Dynamometer Evaluation of Plasma-Catalyst for Diesel NOx Reduction

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PNNL

For Presentation at DOE Diesel Engine Emission Reduction

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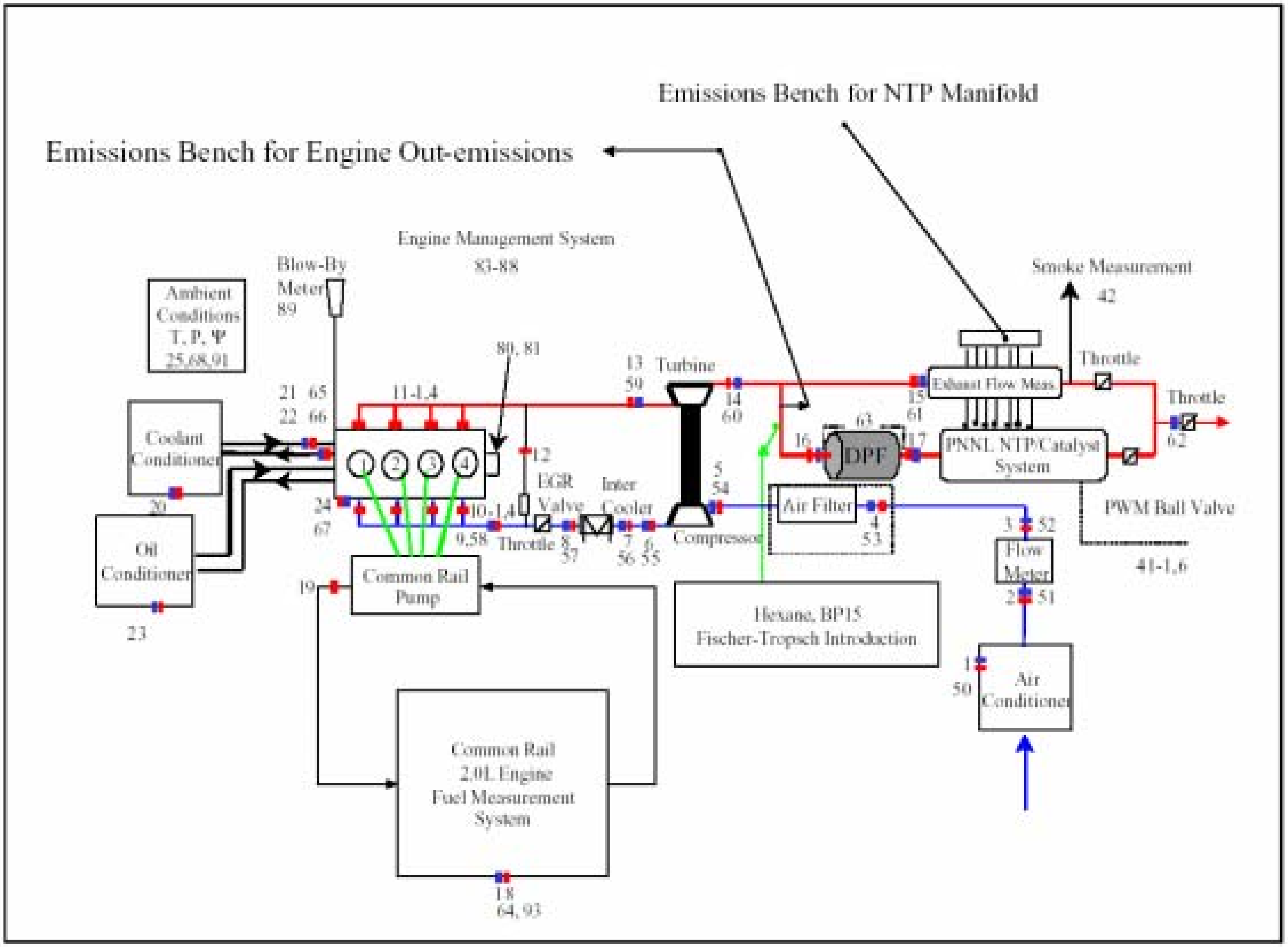
Introduction

- Engine dynamometer evaluation of plasma-catalyst system
  - 3-stage plasma-catalyst system – over 90% on bench
  - Downstream of (non-catalyzed) DPF
- Laboratory follow up and analysis
- CRADA project
  - USCAR LEP
    - Ford, GM, DaimlerChrysler
  - PNNL
- Tests at FEV and Ford Research Lab
- Plasma and catalyst hardware from PNNL
  - Catalyst modified from supplier samples

Engine Description



Engine Specifications

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Engine Process - Diesel

Engine Type - 4-stroke

Number of Cylinders - 4

Total Engine Displacement cm^3 1943

Bore Diameter mm 82

Stroke mm 92

Stroke/Bore Ratio - 1.122

Compression Ratio e - 19 : 1

Maximum Cylinder Pressure bar 150

Squish Height mm 0.8

Piston Bowl Volume cm^3 20.8

Valves per Cylinder - 4

Swirl Level - 1.8 – 1.9

Maximum Boost Pressure bar 2.05

Rated Power @ 4200 rpm kW 81

Plasma-Catalyst Unit

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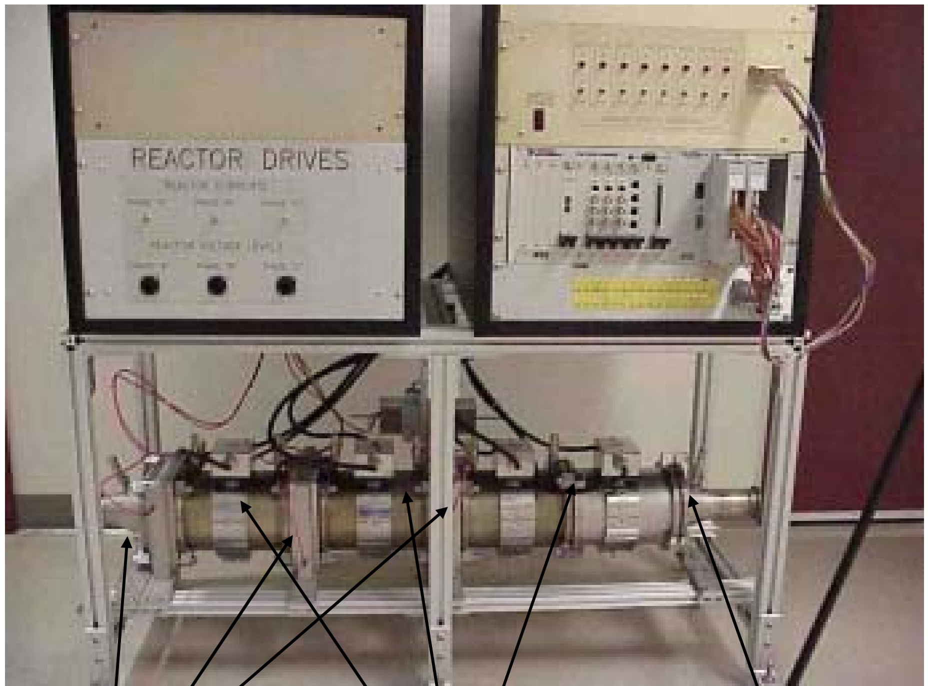
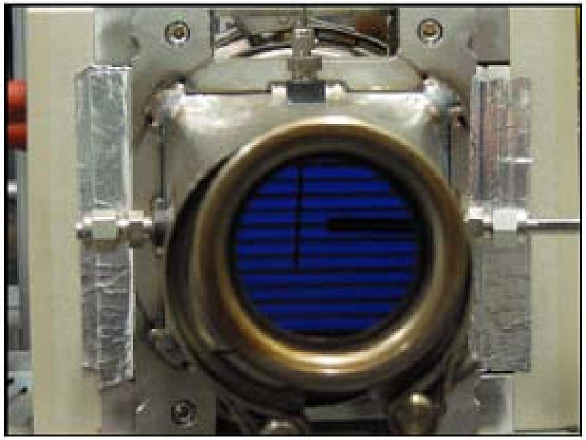


3 plasma stages

3 catalyst stages
with heaters

Oxidation Catalyst
With heater

Plasma Unit



Tube Array Reactor

BaY with Hexane Reductant

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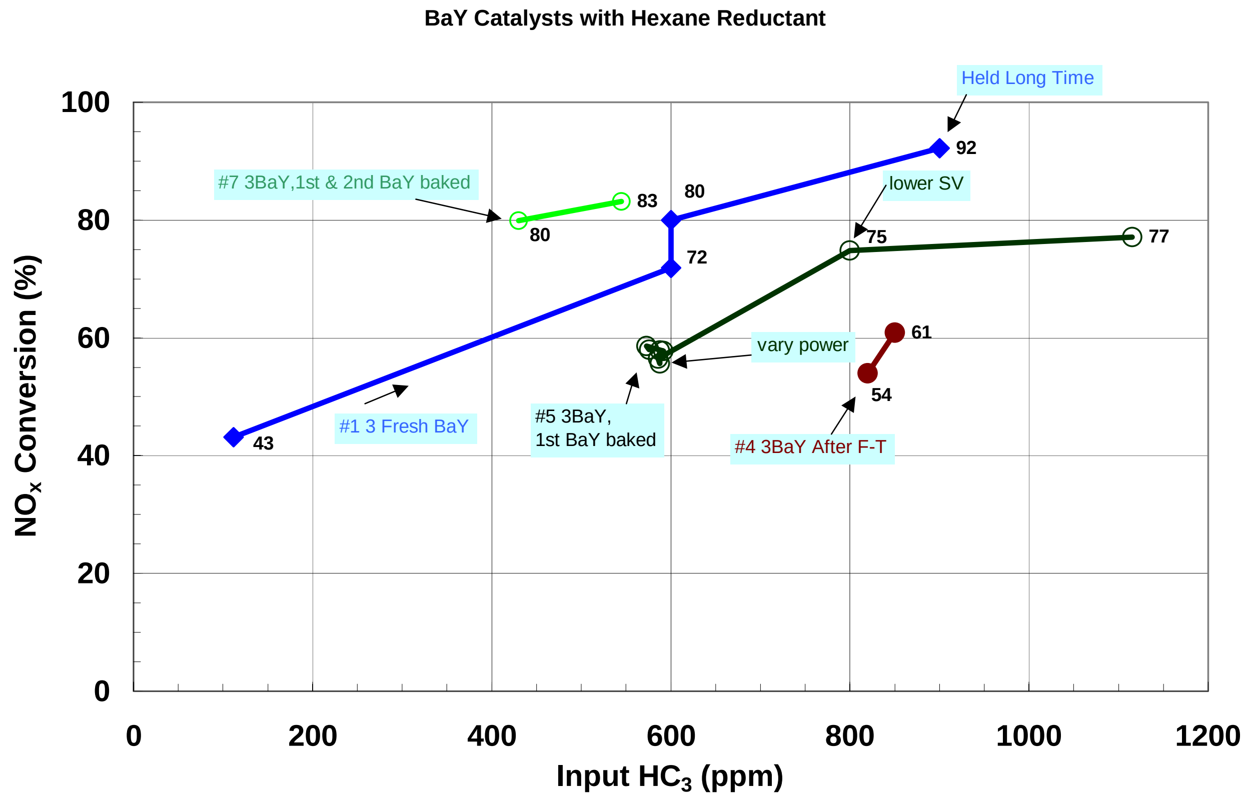
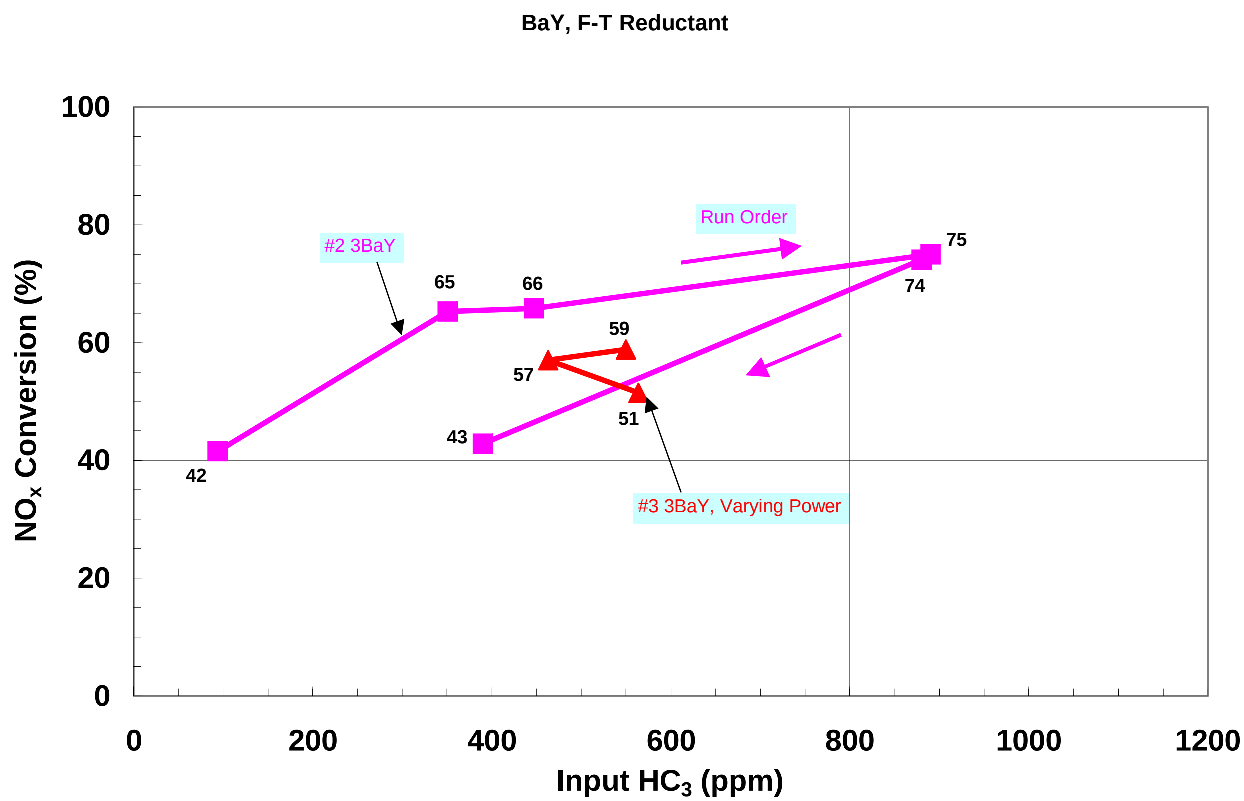


Good initial conversion using hexane reductant
92% NOx conversion for several hours at 230°C
6K space velocity (very low!)

BaY with Fischer-Tropsch



Good initial conversion using F-T reductant
But gradual drop with time
75% NOx conversion peak, dropping to ~50%

BaY/Al_2O_3 with Diesel

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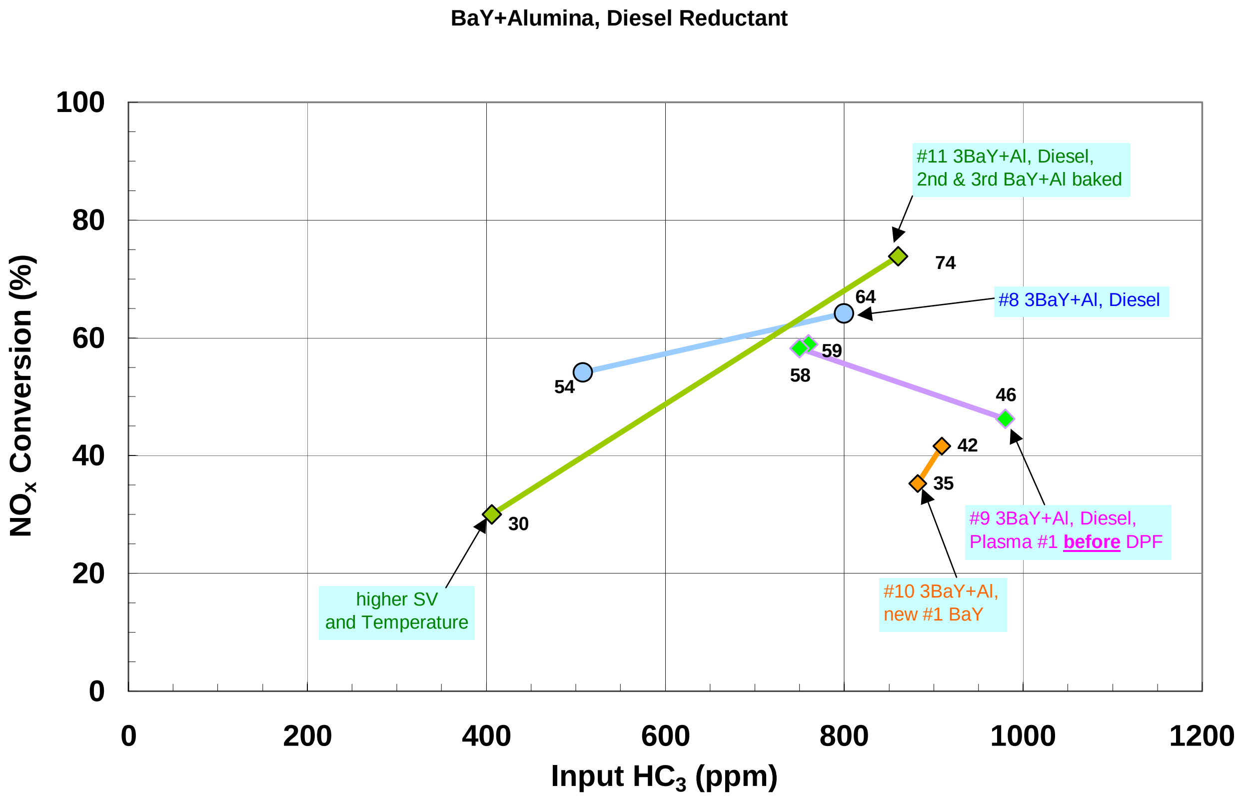

Good initial conversion using diesel fuel reductant
Rapid drop with time

Catalyst Visual

Catalyst coating uneven
Results in flow maldistribution
Increases effective space velocity

General Observations

- Good initial conversion
  - Approaches bench test data
- BaY performance degraded rapidly with F-T or diesel reductant
  - Catalysts discolor
  - Conversion largely recovered by baking 500°C in air

Post Mortem Tests

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- Cores cut from engine test catalyst brick "BaY1" – front catalyst
- Gas Bench (single stage plasma-catalyst)
  - 200°C activity before and after heating
  - Efficiency recovery with C_3H_6 ramps
  - C_3H_6 versus diesel reductant
  - Recovery after diesel fuel exposure
- Thermogravimetric (TG)

Thermal Cycle

- Would catalyst recover in normal driving (without high temperature)?
- Tested engine-used core in normal gas blend with “new” thermal cycle
  - Reductant is C_3H_6 – C_3H_8
- Gradual efficiency recovery

Thermal Cycle

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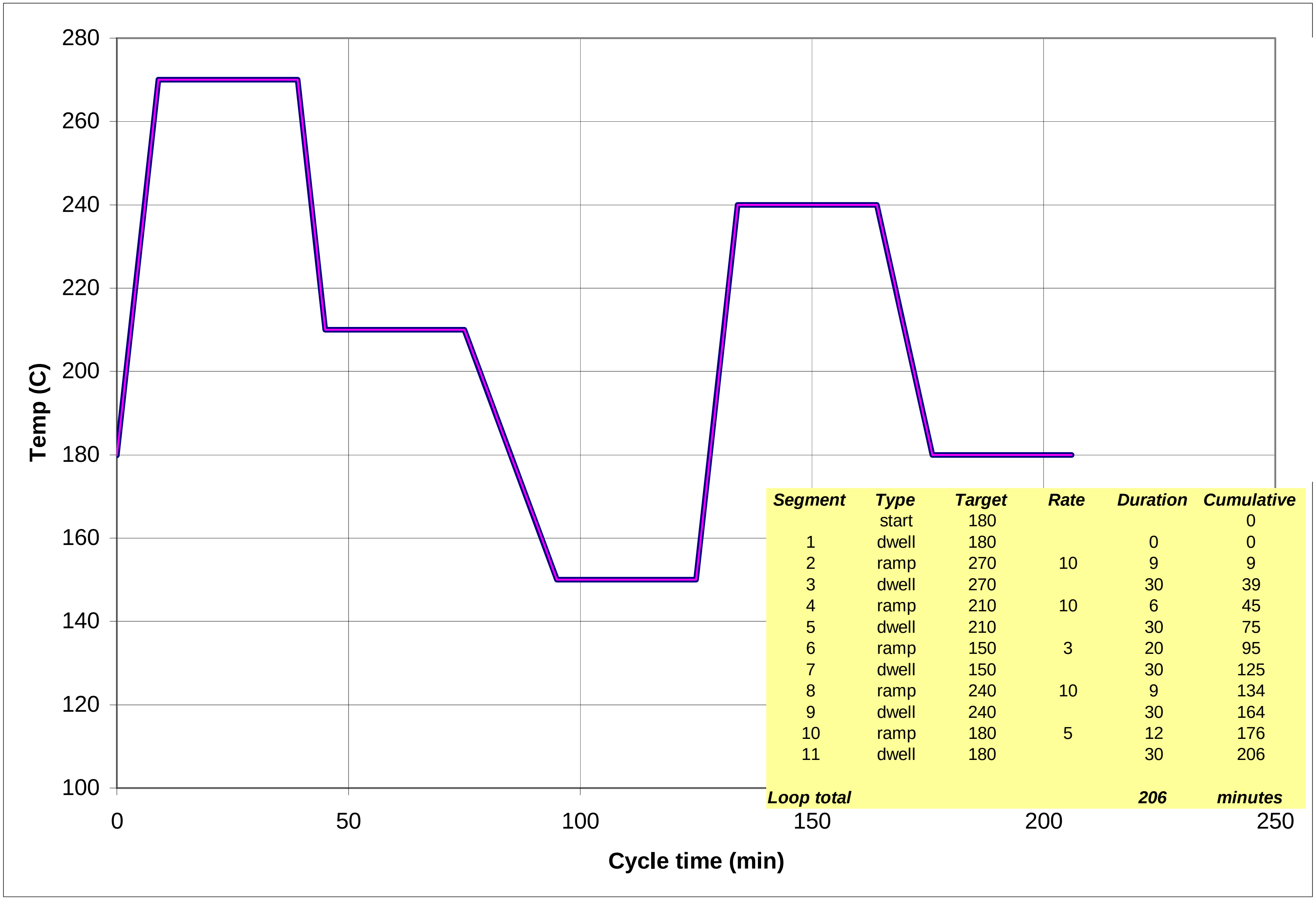
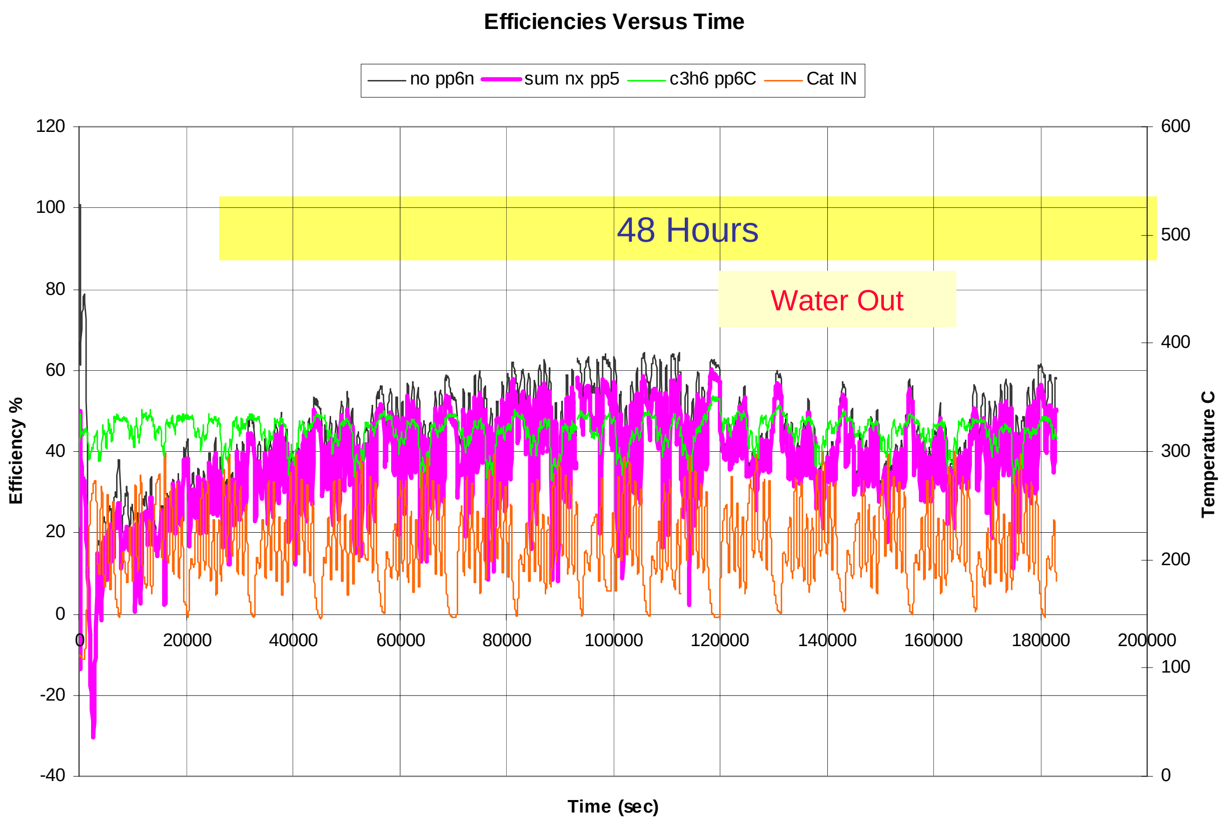


Segment	***Type***	***Target***	***Rate***	***Duration***	***Cumulative***
	start	180			0
1	dwell	180		0	0
2	ramp	270	10	9	9
3	dwell	270		30	39
4	ramp	210	10	6	45
5	dwell	210		30	75
6	ramp	150	3	20	95
7	dwell	150		30	125
8	ramp	240	10	9	134
9	dwell	240		30	164
10	ramp	180	5	12	176
11	dwell	180		30	206
Loop total				***206***	***minutes***

- Temperature values cover ~80% of FTP cycle
- dT/dt low
- 30 minute dwell to assure “steady” value at each temperature
- 3 ramp rates – but all are “slow”
- 206 minutes = 3 hours 26 minutes per cycle

Conversion versus Time



- Gradual recovery of NOx conversion
- Previous test of PNNL in-situ BaY "fresh" core averaged 45%
- Fraction of exit NOx which is NO gradually rises

Cycling Conclusions

- Efficiency gradually recovers
  - Maximum temperature 300°C
  - Propene/propane reductant
  - Color at end is light tan
  - Takes a long time!

Bench Test with Diesel Fuel

- What caused the “coking” and can we duplicate it?
- Same sample catalyst
- Pumped diesel fuel onto heated wick
  - Nominal 1500 ppmC_1
  - Very messy, large storage in lines!
  - Long settling times
  - Replaced propene/propane reductant

Conversion Results

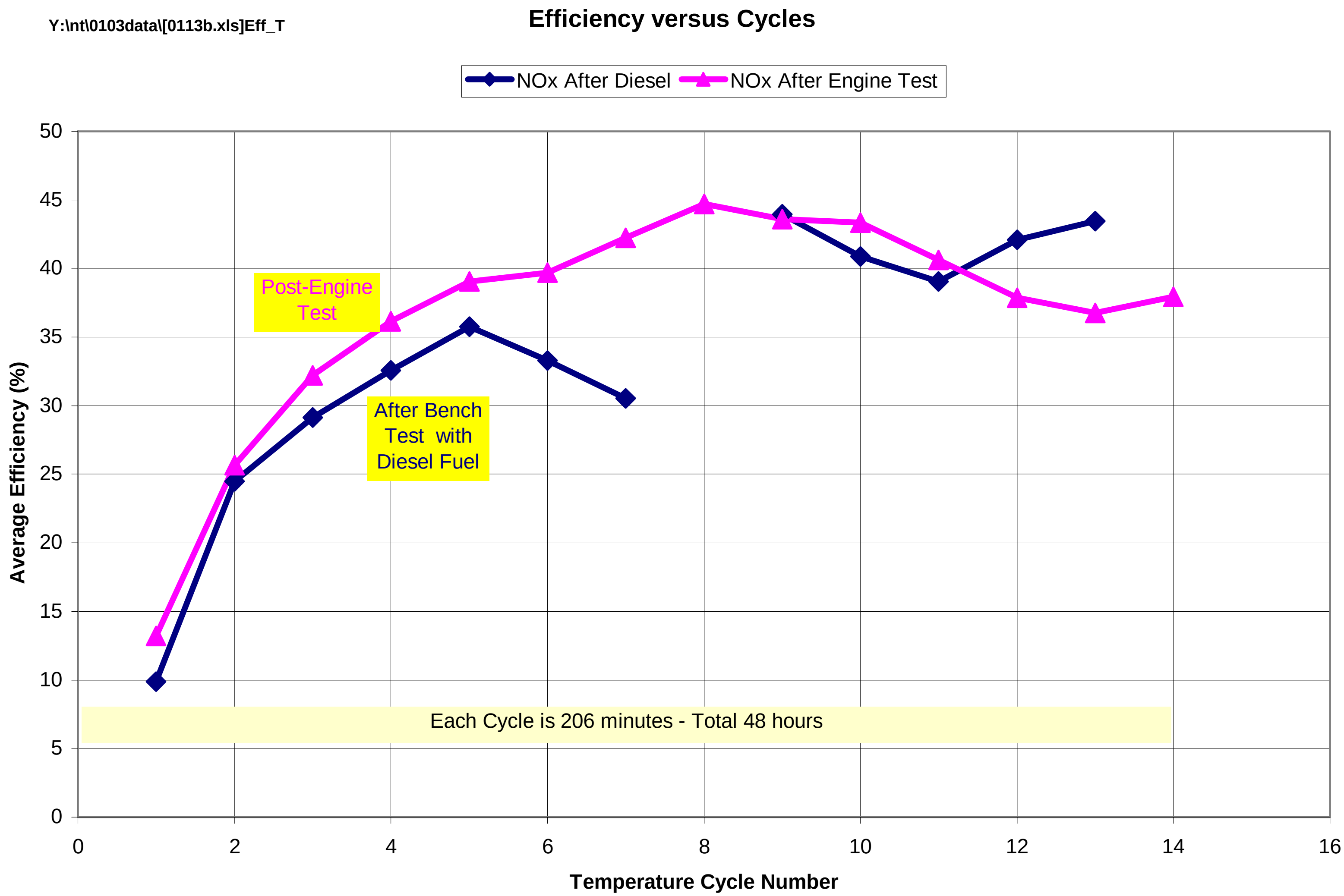
	NO	*NO2*	*SumNOx*	*FID*	*CLA*	
Input concentration	250	0	250	1300	252	
After plasma-catalyst	190	11	205	1040	213	
Conversion	24%		18%	20%	15%	

- 15-18% apparent NOx conversion
- HC conversion ~20%
- Catalyst turned brown within an hour

Repeat Cycling

- Does it recover the same way?
- Following test with diesel reductant
- Ran same cycles with propene/propane reductant

Efficiency Recovery



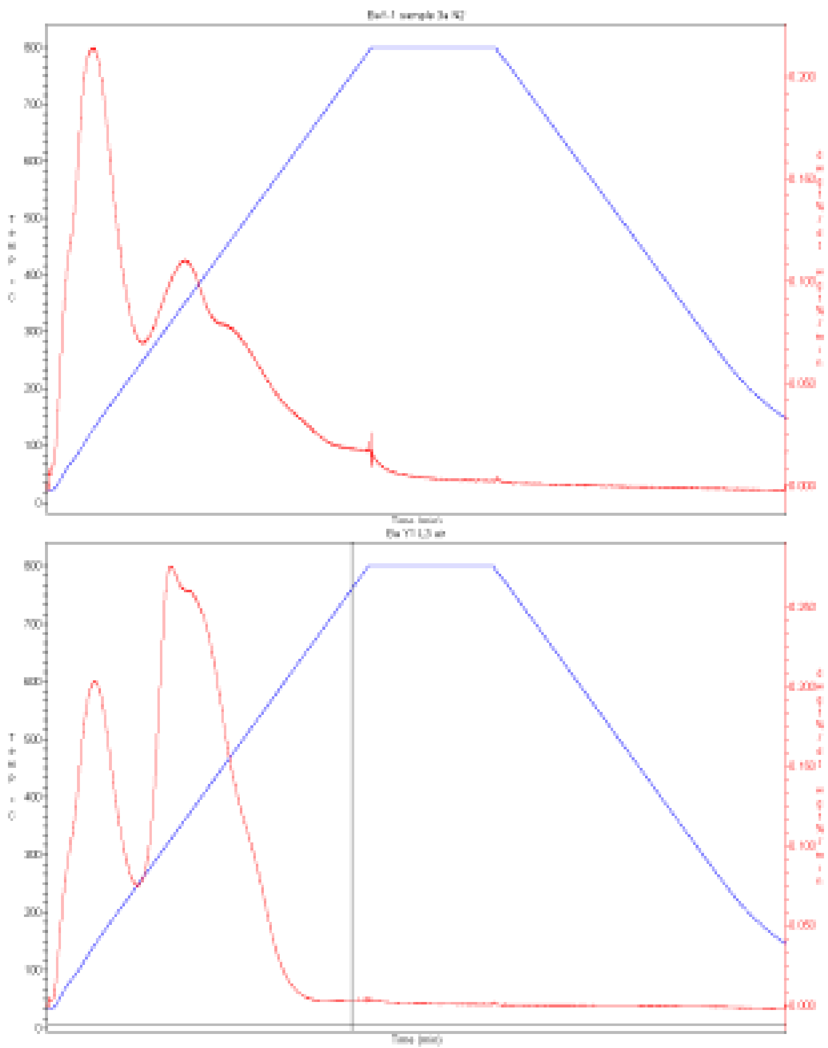
Conclusions

- Diesel fuel as a reductant causes deactivation very similar to engine testing
- Catalyst recovers when heavy HC removed, although slowly
- Deactivation is rapid
- How does this happen?

TG Analysis

Sample	*Gas during test*	*Initial appearance*	*Finial appearance*
L3A	N_2	Brown	Black
L3B	Air	Brown	White
L3B diesel	Air	Tan	White
L3A	Air	Black	White

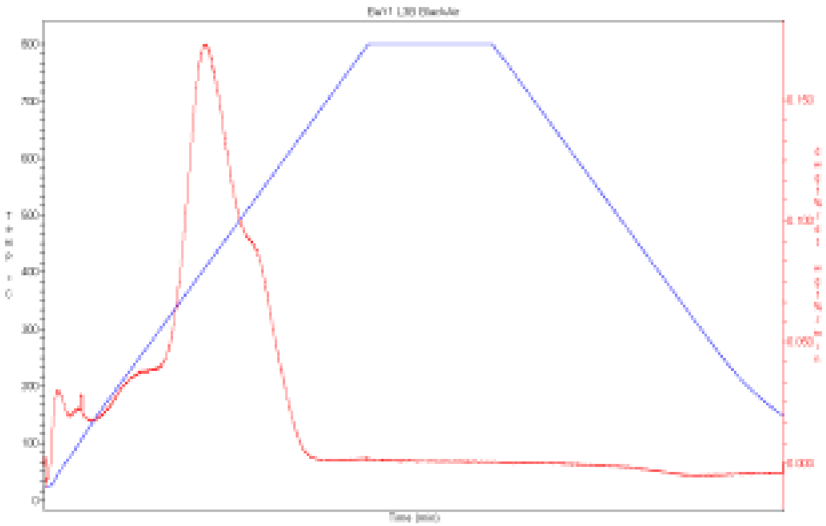
Air versus N_2



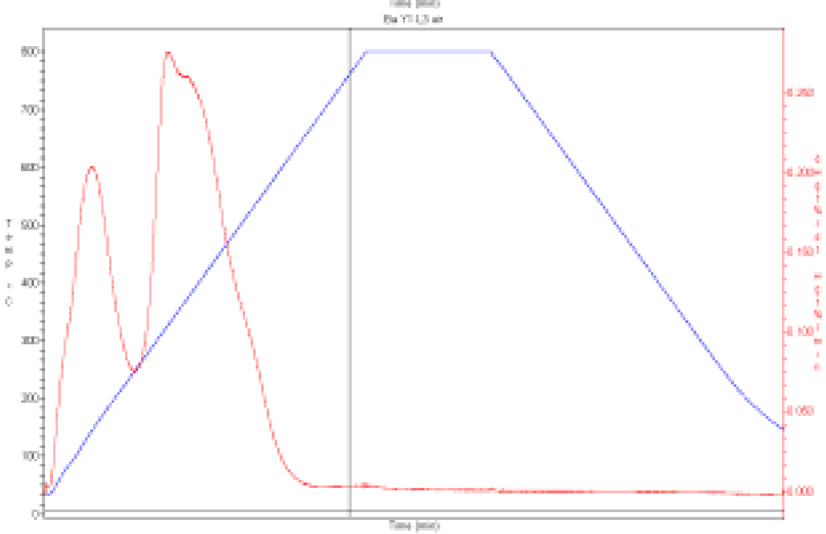
Heating in N_2

Heating in air

Air after N_2



Heating in air, following heating in N_2



Heating in air (reference)

Diesel Fuel

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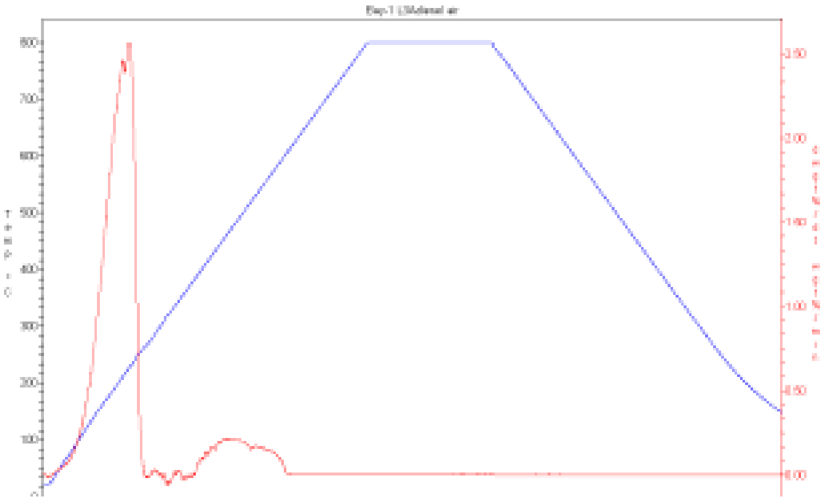
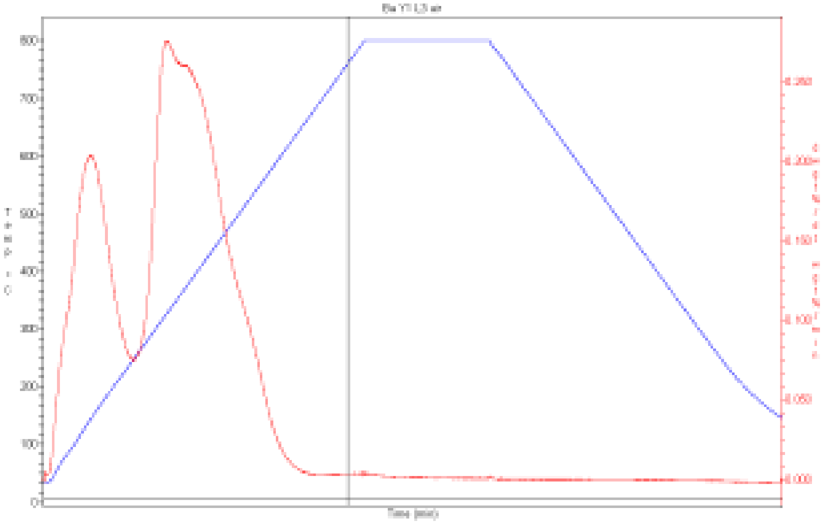


Heating in air after soak in diesel fuel



Heating in air (reference)

TG Conclusions

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- Low temperature desorption
  - ~100-250°C
  - Diesel fuel condensed on surface
  - Present in air or N_2
- High temperature desorption
  - Not present in N_2
  - Oxidation of adsorbed “HC” species
- Which affects conversion?
  - Efficiency recovers after cycling < 300°C
  - Thus, low temperature portion is most critical

Conclusions

- High efficiency of bench testing is possible for short times in engine exhaust
- Diesel reductant deactivates catalyst rapidly
- Thermal regeneration is possible but slow

Acknowledgements

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