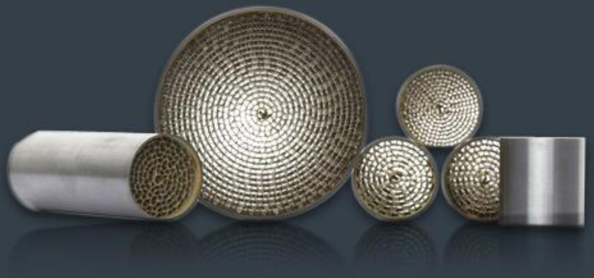
dedicated to innovative catalyst
research equipment that saves
resources and expenditure

cat·age·n

CATALYST AGEING TECHNOLOGY



Introduction

- Dr Andrew Woods (CEO of Catagen Ltd)

A Queen's University, Belfast Spin Out Business (Based in Northern Ireland)

SAE Snowmobile Chalk Talk:

– Aging and Characterisation of Catalytic Converters

Contents

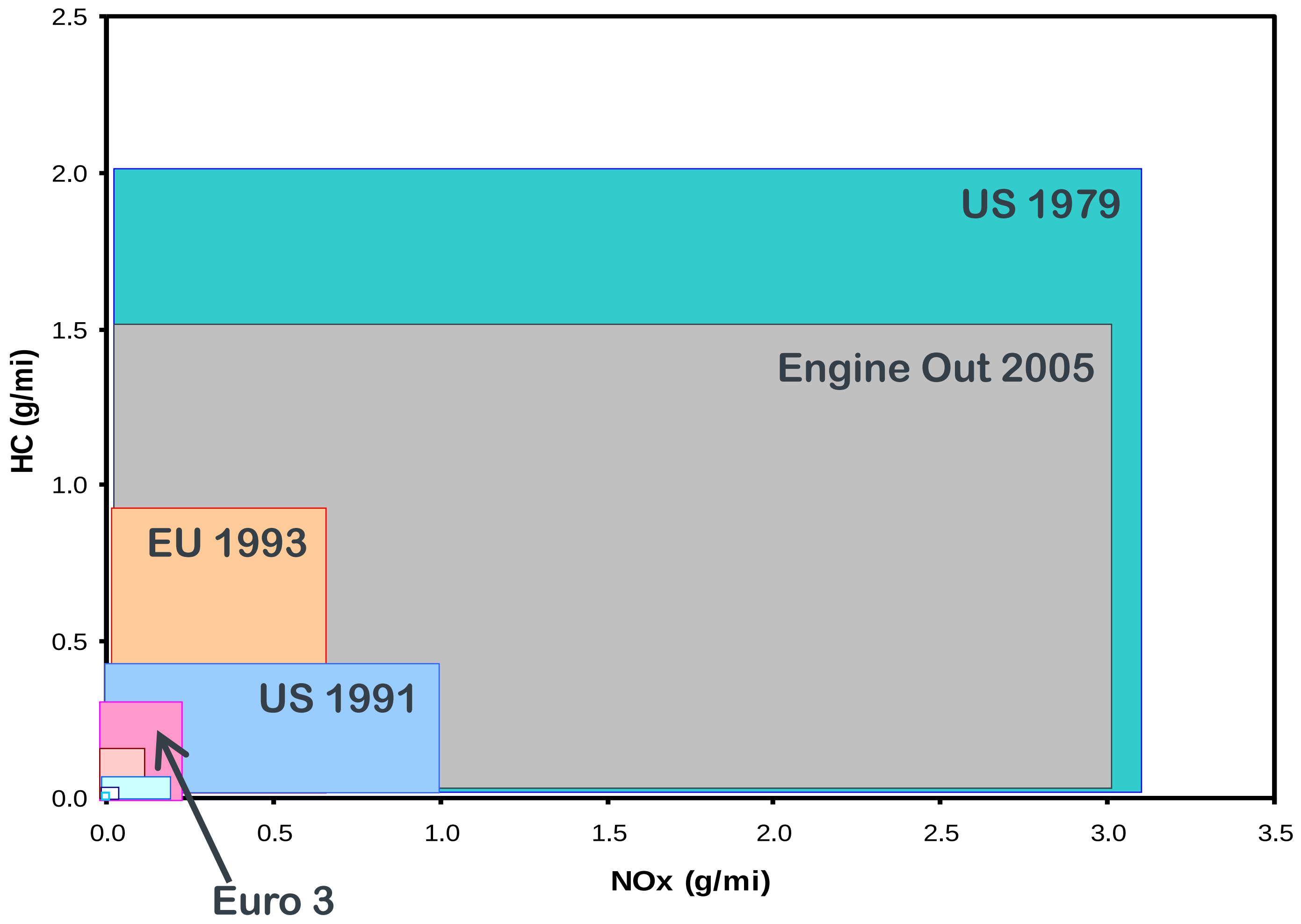
- Meeting the Challenge – Emissions Standards Worldwide
- History of Catalytic Converters and Government Legislation
- Emissions Durability in Recreational Vehicles
- Mechanisms of Catalyst Deactivation
- History of Demonstrating Durability of Emission Systems
- Recreating Engine out Conditions Cost Effectively – Catagen
- Performance Testing/Characterization of Catalysts
- Conclusion

CATAGEN CATALYST AGEING TECHNOLOGY

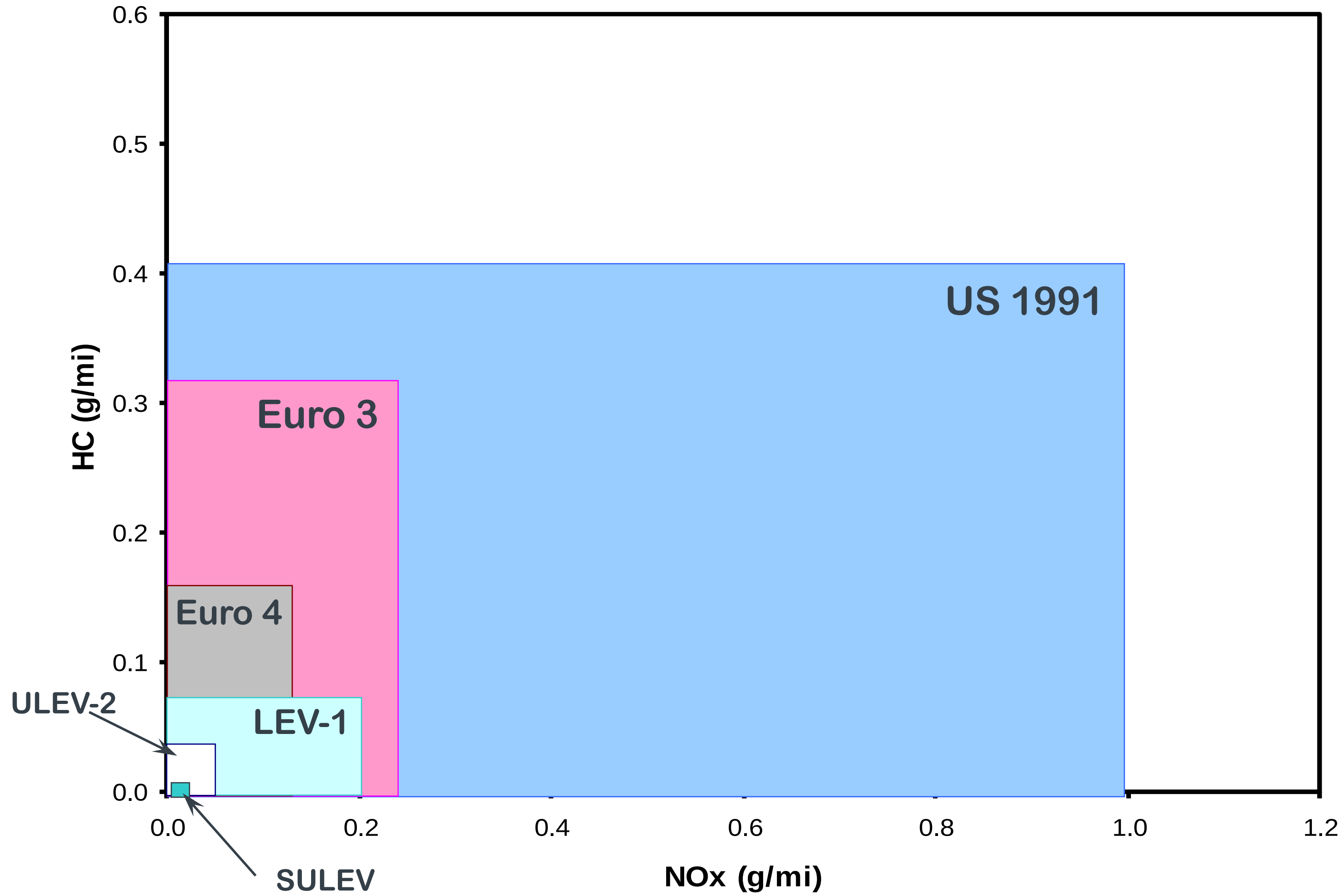
Meeting the Challenge

- To Meet Emissions Standards Worldwide
- Requires effective after-treatment (Catalytic Converter Systems) with reductions of :
    - 95% for US LEV 1
    - 96% for Euro 4
    - 98% for US ULEV 2
    - >99% for US SULEV
- **Durability of Emissions Applied**
    - LEV & ULEV at 50,000 miles
    - U.S. Tier2 = LEV2 and **ULEV2 at 120,000 miles**
    - SULEV at 120,000 miles **(PZEV at 150,000 miles)**
- **SULEV & PZEV are toughest worldwide**

Emissions History



A Closer Look



The Basics - TWC

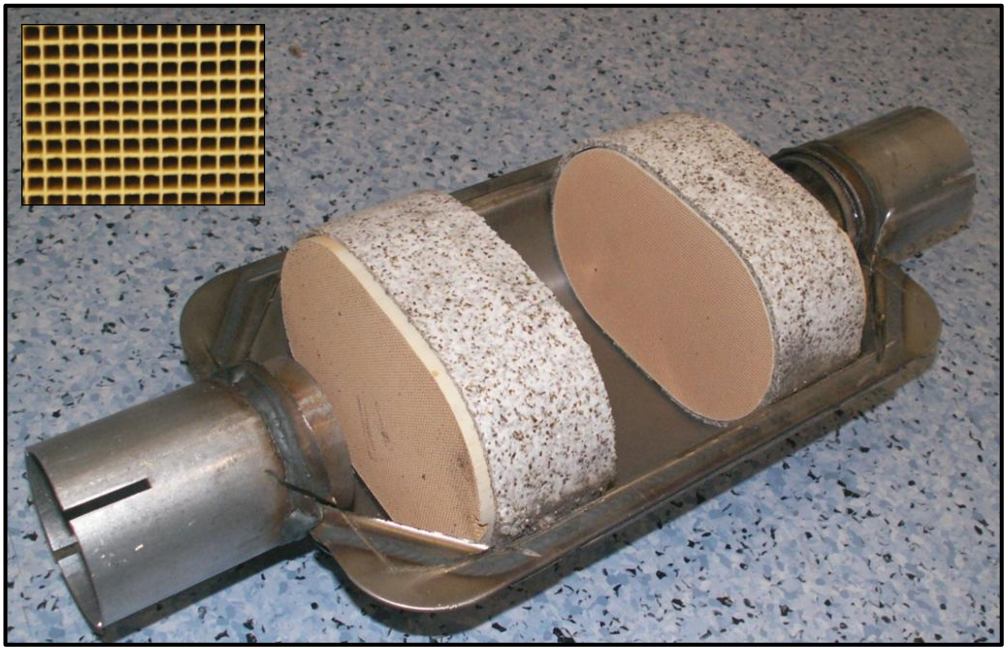


Figure 3: Three-Way Catalytic Converter in Open Can With Matting

Basic Global Reactions in a TWC

$$NO_X + \mathrm{Re}\,duction \xrightarrow{Pt\&Rh} N_2 + Other$$

$$SlowHC + Oxidation \xrightarrow{Pt\&Pd} xCO_2 + yH_2O$$

$$CO + Oxidation \xrightarrow{Pd\,Pt\&Rh} CO_2$$

$$FastHC + Oxidation \xrightarrow{Pt\&Pd} xCO_2 + yH_2O$$

Fresh Catalyst

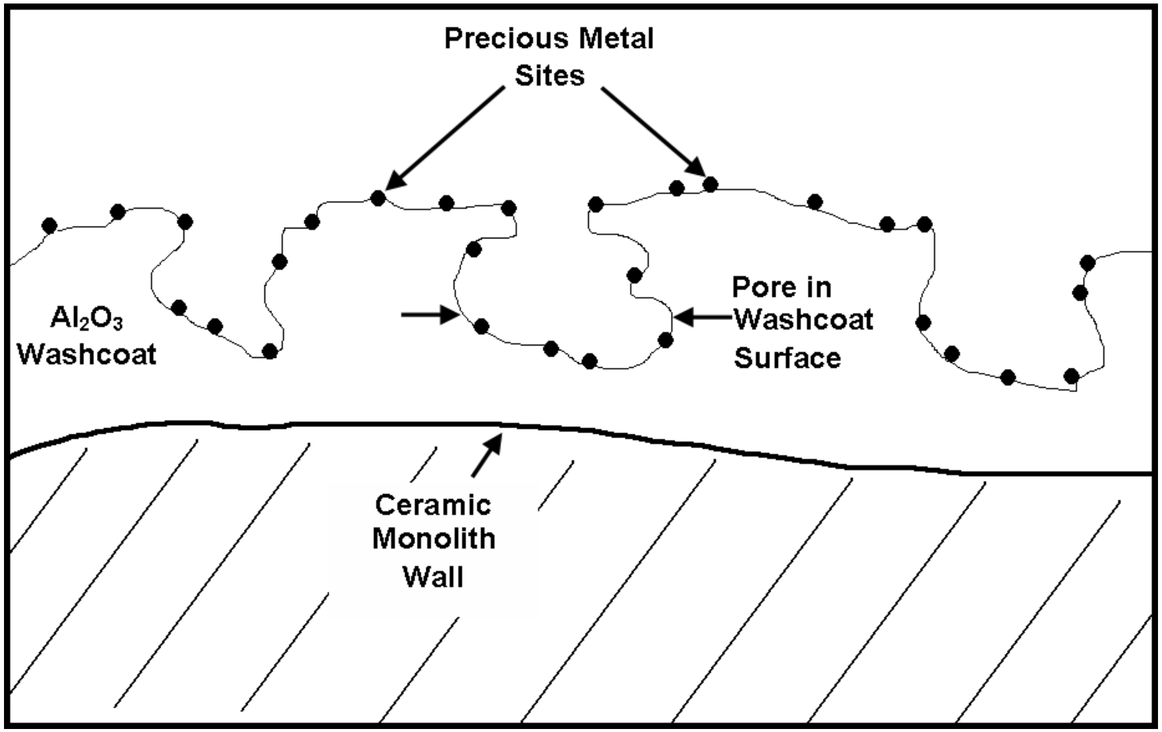


Figure 4: Conceptual Model of Catalytic Sites on Washcoat Bonded to a Monolith

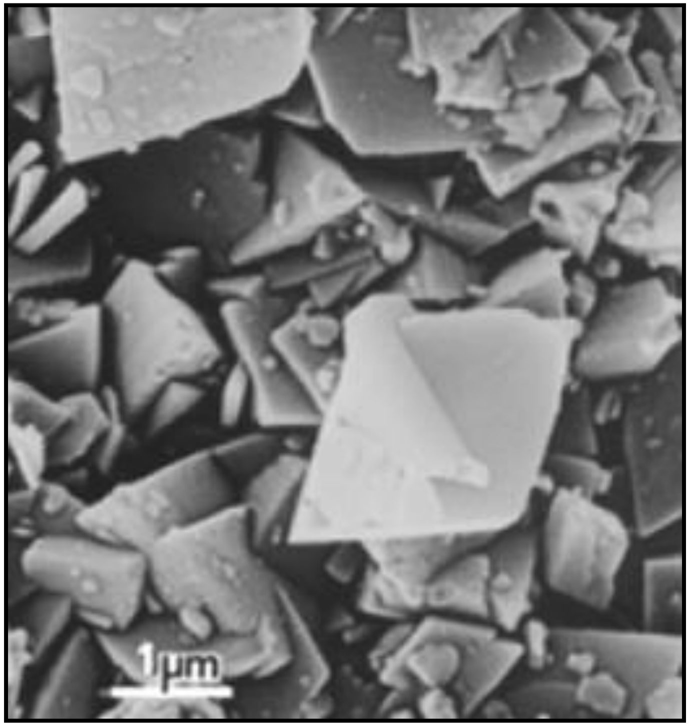


Figure 5: SEM Micrograph of Fresh Catalyst

Catalyst Deactivation

Factors Affecting Catalyst Deactivation:

- – Temperature effects on catalyst – Thermal Deactivation US-EPA Recognise this contributing 95% of total degradation
- – Poisoning of Catalyst (Contaminants in Fuel)
- – Fouling of Catalyst (Combustion Related Contaminants – Soot/Oil)
- – Structural breakdown of catalyst (Mechanical Shock)

Thermal Effects

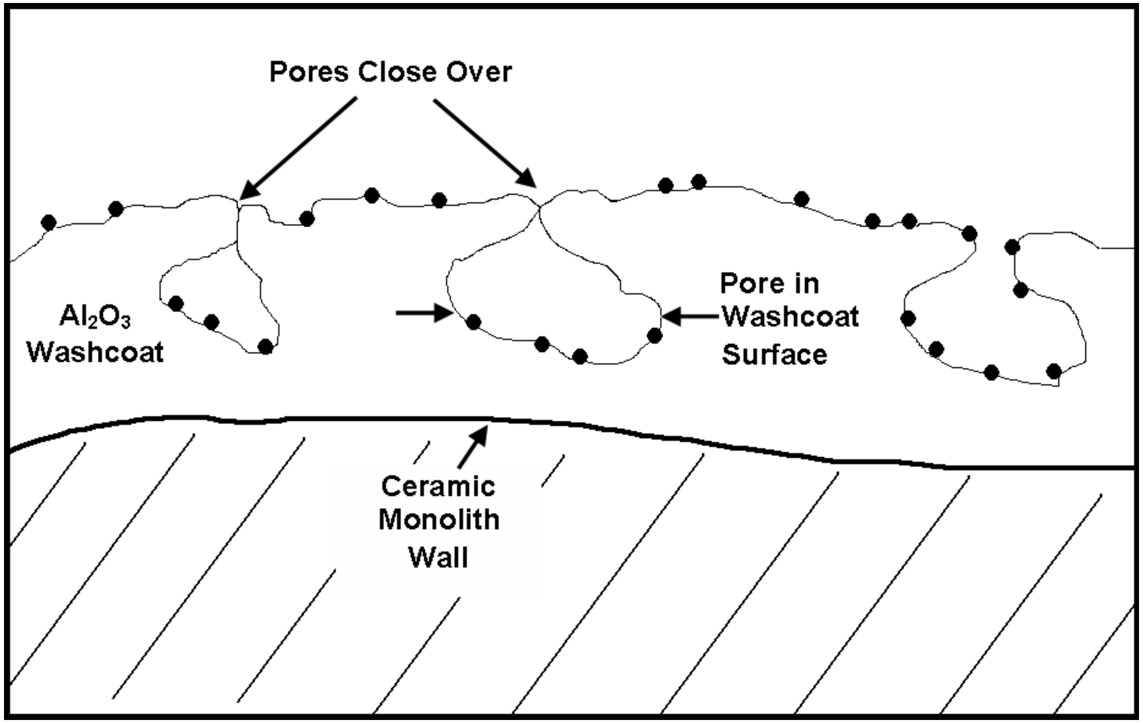


Figure 6: Conceptual - Phase Changes in Washcoat – Thermal Effects

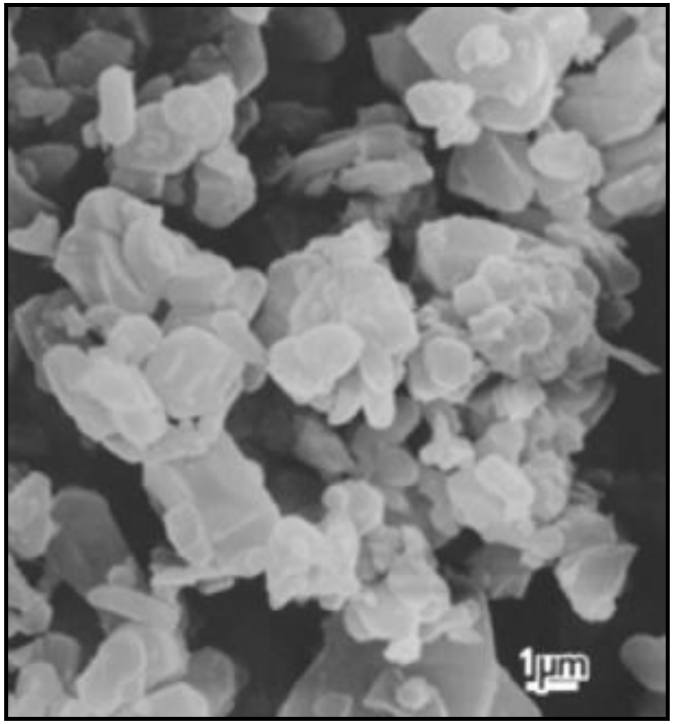


Figure 7: SEM Micrograph Alpha Alumina, α-Al2O3

Thermal Effects

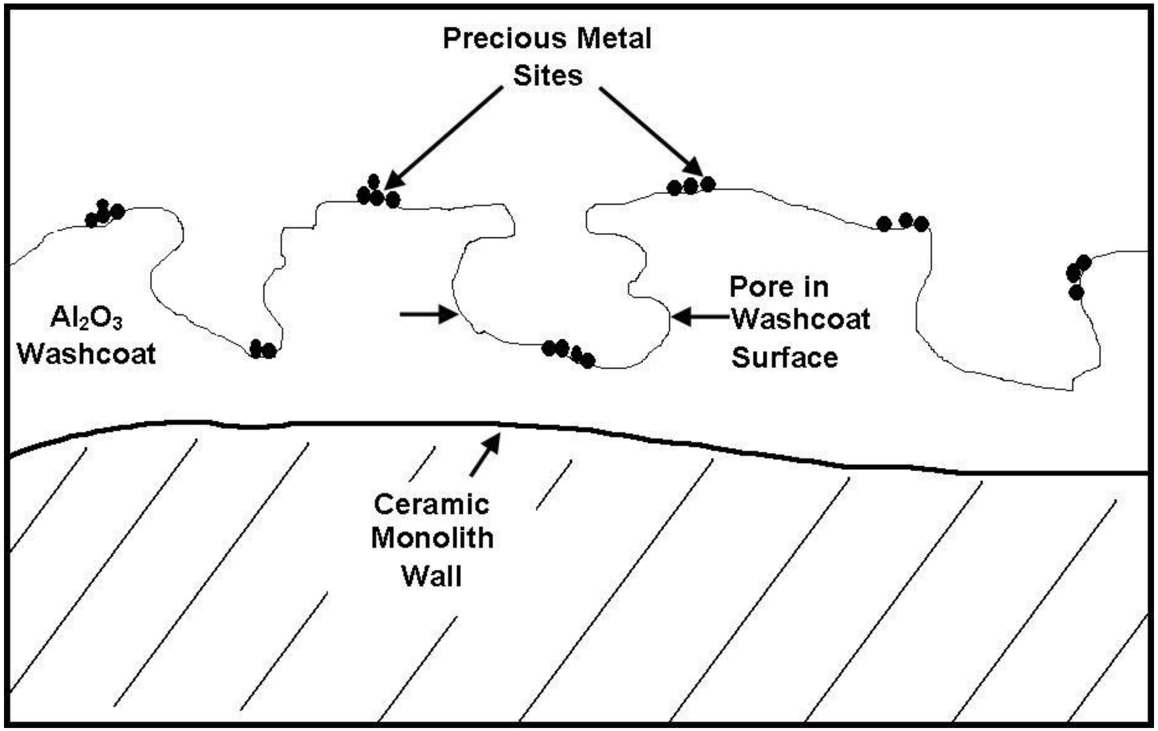


Figure 8: Conceptual -Thermal Sintering of Precious Metal

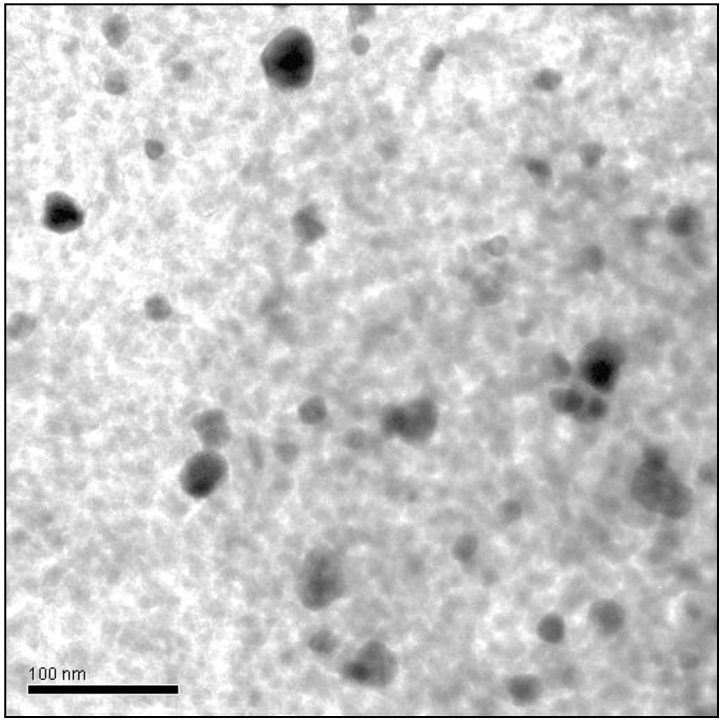


Figure 9: TEM Micrograph of PM Sintering

Fouling of Catalyst

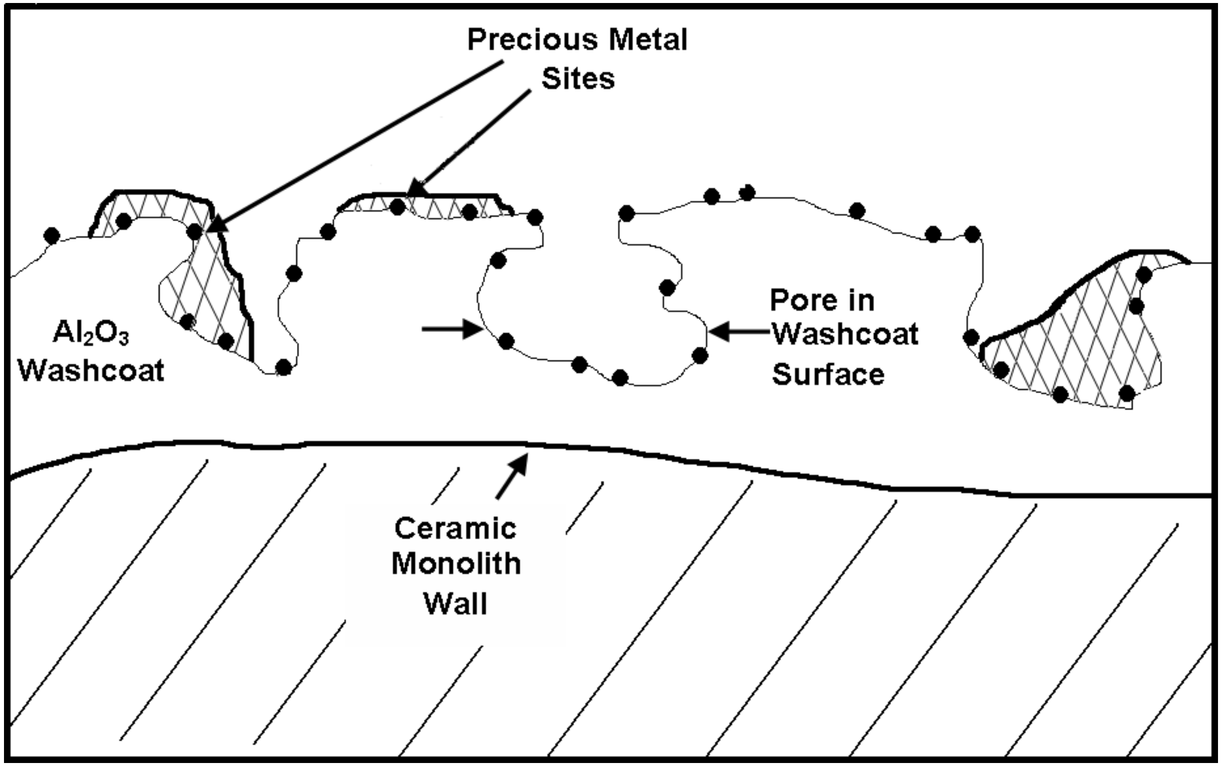


Figure 10: Conceptual –Fouling /Masking of Precious Metal – Heavy Contaminants – Unburnt Oil Etc

catagen
CATALYST AGEING TECHNOLOGY

Catalyst Poisoning

Trace Contaminants Found in Fuel – Cause Alloying and Poisoning of Precious Metals:

- Phosphorous (*P*)
- Chlorine (*Cl*)
- Selenium (*Se*)
- Sodium (*Na*)
- Lead (*Pb*)
- Antimony (*Sb*)
- Cadmium (Cd)

Sulphur (*S*)
Arsenic (*As*)
Tellerium (*Te*)
Calcium (*Ca*)
Tin (*Sn*)
Mercury (Hg)

Fleet Data

Equating Fleet Data to Demonstrate Catalyst Durability for Legislation

Vehicle Fleet Histogram Data – Catalyst Temperatures

Equated to High Temperature Engine Test Cell Aging – Typically 800-1100C

USING US-EPA BAT EQUATION

Application of BAT

- Basic Integral Equation $$t_I = \int t_h \, e^{\left(-R/T_v\right)}$$

  Where t_h is the time at temperature T_v

- This can be applied to any drive cycle or other test
- t_I is then the temperature time integral characteristic of aging
- From this a new aging time t_e can be calculated at reference temp T_r
- This can also be used to match a specific bench ageing profile where
- Equivalent Bench Time $$t_e = t_I \, e^{\left(R/T_r\right)}$$

- For example 2500 hrs of FTP drive cycle on a PZEV vehicle matches to 80hrs of bench ageing at 800ºC

Snowmobile Emissions

Phase	Model year	Phase-in (percent)	Emission standards HC	Emission standards CO	Maximum limits HC	Maximum limits CO
Phase 1	2006	50	100	275		
Phase 1	2007–2009	100	100	275		
Phase 2	2010 and 2011	100	75	275		
Phase 3	2012 and later	100	see equation		150	400

From Regs

$$\mathit{Total\ Emissions} = \left(1 - \frac{HC}{150}\right) \times 100 + \left(1 - \frac{CO}{400}\right) \times 100 \geq 100$$

Or more simply

$$\mathit{Total\ Emissions} = \left(\frac{HC}{150} + \frac{CO}{400}\right) \leq 100\,\%$$

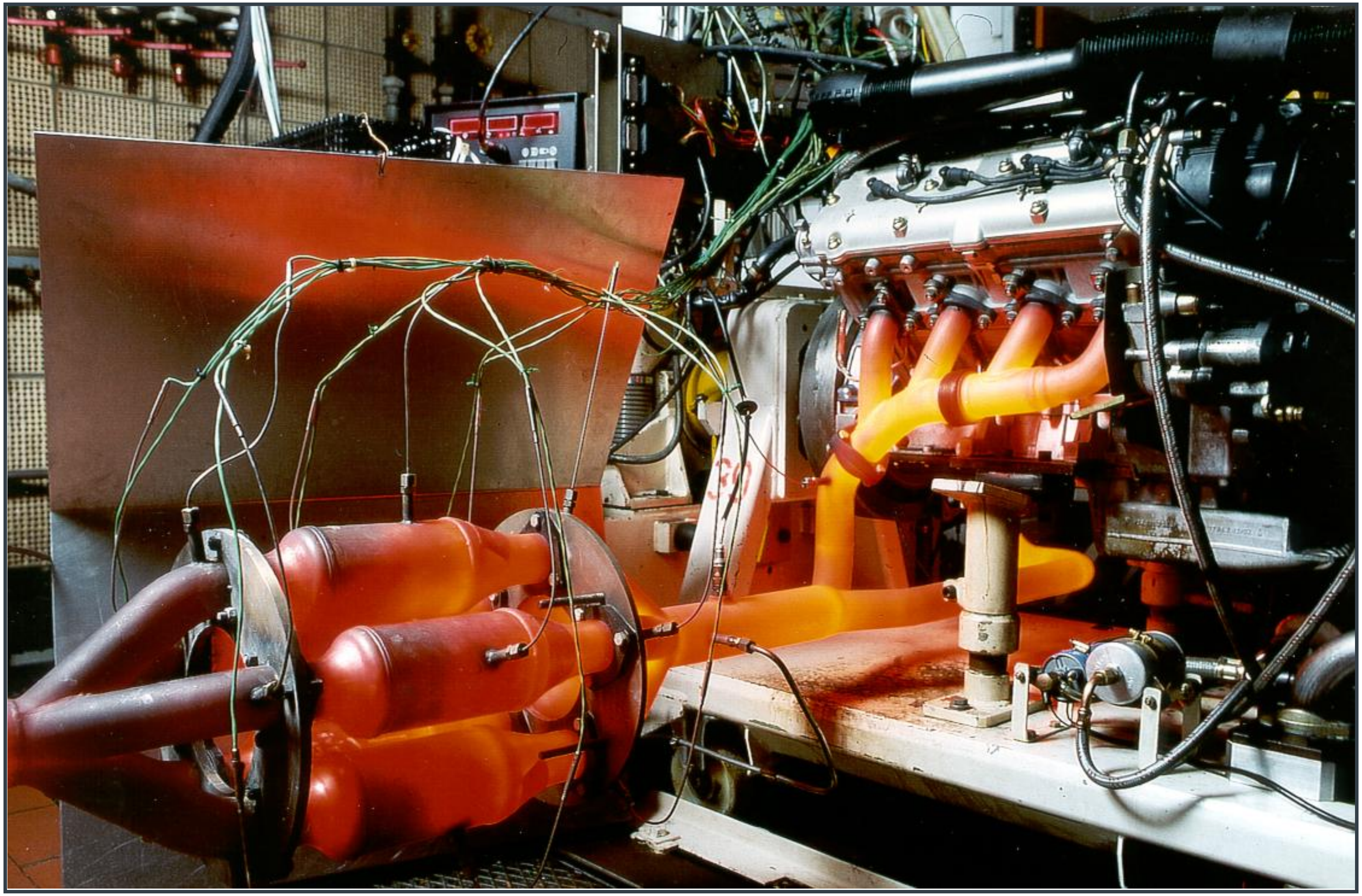
EPA Title 40 Part 1051: Control of Emissions from Recreational Engines and Vehicles
EPA: 40 CFR Parts 60, 63, et al. Control of Emissions from Nonroad Spark-Ignition Engines and Equipment; Proposed Rule 2007 - Emissions Durability Proposal

The Problem

The Issues:

- To Meet Ever Increasing Global Endurance Emissions Targets
- Catalysts need to be Constantly Improved
- Understanding of Deactivation Important to Assess And Improve Catalyst Formulations
- In House Endurance Testing Difficult and Costly
- On Road Catalyst Ageing – Dependant heavily on driving traits
- Dynamometer Ageing – Useful but Expensive!

The Problem



From: Emissions and Health Unit Institute of Environment and Sustainability EC-JRC Ispra

Alternative Solutions

Chamber Furnace Ageing:

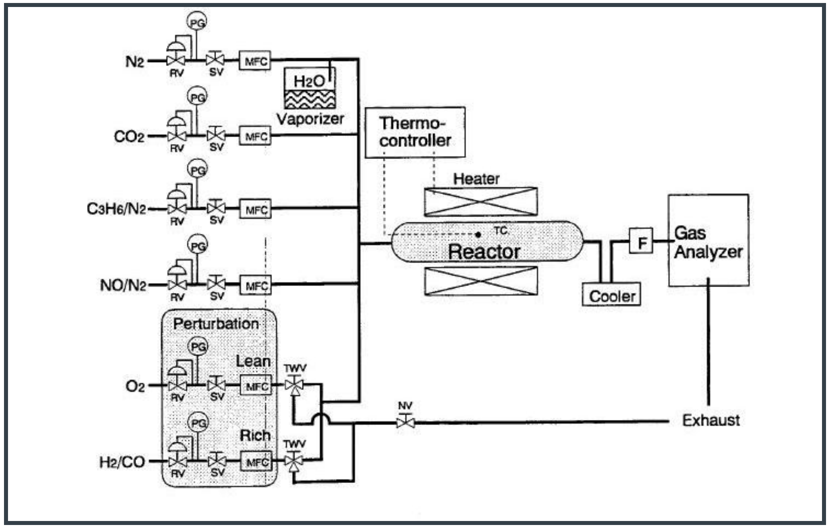
- Thermal Ageing
- Very Difficult to Equate to Road Ageing
- No Flow of Gases – Mostly carried out in air causes high degradation
- Low Cost

Examples:

QUB Chamber Furnace Ageing

Total Synthetic Gas Ageing:

- Typical Synthetic Gas Reactors
- Gas Exhausts to Vent
- Very Costly



SAE 960795

Examples:

Published work shows Ford, GM, JM and Research Institutions have all experimented with this

Alternative Solutions

FOCAS Burner Based Ageing:

- Spin Out Technology from SWRI – Texas
- Commercially Available
- Cost Saving Benefits

http://www.swri.org/4org/d03/engres/focas/aging/default.htm

Alternative Solutions

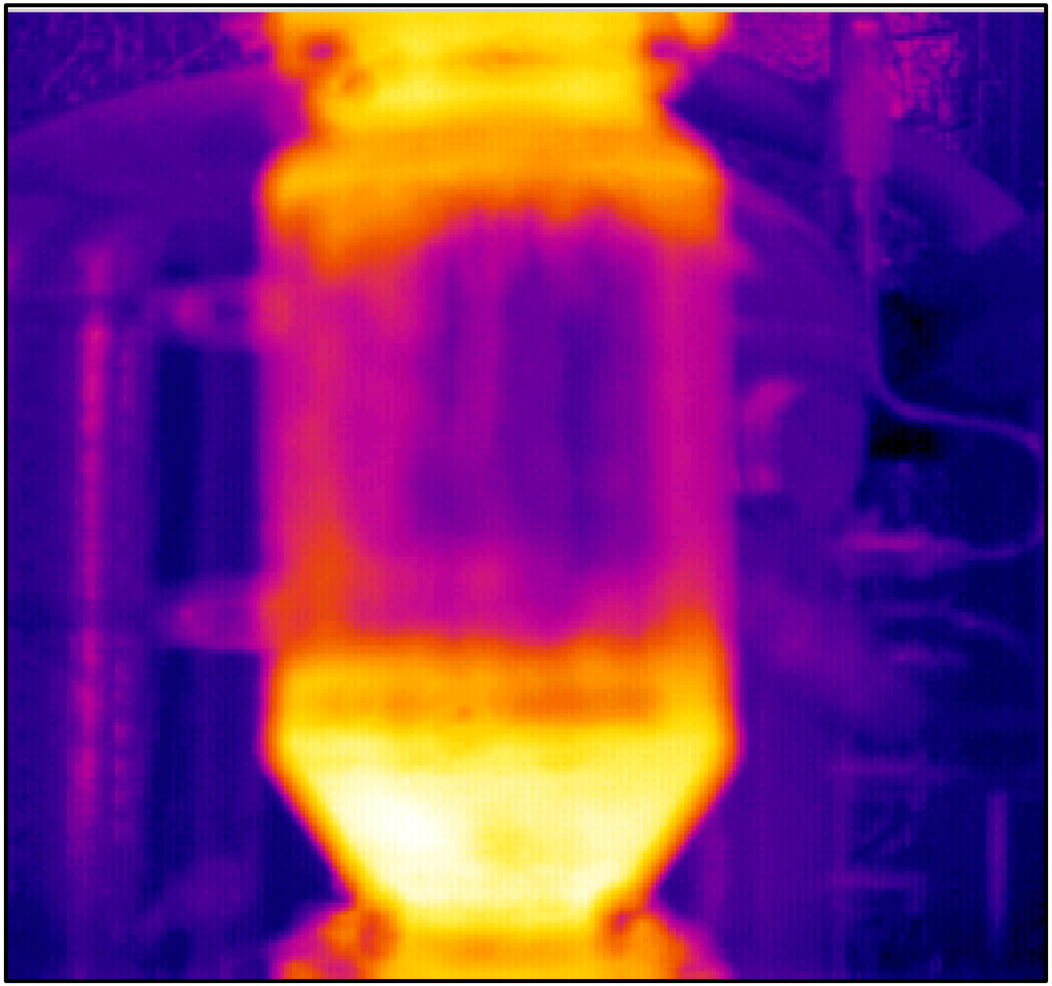
Other Burner Examples

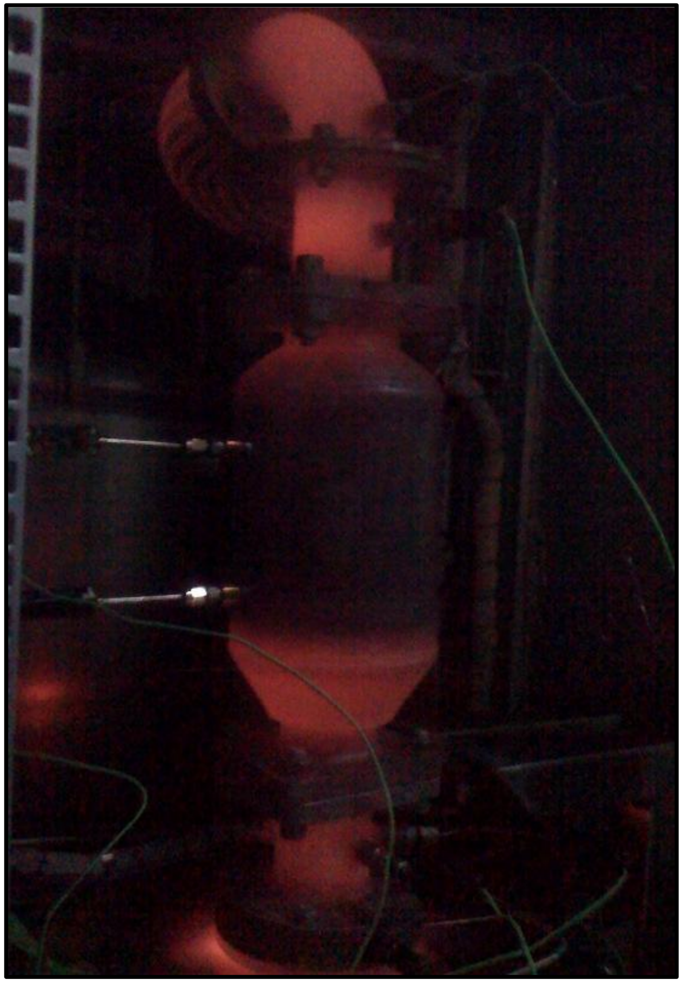
- FEV (Germany), Ford (US), and Schenck (Now Horiba) have all experimented with Burner Technology
- Schenck had offered it as a product in the past
- Queen's University, Belfast – Experimented with Burners in Late 90's – Control Issues (MSc Degree)
- Thermal Control Issue – Decided to Go Down another Research Route

Making economic and
environmental sense
of catalyst ageing

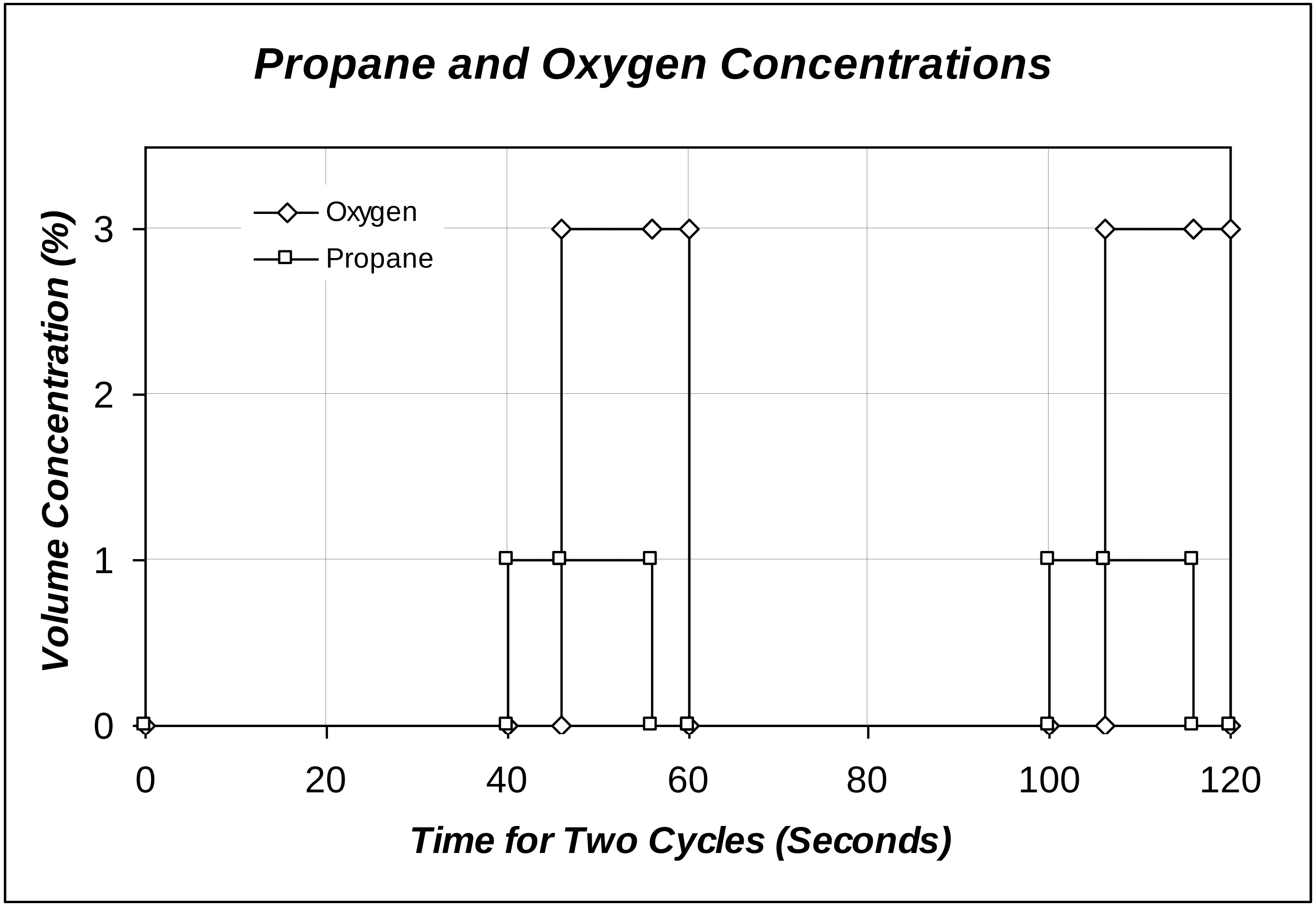

labcat
cat-age-n

Labcat Aging Cat



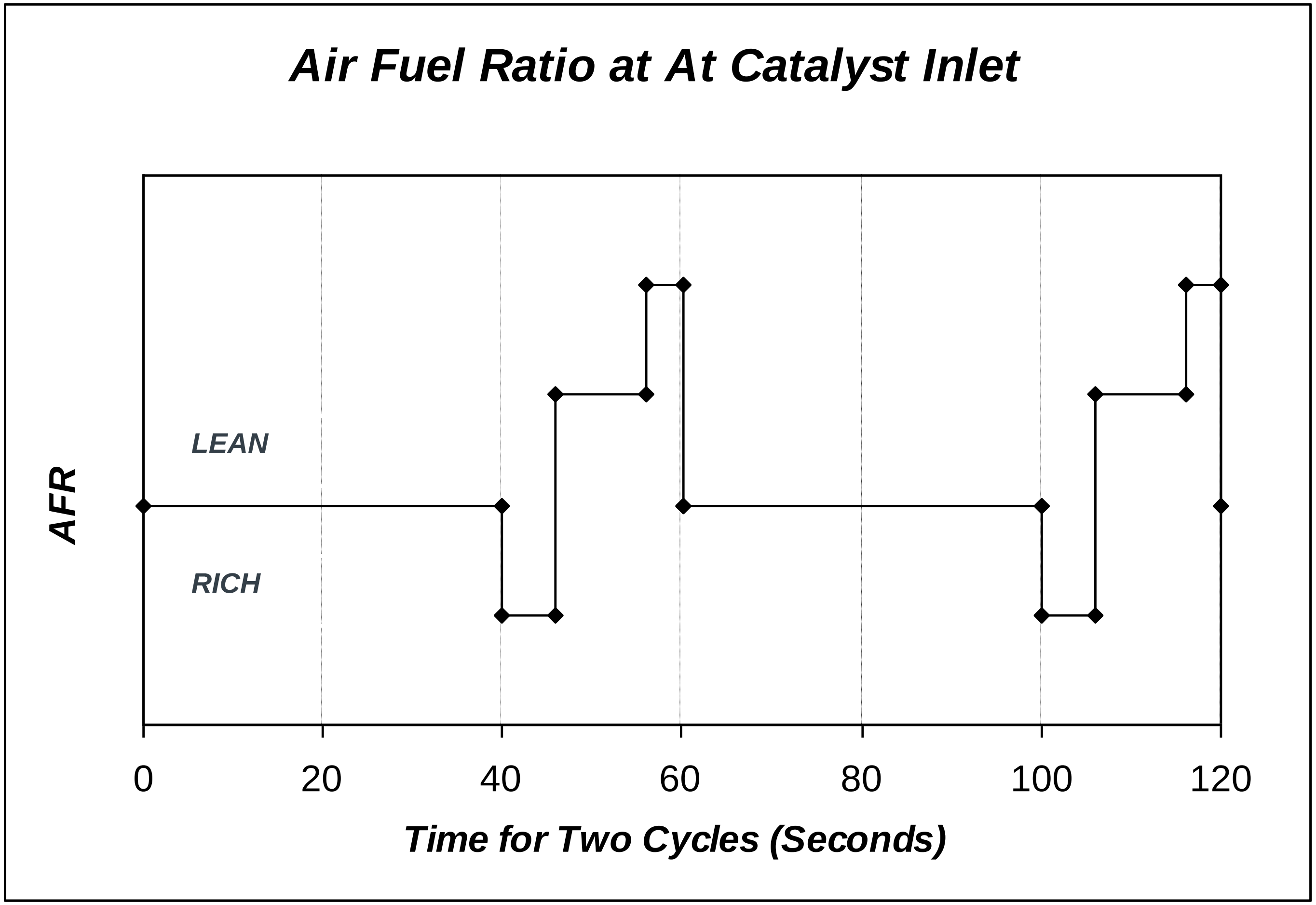


RAT Cycle

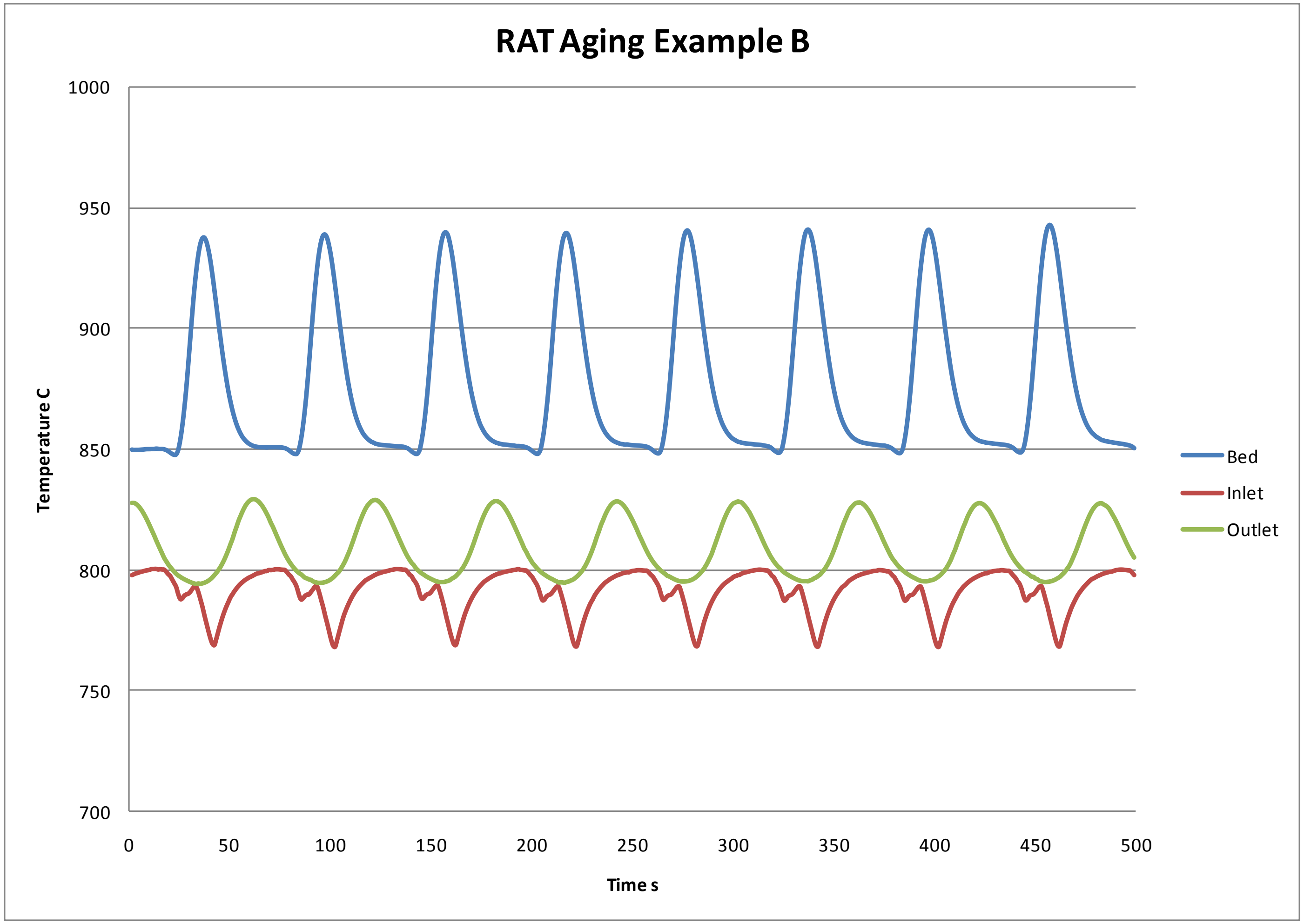


Propane and Oxygen Concentrations
Oxygen
Propane
Volume Concentration (%)
0
1
2
3
0
20
40
60
80
100
120
Time for Two Cycles (Seconds)

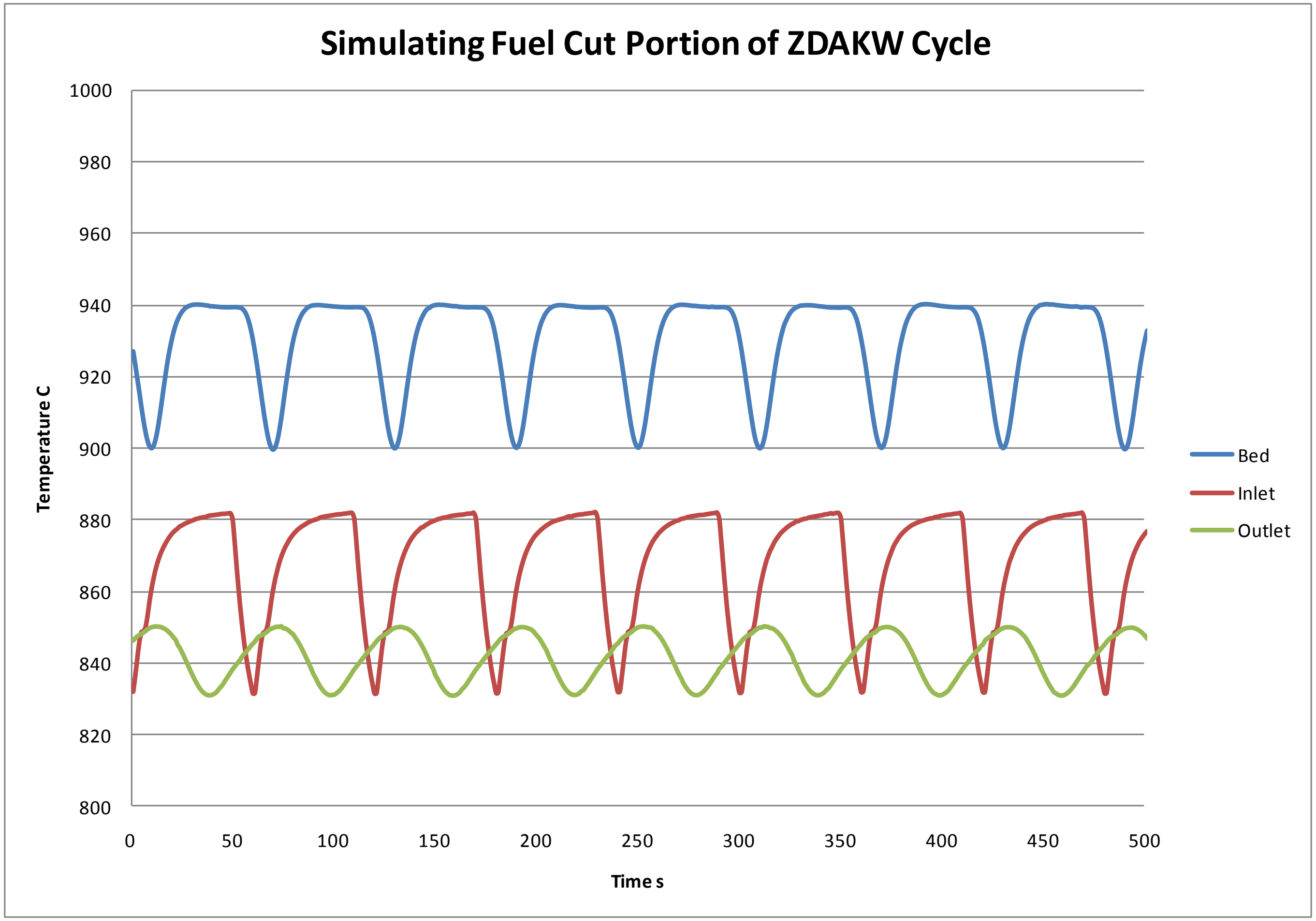
AFR RAT Cycle



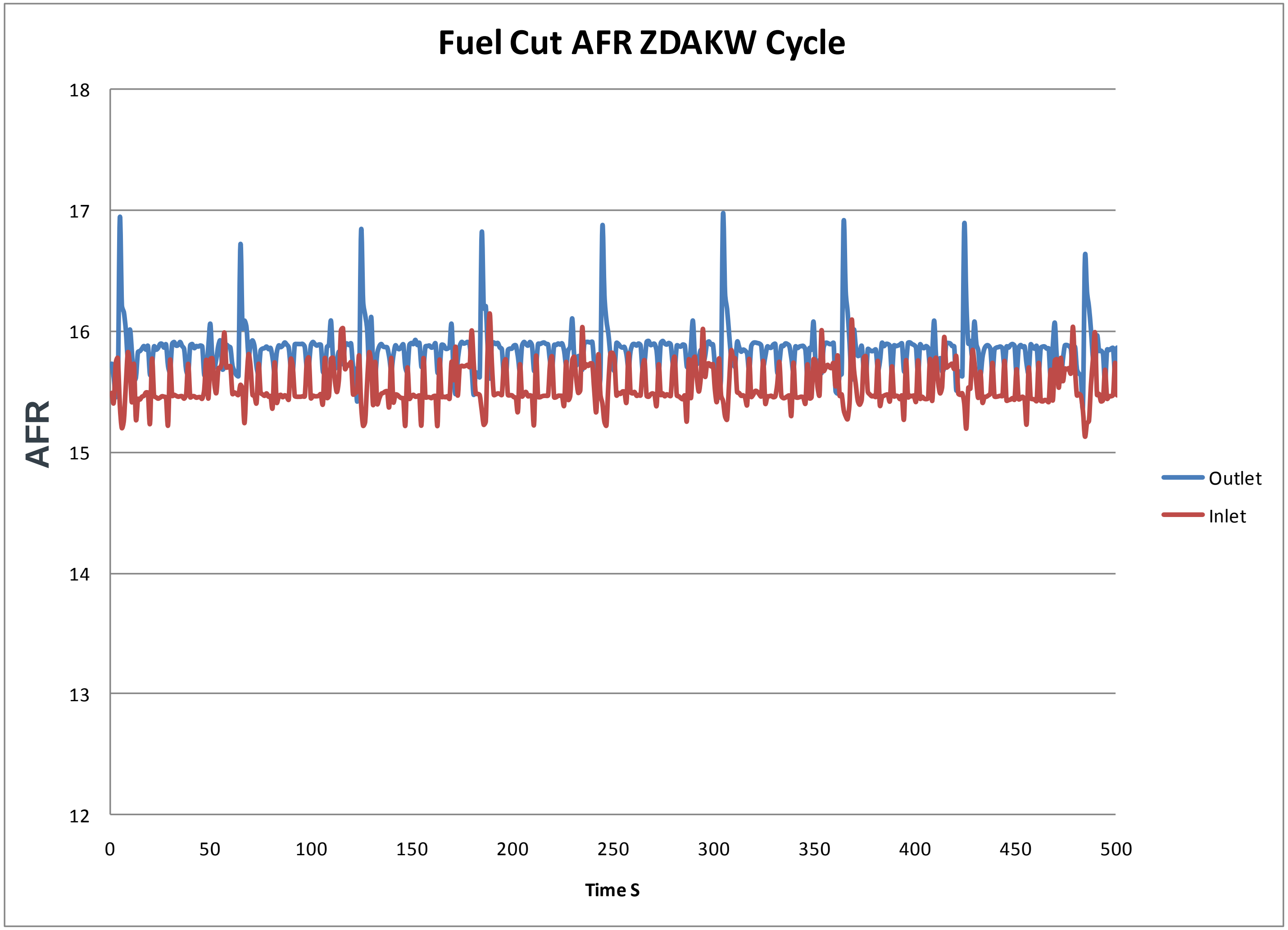
Aging Results



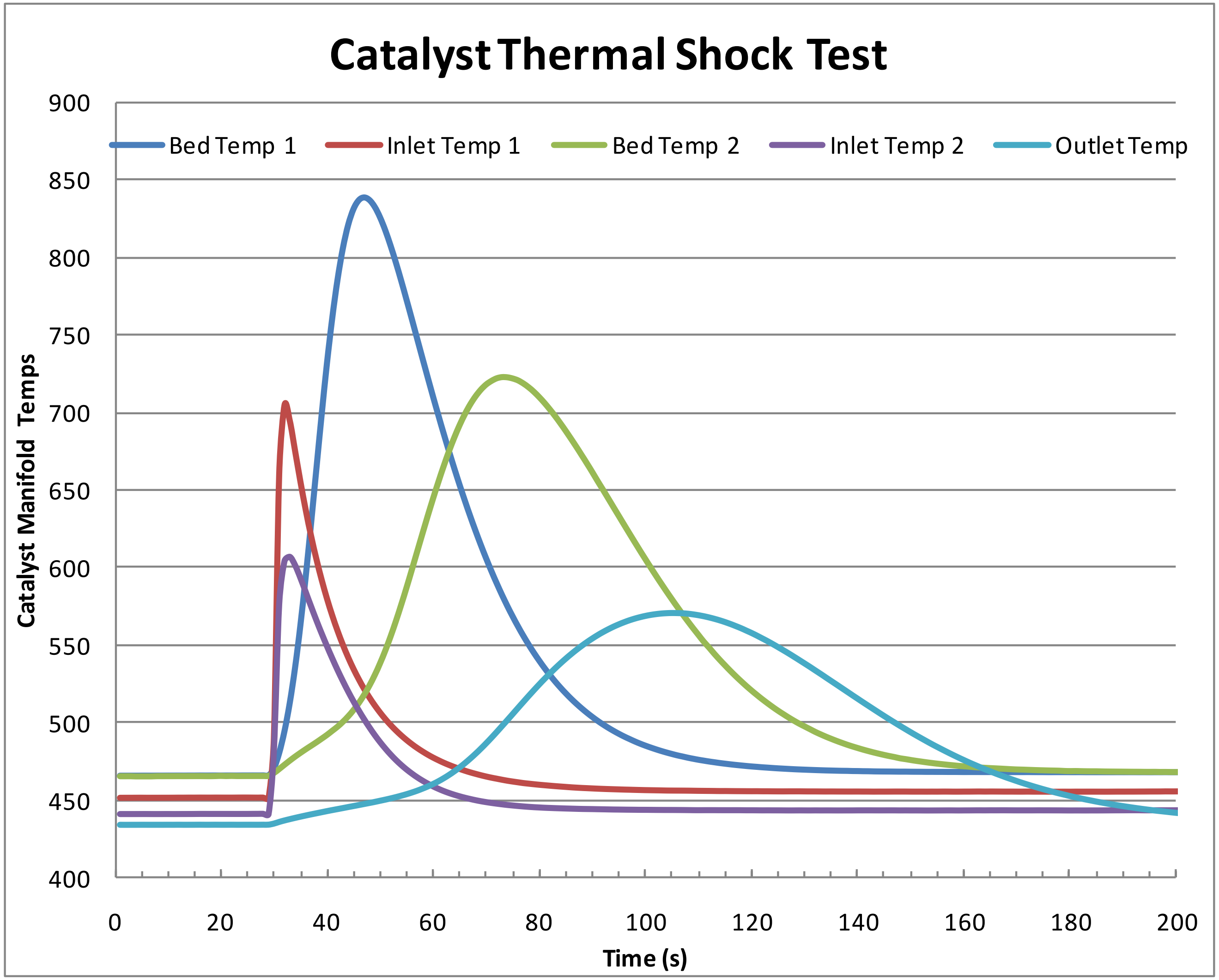
Aging Results



Aging Results



Thermal Shock

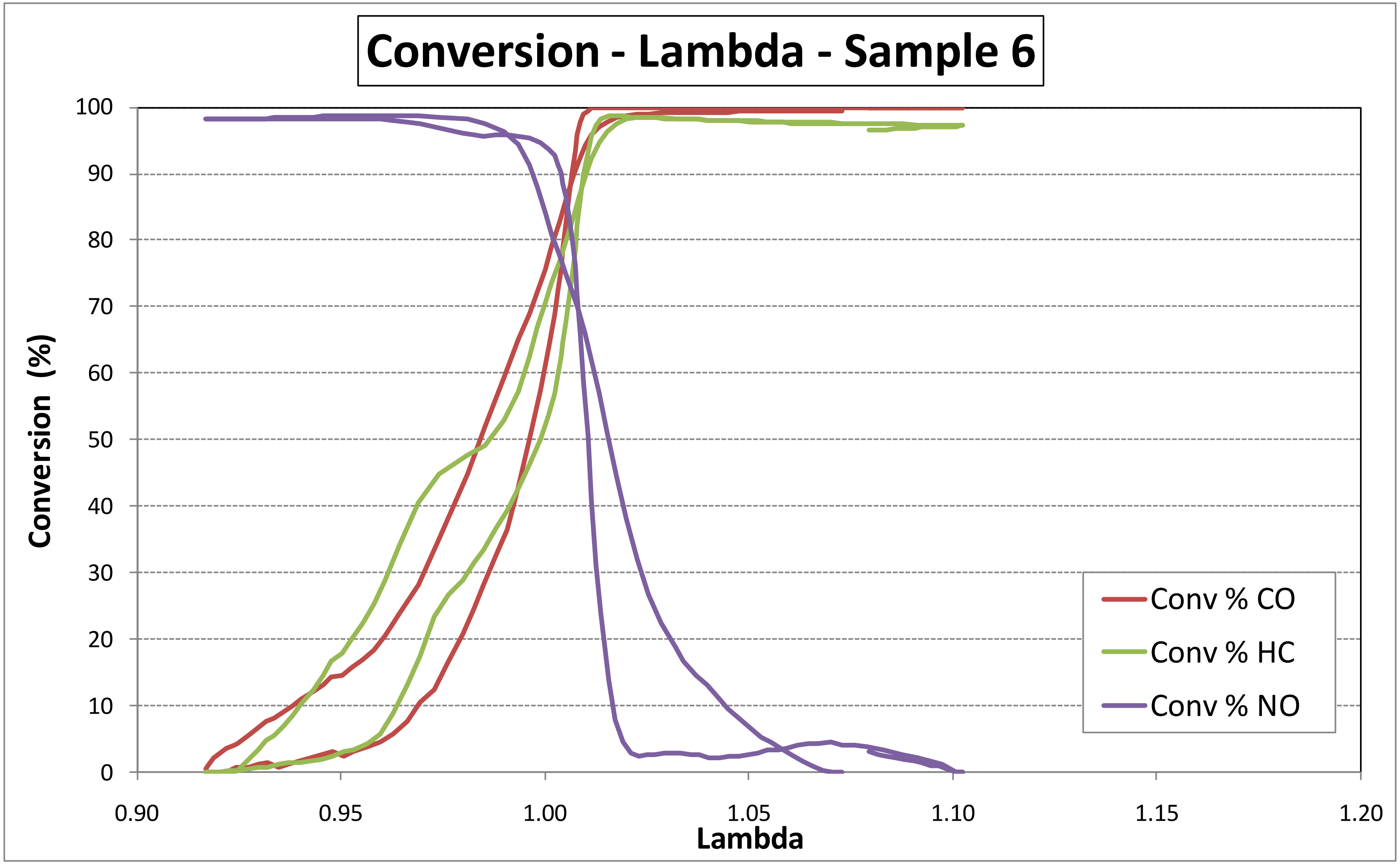


Catalyst Inlet Ramp Rate = 170ºC/Second

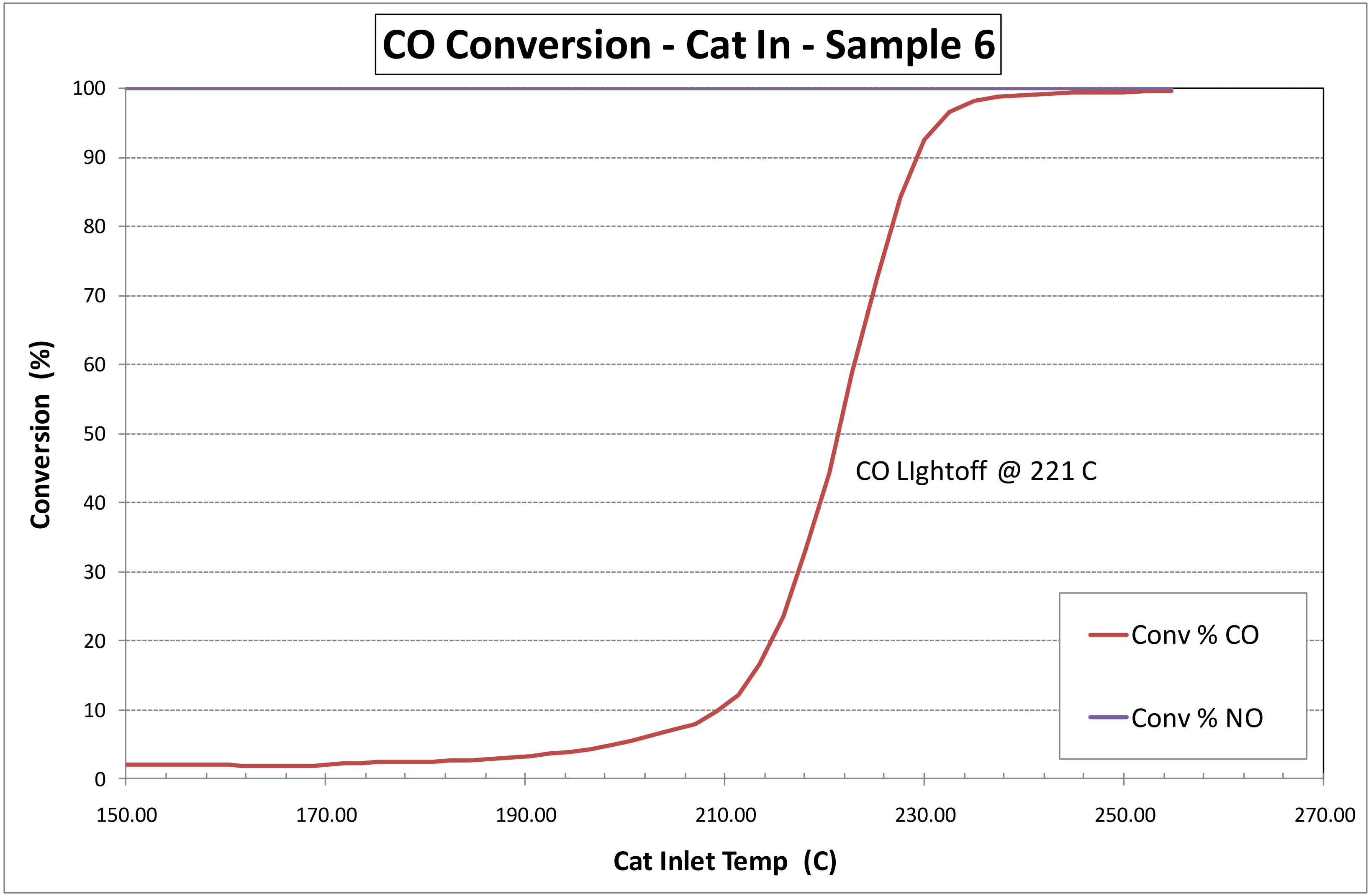
Performance Testing

catagen
CATALYST AGEING TECHNOLOGY

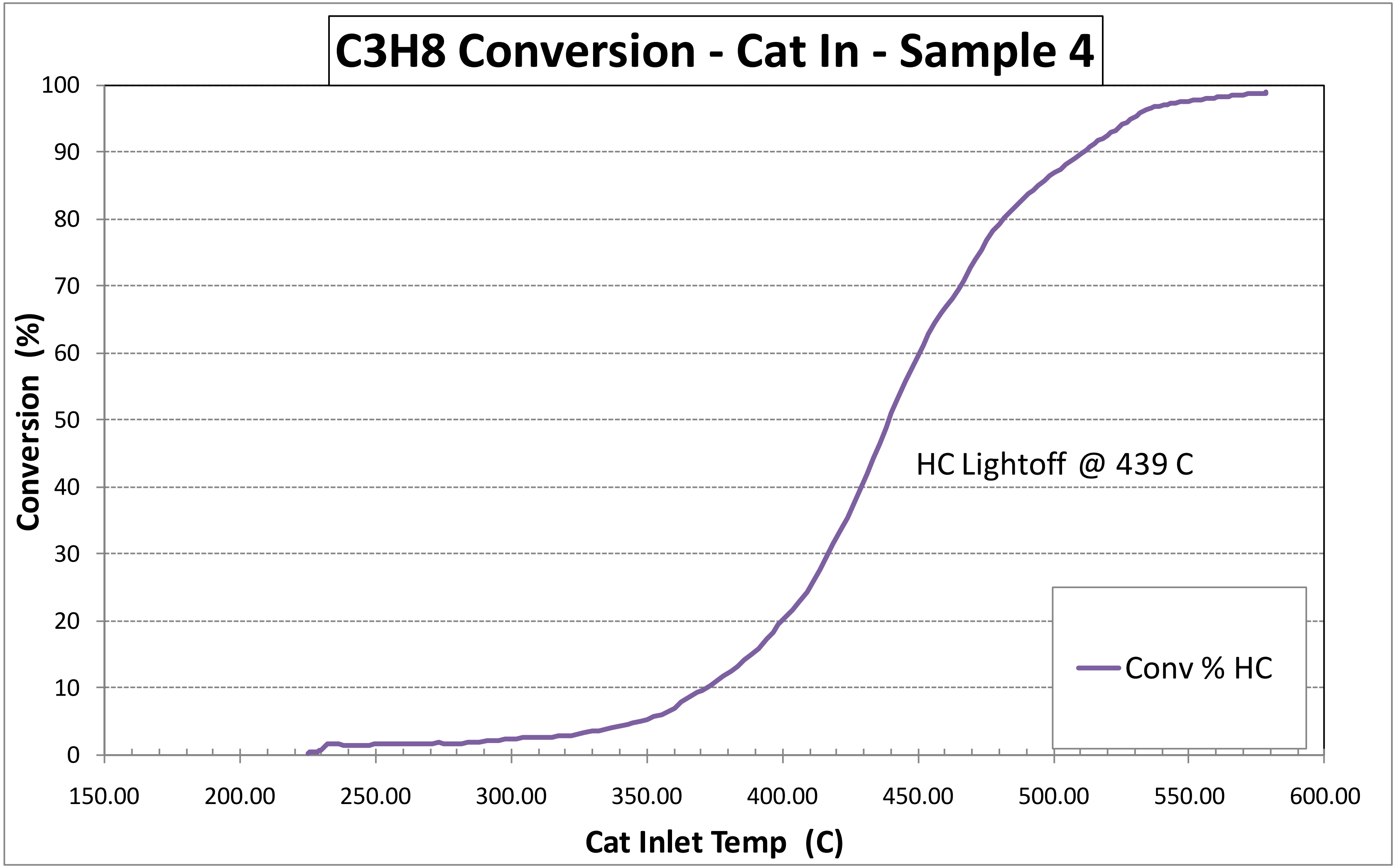
Sweep Test Sample



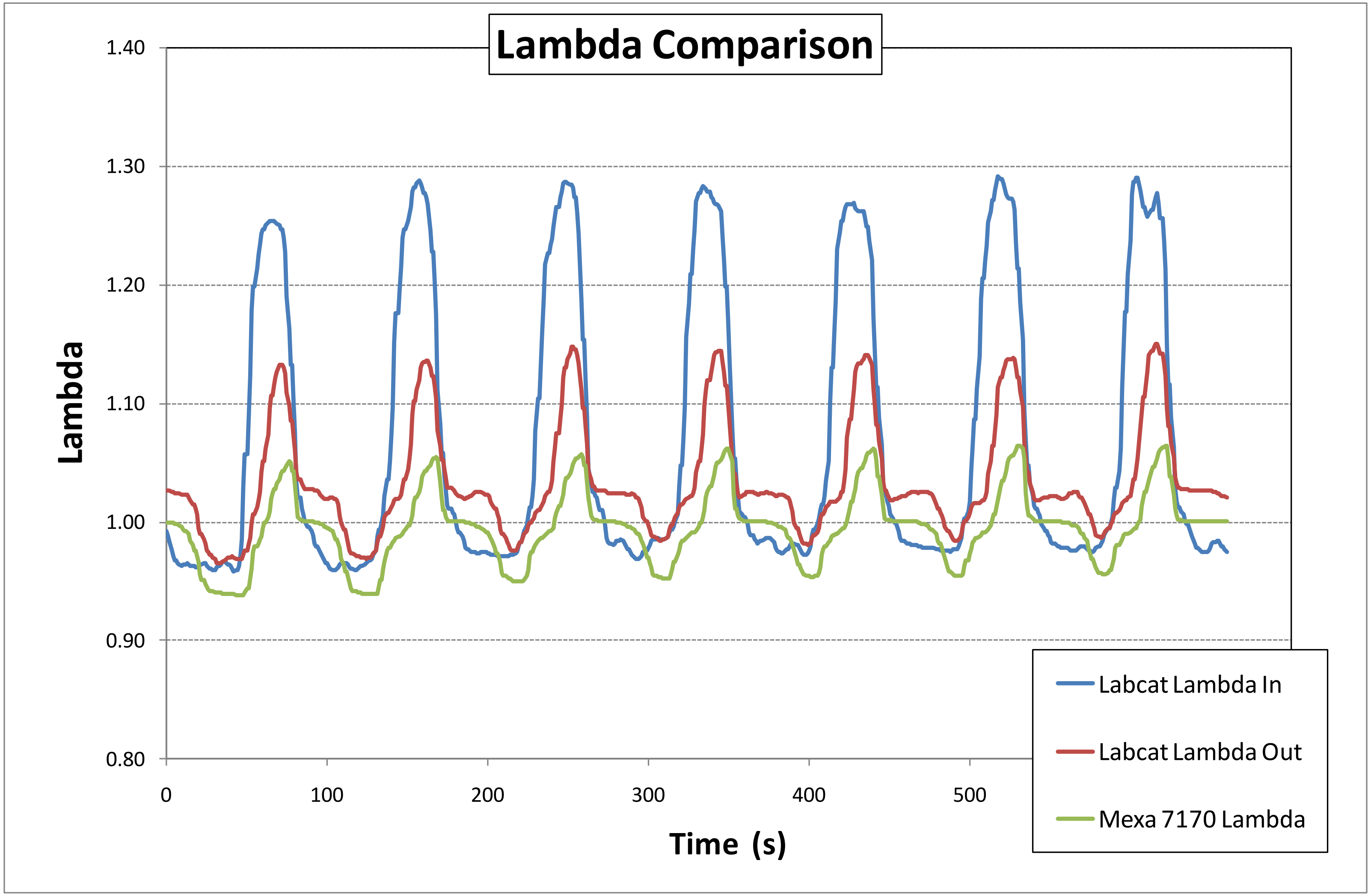
CO Lightoff Sample



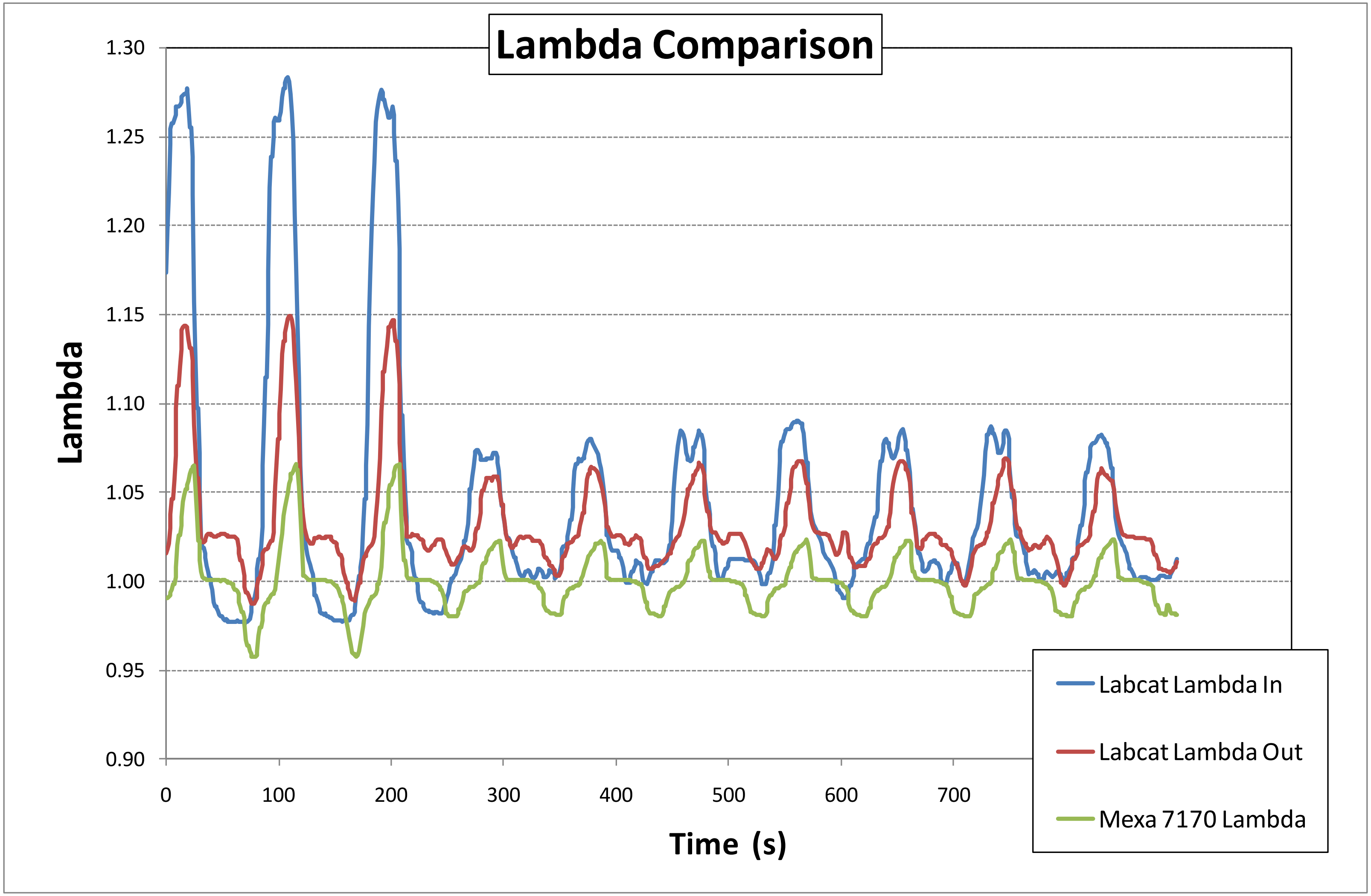
C3H8 Lightoff Sample



OSC Test Sample



OSC Test Sample



PRODUCT RANGE

MAXCAT 200g/sec

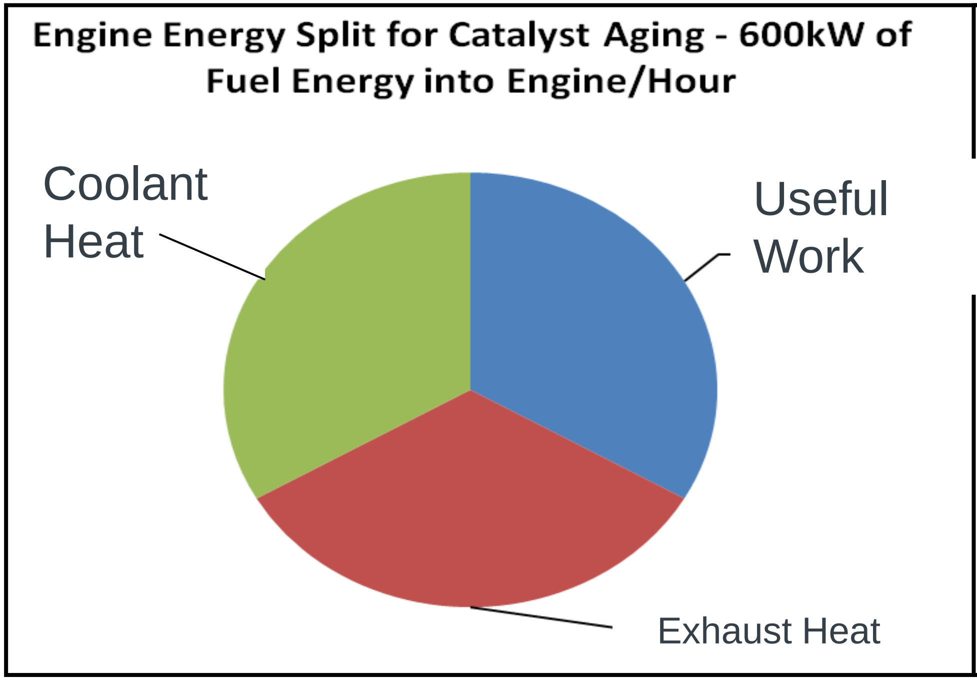
TESTCAT 50g/sec

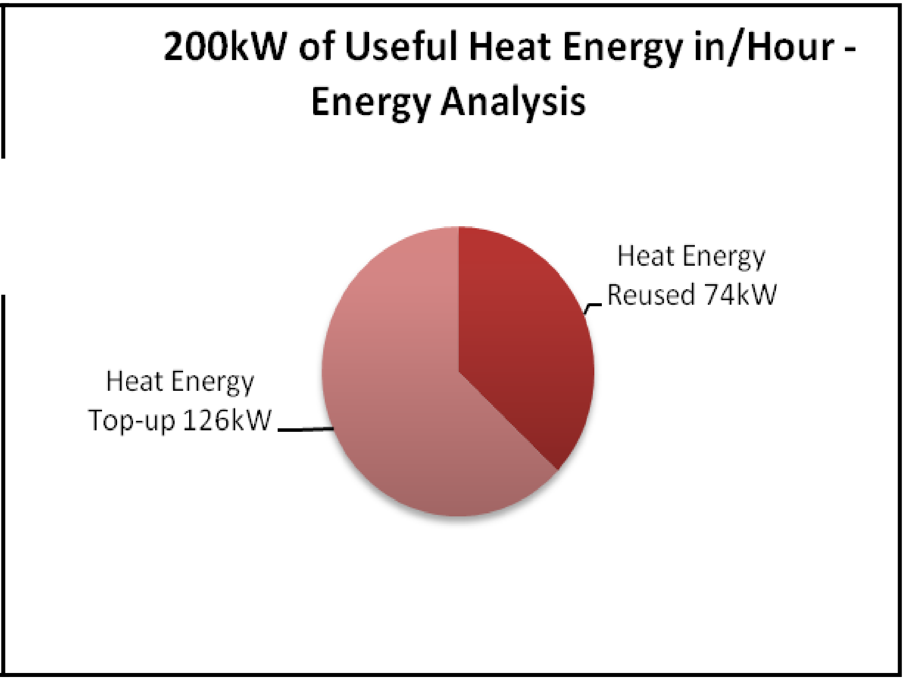
LABCAT 20g/sec Flow

ENERGY

MAXCAT EXAMPLE

- Removes the need for Gasoline & Energy Efficient!





Gasoline Energy **95% Electrical 5% Propane**

- Catagen systems require 80% less energy = Cost Savings! Typical Reduction in Operating Cost 70-85%

catagen CATALYST AGEING TECHNOLOGY

OTHER BENIFITS

- No Need for Engine Test Bed Facilities – Laboratory Environment (Cost)
- Estimated 1 Technician to Operate 3 Catagen Machines – Personnel Reduction
- Remote monitoring facilities/IPad Applications/Remote Alarms – SMS/Email
- Aging and Performance Carried out on Same System
- Highly Repeatable Tests, Easy Experimentation & Analysis
- 98% CO_2 Reduction at Source
- Safety TUV Certification, CE Marking, NFPA 79

SUMMARY

- Catalyst Durability a Key Component Global Air Quality
- Legislation:

  Faster Light-off Requirements

  Lower Emissions Levels

  Longer Durability Requirements

  Expanding into New Geographical Territories

  Expanding into Other Engine Applications (Beyond Auto)

  In Catagen – Developed a tool to aid the industry

CATALYST AGEING TECHNOLOGY

Thanks For Listening

‘And Good Luck to All the Teams Participating in SAE 2011’