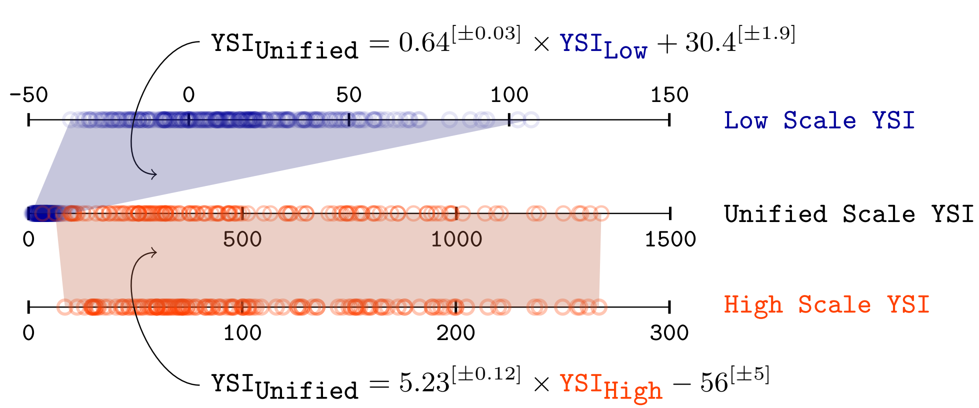
○ Simulation of smoke point data requires a series of full 2D simulations at varying fuel flowrates

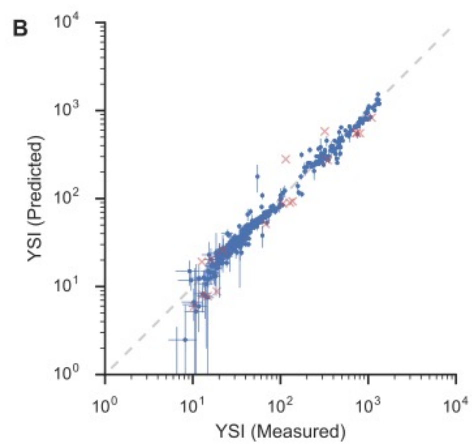


Technical Accomplishments and Progress

Developed a comprehensive YSI database for fuel hydrocarbons

- Measurements from 4 previous publications combined onto a single scale
- **The database contains over 400 compounds, including alkanes, isoalkanes, naphthenes, alkanes, aromatics, naphthalenes, alcohols, ethers, and esters**
- The database is permanently available to all stakeholders via the Harvard Dataverse: https://doi.org/10.7910/DVN/7HGFT8
- **Database was the basis for a machine learning model that can predict YSI for new hydrocarbons (collaboration with Peter St. John, NREL)**
- This model is actively being used by the HPF team for screening new blendstocks



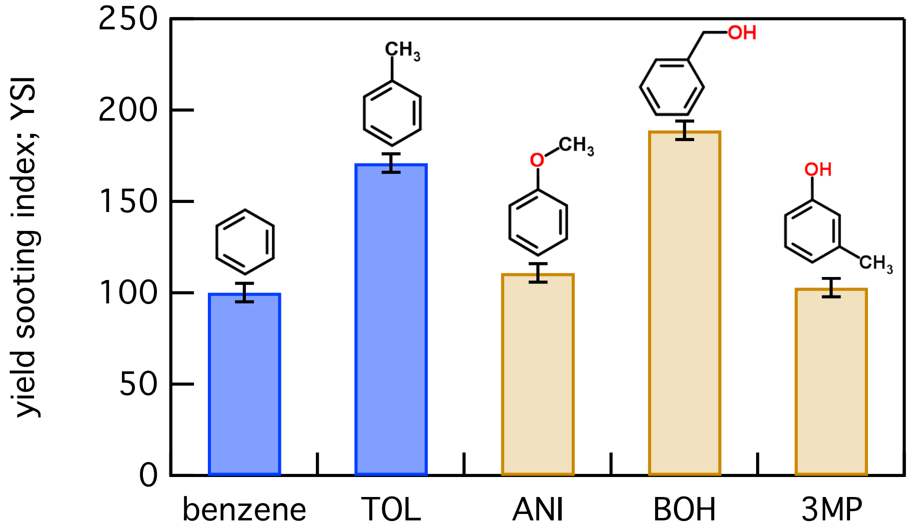


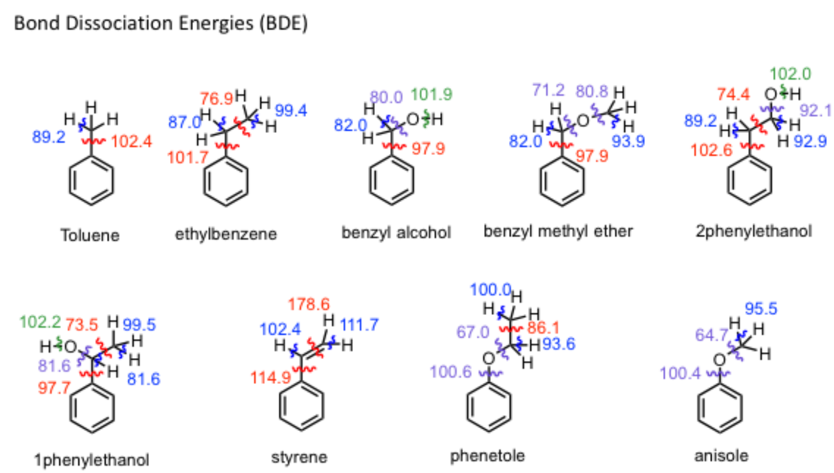
D.D. Das, P.C. St. John, C.S. McEnally, S. Kim, L.D. Pfefferle, "Measuring and predicting sooting tendencies of oxygenates, alkanes, alkenes, cycloalkanes, and aromatics on a unified scale", *Combustion and Flame*, 2018, 190:349-364.

Technical Accomplishments and Progress

Measured YSIs of aromatic hydrocarbons with oxygenated side-chains

- Results so far for 15 oxygenated aromatics and 4 related hydrocarbons
- **Oxygen can significantly reduce the sooting tendency of aromatic hydrocarbons, but the effects depend on the specific chemical form of the oxygen**
- Chemical pathways that explain the results were identified using DFT bond dissociation energies (collaboration with Seonah Kim, NREL)
- Simulations of the measured YSIs using kinetic mechanism developed within C-optima are ongoing (collaboration with Bill Pitz, LLNL and Bill Green, MIT)



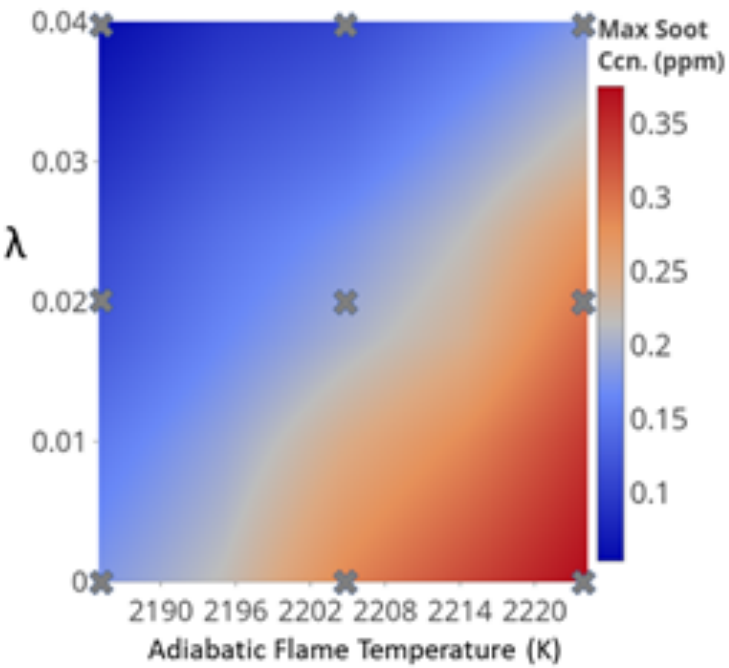


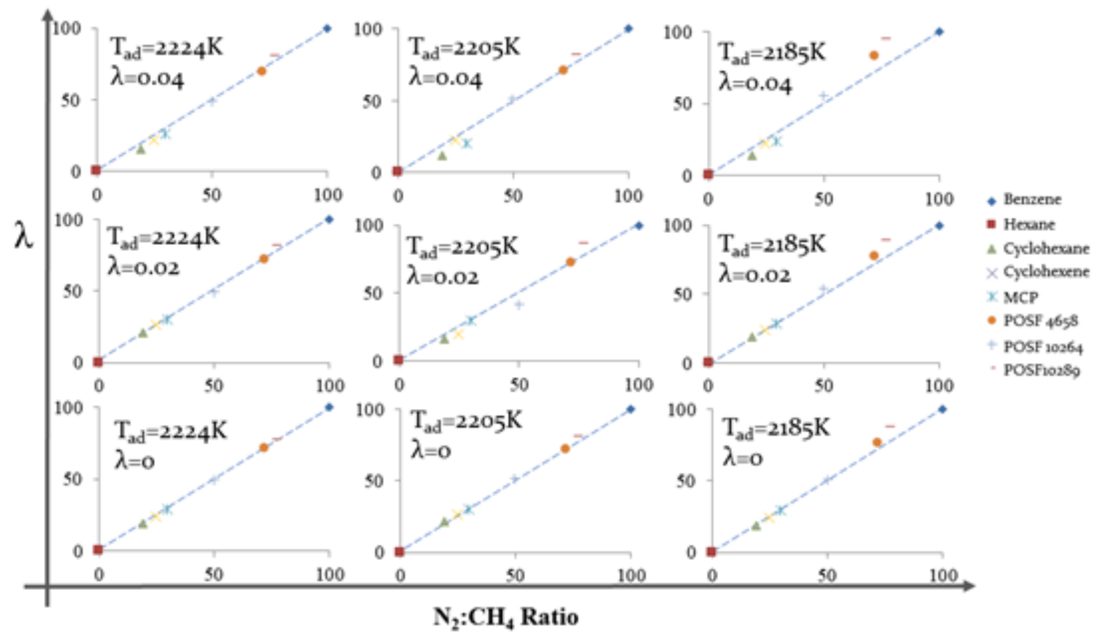
B.P. Beekley, C.S. McEnally, P.C. St. John, S. Kim, A. Jain, H. Kwon, Y. Xuan, L.D. Pfefferle, "Sooting Tendencies of Aromatic Hydrocarbons with Oxygen-Containing Side-Chains," Presented at 2018 Spring ESSCI Meeting, https://doi.org/10.6084/m9.figshare.5993527.v1

Technical Accomplishments and Progress

Determined that YSI is insensitive to temperature and air/fuel ratio

- Measurements verified that soot concentrations go down when flame temperature decreases or primary air/fuel ratio increases
- However, these changes are similar for all dopants, so YSIs are not affected
- **Demonstrated that larger value of YSI corresponds to larger soot formation over wide range of temperature and air/fuel ratio**

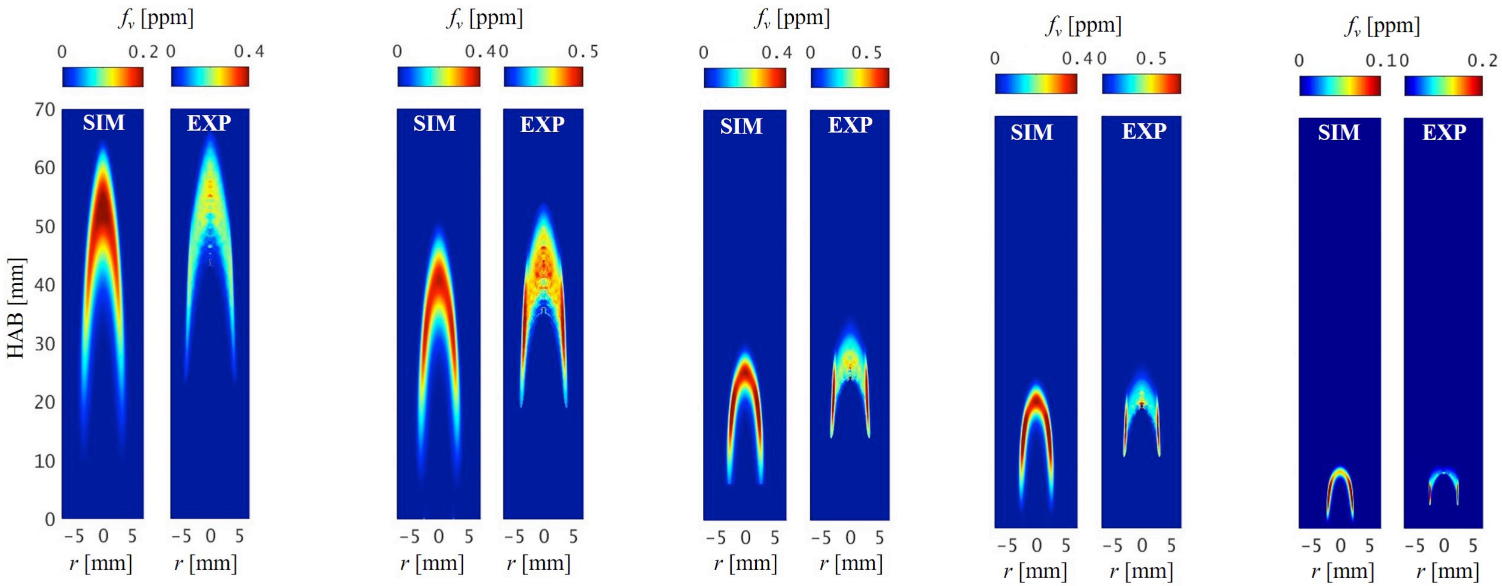




M. Montgomery, D.D. Das, C.S. McEnally, L.D. Pfefferle, "Analyzing the robustness of the yield sooting index as a measure of sooting tendency", *Proceedings of the Combustion Institute*, 2018, accepted.

Validated the methane chemistry mechanism and the soot model with simulations of methane flames with variable Oxygen Index

- Flame sizes and shapes were well predicted by the simulations
- Trends in soot yield and distribution were well predicted by the simulations
- **The computational models can accurately simulate the baseline YSI flame – comparisons between measured and computed YSIs indicate the quality of the chemical kinetic mechanisms for the dopant**



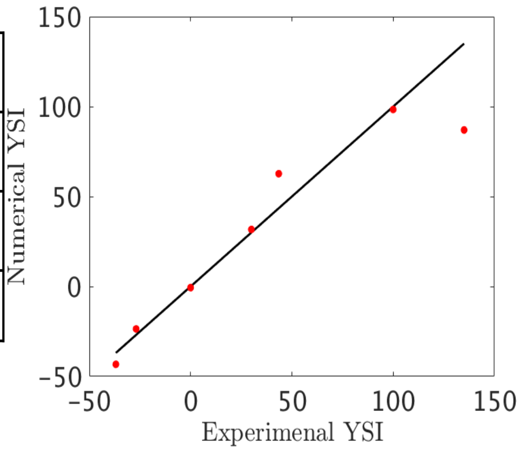
A. Jain, D.D. Das, D., C.S. McEnally, L.D. Pfefferle, Y. Xuan, "Experimental and numerical study of variable oxygen index effects on soot yield and distribution in laminar co-flow diffusion flames", *Proceedings of the Combustion Institute*, 2018, accepted.

Technical Accomplishments and Progress

Completed proof-of-concept simulations of YSI for a range of test fuels

- The computational framework for YSI calculation was validated
- The YSI calculations were computationally efficient
- Large chemical kinetic mechanisms can be directly used without reduction
- More than 10 test compounds were simulated for proof-of-concept
- **The YSI concept and the flamelet-based model allow very large mechanisms to be tested for their ability to predict soot formation**

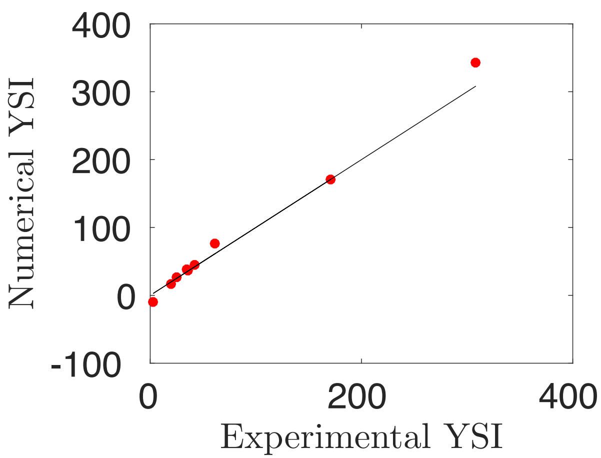
	LLNL Skeleton	LLNL Semi-detailed	LLNL Full
No. of Species	372	697	1372
No. of Reactions	3620	7377	11612
Simulation time	~20 min	~1 h	~6 h

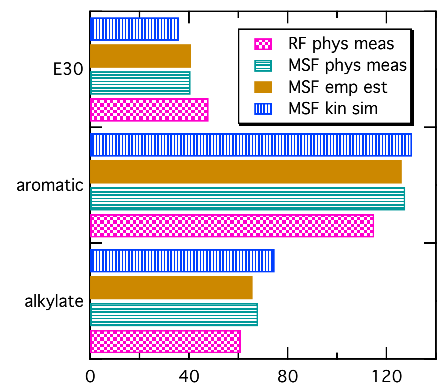


Technical Accomplishments and Progress

Measured and simulated the YSIs of 3 of the Co-Optima test gasolines and of surrogate mixtures formulated for them at ORNL/LLNL

- Fuel samples and DHA from Magnus Sjöberg (Sandia) and Bob McCormick (NREL)
- The LLNL mechanism was merged with an aromatic growth sub-mechanism
- The YSIs of the 8 fuel components in the surrogates were simulated and agree with measurements (include n-alkanes, isoalkanes, aromatics, 1-hexene, ethanol)
- The simulated surrogate YSIs agree well with the YSIs measured for the real fuels
- **The chemical kinetic model accurately predicts the sooting properties of the test gasolines, and the surrogates accurately mimic their sooting behavior**





C.S. McEnally, Y. Xuan, P.C. St. John, D.D. Das, A. Jain, S. Kim, T.. Kwan, L.K. Tan, J. Zhu, L.D. Pfefferle, "Sooting tendencies of Co-optima test gasolines and their surrogates", *Proceedings of the Combustion Institute*, 2018, accepted.

Response to Previous Year Reviewers' Comments

- Not applicable – this project began in May 2017 and was not reviewed last year

Collaboration and Coordination with Other Institutions

- This project is a collaboration between
  - Yale University
  - Penn State University
- Extensive collaboration with Co-optima
  - NREL
  - Sandia
  - PNNL
  - ANL
  - LLNL
  - MIT
  - UConn

Remaining Challenges and Barriers

- Many biomass-derived blendstocks contain chemical functional groups that differ from conventional fuels
- A particulate emissions index exists for GDI engines (i.e., PMI) but not for compression ignition engines
- Only a small fraction of existing chemical kinetic mechanisms have been validated for soot formation

Proposed Future Research

- Measure YSIs for additional fuels and hydrocarbons
  - MCCI blendstocks proposed by Co-optima
  - Biomass-derived fuels produced by the High Performance Fuel team
  - Fuels with NMR compositional data measured at PNNL.
- Develop particulate emissions index for predicting emissions from MCCI engines based on YSI, cetane number, etc.
- Simulate measured YSIs using additional mechanisms
- Any proposed future work is subject to change based on funding levels.

Summary

- Relevance and Approach.
  - Yield Sooting Index (YSI) is a novel measure of sooting tendency that works with small sample size (100s of microliters) and enables high throughput
- Accomplishments.
  - Developed a database of YSI measurements for over 400 regular and oxygenated hydrocarbons relevant to IC engine fuels
  - Implemented a flamelet-based model for simulating measured YSIs that allows large chemical kinetic mechanisms to be tested for their ability to predict soot formation

Thank You