dedicated to innovative catalyst research equipment that saves resources and expenditure
• 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
• 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
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

- US 1979
- Engine Out 2005
- EU 1993
- US 1991
- Euro 3
Basic Global Reactions in a TWC

\[ \text{NO}_x + \text{Reduction} \xrightarrow{\text{Pt&Rh}} \text{N}_2 + \text{Other} \]

\[ \text{SlowHC + Oxidation} \xrightarrow{\text{Pt&Pd}} x\text{CO}_2 + y\text{H}_2\text{O} \]

\[ \text{CO + Oxidation} \xrightarrow{\text{Pd, Pt&Rh}} \text{CO}_2 \]

\[ \text{FastHC + Oxidation} \xrightarrow{\text{Pt&Pd}} x\text{CO}_2 + y\text{H}_2\text{O} \]
Figure 4: Conceptual Model of Catalytic Sites on Washcoat Bonded to a Monolith

Figure 5: SEM Micrograph of Fresh Catalyst
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)
Figure 6: Conceptual - Phase Changes in Washcoat – Thermal Effects

Figure 7: SEM Micrograph Alpha Alumina, α-Al2O3
Figure 8: Conceptual -Thermal Sintering of Precious Metal

Figure 9: TEM Micrograph of PM Sintering
Figure 10: Conceptual – Fouling / Masking of Precious Metal – Heavy Contaminants – Unburnt Oil Etc
### Catalyst Poisoning

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

<table>
<thead>
<tr>
<th>trace contaminant</th>
<th>symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorous</td>
<td>$P$</td>
</tr>
<tr>
<td>Sulphur</td>
<td>$S$</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$Cl$</td>
</tr>
<tr>
<td>Arsenic</td>
<td>$As$</td>
</tr>
<tr>
<td>Selenium</td>
<td>$Se$</td>
</tr>
<tr>
<td>Tellerium</td>
<td>$Te$</td>
</tr>
<tr>
<td>Sodium</td>
<td>$Na$</td>
</tr>
<tr>
<td>Calcium</td>
<td>$Ca$</td>
</tr>
<tr>
<td>Lead</td>
<td>$Pb$</td>
</tr>
<tr>
<td>Tin</td>
<td>$Sn$</td>
</tr>
<tr>
<td>Antimony</td>
<td>$Sb$</td>
</tr>
<tr>
<td>Mercury</td>
<td>$Hg$</td>
</tr>
<tr>
<td>Cadmium</td>
<td>$Cd$</td>
</tr>
</tbody>
</table>
Equating Fleet Data to Demonstrate Catalyst Durability for Legislation

Vehicle Fleet Histogram Data – Catalyst Temperatures
Equated to High Temperature Engine Test Cell Aging – Typically 800-1100°C

USING US-EPA BAT EQUATION
Application of BAT

- Basic Integral Equation
  \[ t_I = \int t_h \, e^{(-R/T_v)} \]
  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
  \[ t_e = t_I \, e^{(R/T_r)} \]

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

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model year</th>
<th>Phase-in (percent)</th>
<th>Emission standards</th>
<th>Maximum limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1</td>
<td>2006</td>
<td>50</td>
<td>100 275</td>
<td></td>
</tr>
<tr>
<td>Phase 1</td>
<td>2007–2009</td>
<td>100</td>
<td>100 275</td>
<td></td>
</tr>
<tr>
<td>Phase 2</td>
<td>2010 and 2011</td>
<td>100</td>
<td>75 275</td>
<td></td>
</tr>
<tr>
<td>Phase 3</td>
<td>2012 and later</td>
<td>100</td>
<td>see equation</td>
<td>150 400</td>
</tr>
</tbody>
</table>

From Regs

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

Or more simply

\[
\text{Total Emissions} = \left(\frac{\text{HC}}{150} + \frac{\text{CO}}{400}\right) \leq 100 \%
\]

EPA Title 40 Part 1051: Control of Emissions from Recreational Engines and Vehicles
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!
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

Examples:

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

- **Oxygen**
- **Propane**

**Time for Two Cycles (Seconds)**

**Volume Concentration (%)**

0 20 40 60 80 100 120
Air Fuel Ratio at Catalyst Inlet

Time for Two Cycles (Seconds)

AFR

LEAN

RICH
Simulating Fuel Cut Portion of ZDAKW Cycle

- Bed
- Inlet
- Outlet
Aging Results

Fuel Cut AFR ZDAKW Cycle

AFR

Outlet
Inlet

Time S
Catalyst Thermal Shock Test

- Bed Temp 1
- Inlet Temp 1
- Bed Temp 2
- Inlet Temp 2
- Outlet Temp

Catalyst Inlet Ramp Rate = 170°C/Second
Performance Testing
Conversion - Lambda - Sample 6

Conversion (%) vs Lambda

- Conv % CO
- Conv % HC
- Conv % NO
CO Lightoff Sample

CO Conversion - Cat In - Sample 6

CO Lightoff @ 221 C

Conversion (%)

Cat Inlet Temp (C)
C3H8 Lightoff Sample

C3H8 Conversion - Cat In - Sample 4

HC Lightoff @ 439 C
Lambda Comparison

Time (s)

Lambda

Labcat Lambda In
Labcat Lambda Out
Mexa 7170 Lambda

OSC Test Sample
MAXCAT  200g/sec

TESTCAT  50g/sec

LABCAT  20g/sec Flow
MAXCAT EXAMPLE

- Removes the need for Gasoline & Energy Efficient!

Gasoline Energy

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

95% Electrical 5% Propane
OTHER BENEFITS

- 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% CO₂ 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
Thanks For Listening

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