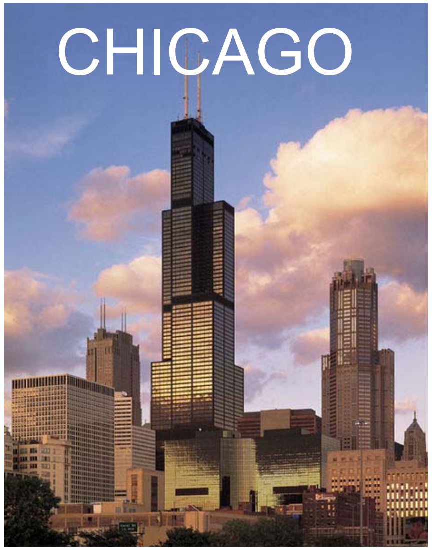
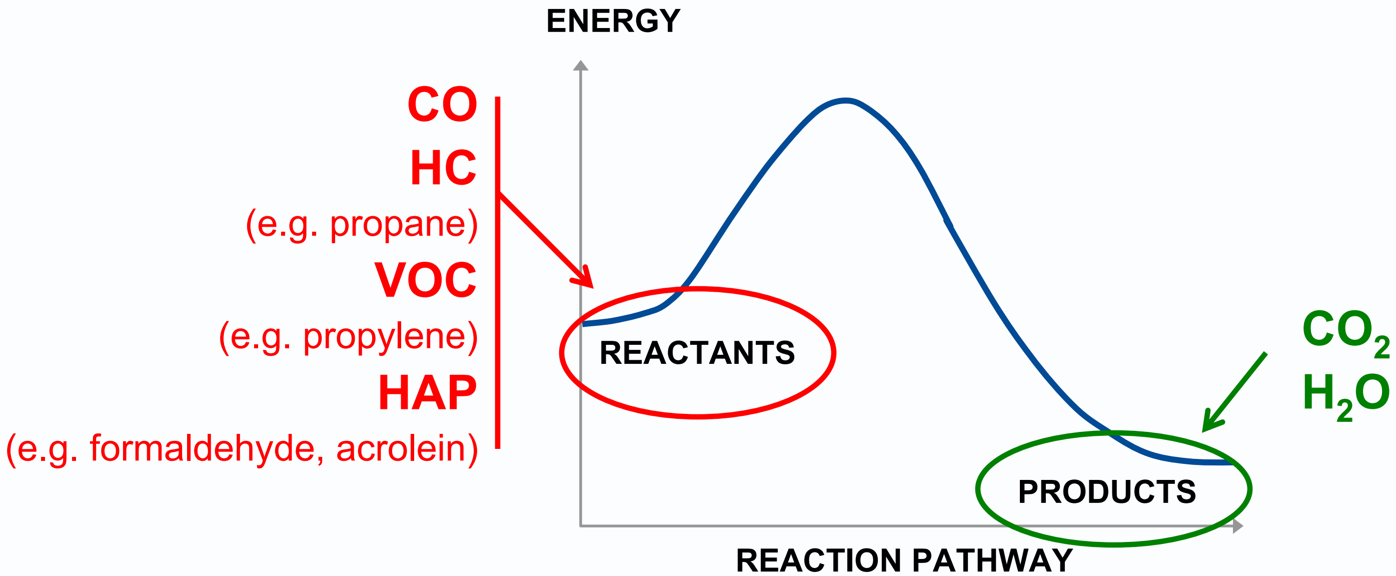
Oxidation Technologies for Stationary Rich and Lean Burn Engines

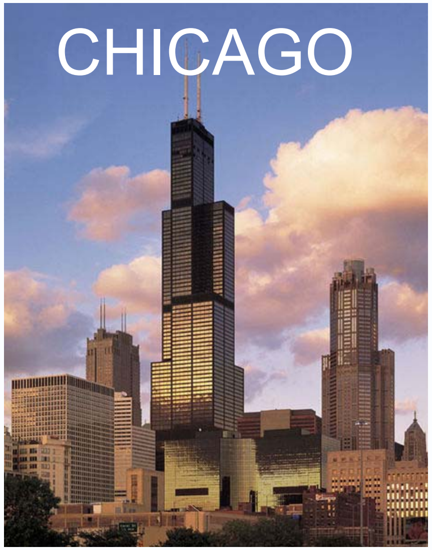
ICAC – LADCO
Advancements in Emission Control and Measurement Technologies for Industrial Applications
March 24-25, 2010
Rosemont, IL

Life without catalysts…



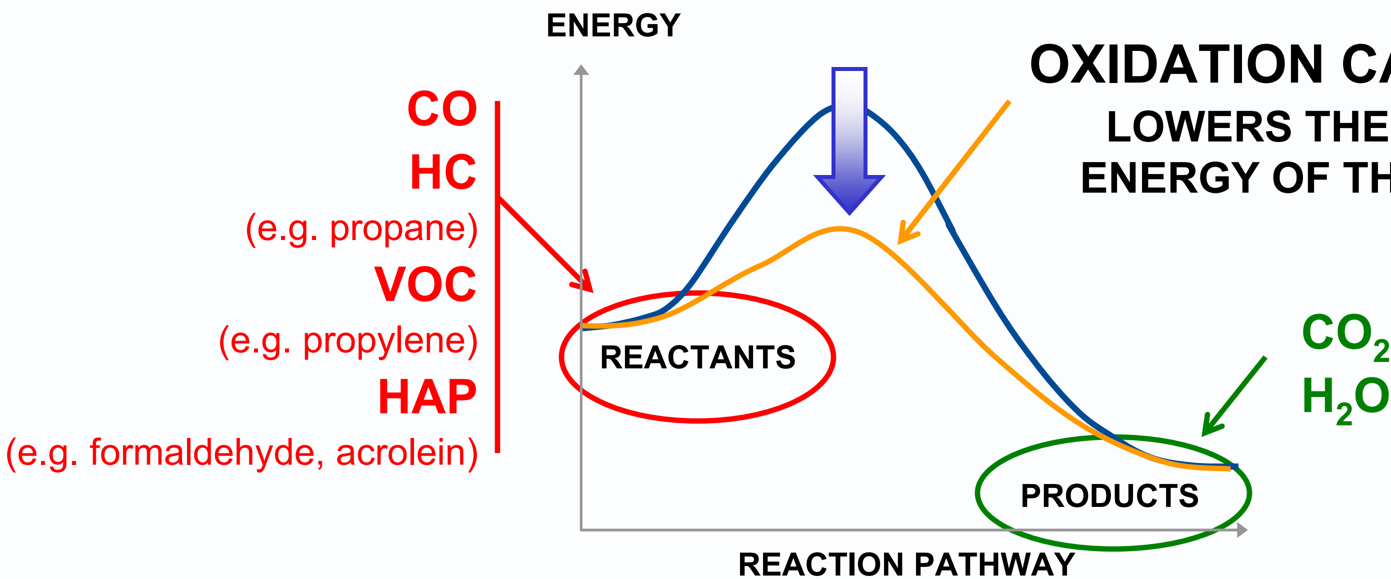


…Life with catalysts



OXIDATION CATALYST

LOWERS THE ACTIVATION ENERGY OF THE REACTION



Oxidation catalyst technology is mature yet still innovative

Application	Fuel	Emissions	Timeframe	Installations
Fork Lift Trucks	LP, Gasoline	CO, HC	Mid-1960s	1,000s
Mining Equipment	Diesel	CO, HC, Odor	Mid-1960s	1,000s
Automobiles	Gasoline, Diesel	CO, HC	1975	100,000,000s
Formaldehyde Plants	-	CO, VOC	Mid-1970s	100s
Process Plants	-	CO, VOC	Mid-1970s	1,000s
Engine Gen Sets	Various	CO, HC, Odor, VOC	1970s	1,000s
Turbines	Various	CO	Mid-1980s	100s
Boilers	Various	CO	Late-1980s	10s
Trucks	Diesel	CO, HC, PM	Mid-1990s	1,000,000s
Buses	Diesel	CO, HC, PM	Late-1990s	10,000s

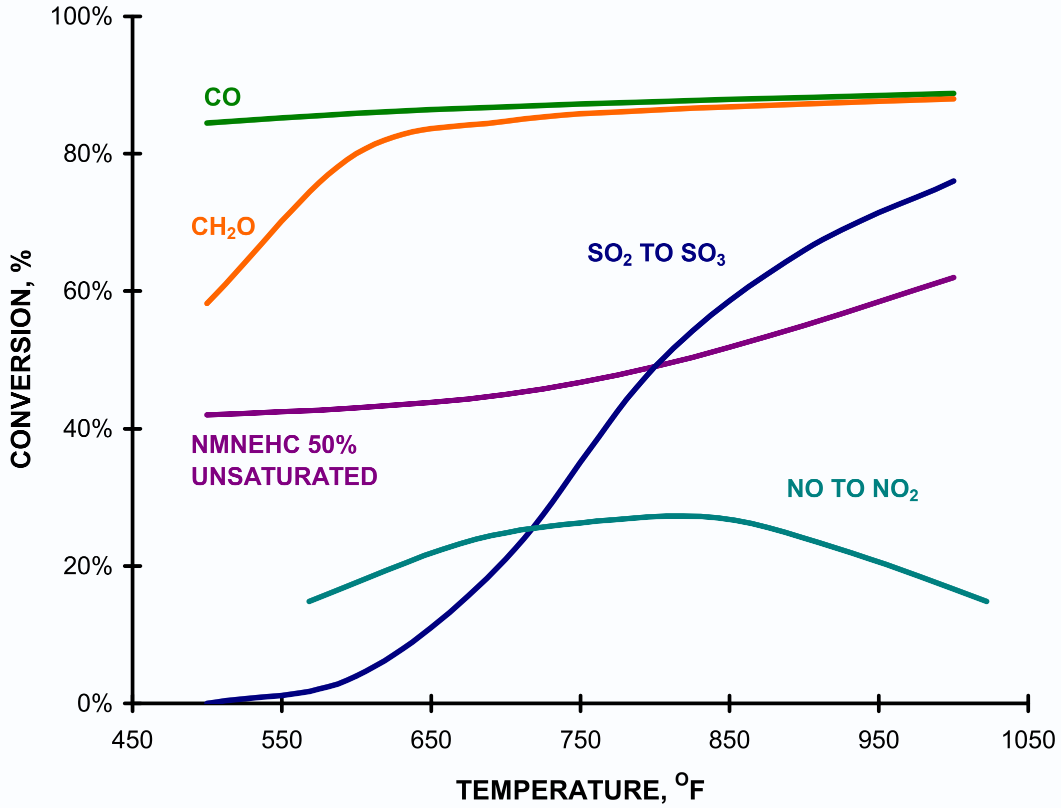
- **Latest challenges for oxidation catalyst technology include biofueled applications and ammonia slip abatement downstream of SCR systems**

Overview

- Oxidation catalyst technologies
  - NSCR (Three-way catalyst)
  - Diesel Oxidation Catalyst (DOC)
  - Oxidation Catalyst
- Advances in emission control
  - Substrates
  - Systems
  - Selection
- Applications on stationary engines
  - Case study

Oxidation catalyst – General characteristics

CO… HC… VOCs… HAPs… SO_2… NO…



Generic 90% CO conversion case shown…

99% CO conversion possible with additional catalyst volume

Activity

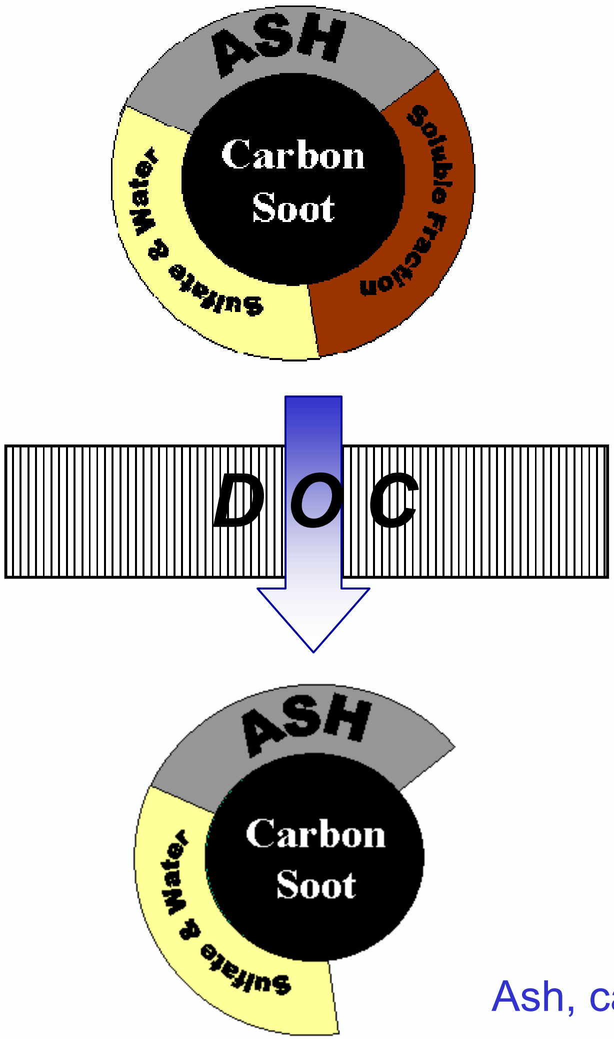
"Passive" technology will oxidize everything that it contacts, but not necessarily to the same degree.

The catalyst performance for each compound typically determined by residence time (i.e. catalyst volume) & operating temperature.

Selectivity

Catalyst formulation may be customized to enhance or inhibit certain reaction pathways.

Diesel oxidation catalyst



Diesel particulate matter – What is it?

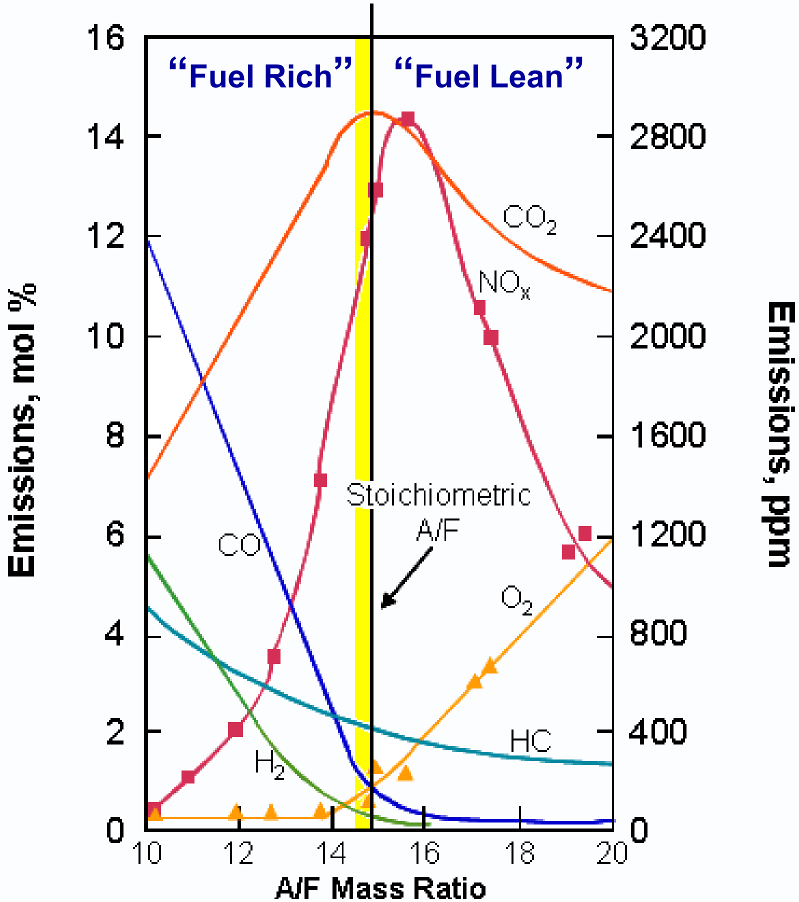
- Carbon soot
- Soluble organic fraction
- Sulfate and water
- Ash

Applicable for diesel fuel < 500 ppm S

Soluble organic fraction	20% - 50% PM reduction
CO & hydrocarbons	> 90%
Aldehydes	> 70%
SO_2	Some oxidation to SO_3
Ash, carbon soot, sulfate & water	No impact

NSCR on rich burn engines
(NSCR = Non-Selective Catalytic Reduction)

Generic engine emissions profile inlet to NSCR catalyst



Engine operates slightly "fuel rich"

Air-fuel ratio controller required to maintain balanced engine emissions (NO_X, CO, HC) for stable catalyst performance

Catalyst depletes O_2 via oxidation reactions then reduces NO_X using remaining CO, H_2, and HC as reagents.

Typical reductions:
- 90% - 99% NO_X
- 90% - 99% CO
- 50% - 90% HC
- 80% - 95% CH_2O
- 80% - 95% HAPs

Oxidation catalyst – Maintenance and lifespan

- If applied properly, an oxidation catalyst technology…
  - NSCR
  - DOC
  - oxidation catalyst
  - ammonia destruction catalyst

…does not need regular maintenance

  - No moving parts
  - No chemical reagents

- However, certain engine “upset” conditions can affect the performance and lifespan of oxidation catalyst technology
  - Thermal deactivation
    - Very high temperatures > 700°C (1300°F) (varies by formulation)
  - Catalyst poisoning from
    - Use of high sulfur diesel fuel (e.g. 2,000 ppm S)
    - Certain lube oil and lube oil additives (e.g. Zn, P)
  - In some cases, catalyst may be regenerated with proper cleaning to extend its useful life

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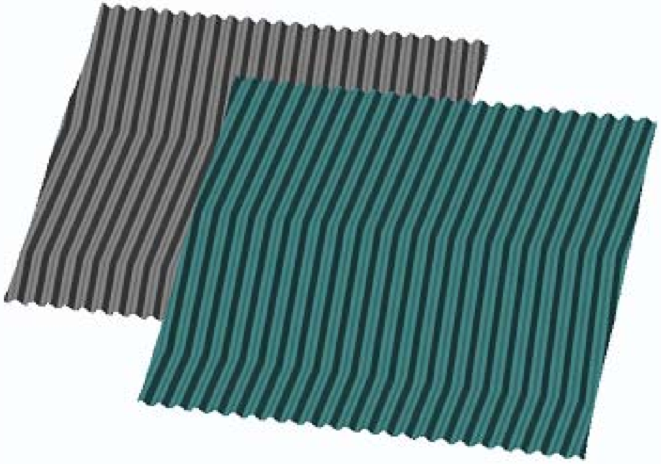
Substrates offer versatility in technology applications

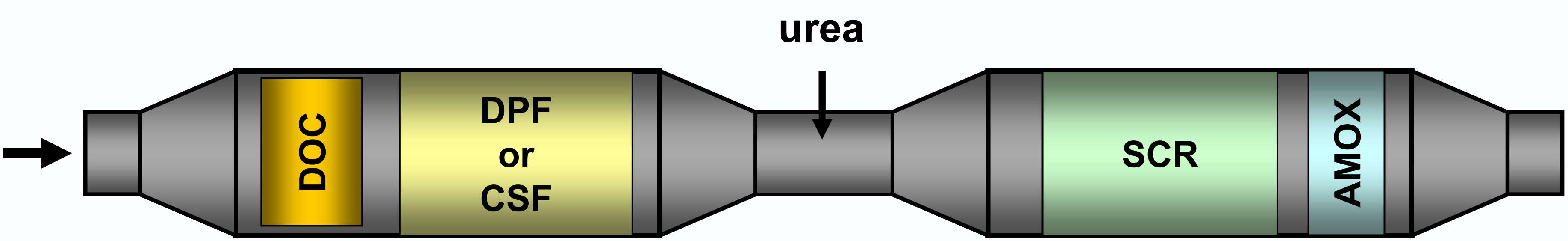
- Metal substrate
  - Low pressure drop
  - High surface area
  - Design flexibility to address application specific constraints on space



- Ceramic substrate
  - Well-suited for washing to extend useful life
  - Resistant to acid gas environments

System packaging of multiple technologies allows for synergies

- Each component in an integrated catalyst technology system is considered for:
  - Its contributions toward the overall required performance
  - Its impact on other installed technologies

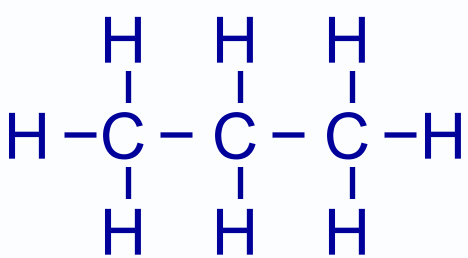


- A **DOC** installed upstream of the particulate collection element may be optimized for <u>activity</u>: high VOC conversion at higher temperatures.
- An ammonia destruction (**AMOx**) catalyst installed downstream of the SCR may be optimized for <u>selectivity</u>: high NH_3 slip conversion to N_2 rather than NO_X, at lower temperatures.

Selection (custom catalyst solutions)
Perspectives on VOCs

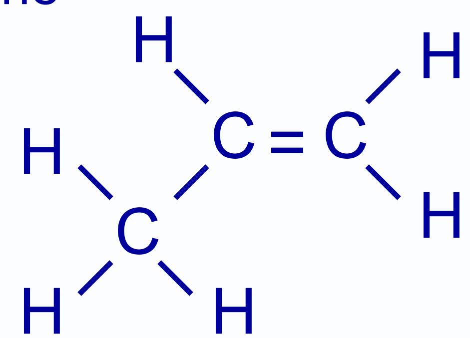
- The term "VOCs" represents a <u>class</u> of compounds (~ 200+ unique "VOCs")
- There is no one compound that may characterize the reaction of all VOCs across a given oxidation catalyst technology

Propane



C3 - saturated compound
Single bonds only
Ignition temp ~ 770F
Difficult to react across catalyst

Propylene

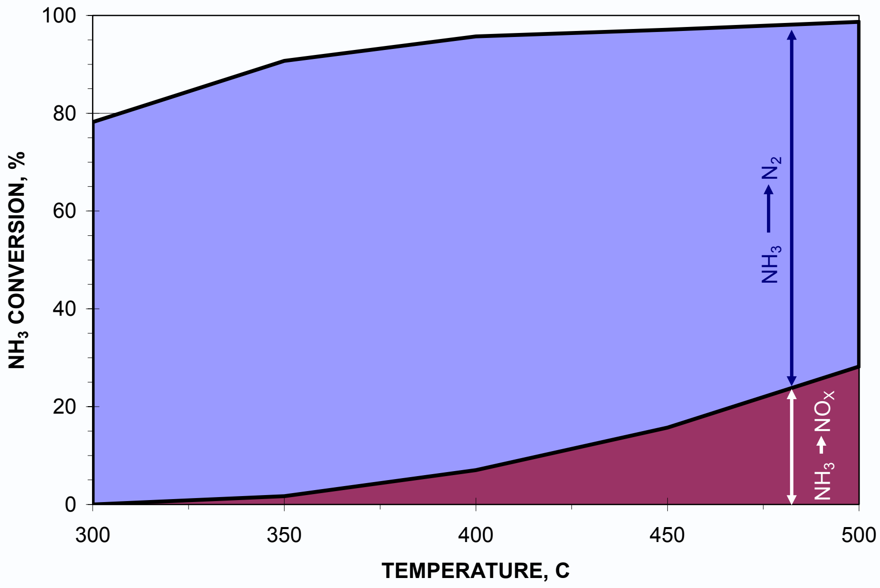


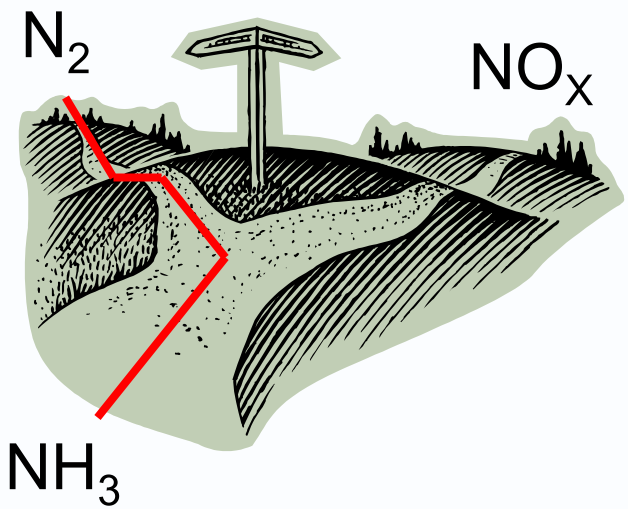
C3 - unsaturated compound
Double bond present
Ignition temp ~ 500F
Easy to react across catalyst

- **Control of specific VOCs may require customized catalyst formulations to offset operating condition limitations (e.g. operating temperature)**

Selection (custom catalyst solutions)
Ammonia Destruction Catalyst (AD)

- Ammonia Destruction Catalyst (AD) installed downstream on an SCR system:
  - Minimizes NH_3 slip emissions
  - Extends working life of SCR systems
  - Promotes reliable operation of load-mapped urea/ammonia injection control systems





Biofuels pose complex challenges for oxidation catalyst technology

May impact catalyst performance as poisons and/or masking agents

Trace contaminants from production processes

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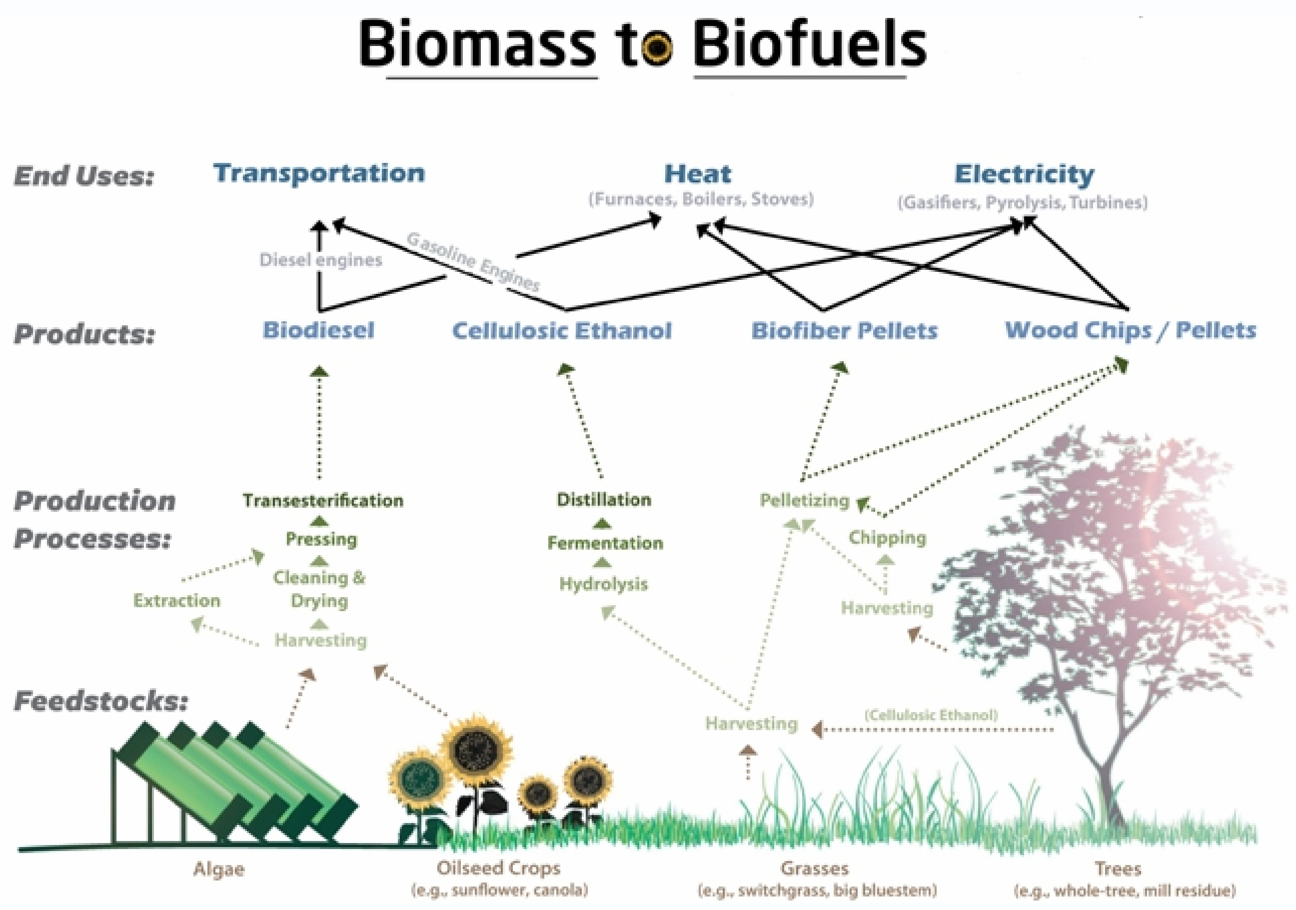
Trace elements in soil & water



Graphic source: Vermont Sustainable Jobs Fund (http://www.vsjf.org/project-details/13/biomass-to-biofuels-resources)

Selection (custom catalyst solutions)
Biofuels for stationary engines

- Catalyst issues posed by biofueled stationary engines:
  - Biodiesel Is An Effective Solvent, Can Dissolve Engine/Component Deposits.
  - Ethanol Corrosive To Pipelines and Older Fuel Systems Components.
  - Trace Contaminants:
    - Processing Catalysts: Na, K, Cu, Ni
    - Alkali Metals and Alkaline Earth Metals: Mg, Ca, Na, K
  - Siloxanes Typical Contaminant in Landfill Gas.
  - Blends Often Used
    - What Is The Real Fuel Specification?

- Early adopters of oxidation catalyst technologies on biofueled stationary engines have been successful in EU (~ 200 engines)

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EPA proposed air toxics limits on stationary engine emissions

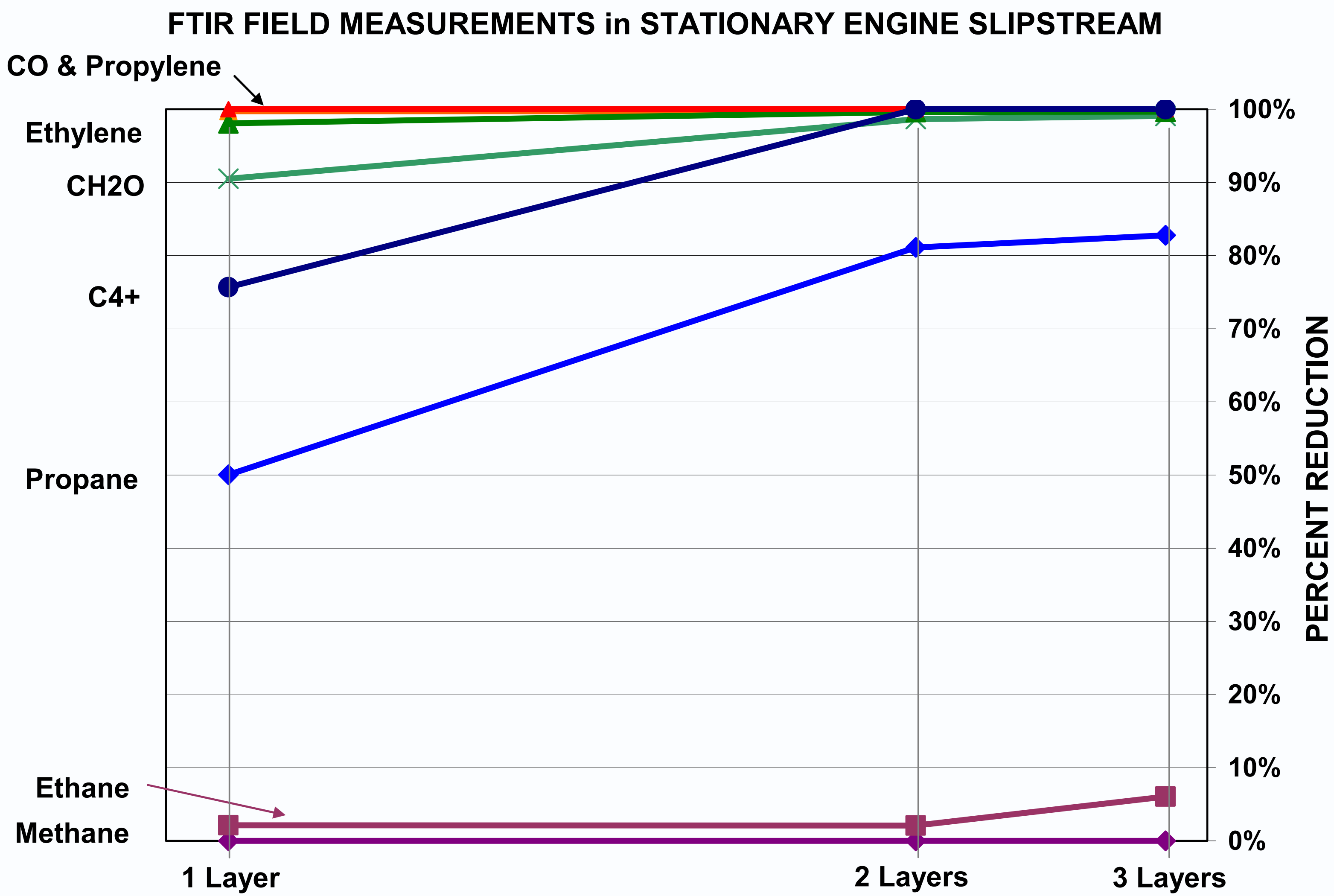
- On 2/26/10, EPA proposed setting emission limits for formaldehyde, benzene, acrolein and other air toxics from certain stationary diesel and gas-fired engines.
- For major sources of air toxics, this rule would only apply to engines that are:
  - Smaller than or equal to 500 horsepower that were constructed or reconstructed before June 12, 2006, or
  - Larger than or equal to 500 horsepower that were constructed or reconstructed before December 19, 2002.
- To meet the proposed emissions requirements, owners and operators of these engines would need to install "after treatment" controls, such as filters or catalysts, to engine exhaust systems, the agency said.
- The EPA estimates that this rule would reduce air toxics emissions by 13,000 tons per year, particle pollution by 2,600 tons and carbon monoxide emissions by 510,000 tons, when fully implemented in 2013.

Source: www.pollutionengineering.com

Case study:
Acrolein emissions control

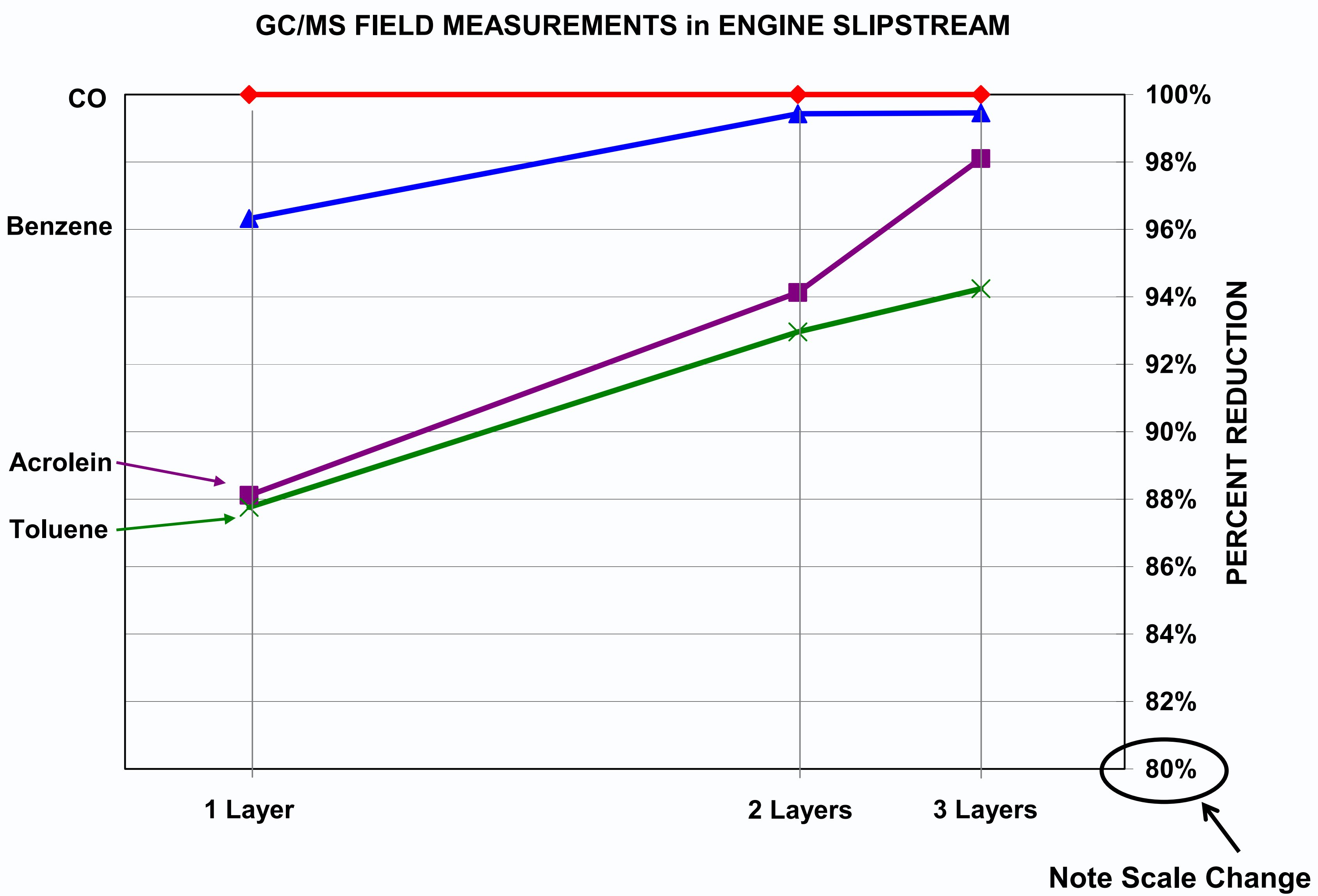
- The problem… in 2005, a 1,000 hp, four stroke, stationary engine operating in Southern California is required to meet an acrolein (HAPs) stack emission requirement of 40 ppbv(wet).
- The solution… custom oxidation catalyst selected and subjected to slipstream reactor testing to prove its performance:
  - 3000 ppbv(wet) acrolein nominal inlet concentration
  - 40 ppbv(wet) acrolein required outlet concentration
    - 98.6% acrolein nominal conversion efficiency
  - 950°F nominal engine stack temperature
    - Slipstream reactor operates at 700 – 900F due to ambient cooling losses
  - Acrolein measurements by GC/MS

Case study:
Field data by FTIR



Note: acetaldehyde emissions (not shown) were below instrument detection limit

Case study:
Field data by GC/MS



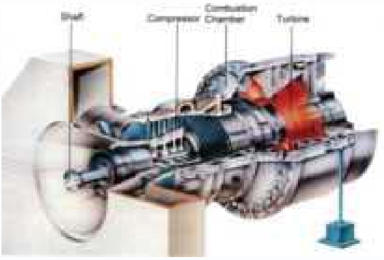
Case study:
Acrolein emissions control

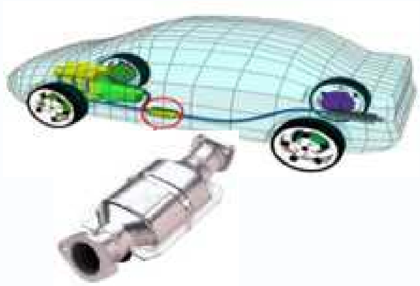
- The result… based on slipstream testing, three layers of oxidation catalyst were installed on the stationary engine.
  - Stack permit testing showed the acrolein emission to be 3 ppbv(wet), well below the 40 ppbv(wet) emission limit
  - Meaningful measurements below the nominal instrument detection limit of 10 ppbv(wet) were possible due to significant hydrocarbon conversion that allowed for very clean chromatogram peaks.
  - Engine stack temperature measured 1,000°F, a 20-40°F increase above nominal associated with catalyst backpressure
    - Higher catalyst operating temperature = higher compound conversion rates
    - Slipstream temperature profile through catalyst layers was less than actual application
      - Nominal 700°F – 890°F slipstream vs. 1000°F application

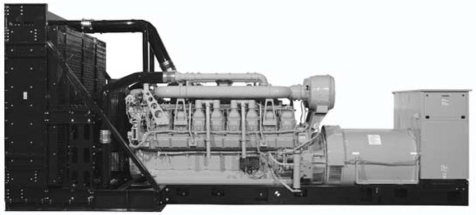
Summary…

- Oxidation catalyst technologies offer:
  - <u>Historically proven success</u>

    of controlling emissions from a wide variety of combustion sources, including stationary engines



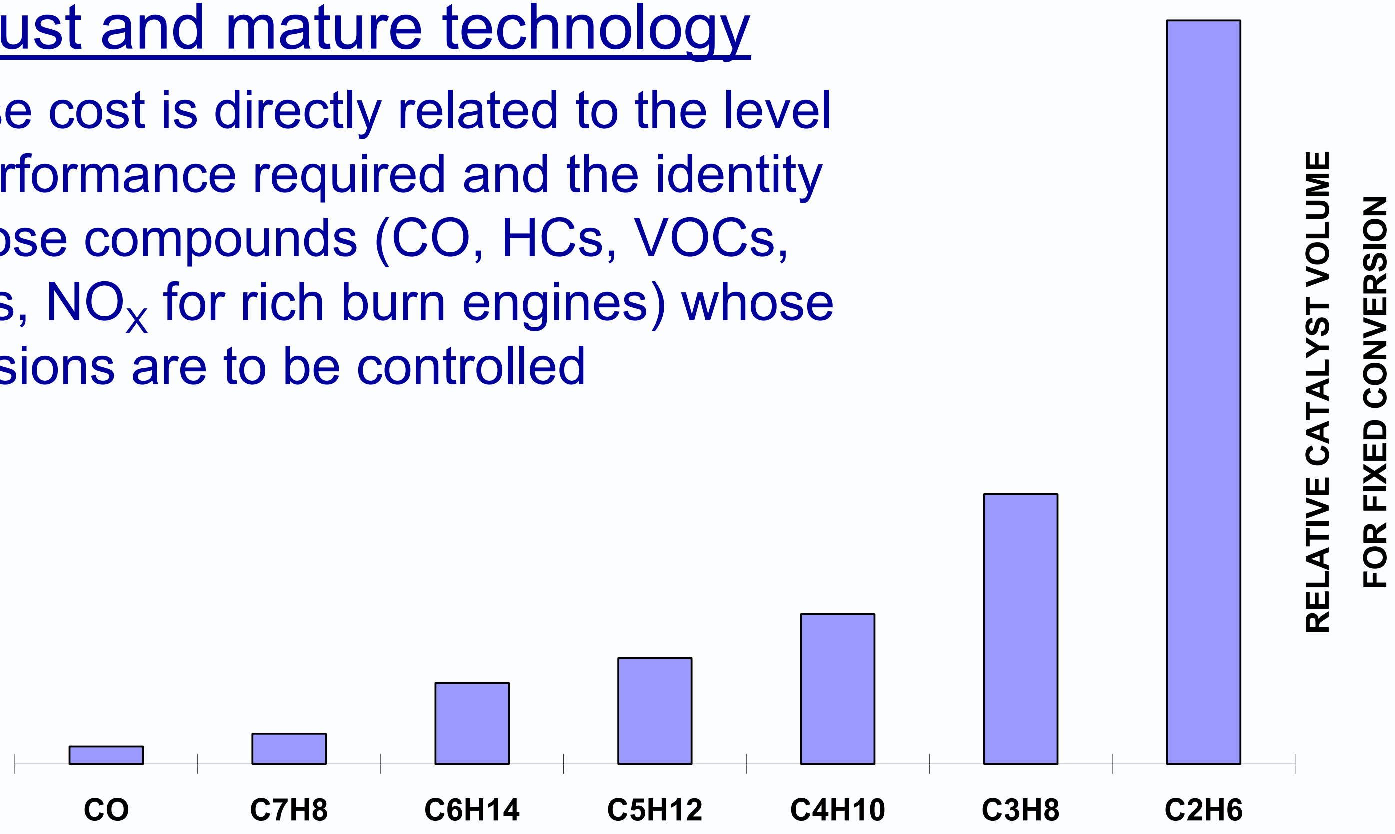




Summary…

- Oxidation catalyst technologies offer:
  - Robust and mature technology

    whose cost is directly related to the level of performance required and the identity of those compounds (CO, HCs, VOCs, HAPs, NO_X for rich burn engines) whose emissions are to be controlled

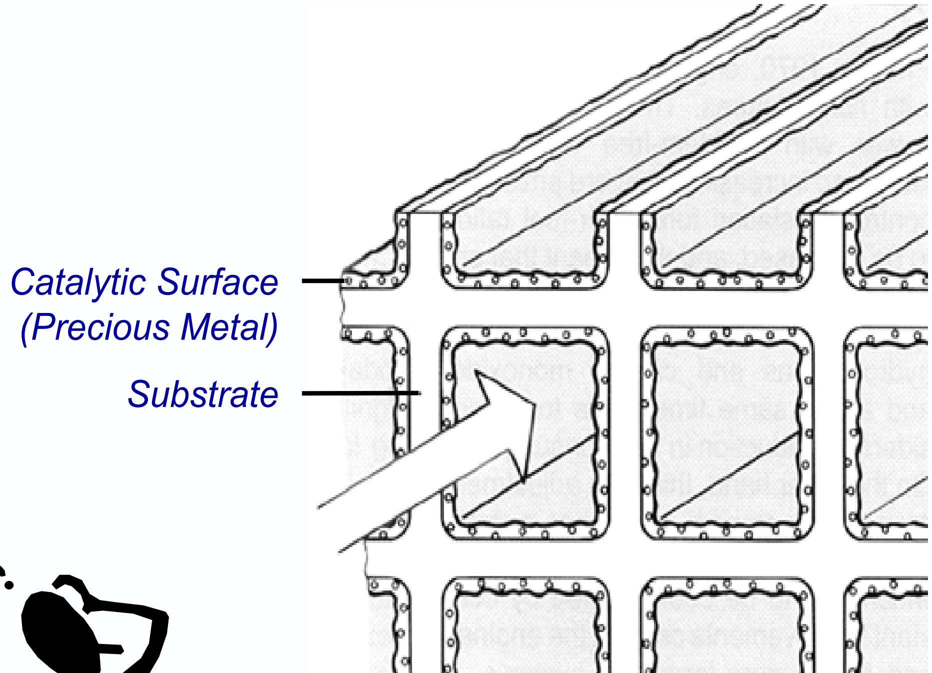


Summary…

- Oxidation catalyst technologies offer:
  - A future of continued innovation

    into new applications and price/performance optimization of existing applications to ensure sustainable development

Questions?



Schematic of honeycomb oxidation catalyst

STAN MACK
BUSINESS MANAGER
STATIONARY SOURCE
stan.mack@basf.com
732-205-6174

WILLIAM HIZNY
TECH. PROJECTS MGR
STATIONARY SOURCE
william.hizny@basf.com
732-322-5516

BASF CATALYSTS LLC
2655 ROUTE 22 WEST
UNION, NJ 07083