Flow Reactor and Kinetic Modeling Progress

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2009 AFOSR MURI Annual Presentation
Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)
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Surrogate Modeling for Real Fuels

- General problem: need data for real fuel and surrogate components and their mixtures in each of the fundamental experimental venues
  - The kinetic *validation database* becomes significantly more complex with the number of components to be used in the surrogate mixture
  - Few data over wide parameter ranges and venues for *pure* components
  - Even fewer data for *mixtures* to validate individual component interactions.
- Experimental difficulties become significantly greater with molecular carbon numbers above 12-14 (keep materials in the gas phase without decomposition)
- Both the model development and validation data requirements favor working with the least number of components.

Modeling Overview

- "Comprehensive" (Westbrook and Dryer, 1981)
  - There is at present no such thing as a kinetic model that fits *all* experimental observations and that will never need revisiting as *"new* validation data become available, mechanism knowledge increases, predicted parameters of interest change……
- The "Hierarchical" modeling -
  - Changes in sub-models are always constrained first and foremost by sub-model validation observations as new constraints are considered.
- Does every potential elementary reaction possible need to be considered?
  - Computational model construction is emerging and will in the long term replace the "art" of model development, but…
  - "Completeness" not guaranteed (as new knowledge on mechanism emerges) and comes with increasing uncertainties in model and numbers of estimated parameters (even if minimization/optimization is applied)
  - *Chemical kinetic purism – put everything in… Engineering interest – make model predictive for the targets pertinent to the application – modeling reduction methods can significantly merge these two interests.*
- MURI is attempting to respond to all of these modeling aspects
- Key - There are scientific, nomenclature, and cultural impediments to merging modeling advances across multiple efforts into cohesive kinetic tools.

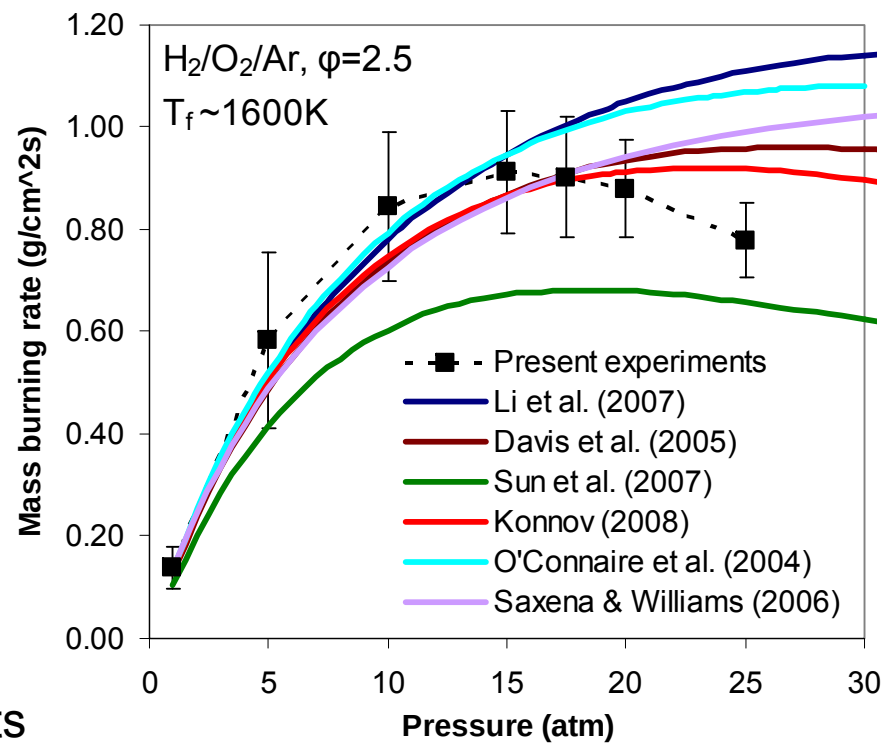
An Example – What is frequently assumed to be well known

New experimental data reveals modeling discrepancies that require re-evaluating model construct and validation for Hydrogen/oxygen at high pressures

Sources of Discrepancies -
- Missing reaction pathways?
- Inaccurate reaction parameters?
- Different thermochemistry?
- Inaccurate pressure fall-off?
- Transport parameters?
- Correct interpretation of data?
- Correct modeling assumptions?

Present case – Models presently in the literature do not reproduce high pressure burning rate data well.

- Though some models prediction similar burning rate predictions, each also predicts considerably different reactive radical species profiles within the flame structure.

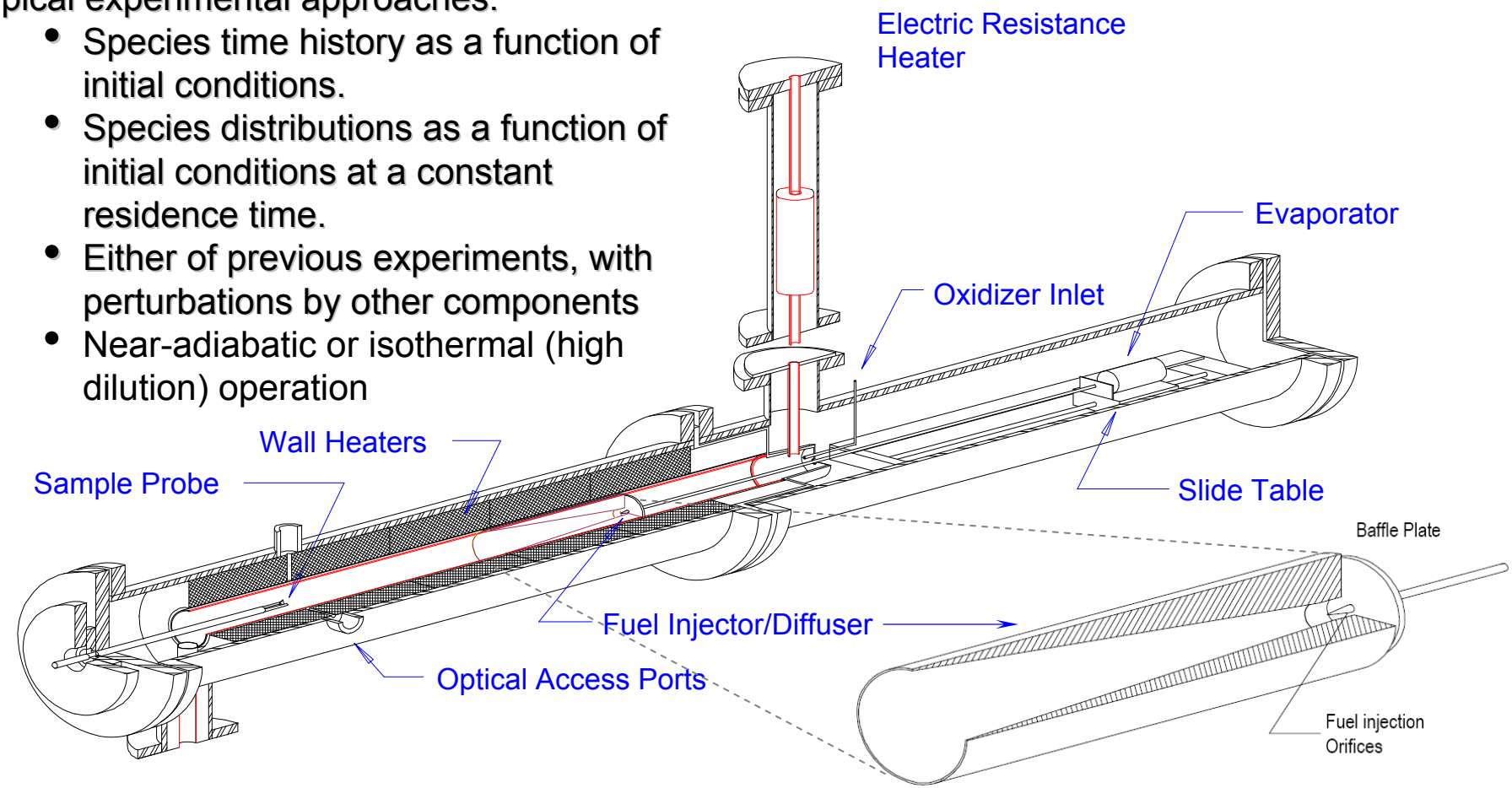


from Burke et al. (2009) Combust Flame (In press)

Princeton Variable Pressure Flow Reactor

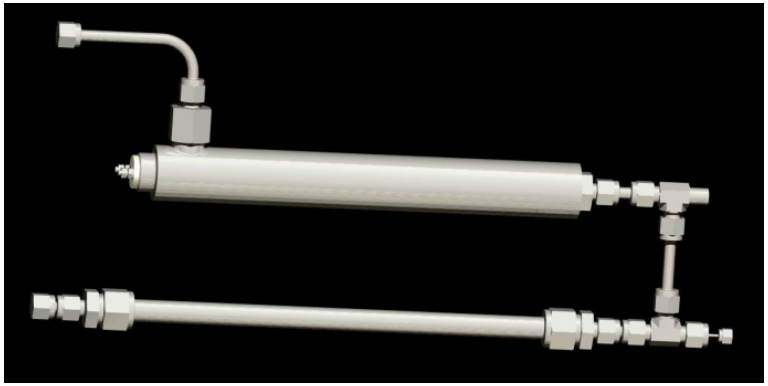
Typical experimental approaches:

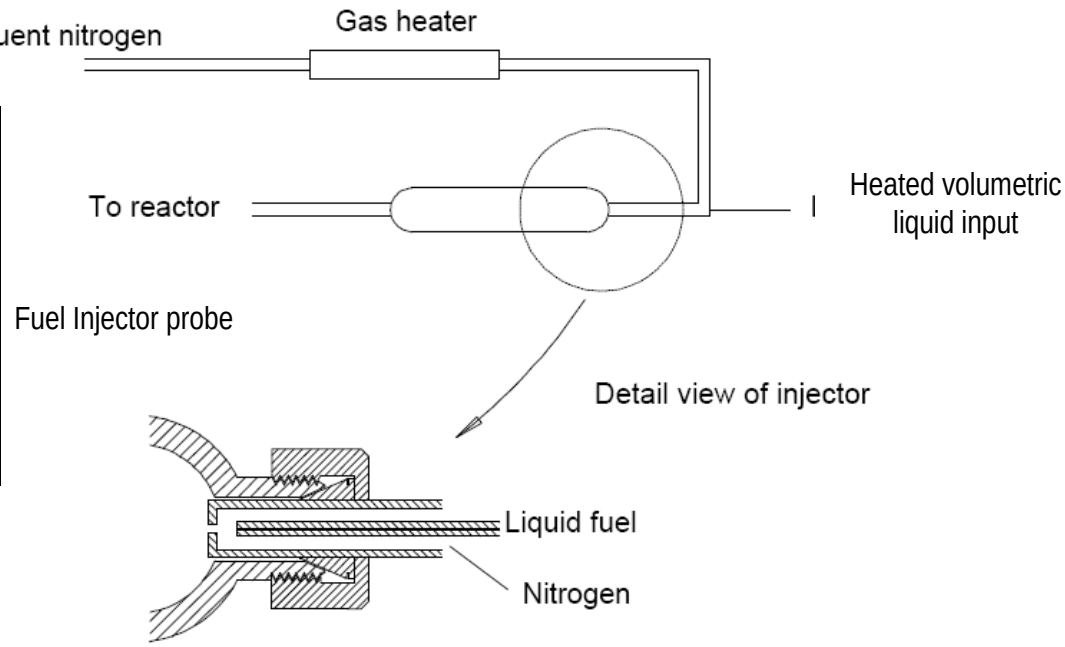
- Species time history as a function of initial conditions.
- Species distributions as a function of initial conditions at a constant residence time.
- Either of previous experiments, with perturbations by other components
- Near-adiabatic or isothermal (high dilution) operation



Reactor Duct Material	Fused Silica	Reactor Section Dia.	10 cm
Pressure:	0.2 - 20 atm	Mass Flow rate:	10 - 30 grams/sec
Temperature:	500- 1200 K	Residence Time:	0.015 - 5 sec

Liquid Fuel Metering and Vaporization System

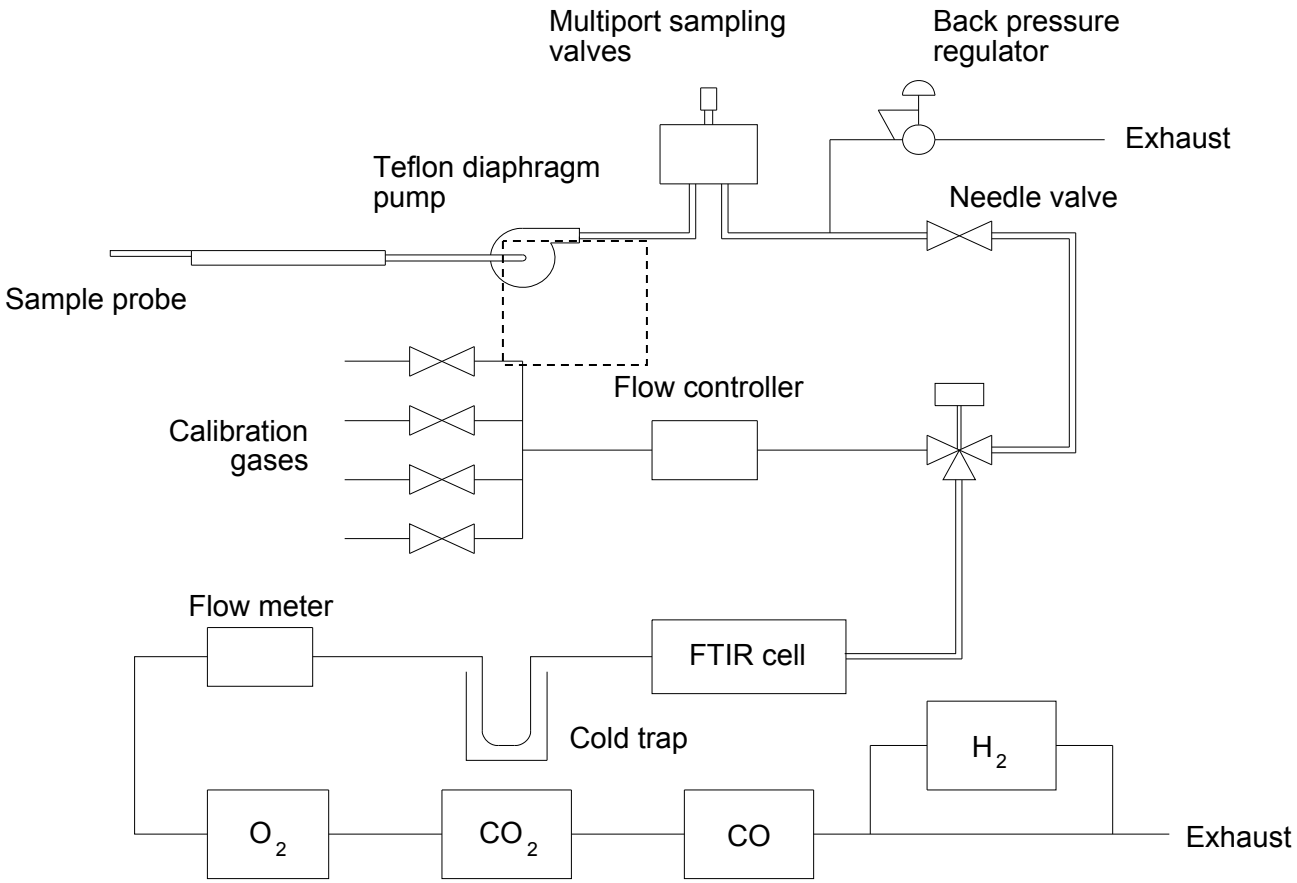




- Recent improvements to deliver vapor for components and mixtures up to C_{16}.
- Revision in analytical system to hot glycol/water cooling of convection quenched sampling probe system to gas storage valve for off-line GC/TC/FID/FTIR

VPFR Sample System Schematic

(Double lines represent heated Teflon tubing)



Updating of on-line FTIR and off-line GC/TC/FID/FTIR analytical tools

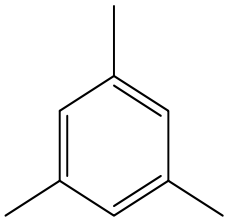
Flow Reactor Experimental Studies

High pressure n-decane; C9 alkylated benzenes

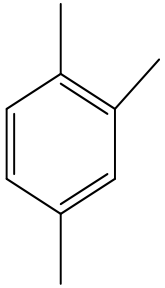
Fuel	T / K	Fuel / ppm	Φ
n-decane	520—1000	1000	pyrolysis &1.0
1,3,5 trimethyl benzene	520—1048	1150	pyrolysis,1.0 & 0.2
1,2,4 trimethyl benzene	520—1048	1150	pyrolysis,1.0 & 0.2
n-propyl benzene	520—1048	1150	pyrolysis & 1.0

Summary of conditions for flow reactor study of surrogate jet fuel pure components.

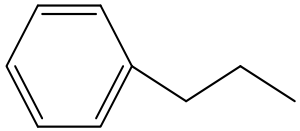
- Pressure held at 12.5 atm for all data sets.



1,3,5 trimethyl benzene



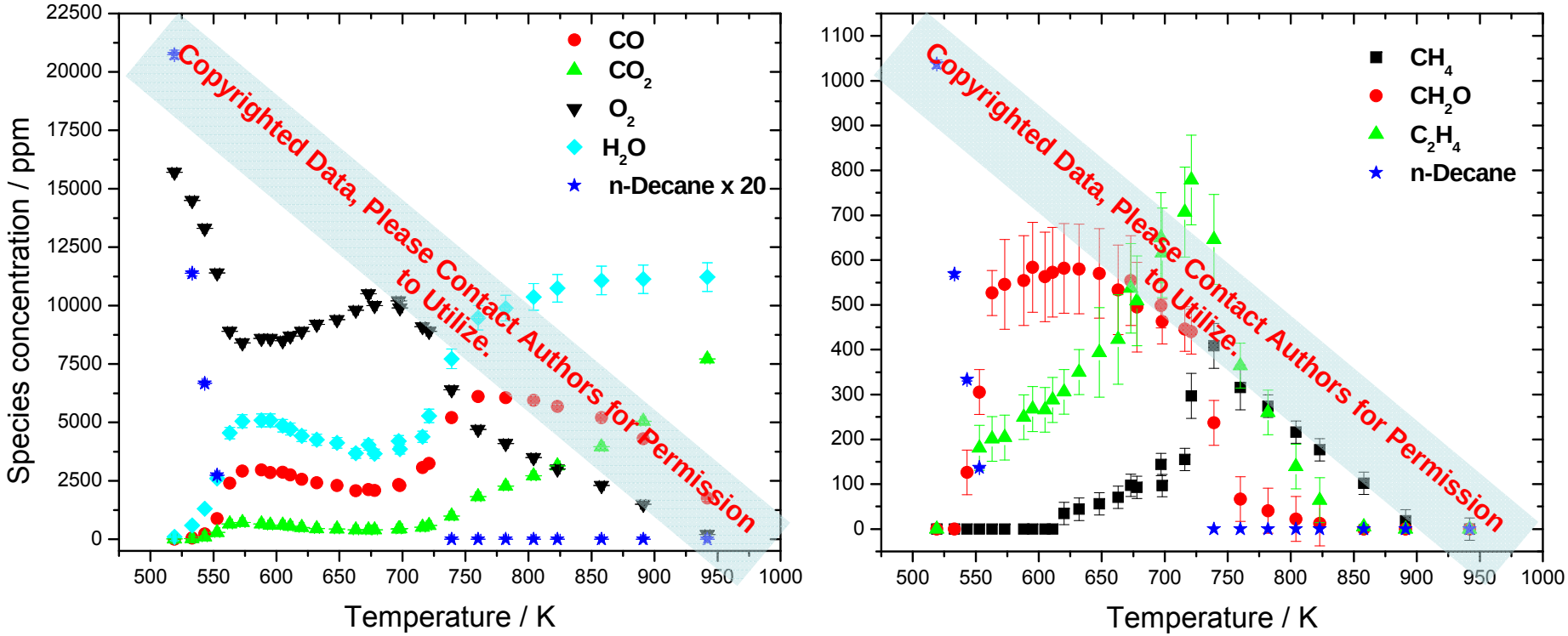
1,2,4 trimethyl benzene



n-propyl benzene

n-Decane Oxidation

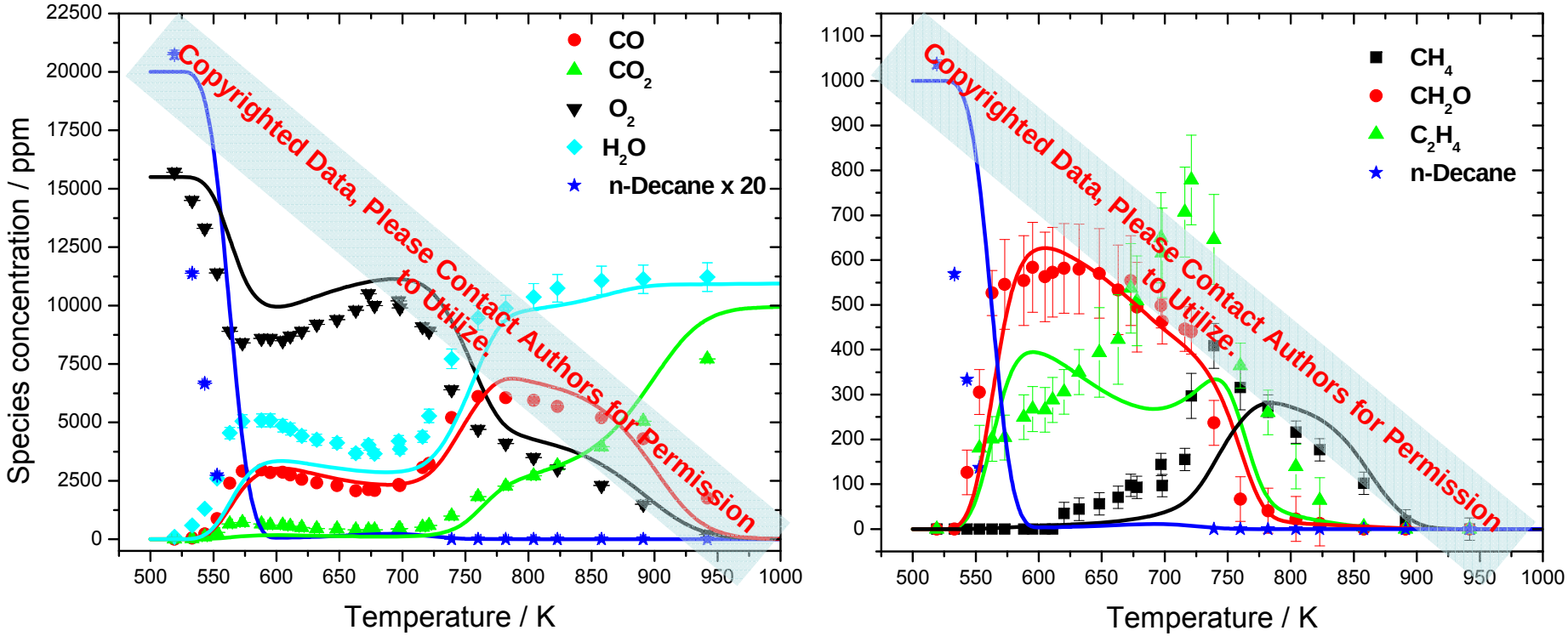
- Extensive reactivity at low temperatures, including pronounced negative temperature coefficient region from ~575 — 700 K.



Experimental data for 1000 ppm n-decane, 15500 ppm O_2, Φ =1.0, τ=1.8s at 12.5 atm.

n-Decane Oxidation

- Kinetic models show generally good reproduction of global reactivity and large intermediates and products, with lesser fidelity for small intermediates.



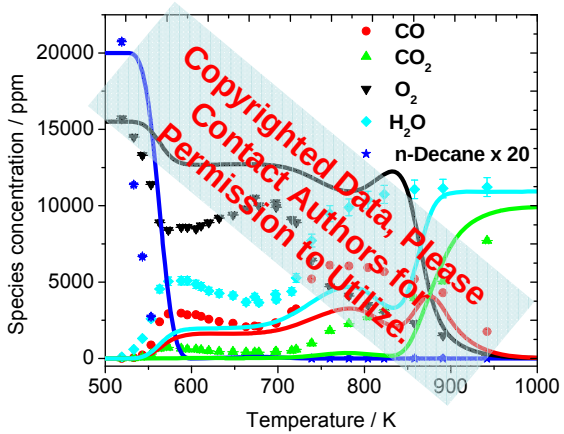
Experimental data (symbols) verses simulation (lines) for 1000 ppm n-decane 15500 ppm O_2, Φ =1.0, τ=1.8s at 12.5 atm.

➢ Westbrook C.K., Pitz W.J., Herbinet O., Curran H.J, and Silke E.J., *Combust. Flame 156 2009 181 — 199.*

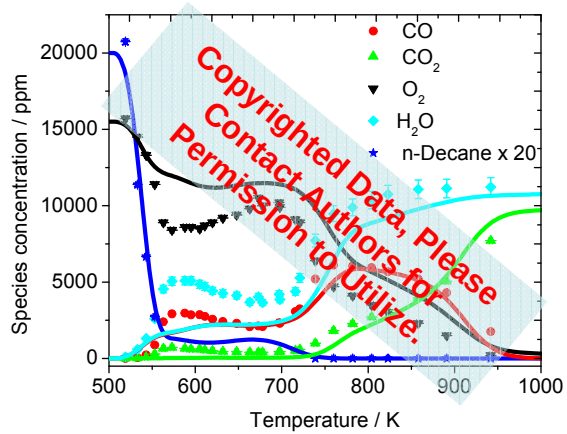
n-Decane Oxidation

- Other models show varying disparities of predictions with the experimental data.

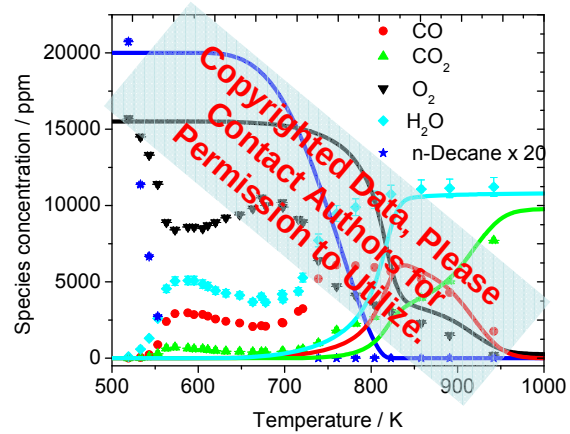
Bikas and Peters.



Gokulakrishnan et al.



JetSurF v 0.2

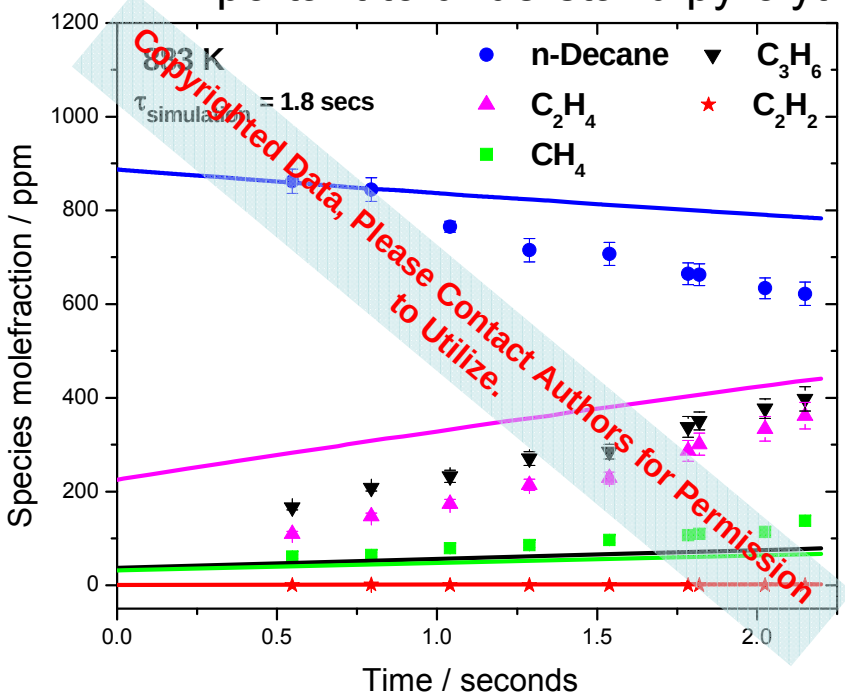


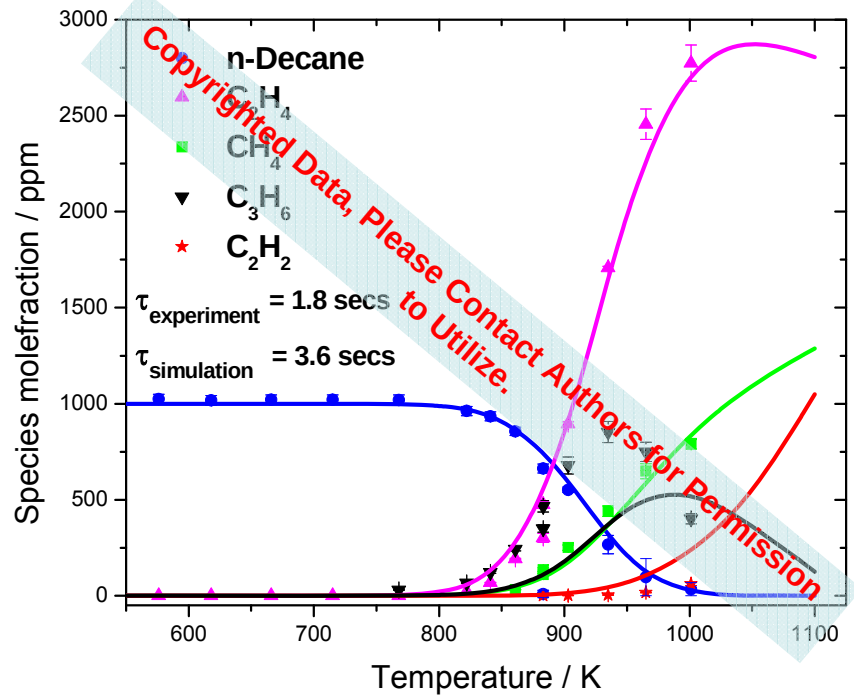
Experimental data (symbols) verses simulation (lines) for 1000 ppm n-decane 15500 ppm O_2, Φ =1.0, τ=1.8s at 12.5 atm.

- Bikas G. and Peters N., *Combust. Flame 2001, 126, 1456 — 1475.*
- Gokulakrishnan, P., Gaines G., Currano J., Klassen M. S. and Roby R. J., ASME Transactions: Journal of Engineering Gas Turbines and Power.
- JetSurF v 0.2, B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, F. N. Egolfopoulos, H. Wang, S. S. Vasu, D. F. Davidson, R. K. Hanson, C. T. Bowman, A. Kelley, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, A. Violi, R. P. Lindstedt, September 2008.

n-Decane Pyrolysis

- Important to understand pyrolytic as well as oxidative behavior





Experimental data (symbols) verses simulation (lines) for 1000 ppm n-decane at 12.5 atm.

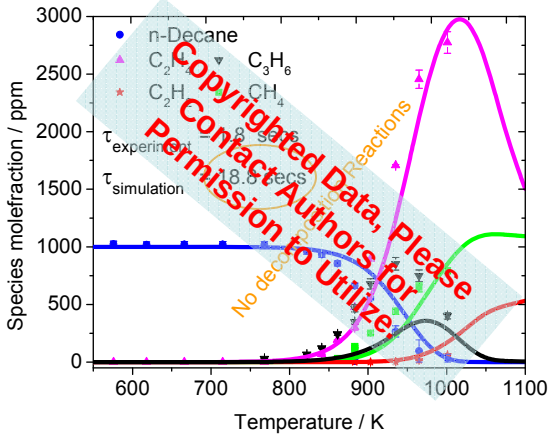
- Predicted pyrolysis rates are slower than observed
- Distribution of intermediates with exception of C_2H_2, C_3H_6 are reasonable.

➢ Westbrook C.K., Pitz W.J., Herbinet O., Curran H.J, and Silke E.J., *Combust. Flame 156 2009 181 — 199.*

n-Decane Pyrolysis

- Large amounts of propene and ethylene formed, but not reproduced at correct temperature.
- Alkyl radical isomerization reactions differ in every model.

Bikas and Peters.



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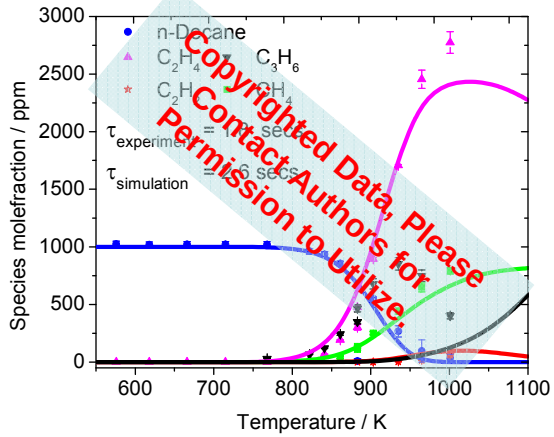

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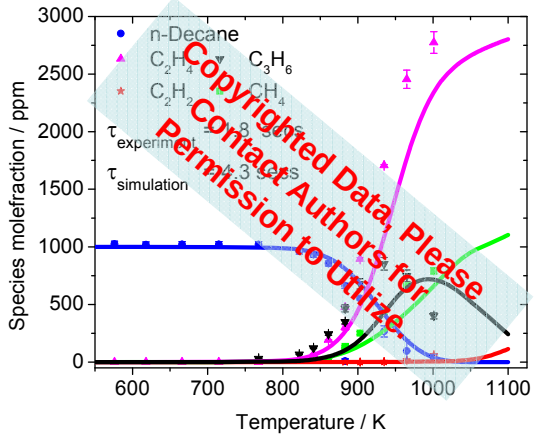

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- Bikas G. and Peters N., *Combust. Flame 2001, 126, 1456 — 1475.*
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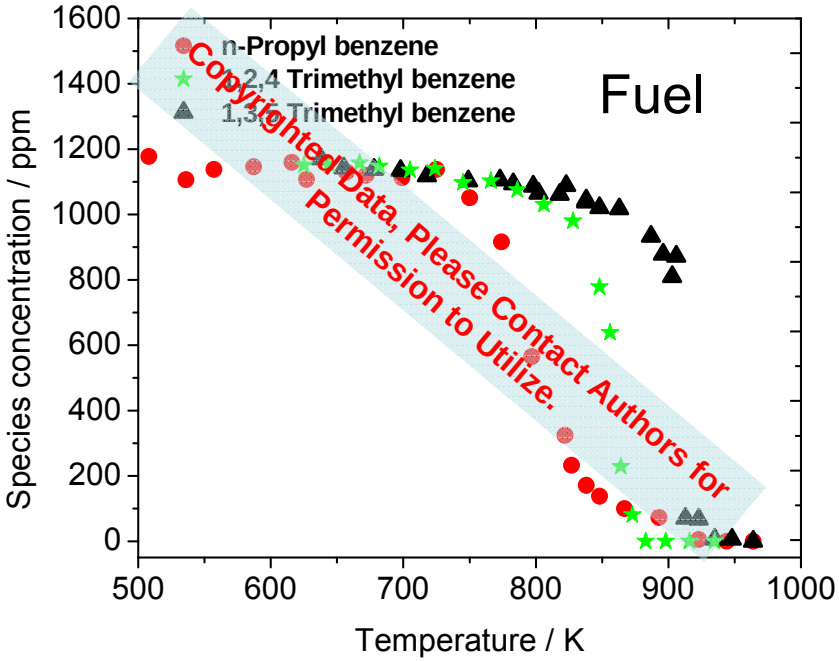
Aromatic Oxidation

- 1,3,5 Trimethyl benzene, 1,2,4 trimethly benzene and n-propyl benzene are selected aromatic surrogate fuel components.
- Blending ratio of these fuels needed to adjust reactivity and TSI of surrogate mixture to match real jet fuels.



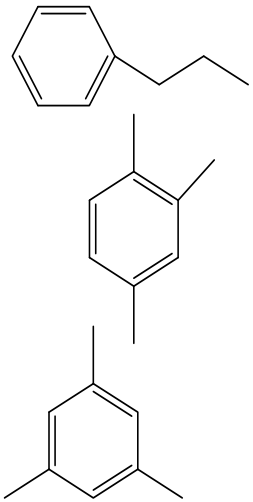
Experimental data for ~1125 ppm fuel, 13500 ppm O_2, Φ=1.0, at 12.5 atm and τ = 1.8 seconds.

Reactivity

n-Propyl benzene

1,2,4 Trimethly benzene

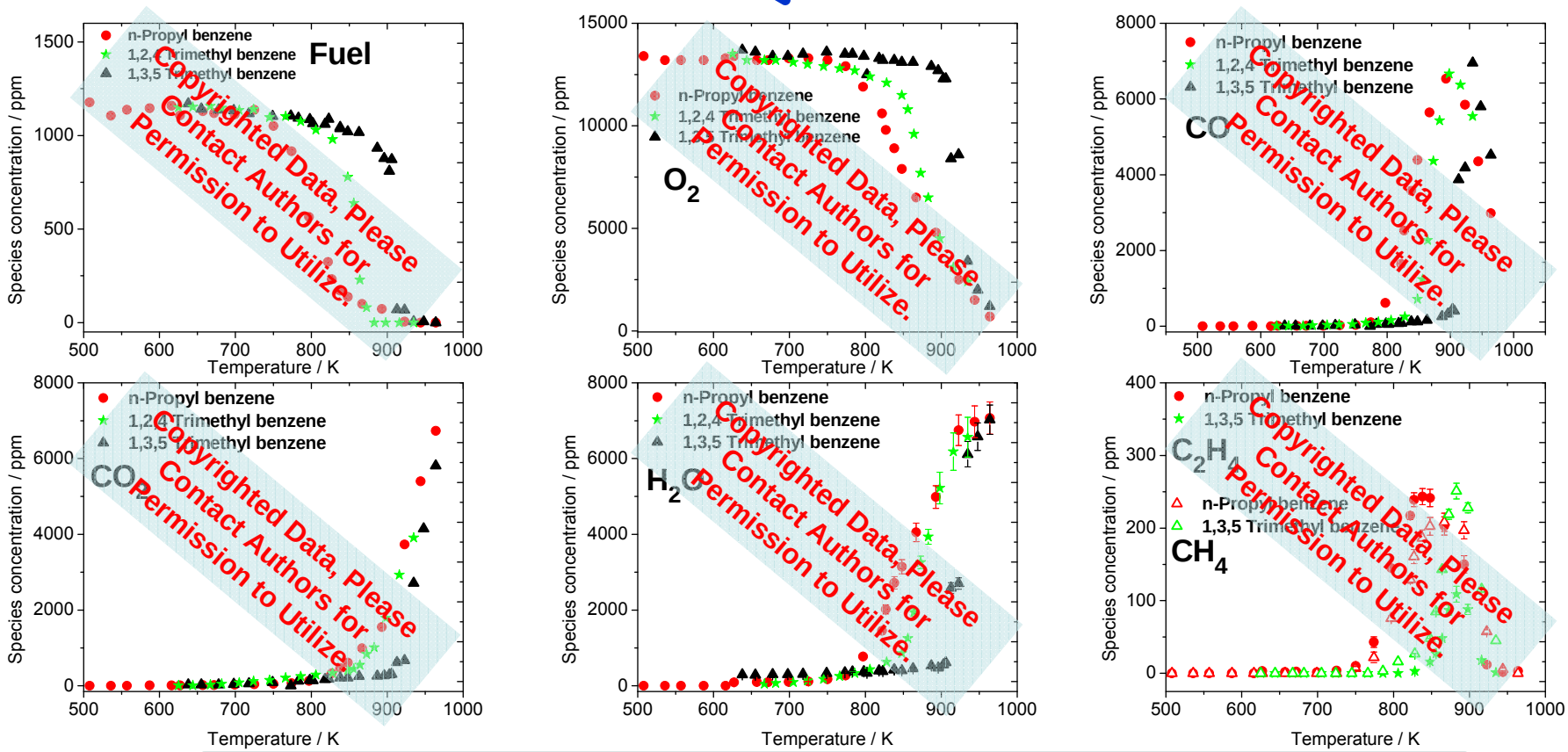
1,3,5 Trimethyl benzene



Aromatic Oxidation

- Other species comparisons ⟹ n-propyl benzene > 1,2,4 TMB > 1,3,5 TMB

Reactivity



Experimental data for ~1125 ppm fuel, 13500 ppm O_2, Φ=1.0, at 12.5 atm and τ = 1.8 seconds.

Aromatic Oxidation

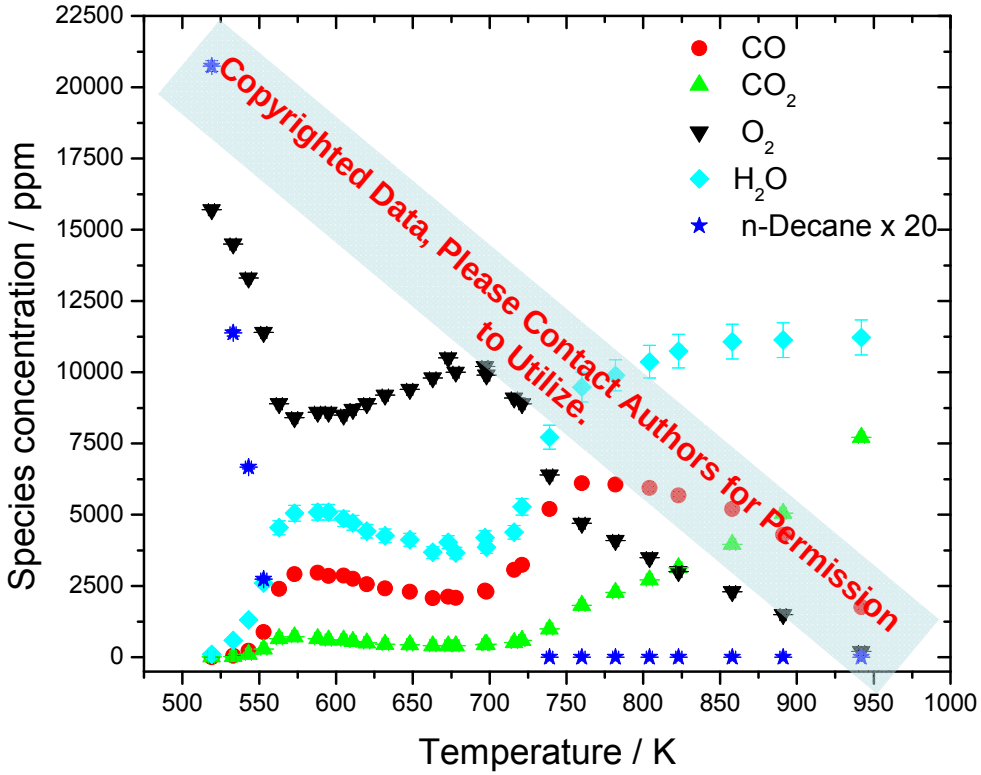
Reactivity ←

- Other parameters ? $\Longrightarrow$ n-propyl benzene > 1,2,4 TMB > 1,3,5 TMB.

Extinction strain rate of aromatic fuels from counterflow diffusion flames.
Adapted from Sang Hee Won, Wenting Sun, Xiaolong Gou and Yiguang Ju.

Oxidation of n-Decane/Aromatic Blends

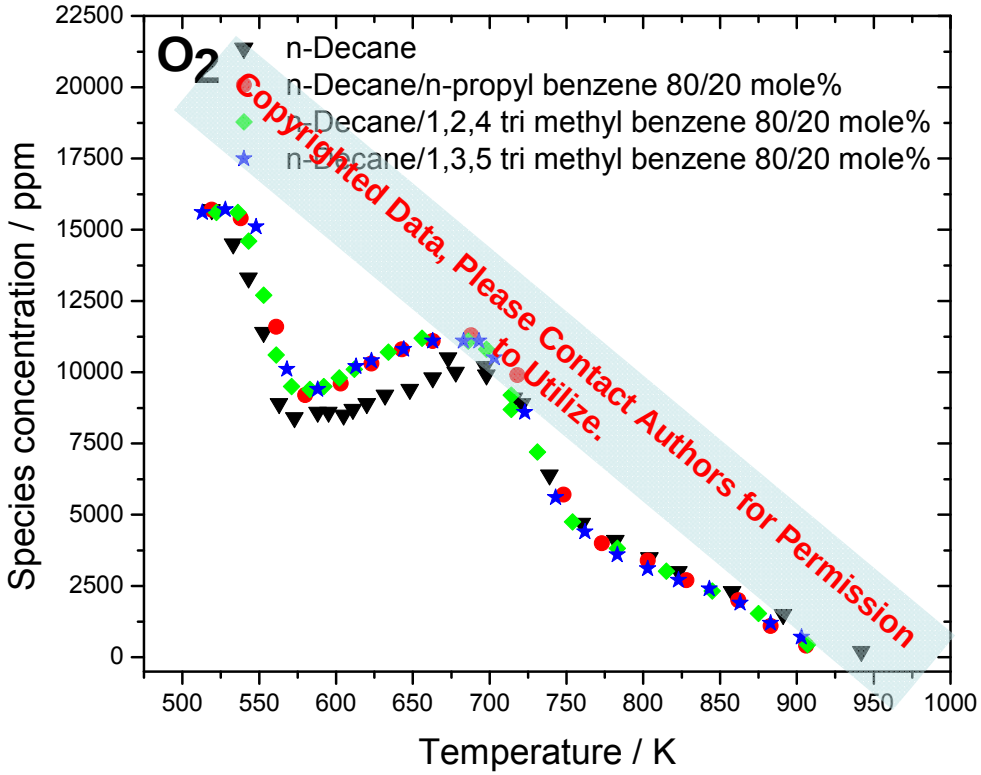
- Expect an inhibitive effect on global oxidation reaction due to presence of aromatics.



Experimental data for 1000 ppm n-decane, 15500 ppm O_2, Φ =1.0, τ=1.8s at 12.5 atm.

- Use [O_2] as indicator of global reactivity.
- Pure n-decane shown here
- Following slide compares oxygen profiles with individual aromatic addition to that here (other species comparisons show similar behavior)

Oxidation of n-Decane/Aromatic Blends



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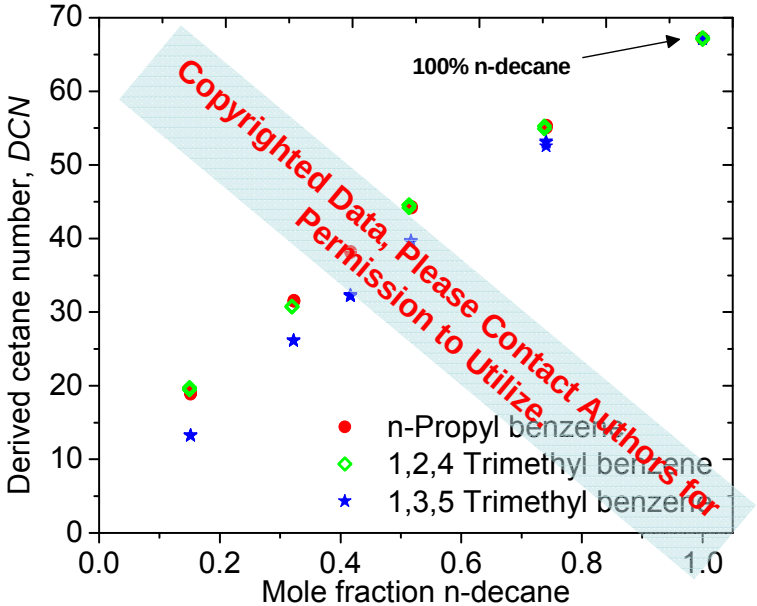
Experimental data for 1000 ppm fuel, 15500 ppm O_2, τ=1.8s at 12.5 atm.

- Test perturbation of reactivity relative to n-decane if 20 mole % of fuel is replaced with aromatic: n-propyl benzene
  1,2,4 tri methyl benzene
  1,3,5 tri methyl benzene
- n-Decane oxidation is insensitive to blending with 20 mole % aromatic at 700K<T< 900K and τ_{res} =1.8s.
- Low temperature oxidation behavior is affected, including magnitude but not temperature range of NTC region.
- Perturbation is due primarily to radical termination from the presence of <u>an</u> aromatic functionality.
- Do we need to consider all three as surrogate components?,

⇒ Other premixed ignition studies to confirm.

Oxidation of n-Decane/Aromatic Blends

- Derived Cetane Nos.(DCNs) of n-propyl benzene/n-decane blends and 1,2,4 trimethyl benzene/n-decane blends almost identical.
- Threshold Sooting Index of 1,2,4 trimethyl benzene ≅ 1,3,5 trimethyl benzene.
- Considering these results, 1,3,5 trimethyl benzene may be more appropriate to utilize as a component than 1,2,4 trimethyl benzene for surrogate formulations.



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Derived cetane numbers for n-decane/aromatic mixtures from Ignition Quality Tester, at ~865K and 20atm.

Smoke points and threshold sooting index (TSI) values. Adapted from A. Mensch, V. Iyer, R. J. Santoro, T. A. Litzinger.

Large Molecule Kinetic Modeling

Paraffins

- n-Alkane (iso-alkane) kinetic models are reasonably well developed:
- Still some fundamental questions regarding low temperature oxidation (fate of RO_2 species) and pyrolytic decomposition.
- Display good reproduction of global oxidation observations under practical conditions: ignition delay, major intermediate production, laminar burning velocity, flame extinction and autoignition.

  ⇒ committed to evaluation and further development of these kinetic models in collaboration with LLNL.

Aromatics

- Oxidation of alkylated aromatic fuels is much less well developed.

  ⇒ Scant experimental data for any aromatic other than toluene.

  ⇒ Even available toluene kinetic models have some shortcoming: most reproduce ignition delay but show less satisfactory agreement against speciation data.
- Must revisit and refine kinetic description of toluene oxidation.

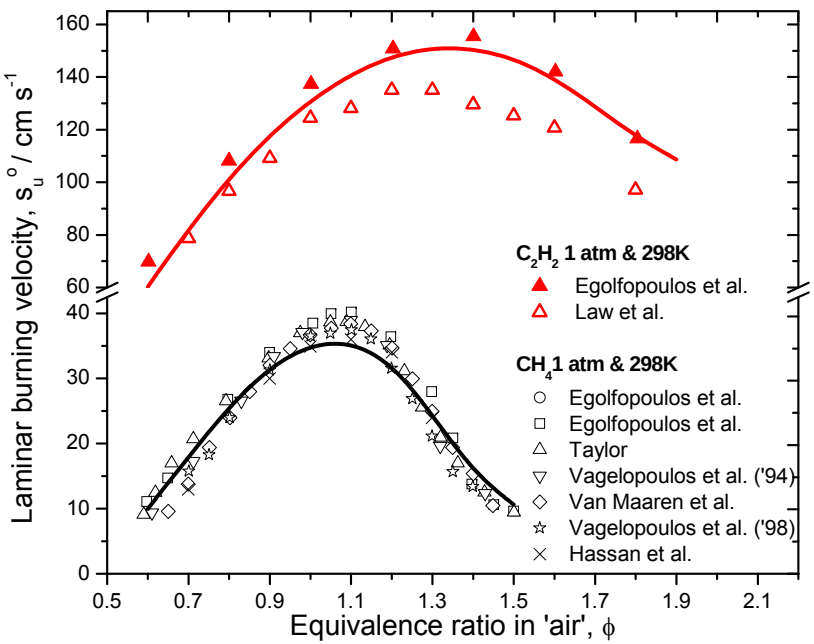
  ⇒ extend kinetic and thermodynamic parameters to larger alkylated aromatics.

Small Species Sub-models

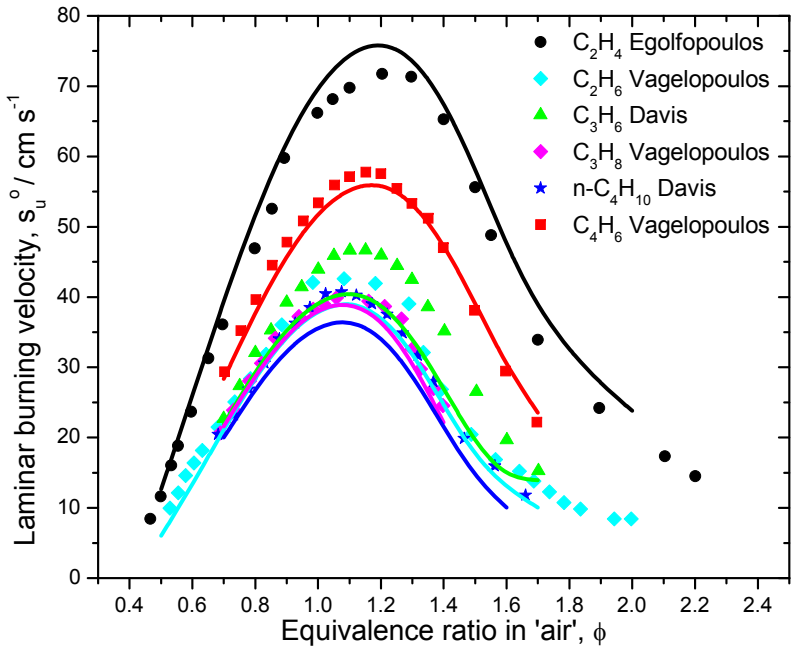
- Logistical challenge of parallel kinetic modeling efforts across a number of research groups => integrated effort would be very beneficial.
- Critical that a common and rigorous base chemistry set evolve.
- **C_4 Sub mechanism development**
  - H_2 — C_1 sub mechanism from Princeton DME studies.
    - Li J., Zhao Z., Kazakov A., Chaos M., Dryer F.L. and Scire J.J. Jr., *Int J Chem Kinet 2007 39 109 — 136.*
    - Zhao Z., Chaos M., Kazakov A., and Dryer F.L., *Int J Chem Kinet 2008 10 1 — 18.*
    - Bikas G. and Peters, N. *Combust Flame 2001 126 1456 — 1475.*
  - C_2 — C_4 sub mechanism from Healy *et al.*
    - Healy D., Curran H.J. , Simmie J.M., Kalitan D.M., Zinner C. M., Barrett A.B., Petersen E.L., and Bourque G., *Combust Flame 2008 155 3: 441 — 448.*
  - Butadiene chemistry from Laskin *et al.*
    - Laskin A., Wang H. and Law C.K., *Int J Chem Kinet 2000 32 589 — 614.*
- Validation database is large and evolving, currently encompassing wide range of conditions and environments for H_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, DME, C_3H_6, C_3H_8, C_4H_6, C_4H_{10}.

Small Species Chemistry

- **C_4 Sub mechanism development – shock tube ignition delay, flow reactor speciation, stirred reactor speciation, rapid compression machine, examplar flame burning rate data here**
- **Identified some areas for further improvements=> continual attention needed**



Laminar burning velocities, s_u^o , of methane and acetylene in 'air'. Experimental data (symbols) verses simulation (lines).



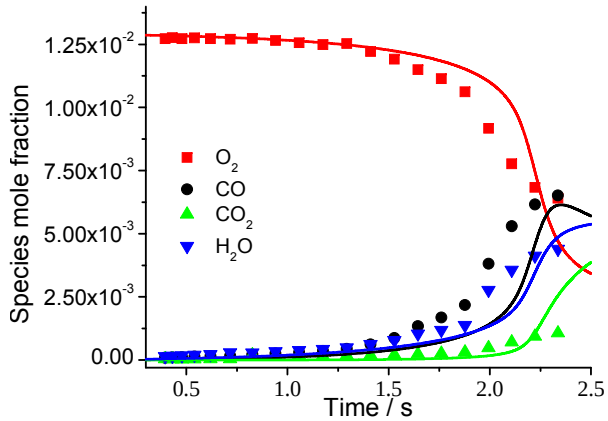
Laminar burning velocities, s_u^o , for fuel /'air' mixtures. Experimental data (symbols) verses simulation (lines).

Toluene Kinetic Model

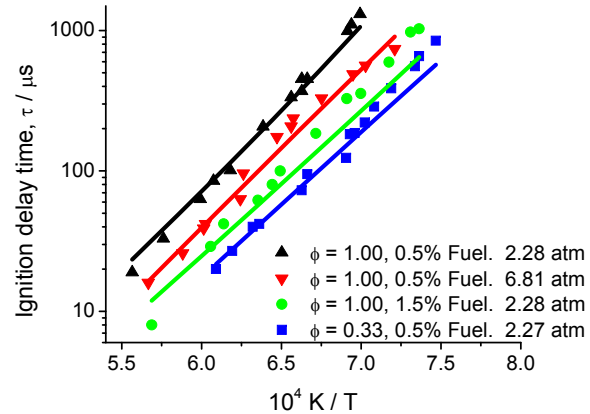
- Toluene sub-mechanism primarily from Bounaceur et al.[1] with important modifications:
  - Rate constants for abstraction from methylic and benzylic sites updated from the recent literature.
  - Toluene decomposition reactions taken from Klippenstein et al.[2]
  - Reactions of benzyl and bibenzyl primarily taken from Sakai[3] and Oehlschlaeger.[4]
  - Important reaction between benzyl and HO_2 taken from daSilva and Bozzelli.[5]
  - Benzyl plus O_2 taken from Murakami et al.[6]
- Benzene sub-mechanism assimilated from the literature.
- Cyclopentadiene from Zhong and Bozzelli[7] with small additions.

[1] R. Bounaceur, I. Da Costa, R. Fournet, F. Billaud, F. Battin-LeClerc, Int J Chem Kinet 37 (2005) 25–49.
[2] S. J. Klippenstein, L. B. Harding, Y. Georgievskii, Proc. Combust. Inst. 31 (2007) 221–229.
[3] Y. Sakai, A. Miyoshi, M. Koshi, W. J. Pitz, Proc. Combust. Inst. 32 (2009) 411–418.
[4] M. A. Oehlschlaeger, D. F. Davidson, and R. K. Hanson, J. Phys. Chem. A ,110 (2006) 6649–6653.
[5] G. da Silva, J. W. Bozzelli, Proc. Combust. Inst. 32 (2009) 287–294.
[6] Y. Murakami, T. Oguchi, K. Hashimoto and Y. Nosaka, J. Phys. Chem. A , 111 (2007), 13200-13208.
[7] X. Zhong and J. W. Bozzelli, J. Phys. Chem. A , 102 (1998) 3537-3555.

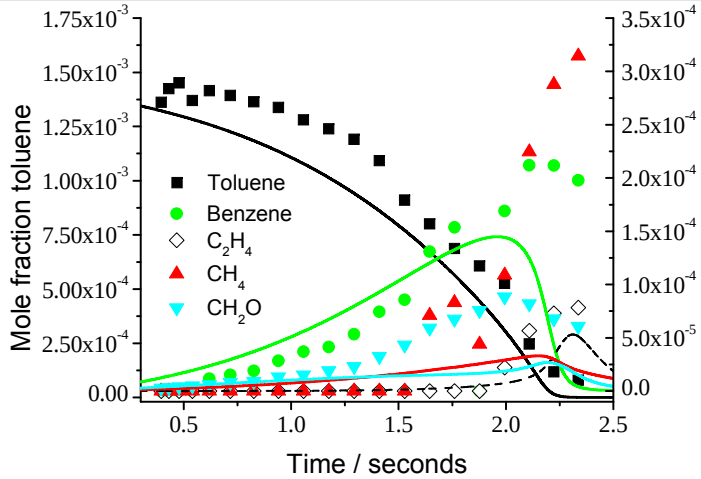
Toluene Model Performance



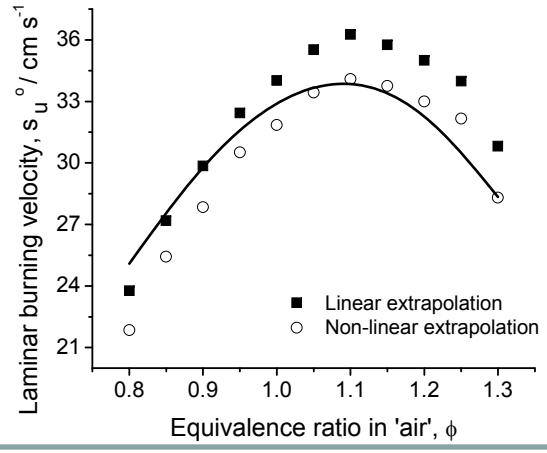
Experimental data from VPFR of 0.14% Toluene, 1.29% O_2 , ϕ = 1.0, 920 K, 12.5 atm. τ = 1.8s. Modeling simulations shifted by 0.3s



Shock Tube ignition delay times of Burcat for Toluene/O_2/Ar.

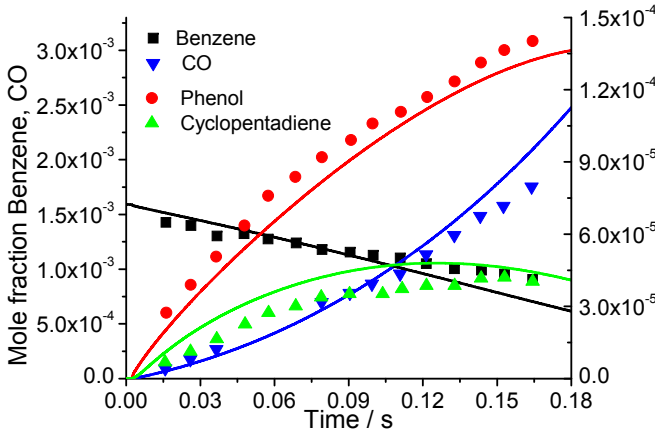


Experimental data from VPFR of 0.14% Toluene, 1.29% O_2 , ϕ = 1.0, 920 K, 12.5 atm. τ = 1.8s. Modeling simulations shifted by 0.3s

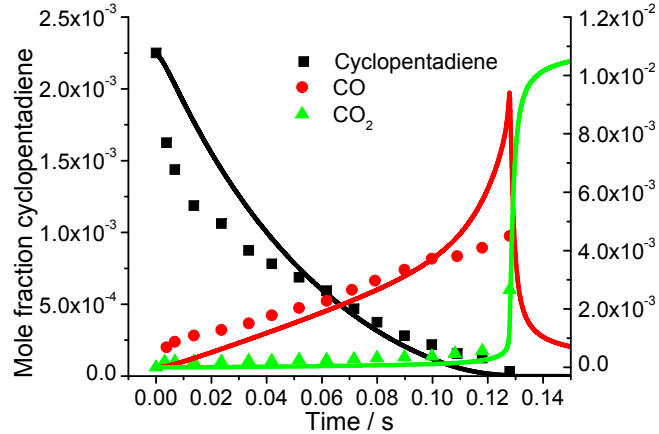


Toluene laminar burning velocities in air, T_i = 298 K, P_i = 1.0 atm. Experiments of Davis (symbols) and modeling simulations.

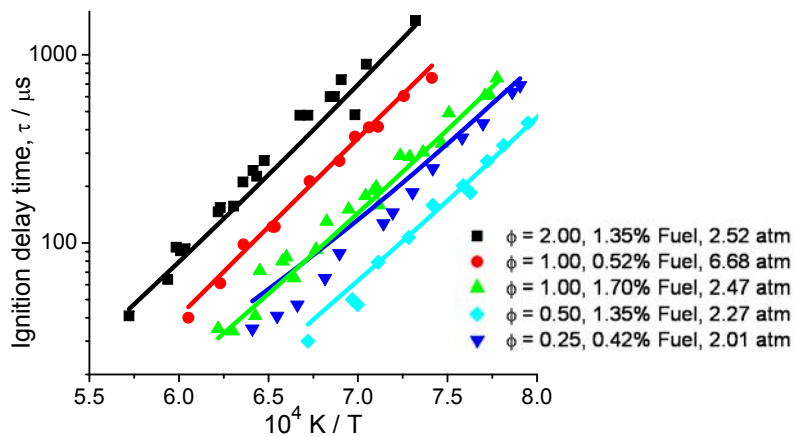
Aromatic Intermediates



Flow rector data (symbols) of Lovell et al.
1591 ppm benzene, ϕ = 1.0, 1096 K and 1.0 atm.



Flow rector data (symbols) of Butler et al.
2243 ppm cyclopentadiene ϕ = 1.03,1198 K and1.0 atm,



Shock tube ignition delays of benzene/O_2/Ar mixtures.
Experiments of Burcat (symbols) and modeling simulations (lines).

Shock tube ignition delays of 1.0% cyclopentadiene/O_2/Ar at 1.0 atm.
Experiments of Orme (symbols) and modeling simulations (lines).

Conclusions

- Low-to-intermediate temperature reactivity of n-decane has been characterized.
- Kinetic models (Westbrook et al.) show generally good reproduction of global parameters.
- Low-to-intermediate temperature reactivity of 1,2,4 /1,3,5 trimethyl benzenes and n-propyl benzene have also been characterized.
  - No oxidation observed below 700 K.
  - Observe reactivity of n-propyl benzene > 1,2,4 TMB > 1,3,5 TMB.
  - Negligible increase in reactivity with increase of Φ.

- Ignition quality testing as well as flow reactor results indicate ignition and oxidation character for blends of 20 mole % 1,2,4 trimethyl benzene and n-propyl benzene are indistinguishable.
  - Combined with TSI differences, 1,3,5 trimethyl benzene and n-propyl benzene components best satisfy surrogate formulation criteria – modeling 1,3,5 is perhaps more straightforward that developing a model for 1,2,4 trimethyl benzene.

Conclusions

- Small species sub-model for C1-C4 has been assembled and is under further development and validation.
- Detailed kinetic model for toluene and other important aromatic combustion intermediates (cyclopentadiene, phenol, benzene) has been advanced.
  - Results impact developing kinetic/thermodynamic parameters and models for the trimethyl benzenes.

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