Development of Advanced Diesel Particulate Filtration (DPF) Systems
(ANL/Corning/Caterpillar CRADA)

Project ID: ACE024

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
- Start: Oct 2006
- Finish: Sept 2009 (extended to 2011)
- 80% Finished

Budget
- Total Project funding (3 yrs)
  - DOE: $1,450K
  - Industry sponsors: $1,450K
- Funding received in FY10
  - $500K
- Funding received in FY11
  - $250K

Barriers
- Increased back pressure and fuel penalty
- Lack of effective regeneration strategies to reduce input energy and deal with low exhaust temperature
- Durability of the system, including filter materials
- Sensor technology

Partners
- Corning and Caterpillar
- University of Illinois – Chicago
- University of Wisconsin – Madison
- ILJIN Electric Co., Korea
- IBIDEN, Japan
Relevance and Objectives

- Existing DPF systems still need to improve filtration/regeneration efficiencies and pressure drops.
- DPF systems need efficient regeneration strategies, which can control thermal run-away.
- A real-time DPF control/management system is required for developing an advanced DPF system with on-board diagnostics (OBD) capability.

- Evaluate pressure drops for catalyzed DPF membranes.
- Investigate the regeneration process via real-time monitoring.
- Predict the transient heat release from DPF regeneration.
  - Evaluate the oxidation rates and kinetic parameters for diesel particulates
- Develop a real-time DPF control/management system that can measure the instantaneous mass of soot deposits in a DPF, control DPF regeneration, and provide OBD signals for DPF operation.
Approach – Overall

DPF experiments for filtration, regeneration, $\mu$-imaging

Soot oxidation experiments with TGA, DSC

Numerical modeling

Diesel Engine

PM mass, filtration efficiency with TEOM
**Approach**

- **Experimental procedure**

  - Diesel PM samples
  - TGA
  - DSC
  - Bisected non-catalyzed Cordierite membrane
  - Soot deposit
  - DPF Test System
  - 2.4L Diesel Engine
  - Residues
DPF bench test system upgraded with heater unit
Pore size distributions were evaluated for catalyzed DPF membranes

Definition of pore size ($D_p$): max diameter of a sphere that can pass through the pore on the surface
Average pore size increased with catalyst coating

- Average pore diameters: 28.4 $\mu$m (#1), 34.2 $\mu$m (#2), 41.9 $\mu$m (#3)
  - With catalyst coating, the number of small micro pores was reduced (blocked by catalyst materials), while the number of medium/large pores relatively increased.
Heavily catalyzed membrane increased back pressure by a factor of two (2) compared to bare membrane.

- Reduced total number of pores with catalyst coating is responsible for the increased pressure drop.
Accurate evaluation of kinetic parameters is important for calculating transient heat release.

- Numerical calculation of transient heat release during regeneration is pursued, because of limited access to the hardware and inaccuracy in measurements.

\[
\dot{Q} = q \times \frac{dm}{dt}
\]

- Heat release per mass \(q\) of diesel particulates has been measured by using a DSC.
  
  \[q_{\text{dry soot}} = 17.2 \text{ kJ/g}, \quad q_{\text{SOF}} = 5.5 \text{ kJ/g}\]

- Oxidation rates can be found by TGA experiments.

\[
r = -\frac{dm}{dt} = A \cdot \exp\left[-\frac{E_a}{RT}\right] \cdot [m]^n \cdot [P_{O_2}]^{n_{O_2}}
\]

- \(r\): Reaction rate
- \(m\): Remaining carbon mass
- \(A\): Pre-exponential factor
- \(E_a\): Activation energy
- \(R\): Universal gas constant
- \(T\): Temperature
- \(n\): Reaction order of carbon
- \(P_{O_2}\): Partial pressure of oxygen
- \(n_{O_2}\): Reaction order of oxygen
Activation energy was evaluated for carbon black

- Model soot: Carbon black (Printex-U)
- Instruments
  - Thermogravimetric analyzer (TGA) → oxidation rate
  - Differential scanning calorimeter (DSC) → heat release
- Experimental conditions
  - Isothermal oxidation (@ 600 °C isothermal)
    - Environment: 40% He + 60% air (overall 12% O₂ concentration)
    - Total flow rate: 100 ml/min
    - Heating rate: 10 °C/min
Reaction order of surrogate soot was successfully evaluated via TG oxidation experiments.

- Model soot sample

- Reaction order of soot sample \((n = 0.78 \pm 0.03)\)

\[
\ln \left[-\frac{\mathrm{dm}}{\mathrm{dt}}\right] = n \ln[m] - \frac{E_a}{R} \cdot \frac{1}{T} + n_{O_2} \ln[P_{O_2}] + \ln[A]
\]
Activation energy for surrogate soot turned out to be comparable to those from other investigations

Model soot sample (n = 0.78) @ ln(m)=0

\[- \frac{dt}{dm} = \frac{-E_a}{R} \cdot \frac{1}{T} + n_{O_2} \ln[P_{O_2}] + \ln[A]\]

slope = \(-\frac{E_a}{R}\)

Activation energy, \(E_a\) (kJ/mol)

137 \(\pm\) 8.7 kJ/mol @ He/air (A. Yezerets, 2005)
168 \(\pm\) 1.0 kJ/mol @ O\(_2\)/Ar (J.P.A. Neeft, 1997)

\[\frac{dm}{dt} \text{ (mg/sec)} = 1.3625 \times 10^5 \exp \left( - \frac{16598}{T \text{ (K)}} \right) \cdot [m]^{0.78} \text{ (mg)}\]
Effects of ambient experimental conditions and analytic methodology need to be examined to accurately evaluate kinetic parameters

- Effects of inert gas and heating rate have not been investigated for evaluation of kinetic parameters, especially in engineering research communities.
- The magnitude of kinetic parameters also depends on the methodology that analyzes the thermogravimetric data.
- Analytic methodologies
  - Isothermal kinetic analysis
  - Non-isothermal kinetic analysis
    - \textit{Integral method}
    - \textit{Iso-conversional method}
    - \textit{Differential method (proposed by Argonne research team)}
Theory of the different analytic methodologies

■ Isothermal kinetic analysis

- \( \alpha = \frac{m_0 - m}{m_0 - m_1} \) (Degree of conversion, \( m \): mass of soot)

- \( \frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \) (Rate of reaction, \( f(\alpha) \): kinetic expression)

- \( f(\alpha) = (1 - \alpha)^n \) Simple assumption

- No effects of heating rate considered.

■ Non-isothermal kinetic analysis

- \( \frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \) (\( \beta = \frac{dT}{dt} \) : Heating rate)

- \( \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_T^{T_0} \frac{A}{\beta} \exp \left(-\frac{E_a}{RT}\right) dT \)

- Integral method
  - \( g(\alpha) = \frac{A E_a}{\beta R} \cdot p(x) \) \[ g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} , \quad p(x) = \int_x^\infty \frac{e^{-u}}{u^2} du , \quad u = \frac{E_a}{RT} \]
  - Coats-Redfern’s approximation, \( p(x) = e^{-x} \frac{x^2-2}{x^2} \), and taking logarithm
  - \( \log \frac{g(\alpha)}{T^2} = \log \left[ \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) \right] - \frac{E_a}{2.3RT} \) (A plot of \( \log \frac{g(\alpha)}{T^2} \) vs. \( \frac{1}{T} \))
Theory (continued)

- Iso-Conversional method (Vyazovkin)
  - \( g(\alpha) = \frac{A E_a}{\beta R} \cdot p(x) \)
  - Used different heating rates, \( \beta_i \) \((i = 1, \ldots, n)\)
  - Approximation: \( p(x) = \frac{e^{-x}}{x} \frac{x^2+10x+18}{x^3+12x^2+36x+24}, \) where \( x = \frac{E_a}{RT} \)

- Differential method (proposed)
  - \( \frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \cdot (1 - \alpha)^n, \) where \( f(\alpha) = (1 - \alpha)^n \)
  - \( \log\left(\frac{d\alpha}{dt}\right) - n \log(1 - \alpha) = -\frac{E_a}{RT} + \log A \)
  - \( E_a \) and \( A \) can be found by plotting left-hand terms vs. \( 1/T \) with a variation of hypothesized \( n \).
*Isothermal Method gives different activation energies depending on inert gases*

- Each data set was evaluated for three different isothermal conditions: 500, 550, and 600 °C.
- Average activation energy: 164.5 (N\textsubscript{2}), 163.9 (Ar), and 149.5 kJ/mole (He)
Integral Method evaluated activation energies quite significantly changing with heating rate (Non-isothermal)

- Activation energy appears to be sensitive to the heating rate for all three inert gas-air mixtures.
- Data for N₂ and Ar show almost identical values.
Iso-Conversioonal Method evaluated the activation energies depending on inert gas

Average activation energy: 145.7 (N₂), 152.8 (Ar), and 127 kJ/mole (He)
Differential Method gives a single value of activation energy suitable for regeneration in DPF systems.

- Relatively even distributions with heating rate were evaluated for \( \text{N}_2 \) and Ar.
- Activation energy converges at the lowest heating rate, regardless of inert gas (155 kJ/mole).

![Graph showing activation energy vs heating rate for different inert gases](image)
## Summary of activation energy values evaluated by different analytic methodologies

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Inert gas</th>
<th>N\textsubscript{2} (kJ/mole)</th>
<th>Ar (kJ/mole)</th>
<th>He (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td></td>
<td>164.5</td>
<td>163.9</td>
<td>149.5</td>
</tr>
<tr>
<td>Non-isothermal</td>
<td>Integral</td>
<td>138 – 155 (Approx. same)</td>
<td>←</td>
<td>138 – 148</td>
</tr>
<tr>
<td></td>
<td>Iso-</td>
<td>145.7</td>
<td>152.8</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>coversional</td>
<td></td>
<td>←</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Differential</td>
<td>155 – 170 (Avg. ≅ 160)</td>
<td>120 – 155</td>
<td></td>
</tr>
</tbody>
</table>

- Comparable molecular weights between N\textsubscript{2} (14) and Ar (18)
- Comparable mass diffusivity and thermal diffusivity between N\textsubscript{2} and Ar
Modified DPF membrane showed an improvement of pressure drop in a short soot loading period.
Extended soot loading revealed an apparent reduction of back pressure in modified membranes

- A heavy-duty single cylinder has been used for soot loading.
- The modified filter allows a lower back pressure during more than 90% time period of a regeneration cycle.
Particulates from LTC with bio fuels showed considerably different morphology

- 1.9 L diesel; 2000 rpm/5.5 bar IMEP; 67% EGR; 9.5% O₂ concentration; 22° BTDC fuel inj.
- Biofuel-derived particles showed smaller in size than those from the ULSD combustion.
- These LTC-derived particles looked more spherical in shape and amorphous in nanostructures than those from conventional stoichiometric diesel combustion.
- This work has been conducted in collaboration with ERC at University of Wisconsin.
Detailed TEM image analysis revealed fuel-dependence of particulate dimensions in LTC

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Soy bean B20</th>
<th>Palm oil B20</th>
<th>ULSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. $D_p$ (nm)</td>
<td>23.2</td>
<td>22.2</td>
<td>23.0</td>
</tr>
<tr>
<td>Avg. $R_g$ (nm)</td>
<td>22.9</td>
<td>27.4</td>
<td>27.5</td>
</tr>
<tr>
<td>$D_f$</td>
<td>1.84</td>
<td>1.83</td>
<td>1.82</td>
</tr>
</tbody>
</table>
Future Work

- FY11
  - Evaluate PM filtration efficiencies at various engine operating conditions.
  - Conduct regeneration experiments.
    - Use catalyst-coated membranes.
    - Provide optical images of thermal reaction in regeneration.
  - Perform thermogravimetric experiments with various flue gases (NO$_x$, HC, CO, CO$_2$, H$_2$O) to evaluate oxidation rates, kinetic parameters, and heat release.

- This work will be continued under a new CRADA contract in collaboration with Corning, Inc.
Summary

- The regeneration system has been completed to fabricate by adding the electric heating system.
- Catalytic coating on DPF membranes changed pore structures and increased back pressure up to a factor of two (2).
- Activation energy turned out to be sensitive to the inert gas and heating rate.
- The proposed Differential Method accurately evaluated an activation energy (155 kJ/mole), which is independent of the inert gas.
- The modified DPF membrane significantly reduced back pressure for the majority of filtration period.
- The use of biofuels for LTC significantly changed particulate morphology, in terms of nano-structures, size (particularly by soy bean fuel), and fractal geometry, compared to those from the conventional diesel combustion.
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