Development of Detailed and Reduced Kinetic Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels:

Drexel Flow Reactor Studies at Low and Intermediate Temperatures

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MACCCR Fuels Research Review

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Program Overview

Objectives:

1) Explore the preignition oxidation behavior of petroleum and alternative jet fuel surrogate components and component mixtures
2) Measure the combustion properties of the surrogate components
3) In Year 3, finish n-dodecane and n-butylcyclohexane studies and move to isocetane and n-propylcyclohexane

Approach:

- React the fuel/oxidizer/diluent systems under well-controlled conditions in our Pressurized Flow Reactor (PFR)
  - » Perform bench scale tests on selected hydrocarbon and hydrocarbon mixtures
  - » Monitor reactivity and collect gas samples as a function of experimental and reactant conditions
  - » Perform detailed chemical analysis of extracted gas samples
- Mechanistic analysis and development
- Provide data for chemical kinetic model development

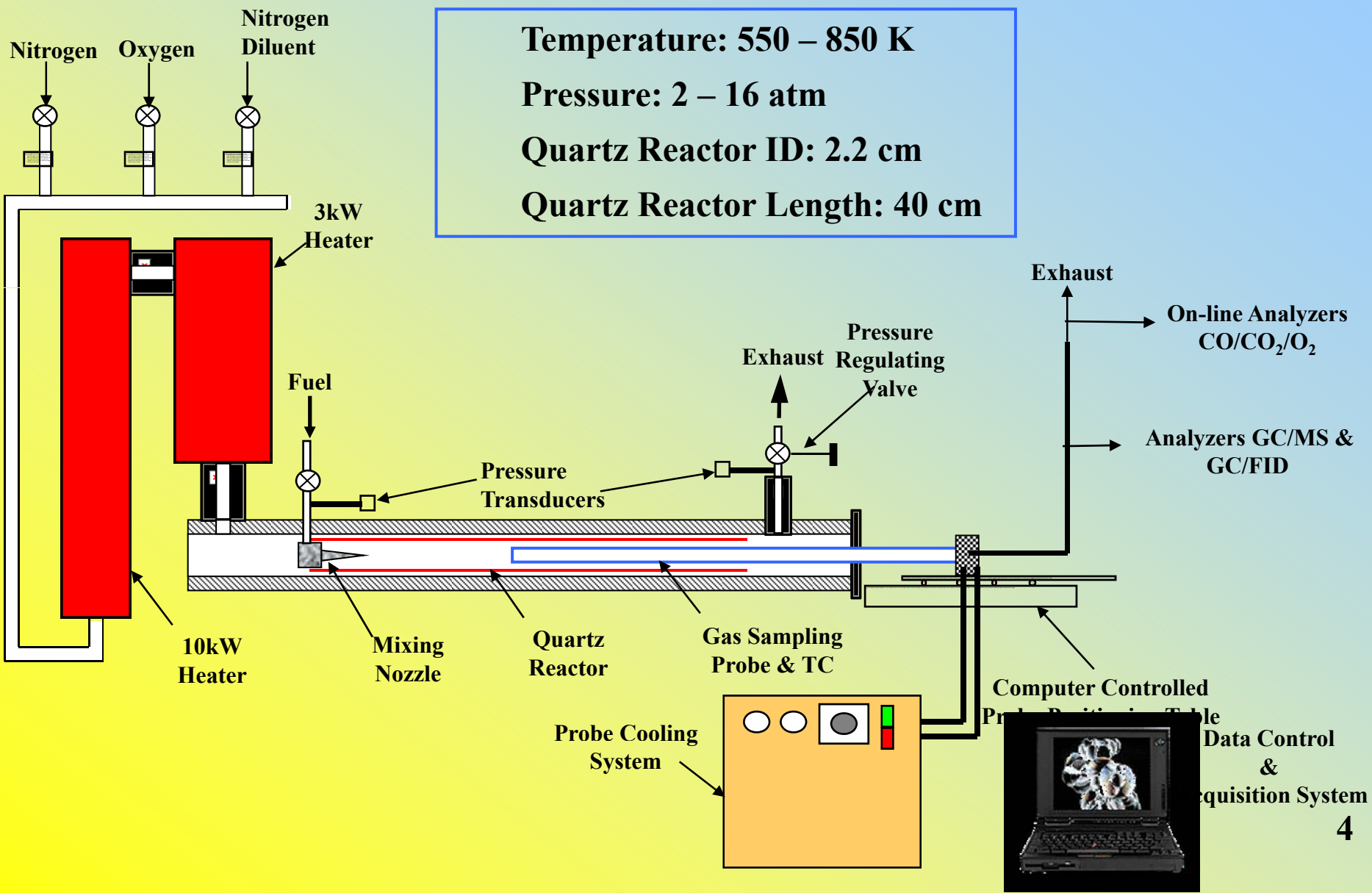
PFR Facility

Temperature: 550 – 850 K

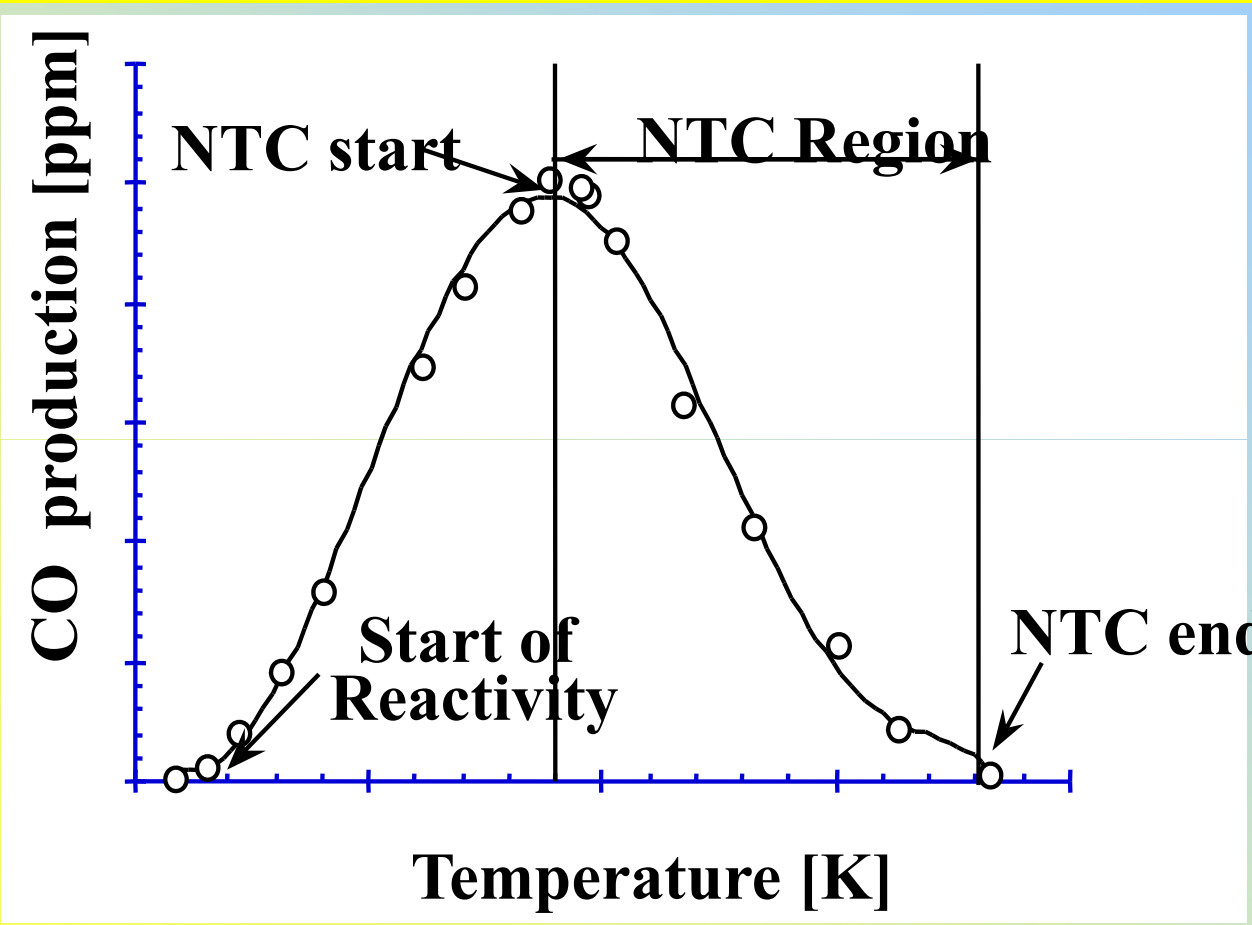
Pressure: 2 – 16 atm

Quartz Reactor ID: 2.2 cm

Quartz Reactor Length: 40 cm



Representative Reactivity Map Profile



- CO is a major indicator of reactivity at low temperatures, we also measure water with the MS which tracks the CO
- Negative Temperature Coefficient (NTC) region is the shift from low to intermediate temperature chemistry

Review of Past E-IPT Work

- **Year One: A series of n-dodecane experiments was conducted at low temperatures (550-850 K) at a range of equivalence ratios (0.2-0.9)**
  - **Mapped NTC region for n-dodecane using measurements of CO and CO_2**
  - **Chemical Analysis of samples produced unacceptably low carbon balances - on average 50%, and as low as 20%, depending on the temperature – intermediates produced from this larger fuel require alternative operational and sampling systems**
- **Year Two: Major sampling train modifications were implemented; operational methodology was changed to eliminate sample "aging" questions.**
  - **Prelim n-dodecane: chemical analysis yielded carbon balances greater than 80%; 115 intermediate species compared to 30 in Year01 work**
  - **Prelim n-butyl cyclohexane: mapped NTC region; carbon balances above 95% for chemical analysis; 65 species identified**

Year 03: E-IPT Effort

- N-dodecane work extended
- N-butyl cyclohexane work extended
- After consultation within the work group – selected isocetane and n-propyl cyclohexane as our next hydrocarbons and completed preliminary experiments
- Comparison of flow reactor experiments

n-Dodecane

- **PFR experimental conditions**
  - **531 +/- 8 ppm $C_{12}H_{26}$**
  - **42100 ppm O_2**
  - **Balance N_2**
  - **Φ=0.23 +/- .05**
  - **τ_{res} = 120 +/- 10 ms**
  - **Pressure = 8.000 +/- 0.025 atm**
- **Overview of results**
  - **Carbon Balances > 80% under all conditions**
  - **131 species measured**
- **Chemical kinetic models – existing low temperature models**
  - **Lawrence Livermore National Laboratory (Livermore)**
    - » **C_8-C_{16} n-alkanes (Westbrook et al., 2009)**
  - **Politecnico di Milano (Milano)**
    - » **Hydrocarbons up to C_{16} (Ranzi et al., 2005)**
  - **Modeled as plug flow reactor module at adiabatic conditions**

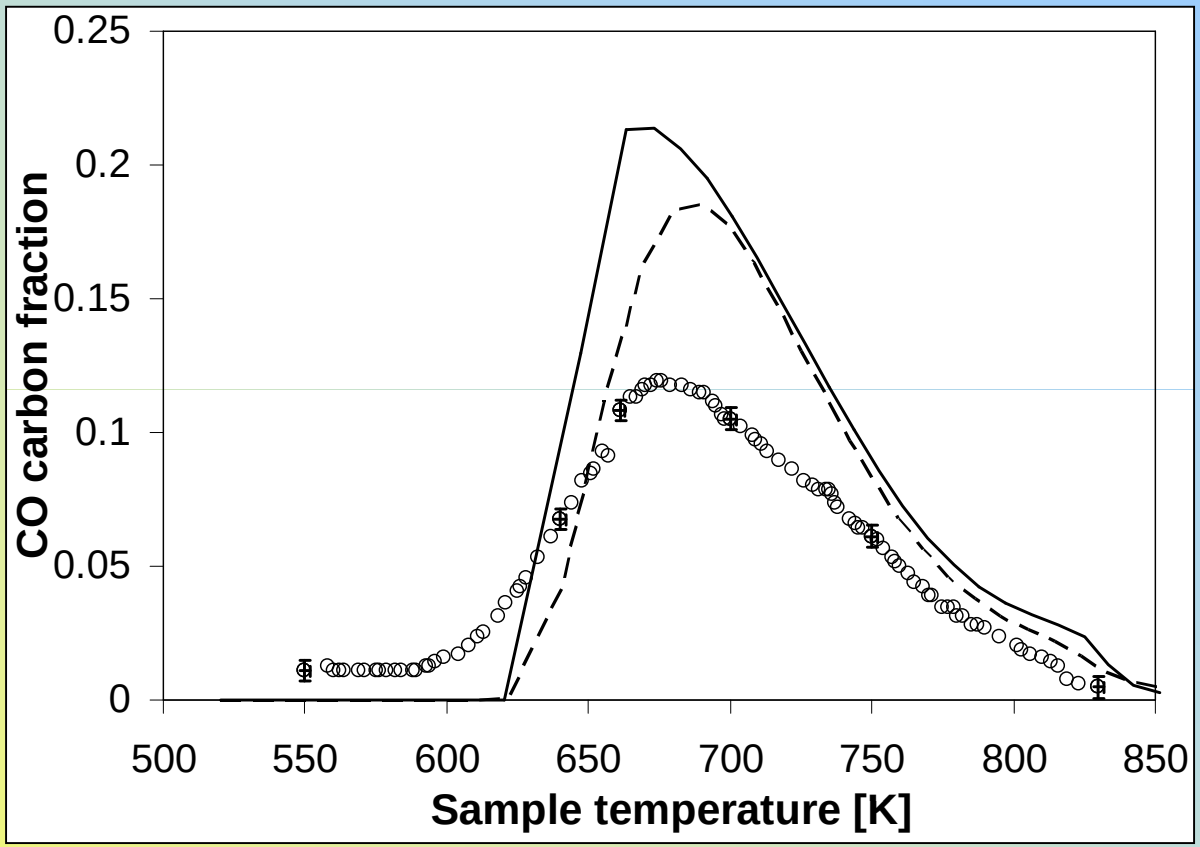
n-Dodecane results

- Reported data are averages of three replicated experiments
- Carbon balances were greater than 80%, and oxygen balances were greater than 97%
- 115 species were identified and measured
- A few major species accounted for 55-80% of the initial carbon
  - CO, CO_2
  - formaldehyde, acetaldehyde, propanal
  - 2-propyl-5-iso-pentyltetrahydrofuran and two incompletely identified C_{12} alkylated tetrahydrofuran isomers
  - 5-methyl-dihydro-2(3H)-furanone, dihydro-2(3H)-furanone
  - ethene, and 3-dodecene

n-Dodecane: CO

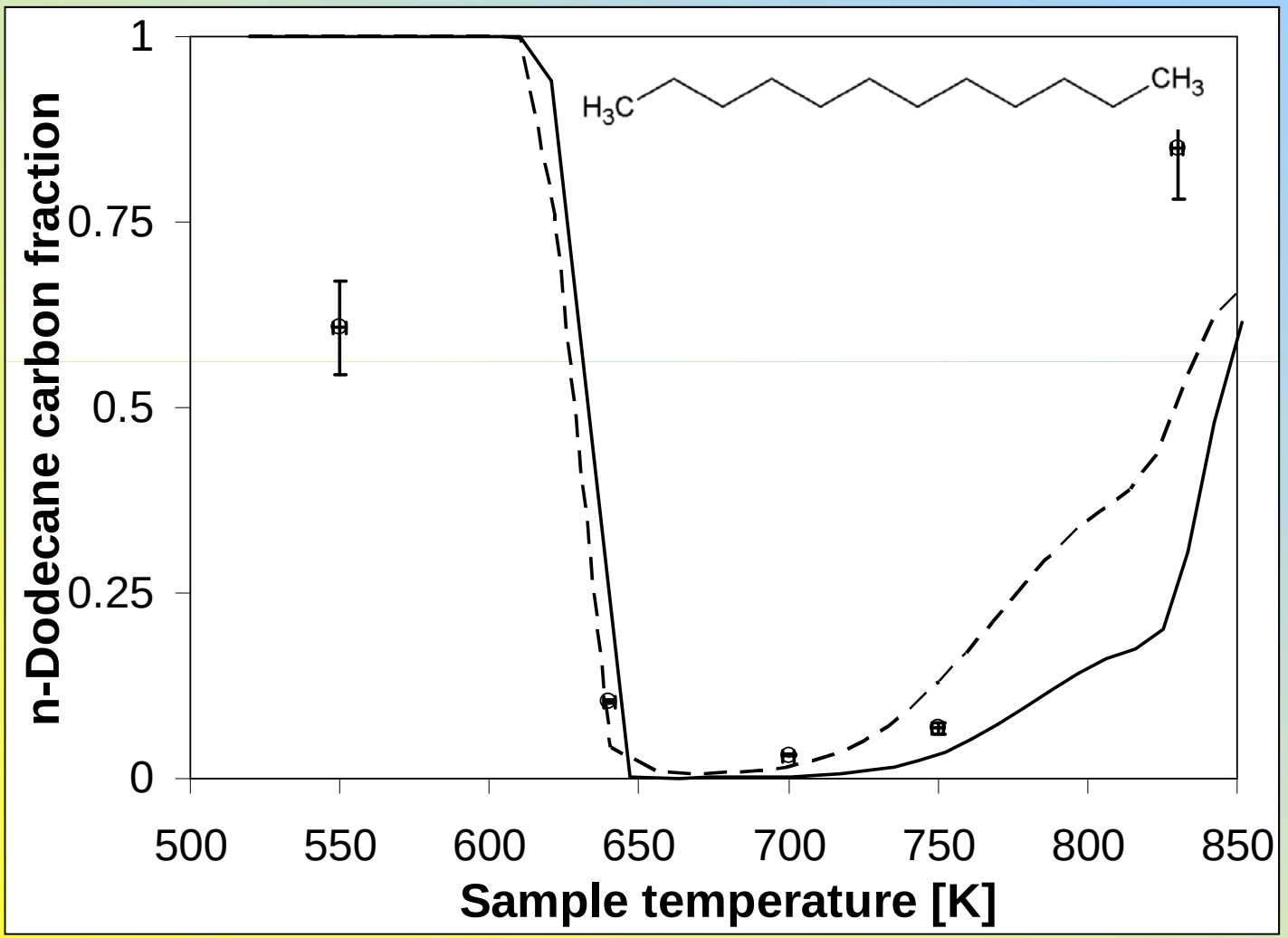
- CO accounted for up to 10% of the carbon
- In the low temperature regime, CO is a good indicator of reactivity and does not oxidize significantly to CO_2

  (Wilk et al., 1989)
- Maximum CO, 760 ppm, occurred at 675 K
  - Start of NTC behavior
- CO_2 followed the CO trend, but at approximately 1/3 the quantity
  - CO_2 can be produced from oxygenates such as cyclic ethers (Glaude et al., 2002) rather than from the oxidation of CO



Carbon fractions for CO:
(○) experimental, (——) Livermore, (– – –) Milano

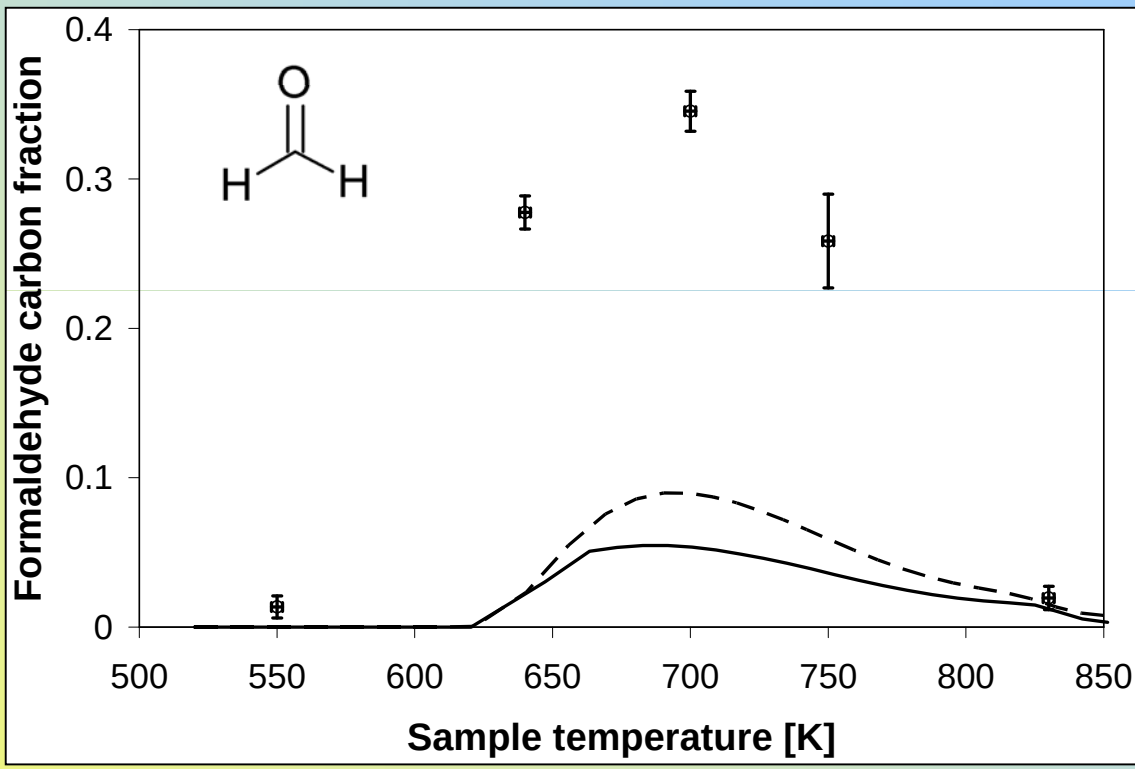
n-Dodecane: Fuel Profile



Carbon fractions for n-dodecane:
(○) experimental, (——) Livermore, (– – –) Milano

n-Dodecane: Formaldehyde

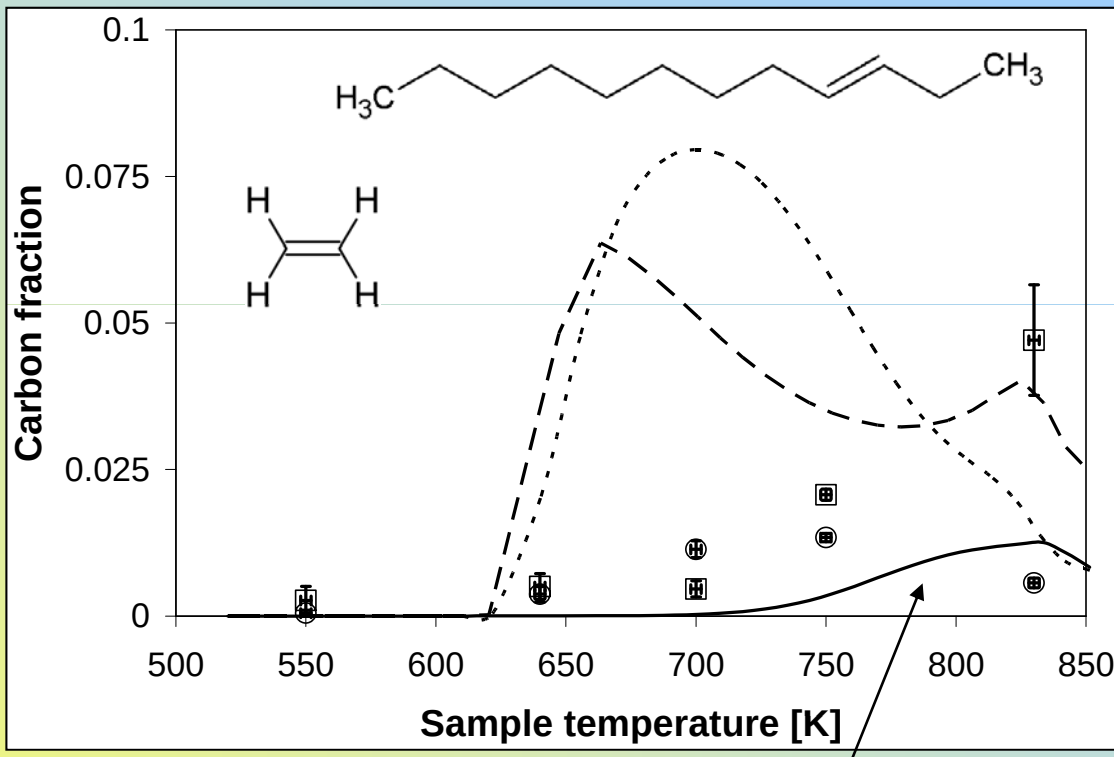
- Formaldehyde was the most abundant aldehyde measured
- At 700 K, the Milano model predicted formaldehyde four times lower, and the Livermore model predicted a level six times lower
- Additionally, acetaldehyde and propanal were also measured
  - Exhibited an increase between 640-750 K similar to formaldehyde
  - Livermore model predicted the profile well, while the Milano model predicted a level five times higher



Carbon fractions for CH_2O:
(○) experimental, (——) Livermore, (– – –) Milano

n-Dodecane: Major Alkene

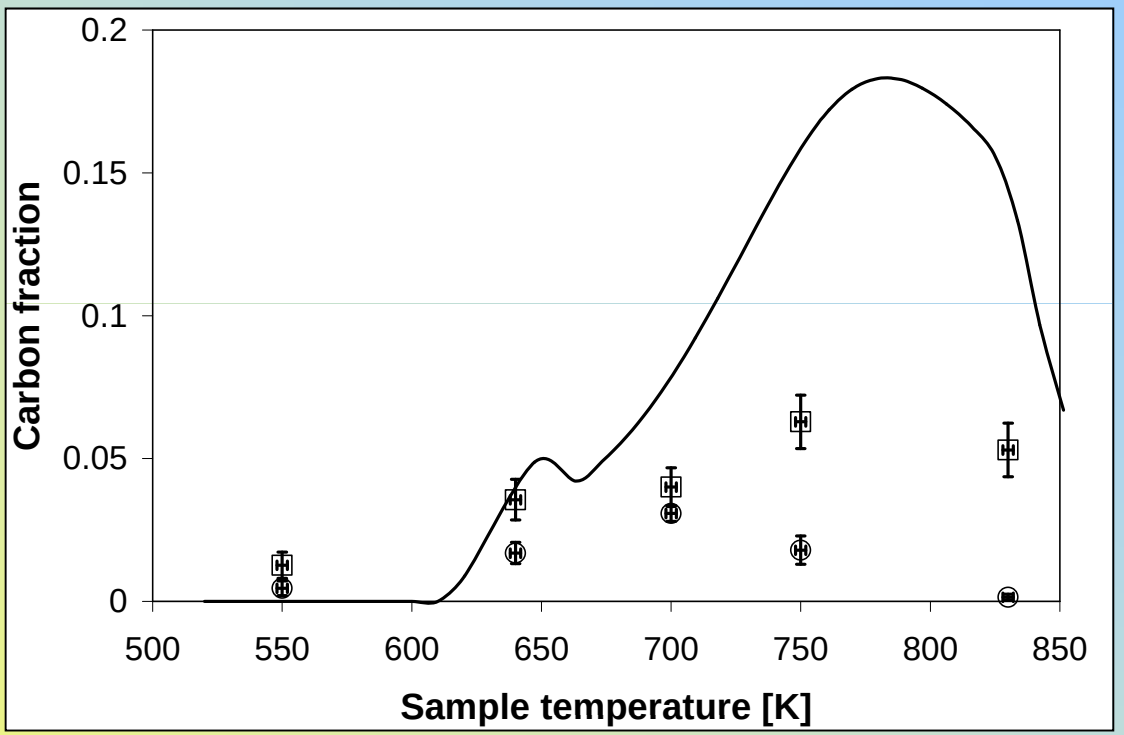
- Ethene and 3-dodecene were the most abundant alkenes
  - Livermore included six dodecene isomers
  - Livermore captured the trend of increasing 3-dodecene with temperature
    - Peak production was under predicted by a factor of four
  - Ethene peaked at 750K
    - Both models over predicted production



Carbon fractions for 3-dodecene: (□) experimental, (——) Livermore; and for ethene: (○) experimental, (– – –) Livermore, (------) Milano

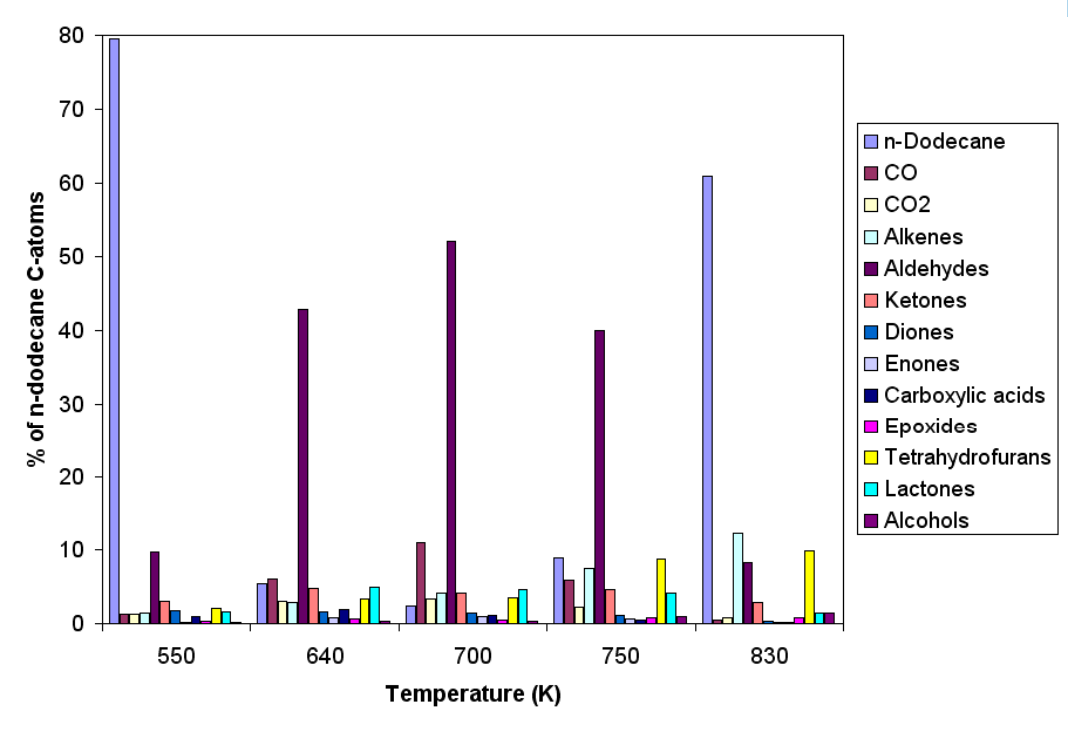
n-Dodecane: Tetrahydrofuran

- C_{12} alkylated THF
- Several lactones were measured
  - 5-methyl-dihydro-2(3H)-furanone dominant lactone
- 5-methyl-dihydro-2(3H)-furanone
  - Similar trend to aldehydes
  - Neither model included lactones
- Engine experiments studying the autoignition of tetrahydrofuran at an intake temperature of 400 K, dihydro-2(3H)-furanone was measured (Leppard, 2001)
  - No lactone production pathways were suggested



Carbon fractions for C_{12} alkylated tetrahydrofurans: (□) experimental, (——) Livermore; and for 5-methyl-dihydro-2(3H)-furanone: (○) experimental

n-Dodecane: Class Analysis



All classes accounting for ≥ 1% of reactant, fractions of reactant and product calculated by C-atoms

Temperature (K)	550	640	700	750	830
Classes accounting for ≥ 5% of reactant, listed in descending order	dodecane, aldehydes	aldehydes, CO, dodecane, lactones, ketones	aldehydes, CO, lactones	aldehydes, dodecane, THF's, alkenes, CO, ketones	dodecane, alkenes, THF's, aldehydes

Highlights of n-Dodecane Year 02+ 03 Work

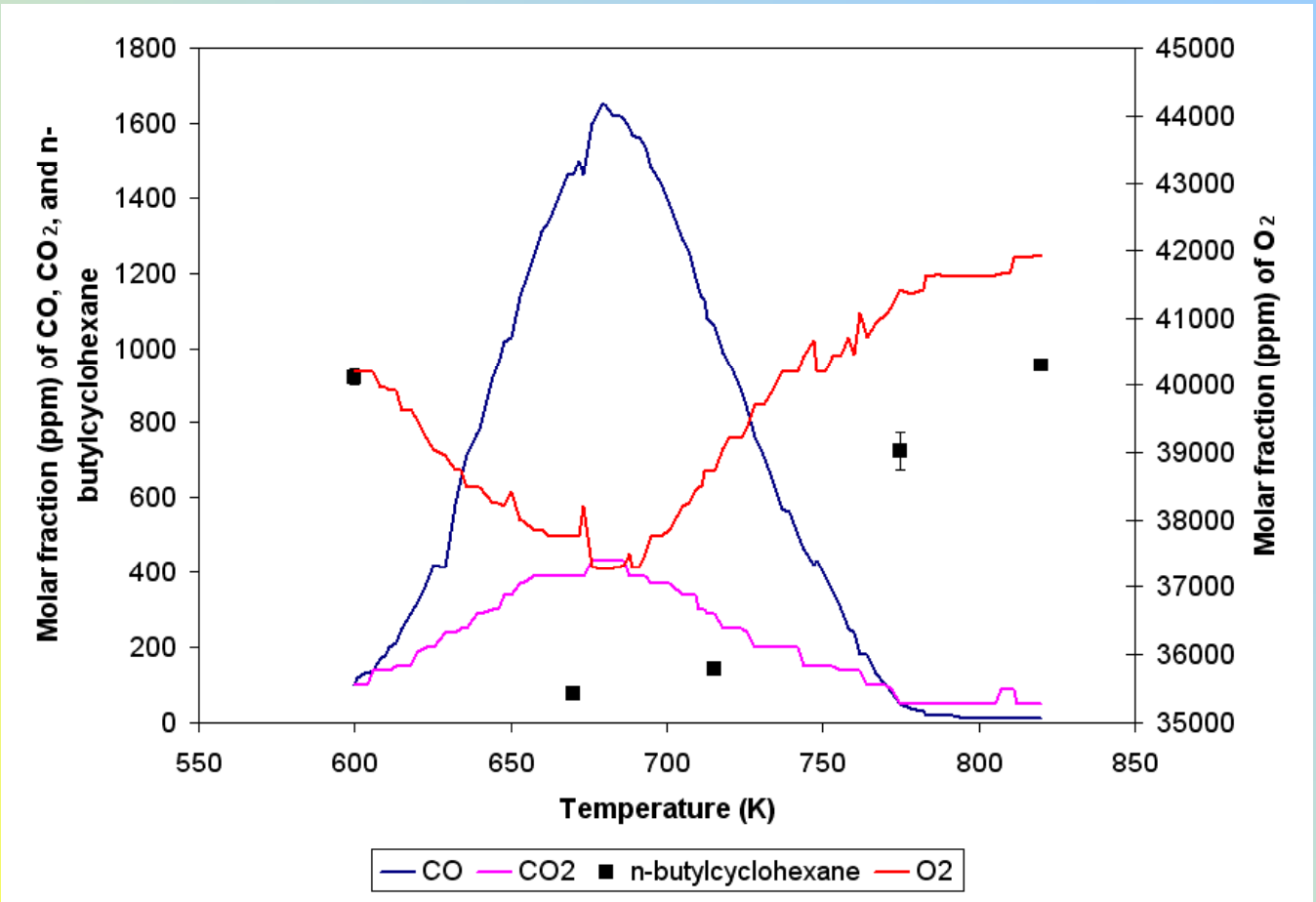
- Modifications to the PFR improved carbon balance which will help for reaction pathway analysis and model development
- CO, CO_2, and aldehydes all peaked at start of NTC
- Different hydrocarbon classes were predominant at different reaction conditions:
  - Low temperature (lactones and ketones)
  - NTC start (lactones)
  - Over NTC region (alkenes, tetrahydrofurans, and ketones)
- Novel observations, compared to past work of lighter hydrocarbons at these temperatures, included the identification of many species with two O atoms - lactones, carboxylic acids, and diones
- Speculation on new pathways: explaining formaldehye/CO ratio and lactone formation
- PhD Completed; Paper at 33rd Sym.; another in preparation

n-Butyl Cyclohexane (n-butyl CHX)

- **PFR experimental conditions**
  - **1080 +/- 20 ppm $C_{10}H_{20}$**
  - **42100 ppm O_2**
  - **Balance N_2**
  - **Φ=0.38 +/- .05**
  - **τ_{res} = 120 +/- 10 ms**
  - **Pressure = 8.000 +/- 0.025 atm**
- **Results overview**
  - **Reported data are averages of three replicated experiments**
  - **Carbon balances were greater than 95%**
  - **65 species were identified and measured**
- **Preliminary modeling (early speculations)**
  - **Add classic low temperature steps to Jet-Surf 1.1 (43 species, 80 rxns)**
  - **Thermochemistry developed and reaction rates built**
  - **Modeled as a plug flow reactor module at adiabatic conditions**

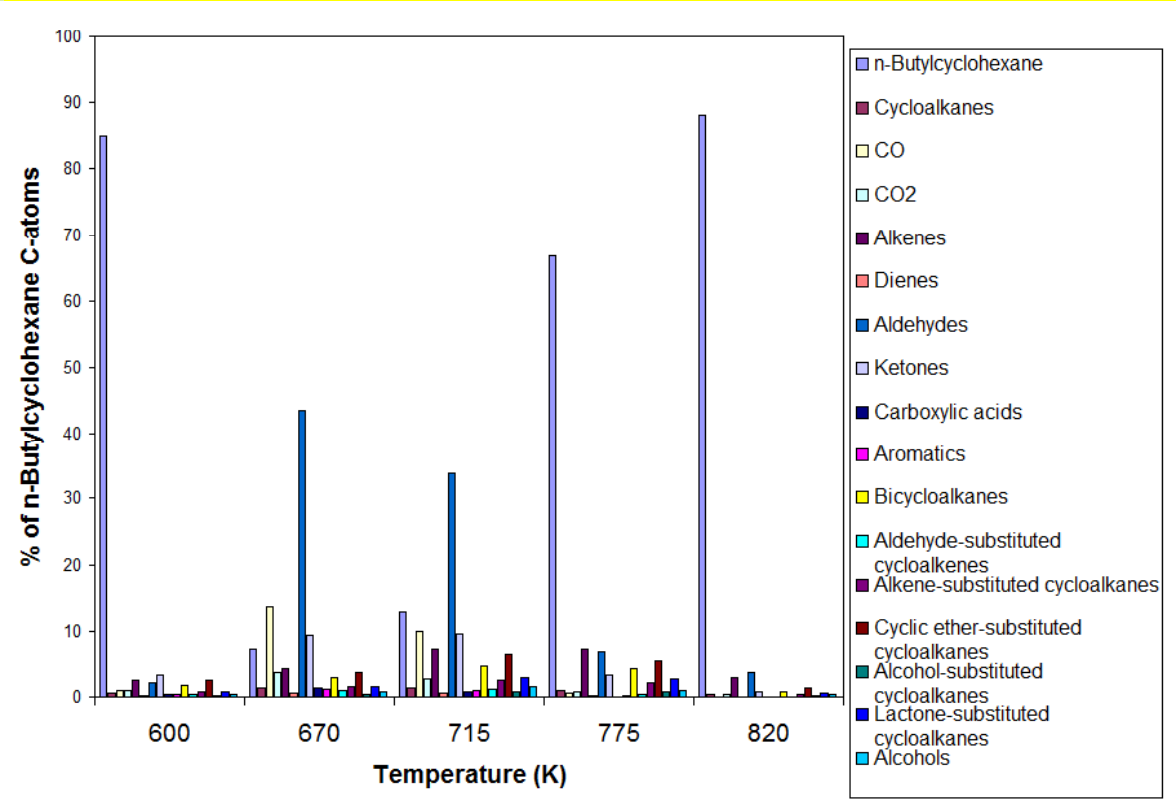
n-butyl CHX: Reactivity Mapping

- 600 K < T < 700 K: increasing reactivity
- T ~ 700 K: NTC start
- 700 K < T < 850 K: NTC region
- Minimum carbon balance 95%; 65 peaks measured



- H_2O was measured using the MS and matched the CO trend

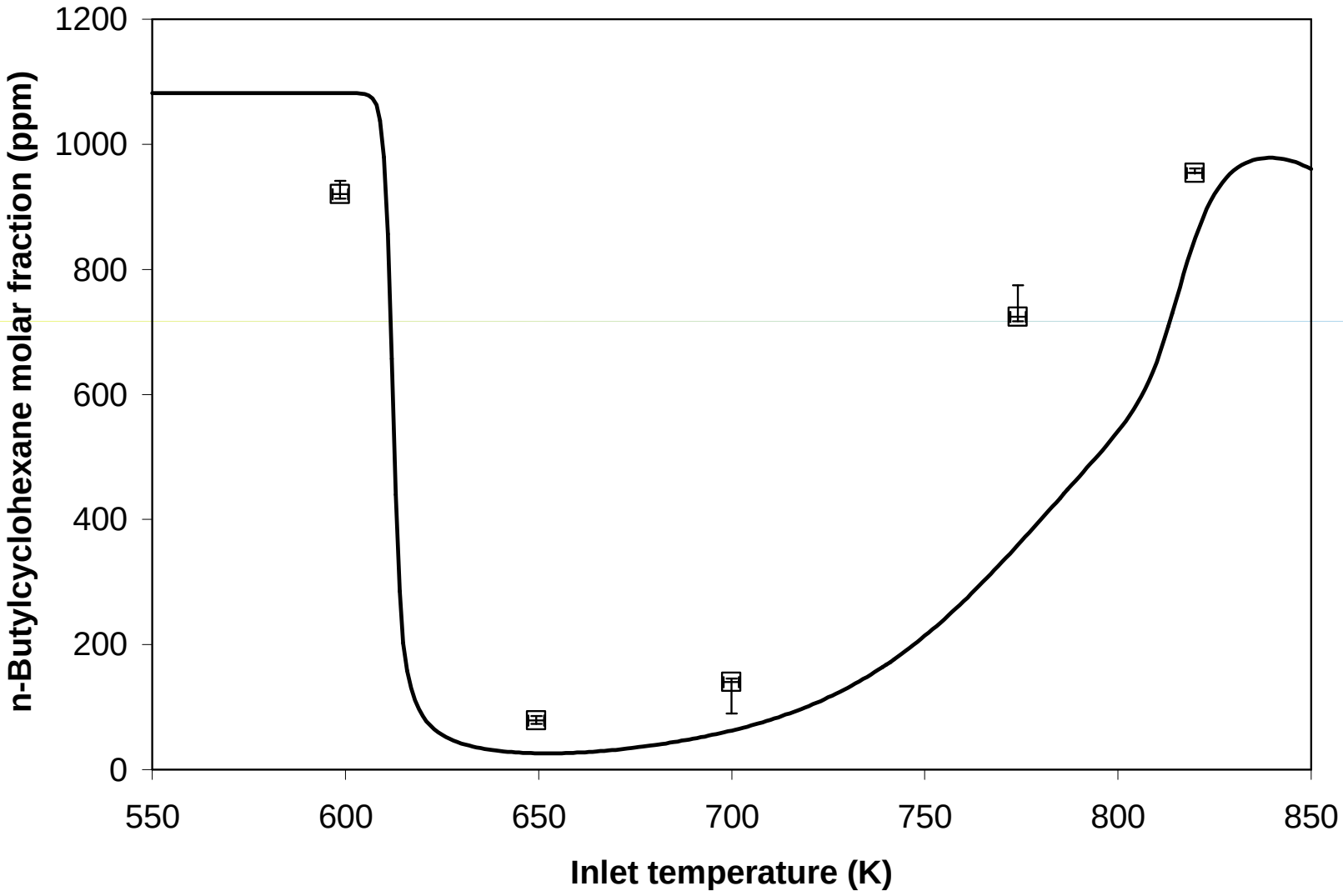
n-butyl CHX: Class Analysis



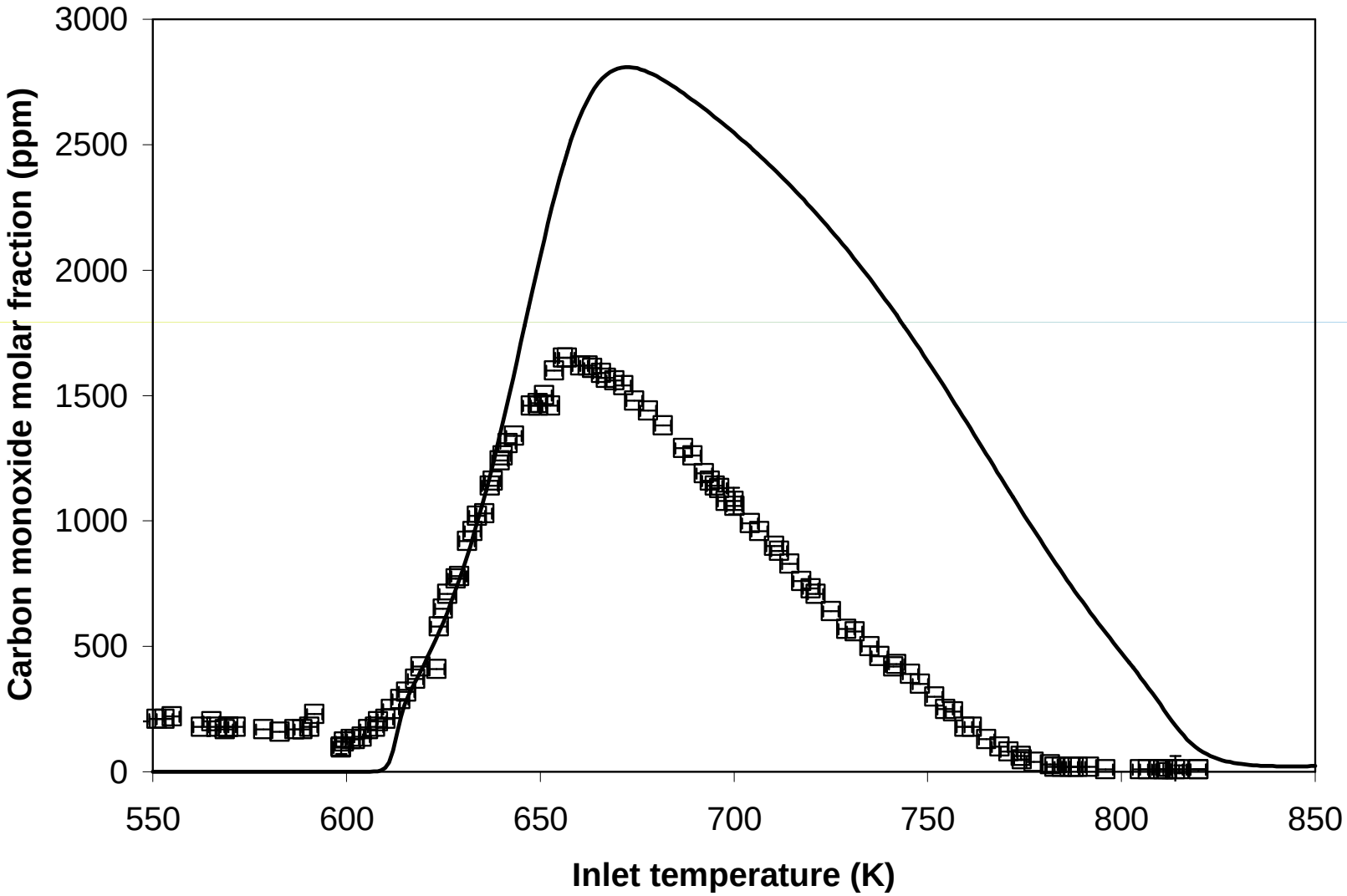
All classes accounting for ≥ 1% of reactant, fractions of reactant and product calculated by C-atoms

Temperature (K)	600	670	715	775	820
Classes accounting for ≥ 5% of reactant, listed in descending order	n-BCH	aldehydes, CO, ketones, n-BCH	aldehydes, n-BCH, CO, ketones, alkenes, cyclic ether-substituted cycloalkanes, bicycloalkanes	n-BCH, alkenes, aldehydes, cyclic ether-substituted cycloalkanes	n-BCH

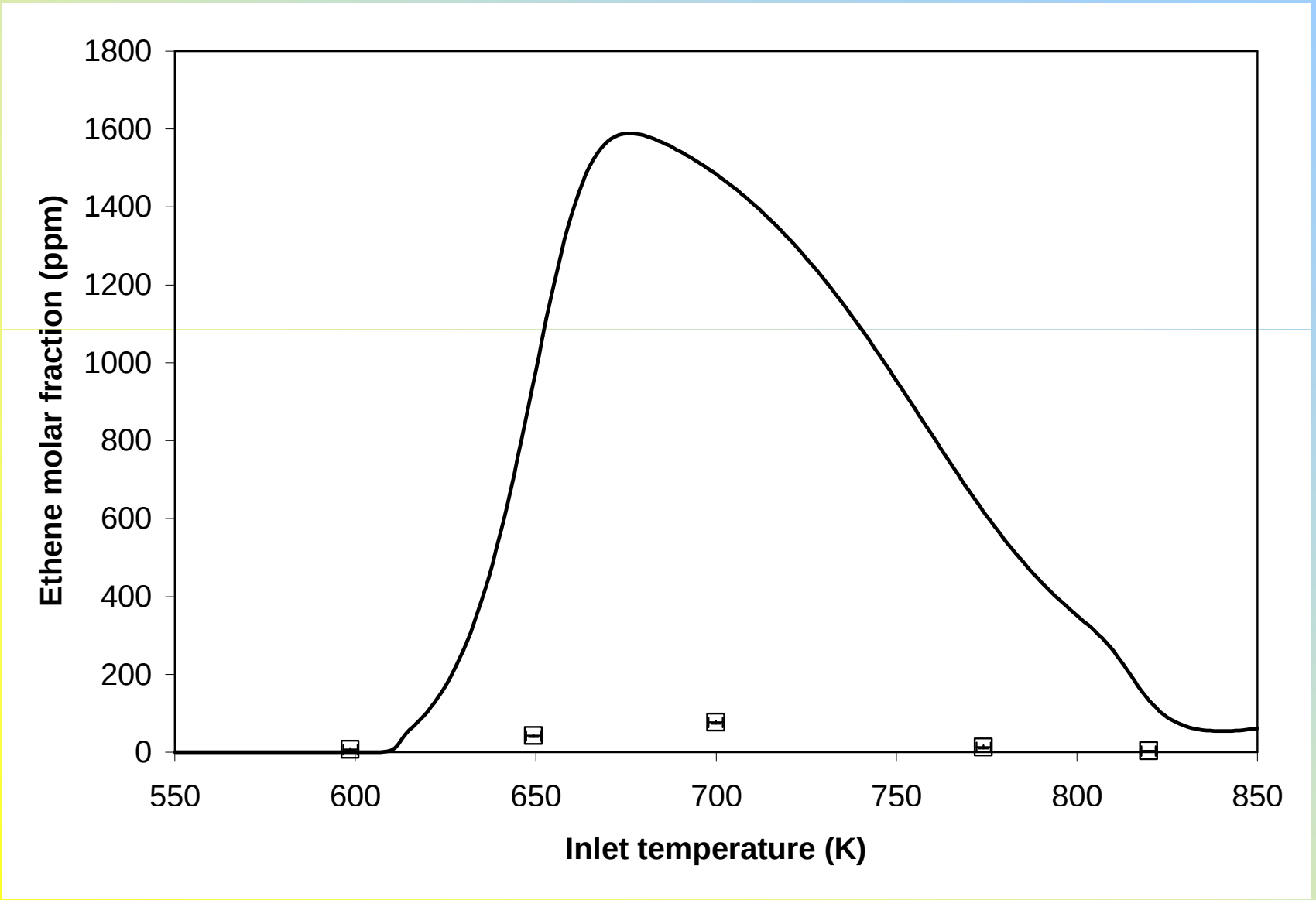
n-butyl CHX Modeling: Fuel Profile



n-butyl CHX Modeling: CO Profile



n-butyl CHX Modeling: ethene



Highlights of n-butyl CHX 02 & 03 Work

- n-Butylcyclohexane experiments were conducted with carbon balances greater than 95% in the new setup, measuring 65 intermediates
- C_{2-4} straight-chain alkenes produced from n-butyl chain
- Larger species measured were cycloalkenes, cycloketones, and multi-ring species (cycloalkane / tetrahydrofuran, cycloalkane / lactone, and dicycloalkane)
- Different classes were predominant at different reaction conditions:
  - low temperature (aldehydes, cycloketones, and acetic acid)
  - over the NTC region (cycloalkenes and multi-ring species)
- Modeling speculation begun
- PhD completed; Manuscript in preparation

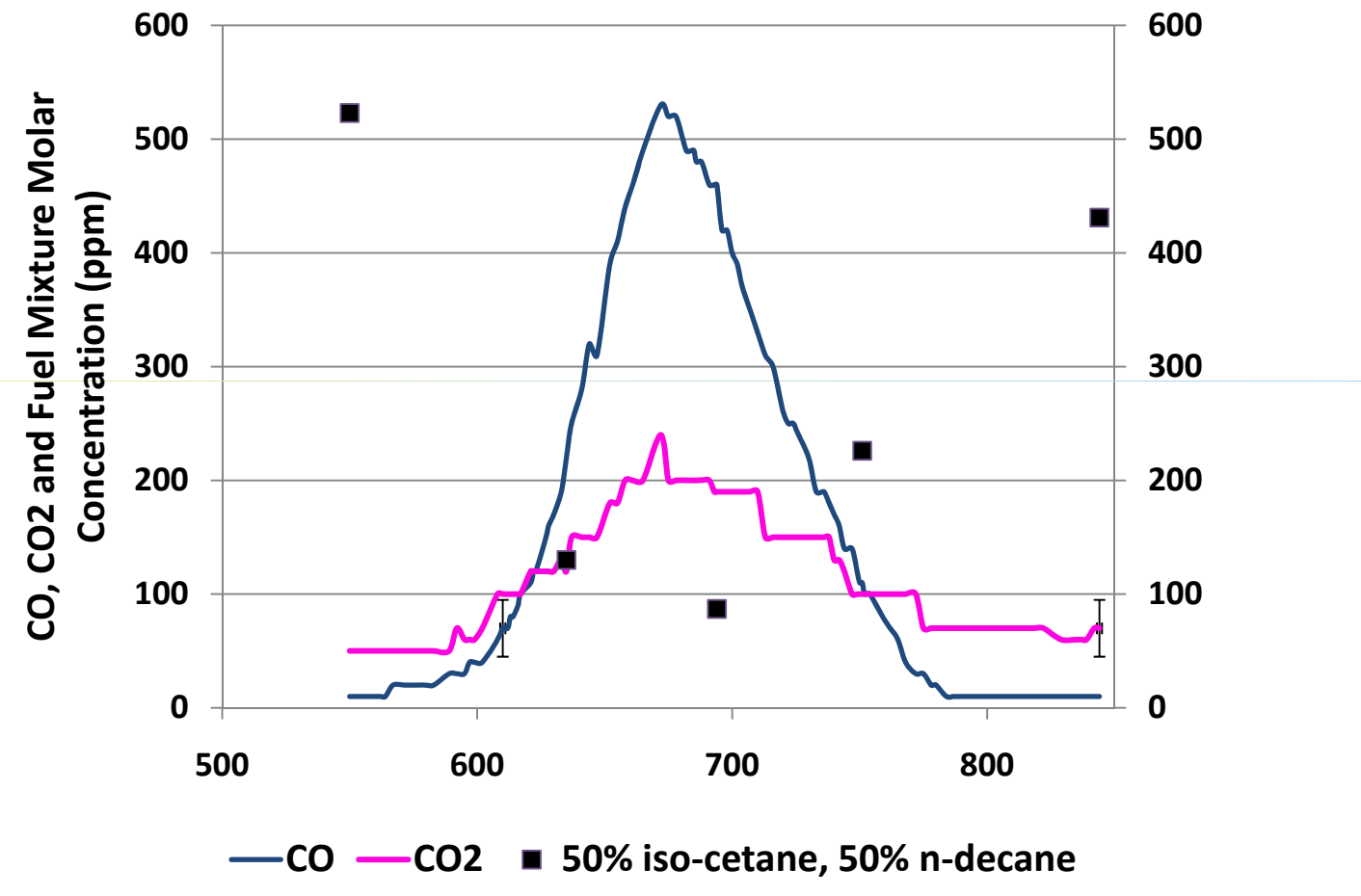
Isocetane

	Neat iso-cetane	50% iso-cetane / 50 % n-decane (by volume)	±
Fuel (ppm)	435	440	-
O_2 (ppm)	42,100	42,100	1250
N_2	balance	balance	-
Pressure (atm)	8	8	0.05
Residence time (ms)	120	120	10
Equivalence ratio	0.25	0.24	0.05

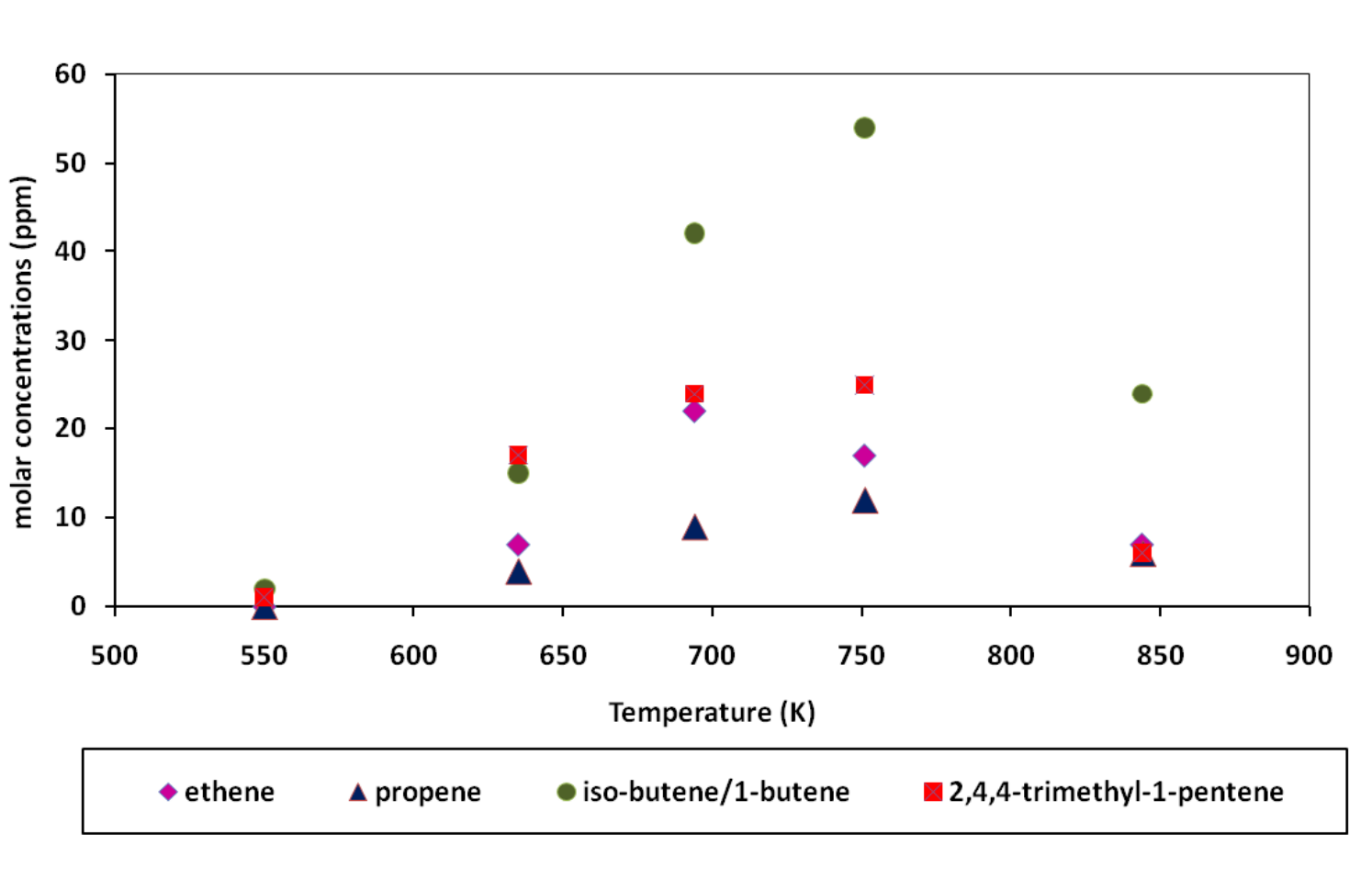
- Initial neat iso-cetane experiment produced insignificant reactivity
- n-decane was chosen as a blending fuel.

50/50: Reactivity Mapping

- 550K < T < 672K: increasing reactivity
- Maximum CO concentration was measured to be 530 ppm at 672K.
- T ~ 672K: NTC start
- 672K < T < 850K: NTC region

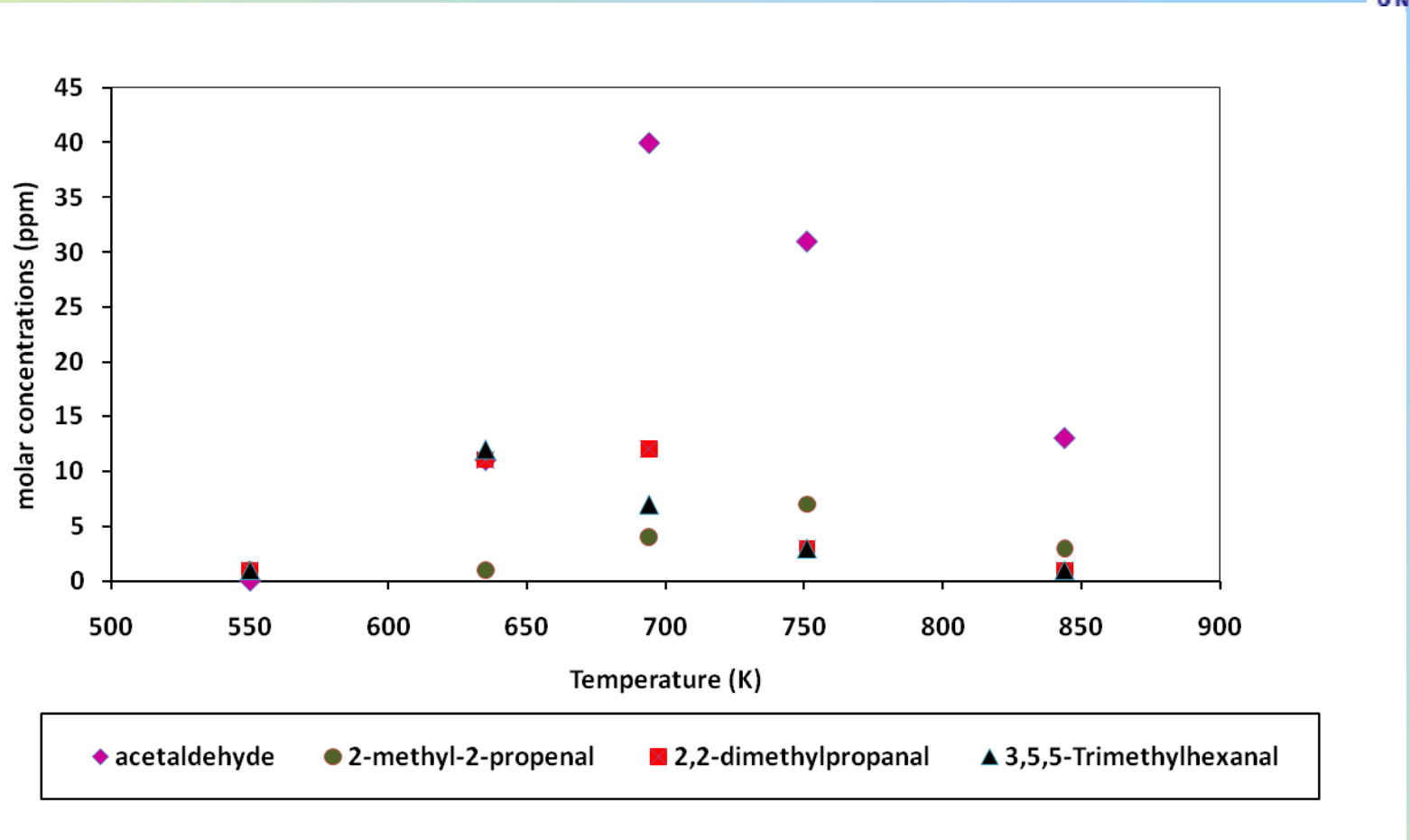


50/50: Alkenes



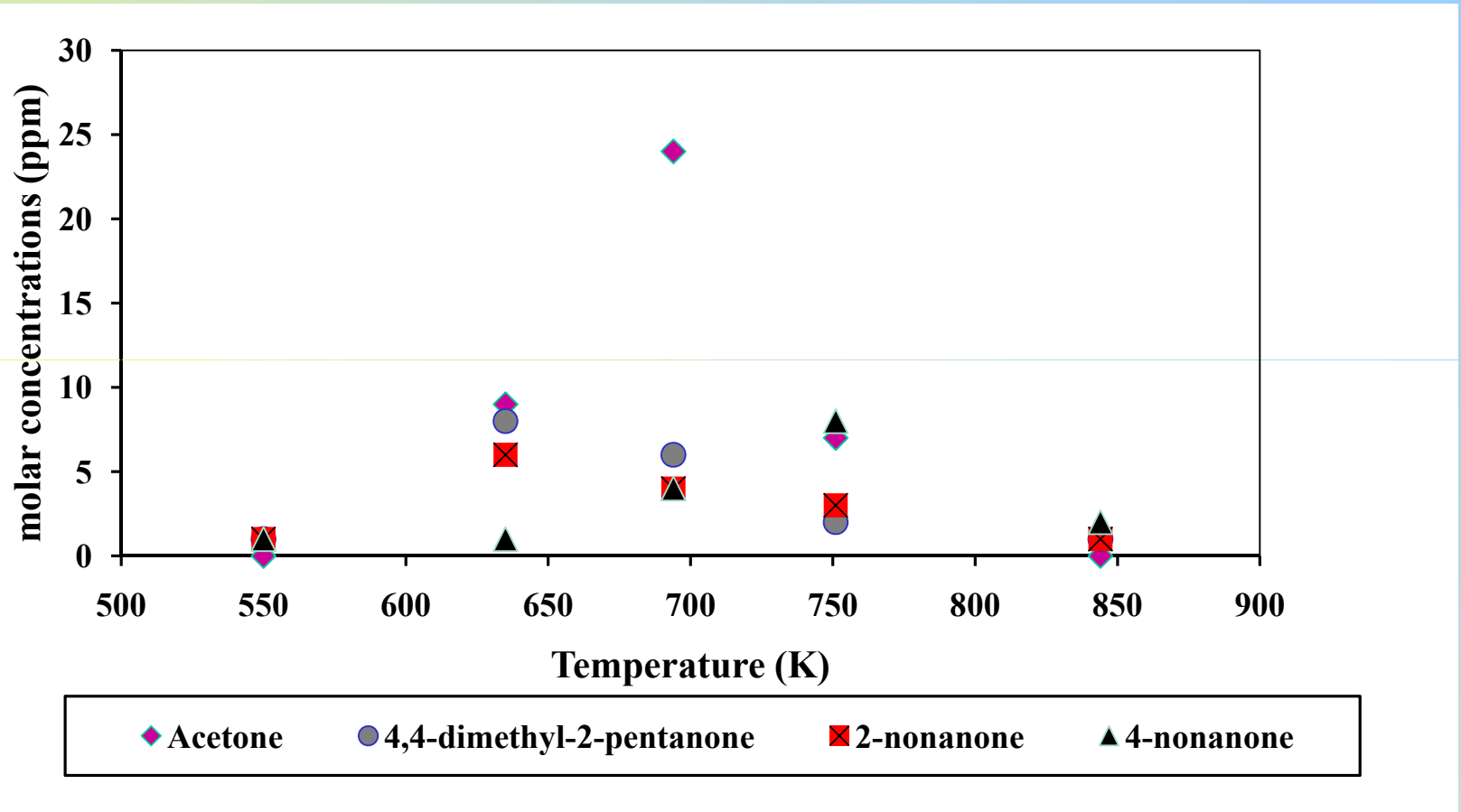
- **Other alkenes were produced at smaller quantities.**

50/50: Aldehydes



- **Formaldehyde was a major intermediate species, but was not quantified.**
- **Other aldehydes were measured at smaller quantities.**

50/50: Ketones



- Acetone was the major ketone identified.
- Formation of 4,4-dimethyl-2-pentanone is from decomposition of iso-cetane.

First Impressions of iso-cetane Oxidation

- Neat iso-cetane was unreactive at our experimental conditions
- n-decane, was selected as a blending fuel (50/50 by volume) with iso-cetane to initiate reactivity
- The 50/50 mixture produced 530 ppm CO and 240 ppm CO_2 at approximately 672 K, the start of the NTC regime
- A large number of intermediate species throughout this temperature range
- Alkenes and aldehydes were predominant in the NTC region
- Ketones peaked at the start of NTC region
- Acetic acid peaked before the start of NTC.

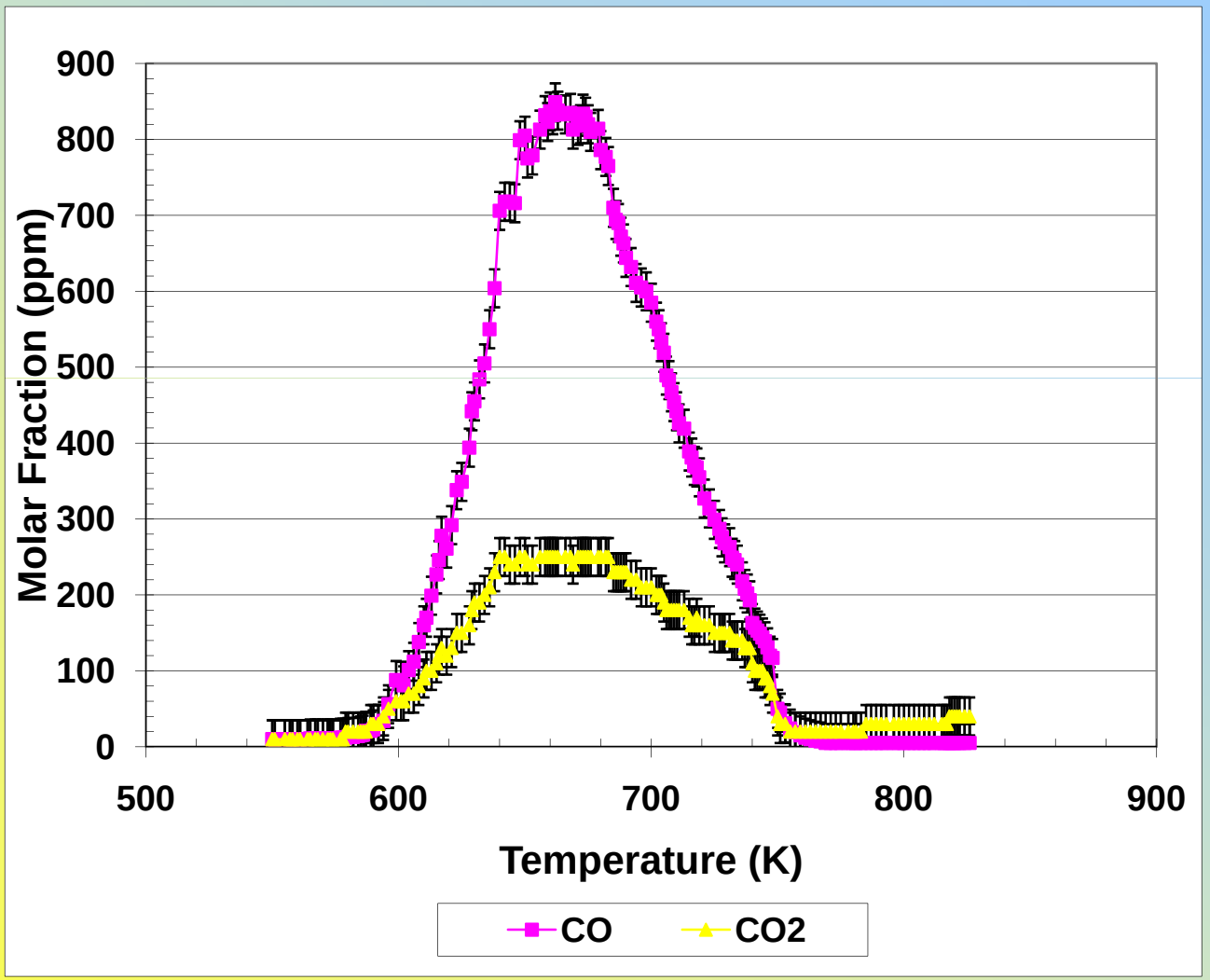
Propylcyclohexane (n-propyl CHX)

	n-propyl CHX	±
Fuel (ppm)	684	8
O_2 (ppm)	42,100	1250
ϕ	0.22	0.05
N_2 (ppm)	balance	-
Pressure (atm)	8.00	0.025
Residence time (ms)	120	10

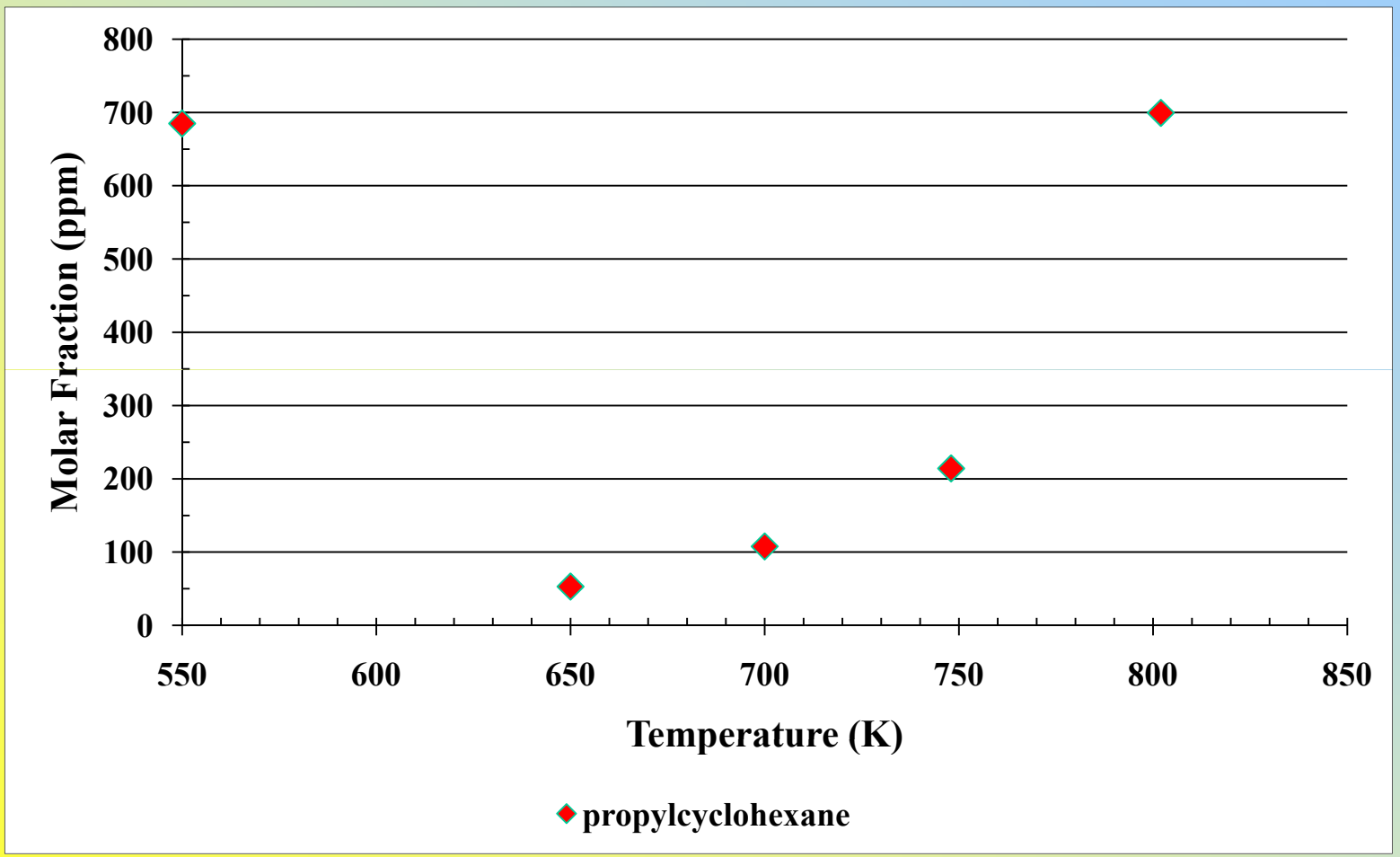
- Fuel concentrations, and intermediate species in the following graphs are results from one experiment. Reproducibility experiments to be performed.
- O_2, equivalence ratio, pressure, and residence time uncertainties are based on instrumental uncertainty.

n-propyl CHX: Reactivity Mapping

- 550K < T < 700K: increasing reactivity
- T ~ 700K: NTC start
- 700K < T < 850K: NTC region
- CO/CO2 trend match past n-Dodecane and n-BCH results

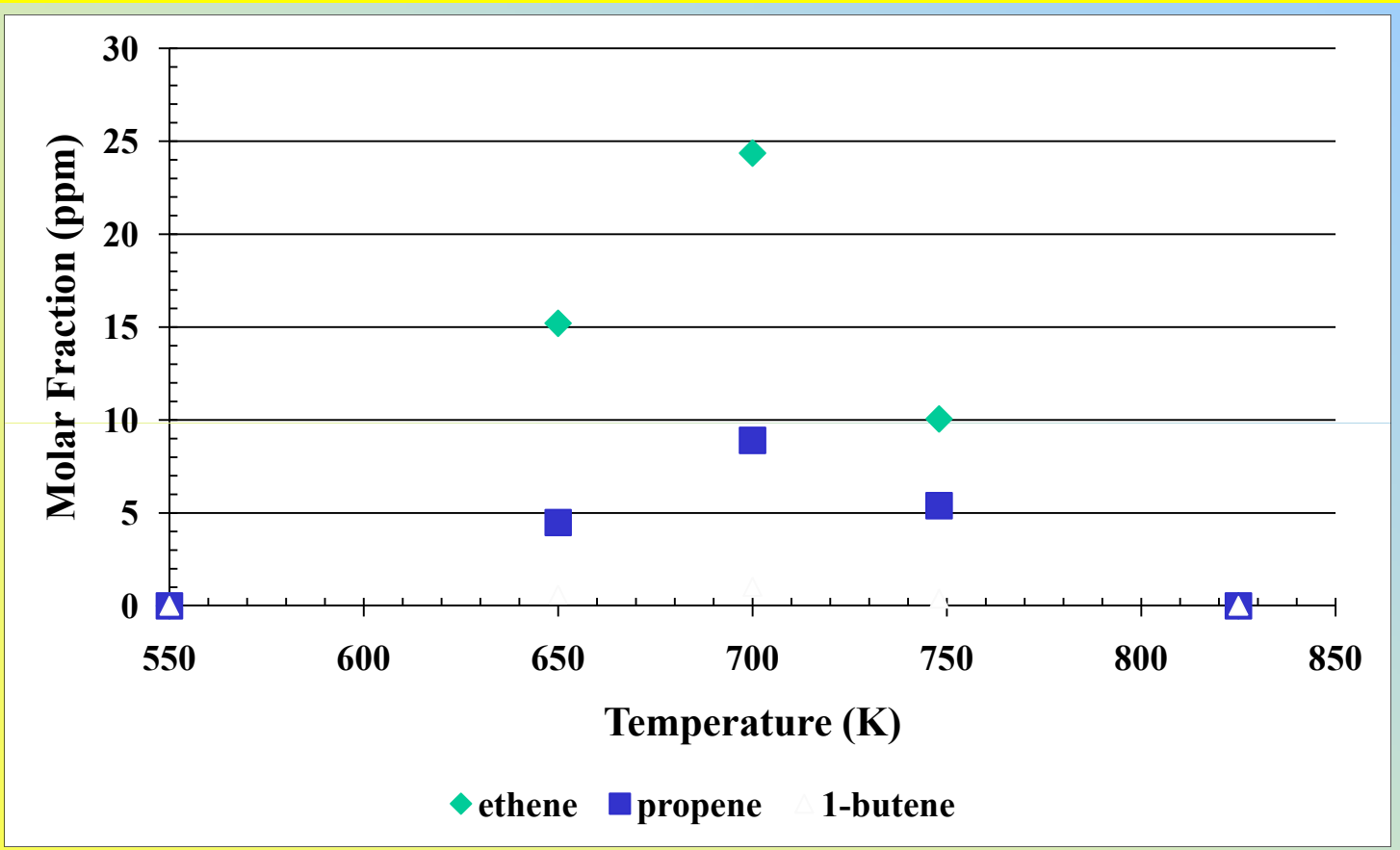


n-propyl CHX: Fuel Profile



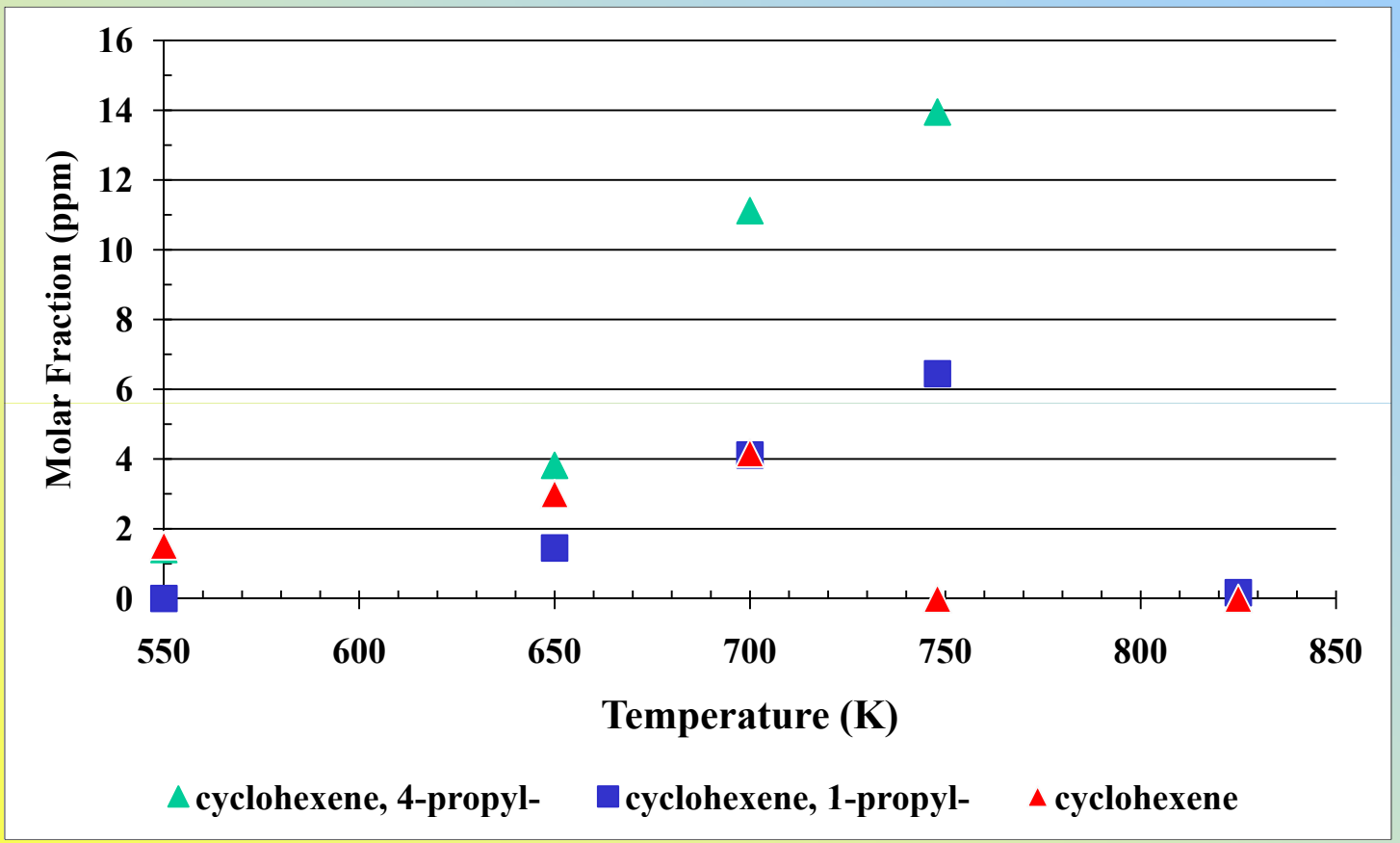
- **Minimum fuel concentration occurs at maximum reactivity around 675 K.**

n-propyl CHX: Straight Chain alkenes



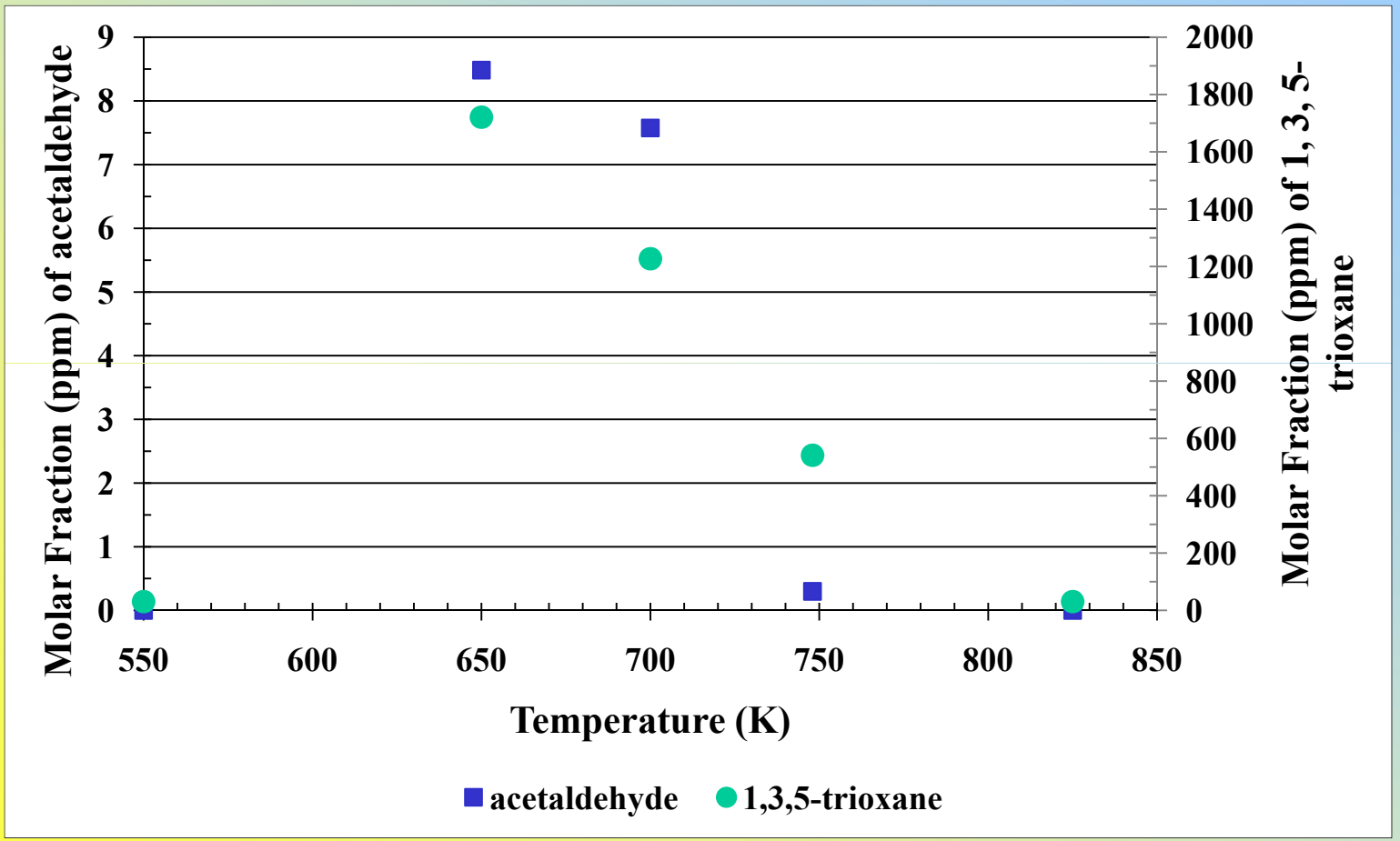
- Ethene, Propene and 1-Butene observed during n-BCH studies at higher concentrations because equivalence ratio was larger.
- 1-Butene production with PCH is much lower than 1-Butene production with n-BCH.

n-propyl CHX: Cycloalkenes



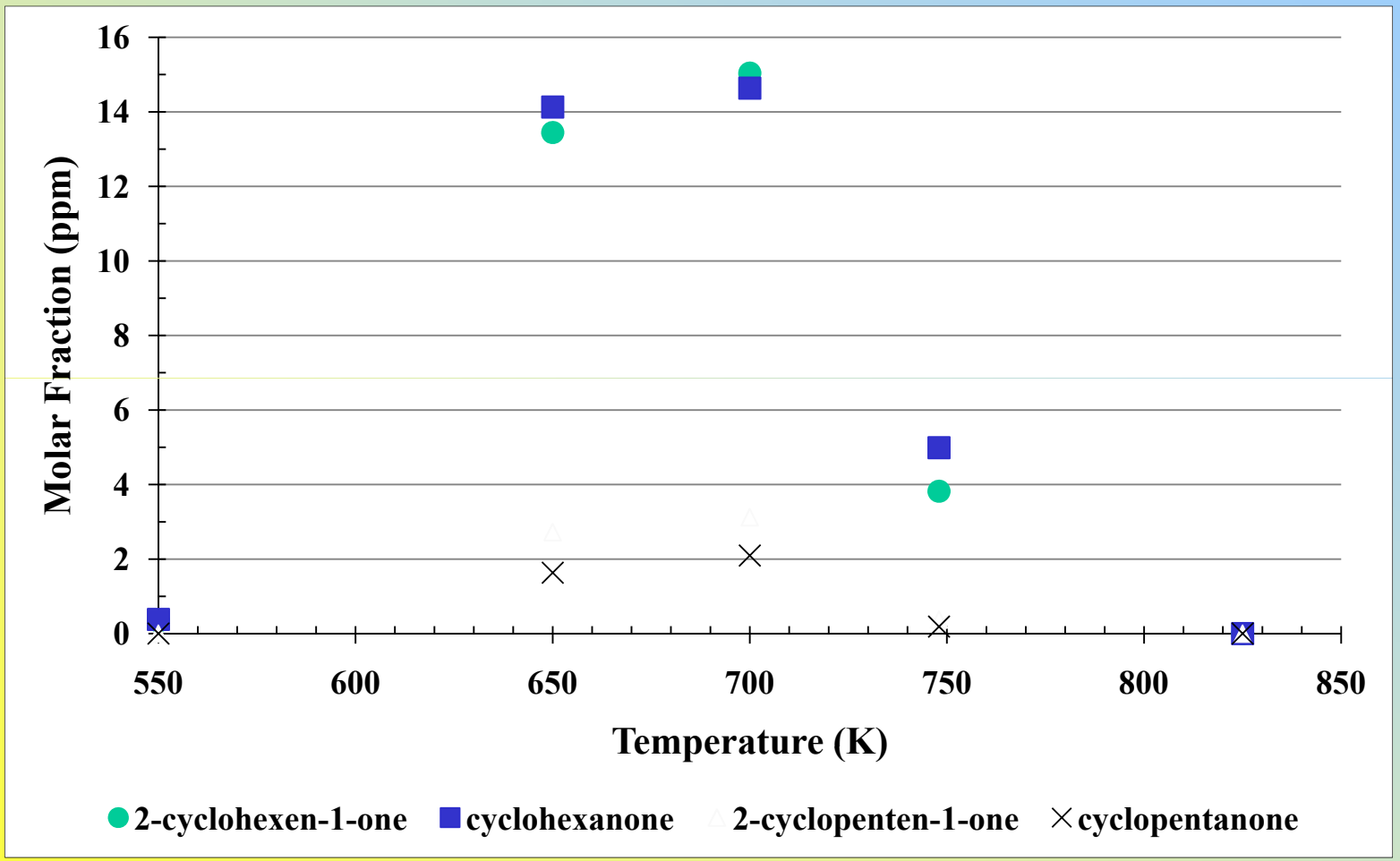
- **Propylcyclohexenes highest in NTC region where overall reactivity is low.**
  -Similar behavior observed with n-BCH.

n-propyl CHX: Aldehydes



- Aldehydes highest around NTC start.
  -Similar behavior observed with n-BCH.
- 1,3,5-Trioxane polymerized from formaldehyde during sampling.

n-propyl CHX: Cycloketones



- **Cyclopentanones and Cyclohexanones peaks near NTC start.**
  -Similar behavior observed with n-BCH.

First Impressions of n-propyl CHX Oxidation

- 1-Butene production with n-propyl CHX is much lower than 1-Butene production with n-butyl CHX.
  - Suggests that Ethene and Propene are produced from propyl chain
- Similar behavior of cycloalkenes, aldehydes, acetic acid and cycloketones observed between n-propyl CHX and n-butyl CHX.
  - Suggests similar mechanisms.
- Different classes were predominant at different reaction conditions:
  - Low temperature (aldehydes, cycloketones, and acetic acid).
  - Over the NTC region (cycloalkenes and multi-ring species).
- More experiments to be performed with PCH.
  - Reproducibility and possibly different conditions.

Future Work

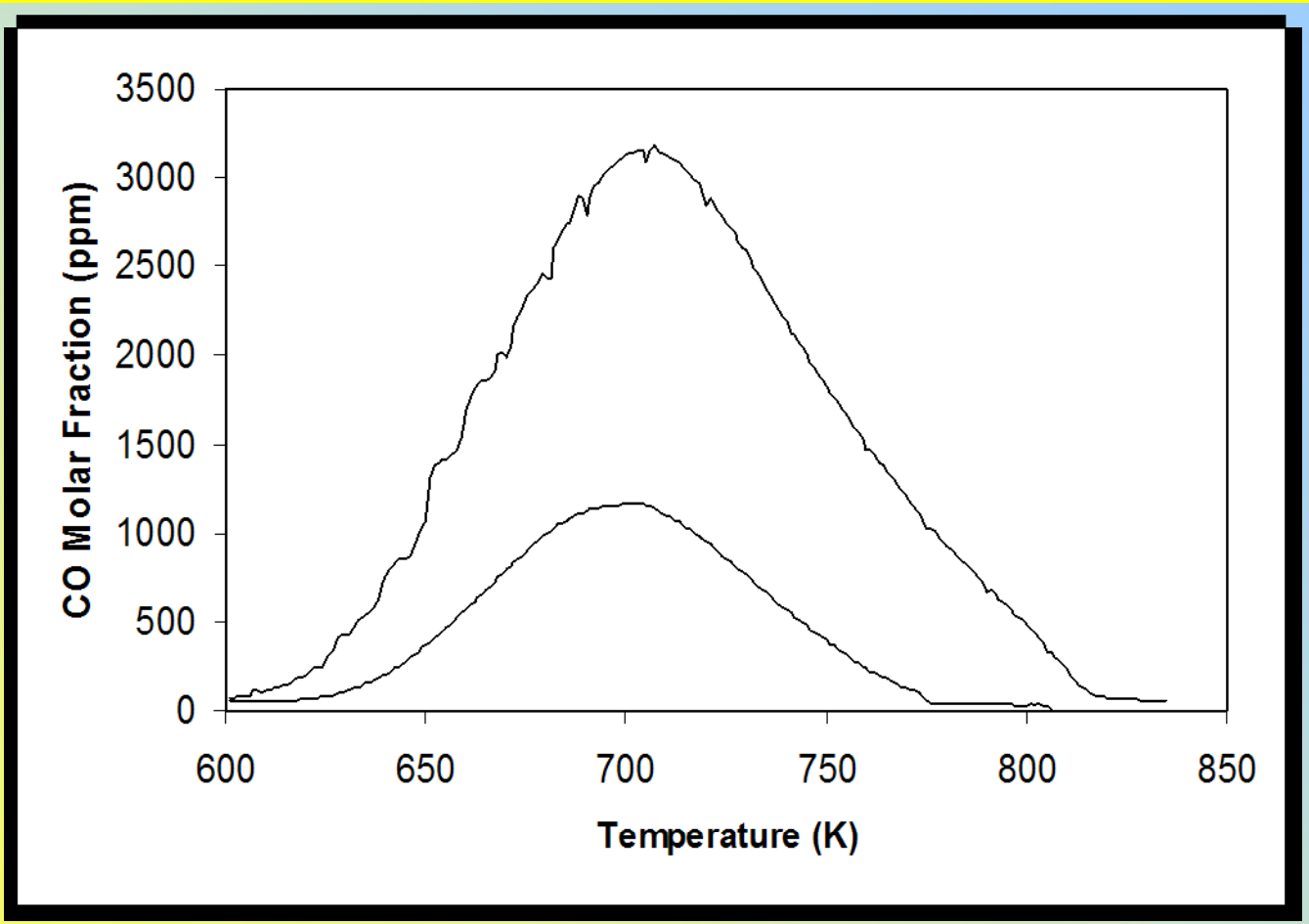
- **Work on some in-house modeling for low temperature data**
- **Replicate experiments to be performed with iso-cetane and propylcyclohexane.**
- **? Move to lightly branched iso alkanes and aromatics?**

Comparing Flow Reactor Measurements

- As data on surrogate component oxidation from several flow reactors have becomes available, it only seems natural to compare results
- Unfortunately, as each of our groups presents measurements it appears that there are major differences among the measurements

DU n-decane reactivity

Lower pressure and lower residence time have slight reduction on NTC start temperature, but cause end of NTC reactivity to be at significantly lower temperature



(Kurman et al., 2007)

- Upper line: 8 atm pressure & 120 ms residence time, Lower line: 4 atm pressure & 75 ms residence time
- 810 ppm n-decane, 0.30 phi

Princeton Data – Comb. & Flame

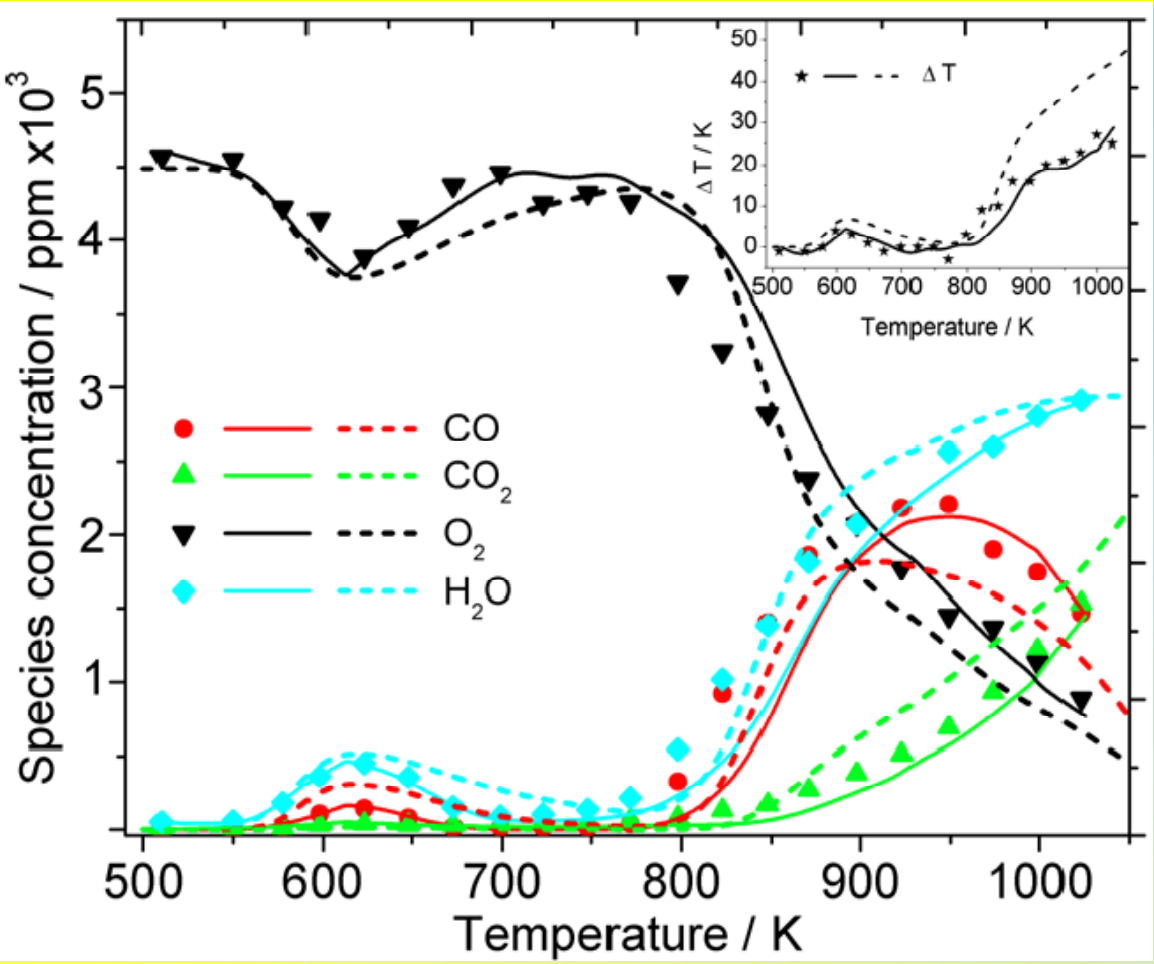
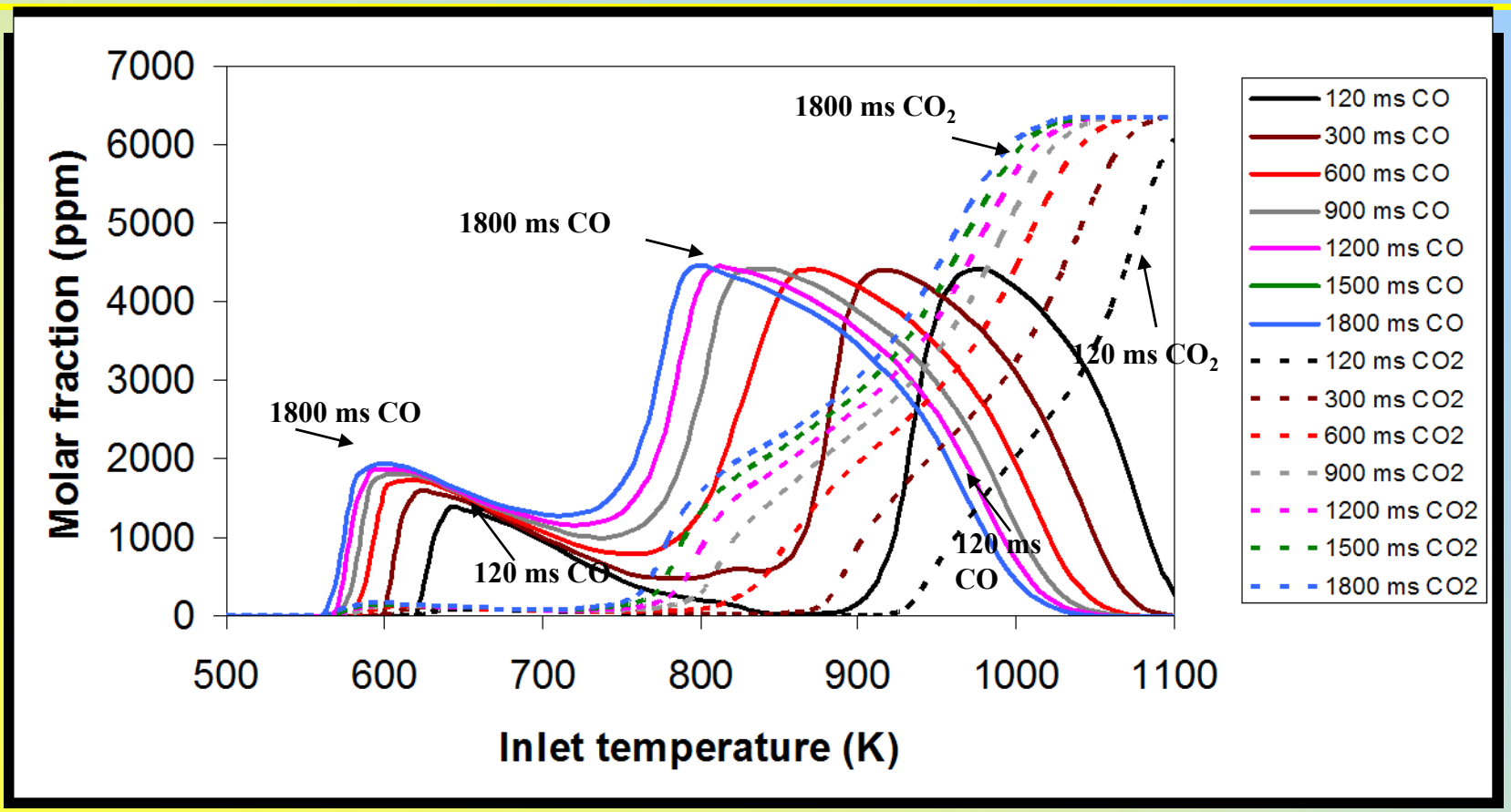


Figure 1 from Dooley et al., 2010: Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, ϕ= 1.0 and τ =1.8s, for POSF-4658 (symbols), POSF-4658 surrogate (solid lines) and model simulation of POSF-4658 surrogate (dashed lines), Inset;ΔT. POSF-4658 surrogate: 42.67/33.02/24.31 mole % n-decane/iso-octane/toluene

CO & CO_2 Predictions as Residence Time Changes



531 ppm n-dodecane / 42,100 ppm O_2 / 957,369 ppm N_2; 0.23 phi; 0.3% carbon by mole; 8 tm; Livermore model (Westbrook et al., 2009) run using plug flow reactor under adiabatic conditions at 10-K intervals. Note: 1500 and 1800 ms CO overlap.

With lower residence time, first-stage and second-stage ignition shift to higher temperatures

- **Thanks**