Ford Motor Company

Temperature Transient Effects in Plasma-Catalysis
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Background

- Ford is working on plasma-catalysis as part of the USCAR LEP CRADA with PNNL
- Developed low temperature NOx catalysts
- Recent cooperation with Caterpillar to jointly evaluate “our” catalyst and “theirs”
- Ford data using a temperature transient test method

Experimental

- Mass flow controllers blend simulated exhaust
- Flow system
  - Dielectric barrier discharge device in first oven
  - Catalyst(s) in second oven
  - Permits feedgas, midbed, downstream samples
  - Sample diluted 5:1 with N_2; water is not removed
- Analysis by high resolution FTIR plus emission analyzer bench (CLA, FID, O_2, CO, CO_2)

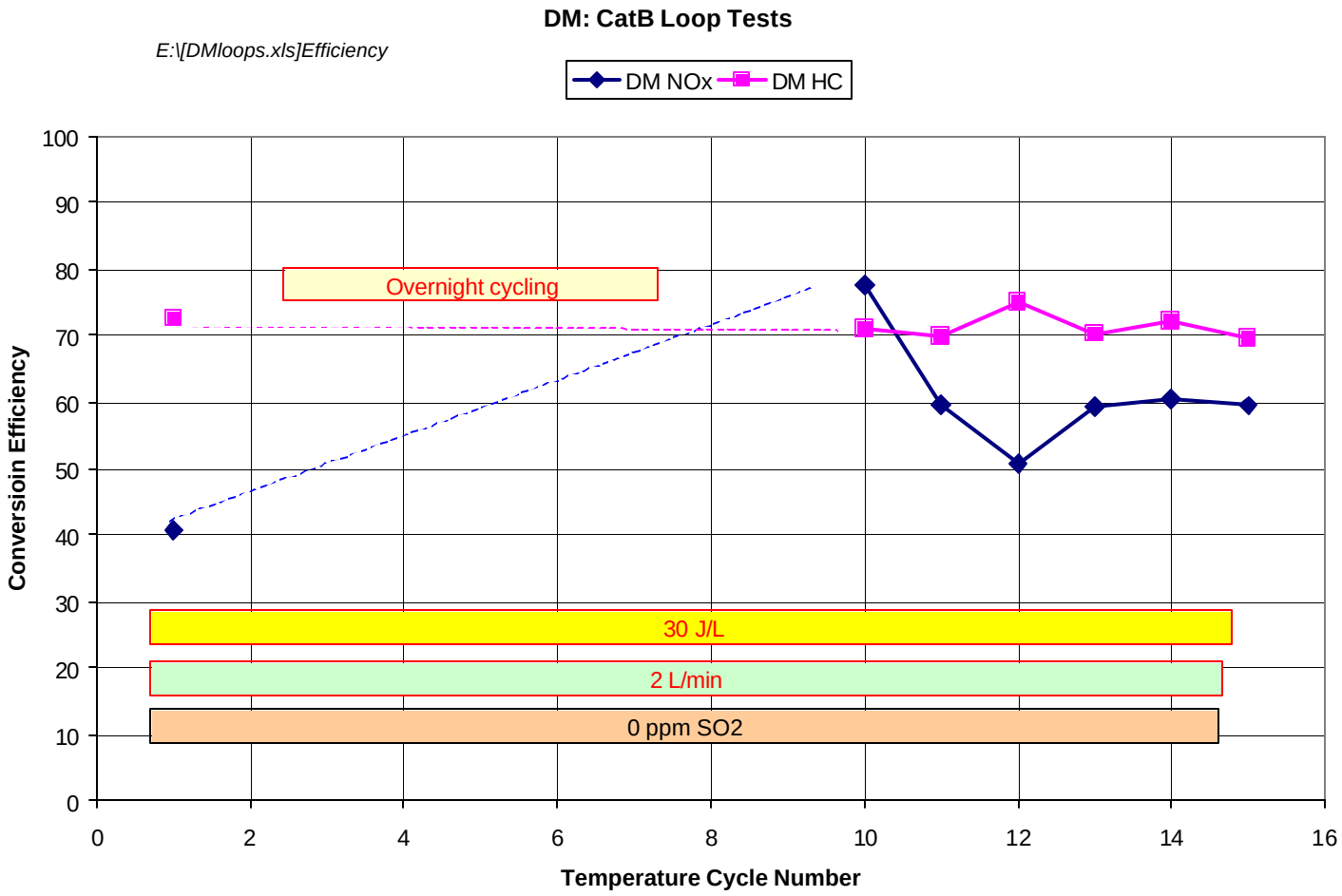
Thermal Cycle Testing

- Temperature ramps: 10 °C/min between about 100°C to 500°C, with 12 minute hold at each end; each cycle is 104 minutes. Both ovens ramp.
- Typically 15-20 hours cycling
- NOT known to correlate with real world aging!
- Gas Blend (unless noted):
  - 260 ppm NO — 1000 ppm CO
  - 0 or 50 ppm SO_2 — 333 ppm H_2
  - 7% CO_2 — 1500 ppmC_1 C_3H_6 7.6 C_1:NOx
  - 7% O_2 — 500 ppmC_1 C_3H_8
  - 1% Ar — 2.8% H_2O

Catalysts Tested

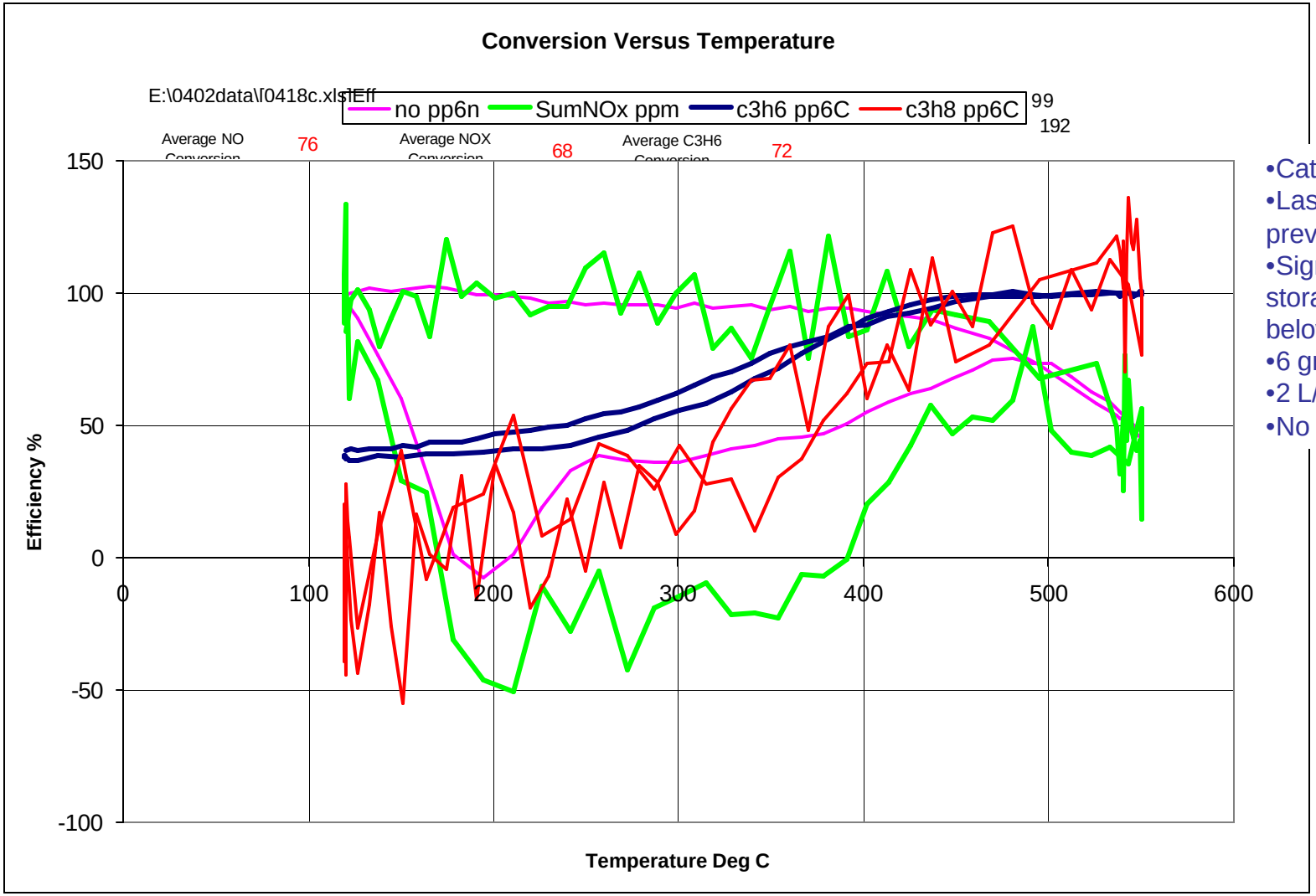
- BaY with added impregnation (BaY+)
  - Prepared by PNNL under the LEP CRADA
- Caterpillar catalyst “B”
  - Provided by Paul Park
  - Alumina based
- Combinations:
  - BaY-alumina-Pt
  - Impregnated Y - CatB (BaY+/B)

Catalyst B Thermal Loops

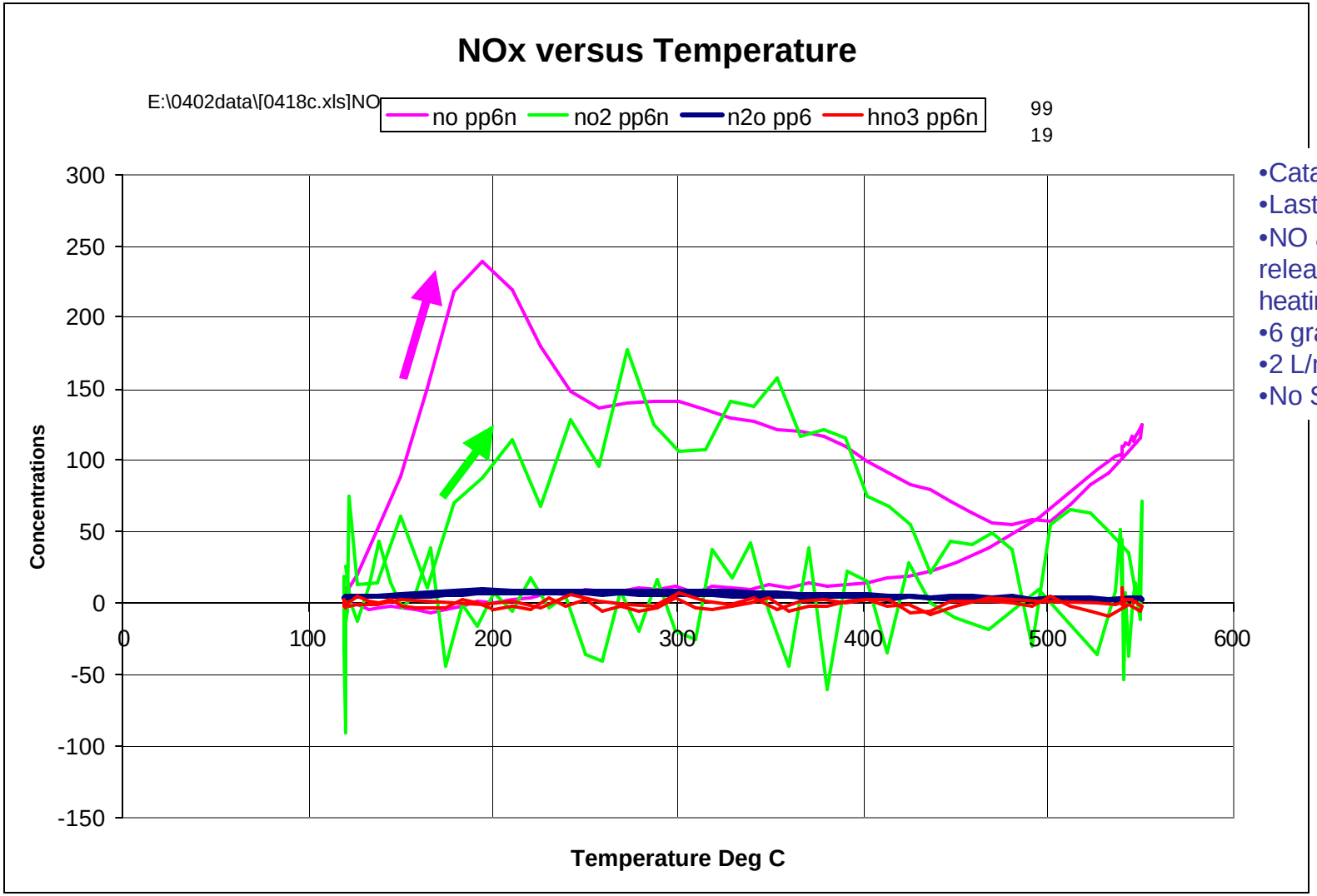


- Alumina based "HD" catalyst
- Data integrated over temperature loops
- Data only recorded during daytime
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2

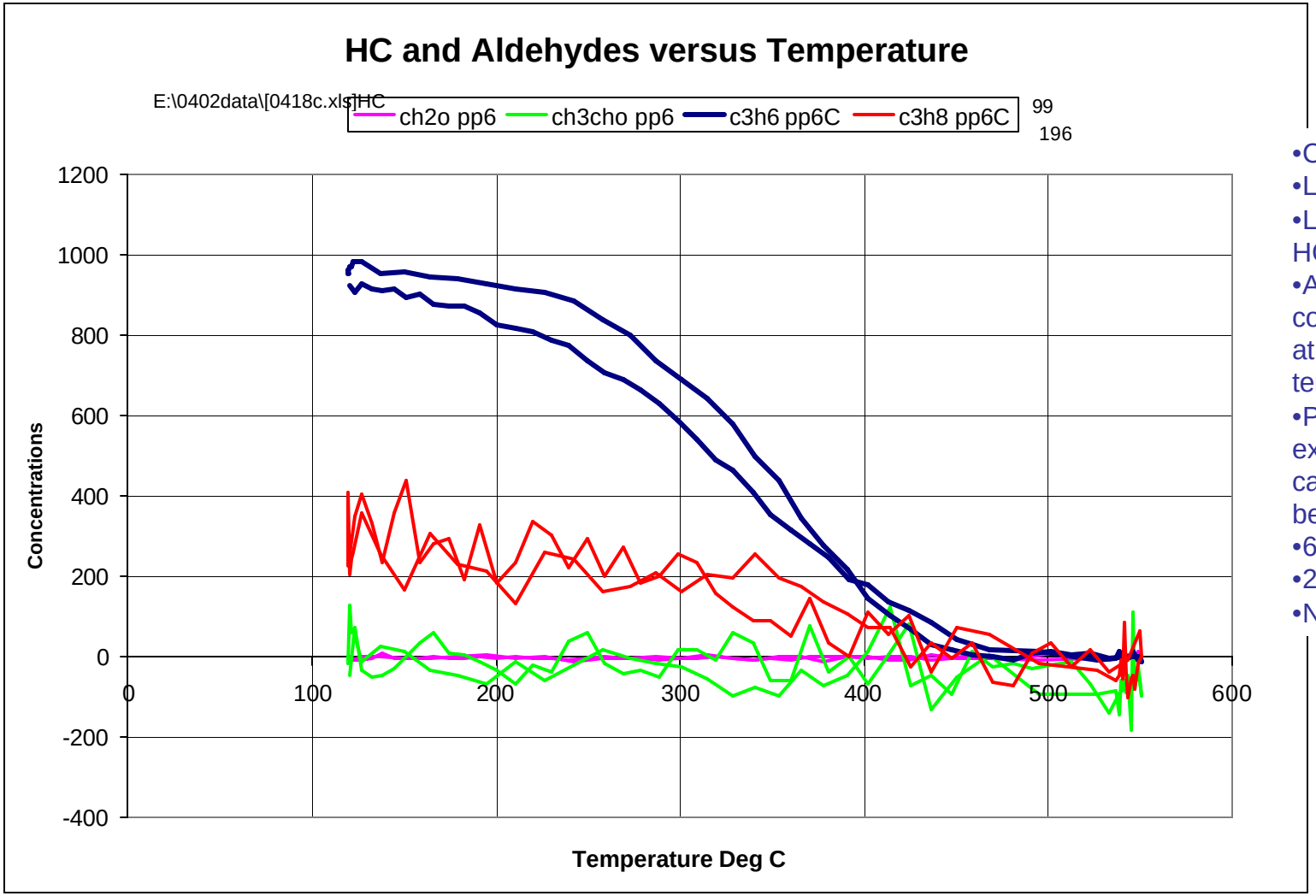
Catalyst B



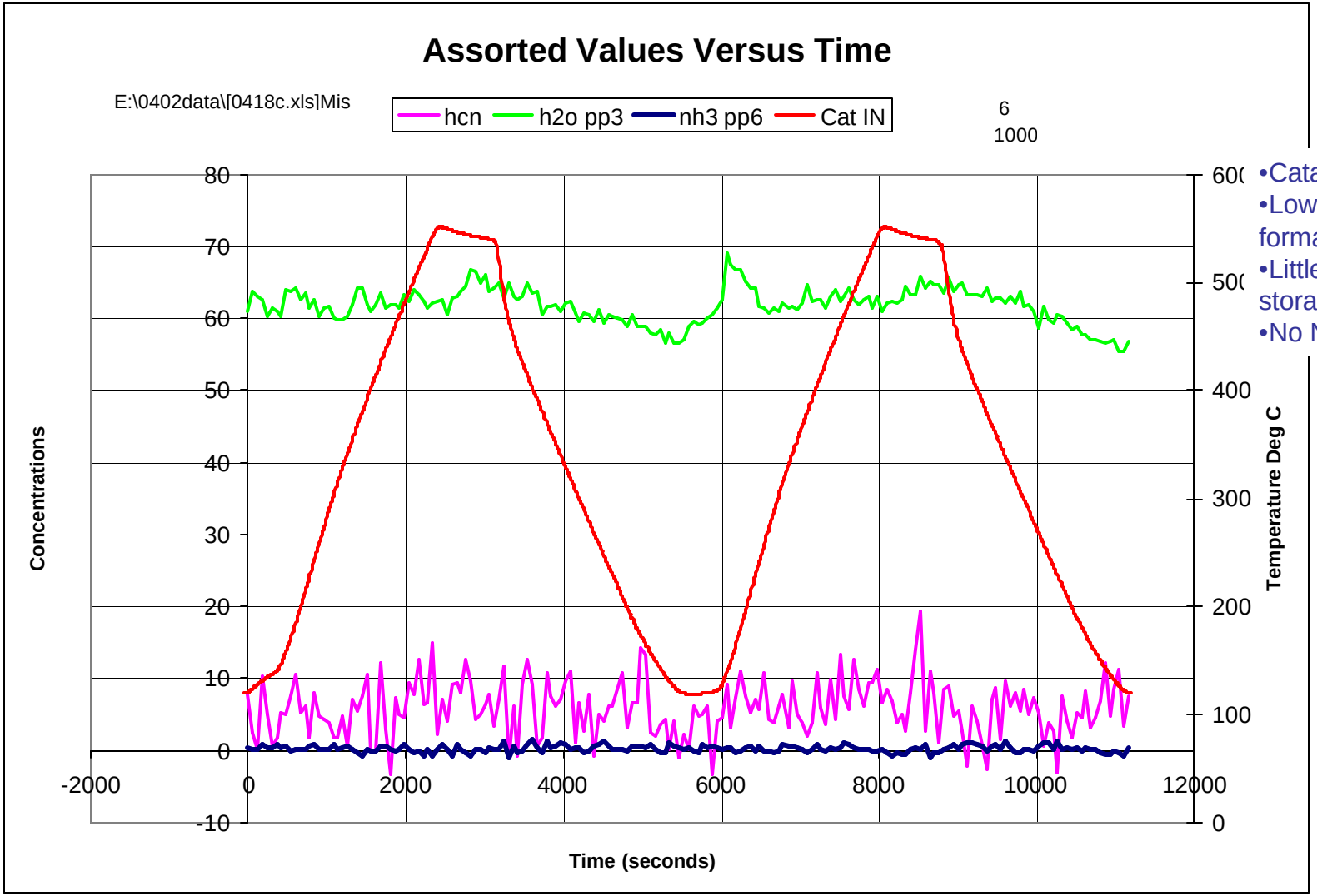
- Catalyst B
- Last loop of previous plot
- Significant NOx storage/release below 350°C
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2



- Catalyst B
- Last loop
- NO and NO_2 released during heating
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2

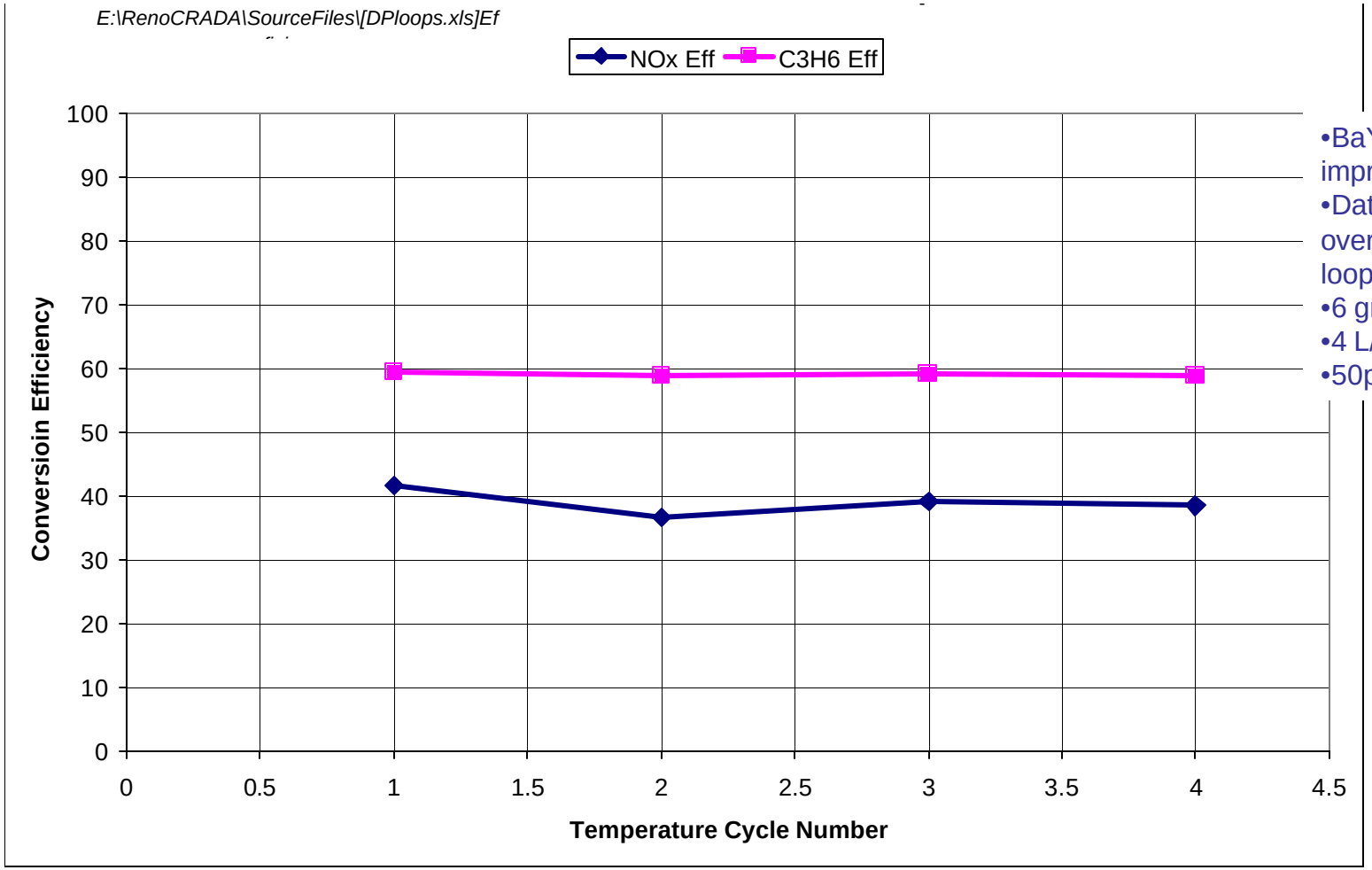


- Catalyst B
- Last loop
- Little storage of HCs
- Aldehydes consumed/stored at all temperatures
- Probably explains why "LD" catalyst needs to be in front
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2

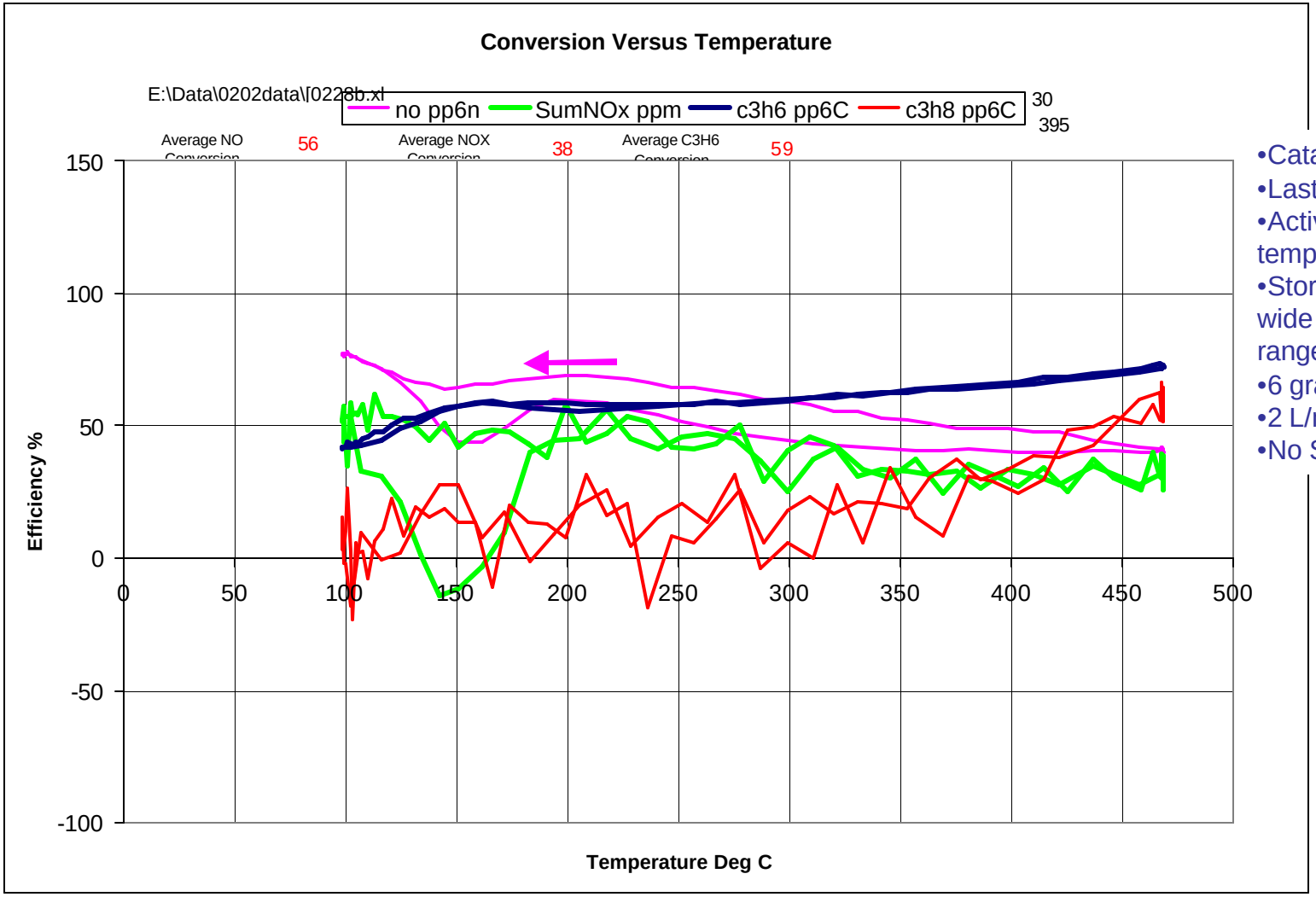


- Catalyst B
- Low HCN formation
- Little water storage
- No NH_3

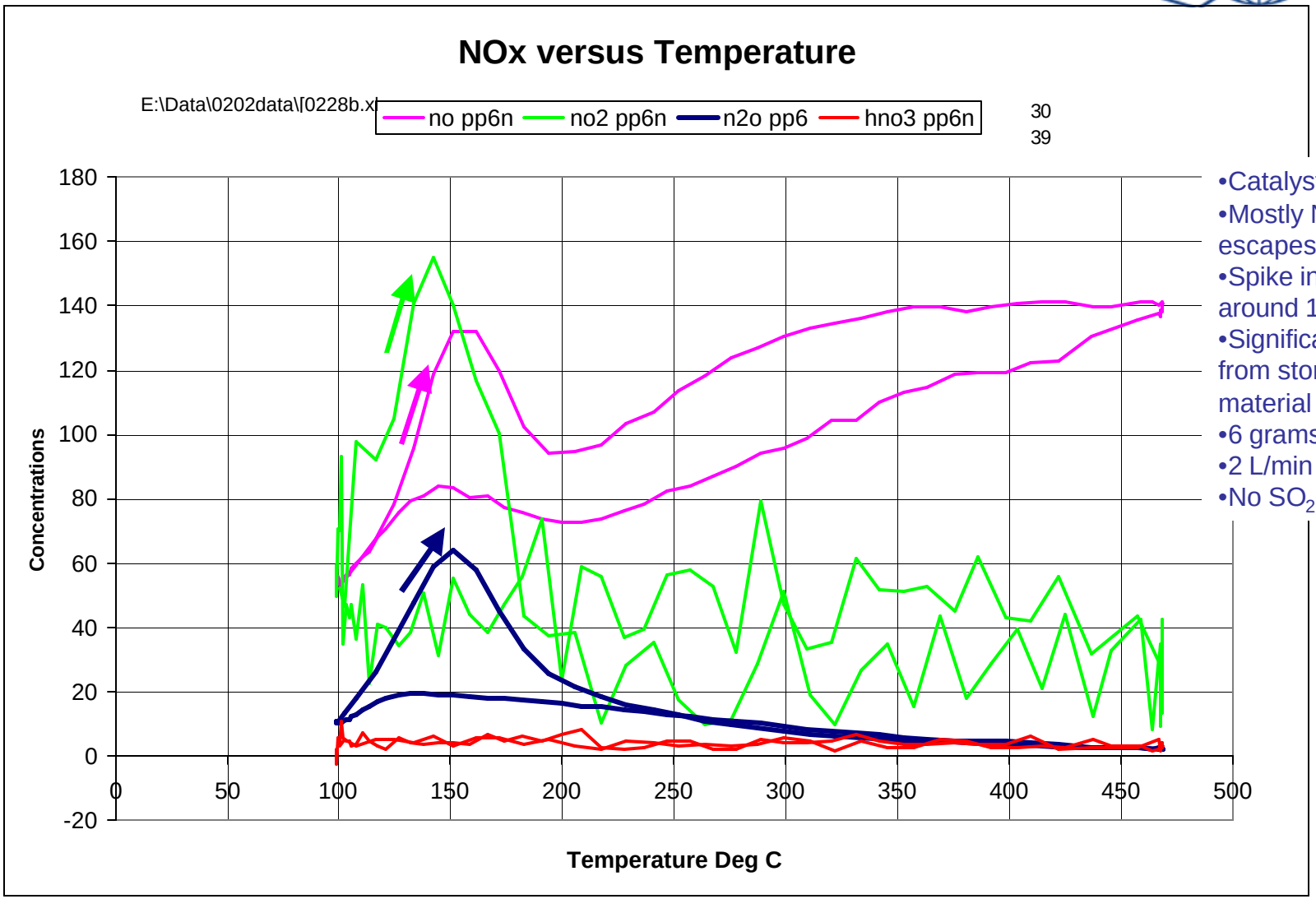
BaY+ Catalyst



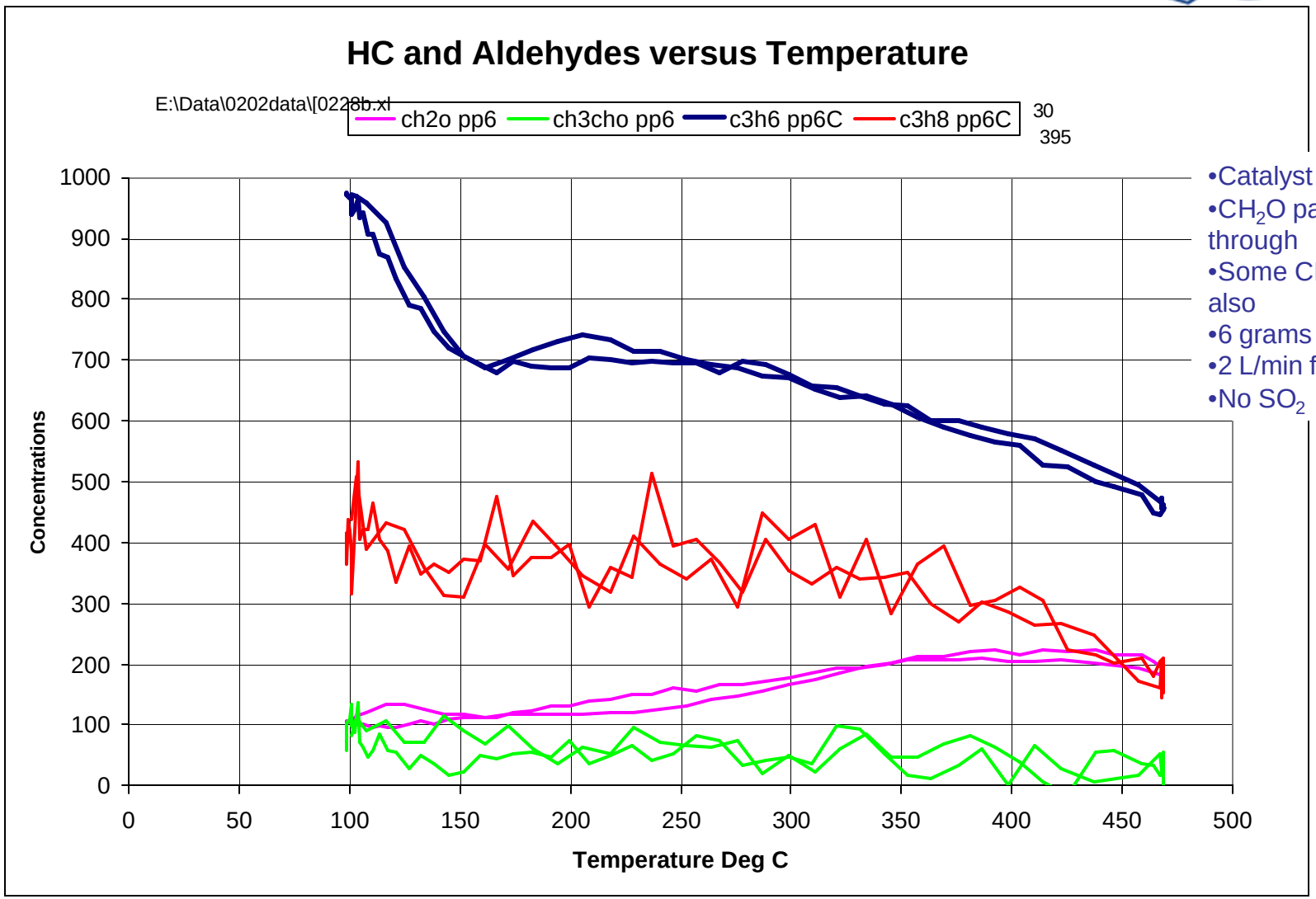
- BaY with added impregnation
- Data integrated over temperature loops
- 6 grams catalyst
- 4 L/min flow rate
- 50ppm SO_2



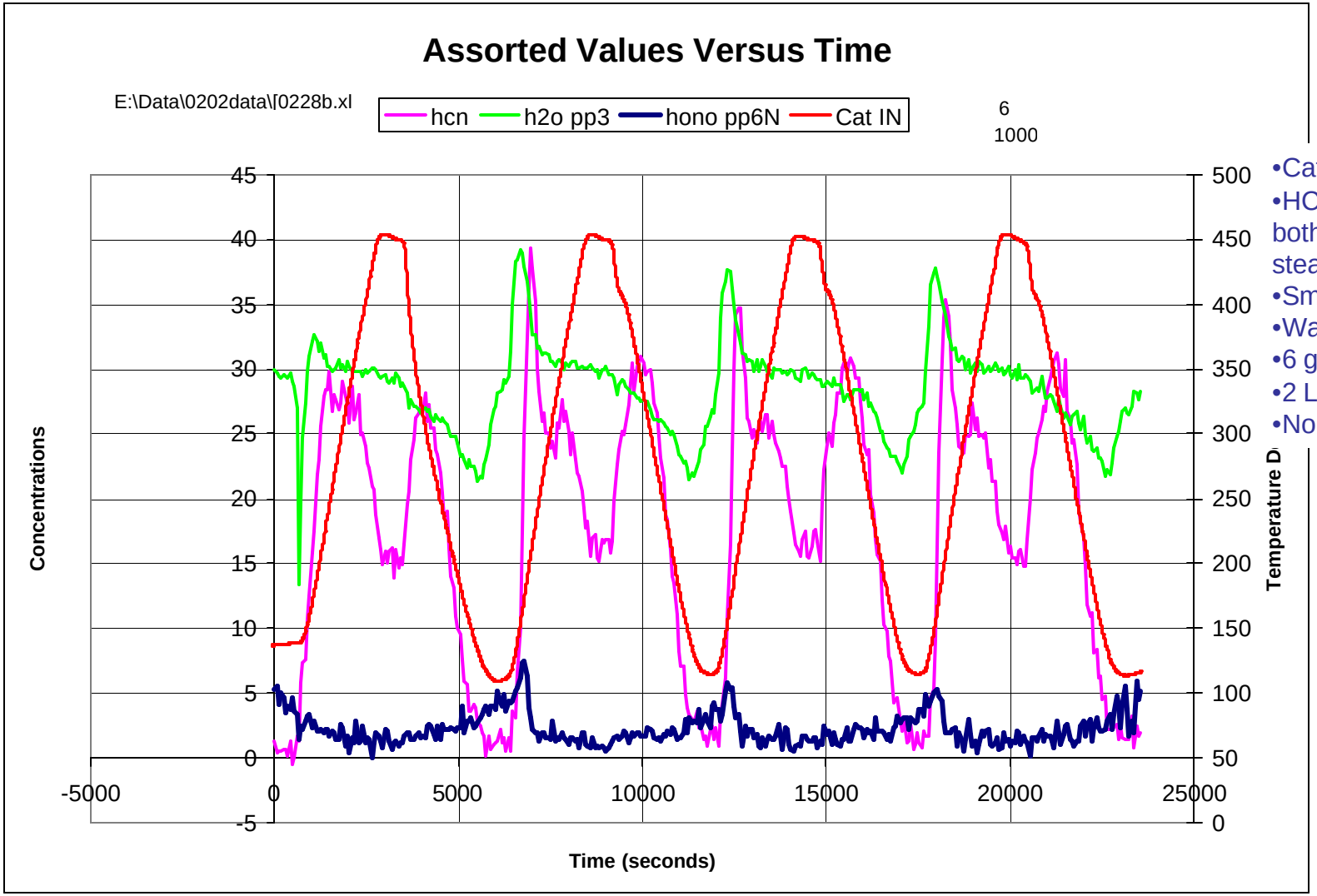
- Catalyst BaY+
- Last loop
- Activity at all temperatures
- Storage over wide temperature range
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2



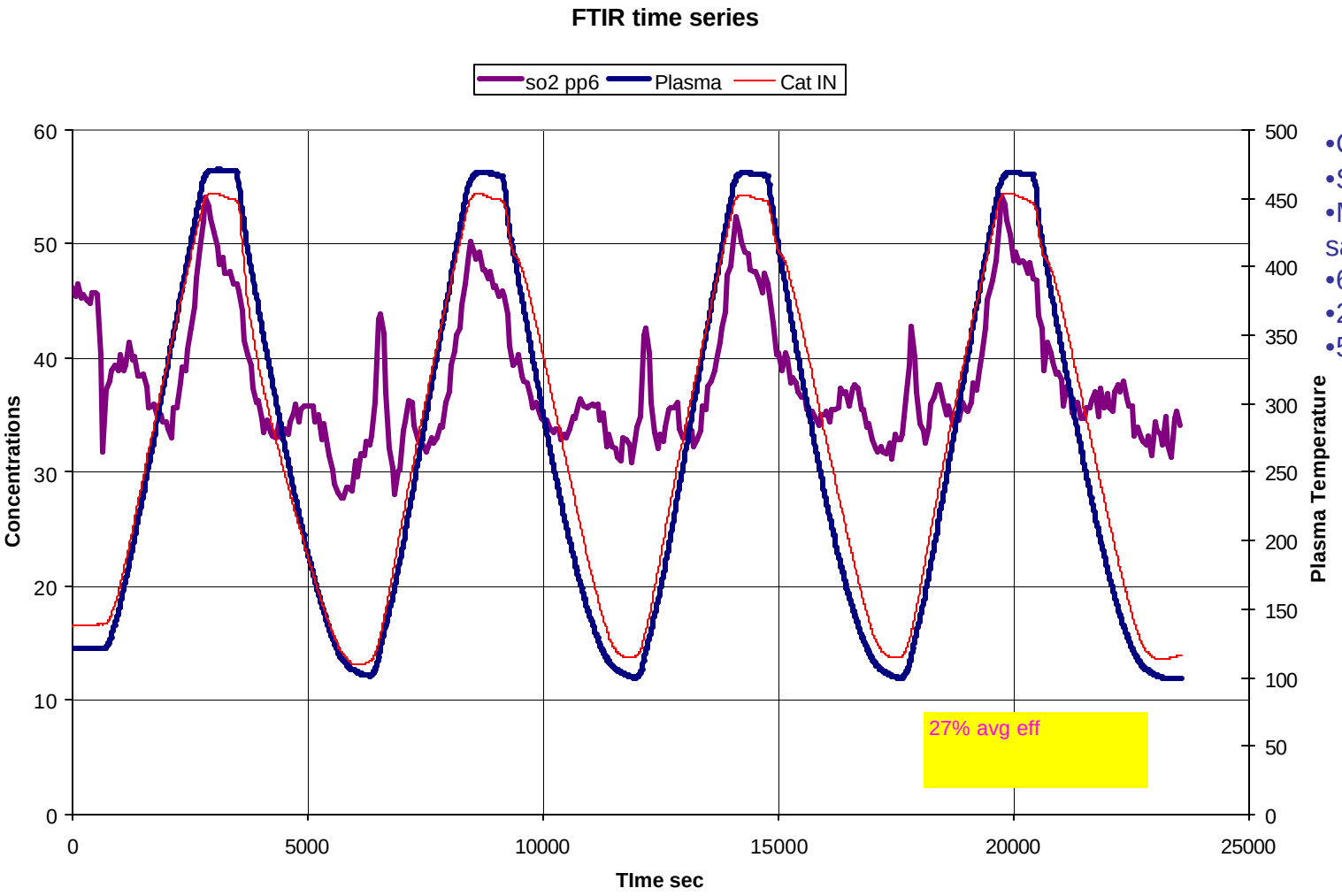
- Catalyst BaY+
- Mostly NO escapes
- Spike in NO_2 around 150°C
- Significant N_2O from stored material
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2



- Catalyst BaY+
- CH_2O passes through
- Some CH_3CHO also
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2

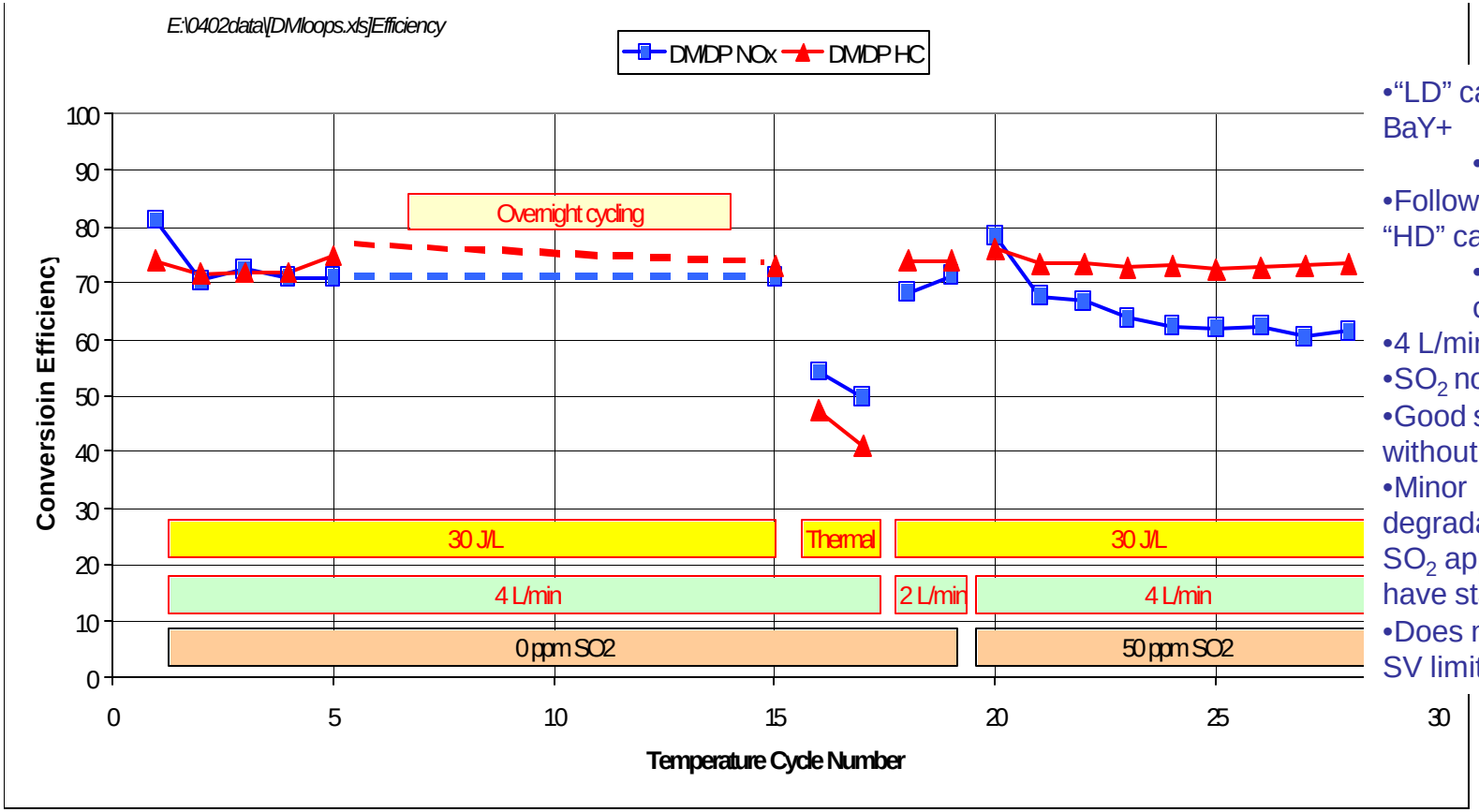


- Catalyst BaY+
- HCN formation – both transient and steady
- Small HONO
- Water storage
- 6 grams catalyst
- 2 L/min flow rate
- No SO_2

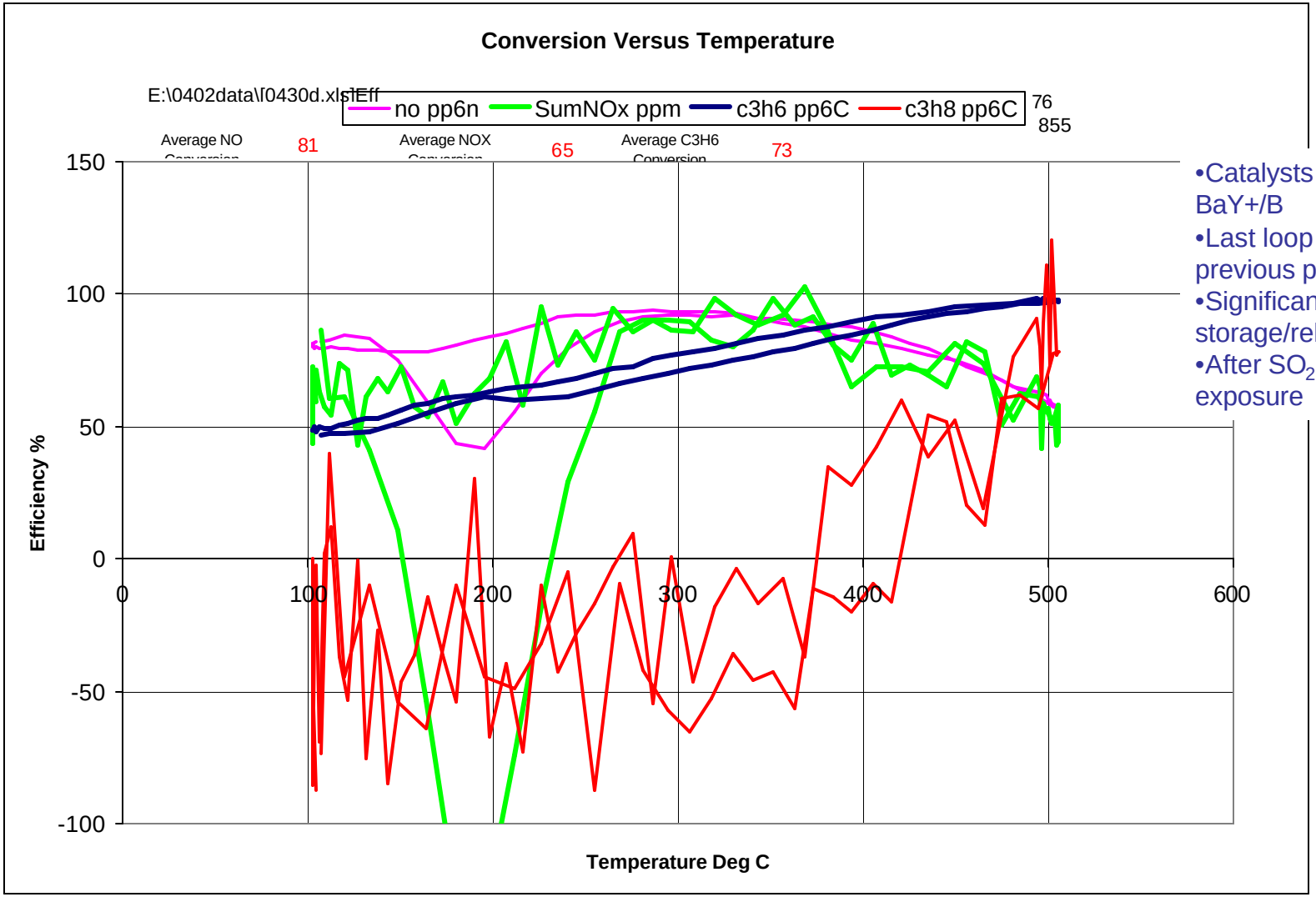


- Catalyst BaY+
- SO_2 storage
- May not be saturated yet
- 6 grams catalyst
- 2 L/min flow rate
- 50ppm SO_2

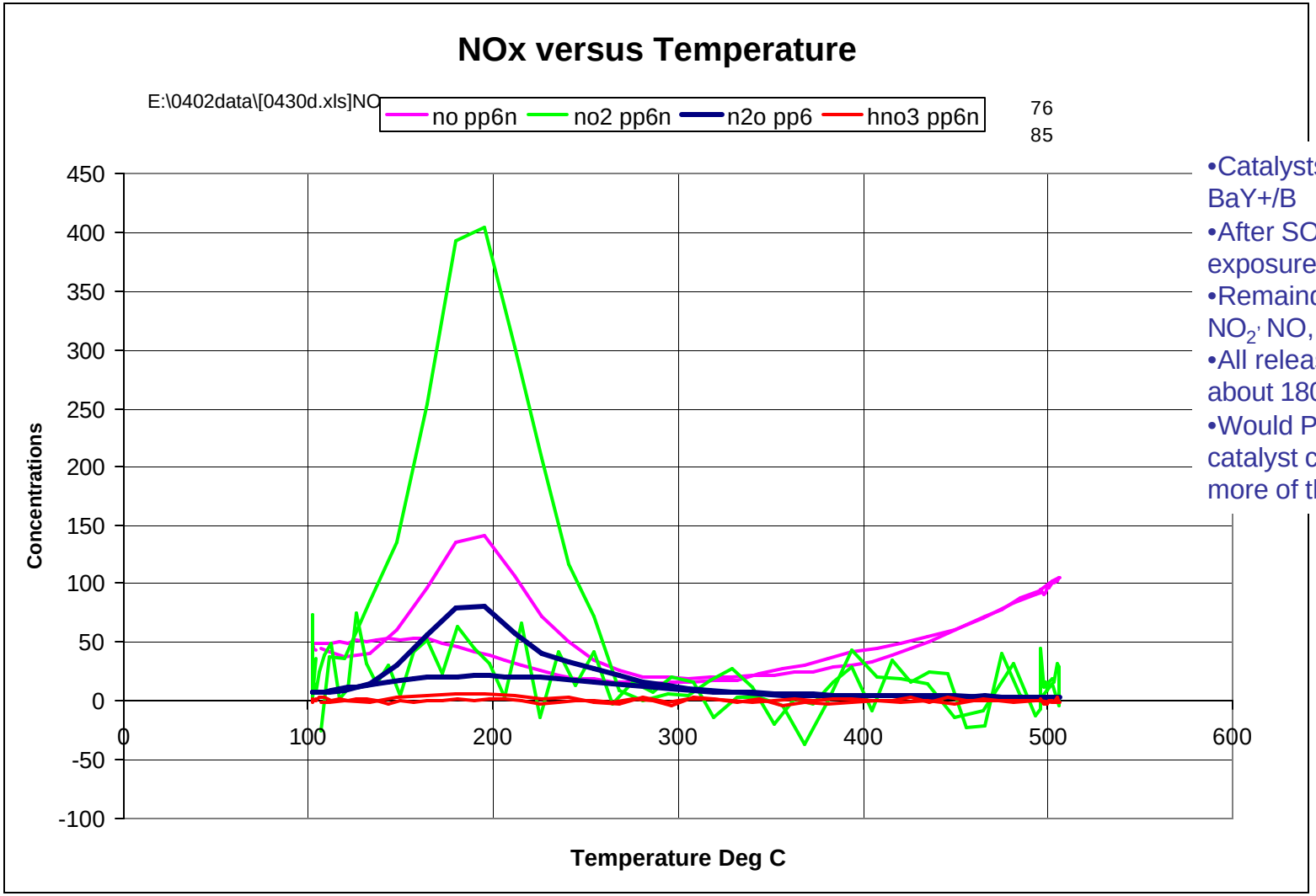
Combination: BaY+/B



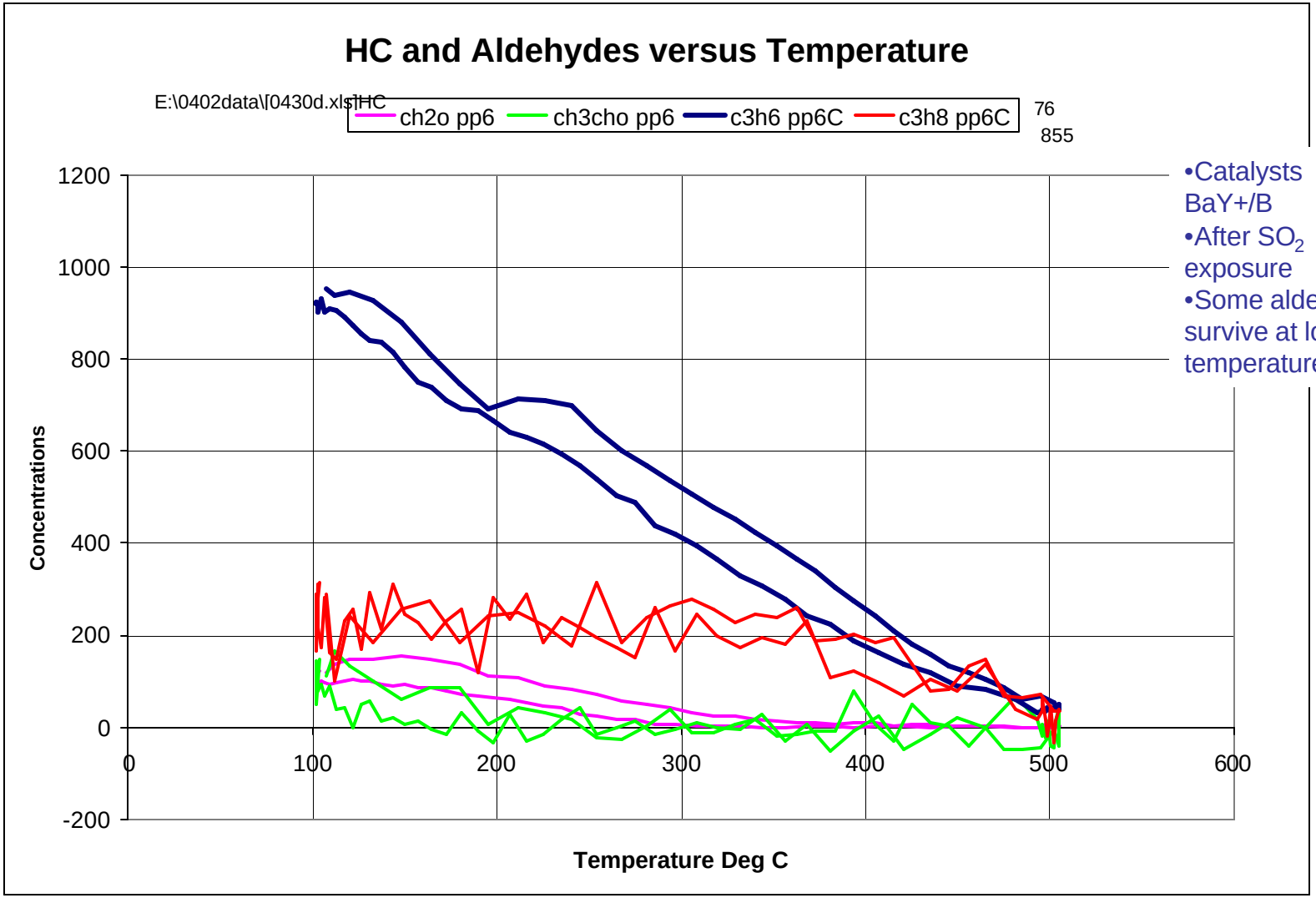
- "LD" catalyst BaY+
  - 6 grams
- Followed by "HD" catalyst B
  - 3 grams catalyst
- 4 L/min flow rate
- SO_2 noted
- Good stability without SO_2
- Minor degradation with SO_2 appears to have stabilized
- Does not appear SV limited



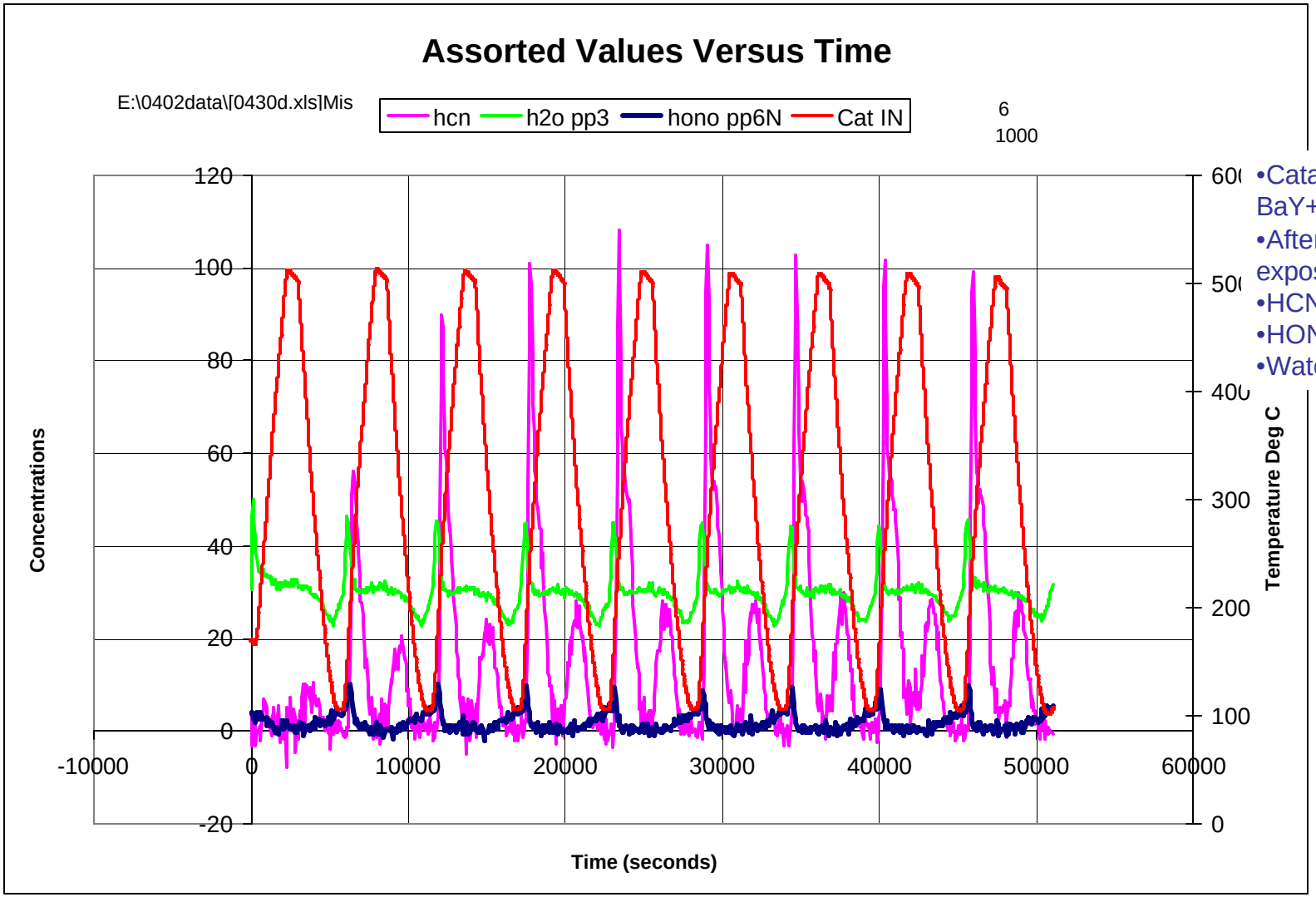
- Catalysts BaY+/B
- Last loop of previous plot
- Significant NOx storage/release
- After SO_2 exposure



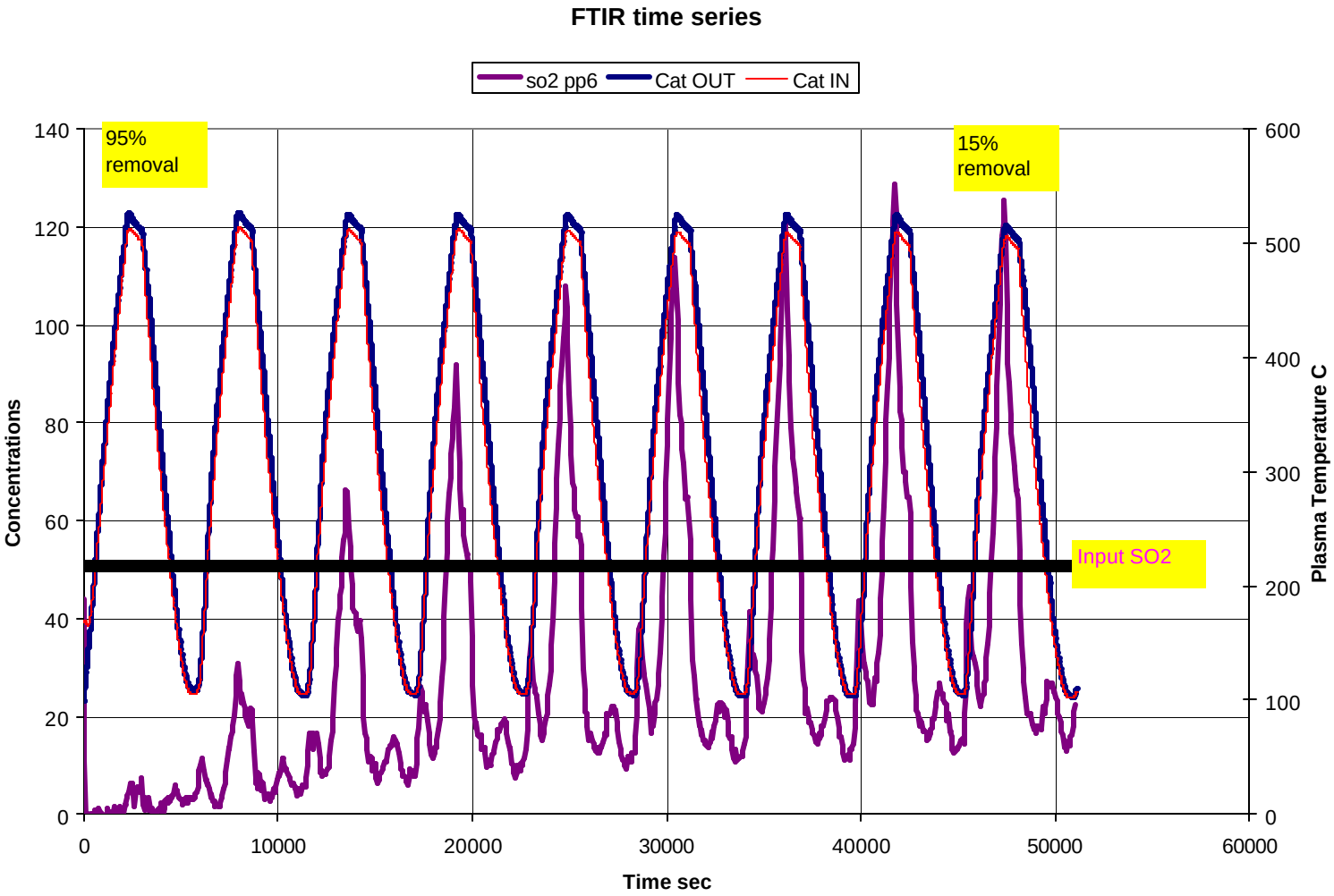
- Catalysts BaY+/B
- After SO_2 exposure
- Remainder is NO_2, NO, N_2O
- All released about 180°C
- Would Pt catalyst convert more of this?



- Catalysts BaY+/B
- After SO_2 exposure
- Some aldehydes survive at low temperature

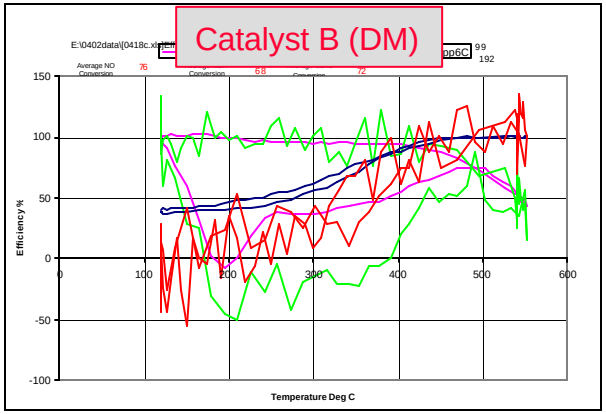


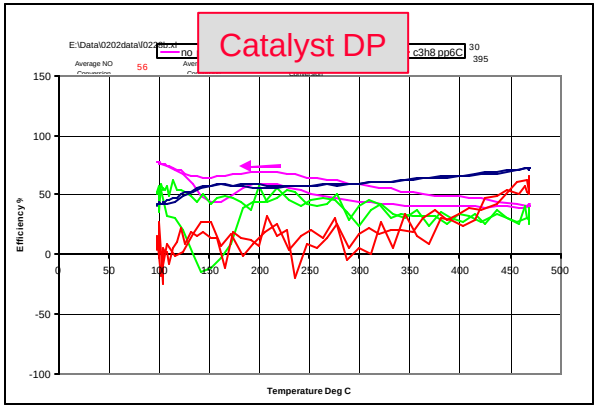
- Catalysts BaY+/B
- After SO_2 exposure
- HCN formed
- HONO
- Water storage

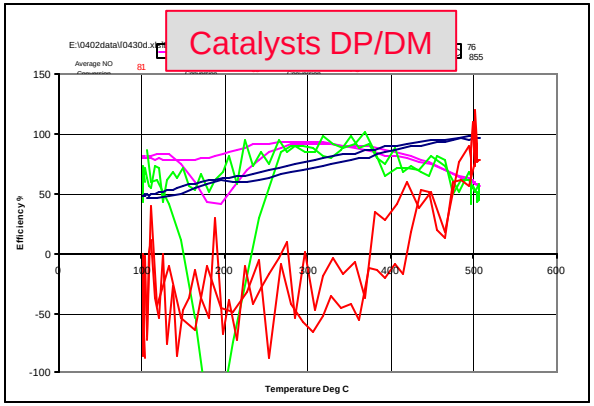


- Catalysts BaY+/B
- SO_2 adsorption
- Nearly saturated after 9 loops (about 15 hours)
- Low correlation between SO_2 storage and NOx conversion
- Some growth in CH_2O slip at low temperature

System Comparison







- HD Catalyst B
- 9K SV
- Conversion at high temperature
- Storage at lower temperatures

- LD catalyst DP
- 29K SV
- Lower conversion, wide range of temperature

- Combination DM/DP
- 29.9+42 K SV
- Good conversion over wide temperature range
- Significant storage
- Needs Pt downstream for HC control

Summary

- Ramp tests are an efficient way to run evaluations and initial aging
  - No known correlation to real world life!
  - Highlight storage/release issues
- Different catalysts have different “slip”
  - NOx speciation
  - Aldehyde and HC speciation
  - Temperature ranges
- Combinations can be much superior to single catalysts
  - Wider temperature range
  - Downstream catalyst “catches” slip from upstream
  - Order of catalysts matters; can’t mix them

Acknowledgements

- This work was performed as part of a CRADA with DOE and PNNL.
- The work was performed at the Ford Research Laboratory.
- Catalyst B was provided by Caterpillar Inc.