

# **Spatial Resolution of Reactant Species Consumption in Diesel Oxidation Catalysts**

**William S. Epling, Karishma Irani and Peter Hou  
University of Waterloo**

**Richard Blint  
General Motors**

# Background and motivation

- Running engines “lean”
  - improved fuel economy
  - less CO<sub>2</sub> emissions
  - But,
    - TWC does not work
    - Upcoming/current regulations limit NO<sub>x</sub> and PM on diesels
- Issues
  - reduction of NO<sub>x</sub> to N<sub>2</sub> in oxygen environment
  - oxidation of soot without melting the exhaust pipe
- Catalytic approach
  - SCR: HC, or NH<sub>3</sub> (urea)
  - NO<sub>x</sub> storage/reduction

# Background and motivation

| Catalyst                            | Reaction type  | Emissions                  |
|-------------------------------------|--|----------------------------|
| Selective catalytic reduction (SCR) | SCR by ammonia/urea<br>$4\text{NO} + 4\text{NH}_3 + \text{O}_2 \leftrightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$<br>$2\text{NO} + 2\text{NO}_2 + 4\text{NH}_3 \leftrightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$          | $\text{NO}_x$              |
| $\text{NO}_x$ adsorbers (traps)     | $\text{NO}_x$ adsorption - lean exhaust,<br>reduction - rich conditions<br>$\text{NO} + 0.5\text{O}_2 \leftrightarrow \text{NO}_2$<br>$\text{BaO} + 2\text{NO}_2 + 0.5\text{O}_2 \leftrightarrow \text{Ba}(\text{NO}_3)_2$ | $\text{NO}_x$ , CO,<br>HCs |
| Soot filters                        | Oxidation<br>$\text{C} + 0.5\text{O}_2 \leftrightarrow \text{CO}$<br>$\text{NO}_2 + \text{C} \leftrightarrow \text{CO} + \text{NO}$<br>$\text{CO} + 0.5\text{O}_2 \leftrightarrow \text{CO}_2$                             | PM                         |

Engine out  $\text{NO}:\text{NO}_2 \rightarrow 90:10$

# Background and motivation for the DOC

- Purpose

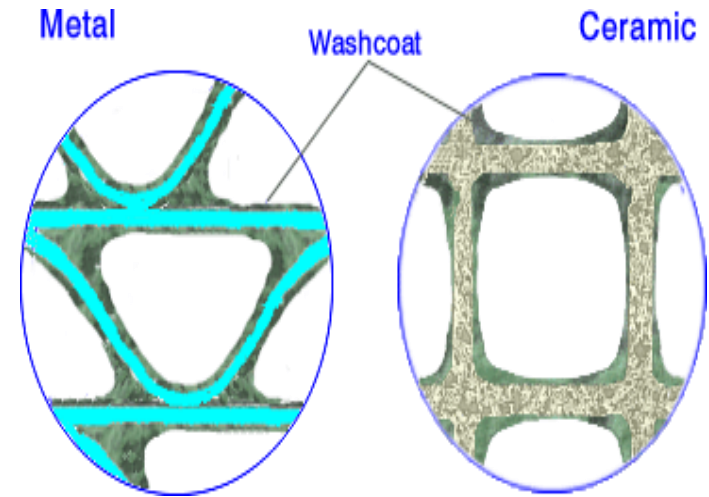
- $\text{NO} + 0.5\text{O}_2 \rightarrow \text{NO}_2$
- $\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$
- $\text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- Heat generation

- Oxidation of NO to NO<sub>2</sub> helps control NO<sub>x</sub> and soot emissions

- DOCs are installed upstream of SCR and NO<sub>x</sub> trap catalysts, as well as soot filters

- Problems:

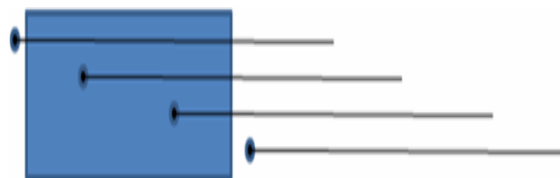
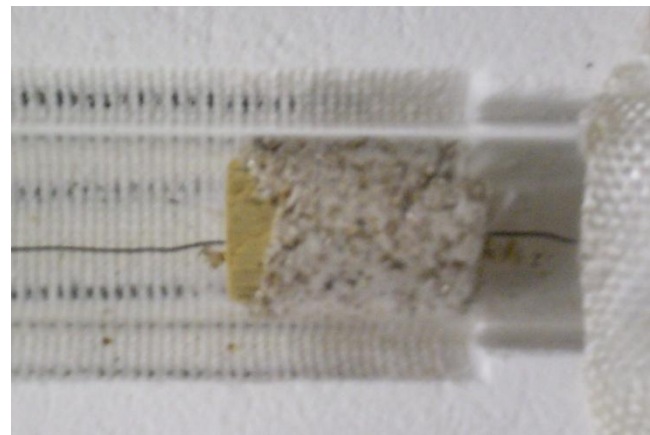
- NO oxidation kinetically and thermodynamically limited
- At low temperature CO, HC poisoning★
- New technologies require low T efficiencies
- Lack of literature on DOCs!



# Experiment Description

Monolith supported Pt-Pd/ $\text{Al}_2\text{O}_3$  model sample, dimensions = 2 x 3.5 cm

Gas analysis - FTIR analyzer  
- Mass spectrometer



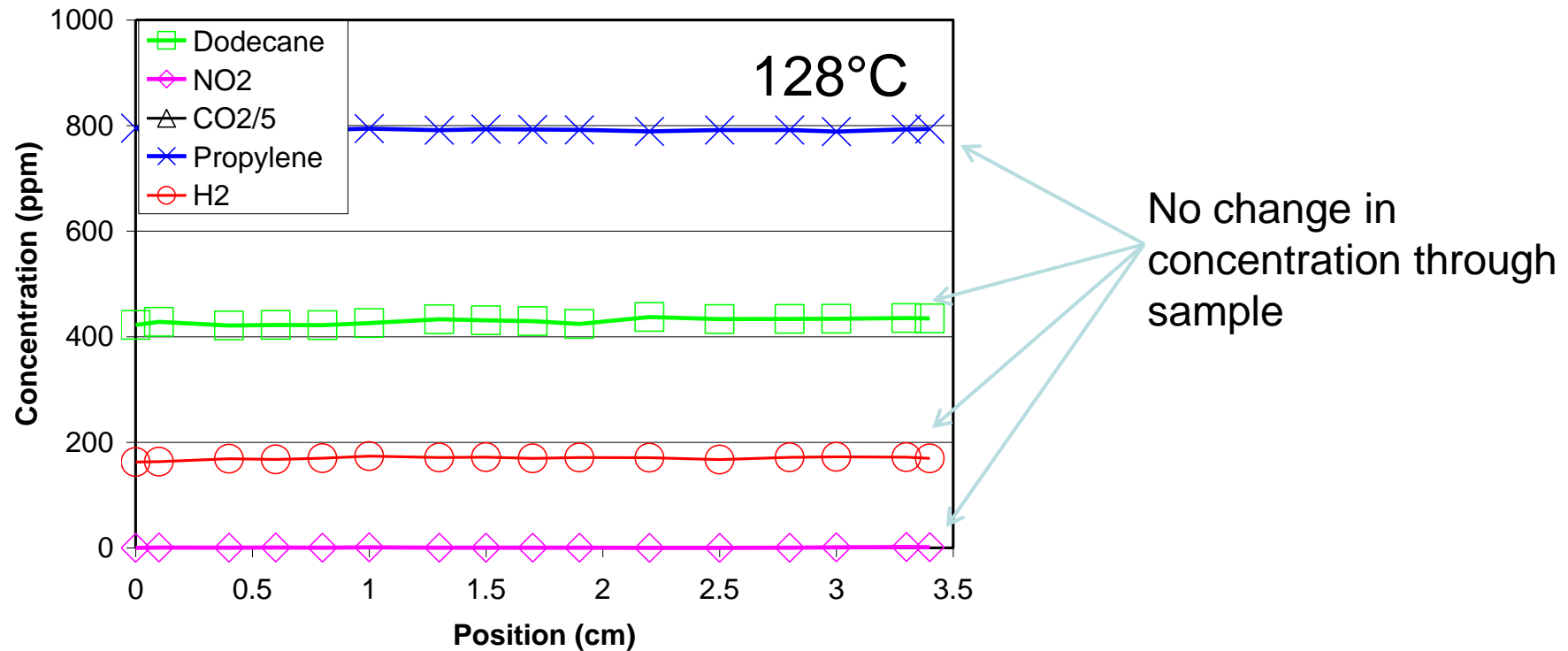
SPACiMS technique  
developed at ORNL

“Steady-state” experiments: constant temperature, vary the capillary position (T ramps and simpler mixture expts also run)

Feed characteristics:

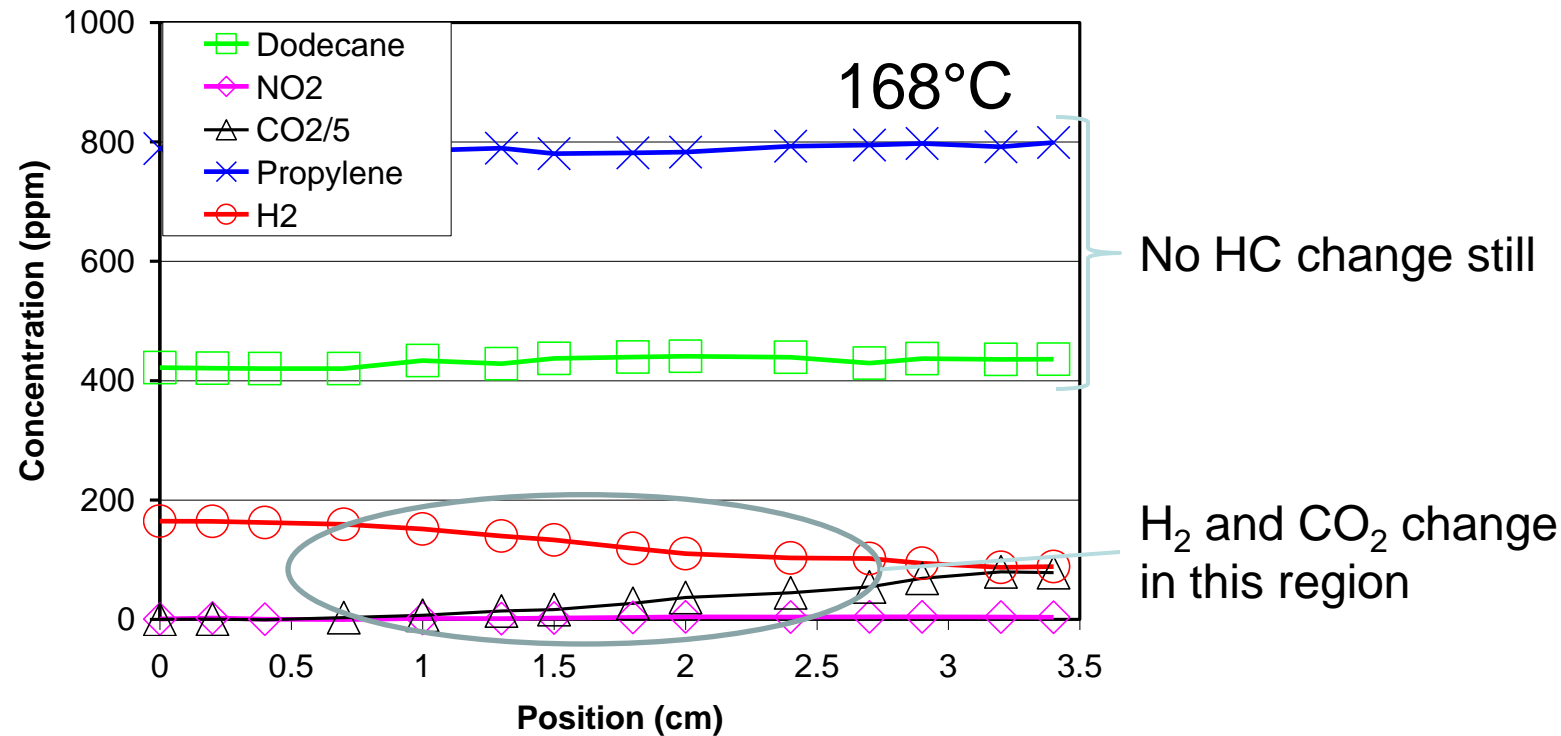
tests included  $\text{C}_{12}\text{H}_{26}$ ,  $\text{C}_3\text{H}_6$ , CO, NO, He, 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ , flowrate = 19.06 L/min (100K SV)

# Results – low T profiles



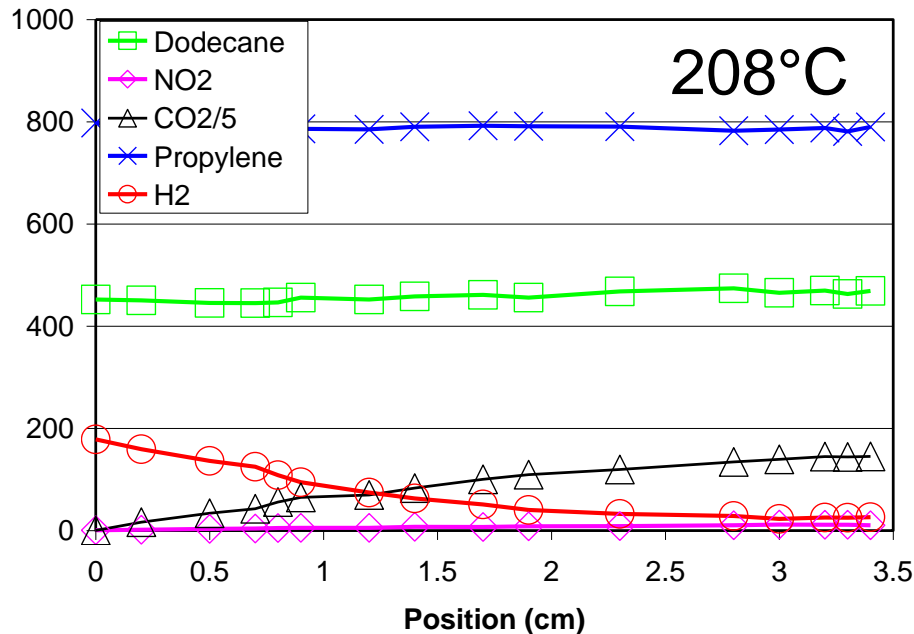
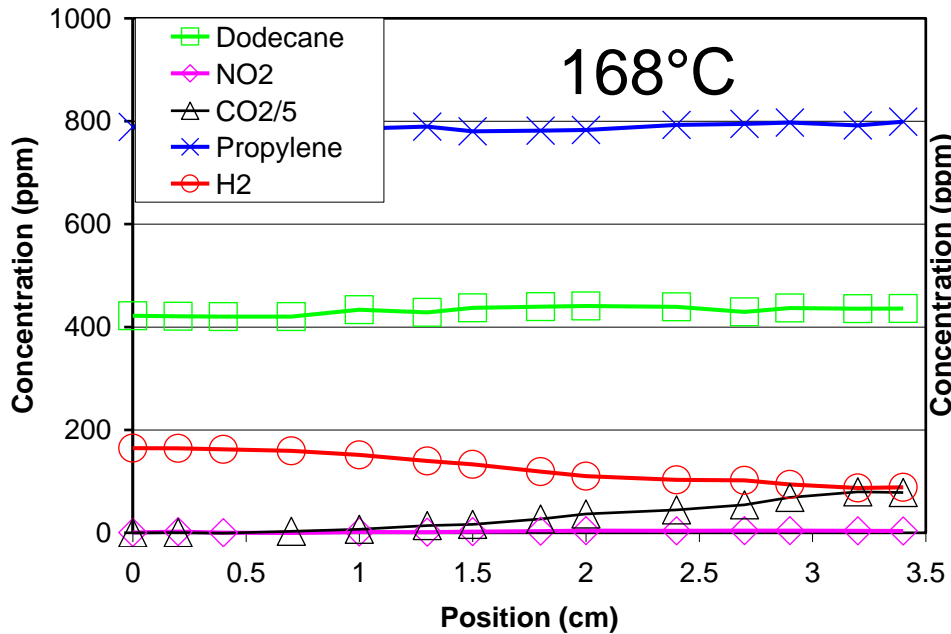
- Concentrations of H<sub>2</sub>, CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>12</sub>H<sub>26</sub> and NO<sub>2</sub> measured at various positions
- No obvious (significant) changes observed – no reaction along the length of sample

# Results – mid T profiles



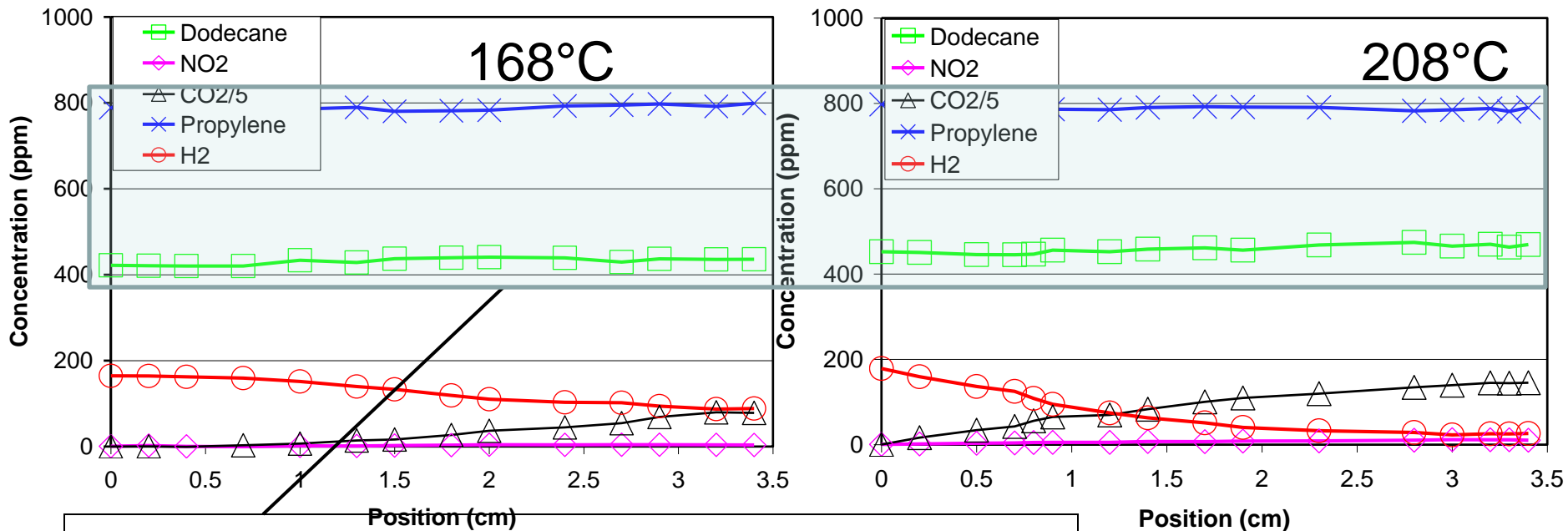
- H<sub>2</sub> drops and CO<sub>2</sub> increases from about 0.75 cm to 3 cm in the sample → oxidation is occurring in this region of the monolith (CO<sub>2</sub> from CO oxidation, 5 C change)
- No obvious (significant) change in HC species concentrations observed – no reaction along the length of sample

# Results – increasing T





# Results – increasing T

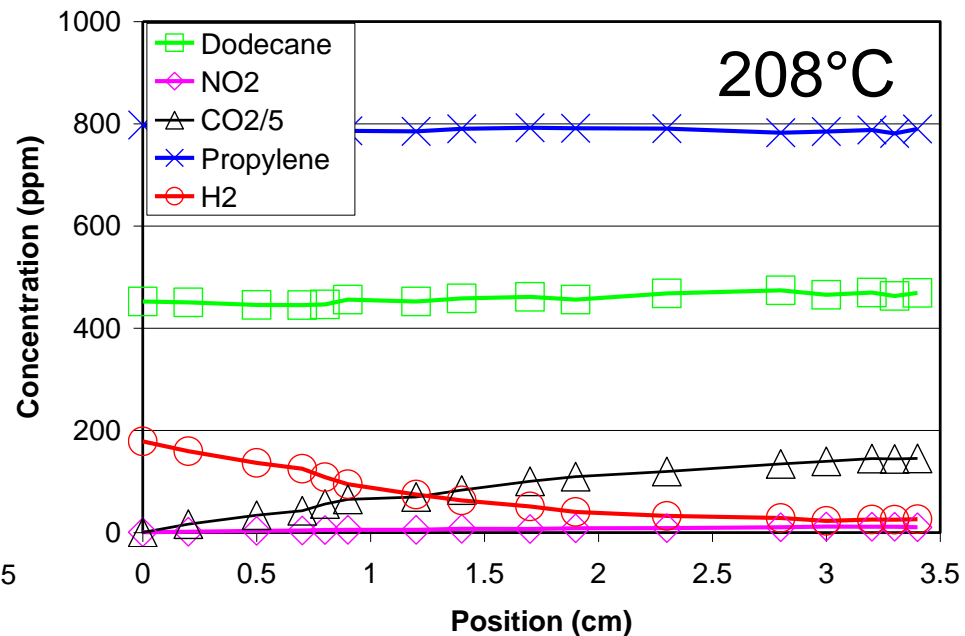
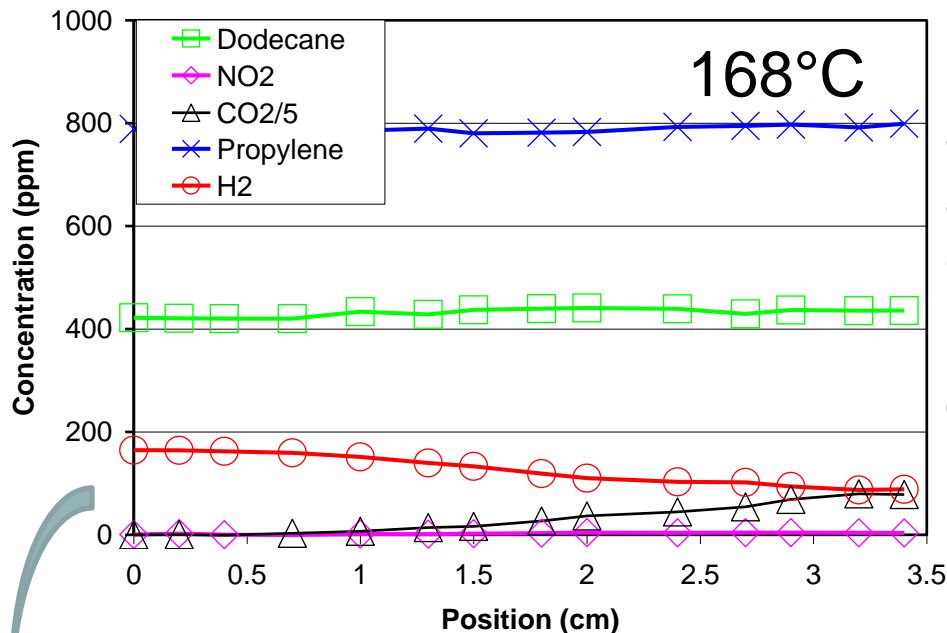


No change in HC species concentrations again – no conversion

H<sub>2</sub> and CO<sub>2</sub> changes begin to occur closer to the sample inlet with the increase in T

- back-to-front ignition profile
- no obvious differences in CO vs H<sub>2</sub> light-off

# Results – increasing T

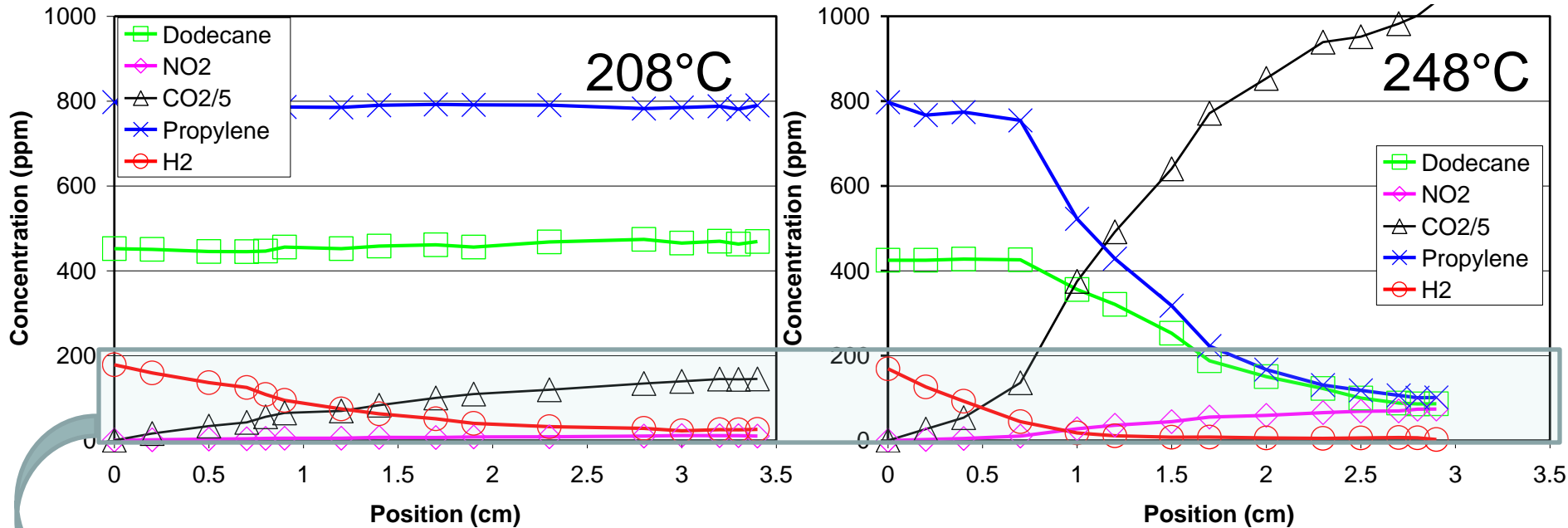


No change in HC species concentrations again – no conversion

H<sub>2</sub> and CO<sub>2</sub> changes begin to occur closer to the sample inlet with the increase in T

- back-to-front ignition profile (~5 C change)
- no obvious differences in CO vs H<sub>2</sub> light-off

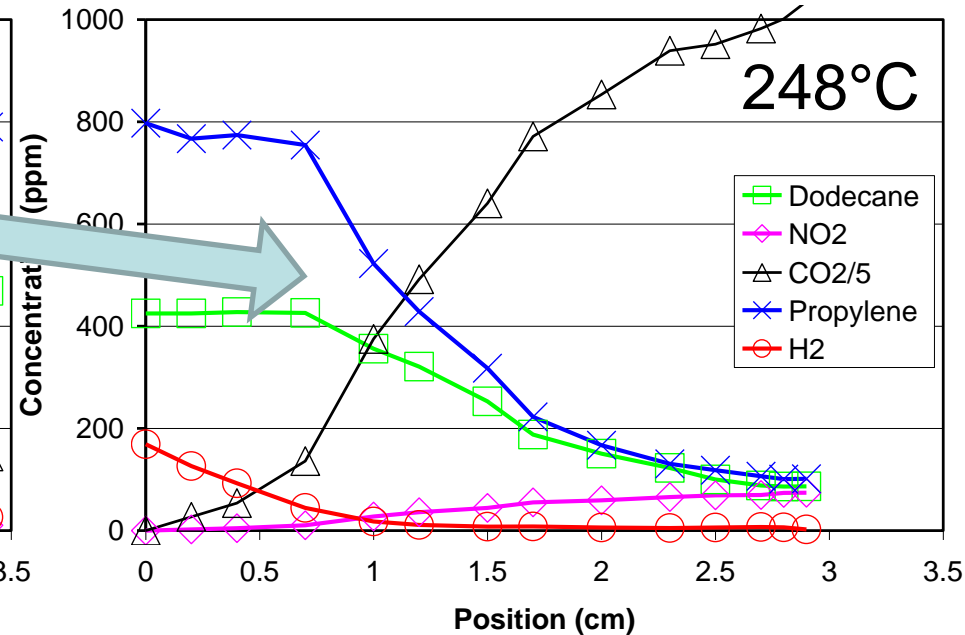
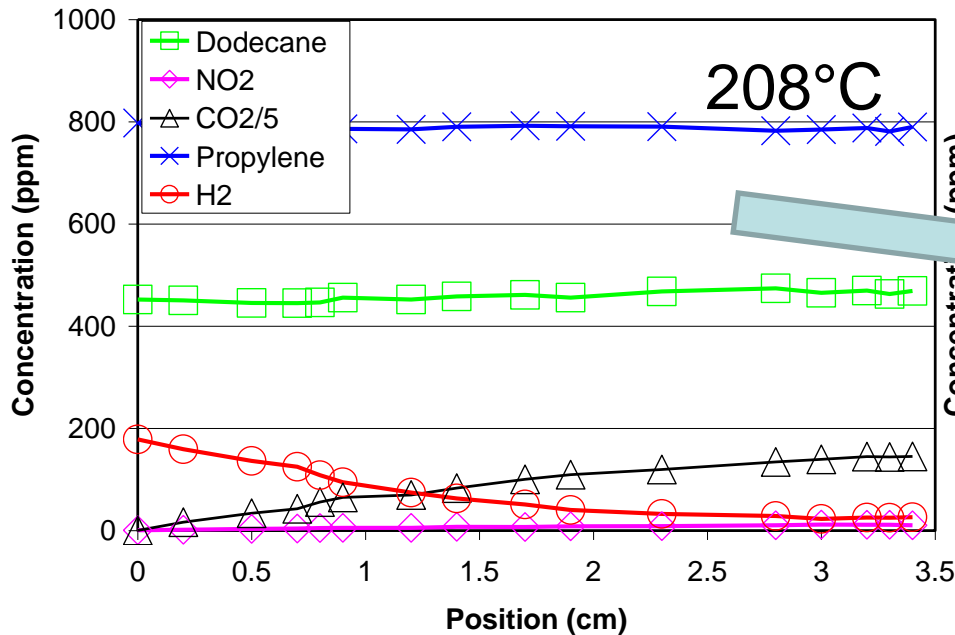
# Results – increasing T



H<sub>2</sub> and CO<sub>2</sub> changes begin to occur closer to the sample inlet with the increase in T

Both C<sub>3</sub>H<sub>6</sub> and C<sub>12</sub>H<sub>26</sub> are being oxidized, with CO<sub>2</sub> increasing as well

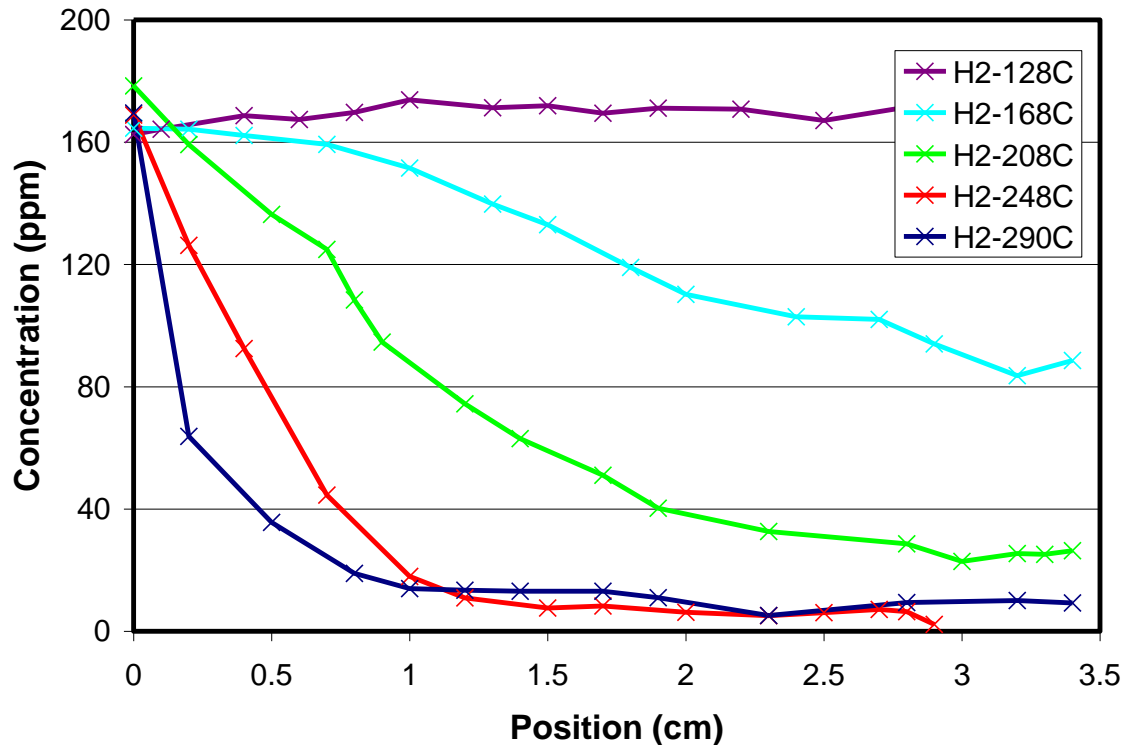
# Results – increasing T



H<sub>2</sub> and CO<sub>2</sub> changes begin to occur closer to the sample inlet with the increase in T

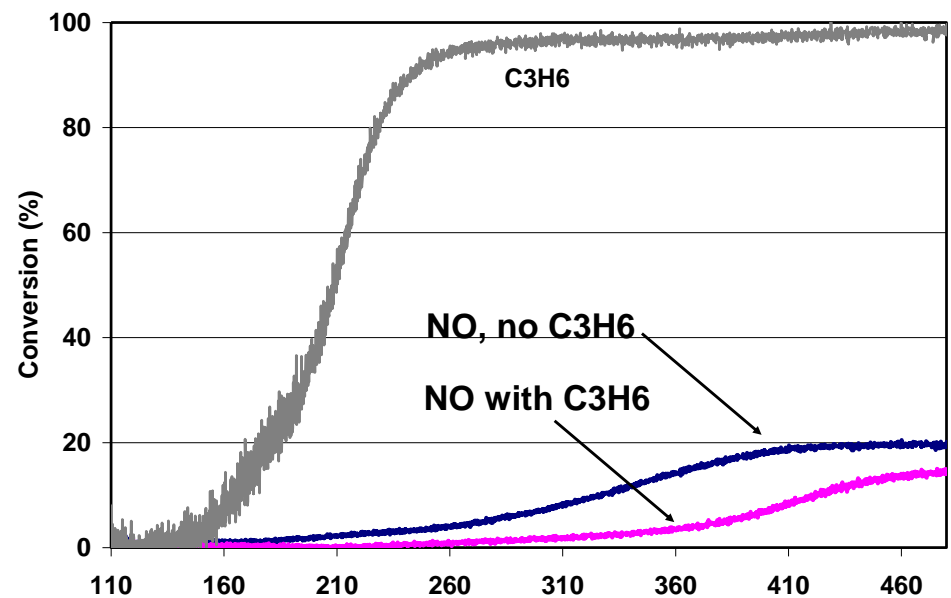
Both C<sub>3</sub>H<sub>6</sub> and C<sub>12</sub>H<sub>26</sub> are being oxidized, with CO<sub>2</sub> increasing as well (55°C change)

# Results – highlighting the oxidation profile



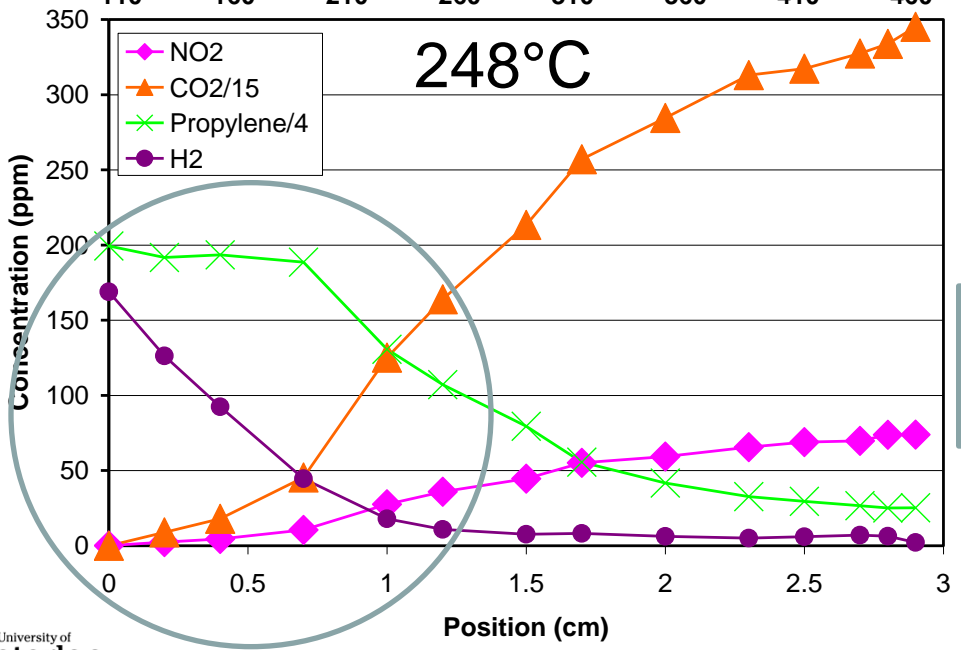
- Oxidation begins between 128 and 168°C
- At 168°C there appears to be an unreactive front portion and then at ~0.5 cm, reaction is observed
- With increasing temperature, the oxidation rate increases and less catalyst is needed to achieve the same conversions

# Results – NO Oxidation inhibition



T ramp experiments – 200 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O, with or without 800 ppm C<sub>3</sub>H<sub>6</sub>

Low T inhibition of NO oxidation clearly observed (NO also inhibits C<sub>3</sub>H<sub>6</sub> oxidation)

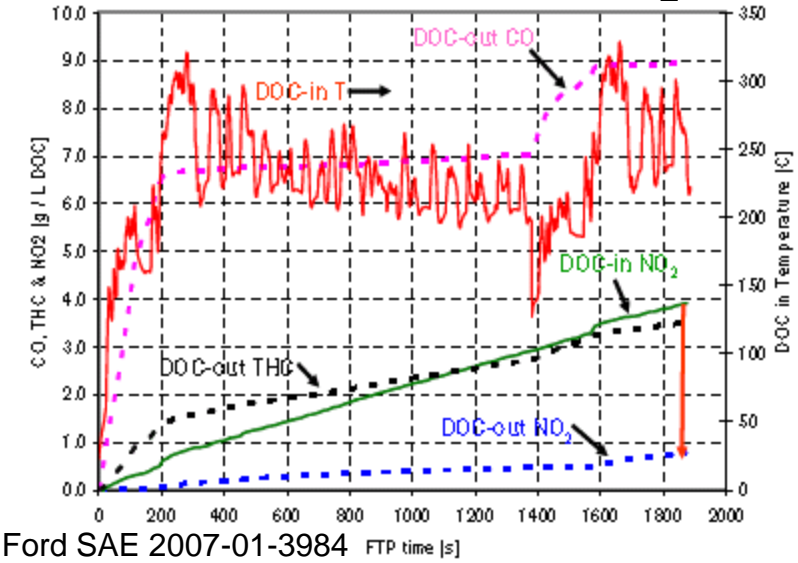


NO<sub>2</sub> oxidation “accelerates”  
 - after H<sub>2</sub> and CO are decreased and  
 - C<sub>3</sub>H<sub>6</sub> begins to drop

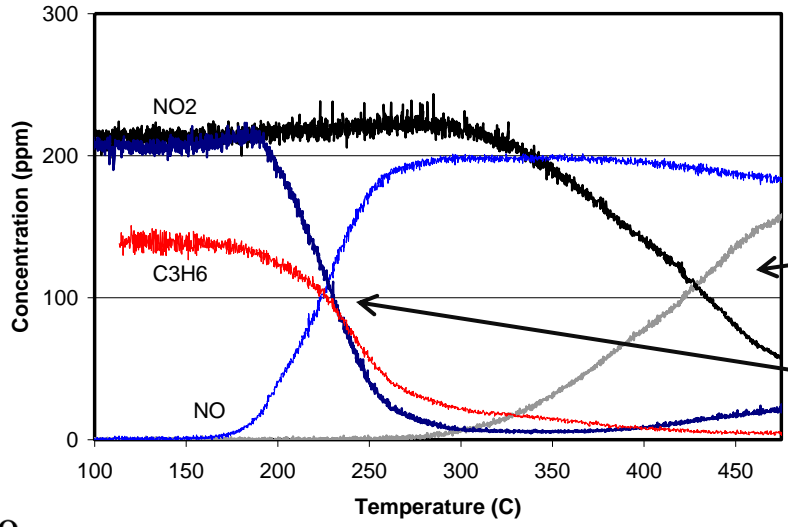
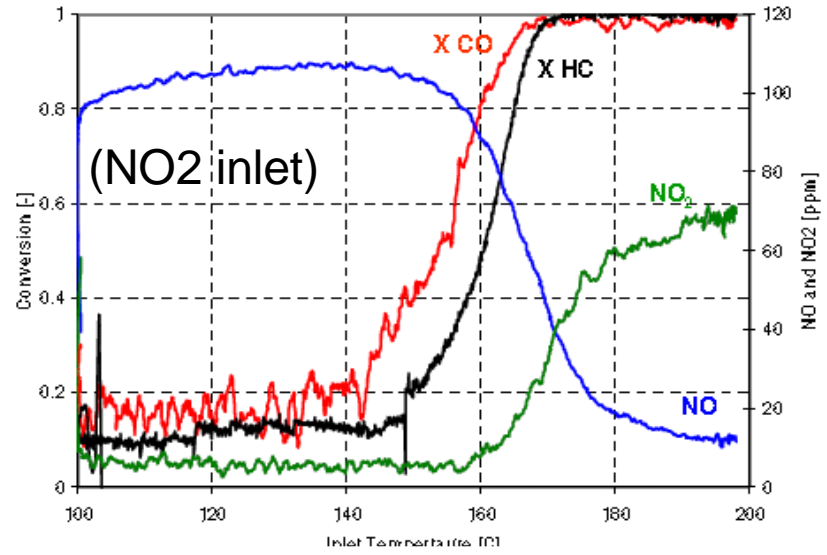
NO oxidation “starts” when CO is gone and C<sub>3</sub>H<sub>6</sub> drops

# Results – NO Oxidation “inhibition”

Aged DOC out has less NO<sub>2</sub> than in



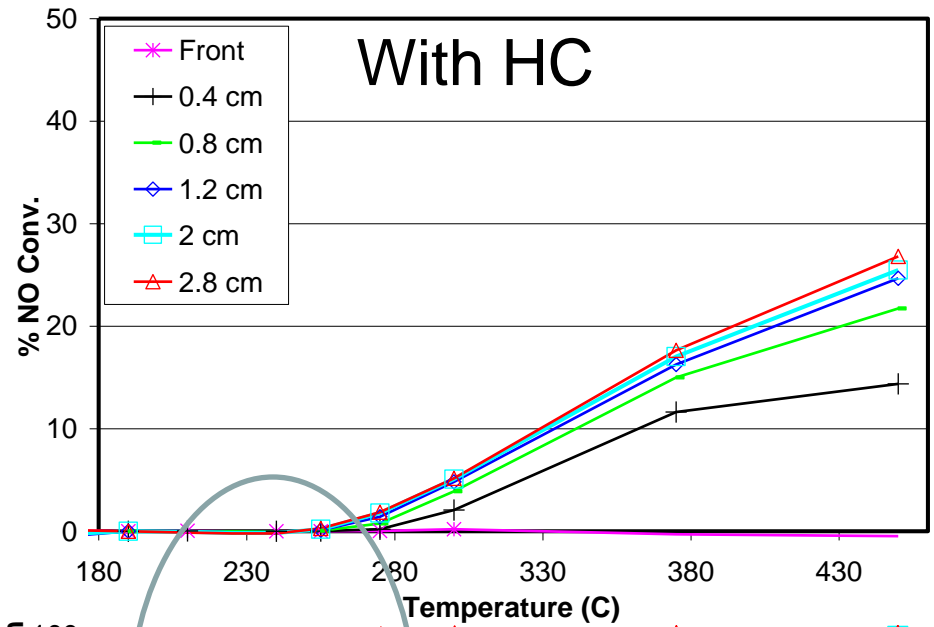
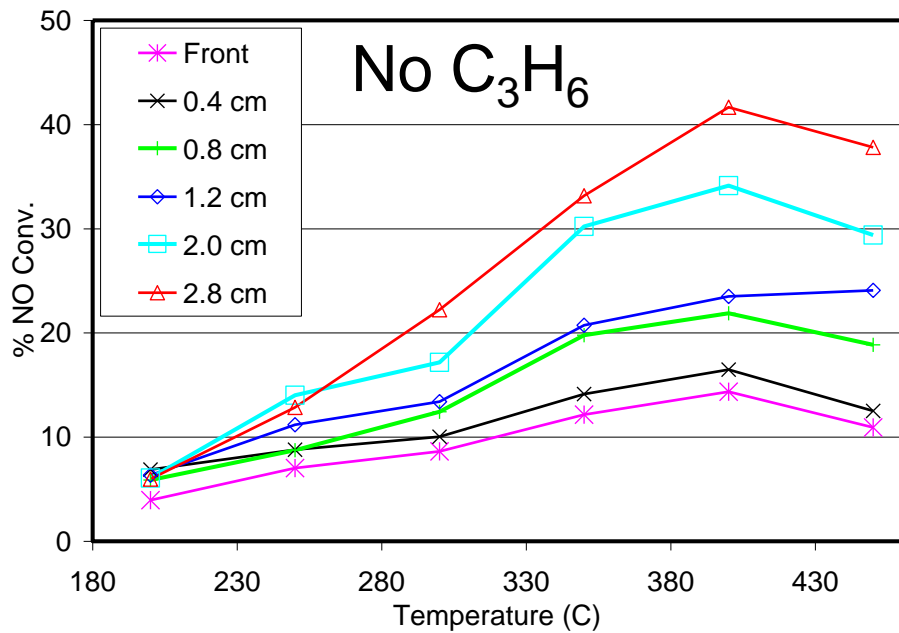
HC inhibition of NO oxidation via NO<sub>2</sub> oxidation of HC



Model DOC shows same trend

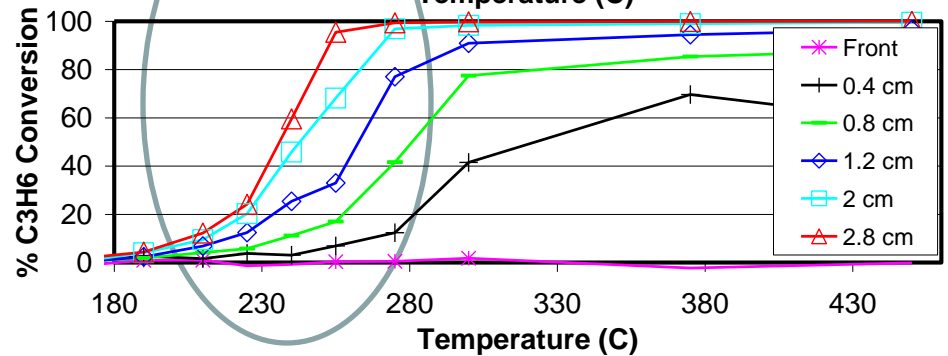
No HC in  
With C<sub>3</sub>H<sub>6</sub> in

# Results – NO Oxidation inhibition



Lower total conversion when HC is added

Higher T required for light off (ultimately causing lower conversion)



NO oxidation observed after C<sub>3</sub>H<sub>6</sub> light-off – C<sub>3</sub>H<sub>6</sub> inhibition  
 Actually – NO<sub>2</sub> is used as an oxidant for C<sub>3</sub>H<sub>6</sub> oxidation



# Conclusions

---

- Spatially-resolved concentrations of  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_{12}\text{H}_{26}$  and  $\text{NO}_2$  were measured within a model DOC
- $\text{H}_2$  and  $\text{CO}$  lit-off prior to  $\text{C}_3\text{H}_6$  and  $\text{C}_{12}\text{H}_{26}$
- Back-to-front light-off was observed under these test conditions
- $\text{CO}$  and  $\text{C}_3\text{H}_6$  inhibition of  $\text{NO}$  oxidation was observed

# Acknowledgements

---

- General Motors, Ontario Centres of Excellence and Natural Sciences and Engineering Research Council of Canada
- Naomi Zimmerman