Fuels, Quality Standards, and Emissions Durability

SOUTHWEST RESEARCH INSTITUTE®

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PERC Fuel Quality Survey

National Fuel Quality Survey
(PERC Docket 20064)

National LPG Survey

- 100 samples taken between 03/19/2015 and 01/18/2016
- Sample distribution based on state population
- Samples taken from bulk-plant tanks and bobtail trucks in 33 lb aluminum forklift cylinders
- Both commercial and HD-5 samples
  - 95% met HD-5 specifications
- 95% of samples passed 0.3 mL oil stain limit for residue
- Two samples exceeded 0.05 mL/100 mL residue volume limit
- Two samples exceeded 80 mg/kg total sulfur (current limit for gasoline and California "HD-10")
  - Only one sample exceeded 123 mg/kg HD-5 limit

LPG Sample Locations

LPG Composition Statistics

Hydrocarbon Composition (D2163)	Unit	Mean	1σ	Min	Max
methane	vol%	0.06	0.07	0.00	0.38
ethane	vol%	3.83	2.26	0.38	10.55
ethylene	vol%	0.00	0.01	0.00	0.04
propane	vol%	94.49	2.33	86.68	98.77
propylene	vol%	0.61	1.44	0.00	10.99
isobutane	vol%	0.82	0.37	0.17	2.17
n-butane	vol%	0.16	0.14	0.01	0.67
trans-2-butene	vol%	0.00	0.00	0.00	0.01
1-butene	vol%	0.00	0.01	0.00	0.03
isobutene	vol%	0.00	0.01	0.00	0.05
cis-2-butene	vol%	0.00	0.00	0.00	0.01
isopentane	vol%	0.00	0.01	0.00	0.05
n-pentane	vol%	0.01	0.01	0.00	0.07
1,3-butadiene	vol%	0.00	0.01	0.00	0.06
butane and heavier	vol%	1.00	0.46	0.34	2.88
pentane and heavier	vol%	0.01	0.02	0.00	0.12

LPG Composition Statistics

Calculated Properties	Unit	Mean	1σ	Min	Max
Vapor Pressure @ 37.8 °C (D2598)	psi	191	10	174	221
Relative Density @ 15.6 °C (D2598)	--	0.50	0.00	0.49	0.51
Motor Octane Number (MON) (D2598)	--	97	0	96	98
Gross Energy Content (GPA 2145)	BTU/gal	89,937	577	88,200	90,958
Sulfur Speciation – ppmw of Compound (D5623M)	**Unit**	**Mean**	**1σ**	**Min**	**Max**
ethyl mercaptan	mg/kg	48	23	0	165
carbonyl sulfide	mg/kg	2	3	0	21
dimethyl sulfide	mg/kg	0	0	0	2
dimethyl disulfide	mg/kg	3	7	0	61
diethyl disulfide	mg/kg	10	27	0	257
benzothiohene	mg/kg	0	2	0	17
Total Sulfur (D6667)	mg/kg	37	14	19	91

Note: Total sulfur statistics exclude 343 mg/kg outlier

LPG Composition Statistics

	Unit	Mean	1σ	Min	Max
Stain Tube Test – Methanol (D5305M)	**ppmv**	462	210	2	1032
Dryness - Valve Freeze (D2713)	**seconds**	all passed	--	> 90	> 90
Copper Strip (D1838)	**rating**	1	0	1	1
LPG Residues by GC (D7756)	**mg/kg**	49	152	10	1307
Residue in LPG (D2158)					
Residue Volume	**mL / 100 mL**	--	--	< 0.05	0.50
Oil Stain Volume	**mL**	1.0	0.5	0.1	1.5

2017 PERC Fuel Quality Survey Plan

- Tentative plan, pending PERC Council approval
- Approximately 70 samples will be collected and tested
  - ASTM D1657 Density by Pressure Hydrometer
  - ASTM D1267 Vapor Pressure
  - ASTM D1838 Copper Corrosion
  - ASTM D2158 Residue in LPG
  - ASTM D2163 Composition by GC
  - ASTM D2598 Relative density, vapor pressure, MON
    - Calculated from D2163
  - ASTM D2713 Moisture Content
  - ASTM D5623 Sulfur Speciation
  - ASTM D6667 Total Sulfur

3-Way Catalyst Light-Off Performance on LPG and the Feasibility of Achieving Near-Zero NOx

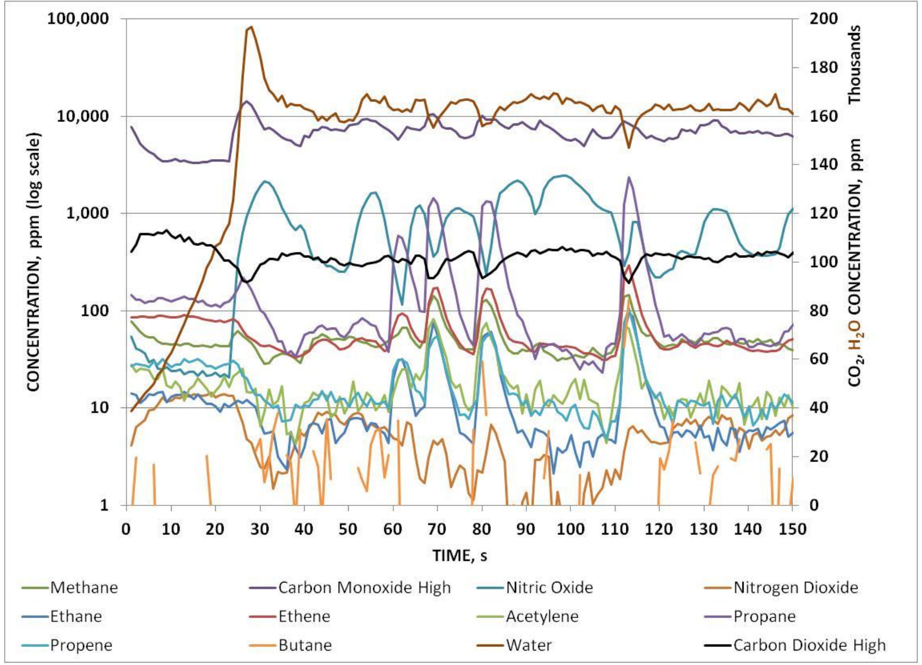
Baseline Data – Cold Start Engine Out Emissions

- HD Otto-Cycle FTP Cold Start Engine Out Emissions Obtained from 2016 MY Propane-Fueled Engine

Gas Mixtures Used for Bench Testing

Mixture based on average concentrations during 30 – 125 seconds of cold FTP cycle

GAS	CONCENTRATION
H_2O	16.4 %
CO_2	10.13 %
CO	[1]2900, 2600, 2100, 1200 ppm
H_2	[1]967, 867, 700, 400 ppm
NO	1013 ppm
CH_4	[1]97, 194, 388, 776 ppm
C_2H_4	63 ppm
C_2H_6	14 ppm
C_2H_2	19 ppm
C_3H_6	18 ppm
C_3H_8	258 ppm
O_2	[1]0.50, 0.51, 0.55, 0.61 %
SO_2	[1]0.625, 1.25, 2.5, 5.0 ppm
[1]CH_4 used as carrier for SO_2	



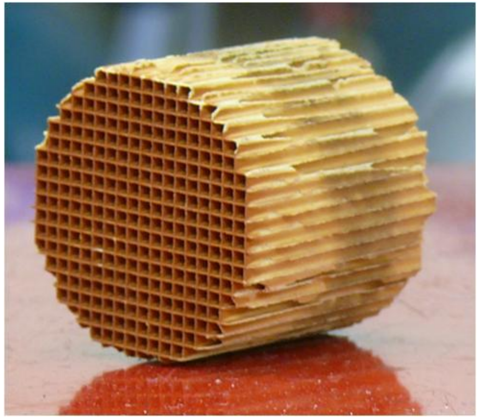
Baseline Data – Test Catalysts

- Both Catalyst Formulations Evaluated Were Commercial Products
  - Formulation A is a low cost, zone-coated gasoline engine catalyst used in some propane applications
  - Formulation B is a natural gas engine catalyst with platinum, that is reported to improve sulfur tolerance
  - The two formulations represent relative extremes in emissions control demand (gasoline easier, natural gas more difficult)

CATALYST	Pt, g/ft^3	Pd, g/ft^3	Rh, g/ft^3	Total, g/ft^3
A	0	10/100/7	2/2/2.6	33
B	1.3	57	1.1	59

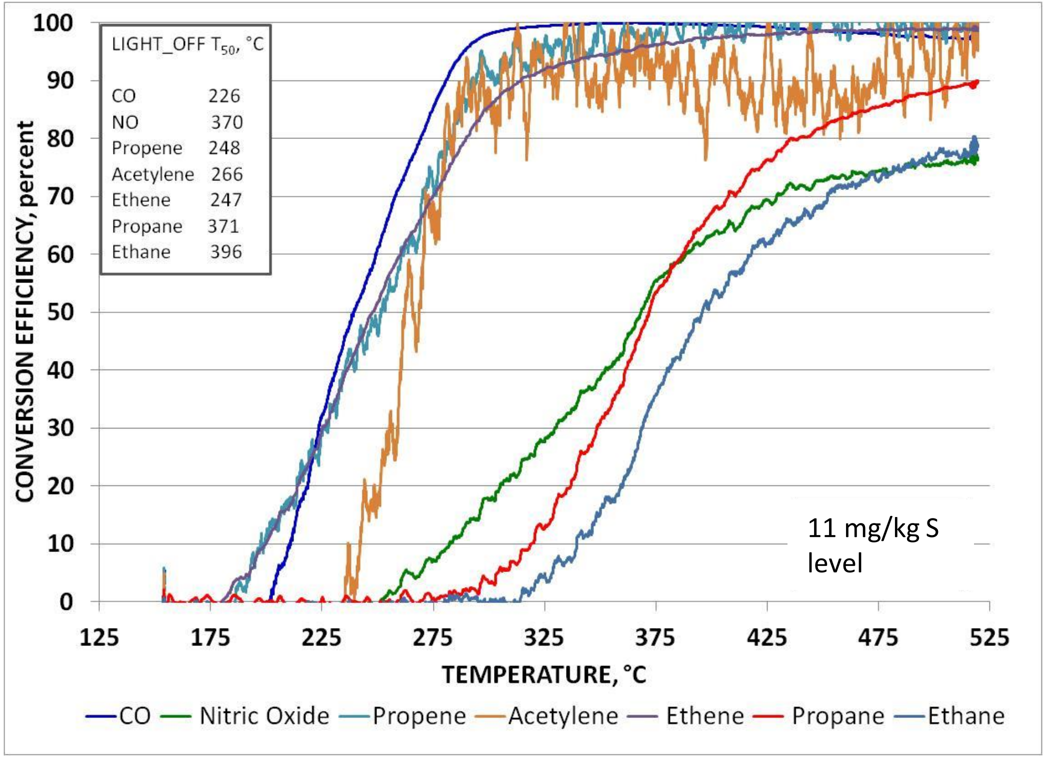
Synthetic Gas Reactor Bench Core Testing

- SwRI's Universal Synthetic Gas Reactor (USGR®) Catalyst Core Testing System



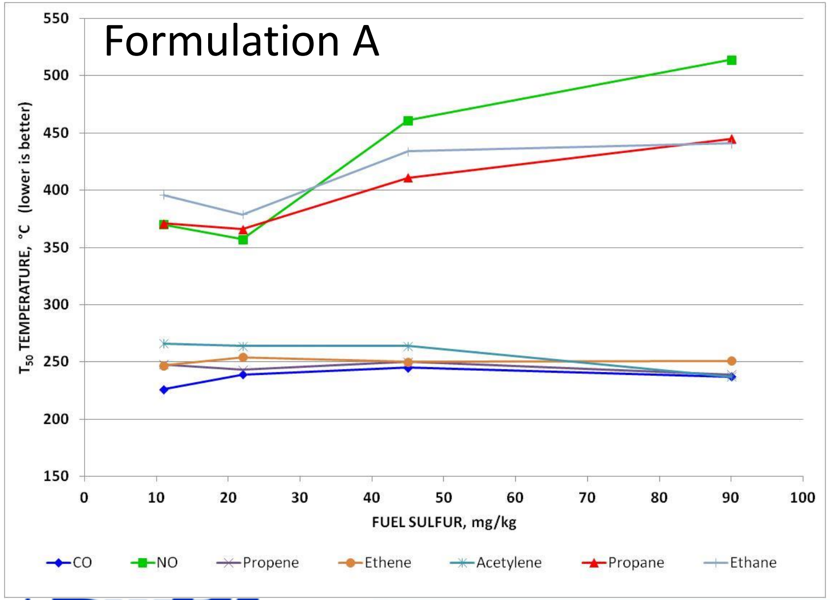
Fresh Catalyst Performance

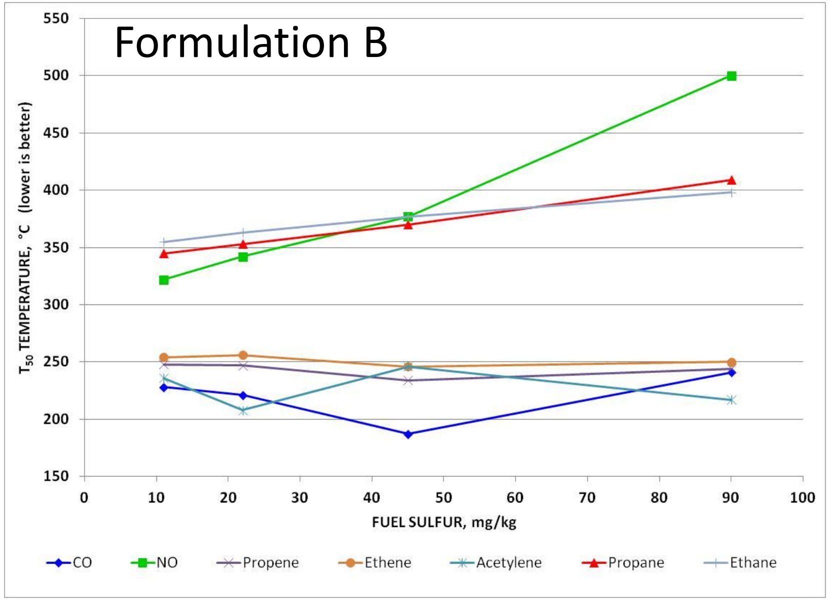
- Example of Processed Test Result
- T_{50} used to Compare Catalysts and Conditions
- Four Fuel Sulfur Equivalent Conditions Tested
  - 11 mg/kg S
  - 22 mg/kg S
  - 45 mg/kg S (field average + 20%)
  - 90 mg/kg S



Comparison of Two Formulations Sensitivity to Fuel Sulfur Content

- Both Formulations are Sensitive to Sulfur Level for NO, Propane and Ethane Control
- Formulation B Exhibited Lower Light-Off Temperatures than Formulation A





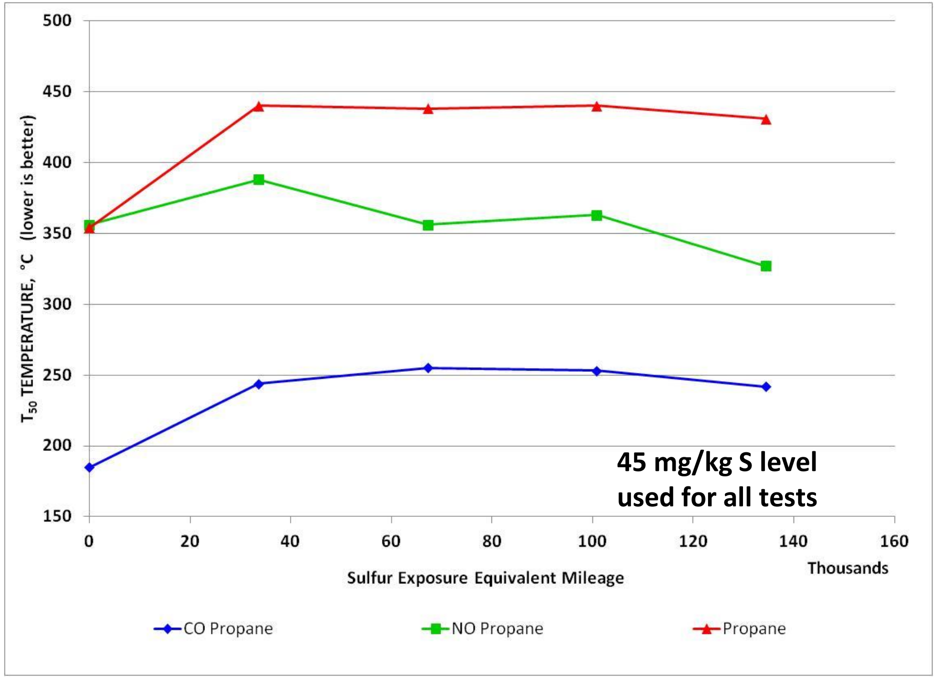
Aging by Sulfur Exposure

- Formulation A was Exposed to High SO_2 Levels, in Increments, to Age to the Equivalent of Full Useful Life
- 16 Hours, 400 °C, λ = 1.02
- 104 ppm SO_2 + O_2, CO_2, CH_4, N_2

  = 33,600 miles using 90 mg/kg S fuel

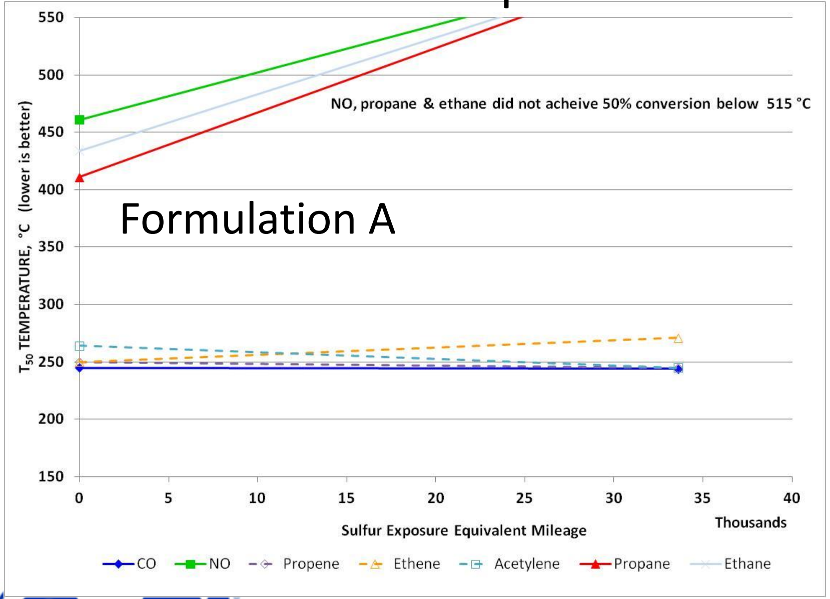
- Deactivation by Sulfur up to 33,600 Miles Equivalent, then Stable

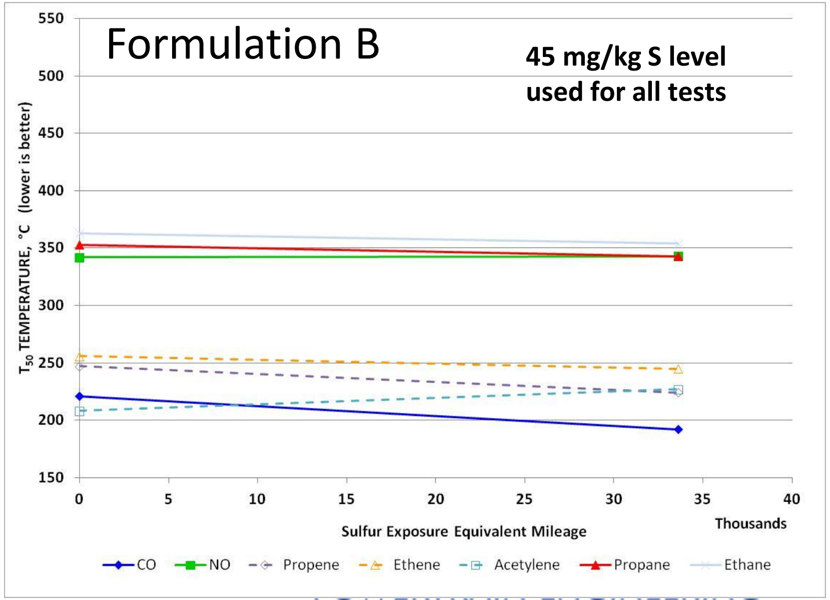
- Formulation B Aged to 33,600 Miles Equivalent for Comparison



Comparison of Aged Sensitivity to Fuel Sulfur Content

- Unlike Formulation A, Formulation B was Stable to Sulfur Exposure
  - Higher precious metal loading
  - Small amount of platinum



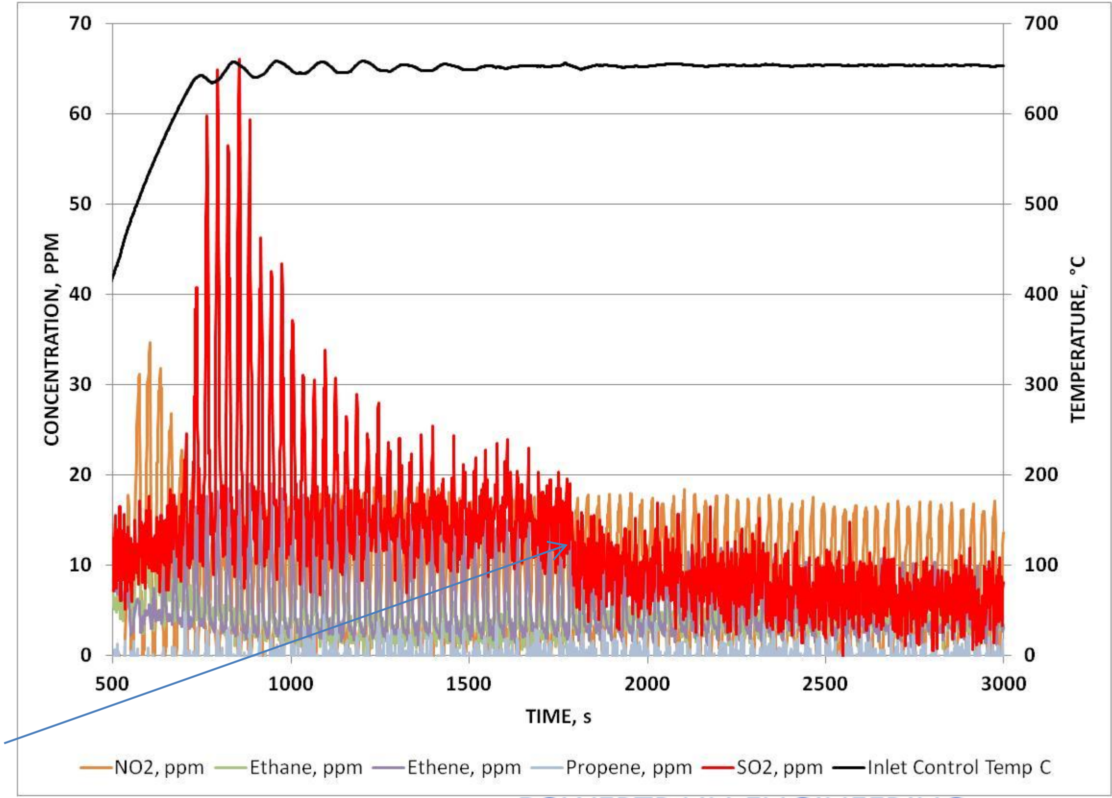


Desulfation

- Formulation A was Desulfated and Retested
  - Full gas mixture
  - Lean : Rich cycle – 20 s Lean : 10 s Rich
    - » Repeat until all evidence of sulfur desorption is gone (FTIR SO_2)
  - 650 ^{o}C catalyst inlet temperature
  - 45 mg/kg fuel sulfur equivalent in feed gases

Desulfation

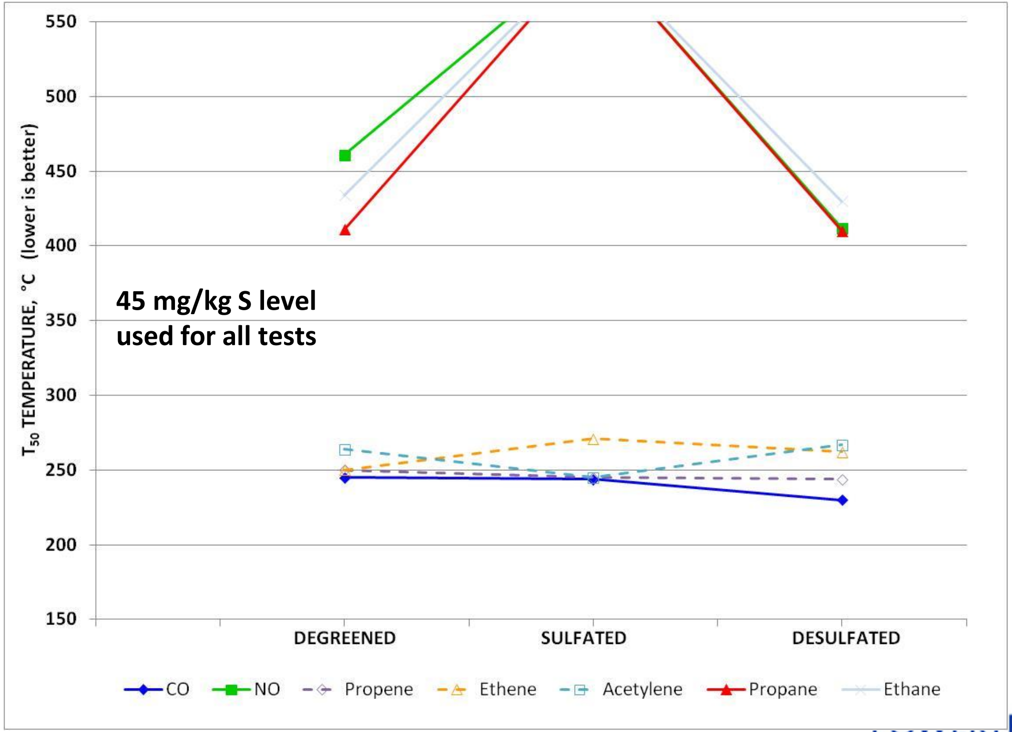
- Desulfation Began Above 600 °C
- Complete Desulfation in About 30 Minutes



SO_2 feed turned off

Effectiveness of Desulfation

- Formulation A was Effectively Regenerated by Desulfation

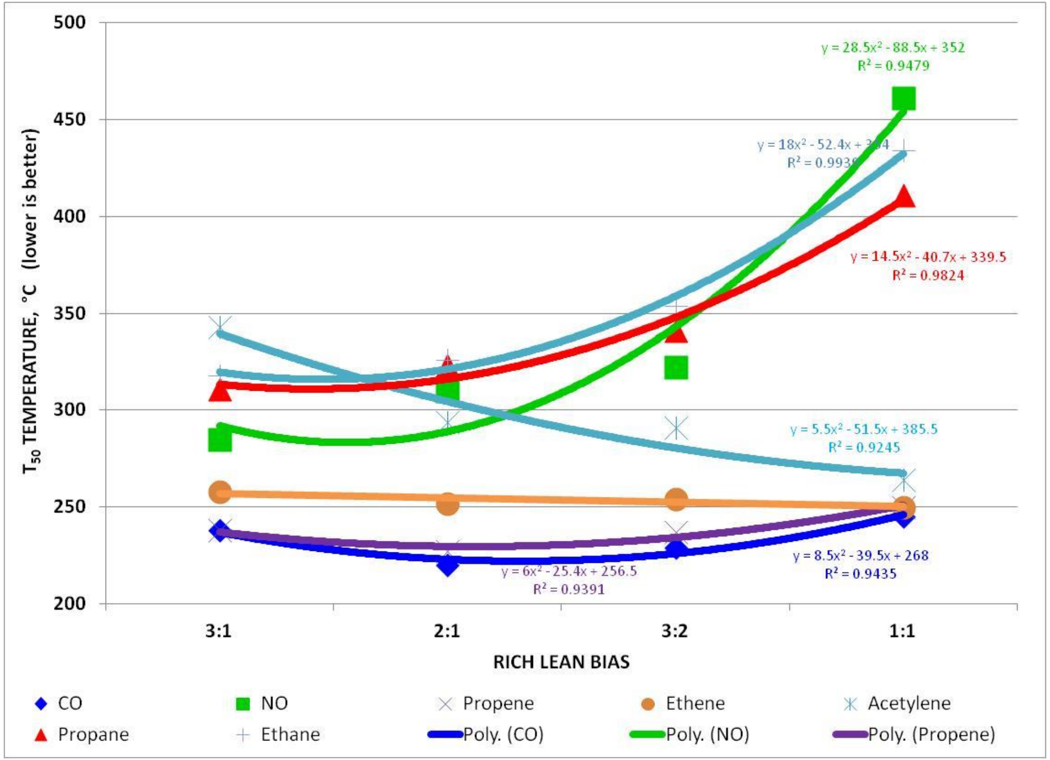


Rich Biasing of Cold Start

- Does a rich bias reduce light-off temperatures (especially NOx)?
- Tests Were Performed Using Formulation A at 45 mg/kg Fuel Sulfur Equivalent With Rich:Lean Perturbations of 3:1, 2:1 and 3:2

Rich Biasing of Cold Start

- Nitric oxide, Propane, Ethane Temperatures Decrease (good)
- Acetylene Temperatures Increase (worse)
- Applying a Rich Bias During Cold Start Can Significantly Improve Cold Start Emissions Performance
    - Even a small bias (R:L 3:2) is sufficient



Conclusions

- Both Formulations Exhibited Increased Light Off Temperatures for NO, Propane and Ethane (saturated hydrocarbons) as a Function of Sulfur Concentration
  - CO and unsaturated hydrocarbons were unaffected
- The Palladium/Rhodium Formulation A was Adversely Affected by Sulfur Exposure Aging
- The Platinum/Palladium/Rhodium Formulation B was Unaffected by Sulfur Exposure Aging
- Sulfur Poisoning was Reversible for Formulation A with a Desulfation
- Cold Start Emissions Performance Could be Improved by Employing a Slight Rich Bias

Questions?

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