



# **Experimental and Modeling Studies of the Combustion Characteristics of F-T Fuels**

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**LEADING THE WAY TO CLEAN COMBUSTION DESIGN**

# Outline

- **Overview**

- Participants
- Objectives of project

- **Results**

- Surrogate blend for F-T and bio-derived jet fuels
- Experimental data obtained at USC
- Mechanism validation
- Mechanism reduction

- **Conclusions**

- Comparisons of F-T and bio-derived jet fuels with conventional fuels
- Outlook for detailed kinetics in CFD simulations

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# Collaborators on this project

- **NASA Glenn (Project oversight)**

- M. Rabinowitz, D. Bulzan
- Award # NNC07CB45C
- 05-2007 through 04-2009

- **University of Southern California (Co-PIs)**

- Profs. F. N. Egolfopoulos and T. Tsotsis
- Y. L. Wang, P. Veloo, Q. Feng, A. Holley



- **Reaction Design**

- E. Meeks (PI)
- C. V. Naik, K. V. Puduppakkam, A. Modak (Co-PIs)
- Consultant: C. K. Westbrook (Co-PI)



reaction  
DESIGN

# Project Objectives

- **Obtain fundamental data on combustion behavior of alternative jet fuels**
  - Fischer-Tropsch and Bio-derived
  - Real fuels and associated model (surrogate) fuels
- **Assemble fuel-chemistry models for simulation**
  - Validate kinetics through comparison with experiment
  - Recommend surrogate blends
  - Provide accurate, reduced mechanisms
- **Identify differentiating characteristics of molecular fuel components**

# Tasks undertaken to meet objectives

- **Fuels survey and analysis**
  - F-T fuels
  - Bio-derived fuels
- **Flame experiments for liquid / heavy fuels**
  - Laminar flame-speed and flame-extinction limits
  - Augmentation of diagnostics to measure  $\text{NO}_x$  and soot
- **Surrogate-model assembly and testing**
  - Build from state-of-the-art detailed mechanisms
  - Refine  $\text{NO}_x$  sub-model
  - Flame modeling, including  $\text{NO}_x$  and soot formation
- **Mechanism reduction for targeted conditions**

# Ultimately, we want fuel-combustion mechanisms suitable for CFD simulation

- 1. Identify appropriate surrogate components for targeted alternative jet fuels**
- 2. Assemble & test component mechanisms against available experimental data**
- 3. Determine appropriate component-blending method to match real-fuel properties**
- 4. Test surrogate blend against real fuel behavior**
- 5. Reduce surrogate mechanism for targeted conditions**

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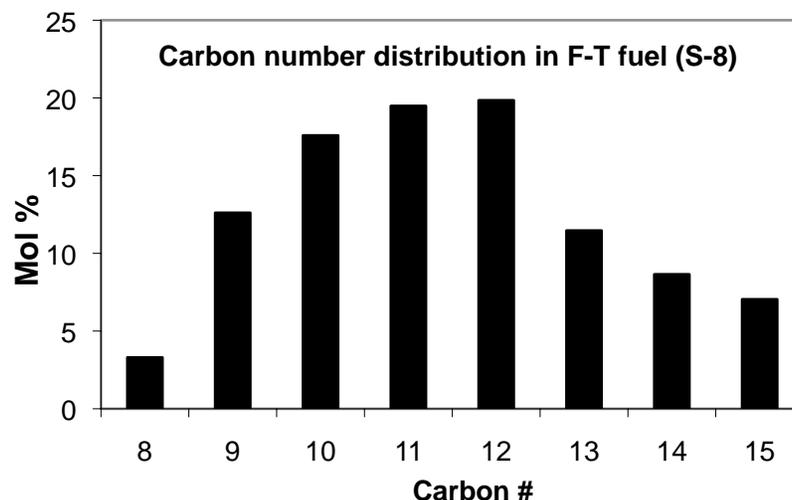
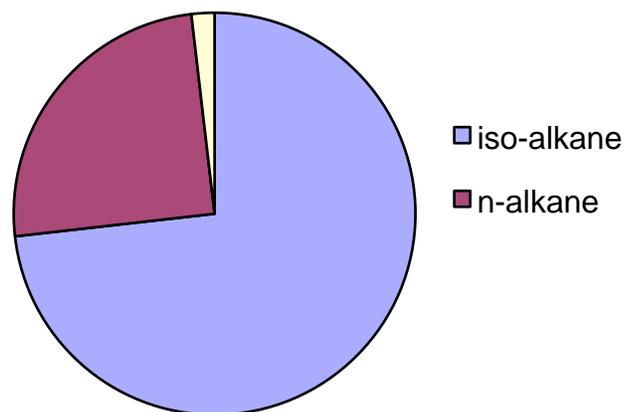
# Fuel data was collected to determine appropriate fuel surrogates

- **2 F-T samples obtained from the Air Force**
  - Courtesy of Tim Edwards, AFRL
  - GC/MS data provides class/size composition of fuels
  - Cetane number (IQT data) and distillation points
- **Bio-derived jet fuel (R-8) also acquired from AF**
  - Same general characteristics as F-T samples
  - Detailed chemical analysis not available

# F-T fuel analysis shows predominance of iso-alkanes with very little branching

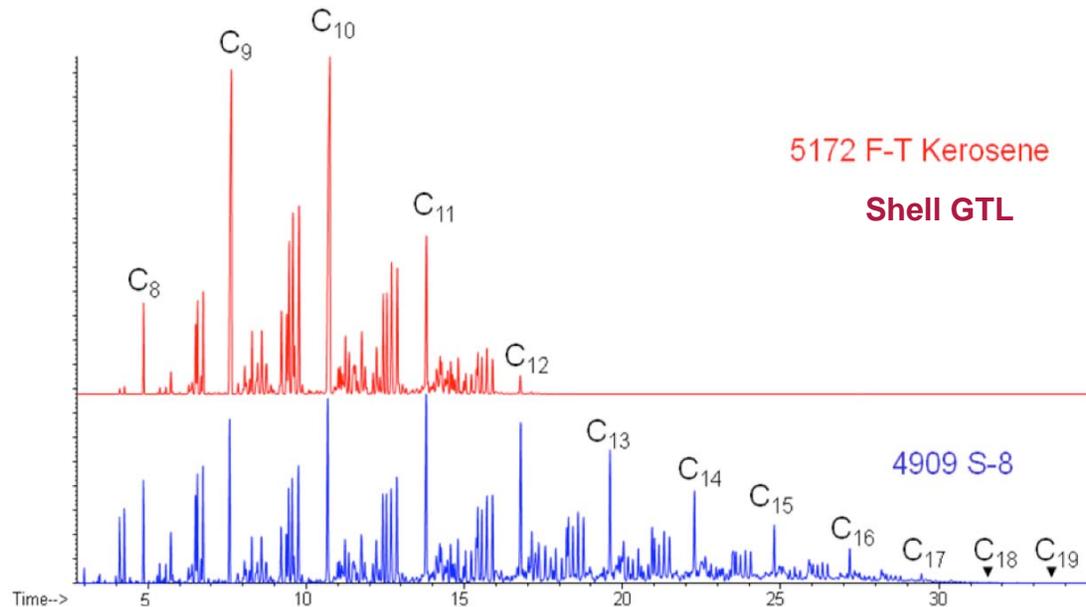
- **Summary results for S-8 (Syntroleum) sample: (based on GCMS analysis courtesy of Tim Edwards of AFRL)**

F-T fuel (S-8) analysis, mol%



- **Most of the iso-paraffins consist of only one methyl branch on a long and straight alkane chain**

# F-T fuel from different sources are similar, but have different C# distribution



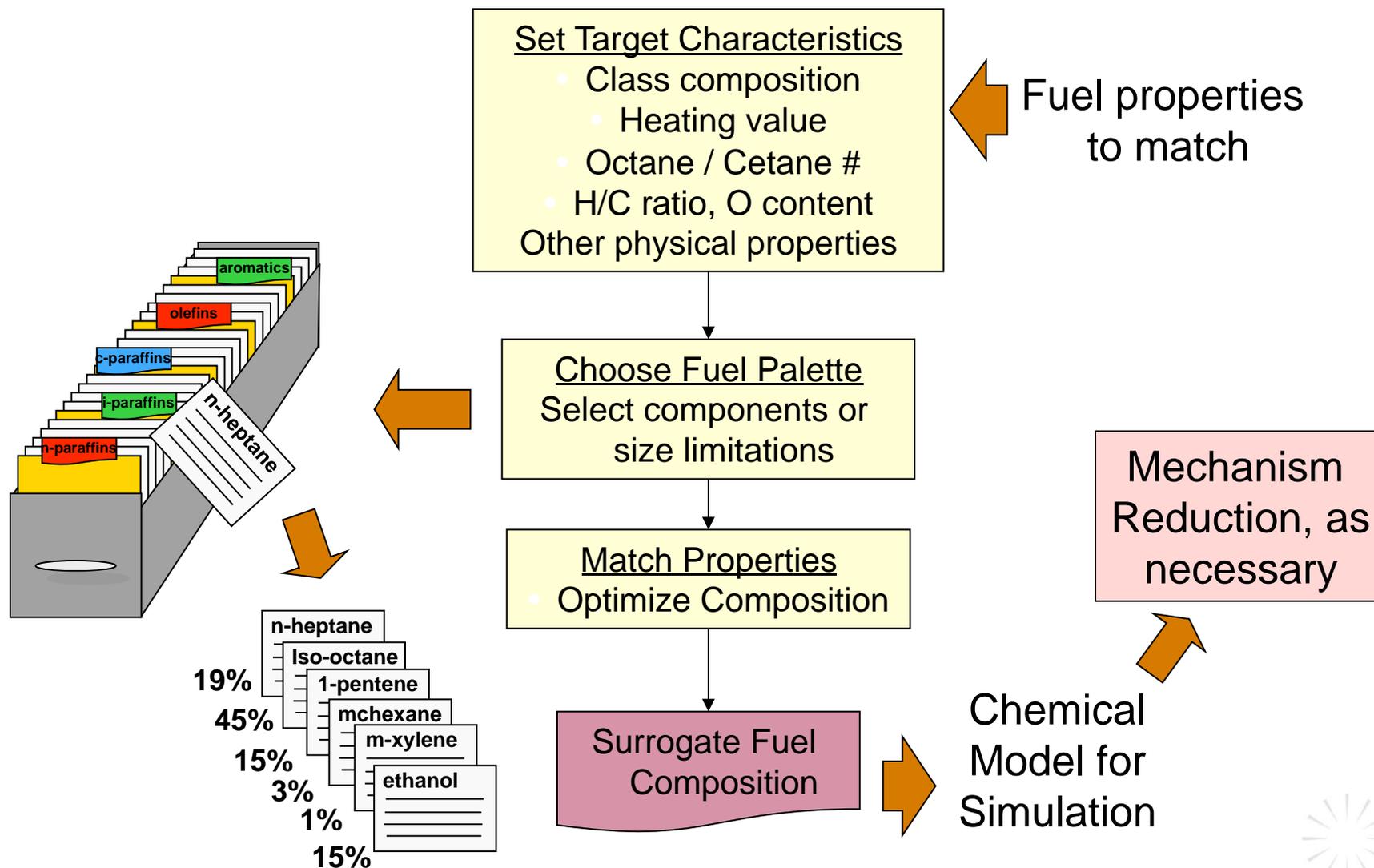
| Cetane Numbers | IQT   | ASTM D976 |
|----------------|-------|-----------|
| Shell GTL      | 59.67 | 68        |
| Syntroleum S-8 | 59.08 | 57        |

## ● Highlights about composition

- Mostly 1 or 2 methyl side chain alkanes
  - \* Side chains responsible for lower cetane numbers of large alkanes
- C# varies significantly
  - \* C<sub>7</sub>-C<sub>17</sub> for S-8 with C<sub>8</sub>-C<sub>13</sub> consist majority of composition
  - \* C<sub>8</sub>-C<sub>12</sub> for Shell
- Cetane number is ~60



# Reaction Design has developed a Surrogate Blend Optimizer to match fuel properties



# We determined surrogate blends based on properties that are important for simulation

- **Iso-octane included to match Cetane Number**

- Although highly branched, captures effect of low-branch components
- We had a well validated mechanism consistent with other mechanisms

|                                   | Shell GTL Surrogate | Shell GTL Targeted Properties (Measured) | S-8 Surrogate | S-8 Targeted Properties (Measured) |
|-----------------------------------|---------------------|--|---------------|------------------------------------|
| <b>Surrogate Blend Definition</b> |                     |  |               |                                    |
| iso-Octane (mol %)                | 28                  |  | 32            |                                    |
| n-Decane (mol %)                  | 61                  |  | 25            |                                    |
| n-Dodecane (mol %)                | 11                  |  | 42            |                                    |
| <b>Properties Comparison</b>      |                     |  |               |                                    |
| Cetane Number                     | 61                  | 61                                       | 61            | 60                                 |
| H/C molar ratio                   | 2.21                | 2.17                                     | 2.20          | 2.17                               |
| Lower Heating Value (MJ/kg)       | 45                  | 44                                       | 44            | 44                                 |
| T50 boiling point (K)             | 404                 | 445                                      | 447           | 474                                |

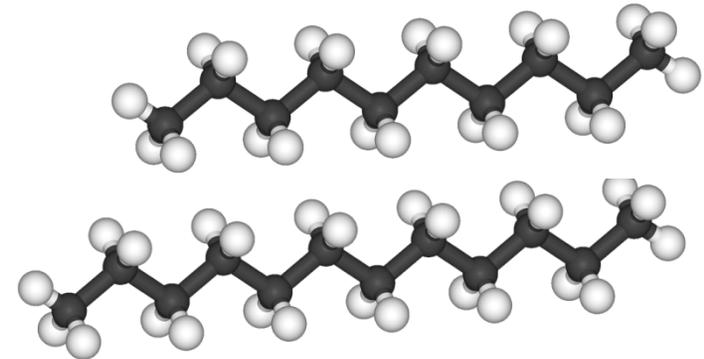


# The F-T surrogate mechanism was assembled based on previous work

- **n-decane and n-dodecane**

- From Westbrook et al. (2008) mechanism of n-alkanes

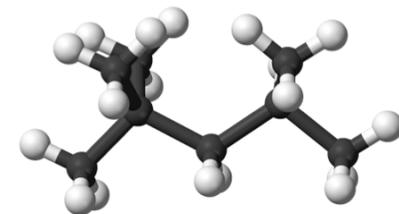
- \* Removed species > C12
- \* Removed low-temperature kinetics to focus on flames
- \* Added estimates of transport parameters



- **iso-octane mechanism merged in**

- From Curran et al. (2002)

- \* high-temperature reactions only



- **Enforced self-consistent rate rules and thermodynamics**

- SMILES strings identified for all species

# Improvements were made to address over-prediction of laminar flame-speeds

- **Sensitivity analysis pointed to C<sub>0</sub>-C<sub>3</sub> chemistry as sources of systematic error**
- **Changes made to C<sub>0</sub>-C<sub>3</sub> core chemistry:**
  - H<sub>2</sub> oxidation
    - \* Updated based on recent studies by Curran et al. (2004) and Dryer et al. (2007)
    - \* Updated  $\ln H_f^{298K}$  for OH and HO<sub>2</sub>
    - \* **Significant effect on flame speeds**
  - C<sub>1</sub> oxidation
    - \* Updated based on Petersen et al. (2007)
  - C<sub>2</sub> and C<sub>3</sub> oxidation
    - \* Updated based on Naik and Dean (2006)
    - \* All reverse rate constants based on microscopic reversibility

# A NO<sub>x</sub> sub-mechanism was assembled, including low- and mid-temperature pathways

- **Based on recent mechanisms reported in literature**
  - GRI 3.0 NO<sub>x</sub> sub-mechanism – High-T
  - Dagaut, Glarborg, et al. 2008 mechanism – Mid-T
    - \* Complete and up-to-date HCN chemistry, as well as N<sub>2</sub>O and NNH chemistry
  - Rasmussen, Glarborg, et al. 2008 mechanism – Low-T
    - \* NO<sub>x</sub>-HC interactions



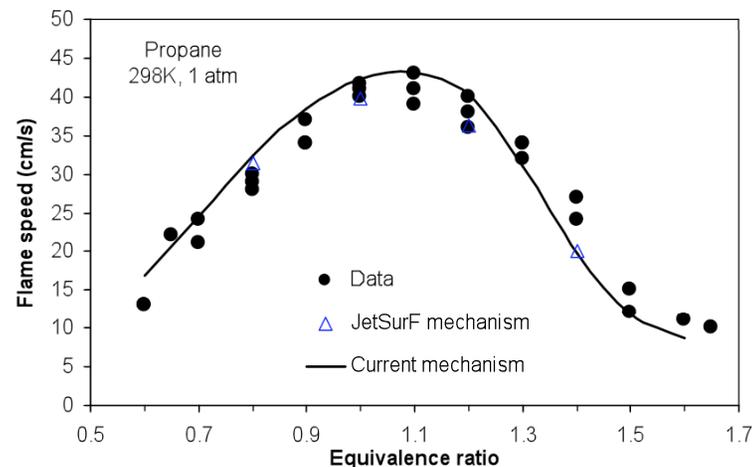
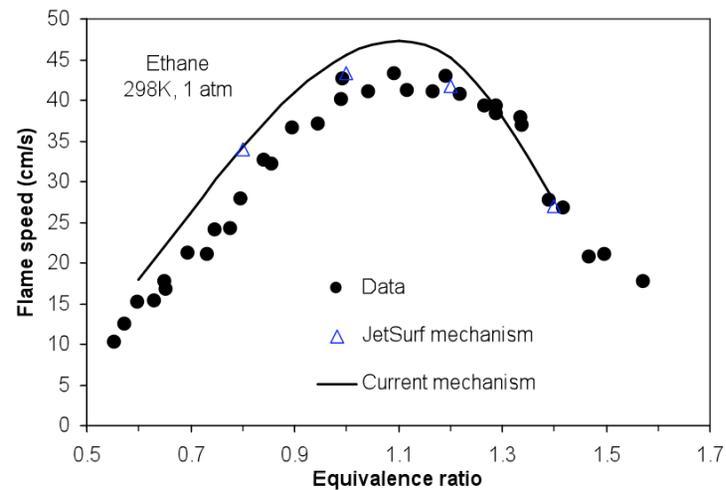
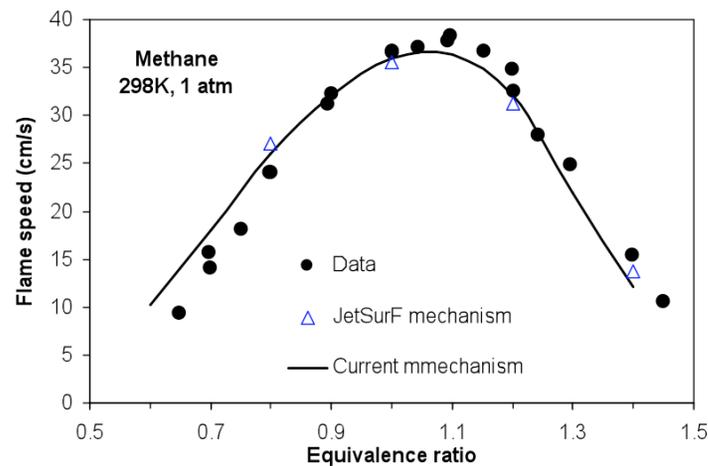
- **Final NO<sub>x</sub> sub-model includes fuel-NO<sub>x</sub> sensitization and self-consistent set of thermodynamic properties**

# Detailed mechanisms were systematically reduced to high-temperature versions

- **High-temperature mechanisms extracted based on chemistry logic**
  - Remove species deemed to be only important for low-temperature chain-branching
    - \* Ketohydroperoxides and QOOH species
  - Remove reactions associated with removed species
- **Method based on unique species identifiers**
  - SMILES strings tag each species in system
  - Independent of any species naming convention
  - Allows full automation for mechanism operations
- **Resulting mechanism:**
  - 681 species, 3934 reactions

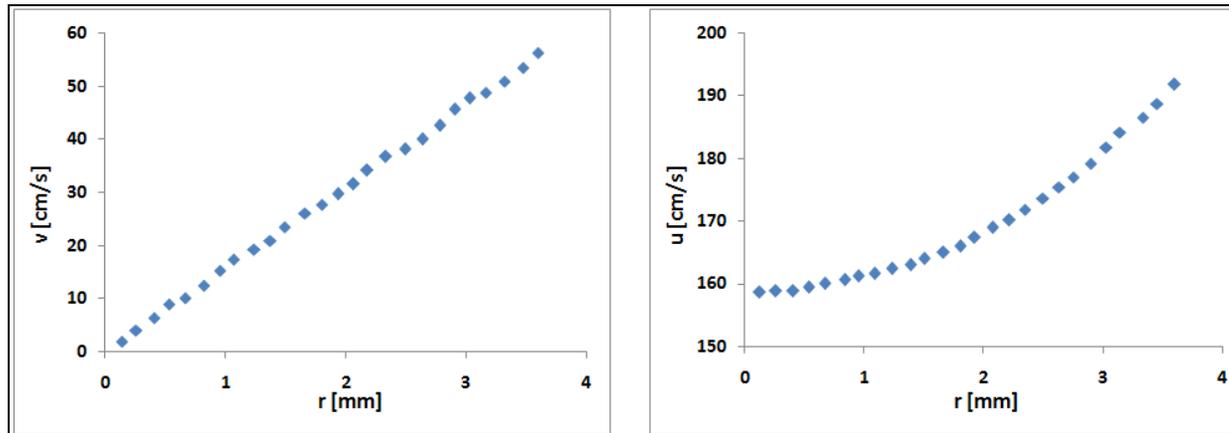
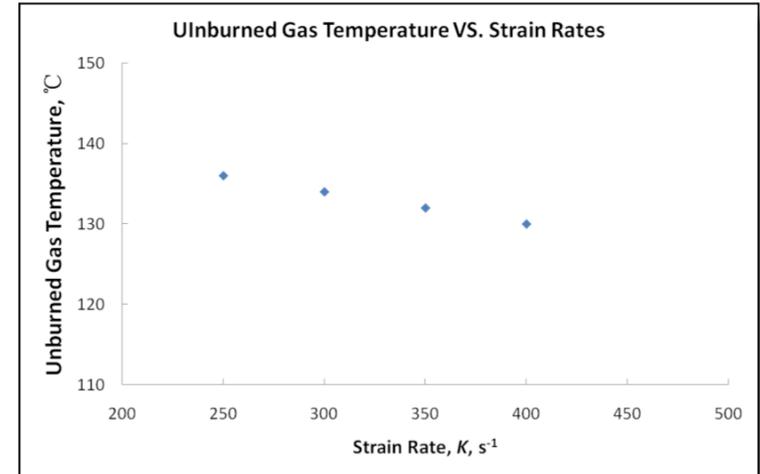
# Improved mechanism provides reliable flame-speed predictions for n-alkanes

- Tested with smaller alkane data from the literature first
- Compares well with USC JetSurF mechanism



# Extensive study at USC resulted in high-quality, reproducible data for liquid fuels

- **Effect of flow rate (strain rate) on unburned gas temperature**
  - Temperature correction required
- **Effect of radial location of measurement for velocities**
  - Consistent placement very close to centerline required for reproducibility



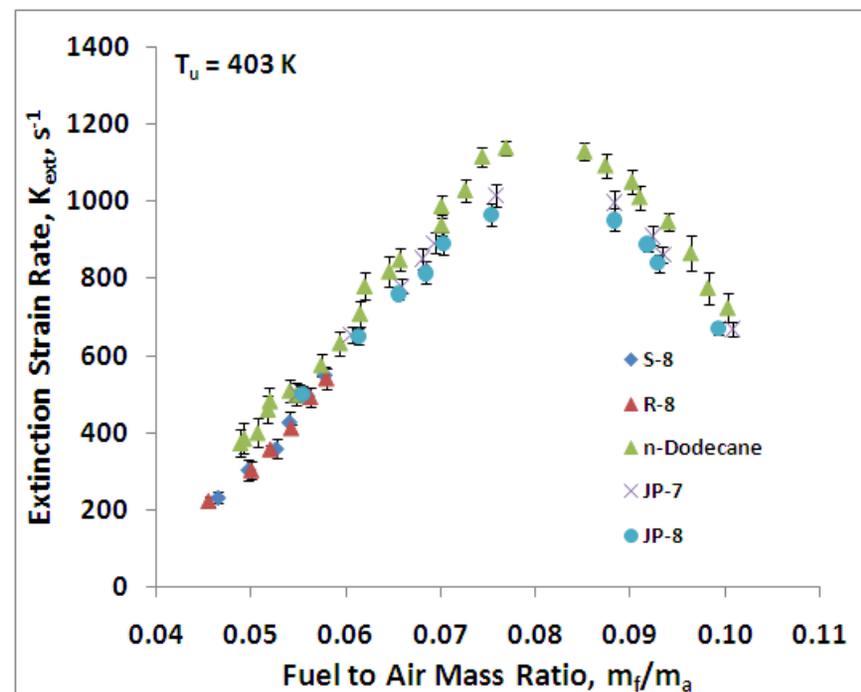
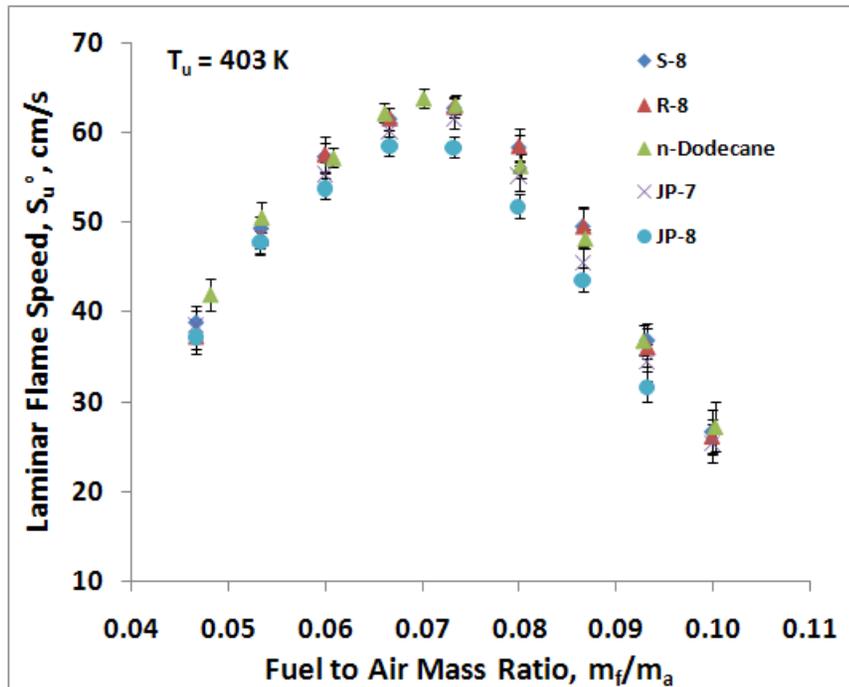
# A wide range of data was collected at USC for fuel comparison and model validation

- **Laminar flame speeds**
- **Laminar flame extinction strain rates**
- **NO<sub>x</sub> in premixed flames**
- **Ignition temperature for premixed flames**
  
- **Data was collected for real jet fuels and surrogate components**



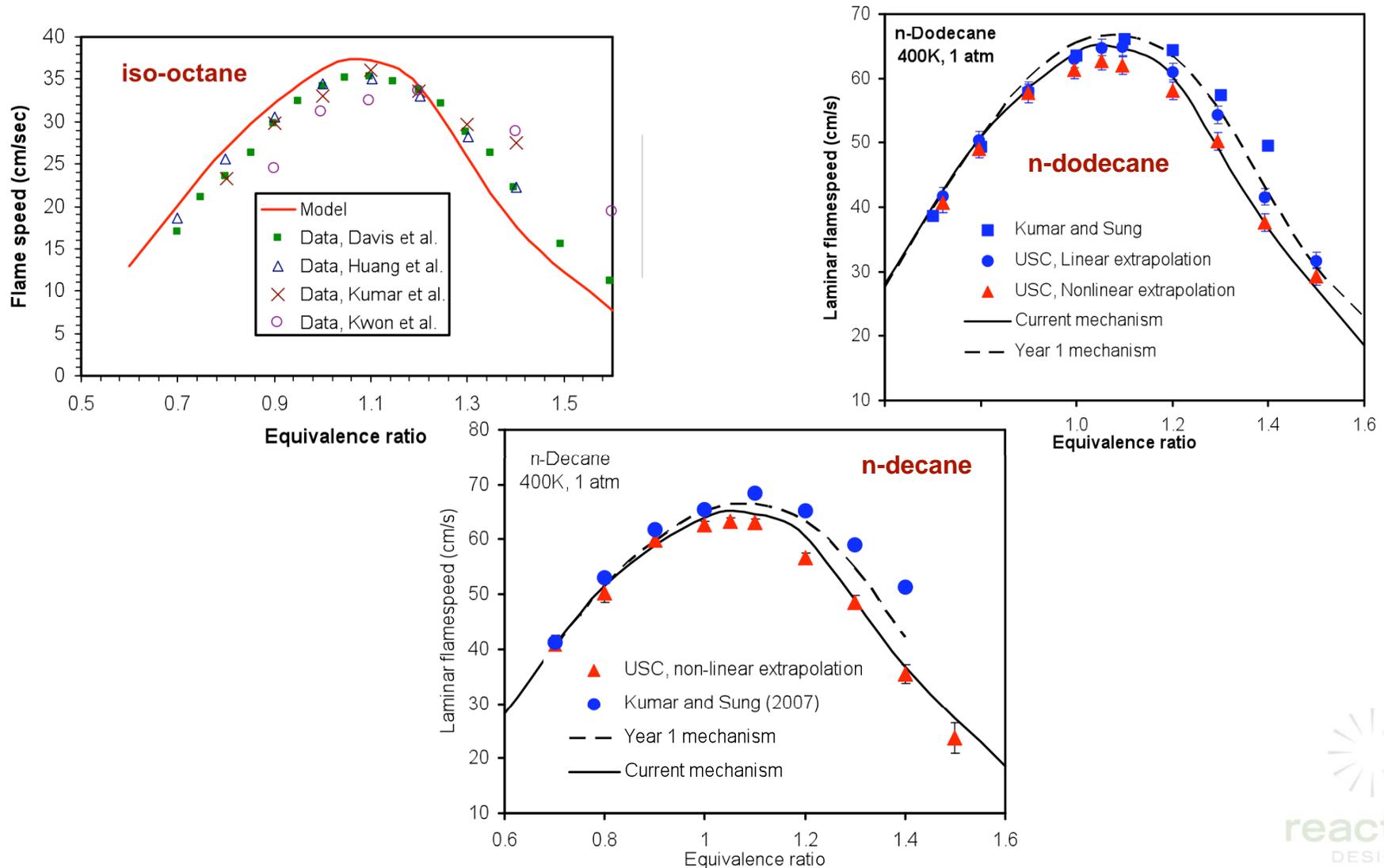
# Results show strong similarity between fuels for flame propagation and extinction

- **JP-7, S-8, R-8 and n-dodecane give same flame speeds**
  - JP-8 is slightly lower
- **JP-7, S-8, R-8 show the same extinction strain rates**
  - n-dodecane is slightly higher



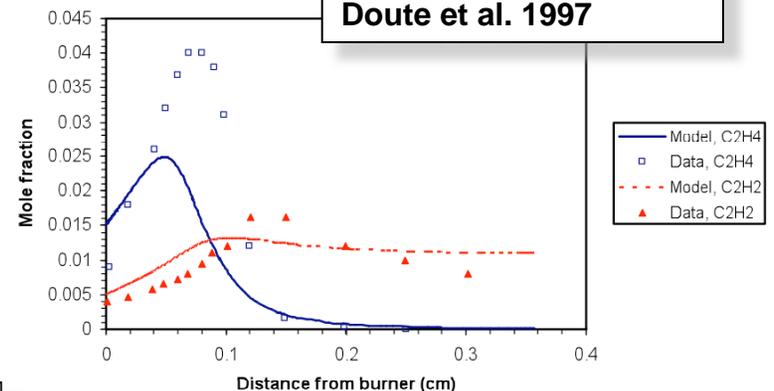
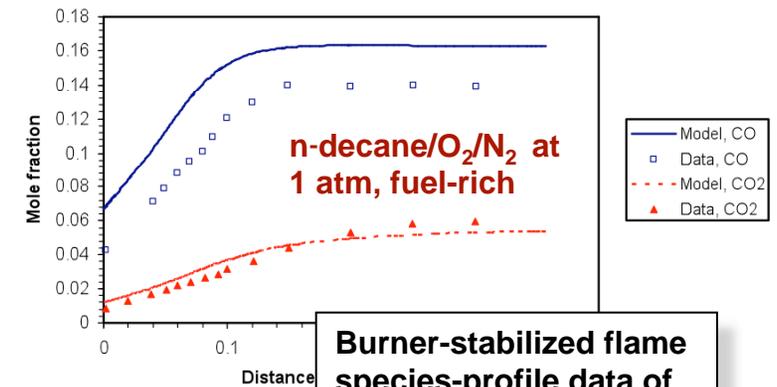
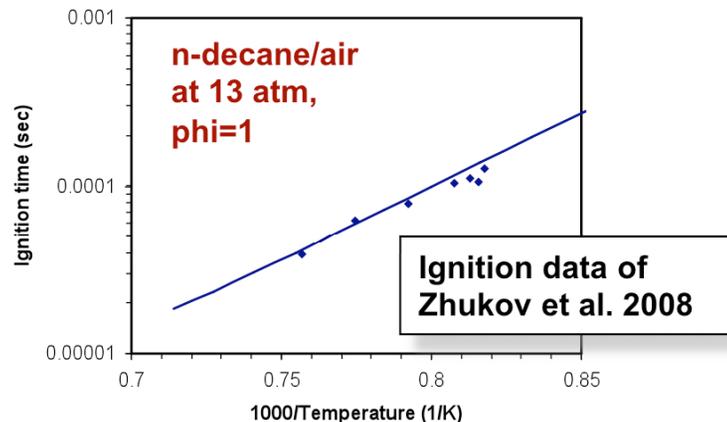
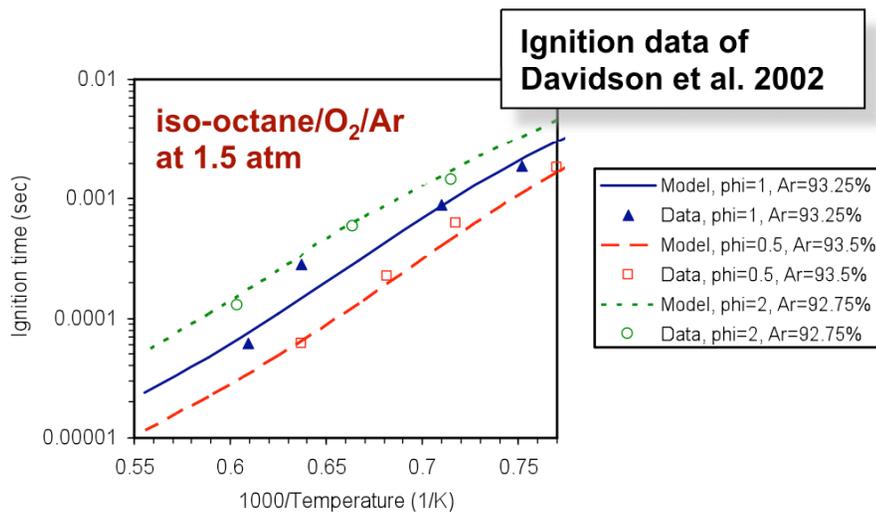
# We performed a large number of simulations to validate our chemistry model

## ● Laminar flame-speeds for three surrogate components:



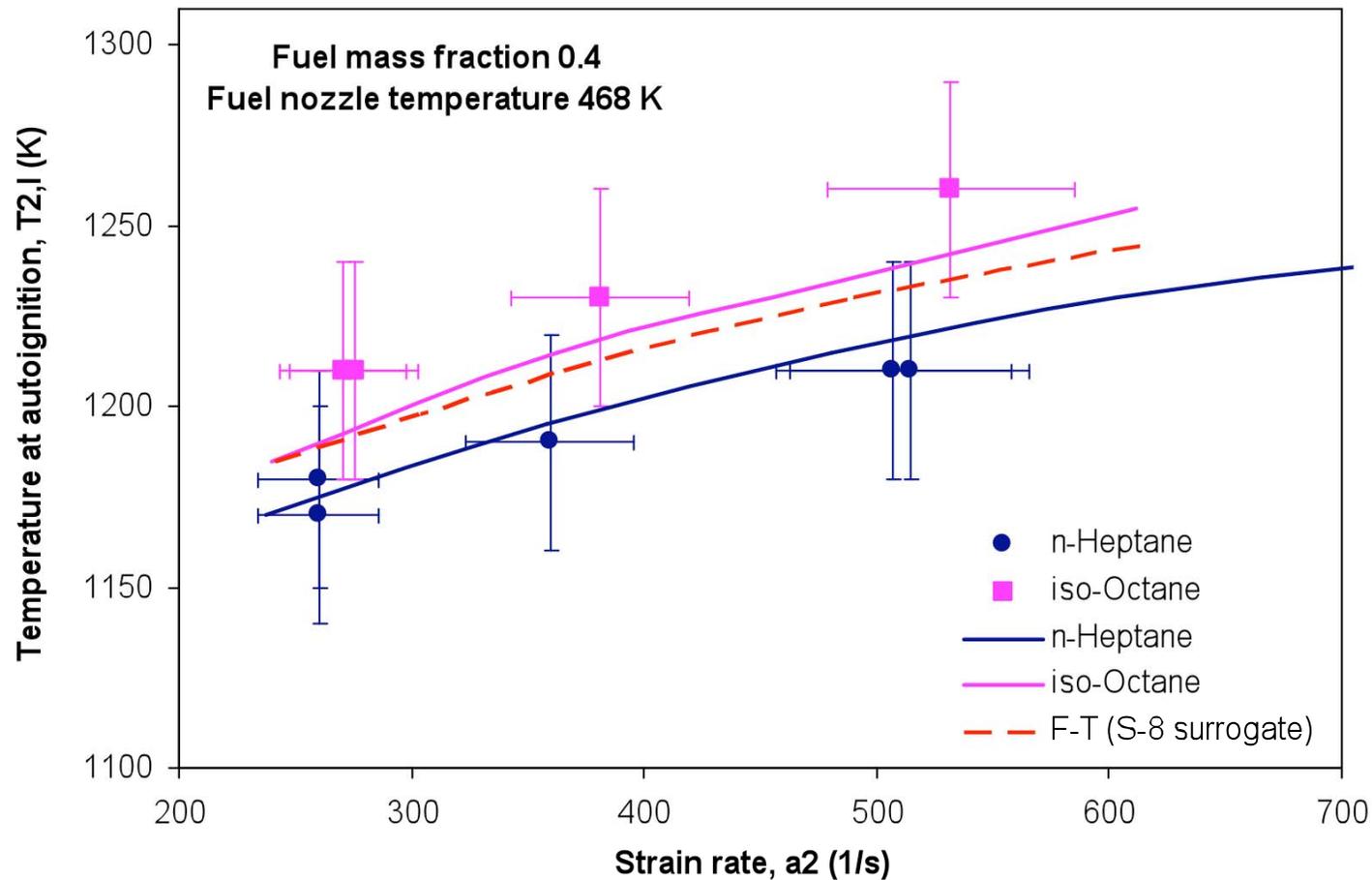
# We compared the model to literature data, as well as to USC flame data

- Ignition-delay time and species profiles in flames for surrogate-fuel components



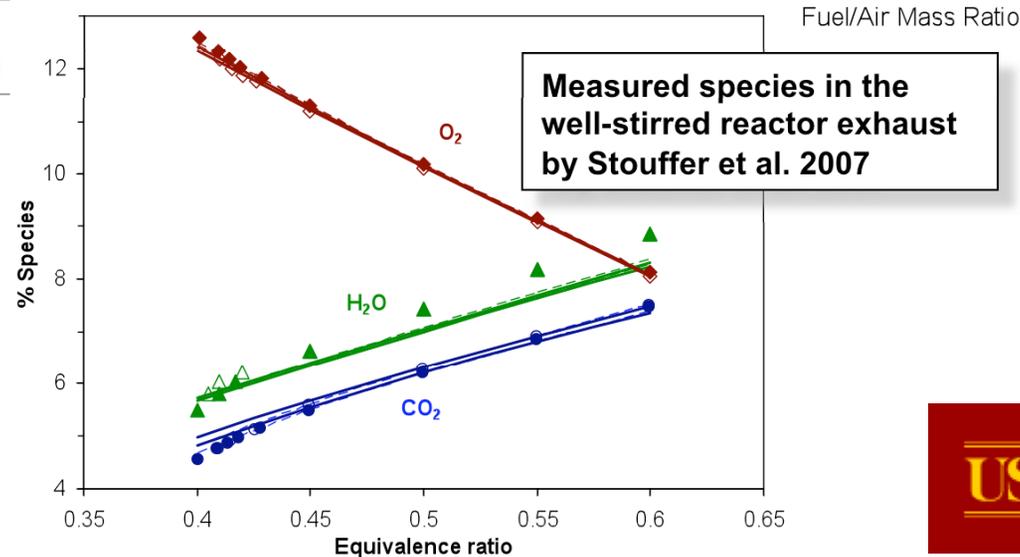
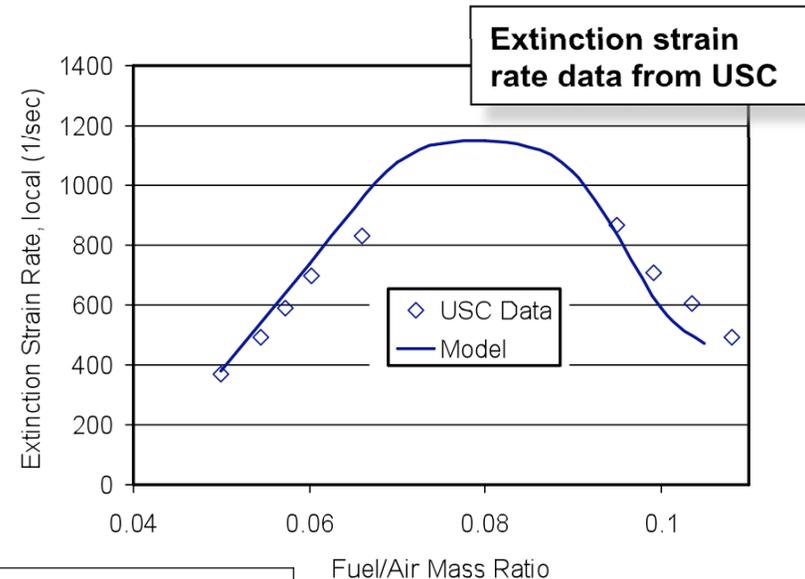
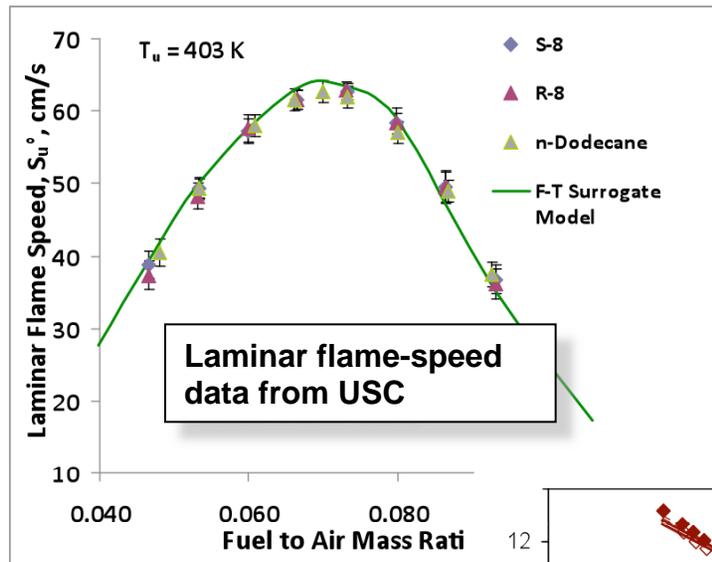
# We also looked at very recent ignition temperature measurements

- Data from Bieleveld et al. 2009



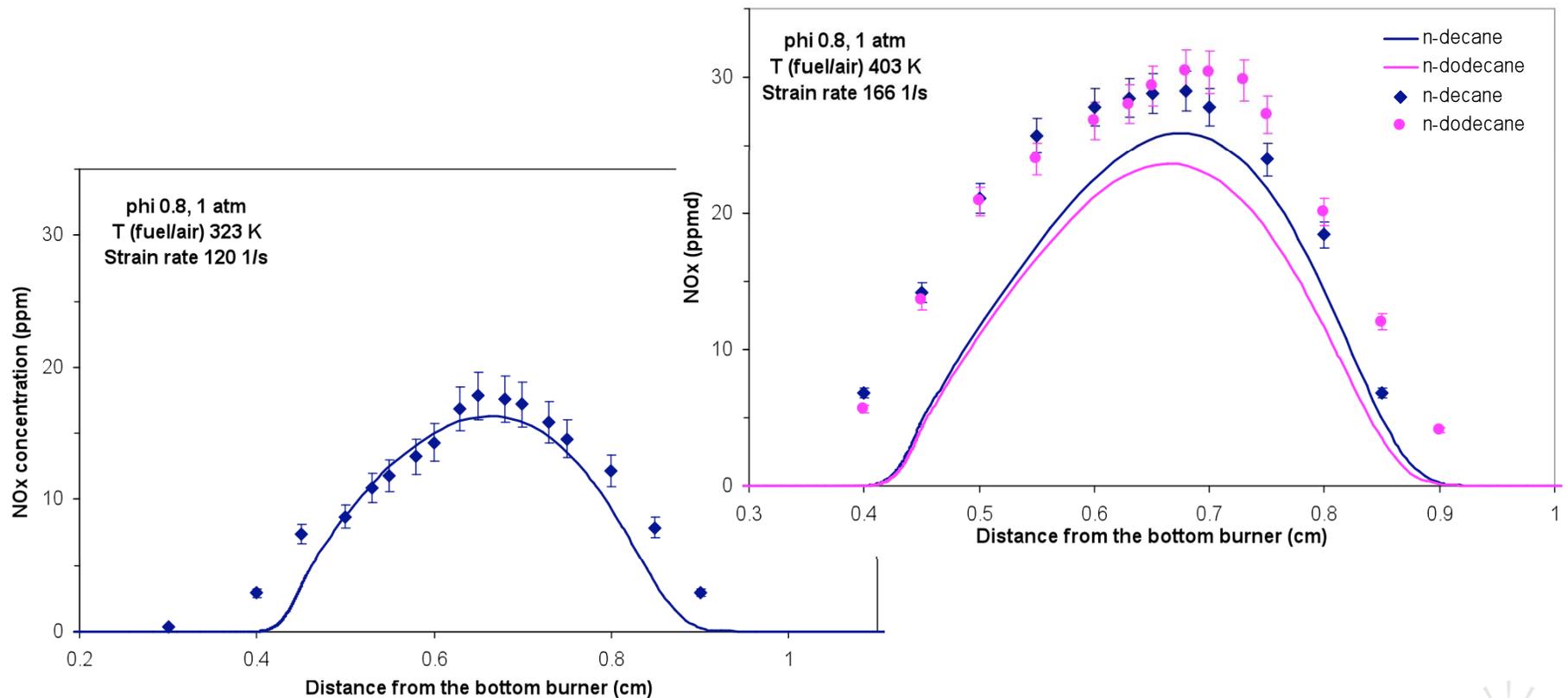
# Comparisons of the surrogate model with F-T fuel data show good agreement

- Flame-speed, flame-extinction, and species data for F-T fuel sample, S-8



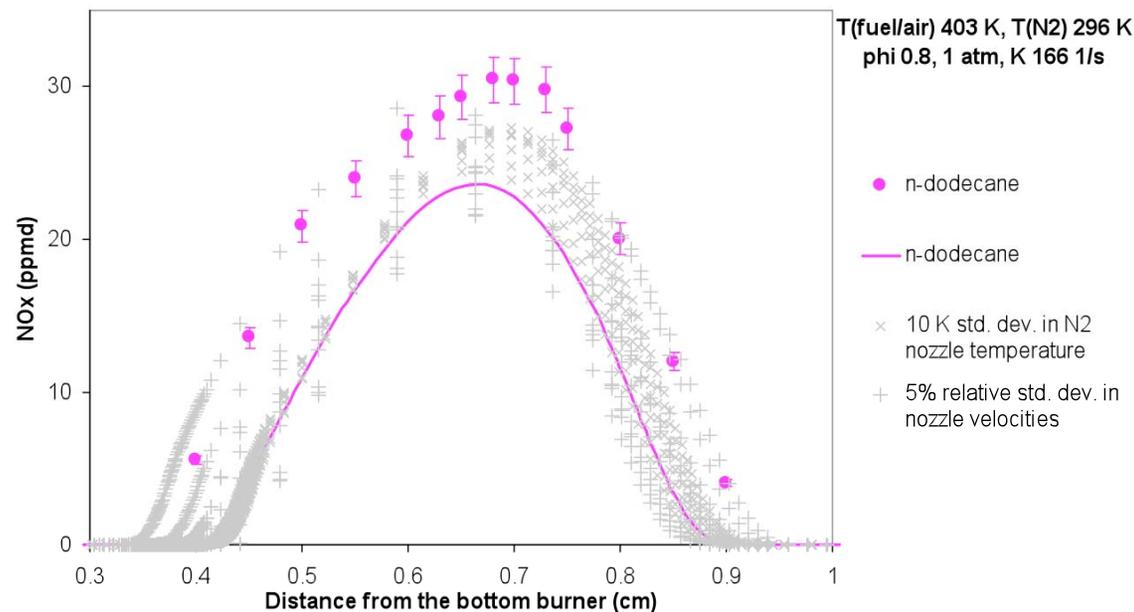
# The $\text{NO}_x$ sub-mechanism has also been tested against USC flame data

- Agreement not as good for larger hydrocarbons



# Uncertainty and reaction path analysis suggest discrepancy may be due to data

- Reaction path analysis show same dominant reactions under both conditions
- Uncertainty analysis suggests small perturbations in velocity or temperature measurements could account for difference

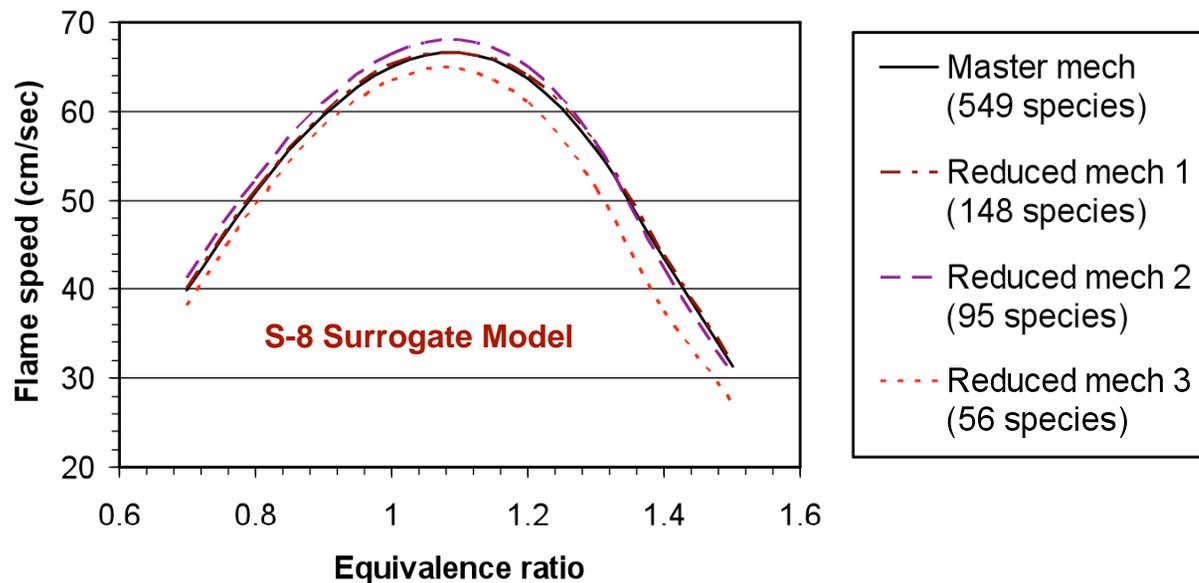


# Two automated mechanism-reduction methods in CHEMKIN have been tested

- **Directed Relation Graph (DRG) method**
  - Produces skeletal mechanism
  - Maintains original rates and species identity
- **Computational Singular Perturbation (CSP) method**
  - More severe reduction, based on quasi-steady assumptions
  - Global, lumped reactions solved for active species
  - Algebraic set of equations solved for non-active species
  - Requires skeletalization (DRG) as preliminary step in reduction
- **Both methods are fully integrated into a (pre-release) version of CHEMKIN-PRO**

# Results show that accuracy can be maintained with about 85% reduction

| Mechanism                             | # of species after DRG reduction | # of species after subsequent CSP reduction |
|---------------------------------------|----------------------------------|---|
| Master mechanism contains 549 species |                                  |   |
| Reduced mech 1                        | 174                              | 148   |
| Reduced mech 2                        | 95                               | 95 (no CSP applied)                         |
| Reduced mech 3                        | 64                               | 56  |



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# Conclusions (1 of 2)

- **Comparing F-T fuels to bio-derived jet fuels, we find no difference in behavior**
- **Despite differences in the C# distribution for two F-T fuels, the flame speed & extinction were the same**
  - Long-chain normal alkanes > C6 have similar flame behavior
  - Still may be important to distinguish for NO<sub>x</sub> emissions
- **Comparing F-T fuels with JP-7 and JP-8, we found that the F-T fuels have same laminar flame-speed as JP-7**
- **n-dodecane also shows similar flame behavior as F-T**
  - This is a reasonable 1-component surrogate for flame-speed and extinction behavior only
  - Need more complex surrogate for other fuel properties and emissions

## Conclusions (2 of 2)

- **Our chemistry model underwent much improvement during the course of the project**
  - Flame-speed, flame-extinction, ignition and  $\text{NO}_x$  predictions are within experimental uncertainty
- **A 3-component fuel surrogate for the F-T and bio-derived jet fuels matches data well**
  - n-dodecane, n-decane, iso-octane
- **Automated mechanism reduction provides a practical model for use with CFD**
- **The chemistry models are available and will be published with NASA's approval**
- **A new CHEMKIN-based extinction model is currently in beta testing**