Lawrence Livermore National Laboratory

Improving alternative fuel utilization: detailed kinetic combustion modeling & experimental testing

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DOE National Laboratory Alternative Fuels R&D
Merit Review and Peer Evaluation
Washington, DC

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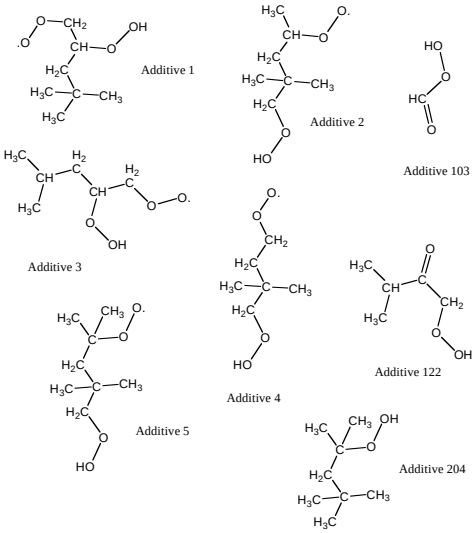
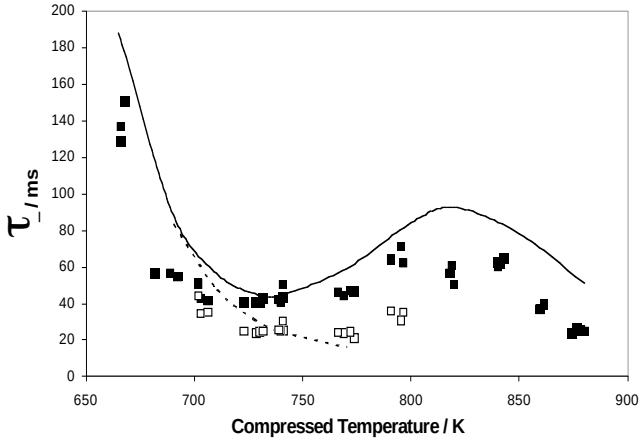
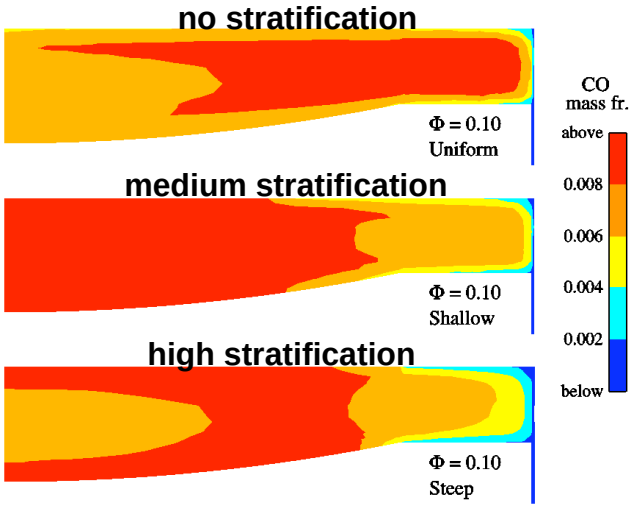
Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

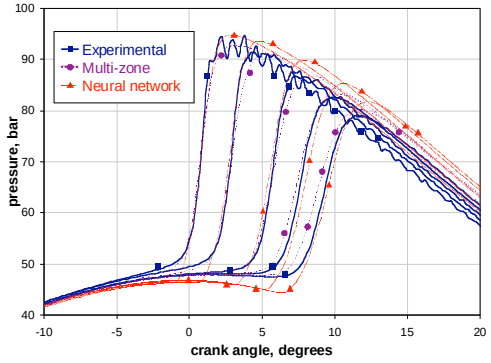
Goals/Objectives: Enable efficient utilization of alternative fuels through detailed chemical kinetic and fluid mechanics analysis





Chemical kinetic model development and validation





High fidelity engine analysis and chemical kinetic model testing at engine conditions

FY2007 Reviewer's Comments and Response

- ***Understand if indeed methyl decanoate is a representative surrogate for biodiesel. Another project indicated deficiencies.*** **Our work has demonstrated good agreement between numerical results for methyl decanoate and experimental results for rapeseed oil**

- ***Can the combustion kinetic modeling be combined with flow reactor studies to get better validation data and a deeper understanding?*** **Much of our validation is conducted at flow reactor conditions.**

- ***Some of the tasks and data were also presented in the combustion session.*** **There is overlap between the "Combustion" and the "Alternative Fuels" part of our work. We minimize overlap in the presentations by clearly distinguishing results most relevant to the combustion session from those most relevant to the alternative fuels session.**

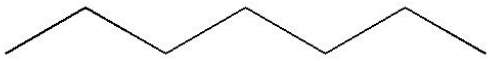
FCVT Barriers: our work is sharply focused on addressing technical barriers that limit applicability of alternative fuels

- ***Inadequate data and predictive tools for property effects on combustion and engine optimization:*** **Our detailed models enable high fidelity analysis for engine optimization**

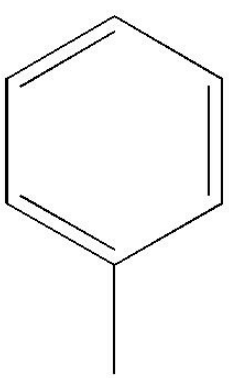
- ***Inadequate data and predictive tools for fuel effects on emissions and emission control system impacts:*** **Our high fidelity chemical kinetic models are applicable to emissions predictions (HC, CO, NO_x and PM) in HCCI and other low temperature combustion regimes**

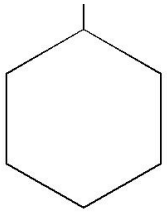
- ***Inadequate knowledge base on the technical and economic impacts of non-petroleum fuels:*** **Our analysis tools enable clean and efficient utilization of alternative fuels such as biodiesel**

Approach: We are developing high fidelity surrogate models through testing and tuning with our innovative engine analysis codes



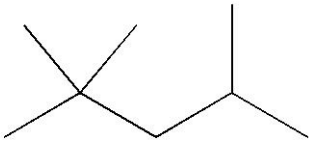
n-heptane



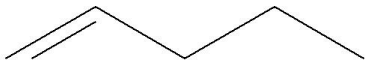


methylcyclohexane

toluene



iso-octane

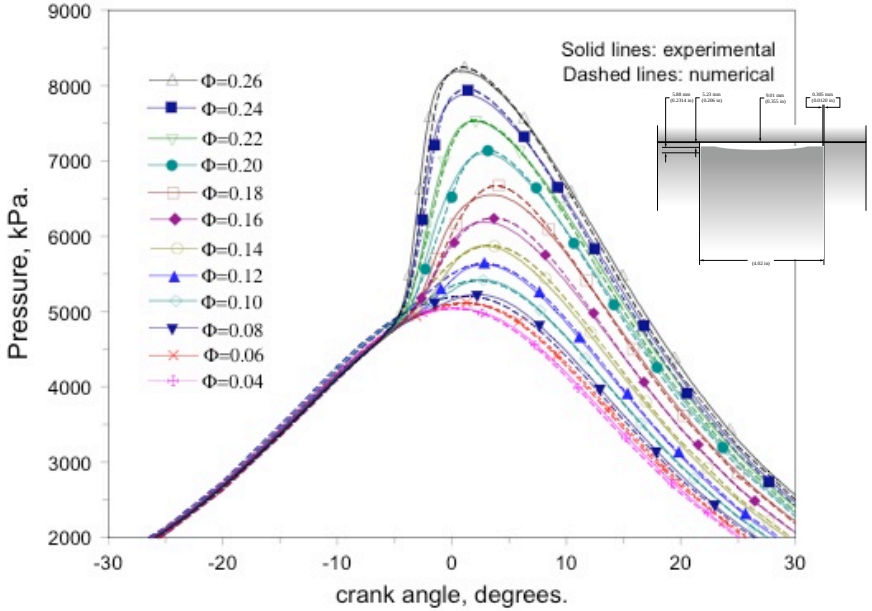


1-pentene

Detailed kinetics of gasoline surrogates

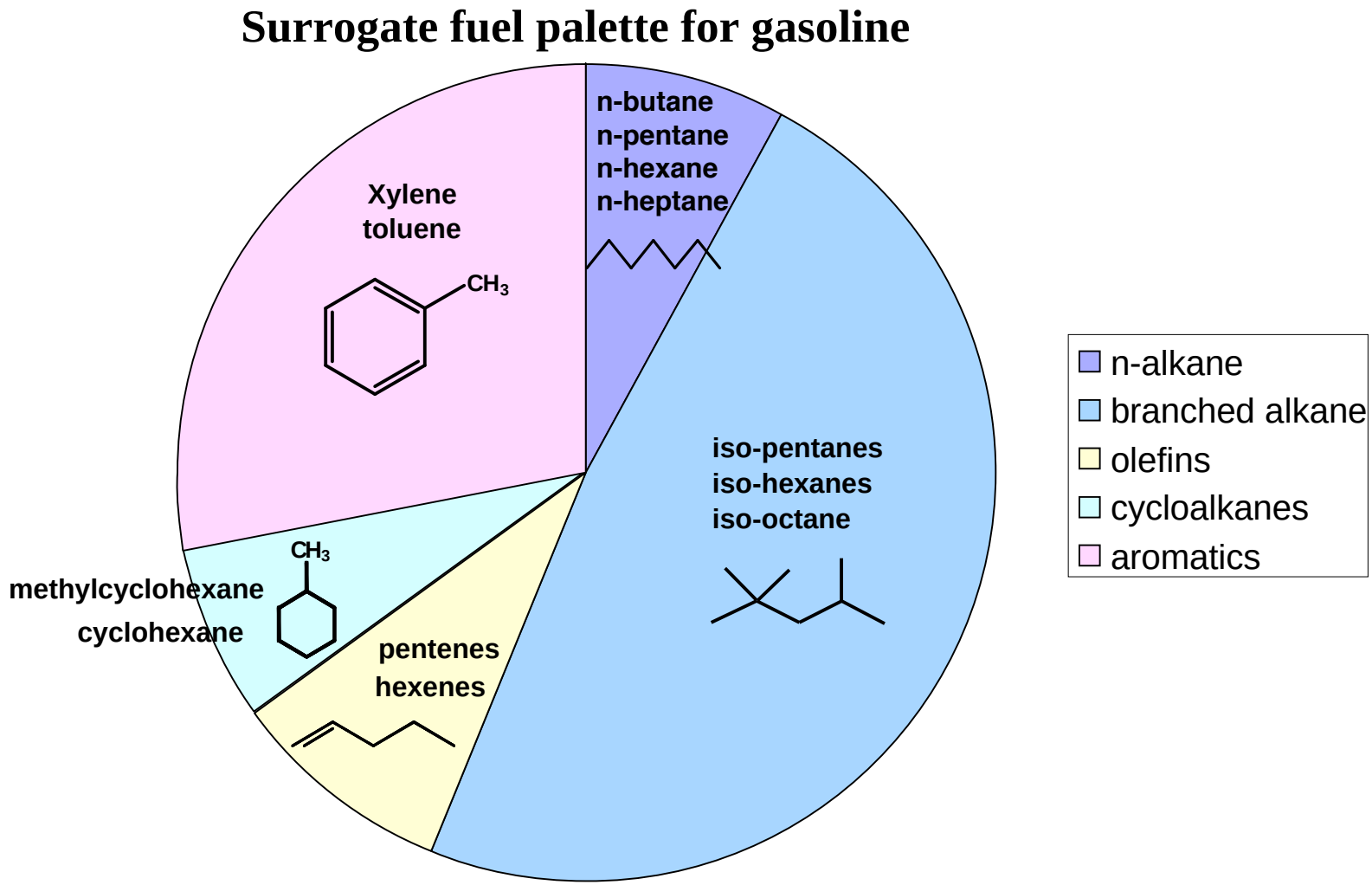
testing

tuning



High fidelity engine models

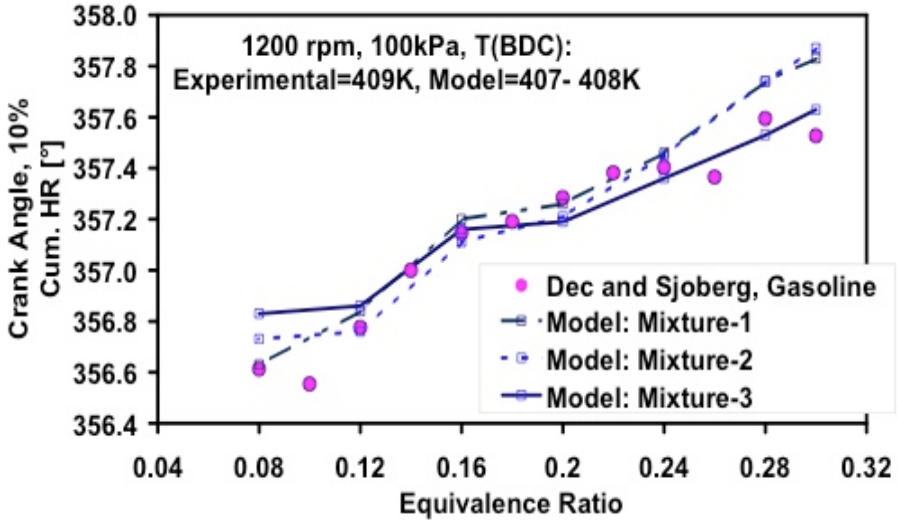
Technical accomplishment summary: developing high fidelity *surrogate* chemical kinetic models for practical fuels (diesel, gasoline, biodiesel)



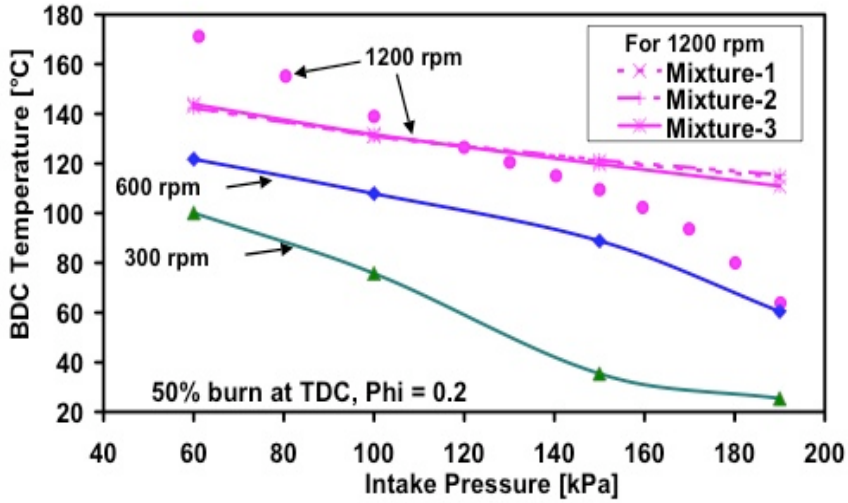
Our gasoline surrogate model includes detailed mechanisms for all the chemical classes

We have proposed and tested three gasoline surrogate mechanisms

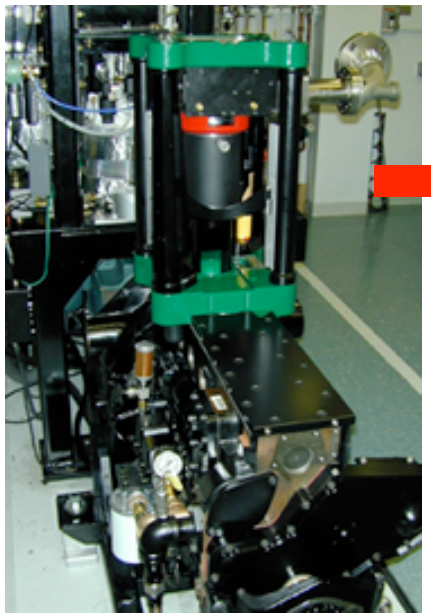
% Molar Composition	Mixture 1	Mixture 2	Mixture 3
iso-Octane	60	40	40
n-Heptane	8	10	20
Toluene	20	10	10
Methyl cyclohexane	8	40	30
1-Pentene	4	0	0
RON (linear)	92.9	82.2	74.5
MON (linear)	90.6	80.0	72.7
RON (blend)	96.3	92.9	82.5
MON (blend)	92.9	84.9	76.3



- **Mixture 1: average gasoline composition**
- **Mixture 2: similar octane number as gasoline**
- **Mixture 3: enhanced reactivity**



We have recruited LLNL's analytical chemistry group for detailed evaluation of small hydrocarbon species in HCCI exhaust



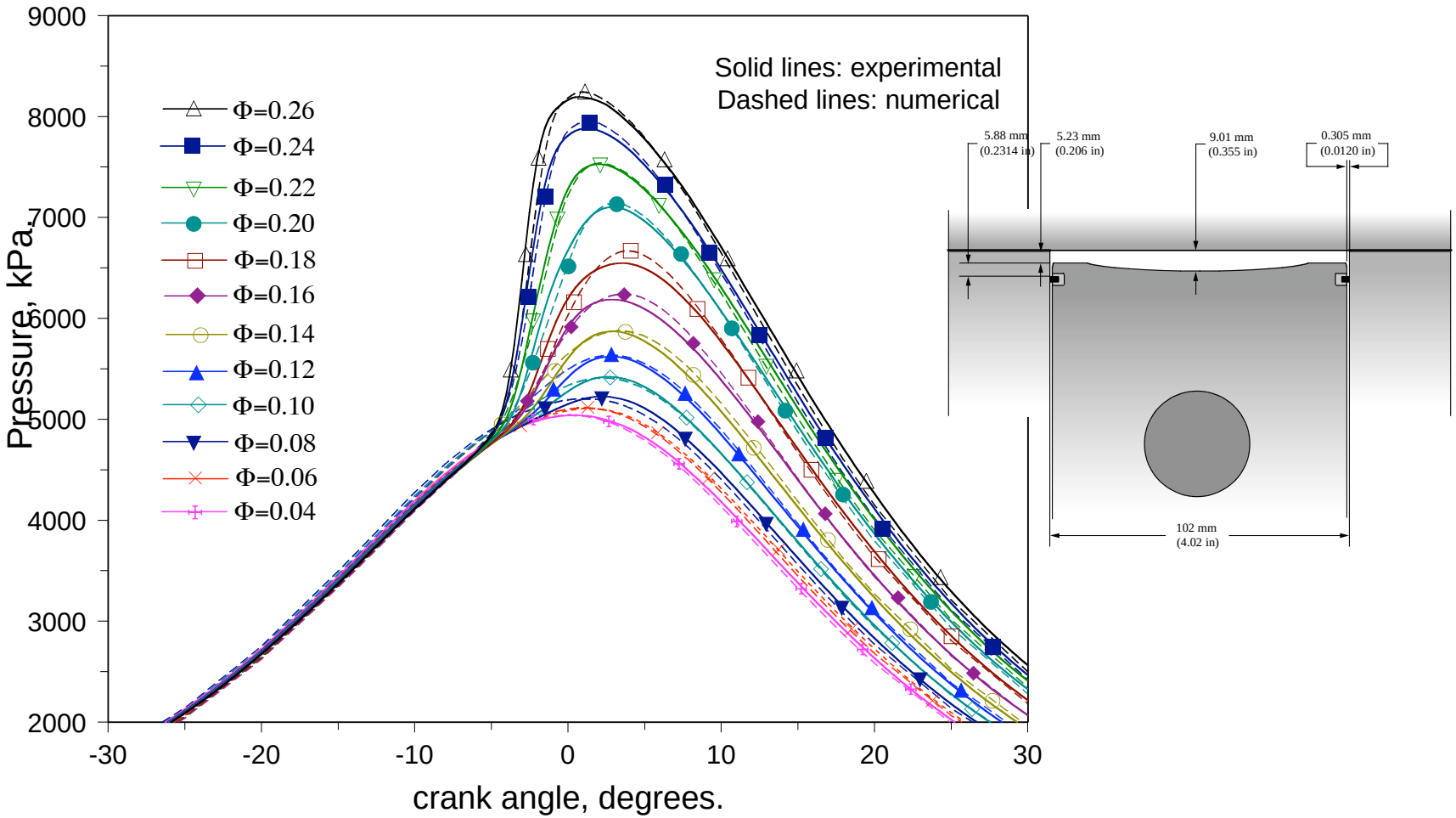
Sandia Engine

Tedlar bags

Purge and Trap

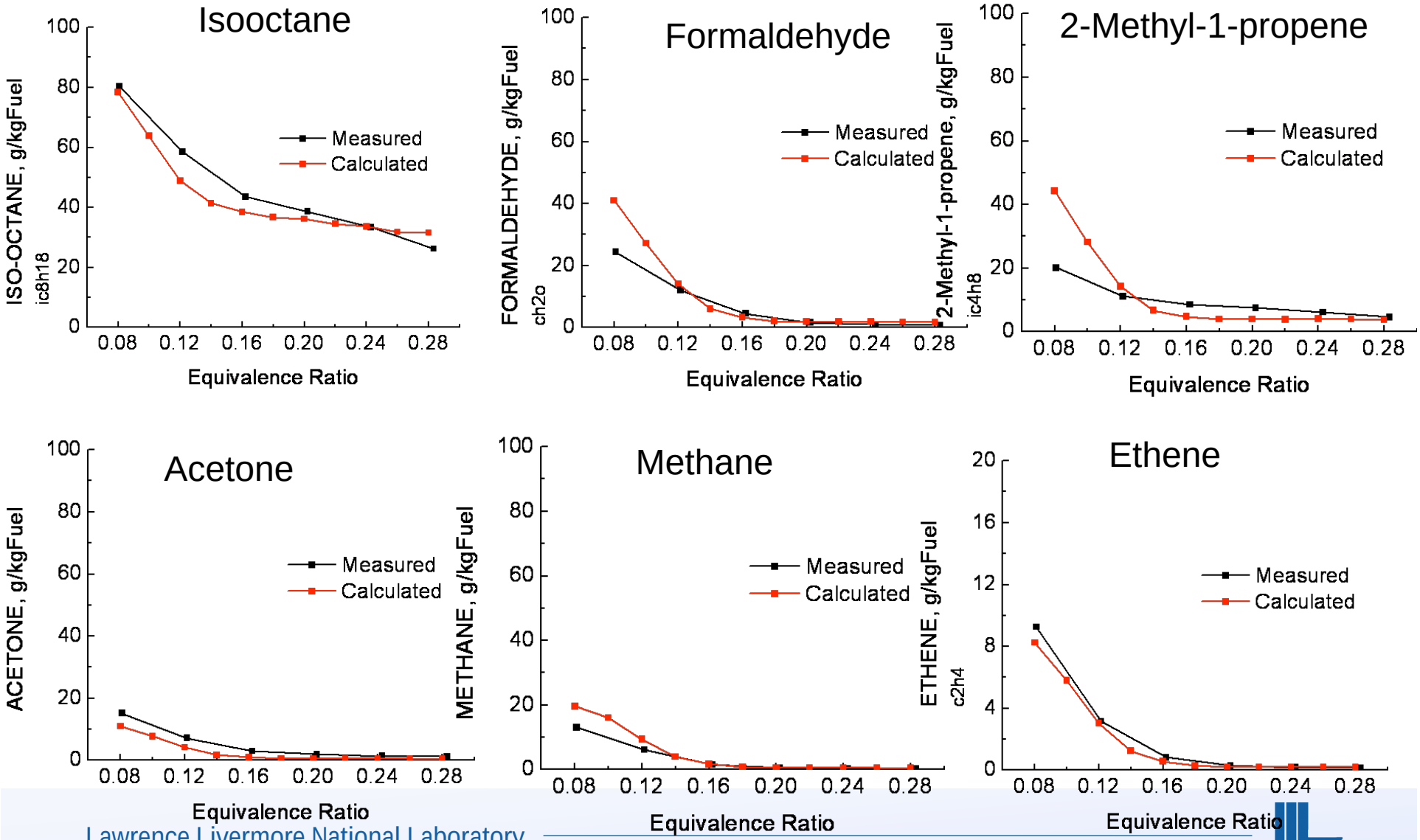
Gas chromatography mass spectrometer (GC-MS)

Our innovative numerical techniques have enabled fast, high fidelity analysis of homogeneous and partially stratified combustion

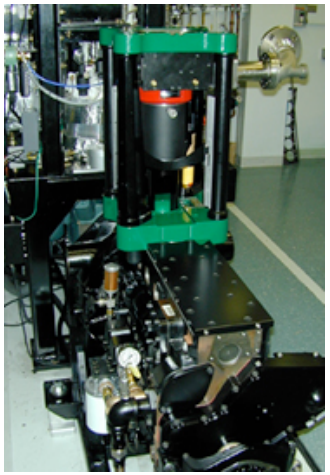


Unprecedented level of agreement obtained between experimental (Sandia) and numerical (LLNL) results

We have demonstrated *unprecedented* modeling fidelity accurately predicting exhaust composition of 50 species

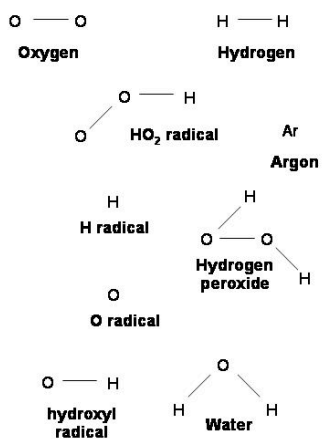


We are combining our chemical kinetics codes, engine models, and analytical chemistry to deliver high fidelity surrogate models

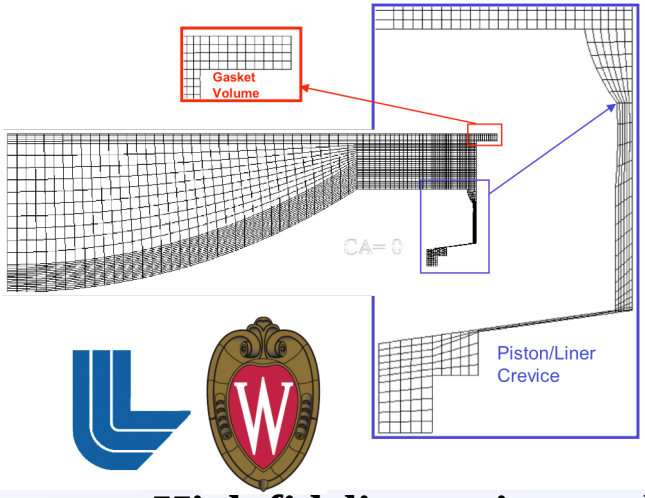


High quality HCCI engine experiments (Sandia)

Analytical chemistry for detailed exhaust speciation



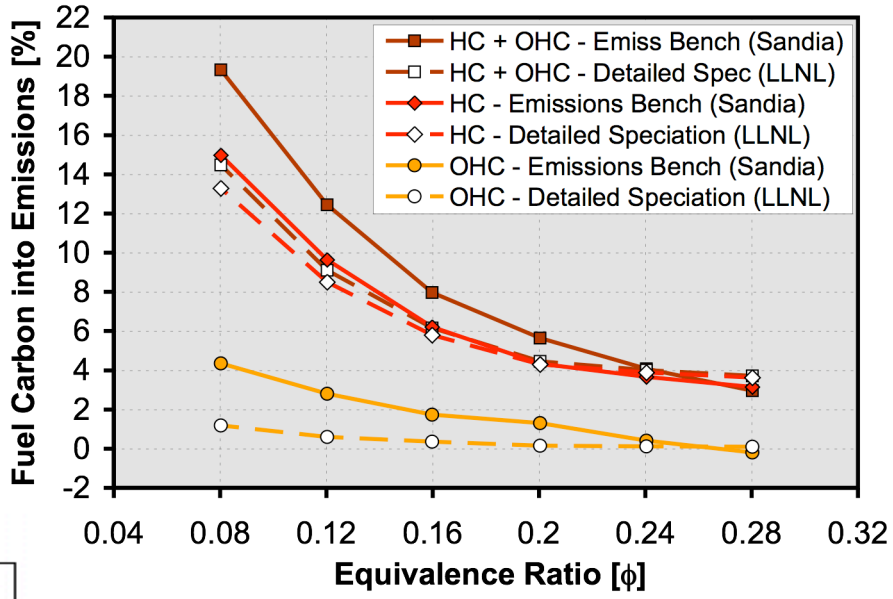
Extensively validated chemical kinetic models

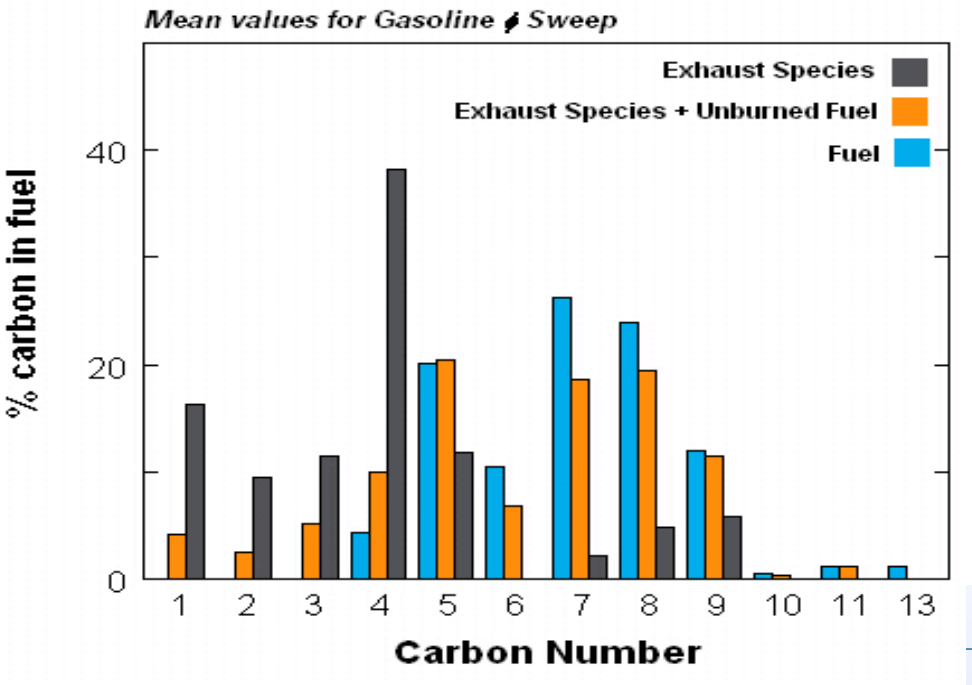


High fidelity engine analysis

We have conducted detailed speciation experiments at Sandia HCCI engine with Chevron-Phillips reference gasoline

- **Conducted both phi-sweep and stratified charge experiments**
- **18 samples collected in triplicate**
- **Emission bench and detailed species in good agreement**

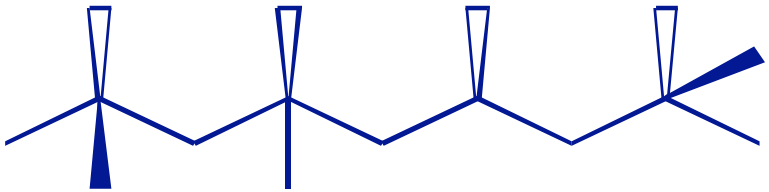




- **70 individual exhaust species identified and quantified**
- **11 different authentic standards used for quantification**
- **>1000 individual analyses reported**

We are developing chemical kinetic mechanisms for representative & surrogate diesel/biodiesel species

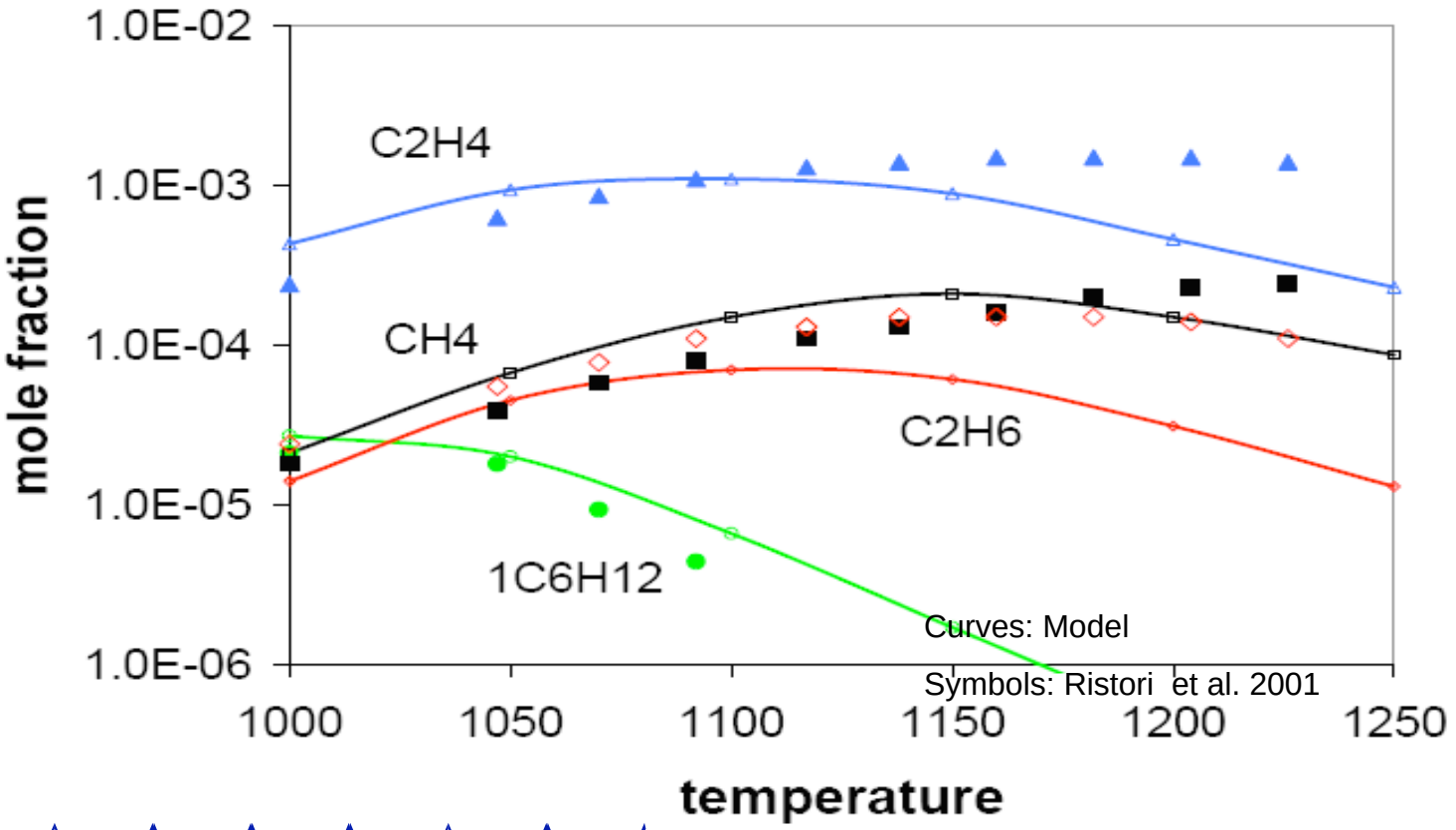
N-hexadecane
- **Diesel primary reference fuel**
- **Representative of diesel fuel**



2,2,4,4,6,8,8 heptamethylnonane
- **Diesel primary reference fuel**

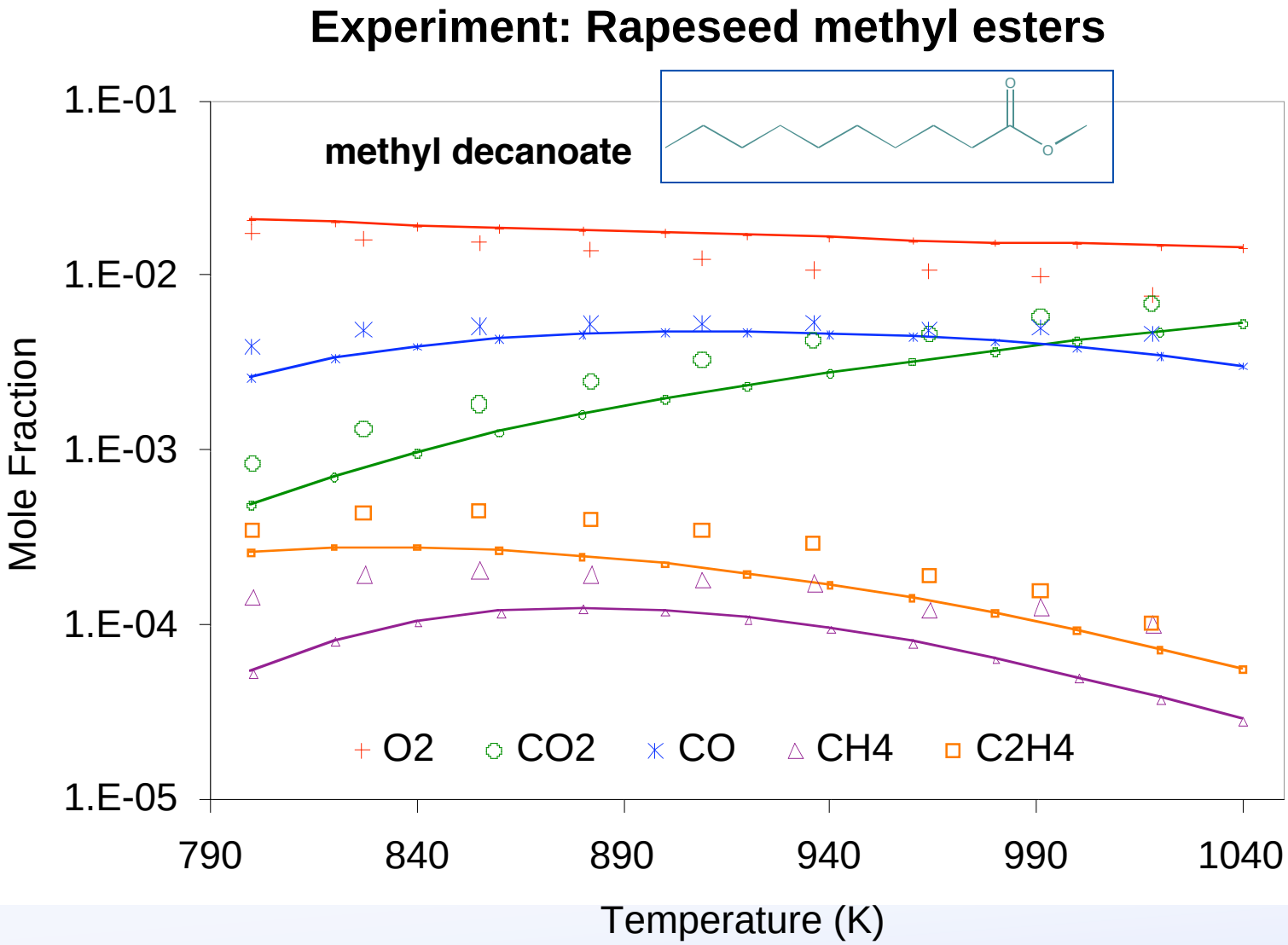
methyldecanoate
- **Biodiesel surogate**

n-Hexadecane model agrees well with experiments and it is ready for detailed diesel engine analysis

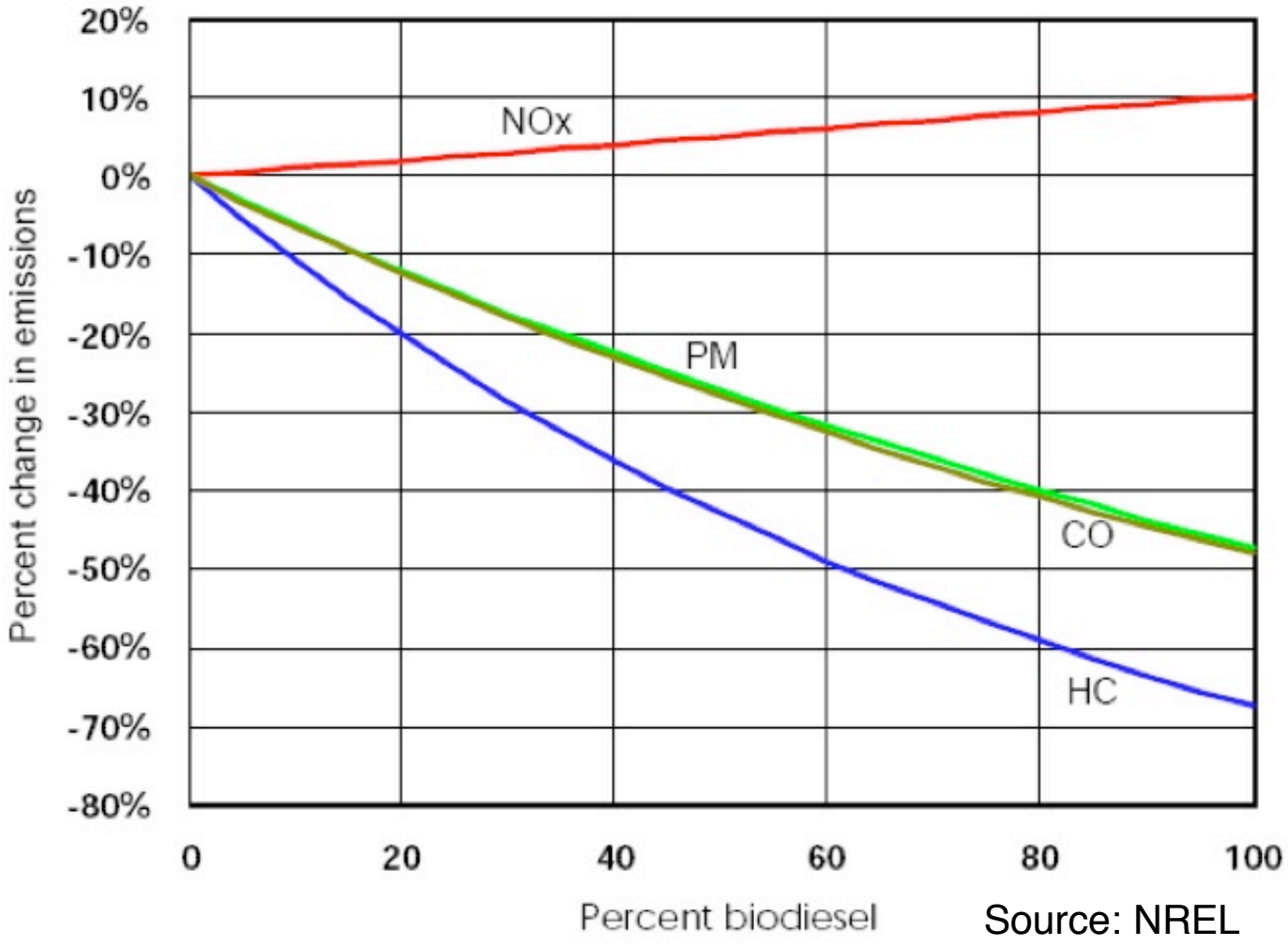


In stirred reactor at 1 atm and 1000-1250K

Biodiesel surrogate methyl decanoate accurately predicts ignition chemistry relative to rapeseed oil combustion

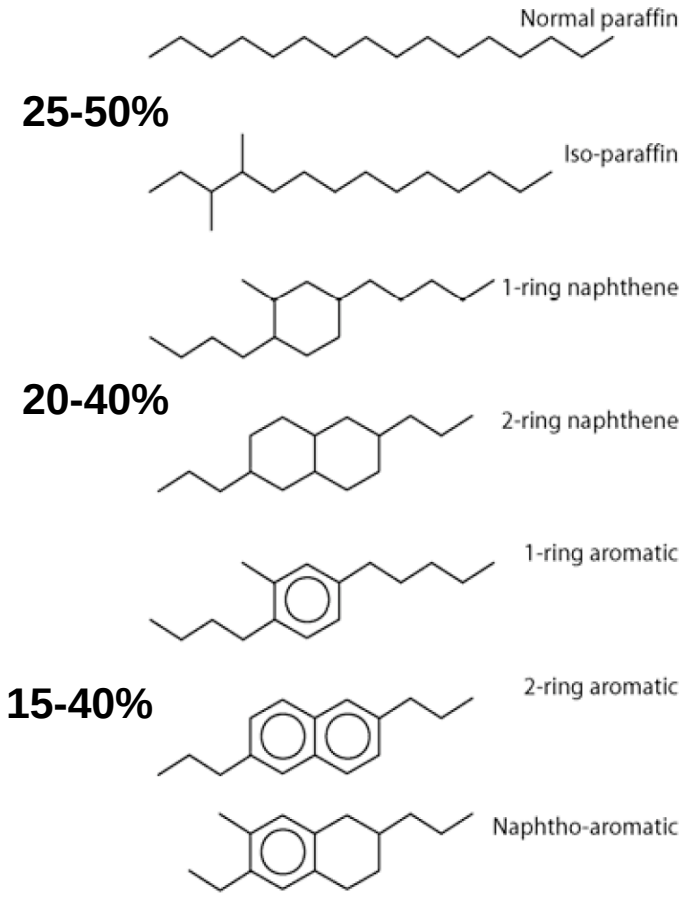


Biodiesel fuels contribute to lower HC, CO and PM emissions, but increase the level of NO_x emissions

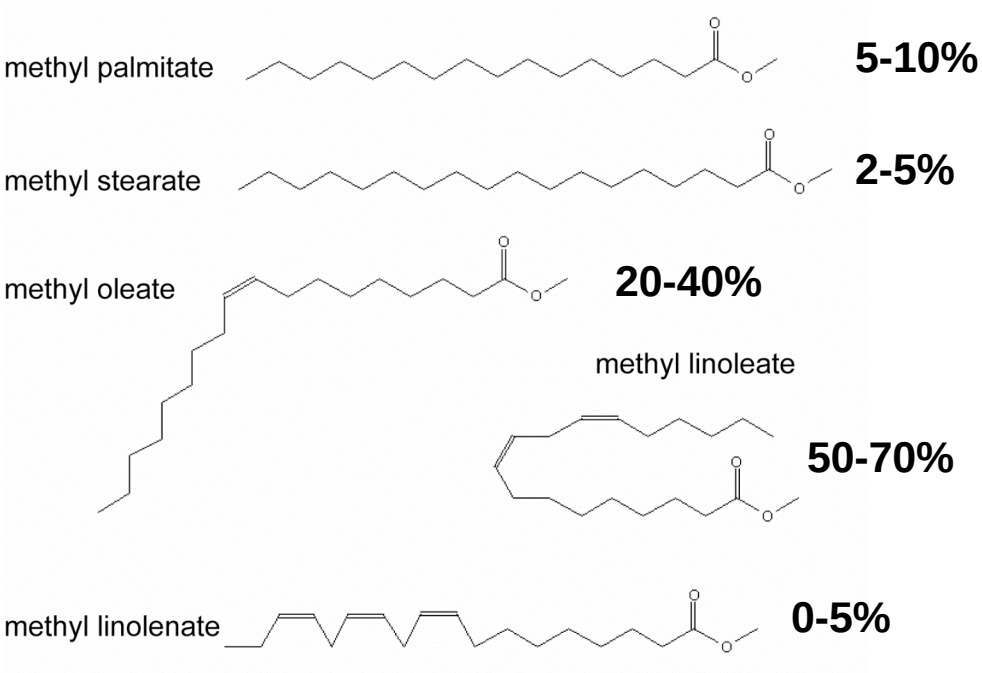


Source: NREL

Is there a chemical reason for the increase in NO_x with biodiesel?

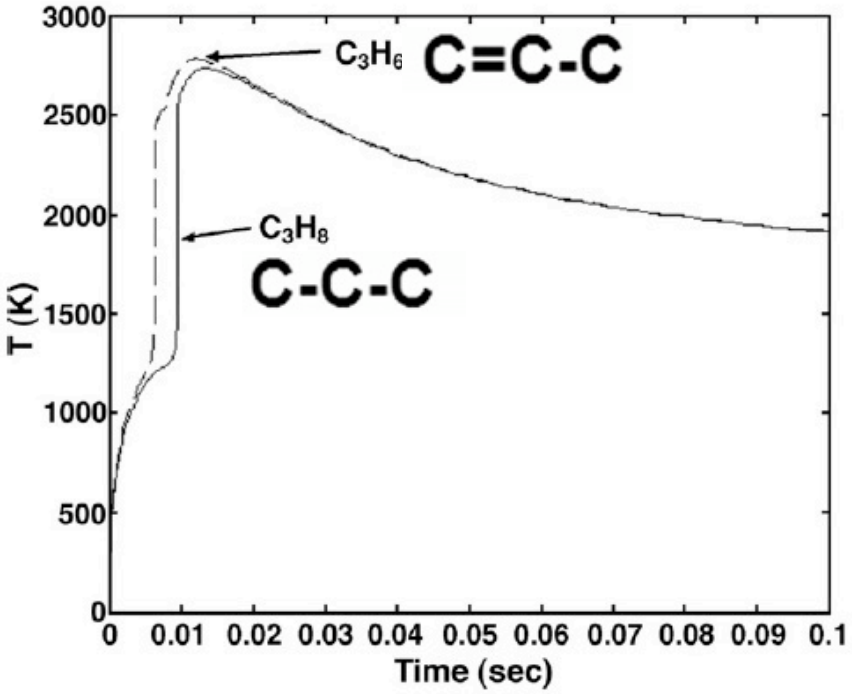


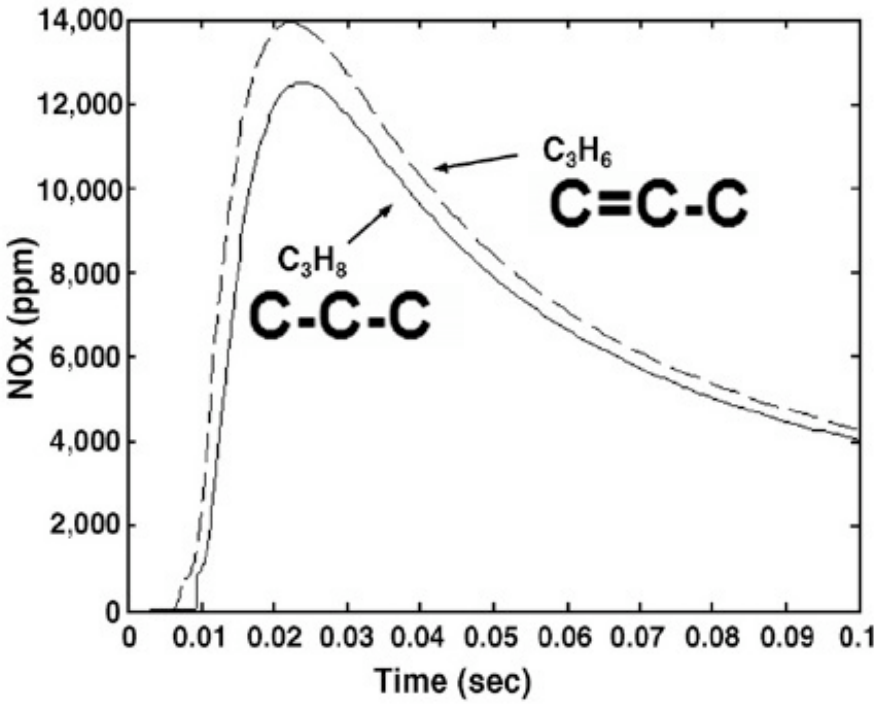
Representative molecules in diesel fuel (Farrell et al., 2007)



Main species in biodiesel

Conclusion: biodiesel burns hotter because it has multiple double bonds
Hotter burn increases NO_x





Technical Publications during FY08

- C. K. Westbrook, W. J. Pitz, O. Herbinet, H. J. Curran and E. J. Silke, "A Detailed Chemical Kinetic Reaction Mechanism For n-Alkane Hydrocarbons From n-Octane to n-Hexadecane," *Combust. Flame* (2008) Submitted.
- E. J. Silke, W. J. Pitz, C. K. Westbrook, M. Sjöberg and J. E. Dec, "Understanding the Chemical Effects of Increased Boost Pressure under HCCI Conditions", 2008 SAE World Congress, Detroit, MI, SAE 2008-01-0019, 2008.
- R. P. Hessel, D. E. Foster, S. M. Aceves, M. L. Davisson, F. Espinosa-Loza, D. L. Flowers, W. J. Pitz, J. E. Dec, M. Sjöberg and A. Babajimopoulos, Modeling Iso-octane HCCI using CFD with Multi-Zone Detailed Chemistry; Comparison to Detailed Speciation Data over a Range of Lean Equivalence Ratios, SAE 2008-01-0047, 2008.
- Sakai, Y., Ozawa, H., Ogura, T., Miyoshi, A., Koshi, M. and Pitz, W. J., "Effects of Toluene Addition to the Primary Reference Fuel at High Temperature," SAE Commercial Vehicle Engineering Congress & Exhibition, Chicago, IL, 2007.
- Y. Sakai, A. Miyoshi, M. Koshi and W. J. Pitz, "A Kinetic Modeling Study on the Oxidation of Primary Reference Fuel–Toluene Mixtures Including Cross Reactions between Aromatics and Aliphatics", *Proc. Combust. Inst.,* Montreal, Canada, submitted, 2008.
- K. Seshadri, T. Lu, O. Herbinet, S. Humer, U. Niemann, W. J. Pitz and C. K. Law, "Ignition of Methyl Decanoate in Laminar Nonpremixed Flows," *Proceedings of The Combustion Institute* (2008) Submitted.
- C. K. Westbrook, W. J. Pitz, P. R. Westmoreland, F. L. Dryer, M. Chaos, P. Osswald, K. Kohse-Hoinghaus, T. A. Cool, J. Wang, B. Yang, N. Hansen and T. Kasper, "A Detailed Chemical Kinetic Reaction Mechanism for Oxidation of Four Small Alkyl Esters in Laminar Premixed Flames", *Proc. Combust. Inst.,* Montreal, Canada, submitted, 2008.
- Joel Martinez-Frias, Salvador M. Aceves, Daniel L. Flowers, "Improving Ethanol Life Cycle Energy Efficiency by Direct Utilization of Wet Ethanol in HCCI Engines," Journal of Energy Resources Technology, Vol. Vol. 129, No. 4, pp. 332-337, 2007.
- George A. Ban-Weiss, J.Y. Chen, Bruce A. Buchholz, Robert W. Dibble, "A Numerical Investigation into the Anomalous Slight NOx Increase when Burning Biodiesel: A New (Old) Theory," Fuel Processing Technology, Vol. 88, pp. 659-667, 2007.

Collaboration: We have long standing partnerships with industry, national labs, and academia

- Industry Partners:
  - ***Collaborative modeling and analysis of experiments***

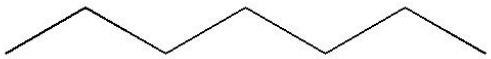
- National Labs and Universities:
  - ***Modeling tools, experiments, analysis***


Other collaborative activities

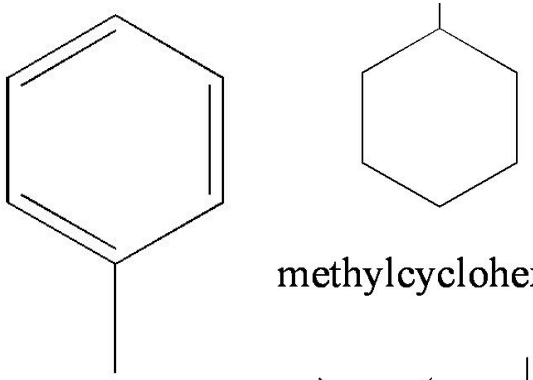
- **Ongoing participation at MOU meetings with vehicle and engine manufacturers**
- **Fuels for Advanced Combustion Engines (FACE) working group**
- **Surrogate fuel working group with representatives from industry (Exxon, Caterpillar, Chevron, United Technologies)**
- **Basic Energy Sciences panel on advanced combustion**
- **SAE HCCI symposium, Lund, Sweden, 2 invited seminars**
- **Chalmers University, Opponent in Ph.D. exam**
- **8 PhD and >15 MS through collaboration and direct support**

- **Several collaborative publications involving National Laboratories and Universities in the US and abroad:**
  - **SAE**
  - **The Combustion Institute**
  - **International Journal of Engine Research**
  - **Combustion Theory and Modeling**
  - **Journal of Energy Resources Technologies**
  - **IEEE Control Systems Technology**

Future plans: We will deliver high fidelity surrogate models for gasoline and diesel fuels

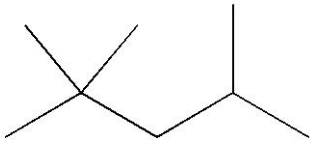


n-heptane

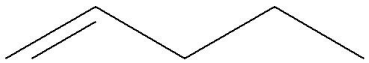


methylcyclohexane

toluene



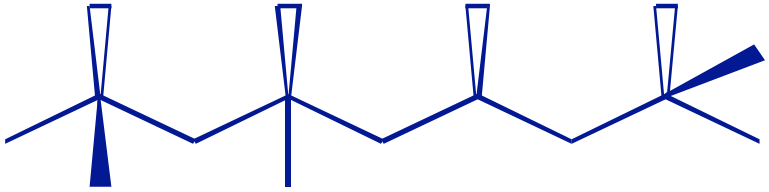
iso-octane



1-pentene

gasoline surrogate

n-hexadecane

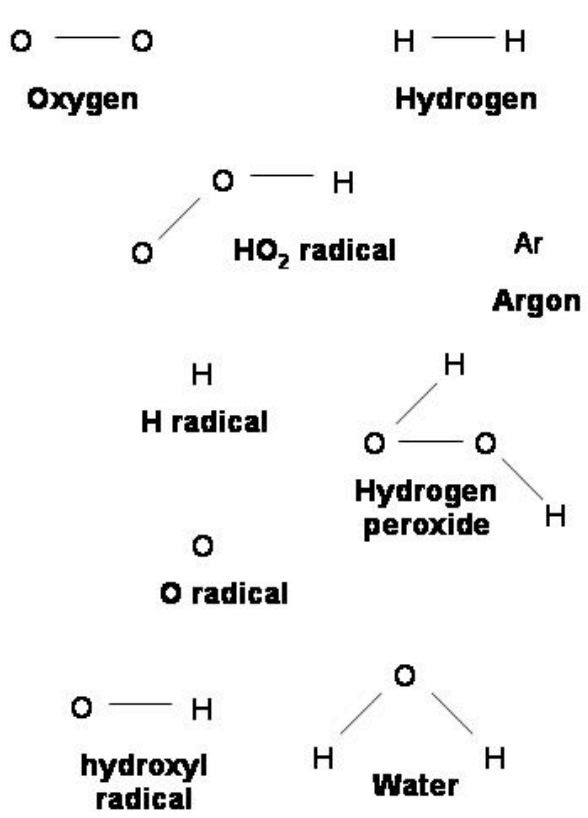


2,2,4,4,6,8,8 heptamethylnonane

methyldecanoate

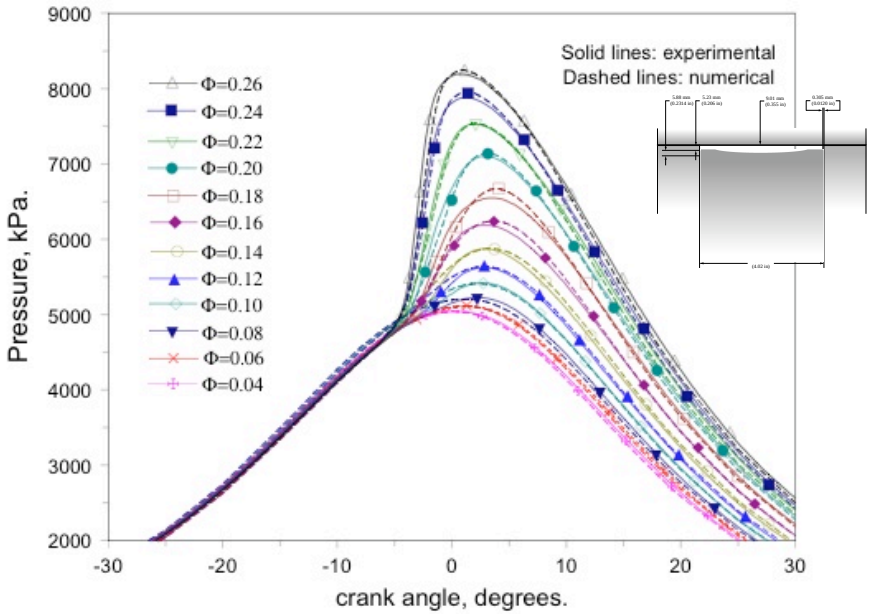
diesel/biodiesel surrogate

Summary: We are combining our chemical kinetics codes, engine models, and analytical chemistry to deliver high fidelity surrogate models



testing

tuning



Detailed chemical kinetics

High fidelity engine models