Surrogate Fuel Formulation Concepts and Associated Kinetic Studies

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Multi Agency Coordination Committee for Combustion Research
Fuels Summit

Princeton University, September 20th–22nd 2010

Overview

- MURI concept to identify surrogate fuel components.
- n-alkyl benzene oxidation.
- Flow reactor oxidation of 1st/2nd generation surrogates vs POSF 4658.
- 1st generation surrogate kinetic model performance, future modeling direction.
- Cycloalkanes in surrogate fuel formulations.
- Can surrogate performance be improved?

MURI Strategy to Jet Fuel modeling

➢Identify critical fuel properties which manifest in important practical gas phase combustion chemistry behaviour of target fuel:

- Adiabatic flame temperature
- Local air fuel stoichiometry
- Enthalpy of combustion
- Flame velocity

} Ratio of hydrogen to carbon (H/C)

- Fuel diffusive properties → Molecular Weight (MW)
- Sooting propensity → Threshold Sooting Index (TSI)
  via smoke point measurement
- Global chemical kinetics/ Overall radical production

} Derived Cetane Number (DCN),
macro ignition measure via Ignition Quality Tester

➢Surrogate mixture must emulate these parameters, but how?

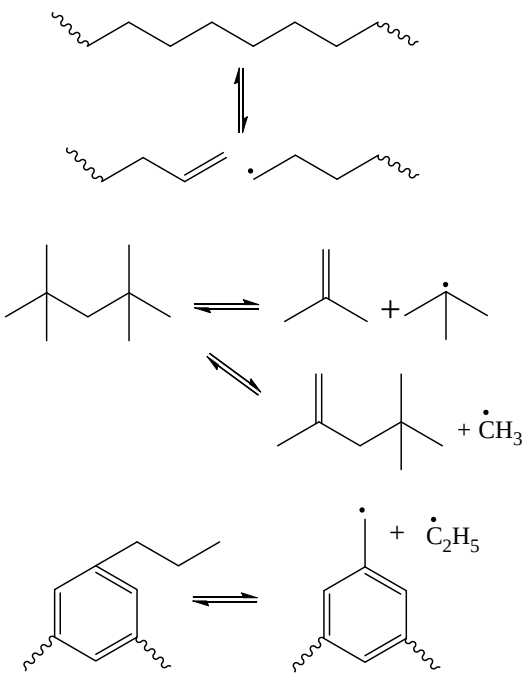
➢Surrogate should represent **distinct molecular class** composition of real fuel reacting flux => ***n*–alkyl, alkenyl and aromatic.**

➢ **Interaction of distinct chemical functionalities in radical generation is manifested in real fuel behaviour.**

MURI Strategy to Jet Fuel modeling

- Must identify distinct chemical functionalities.

MURI 1st and 2nd Generation Surrogates

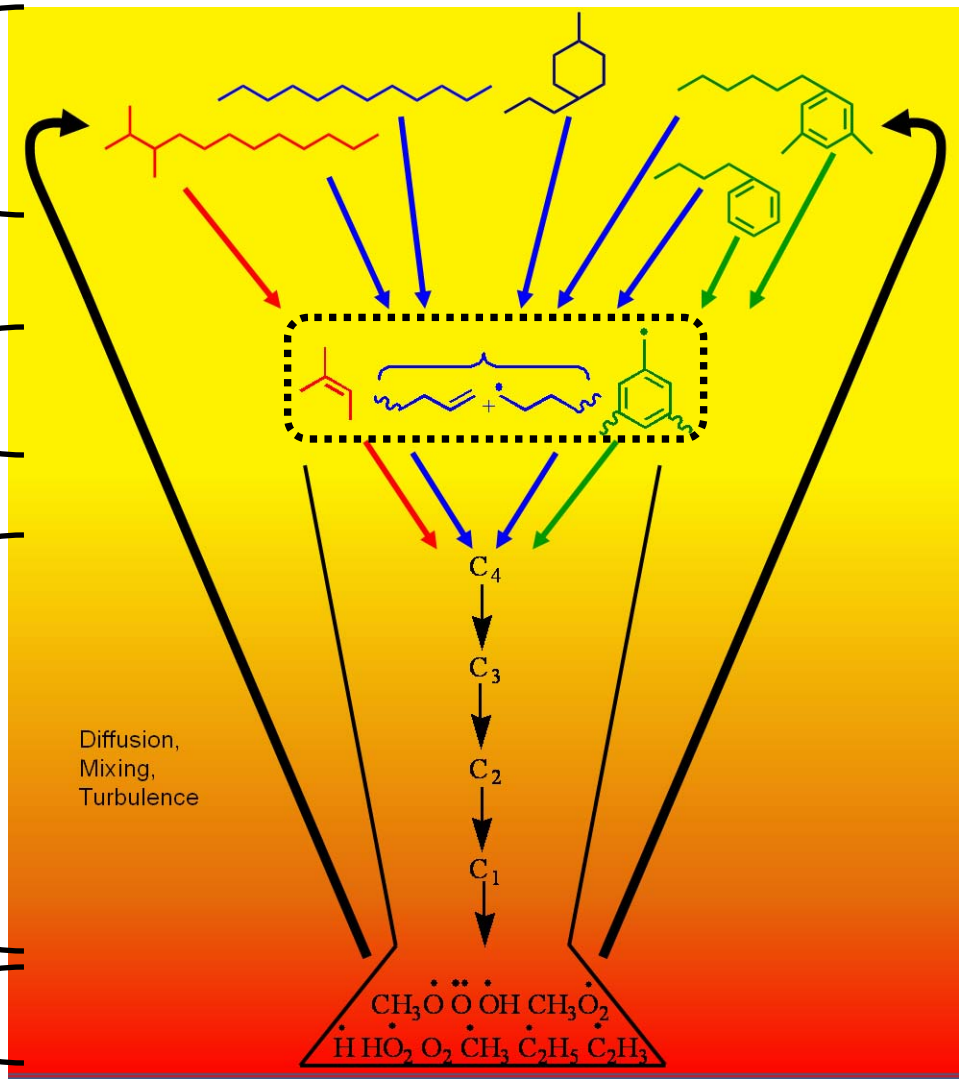


Real fuels have many generic chemical functionalities

Much fewer distinct chemical functionalities after initial oxidation

Distinct chemical functionalities affect small species population which affect radical pool identity and population

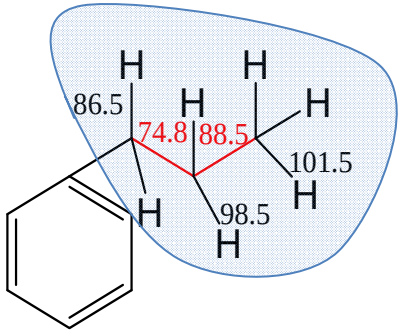
Radical pool population controlling in combustion chemistry



n-alkyl Benzene Oxidation

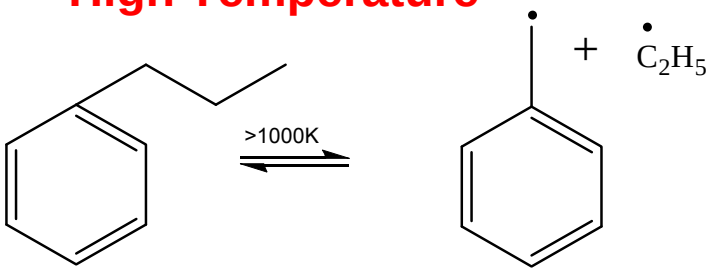
n-propyl benzene oxidation and distinct functionality concept

- n-propyl benzene (n-alkyl benzenes) exhibit(s) very weak C-C bond dissociation energies.
- This allows modeling of **high temperature global** combustion properties to be simplified.
- Construct model only considering oxidation of alkyl chain, divides high T and low T phenomena.



n-propyl benzene bond dissociation energies, kcal mol^{-1}

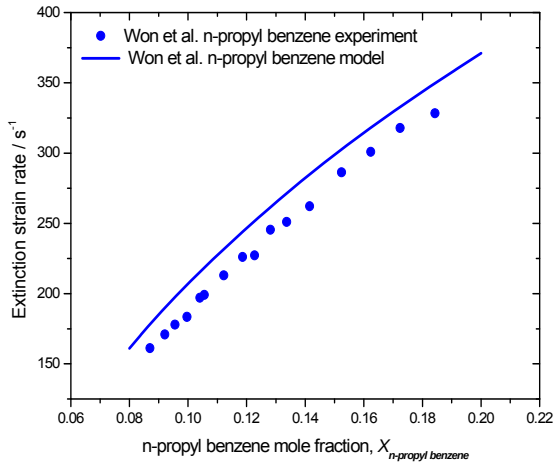
High Temperature



Allowed in model => Good agreement against high T global phenomena

S.H. Won, S. Dooley, F.L.Dryer, Y. Ju Proc. Combust, Inst. in press 2010,

Extinction



Strain rates of extinction for counter flow diffusion flames at 1 atm, n-propyl benzene.

Autoignition

See Presentation of M. Oehlschlaeger, this symposium

Shock tube Ignition delay times for n-propyl benzene, φ= 1.0 in air at ~20 atm.

n-alkyl Benzene Oxidation

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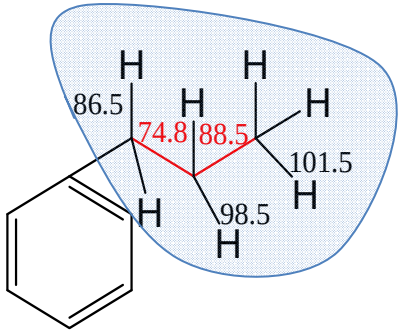
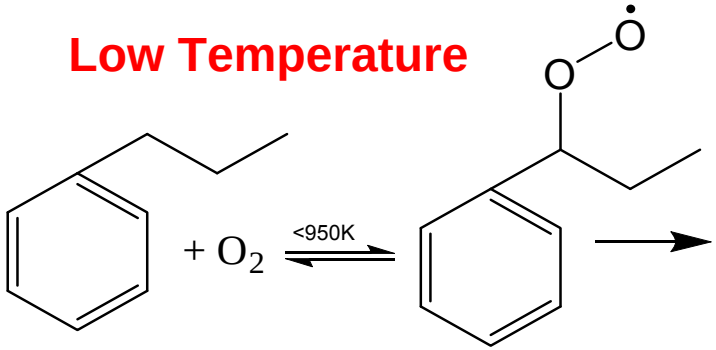


n-propyl benzene bond dissociation energies, kcal mol^{-1}

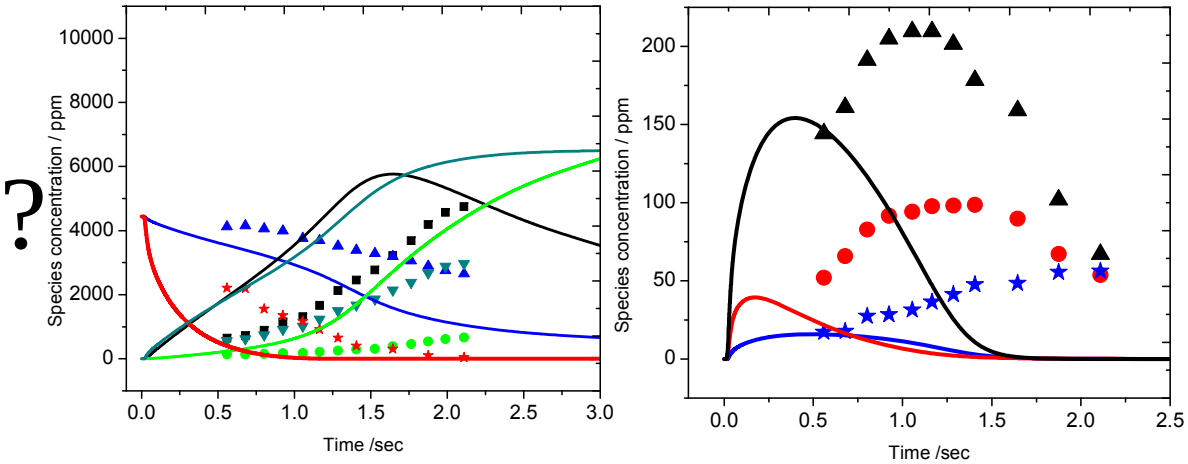
Low Temperature



R +O_2 chemistry not allowed at fuel level in model leading to poor agreement at lower temperatures

S.H. Won, S. Dooley, F.L. Dryer, Y. Ju Proc. Combust, Inst. in press 2010,

Flow reactor Oxidation at 848K



Flow reactor oxidation data. Experiment (symbols) and model computations (Lines).

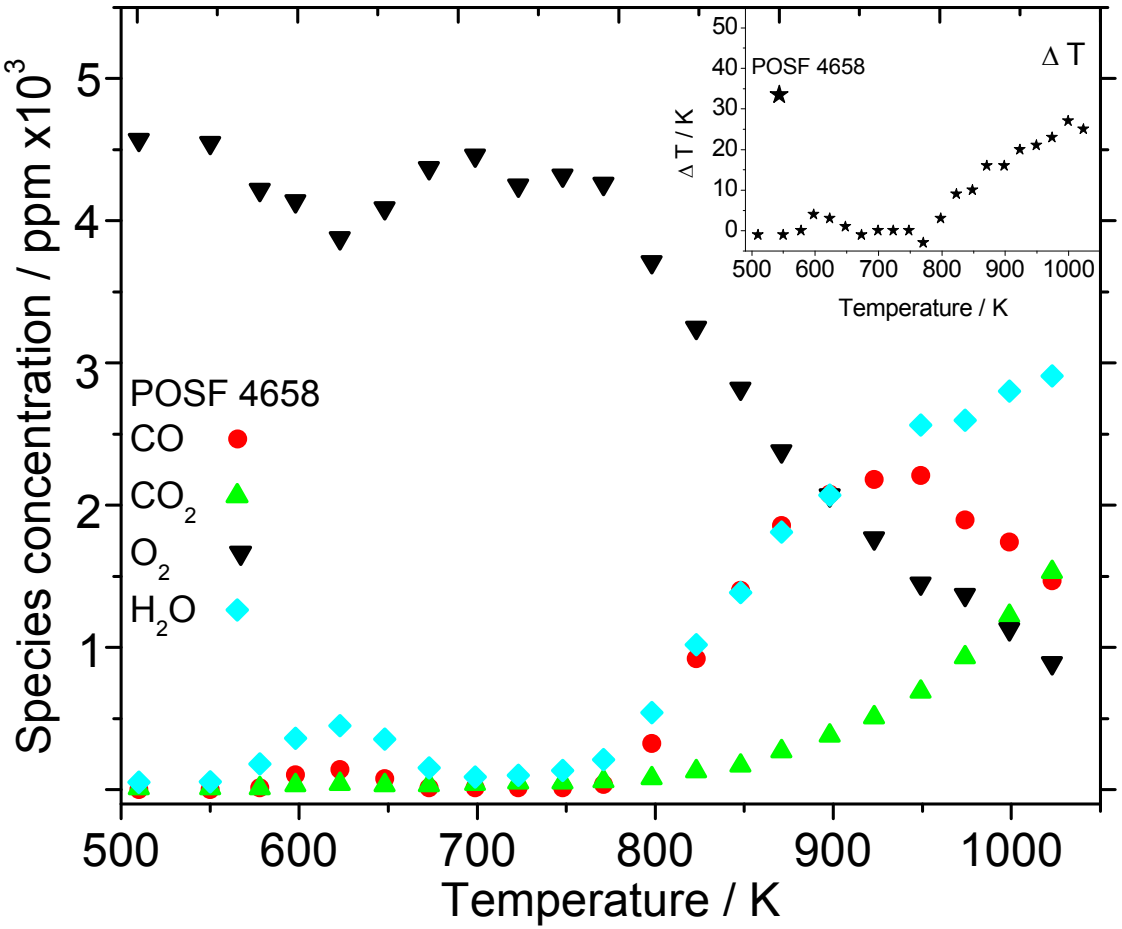
1st Generation Surrogate

Mole Fraction			DCN	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658			47.1	1.957	142.01	21.4
***n*-decane**	***iso*-octane**	**Toluene**				
0.4267	0.3302	0.2431	47.1	2.01	120.7	14.1

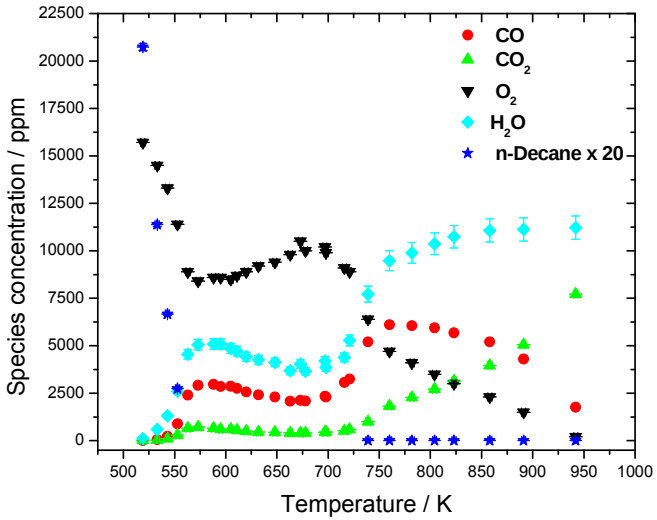
Surrogate Formulation

- Molecular weight may not be emulated with these components. (How important is that to combustion chemistry targets?)
- POSF 4658 vs Surrogate, $C_{10.17}H_{19.91}$ vs $C_{8.61}H_{17.27}$
- H/C and TSI may not be emulated by the same mixture.
- *n*–decane/*iso*–octane/toluene allows for assessment of current kinetic modeling capabilities and all range of conditions for JP fuels.

POSF 4658 vs 1st Generation Surrogate: Oxidation

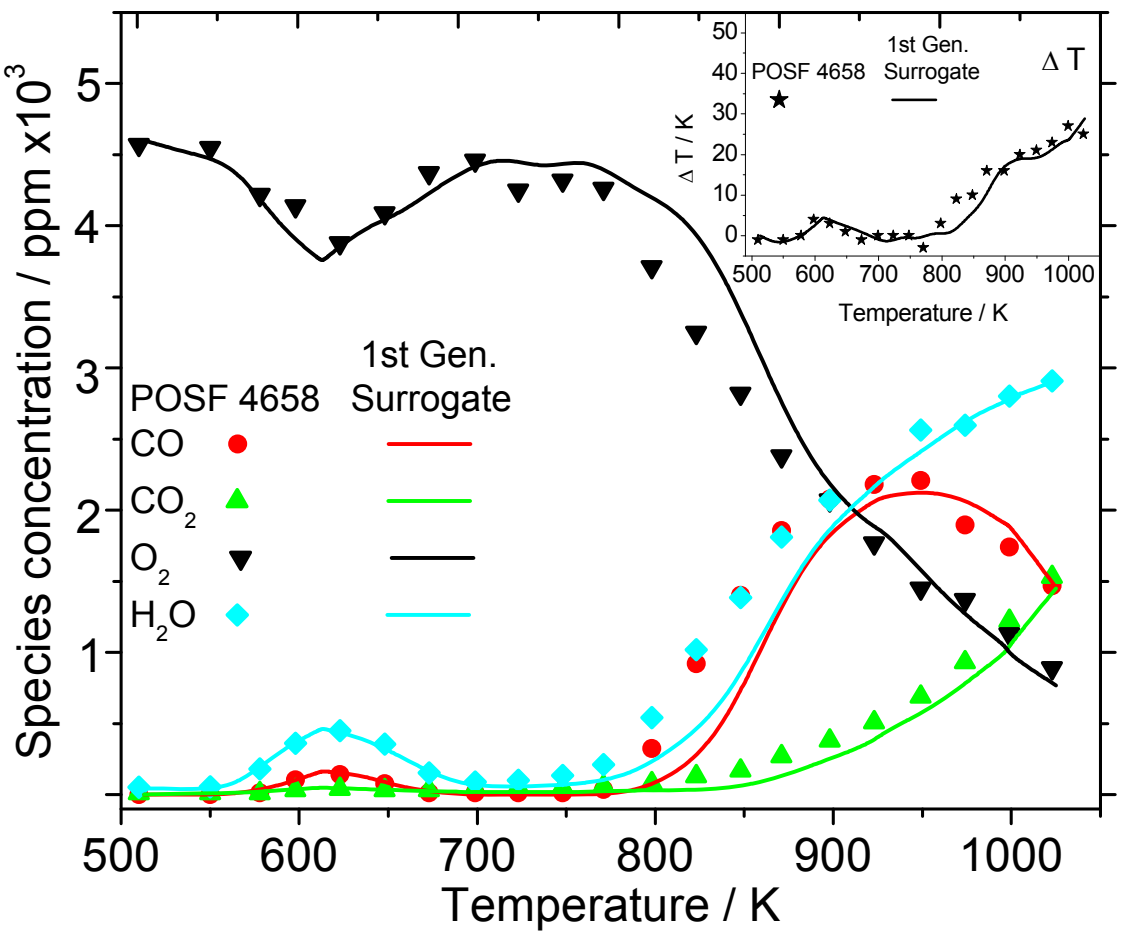


- Fuel dilute conditions, 0.3% carbon as fuel allows heat release to be regulated.



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, $\phi = 1.0$ and $t = 1.8$s, for POSF-4658 (symbols), Inset;ΔT.

POSF 4658 vs 1st Generation Surrogate: Oxidation



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, ϕ= 1.0 and t =1.8s, for POSF-4658 (symbols) and 1st generation POSF-4658 surrogate (solid lines), Inset;ΔT.

- Fuel dilute conditions, 0.3% carbon as fuel allows heat release to be regulated.
- 0.3 % carbon and ϕ=1.0
- POSF 4658 vs Surrogate 294 vs 348 "ppm" fuel 4548 vs 4496 ppm O_2
- Heat release rate is well emulated

1st Generation POSF 4658 Surrogate

Mole Fraction			DCN	H/C	MW / g mol^{-1}	TSI
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***n*-decane**	***iso*-octane**	**Toluene**				
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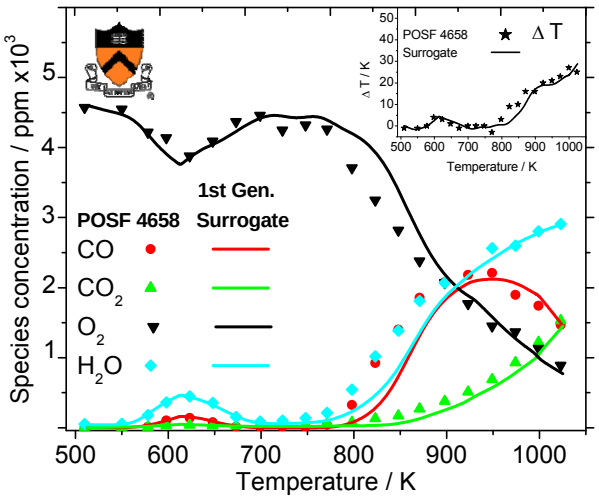
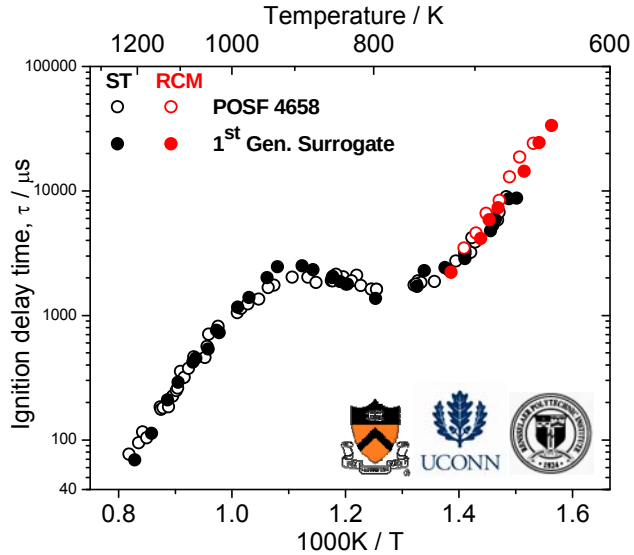
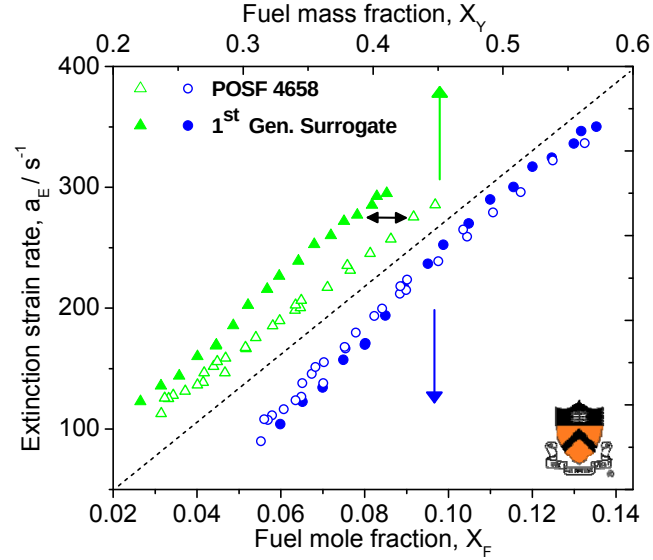


Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, φ= 1.0 and *t* =1.8s, for POSF 4658 and 1st generation POSF 4658 surrogate. Inset;ΔT.



Ignition delay times, φ= 1.0 in air at ~20 atm for POSF 4658 and 1st generation POSF 4658 surrogate.



Strain rates of extinction for counter flow diffusion flames at 1 atm, for POSF 4658 and 1st generation POSF 4658 surrogate.

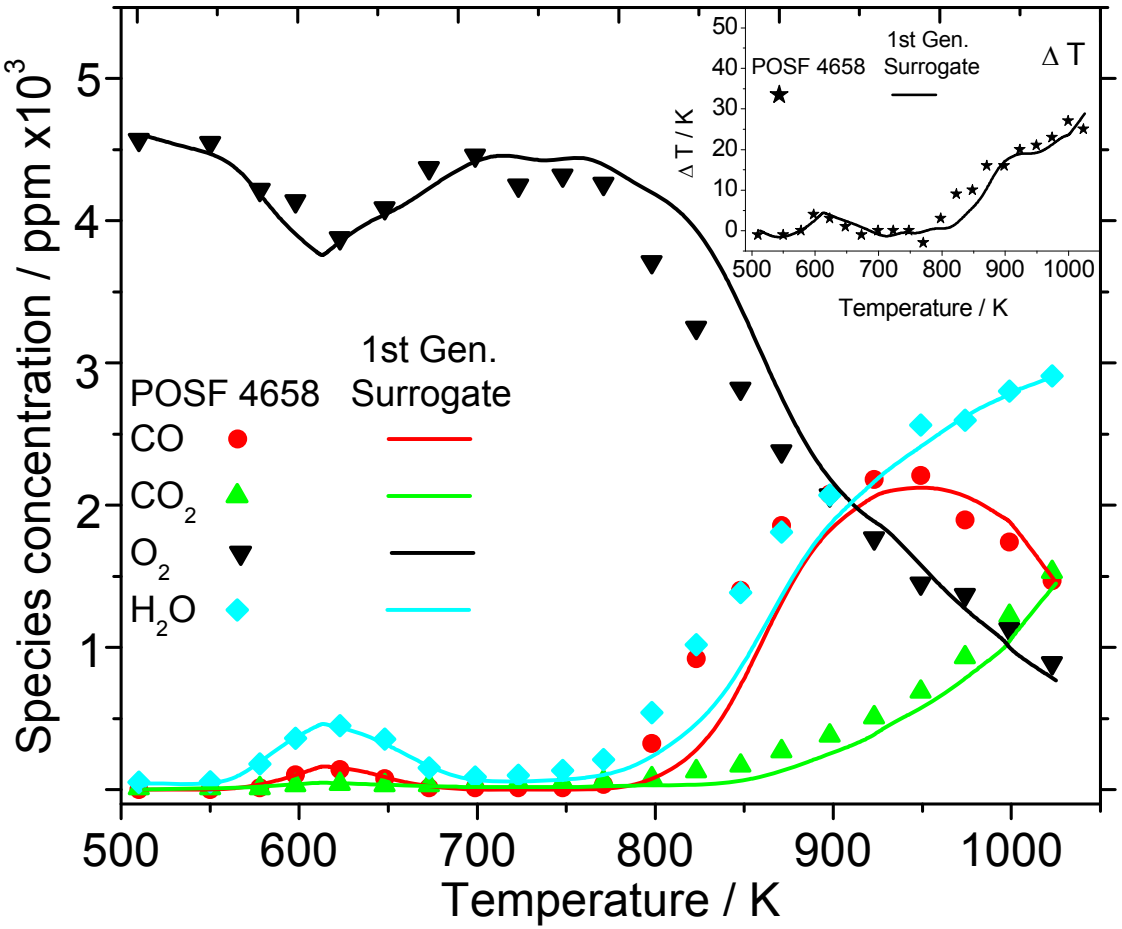
2nd Generation POSF 4658 Surrogate

2nd Generation Surrogate Formulation

- Molecular weight may not be emulated with *n*–decane/*iso*–octane/toluene and H/C and TSI may not be emulated simultaneously.
- Must use larger alkane to adjust DCN and alkylated aromatics to adjust H/C independent of TSI, as TSI ∝ aromatic content.
- More reactive aromatics may improve emulation of end of NTC region.
  => ***n*–dodecane/*iso*–octane/ propyl benzene / 1,3,5 trimethyl benzene**
  Can match all combustion property constraints.
- Parameterise DCN as before, 35 mixtures for 4 components versus 14 for 3 components.

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	0.29	0.07	0.23				

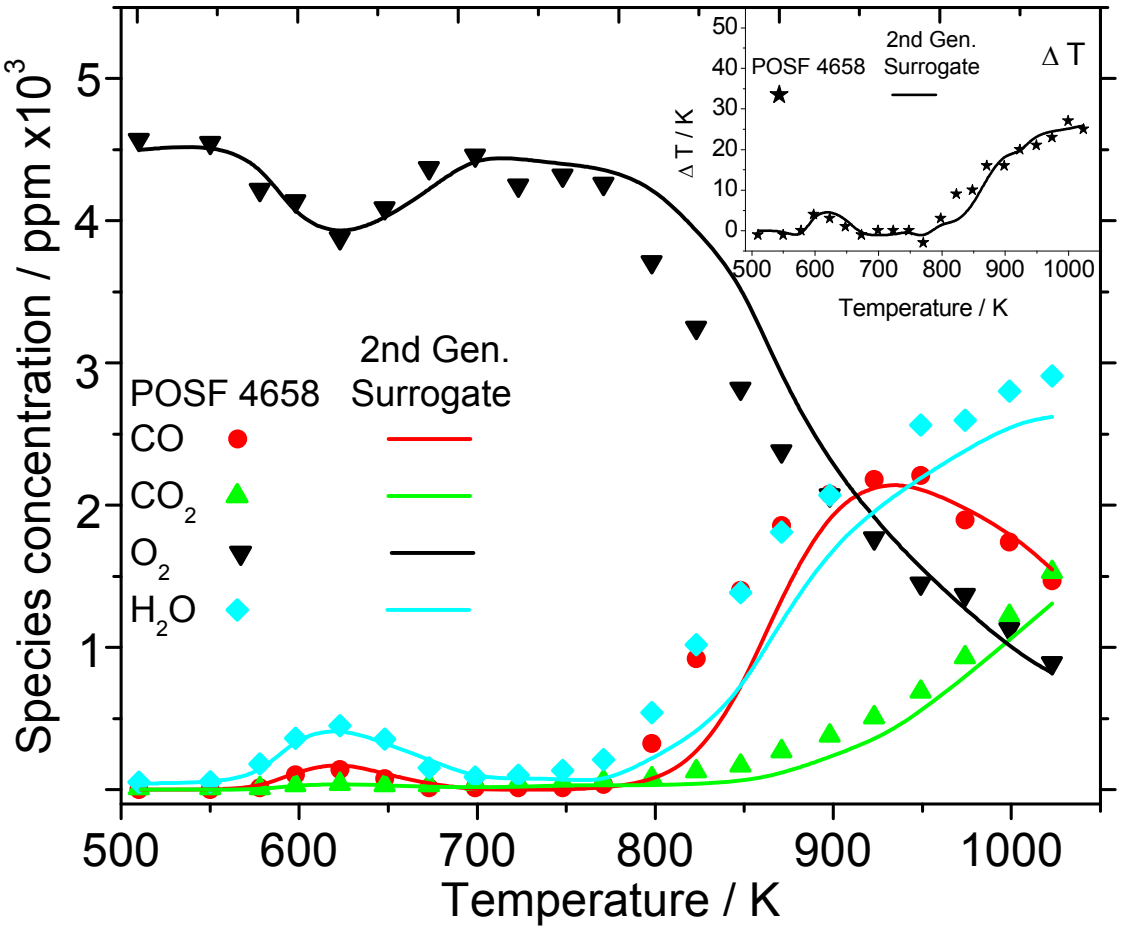
POSF 4658 vs 1st Gen. Surrogate: Oxidation



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, ϕ= 1.0 and t =1.8s, for POSF-4658 (symbols), 1st generation surrogate (solid lines), Inset;ΔT.

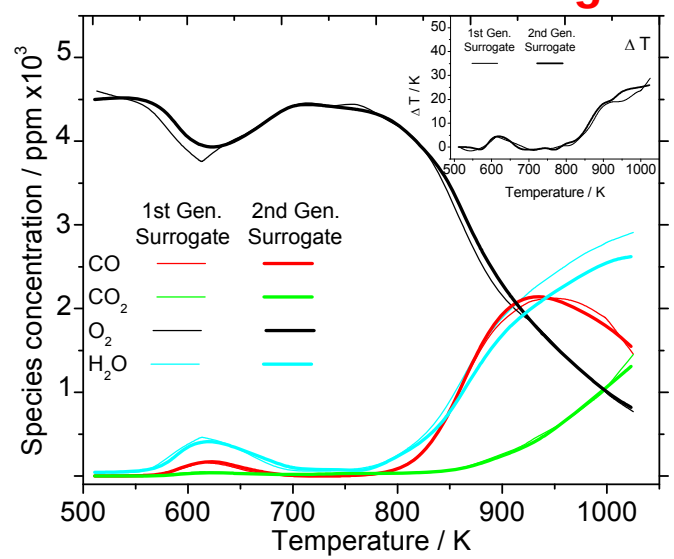
- Fuel dilute conditions, 0.3% carbon as fuel allows heat release to be regulated.
- 0.3 % carbon and ϕ=1.0
- POSF 4658 vs 2nd gen Surrogate
  294 vs 300 "ppm" fuel
  4548 vs 4500 ppm O_2

POSF 4658 vs 2nd Gen. Surrogate: Oxidation



•0.3 % carbon and ϕ=1.0

1st vs 2nd Gen. Surrogate



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, ϕ= 1.0 and t =1.8s, for POSF-4658 (symbols), 2nd generation surrogate (solid lines), Inset;ΔT. RHS 1st generation surrogate versus 2nd generation surrogate.

2nd Generation POSF 4658 Surrogate

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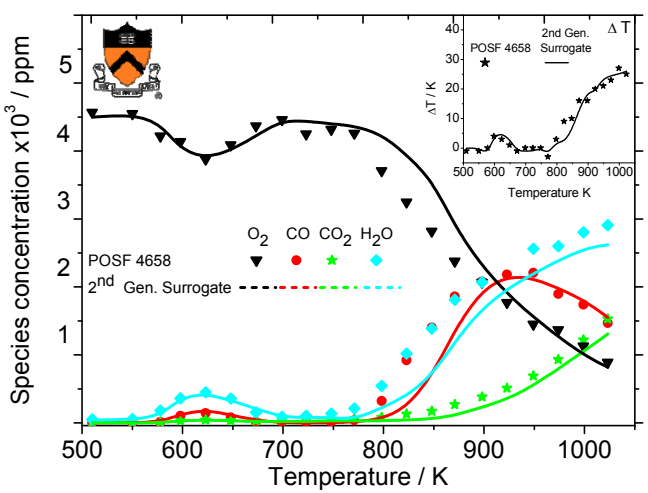

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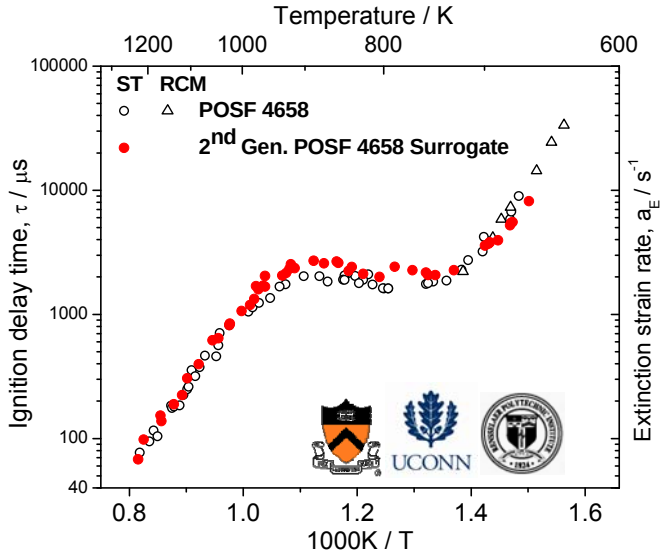

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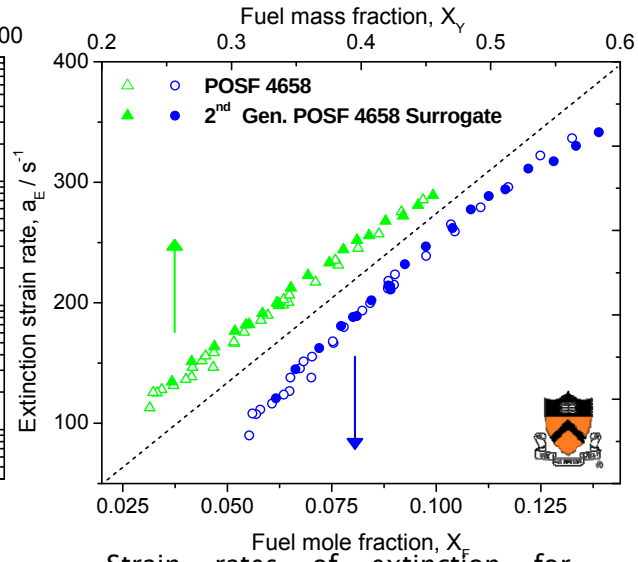

Strain rates of extinction for counter flow diffusion flames at 1 atm, for POSF 4658, 1st generation POSF 4658 surrogate and 2nd generation POSF 4658.

1st Generation Surrogate Kinetic Model

- *n*-decane/*iso*-octane/toluene detailed kinetic model.
  - *n*-decane => Westbrook et al. (LLNL) 2008. => Overall good
  - *iso*-octane => Mehl et al. (LLNL revision of Curran et al.) 2010. =>Overall good
  - Toluene => Princeton, (Metcalfe, Dooley and Dryer) 2010.=> Extensive revision available soon

C.K. Westbrook, W.J. Pitz, O. Herbinet, H.J. Curran, E.J. Silke, Combust. Flame, 156 (2009) 181–199.
Marco Mehl, Personal communication Nov 2009.
H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, Combust. Flame 129 (2002) 253–280.
W.K. Metcalfe, S. Dooley, Dryer F.L, in preparation 2010.
R. Bounaceur, I. Da Costa, R. Fournet, F. Billaud, F. Battin-Leclerc, Int J. Chem. Kin. 37 (2005) 25-49.

Common C_0–C_4 assembled and tested by Princeton.

- H_2/O_2 from Li et al. and C_1 chemistry of Zhao et al. to $CH_3+CH_3(+M)=C_2H_6(+M)$.
- C_2 to C_4 of Healy et al.
- Laskin et al. for higher alkenyl type species.

- Do not consider "cross reactions"(!), 1600/6600 species/reactions.
- Transport from literature review => aromatics, oxygenates, alkyl/alkenyls.

J. Li, Z. Zhao, A. Kazakov, M. Chaos, F.L. Dryer, J.J. Scire Jr., Int. J. Chem. Kinet. 39 (2007) 109–136.
Z. Zhao, M. Chaos, A. Kazakov, F.L. Dryer, Int. J. Chem. Kinet. 10 (2008) 1–18.
D. Healy, H.J. Curran, J.M. Simmie, et al.Combust. Flame 155 (2008) 441–448.
A. Laskin, H. Wang, C.K. Law, Int. J. Chem. Kinet. 32 (2000) 589–614.
F.M. Mourits, F.H.A. Rummens, Can. J. Chem. 55 (1977) 3007–3020.
H. Wang, M. Frenklach, Combust. Flame 96 (1994) 163–170.

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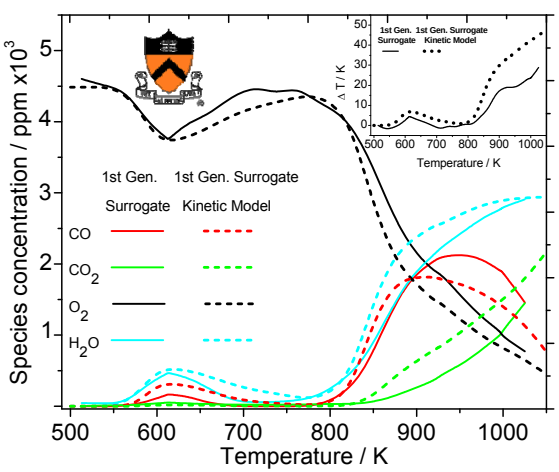
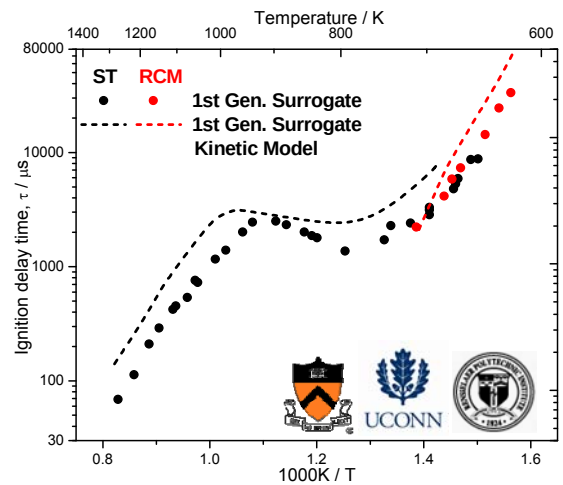
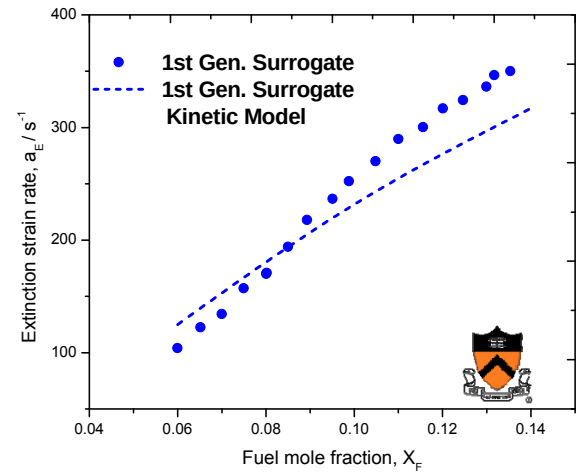


Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, φ= 1.0 and *t* =1.8s, for POSF-4658, 1st generation POSF-4658 surrogate and model simulation of 1st generation POSF-4658 surrogate, Inset;ΔT



Ignition delay times, φ= 1.0 in air at ~20 atm for POSF-4658, 1st generation POSF-4658 surrogate and 1st generation POSF-4658 surrogate kinetic model simulation



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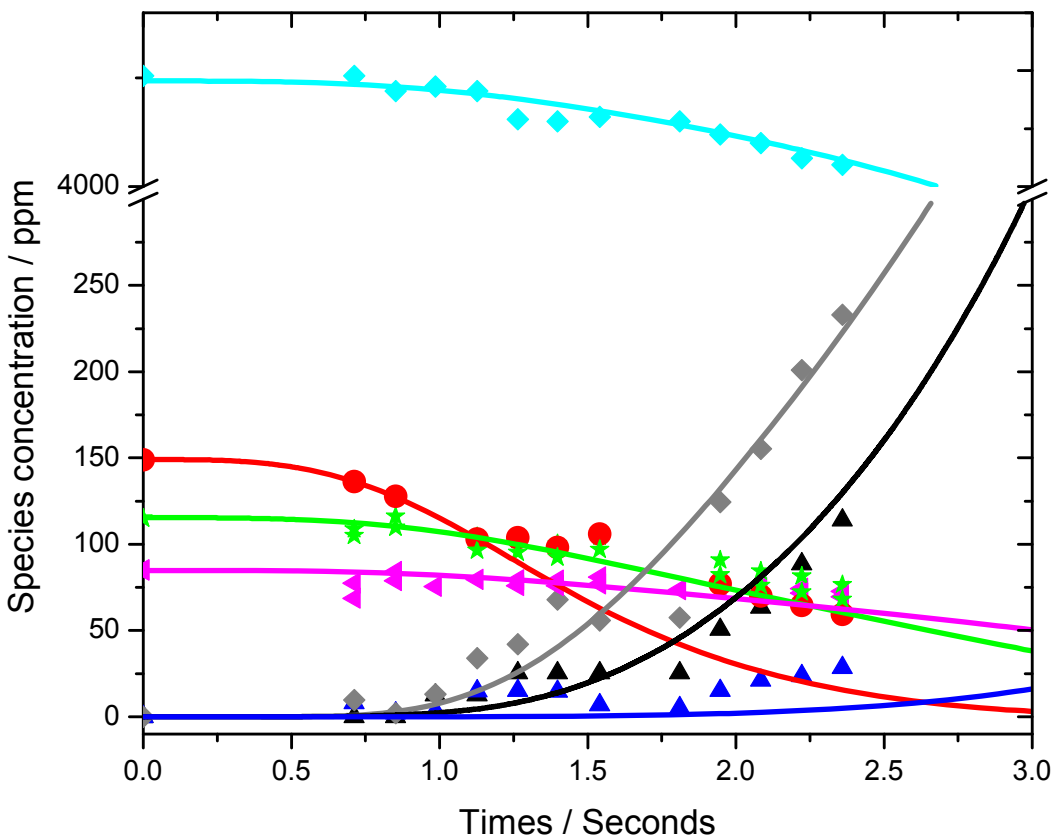
Analysis of 1st Generation Surrogate Kinetic Model



Flow reactor oxidation data for 1st Generation surrogate.

- Model shows that n-decane is principally active in radical generation=> exclusively so at lowest temperatures.

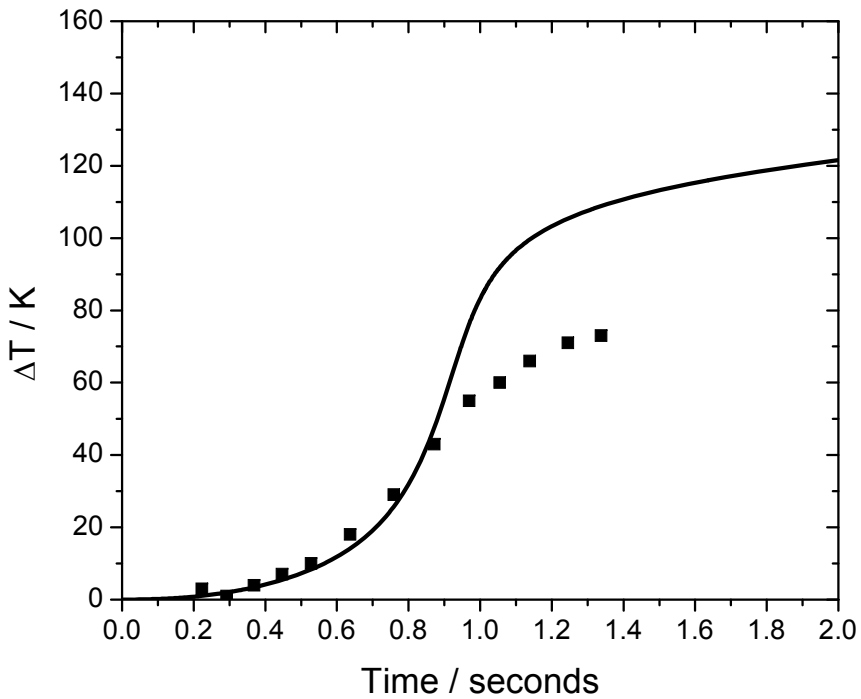
- Excellent emulation of POSF 4658 at low Ts indicates quantity of n-alkyl fragments have been approx. correctly prescribed in surrogate.

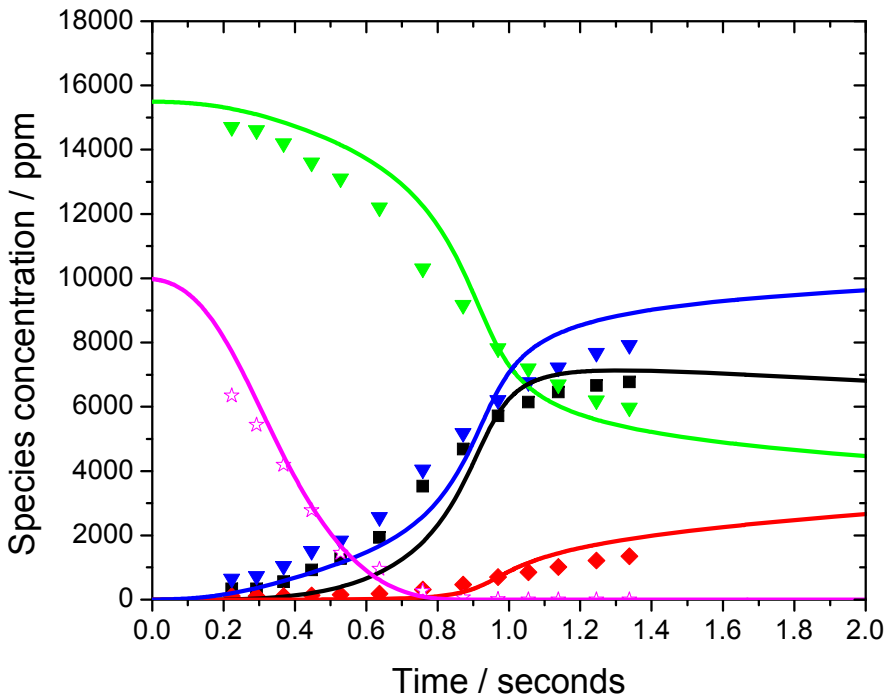
- Aromatic/iso-alkanes can not produce radicals as competitively, slowing overall reaction.

- iso-octane/toluene start to contribute to radical generation above 800K and 900K respectively.

n-Alkane Oxidation: n-Decane

- Analysis indicates n-alkane oxidation of huge importance.
- Current models have room for improvement.





Experimental data (symbols) versus simulation (lines) for n-decane oxidation

Time Shift = 0s

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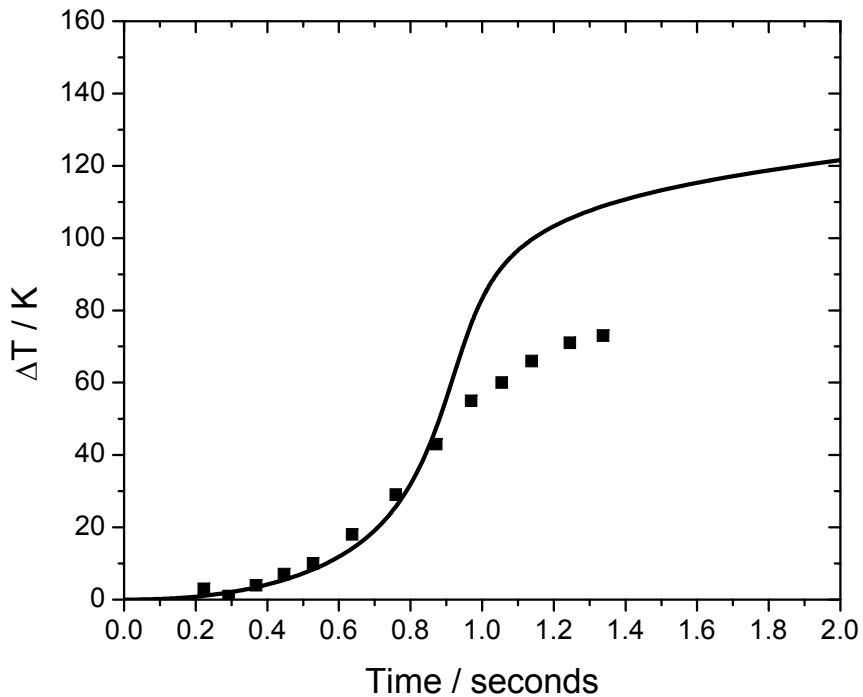

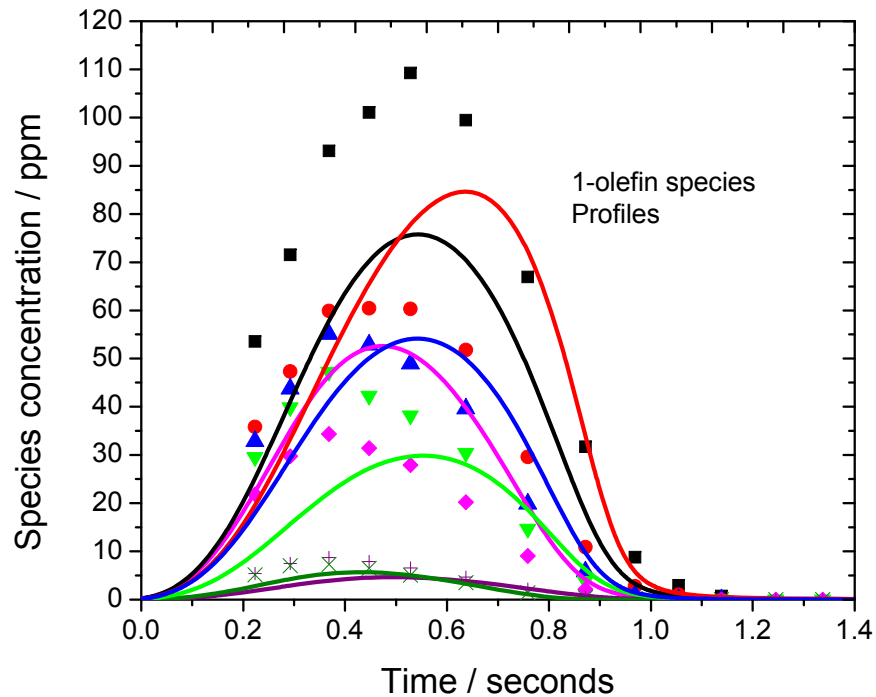

Experimental data (symbols) versus simulation (lines) for n-decane oxidation.

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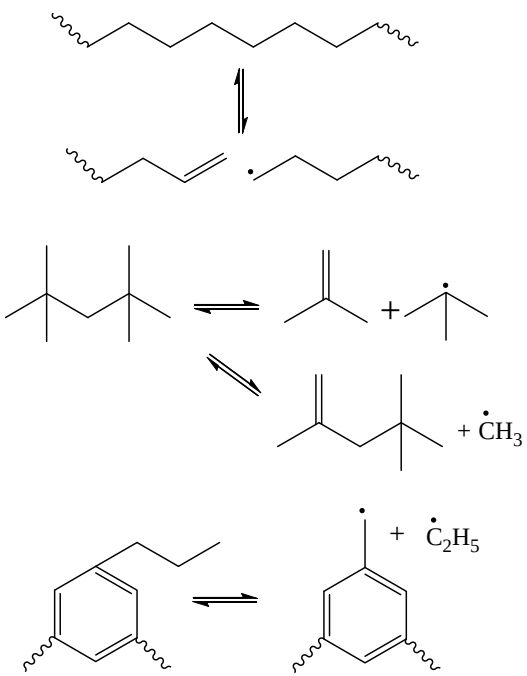
Cycloalkanes in MURI Strategy to Jet Fuel modeling

- Must identify distinct chemical functionalities.

MURI 1st and 2nd Generation Surrogates

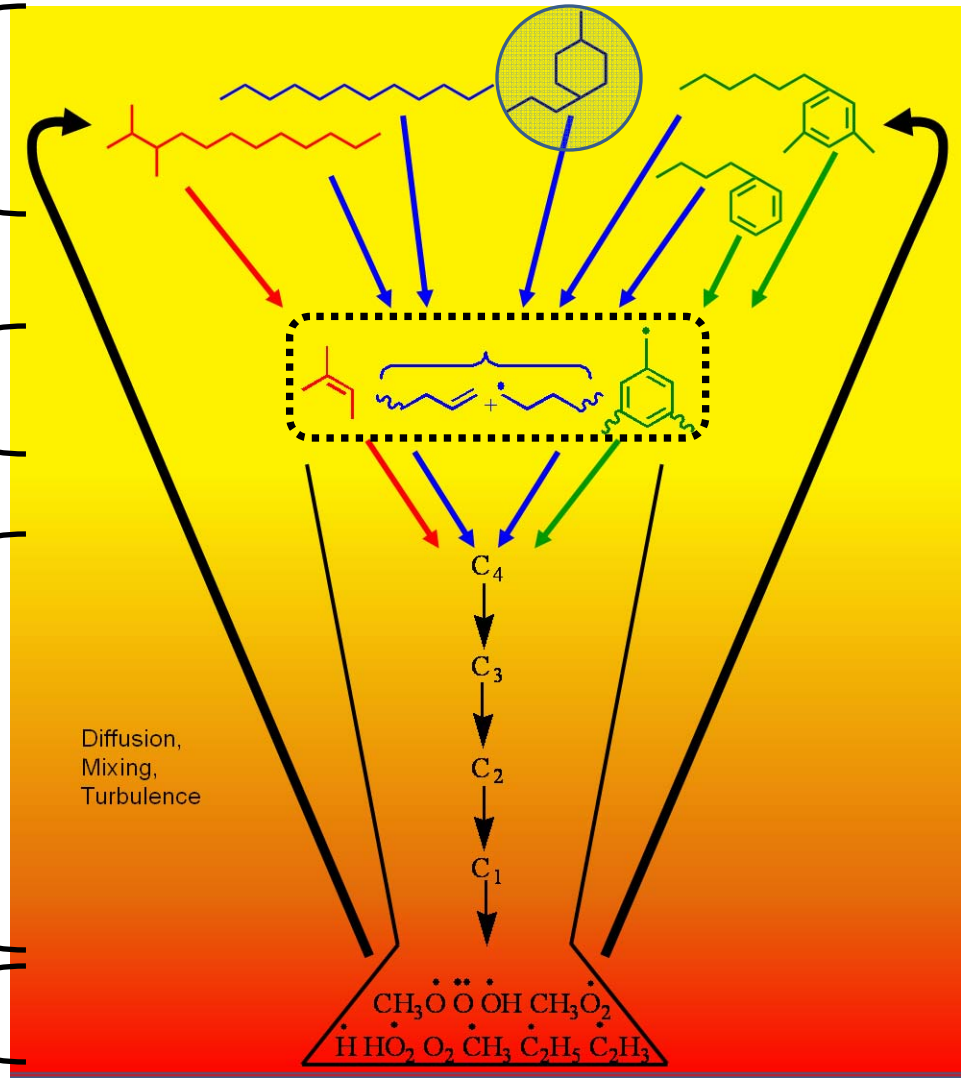


Real fuels have many generic chemical functionalities

Much fewer distinct chemical functionalities after initial oxidation

Distinct chemical functionalities affect small species population which affect radical pool identity and population

Radical pool population controlling in combustion chemistry



Cycloalkanes within MURI Surrogate Formulation Strategy?

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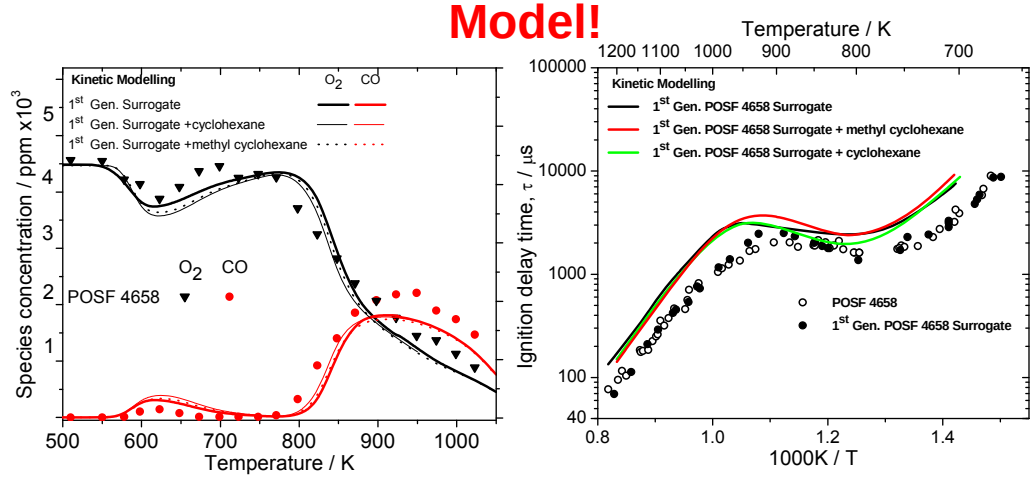
	0.427	0.33	0.243					
1st generation surrogate + cylclohexane	*n*-decane	*iso*-octane	Toluene	Cylclohexane	46.8	1.99	117.9	11.1
	0.482	0.175	0.178	0.165				
1st generation surrogate + methyl cyclohexane	*n*-decane	*iso*-octane	Toluene	Methyl cyclohexane	47.8	1.98	118.2	11.2
	0.422	0.174	0.179	0.225				

- Formulate 2 additional surrogates containing cycloalkanes: cyclohexane and methyl cyclohexane.
- Incorporate LLNL cyclohexane[1] and methyl cyclohexane[2] chemistries into Jet-A model[3], is cylcoalkyl functionality having a significant effect?
- Model results say no.

Model!



flow reactor and shock tube oxidation of 1st generation surrogate *versus* 1st generation surrogate + methyl cyclohexane. Model computations (lines), experiments (symbols).

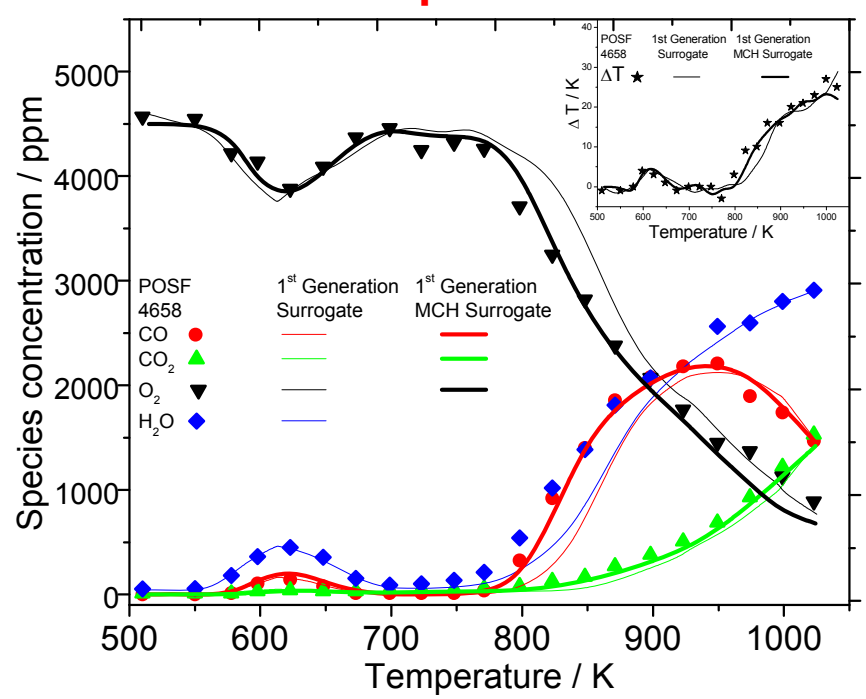
1) E.J. Silke, W.J. Pitz, C.K. Westbrook, *J. Phys. Chem. A* 111 (2007) 3761-3775.
2) W.J. Pitz, C.V. Naik, T.N. Mhaolduin, C.K. Westbrook, H.J. Curran, J.P. Orme, J.M. Simmie, *Proc. Combust. Inst.* 31 (2007) 267-275.
3) S.Dooley, S. H. Won, M. Chaos, J.Heyne, Y. Ju F.L. Dryer, K. Kumar, C.-J. Sung, H. Wang, M.Oehlschlaeger, R. J. Santoro, T. A. Litzinger, Combust. Flame *in press* 2010.

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				

- What does experiment say?
- Low temperature (<800K) behaviour is almost identical to 1st Generation surrogate.
- Observe a shift of approx. 25-30K to cooler temperature in "hot ignition" condition.
- How significant is this to the engine design scenario?

Experiment!



Flow reactor oxidation 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.

Conclusions and Remaining Questions

- Surrogate formulation strategy is promising, tested surrogates closely emulate the chemical kinetic related behavior of real life Jet-A POSF 4658.
- Emulation quality improves with a richer chemical structural palette, cycloalkanes, weakly isomerised alkanes?

  => Is it worth incorporating these given the kinetic modeling price to be paid?
- To what level must constraining parameter be matched, likely dependent on condition of study and fuel?
- One surrogate one fuel? Intermediate species? 2-stage ignition?
- Kinetic modeling for n-decane/iso-octane/toluene is qualitatively accurate but not precise, promising "a priori" agreement.
- More detailed and quantitative understanding of n-alkyl fragment oxidation required to improve real fuel oxidation models.
- Paper is published in Combust. Flame, on line now.

  S. Dooley et al. Combust. Flame. in press 2010 doi:10.1016/j.combustflame.2010.07.001

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