The background features a large, faint watermark of the Rensselaer Polytechnic Institute seal. The seal is circular and contains a central shield with various symbols, including a cross and a gear. The text "RENSSELAER POLYTECHNIC INSTITUTE" is written around the perimeter of the seal, and the year "1824" is at the bottom.

The autoignition of jet fuels,  
surrogates, and components

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## Goal: *a priori* predictive kinetic modeling for real fuels

- Real fuels

- Jet fuels: traditional (Jet A, JP-x) and alternative (FT, other)
- Components and surrogates

- Predictive

- Experimental uncertainties: ~10-20% for ignition delay
- Modeling uncertainties: at present significantly larger than those for experiments; perhaps  $\times 2$  at high T and  $\times 10$  at low T for ignition delay for large HCs at elevated pressures
- Status: *a priori* kinetics schemes differ  $\times 1-10$  with experimental ignition delay
  - experiment - model = *function* (conditions, fuel)

## Kinetic targets, including ignition delay, provide...

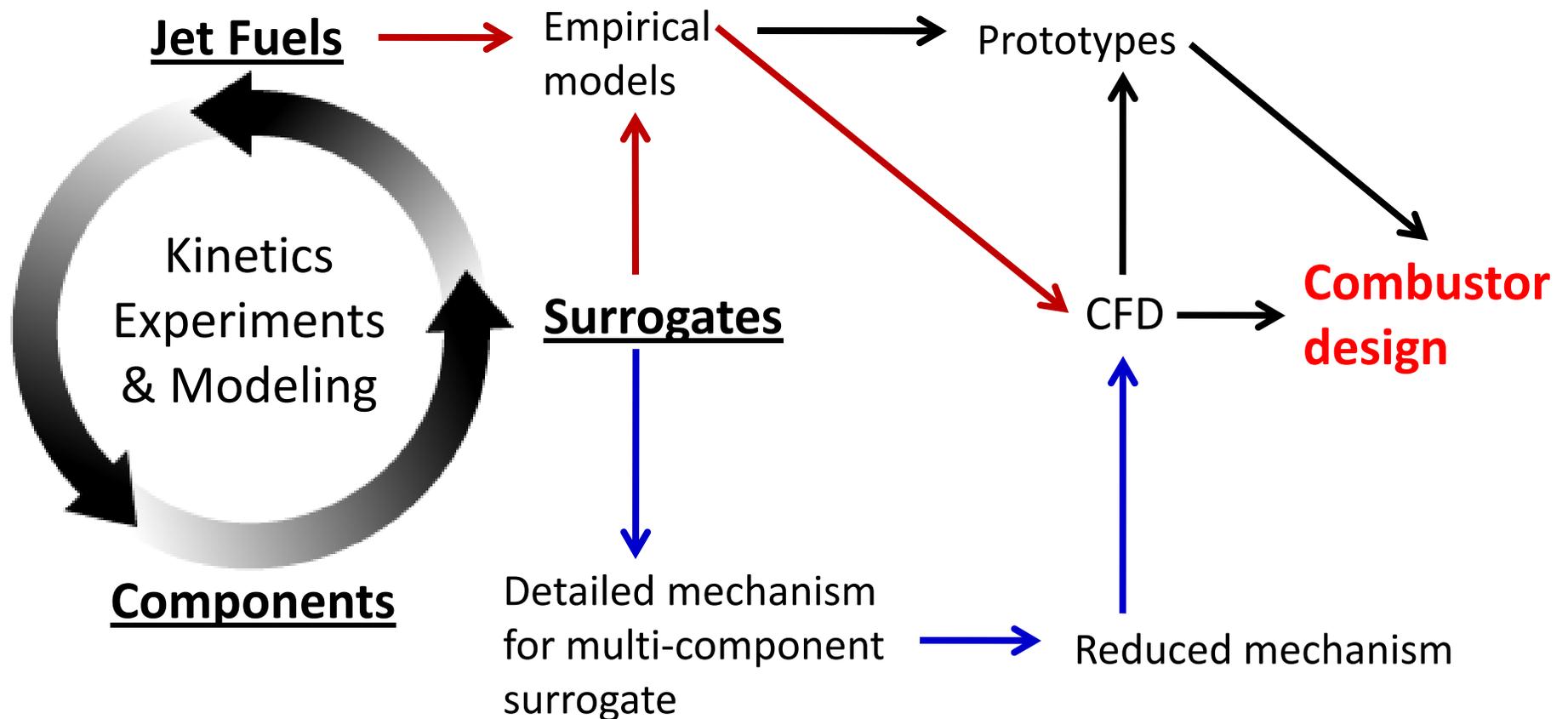
- Validation/assessment/development of detailed and reduced kinetic mechanisms
- Direct insight into fuel chemistry
  - Influence of molecular structure on reactivity
  - Influence of fuel variability
- Assessment of surrogates and surrogate formulation methodologies
- Data that can be used directly in combustor design via reduced-order models

## *Should* come from...

- Well-characterized experiments at *practical/useful* conditions where transport processes are well understood or of negligible importance
- e.g., **shock tubes**, rapid compression machines, flow reactors, flames, JSRs, etc.

Jet fuels are **compositionally complicated** (100s of distinct components) and **variable**

- Requires an integrated research focus on individual components, surrogate mixtures for specific jet fuels, and jet fuels



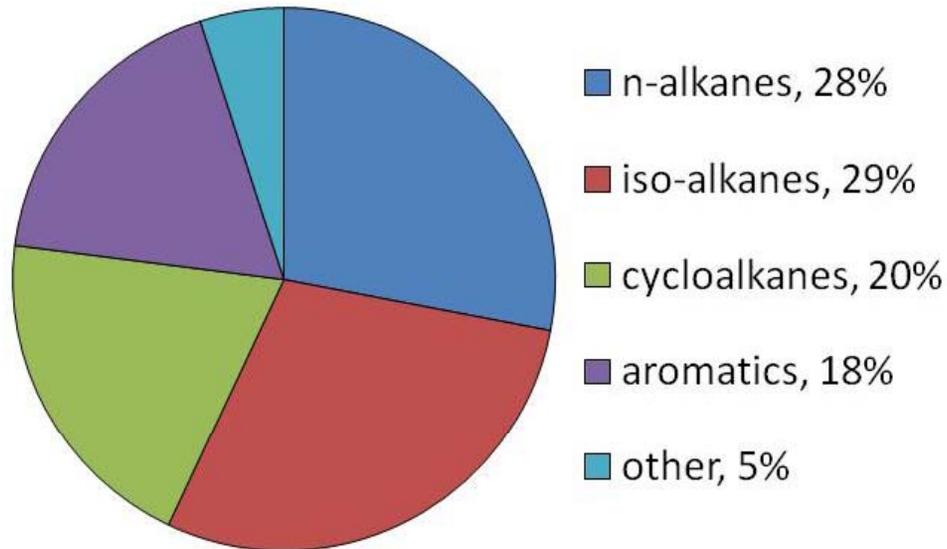
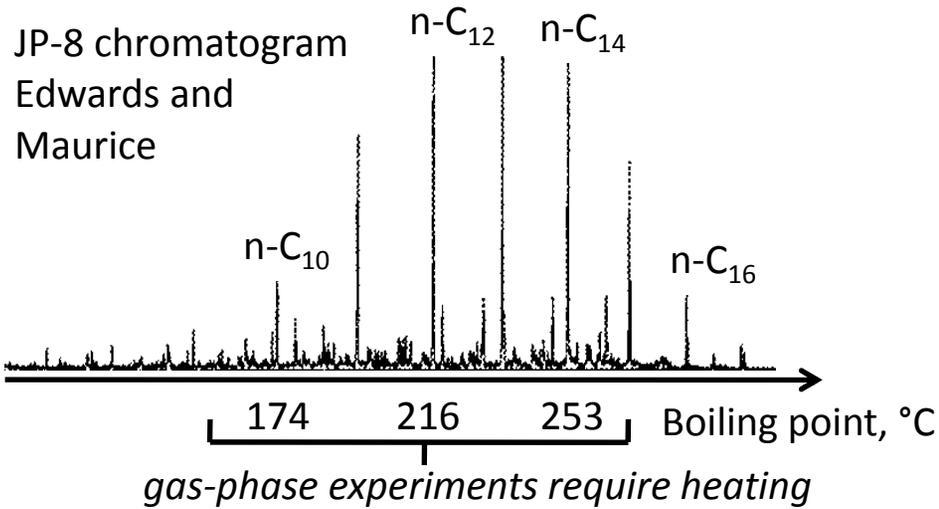
# RPI jet fuel studies

- **Shock tube ignition delay time** studies for:
  - Jet fuels: specific Jet A w/ and w/o JP-8 additive package
  - Surrogates: AFOSR-MURI, RPI, literature
  - Components: chosen due to relevance to Jet A (JP-8) and diversity of organic structure

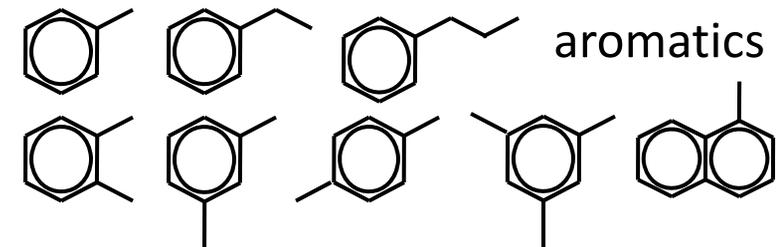
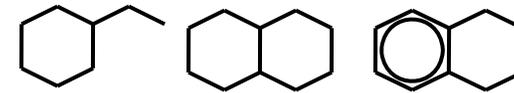
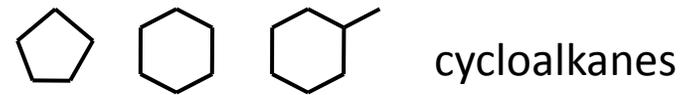
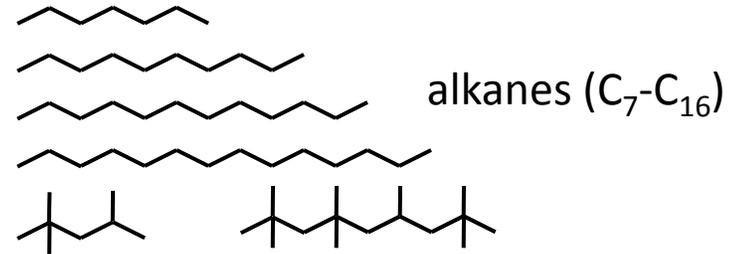
## Payoff

- Fundamental kinetics: support the development of detailed kinetic mechanisms, classify the reactivity of variety of organic structures
- Surrogate formulation: provide surrogate vs jet fuel comparisons/assessment and targets for the development of surrogate models
- Direct path for implementation of kinetics in design: reduced-order models

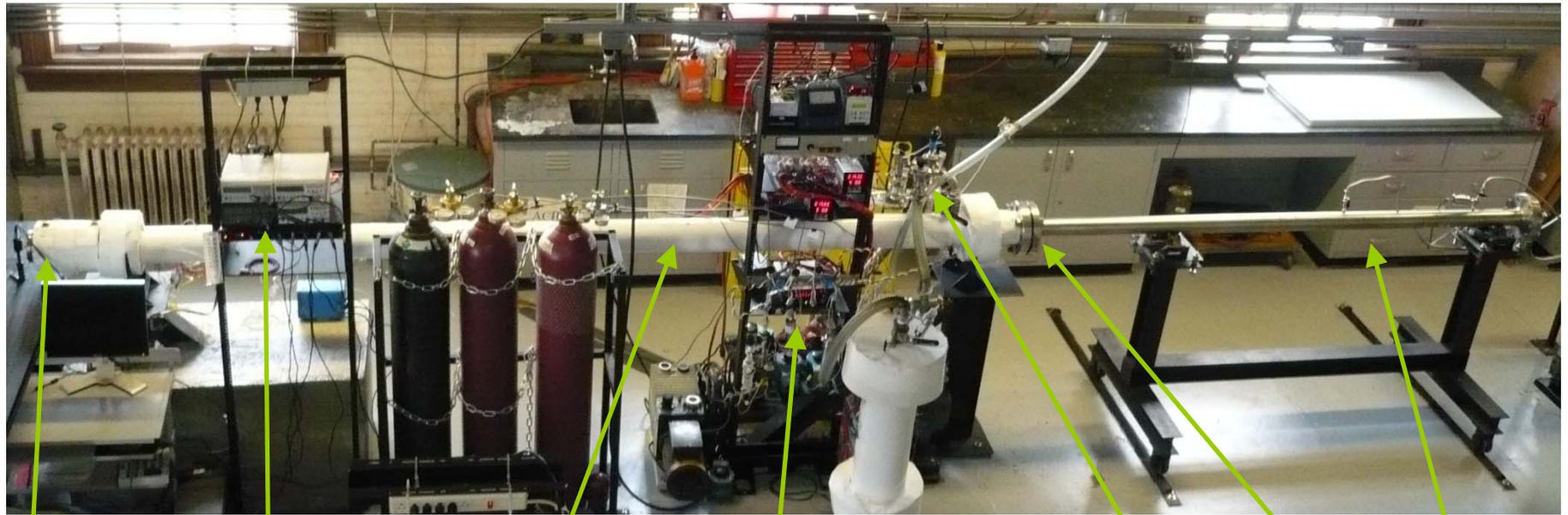
# Component palette



## Compounds recently studied at RPI



# RPI shock tube facility



Test location w/  
optical access

Shock velocity  
detection

Heated and insulated  
driven section

Mixing manifold

Heated and insulated  
mixing vessel

Vacuum section

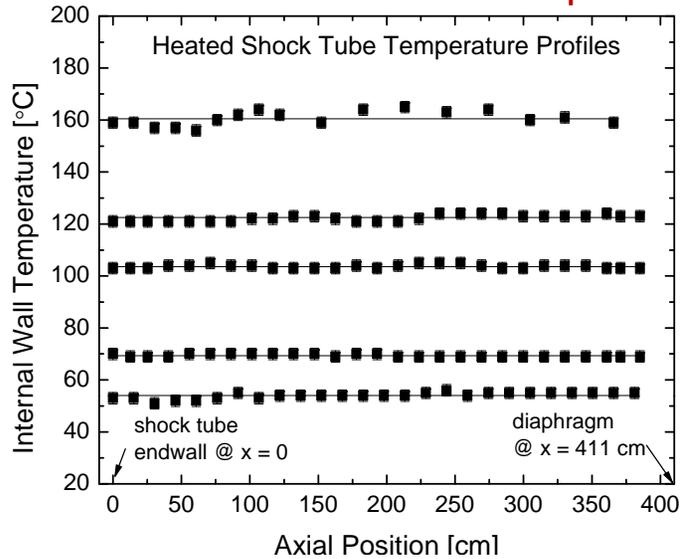
Diaphragm

Driver

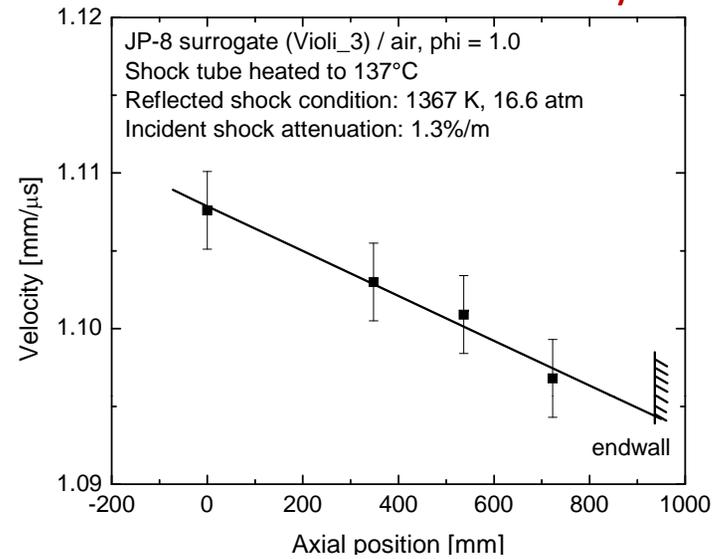
- Inner diameter = 5.7 cm
- Reflected shock pressures up to 200 atm
- Initial temperatures up to 200°C
- Designed for kinetic studies of low vapor pressure fuels (jet fuels) at engine-like elevated pressures

# Shock tube characteristics

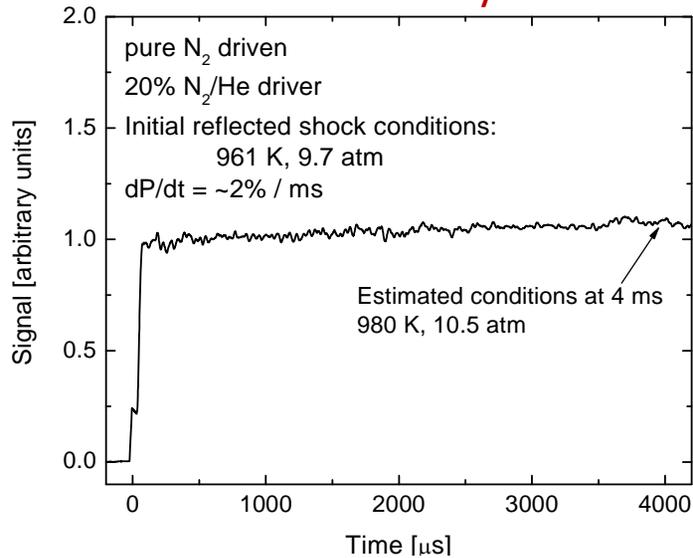
## Heated Shock Tube Temperature



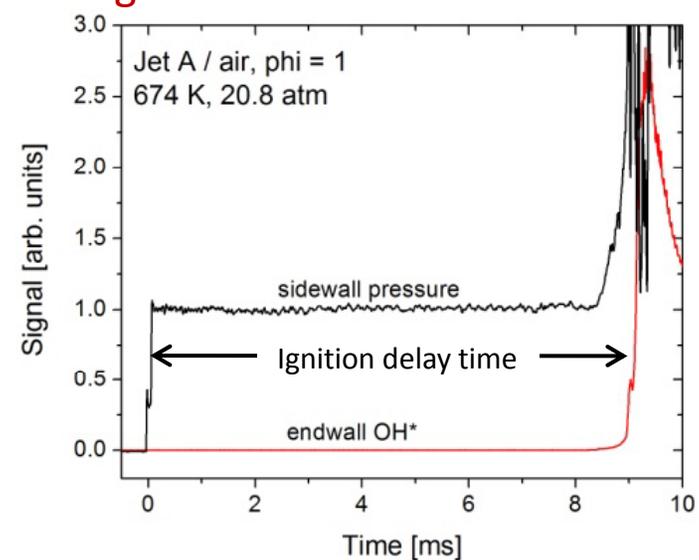
## Incident Shock Velocity



## Non-Ideal Gasdynamics



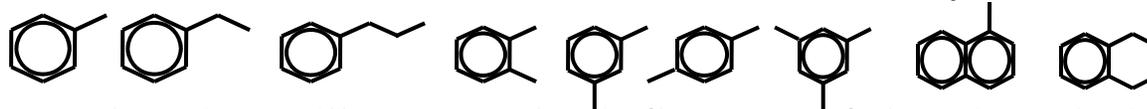
## Ignition Time Measurement



# Example component data: aromatics

Preliminary data removed

- Measurements have been made for seven monocyclic and two bicyclic compounds

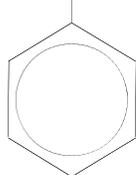


- Ignition delay times illustrate the influence of the side chains
- Wide range in high-temperature ignition for aromatics: important in surrogate selection

# Aromatics

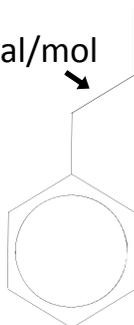
toluene

104 kcal/mol  
C-C



n-propylbenzene

77 kcal/mol  
C-C



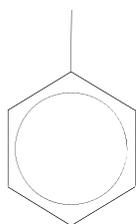
Side chains:

- Primary C-H bonds ~89-90 kcal/mol
- Secondary C-H bonds ~87-88 kcal/mol

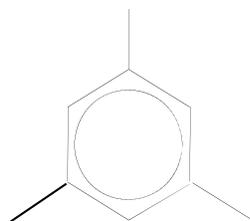
**C<sub>2</sub> and longer alkyl side chains introduce weak C-C bonds**

- Faster fuel consumption via decomposition and metathesis reactions
- Potential for radicals other than benzyl

toluene



1,3,5-trimethylbenzene



- Additional of methyl groups stabilizes the ring: increases the probability of unreactive benzylic radicals and decreases probability of more reactive phenylic radicals

# Aromatic kinetic modeling

Preliminary data removed

n-propylbenzene

- Good agreement with NUI Galway shock tube measurements
- Good agreement with Won et al. kinetic modeling for  $T > 900$  K
- Low-T deviation: gas dynamics or other non-kinetic experimental phenomena or  $\text{RO}_2$  chemistry in the propyl side chain (not included in model)?

# nPB reflected shock pressure profiles

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## **Ignition delay times**

- Good agreement at ~950 K
- Experiment is faster than model at ~850 K

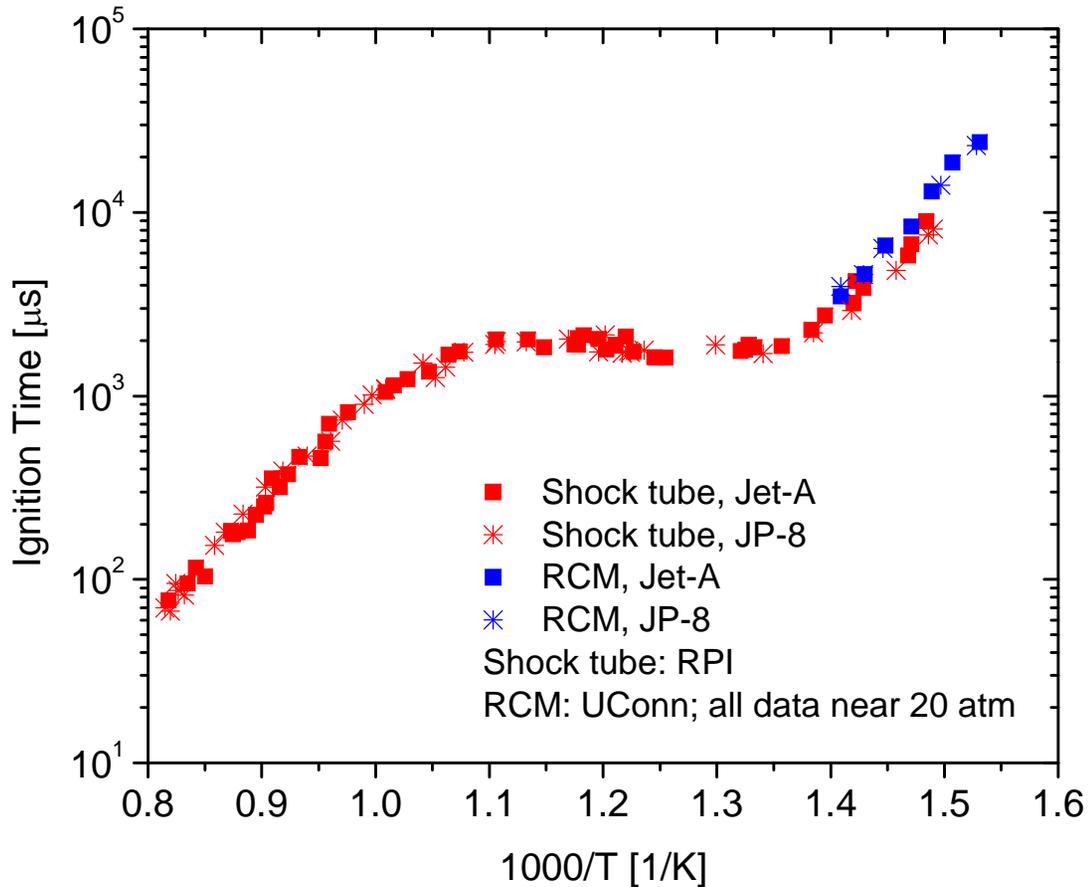
## **Induction period energy release**

- Good agreement at 950 K
- Experiment exhibits greater energy release prior to ignition than model at ~850 K

# Reactivity of HC components

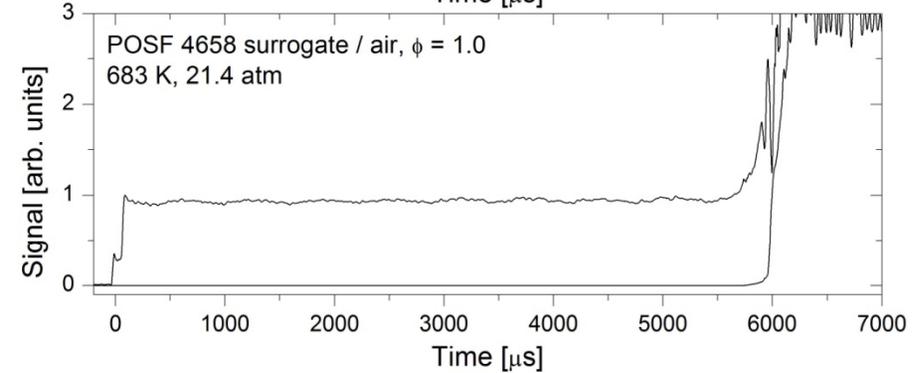
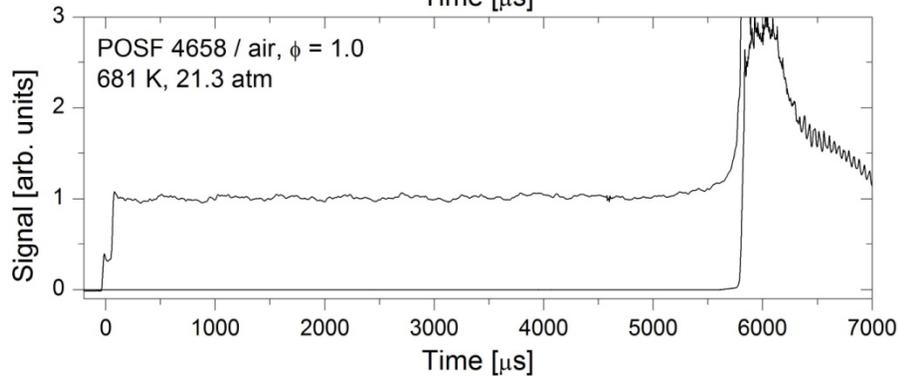
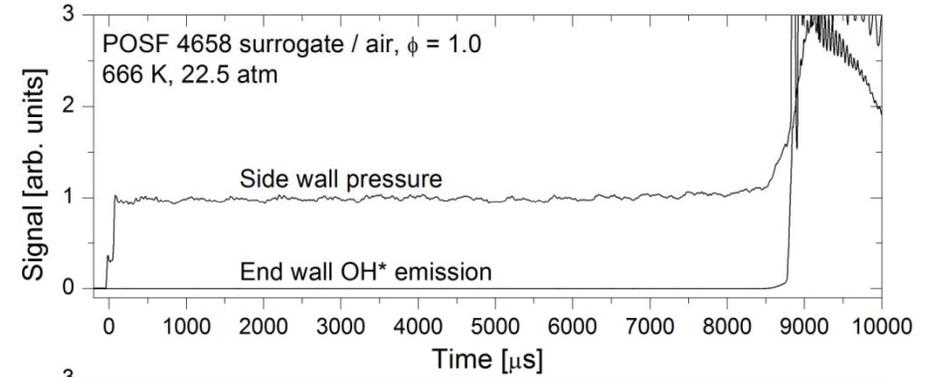
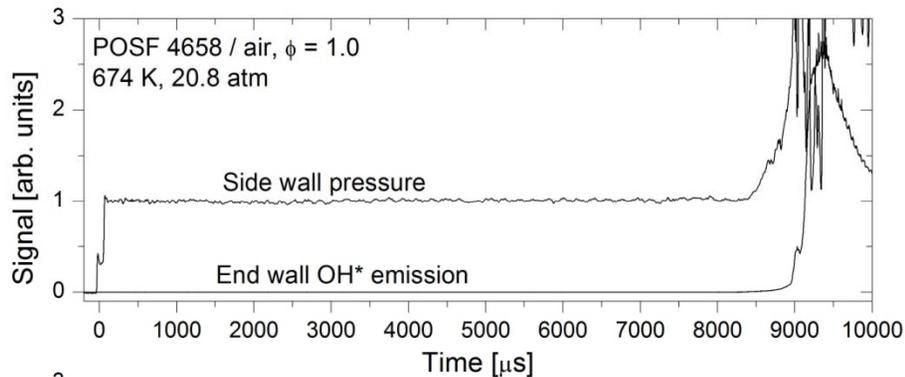
- Series of RPI autoignition studies for components provides quantitative kinetic targets and leads to following observations regarding reactivity
- **Large n-alkanes:** ignition times slightly decrease with increasing chain length; at high to moderate T, to first order, autoignition independent of chain length
- **Branched alkanes:** High- to moderate-T autoignition controlled by fraction of non-primary H atoms and rate of thermal decomposition
- **Substituted-aromatics:** side chain length/proximity/number primarily controls high-T autoignition; very little low-T reactivity
- **Substituted-cyclohexanes:** slight stabilization with increased side chain length
- Reactivity observations are important for surrogate formulation
  - First step might be to compare jet fuel and component data
- Data have led to refinements/validation of kinetic modeling

# Ignition delay for jet fuels



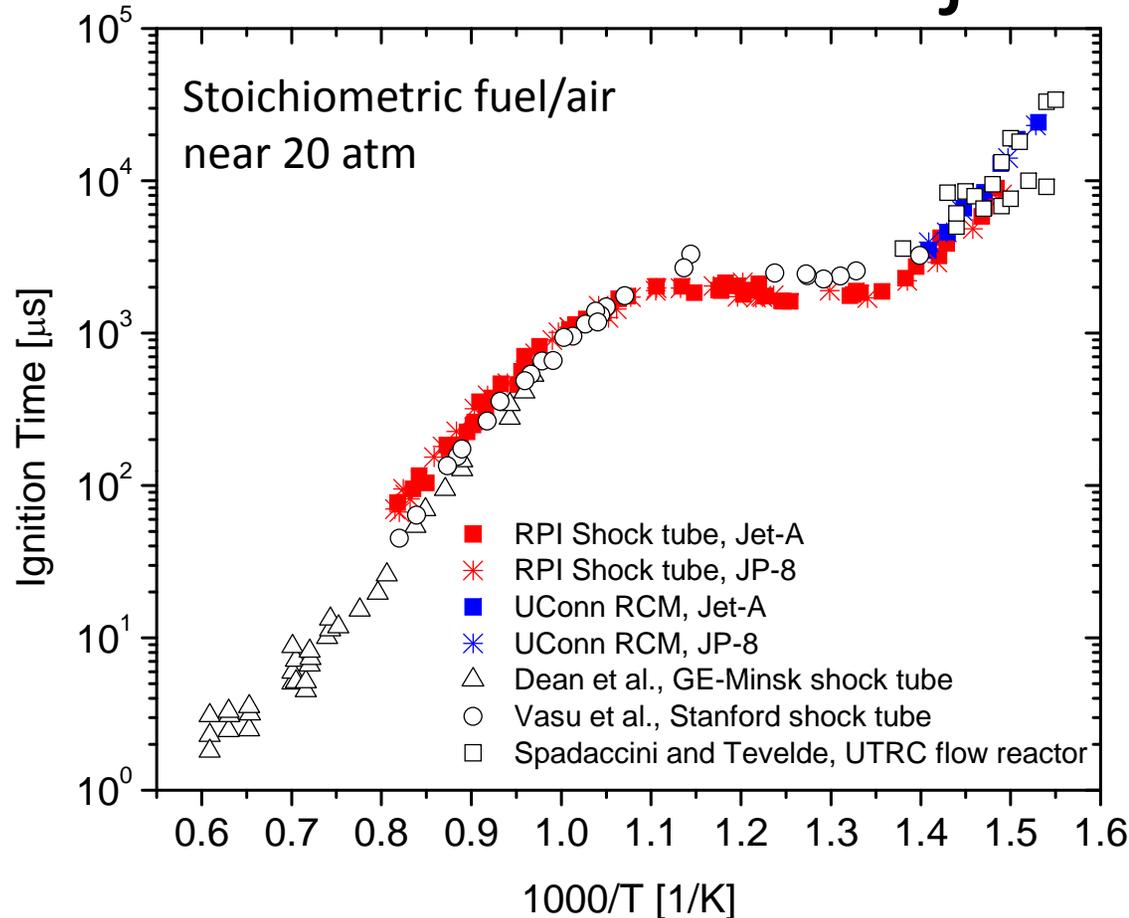
- Jet-A (POSF 4658): average Jet-A blended at WPAFB (Tim Edwards) from several Jet-A fuels
- JP-8: POSF 4658 w/ JP-8 additive package
- No discernible influence on autoignition by additive package
- Good agreement with RCM data (Sung, UConn) at lower temperatures

# Reflected shock pressure histories



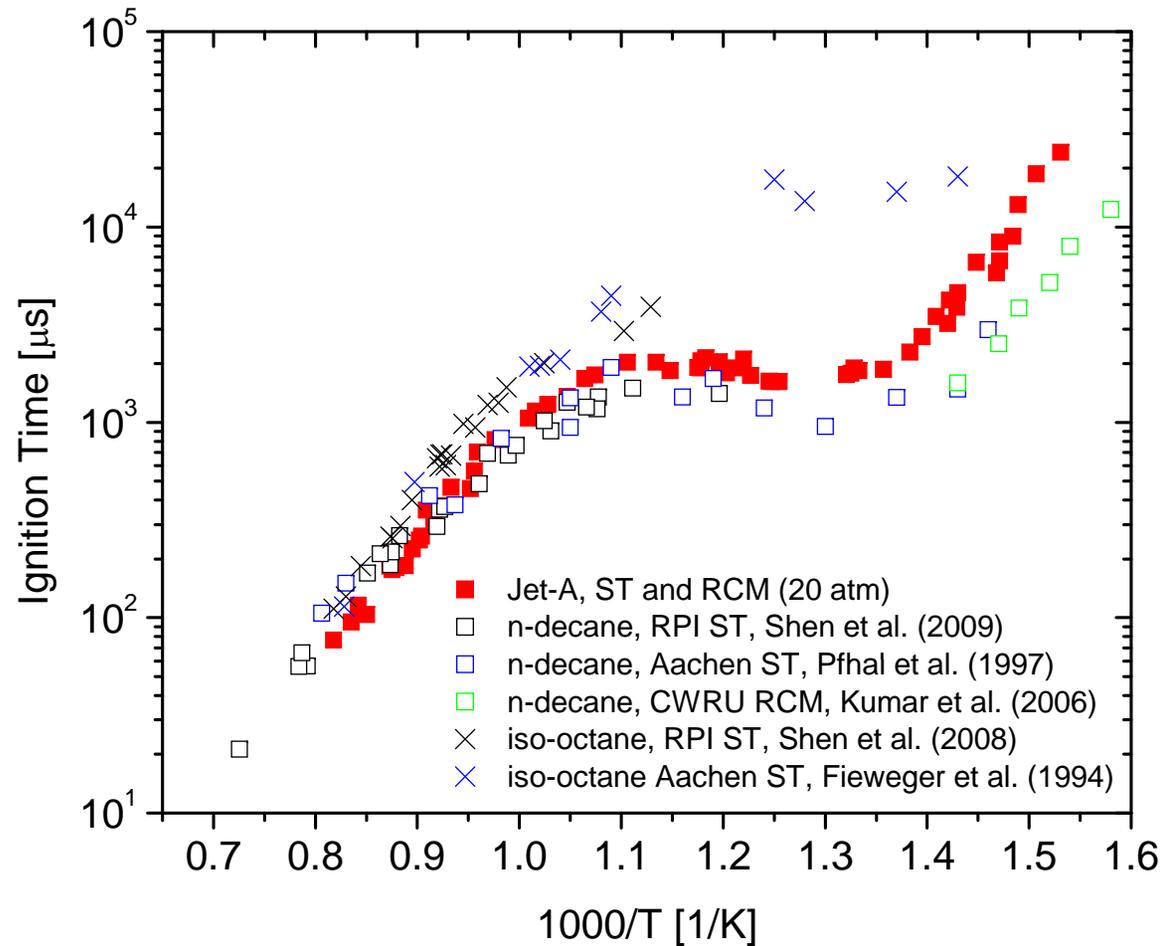
- Well behaved pressure profiles for <10 ms with N<sub>2</sub>/He tailored driver gases
- Very little gasdynamic pressure rise (<1%/ms) for jet fuel/air and surrogate/air mixtures at very low temperatures (670-680 K) for reflected shock experiments
- Gasdynamic pressure rise varies from 0-2%/ms depending on desired reflected shock pressure and temperature

# Comparison with literature jet fuel data



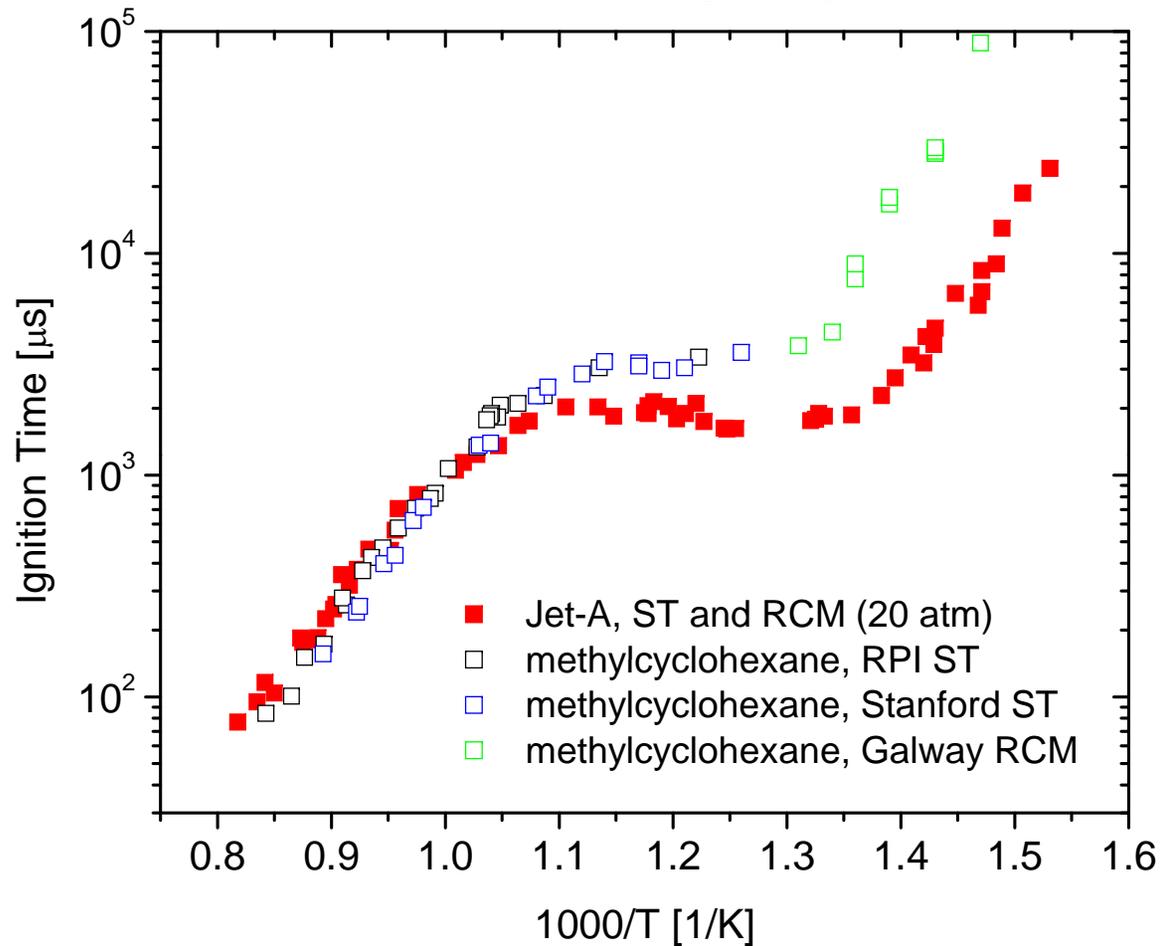
- Dean et al. GE/Minsk, shock tube: scaled from  $\sim 8$  atm to 20 atm using  $\tau \sim P^{-1}$
- Vasu et al. Stanford, shock tube: no pressure scaling
- Spadaccini and Tevelde UTRC, flow reactor: no pressure scaling
- Most of the deviations in data sets are due to pressure differences/scaling and differences in fuel/air mixtures

# Jet fuel vs alkanes



- n-alkane ignition delay times shorter than jet fuel
- Highly branched iso-alkane ignition delay times longer than jet fuel
  - Dependent on degree of branching

# Jet fuel vs methylcyclohexane



- MCH ignition delay times similar to jet fuel at high temperature and longer at low temperature
- Other substituted cyclohexanes likely behave similarly but have received little kinetic investigation

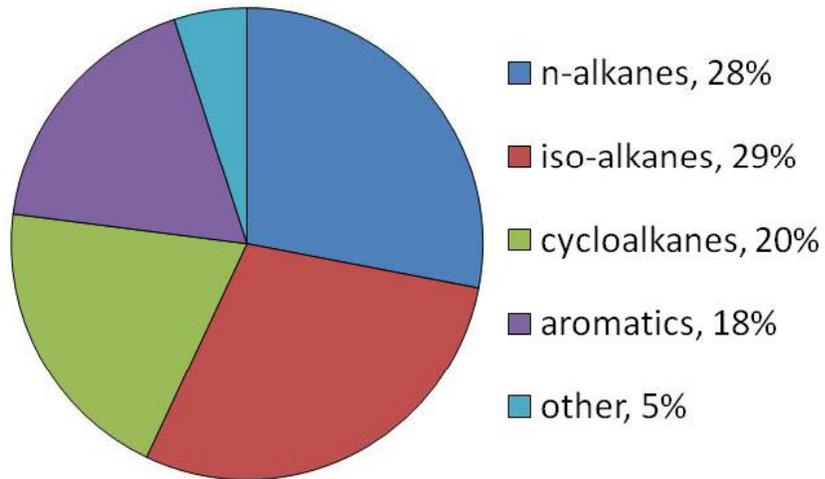
# Jet fuel vs aromatics

Preliminary data removed

- Aromatic ignition delay times longer than jet fuel
- Significant differences in aromatic reactivity
  - Aromatic must be chosen carefully for reactivity and soot formation considerations

# Surrogates and targets

## JP-8 composition



100s of distinct species

Jet fuel prohibitively complex to model  
→ must model w/ surrogate

## JP-8 physical properties

- H/C ratio = 1.84-2.07,  $H/C_{avg} \approx 1.9$
- MW  $\approx 153$  kg/kmol
- Aromatic liquid content  $\approx 20\%$
- Liquid density  $\approx 804$  kg/m<sup>3</sup>

## Potential targets

- Physical properties
- Organic compositional distribution
- Ignition/oxidation
  - ignition times, species histories/profiles, flame speed/extinction/ignition
- Cetane number, CN = 32-57,  $CN_{avg} \approx 44$
- Soot, TSI = 16-26,  $TSI_{avg} \approx 18$
- Distillation curve
- Transport

## Other factors

- Simplicity vs complexity
  - number and structure of components
- State of kinetic modeling
- Cost

# MURI surrogate 1

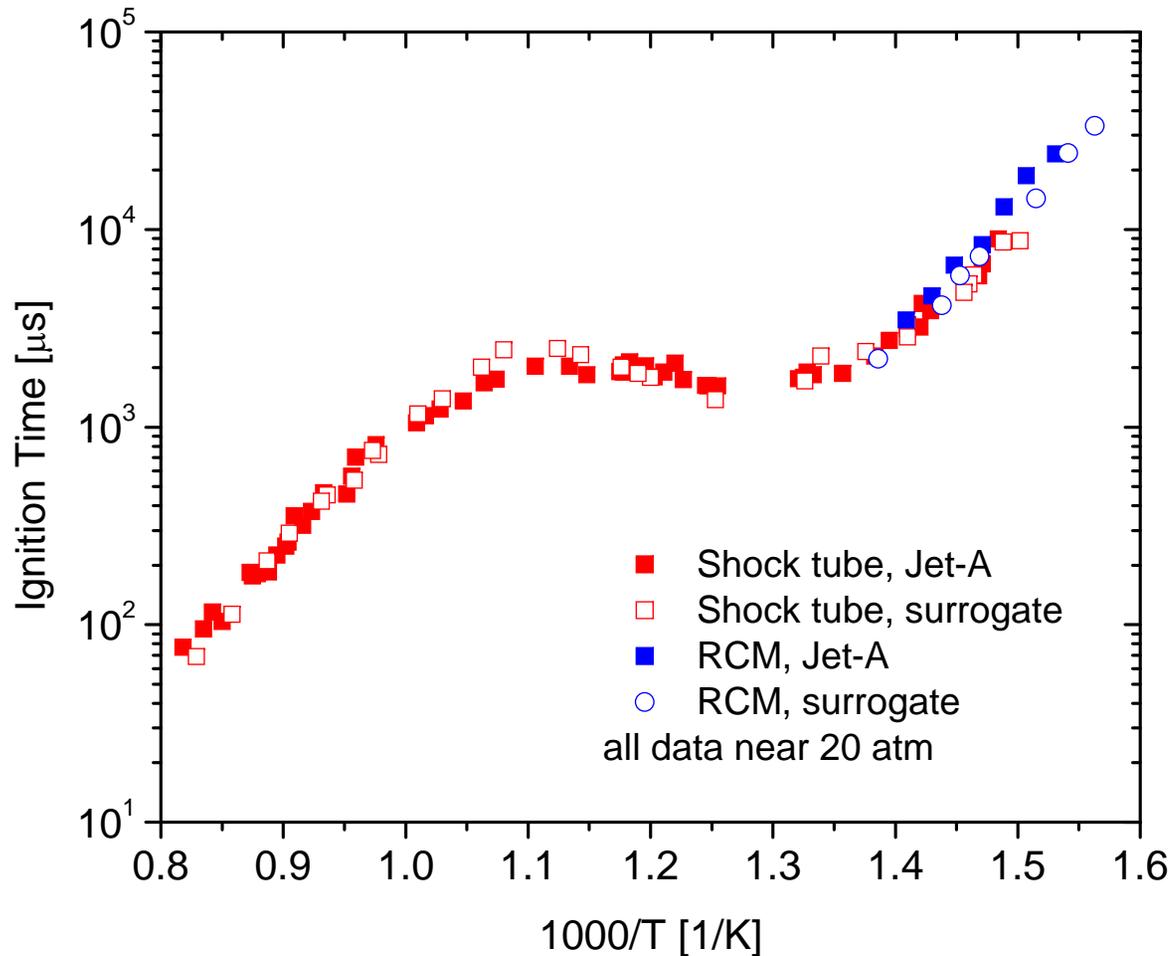
## Methodology:

- Restricted to three components for which models are widely available
- Match **H/C, DCN, and aromatic content** of POSF 4658 (“average” Jet A from Dr. Tim Edwards, AFRL)
- Test surrogate vs POSF 4658: flow reactor, flame extinction, ignition delay (shock tube and RCM)

	molar	liquid vol
n-decane	42.7%	50.8%
iso-octane	33%	33.3%
toluene	24.3%	15.8%

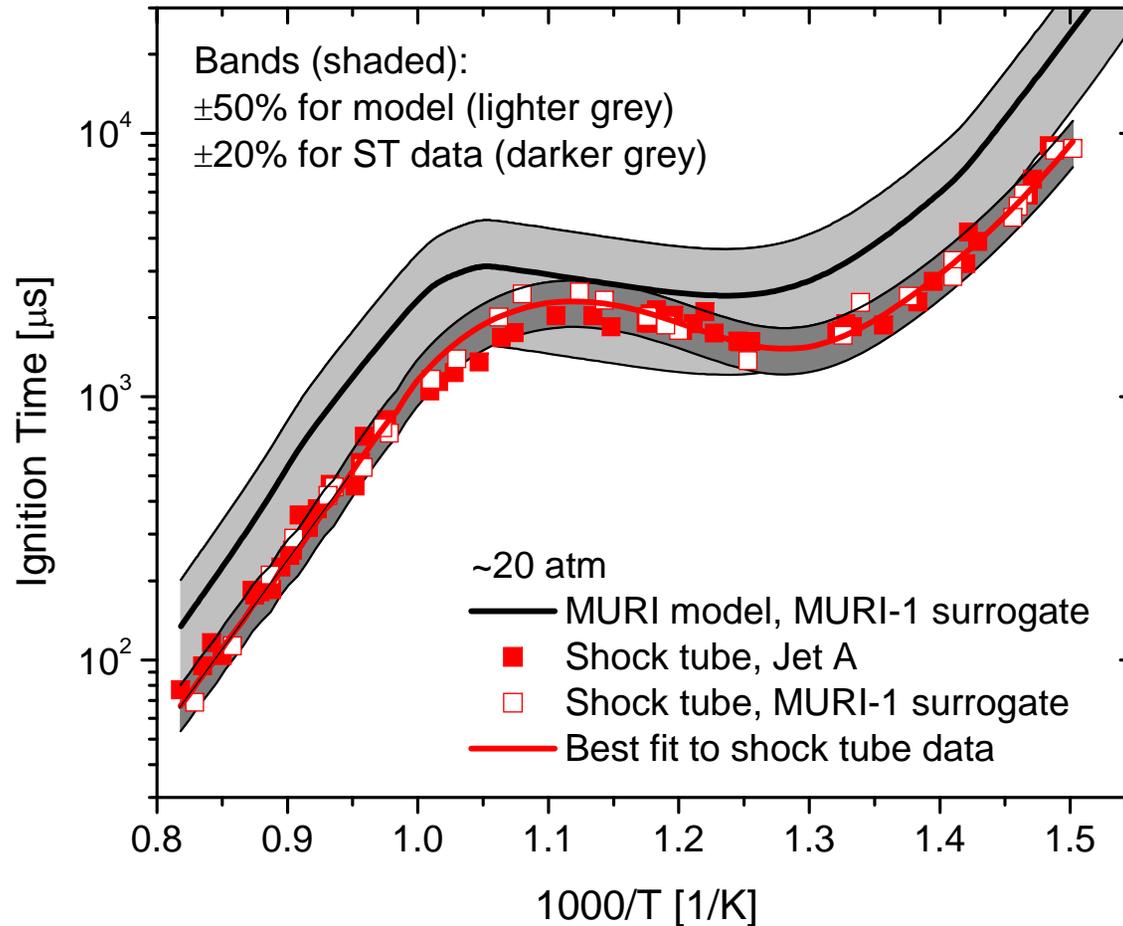
Fuel	H/C	MW	Aromatic liquid %	Liquid density [kg/m <sup>3</sup> ]	Cetane	TSI
JP-8, literature	1.84-2.07, avg = 1.9	~153	~20	~804	CN = 32-57, avg = 44	16-26, avg = 18
POSF 4658	<u>1.957</u>	142	<u>18.4</u>	799	<u>DCN = 47.1</u>	21.4
MURI Sur 1	<u>2.01</u>	121	<u>15.8</u>	750	<u>DCN = 47.1</u>	14.1

# MURI surrogate 1 vs jet fuel



- Surrogate experimentally mimics jet fuel autoignition well
- Fairly good agreement between ST and RCM

# MURI surrogate 1 vs kinetic modeling



- *a priori* kinetic modeling longer than experiment by  $\sim 2\times$
- Transition temperature from high-T to NTC differs:  
model  $\sim 950$  K, experiment  $\sim 900$  K

# MURI surrogate 2

## Methodology:

- Use larger n-alkanes and aromatics representative of those found in Jet A
  - n-dodecane, iso-octane, n-propylbenzene, and 135-trimethylbenzene
- Match **H/C, DCN, aromatic content, TSI, and MW** of POSF 4658
- Test surrogate vs POSF 4658: flow reactor, flame extinction, ignition delay (shock tube and RCM)

Preliminary data removed

# MURI surrogate 2 vs jet fuel

Preliminary data removed

- More complex four-component surrogate experimentally mimics jet fuel autoignition well

# MURI surrogate 2 vs kinetic modeling

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- *a priori* kinetic modeling only slightly longer than experiment at high to moderate T, longer at low T
- Transition temperature from high T to NTC differs: model ~950 K, experiment ~900 K

# RPI surrogate 1

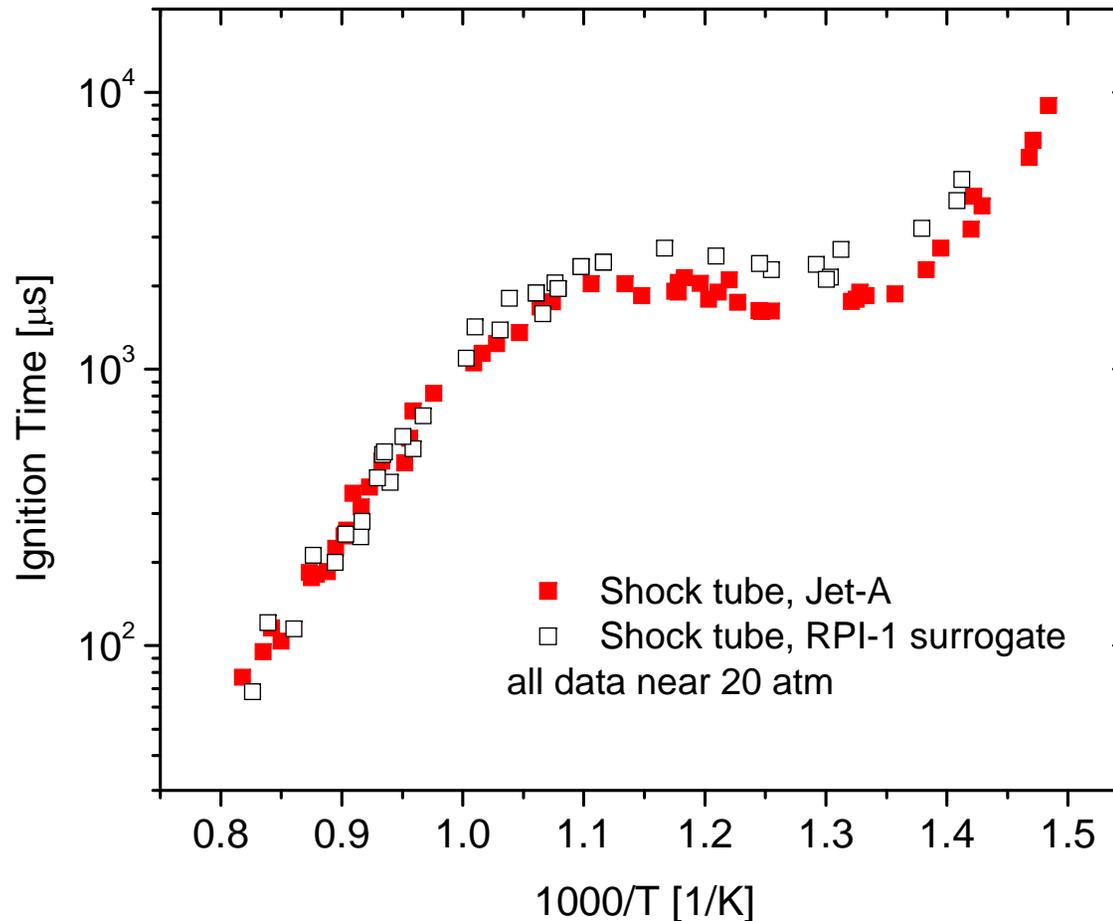
## Methodology:

- Choose HC components to approximate the relative distribution of typical jet fuel by organic class (n-alkane, iso-alkane, cycloalkane, aromatic)
- Match **H/C, DCN, aromatic content, TSI, MW, and liquid density** of literature average JP-8: heavier components chosen to match MW and liquid density

	molar	liquid vol
n-tetradecane	25.8%	35%
iso-cetane	16.8%	25%
methylcyclohexane	30%	20%
n-propylbenzene	27.4%	20%

Fuel	H/C	MW	Aromatic liquid %	Liquid density [kg/m <sup>3</sup> ]	Cetane	TSI
JP-8, literature	1.84-2.07, avg = <u>1.9</u>	~ <u>153</u>	~ <u>20</u>	~ <u>804</u>	CN = 32-57, avg = <u>44</u>	16-26, avg = <u>18</u>
POSF 4658	1.957	142	18.4	799	DCN = 47.1	21.4
RPI Sur 1	<u>1.87</u>	<u>151</u>	<u>20</u>	<u>792</u>	<u>DCN = 42.8</u>	<u>16.7</u>

# RPI surrogate 1 vs jet fuel



- Captures high-temperature autoignition
- Slight deviations at moderate to low temperatures consistent with differences in DCN: 42.8 for surrogate vs 47.1 for Jet A (POSF 4658)
  - Motivates studies jet fuels and surrogates with variation in DCN

# Summary

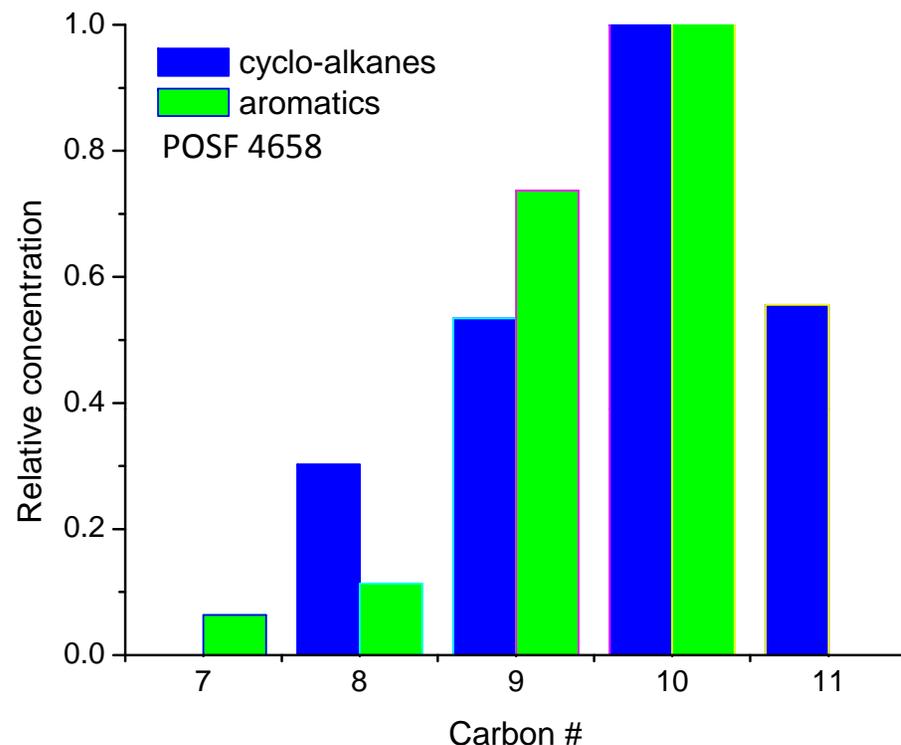
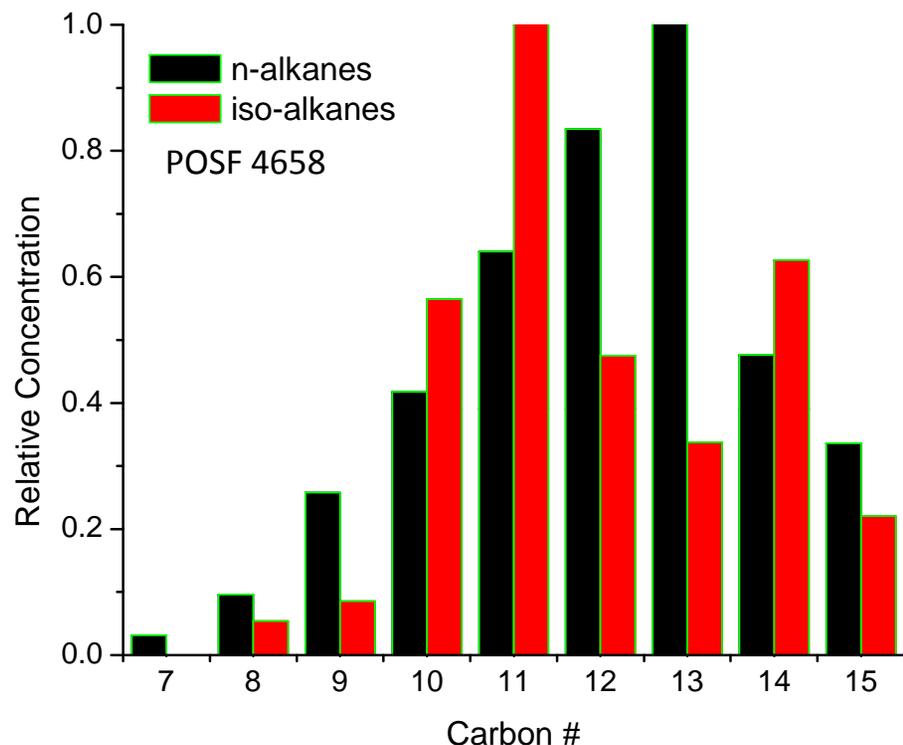
- Ignition delay data is available for jet fuels, components, and surrogates
  - Provide direct insight into fuel chemistry (reactivity vs structure)
  - Aide in development of kinetic mechanisms
  - Allow assessment of surrogates and surrogate formulation methodologies
- Surrogate formulation methodology hypothesized by the MURI team has been successful for formulating surrogates with reactivity (ignition delay) mimicking a specific jet fuel (POSF 4658)
  - Tested for three surrogates
    - n-decane, iso-octane, toluene
    - n-dodecane, iso-octane, n-propylbenzene, 135-trimethylbenzene
    - n-tetradecane, iso-cetane, methylcyclohexane, n-propylbenzene

# Closing points on surrogates: jet fuel composition

## NIST (Bruno) characterization of POSF 4658

name	CAS no.	area percentage	name	CAS no.	area percentage
<i>n</i> -heptane	142-82-5	0.125	2,3-dimethyl decane	17312-44-6	0.681
ethyl cyclohexane	108-87-2	0.198	1-ethyl-2,2,6-trimethyl cyclohexane	71186-27-1	0.364
2-methyl heptane	592-27-8	0.202	1-methyl-3-propyl benzene	1074-43-7	0.569
toluene	108-88-3	0.320	aromatic	NA	0.625
<i>cis</i> -1,3-dimethyl cyclohexane	638-04-0	0.161	5-methyl decane	13151-35-4	0.795
<i>n</i> -octane	111-65-9	0.386	2-methyl decane	6975-98-0	0.686
1,2,4-trimethyl cyclohexane	2234-75-5	0.189	3-methyl decane	13151-34-3	0.969
4-methyl octane	2216-34-4	0.318	aromatic	NA	0.540
1,2-dimethyl benzene	95-47-6	0.575	aromatic	NA	0.599
<i>n</i> -nonane	111-84-2	1.030	1-methyl-(4-methylethyl) benzene	99-87-6	0.650
<i>x</i> -methyl nonane	NA	0.597	<i>n</i> -undecane	1120-21-4	2.560
4-methyl nonane	17301-94-9	0.754	<i>x</i> -methyl undecane	NA	1.086
1-ethyl-3-methyl benzene	620-14-4	1.296	1-ethyl-2,3-dimethyl benzene	933-98-2	1.694
2,6-dimethyl octane	2051-30-1	0.749	<i>n</i> -dodecane	112-40-3	3.336
1-methyl-3-(2-methylpropyl) cyclopentane	29053-04-1	0.285	2,6-dimethyl undecane	17301-23-4	1.257
1-ethyl-4-methyl benzene	622-96-8	0.359	<i>n</i> -tridecane	629-50-5	3.998
1-methyl-2-propyl cyclohexane	4291-79-6	0.370	1,2,3,4-tetrahydro-2,7-dimethyl naphthalene	13065-07-1	0.850
1,2,4-trimethyl benzene	95-63-6	1.115	2,3-dimethyl dodecane	6117-98-2	0.657
<i>n</i> -decane	124-18-5	1.67	2,6,10-trimethyl dodecane	3891-98-3	0.821
1-methyl-2-propyl benzene	1074-17-5	0.367	<i>x</i> -methyl tridecane	NA	0.919
4-methyl decane	2847-72-5	0.657	<i>x</i> -methyl tridecane	NA	0.756
1,3,5-trimethyl benzene	108-67-8	0.949	<i>n</i> -tetradecane	629-59-4	1.905
<i>x</i> -methyl decane	NA	0.613	<i>n</i> -pentadecane	629-62-9	1.345

# Closing points on surrogates: jet fuel composition



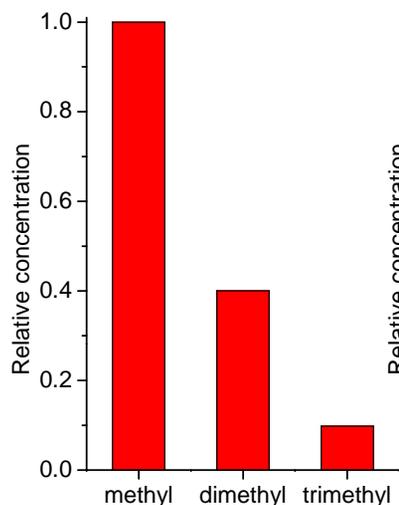
**To match many macroscopic combustion properties (ignition delay, DCN, TSI, H/C, etc.)**

- Not necessary to restrict the surrogate to the organic distribution and/or the organic structures found in jet fuels (e.g., iso-octane and iso-cetane are not found in jet fuels)

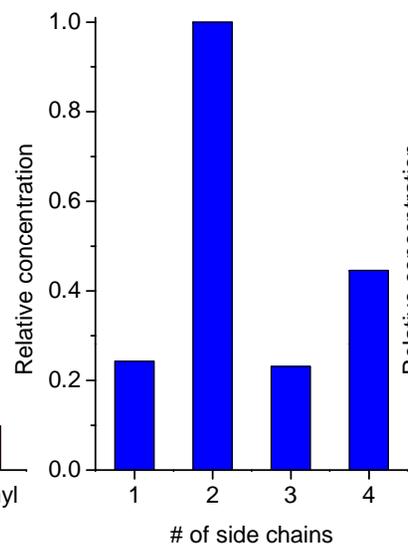
In order to match other physical properties (distillation), microscopic kinetic targets (detailed speciation), and perhaps some macroscopic targets (ignition delay) for a larger range of conditions it may be desired to make the surrogate look more like the jet fuel, in terms of structure and diversity of structure (larger number of components).

# Closing points on surrogates: branching/substitution

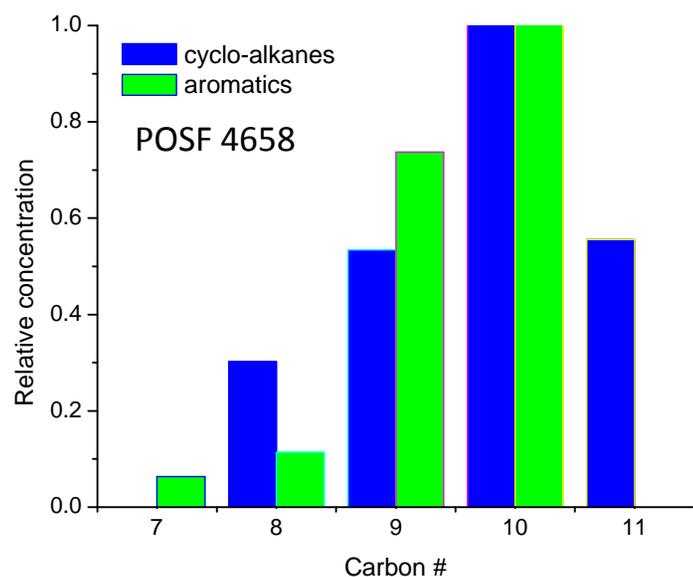
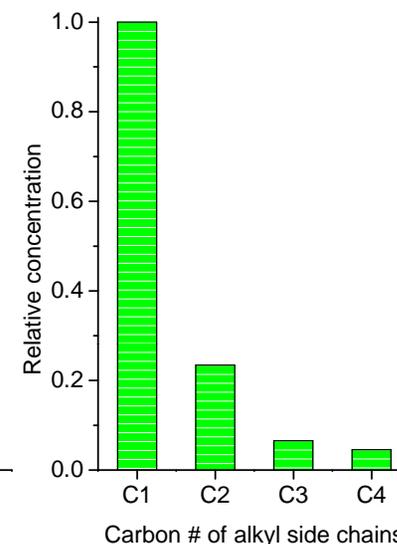
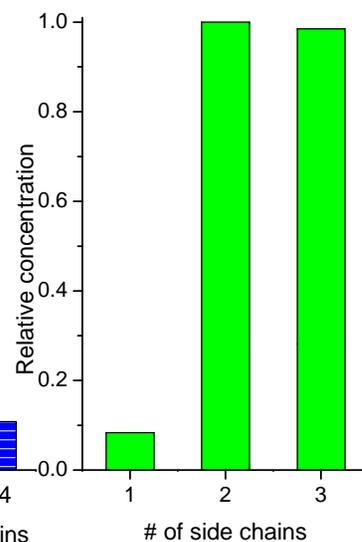
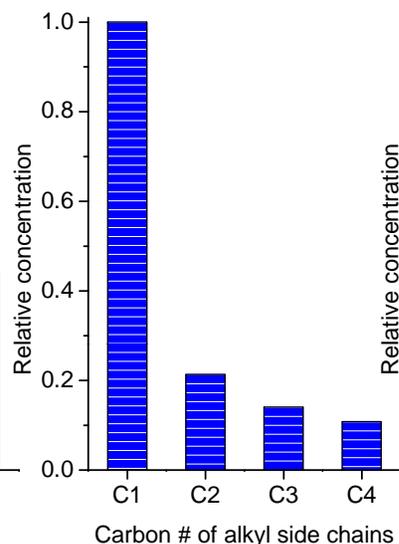
iso-alkanes



cyclo-hexanes



aromatics



If greater structural similarity is desired, need to consider:

- Lightly branched alkanes
  - extension of current n- and iso-alkane kinetics
- Cyclo-hexanes (C<sub>8</sub>-C<sub>11</sub>) with multiple small alkyl side chains
  - extrapolation of MCH kinetics
- Aromatics (C<sub>8</sub>-C<sub>10</sub>) with 2 or 3 small alkyl side chains
  - extrapolation of toluene kinetics

# Future work

## Jet Fuels

- Fuel variability: range of fuels (Jet A, JP-8, S-8, IPK, etc) with differing DCN
- Conditions
  - Lower and higher pressures of relevance to main combustors, after burners, and diesel engines
  - Equivalence ratio
  - Vitiation? – afterburners

## Surrogates

- Sensitivity to compositional perturbations: variation of the same set of components to mimic a range of jet fuels

## Components

- Lightly branched alkanes
- More complex cyclo-hexanes and aromatics
- Olefin compounds that are found in the intermediate soup during the oxidation of paraffins

# Acknowledgements

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- Collaborators: Prof. Fred Dryer, Dr. Stephen Dooley (Princeton) and MURI team, Drs. Charlie Westbrook and Bill Pitz (LLNL)
- Students: Haowei Wang, Dr. Jeremy Vanderover (GE), Dr. Shawn Shen (Raytheon)
- Fuel: Dr. Tim Edwards (AFRL)

Questions?