# Rapid Aging Protocol for Lean NOX Traps

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# Background / Interest

- Emphasis on mechanisms, not durability testing
- Need for harmonization of aging methods
- Need to leverage TWC experience where appropriate
- Sponsored by Diesel Crosscut Team
- Funded by Office of FreedomCAR and Vehicles Technologies
- Coordinating with CLEERS focus group for LNT

- Two lab collaboration, ORNL and PNNL

# Project plan

- FY 2003
  - Interview interested parties
  - Literature search
  - Develop project plan
  - Acquire materials and resources
- FY 2004
  - Lean / rich thermal aging
  - Extended sulfur poisoning
  - Phosphorous poisoning (related project)
  - Catalyst performance measurements
  - Catalyst structural and materials analysis
  - Report results

# Interviews

- **Interviewed Cummins, Delphi, Umicore, Engelhard, Ford, ORNL, CLEERS, U. Kentucky, EPA, PNNL, Diesel Crosscut, Johnson Matthey, Caterpillar, U. Maryland, Detroit Diesel, Emerichem, NREL**

- **“We need a systematic evaluation of durability outside of commercial interests.**
- **“We need a standard way to compare different suppliers for performance and durability.**
- **“Can the project be expanded to include other types of diesel aftertreatment?**
- **“Time-line is very short, durability requirements very high**
- **“Complimentary to APBF-DEC**

- **Based in technical input, research plan for FY 2004 was put together**

# Aging mechanisms

- Importance of various mechanisms is very catalyst dependent
- Aging will affect both capacity and rates
- PM aging mechanisms
  - Sintering
  - Loss of connectivity with sorbate
- Sorbate aging mechanisms
  - Sintering
  - Pooling, migration
  - Reaction with washcoat, PM, or substrate
- Support aging mechanisms
  - Phase change
  - Loss of surface area
  - Reaction with other system components

# Thermal damage

- High temperatures during desulfation
- Localized hot spots
- Damage increases exponentially with temperature
- Temperatures are commonly increased to accelerate aging
- Rich – lean transition rate very important

# Poisoning

- Sulfur poisoning
  - Sulfur will always be an issue – even with ultra low sulfur fuel, low sulfur lubes, and sulfur traps
  - Sulfur chemistry (in fuel and lube) is probably important
  - Sulfur experiments can (probably) be accelerated with higher sulfur concentrations
  - How excess sulfur is added is probably important
  - It would be useful to explore formation of polysulfides, large sulfate crystals, sulfur-adsorbate compounds, deep sulfates, elemental sulfur, etc.
  - There may be washcoat thickness effects
  - Sulfur adsorbs differently during lean and rich operation
- Other poisoning
  - How poisons are added, concentration dependence, chemistry dependence, differences from gasoline

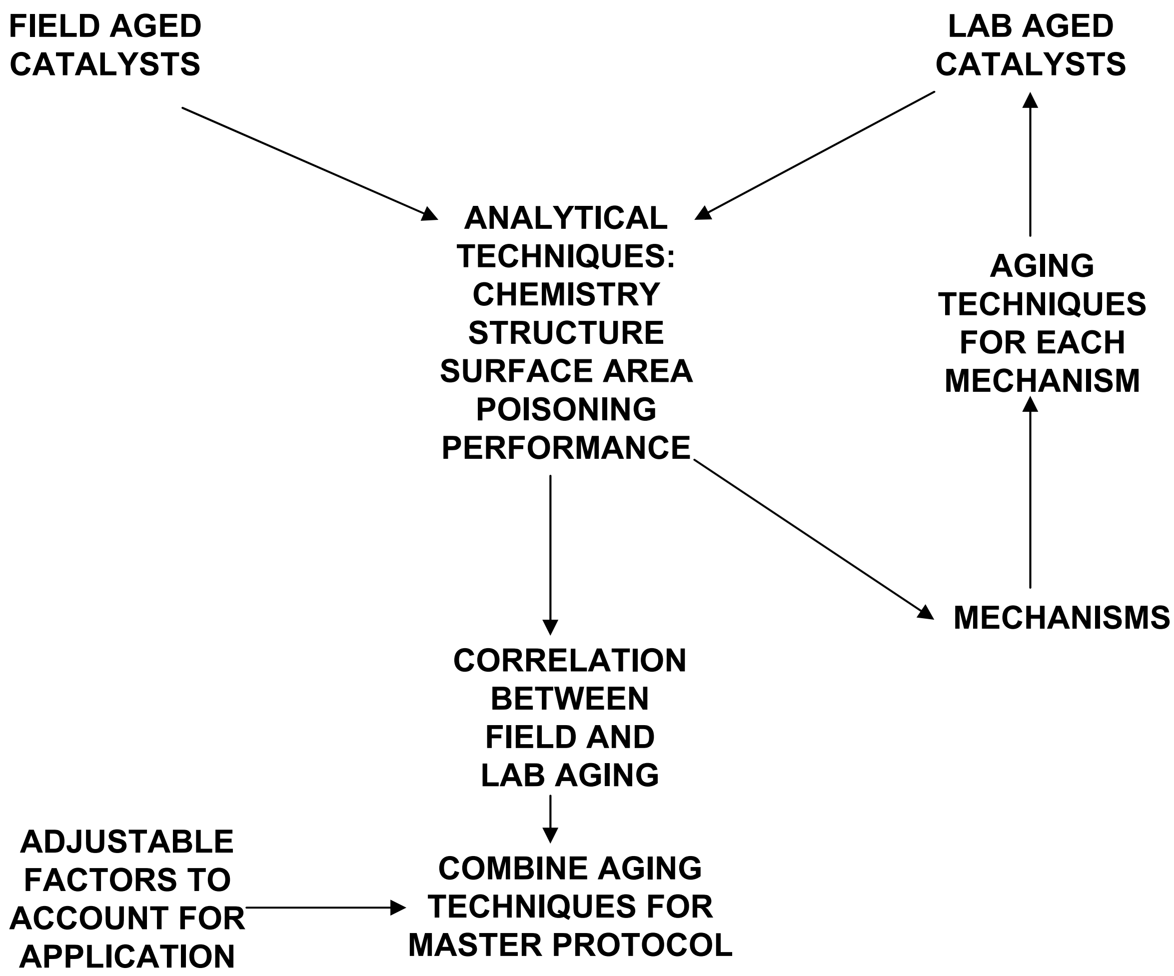
# Correlation and cycle development

- Biggest issue is correlating to actual life
- Must compare to field aged catalysts to ensure that we are staying within realistic envelop of actual mechanisms
- There is a huge difference between arbitrary aging cycles used for catalyst development and true correlation to in-use aging
- Normally, engine and vehicle manufacturers develop aging cycles and catalyst companies apply them to qualify their products
- Cycles are generally proprietary
- EPA approves but does not specify aging cycles
- It may be possible to develop a common cycle for aging, but details of time, temperature, and A/F ratios will be dependent on application, system design, control strategy, and catalyst formulation

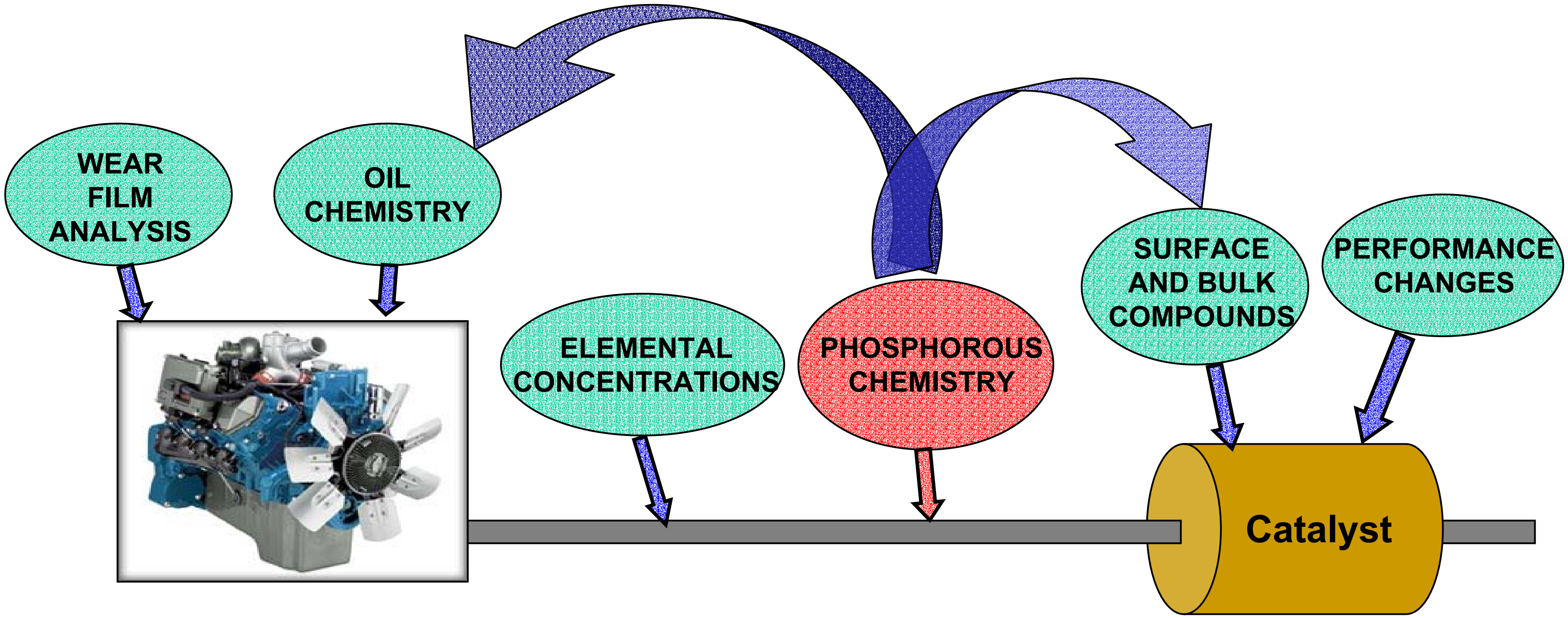
# Control strategy notes

- System components and their sequence is very important
- High temperature transition from rich to lean is very important
  - Slow or staged transition to reduce ‘fuel-cut’ damage
  - Limit oxygen exposure to HC saturated catalysts
  - Allow catalyst to cool before fully lean
- Dithering of A/F during regeneration
  - Controls maximum temperature
  - Faster regeneration and desulfation
  - Reduces H2S formation
- Presence of excess HC or unreacted O2 is important
- Method for determination of A/F is important – calculated or measured

# Framework for development of rapid aging protocol



# Exhaust Phosphorous Chemistry (related project)




Can exhaust phosphorous chemistry measurements provide a link between additive chemistry and catalyst reactions?

# Exhaust Phosphorous Chemistry

| LUBE OIL + ENGINE | EXHAUST CHEMISTRY | CATALYST |
| --- | --- | --- |
| ZDDP | ZDDP – | |
| | | GLASSY COATINGS |
| | ZnPO4 | |
| Ca → | | |
| | P2O5 | FLUFFY COATINGS |
| Mg → | | |
| Mn → | Other phosphates | BULK WASHCOAT COMPOUNDS |
| NOX → | Nitrates | |
| SO3 → | Sulfates | |

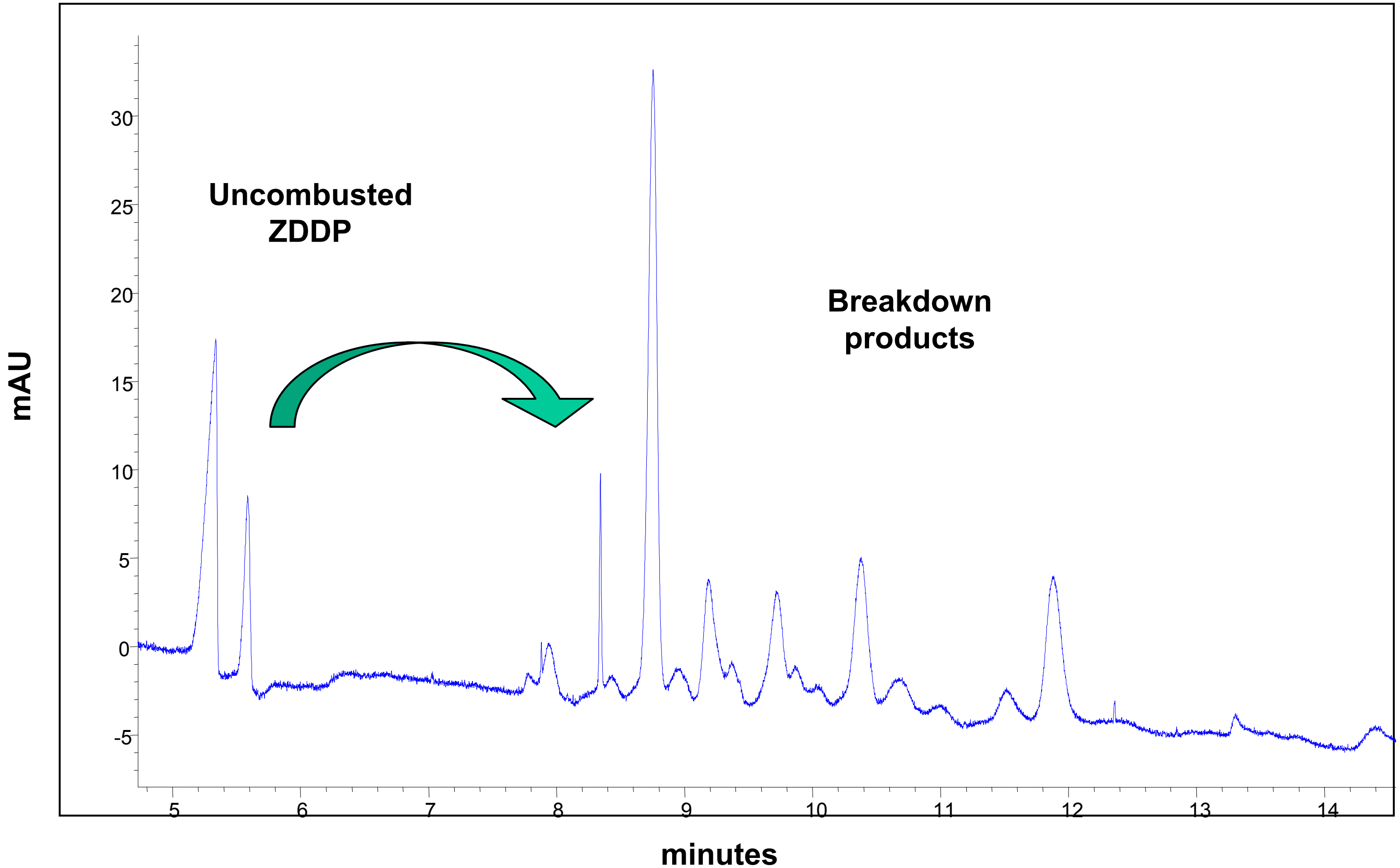
# Phosphorous - sampling and analysis

- **Measurement capability development**
  - **chemistry and compound identification**
- **How do engine / lube oil changes affect exhaust chemistry?**
  - **Additive chemistry and formulation**
  - **Presence of other metals: Ca, Ba, Na, Mn**
  - **Pathway of introduction**
- **How do exhaust chemistry changes affect catalyst?**
  - **Surface compounds**
  - **Bulk washcoat compounds**
  - **Activity, performance**

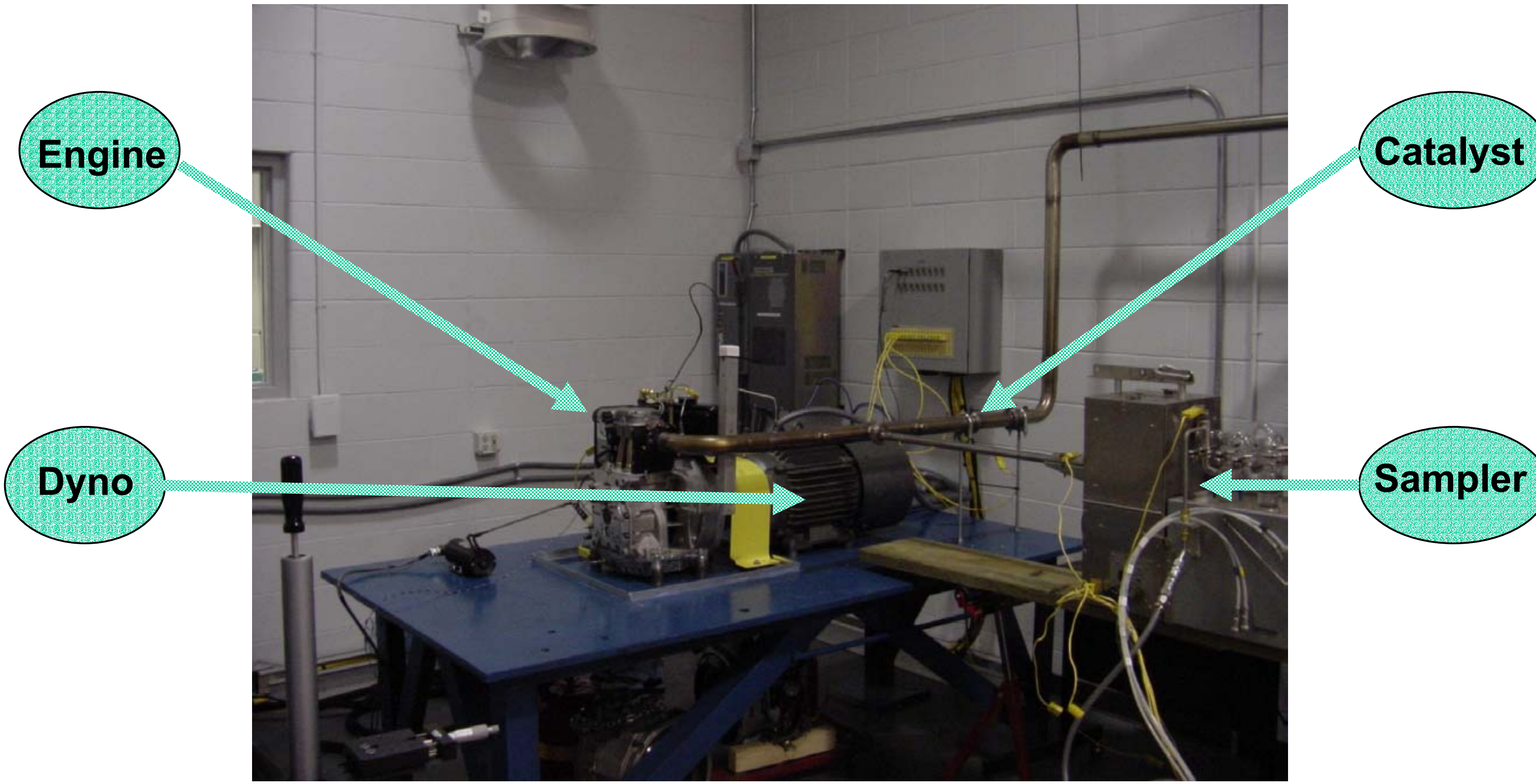
# Exhaust Phosphorous Chemistry

## ZDDP in engine exhaust

### Capillary electrophoresis, 230 nm UV adsorption



# Experimental set-up

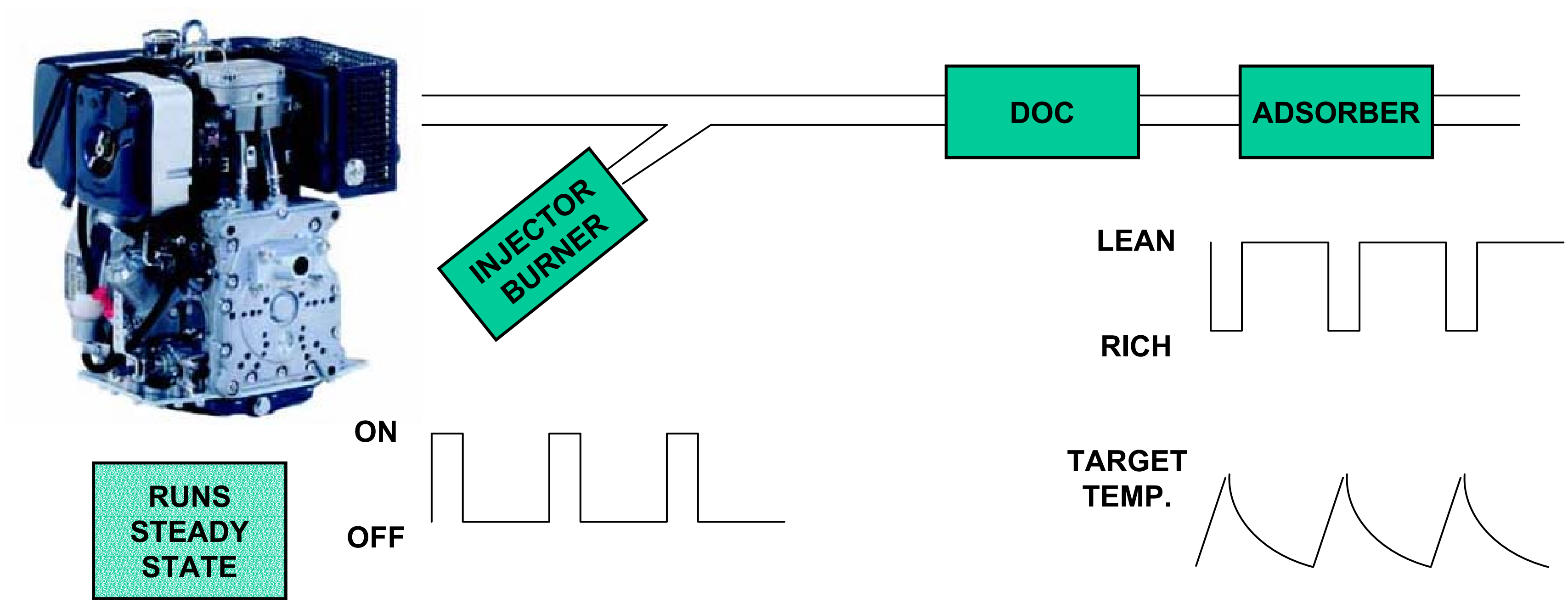


# Catalyst and holder

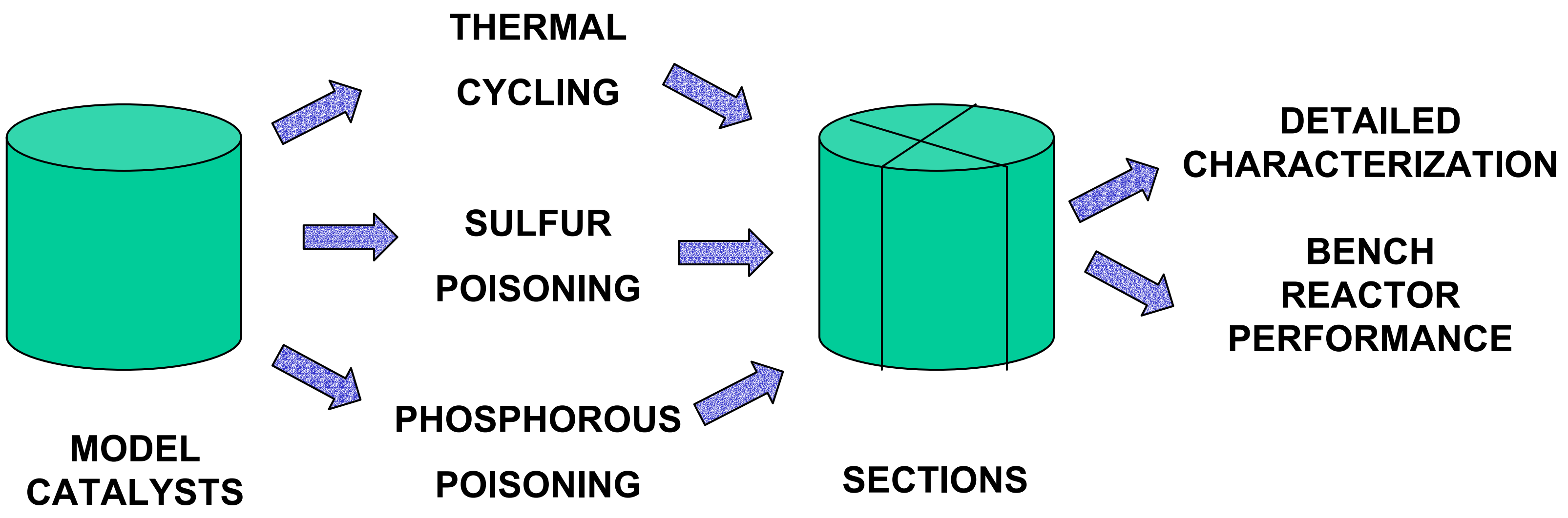
# Materials

- Engine
  - Hatz
    - 500 cc single cylinder DI diesel
- ZDDP additives, formulated oils
  - Lubrizol
  - Elco
- Catalyst substrates
  - NGK
    - Cordierite, 200 cpsi, 12 mil, 2” dia x 3” long
- Model catalysts
  - Engelhard Corporation
    - Diesel NOX adsorber catalyst (Pt, barium, alumina)
  - Emerachem
    - Diesel NOX adsorber catalyst (Pt, potassium, alumina)

# Lean – rich thermal cycling



# Rapid aging test plan



# Characterization and bench performance

- **Characterization**
  - **Materials surface area and particle size**
  - **Materials distribution / migration**
  - **Poisoning compounds**
- **Bench performance**
  - **Effective temperature range**
  - **Storage capacity**
  - **Performance vs. lean / rich duty cycle**

# Current status

- Seeking feedback, assistance, support
  - Diesel Crosscut – 9/12/03
  - CLEERS – 9/23/03
- Project in FY 2004 AOP, appears to be approved
- Continue to formulate plan
- Continue to procure materials and set up experiments
- We need to partner relative to field aged catalysts
- Begin experimental work FY 2004