Stationary Engine Emission Controls

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Outline

- What is a catalyst?
- How does a catalyst work?

  - **Three Way Catalyst** (aka NSCR or TWC) for Rich Burn Engines
  - **Two Way Catalyst** (aka Oxidation of DOC) for Lean Burn Engines
  - **Selective Catalytic Reduction Systems** (aka SCR) for Lean Burn Engines
  - **Diesel Particulate Filter System** (aka DPF) for Lean Burn Diesel Engines
What is a catalyst?  
Is it a black box???
A catalyst is NOT a black box!
It is a substance that accelerates a chemical reaction

- A catalyst is a material that increases the rate of a chemical reaction while not undergoing any permanent change.
- This results in the chemical reaction occurring at a lower temperature and more quickly.
- Catalysts do not perform miracles, the reactions they perform have to be “allowed” chemically.
- Catalysts are designed to speed up the desired reactions, but not the undesired reactions.
Common substances are:

Platinum Group Metals (PGM)
Common Uses of PGM Include...

- Makes People Happy
- Makes People Wealthy
- Makes People Healthy
Environmentally PGM is used for ...

- Makes our environment cleaner
- Makes our energy sources greener
How does it work?
Different applications require different catalysts

Section 1: Three way catalysts
Section 2: Two way catalysts
Section 3: SCR systems
The A/Fuel ratio (Lambda) is critical, as the area of operation is with excess reductants (HC, CO). Exhaust composition is extremely important to the proper catalyst for the application.

Rich (Exhaust O₂ 0.3% – 0.5%)  Stoic (Reductants not in excess)

Both oxidation reactions and reduction reactions are taking place in TWC catalyst.

Oxidation Reactions
- CO + 1/2O₂ → CO₂
- CH₄ + 2O₂ → CO₂ + 2H₂O

Reduction Reactions
- 2NO + 2CO → N₂ + 2CO₂
- 4NO + CH₄ → 2N₂ + CO₂ + 2H₂O
Three Way – Rich Burn Catalyst Components

- **Substrate** – A high geometric surface area support for the washcoat.
- **Washcoat** – High surface area support for the catalyst, strong adhesion to the substrate.
- **Promoters** – Stabilise washcoat, modify sulphur chemistry.
- **Oxygen Storage Component** – Improve operating window, OBD.
- **Platinum Group Metal (PGM): Pt, Pd, Rh** – Active sites, have correct electronic structures to interact with HC, CO, NOx and O$_2$. 

Rich Burn Engines Run Around $\lambda = 1$

- CO and NOx levels are related to the amount of exhaust $O_2$

- AFR control relies on $O_2$ levels
  - Conventional controls uses “set point” control
  - Tries to control at a very narrow set point

Courtesy of
Combination Catalytic Converters and Engine Silencers Example

Catalyst access location

Silencer portion
Three Way – Rich Burn
Summary

- Three way catalyst control NOx, CO and HC emissions

- Three way catalyst effectiveness is very dependent on exhaust chemistry (lambda), operate at or below stoich and are used with Rice Burn engines

- A/F ratio control is critical for effectiveness
How does it work?
Different applications require different catalysts

Section 1: Three way catalysts
Section 2: Two way catalysts
Section 3: SCR systems
The Air Fuel ratio (Lambda) is not as critical as the area of operation is with excessive $O_2$. The type of hydrocarbon (HC) being oxidized is extremely important in selecting the proper catalyst.

- **Oxidation Reactions**
  - $CO + \frac{1}{2}O_2 \rightarrow CO_2$
  - $HC + O_2 \rightarrow CO_2 + H_2O$
  - *In this case HC is “any” HC, HAP, VOC*

Only oxidation reactions are taking place.
Hydrocarbon oxidation across a catalyst is dependent on the hydrocarbon species and varies between easy to difficult.

Order of difficulty

- Methane > ethane > propane > butane
- Saturated HC > Unsaturated HC
- Unsaturated HC > CO

Different catalysts are needed for different hydrocarbons
Two Way – Lean Burn – Oxidation Catalyst – DOC

Catalyst Components

- **Substrate** – A high geometric surface area support for the washcoat.
- **Washcoat** – High surface area support for the catalyst, strong adhesion to the substrate.
- **Promoters** – Stabilise washcoat, modify sulphur chemistry.
- **Platinum Group Metal (PGM): Pt, Pd** – Active sites, have correct electronic structures to interact with HC, CO, and O₂.
Spark Ignited Natural Gas Lean Burn Catalytic Converters Example

- 20 x Caterpillar G3516, 1,125 hp
- 93% CO Conversion
Two Way – Lean Burn – Oxidation Catalyst – DOC

Summary

- Oxidation catalyst selection is very dependent on hydrocarbon species
  - Catalyst activity is a combination of design materials as well as the optimizing for operating parameters

- Oxidation catalyst deactivation is similar to TWC catalyst
  - Deactivation of the catalyst is a result of the operating Environment
  - Temperature, poisons, and masking
  - Thermal deactivation is irreversible
  - Chemical washing can restore significant amount of activity due to “typical” poisons
Catalyst Applied as Thin Coating on Substrate
Optical micrographs
Catalyst Degradation

- There are several factors that effect the durability of a catalyst

- The major causes of activity degradation are:
  - Thermal Overheating ~ by engine misfire
  - Poisoning ~ by Pb, P, S, etc.
  - Masking of the surface ~ by PbSO$_4$, SiO$_2$
  - Fouling ~ by debris from engine exhaust system
Sintering

Agglomeration or densifying of the support material that carries active catalyst – reduces the total catalyst surface area exposed to the process stream. Each catalyst has a recommended temperature “window of operation.” At temperatures within this window, desired operation will occur. At temperatures above this window – 1,400 F and higher – sintering can occur. Sintering, in effect, the collapse of the catalyst surface, is a slow process. Short exposure to elevated temperatures results in less sintering than long exposure.
Masking Of Catalyst

Masking
- In this case, reduced catalyst activity is caused by a gradual accumulation of non-combusted or inorganic solid material on the catalyst surface, preventing passage of exhaust gas from the exhaust stream to the catalyst sites. Masking problems typically arise from dust or dirt, metal oxides formed in the process, corrosion products from within the duct system, or organic char from too-low operating temperatures.
Poisoning

Deactivation resulting from the chemical interference of materials in the process stream with the catalyst itself. “Active” precious metal sites become “inactive,” reducing catalyst performance. Excessive amounts of halogens, phosphorous or certain metals may cause this problem. However, most often, catalysts believed to be permanently poisoned can be regenerated, using procedures that have been developed for this purpose.
Fouling of Catalyst

- Plugging of catalyst cells by debris
- Generally reversible
How does it work?
Different applications require different catalysts

Section 1: Three way catalysts

Section 2: Two way catalysts

Section 3: SCR systems
In typical stationary lean burn engine emissions, the O\(_2\) concentration is \(\sim 1000x\) greater than NOx. Most of the reducing agents react faster with the oxygen than NOx:

\[
\begin{align*}
2\text{H}_2 + \text{O}_2 & \rightarrow 2\text{H}_2\text{O} \\
2\text{CO} + \text{O}_2 & \rightarrow 2\text{CO}_2 \\
(\text{HC}) + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{NH}_3 + \text{O}_2 & \rightarrow \text{NO} + \text{H}_2\text{O}
\end{align*}
\]

NH\(_3\) can be an exception if a selective catalytic reduction (SCR) catalyst is present.
• Reduce NOx (NO + NO₂) emissions in oxidizing atmosphere using a reducing agent and a catalyst:
  • Anhydrous NH₃
  • Aqueous NH₃
  • Urea
• Reduce NOx by 95%+
• Temperature range ~550°F to ~950°F (perfect for engines)
• Considered BACT

• Compare vs. Selective Non–Catalytic Reduction (SNCR)
• Reduce NOx by 60%+
• Temperature range ~1600°F to 1800°F (too high for engines)
Stoichiometric reaction of NOx molecules at the catalytically active surface with reducing agent Ammonia:

- $4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$
- $\text{NO}_2 + 4 \text{NH}_3 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}$
- $\text{NO} + \text{NO}_2 + 2 \text{NH}_3 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O}$

Ammonia source is typically urea

- $(\text{NH}_2)_2\text{CO} \rightarrow \text{NH}_3 + \text{HNCO}$ decomposition
- $\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2$ hydrolysis
- $(\text{NH}_2)_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2$

One urea yields two NH$_3$

- $4 \text{NO} + 2(\text{NH}_2)_2\text{CO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 4 \text{H}_2\text{O} + 2 \text{CO}_2$
SCR – Lean Burn Catalyst Composition

$V_xO_y$ (0.3 to 5%) Analyzed as vanadium(V) oxide commonly known as vanadium pentoxide, is the most important compound of vanadium. In addition, binding and plasticizer materials.

$WO_3 / MoO_3$ Tungsten(III) oxide ($WO_3$) is a compound of tungsten and oxygen.

$TiO_2$ - Titanium dioxide, also known as titanium(IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula $TiO_2$. When used as a pigment, it is called titanium white, Pigment White 6, or CI 77891.
SCR – Lean Burn
NOx Reduction and Temperature

Dashed Line: NH₃ Slip
Temperature (°F)
SCR – Lean Burn
General Arrangement

- Clean Exhaust
- Optional NOx Process Monitor
- Optional Oxidation Catalyst or DPF
- Reagent Injection Lance
- SCR Catalyst Housing
- Mixing Duct
- Reagent Feed
- Air Feed
- SCR Injection System
- Diesel or Lean Burn Natural Gas Engine
- HAP Guard or Soot Alert
- Reagent Feed
- Compressed Air
- Level Sensor
- Reagent Storage Tank
SCR – Lean burn
Example – Combined Heat & Power

- 96% NOx Reduction
- 93% CO Reduction
- 60% VOC Reduction
- 3.7 ppmvdc NOx Max
- 3.0 ppmvdc NOx Achieved
- Hybrid Injection w/CEMS
SCR – Lean burn
Example – Gas Compression

- 2 x G3616LE (4,735 hp) Prime Gas Compression
- 75% NOx / 95% CO / 72.2% VOC Reduction
- Tempering Blowers to Limit SCR Temperature
- Hybrid Urea Injection Control w/NOx Sensor
- ~5 inH₂O Total System Backpressure
SCR – Lean burn
Example – Gas Drilling

- CAT 3512 Engines
- 3 Rig Engines Load Share
- 24 SCR Systems Total
- 90% NOx Reduction
- Skid Mounted
- Remote Locations
SCR – Lean Burn
Example – Peak Shaving

- CAT G3516 – 750kW
- SCR and CO catalyst
- Natural gas fueled
- 80% NOx / 93% CO / 70% VOC reduction
SCR Systems – Lean Burn

Summary

• Base metal catalyst with no Platinum Group Metals (PGM)
• Not a passive catalyst system; requires a reductant
• Customized to customer specifications and footprint
• Equipment scope is more than catalyst and a housing:
  • Reductant injection system, Mixing Duct, Reductant Tank, etc.
• Reductant injection system must be robust
  • Dosing too low = low NOx reduction
  • Dosing too high = excessive NH₃ slip
• Different operating temps than Two Way and Three Way
  • Two Way and Three Way must operate at <1250°F
  • Urea-based SCR must operate at 575°F – 950°F
Fine and ultra-fine particulate matter is emitted by diesel engines from incomplete combustion of the fuel. It is comprised of the following:

- Carbon soot
- Soluble Organic Fraction (SOF) – unburnt HC’s
- Sulfate and water
- Ash (includes heavy metals)
1. DOC oxidizes the SOF to CO₂ and H₂O
2. DOC converts engine out NO to NO₂
3. Soot and ash are collected in the filter
4. The filter is regenerated by the NO₂ reacting with the soot
5. Filter is periodically cleaned to remove the ash
In the DPF, NO₂ is generated over the Diesel Oxidation Catalyst to oxidize the soot which has been trapped on the filter.
Diesel Particulate Filter
Highly Efficient Wall Flow Filter

Exhaust gas flows through filter, depositing PM on filter

Every other channel blocks gas flow
Diesel Particulate Filter Assembly

DOC

Soot Filter
Various Diesel Particulate Filter Sizes in Operation

Number of DOC/Filters per CRT from 1 to 50+
DPF Systems – Lean Burn Diesel Engines

Summary

• Combines DOC with filter

• A passive system that uses engine exhaust temperature

• Reduces PM by ~85%, CO ~90% and HC ~70%

• Filter is regenerated by chemical reaction of $\text{NO}_2$ and PM

• Existing Tier 2 engines comply with Tier 4 PM, CO and HC

• Combine with SCR to make Tier 2 compliant with Tier 4
Summary

- What is a catalyst? – Material that allows chemical reaction at lower temperature
- How does a catalyst work – Reduces activation energy for reaction

- Three Way Catalyst for Rich Burn Engines reduces NOx, CO and HC
- Two Way Catalyst for Lean Burn Engines reduces CO and HC
- Selective Catalytic Reduction Systems for Lean Burn Engines Reduces NOx
- Diesel Particulate Filter System for Lean Burn Diesel Engines Reduces CO, HC and PM
Thank You!

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