Collaborative Combustion Research with BES

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Overview

Timeline

- **Project started FY 2011**
- **Project directions and continuation are evaluated annually**

Budget

- **Project funded by DOE / VTP**
  - → **FY12 funding: $315 k**
  - → **FY13 funding: $320 k**
  - → **FY14 funding: $325 k**

Barriers

- **Lack of fundamental knowledge of advanced engine combustion regimes**
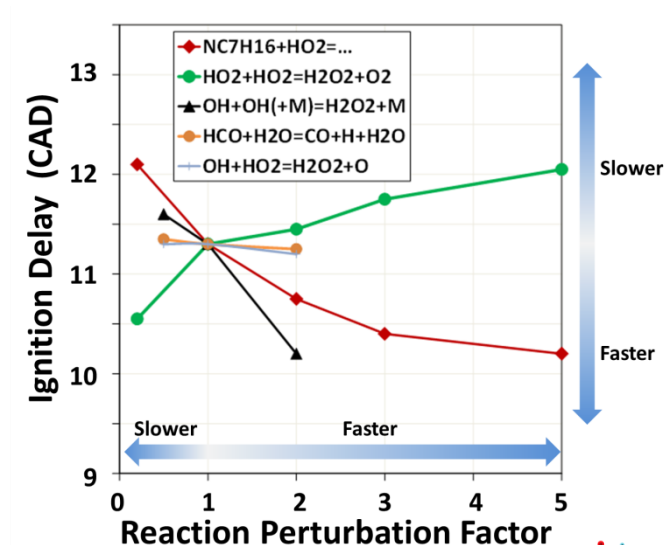- **Lack of modeling capability for combustion and emission control**

Partners

- **ANL – GCI engine, GSA tools, sub-mechanism improvement, alt. additives**
- **LLNL – fuel mechanism development / validation, gasoline surrogate formulation, local sensitivity analysis**
- **KAUST, Chevron – fuels**
- **UW-ERC – data sharing for CFD model**
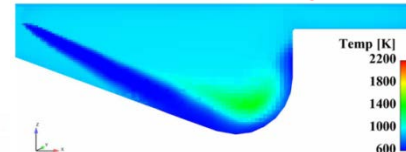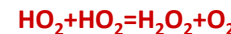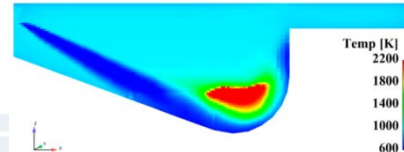- **International RCM Workshop**

Objectives and Relevance to DOE

- **Acquire fundamental data, and develop / validate / refine chemical kinetic and relevant models for transportation-relevant fuels (conventional and future gasolines, diesels and additives) at conditions representative of advanced combustion regimes, leveraging collaborations with BES-funded groups, and researchers across the broader community.**

- **Predictive simulations with these models, which require low associated uncertainties, could be utilized to overcome technical barriers to low temperature combustion (LTC), and achieve required gains in engine efficiency and pollutant reductions.**
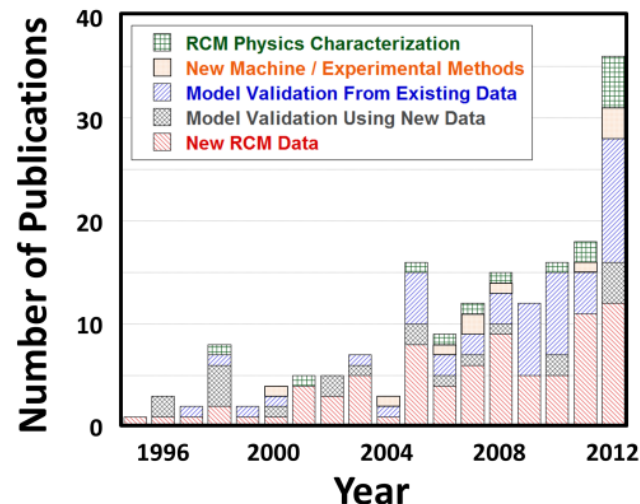

doi:10.1021/jz400874s

$HO_2+HO_2=H_2O_2+O_2$

Project Approach
RAPID COMPRESSION MACHINE

- **Utilize ANL's twin-piston RCM to acquire autoignition data**

- **Employ novel data analysis tools and advanced diagnostics**
  - **Physics-based, reduced-order system model**
  - **Developing time-resolved gas sampling and speciation**
- **Develop and synergistically improve kinetic models using novel probing techniques (e.g., GSA) and detailed calculations of sensitive processes (e.g., individual reaction rates)**

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Project Approach
RCM SYSTEM MODEL

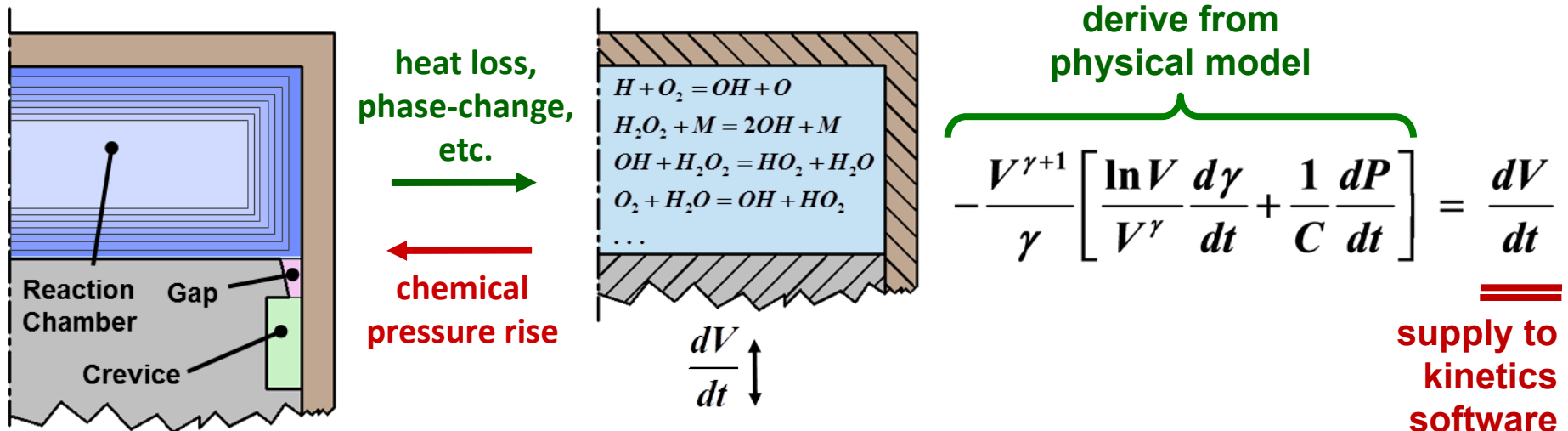- **Physics-based, reduced-order model coupled with chemical kinetics software – accounting for physical-chemical interactions during experiments (e.g., LTHR + crevice flows)**

  - **Computationally-efficient approach improves simulation fidelity**
  - **Facilitates utilization of additional metrics for mechanism validation / refinement (e.g., ROHR (1st, 2nd stages))**

heat loss, phase-change, etc.

chemical pressure rise

$$H + O_2 = OH + O$$
$$H_2O_2 + M = 2OH + M$$
$$OH + H_2O_2 = HO_2 + H_2O$$
$$O_2 + H_2O = OH + HO_2$$
$$\ldots$$

$$\frac{dV}{dt}$$

derive from physical model

$$-\frac{V^{\gamma+1}}{\gamma}\left[\frac{\ln V}{V^{\gamma}}\frac{d\gamma}{dt} + \frac{1}{C}\frac{dP}{dt}\right] = \frac{dV}{dt}$$

supply to kinetics software

Reaction Chamber Gap Crevice

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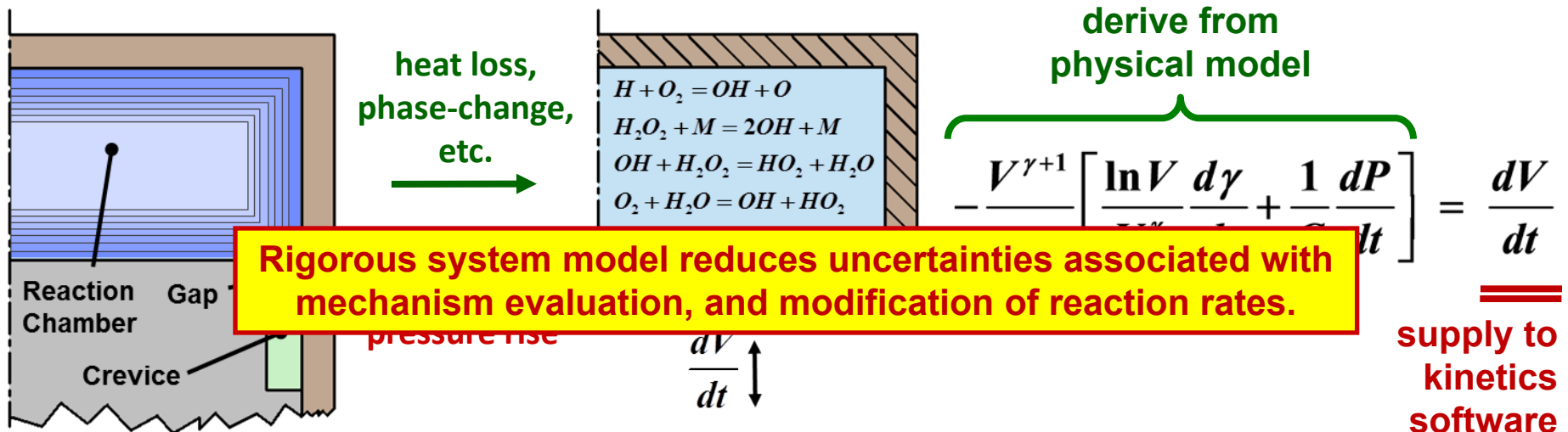 - **Facilitates utilization of additional metrics for mechanism validation / refinement (e.g., ROHR (1st, 2nd stages))**

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supply to kinetics software

pressure rise

$\frac{dV}{dt} \downarrow$

Rigorous system model reduces uncertainties associated with mechanism evaluation, and modification of reaction rates.

doi:10.1016/j.combustflame.2012.07.010

Project Milestones
FY2014 BUDGET – $325K

Task	Milestone	Status
1	Renovate RCM laboratory facilities. Move to refurbished, 1500 sq. ft. room to house twin-piston and single-piston RCMs, with space for additional equipment.	Completed
2	Acquire ignition delay measurements for gasoline fuels + reactivity modifiers. a) 2-ethyl-hexyl nitrate (2EHN) ($C_8H_{17}NO_3$); b) di-tert-butyl-peroxide (DTBP) ($C_8H_{18}O_2$).	Completed Jul '14
3	Develop, validate chemical kinetic model for gasoline fuels + reactivity modifiers. (model complete, validation 50% complete)	Sep '14
4	Formulate methodology to extract heat release information from RCM experimental data. (85% complete)	May '14
5	Implement GSA for gasoline surrogate kinetic mechanism, using multiple targets (e.g., ignition delay time, heat release rate).	Aug '14
6	Demonstrate capabilities of new single-piston RCM using volatile and involatile, single-component fuel surrogates.	Sep '14

Collaborative Combustion Research with BES, 2014 DOE Merit Review

Technical Accomplishments / Progress
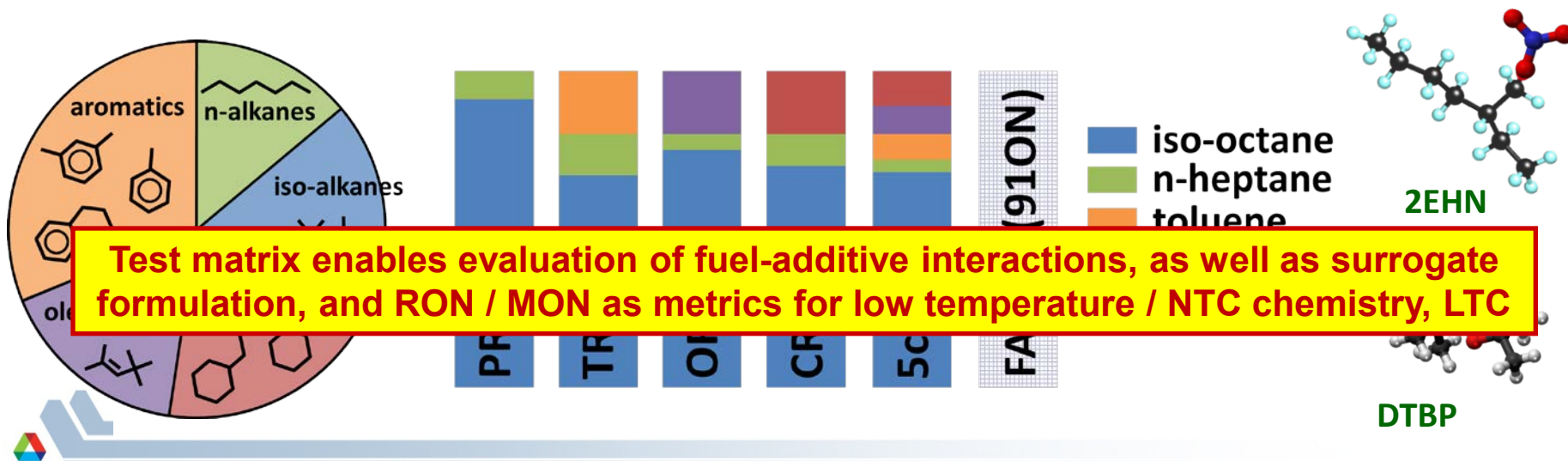## INVESTIGATING REACTIVITY MODIFIERS

- **Additives used to (dynamically) control combustion in advanced regimes (e.g., LTC, RCCI), multi-mode switching**

    - **Need to adequately model sensitizing effect on ignition timing and combustion. Are there optimal additives for ACEs?**

    - **Fuel / additive sensitization studied using gasoline surrogates, and full-boiling range gasoline, doped with various compounds**

    - **Developing / validating chemical kinetic models for blends, to fundamentally understand kinetic and exothermic influences**

Technical Accomplishments / Progress
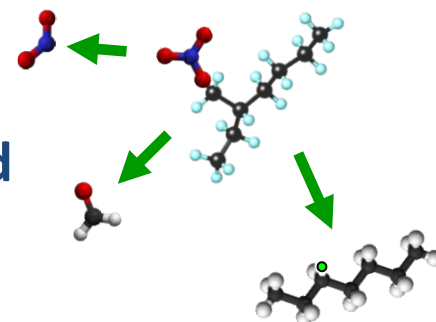## INVESTIGATING REACTIVITY MODIFIERS

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2EHN

DTBP

iso-octane
n-heptane
toluene

Test matrix enables evaluation of fuel-additive interactions, as well as surrogate formulation, and RON / MON as metrics for low temperature / NTC chemistry, LTC

Technical Accomplishments / Progress

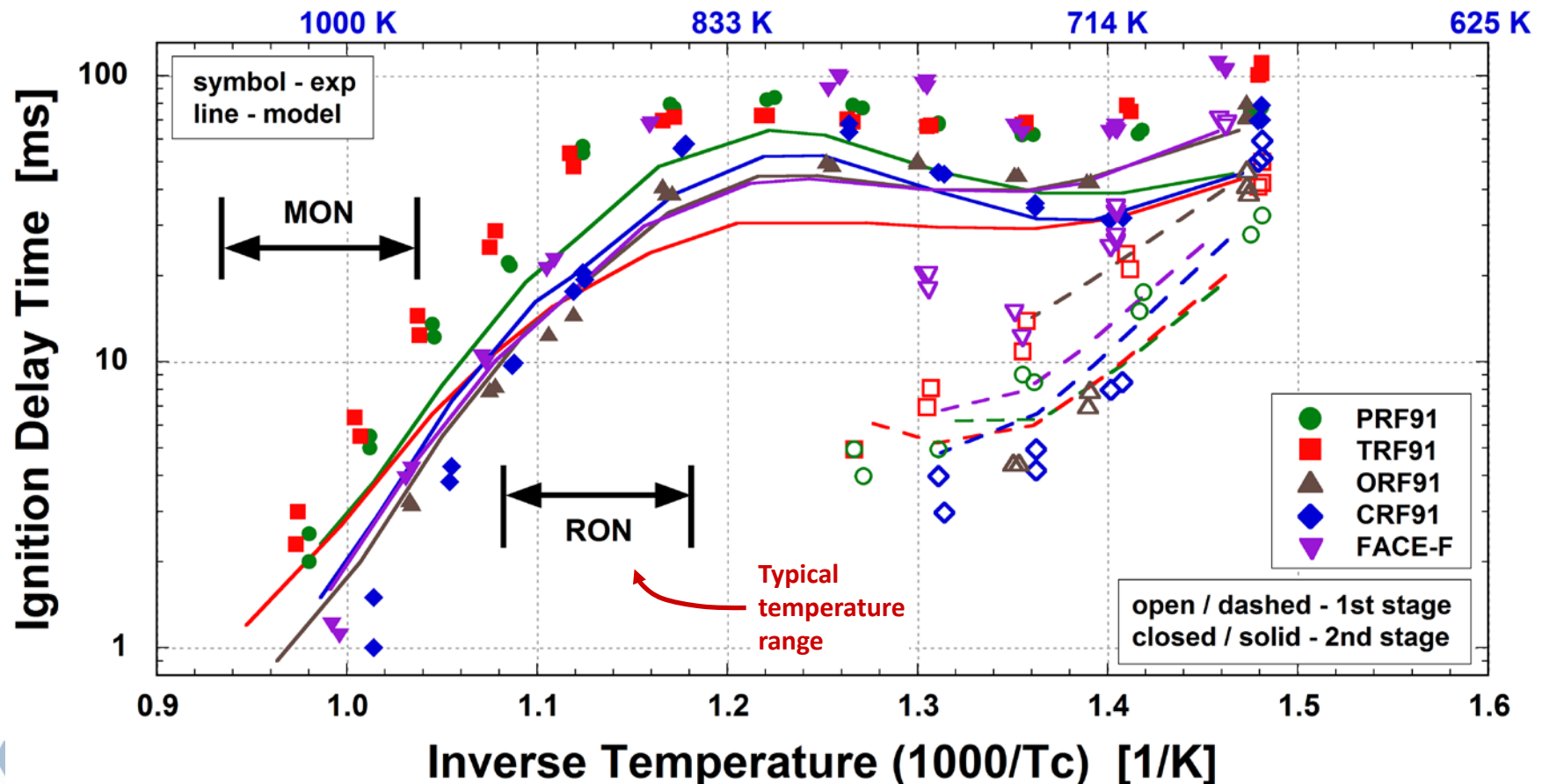## ASSEMBLED CHEMICAL KINETIC MODEL

- **Detailed mechanism with 2000 species, 8800 reactions**

- **Base, 5-component gasoline surrogate model (LLNL)**
  - **n-heptane, iso-octane, toluene, 2-hexene, methyl-cyclohexane**

- **Additive sub-mechanisms**
  - **2EHN unimolecular decomposition**
  - **DTBP breakdown via scission of O-O, or C-O bond**

- **Nitrogen chemistry (detailed and skeletal)**
  - **GRIMech 3.0 (prompt, thermal NOx, etc.)**
  - **Glarborg / Dagaut (HONO, extended HCN, etc.)**
  - **Fuel-specific (NO/NO$_2$ abstraction, addition, etc.)**
  - **Detailed nitrogen chemistry adds 200 species, 1400 reactions; skeletal sub-mechanism adds 5 species, 29 rxns**

Technical Accomplishments / Progress
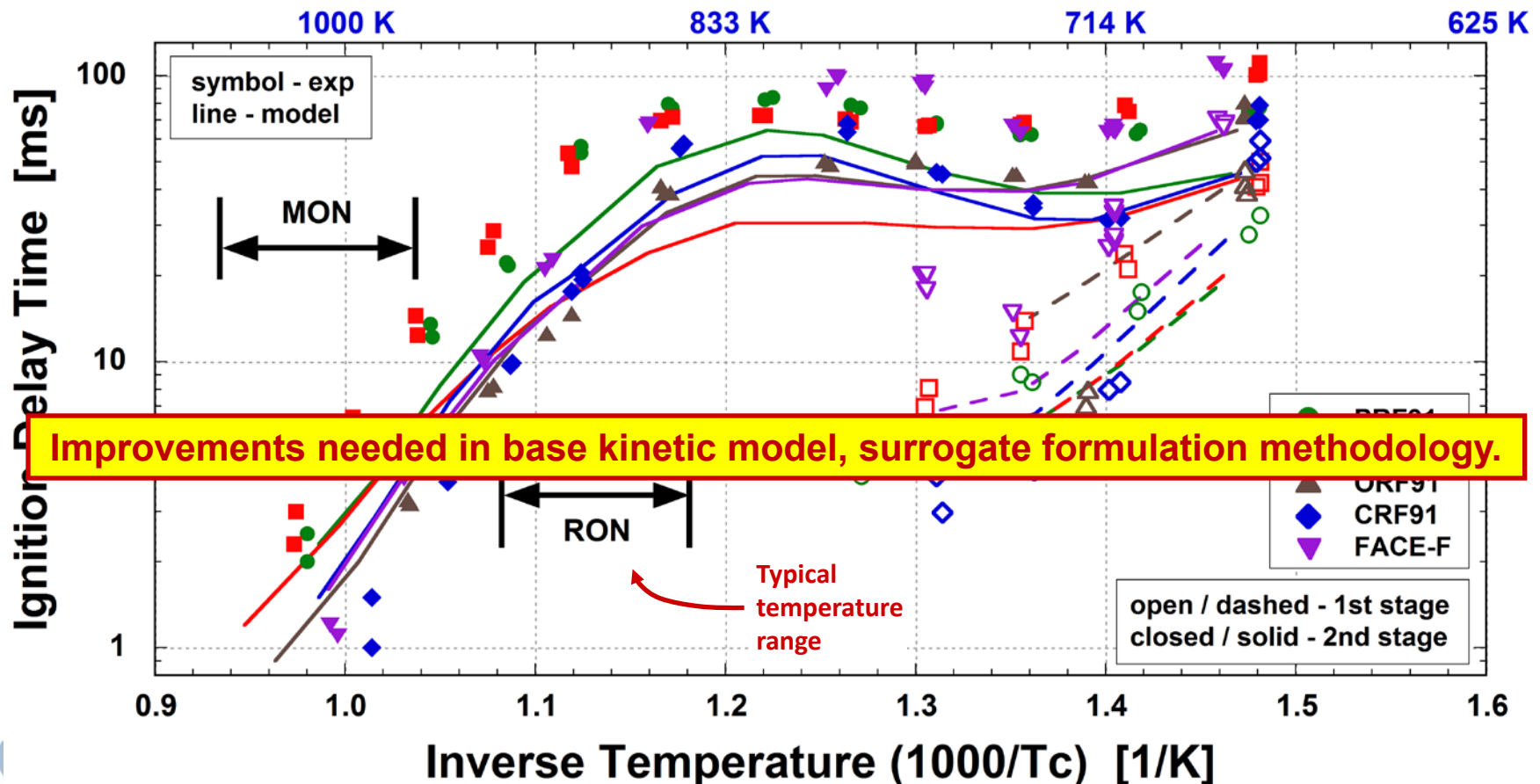
RCM Experiment, Model Comparison

- **Undoped blends / FACE-F; $\phi = 1.0$; p = 20 bar; 11% O_2**
  - **Discrepancies between base model, undoped fuel blends**
  - **3-component blends do not capture FACE-F gasoline behavior**

Technical Accomplishments / Progress
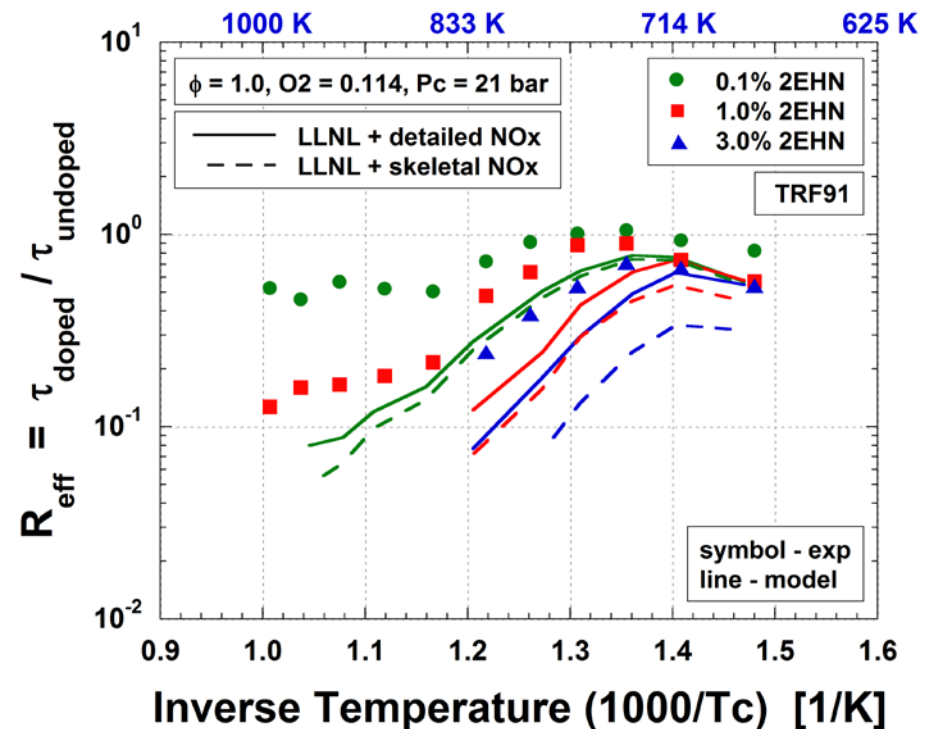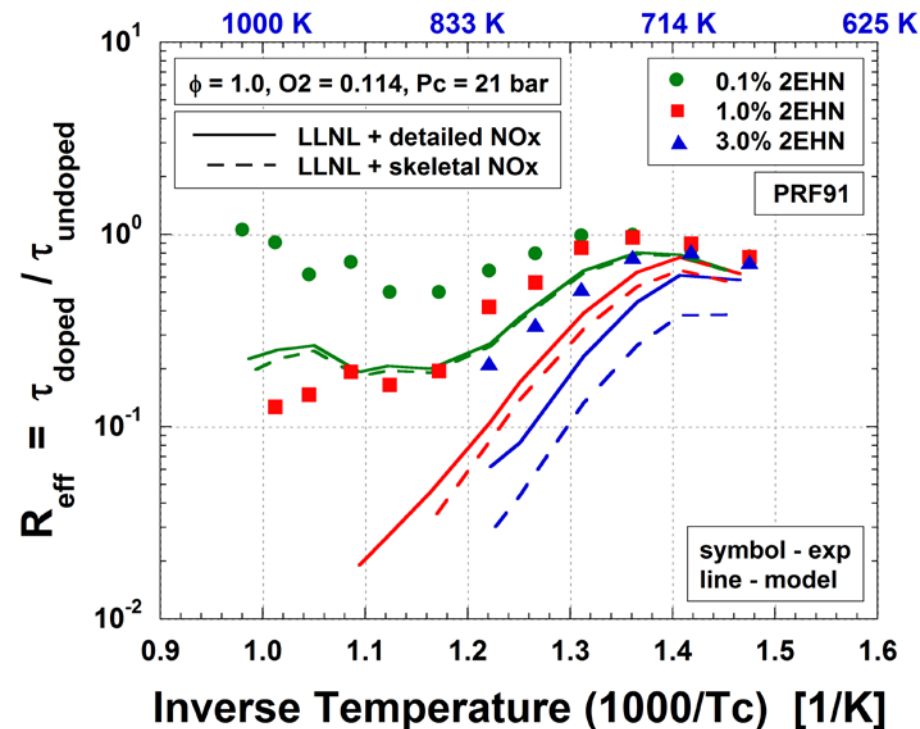## RCM EXPERIMENT, MODEL COMPARISON

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  - **3-component blends do not capture FACE-F gasoline behavior**

Improvements needed in base kinetic model, surrogate formulation methodology.

Technical Accomplishments / Progress

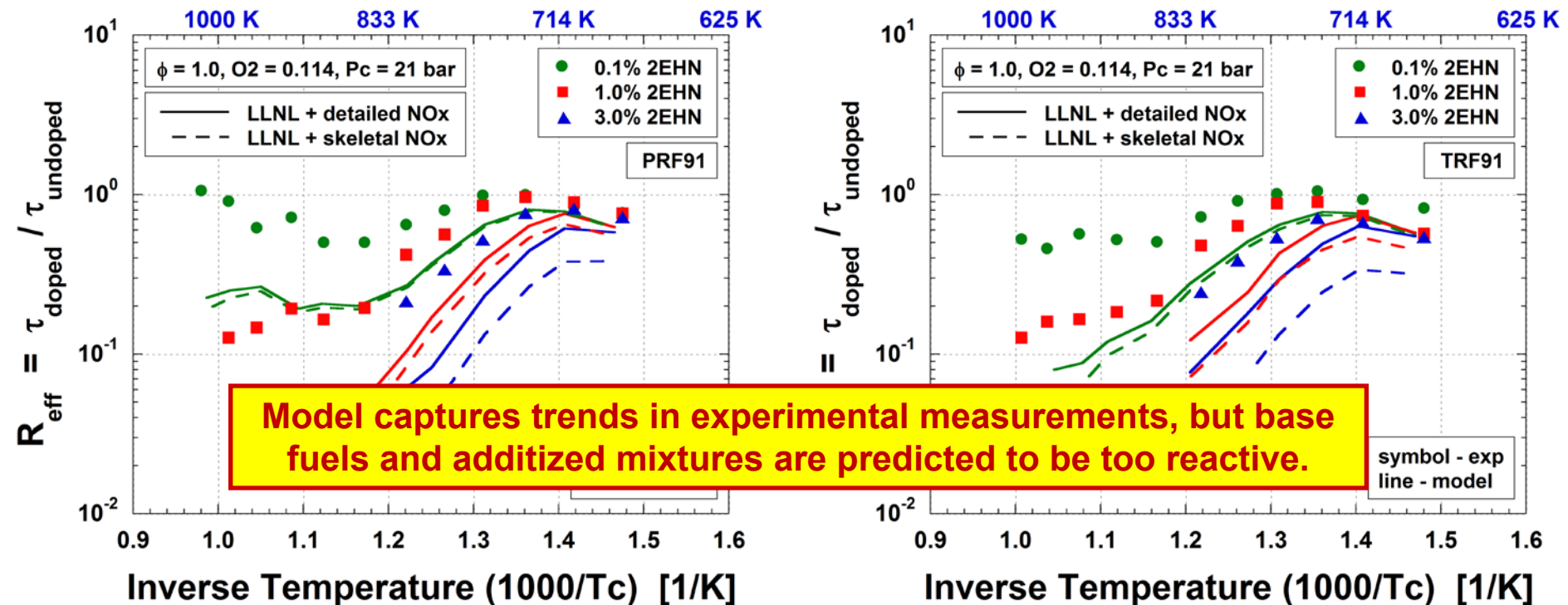## RCM EXPERIMENT, MODEL COMPARISON

- **PRF91 + 2EHN / TRF91 + 2EHN, ϕ = 1.0, p = 20 bar, 11% O_2**
  - **Fairly similar reactivity modification for PRF91 and TRF91**
  - **Effects of additives are over-predicted by model (LTHR, τ)**
  - **Detailed NOx chemistry important only at high doping fractions**

Technical Accomplishments / Progress

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- **Detailed NOx chemistry important only at high doping fractions**

Model captures trends in experimental measurements, but base fuels and additized mixtures are predicted to be too reactive.

Technical Accomplishments / Progress

MODEL INDICATIONS – LOCAL SENSITIVITY ANALYSIS

- **Constant volume, adiabatic simulations, T = 684, 836 K**

- **PRF91 + 2EHN, ϕ = 1.0, p = 20 bar, 11.4% O2**

  - As fuel is doped, typical pathways for low / intermediate temperature chemistry are perturbed, e.g., RO_2 = QOOH.

  - CH_2O / CH_3O_2 / HCO reactions become increasingly important at all times in the induction process. 2EHN decomposition is sensitive at lower temperatures, but not at higher T since it is too fast. Reactions involving the 3-heptyl radical (2EHN-derived) are important at induction times (low T), and at all induction times for higher T. $HONO_2$ and CH_3NO_2 formation / destruction are the only NOx reactions that appear to be sensitive at lower and higher T, respectively, but only at early induction times.

- **TRF91 + 2EHN, ϕ = 1.0, p = 20 bar, 11.4% O2**

  - With doping, TRF91 is more sensitive than PRF91 to 3-heptyl radical reactions (from 2EHN decomposition). CH_2O / CH_3O_2 / HCO reactions are slightly less important compared to PRF91.

  - $NO+HO_2=NO_2+OH$ is the only NOx reaction that appears to be sensitive for the TRF91 blend at these conditions, and only at the highest doping level.

Technical Accomplishments / Progress

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  > **2EHN sensitizes base fuel chemistry; adequacy of surrogate model is important.**
  > **NOx chemistry sensitive to just a few reactions.**
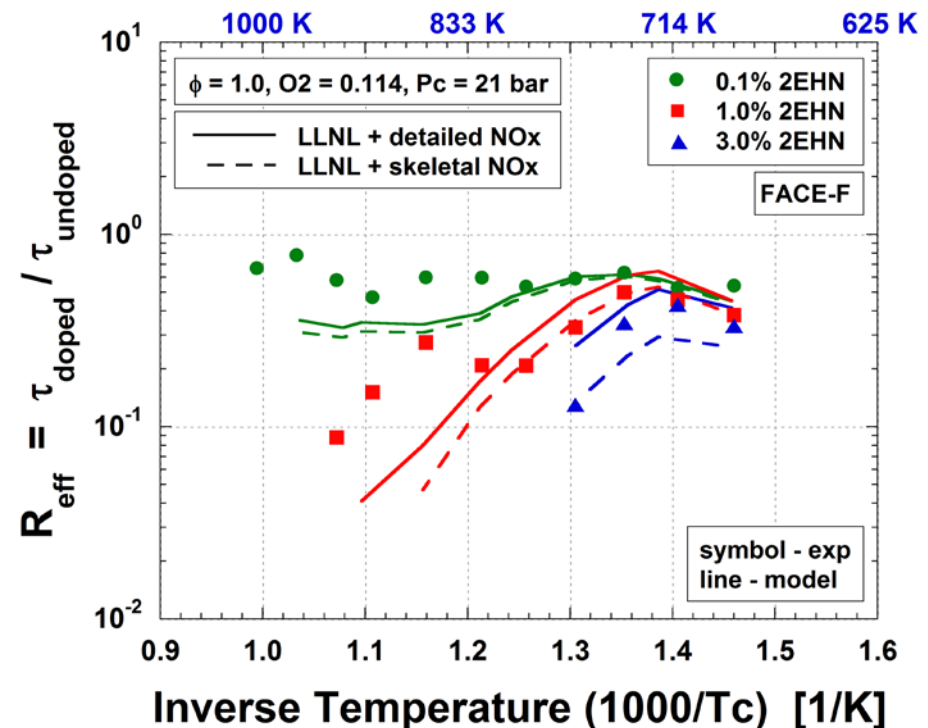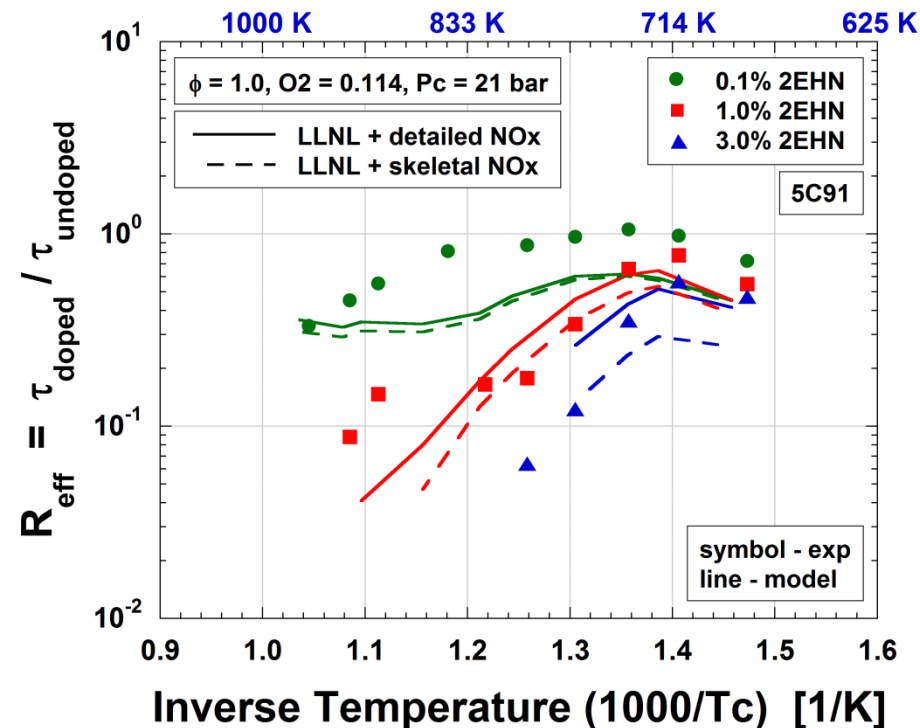 > **→ More work required to better understand, improve kinetic model.**

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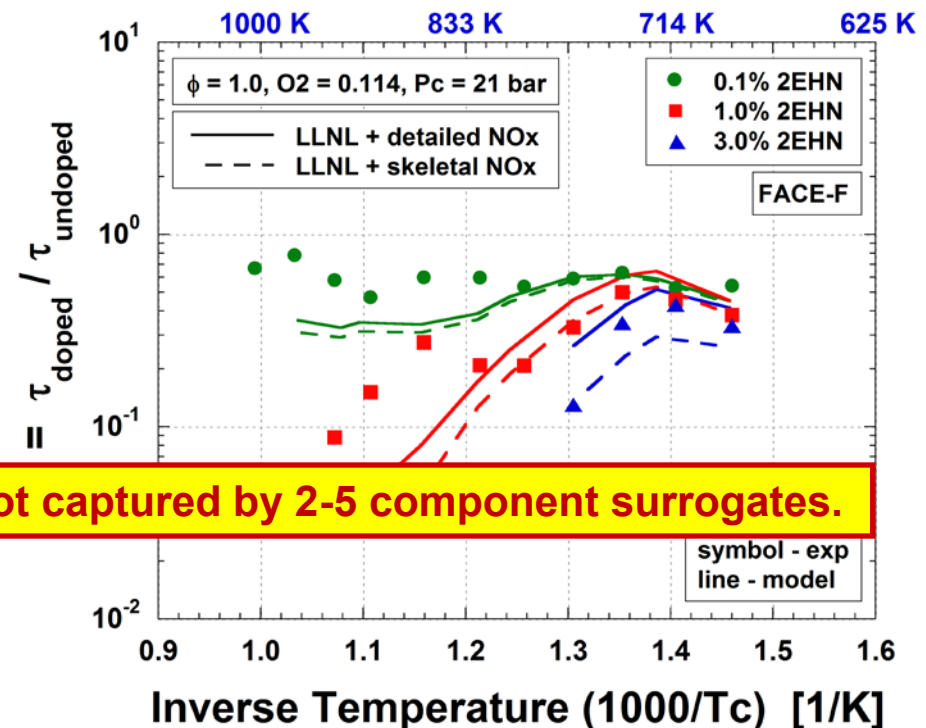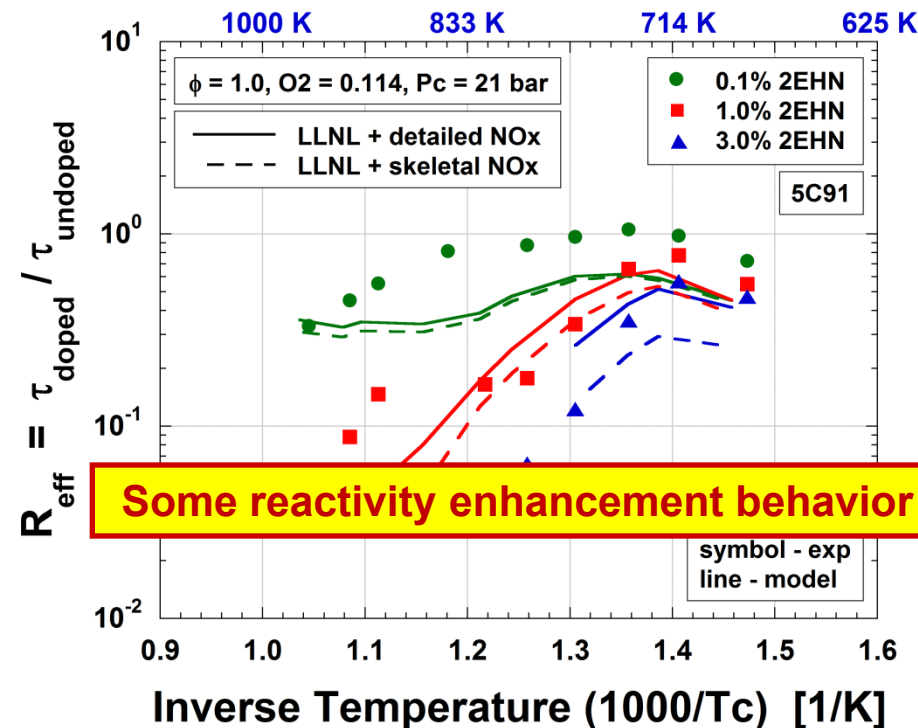
RCM EXPERIMENT, MODEL COMPARISON

- **5C91 + 2EHN / FACE-F + 2EHN, ϕ = 1.0, p = 20 bar, 11.4% O2**

  - **FACE-F seems to be more sensitive to 2EHN additive, particularly at lower temperatures; indications of interactions between gasoline constituents, not seen in surrogate blends**

  - **Similar reactivity trends at intermediate temperatures (T > 833 K)**

RCM EXPERIMENT, MODEL COMPARISON

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Some reactivity enhancement behavior not captured by 2-5 component surrogates.
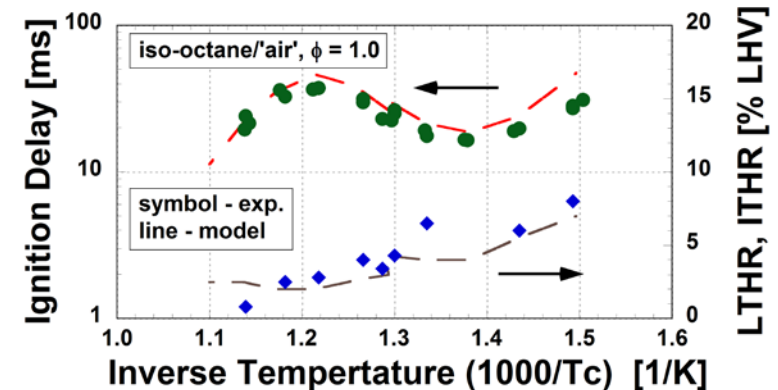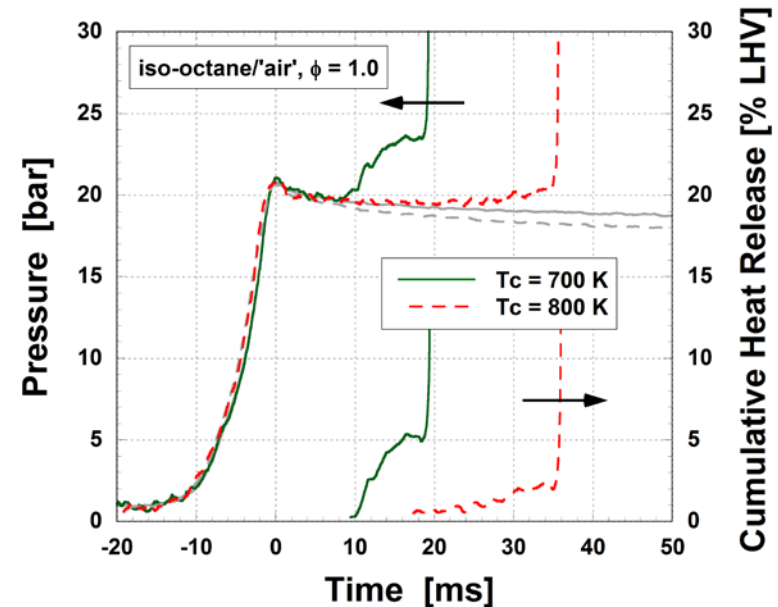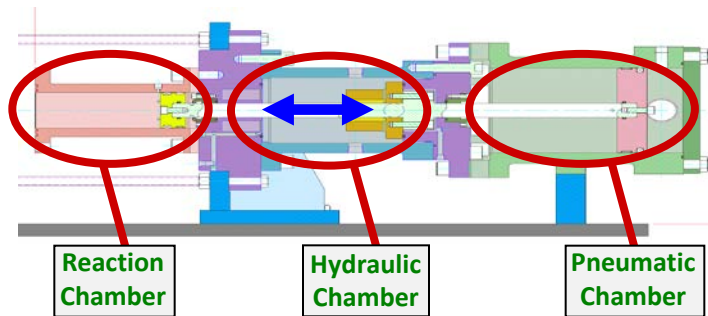
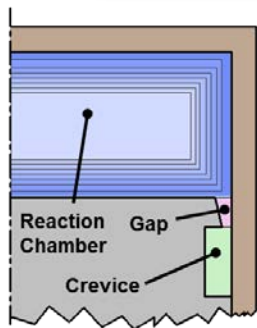# Technical Accomplishments / Progress
RCM HEAT RELEASE ANALYSIS

■ **Useful to characterize preliminary stages of autoignition**

- **Quantifying LTHR / ITHR via application of energy balance to gas in RCM's reaction chamber**

$$\dot{Q}_{chem} = \frac{d}{dt}(mu)_{RC} + \dot{Q}_{wall} - \sum \dot{H}_i + \sum \dot{H}_e + P\frac{dV}{dt}$$

Heat release rate — **Reaction Chamber sensible energy** — **Heat loss to RC walls** — **Enthalpy flow from / to piston crevices** — **Piston compression / expansion**

iso-octane/'air', $\phi = 1.0$

Tc = 700 K
Tc = 800 K

Reaction Chamber Gap
Crevice

Reaction Chamber **Hydraulic Chamber** **Pneumatic Chamber**

iso-octane/'air', $\phi = 1.0$

symbol - exp.
line - model

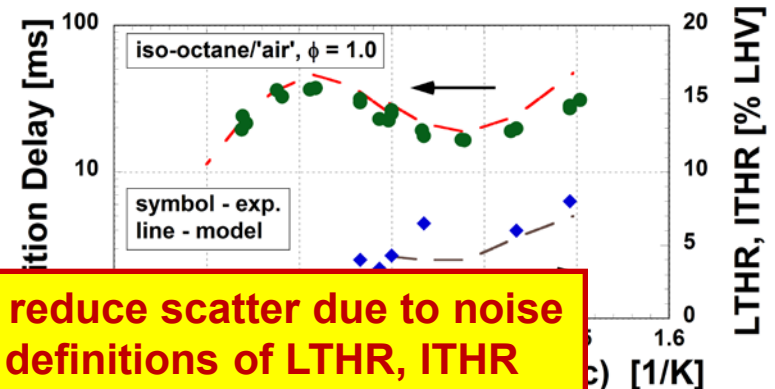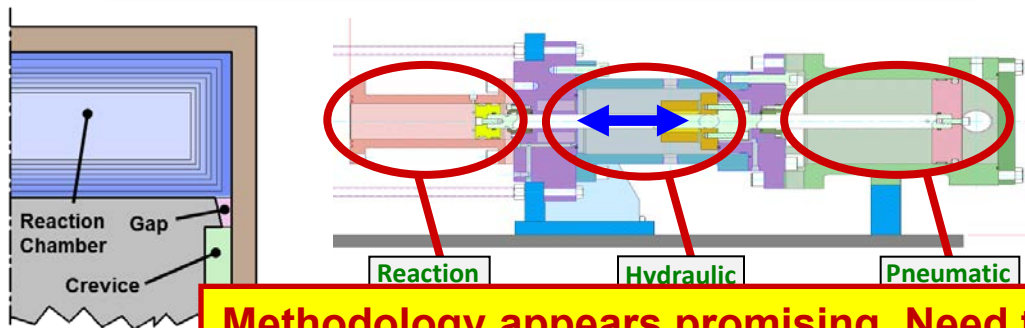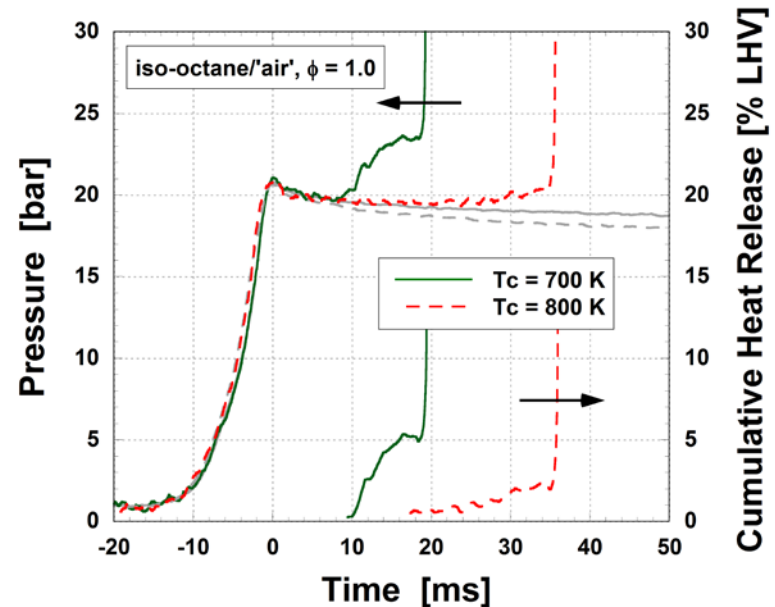Collaborative Combustion Research with BES, 2014 DOE Merit Review

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Technical Accomplishments / Progress

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Heat release rate · **Reaction Chamber sensible energy** · **Heat loss to RC walls** · **Enthalpy flow from / to piston crevices** · **Piston compression / expansion**

iso-octane/'air', φ = 1.0

Tc = 700 K
Tc = 800 K

Pressure [bar] vs Time [ms], Cumulative Heat Release [% LHV]

Reaction Chamber Gap
Crevice

Reaction   Hydraulic   Pneumatic

iso-octane/'air', φ = 1.0

symbol - exp.
line - model

Ignition Delay [ms], LTHR, ITHR [% LHV]

Methodology appears promising. Need to reduce scatter due to noise in measurements, model uncertainties, definitions of LTHR, ITHR

Collab

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Collaborations

COMMUNITY-WIDE ACTIVITIES

- **ANL-led, International RCM Workshop:** patterned after ECN to better understand LTC phenomena using RCMs, esp. auto-ignition chemistry, turbulence-chemistry interactions, etc.

  - **Participation includes experimentalists, modelers, theoreticians**

  - **14 RCM laboratories contributing to first standardized tests using iso-octane; bi-component, other blends to follow**

  - **Establishing consensus for 'Best Practices'**
    - ➡ **approaches for reporting / analyzing / comparing data**
    - ➡ **approaches for simulating the experiments**

http://www.transportation.anl.gov/rcmworkshop/

Collaborations

ONGOING INTERACTIONS

- **DOE Working Groups on HCCI and diesel engines:** results presented at Advanced Engine Combustion MOU

- **ANL:** global sensitivity analysis, mechanism development / refinement, gasoline LTC – reactivity modifiers, new additives

- **LLNL:** fuel mechanism development / validation, gasoline surrogates and additives

- **KAUST / Chevron:** fuel supply

- **U. Wisconsin ERC:** data / models using reactivity modifiers

- **Other universities:** NUI Galway (kinetic models), UIC (biodiesels), U. Michigan, U. Akron and Vrije Universiteit Brussel (reduced-order physical models), Marquette U. (aerosol-fueling)
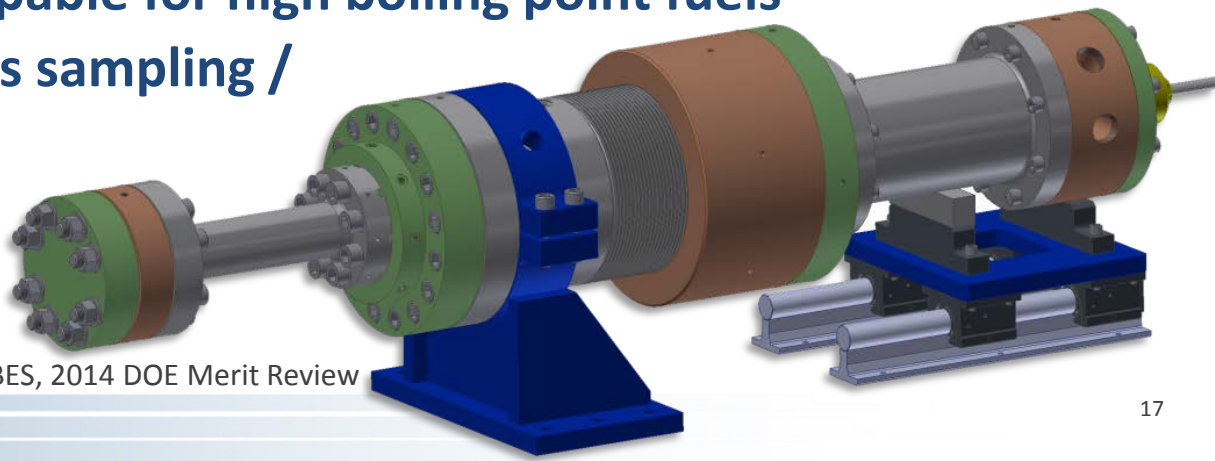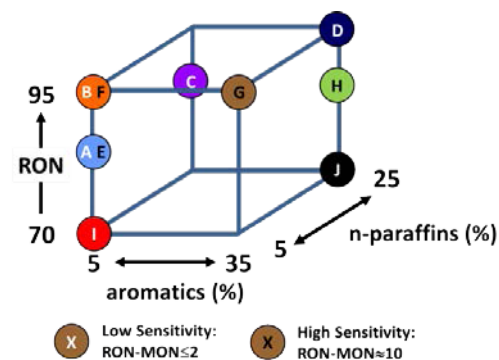
Remaining Challenges

- **Improvements to chemical kinetic mechanism require deeper understanding of model behavior, uncertainties associated with low temperature chemistry pathways of base model**

- **Understanding the sensitization of full boiling-range gasoline via low order (2-5 component) surrogates requires improved capability to formulate surrogates**

- **Ignition delay time, and preliminary heat release are integrated metrics for ignition chemistry, constraints exist with their utility; additional diagnostics could improve development / validation efforts**

Future Work
FY2014 / FY2015

- **Integrate RCM system model with model probing tools (GSA), and stratified reactor approach to improve capabilities of chemical kinetic predictions**

- **Conduct additional experiments and modeling with gasoline and additives**

  - **Improve formulation of low-order surrogates**

  - **Utilize FACE gasolines, ethanol/gasoline blends**

- **Demonstrate new single-piston RCM (funded via ANL LDRD)**

  - **Aerosol-fueling capable for high boiling point fuels**

  - **Integrated with gas sampling / analytical unit**

Response to Reviewer's Comments

- **RCM work provides a good addition to work done via other methods. RCM system model helps to improve accuracy of the chemistry results. Project is an enabler for others exploring reactivity of possible transportation fuels, and to identify shortcomings in chemistry models to focus improvements. More data on fuels of interests to DOE should be presented next year.**

  - **FY2014 activities continue with enhanced experimental facilities and rigorous approach to modeling the system. New data analysis techniques are developed for mechanism comparison. Datasets acquired for gasoline-relevant surrogate blends, and full boiling-range gasoline.**

- **The project should highlight connections to engine efficiency and pollutant reduction, and how selection of reactivity modifiers and long-term development of fuel chemistry can affect these. Identify expectations of, and interactions with industry.**

  - **FY2014 activities continue interactions with ANL GCI engine project, and UW-ERC to identify potential of additives via experiments and simulations. Industrial feedback / interactions acquired through industry working groups such as the Advanced Engine Combustion MOU, and CRC's Fuel for Advanced Combustion Engine Committee.**

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Summary

- **Objective**
  - Acquire data / develop models for transportation-relevant fuels at advanced engine conditions

- **Approach**
  - Utilize ANL's RCM and novel data analysis tools, leverage expertise of BES-funded researchers to synergistically develop predictive models

- **Technical Accomplishments**
  - Acquired extensive datasets and developed kinetic model to understand and predict effects of a common reactivity modifier, 2EHN
  - Utilizing facilities and physics-based, RCM system model to derive and apply new metrics (e.g., ROHR) for validating / refining kinetic models

- **Collaborations**
  - National labs, universities and industry; International RCM Workshop

- **Future Work**
  - Reactivity modifiers, FACE gasolines, model improvement tools, and new experimental apparatus with expanded capabilities
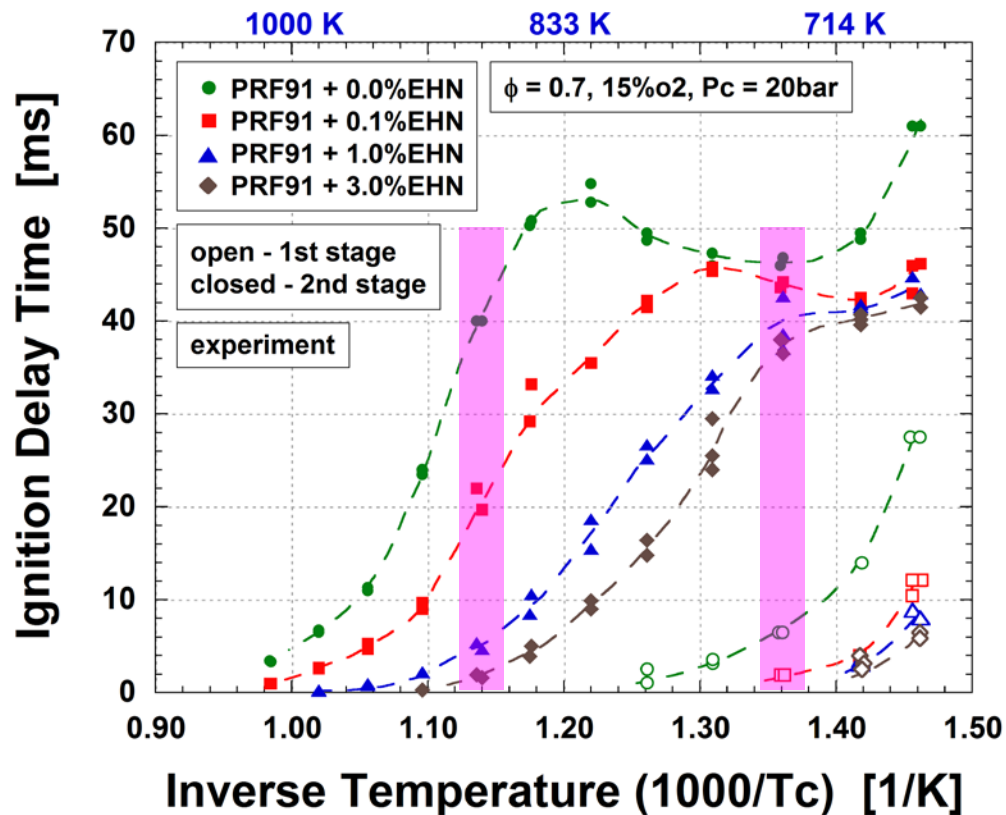
Technical Back-Up Slides

(Note: please include this "separator" slide if you are including back-up technical slides (maximum of five). These back-up technical slides will be available for your presentation and will be included in the DVD and Web PDF files released to the public.)
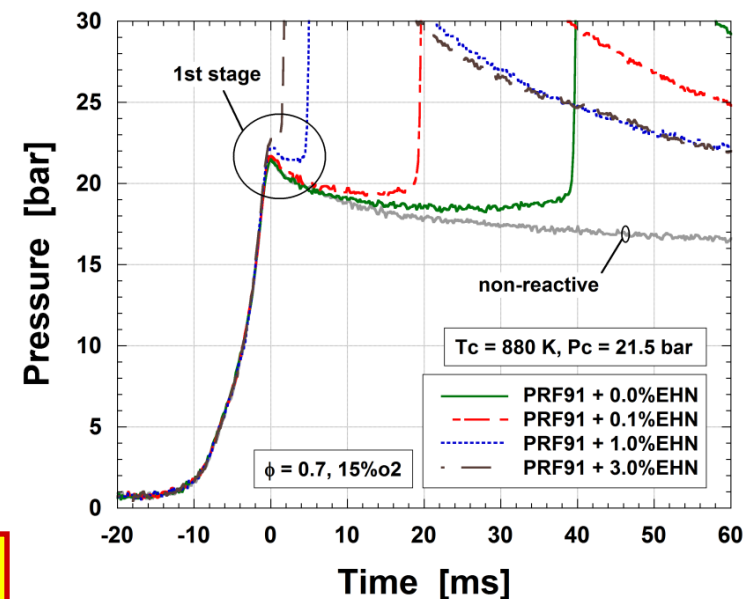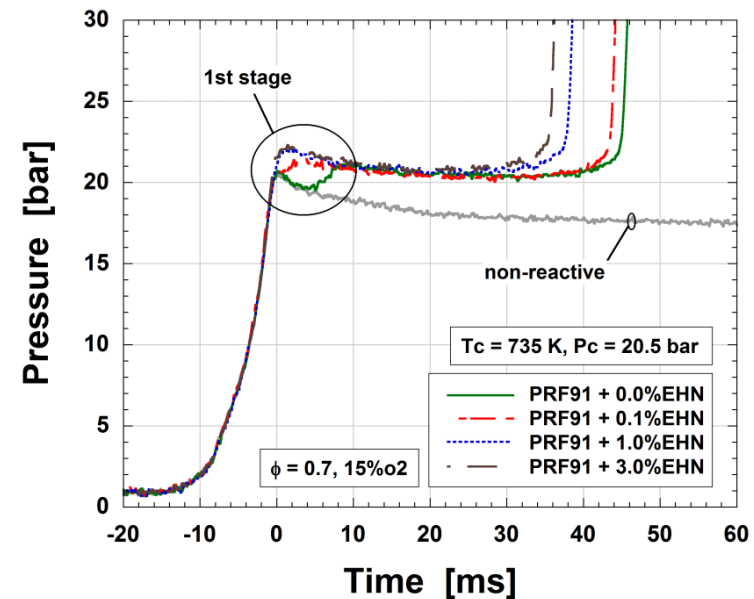
Experimental Measurements
REACTIVITY MODIFIERS

■ **PRF91 + EHN, experiments**

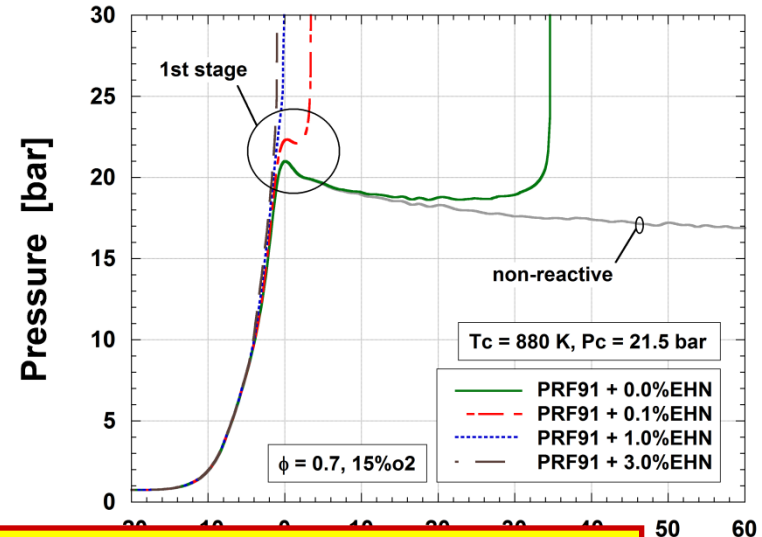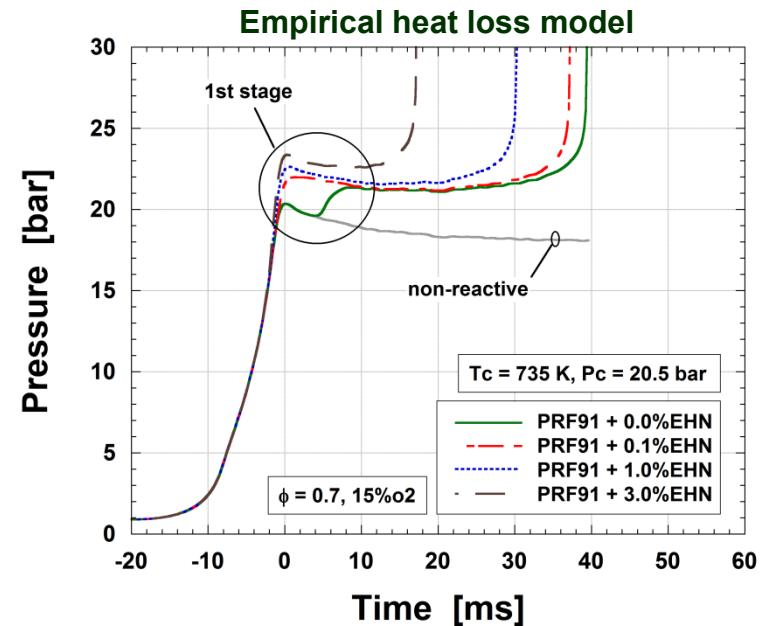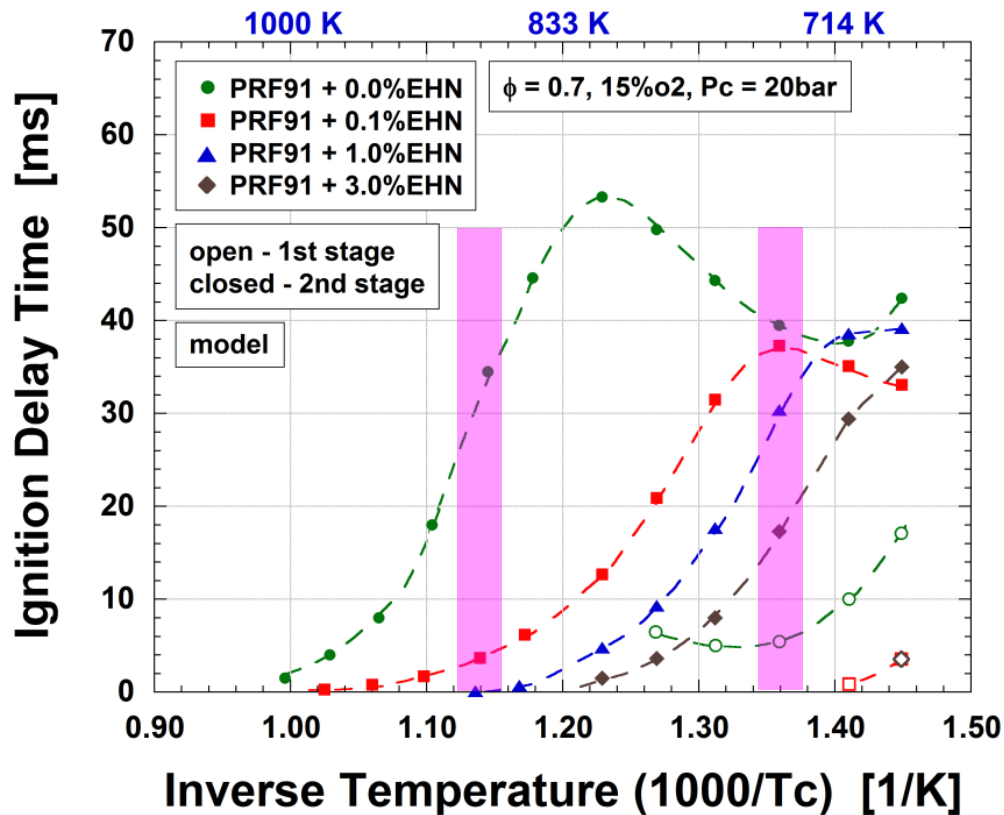- **Early heat release with most additive concentrations**

EHN influential throughout NTC regime

Chemical Kinetic Simulations

REACTIVITY MODIFIERS

- **PRF91 + EHN, simulations**

  - **Over-predicting additive effects; excessive LTHR, esp. at higher T**

Sensitization with low temperature fuel chemistry needs better understanding