Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

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Summary of the AFOSR 2007 MURI Topic #12

Science-Based Design of Fuel-flexible Chemical Propulsion/Energy Conversion Systems

July 1, 2007 – June 30, 2012

MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)

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Advisory Board: Tim Edwards (AFRL), John Farrell (Exxon Mobil), Catalin Fotache (UTRC), Hukam Mongia (GE/Purdue), William Pitz (LLNL), Wing Tsang (NIST)

Improved Methods for Evaluating and Emulating Real Jet Fuel Properties on Combustion

- Enhanced efficacy in evaluating the effects of fuel property variations on existing propulsion system performance and emissions.
- Improved paper design and development for advancing existing and developing new propulsion/combustion concepts.

Military F119-100

In emulating multiphase combustion in real combustors, must all physical and chemical processes be represented to the same level of detail and accuracy to achieve satisfactory predictions?

- ***Experimental* evidence is needed that delineates the relative importance of physical and chemical kinetic properties on multi-phase combustion behavior at conditions encompassing those found in real combustors.**

Turbine Fuel Aviation Kerosene Type Specification

(MIL-DTL-83133)

ASTM D1319 Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
(Aromatic, olefin, saturate fractions)

ASTM D6379 Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index

ASTM D3343 Standard Test Method for Estimation of Hydrogen Content of Aviation Fuels
(Correlation method based on petroleum data)

ASTM D1322 – Standard test method for smoke point of kerosene and aviation turbine fuel

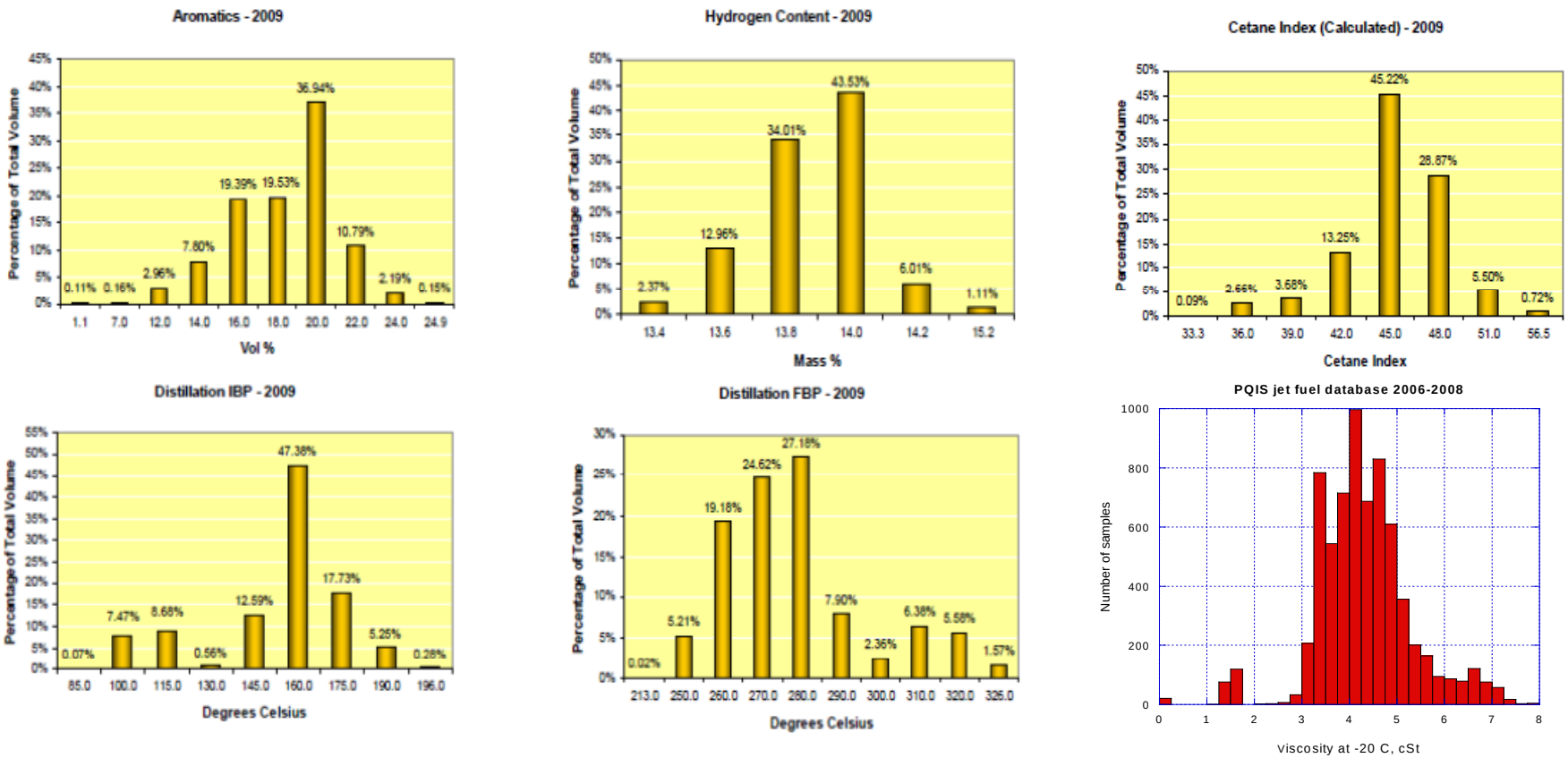
ASTM D976 Standard Test Method for Determining Cetane Index, reported only, no specification
(Correlation method based on petroleum data)

Property	Min	Max	Test Methods ASTM Standards
Color, Saybolt		1/	D156 2/ or D6045
Total Acid number, mg KOH/gm		0.015	D3242
Aromatics, vol percent		25.0	D1319
Sulfur, total, mass percent		0.30	D129, D1266, D2622, D3120, D4294 2/ or D5453
Sulfur Mercaptan, mass percent OR		0.002	D3227
Doctor Test		negative	D4952
Distillation Temperature, °C 3/			D86 2/, D2887
(D2887 limits given in parentheses)			
Initial boiling point		1/	
10 percent recovered		205 (186)	
20 percent recovered		1/	
50 percent recovered		1/	
90 percent recovered		1/	
End point		300(330)	
Residue, vol percent		1.5	
Loss, vol percent		1.5	
Flash point, °C	38	4/	D56, D93 2/ or D3828 4/
Density or Gravity			
Density, kg/L at 15° C OR	0.775	0.840	D1298 or D4052 2/
Gravity, API at 60°F	37.0	51.0	D1298
Freezing point, °C		-47	D 2386 2/, D 5901 or D5972
Viscosity, at -20°C, mm^2/s		8.0	D445
Net heat of combustion, MJ/kg	42.8		D3338 5/ or D4809 2/
Hydrogen content, mass percent	13.4		D3701 2/, D3343
Smoke point, mm, OR	25.0		D1322
Smoke point, mm, AND	19.0		D1322
Naphthalenic, vol percent		3.0	D1840
Calculated Cetane Index		1/	D976 2/
Copper strip corrosion, 2hr at 100°C (212°F)		No. 1	D130
Thermal stability			D3241 7/
change in pressure drop, mm Hg		25	
heater tube deposit, visual rating		<3 12/	
Existent gum, mg/100 ml		7.0	D381
Particulate matter, mg/L		1.0	D2276 8/ or D5452 2/
Filtration time, minutes		15	
Water reaction interface rating		1 b	8/ D1094
Water separation index	9/		D3948
Fuel system icing inhibitor, vol %	0.10	0.15	D5006 10/
Fuel electrical conductivity, ps/m	11/	11/	D2624

Fuels that meet fit-for-use specifications can have significantly different molecular (chemical) compositions and physical properties.

“JP-8”, “Jet A”, “C_nH_m”: Sufficient Definition for Research?

Fraction of delivered JP-8 fuels with specified properties

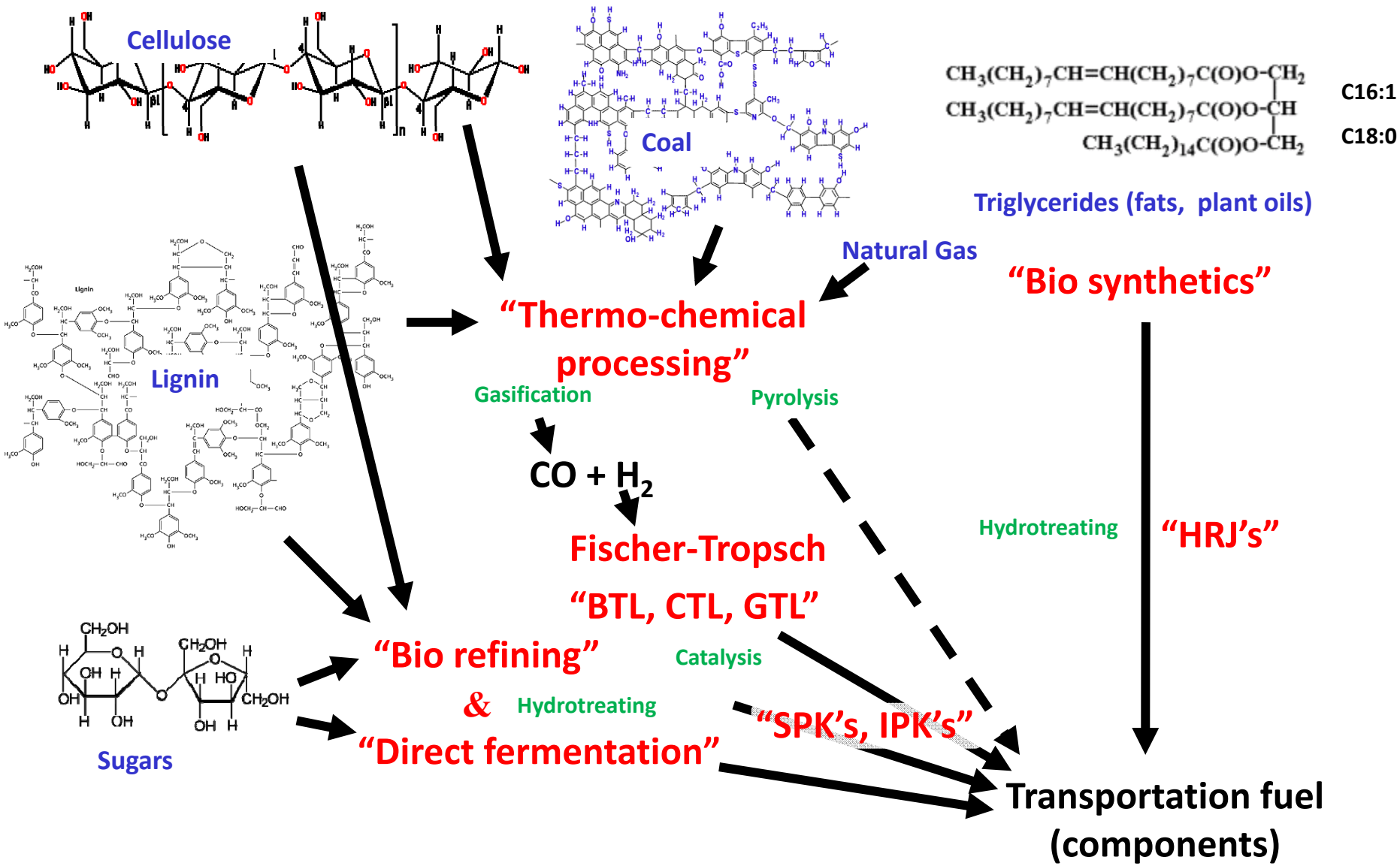


- Certification information aimed at fit-for-use qualification.
- Typical fuel property variabilities are significant.
- **Physical/chemical fuel properties need more precise characterization when attempting to relate fuel properties and gas turbine combustion.**

http://www.desc.dla.mil/DCM/Files/2009PQISreport.pdf

Petroleum Quality Information System

Alternative Fuel Resources and Processing Options

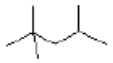
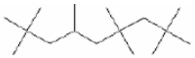
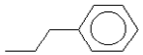


Emulating *Fully Prevaporized* Combustion of a Specific Jet Fuel

What are the critical (fuel) combustion property targets that manifest in important practical combustion behavior of each, individual real fuel, including:

- Adiabatic flame temperature
- Local air fuel stoichiometry
- Enthalpy of combustion
- Flame velocity
- Overall active radical production
- Premixed sooting
- Non-premixed sooting
- Fuel vapor diffusive transport properties
- Autoignition/global kinetics

- Emulate the real fuel with a select mixture of a few pure "surrogate" components. *Which ones? How many components are needed?*
- *How many critical property targets are needed?*
- Each property target for the real fuel, surrogate components and their mixtures need to be easily determined *experimentally.*

Component	Molecular Formula	Structure	NTC
n-Heptane	C_7H_{18}		Yes
n-Decane	$C_{10}H_{22}$		Yes
n-Dodecane	$C_{12}H_{26}$		Yes
Iso-Octane (2,2,4 Trimethylpentane)	C_8H_{18}		Sml
Iso-Cetane (Heptamethylnonane)	$C_{16}H_{34}$		No
Methylcyclohexane	C_7H_{14}		Yes
Toluene	C_7H_8		No
n-Propyl Benzene	C_9H_{12}		?
1,3,5 Tri Methyl Benzene	C_9H_{12}		?
1-methyl naphthalene	$C_{11}H_{10}$		No

Several models available, more refinements, substantial validation.
Several models available, more validations emerging.
Fewer validation data, or models especially for aromatics.
Are weakly branched alkanes needed as components?

Emulating *Fully Prevaporized* Combustion of a Specific Jet Fuel

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- 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 vapor diffusive transport properties → Average Molecular Weight (MW_{avg})
- Autoignition/global kinetics → Derived Cetane Number (DCN) Correlative for macro ignition measure

- Each combustion property target for the real fuel and surrogate mixture can be determined *experimentally*.
- *Selected surrogate components **DO NOT** necessarily need to include a representative molecular species for each of the molecular classes found in the real fuel of interest.*
- *Instead, the surrogate component mixture must reasonably replicate the interaction and composition of the **distinct chemical functionality in the mixture** that are manifested in the real fuel!*

Surrogate Mixture Formulation and Evaluation

1. ***Characterize the specific real fuel:***

- Determine MW_{avg} *(Literature correlation methods=> more direct method needed).*
- Determine empirical formula for C_nH_m using CHN analysis data (ASTM D5291) & MW_{avg}.
- Determine DCN of fuel using Ignition Quality Testing (ASTM D6890).
- Determine TSI from smoke point measurement (ASTM D1322) and MW_{avg}.

All above tests require, only small sample volumes, short analytical times, and no detailed species characterization of the sample, not even quantitative species/class identification.

2. ***Characterize chosen surrogate components and their mixtures:***

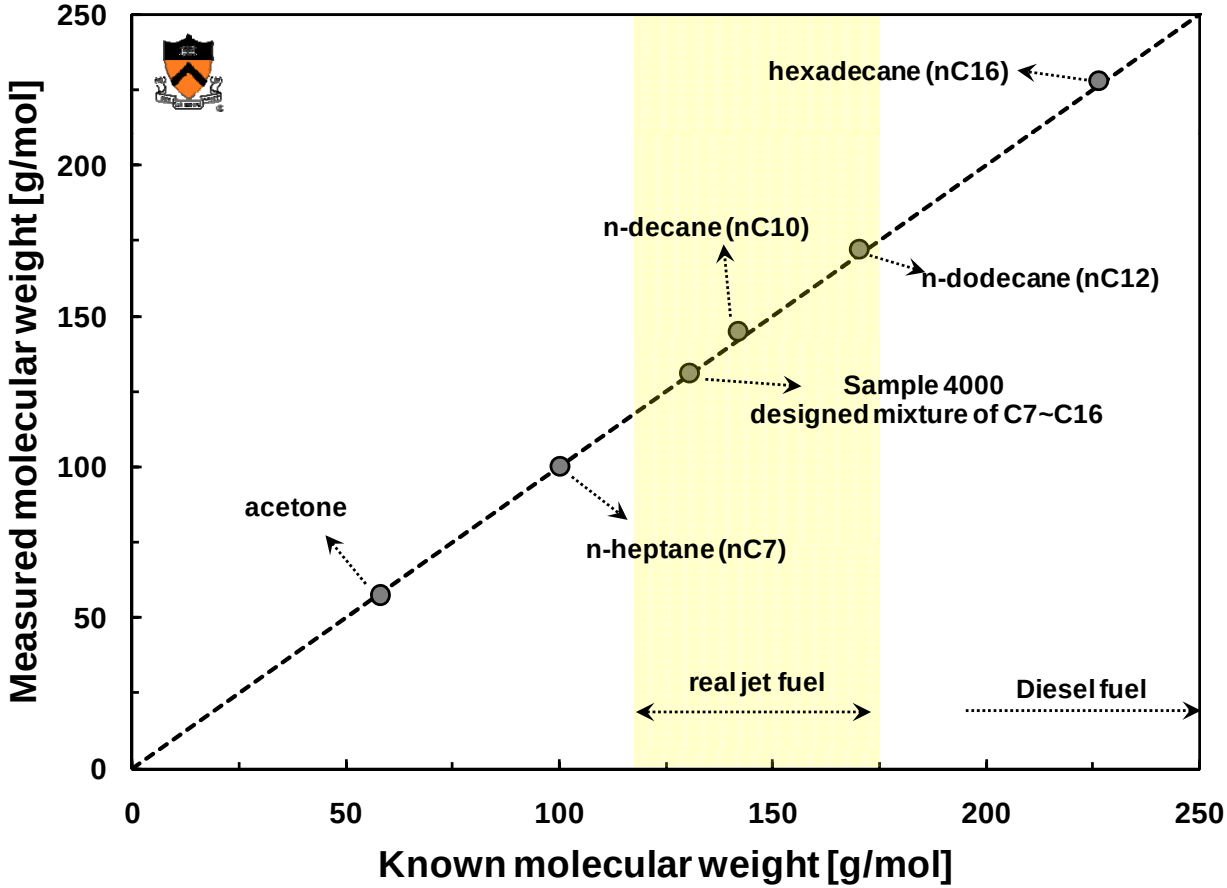
- Develop experimental self-consistent library of TSI values for surrogate components and mixtures.
- Develop experimental self-consistent DCN database for surrogate component mixtures composed of a base n-alkane to which other components that are added yield 30 <DCN<65 (ASTM D6890).

3. ***Emulate the H/C, DCN, TSI, and average molecular weight of specific fuel by choice of surrogate components and their mixture fractions.***

4. ***Compare gas phase experimental observations for specific fuel and the apriori formulated surrogate mixture:***

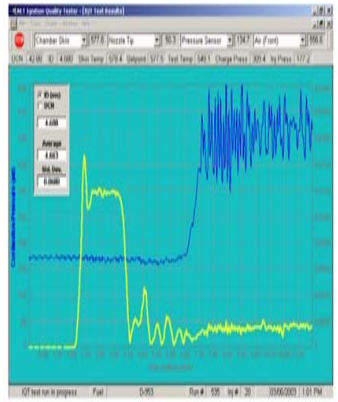
Mw_{Ave} Method Feasibility Demonstration

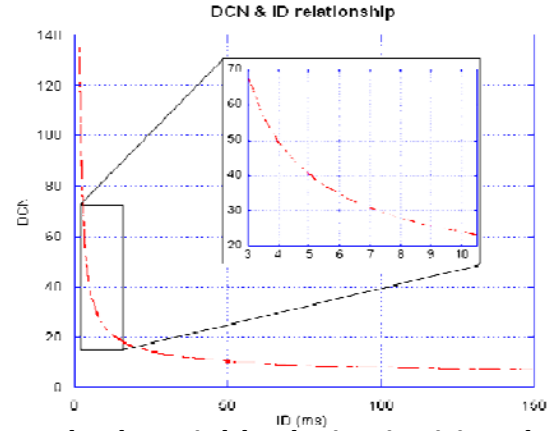
- New Experimental Method. *(Provisional Patent Disclosure filed Feb. 2012)*.
  - *Not available for our prior published work.*
- Requires less than 50 ml sample and takes about 30 minutes.
- Applicable to real gas turbine fuel, surrogate components, and mixtures.
- *Determines MW_{ave} of the sample to generally less than ±1 unit.*



Dooley, Won and Dryer, Princeton University, 2012

Ignition Quality Testing and Ignition Delay Correlations





Single Characterization:

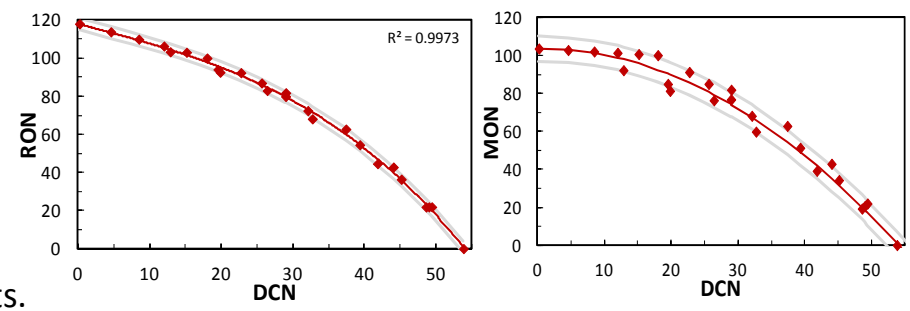
- Total fuel sample ~50 ml
- 15 "warm-up" & 32 recorded injection/ignition events per test ~ 15 minutes
- Ignition delays derived using ASTM D-6890 method are reported as **DCN**'s by correlating data with that of Cetane reference fuels.

Procedure for Jet Surrogate Blends Tests:

- Choose base n-alkane (n-decane, dodecane).
- Define statistical experiments for blending components.
- Obtain **DCN** data for all blend options that produce 30>**DCN**>70.
- Develop regression correlation to predict **DCN** as function of component composition.
- Check regression predictions against new data.

It's just a rapid standardized method to yield relative ignition delays!

Another Example : RON and MON for gasolines



RON-DCN and MON-DCN correlations based on IQT *experimental data for TRF reference gasoline mixture data.* Gray bands are ±3.5 and ±6.5 units from best fit polynomials.

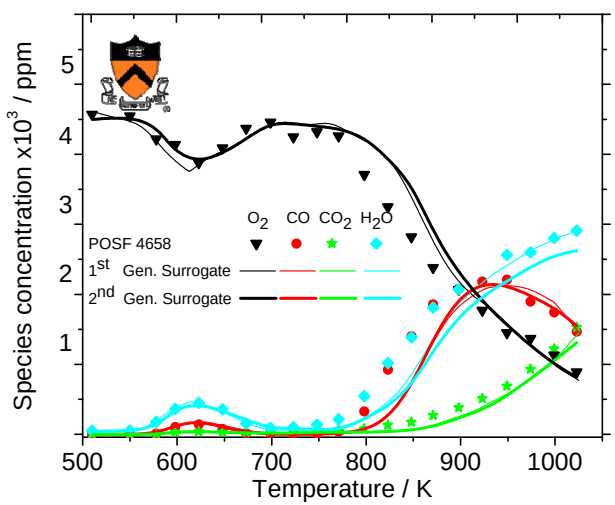
Haas et al. (2012) WIP, 34th Int Symp on Combust, Warsaw Poland, July 30-Aug 3.

A function developed from DCN measurements for 124 separate 2nd generation surrogate mixtures relates the mixtures and the measured DCN's within ± 0.98 DCN. A Matlab based tool will be available on our website in late 2012.

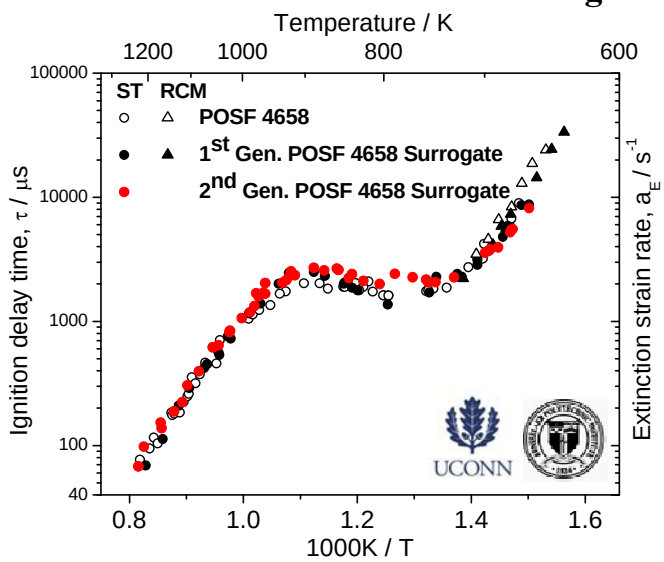
MURI Surrogate Concepts Compared with a Real Jet A Fuel

	Mole Fraction				DCN	H/C	MW / g mol^{-1}	TSI
Target Real Fuel	Jet Aviation Fuel, POSF 4658				47.1	1.95	142.1	21.4
1st Generation Surrogate Fuel	*n*-decane	*iso*-octane	toluene		47.1	2.01	120.7	14.1
	0.423	0.33	0.24					
2nd Generation Surrogate Fuel	*n*-dodecane	*iso*-octane	135TMB	nPB	48.5	1.95	138.7	20.4
	0.40	0.29	0.07	0.23				

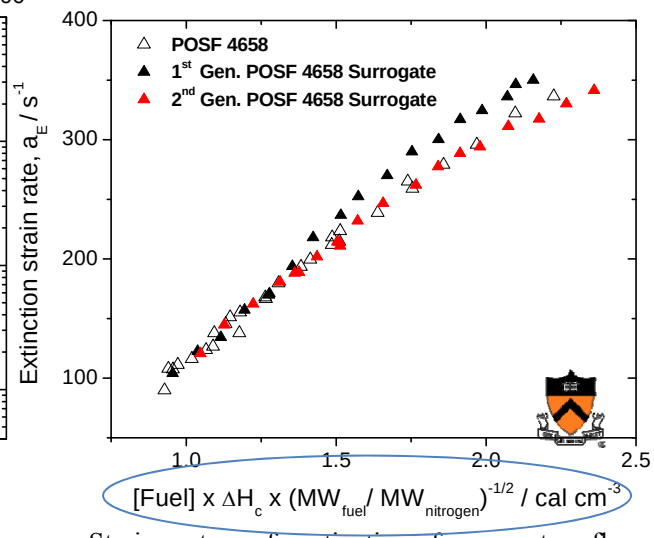
Variable Pressure Flow Reactor, Reflected Shock (ST) and Rapid Compression Machine (RCM) Ignition, Strained Diffusive Extinction Comparisons of 1st and 2nd Gen POSF 4658 Surrogate Mixtures with Real Jet A POSF 4658



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 and 2nd generation POSF 4658 surrogate.



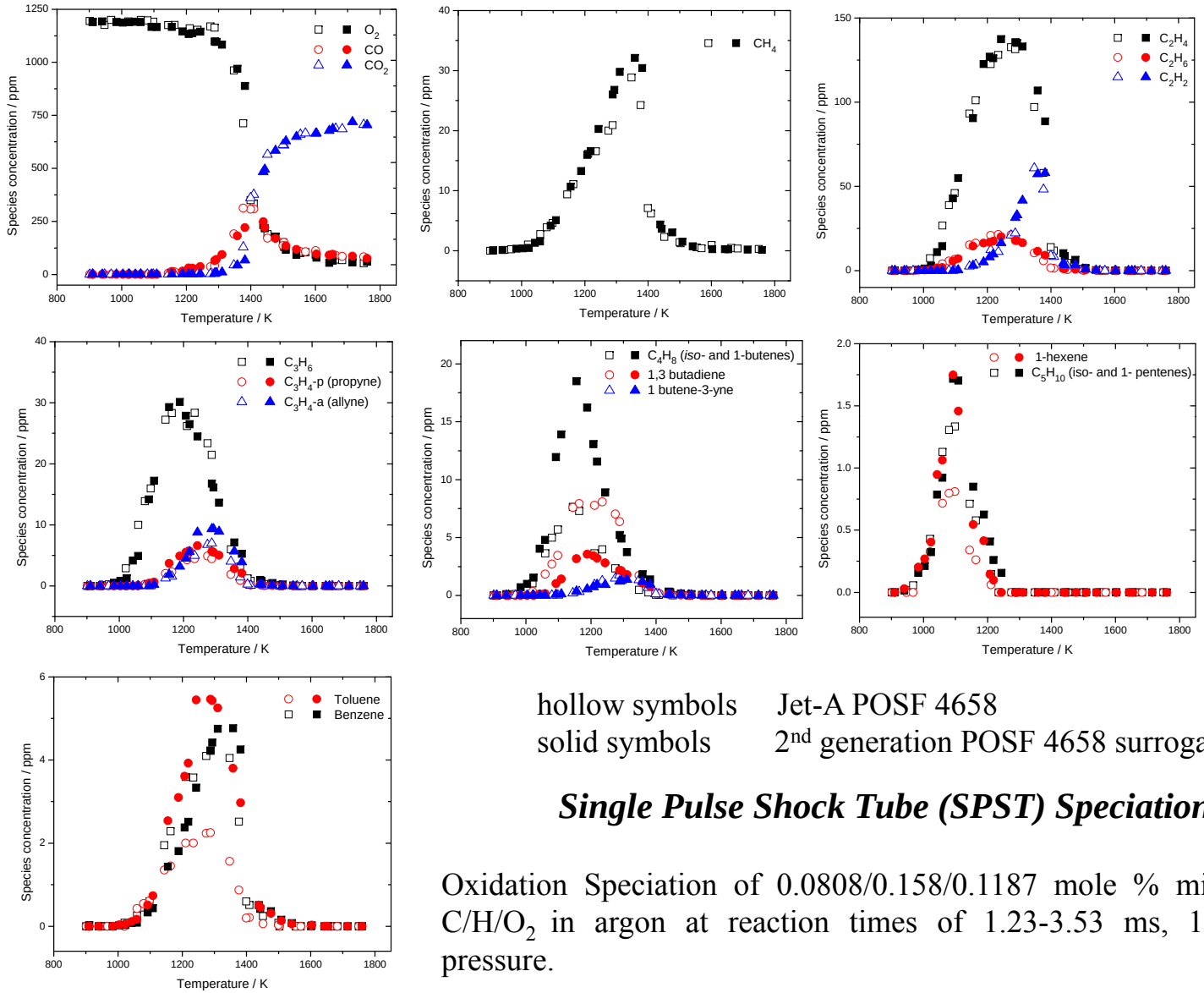
Ignition delay times, φ= 1.0 in air at ~20 atm for POSF 4658, 1st generation POSF 4658 surrogate and 2nd generation POSF 4658.



Strain rates of extinction for counter flow diffusion flames at 1 atm, for 1st and 2nd generation POSF 4658 surrogate fuels v. 4658 surrogate fuels v. Transport Weighted Enthalpy (*TWE) for each fuel.

Dooley et al. *Combust Flame* 159:1444 1466 (2012)
*Won et al. *Combust Flame,*159:541-551(2012)

MURI Surrogate Concepts Compared with a Real Jet A Fuel



hollow symbols Jet-A POSF 4658
solid symbols 2nd generation POSF 4658 surrogate

Single Pulse Shock Tube (SPST) 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, 18-29 atm pressure.

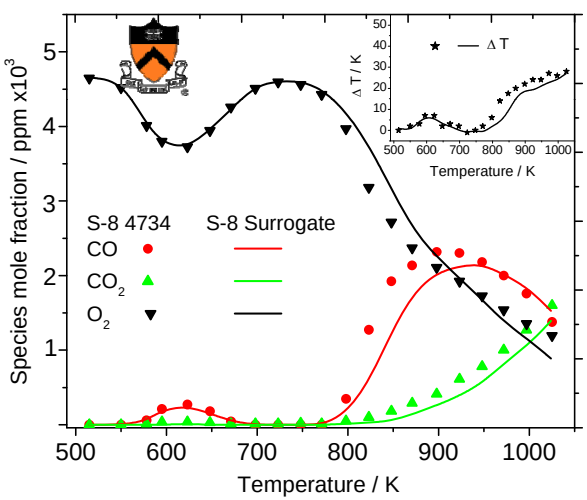
Dooley et al. *Combust Flame 159:1444 1466 (2012)*

S-8 POSF 4734 vs S-8 Surrogate

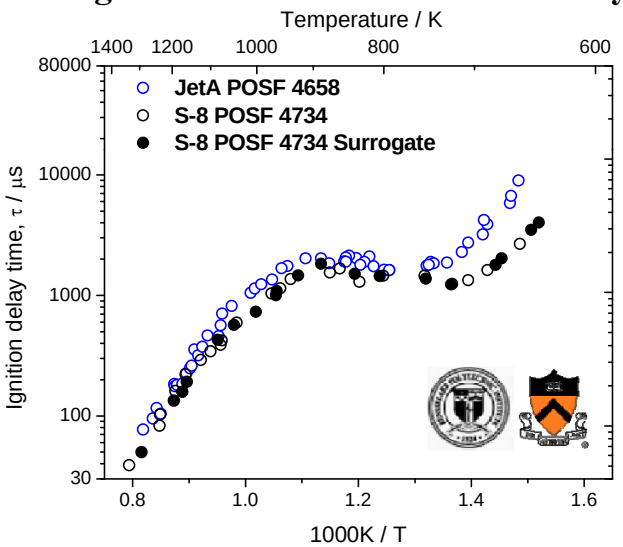
12% n-, 61% mono-methyl; 25% di-methyl, 2% cyclo-alkane synthetic fuel from natural gas

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**			
0.519	0.481	58.7	2.19	143.4

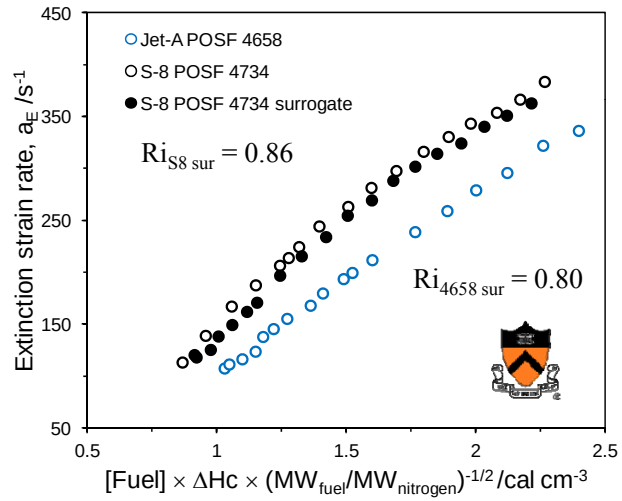
Variable Pressure Flow Reactor, Reflected Shock (ST) Ignition, Strained Diffusive Extinction Comparisons of POSF 4734 Surrogate Mixtures with POSF 4734 Synthetic S-8



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 (Iines), 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.



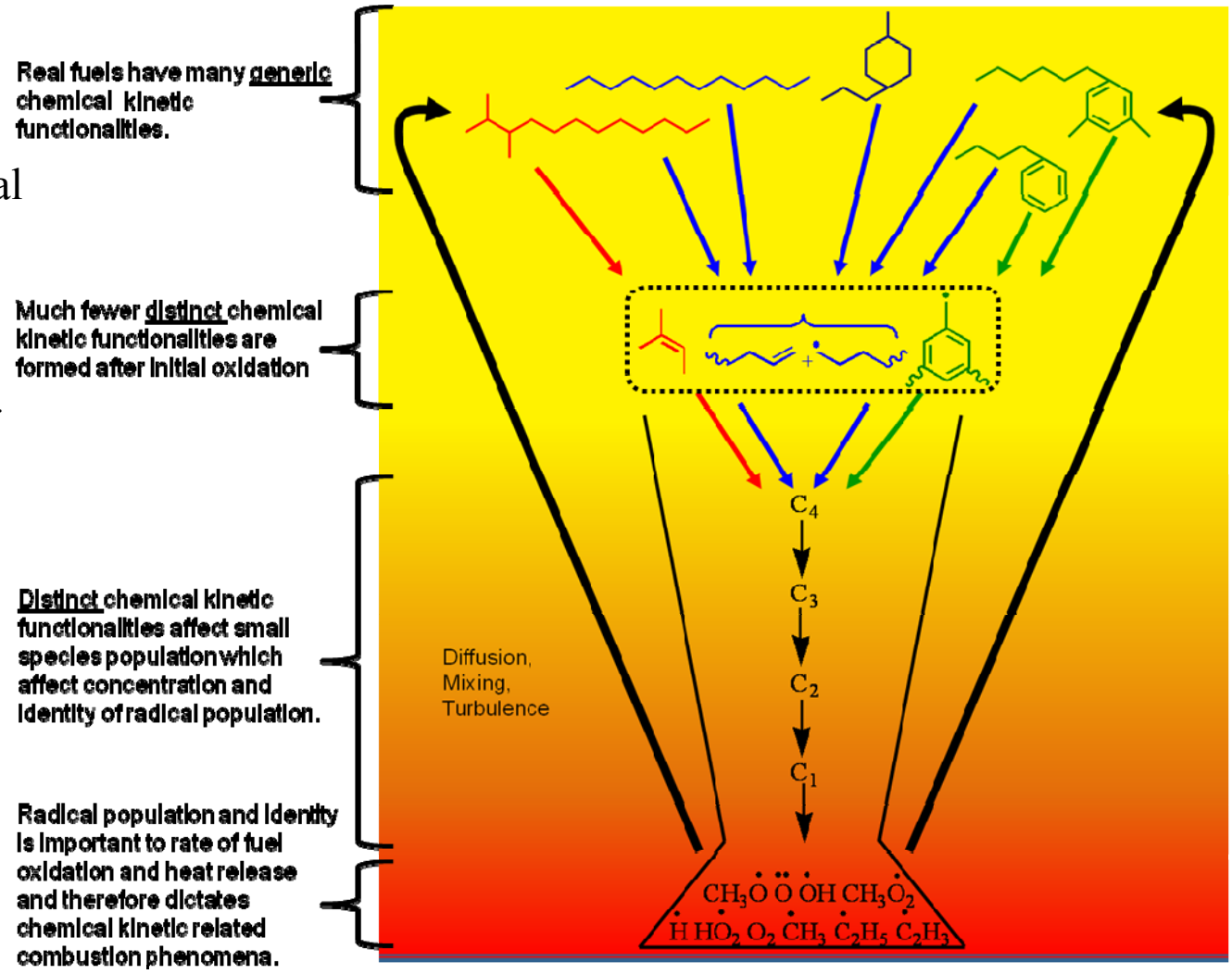
Strain rates of extinction v TWE for counter flow diffusion flames at 1 atm, Jet-A POSF 4658, S-8 POSF-4734 and S-8 POSF 4734 Surrogate.

- Weakly branched alkane behavior can be approximated well without actually using weakly branched surrogate components.

Dooley et al. (2012) *50th AIAA Aerospace Sciences Meeting*, 2012. AIAA-2012-619-419
Dooley et al. *Combust Flame* (2012)159: 3014 3020

MURI Strategy to Emulating Real Fuel Prevaporized Combustion

- Molecular structure correlations can yield the distinct chemical functional information for a real fuel if chemical composition is known (or perhaps from NMR spectral analysis)….
- *But, experimental (fuel) combustion property targets used here apparently provide sufficient constraints with much less effort!*
- *There is considerable flexibility in choosing appropriate surrogate components.*

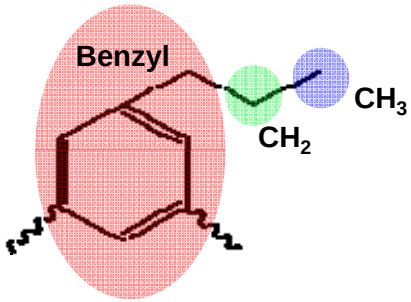


Initial fuel molecular structural issues might become more relevant at low and NTC oxidation conditions (ROOH and QOOH isomerization reactions).

Dooley et al.*Combust Flame* 159::444 1466 (2012)
Dooley et al. *Combust Flame* 159:3014 3020 (2012)

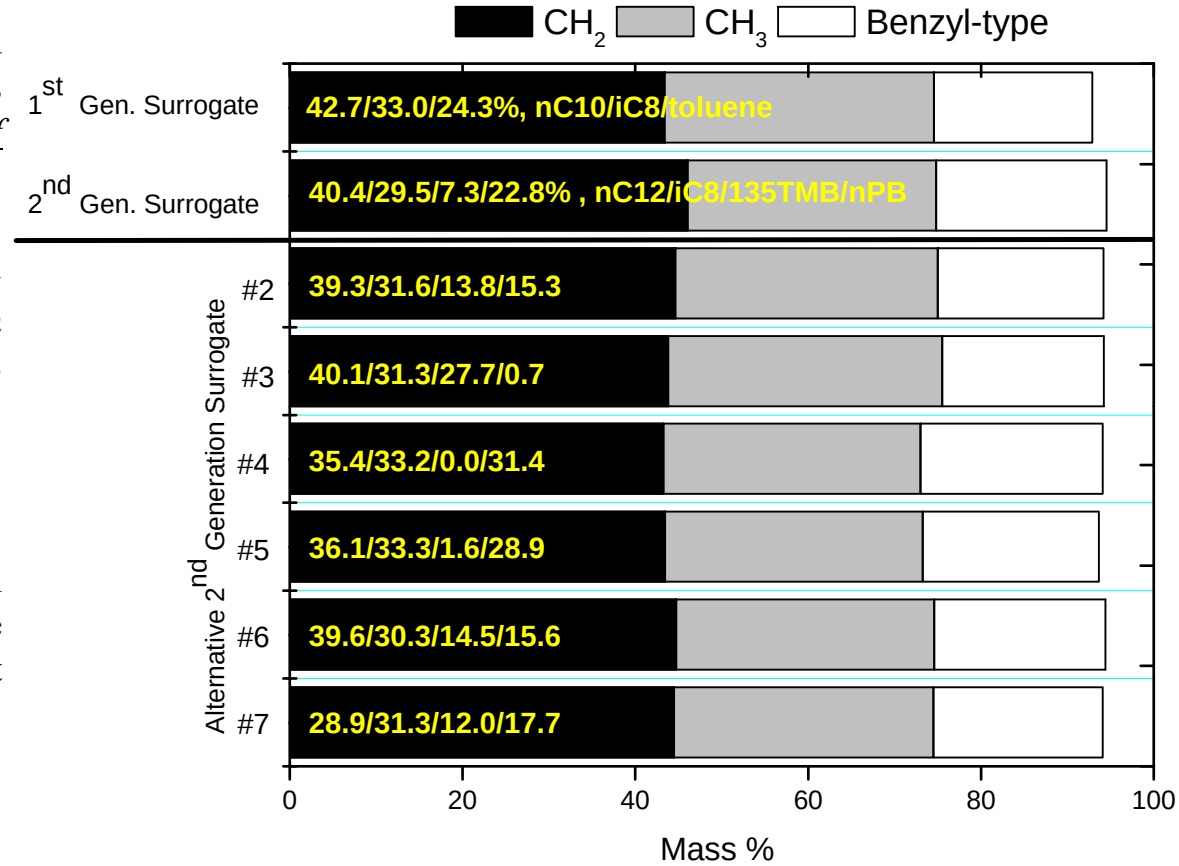
MURI Strategy to Emulating Real Fuel Prevaporized Combustion

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



one Benzyl
+ *one* CH_2
+ *one* CH_3

- Each Molecular structure may contain several of the same groups and thus the molecules themselves do not represent linearly independent parameters.



Molecular group mass comparisons for 1st Gen (n-decane/iso-octane/toluene 42.7/33.0/24.3 mole %), 2nd gen (n-dodecane/iso-octane/1,3,5 trimethylbenzene/n-propylbenzene 40.41/29.48/7.28/22.83 mole %) and six ~equally possible *alternative* 2nd gen POSF 4658 surrogate fuel mixtures.

Surrogate mixture compositions with ~ equivalent property targets yield ~same functional group compositions with different surrogate components and even with different mixtures of the same components!

Dooley et al. *Combust Flame* 159, 1444 1466 (2012)

MURI Strategy to Emulating Real Fuel Prevaporized Combustion

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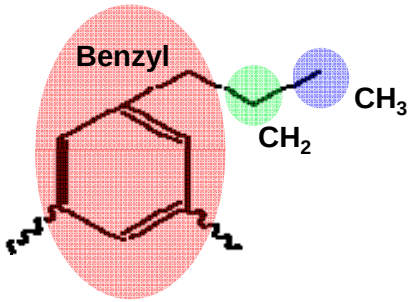

one Benzyl
+ *one* CH_2
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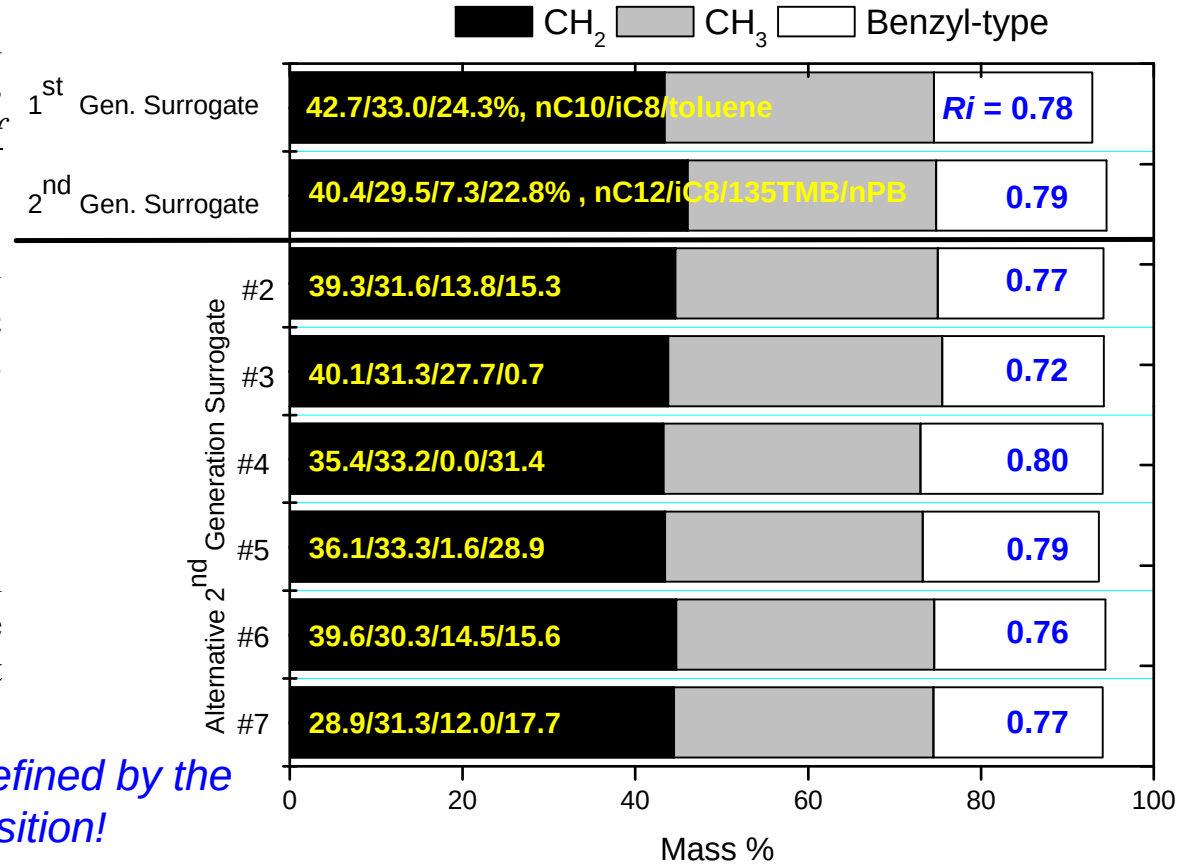

Radical index (Ri) = is also defined by the 2nd generation mixture composition!

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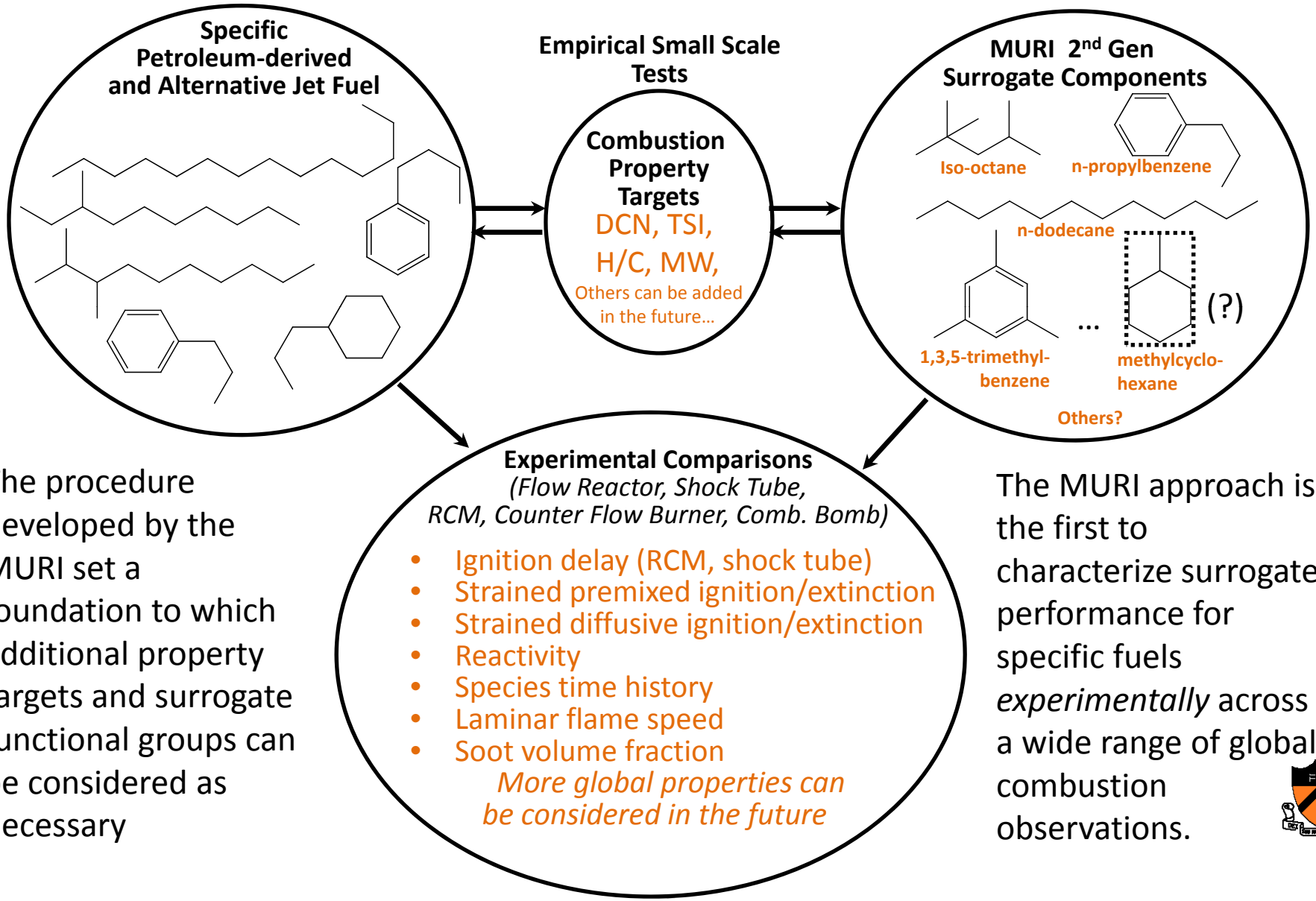
Dooley et al.*Combust Flame* 159,:444 1466 (2012)

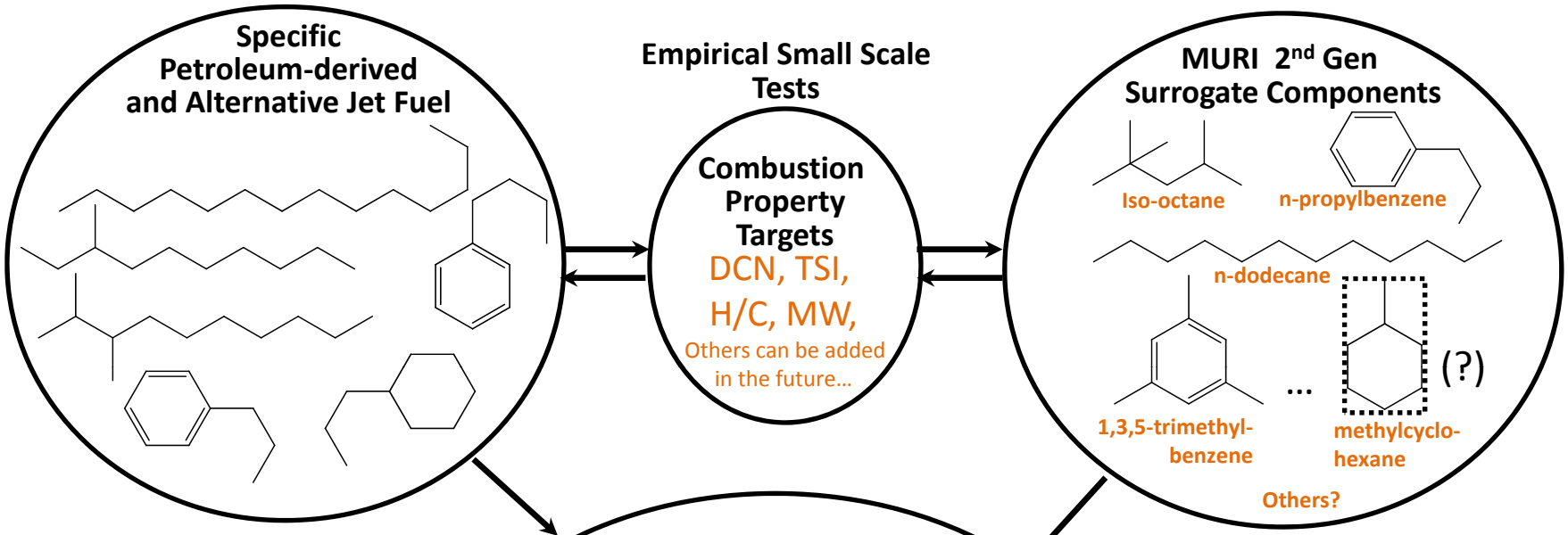
Proofing Surrogate Mixture Emulation of Fully Prevaporized Global Combustion Behaviors of a Real Fuel



The procedure developed by the MURI set a foundation to which additional property targets and surrogate functional groups can be considered as necessary

The MURI approach is the first to characterize surrogate performance for specific fuels *experimentally* across a wide range of global combustion observations.

Proofing Surrogate Mixture Emulation of Fully Prevaporized Global Combustion Behaviors of a Real Fuel



If two fuels have the same property targets, they will have the same fully prevaporized global combustion properties =>*Solvent Surrogate Mixtures!*

Experimental Comparisons
(Flow Reactor, Shock Tube, RCM, Counter Flow Burner, Comb. Bomb)

- Ignition delay (RCM, shock tube)
- Strained premixed ignition/extinction
- Strained diffusive ignition/extinction
- Reactivity
- Species time history
- Laminar flame speed
- Soot volume fraction

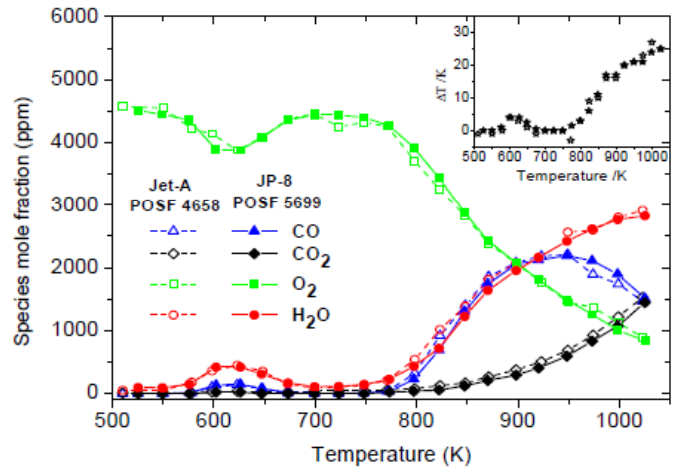
More global properties can be considered in the future to further proof the technique

Two fuels with the same property targets => *Kinetic/transport Models based on 2nd Gen pure component surrogate mixture should apply for emulating both fuels.*

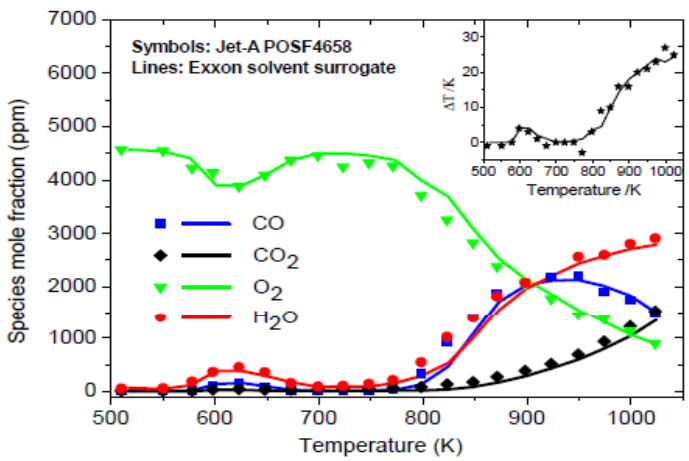
Surrogate Mixtures of Solvent Cuts for a Real Jet A & JP-8

Fuel				DCN Predicted	DCN Measured	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658				-	47.1 ± 0.3	1.95	142 ±20	21.4*
2nd Generation POSF 4658 Surrogate (mole %)				47.1	48.6 ± 0.4	1.96	138.7	20.4*
n-dodecane	iso-octane	1,3,5 trimethyl benzene	n-propyl benzene					
40.4	29.5	7.3	22.8					
*Jet-A POSF 4658 Solvent Cut Surrogate Mixture (mole %)				47.4	47.3	2.03	162.1	21.4
Nor-Par 12	Iso-Par L	Aromatic150						
42.78	40.62	16.6						
JP-8 POSF 5699*					49.3	1.94	153 (est.)	22.3
**JP-8 POSF 5699 Solvent Cut Surrogate Mixture (mole%)					49.4	1.93	165.6 (est.)	20.8
EXXSOL D95	IPK UN1223	Aromatic100						
70.51	13.13	16.36						

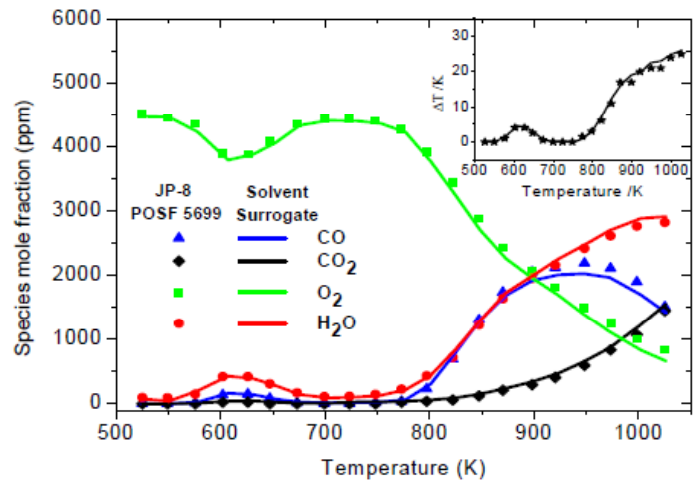
*Jahangirian et al (2011) Fall Eastern States Section of the Combustion Institute, UCONN, Storrs, CT Oct. 9-12.
**Iyer et al (2011), Fall Eastern States Section of the Combustion Institute, UCONN, Storrs, CT Oct. 9-12.



JET A POSF4658 vs. JP-8 POSF 5699



JET A POSF 4658 vs. POSF 4658 Exxon Nor Par Solvent Cut Surrogate Mixture

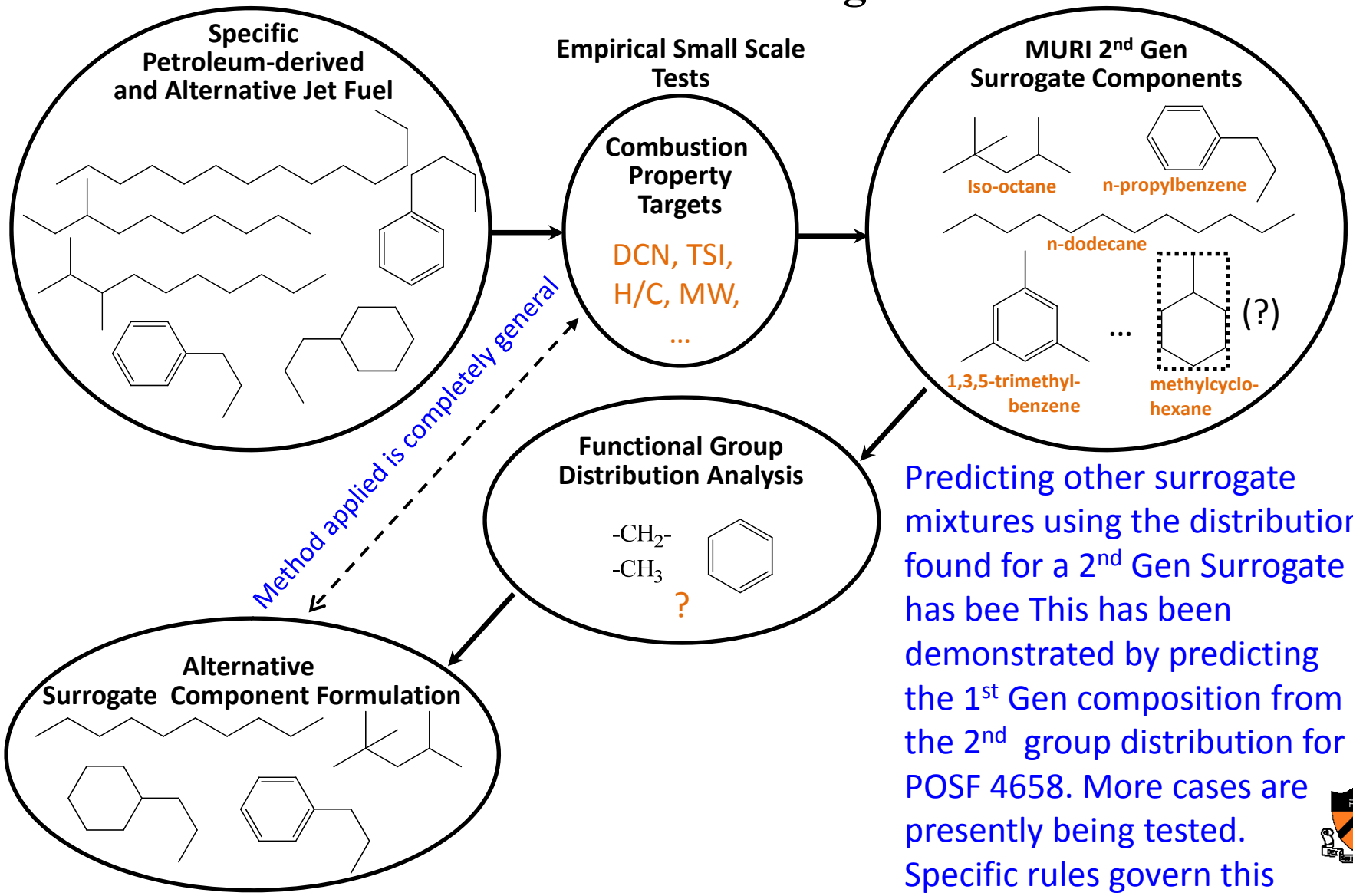


JP-8 POSF5699 vs. POSF 5699 Solvent Cut Surrogate Mixture (D-95/A100/IPK)

(VPFR) Reactivity and Heat Release Data Comparisons: 12.5 atm pressure, 1.8 s residence time, 0.3 % (molar) carbon, φ .=1 .

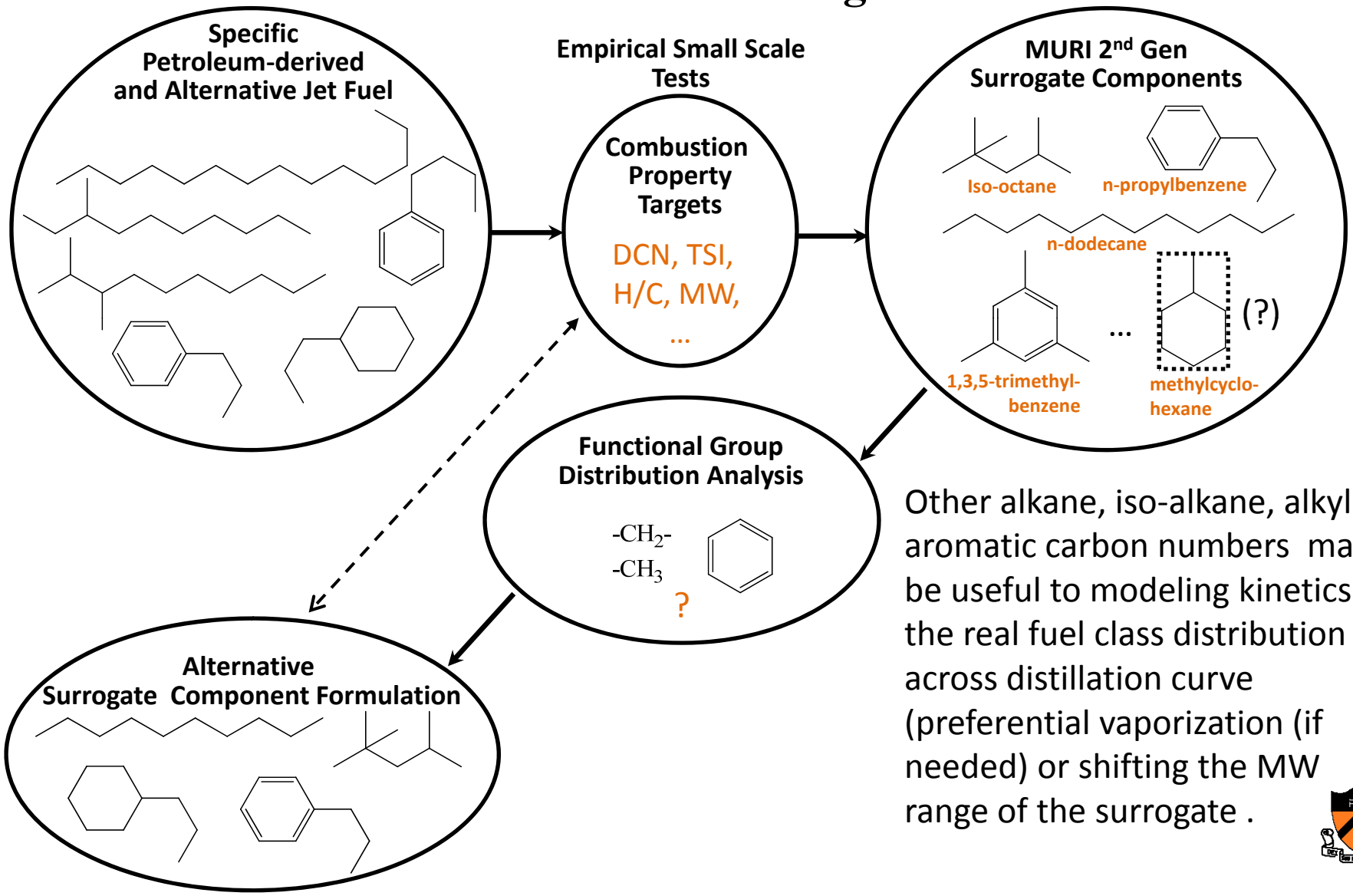
Jahangirian et al. *Eastern States Section of the Combustion Institute* , Storrs, CT Oct. 9-12, 2012
Jahangirian et al. (2012), *Fuel,* to be Submitted
Iyer et al *50th AIAA Aerospace Sciences Meeting*, 2012. *AIAA-2012-621-917*

Deriving Other Surrogate Component Mixtures from the MURI 2nd Generation Surrogate Mixture



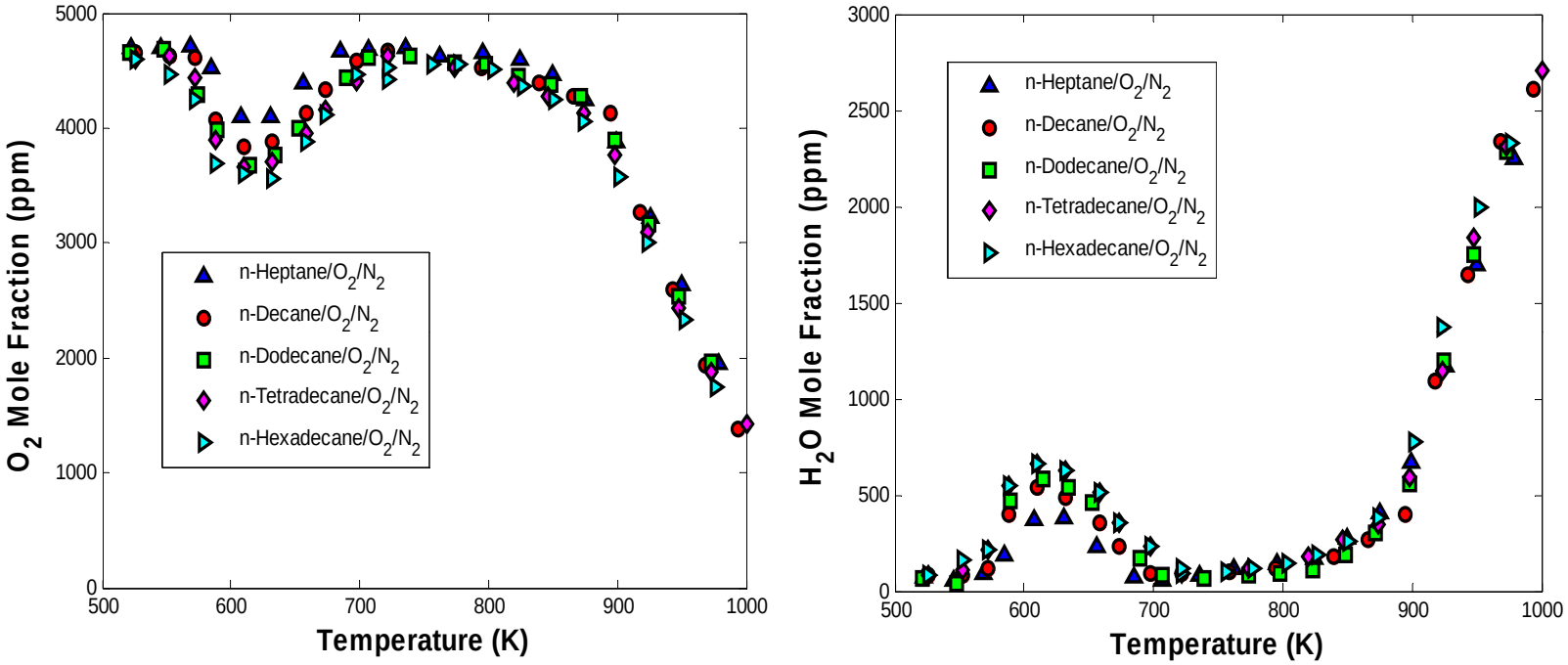
Predicting other surrogate mixtures using the distribution found for a 2nd Gen Surrogate has bee This has been demonstrated by predicting the 1st Gen composition from the 2nd group distribution for POSF 4658. More cases are presently being tested. Specific rules govern this method

Deriving Other Surrogate Component Mixtures from the MURI 2nd Generation Surrogate Mixture



Other alkane, iso-alkane, alkyl aromatic carbon numbers may be useful to modeling kinetics of the real fuel class distribution across distillation curve (preferential vaporization (if needed) or shifting the MW range of the surrogate .

Reactivity Comparison of $C_7 - C_{16}$ *n*-Alkanes

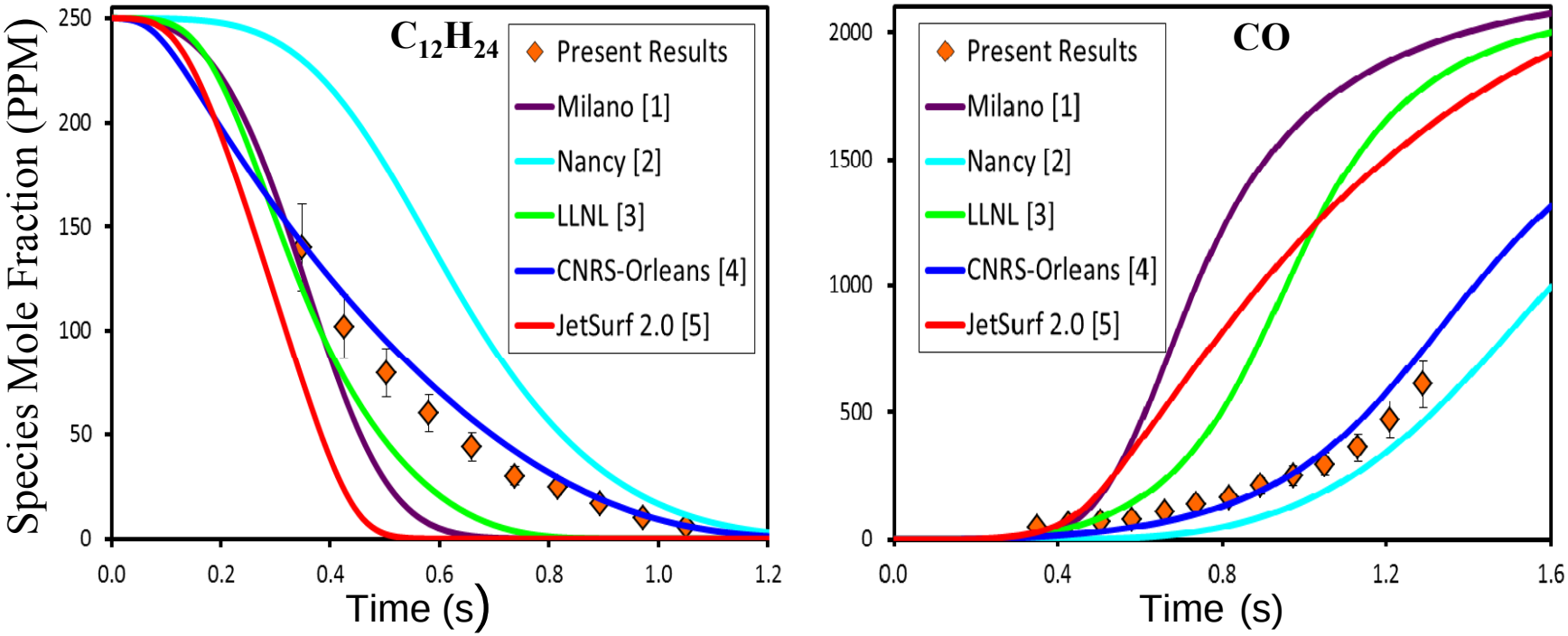


VPFR Reactivity of n-Alkanes: ϕ =1.0, P=8 atm, t=1.0 s, 0.3 % Carbon (molar) Content

- Few Data elsewhere comparing this wide of carbon numbers at a single condition.
- Activity in low temperature region scales with DCN (56=>100), even for phi=1.
- Activity differences result in more heat release in first stage as carbon number increases.
- Reactivity above hot ignition is essentially the same for all of the alkane carbon numbers.

Veloo and Dryer, WIP Poster, 34th Int Symp on Combustion (2012)

Model Comparisons with VPFR *n*-Dodecane Oxidation Data



VPFR n-Dodecane oxidation: f=1.0, P=8 atm, T_i=881 K, 0.3 % Carbon (molar), no time shift

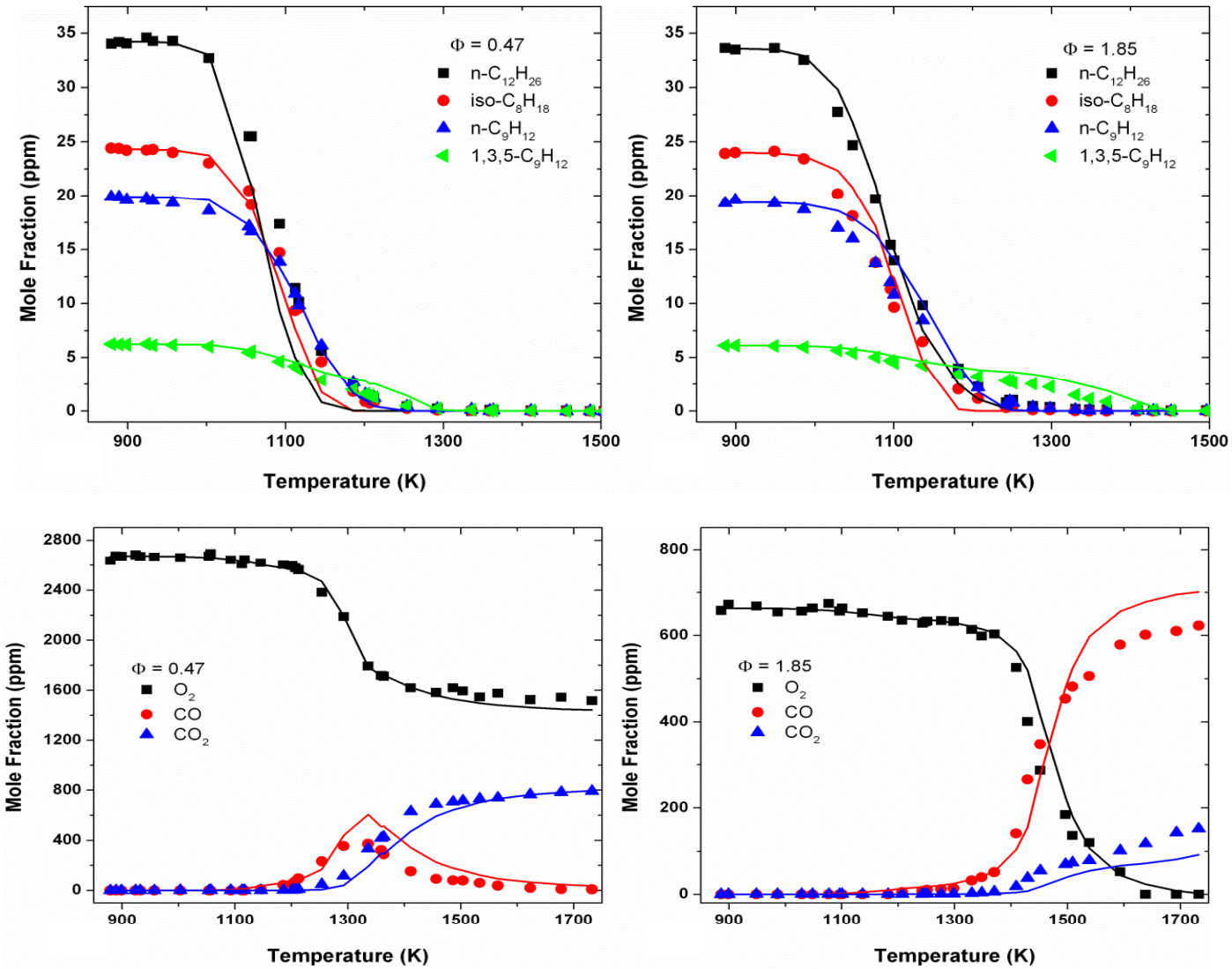
- All of the models except Mze-Ahmed are too fast.
- No time shifting can improve comparisons.
- $R+O_2$ => olefins + HO_2 remains important even at~900 K. (absent from Jet Surf 2.0).
- Detailed comparisons similar to those presented for n-decane oxidation are available.

1. Ranzi et al. Ind. Eng. Chem. Res. 44 (2005) 5170-5183.
2. Biet et al. Energy Fuels 22 (4) (2008) 2258–2269.
3. Sarathy et al. Combust. Flame 158 (2011) 2338–2357.
4. Mzé-Ahmed et al Energy Fuels, 10.1021/ef300588j.
5. Wang, et al. JetSurF version 2.0, <ttp://melchior.usc.edu/JetSurF/JetSurF2.0>

Detailed High Pressure Experimental and Modeling of Aromatics, Jet A, and Alkanes (UIC)

- S. Klotz, K. Brezinsky, I. Glassman, "Modeling, the Combustion of Toluene-Butane Blends", *Proc. Combust Ins* (1998) 27:337-344. *Base Model for Toluene. AFOSR No. 91-0431.*
- R. Sivaramakrishnan, R.S. Tranter 1, K. Brezinsky, "High-pressure, High-temperature Oxidation of Toluene", *Combust Flame* 139 (2004) 340–350. *Base model for higher alkyl aromatics. DOE/BES DE-FG0298ER14897.*
- S. Gudiyella, T. Malewicki, A. Comandini, K. Brezinsky, "High Pressure Study of m-Xylene Oxidation", *Combust Flame* 158 (2011) 687–704. *Base model for higher alkyl aromatics. SERDP, PN WP1575.*
- S. Gudiyella, K. Brezinsky, "High Pressure Study of n-Propylbenzene Oxidation", *Combust Flame* 159 (2012) 940–958.
- S. Gudiyella, K. Brezinsky, High Pressure Study of 1,3,5-Trimethylbenzene Oxidation", *Combust Flame* (2012). http://dx.doi.org/10.1016/j.combustflame.2012.06.014
- S. Gudiyella, K. Brezinsky. The High Pressure Study of n-Propylbenzene Pyrolysis, *Proc. Combust.Inst.* (2012) 34. http://dx.doi.org/10.1016/j.proci.2012.05.007
- T. Malewicki, K. Brezinsky, "Experimental and Modeling Study on the Pyrolysis and Oxidation of n-Decane and n-Dodecane", *Proc Combust Ins* (2012) 34. http://dx.doi.org/10.1016/j.proci.2012.06.156.
- T. Malewicki, A. Comandini, K. Brezinsky, "Experimental and Modeling Study on the Pyrolysis and Oxidation of iso-Octane", *Proc Combust Ins* (2012) 34. http://dx.doi.org/10.1016/j.proci.2012.06.137
- T. Malewicki, S. Gudiyella, K. Brezinsky. Experimental and Modeling Study on the Oxidation of Jet A and the 2nd Generation Surrogate Fuel, *Combust Flame* (In review).

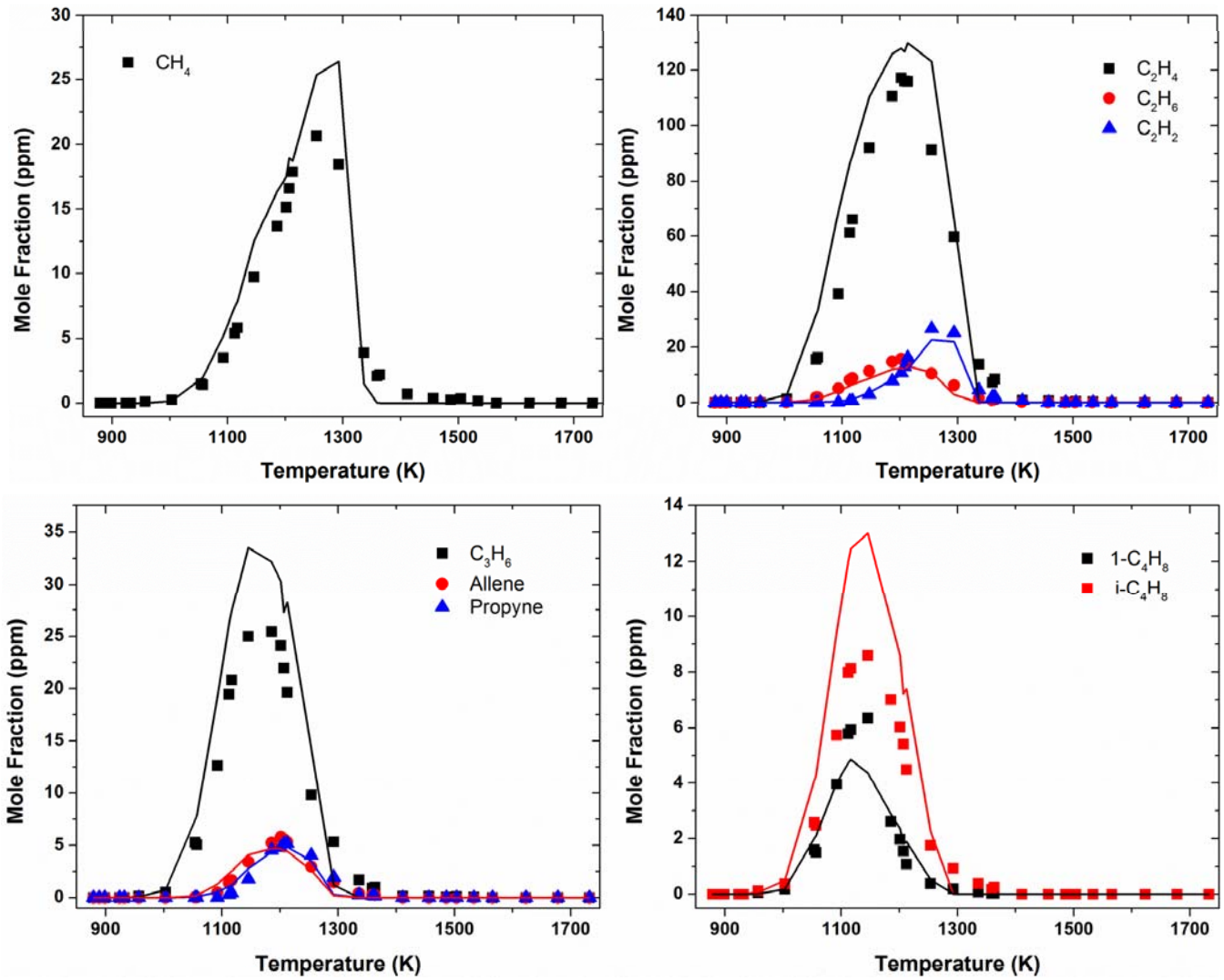
n-C_{12}/Iso-C_8/n-PB/135-TmB Surrogate Modeling (UIC)



Jet A POSF 4658 Surrogate Composition, P_{NOM} = 25 atm, t = 1.34-3.36 ms, Symbols - Data, Lines - Model

Malewicki, et al *Combust Flame* 2012, (In review).

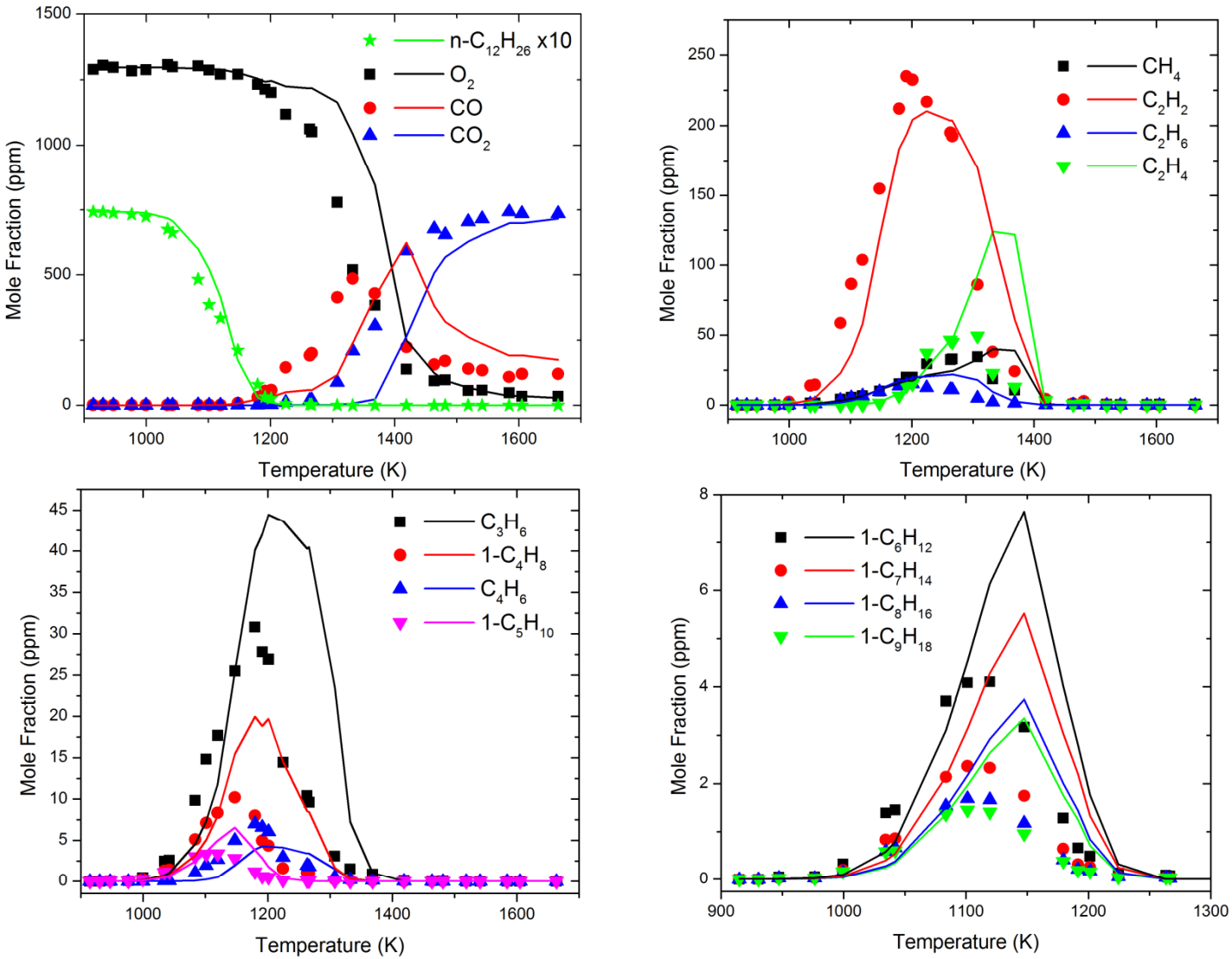
n-C_{12}/Iso-C_8/n-PB/135TmB Surrogate Modeling (UIC)



Jet A POSF 4658 Surrogate Composition, P_{NOM} = 25 atm, t = 1.34-3.53 ms, Φ = 0.47
Symbols - Data, Lines - Model

Malewicki, et al *Combust Flame* 2012, (In review).

n-Dodecane Shock Tube Speciation versus JetSurf 2.0

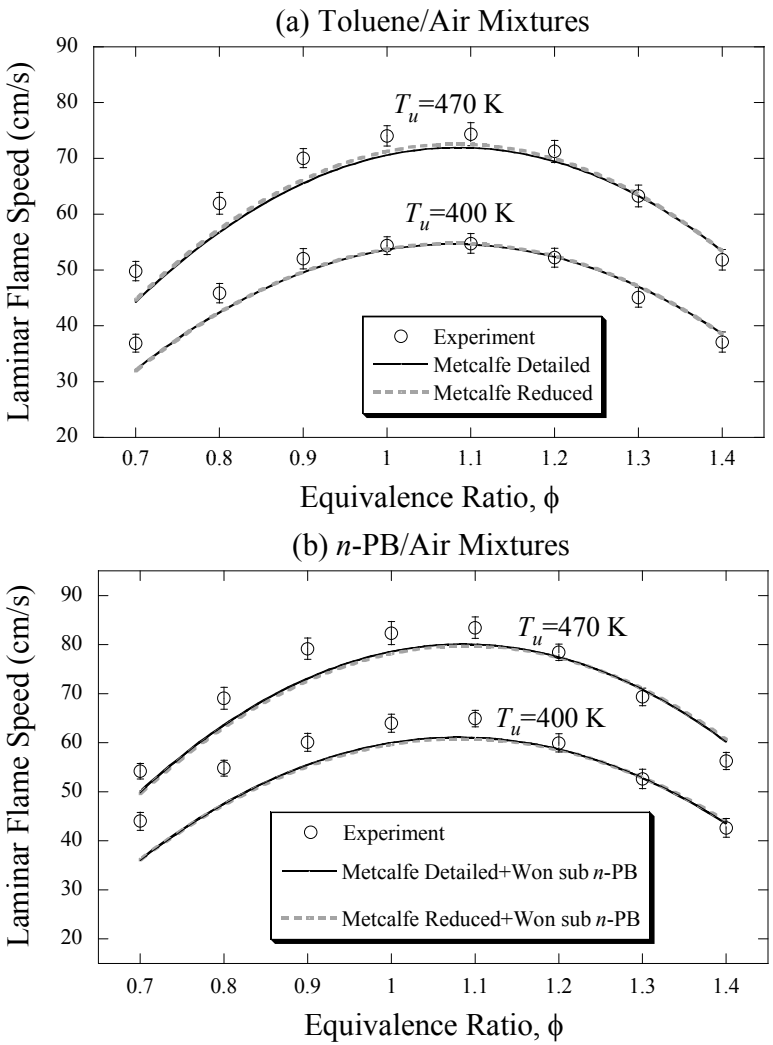


ϕ = 1.06, P = 42.8-58.0 atm, t = 1.15-2.29 ms, Symbols - Data, Lines - Model

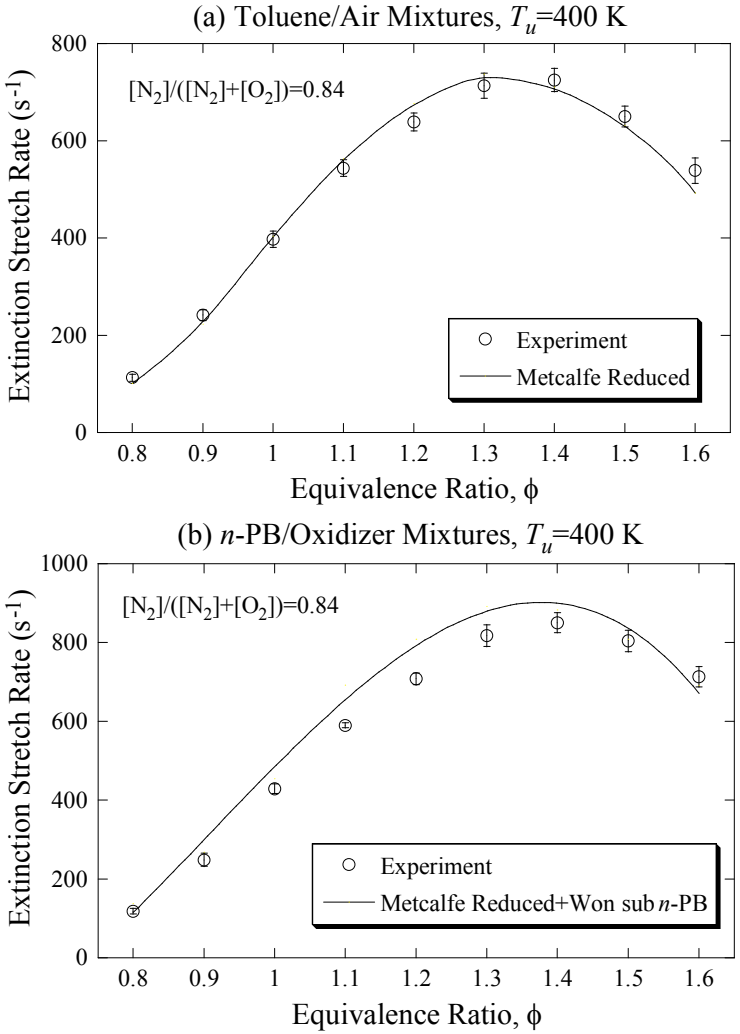
Efforts for Modeling Combustion Targets (PU)

- S. Dooley , S.H. Won , M. Chaos, J. Heyne, Y. Ju, F. L. Dryer, K. Kumar, C-J. Sung, H. Wang, M. A. Oehlschlaeger, R.J., Santoro, T. A. Litzinger. A Jet Fuel Surrogate Formulated by Real Fuel Properties, *Combust Flame* (2010) 157:2333-2339.
- S. Jahangirian, S. Dooley, F.M. Haas, F.L. Dryer. A Detailed Experimental and Kinetic Modeling Study of n-Decane Oxidation at Elevated Pressures, *Combust Flame* (2012) 159:30-43.
- S.H. Won, S. S. Dooley, F.L. Dryer, Y. Ju. Kinetic Effect of Molecular Structure on Extinction Limit of Aromatic Diffusion Flames, *Proc Combust Ins* 33, 1163–1170 (2011).
- S.H. Won, S. Dooley, F. L. Dryer, and Y. Ju, A Radical Index for the Determination of the Chemical Kinetic Contribution to Diffusion Flame Extinction of Large Hydrocarbon Fuels, *Combust Flame* (2011) 159:541-551.
- W. K. Metcalfe, S. Dooley, F. L. Dryer. "Comprehensive Detailed Chemical Kinetic Modeling Study of Toluene Oxidation", *Energy Fuels* (2011) 25:4915-4936.
- X. Hui, K. Kumar, C. J. Sung, S. Dooley, F. L. Dryer. Laminar Flame Speeds and Extinction Stretch Rates of Selected Aromatic Hydrocarbons, *Fuel* (2012) 97:695–702.
- 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, T.A. Litzinger, R.J. Santoro, T. Malewecki, K. Brezinsky. The Experimental Evaluation of a Methodology for Surrogate Fuel Formulation to Emulate Gas Phase Combustion Kinetic Phenomena, *Combust Flame* (2012) 159: 1444-4466.
- S. Dooley, S.H. Won, Y. Ju, F.L. Dryer, H. Wang, M. A. Oehlschlaeger. The Combustion Kinetics of a Synthetic Paraffinic Jet Aviation Fuel and a Fundamentally Formulated, Experimentally Validated Surrogate Fuel, *Combust Flame* (2012) 159: 3014-3020.
- S. Dooley, F.L. Dryer, T.I. Farouk, S.H. Won, "A Reduced Kinetic Model for the Combustion of Jet Propulsion Fuels", 51st AIAA Aerospace Sciences Meeting, Grapevine, Texas. 7-10 January 2013. Abstract Accepted.

Laminar Premixed Predictions for Toluene, n-PB



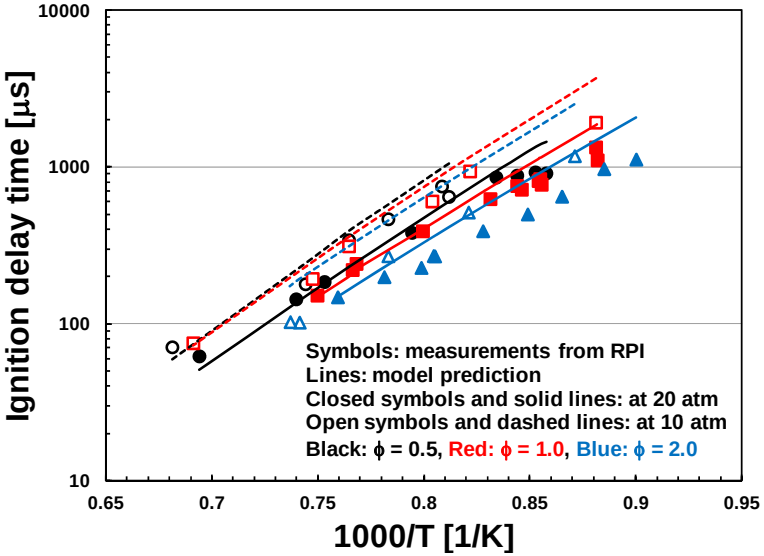
Comparison of experimental and computed laminar flame speeds for (a) toluene/air mixtures, and (b) *n*-PB/air mixtures.

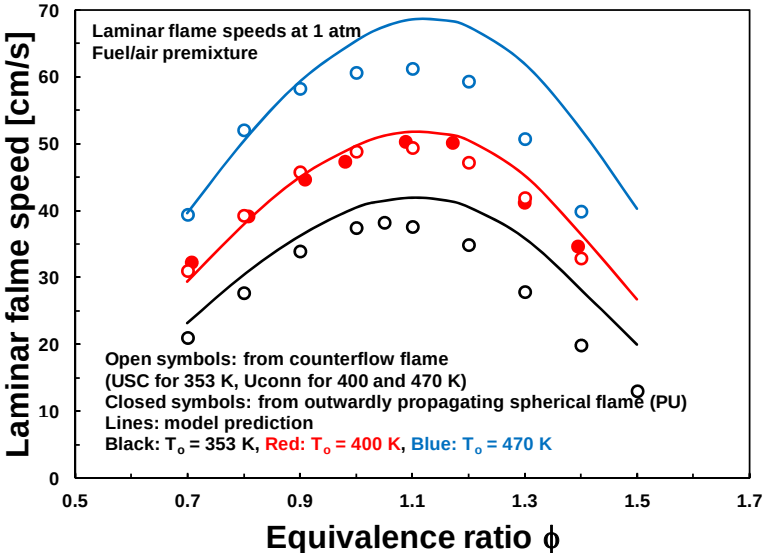


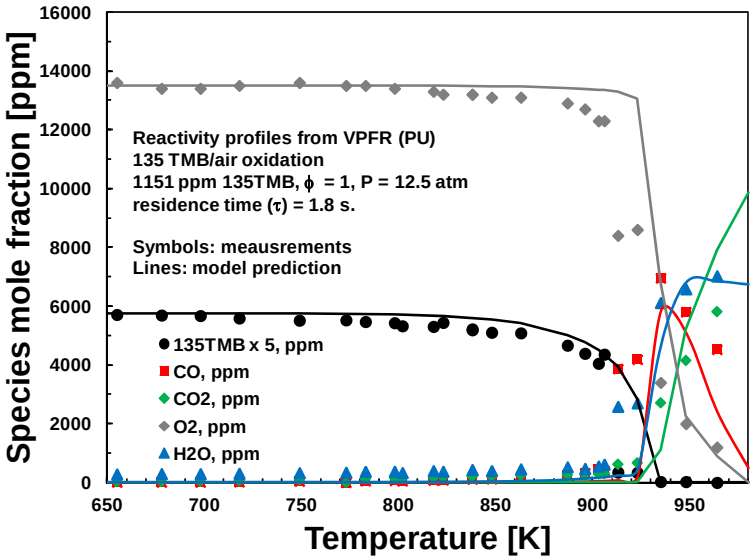
Comparison of experimental and computed extinction stretch rates for (a) toluene/oxidizer mixtures, and (b) *n*-PB/oxidizer mixtures.

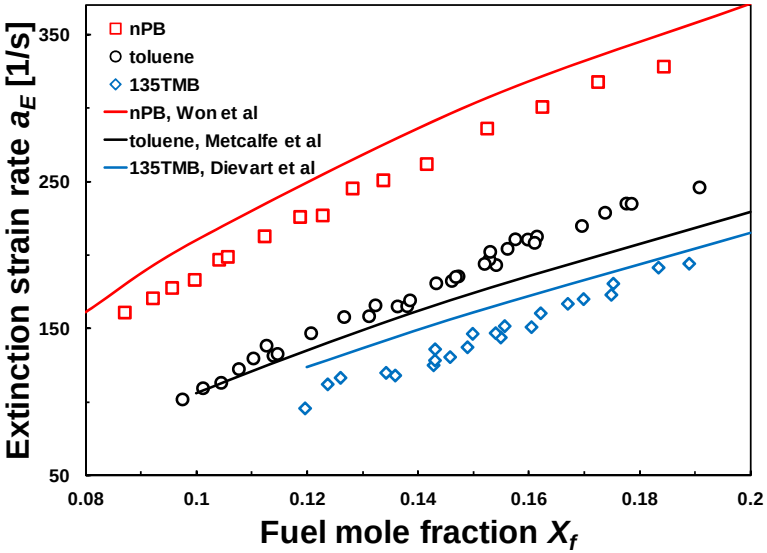
Hui et al., *Fuel* (2012) 97:695–702

Model Performance: 135-TmB

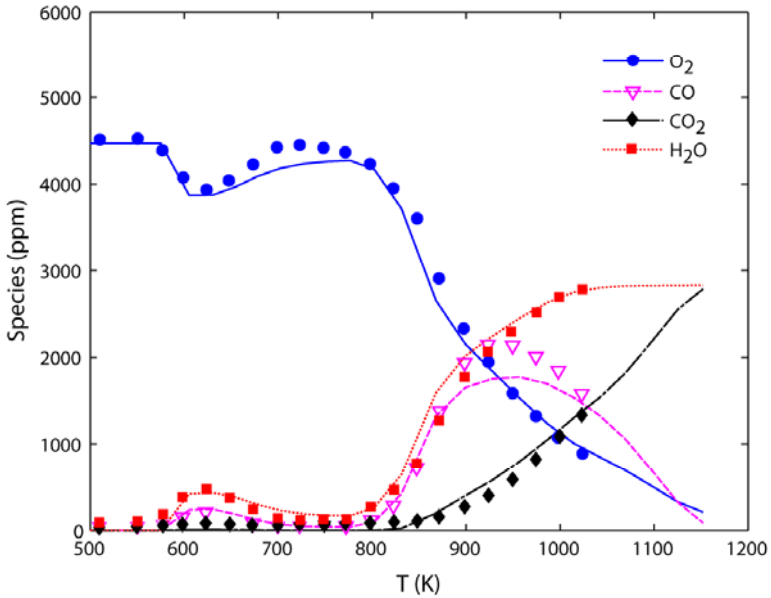




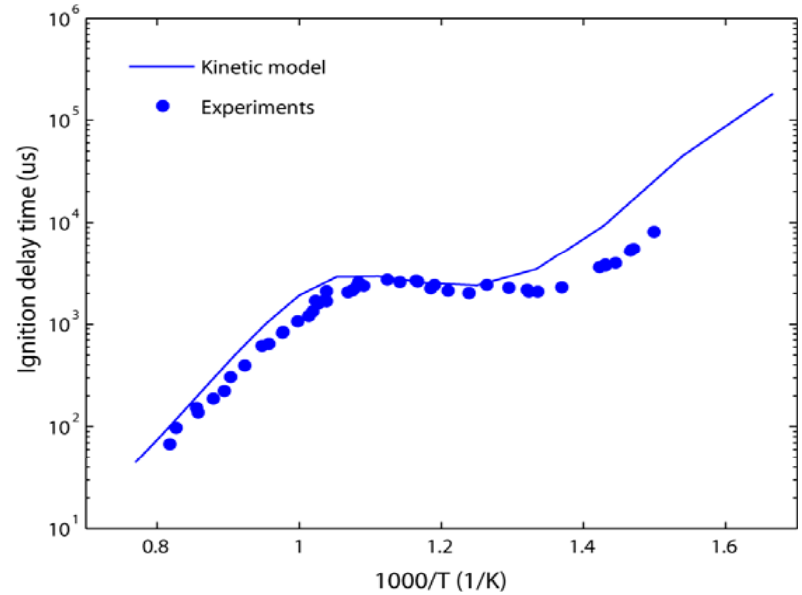




2nd Generation Surrogate Modeling (PU)

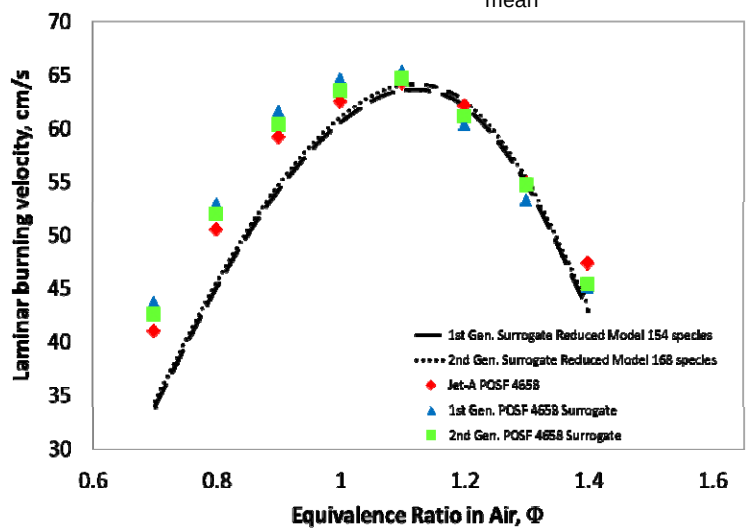


VPFR Flow reactor oxidation data for conditions of 12.5 atm, 0.3 mole % carbon, Φ= 1.0 at 1.8 s residence time.



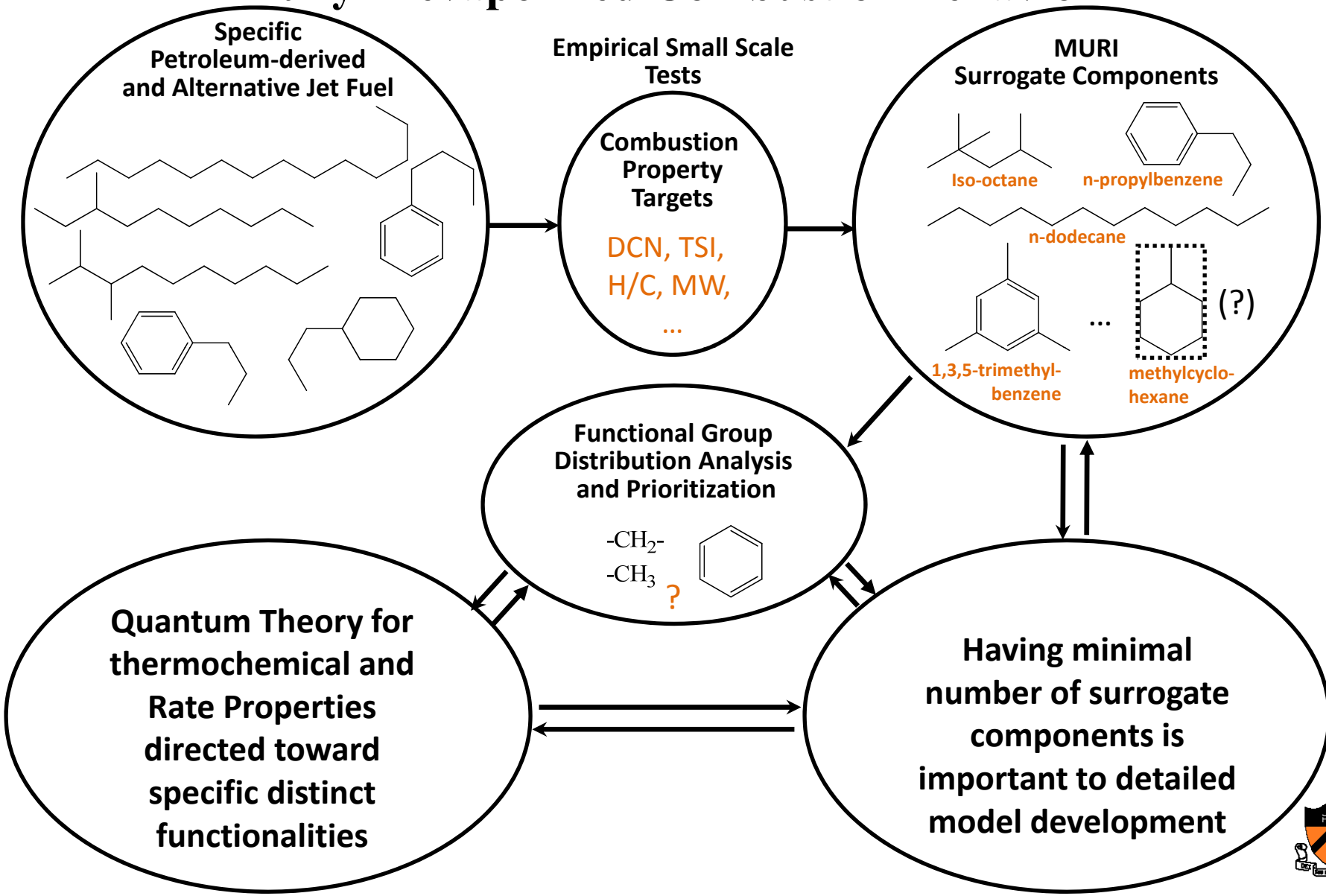
Ignition delay , Φ= 1.0, air, P= 17-22 atm. Simulations conducted at P_{mean}= 20 atm.

Jet A POSF 4658 2nd generation (n–C_{12}/iso-C_8/n-PB/135-TmB (40.41/29.48/7.28/22.83 mole %) surrogate mixture. Lines represent kinetic model and symbols represent experimental data. Refinements are continuing.

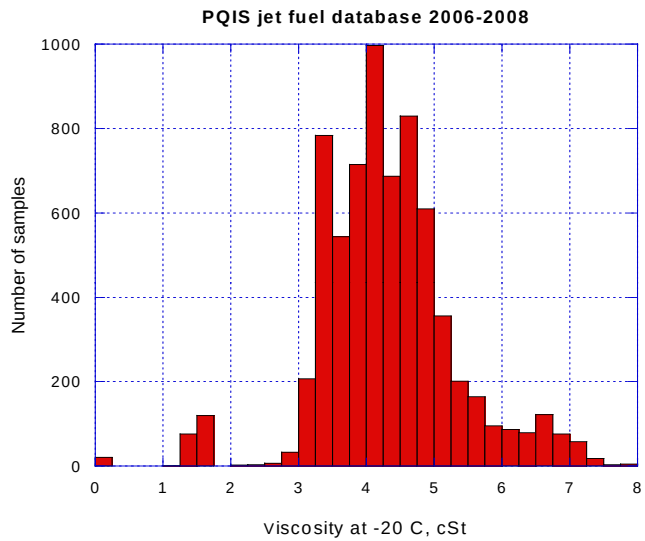


Laminar flame speed measurements at 1 atm pressure, 298 K

Surrogate Impacts on Model Development for Emulating Real Fuel Fully Prevaporized Combustion Behavior

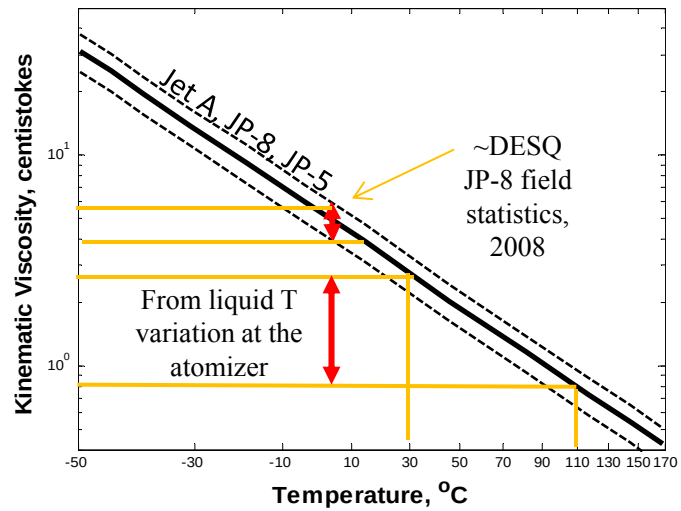


Viscosity Variations for Jet Fuels



http://www.desc.dla.mil/DCM/Files/2009PQISreport.pdf

Petroleum Quality Information System



from *Handbook of Aviation Fuel Properties—2004 Third Edition, CRC Report No. 635, CRC*, Inc., Alpharetta, GA 30022.

- Temperature dependence is essentially the same for all jet fuels (Jet A, JP-8, and JP5).
- Heat transfer coupling of combustion and atomizer region affects liquid temperature at the atomizer.
- Variation of liquid temperature can cause property variations larger than those found as field variations in reference viscosity.
  - Fuels are used as heat transfer fluids in strategic aircraft!

Summary

- Surrogate mixtures constructed by emulating combustion property targets of a specific real fuel is a viable, *foundational* emulation concept *for both petroleum-derived and non-petroleum derived (alternative) fuels*.
- The mix of distinct chemical functionalities present in fully prevaporized combustion of the real fuel is more relevant to mixture formulation than attempting to emulate detailed real fuel organic molecular structure distribution.
- *Including weakly branched alkanes as a discrete class in detailed kinetic surrogate models appears unnecessary at present. Other functional groups can be added as necessary (e.g. cycloalkyl…)*
- Testing surrogate fuel concepts by *experimental* comparisons of real fuel and surrogate candidate mixture results is *far superior* to comparing candidate surrogate mixture model predictions against real fuel data in testing concepts. (*Current models reasonably replicate global behaviors, but not necessarily details).*
- Significant challenges remain in refining kinetic *mechanistic* as well as *kinetic rate*, *thermochemical data*, and *transport data* in order to achieve improved emulation of even alkane oxidation => *speciated fuel destruction/oxidation data are essential for quantitative detailed kinetic model validation.*
- Minimizing the numbers and types of surrogate components is a *critical determinant* to achieving well-validated models that will be tractable for computational simulations.
- *Finally: Surrogate mixtures for a real fuel can be formulated from hydrocarbon solvent cuts (or distillation fractions there-from) that all have the same fully prevaporized combustion behaviors. Along with matching 2nd generation formulation, these mixtures can be utilized in fully prevaporized and multiphase experiments to evaluate the relative importance of physical and chemical kinetic fuel properties on real gas turbine combustion properties.*