Surrogate Mixtures for Real Fuels; Concepts and Associated Kinetic Studies of Surrogate Components

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MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)
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Overview

- Review of the MURI surrogate construction methodology
- Comparison of 1st and 2nd Generation Surrogates with Jet A POSF 4658
  - New Combustion Target Comparisons
    - Premixed Laminar Flame Targets
    - High Pressure Speciation Target
- SPK Real Fuels and a 2nd Generation Surrogate for S-8 POSF 4734
- Contributions of Weakly Branched Iso-alkanes to real fuel behavior.
  - 2-methyl Heptane Experiments vs. Recent Modeling from LLNL
  - Tri-methyl Alkyl Isomer Experimental Comparison with an n-Alkane, S-8 POSF 4734 and POSF 4734 surrogate mixture (all with similar DCN)
- Further Progress on n-Alkane Modeling and Validation
- Aromatics – Modeling Progress
  - n-Propyl Benzene (nPB)
  - 1,3,5 Trimethyl Benzene (1,3,5 TmB)
- Some Brief Comments on Integration of Physical and Chemical Properties in Surrogate Formulation
- Summary and Continuing Efforts

MURI Strategy for Modeling a Specific Jet Fuel

Identify critical fuel property targets that manifest in important practical combustion behavior of each real fuel:

- Adiabatic flame temperature
- Local air fuel stoichiometry
- Enthalpy of combustion
- Flame velocity
- Overall active radical production
- Premixed sooting

} Ratio of Hydrogen to Carbon (H/C)

- Non-premixed sooting → Threshold Soot Index (TSI), By standardizing smoke point measurement
- Fuel diffusive transport properties → Average Molecular Weight (MW_{avg})
- Autoignition/global kinetics → Derived Cetane Number (DCN), Correlative for macro ignition measure

- All property target values for real fuel and surrogate components determined experimentally.
- Surrogate fuel components and mixture do not have to necessarily include all of the molecular classes found in the real fuel of interest.
- The components and their mixture must reasonably replicate the interaction and composition of distinct chemical functionalities manifested in the real fuel!

1st and 2nd Gen Surrogates for POSF 4658

Test MURI concept by replicating property targets for Jet A POSF 4658

Mole Fraction					DCN	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658					47.1	1.957	142.01	21.4
1st Generation surrogate	*n*-decane	*iso*-octane	Toluene		47.1	2.01	120.7	14.1
	0.427	0.33	0.243					
2nd Generation surrogate	*n*-dodecane	*iso*-octane	Mesitylene	n-propyl benzene	48.5	1.95	138.7	20.4
	0.40	029	0.07	0.23				

1st Generation Formulation - n-C_{10}/iso-C_8/toluene

- Allow for analyses using more well-developed kinetic model components.
- Three component formulation can match H/C and DCN, but not TSI as well, and can never emulate MW_{avg} of the fuel.

2nd Generation Formulation – n-C_{12}/iso-C_8/n-PB/1,3,5 TmB

- Can replicate all property targets of nearly all jet fuels.
- Larger MW components, multiple aromatics (same MW) facilitate property matching.
- Significant needs in database/model development and validation, so first:

Experimentally **compare Jet A POSF 4658 and its surrogates in a wide range of venues (VPFR reactivity, ST/RCM ignition delay, diffusive strained ignition,** ***premixed burning rate and strained extinction, SPST speciation, sooting*****), and conditions (dilute fuel/O_2, fuel/air, range of pressures and temperatures).**

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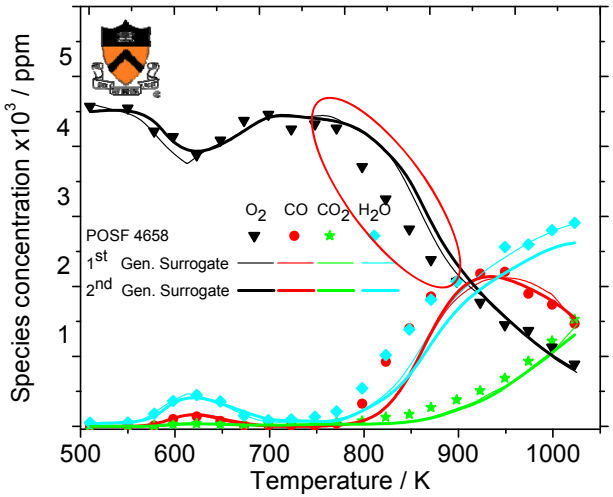
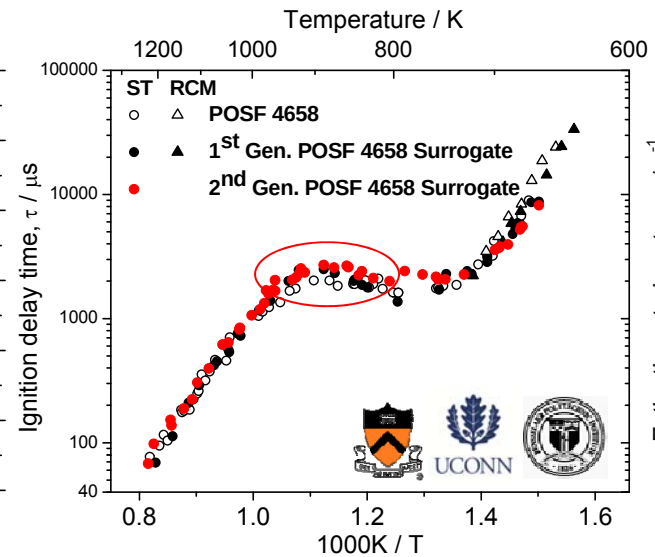
First reported by UCONN, UIC teams, this review

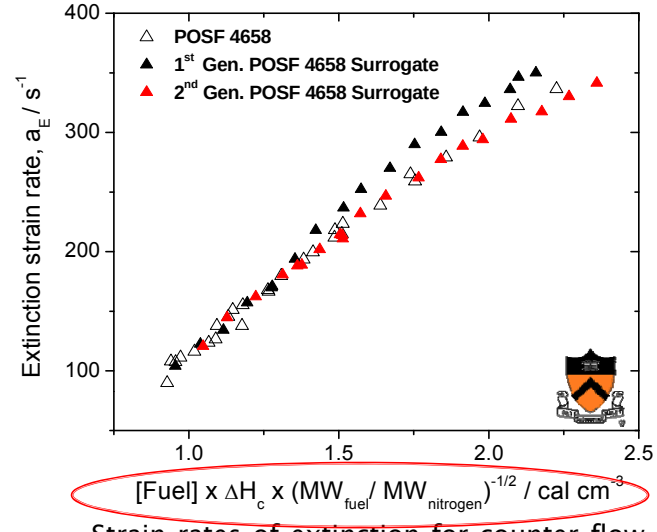
1st and 2nd Gen Comparisons with Jet A POSF 4658



Flow reactor oxidation data for conditions of 12.5 atm, φ= 1.0 and *t* =1.8s, for Jet A POSF 4658, 1st gen and 2nd gen POSF 4658 surrogate mixtures. All experiments at 0.3% mole carbon content.



Ignition delay times, φ= 1.0 in air at ~20 atm for Jet A POSF 4658, 1st gen and 2nd gen POSF 4658 surrogate mixtures.



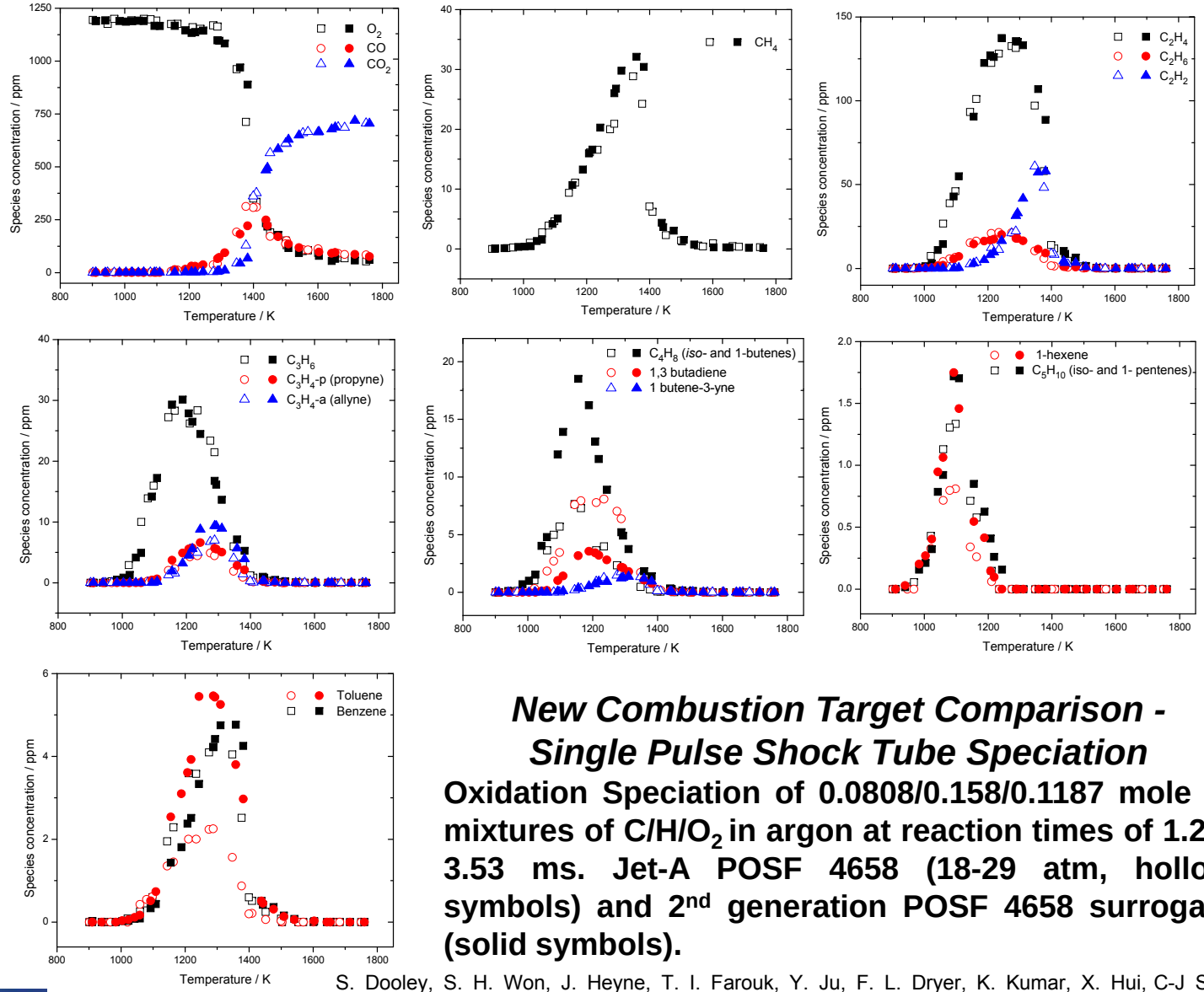
Strain rates of extinction for counter flow diffusion flames at 1 atm, for 1st and 2nd generation POSF 4658 surrogate fuels v. *Radical Index for each fuel

- **1st and 2nd generation surrogates produce nearly identical emulations of the real fuel behavior with significantly different initial surrogate components.**
- **Consistent, small differences in real fuel behavior and surrogate behavior in the hot ignition regime (surrogates very similar).**
- **Replicating molecular weight important to diffusive extinction comparisons.**

*S. H. Won, S. Dooley, F.L. Dryer, Y. Ju, *Combust. Flame.. Accepted, August 2011.*

S. Dooley, S. H. Won, J. Heyne, T. I. Farouk, Y. Ju, F. L. Dryer, K. Kumar, X. Hui, C-J Sung, H. Wang, M. A. Oehlschlaeger,V. Iyer, T. A. Litzinger, R. J. Santoro, T. Malewicki, and K.Brezinsky. *Combust Flame* (2011). *In review.*

Jet A POSF 4658 and 2nd Gen POSF 4658 Speciation

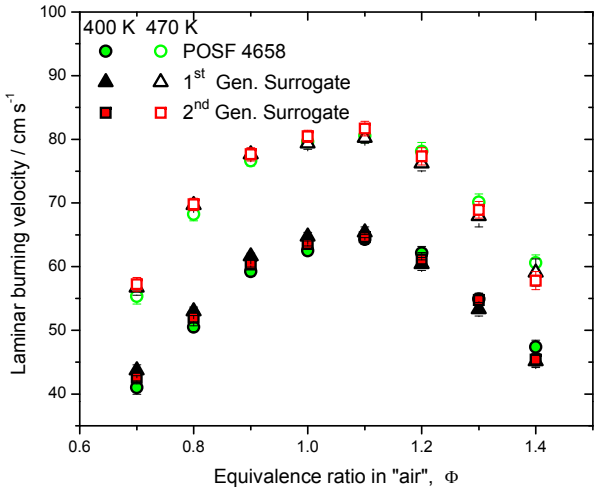


New Combustion Target Comparison - Single Pulse Shock Tube Speciation

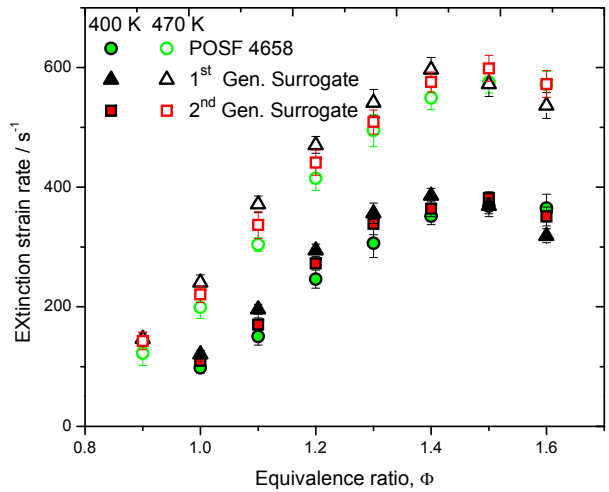
Oxidation Speciation of 0.0808/0.158/0.1187 mole % mixtures of C/H/O_2 in argon at reaction times of 1.23-3.53 ms. Jet-A POSF 4658 (18-29 atm, hollow symbols) and 2nd generation POSF 4658 surrogate (solid symbols).

S. Dooley, S. H. Won, J. Heyne, T. I. Farouk, Y. Ju, F. L. Dryer, K. Kumar, X. Hui, C-J Sung, H. Wang, M. A. Oehlschlaeger,V. Iyer, T. A. Litzinger, R. J. Santoro, T. Malewicki, and K.Brezinsky. *Combust Flame* (2011). *In review.*

Jet A POSF 4658, 1st, & 2nd Gen POSF Premixed Flames



Laminar burning velocities at 1 atm: Jet-A POSF 4658 (circles), 1st gen (triangles) and 2nd gen (squares) POSF 4658 surrogates.



Extinction strain rates for premixed Fuel/O_2/N_2 at 1 atm: Jet-A POSF 4658 (circles), 1st gen (triangles) and 2nd gen (squares) POSF 4658 surrogates. $N_2/(N_2+O_2)$ =0.86.

New Combustion Target Comparison
Premixed Laminar Flame Properties

Premixed laminar flame properties of Jet-A POSF 4658, 1st and 2nd gen POSF 4658 surrogate s at T_u = 400 K. (solid symbols) and 470 K (hollow symbols) in "Air": $N_2/(N_2+O_2)$ =0.86.

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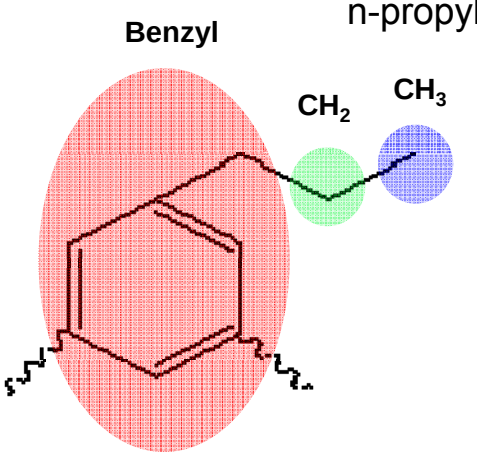
S. Dooley, S. H. Won, J. Heyne, T. I. Farouk, Y. Ju, F. L. Dryer, K. Kumar, X. Hui, C-J Sung, H. Wang, M. A. Oehlschlaeger,V. Iyer, T. A. Litzinger, R. J. Santoro, T. Malewicki, and K.Brezinsky. *Combust Flame* (2011). *In review.*

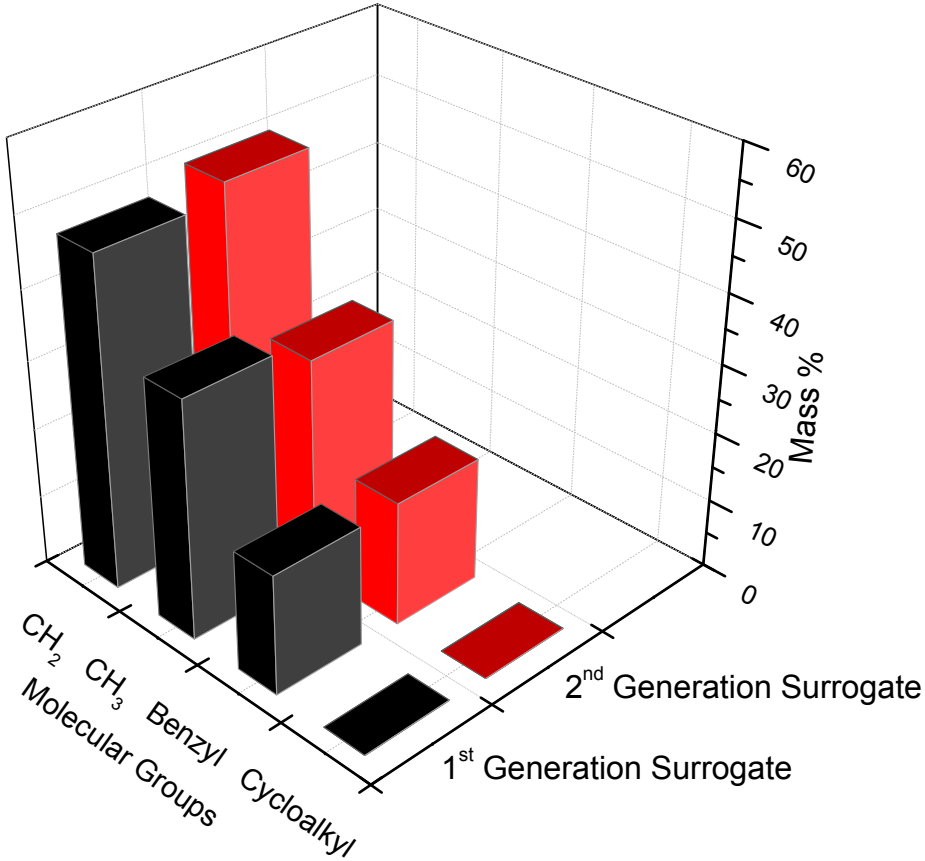
1st vs 2nd Generation Surrogate Chemical Properties

- Group additivity type analysis performed on 1st and 2nd generation surrogate fuels shows high degree of *Commonality of Chemical Groups* on a mass basis.

For example:

Benzyl
+ CH_2
+ CH_3
n-propylbenzene



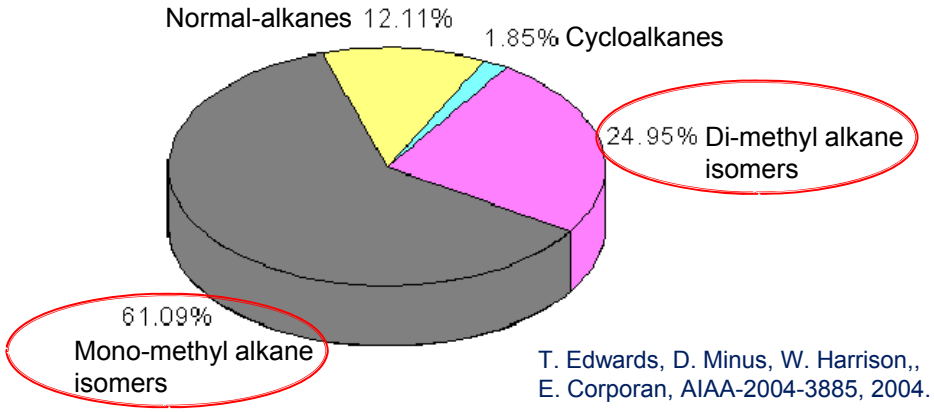


- *Different distinct groups available in each molecular class in the real fuel can contribute to the sums of all distinct chemical groups found in the composition.*

S. Dooley, S. H. Won, J. Heyne, T. I. Farouk, Y. Ju, F. L. Dryer, K. Kumar, X. Hui, C-J Sung, H. Wang, M. A. Oehlschlaeger,V. Iyer, T. A. Litzinger, R. J. Santoro, T. Malewicki, and K.Brezinsky. *Combust Flame* (2011). *In review.*

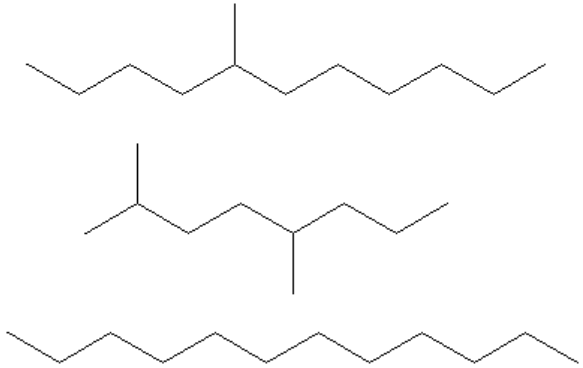
Paraffinic Kerosene Surrogates

- SPK and HRJ Jet fuel compositions have no aromatics, but will likely be mixed with petroleum derived jet fuel or have synthetic aromatics added for compatibility with legacy engine systems. *S-8 POSF 4734 is such an SPK feedstock produced from natural gas.*
- Prior surrogate mixtures for S-8 have been constructed by others previously.
  - Gokulakrishnan et al. (2007) AIAA 2007-5701
  - Naik et al., (2010), doi:10.1016/j.combustflame.2010.09.016.
- Can a simple 2nd generation surrogate mixture (no mono-methyl/di-methyl iso-alkanes) replicate the combustion behavior of S-8 (major amounts of methylated iso-alkanes)?



T. Edwards, D. Minus, W. Harrison,, E. Corporan, AIAA-2004-3885, 2004.

Identified components and ~ proportions for S-8 POSF 4734

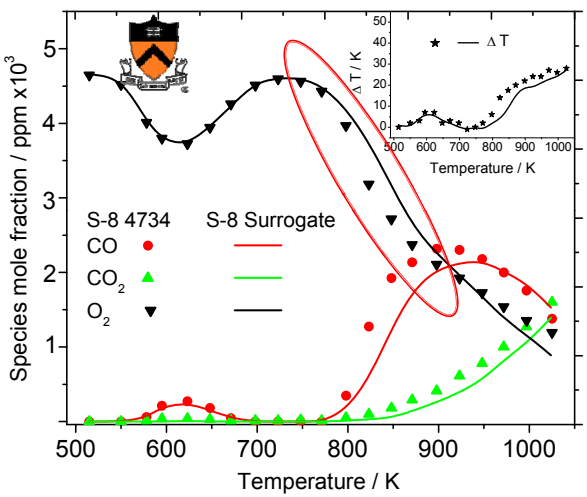


Exemplar generic molecular class composition of S-8

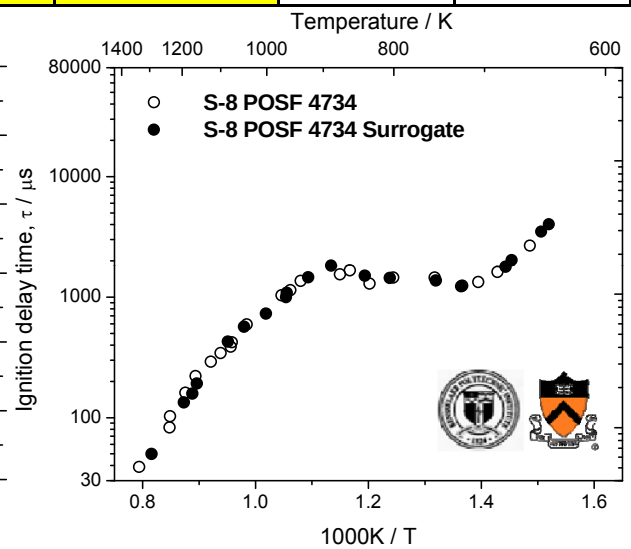
- Select surrogates to represent expected chemical functionalities of **<u>fragments</u>** formed from S-8 combustion => *n*– & *iso*– alkyl and alkenyl for synthetic fuels.
- No utility in matching TSI combustion property as it is very low for all saturated HC's.

S-8 POSF 4734 vs S-8 Surrogate

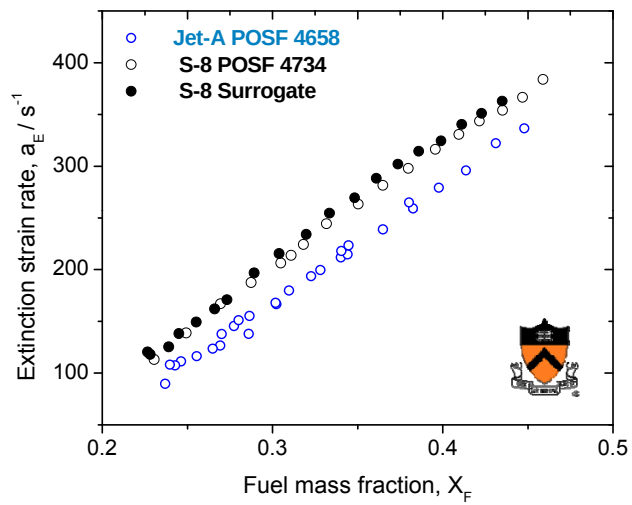
Mole Fraction		DCN	H/C	MW / g mol^{-1}
S-8 POSF 4734		58.7±0.3	2.14-2.19	163.4±15
***n*-dodecane**	***iso*-octane**			
0.5189	0.481	58.87	2.19	143.4



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, φ= 1.0 and *t* =1.8s for S-8 POSF 4734 (symbols) and S-8 POSF 4734 Surrogate (lines), Inset; *ΔT*.



Reflected Shock ignition delay times, ϕ= 1.0 in air at ~20 atm for S-8 POSF 4734, S-8 POSF 4734 Surrogate.



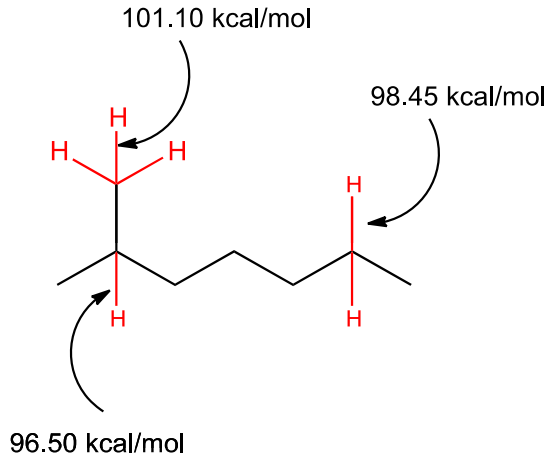
Strain rates of extinction for counter flow diffusion flames at 1 atm, Jet-A POSF 4658, S-8 POSF-4734 and S-8 POSF 4734 Surrogate.

- Similar discrepancies for VPFR reactivity also noted in more complex case of Jet-A POSF 4658, 1st & 2nd gen. POSF 4658 surrogates.
- S-8 surrogate approximates kinetic and transport properties well; MW_{avg} disparity is less important for $MW_{avg's}$ > 120 g mol^{-1}.

S. Dooley, S.H. Won, S. Jahangirian, Y. Ju, F.L. Dryer, H. Wang, M.A. Oehlschlaeger , AIAA Aerospace Sciences Meeting, 2011 & 2012.

Weakly Branched Alkane Kinetic Models: 2-Methylheptane

- The most prominent *iso*-alkanes present in petroleum derived jet and diesel fuels contain one or two methyl branches.†
- Major research gaps exist in modeling weakly branched *iso*-alkanes.†
- 2-Methylalkanes are less reactive under auto-ignition conditions than *n*-alkanes of the same chain length.
- At low temperature and NTC regions, $^{\bullet}RO_2$ isomerization reactions can be inihibited by where methyl groups are located.
- Sarathy et al. and co-workers† have recently developed and validated a detailed kinetic model.
- The present collaboration‡ is nearing completion and encompasses VPFR, shock tube, and RCM validations and further model refinements.
- VPFR Reactivity data show:
  - Substantial low temperature reactivity and pronounced NTC behavior.
  - Iso-butene and propene are significant intermediates above hot ignition.



Structure and C-H bond dissociation energies (kcal mole^{-1}) of 2-methylheptane.

† S. M. Sarathy; C. K. Westbrook; M. Mehl; W. J. Pitz; C. Togbe; P. Dagaut; H. Wang; M. A. Oehlschlaeger; U. Niemann; K. Seshadri; P. S. Veloo; C. Ji; F. N. Egolfopoulos; T. Lu, *Combustion and Flame (*2011). DOI:10.1016/j.combustflame.2011.05.007

‡ S. Jahangirian, D. Healy, S.M. Sarathy, S. Dooley, M. Mehl, W.J. Pitz, F.L. Dryer, H.J. Curran, C.K. Westbrook. To appear: ESS 2011, manuscript in preparation.

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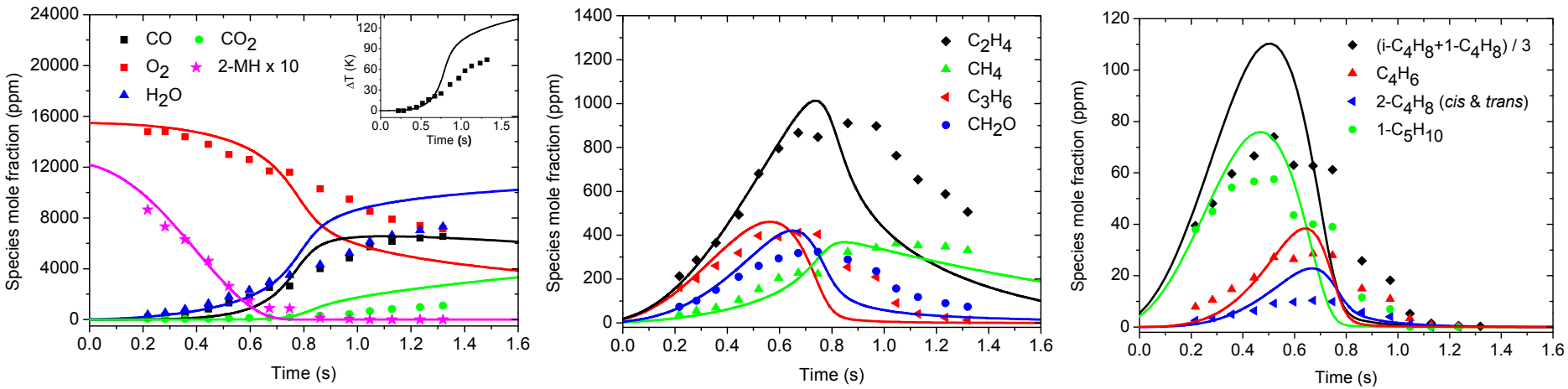
Weakly Branched Alkanes: 2-Methylheptane



Flow reactor oxidation of 2-methylheptane/O_2/N_2 at 8 atm and 840 K, time shift: 0.21 s.
Model: Sarathy et al. (2011)

- Noticeable amounts of 2-methyl alkenes were identified under these conditions.
- The model predictions are satisfactory for most intermediate species, except sum of *iso*-butene and 1-butene and some C_3 oxygenates.
- The model is under further refinement: larger fuel fragments, iso-butene, and C_2 chemistry predictions can benefit from further refinement.
- *Small fragment distinct chemical functionalities can likely be estimated with n-alkane, iso-octane mixtures.*

- S. M. Sarathy; C. K. Westbrook; M. Mehl; W. J. Pitz; C. Togbe; P. Dagaut; H. Wang; M. A. Oehlschlaeger; U. Niemann; K. Seshadri; P. S. Veloo; C. Ji; F. N. Egolfopoulos; T. Lu, *Combust Flame. D*oi:10.1016/j.combustflame.2011.05.007

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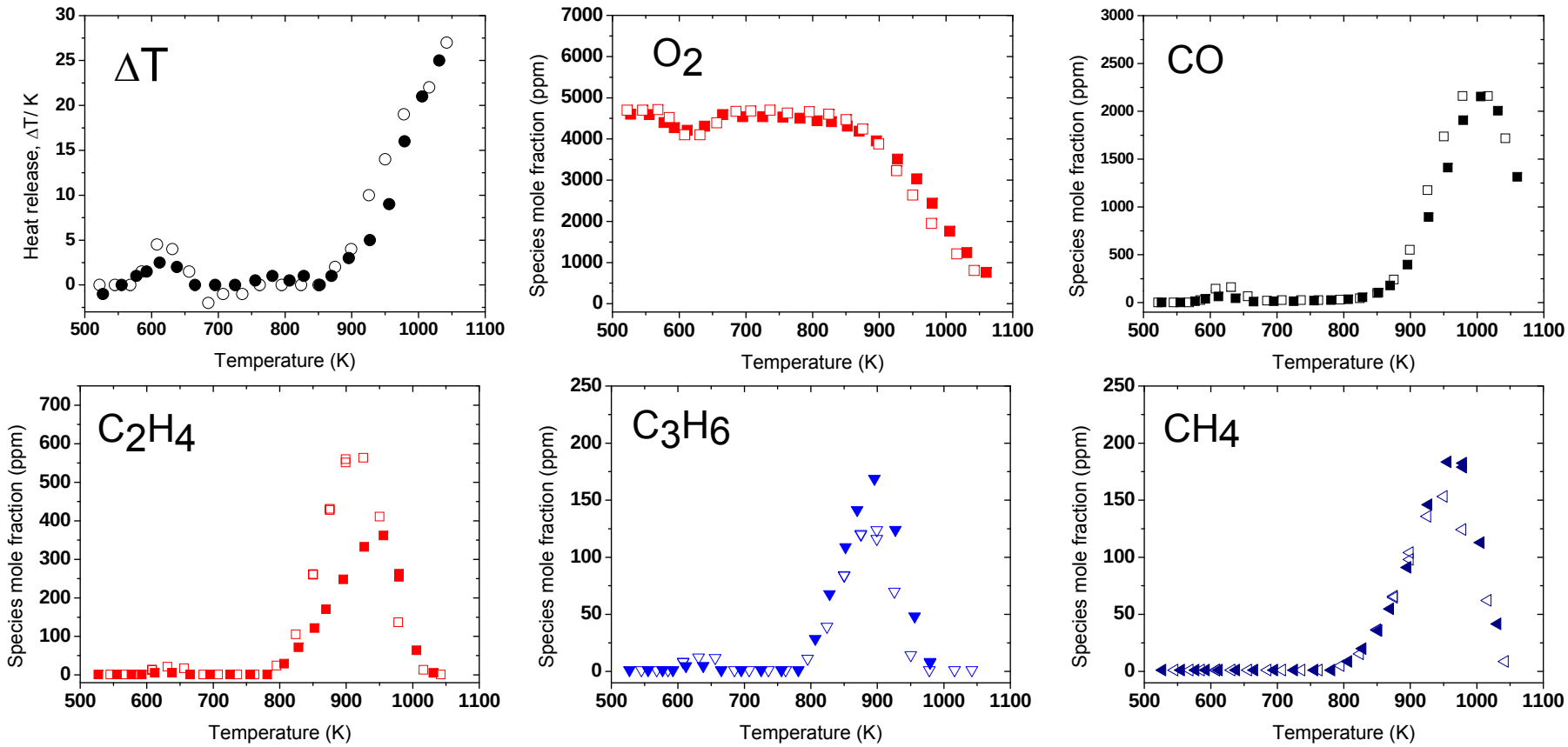
Weakly Branched iso-Alkanes: a Trimethyl-isomer

- This iso-alkane, n-C7, and S-8 POSF 4734 real fuel all have very similar DCN's , and very low TSI. Here we compare VPFR reactivities for the **Tri-methyl isomer** and **n-heptane**

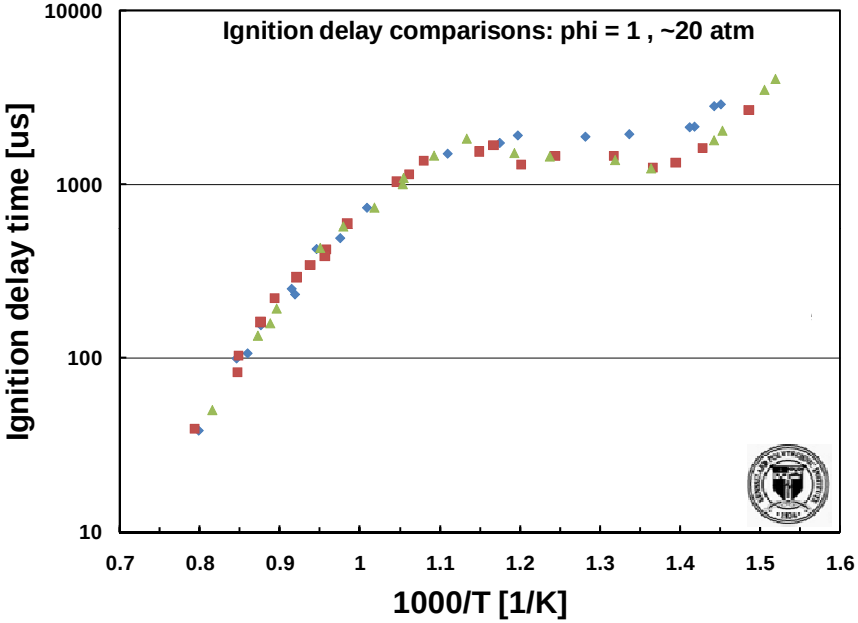


VPFR reactivity data for n-heptane (open symbols) and trimethyl-iso-alkane (solid symbols) ; P= 8 atm with same initial carbon content. The fuels in this study have nearly the same DCN.

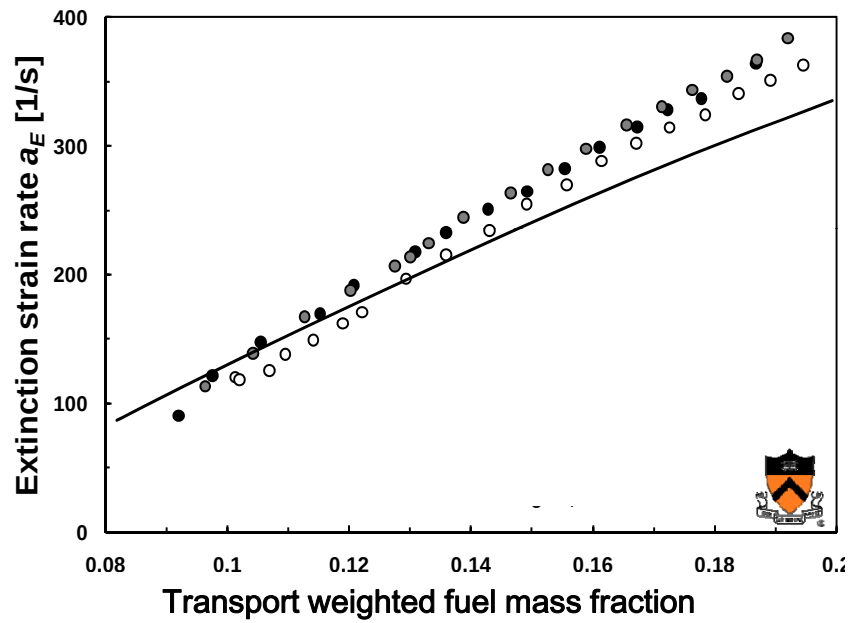
- Species time-history experiments trace ~45 species using GC/MS, ~20 species quantified so far.

Weakly Branched iso-Alkanes: a Trimethyl-isomer

- Here we compare the reflected shock ignition delays and diffusive extinction strain rates for **S-8 POSF 4734**, **S-8 Surrogate**, and the **tri-methyl isomer**.
- All three fuels have nearly identical DCN.



Reflected Shock Ignition Delays for: weakly branched trimethyl isomer (diamonds), S-8 POSF 4734 (squares) & S-8 POSF surrogate (triangles). P ~20 atm, Phi = 1.

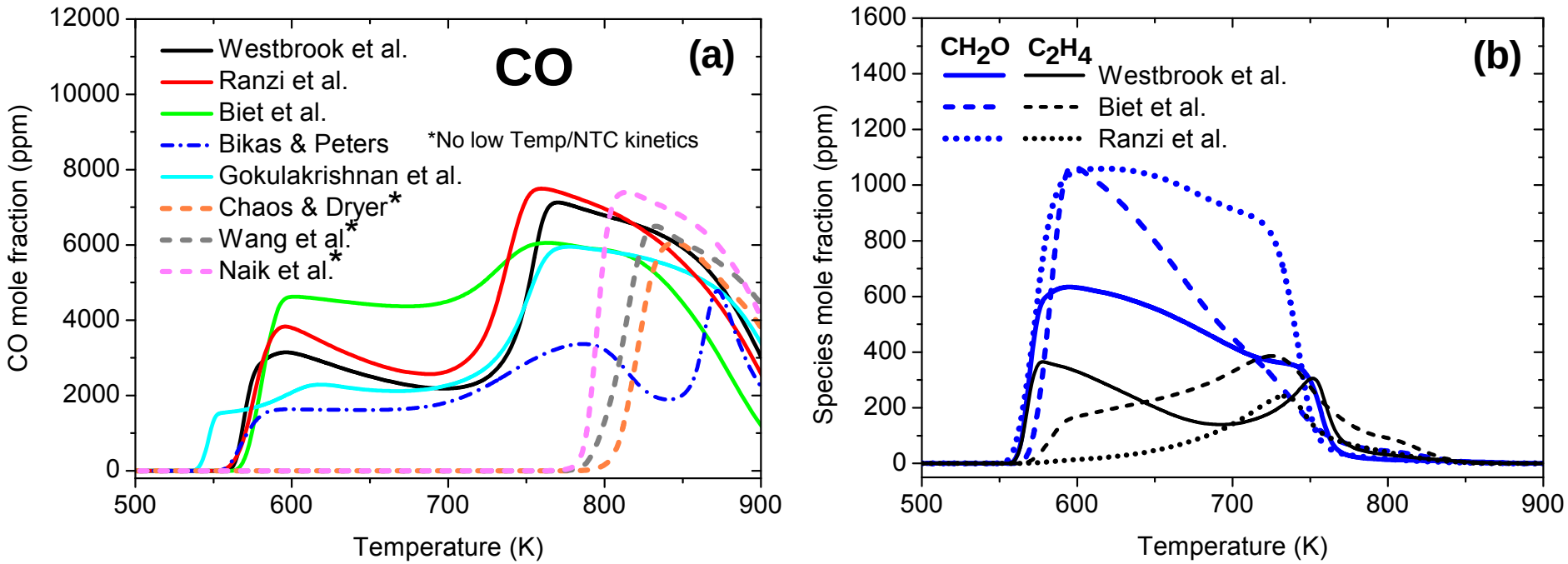


Strain rates of extinction for counter flow diffusion flames at 1 atm for branched trimethyl isomer (gray filled circles), S-8 POSF 4734 (flack filled squares) & S-8 POSF surrogate (open circles).

- Low temperature ignition of trimethyl isomer are expected to be longer as, shown by shock tube results (*but DCN's of all three materials are very similar*).

Reactivity Predictions for n-Alkanes: n-Decane

Normal-alkane fractions of real fuel are essential to determining radical pool generated during fuel oxidation => significant differences exist among model predictions.

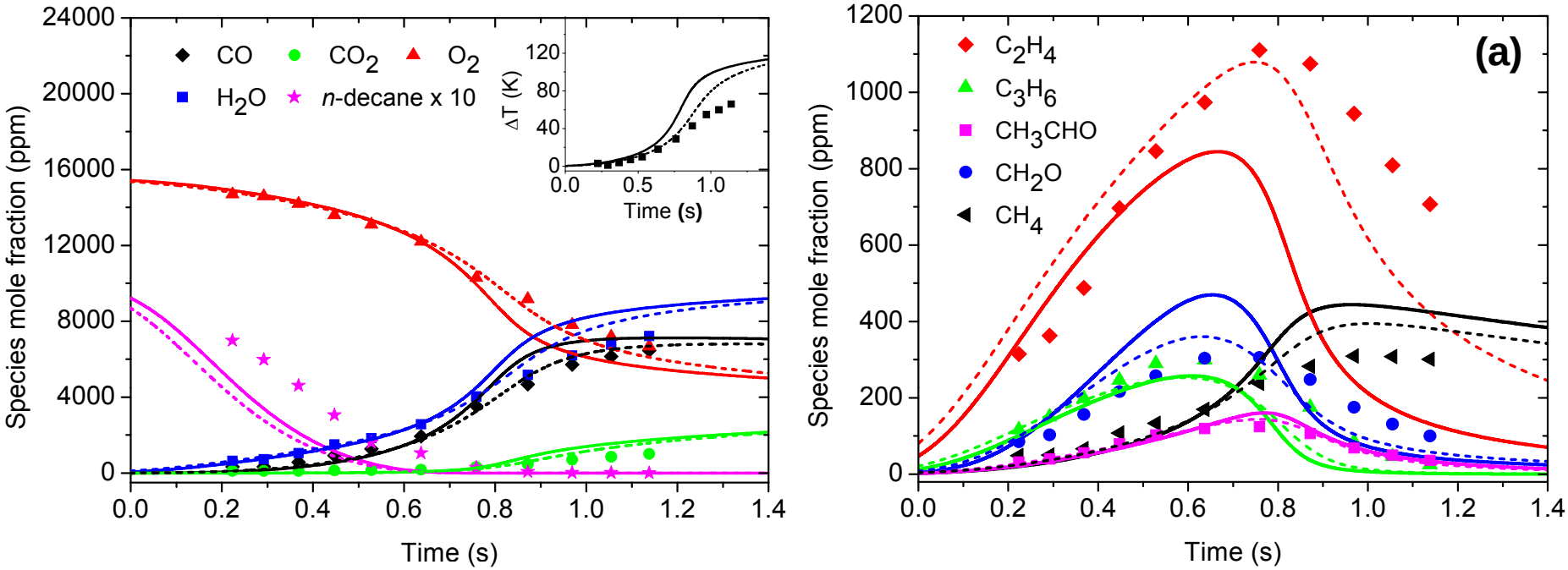


Computed species profiles for VPFR reactivity conditions with *n*-decane/O_2/N_2 1000/15500/983500 ppm at 1.8 s and 12.5 atm.

- *Westbrook CK, Pitz WJ, Herbinet O, Curran HJ, Silke EJ (2009). Combust. Flame 156: 181-199.*
- *Biet J, Hakka MH, Warth V, Glaude PA, Battin-Leclerc F (2008). Energy Fuels 22: 2258-2269.*
- *Ranzi E (Accessed December 2010): available at: http://www.chem.polimi.it/CRECKModeling/kinetic.html.*
- *Bikas G, Peters N (2001). Combust. Flame 126: 1456-1475.*
- *Gokulakrishnan P, Gaines G, Currano J, Klassen MS, Roby RJ (2007) J Eng Gas Turbines Power-Trans ASME 129: 655-663.*
- *Naik CV, Puduppakkam KV, Modak A, Meeks E, Wang YL, Feng Q, Tsotsis TT, Combustion and Flame In Press*
- *Chaos M, Kazakov A, Zhao Z, Dryer FL, Zeppieri SP (2005). US Eastern States Fall Technical Meeting of the Combustion Institute, paper 2549.*
- *Wang et al., (September 19, 2010) JetSurF version 2.0, (http://melchioruscedu/JetSurF/JetSurF20)*

S. Jahangirian; S. Dooley; F. M. Haas; F. L. Dryer (2011). *Combust Flame.* DOI:10.1016/j.combustflame.2011.07.002

n-Decane Temporal Speciation Predictions



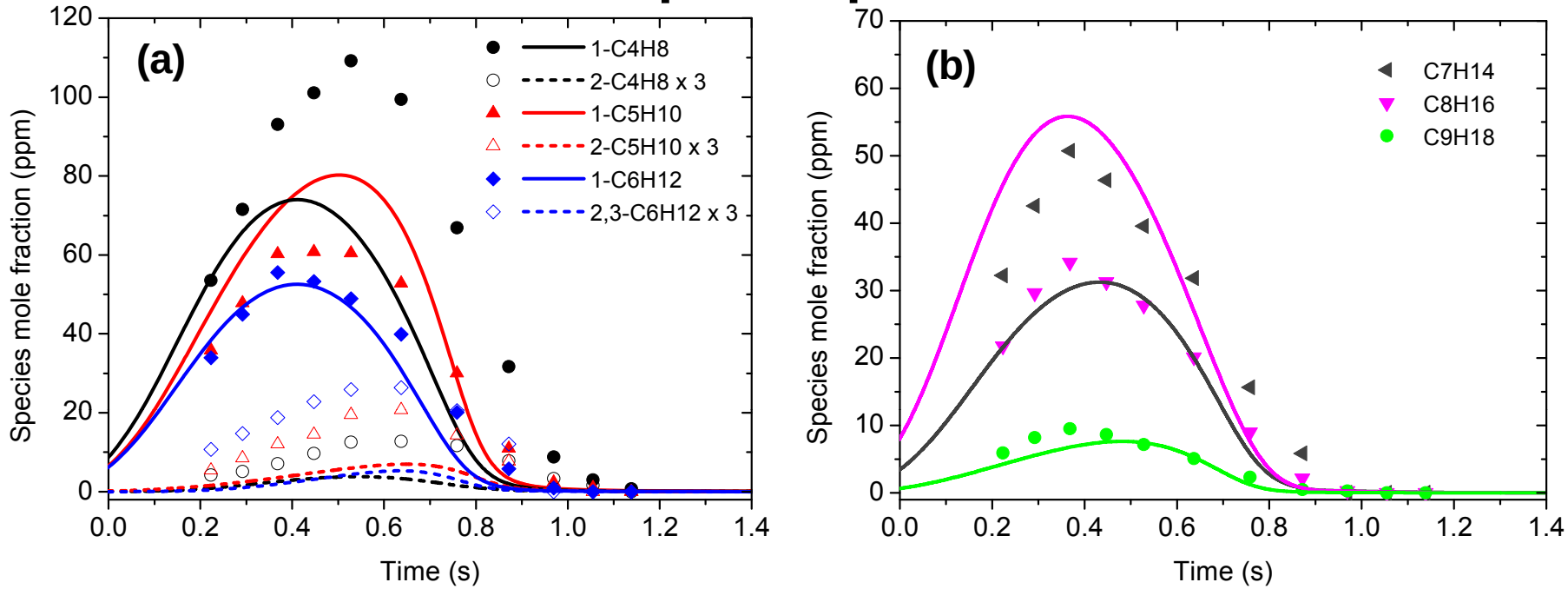
VPFR oxidation of *n*-decane/O_2/N_2 1000/15500/983500 ppm at 8 atm and 830 K.

Solid lines: **Original** Westbrook et al. model; Dashed lines: **Updated** Westbrook et al. model

- Detailed temporal fuel speciation during initial fuel destruction significantly constrains model predictions. But small species chemistry is also important.
- Updating of C_2 *chemistry* leads to significant improvements in prediction of ethylene, formaldehyde, and methane measurements.

- S. Jahangirian; S. Dooley; F. M. Haas; F. L. Dryer (2011). *Combust Flame.* DOI:10.1016/j.combustflame.2011.07.002
- Westbrook CK, Pitz WJ, Herbinet O, Curran HJ, Silke EJ (2009). *Combust. Flame* 156: 181-199.

n-Decane Temporal Speciation: Olefins



VPFR oxidation of *n*-decane/O_2/N_2 1000/15500/983500 ppm at 8 atm and 830 K.

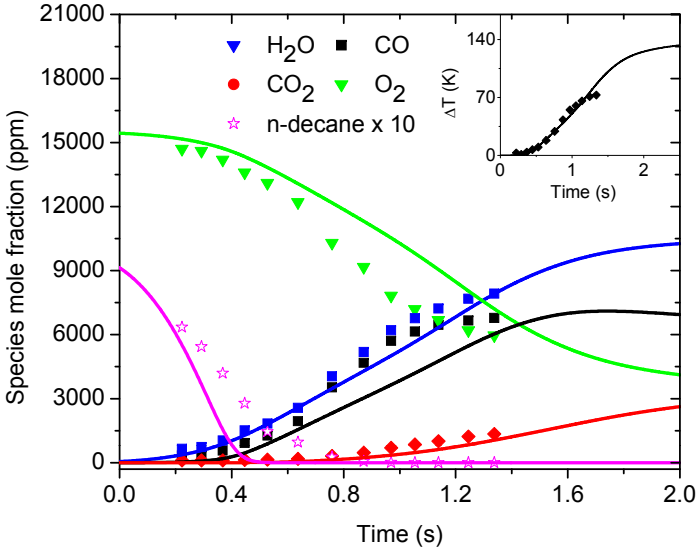
- Significant amounts of large olefins (predominantly, but not exclusively 1-olefins) are observed.
- Beta-scission chemistry as well as •R+O_2 chemistry are both critical to predicting high molecular weight intermediate species, particularly olefins.
- Concerted elimination reaction of •RO_2 to form an olefin and •HO_2 appears of substantial import for improving model predictions against these data.

- S. Jahangirian; S. Dooley; F. M. Haas; F. L. Dryer (2011). *Combust Flame.* DOI:10.1016/j.combustflame.2011.07.002
- Westbrook CK, Pitz WJ, Herbinet O, Curran HJ, Silke EJ (2009). *Combust. Flame* 156: 181-199.

n-Decane Temporal Speciation Predictions: JetSurf 2.0

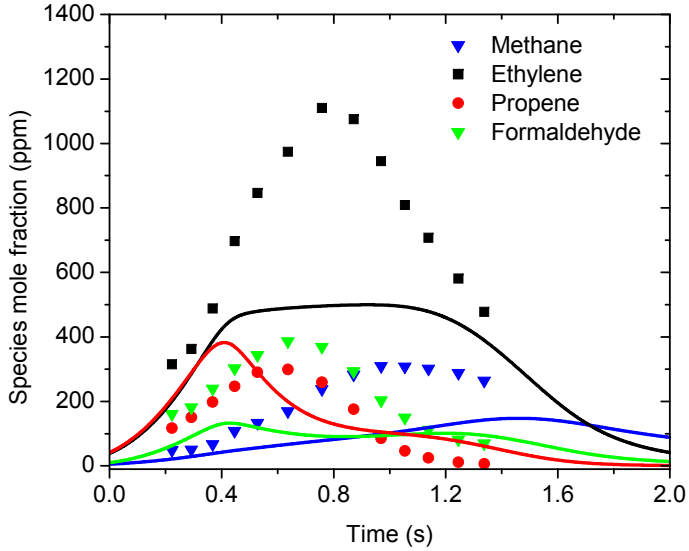
- *JetSurf 2.0* model predictions are good for heat release and satisfactory for major species, but show at least a factor of two disparity for major intermediates, e.g., ethylene, formaldehyde, 1-butene, 1-pentene, and 1-hexene.

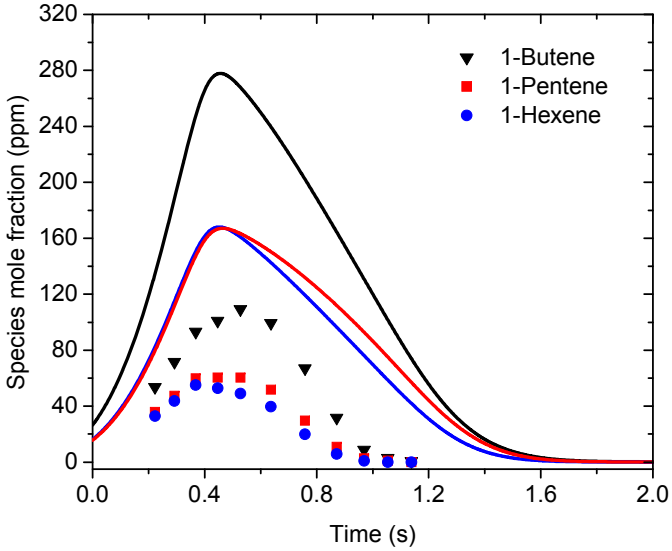
- H. Wang, E. Dames, B. Sirjean, D. A. Sheen, R. Tangko, A. Violi, J. Y. W. Lai, F. N. Egolfopoulos, D. F. Davidson, R. K. Hanson, C. T. Bowman, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, R. P. Lindstedt, A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures, JetSurF version 2.0, September 19, 2010 (http://melchior.usc.edu/JetSurF/JetSurF2.0).



Solid lines: **JetSurf 2.0 model**;

Symbols: Experiment



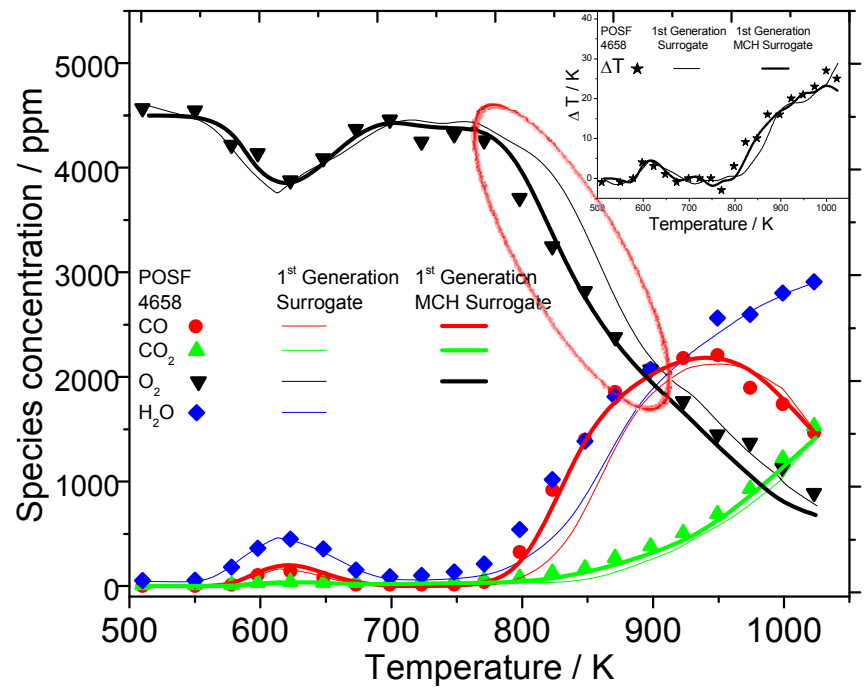


VPFR oxidation of *n*-decane/O_2/N_2 1000/15500/983500 ppm at 8 atm and 830 K.

Cycloalkanes within MURI Surrogate Formulation Strategy?

Mole Fraction					DCN	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658					47.1	1.957	142.01	21.4
1st generation surrogate	*n*-decane	*iso*-octane	Toluene		47.1	2.01	120.7	14.1
	0.427	0.33	0.243					
1st generation surrogate + methyl cyclohexane	*n*-decane	*iso*-octane	Toluene	Methyl cyclohexane	47.8	1.98	118.2	11.2
	0.422	0.174	0.179	0.225				

- Cycloalkanes are a significant fraction of Jet A POSF 4658 composition.
- Is it important any characteristic functional groups present in cycloalkanes?
- *Experimentally VPFR reactivity at Low temperature (<800K) is almost identical to that of 1st Generation surrogate.*
  - Shift of approx. 25-30K to cooler temperature in "hot ignition" condition.
  - Behavior of 1st/MCH surrogate appears to more closely replicate Jet A POSF 4658 in transition to hot ignition...the significance of the improvement remains to be fully evaluated.

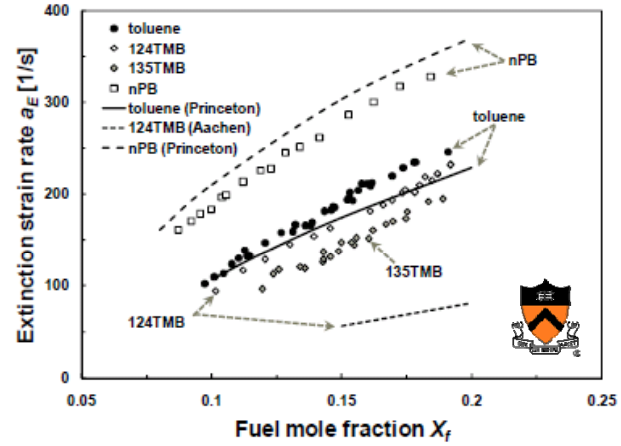


VPFR reactivity data for conditions of 12.5 atm, 0.3% carbon, φ= 1.0 and *t* =1.8s, for POSF-4658 (symbols), 1st generation surrogate (light lines), *and* 1st generation surrogate + methyl cyclohexane (solid lines). Inset;ΔT.

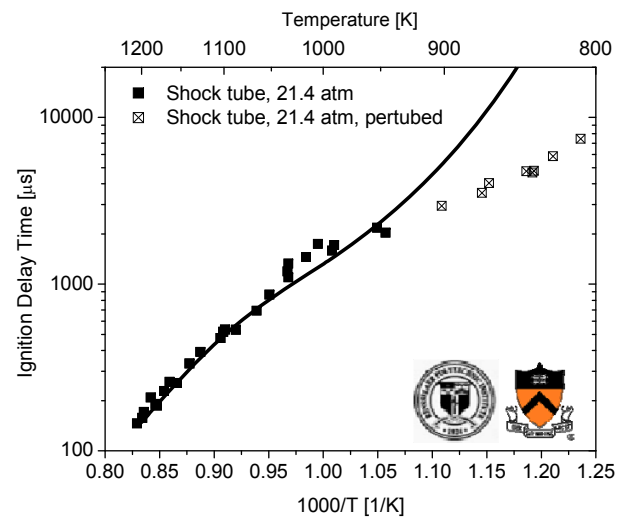
n-Propylbenzene (nPB) Kinetic Modeling

- Won et al. (2010) created a simple model for n-PB based upon the Toluene kinetic model of Metcalfe et al. (2011) with additional reactions that emphasized that fuel consumption would take place principally by oxidation or decomposition of alkyl side chain.
- Model qualitatively reproduced counterflow diffusion flame strained extinction data.
- Comparison of predictions for reflected shock ignition also could be improved upon.
- Lower temperature departure of the data and predictions could not be resolved by radical-oxygen addition reactions.
- VPFR reactivity experiments show that nPB exhibits no significant low temperature or negative temperature coefficient behavior.

- Won, S. H., Dooley, S., Dryer, F. L., Ju, Y. (2011). *Proc. Combust. Ins.* 33, 1163-1170.
- Metcalfe, W.K., Dooley, S., Dryer, F. L. (2011). Energy & Fuels, In Press.
- Wang, H., Oehlschlaeger, M. A., Dooley, S., Dryer, F. L. (2011). *7th U.S. National Combust. Meeting*, Atlanta, Georgia.



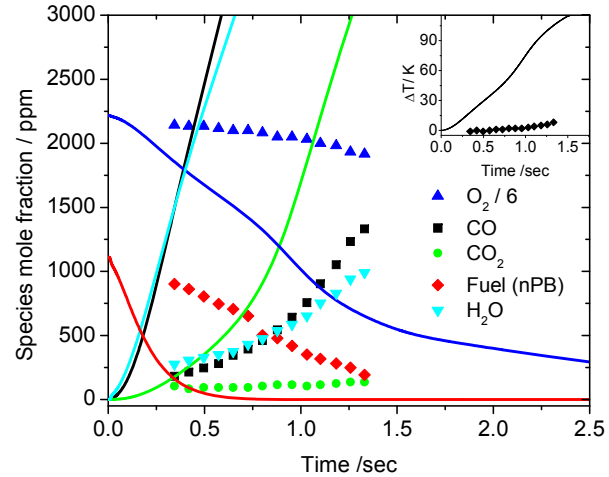
Counterflow diffusion flame strained extinction measurements by Won et al.

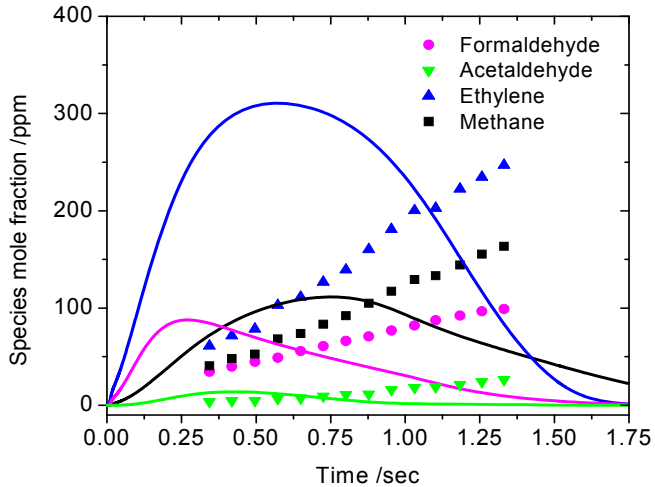


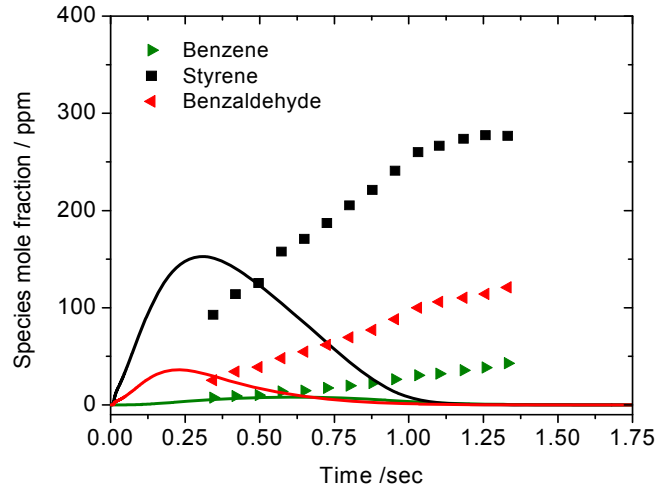
Ignition delays for nPB/air φ = 1.0 at ~21 atm. Data (symbols); Predictions (line).

n-PB Temporal Speciation at 8 atm, 885 K

- This dataset has a carbon balance of 90-100 %.
- Small heat release (< 8 K) occurs over whole time range in measurements.
- Styrene, most abundant intermediate large carbon number intermediate.
- Minor intermediates species: acetylene, ethane, propylene, toluene, and ethylbenzene. Traces of C_4 olefins, butadiane and bibenzyl are observed.
- Wang et al model predictions are too fast.







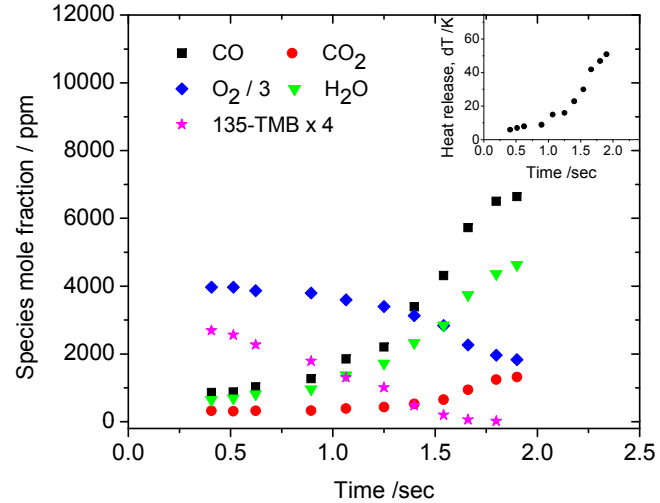
VPFR Species Time History for oxidation of n-Propylbenzene/O_2 (1110/13300 ppm in balance N_2) at 8 atm and 885 K (Symbols: Experiment, Lines: Wang et al. model)

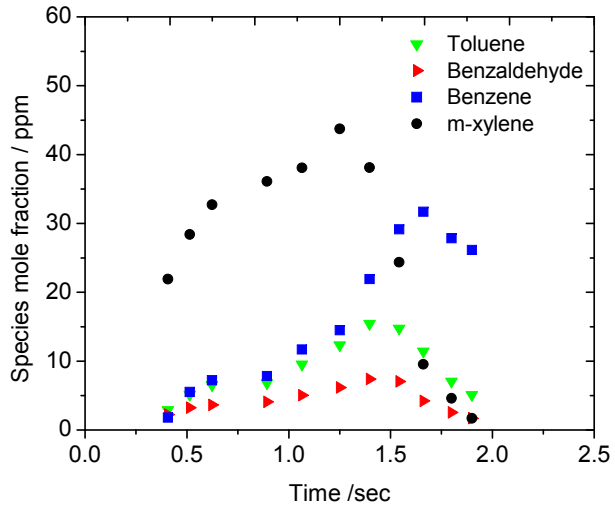
Data: S. Jahangirian, T. Farouk, S. Dooley, F. L. Dryer , 7th ICCK, MIT, Cambridge, MA, July 2011.

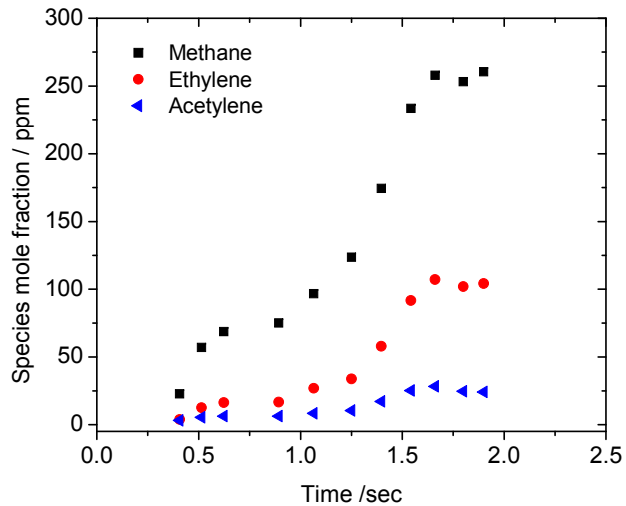
Model: Wang, H., Oehlschlaeger, M. A., Dooley, S., Dryer, F. L. (2011). *7th U.S. National Combust. Meeting*, Atlanta, Georgia.

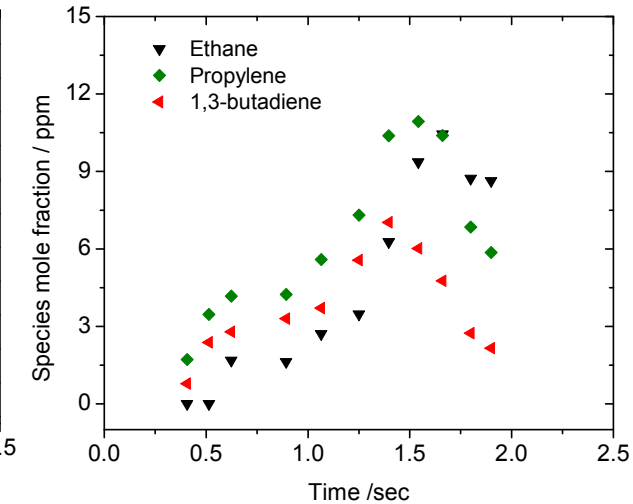
VPFR 1,3,5-TmB Temporal Speciation at 12.5 atm, 930 K

- Development of a model for 1,3,5-trimethyl benzene is in progress.
- Three abundant aromatic intermediates are: *m-xylene > benzene > toluene > benzaldehyde.*









VPFR temporal speciation of 1,3,5-trimethyl benzene/O_2 (1110/13300 ppm in balance N_2). Initial conditions: P=12.5 atm, φ=1.0, T=930K.

S. Jahangirian, S. Dooley, and F.L. Dryer, *240th American Chemical Society National Meeting*, Advances in Fuel Science & Technology, Boston, MA, August 22–26, 2010.

Physical Property of Surrogate Fuels

Surrogate Fuel Formulation

Emulation of Physical Properties

Physical Property Targets:

- Distillation Curve
- Density
- Viscosity
- Thermal Conductivity

Emulation of Combustion Phenomena

Combustion Property Targets:

- Average Fuel Molecular Weight
- Hydrogen/Carbon Molar Ratio
- Cetane Number
- Threshold Sooting Index

- Little attention on how to integrate successful approaches to each issue into a framework for the mutual evaluation of the two issues.
  - Liquid fuel combustion phenomena depend of the gas phase reaction for chemical heat release, liquid fuel properties dictate vaporization and mixing process – multiphase problem.
  - Surrogate formulation emulating both physical properties of the target real fuel in addition to combustion kinetic properties across the distillation curve.

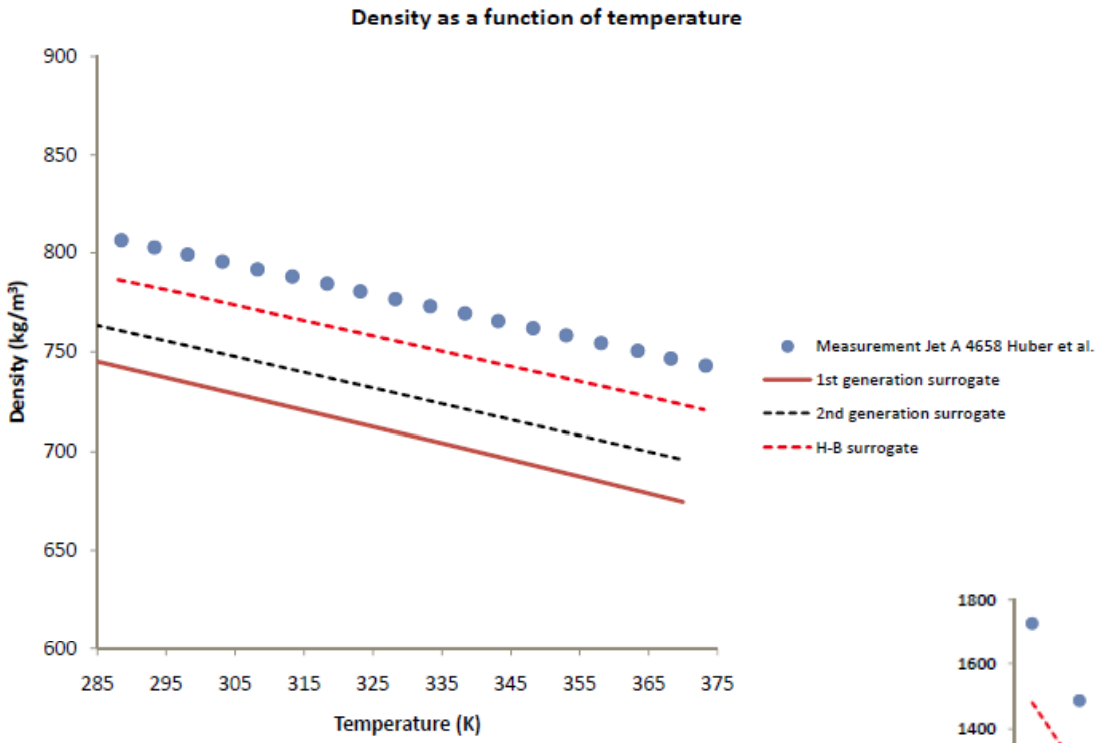
Physical Property Consideration

- Equation of state (EOS) to determine the liquid phase thermo-physical properties – Helmholtz form of equation of state due to its high accuracy.
- NIST REFPROP (Reference Fluid Thermodynamic and Transport Property) and ThermoData Engine (TDE).
- Top – down approach: Liquid phase physical property evaluation once the surrogate fuel has been formulated to match the combustion property targets.

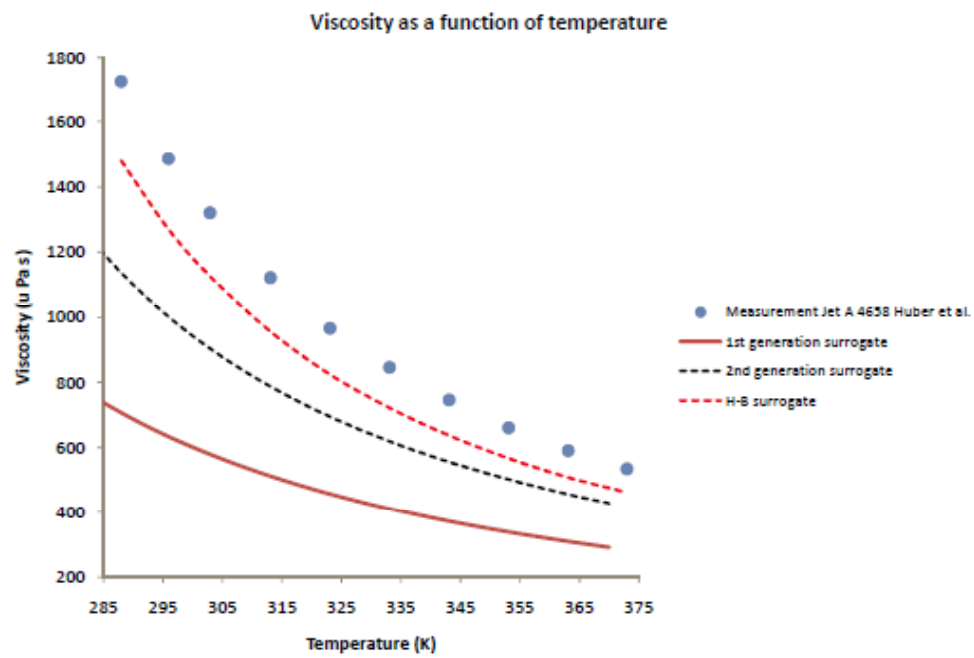
Mole Fraction					DCN	H/C	MW/ g mol^{-1}	TSI
Jet-A POSF 4658					47.1	1.957	142.01	21.4
1st Generation Surrogate	*n*-decane	*iso*-octane	toluene		47.1	2.01	120.7	14.1
	0.427	0.33	0.243					
2nd Generation Surrogate	*n*-dodecane	*iso*-octane	1,3,5 TmB	n-PB	48.5	1.95	138.7	20.4
	0.40	0.29	0.07	0.23				
***H-B Surrogate**	*n*-dodecane	Tetradecane	1,2,4 TmB		60.4	1.89	158.3	28.7
	0.288	0.304	0.408					

*Bruno, and Huber (2010)). Energy Fuels: DOI:10.1021/ef1004978

Liquid Phase Properties



- MW_{avg} is considered as a combustion property target to constrain mass diffusive issues.
- MW_{avg} is appropriate to some degree as a measure of other physical properties.
- 2nd generation surrogate density is estimated to be ~ 5-6% lower than measurements.



- 2nd generation viscosity deviates by ~45 – 25% from 273 – 373 K, but is likely to deviate minimally at the operating temperatures of gas turbines.

Moving Forward on Physical/Chemical Property Integration

Mole Fraction					DCN	H/C	MW/ g mol^{-1}	TSI
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	0.40	0.29	0.07	0.23				

Constraint in the lightly branched alkanes – higher molecular weight isomer might benefit matching combustion targets …also there are other ways of accomplishing the appropriate result.

- The straight chain alkane fraction can be represented as a distribution of alkanes (e.g. nC_6 – nC_{16}) instead of just a single component.
- Chemical kinetics of straight chain alkanes is well defined.
- The distribution of alkanes will increase the average molecular weight and hence permit flexibility in emulating liquid phase physical properties.

Summary(1)

Surrogate Fuel Formulation for emulating fully vaporized real fuel combustion

- **MURI property target approach has been refined and comprehensively tested!**
  - Property targets reflect the integral interactions of the important discrete chemical functionalities present in the fuel.
  - The method permits flexibility in selecting surrogate mixture components and results in non-unique compositions that emulate the specific combustion property targets.
  - Experimental replication of real fuel global combustion properties is typically in better agreement than detailed model predictions based upon surrogate composition.
- **A four component, 2nd Gen surrogate mixture of n-C_{12}/iso-C_8/n-PB/1,3,5 TmB can replicate the combustion property targets of petroleum derived fuels, alternative fuel feed stocks and their blends with petroleum.**
  - Weakly branched isomer and cyclo alkane components generally produce only minor changes in surrogate performance (but can be added within the context of the MURI formulation methodology).
- **Efforts emphasize improving accuracy of individual component and mixture model predictions for the 2nd Gen surrogate.**
  - MURI contributing heavily to enhance experimental databases for all components with special emphasis on aromatics.
  - Significant model advancements have been achieved for toluene, xylenes, n-PB, and 1,3,5 TmB.
  - 2nd generation surrogate model development underway.

Summary(2)

Integrating Surrogate Fuel Physical and Chemical Kinetic Properties

- **Properties, especially distillation curve and vapor-liquid equilibrium, require molecular weight and functional group distributions.**
  - Relative importance of physical properties and chemical kinetic properties to multiphase combustion behavior observations in gas turbine environments need experimental evaluation (e.g. “Rules and Tools program”).
  - ***What uncertainties in the respective property emulations are acceptable?***
- **The MURI surrogate formulation has been confirmed to encompass using hydrocarbon solvent fractions to formulate surrogate mixtures.**
  - Surrogate solvent formulation economics permit applied testing applications of the techniques.
    - Surrogate Solvent kinetics can still be emulated by those for smaller numbers of pure components.
  - Surrogate solvent formulations can be used to independently vary distillation curve, and molecular class distributions over the curve while maintaining the same fully prevaporized combustion kinetic behavior.

Continuing MURI Efforts

- Demonstrate added cases of surrogate mixture comparisons with other gas turbine fuel samples over wide range of fundamental venues.
  - Larger database of combustion property targets already under construction for other POSF's.
- Collaborate in test/proof that solvent surrogate formulation approach can connect fundamental MURI mixture formulation concept and applied research testing.
- Provide further validation data for n-dodecane, n-decane, iso-octane, and alkyl aromatics in kinetic transition to high temperature (beta scission/chemical branching behavior); higher MW alkanes also of interest.
- Improve alkane and aromatic oxidation kinetic models for surrogate mixtures.
- Further evaluate/validate MCH kinetic modeling and inclusion of MCH as a surrogate component.
- Produce MURI mixture kinetic model and appropriate reductions for validation/application.
- Further evaluate MURI surrogate mixtures to emulate real fuel sooting behavior in fundamental and applied venues.

Acknowledgements

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Future Drivers

- **Current science findings can assist in unraveling property/combustion kinetic effects in multi-phase, applied combustion experiments.**
- **Even the most developed and studied kinetic models require further refinement to replicate real fuel behavior as well as achieved in experimental comparisons of real fuel and the formulated surrogate mixtures.**
- **Normal-alkane chemistry is controlling but aromatic chemistry is limiting.**
  - Improved kinetic models for aromatics are essential.
- **Engineering Questions of continuing importance!**
  - What level of emulation of real fuel properties must surrogates meet?
  - Gas phase kinetic property targets?
  - Kinetic model predictive accuracy requirements?
  - Physical property predictive accuracy requirements?
  - Optimal liquid fuel physical and chemical property integration?