Non-NH3 SCR Performance in an LNT/SCR Lean Exhaust System

Mark A. Dearth*, Giovanni Cavataio, Joseph Theis, Lifeng Xu,
R.W. McCabe Ford Motor Company RIC

And

Mark Crocker, University of Kentucky CAER

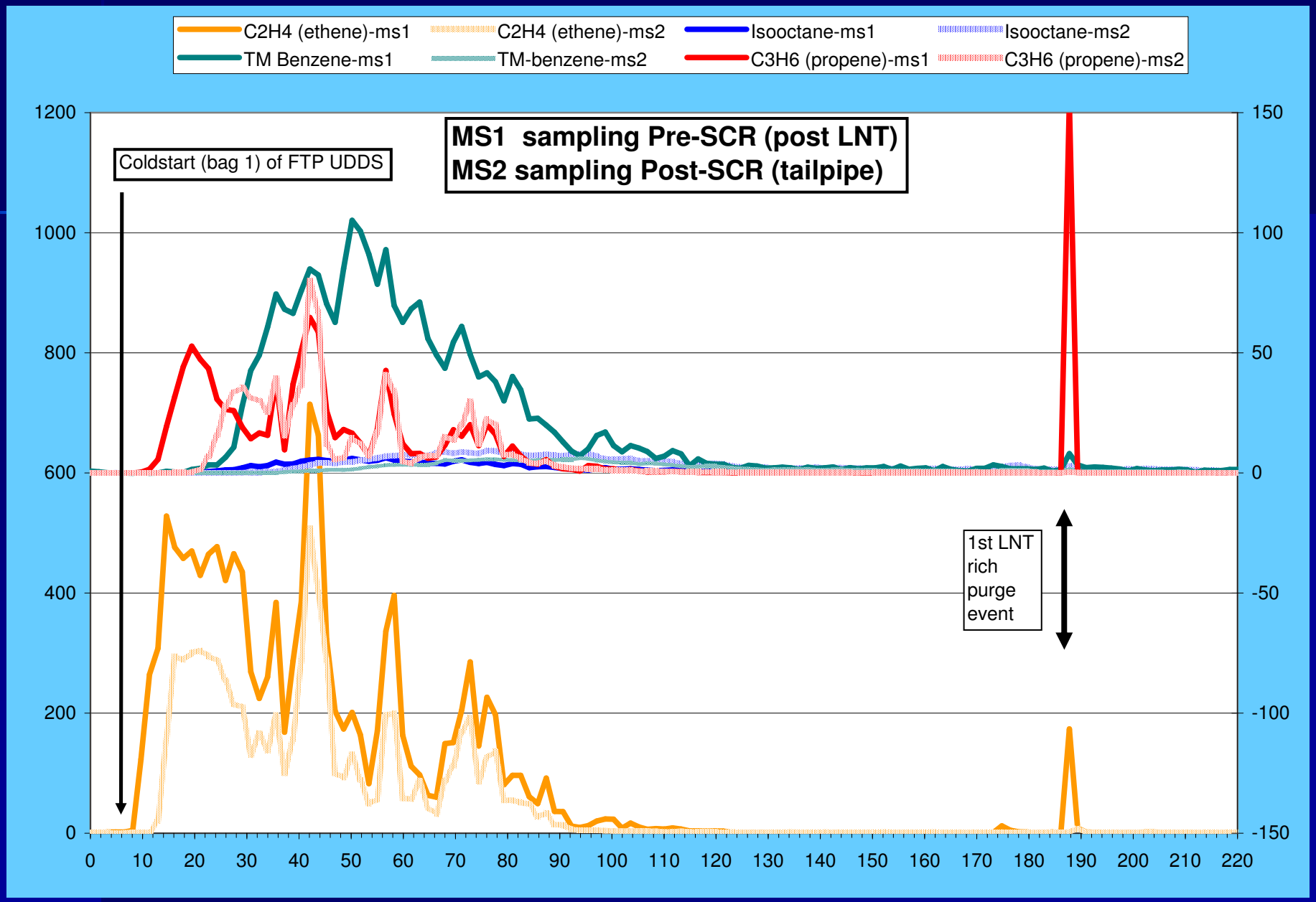
Talk Outline

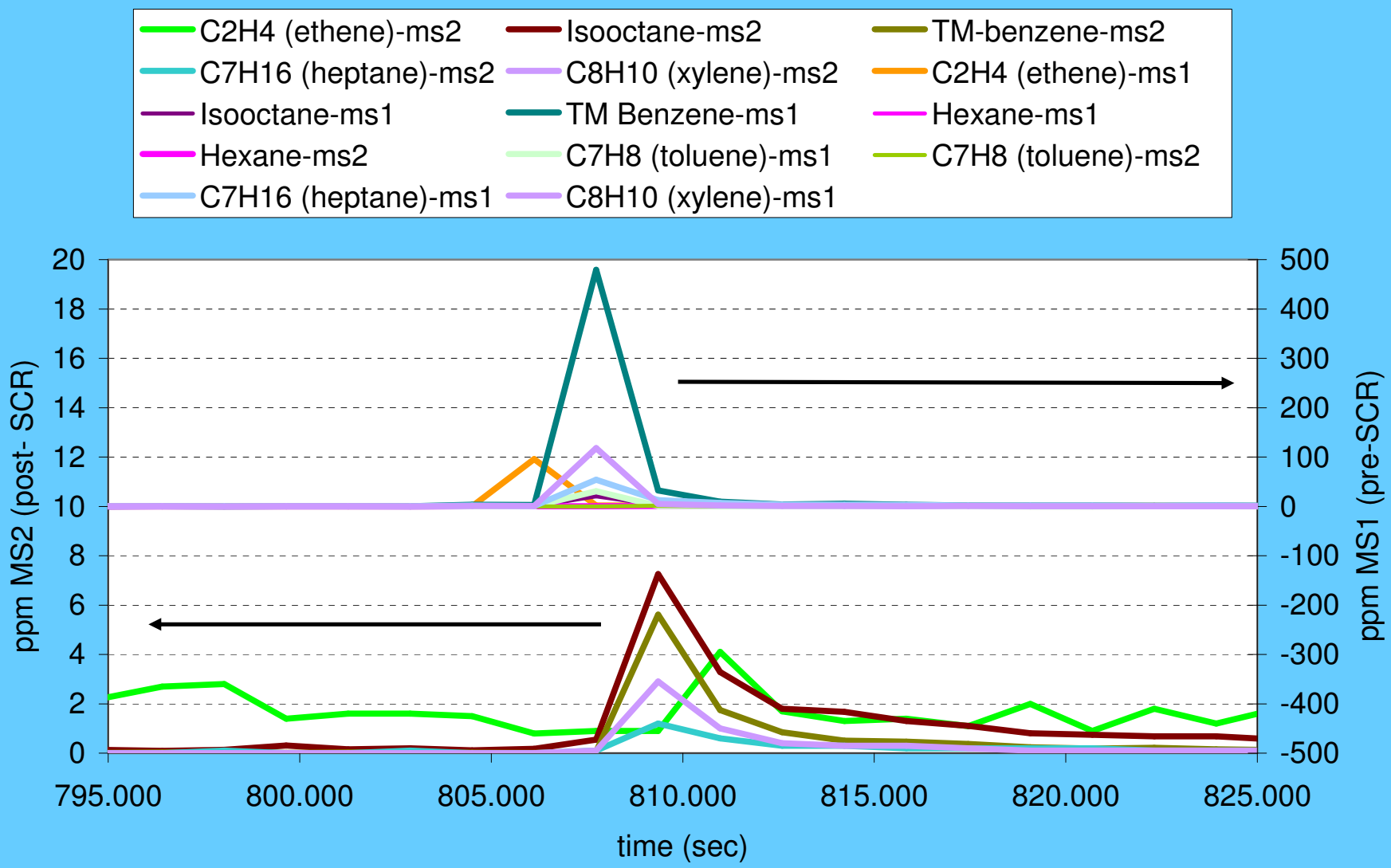
- Vehicle studies of LNT-SCR HC interactions.
- Laboratory studies of LNT-SCR system and benefits.
- Laboratory confirmation of ethylene and propylene interaction with Cu-SCR.
- Summary of results.

LNT+SCR vehicle dynamometer studies

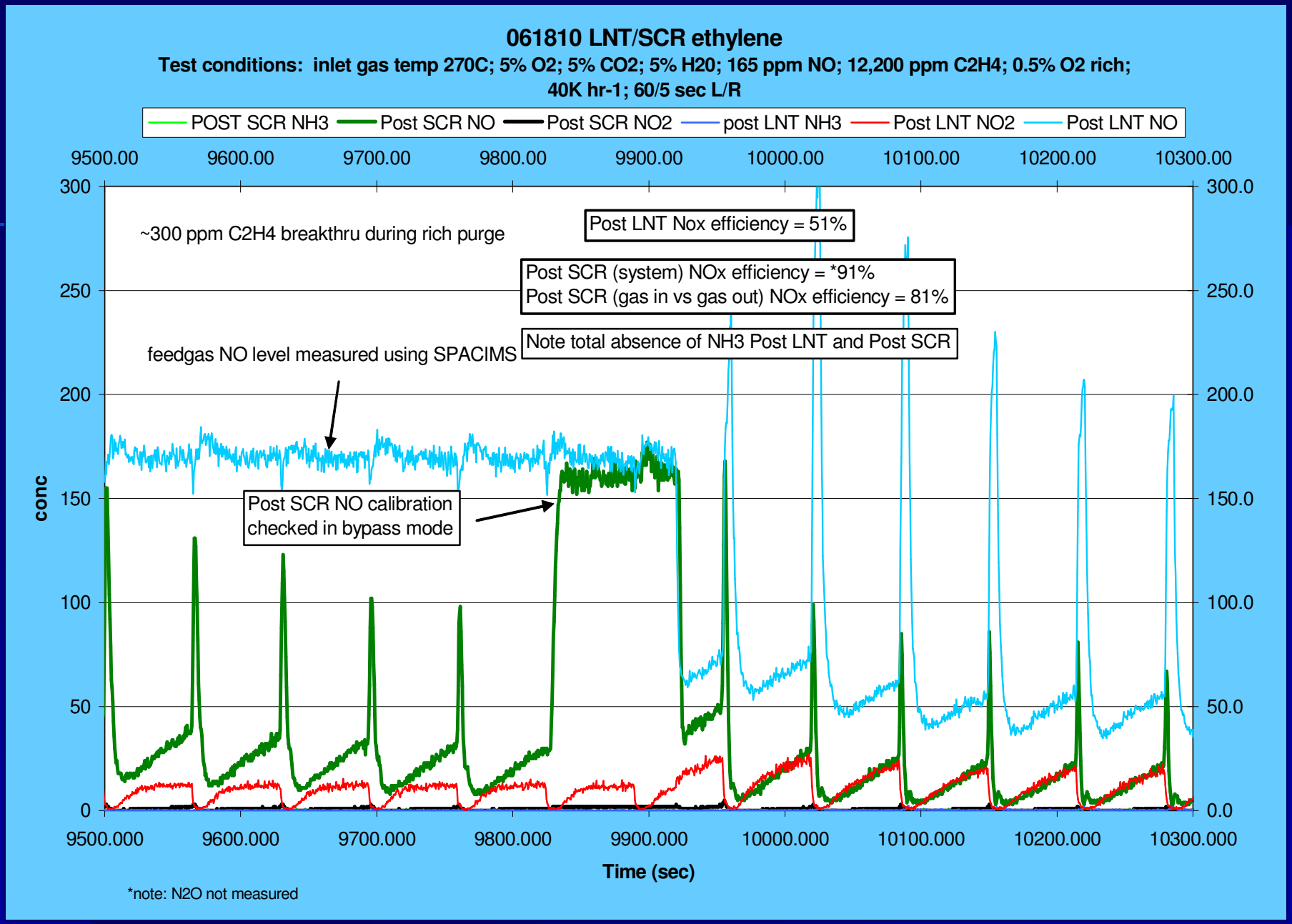
Experimental 4.4L V-6 TDI F150 with DOC/LNT/SCR/cDPF

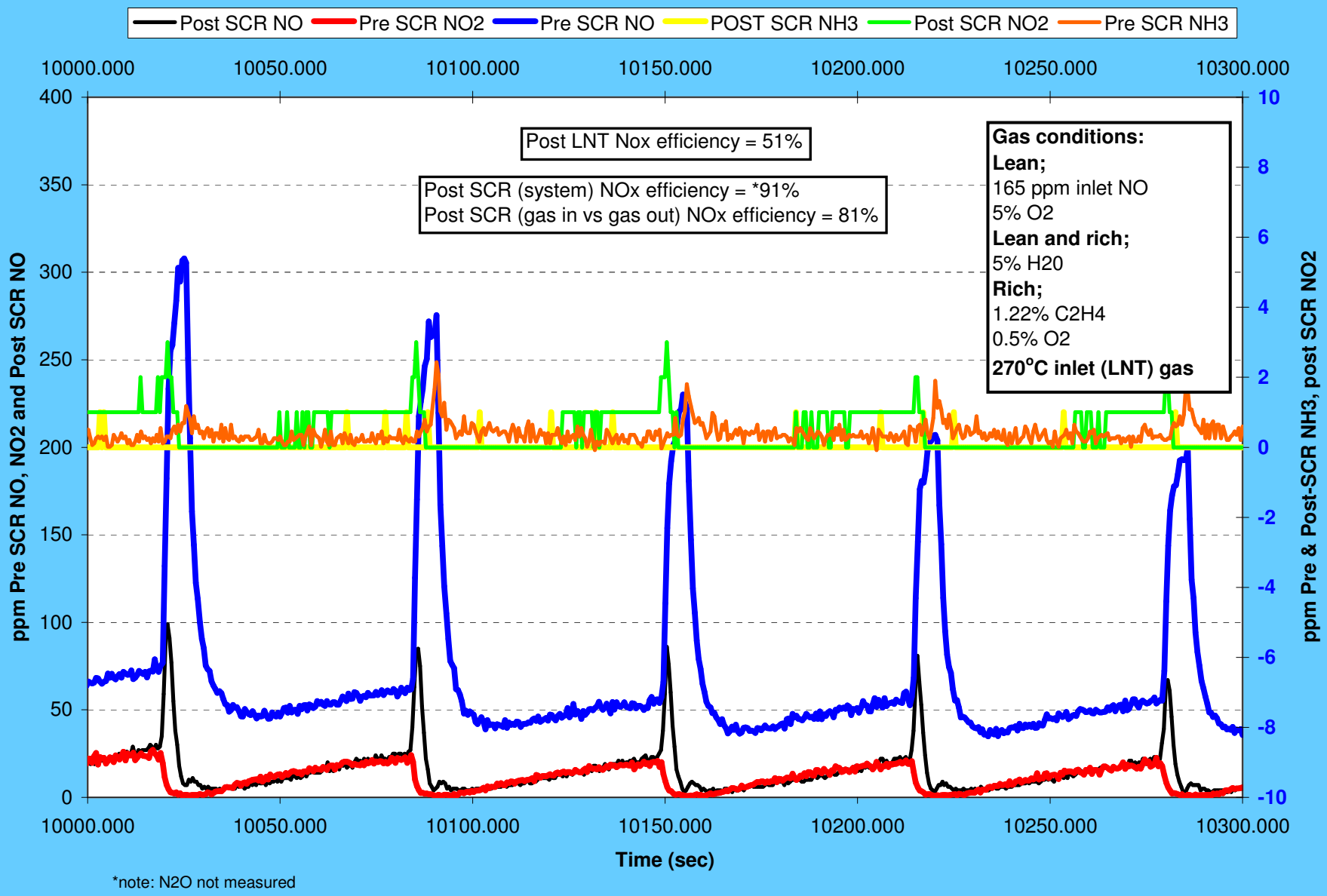
Coldstart data collected after lean-only (no rich purges) HFET/US06 high temp/high speed pre-conditioning.


C2H4 (ethene)-ms1
C2H4 (ethene)-ms2
Isooctane-ms1
Isooctane-ms2
TM Benzene-ms1
TM-benzene-ms2
C3H6 (propene)-ms1
C3H6 (propene)-ms2
MS1 sampling Pre-SCR (post LNT)
MS2 sampling Post-SCR (tailpipe)
Coldstart (bag 1) of FTP UDDS
1st LNT rich purge event
1200
1000
800
600
400
200
0
150
100
50
0
-50
-100
-150
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220

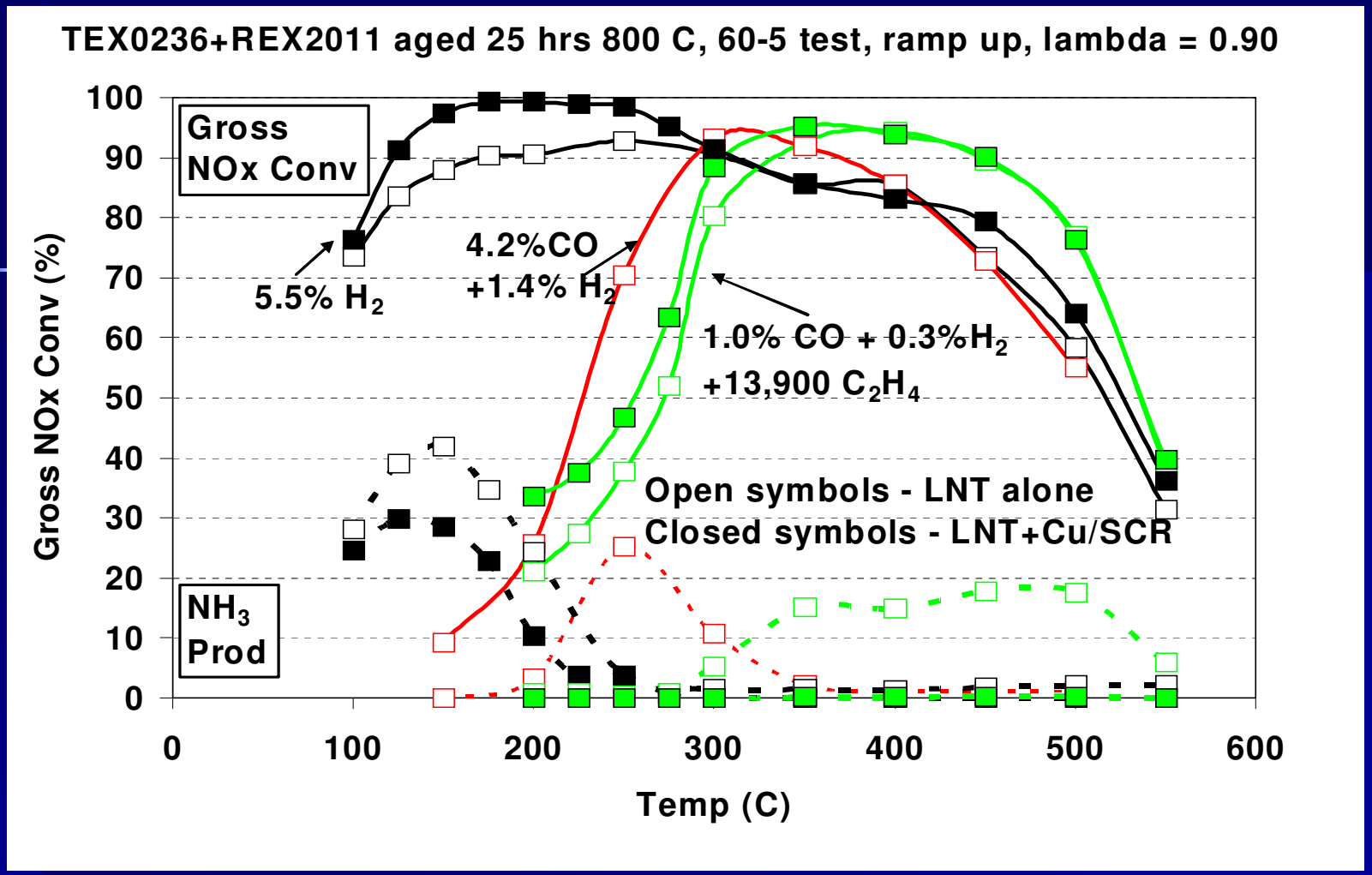

Pre and Post SCR HCs by Dual MS
C2H4 (ethene)-ms2
Isooctane-ms2
TM-benzene-ms2
C7H16 (heptane)-ms2
C8H10 (xylene)-ms2
C2H4 (ethene)-ms1
Isooctane-ms1
TM Benzene-ms1
Hexane-ms1
Hexane-ms2
C7H8 (toluene)-ms1
C7H8 (toluene)-ms2
C7H16 (heptane)-ms1
C8H10 (xylene)-ms1
ppm MS2 (post- SCR)
ppm MS1 (pre-SCR)
time (sec)
20
18
16
14
12
10
8
6
4
2
0
500
400
300
200
100
0
-100
-200
-300
-400
-500
795.000
800.000
805.000
810.000
815.000
820.000
825.000

LNT+SCR flow reactor studies


061810 LNT/SCR ethylene
Test conditions: inlet gas temp 270C; 5% O2; 5% CO2; 5% H20; 165 ppm NO; 12,200 ppm C2H4; 0.5% O2 rich; 40K hr-1; 60/5 sec L/R
POST SCR NH3
Post SCR NO
Post SCR NO2
post LNT NH3
Post LNT NO2
Post LNT NO
~300 ppm C2H4 breakthru during rich purge
Post LNT Nox efficiency = 51%
Post SCR (system) NOx efficiency = *91%
Post SCR (gas in vs gas out) NOx efficiency = 81%
Note total absence of NH3 Post LNT and Post SCR
feedgas NO level measured using SPACIMS
Post SCR NO calibration checked in bypass mode
conc
Time (sec)
*note: N2O not measured

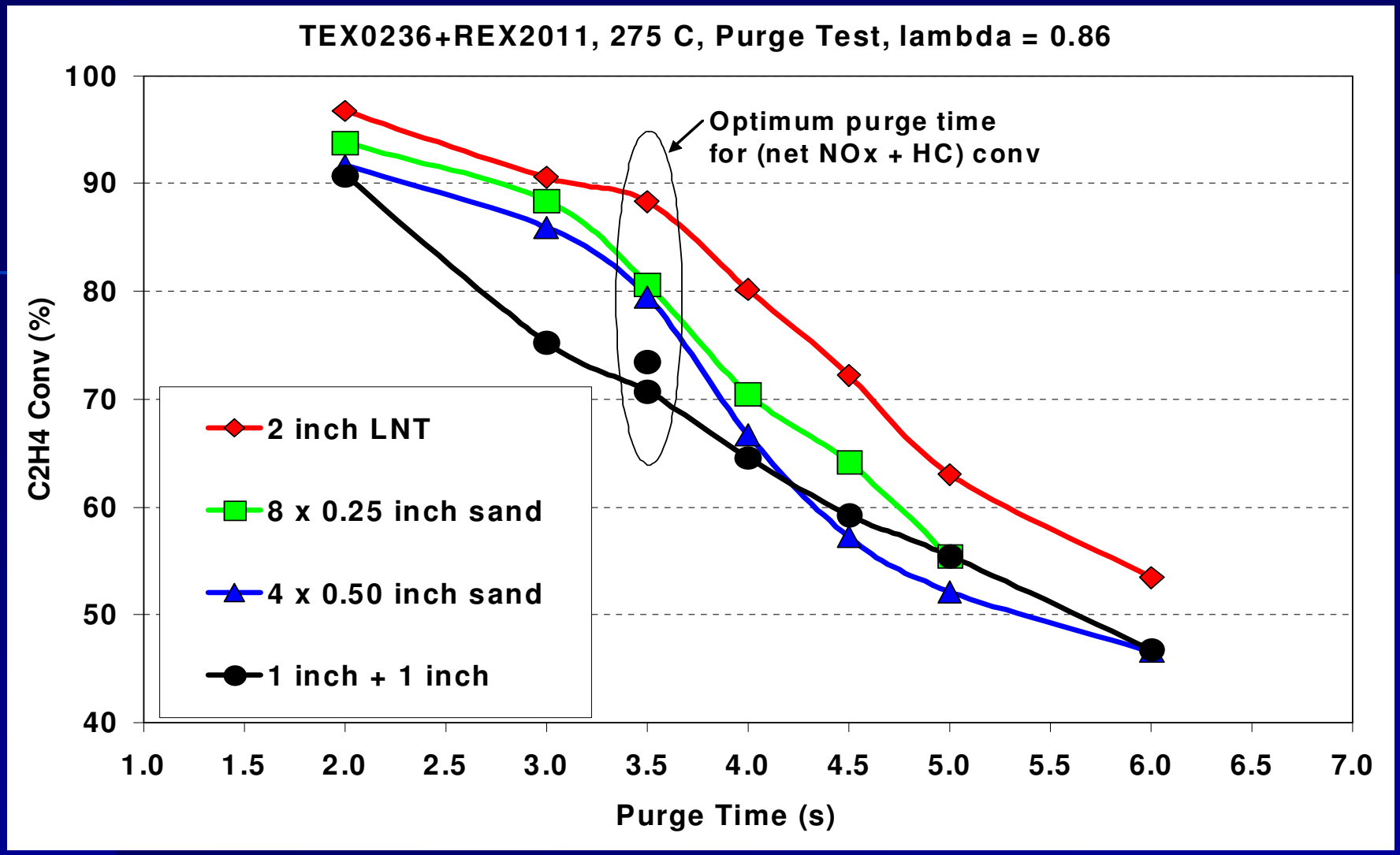


*note: N2O not measured



High H_2 level produce NH3 and improve the NOx performance at low temperatures, while high C_2H_4 levels produce NH3 and improve the NOx performance at high temperatures.

> Vehicle applications – match reductant composition to exhaust temperatures using calibration (e.g., injection timing)



Sandwich designs improve C_2H_4 conversion due to adsorption/desorption of C_2H_4 on SCR catalyst during purge, SCR releases some during lean periods, downstream LNT converts it

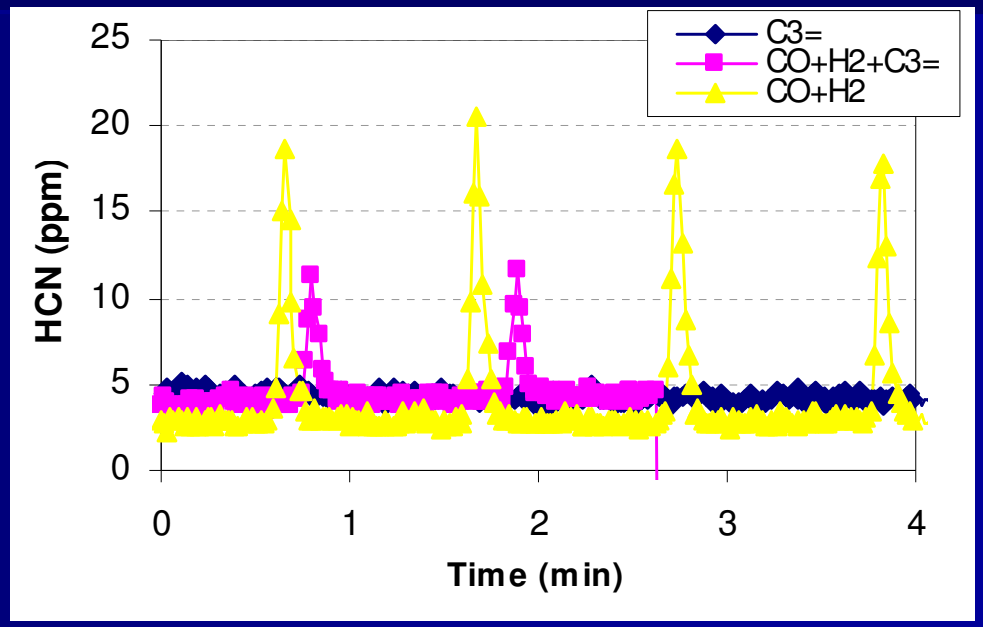
> Need to minimize HC slip, crucial for meeting low HC emission standards

SCR+HCs flow reactor studies

Speciation Study of LNT Exhaust Gas

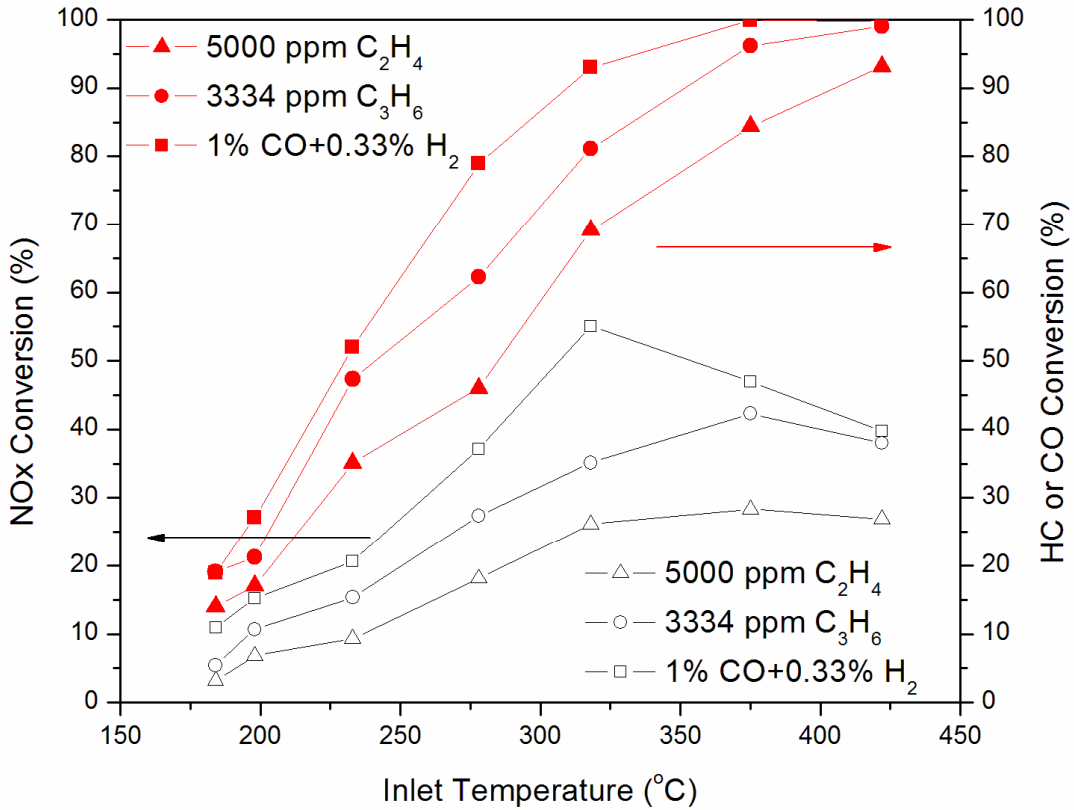
- FT-IR applied to study formation of potential NOx reductants over LNT (other than NH_3); only HCN is consistently observed, but in low concentrations
- Hence, formation of organo-nitrogen species over LNT does not appear to be important

➢ Slipped hydrocarbon is responsible for NOx reduction in SCR catalyst



Measured HCN downstream of LNT during lean/rich cycling (for 3 different reductant mixtures)

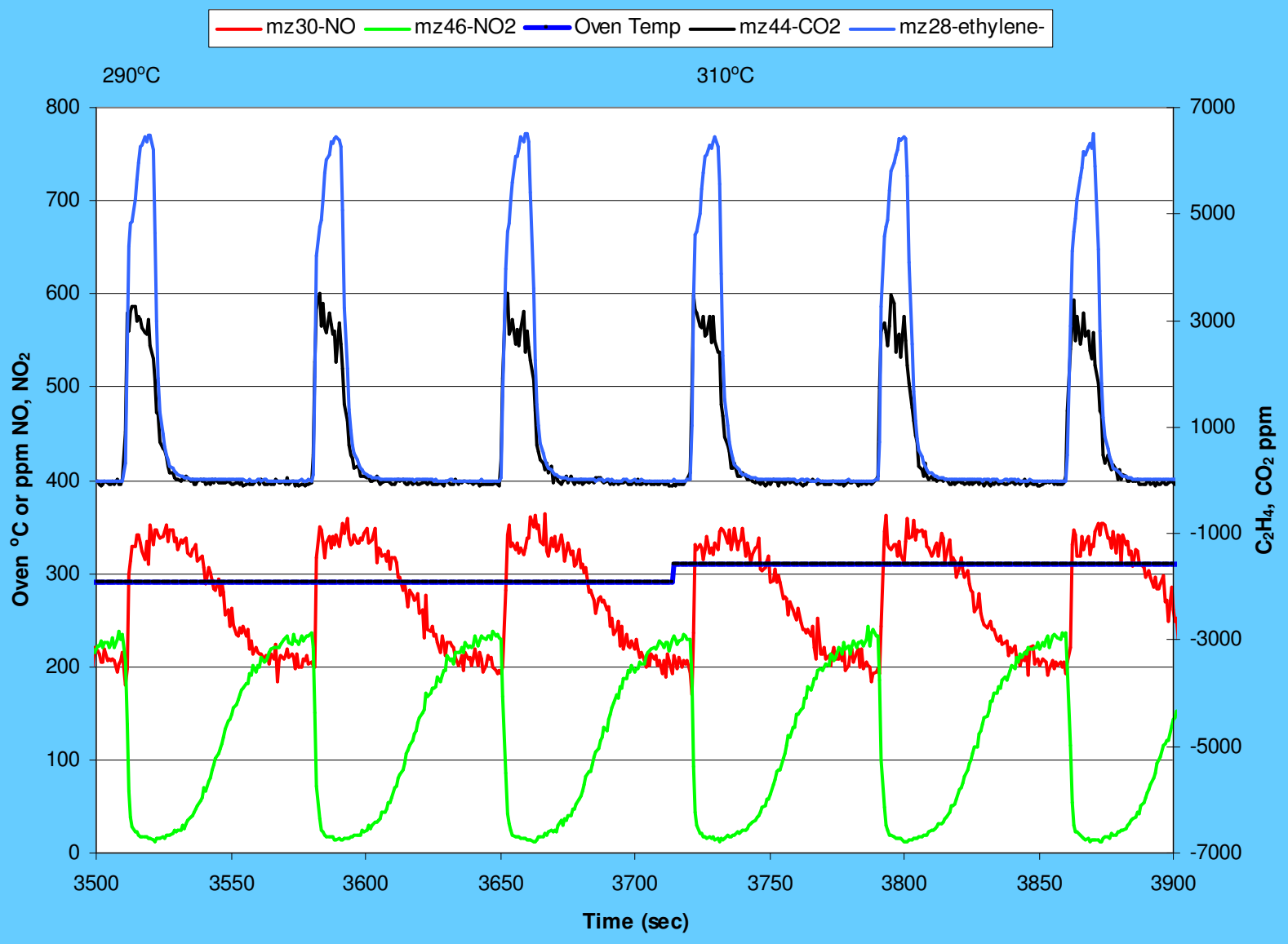
Steady State Reaction over SCR Catalyst

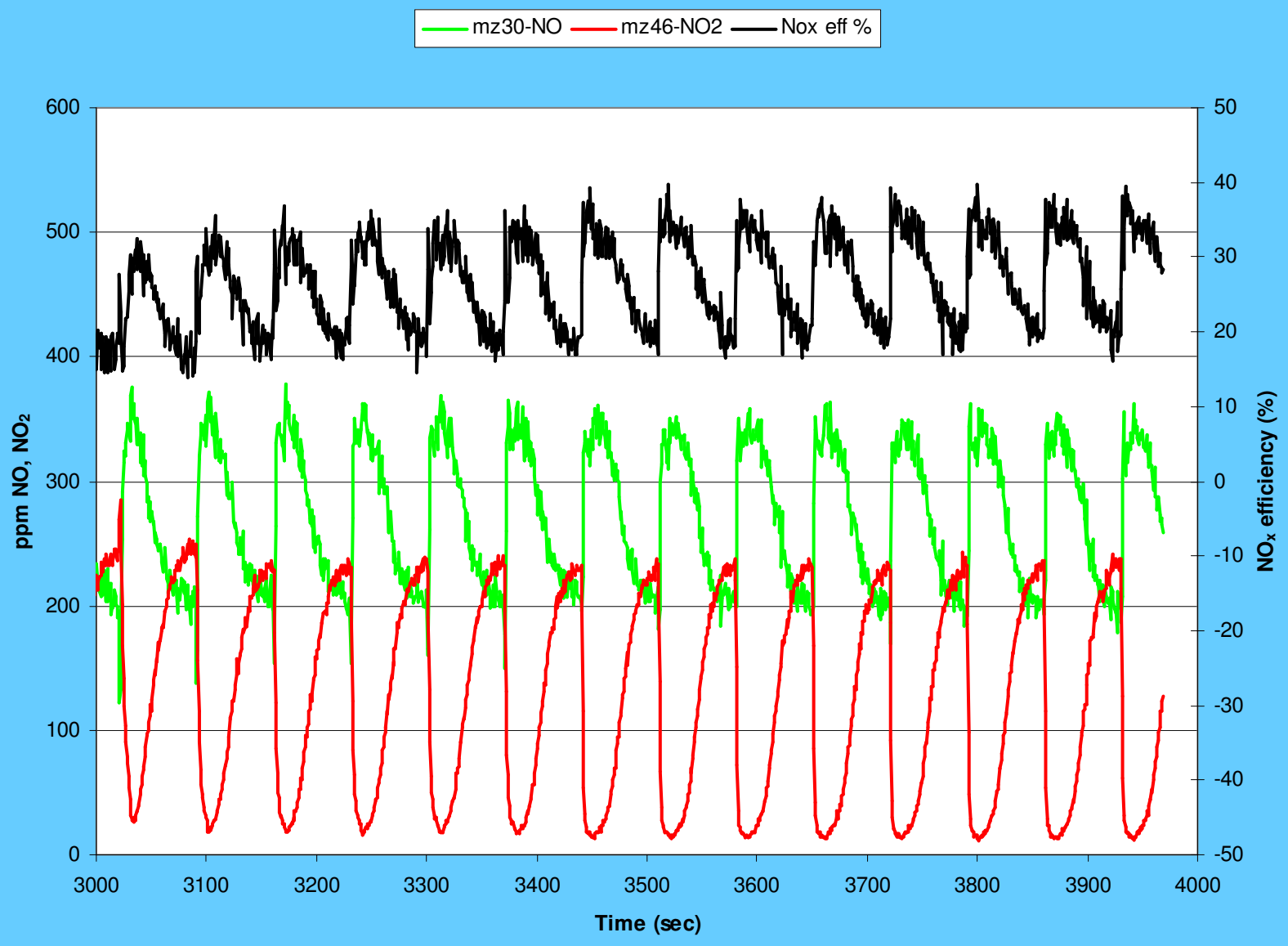


Feed gas:
300 ppm NO, 5%CO_2, 5%H_2O, 1%O_2 , N_2 balance, GHSV = 30,000 h^{-1}, reductant as shown

- SCR catalyst is active for NOx reduction using ethylene, propylene and CO/H_2 as reductants
- Can be significant for NOx conversion under conditions when there is little formation of NH_3

NO_x (300 +240 ppm NO_2+NO) conversion @ 290°C-310°C across SCR using C_2H_4 (10000 ppm)
60/10 sec L/R cycling 5% H_2O, 5% O_2, 0.5% O_2 rich




NOx (300 +240 ppm NO2+NO) conversion @ 270°C-310°C across SCR using C2H4 (10000 ppm)
60/10 sec L/R cycling 5% H2O, 5% O2, 0.5% O2 rich
mz30-NO
mz46-NO2
Nox eff %
ppm NO, NO2
NOx efficiency (%)
Time (sec)
600
500
400
300
200
100
0
50
40
30
20
10
0
-10
-20
-30
-40
-50
3000
3100
3200
3300
3400
3500
3600
3700
3800
3900
4000

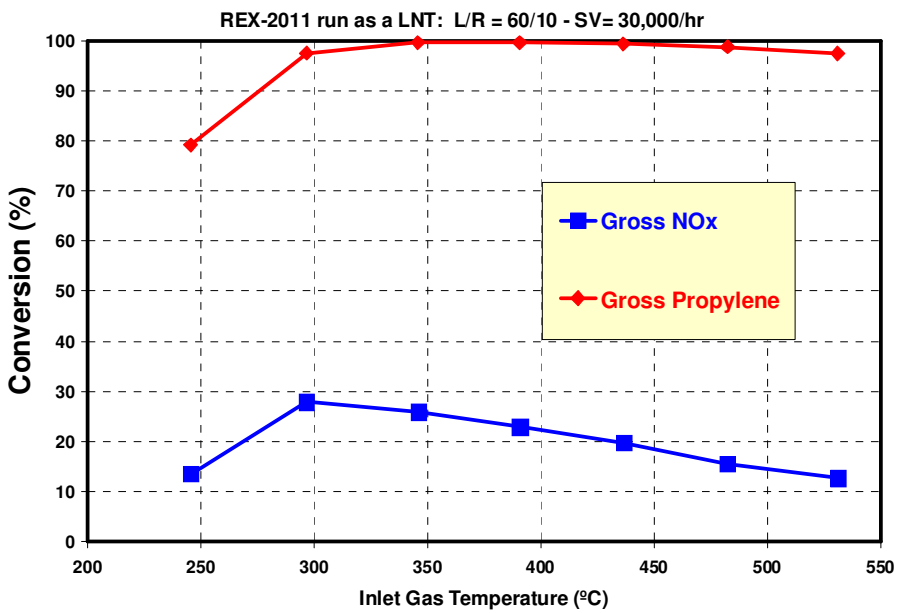
Overall Average Conversion of Lean and Rich Duration

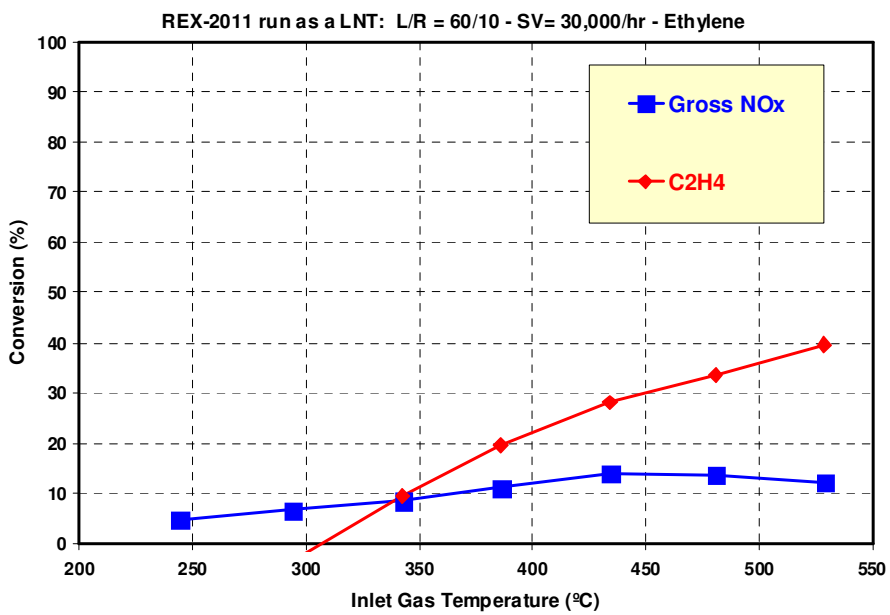
Propylene

CASE 1 PROPYLENE with NO		
	Lean Mode	Rich Mode
Time (s)	60	10
Lambda	~ 2.00	0.99
NO	200ppm	200ppm
NO_2	0	0
O_2	10%	0%
C_3H_6	0ppmC1	5000ppmC1
C_2H_4	0	0
CO_2	5%	5%
H_2O	5%	5%
N_2	balance	balance

Ethylene

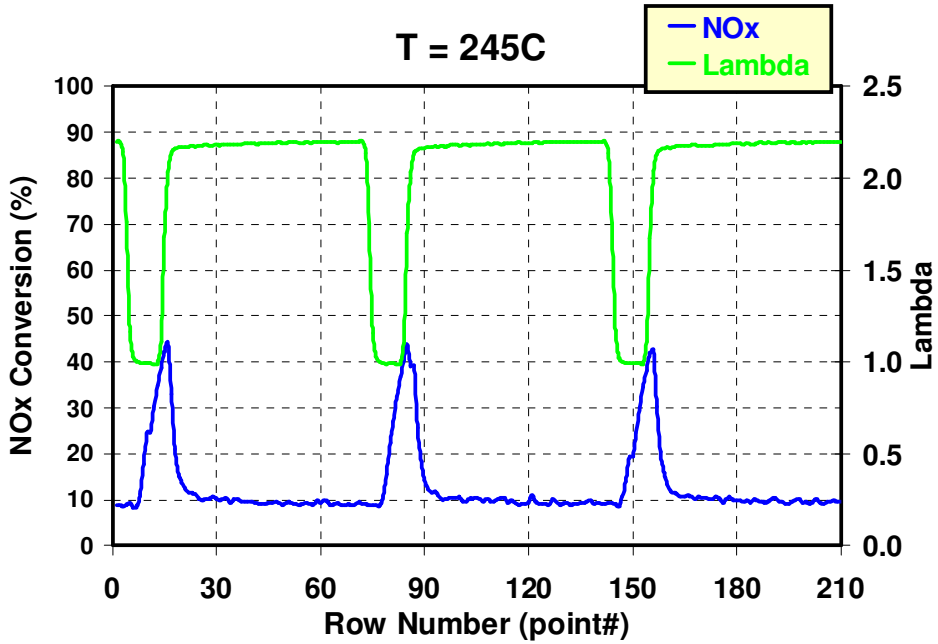
CASE 2 ETHYLENE with NO		
	Lean Mode	Rich Mode
Time (s)	60	10
Lambda	~ 2.00	0.99
NO	200ppm	200ppm
NO_2	0	0
O_2	10%	0%
C_3H_6	0	0
C_2H_4	0ppmC1	5000ppmC1
CO_2	5%	5%
H_2O	5%	5%
N_2	balance	balance

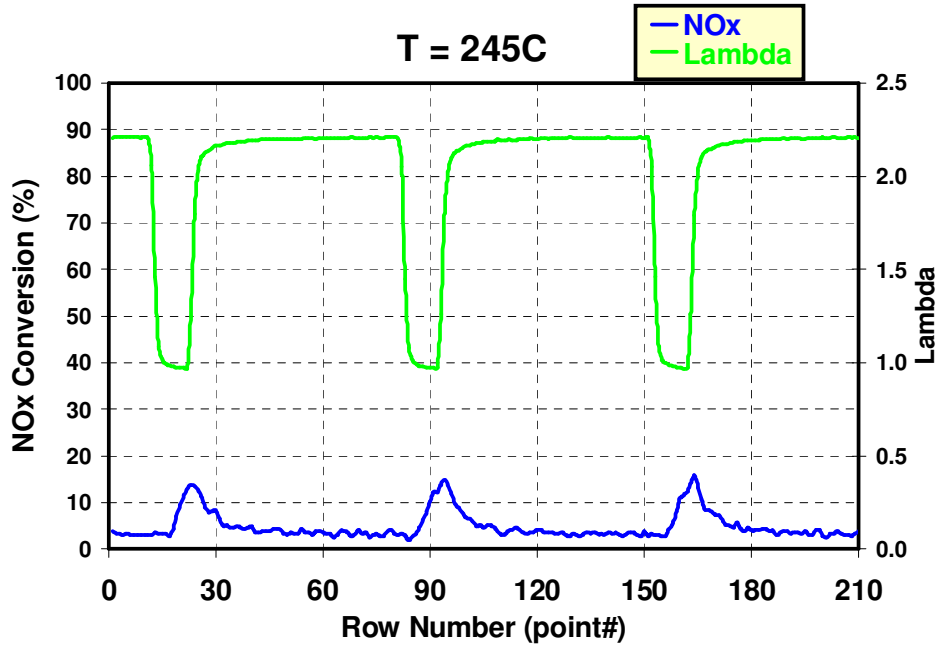


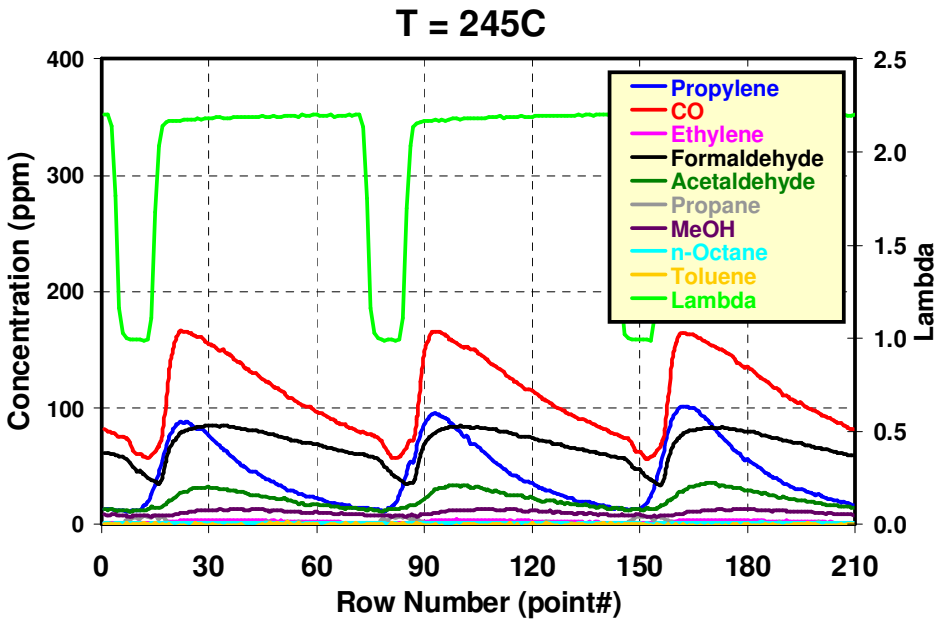


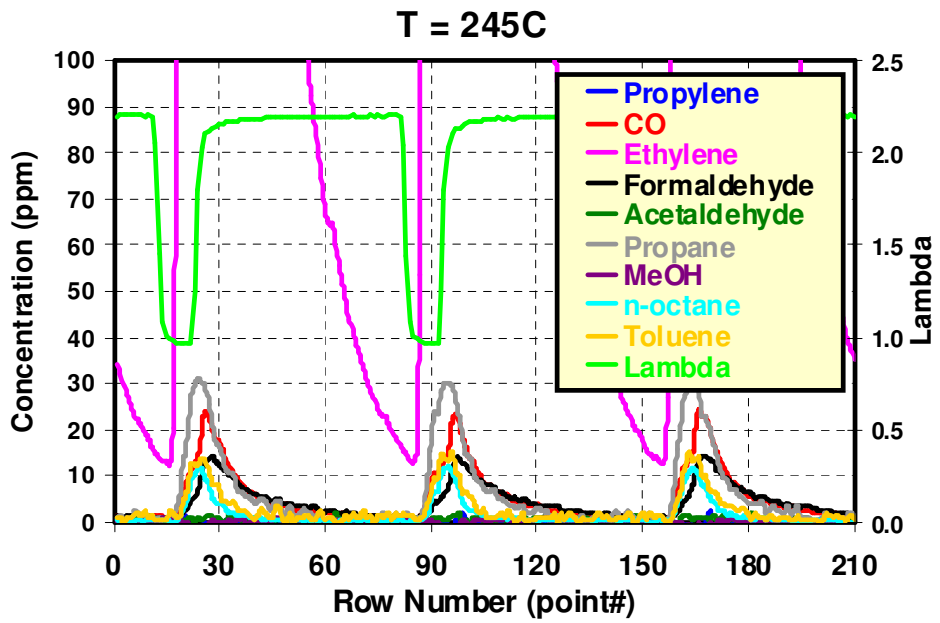
Propylene

Ethylene



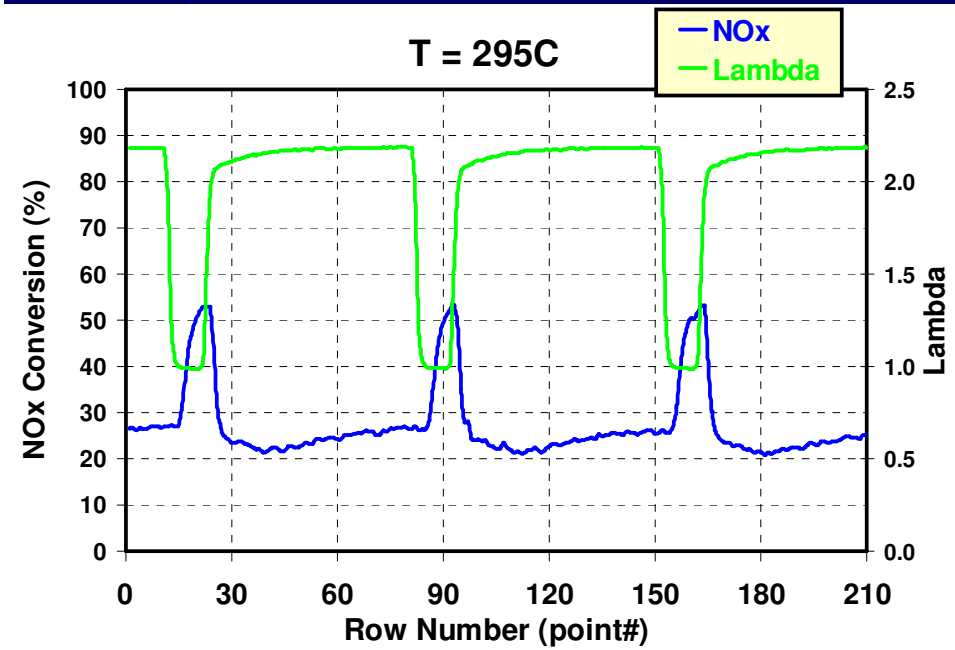


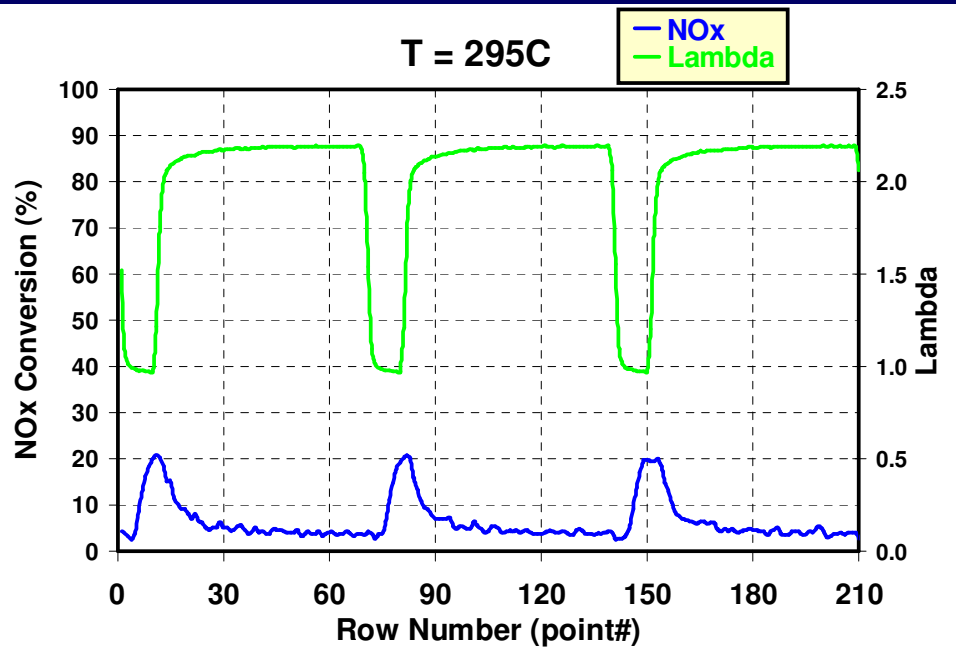


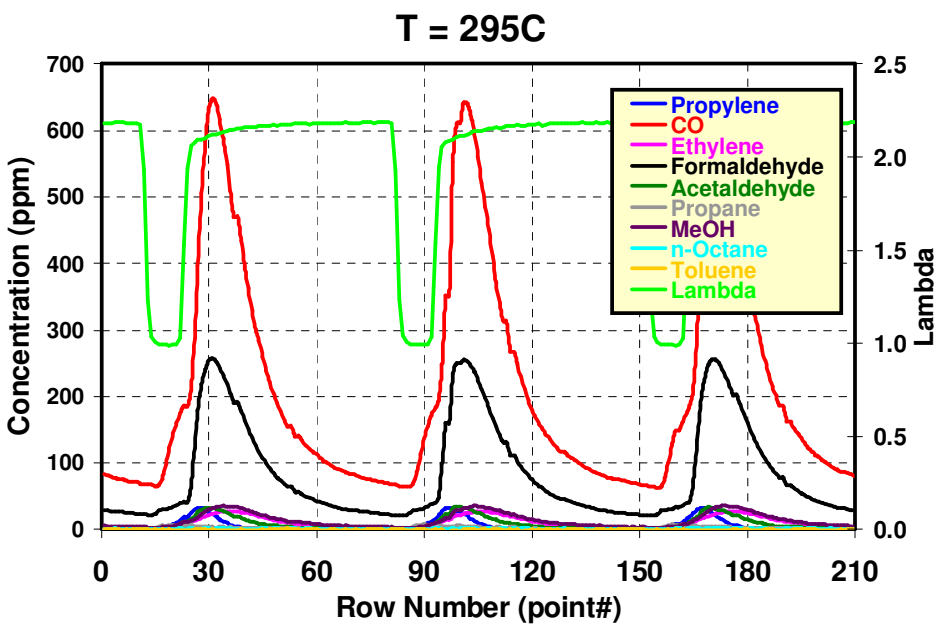


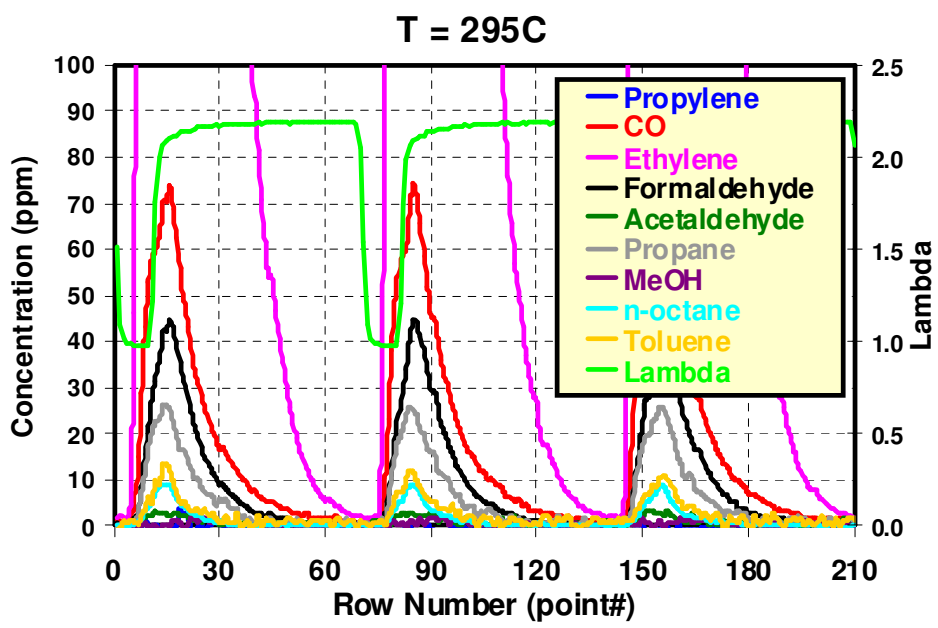
Propylene

Ethylene



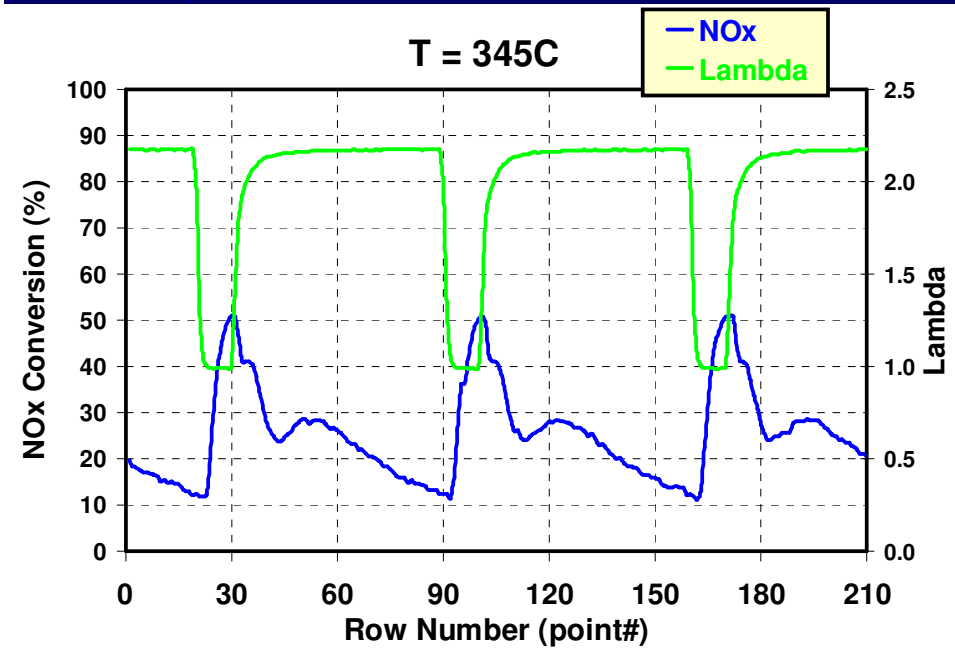


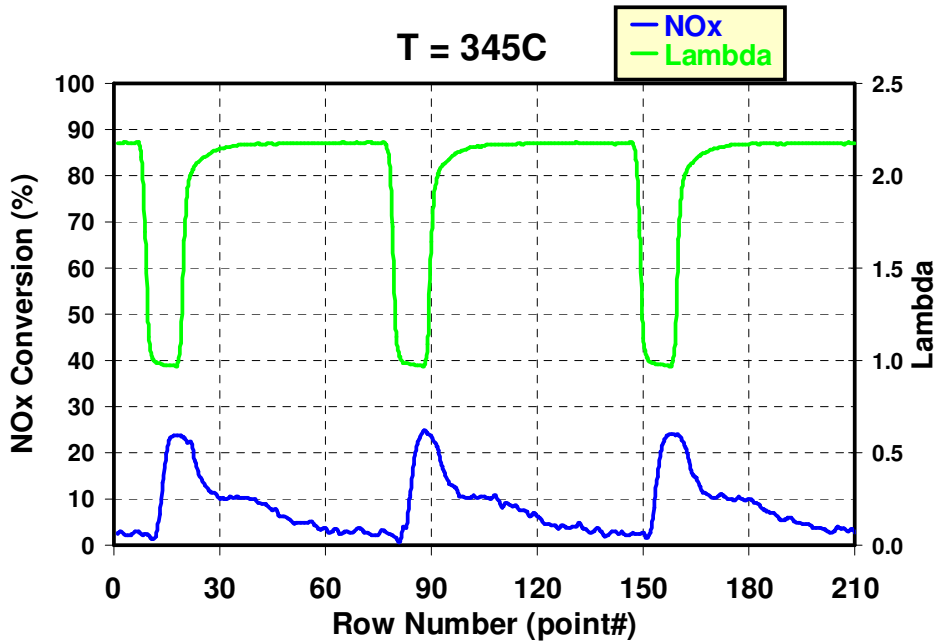


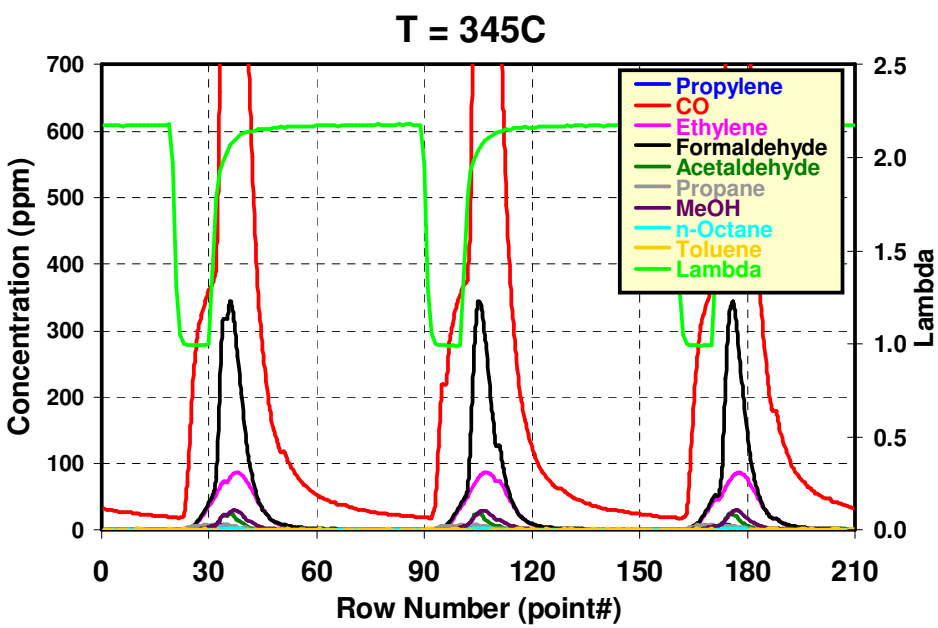


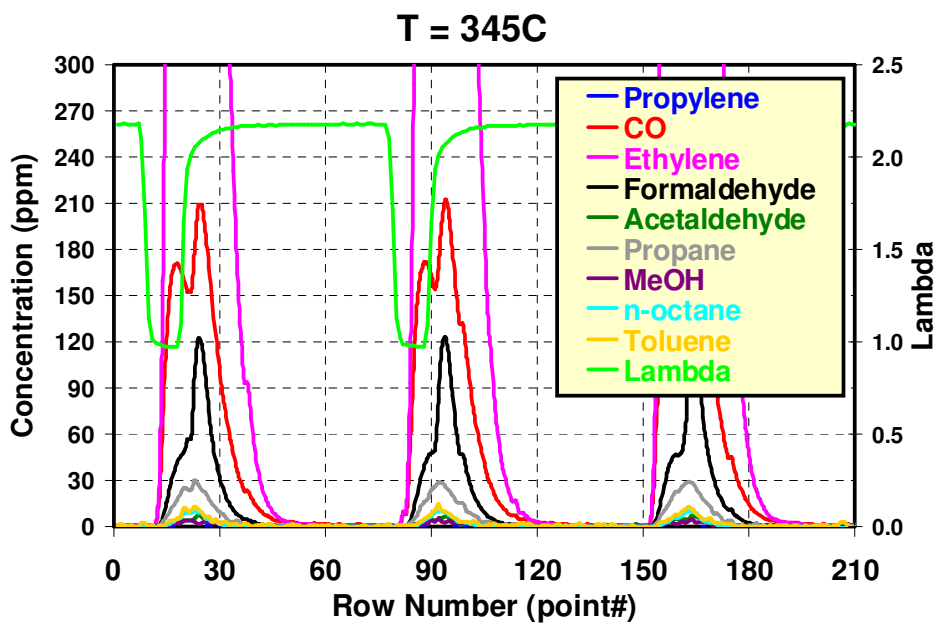
Propylene

Ethylene



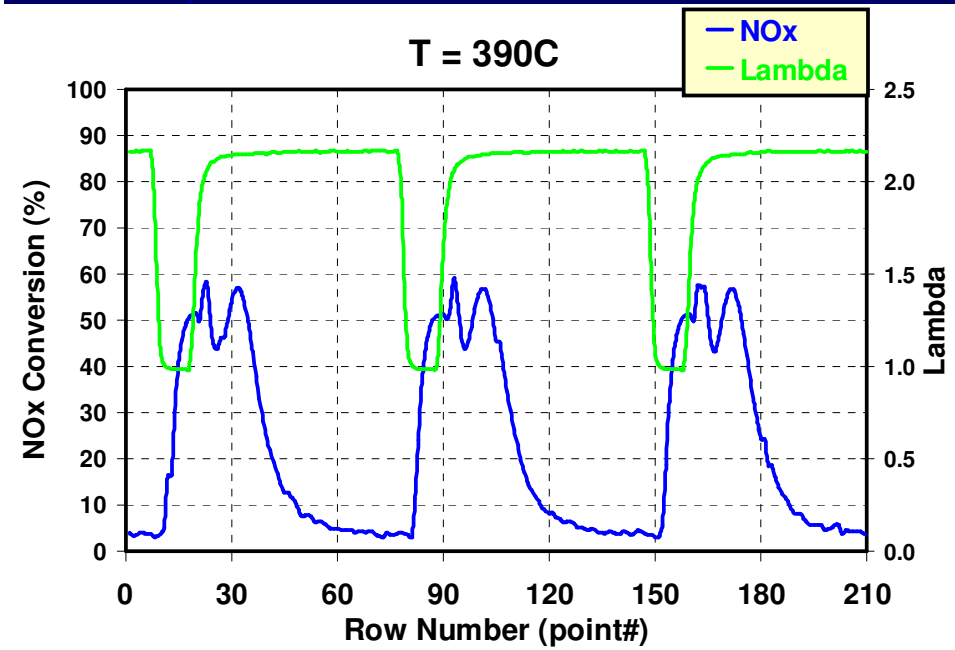


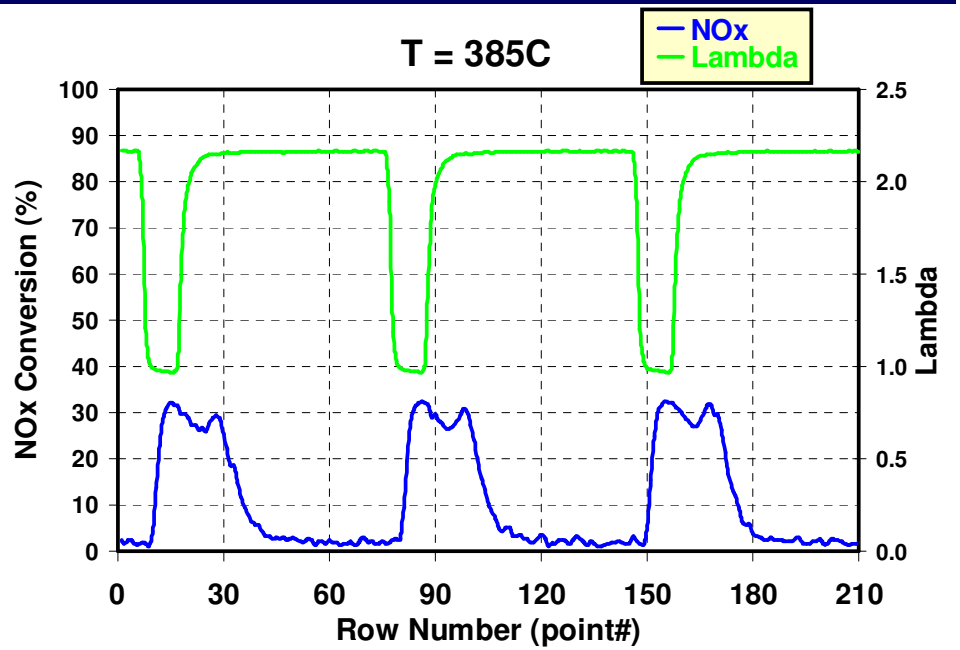


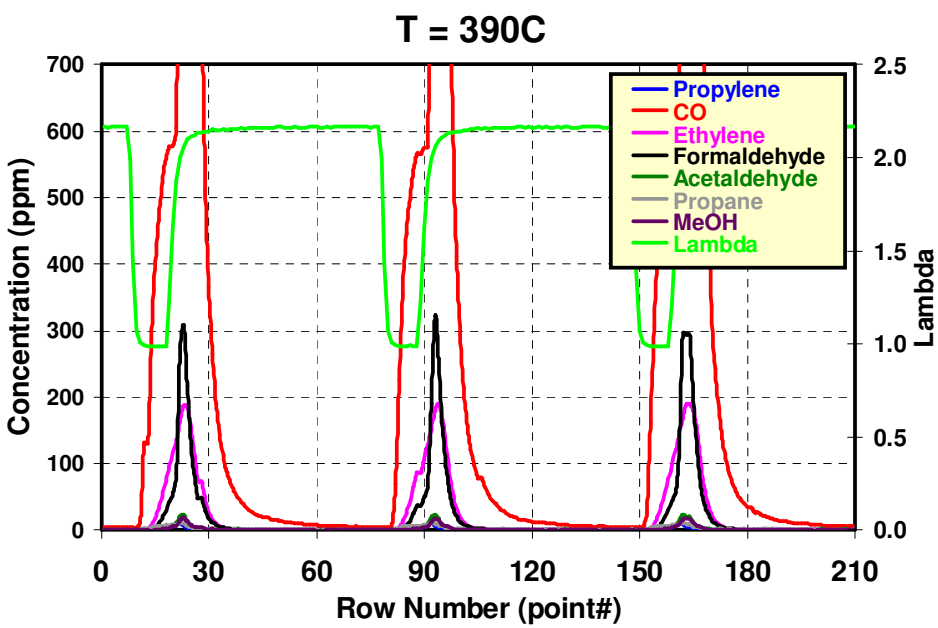


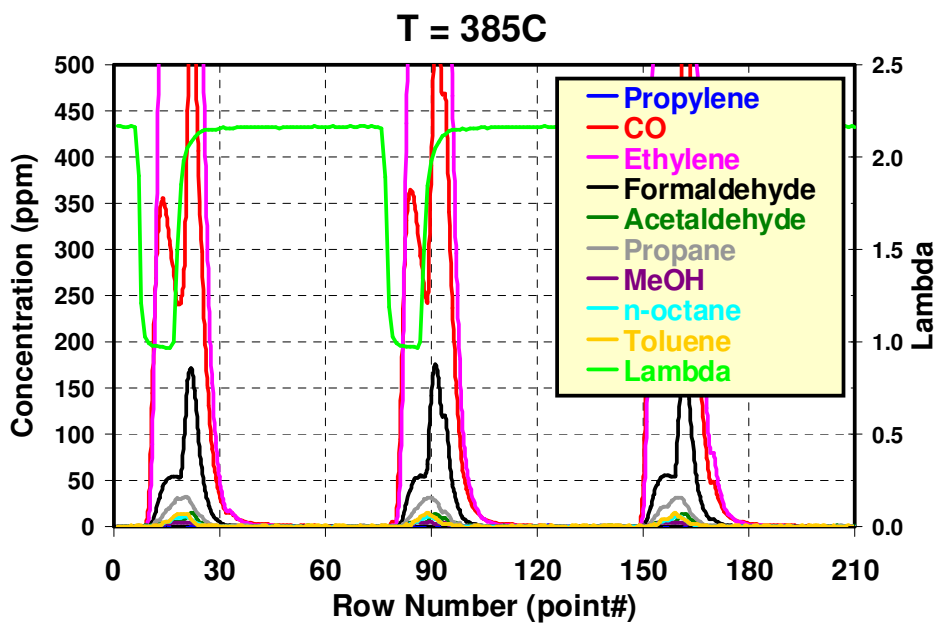
Propylene

Ethylene

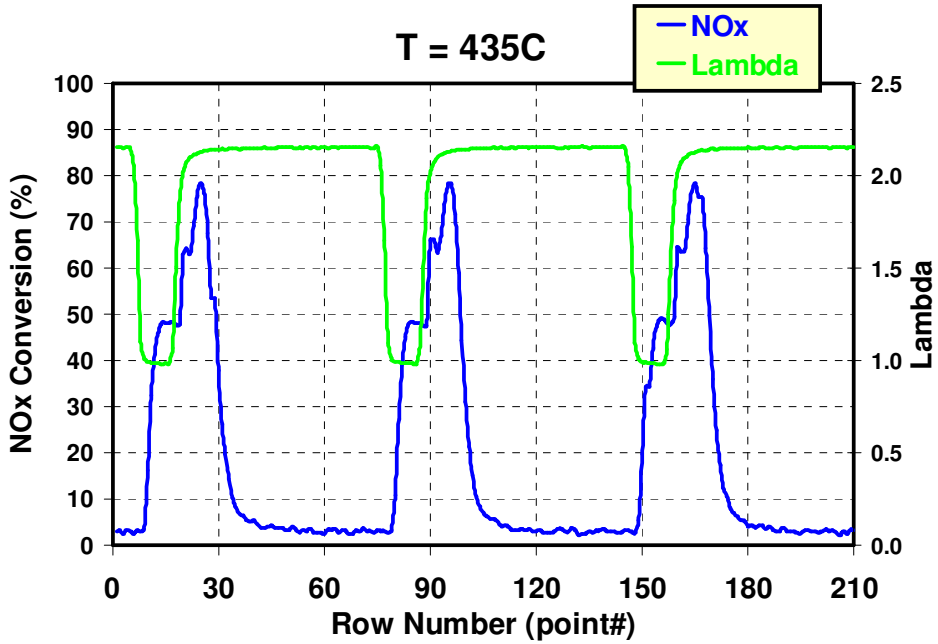


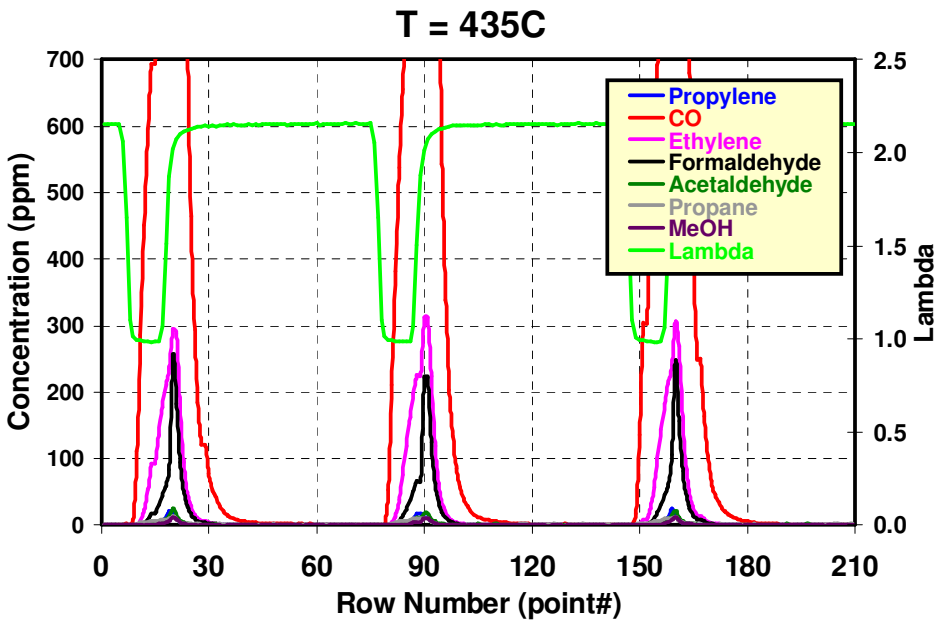




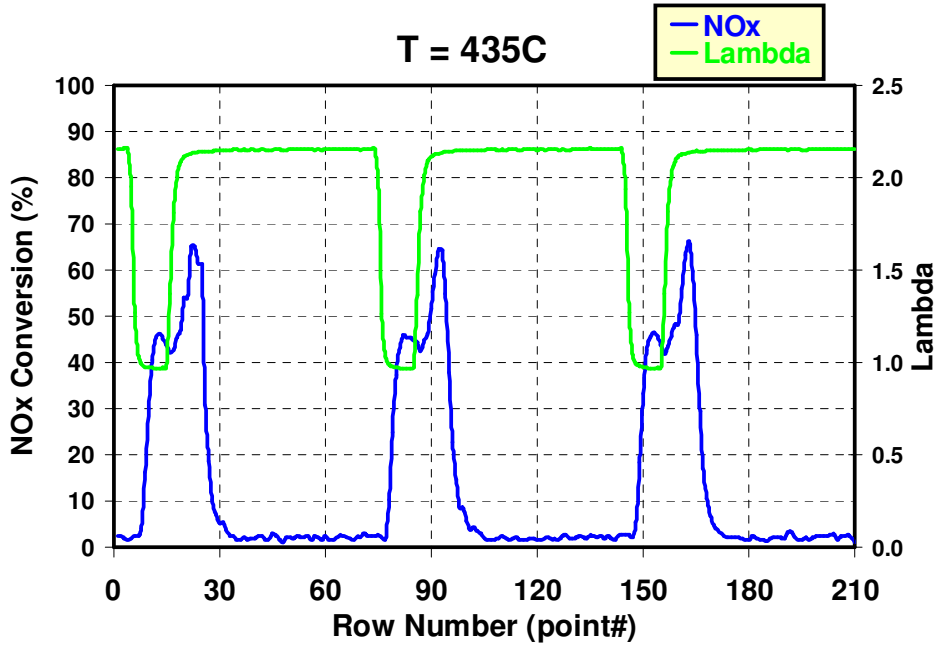


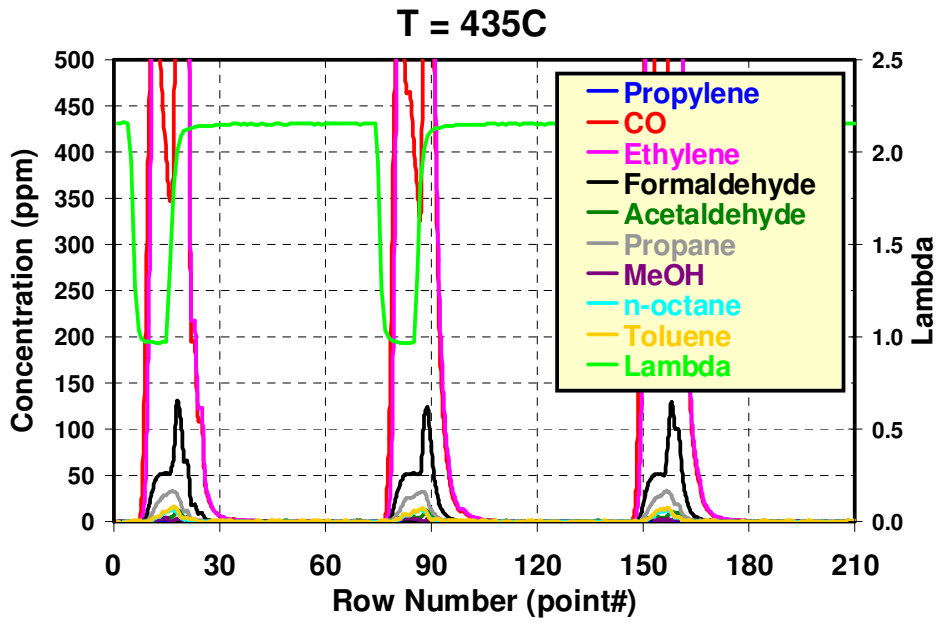
Propylene





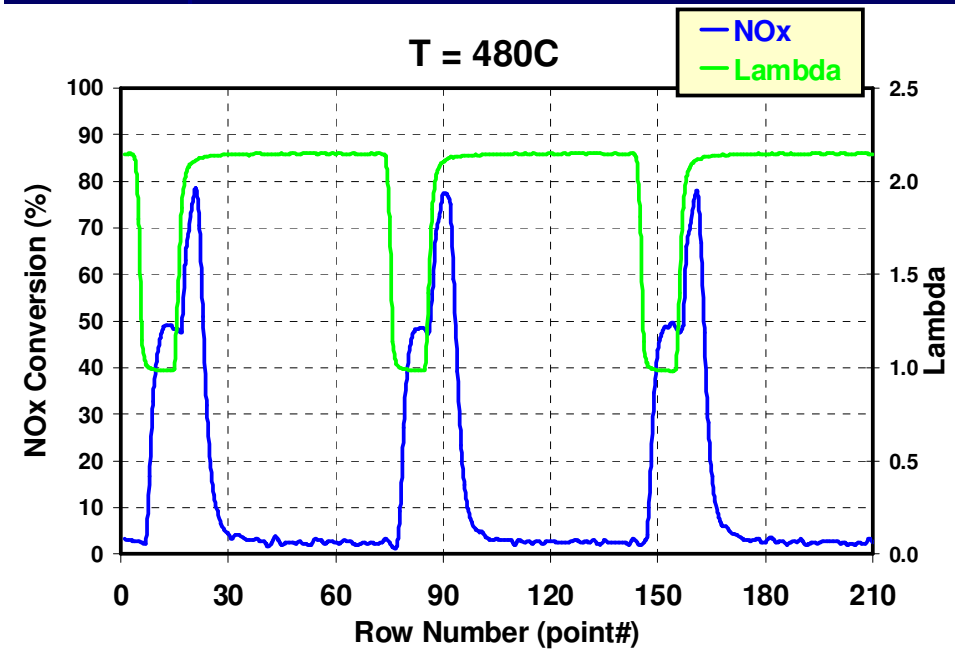
Ethylene

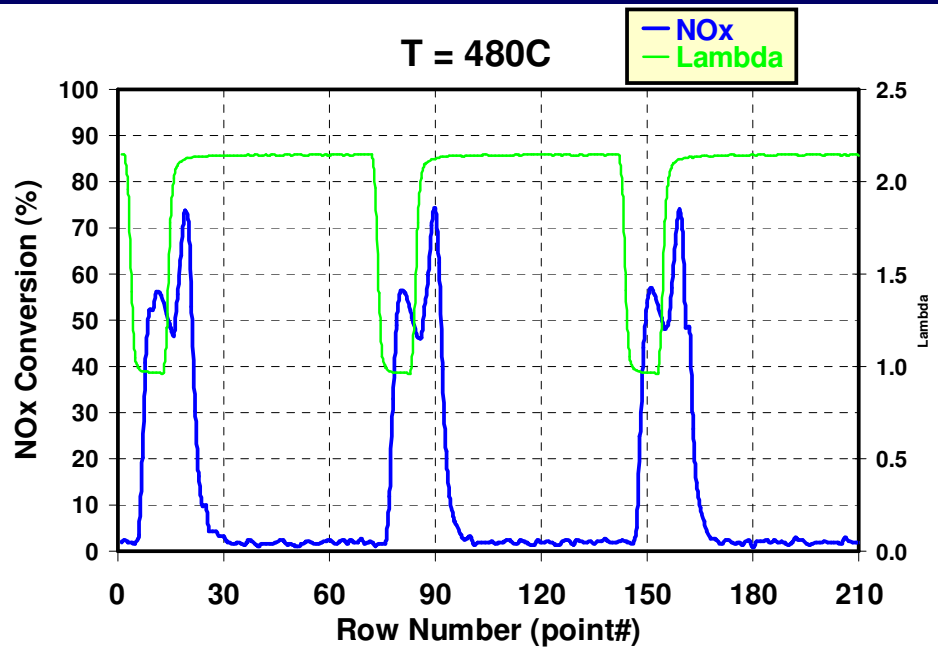


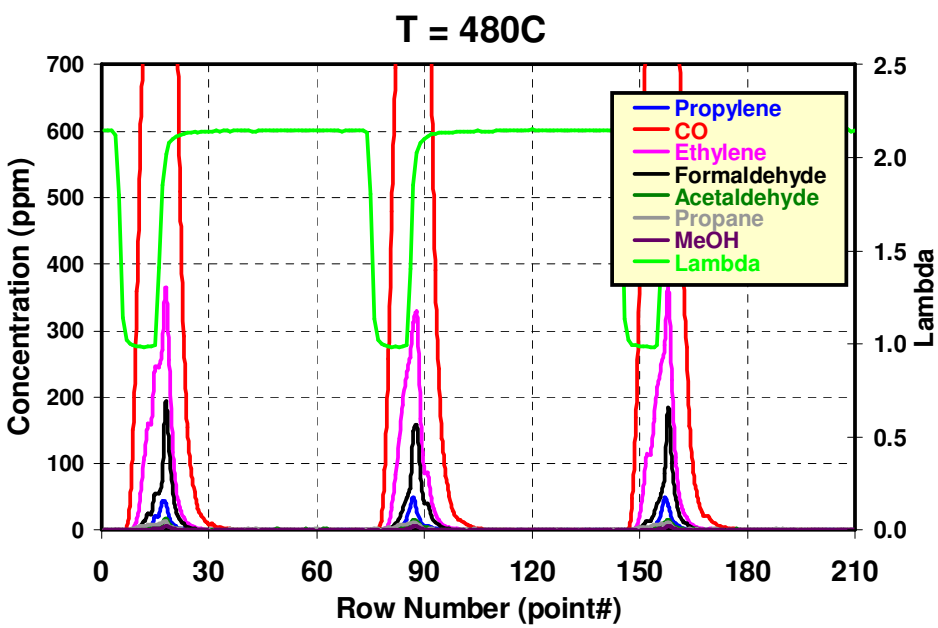


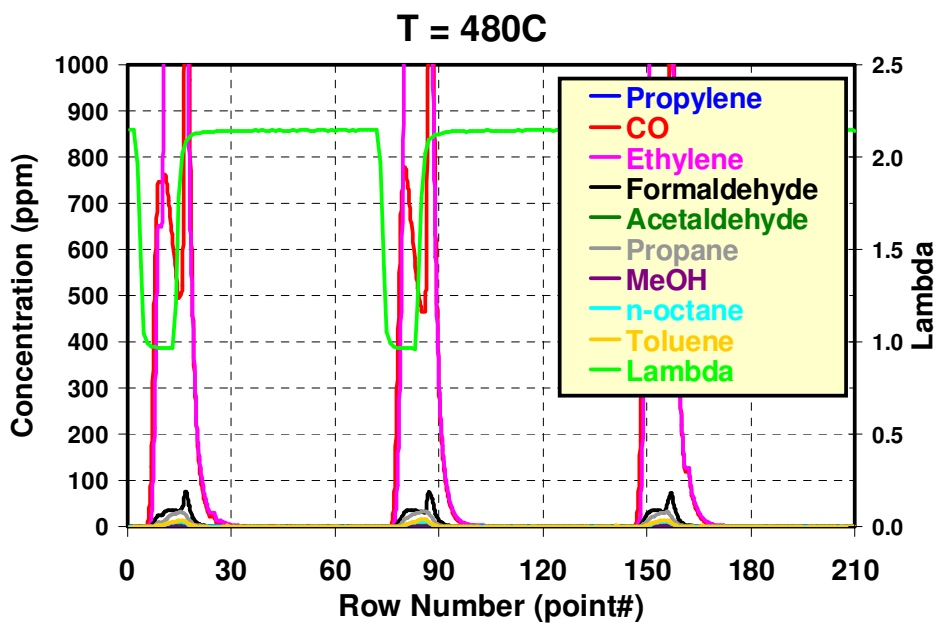
Propylene

Ethylene



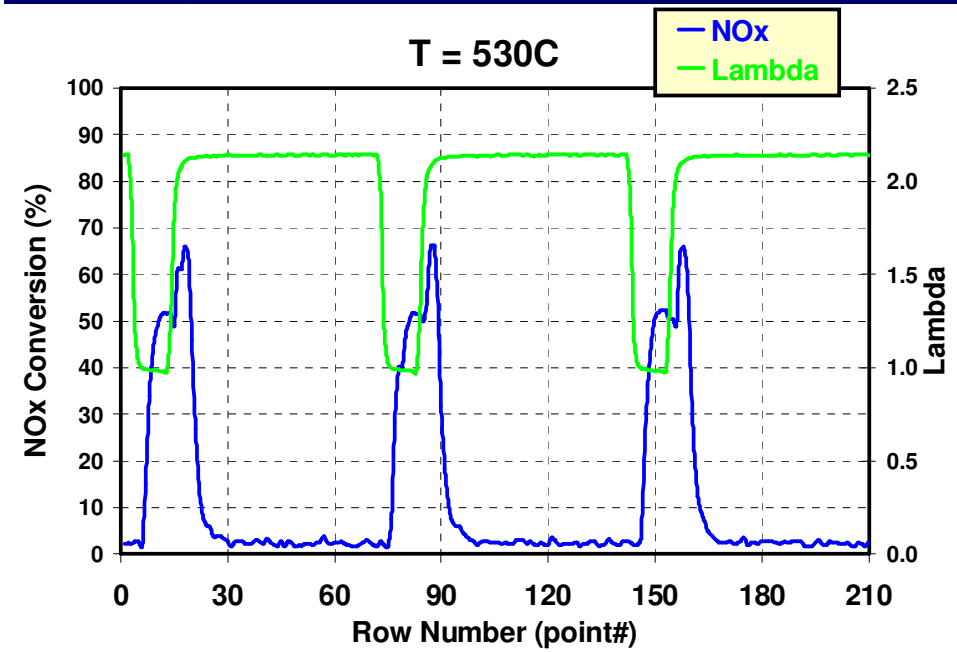


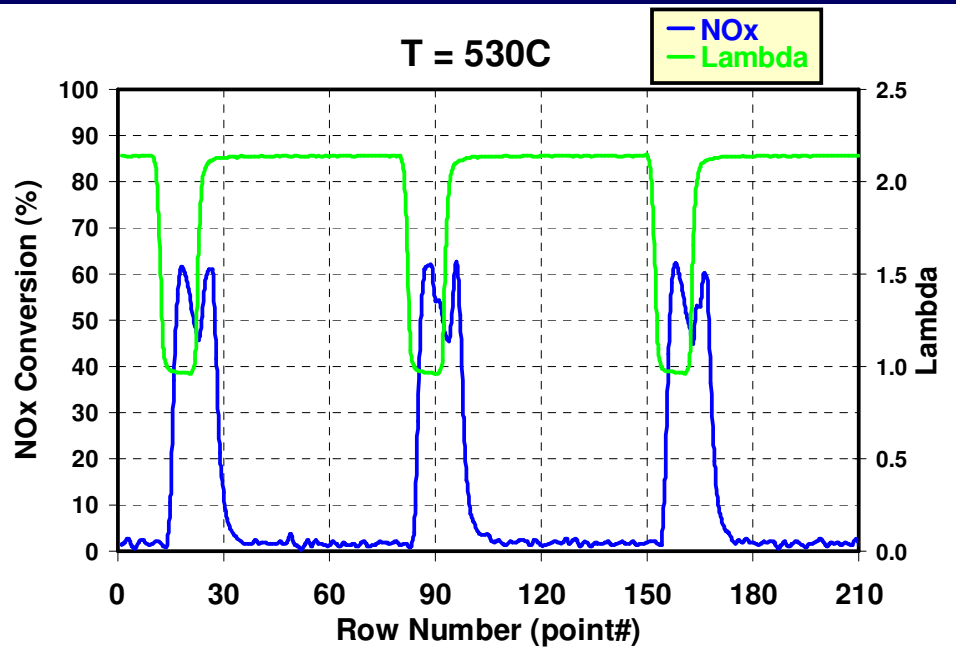


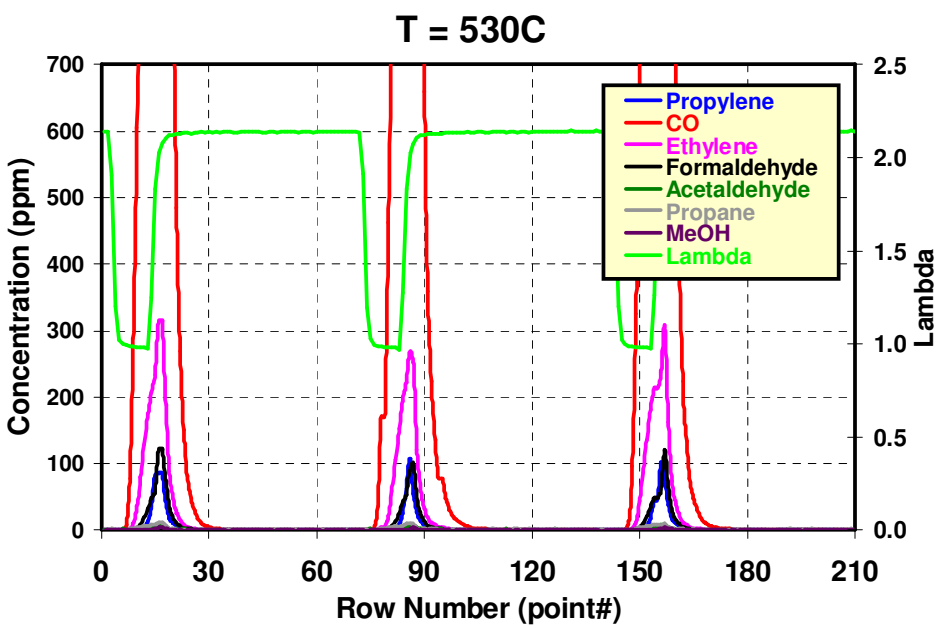


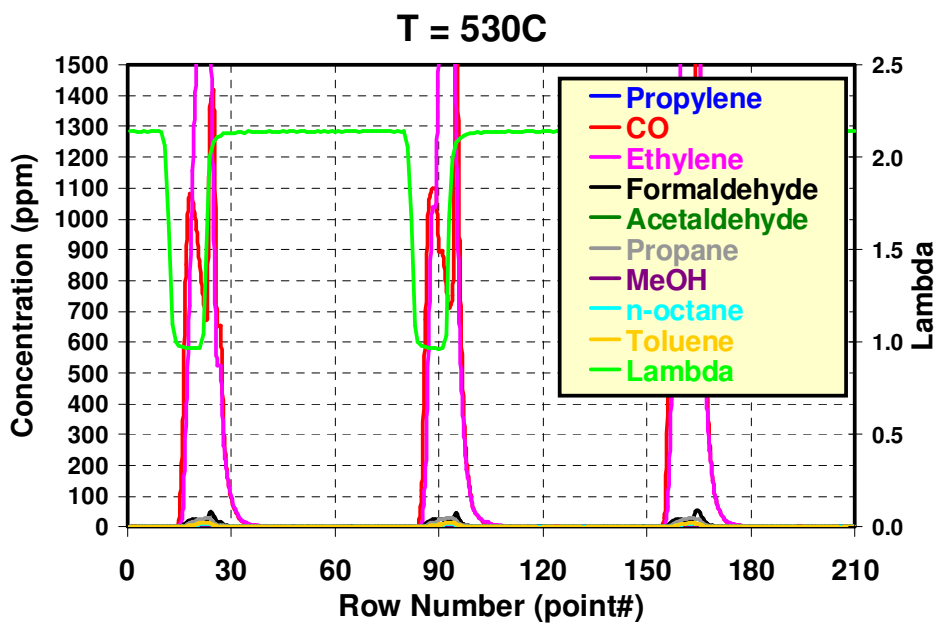
Propylene

Ethylene









Conclusions

- Reactor studies have shown that a hydrocarbon-based NOx reduction mechanism (ethylene and propylene studied) can operate in the SCR catalyst in parallel with the NH_3-SCR mechanism. A significant amount of HC can be stored even at high temps.
- The hydrocarbon pathway is characterized by high NO_2 conversion.
- HCs other than ethylene and propylene also interact, but Pi bond containing molecules are favored.
- A reductant starved condition favors the interaction (non-urea system).
- NO_2 is reduced (in part) to NO at higher inlet levels of NO_2+NO.
- HCs are oxidized to form CO perhaps more than CO_2 across the CuSCR.
- The LNT+SCR system adapts (as the LNT ages) to maintain high HC and NOx conversion efficiency (at the expense of CO?).