An Improved Reaction Mechanism for Combustion of Core (C_0-C_4) Fuels

reaction DESIGN

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LEADING THE WAY TO CLEAN COMBUSTION DESIGN

Outline

- Why core hydrocarbons?
- Issues with existing reaction mechanisms
- Modeling approach
- Extensive model validation
- Concluding remarks

Core hydrocarbons include all gaseous fuels

- **Natural gas**
  - 425,000 wells in the US
  - 105 trillion cubic feet worldwide
- **Syngas, coal gas**
  - From gasification of coal, biomass
  - In-situ coal gasification
- **Biofuels**
  - Ethanol, butanol
- **H_2, C_1-C_4 hydrocarbons**
  - Selected oxygenates

Natural gas well, 1907.

A coal-gas powered taxicab in England, 1920.

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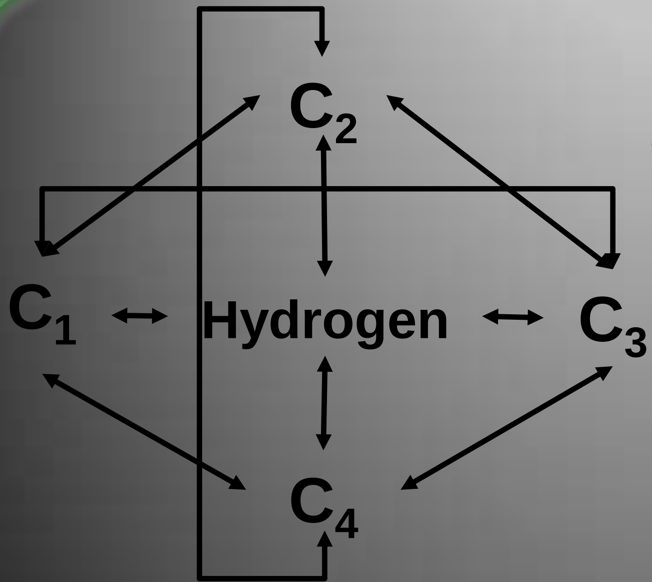
Core hydrocarbons chemistry is core to heavier liquid fuels



Oxygenated species

NO_x chemistry

Unsaturated species

PAH precursors

Liquid hydrocarbon combustion and emissions

Outline

- What are core hydrocarbons?
- **Issues with existing reaction mechanisms**
- Modeling approach
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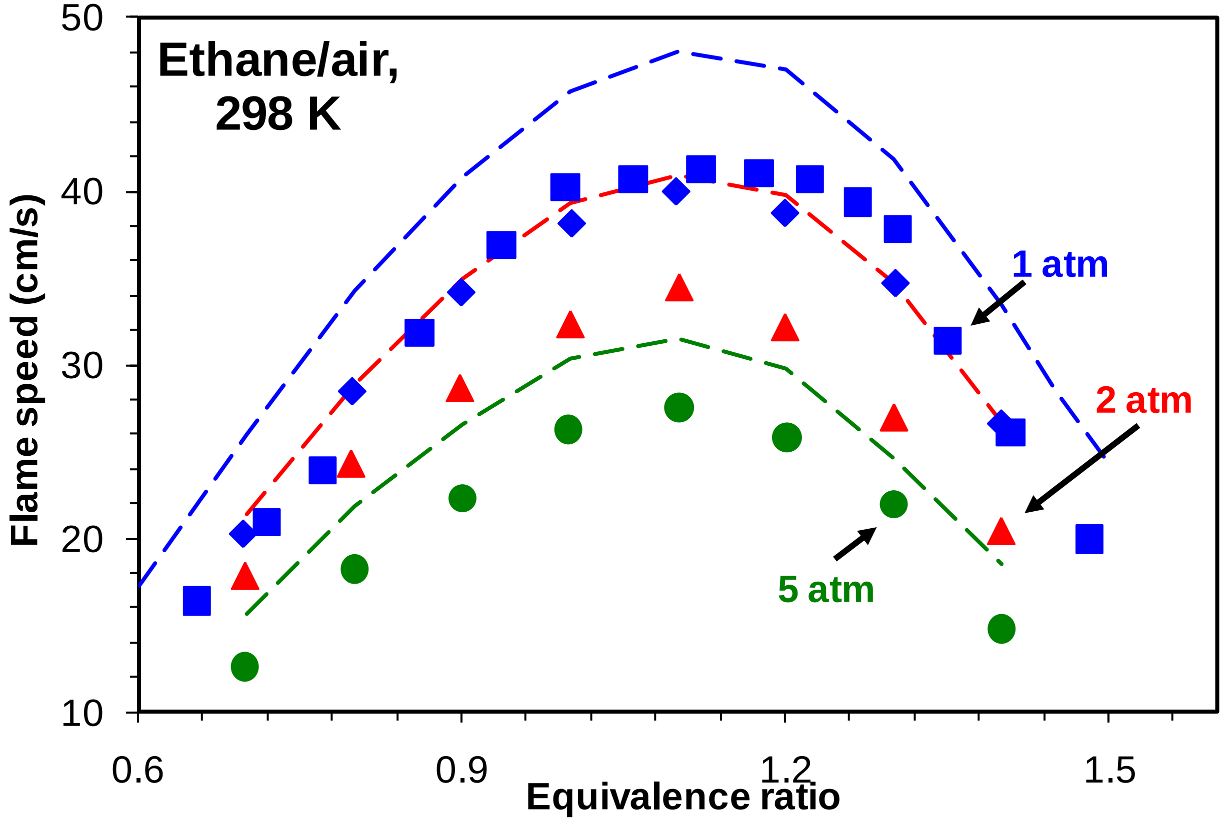
Typical issues with many existing reaction mechanisms

1. **Applicability**
   – Not comprehensive enough
2. **Accuracy**
   – Not accurate enough for broad range of conditions
3. **Extensive validation**
   – Limited validation range and types of experiments

Core chemistry in large mechanisms may not be accurate or validated

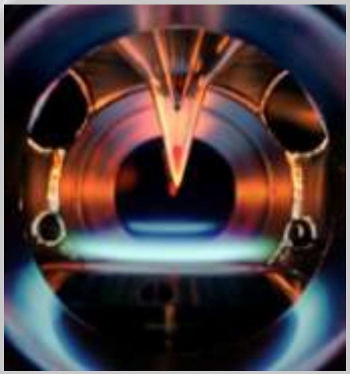


- **LLNL *n*-heptane mechanism overpredicts ethane flame speeds**

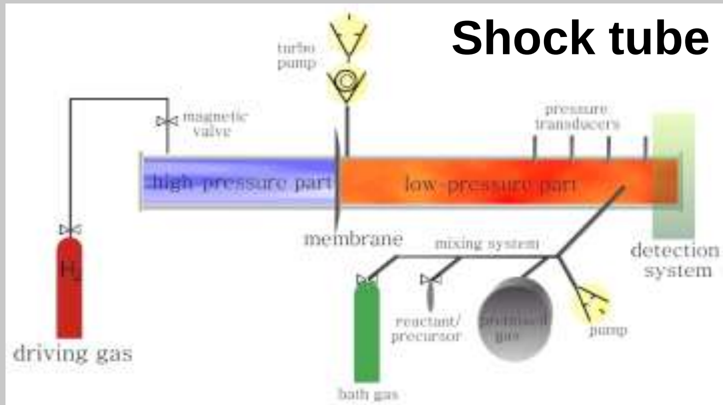
Data from Jomaas et al. 2005

- **Predictions for unsaturated components are worse**

Often mechanisms are validated for one or two types of experiments



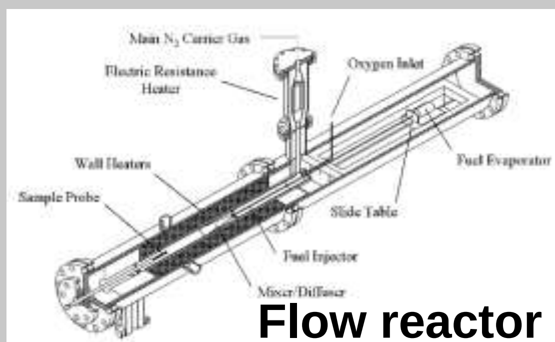
Laminar flames



Shock tube

Stirred reactor

RCM



Flow reactor

Opposed-flow reactor

- **Together they cover the conditions in practical applications (engines, turbines)**

Legacy fuel models are not suitable for applications at high-P and low-T

Natural Gas Components	Composition
Methane	70-90 %
Ethane, Propane, Butane	0-20 %
CO_2	0-8 %
N_2, H_2S	0-5 %

Core hydrocarbons (C_0-C_4)

– GRI-mech limited to methane

Complex Negative Temperature Coefficient (NTC) behavior <1000 K

– Autoignition of fuels critical for engines and turbines

Existing core mechanisms may not be comprehensive

- **Dependencies between various small species**
  - e. g. ethylene chemistry also involves C_4 species
  - e.g. $CH_4 \longleftrightarrow CH_3 \overset{O_2}{\longleftrightarrow} CH_3O\bullet$, $CH_3O\bullet \overset{H}{\longleftrightarrow} CH_3OH$, $CH_3O\bullet \overset{CH_3}{\longleftrightarrow} CH_3OCH_3$
- **Missing components and inconsistencies may affect *predictive* nature**
  - Be careful in merging various mechanisms

Need comprehensive, accurate, and validated core reaction mechanism

Outline

- What are core hydrocarbons?
- Issues with existing reaction mechanisms
- **Modeling approach**
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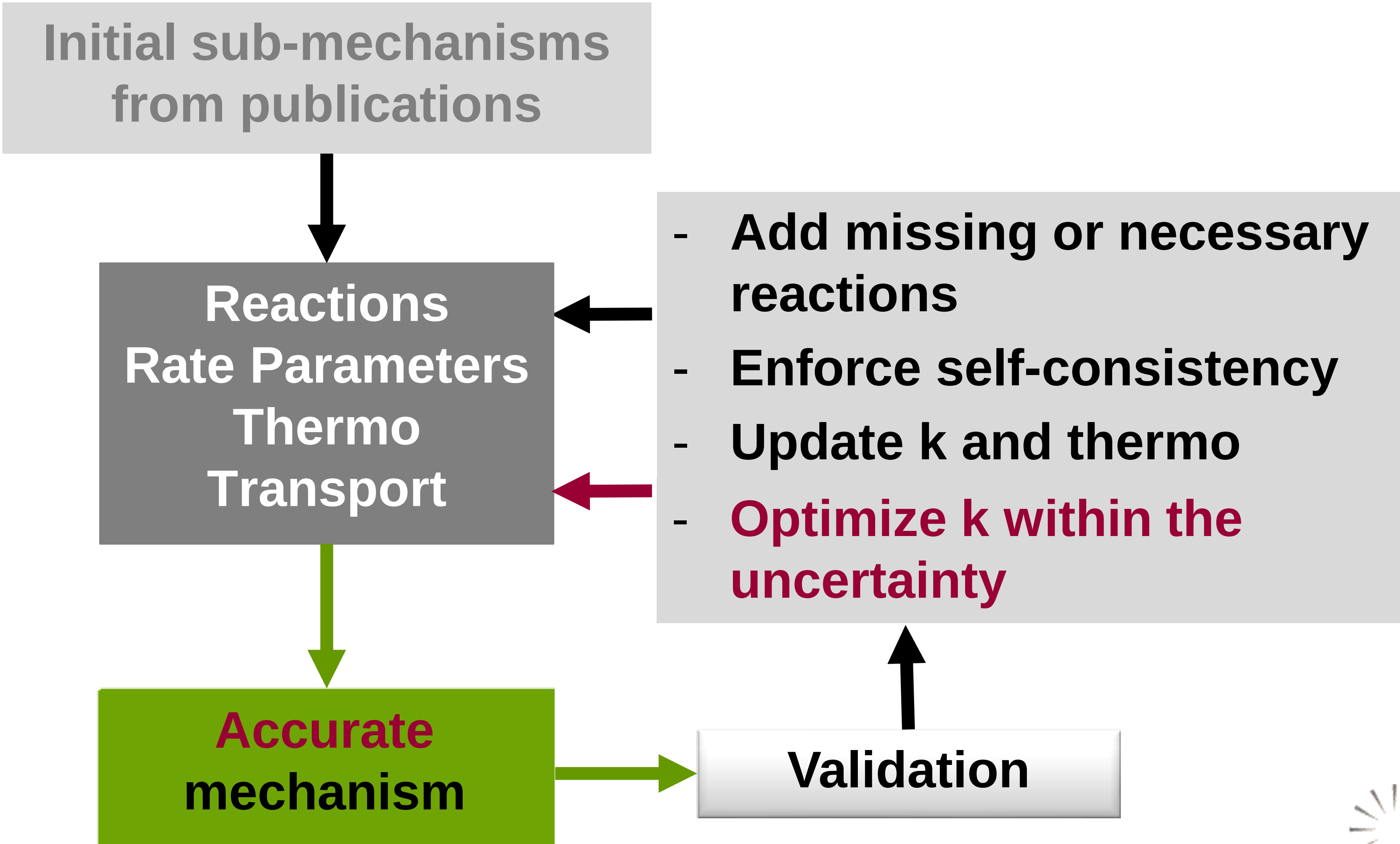
The mechanism is generated in a systematic way



RD2010 core mechanism is comprehensive

- **Starting component sub-mechanisms from various sources**
  - Merged to a consistent base
- **Included low- and high-temperature pathways**
- **Updated rate constants based on recent studies**
  - Pressure-dependent rate constants for important reaction systems
- **18 fuel components**
  - 1161 species and 5622 elementary reactions
  - Saturated, un-saturated, oxygenates
  - NO_x, soot precursors up to benzene

The core mechanism is optimized for accuracy

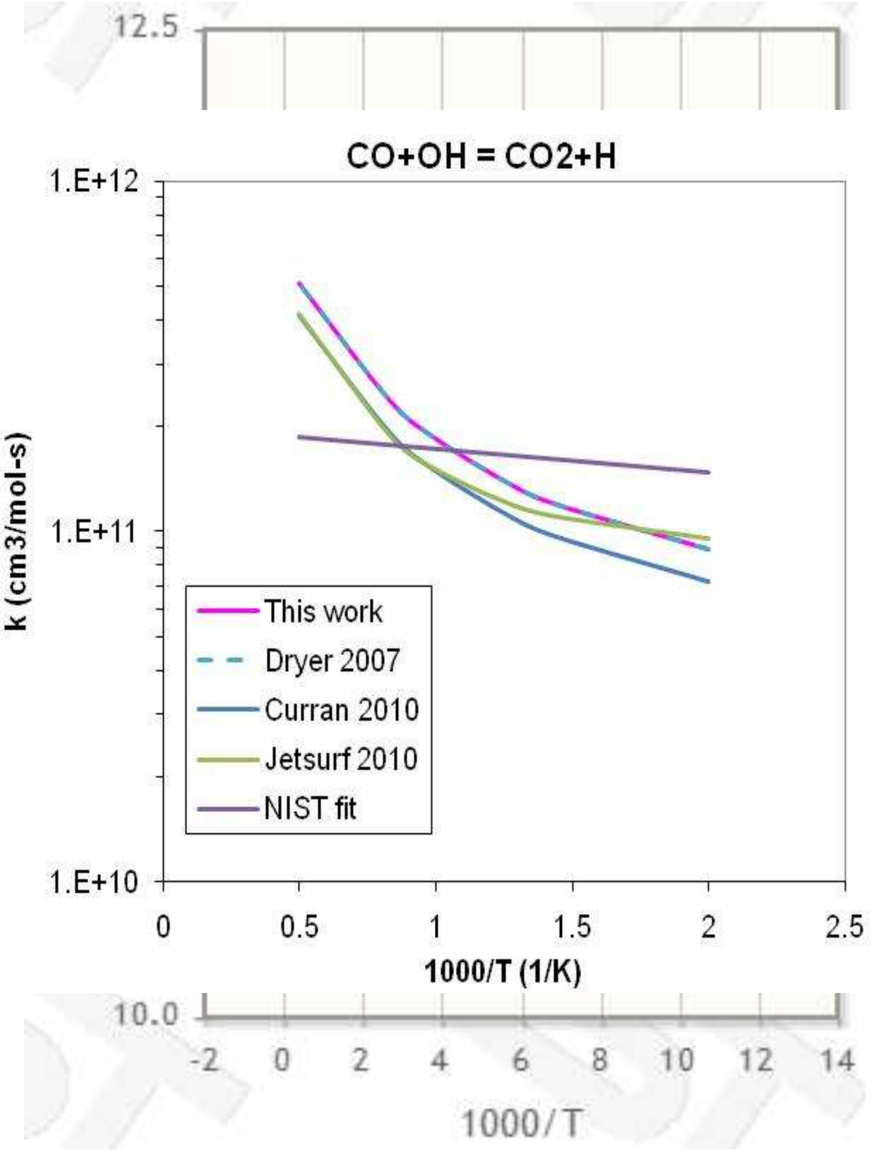
- **Optimized rate constants for less than 5% of the reactions**
  - Within the expected uncertainty

Reaction	A	n	Ea	Ref.
$H+O_2 = O+OH$	3.55E+15	-0.406	1.66E+04	[12]
$CO+OH = CO_2+H$	2.20E+05	1.89	-1.16E+03	[12], A*1.24
$HCO+M = H+CO+M$	4.75E+11	0.7	1.49E+04	[11][a]
$H+OH+M = H_2O+M$	4.50E+22	-2	0.00E+00	[19][a]
C_3H_5-a+H(+M) = C_3H_6(+M)	2.00E+14	0	0.00E+00	[13]
Low pressure limit:	1.33E+60	-12	5.97E+03	
Troe parameters: 0.02, 1.10E+03, 1.10E+03, 6.86E+03				
CH_3+CH_3(+M) = C_2H_6(+M)	9.21E+16	-1.17	6.36E+02	[12][a]
Low pressure limit:	1.14E+36	-5.246	1.71E+03	
Troe parameters: 0.405, 1.12E+03, 69.6, 1.00E+10				
$CH_3+HO_2 = CH_3O+OH$	1.00E+12	0.269	-6.88E+02	[12]
$CH_4+H = CH_3+H_2$	6.14E+05	2.5	9.59E+03	[12]
$HO_2+HO_2 = H_2O_2+O_2$	4.20E+14	0	1.20E+04	[18][b]
	1.30E+11	0	-1.63E+03	
$CH_4+HO_2 = CH_3+H_2O_2$	1.13E+01	3.74	2.10E+04	[12]
Collision efficiencies: CH_4 2.0, CO 1.9, CO_2 3.8, C_2H_6 3.0, H_2O 6.0, H_2 2.0, Ar 0.7				

Example of the CO+OH = CO_2+H rate constants

- **118 records in the NIST database**
  - 91 experimental data
  - 20 theoretical calculations
  - 7 review recommendations
  - 1981-2007 data fit
    - k = 2e11 * exp(-300/RT)

- **Recent data**
  - Agree within 25%
- **Typical uncertainty ~ factor of 2**



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Fundamental data are the best for reaction mechanism validation

- **Reduced impact of transport ➔ More focus on chemistry**

11 saturated fuel components

Neat fuels	Laminar flame speed	Shock tube	Flow reactor	Stirred reactors	Burner flames
Hydrogen	√*	√			
Formaldehyde			√		
Methane	√	√		√	
Methanol				√	
Ethane		√		√	
DME	√	√	√		
Ethanol	√				
Propane	√				
n-Butane	√	√			
iso-Butane		√			
n-Butanol	√	√		√	
NOx				√	√

Broad range of conditions covered

- **Saturated fuels**

Experiment type	T (K)	P (atm)	ϕ	Dilution of oxidizer %*
Laminar flame speeds	295 to 453	1 to 5	0.6 to 1.6	0 to 15
Shock-tubes	650 to 1800	1 to 340	Pyrolysis, 0.3 to 3	0 to >98
Flow reactors	500 to 948	1.5 to 12.5	0.005 to 1.19	97.6 to 98.8
Stirred reactors	700 to 1100	1-10	0.1 to 1	97.1 to 97.9
Burner-stabilized flames	300	1 to 14.6	0.6 to 0.8	N_2/O_2 : 2.2/1 for oxidizer

- **Dilution with N_2, Ar, or H_2O with air or O_2 as oxidizer.**

Broad range of conditions covered for un-saturated components and blends

- **Un-saturated fuels**

Experiment type	T (K)	P (atm)	ϕ	Dilution of oxidizer %
Laminar flame speeds	298	1-5	0.6-2	0-16.5
Shock-tubes	1050-2250	0.85-9	0.5-2	0-97
Flow reactors	700-1350	1	0.05-1.4	97.9-99.7
Stirred reactors	700-1100	1-10	0.1-1.5	96-99.5

- **Fuel blends**

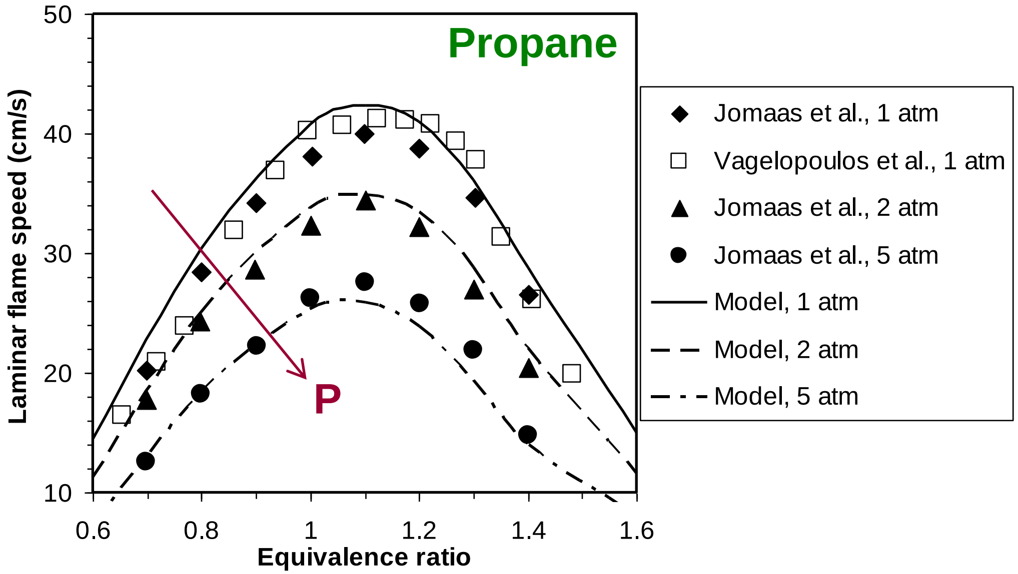
Experiment type	T (K)	P (atm)	ϕ	Dilution of oxidizer %
Laminar flame speeds	298	1-2	0.5-4.5	0-16.5
Shock-tubes	1020-1750	1-256	0.5-3	92-99.9
Stirred reactors	950-1450	1-10	0.3-2	66.1-98.5

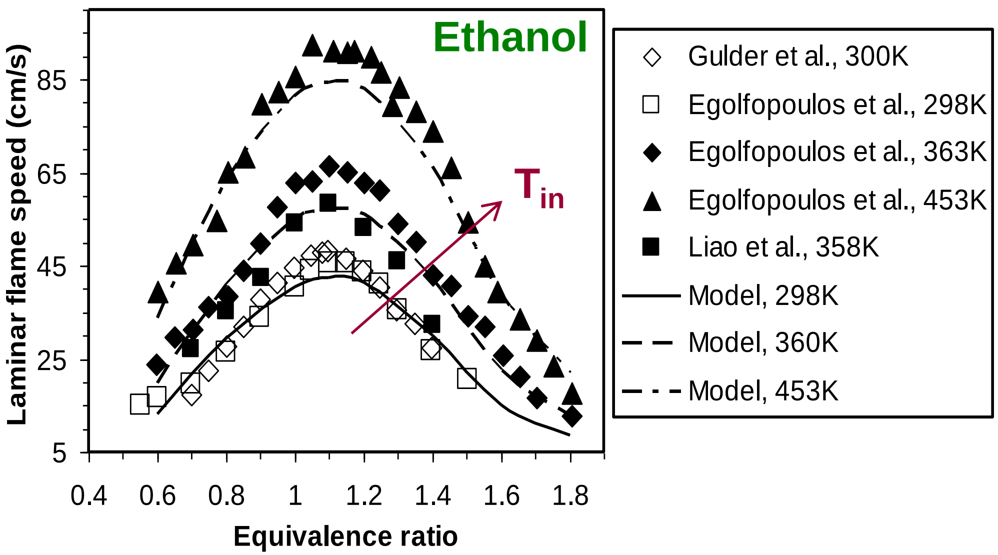
Over 90+ comparison plots for validation

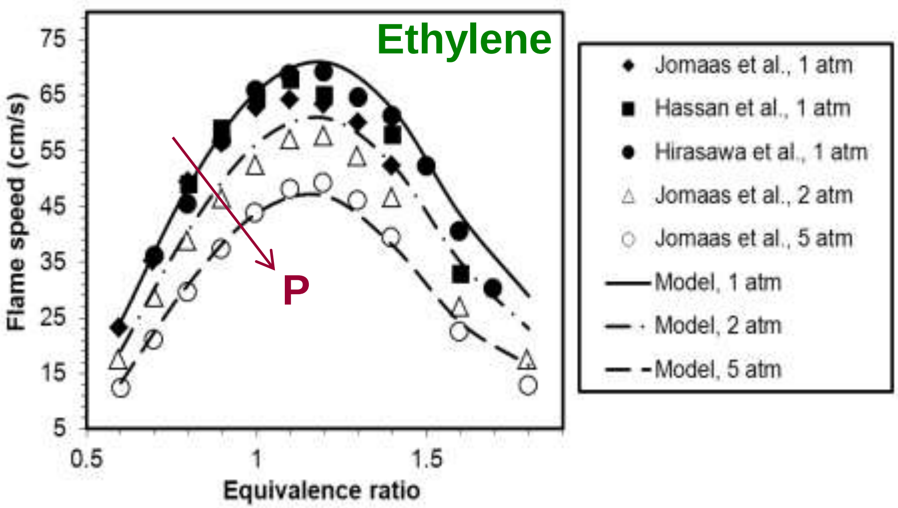
- **A comparison plot contains one or more data sets**
- **Overview of comparisons**
  - Grouped by experiment types
- **Lines – predictions**
- **Symbols – published experimental data**

Laminar flame speeds: Fuel, *T*, *P*, and ϕ effects captured

Fuel/air







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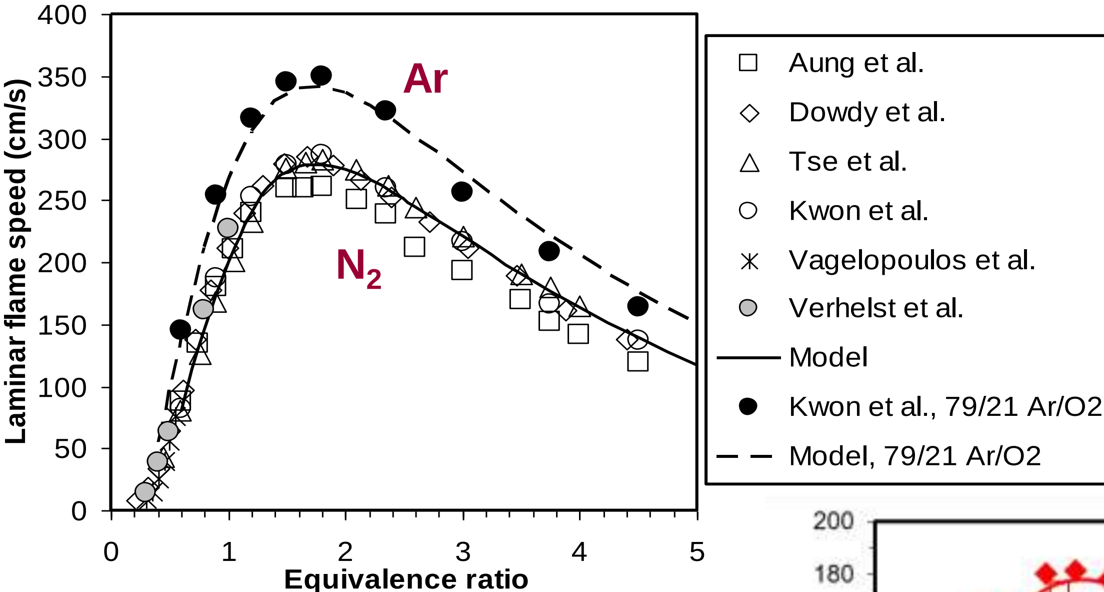
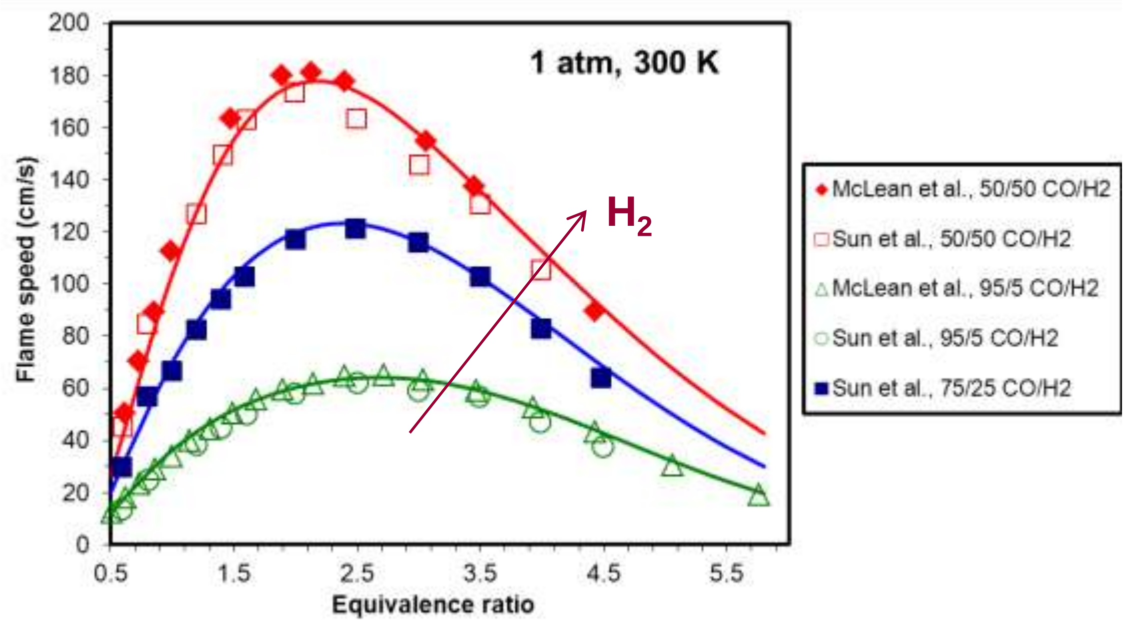
Laminar flame speeds: Diluents and composition effects captured

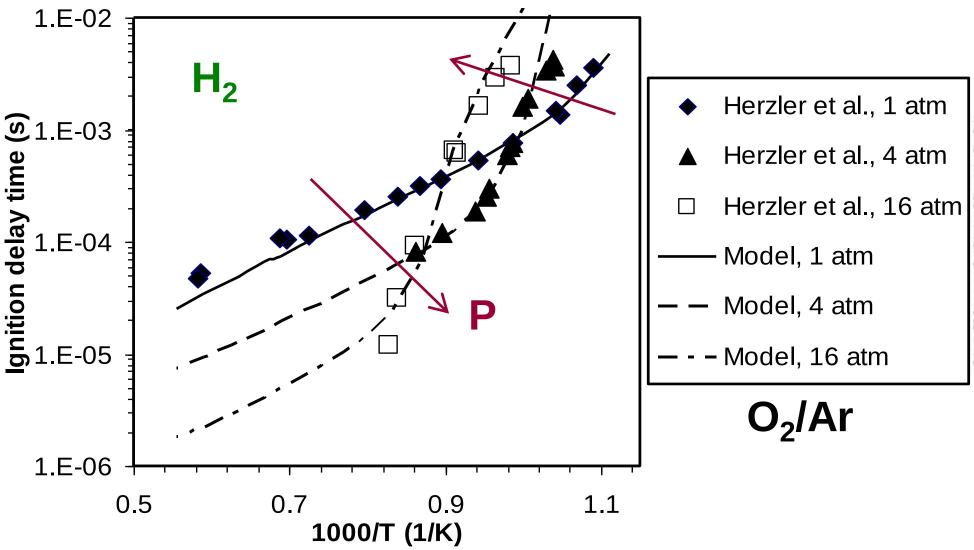


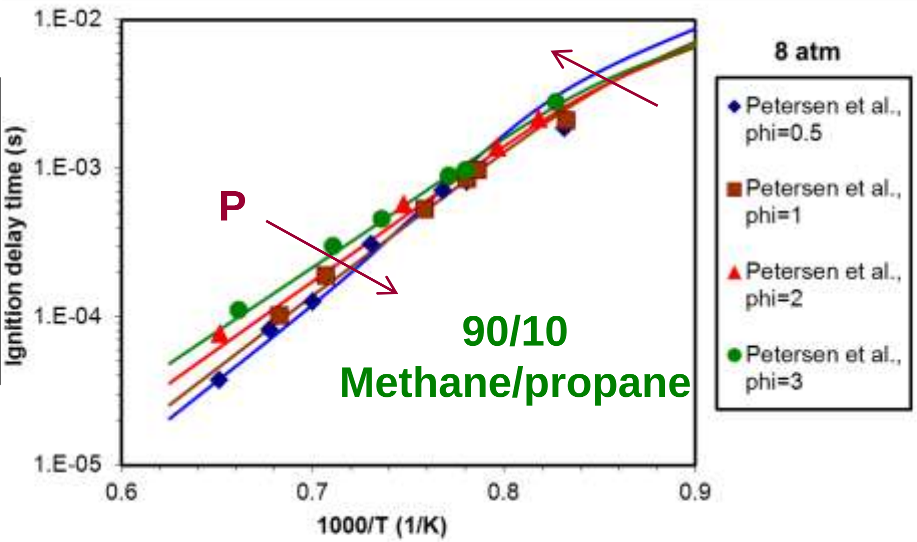
- **H_2 with N_2 or Ar**

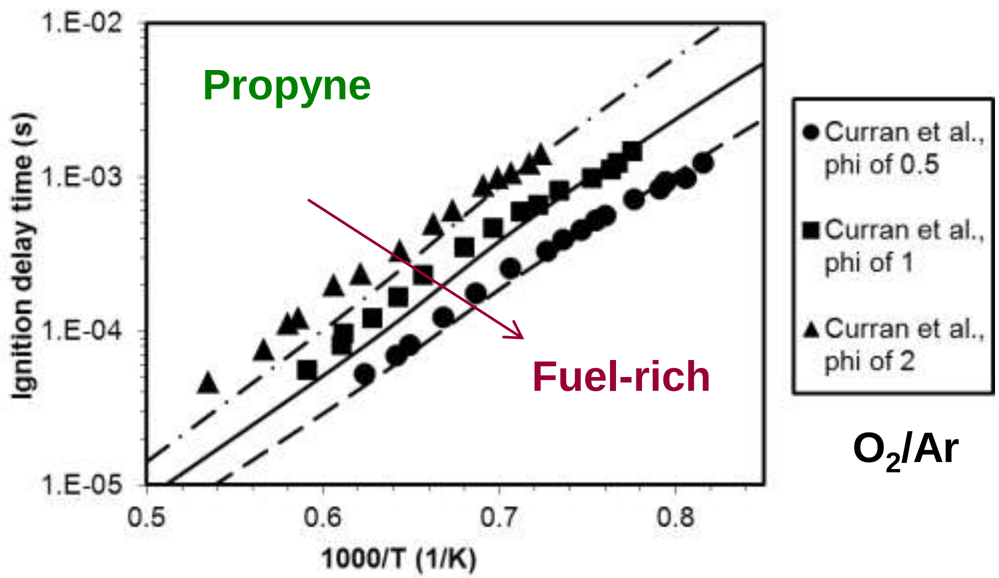


- **Syngas with 50/50 to 95/5 CO/H_2**

Autoignition delay times: Effects of fuel, *T*, *P*, and ϕ captured







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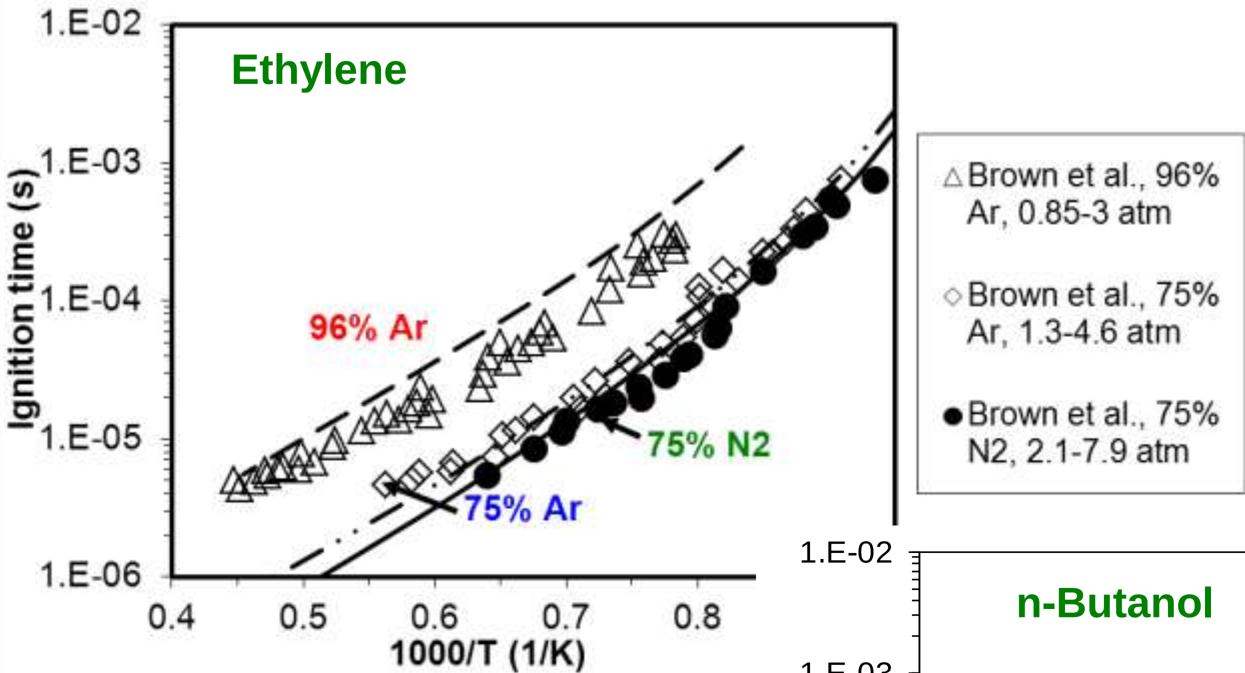
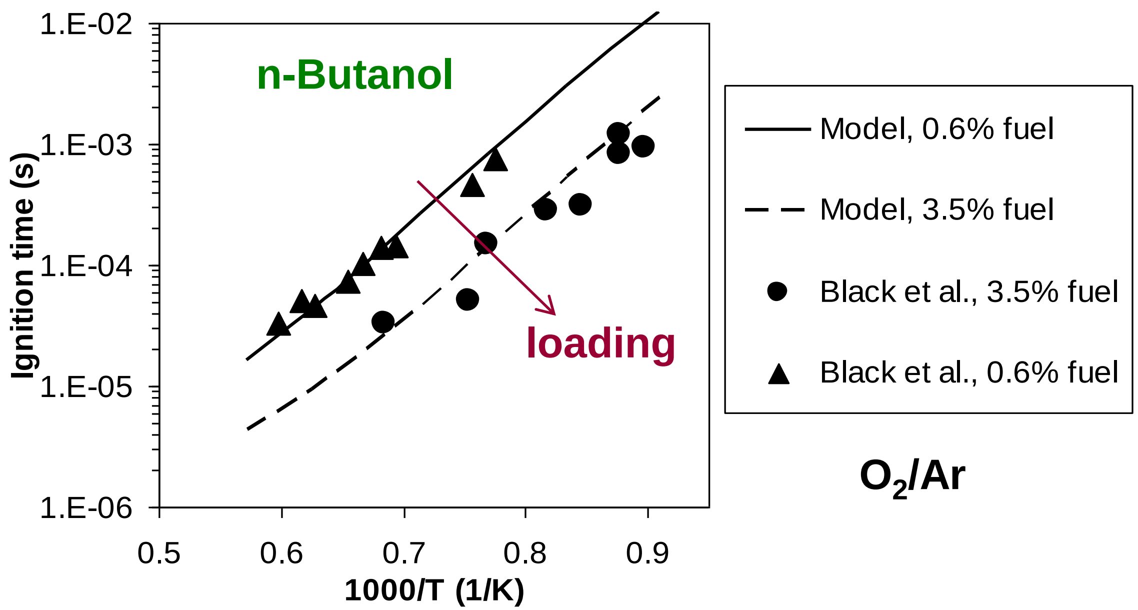
Autoignition delay times: Effects of loading and diluents captured





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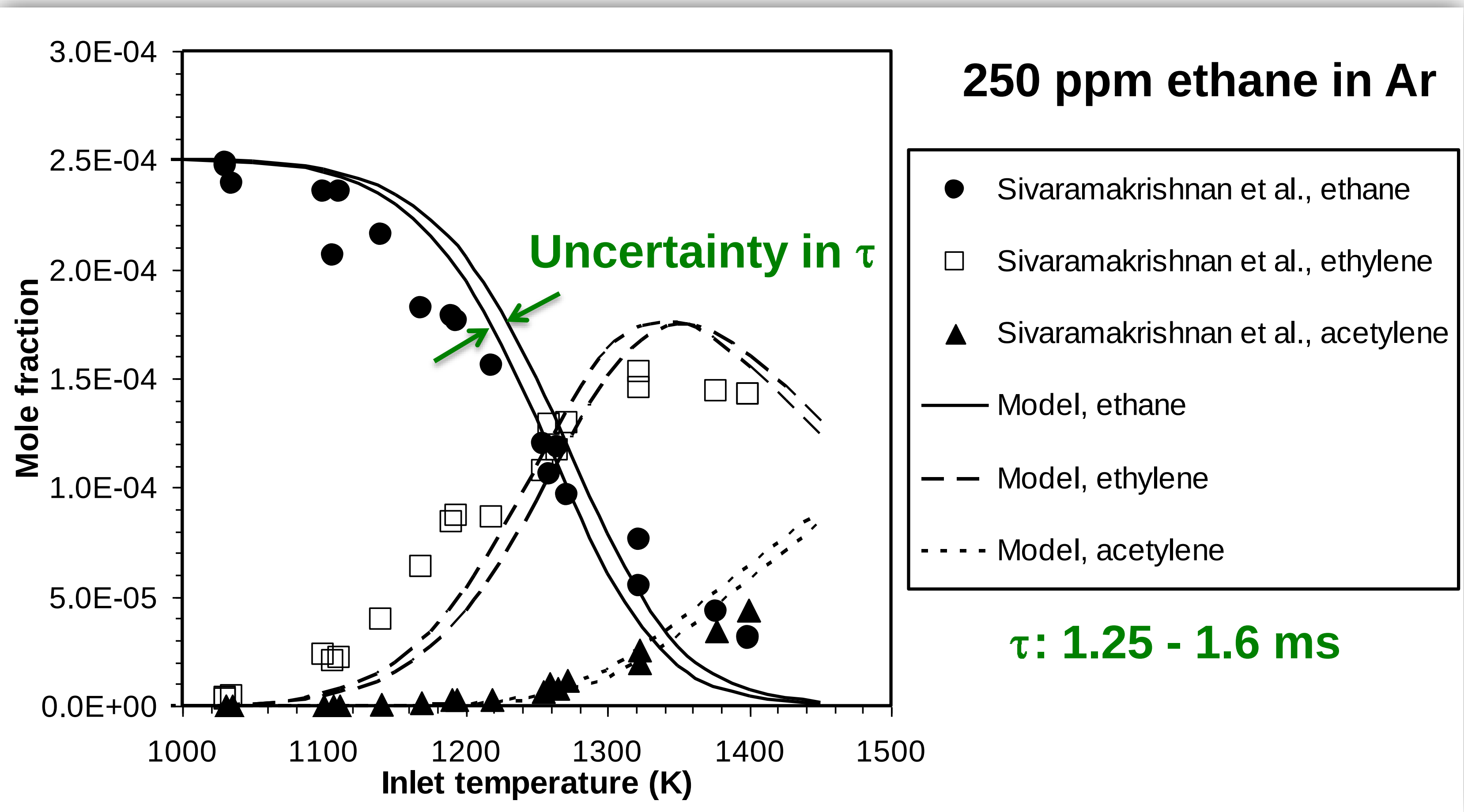
Species profiles: Shock-tube
Accurate predictions at very high pressures



- **Pyrolysis at 340 bar**

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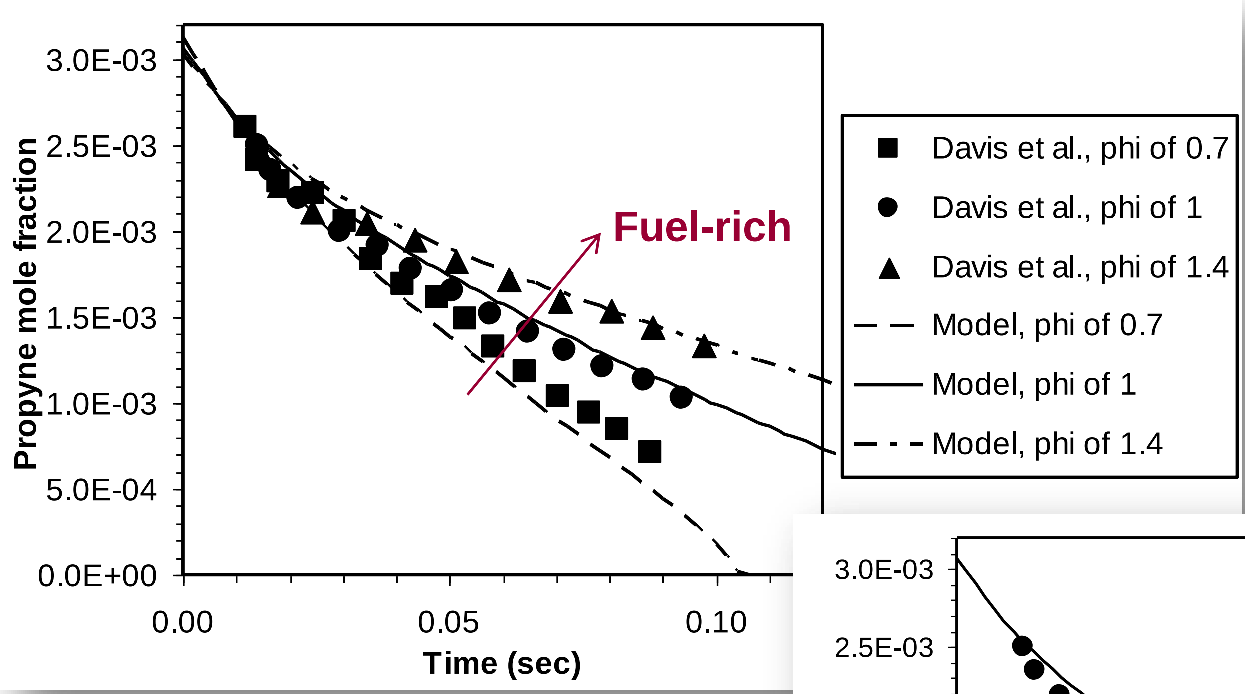
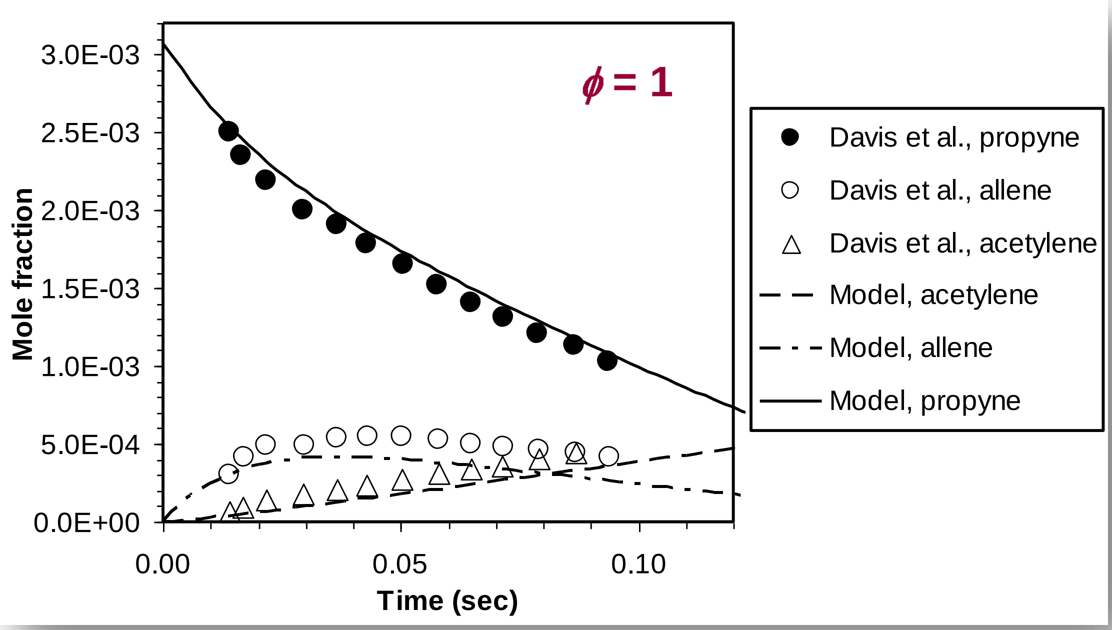
Species profiles: Flow-reactor
Effect of ϕ on propyne oxidation captured

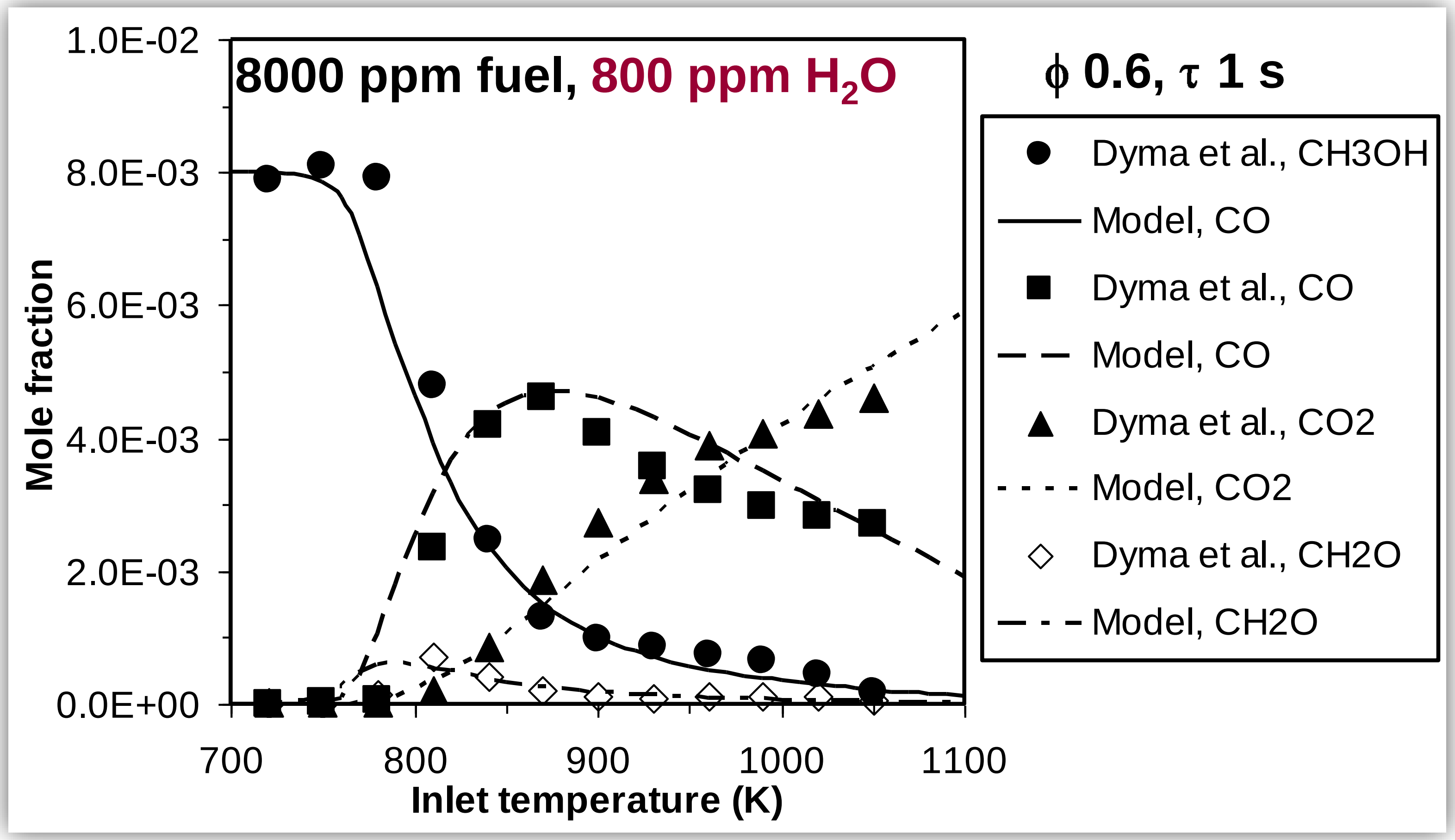


- **1170 K, 1 atm, 0.03% fuel**

- **Products acetylene and allene predicted well**
  - Important PAH precursors

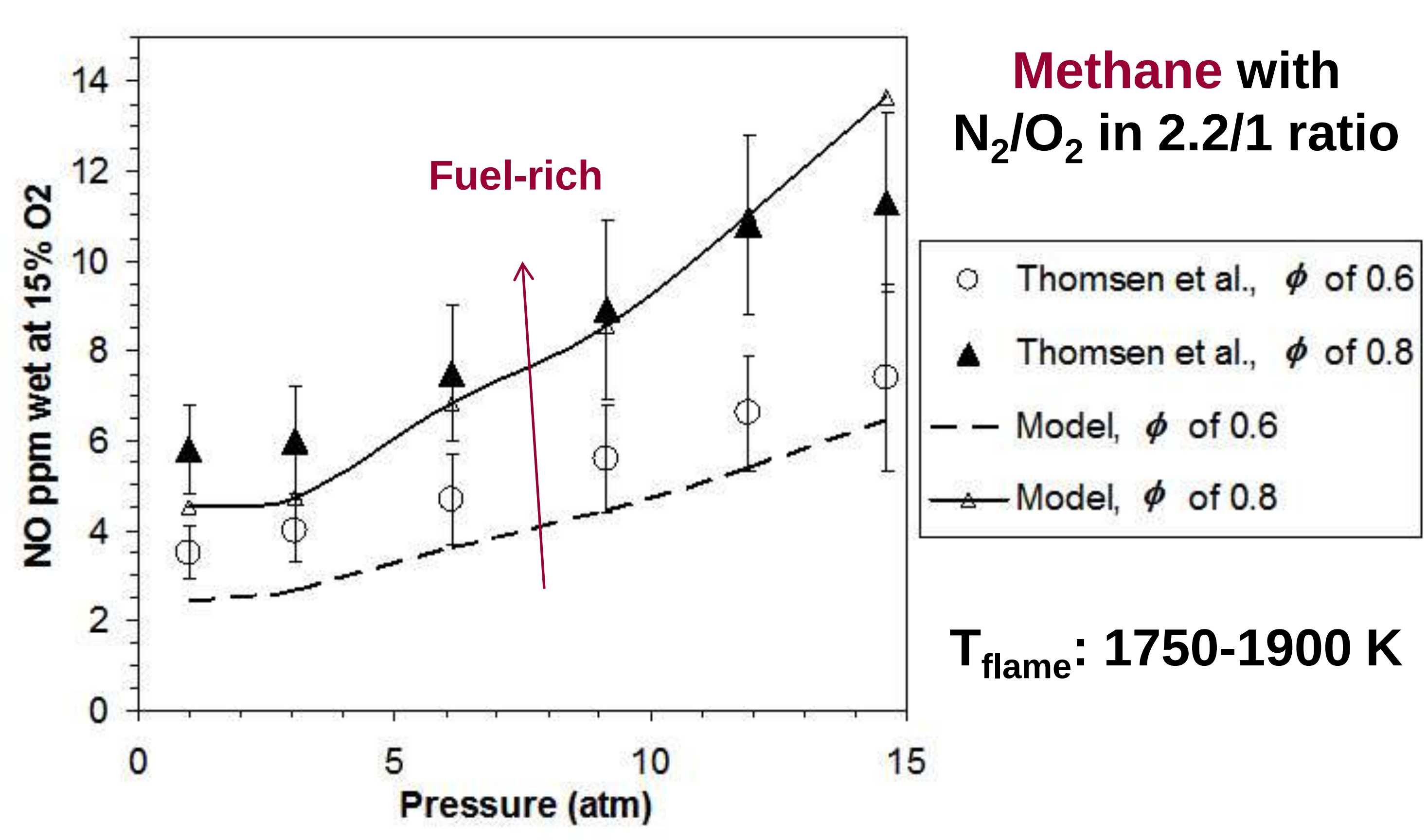


Species profiles: Stirred-reactor
Products evolution in methanol captured



- **Methanol oxidation at 10 atm in a stirred-reactor**

NO_x emissions from premixed flames: Pressure and ϕ effects captured



Methane with N_2/O_2 in 2.2/1 ratio

T_{flame}: 1750-1900 K

- **High-pressure premixed flames**
  - Radiation heat losses included in CHEMKIN-PRO

Outline

- What are core hydrocarbons?
- The problem and our modeling approach
- Extensive model validation
- **Concluding remarks**

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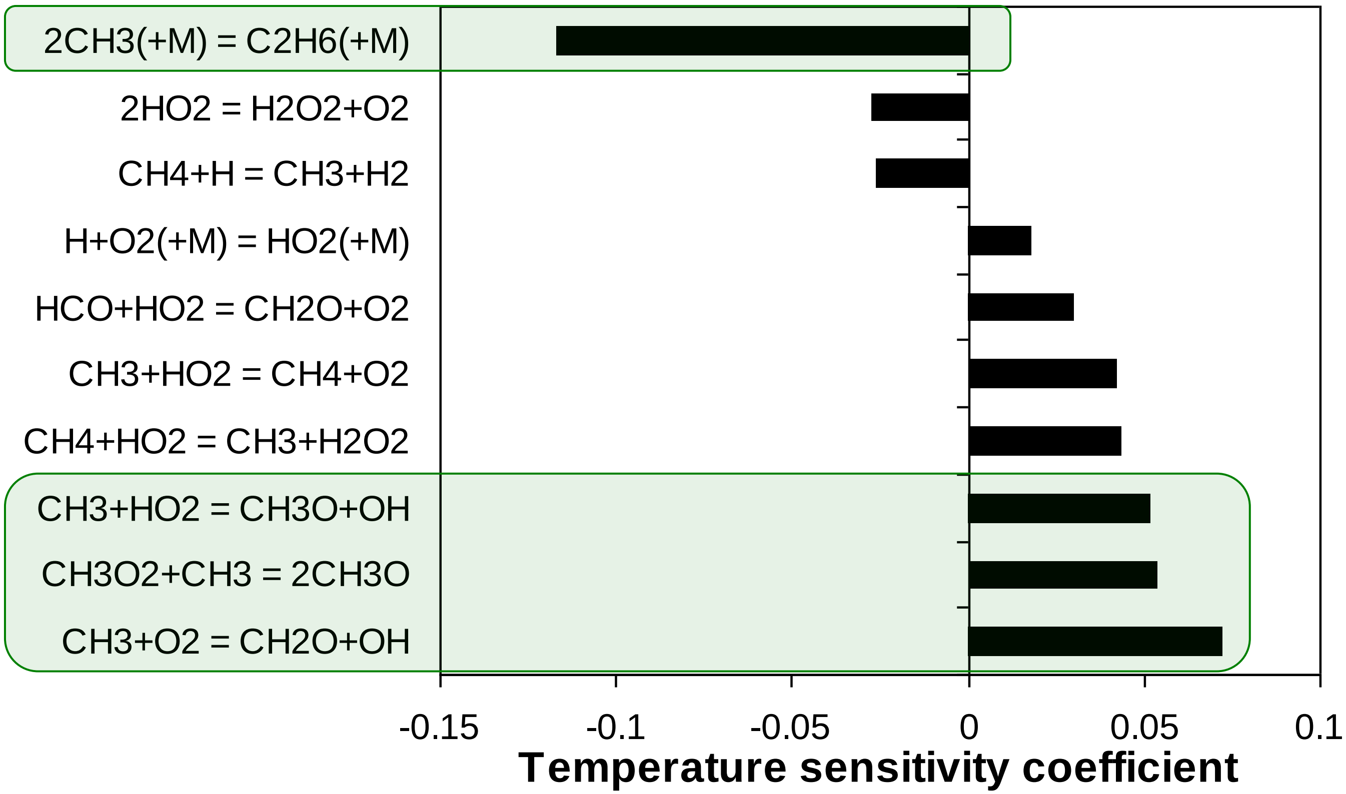
Accurate predictions need comprehensive core mechanism

- **Sensitivity analysis for autoignition delay time**

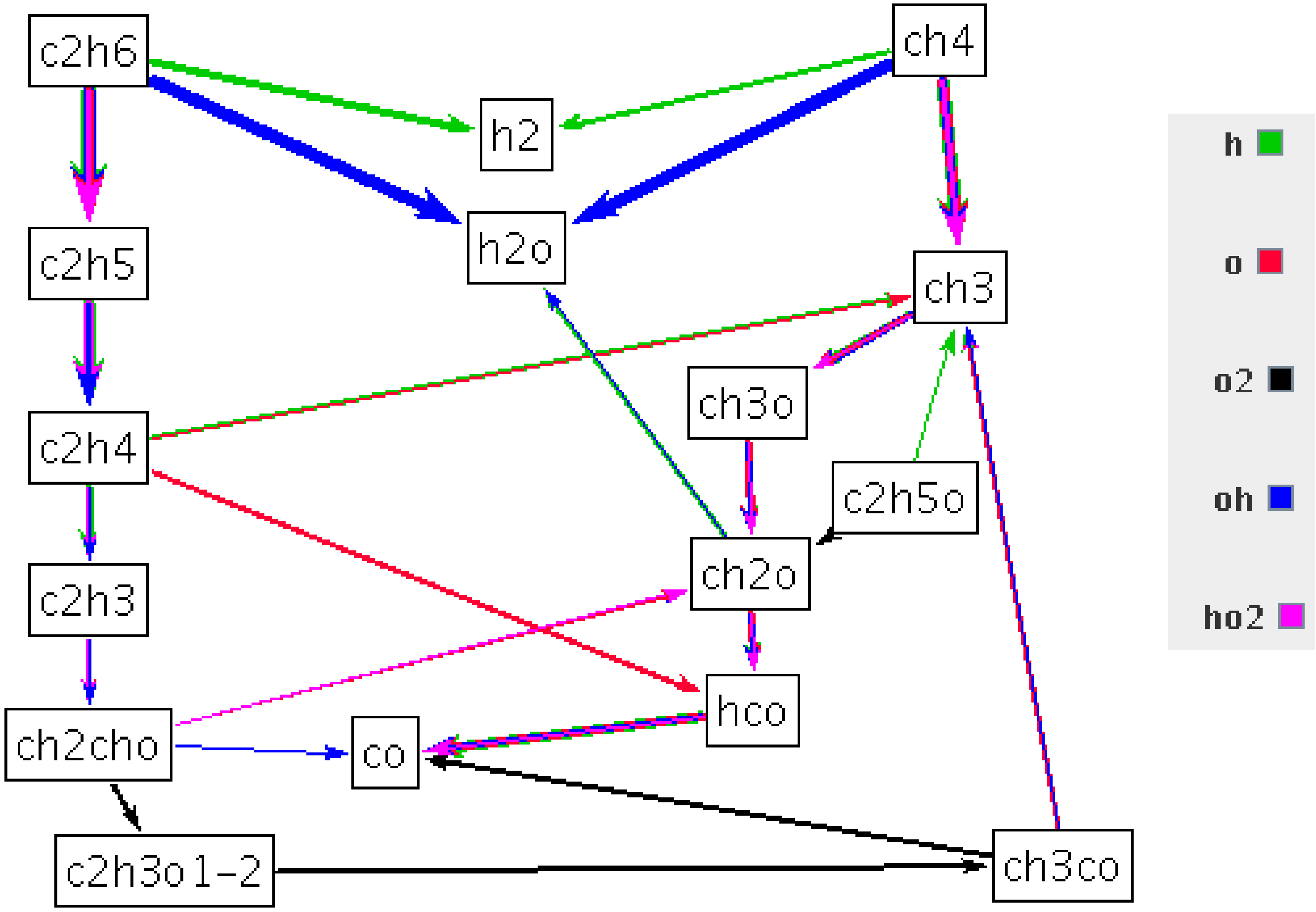


Methane/air, ϕ 3
140 atm, 1400 K

Acetaldehyde ↔ Ethylene ↔ Ethane ↔ Methane ↔ Formaldehyde, Ethanol

Comprehensiveness of the core mechanism even more important for blends

70/30 Methane/ethane - air autoignition at 20 atm, phi 0.5, 1400 K, 10 % conversion



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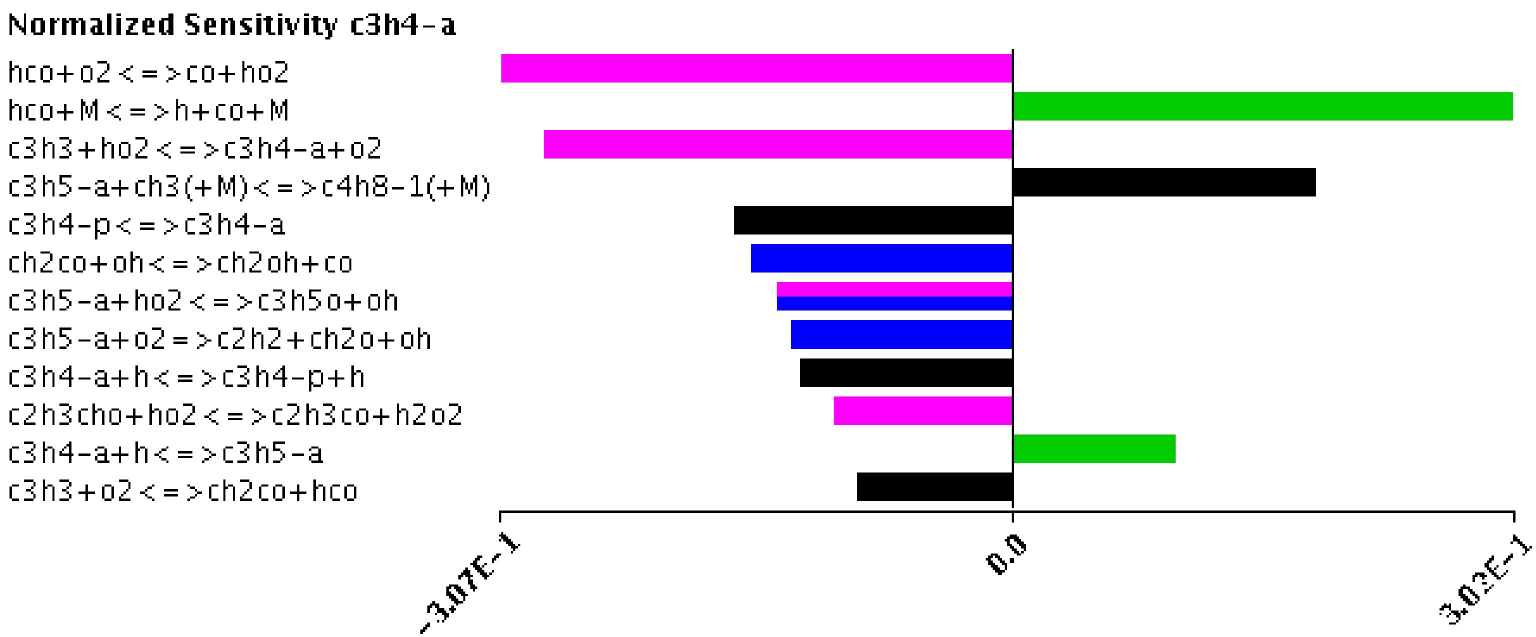
Chemistry of unsaturated fuels is more involved than their saturated counterparts

- **Allene oxidation in a stirred-reactor**
  - 1000 K, 10 atm, 1.5 s, and phi of 1.5



- **Reactions of C1 and C2 most sensitive**
- **Reactions of C4 and C5 also important**
  - C5H6+H <= C2H2+C3H5-a

Summary

- **Successful development of a detailed core (H_2, C_1-C_4) reaction mechanism**
  - Comprehensive: 18 neat fuels and their 8+ blends
    - Includes oxygenated fuels
    - NO_x, and PAH precursors
- **Successful validation using broad range of conditions and experiments**
  - Over 90+ comparison plots using 30 years of the data from the publications

* Results on saturated components to appear in J. Eng. Gas Turbines Power

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Thank You