Flame Studies of Jet Fuels and Surrogate-Related Neat Hydrocarbons

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&
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Period of performance: 9/1/11 – 8/31/14

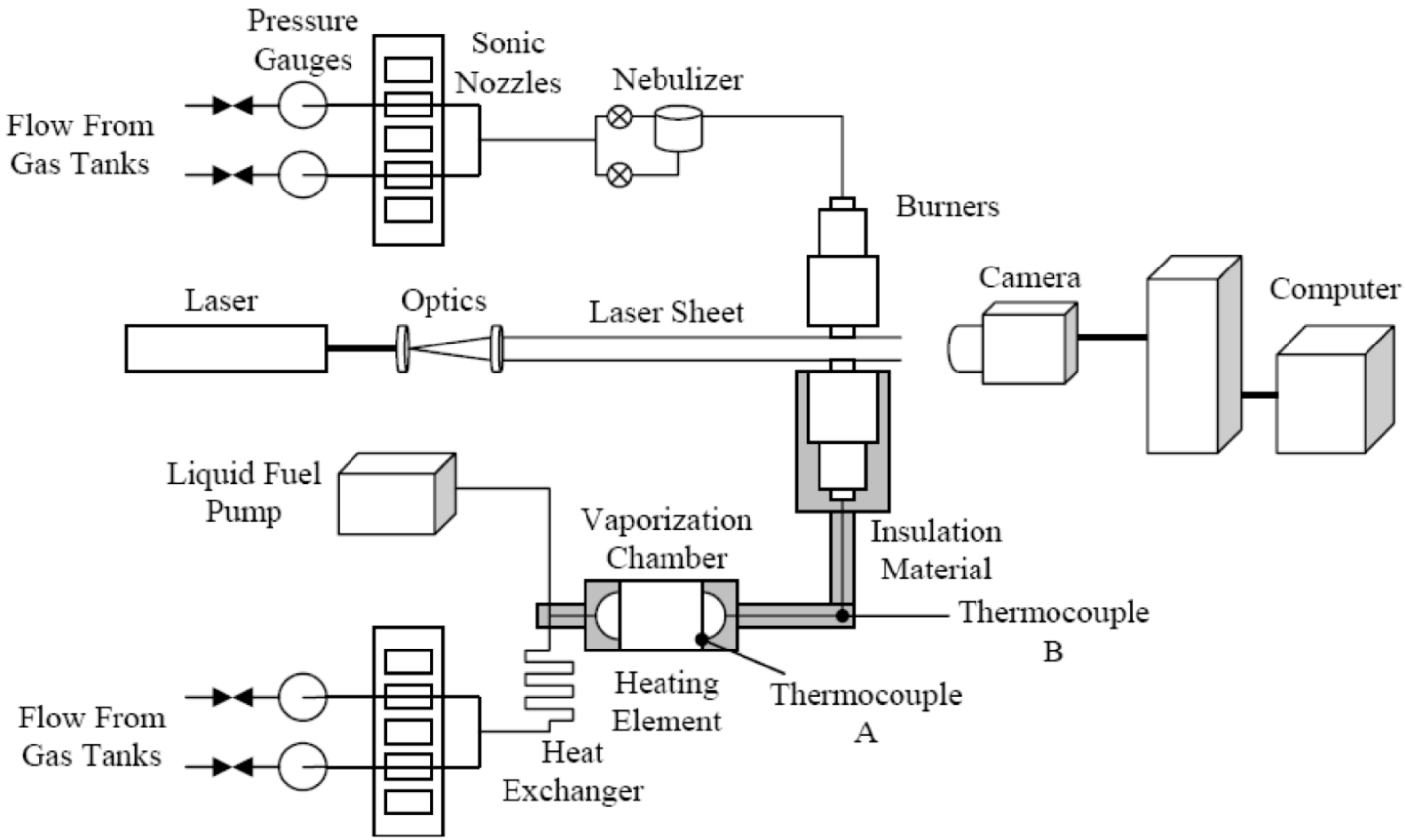
General Objectives

1. **To determine experimentally archival global fundamental flame properties (ignition, propagation, extinction) for:**
   - **Selected jet fuels**
   - **Single-component hydrocarbons**
   - **Mixtures of chosen hydrocarbons**

2. **To model experiments using detailed description of chemical kinetics and molecular transport.**

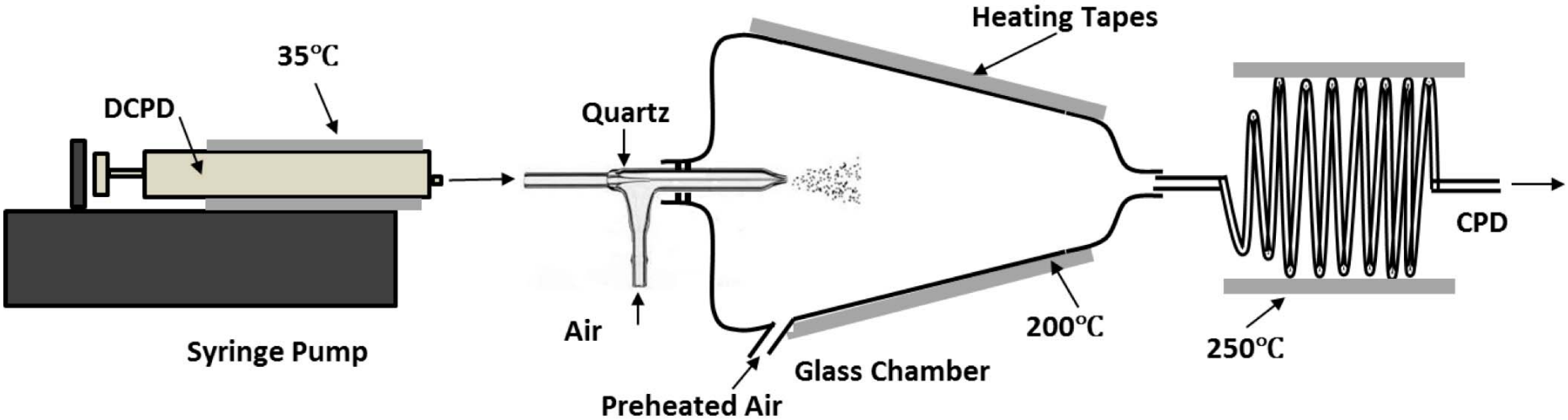
3. **To provide insight into the chemical and physical mechanisms that control the oxidative characteristics of large MW hydrocarbon flames.**

Experimental Approach (1)



- **Flame stability has improved notably through extensive revisions of:**
  - **Liquid fuel injection**
  - **Silicon oil droplets injection, to perform DPIV measurements**

Experimental Approach (2)



- **Special provisions to study cyclopentadiene (CPD)**
  - **Requires di-cyclopentadiene (DCPD) as the fuel source**
    - **Solid at room temperature**
    - **Melts at 32.5°C**
    - **Boils at 170°C**
    - **Readily decomposes to CPD above 150°C**

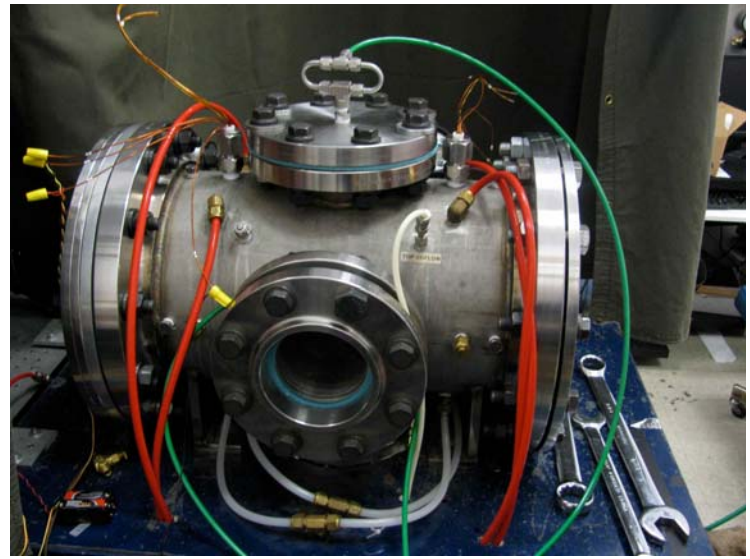
  - **Experimental procedure**
    - **DCPD melted first in a 32.5°C heated oil bath**
    - **Injected using a syringe pump heated at 35°C into a vaporization chamber kept at 200°C**
    - **Mixture passed through a heated coil kept at 250°C, with residence time 5~6 seconds**
    - **DCPD monomerizes to CPD by ~97% with isoprene (i.e. 2-methyl-1,3-butadiene) being the main impurity (Butler & Glassman 32nd Symposium)**

Experimental Approach (3)

- **Use of counterflow configuration (4 atmospheric and 3 high-pressure rigs)**

Twin premixed flames

Single premixed / non-premixed flame

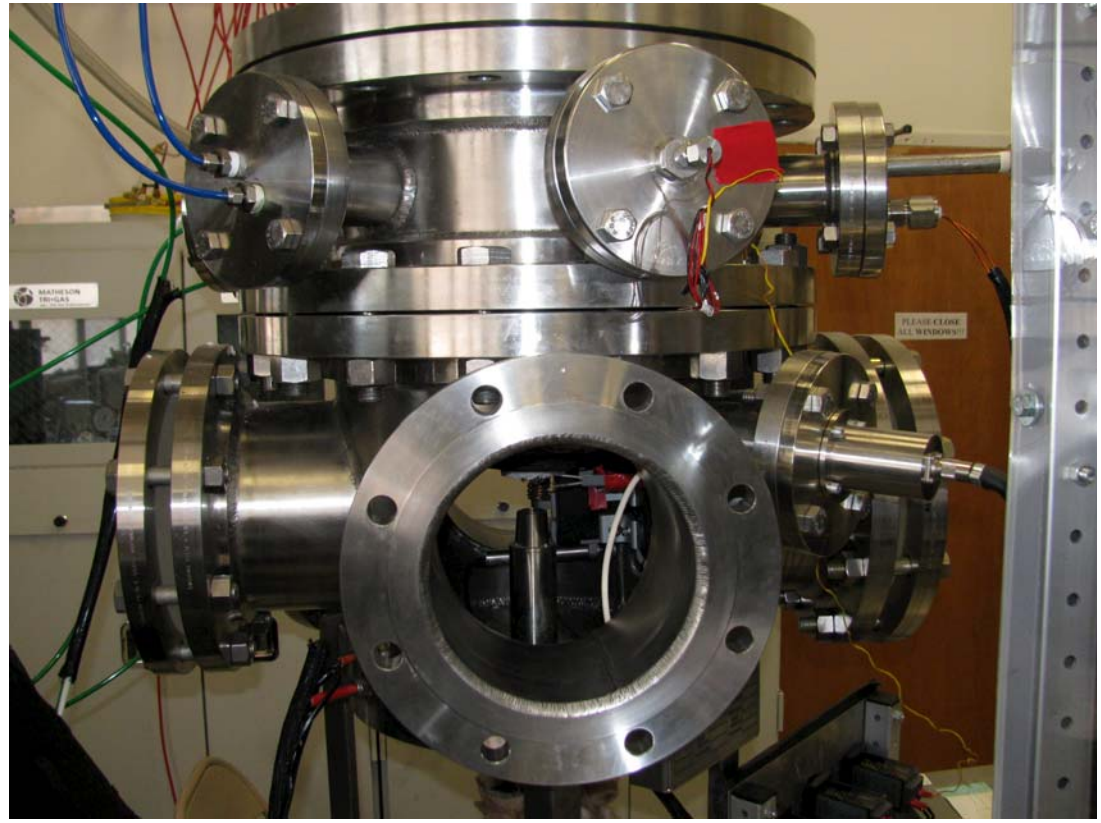


- **Pressure chamber:**
  - **Pressure range 0.1-20 atm**
- **Diagnostics:**
  - **Digital Particle Image Velocimetry (DPIV)**
  - **Thermocouples**
  - **Intrusive NO_x sampling**
  - **Laser extinction**

Experimental Approach (4)

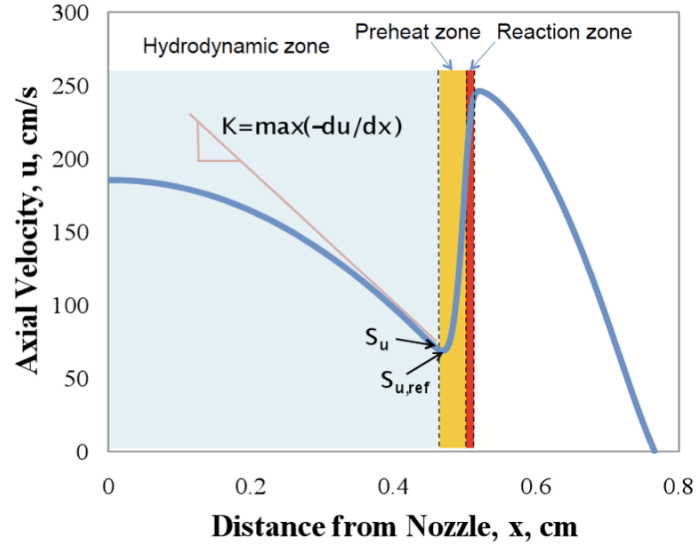
- **Use of counterflow configuration**

Original flame ignition facility, p = 1 atm

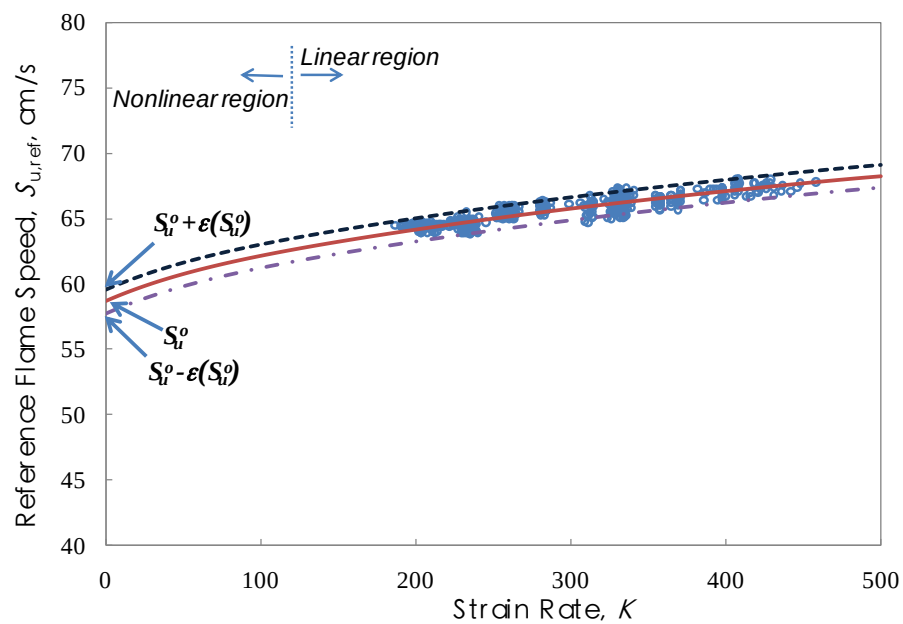


Newly constructed flame ignition facility, $0.1 \leq p \leq 20$ atm

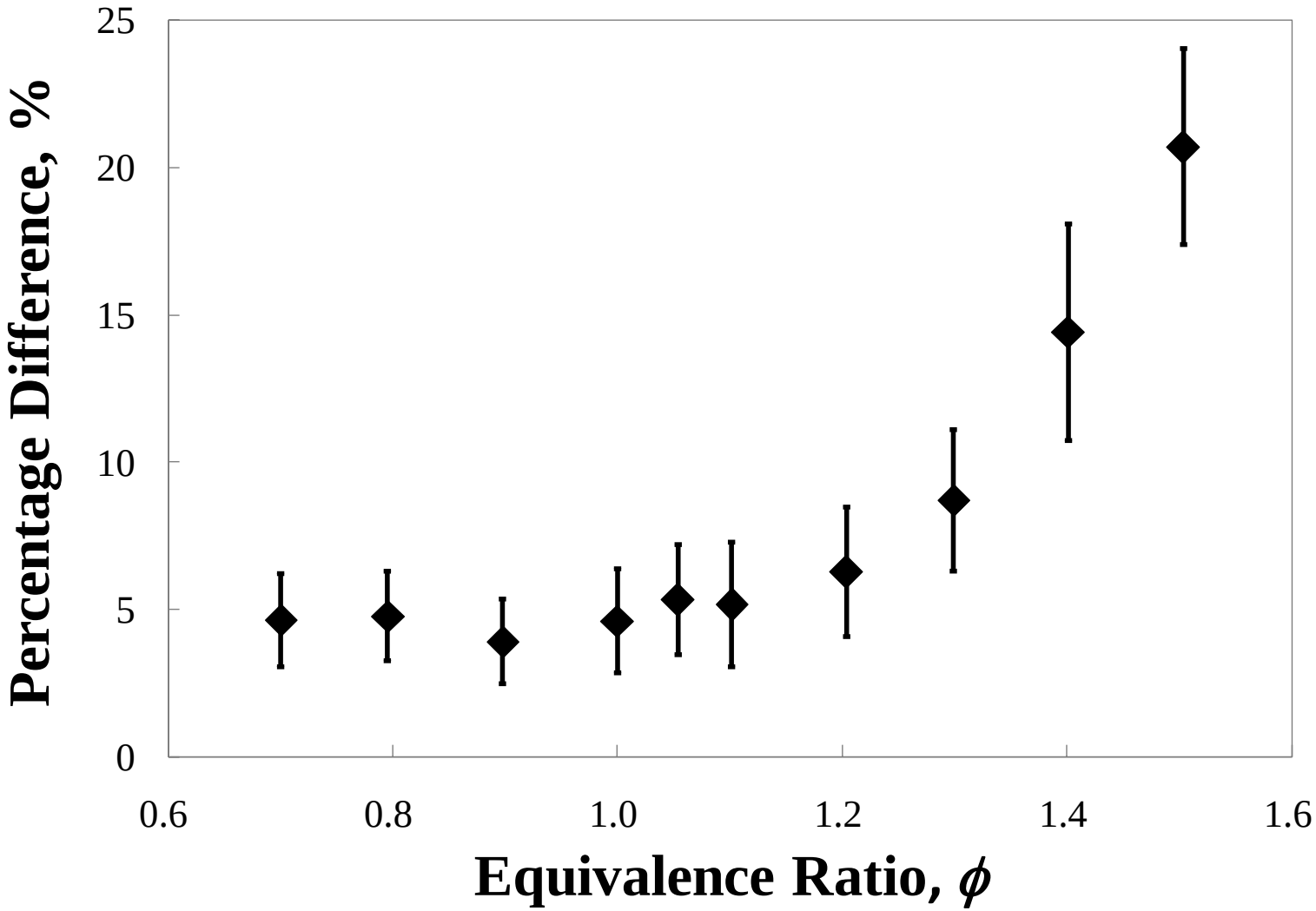
Experimental Approach (5)



- **Laminar flame speeds, S_u^o**
  - **Monitor $S_{u,ref}$ vs. K**
  - **Non-linear extrapolations – computationally assisted**
- **Extinction strain rate, K_{ext}:**
  - **K at the state of extinction**
- **Ignition temperature, T_{ign}:**
  - **T at the hot boundary resulting in ignition**

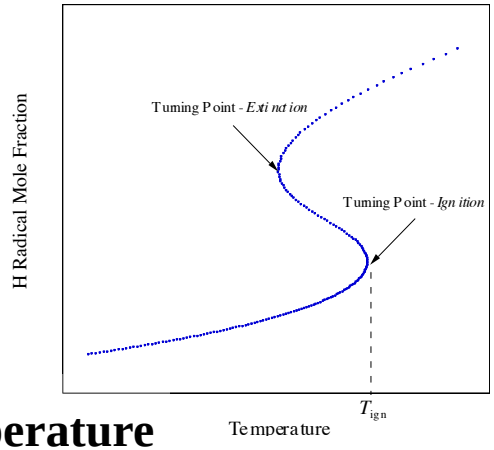


Experimental Approach (6)



Average difference between linear and non-linear extrapolations for C_5-C_{12} *n*-alkane/air flames.

Numerical Approach



- Use of CHEMKIN-II-based codes
- Proper description of "turning-point" behavior
- Mathematically rigorous determination of logarithmic sensitivity coefficients: $\partial(\ln Y)/\partial(\ln X)$
  - Y: laminar flame speed / extinction strain rate / ignition temperature
  - X: A-factor / $D_{i\text{-}N2}$
- Use of JetSurF (http://melchior.usc.edu/JetSurF) kinetic model(s) developed by Wang and coworkers.
- Additional models for aromatics and iso-alkanes

- ***All numerical results have been produced by solutions that:***
  - ***Were properly converged, i.e. in highly resolved grids***
  - ***Included the effects of thermal radiation and Soret***
  - ***Included full multi-component transport formulation***
  - ***Included all pertinent experimental boundary conditions, such as velocity gradients at the burners exits***

Challenges

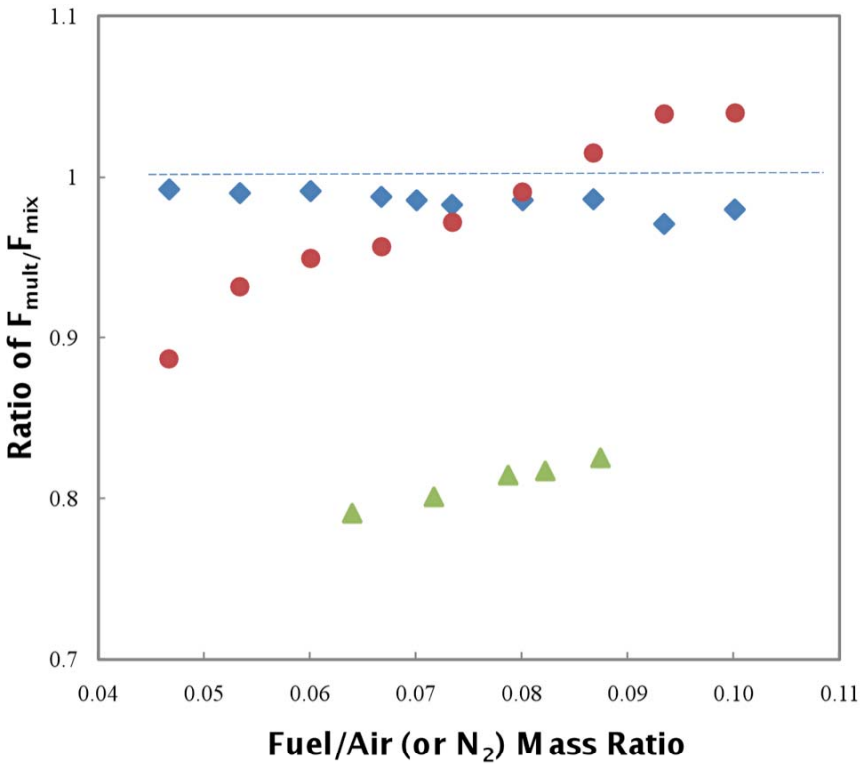
1. **Low fuel vapor pressure:**
   - **fuel heating**
   - **fuel cracking**
   - **fuel condensation**
   - **final mixture composition needs to be tested independent using, e.g., gas chromatography.**

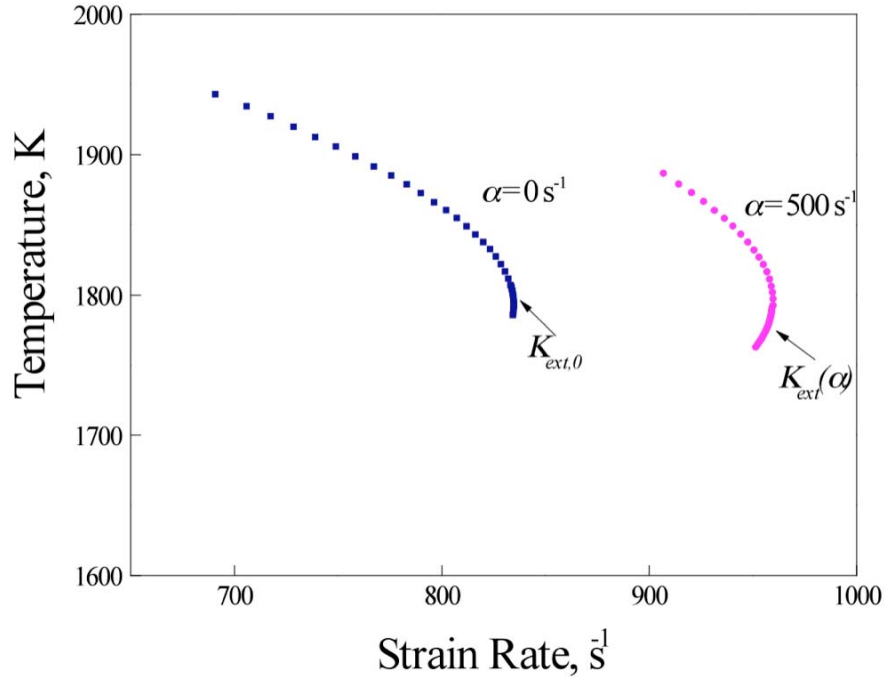
2. **Experiments are complicated notably as pressure increases.**

3. **The large molecular weight discrepancy between fuel and oxidizer can complicate experimental data interpretation.**

4. **Computed results can be compromised by:**
   - **using simplifying assumptions for the transport coefficient formulation due to the large size of kinetic models**
   - **not accounting properly for the experimental boundary conditions**

Two Potential Sources of Error





Computed S_u^o (◆) and K_{ext} for premixed (●) and non-premixed (▲) flames using the multi-component transport formulation and scaled by the attendant values obtained using the mixture-averaged transport formulation.

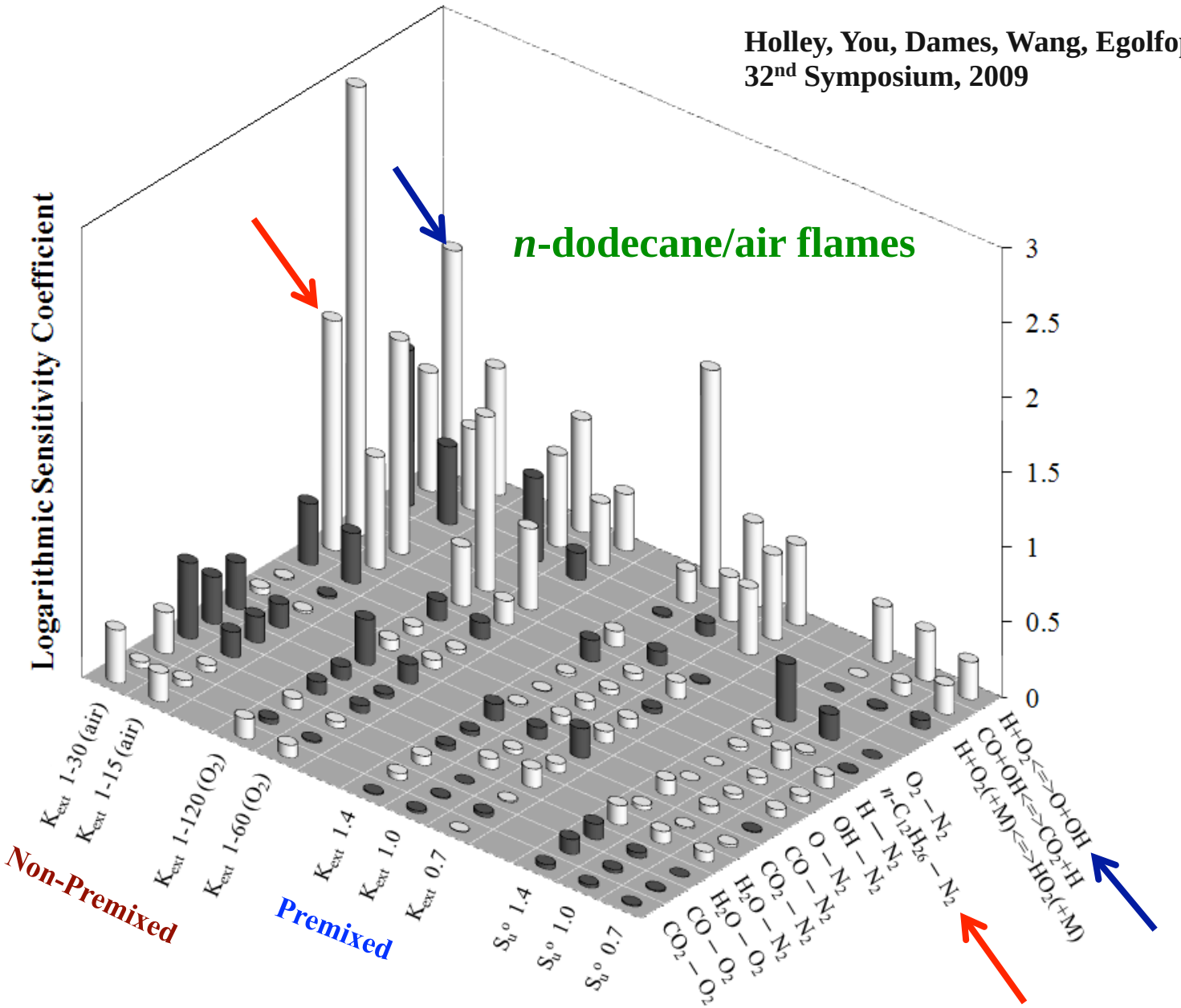
(Egolfopoulos and coworkers, JPP, 2011)

Computed responses of the extinction strain rate on the velocity gradient at the burner exit *a*. The computations were carried out for a stoichiometric *n*-$C_{12}H_{26}$/air flame at T_u = 403 K.

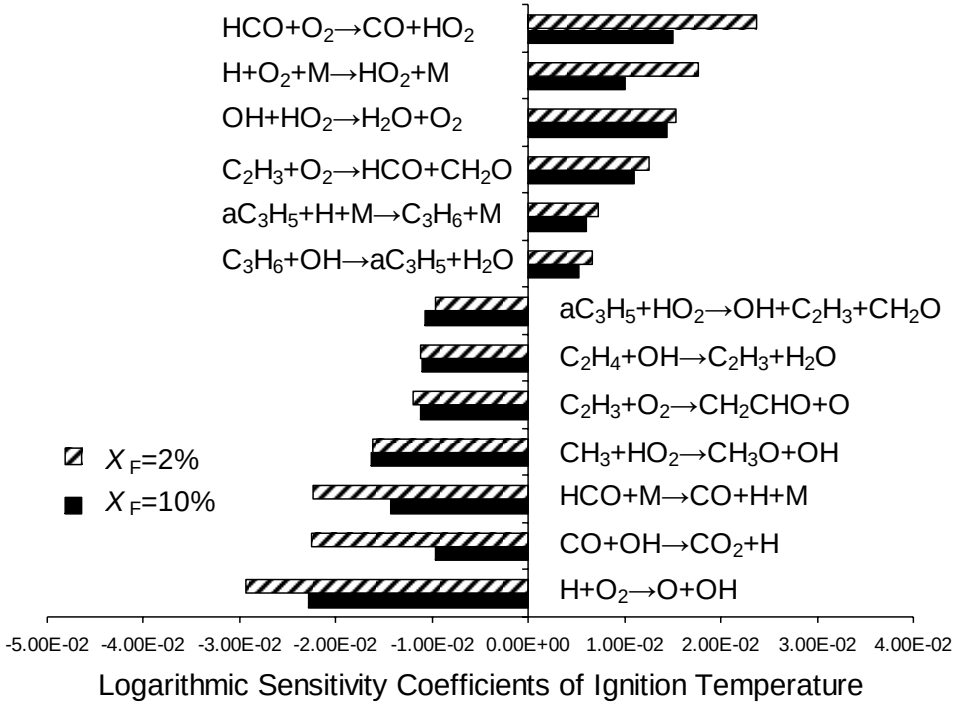
(Wang, Egolfopoulos and coworkers, CNF, 2010, 2011)

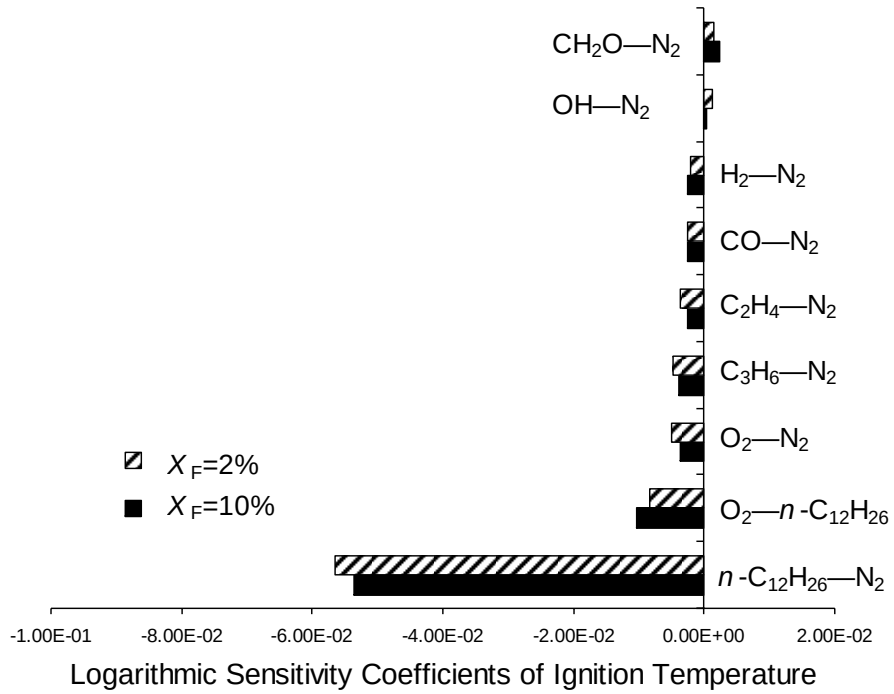
Flame Propagation/Extinction: What do we Learn?

Holley, You, Dames, Wang, Egolfopoulos, 32nd Symposium, 2009



Flame Ignition: What do we Learn?





kinetics ***transport***

***n*-dodecane/air non-premixed flames**

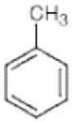
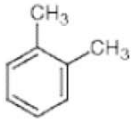
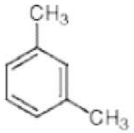
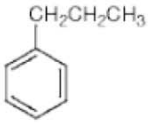
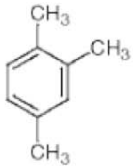
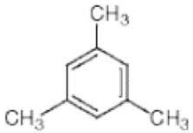
Up to Date Progress

	C_4-C_{12} *n*-alkanes	cycloalkanes	*iso*-alkanes	aromatics	fuel mixtures	jet fuels
Laminar flame speeds (1 atm)	C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12}	cyclohexane (CHX) methyl-CHX ethyl-CHX *n*-propyl-CHX *n*-butyl-CHX cyclopentadiene	*iso*-butane 2-methyl-heptane 3-methyl-heptane 2,5-dimethyl-hexane *iso*-octane	benzene (B) toluene *n*-propyl-B 1,2,4-TMB 1,3,5-TMB *o*-xylene *m*-xylene *p*-xylene	*n*-C_{12}+MCHX *n*-C_{12}+toluene	JP-7 JP-8 S-8 R-8 Shell-GTL
Flame ignition (1 atm)	C_3, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12}	cyclohexane (CHX) methyl-CHX ethyl-CHX *n*-propyl-CHX *n*-butyl-CHX	2-methyl-heptane 3-methyl-heptane 2,5-dimethyl-hexane 2,7-dimethyl-octane *iso*-octane			
Flame extinction (1 atm)	C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12}	CHX methyl-CHX *n*-butyl-CHX cyclopentadiene		benzene toluene *n*-propyl-B 1,2,4-TMB 1,3,5-TMB *o*-xylene *m*-xylene *p*-xylene		JP-7 JP-8 S-8 R-8 Shell-GTL

Propagation and Extinction of

Benzene, Alkylbenzene, and Cyclopentadiene Flames

Aromatic Compounds Considered and Representative T_{ad}'s

Chemical name	Purity, %	Formula	Structure	T_{ad} (K)*
benzene	>99.5	C_6H_6		2373
toluene	>99.5	C_7H_8		2359
o-xylene	>98%	C_8H_{10}		2349
m-xylene	>99%	C_8H_{10}		2349
p-xylene	>99%	C_8H_{10}		2349
n-propylbenzene	>99%	C_9H_{12}		2347
1,2,4-trimethylbzene	>98%	C_9H_{12}		2343
1,3,5-trimethylbzene	>97%	C_9H_{12}		2342

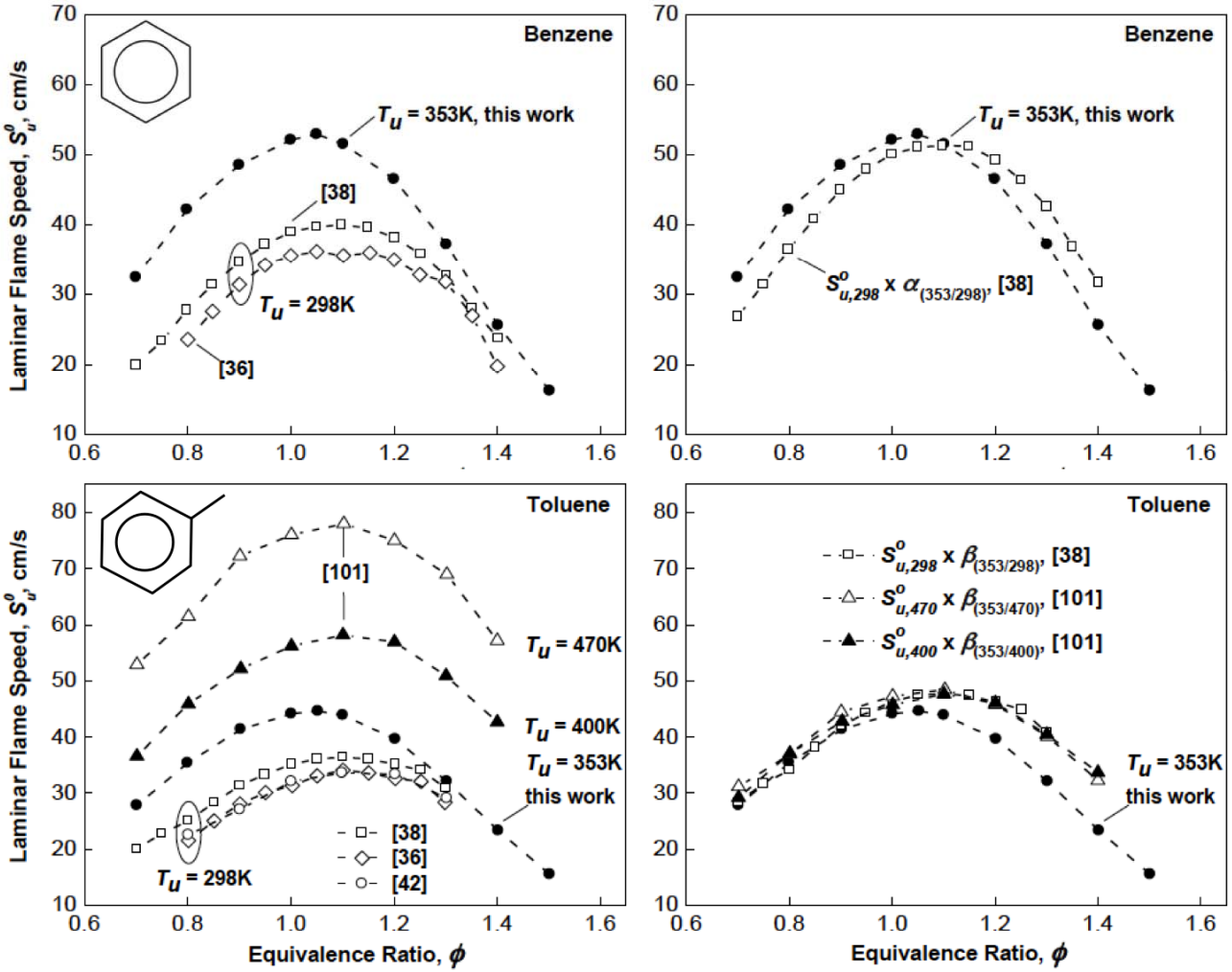
*Adiabatic flame temperature calculated for stoichiometric fuel-air mixture at T_u= 353 K and p = 1 atm.

> 14~31 K

> 10~17 K

Within 7 K

Laminar Flame Speeds of Benzene/Air and Toluene/Air Flames



T_u = 353 K

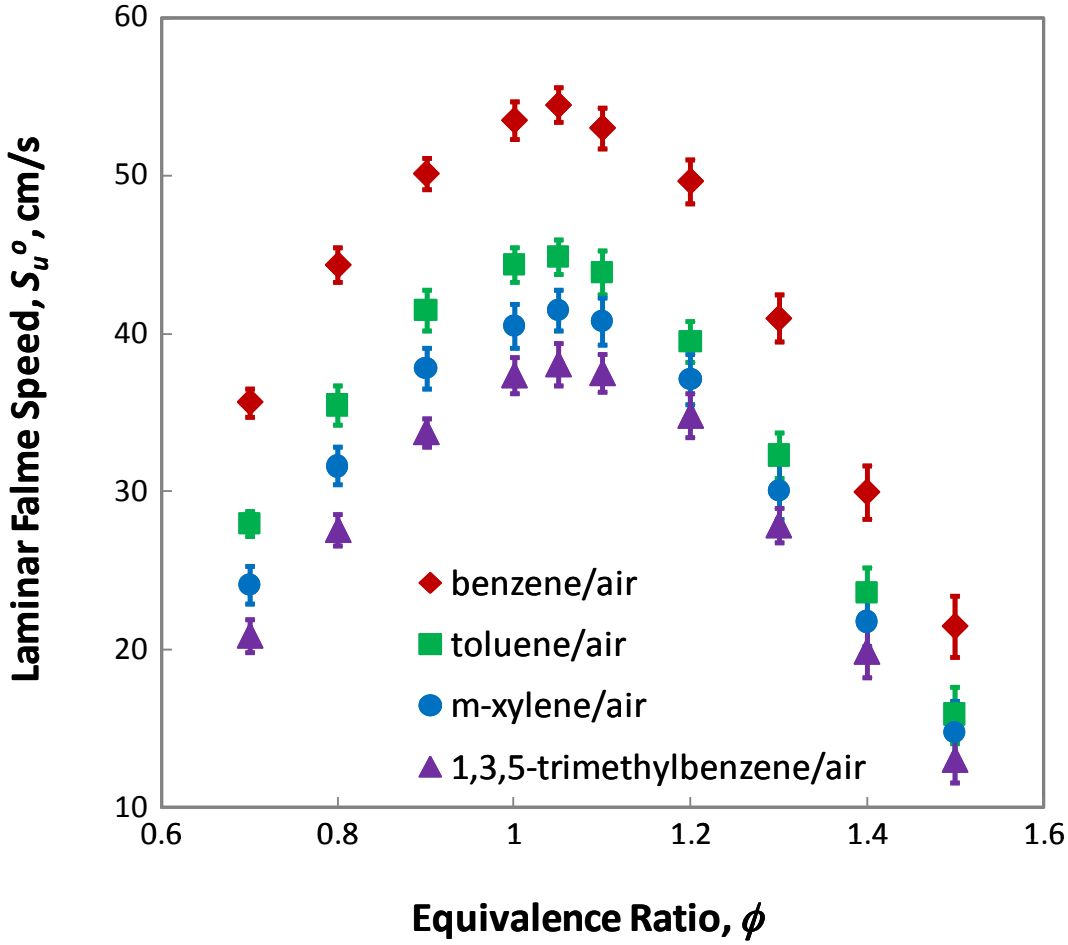
[36] S.G. Davis, H. Wang, K. Brezinsky, C.K. Law, Proc. Combust. Inst. 26 (1996) 1025-1033.

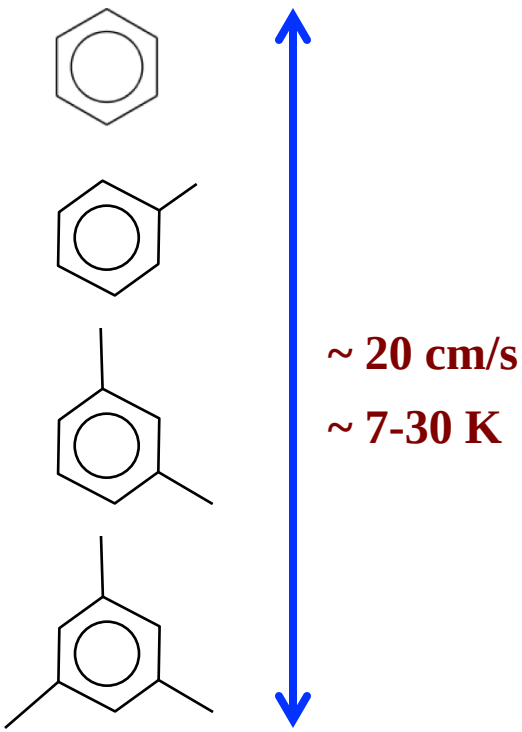
[38] S.G. Davis, C. K. Law, Combust. Sci. Technol. 140 (1-6) (1998) 427-449.

[42] T. Hirasawa, C.J. Sung, A. Joshi, Z. Yang, H. Wang, C.K. Law, Proc. Combust. Inst. 29 (2002) 1427-1434.

[101] K. Kumar, C. J. Sung, Energy Fuel 24 (2010) 3840-3849.

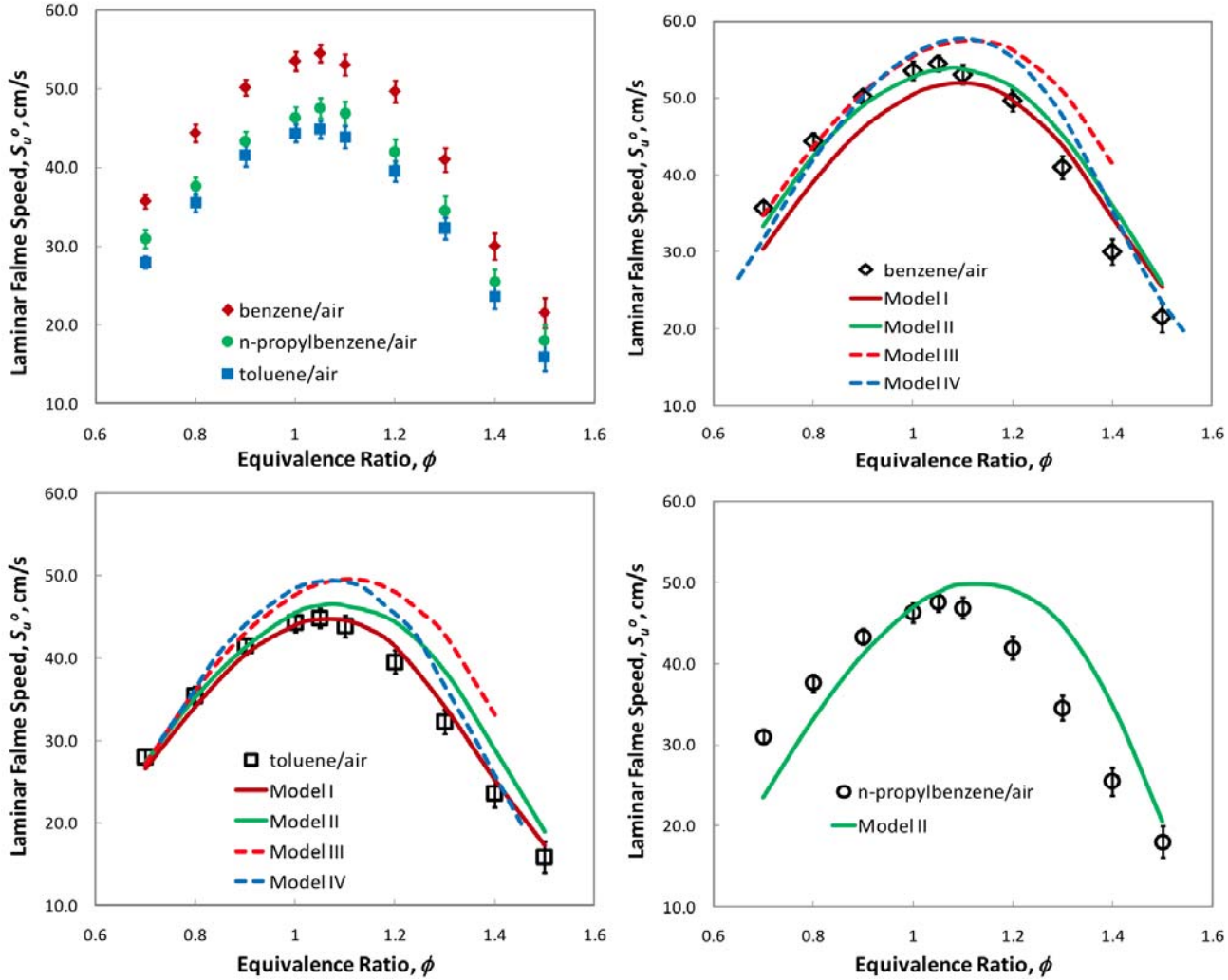
Effect of Methylation on Laminar Flame Propagation



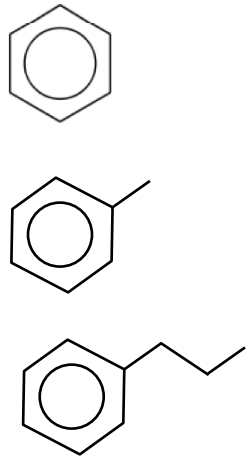


T_u = 353 K

Benzene, Toluene, and n-Propylbenzene Flames

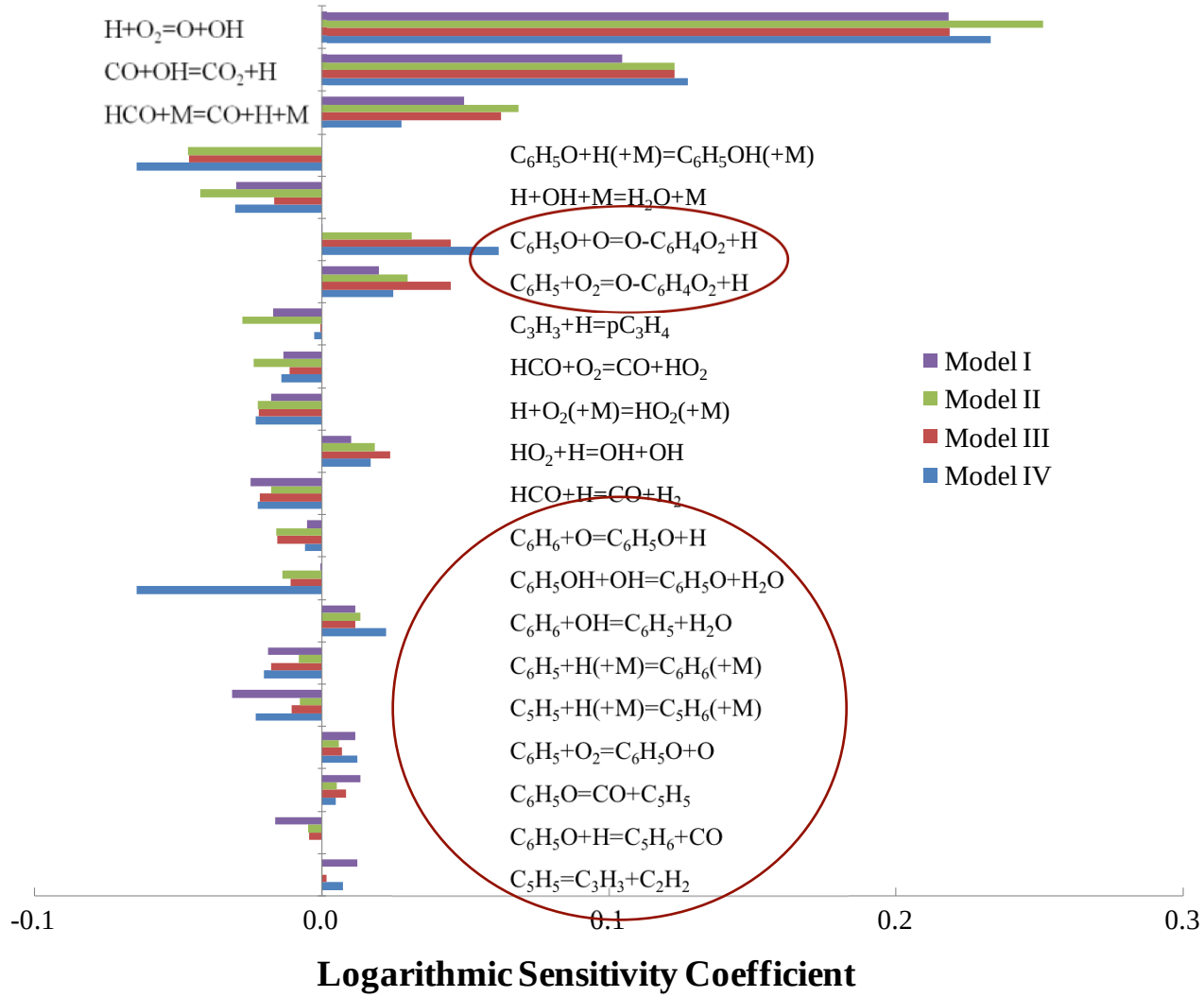


T_u = 353 K



Model I: H. Wang, X. You, A. V. Joshi, S.G. Davis, A. Laskin, F.N. Egolfopoulos, and C.K. Law, USC Mech Version II (2007). (Benzene, Toluene)
Model II: S. Dooley, S.H. Won, M. Chaosa, J. Heynea, Y. Jua, F.L. Dryer, K. Kumar, C-J. Sung, H. Wang, M.A. Oehlschlaegerc, R.J. Santoro, and T.A. Litzinger, Combust. Flame (2010). (Benzene, Toluene, *n*-Propylbenzene)
Model III: F. Battin-Leclerc, R. Bounaceur, N. Belmekki, and P.A. Glaude, Int. J. Chem. Kinet. (2006). (*o*-, *m*-, *p*-xylene)
Model IV: K. Narayanaswamy , G. Blanquart, and H. Pitsch, Combust. Flame (2010). (*m*-xylene)

Kinetic Effects on Flame Propagation of ϕ=1 Benzene Flame



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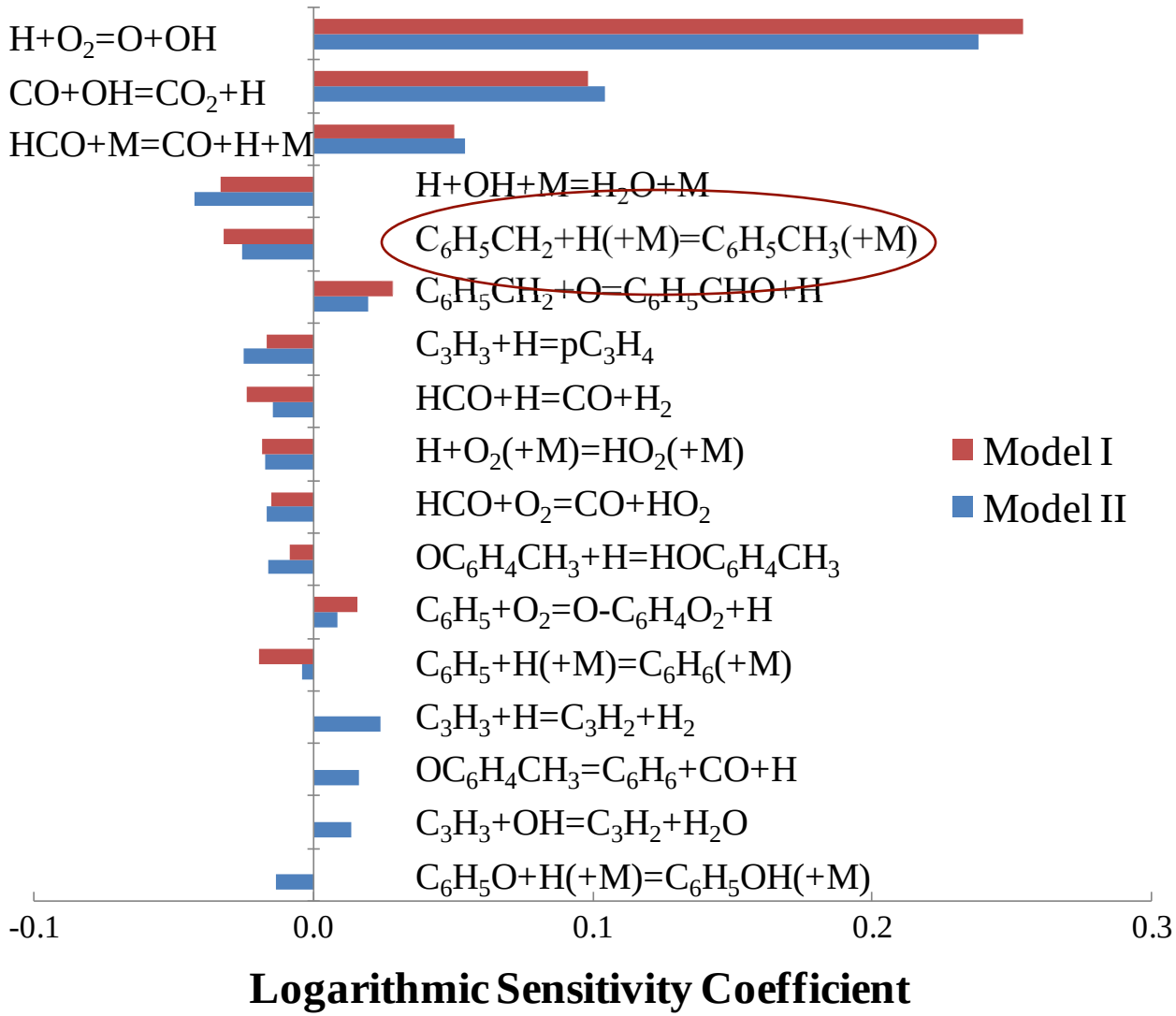
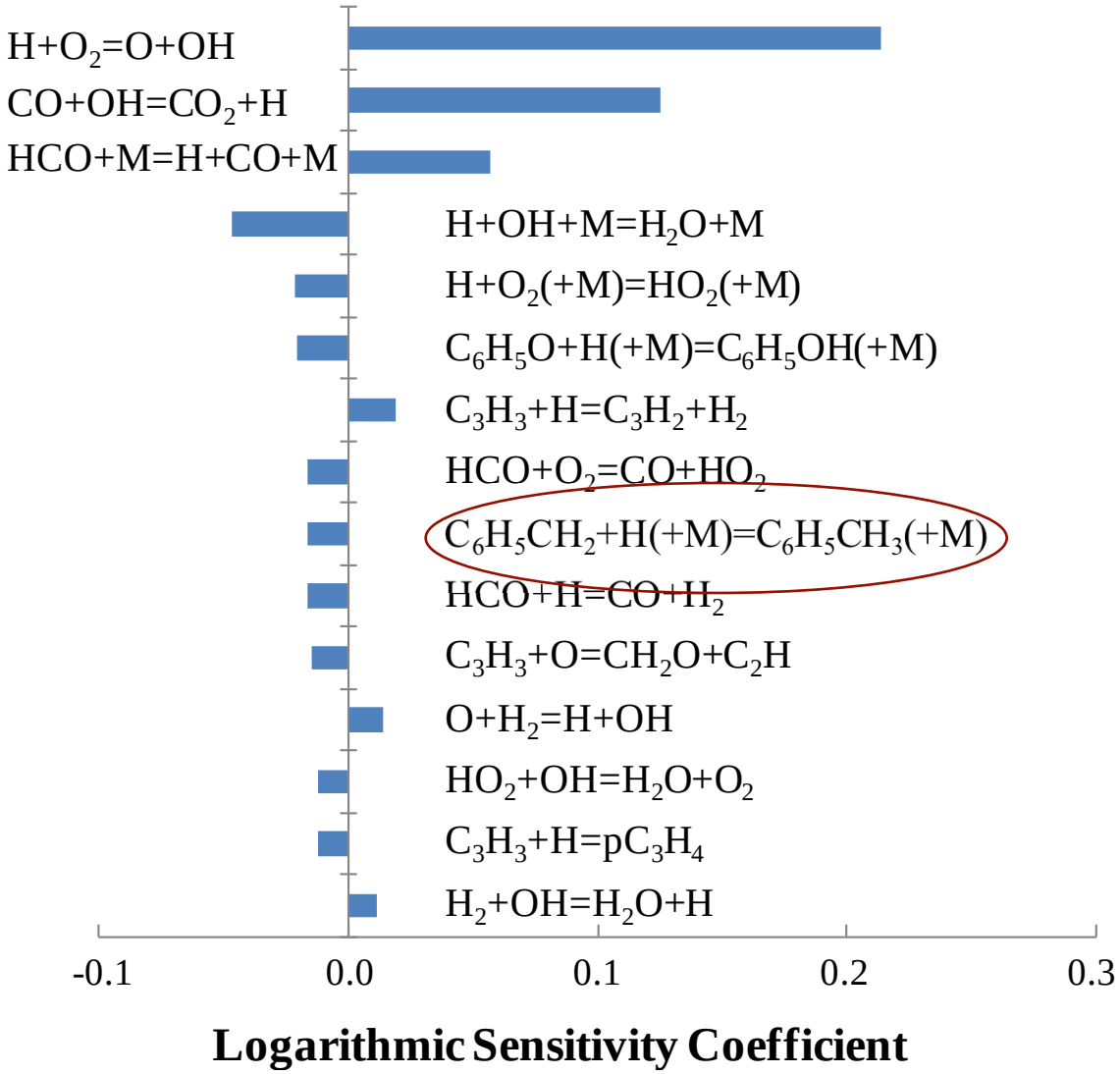
Model IV: K. Narayanaswamy , G. Blanquart, and H. Pitsch, Combust. Flame (2010). (*m*-xylene)

Kinetic Effects on Flame Propagation of ϕ=1 Toluene Flame



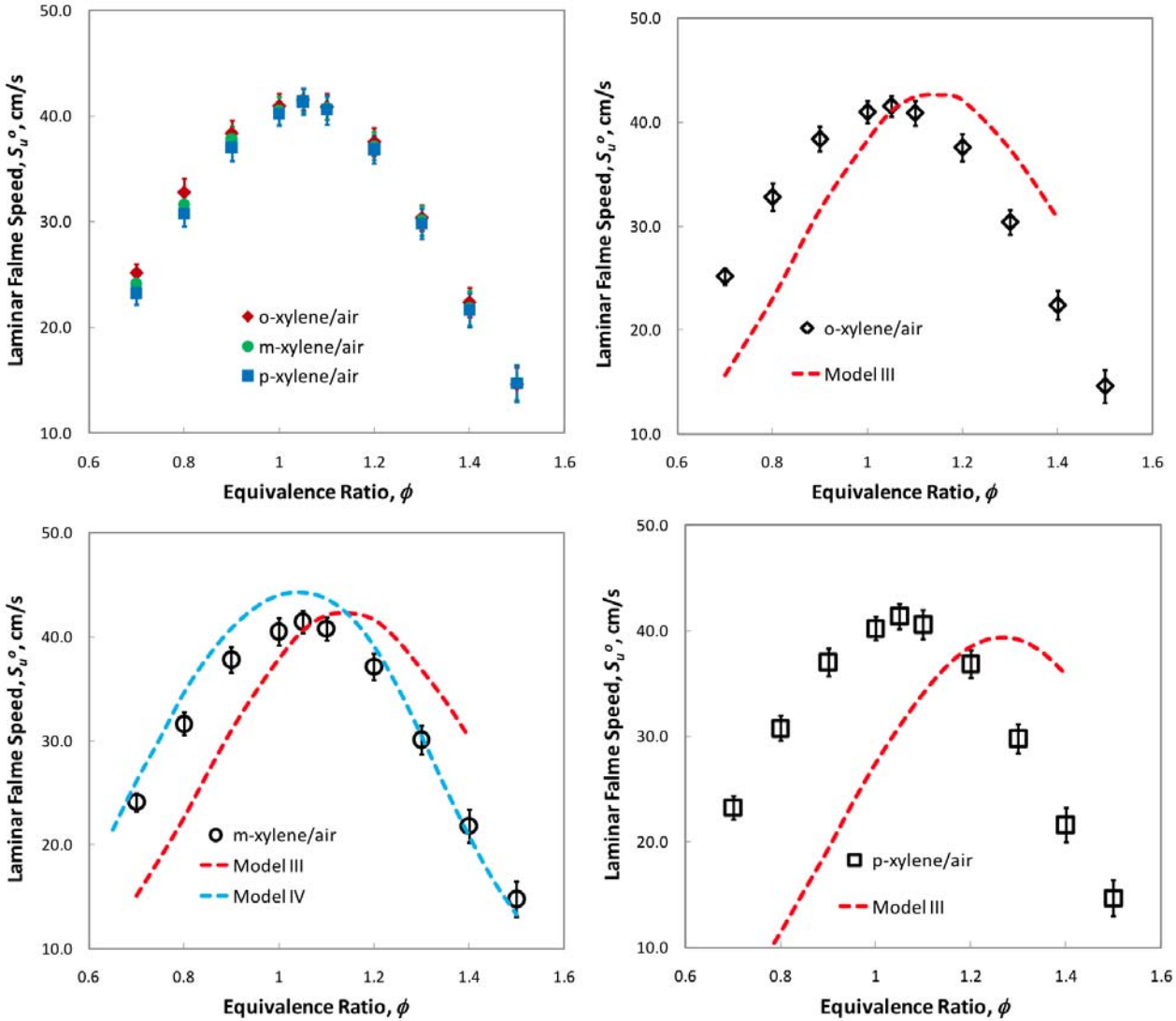
<u>Model I:</u> H. Wang, X. You, A. V. Joshi, S.G. Davis, A. Laskin, F.N. Egolfopoulos, and C.K. Law, USC Mech Version II (2007). (Benzene, Toluene)
<u>Model II:</u> S. Dooley, S.H. Won, M. Chaosa, J. Heynea, Y. Jua, F.L. Dryer, K. Kumar, C-J. Sung, H. Wang, M.A. Oehlschlaegerc, R.J. Santoro, and T.A. Litzinger, Combust. Flame (2010). (Benzene, Toluene, *n*-Propylbenzene)

Kinetic Effects on Flame Propagation of ϕ=1 n-Propyl-Benzene Flame

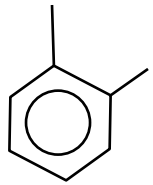


<u>Model II:</u> S. Dooley, S.H. Won, M. Chaosa, J. Heynea, Y. Jua, F.L. Dryer, K. Kumar, C-J. Sung, H. Wang, M.A. Oehlschlaegerc, R.J. Santoro, and T.A. Litzinger, Combust. Flame (2010). (Benzene, Toluene, *n*-Propylbenzene)

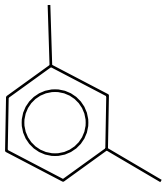
Xylene Isomers Flames



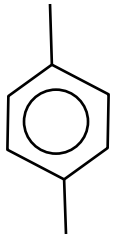
T_u = 353 K



o-xylene



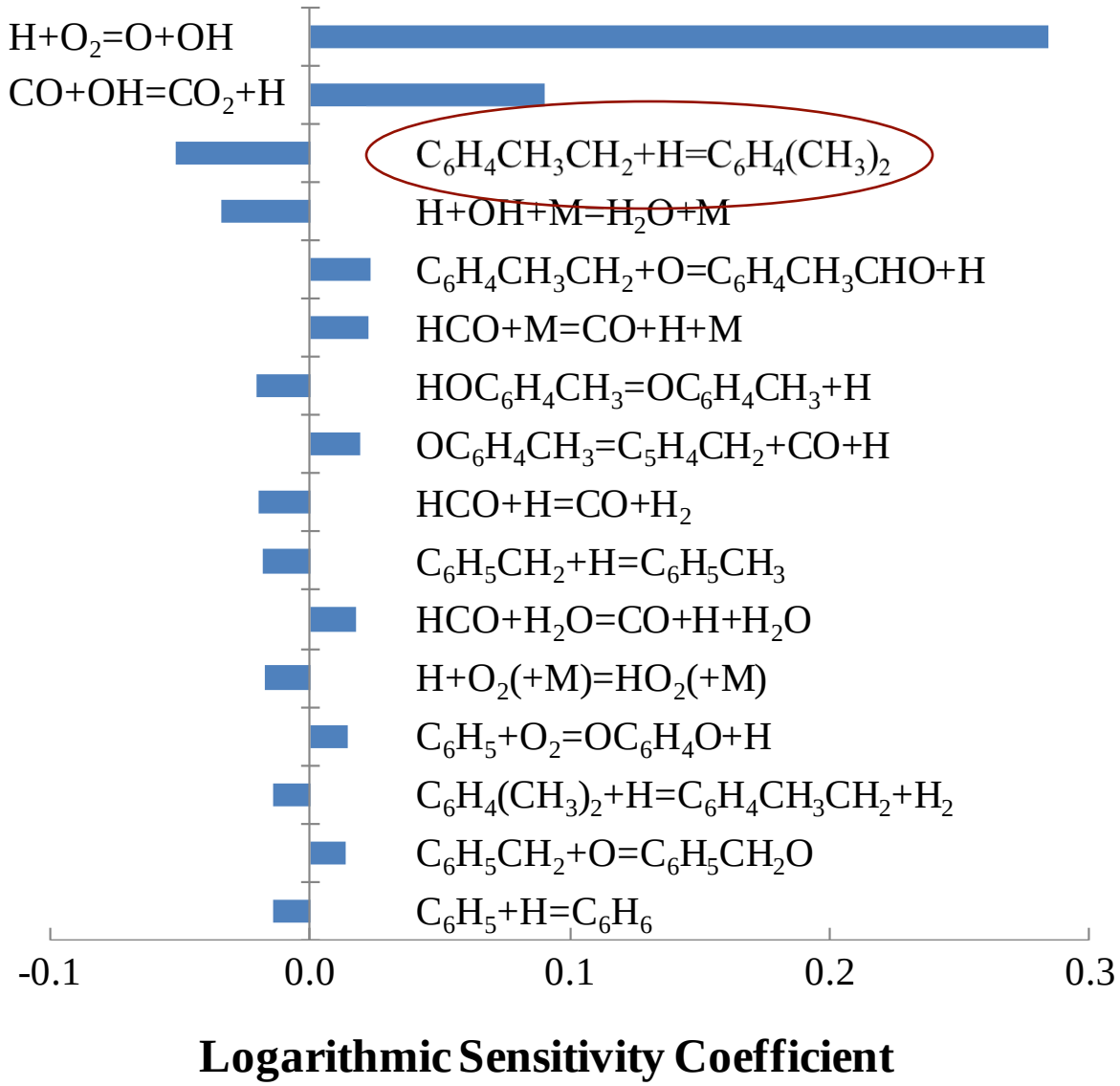
m-xylene



p-xylene

<u>Model III:</u> F. Battin-Leclerc, R. Bounaceur, N. Belmekki, and P.A. Glaude, Int. J. Chem. Kinet. (2006). (*o*-, *m*-, *p*-xylene)
<u>Model IV:</u> K. Narayanaswamy , G. Blanquart, and H. Pitsch, Combust. Flame (2010). (*m*-xylene)

Kinetic Effects on Flame Propagation of ϕ=1 m-Xylene Flame

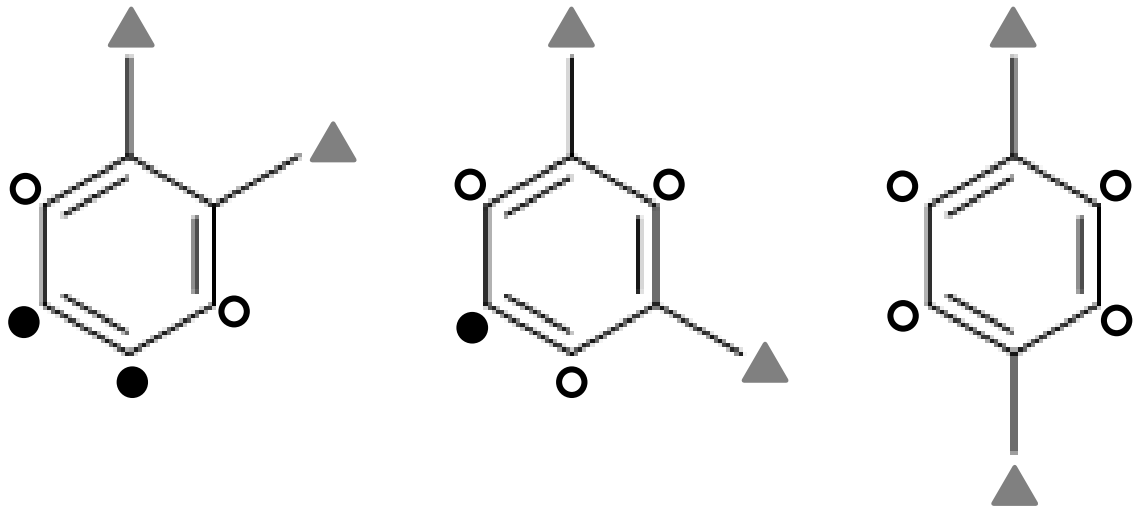


<u>Model IV:</u> K. Narayanaswamy , G. Blanquart, and H. Pitsch, Combust. Flame (2010). (*m*-xylene)

Reactivity of Xylene Isomers Flames

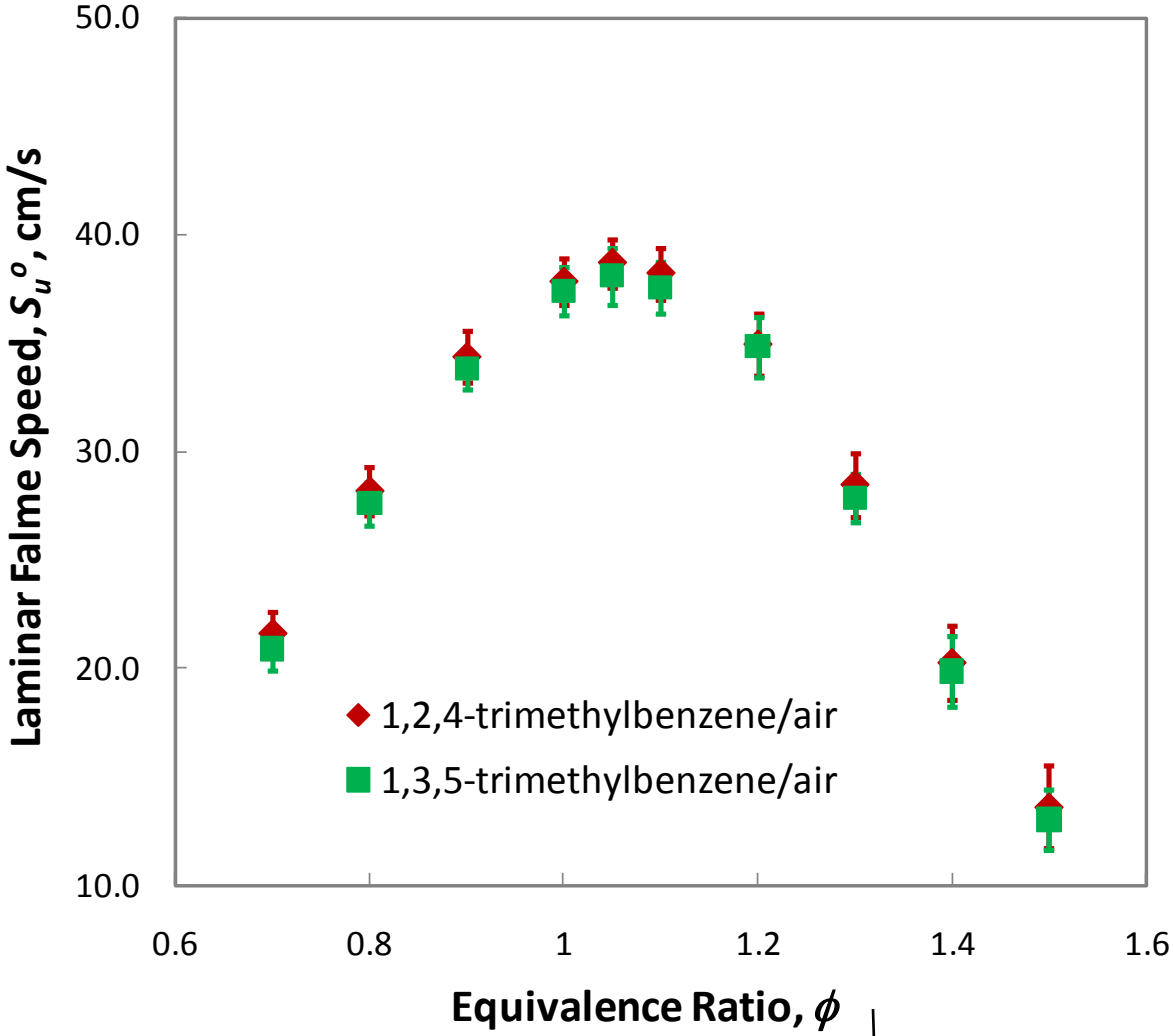
Reactivities: ***o*-xylene** **>** ***m*-xylene** **>** ***p*-xylene**

Mechanism for T > 1400 K:

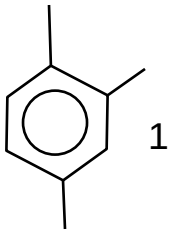


o- *m-* *p-*

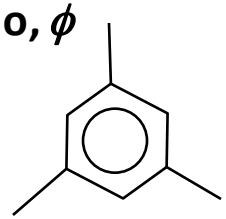
Trimethylbenzene Isomers Flames



T_u = 353 K

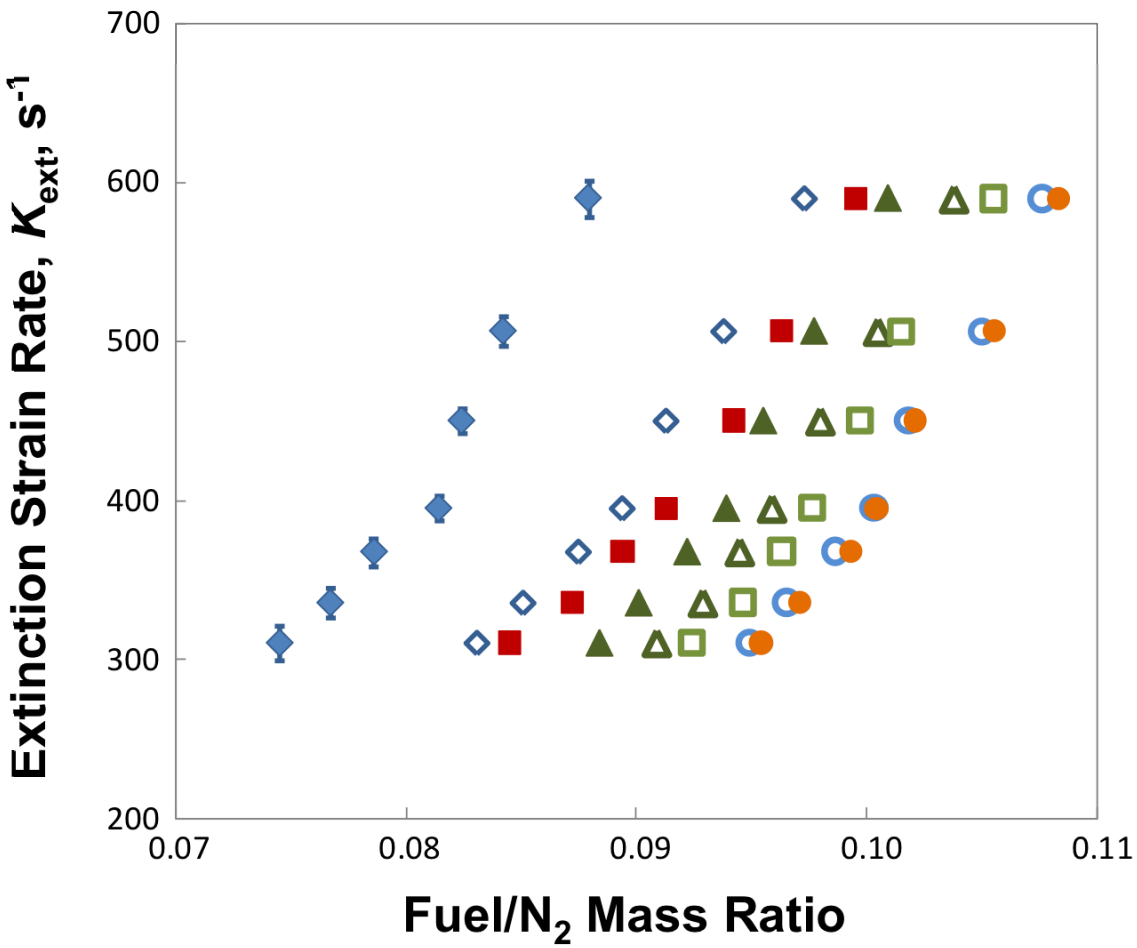


1,2,4-trimethylbenzene

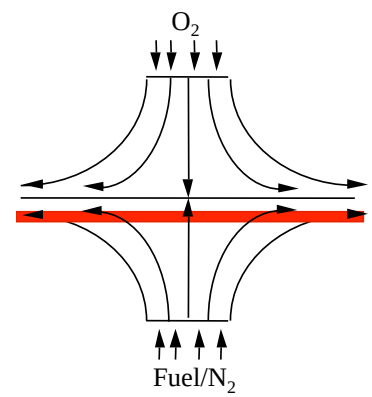


1,3,5-trimethylbenzene

Extinction of Non-Premixed Aromatics Flames

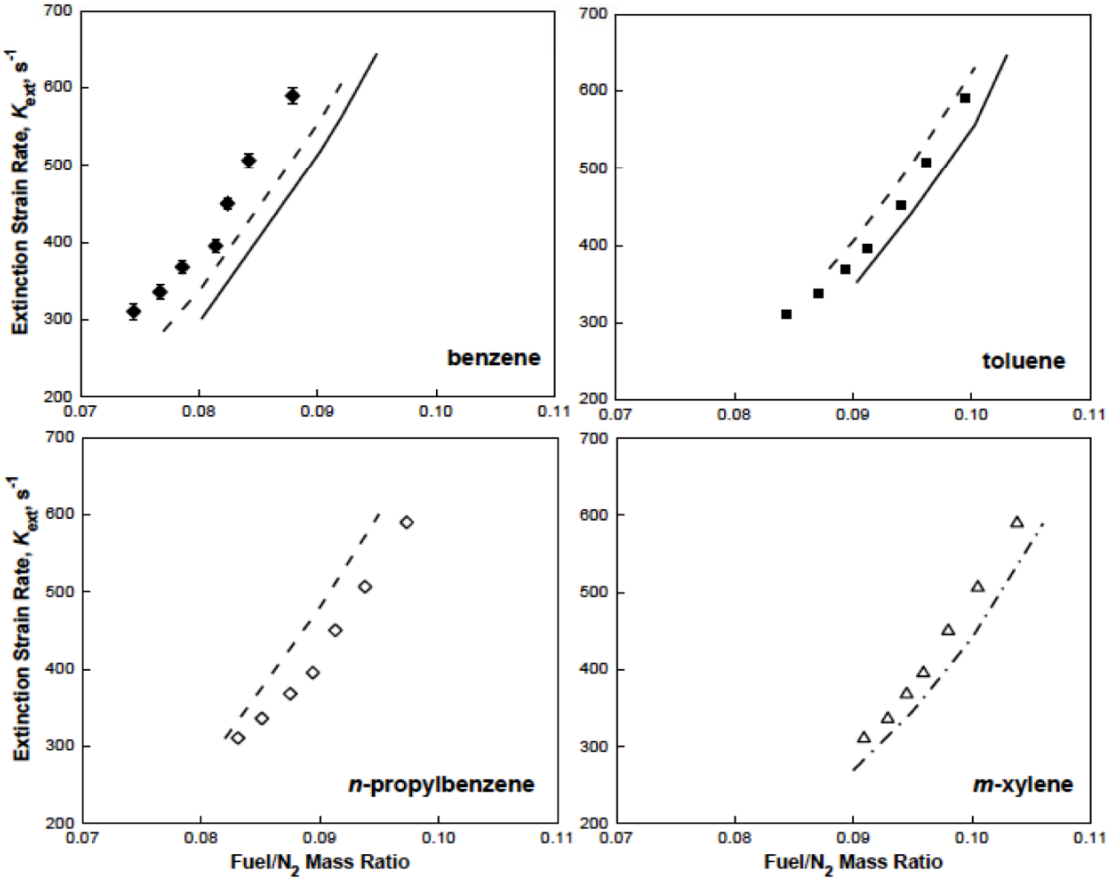


T_u = 353 K

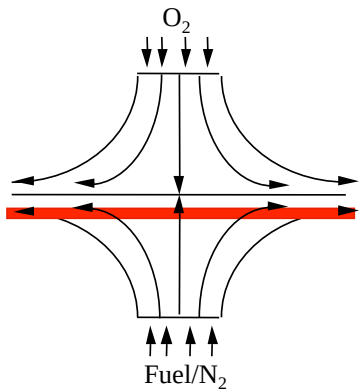


Experimentally determined extinction strain rate of non-premixed flames of (◆) benzene-, (◇) *n*-propylbenzene-, (■) toluene-, (▲) *o*-xylene-, (△) *m*-xylene-, (□) *p*-xylene-, (○) 1,2,4-trimethylbenzene-, and (●) 1,3,5-trimethylbenzene-N_2 mixtures against O_2 at T_u = 353 K and p =1 atm. 2σ uncertainty is similar for all fuels studied, and is shown for benzene only.

Extinction of Non-Premixed Aromatics Flames



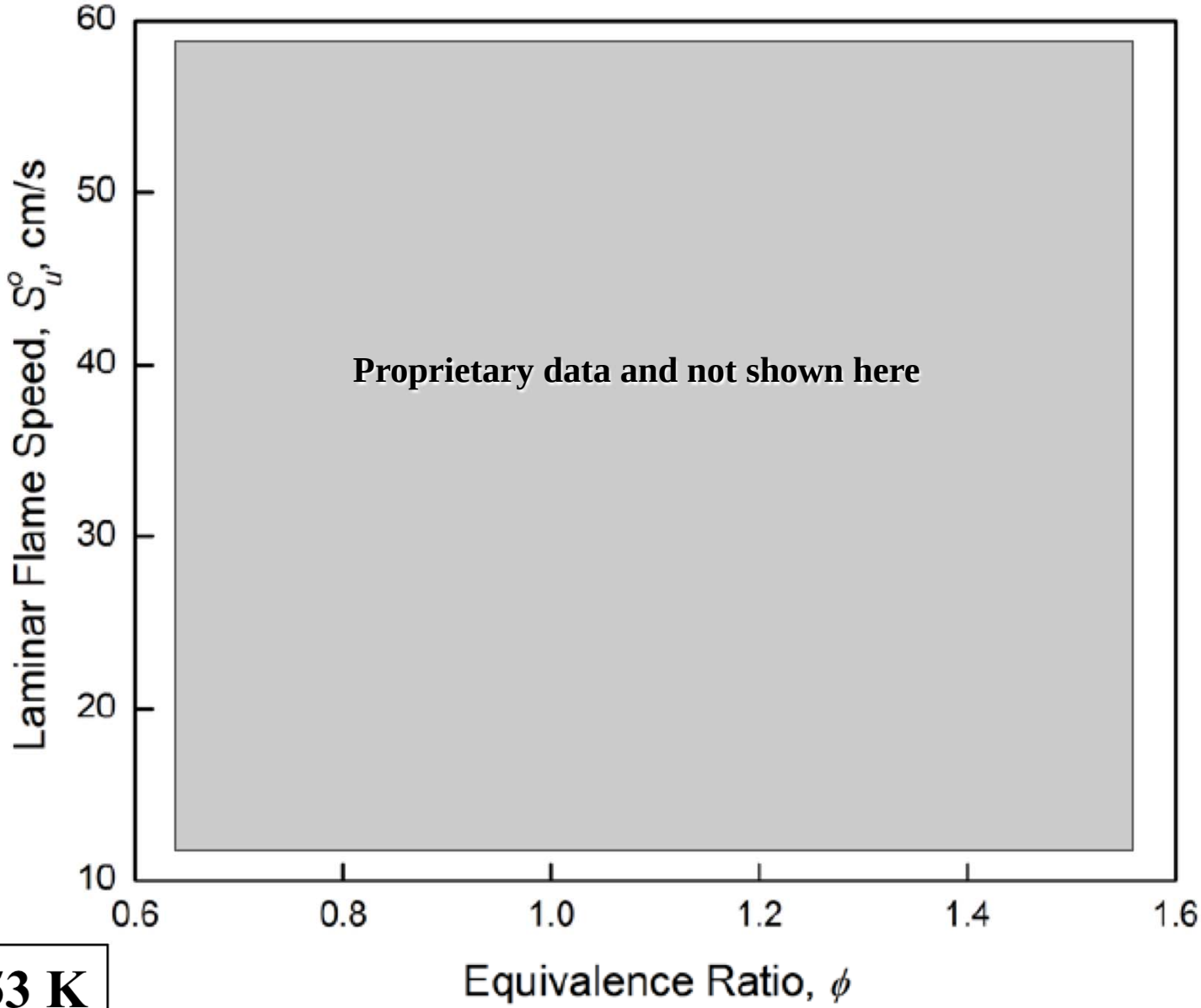
T_u = 353 K



Comparison of experimental (symbols) and computed extinction strain rates for non-premixed flames at $T_u = 353$ K and $p = 1$ atm. Symbols: experimental data; lines: simulations using Model I (solid lines), Model II (dashed lines), and Model IV (dash-dotted line).

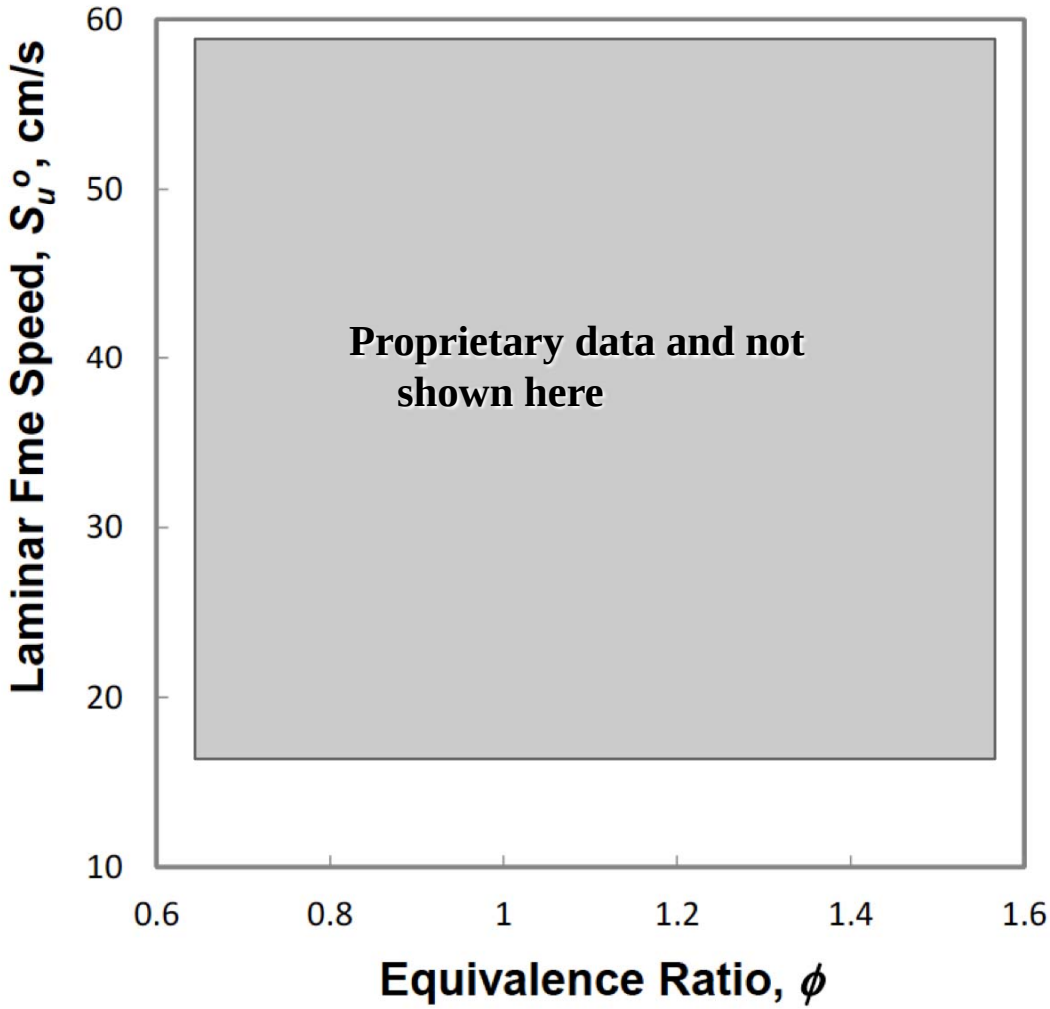
Model I: H. Wang, X. You, A. V. Joshi, S.G. Davis, A. Laskin, F.N. Egolfopoulos, and C.K. Law, USC Mech Version II (2007). (Benzene, Toluene)
Model II: S. Dooley, S.H. Won, M. Chaosa, J. Heynea, Y. Jua, F.L. Dryer, K. Kumar, C-J. Sung, H. Wang, M.A. Oehlschlaegerc, R.J. Santoro, and T.A. Litzinger, Combust. Flame (2010). (Benzene, Toluene, *n*-Propylbenzene)
Model III: F. Battin-Leclerc, R. Bounaceur, N. Belmekki, and P.A. Glaude, Int. J. Chem. Kinet. (2006). (*o*-, *m*-, *p*-xylene)
Model IV: K. Narayanaswamy , G. Blanquart, and H. Pitsch, Combust. Flame (2010). (*m*-xylene)

Propagation of Cyclopentadiene Flames



$T_u = 353$ K

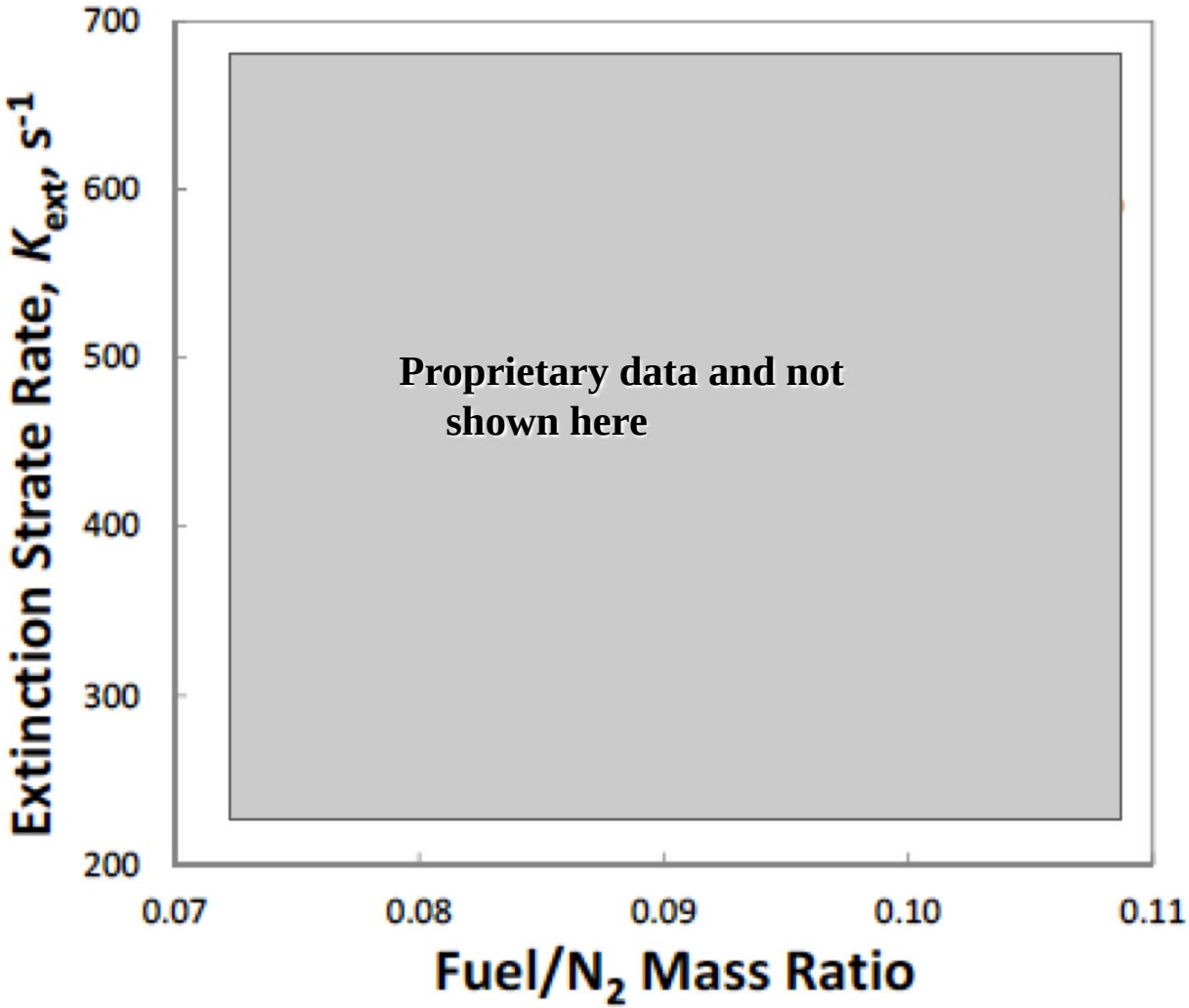
Propagation of Cyclopentadiene Flames



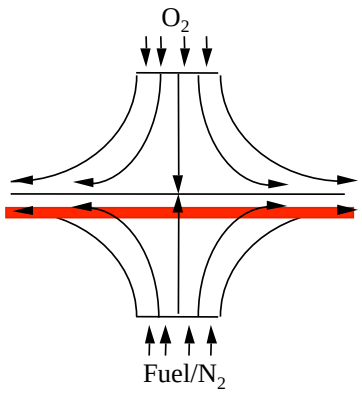
$T_u = 353$ K

Model I: H. Wang, X. You, A. V. Joshi, S.G. Davis, A. Laskin, F.N. Egolfopoulos, and C.K. Law, USC Mech Version II (2007). (Benzene, Toluene)
Model II: S. Dooley, S.H. Won, M. Chaosa, J. Heynea, Y. Jua, F.L. Dryer, K. Kumar, C-J. Sung, H. Wang, M.A. Oehlschlaegerc, R.J. Santoro, and T.A. Litzinger, Combust. Flame (2010). (Benzene, Toluene, *n*-Propylbenzene)

Extinction of Non-Premixed Cyclopentadiene Flames

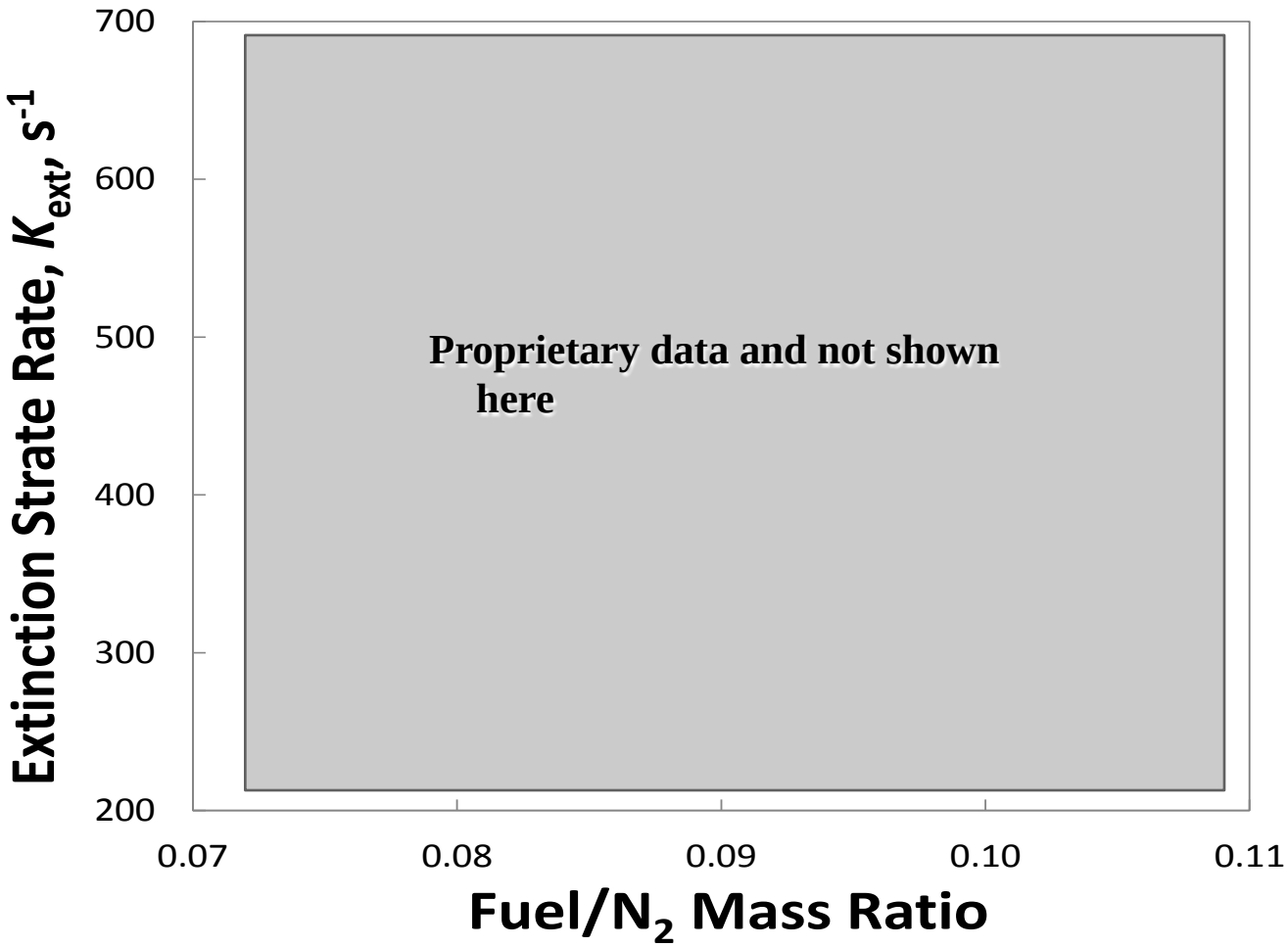


T_u = 353 K

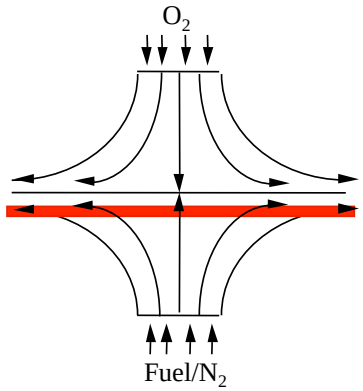


Experimentally determined K_{ext}'s of non-premixed (◆) benzene/N_2, (x) CPD/N_2, (◇) nPB/N_2, (■) toluene/N_2, (▲) *o*-xylene/N_2, (△) *m*-xylene/N_2, (□) *p*-xylene/N_2, (○) 1,2,4-TMB/N_2, and (●) 1,3,5-TMB/N_2 against O_2 flames at T_u = 353 K and p =1 atm.

Extinction of Non-Premixed Cyclopentadiene Flames



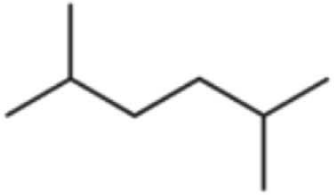
T_u = 353 K



Comparison of experimentally and numerically determined K_{ext}'s for non-premixed flames at T_u = 353 K and p =1 atm. Symbols: experimental data, (◆) benzene/N_2, (x) CPD/N_2, (◇) nPB/N_2, (■) toluene/N_2, and (△) *m*-xylene/N_2. Lines: numerical simulation, (····) Model I, (—) Model II, and (- - -) Model IV.

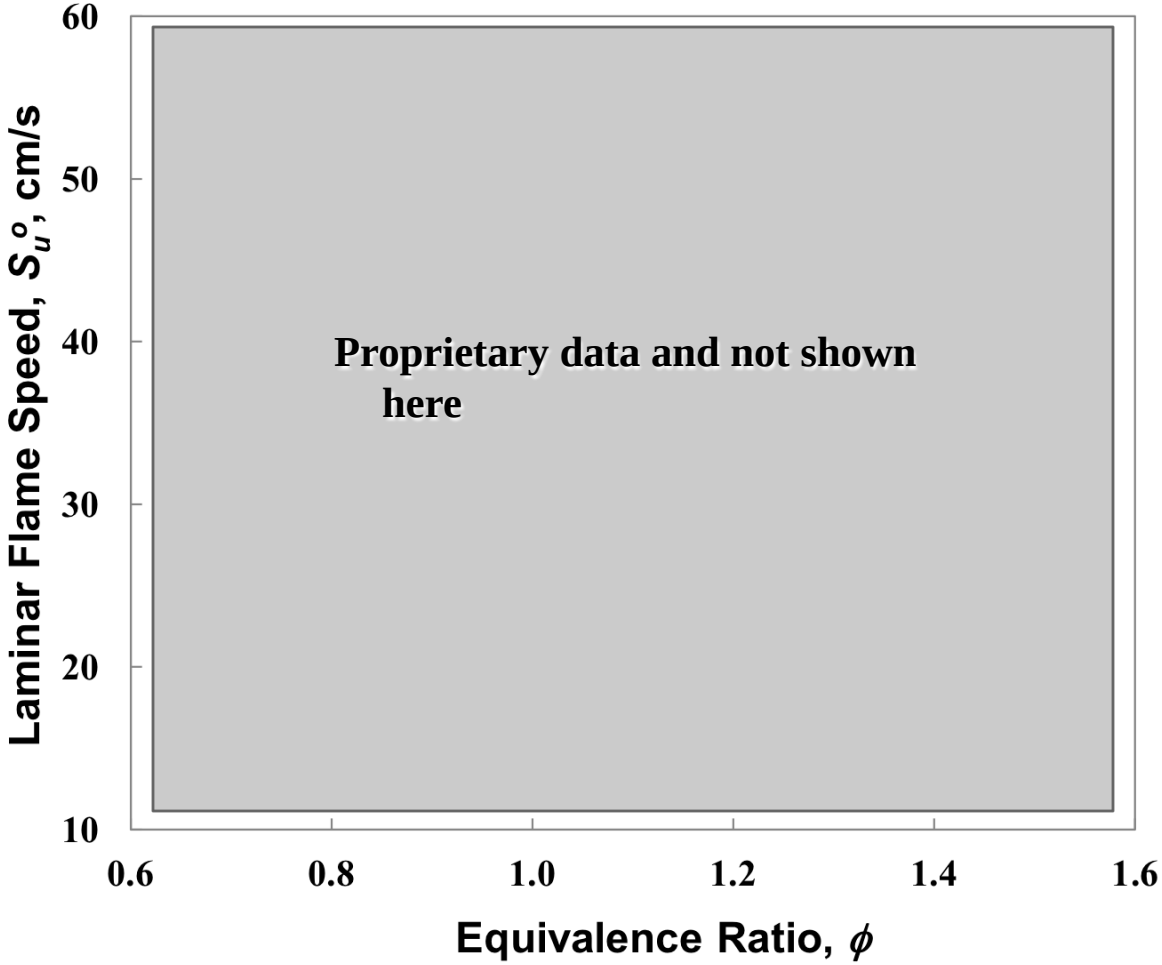
Propagation of Flames of C_8 Isomers

C_8 Isomers Considered

Chemical name	Purity, %	Molecular Formula	Structure	T_{ad}, ϕ=1.0
n-octane	>97	C_8H_{18}		2306 K
2-methylheptane (2-MHP)	>98	C_8H_{18}		2304 K
3-methylheptane (3-MHP)	>98	C_8H_{18}		2304 K
2,5-dimethylhexane (DMH)	>98	C_8H_{18}		2303 K
2,2,4-trimethylpentane (*iso*-octane)	>99	C_8H_{18}		2300 K

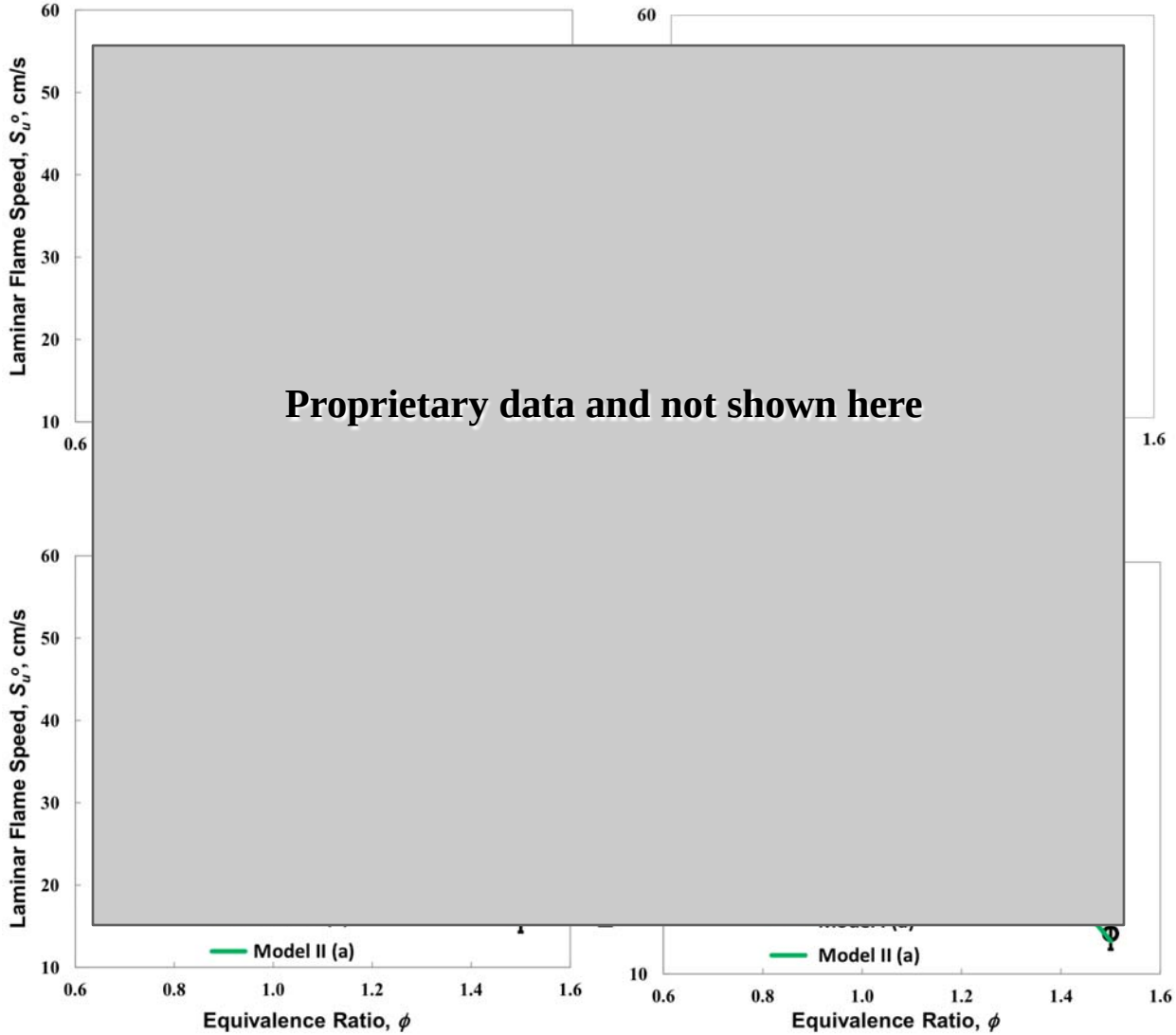
~ 6 K

Laminar Flame Speeds – Comparison of Experimental Data



Experimentally determined S_u^o's of (◆) *n*-octane/air [43], (■) 2-methylheptane/air [42], (△) 3-methylheptane/air, (●) 2,5-dimethylhexane/air, and (▲) *iso*-octane/air mixtures at T_u = 353 K and p = 1 atm.

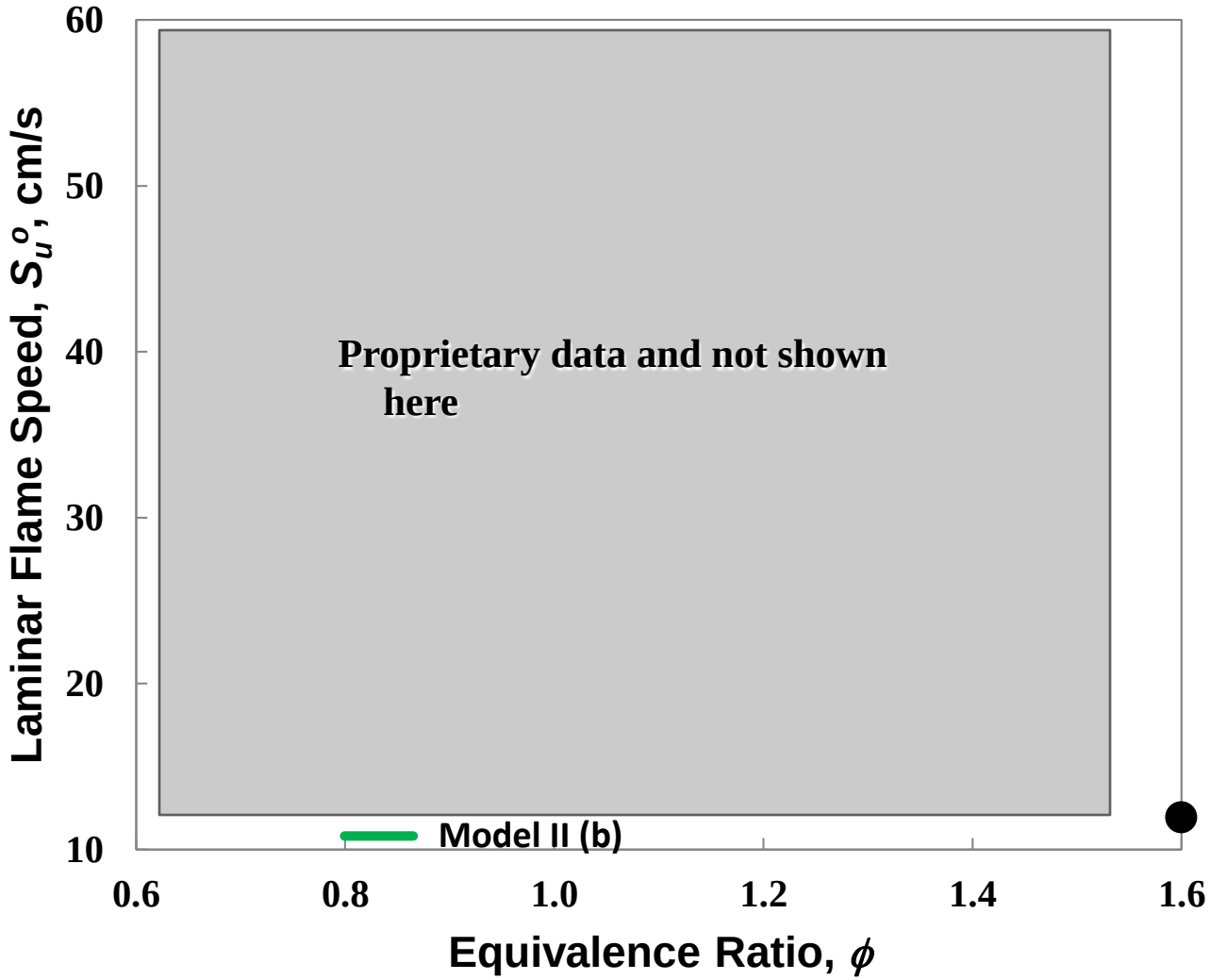
Laminar Flame Speeds: Comparison of Data and Simulations



(c) (d)

Model I: LLNL Model (Sarathy, Pitz, Westbrook)
Model II: LLNL octane isomer kinetics superimposed on to USC Mech II.

Laminar Flame Speeds of iso-Octane/Air Mixtures: Comparison of Data and Simulations



Model I: LLNL Model (Sarathy, Pitz, Westbrook)
Model II: LLNL octane isomer kinetics superimposed on to USC Mech II.

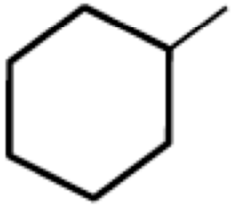
Ignition of Non-Premixed Flames of:

* *Cyclohexane*
* *Mono-Alkylated Cyclohexane*
* *Iso-Alkane*

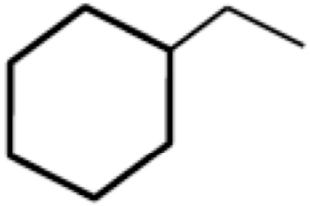
Cyclo-Alkanes Considered

Cyclohexane

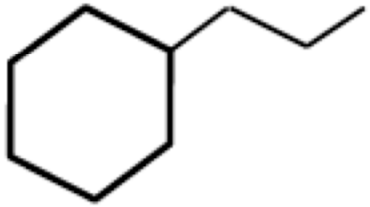
***methyl*-Cyclohexane**



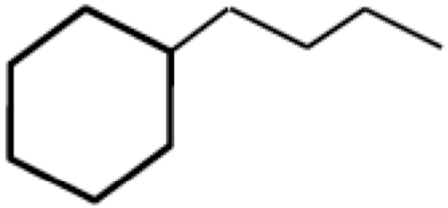
***ethyl*-Cyclohexane**



***n-propyl*-Cyclohexane**

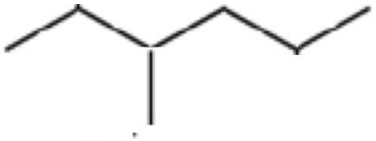


***n-butyl*-Cyclohexane**

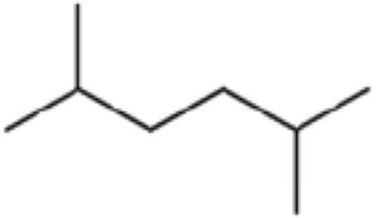


Iso-Alkanes Considered

3-methylheptane (C_8)

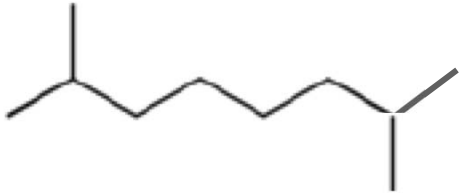


2,5-dimethylhexane (C_8)



2,2,4-trimethylpentane (iso-octane) (C_8)

2,7-dimethyloctane (C_{10})

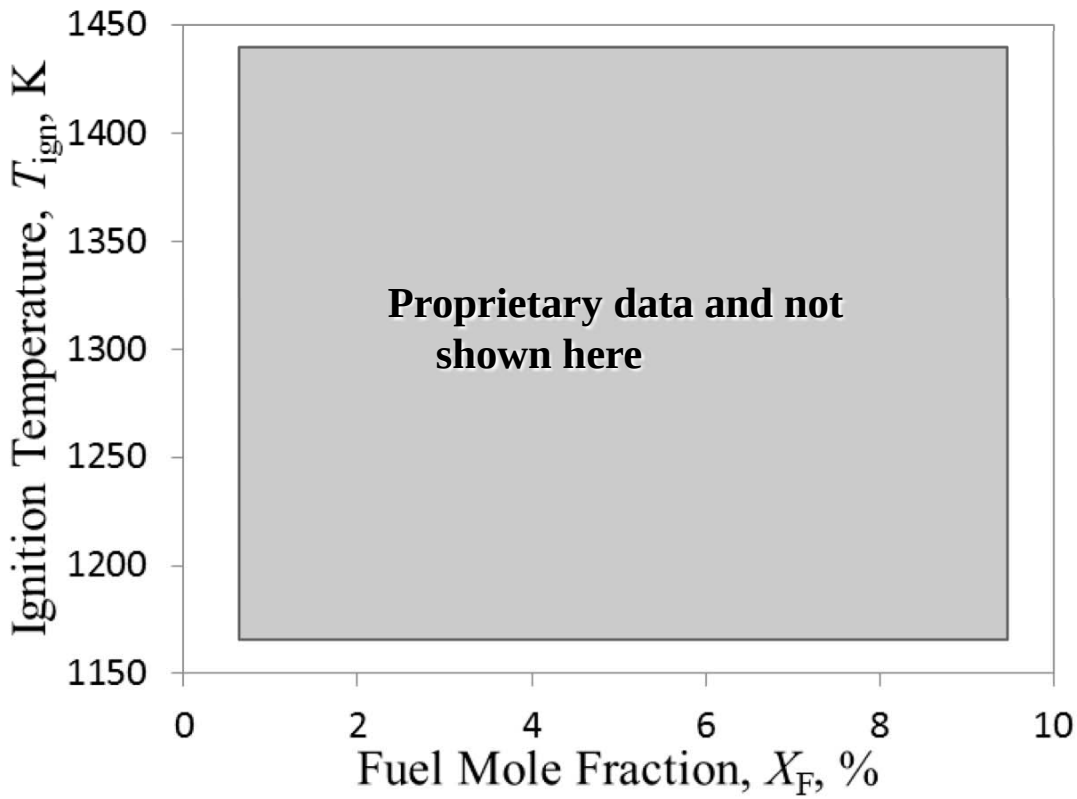


and compared with

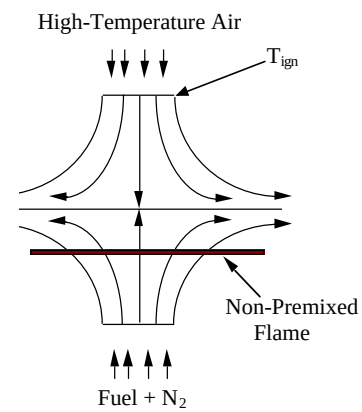
***n*-octane**

***n*-decane**

Ignition of Cyclohexane and n-Hexane Flames: Experiments and Theory

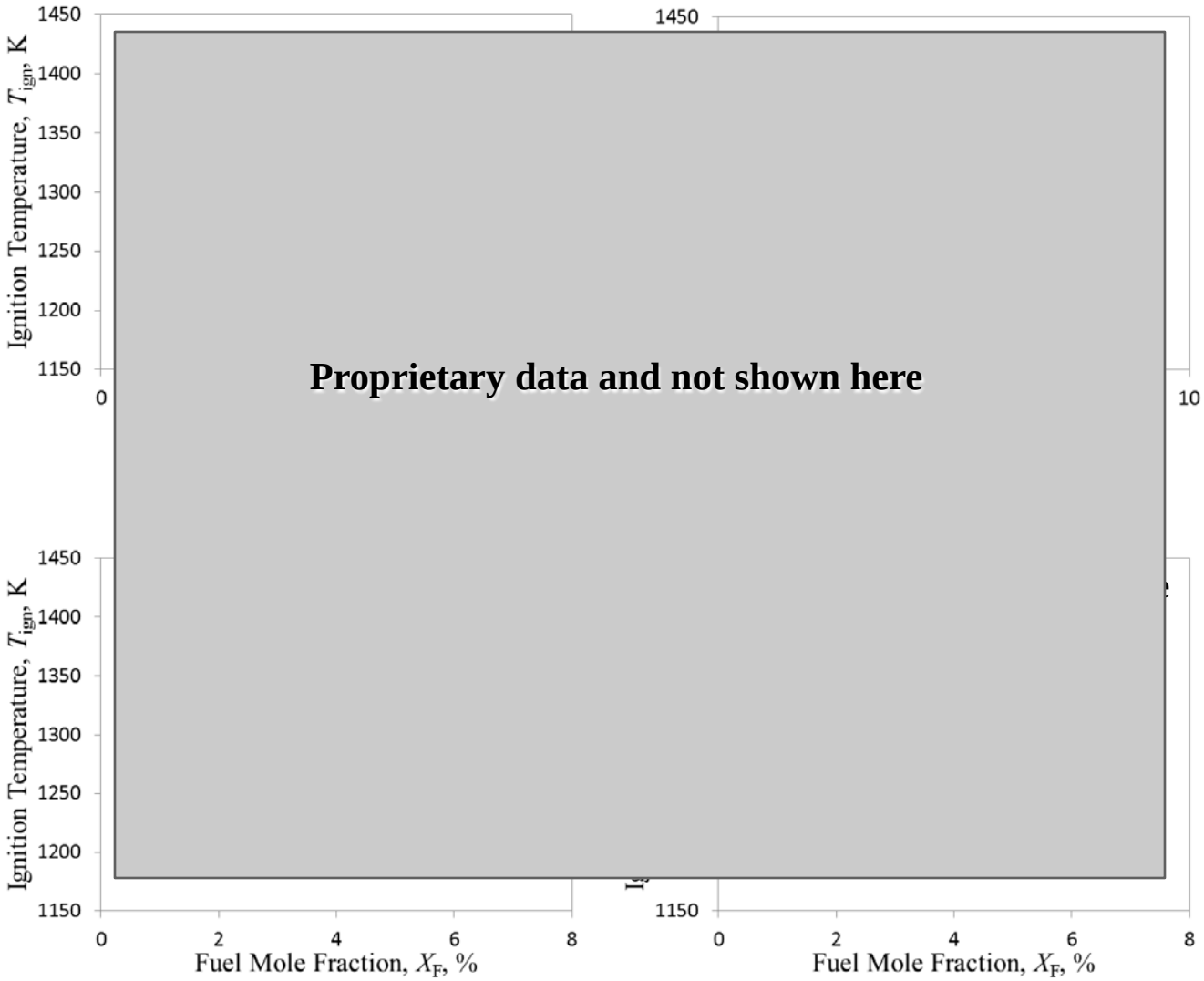


T_u = 373 K
K_{local} = 120 s^{-1}



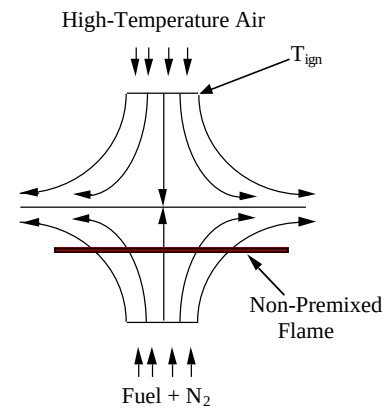
Experimental and computed T_{ign} of non-premixed cyclohexane (♦)(---) and n-hexane (▲)(—) flames.

Ignition of Mono-Alkylated Cyclohexane Flames: Experiments and Theory

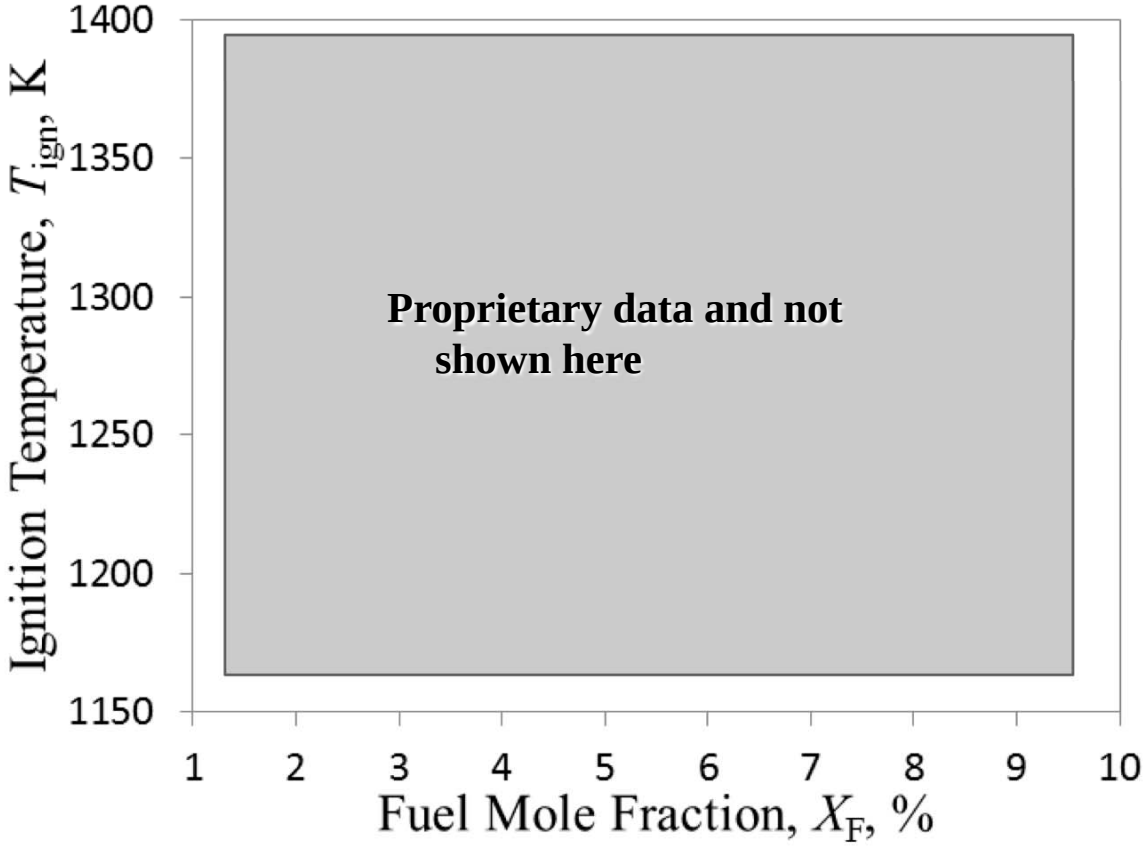


(c) (d)

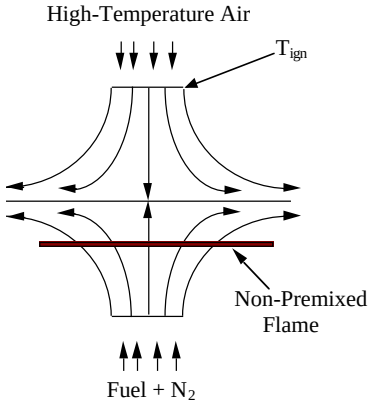
T_u = 373 K
K_{local} = 120 s^{-1}



Ignition of n-Hexane, Cyclohexane, and Mono-Alkylated Cyclohexane Flames: Comparison of Experimental data

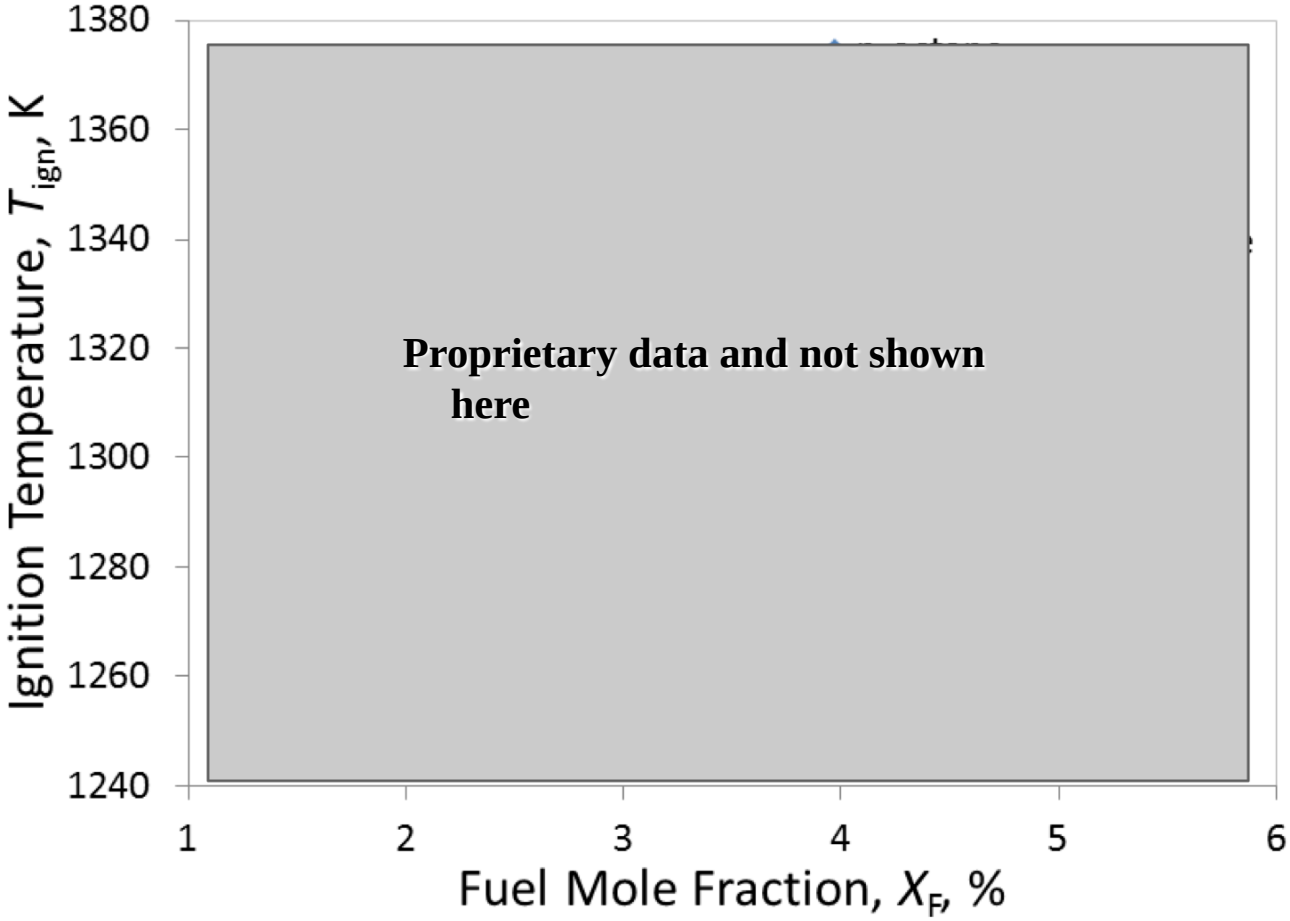


T_u = 403 K
K_{local} = 125 s^{-1}

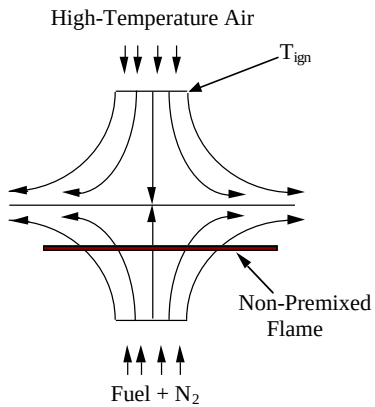


Comparison of experimentally determined T_{ign}'s; (♦) cyclohexane, (□) *methyl*-cyclohexane, (Δ) *ethyl*-cyclohexane, (○) *n-propyl*-cyclohexane, (ж) *n-butyl*-cyclohexane, (▲) *n*-hexane.

Ignition of C_8 Isomer Flames: Effect of Fuel Branching

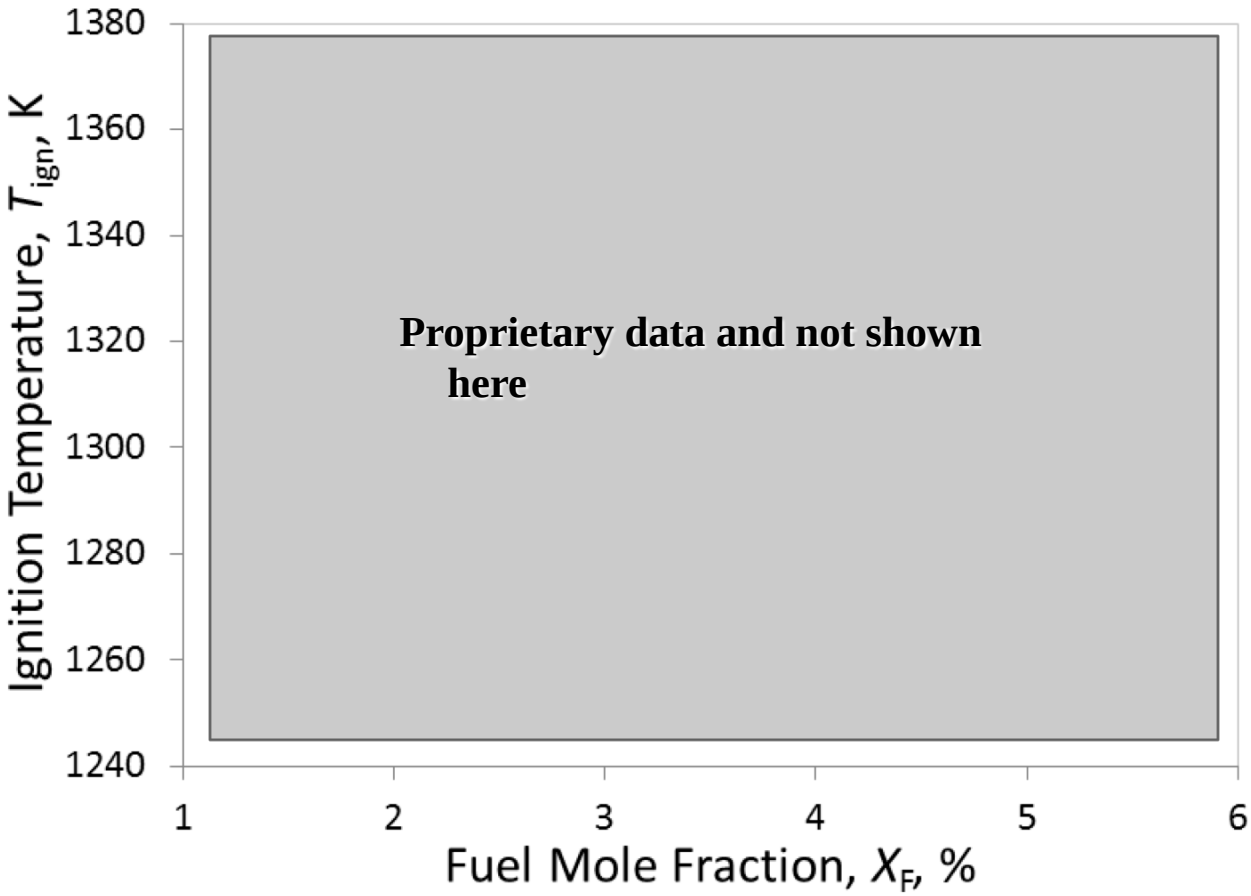


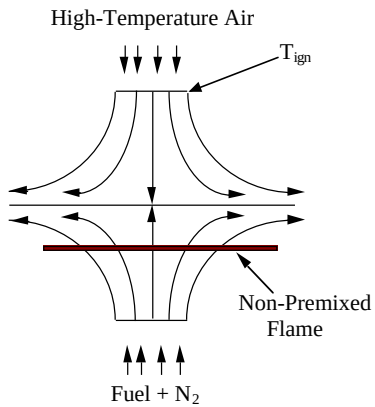
T_u = 403 K
K_{local} = 125 s^{-1}



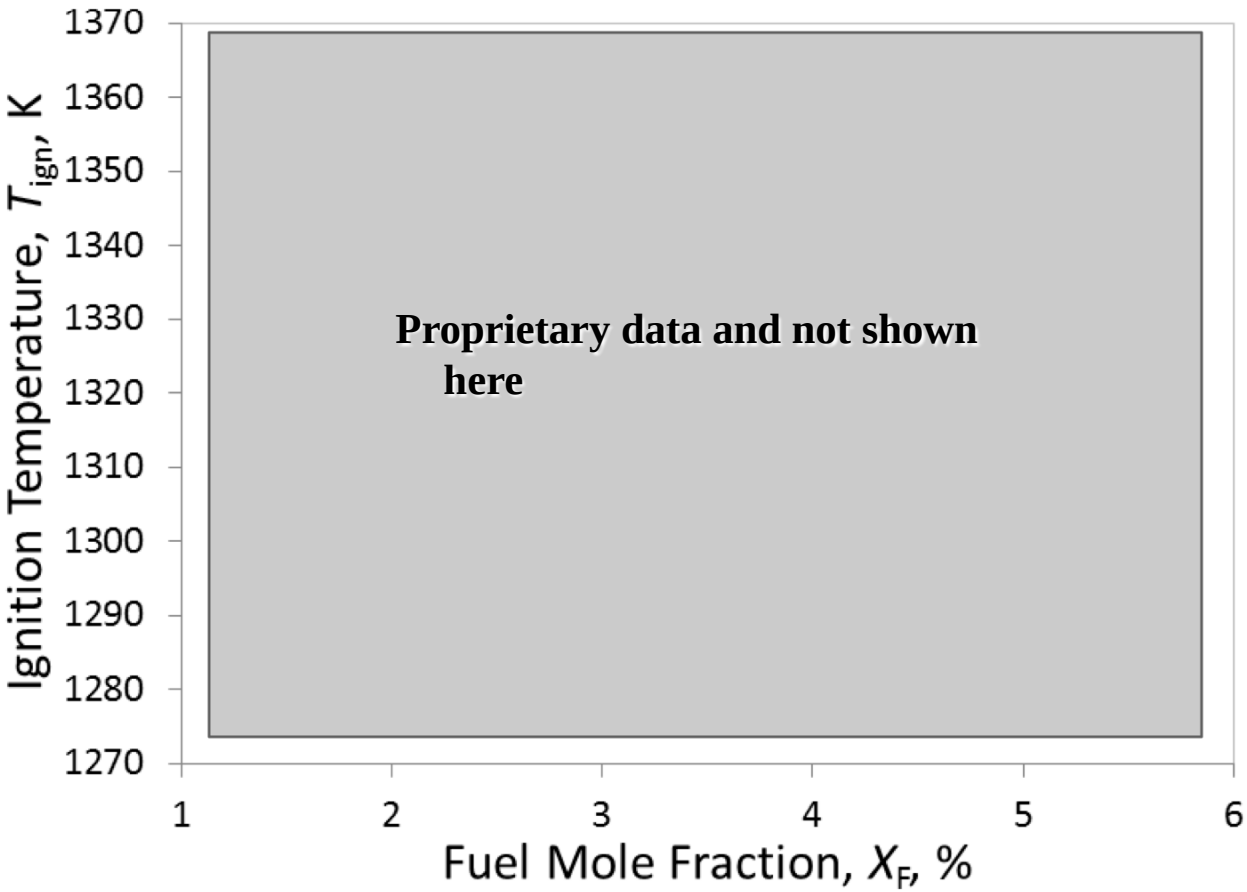
Ignition of C_{10} Isomer Flames: Effect of Fuel Branching

T_u = 403 K
K_{local} = 125 s^{-1}

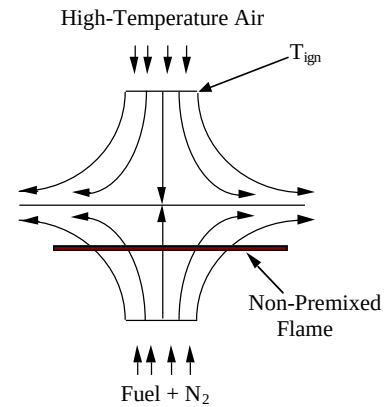




Ignition of iso-Alkane Flames: Effect of Carbon Number



T_u = 403 K
K_{local} = 125 s^{-1}



Concluding Remarks

1. **Experimental data on laminar flame ignition, propagation, and extinction have been determined at 1 atm for:**
   - » ***n*-, *cyclo*-, *iso*-alkanes**
   - » **aromatics**
   - » **binary fuel mixtures**
   - » **jet fuels**

2. **Fuel-related chemistry affects flame propagation as follows:**
   - » ***n*-alkanes: minimally due to rapid cracking of fuel molecule**
   - » ***cyclo*-alkanes: somewhat through the distribution of the cracked products**
   - » ***iso*-alkanes: somewhat through the distribution of the cracked products**
   - » **aromatics: notably due to stability of the aromatic ring**

3. **Some remaining issues related to flame studies:**
   - » **Experimental data need to "converge," e.g. laminar flame speeds**
   - » **Data for such high MW fuels at high pressures**
     - **critically needed**
     - **hard to obtain**
   - » **Notable deficiencies of aromatics kinetics**
   - » **Probe kinetic couplings between fuels further**
   - » **Accurate description of transport properties of large MW fuels**