Detailed Studies on the Oxidation of Surrogate Fuel Components and Surrogates of JP-8

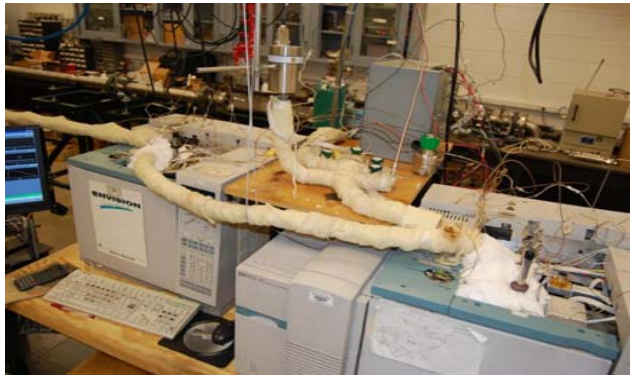
Prof. Kenneth Brezinsky
Department of Mechanical and Industrial Engineering
University of Illinois at Chicago

2010 MURI AFOSR Annual Presentation
Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)
FUELS RESEARCH REVIEW
Princeton, NJ
September 22nd, 2010

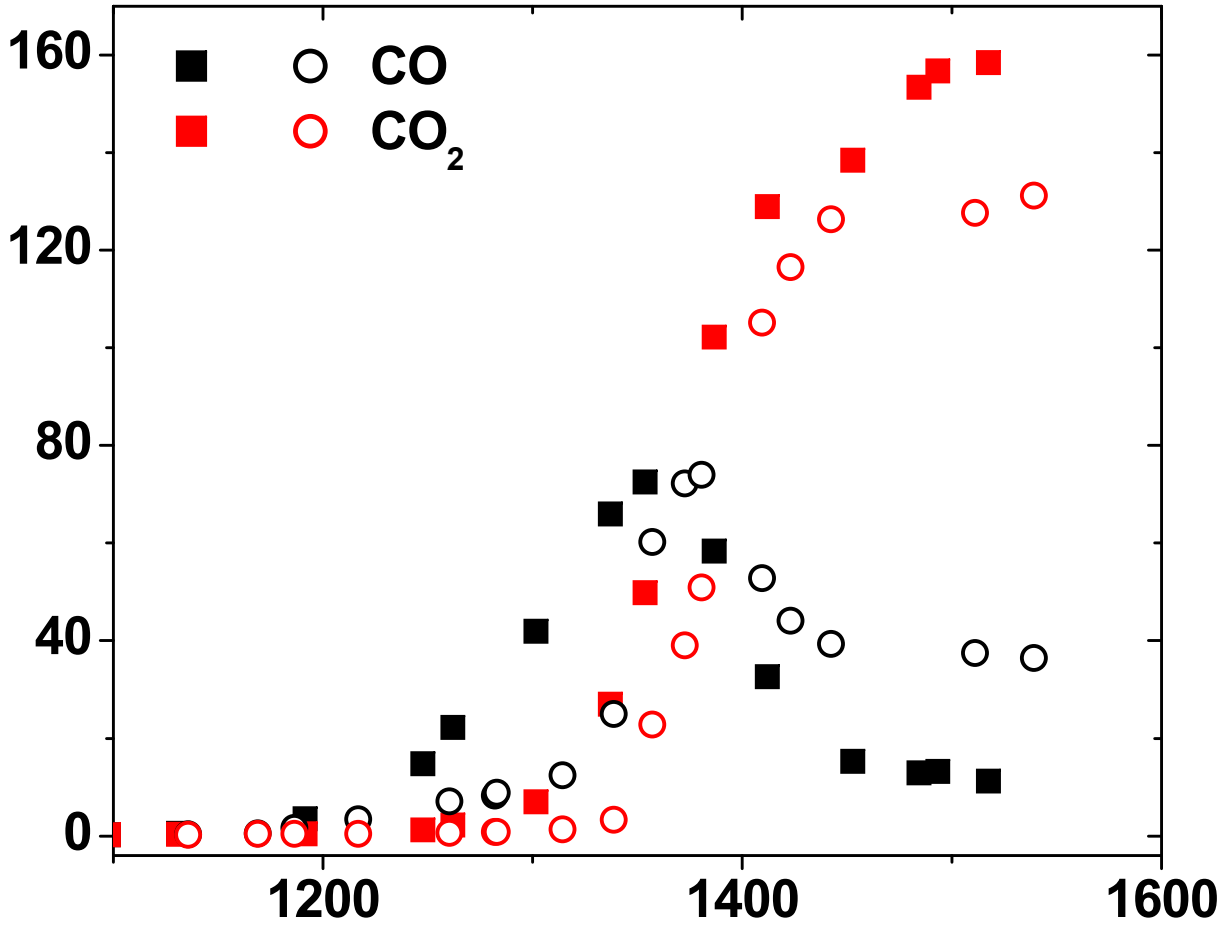
High Pressure Single Pulse Shock Tube (HPST)

- HPST Operating Conditions
  - Temperatures: 800-2500 K
    Pressures: 25 – 1000 bar
    Reaction times: 1.0 – 3.0 ms
  - Single Pulse Shock Tube heated to 100°C



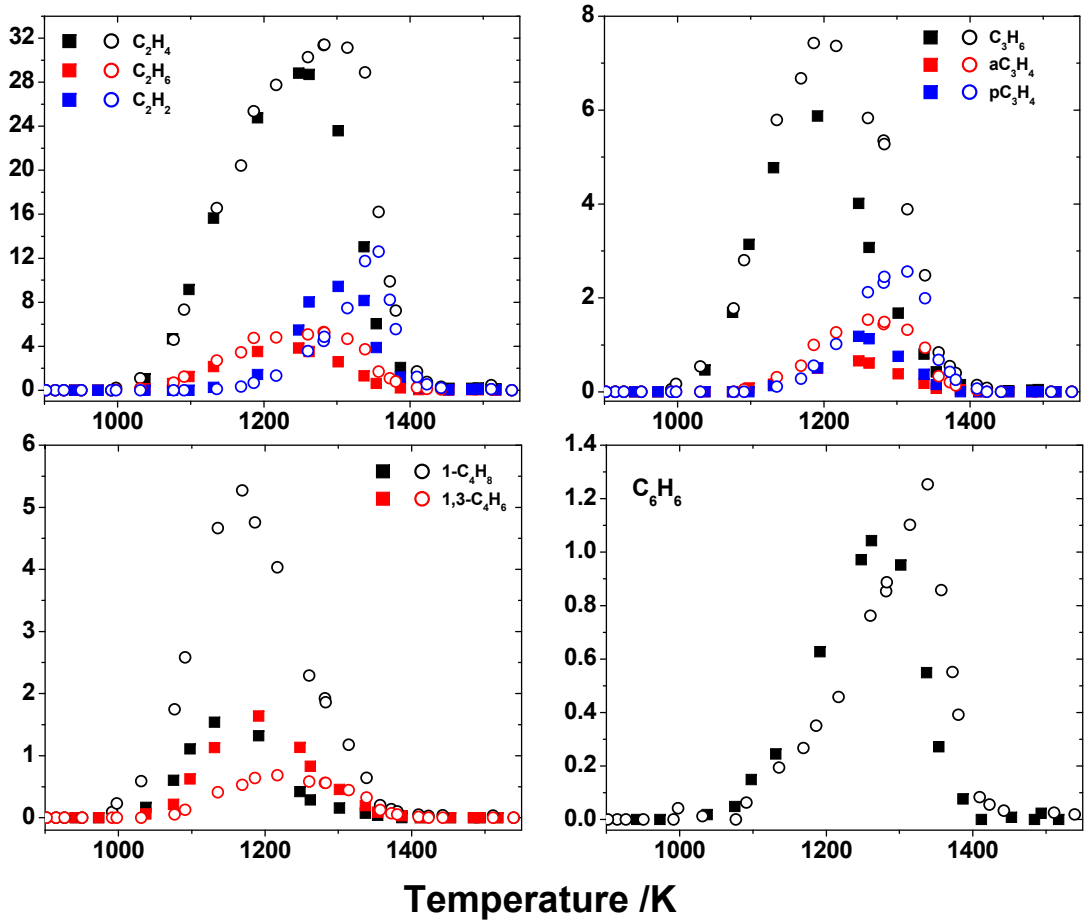
- Analytical Setup
  - Stable species analyzed using the GCs
    - TCD and FID x2 (used for quantification)
    - MS (used only for identification)
  - GC transfer lines heated to 150°C

1st Generation Surrogate versus POSF 4658



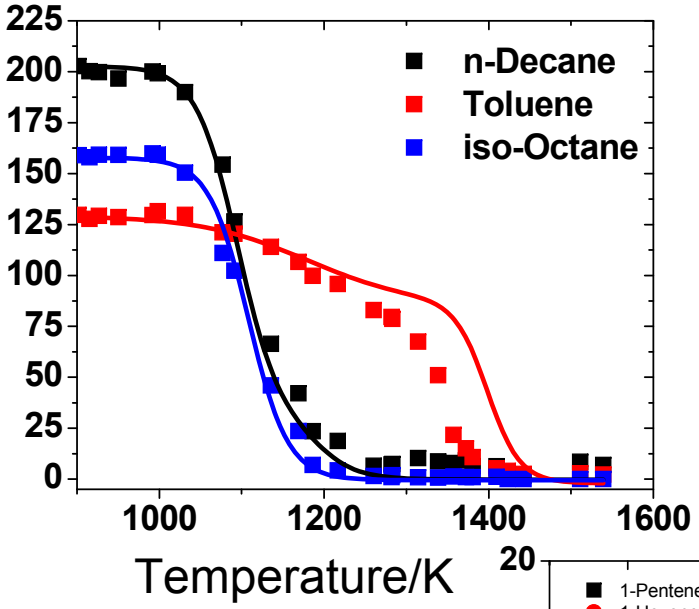
POSF 4658 [■ ■] 1st Gen. Surrogate [○ ○]

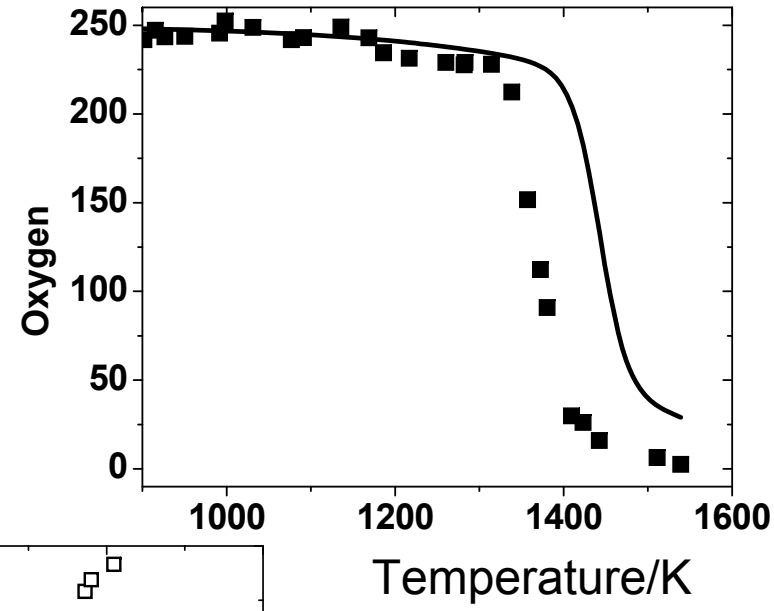
Comparison of 1st Gen. Surrogate and POSF 4658

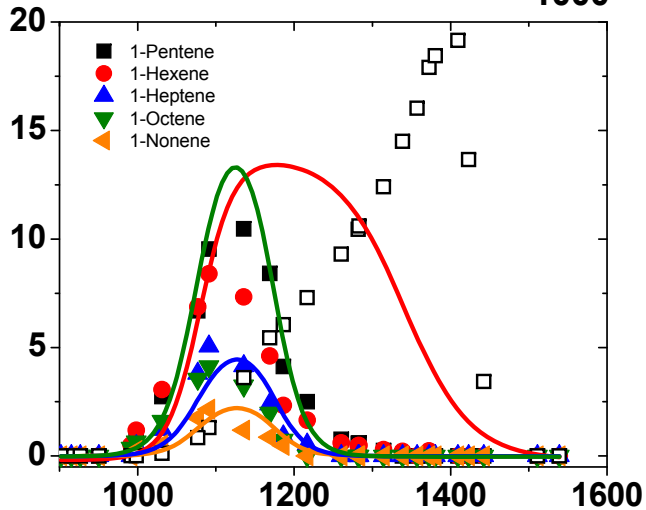


POSF 4658 [■ ■ ■] 1st Gen. Surrogate [○ ○ ○]

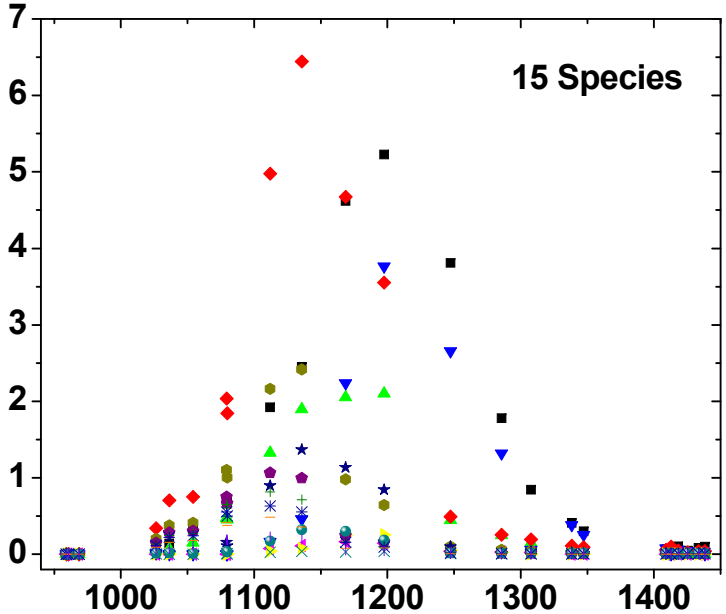
1st Generation Surrogate Experiments Comparison with Model

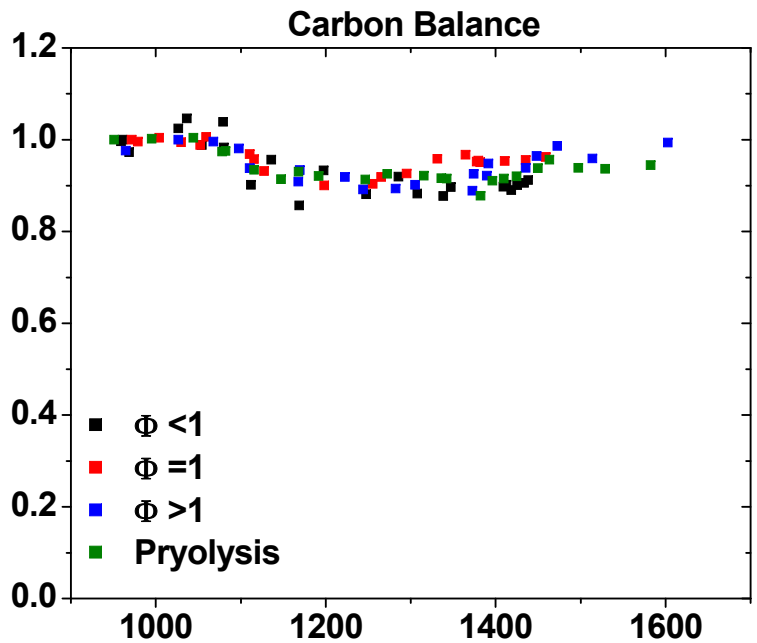






n-Decane Experimental Data





Temperature /K

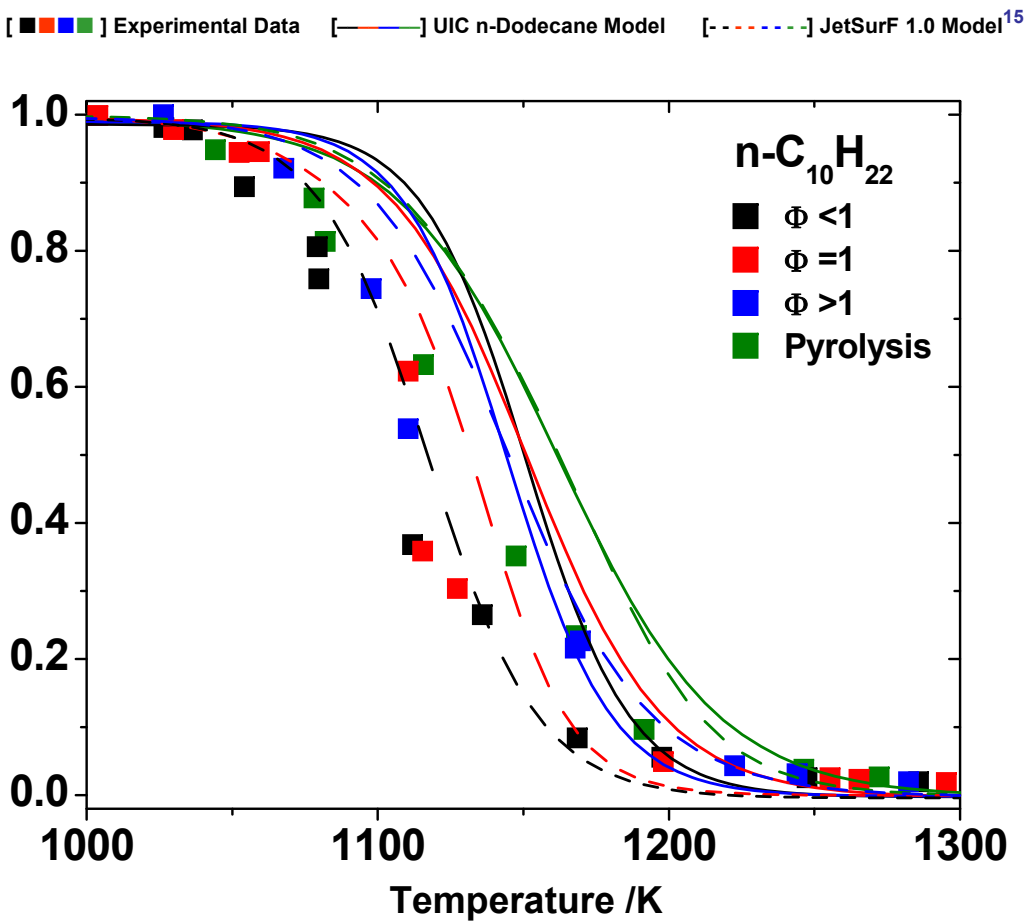
- Measured Species
  - Carbon monoxide, carbon dioxide, methane, ethylene, ethane, acetylene, propylene, propadiene, propyne, 1-butene, 1,3-butadiene, 1-buten-3-yne, 1,3-butadiyne, 1-pentene, 1,3-pentadiene, 1-hexene, benzene, 1-heptene, 1-octene, 1-nonene

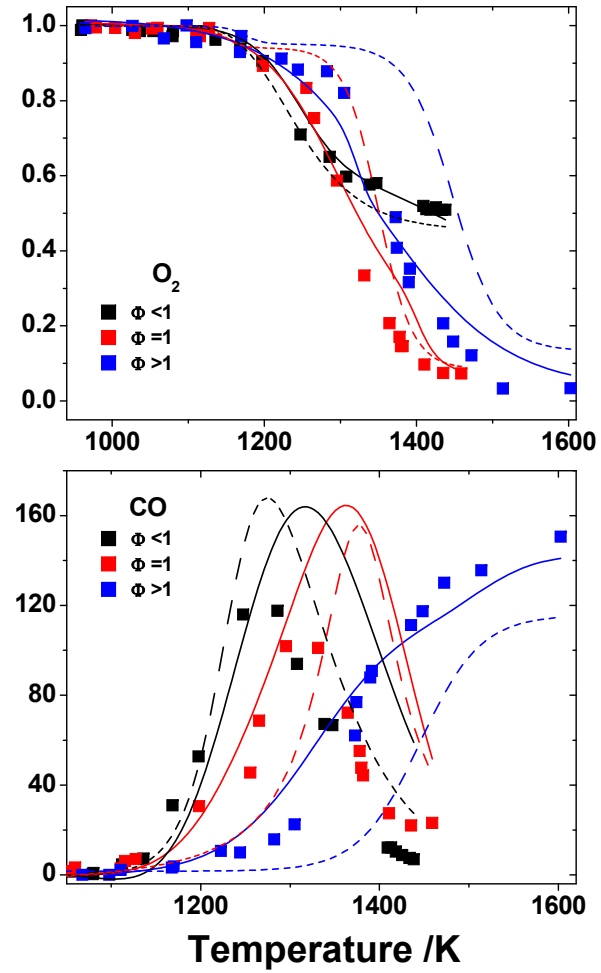
n-Decane Experiments and Modeling

- UIC n-Decane/n-Dodecane Model
  - C1-C4 base mechanism-MURI small species chemistry model[1]
  - C5-C12 from Jet Fuel MechI (2007)[12]
  - General reactions were added/changed to achieve better agreement with the pyrolysis experimental data
    - Additional reactions for 1-alkenes (C5-C9), n-decane → decyl, acetylene, 1,3-butadiyne, propylene decay, and benzene were added[13,14] were added
    - Updated key reactions in the c1-c4 base mechanism

12. You, X., Egolfopoulos, F. N., Wang, H., Proceedings of the Combust. Institute (2009), 32(Pt. 1), 403-410
13. Sivaramakrishnan, R., Tranter, R. S., Brezinsky, K., Journal of Physical Chemistry A (2006), 111(30), 9388-9399
14. Sivaramakrishnan, R., Brezinsky, K., Vasudevan, H., Tranter, R. S., Combust. Sci. and Tech (2006), 178(1-3), 285-305

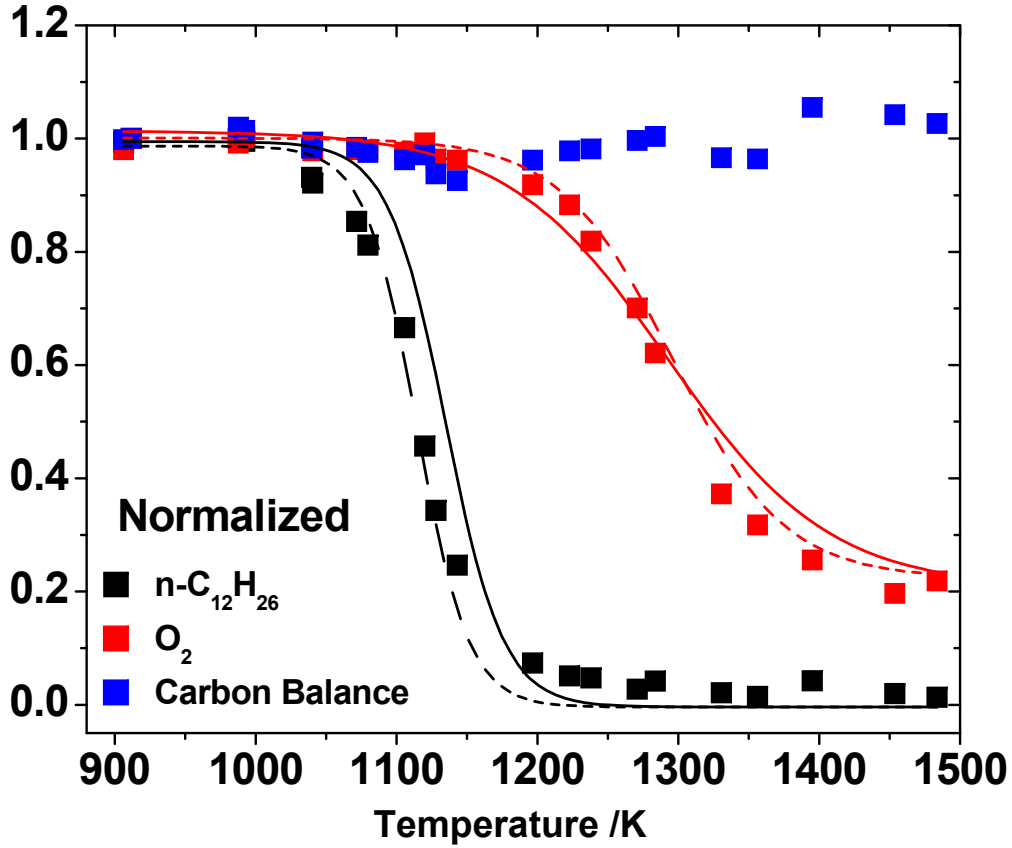
n-Decane Experimental Data and Modeling

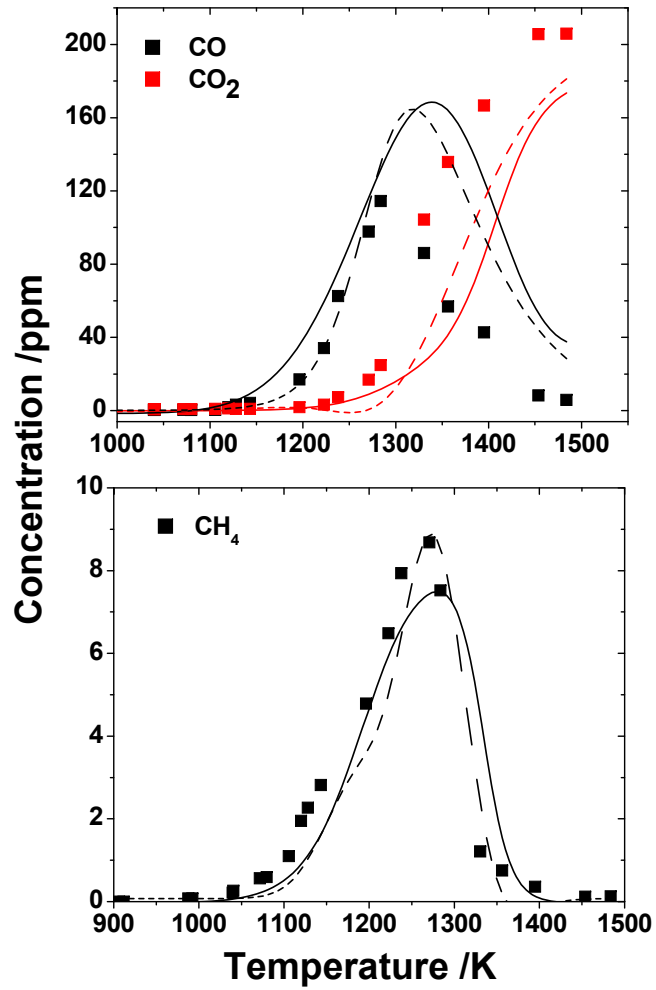




15. B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, F. N. Egolfopoulos, H. Wang, S. S. Vasu, D. F. Davidson, R. K. Hanson, H. Pitsch, C. T. Bowman, A. Kelley, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, A. Violi, R. P. Lindstedt, A high-temperature chemical kinetic model of *n*-alkane oxidation, JetSurF version 1.0, September 15, 2009 (http://melchior.usc.edu/JetSurF/Version1_0/Index.html).

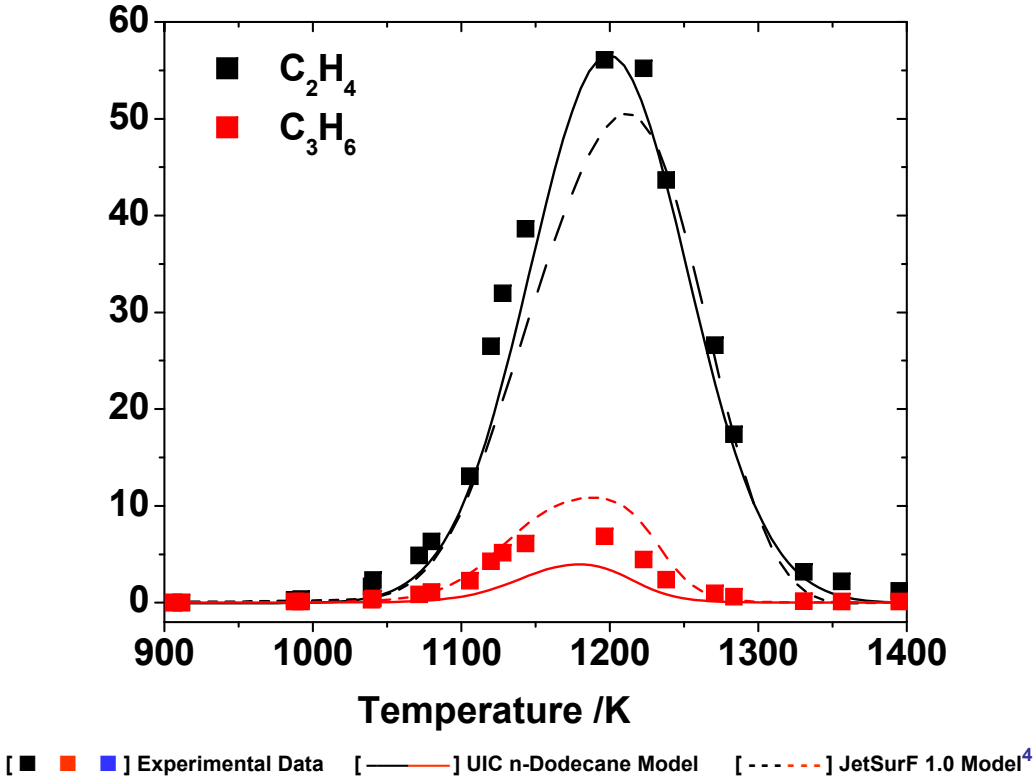
n-Dodecane Experimental Data and Modeling

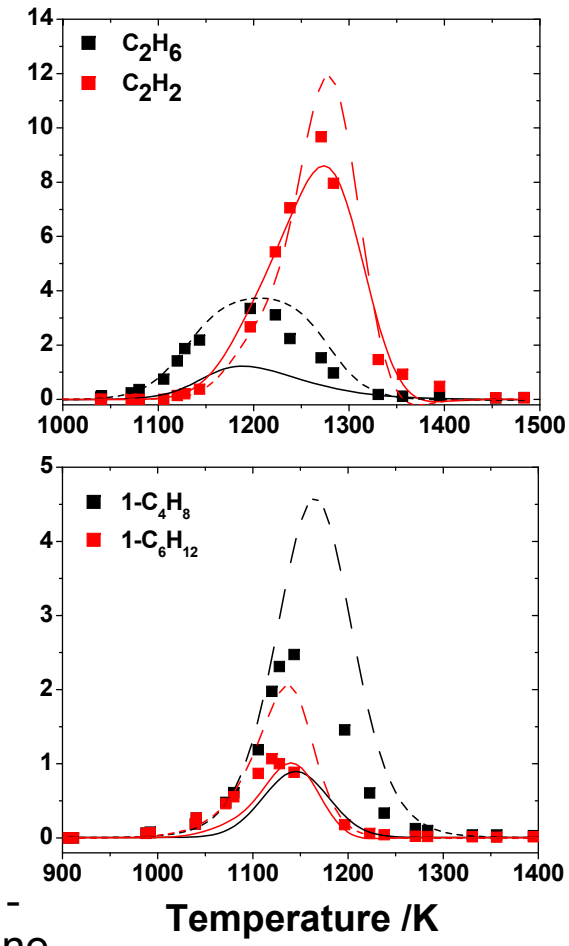




[■ ■ ■] Experimental Data [———] UIC n-Dodecane Model [- - - - - -] JetSurF 1.0 Model[4]

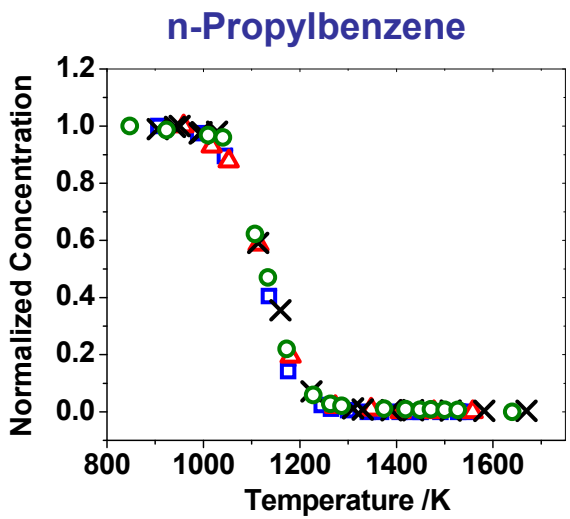
n-Dodecane Experimental Data and Modeling

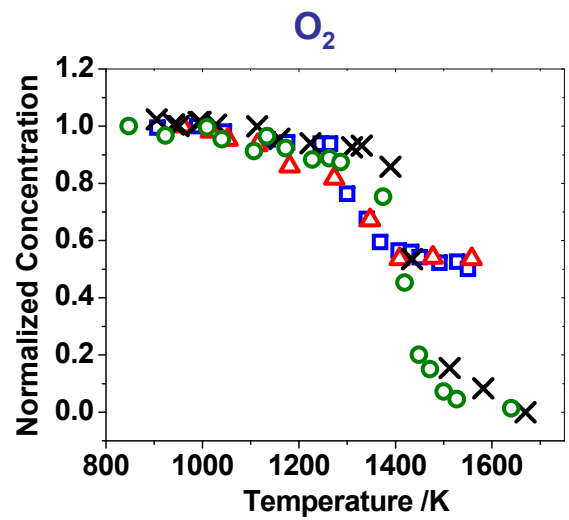




- Additional species not shown
  - propadiene, propyne, 1,3-butadiene, 1-buten-3-yne, 1-pentene, 1,3-pentadiene, benzene, 1-heptene, 1-octene, 1-nonene, 1-undecene

n-Propylbenzene Oxidation Experiments





[Δ]-Φ < 1, [□]-Φ <1, [o]-Φ >1, [X]- Φ >1

The decay of n-propylbenzene and oxidizer

- independent of pressure
- dependent on Φ

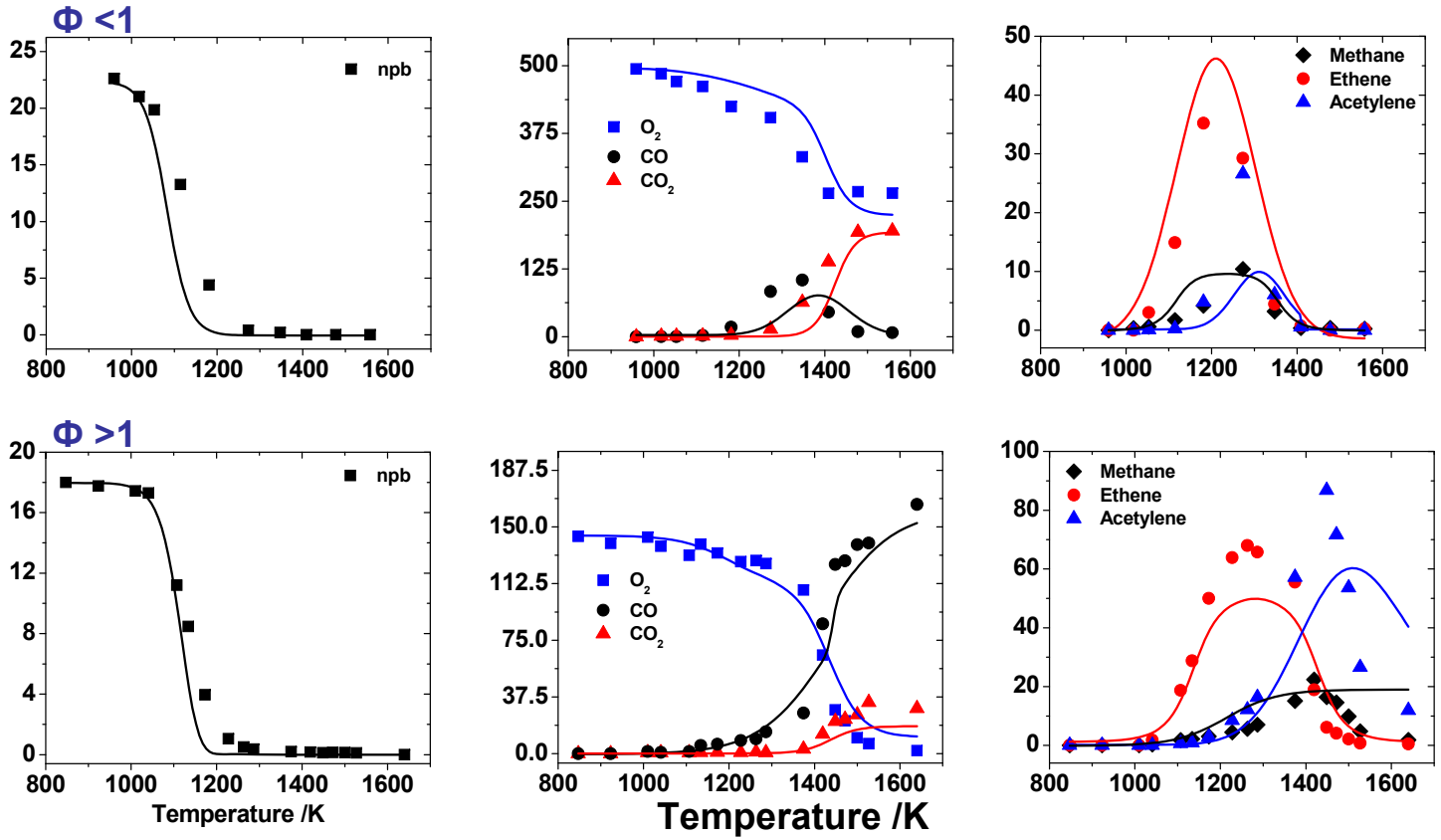
n-Propylbenzene Oxidation Modeling*

- UIC n-Propylbenzene Oxidation Model developed to predict single ring aromatics and aliphatics from fuel.
- Model sub-mechanisms
  - C0-C4 chemistry – MURI small species chemistry model[1]
  - C5-C8 chemistry
    - High Pressure Toluene Oxidation Model[2]
    - High Pressure Toluene Pyrolysis Model[3,4]
  - n-Propylbenzene oxidation chemistry
    - Qi Chen and Froment n-propylbenzene pyrolysis mechanism[5]
    - Rate constants of oxidation reactions based on analogous reactions of propane and toluene

*Manuscript in preparation

1. S. Dooley et al., Combust. Flame (2010) doi:10.1016/j.combustflame.2010.07.001
2. R. Sivaramakrishnan., R. S. Tranter., K. Brezinsky., Proc. Combust. Inst., 30 (2005) 1165-1173.
3. R. Sivaramakrishnan, R. S. Tranter and K. Brezinsky., J. Phys. Chem A 110 (2006) 9388-9399.
4. R. Sivaramakrishnan, R. S. Tranter and K. Brezinsky, J. Phys. Chem. A. 110 (2006) 9400-9404.
5. Qi Chen and Gilbert F. Froment., J. of Analytical and Applied Pyrolysis 21 (1991) 51-77

n-Propylbenzene Oxidation Model Results



[■] Experimental Data [—] UIC n-Propylbenzene Model

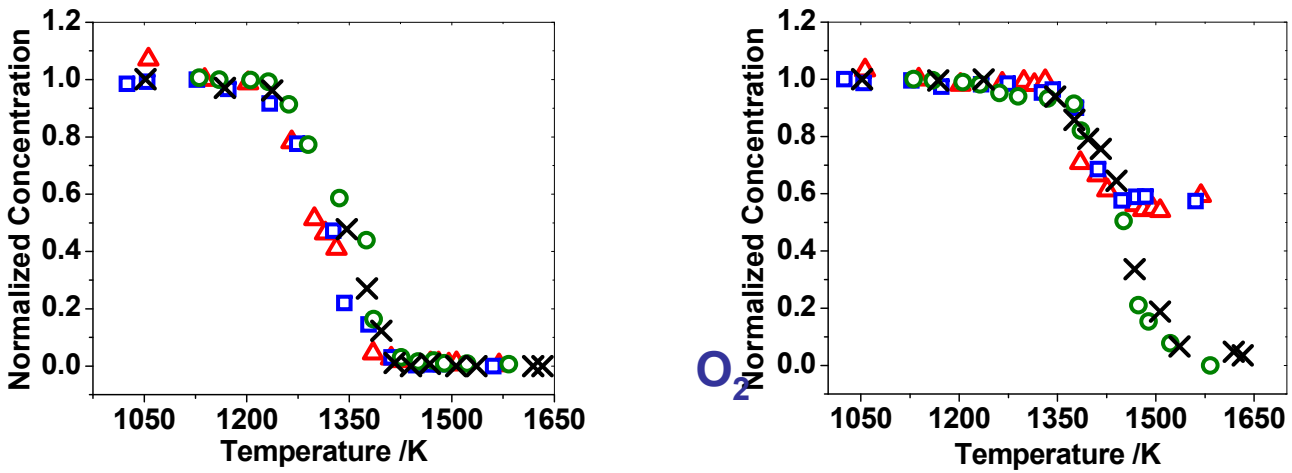
Analysis of the Simulation

- Models shows good agreement for the decay of the fuel, O_2, CO and CO_2
- Shows satisfactory profiles for the formation of major intermediates for $\Phi < 2$
- Polycyclic aromatic hydrocarbon chemistry should be included for complete predictions

m-Xylene Oxidation Experiments

- Experiments and modeling of m-xylene performed to assist development of 1,3,5-trimethylbenzene model

m-Xylene



[Δ]-Φ <1, [□]-Φ <1, [o]-Φ >1 [X]- Φ >1

The decay of m-xylene and oxidizer

- independent of pressure
- dependent on Φ

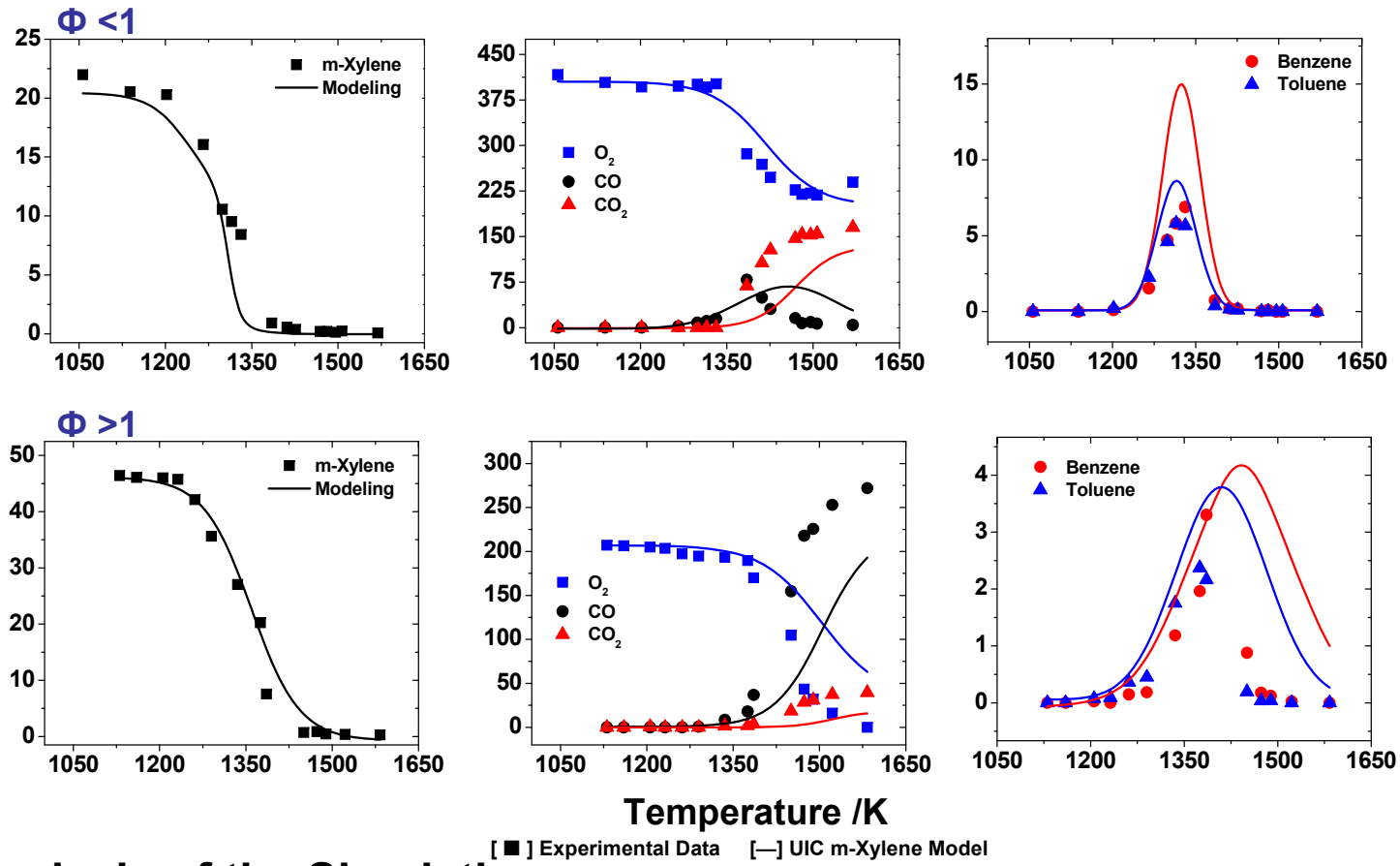
m-Xylene Oxidation Modeling*

- UIC m-Xylene Oxidation Model developed to predict single ring aromatic hydrocarbons and aliphatic compounds from fuel
- Rate constants of the oxidation reactions of m-xylene based on analogous reactions of toluene[2]
- Rate constants of the important steps updated from
  - High pressure CO/H_2 mechanism[6]
  - High pressure ethane oxidation model[7]
  - High pressure toluene pyrolysis model[3,4]
- Thermochemistry of m-xylene and it's oxygenated intermediates taken from Gail and Dagaut[8] and Battin-Leclerc et al.[9]
- Included reactions of methylcylcopentadiene, dimethylcyclopentadiene, p-xylylene and fulvenallene oxidation

*Manuscript submitted to Combustion and Flame

6. R. Sivaramakrishnan, A. Comandini, R. S. Tranter, K. Brezinsky, S. G. Davis, H. Wang, Proc. Combust. Inst. 31 (2007) 429-437.
7. R.S. Tranter, A. Raman, R. Sivaramakrishnan, K. Brezinsky, Int. J. Chem. Kinet. 37 (2005) 306-331.
8. S. Gail, P. Dagaut, Combust. Sci. Technol. 179 (2007) 813-844.
9. F. Battin-Leclerc, R. Bounaceur, N. Belmekki, P. A. Glaude, Int. J. Chem. Kinet. 38 (2006) 284-302.

m-Xylene Oxidation Model Results

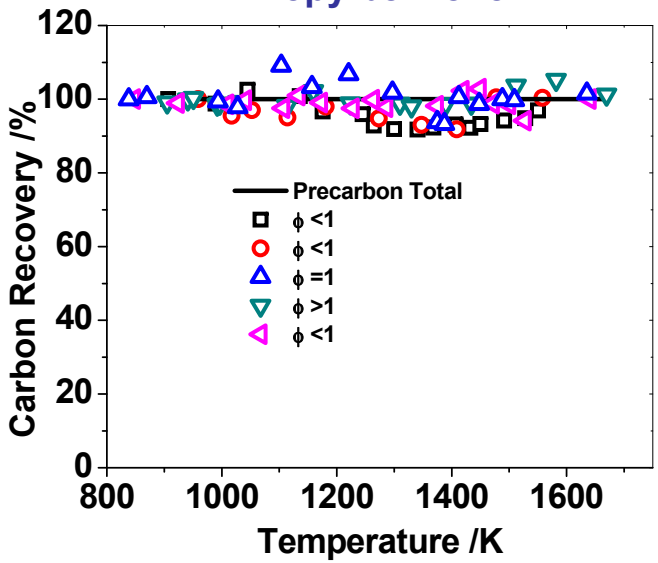


Analysis of the Simulation

- Models shows good agreement for the decay of the fuel, O_2, CO and CO_2
- Shows satisfactory profiles for the formation of major intermediates for $\Phi < 4$
- Large molecule and soot precursors formation steps should be included for better predictions

Carbon Balance

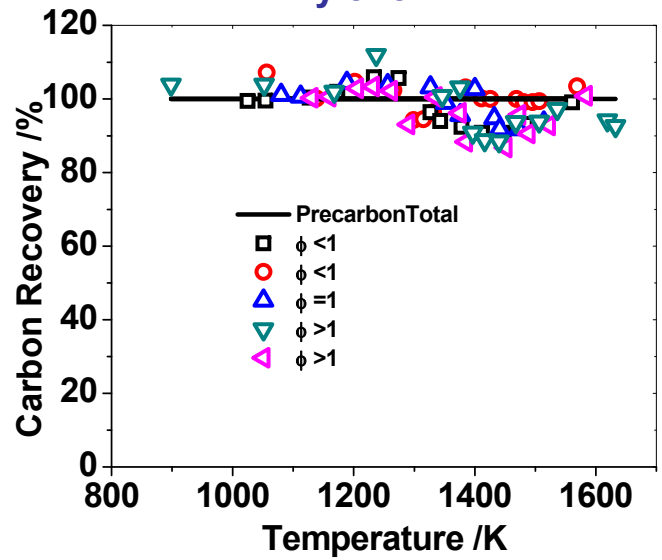
n-Propylbenzene



▪Carbon Recovery > 92% for all datasets

- **Quantification of aliphatics *(11 species)***
  - Major intermediates: CO, CO_2, methane (CH_4), ethene (C_2H_4), ethane (C_2H_6), acetylene (C_2H_2), diacetylene (C_4H_2) and vinylacetylene (C_4H_4)
  - Minor intermediates: allene (C_3H_4), propyne (C_3H_4), 1,3-butadiene ($C_4H_{6-}13$)
- **Quantification of aromatics *(15 species)***
  - Major intermediates: benzene (C_6H_6), toluene ($C_6H_5CH_3$), benzofuran (C_8H_6O), 3, 3'-dimethylbibenzyl ($C_{16}H_{18}$), indene (C_9H_8), naphthalene ($C_{10}H_8$), 2-ethynylnaphthalene ($C_{12}H_8$), fluorene ($C_{13}H_{10}$) , stilbene ($C_{14}H_{12}$), anthracene ($C_{14}H_{10}$)
  - Minor intermediates: styrene ($C_6H_5C_2H_3$), phenylacetylene ($C_6H_5C_2H$), p-xylene (C_8H_{10}), 1,2-propenylbenzene (C_9H_{10}), biphenylmethane ($C_{13}H_{12}$)

m-Xylene



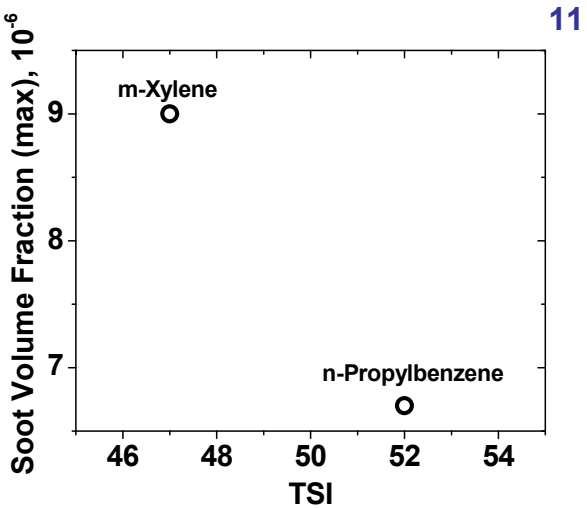
▪Carbon Recovery – drops to 87 % for Φ >1

- **Quantification of aliphatics *(12 species)***
  - Major intermediates: CO, CO_2, methane (CH_4), ethene (C_2H_4), ethane (C_2H_6), acetylene (C_2H_2), diacetylene (C_4H_2) and vinylacetylene (C_4H_4)
  - Minor intermediates: allene (C_3H_4), propyne (C_3H_4), 1,3-butadiene ($C_4H_{6-}13$) and triacetylene (C_6H_2)
- **Quantification of aromatics *(26 species)***
  - Major intermediates: benzene (C_6H_6), toluene ($C_6H_5CH_3$), 3, 3'-dimethylbibenzyl ($C_{16}H_{18}$), indene (C_9H_8), naphthalene ($C_{10}H_8$), 2-ethynylnaphthalene ($C_{12}H_8$), fluorene ($C_{13}H_{10}$) , acenaphthylene ($C_{12}H_8$) and anthracene ($C_{14}H_{10}$)
  - Minor intermediates: cyclopentadiene (C_5H_6), methylcyclopentadiene ($C_5H_5CH_3$), styrene ($C_6H_5C_2H_3$), phenylacetylene ($C_6H_5C_2H$), p-xylene (C_8H_{10}), methylindene ($C_{10}H_{11}$), biphenylene ($C_{12}H_8$), 1,3,6-trimethylnaphthalene ($C_{13}H_{14}$), phenanthrene ($C_{14}H_{10}$), diphenylethyne ($C_{14}H_{10}$), 4-methylfluorene ($C_{14}H_{12}$), 2,2'-dimethylbiphenyl ($C_{14}H_{14}$), 2-methylanthracene ($C_{15}H_{12}$), 2-methylanthracene ($C_{15}H_{12}$), m-tolyl-p-tolyl-methane ($C_{15}H_{16}$), dimtolylmethane ($C_{15}H_{16}$) and pyrene ($C_{16}H_{10}$)

TSI vs. Sooting Tendency

- Threshold Sooting Index (TSI)-measure of the sooting tendency.

Species	TSI[10]
n-Propylbenzene	52
m-Xylene	47



- n-Propylbenzene, m-xylene-similar sooting values-different sooting tendencies

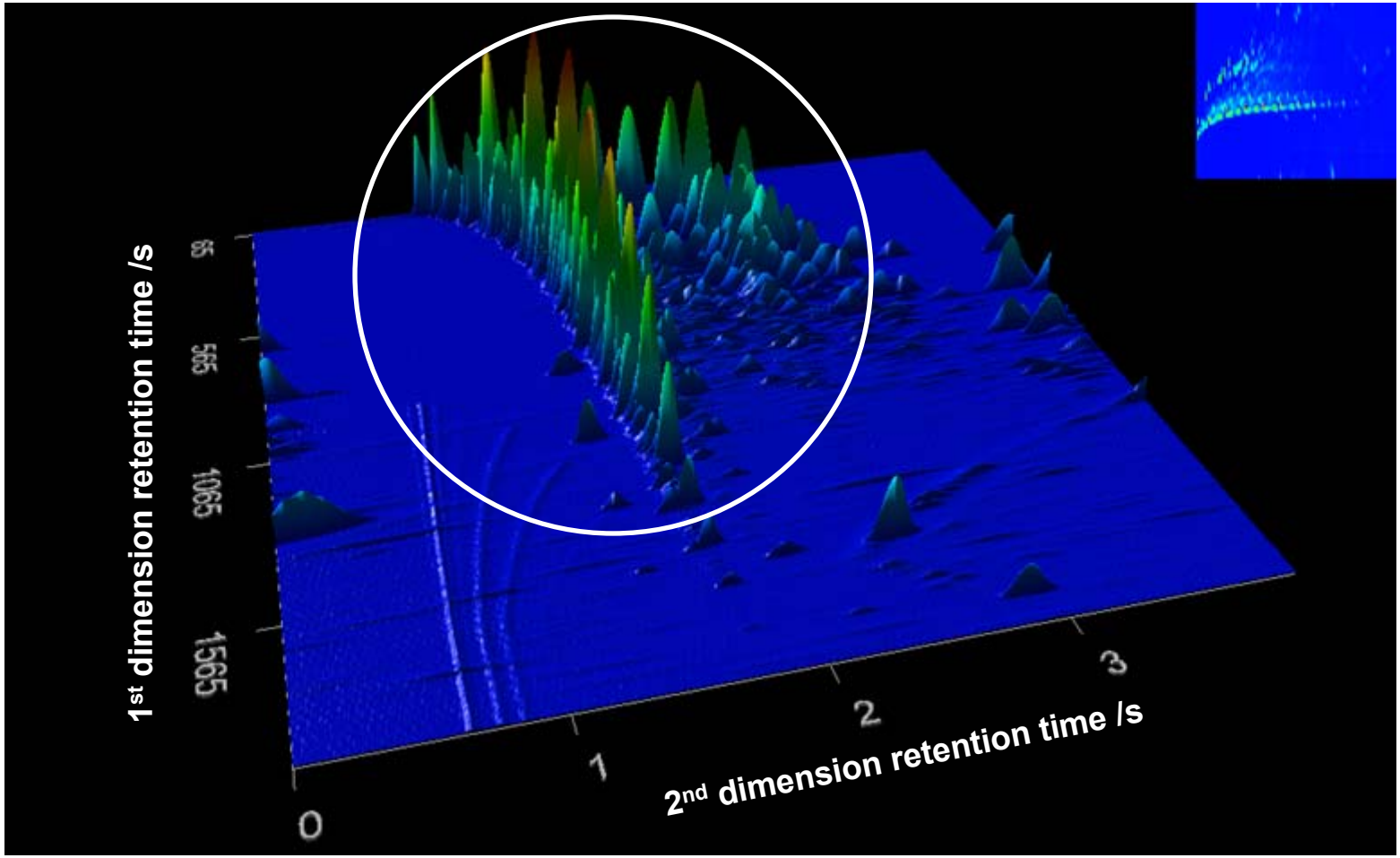
10. A. Mensch, R. J. Santoro, T. A. Litzinger, S.-Y. Lee, Comb. Flame, 157 (2010) 1097-1105.
11. R. J. Gill, D. B. Olson, Comb. Sci. Tech. 40 (1984) 307-315.

Extended Analytical Setup (GC x GC)

- Extended analytical setup
  - Leco GC x GC system
    - 2 x FID detectors
  - Agilent 7890A system
    - 1 x FID, 1 x TCD

Analytical Capabilities

- GC x GC 2-D chromatogram of JP-8



Summary

- Experiments

Fuel	Temperature /K
n-propylbenzene	910-1678
m-xylene	1010-1742
n-decane	950-1602
n-dodecane	906-1483
1st Gen. surrogate	875-1565
PSOF 4658	841-1517

- Modeling
  - *UIC n-Propylbenzene Oxidation Model*: shows satisfactory agreement with the decay of the fuel, oxidizer and formation of the intermediates up to single ringed aromatic hydrocarbons
  - *UIC m-Xylene Oxidation Model*: shows satisfactory agreement with the decay of the fuel, oxidizer and formation of the intermediates up to single ringed aromatic hydrocarbons
  - *UIC n-Decane/n-Dodecane Model:* shows satisfactory agreement with the oxidizer and the formation of heavier intermediates

Future Work

- Experiments
  - 1,3,5-Trimethylbenzene oxidation experiments at 30 and 60 atm
  - iso-Octane and n-dodecane oxidation experiments at 30 and 60 atm
  - Oxidation experiments of the 1st and 2nd Generation Surrogate (n-dodecane/iso-octane/1,3,5-trimethylbenzene/n-propylbenzene) at 30 and 60 atm
  - POSF 4658, JP-8 oxidation
- Modeling
  - Development and validation of the 1,3,5-trimethylbenzene oxidation model
  - Include the polycyclic aromatic hydrocarbon chemistry in m-xylene and n-propylbenzene oxidation models
  - Further develop the n-Decane/n-Dodecane Oxidation Model

Acknowledgements

- AFOSR, financial sponsor through MURI FA9550-07-1-0515, PI: Professor F.L. Dryer
- AFOSR DURIP, Dr. J. Tishkoff
- HPST Laboratory Students - Soumya Gudiyella, Tom Malewicki, Andrea Comandini, Alex Fridlyand