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Development of Advanced Diesel Particulate Filtration (DPF) Systems

(ANL/Corning/Caterpillar CRADA)

Project ID: ACE024

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U.S. Department of Energy

UChicago Argonne LLC

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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.

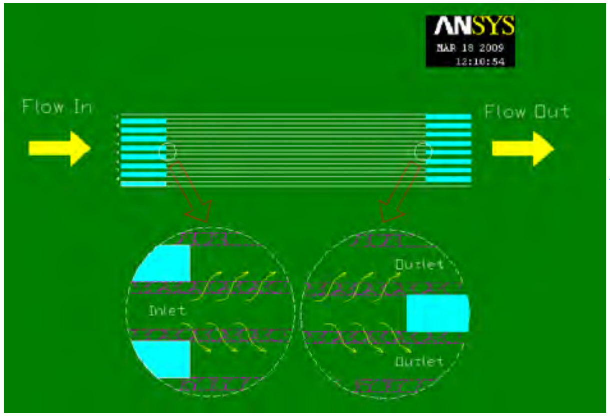
- Evaluate pressure drops for catalyzed DPF membranes.
- Investigate the regeneration process via real-time monitoring.
- Predict the transient heat release from DPF regeneration.
  - Evaluate the oxidation rates and kinetic parameters for diesel particulates
- Develop a real-time DPF control/management 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, μ-imaging

Soot oxidation experiments with TGA, DSC

Diesel Engine

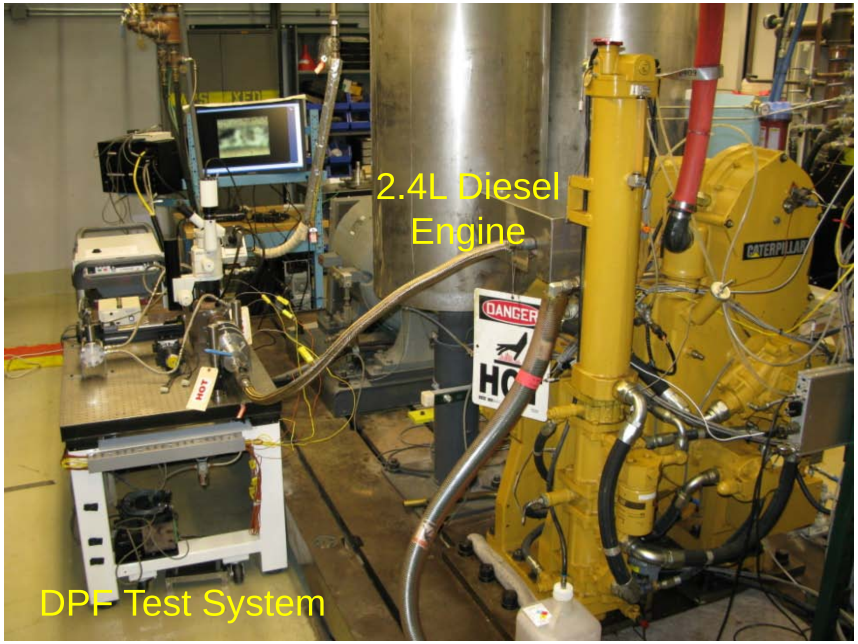


Numerical modeling

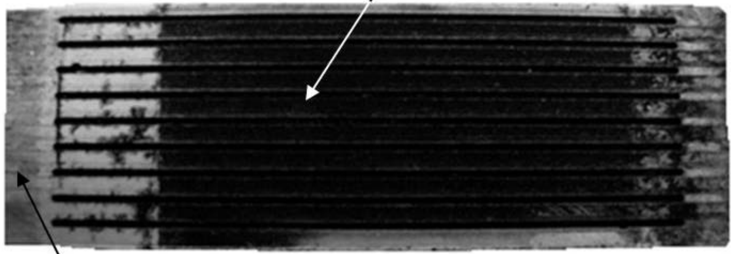
PM mass, filtration efficiency with TEOM

Approach

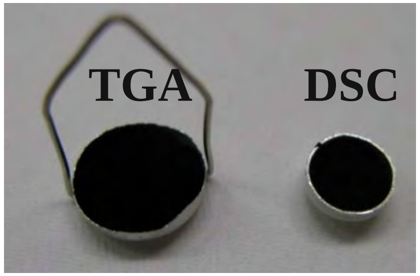
Experimental procedure



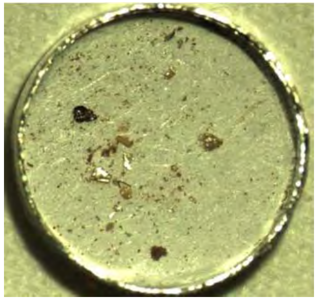
Soot deposit



Bisected non-catalyzed Cordierite membrane

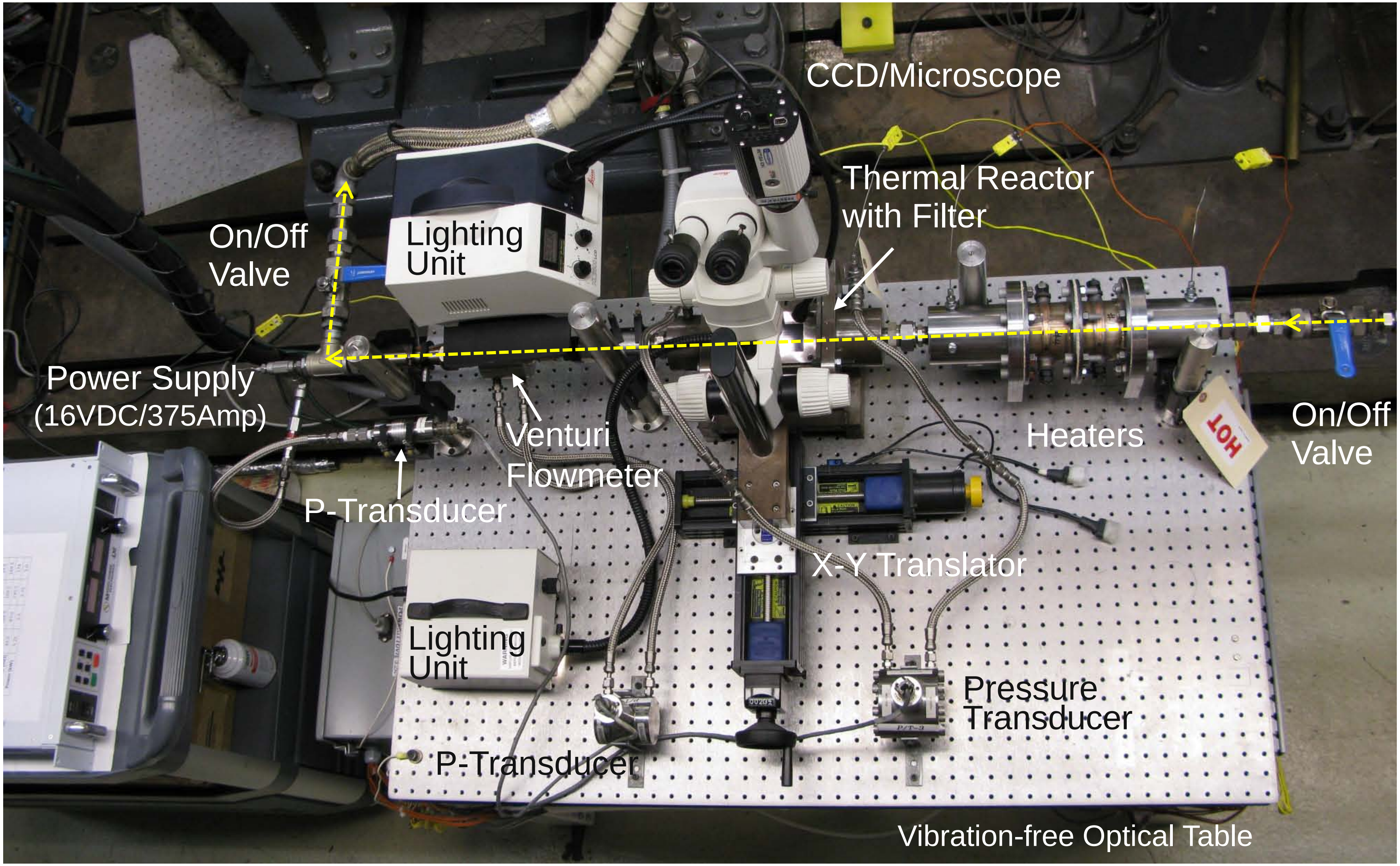


Diesel PM samples

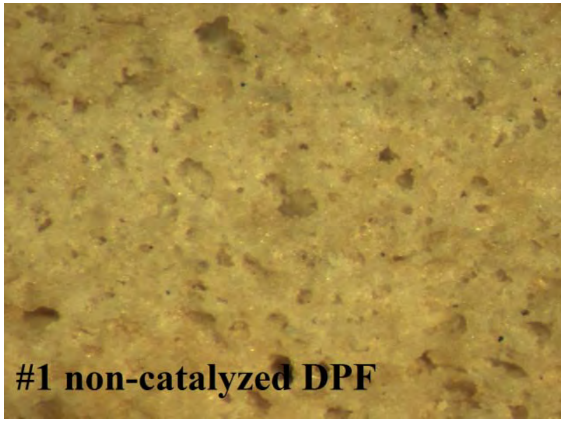


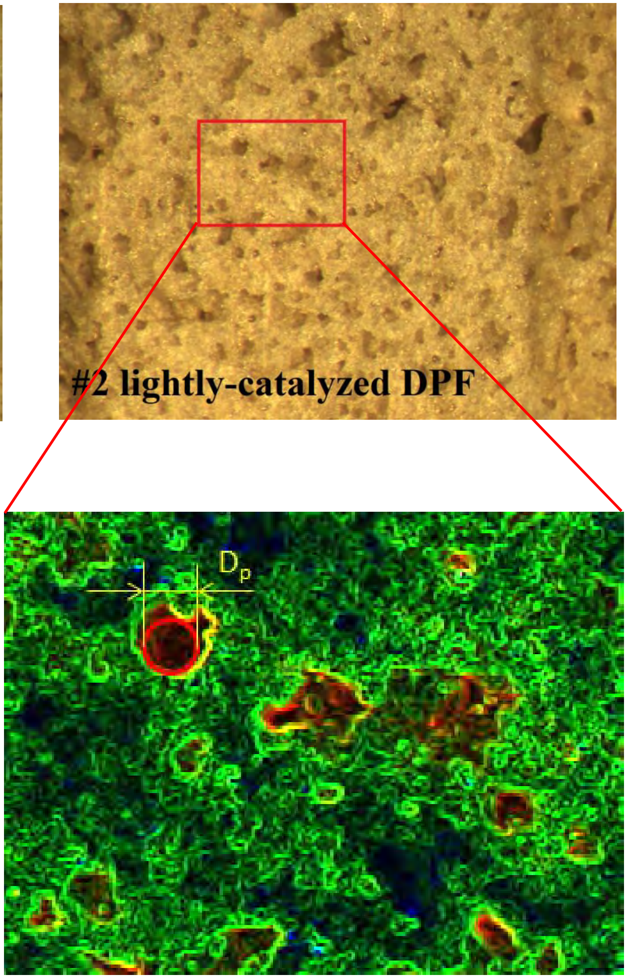
Residues

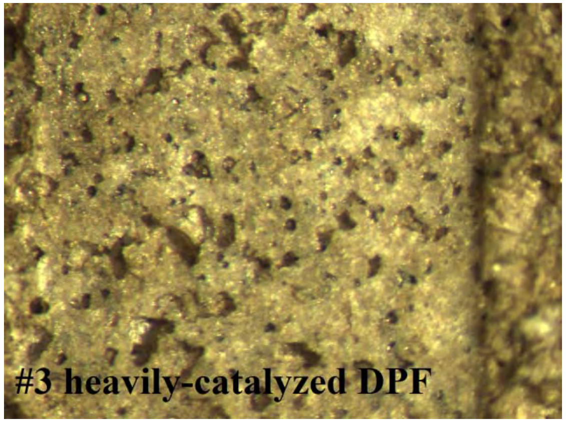
DPF bench test system upgraded with heater unit

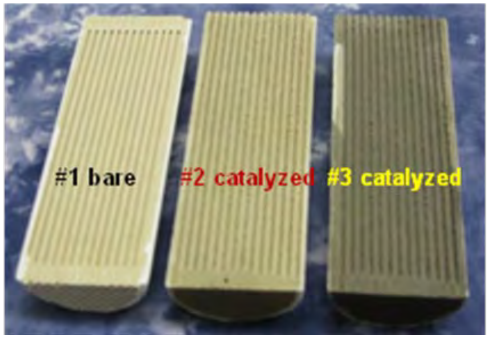


Pore size distributions were evaluated for catalyzed DPF membranes



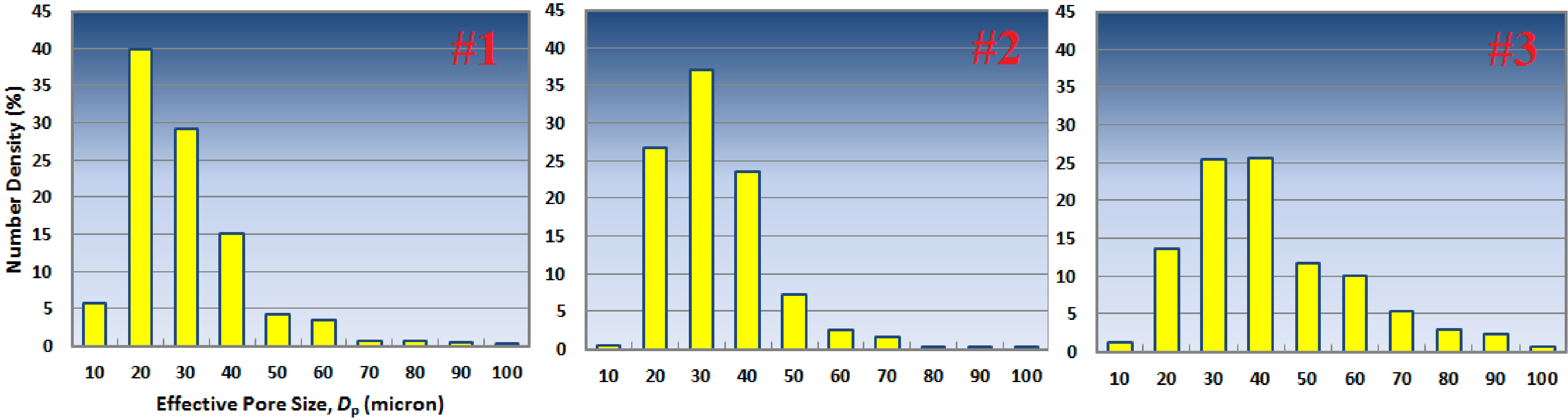






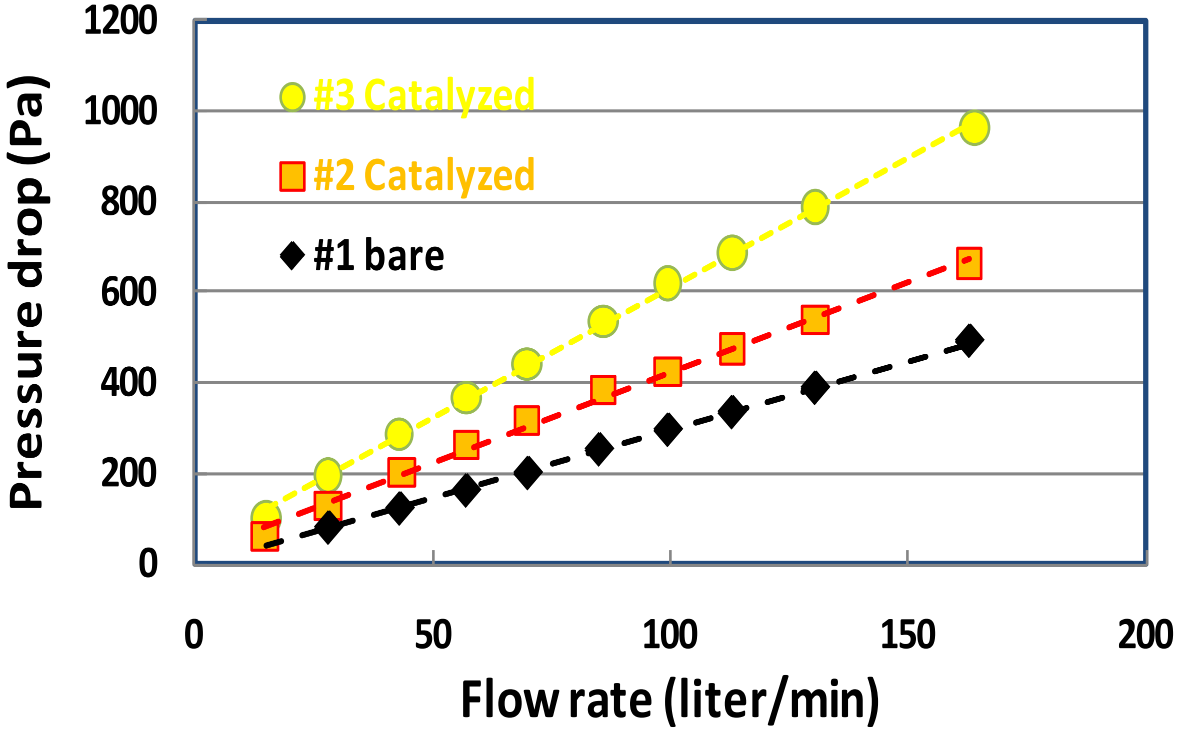
- Definition of pore size (D_p): max diameter of a sphere that can pass through the pore on the surface

Average pore size increased with catalyst coating



- Average pore diameters: 28.4 *µm* (#1), 34.2 *µm* (#2), 41.9 *µm* (#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.

$$\dot{Q} = q \times \frac{dm}{dt}$$

Q [kW]: Transient heat release
q [kJ/g]: Heat release per mass
dm/dt [g/s]: Oxidation rate

- Heat release per mass (q) of diesel particulates has been measured by using a DSC.

$q_{dry\ soot} = 17.2$ kJ/g, $q_{SOF} = 5.5$ kJ/g

- Oxidation rates can be found by TGA experiments

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

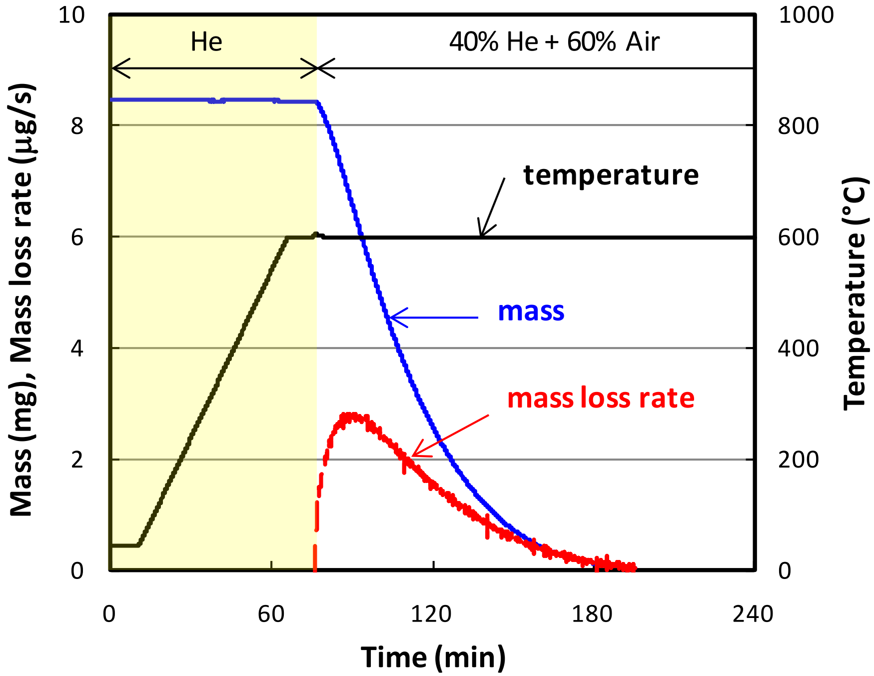
r: Reaction rate
m: Remaining carbon mass
A: Pre-exponential factor
E_a: Activation energy
R: Universal gas constant
T: Temperature
n: Reaction order of carbon
P_{O2}: Partial pressure of oxygen
n_{O2}: Reaction order of oxygen

Activation energy was evaluated for carbon black

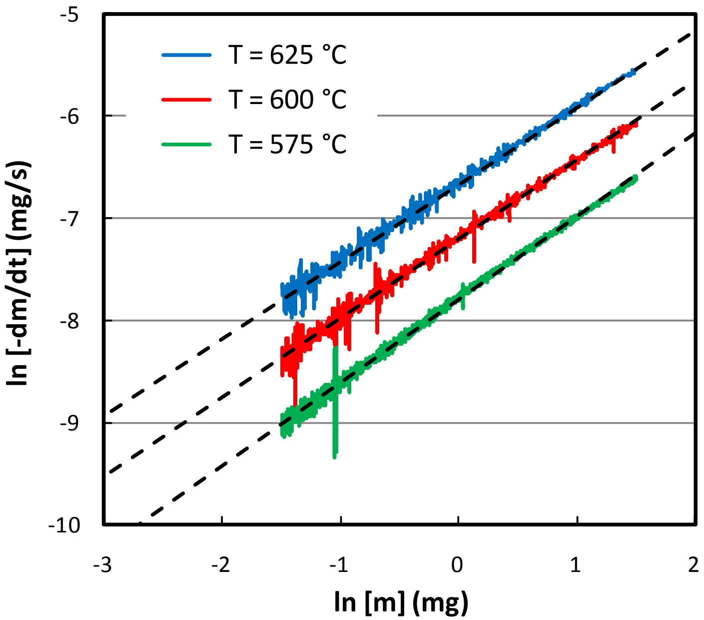
- Model soot: Carbon black (Printex-U)
- Instruments
  - Thermogravimetric analyzer (TGA) → oxidation rate
  - Differential scanning calorimeter (DSC) → heat release
- Experimental conditions
  - Isothermal oxidation (@ 600 °C isothermal)
    - *Environment: 40% He + 60% air (overall 12% O_2 concentration)*
    - *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 ± 0.03**)**



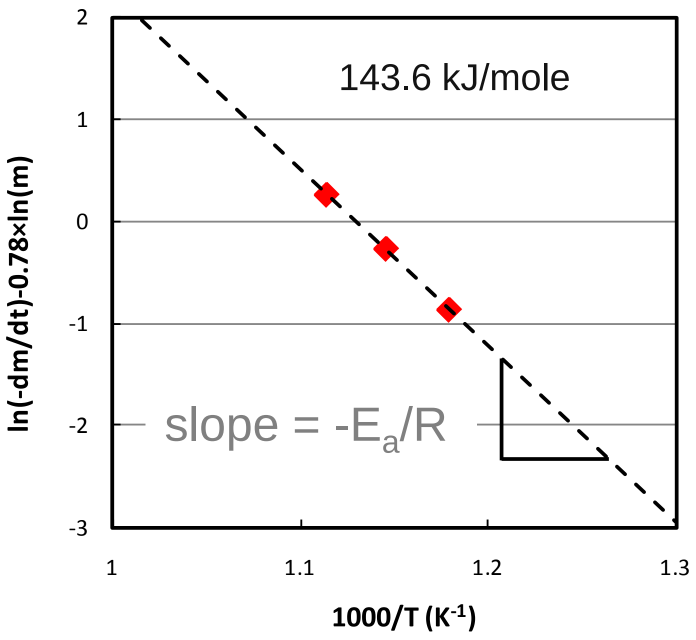
$$\ln\left[-\frac{dm}{dt}\right] = \mathbf{n}\ln[m] - \frac{E_a}{R}\cdot\frac{1}{T} + n_{O_2}\ln\left[P_{O_2}\right] + \ln[A]$$

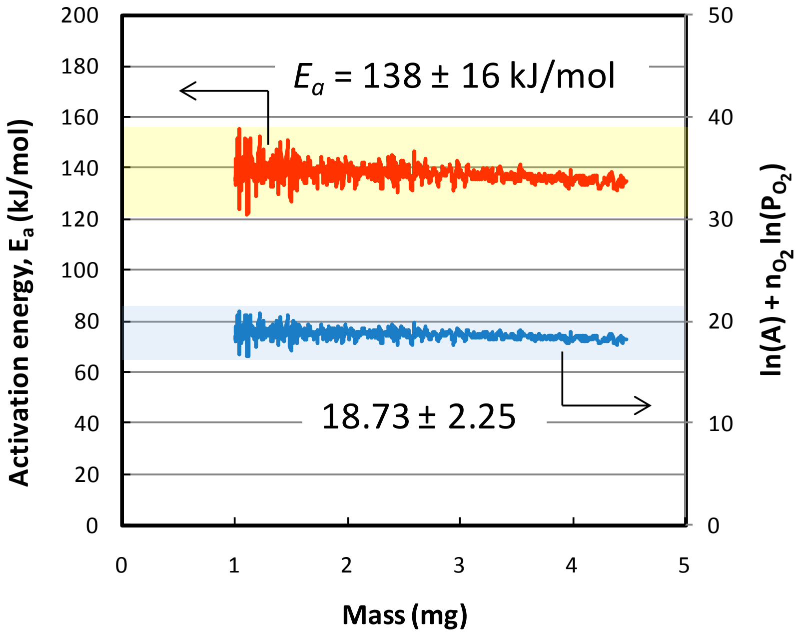
Activation energy for surrogate soot turned out to be comparable to those from other investigations

Model soot sample (n = 0.78)

@ ln(m)=0

137 ± 8.7 kJ/mol @ He/air (A. Yezerets, 2005)
168 ± 1.0 kJ/mol @ O_2/Ar (J.P.A. Neeft, 1997)





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

$$-\frac{dm}{dt}\left(\frac{mg}{sec}\right) = 1.3625\times 10^5 \exp\left[-\frac{16598}{T\ (K)}\right]\cdot[m]^{0.78}\ (mg)$$

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
    - *Integral method*
    - *Iso-conversional method*
    - *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)
  - $\frac{d\alpha}{dt} = A \exp(-\frac{E_a}{RT}) f(\alpha)$ (Rate of reaction, $f(\alpha)$: kinetic expression)
  - $f(\alpha) = (1-\alpha)^n$ Simple assumption
  - No effects of heating rate considered.

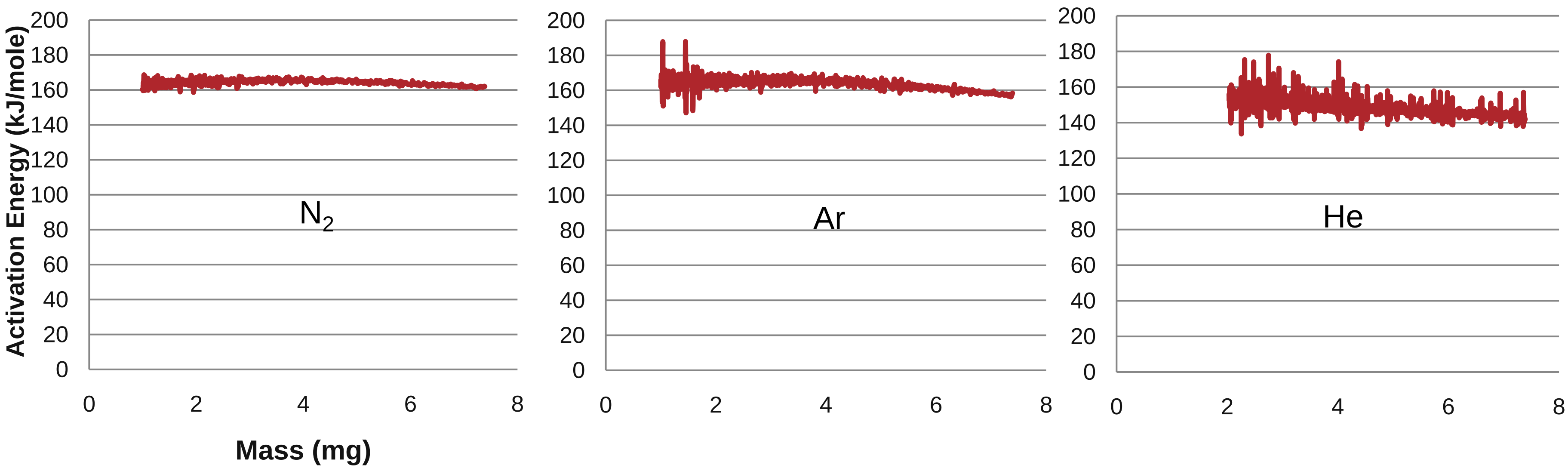
- Non-isothermal kinetic analysis
  - $\frac{d\alpha}{dT} = \frac{A}{\beta} exp(-\frac{E_a}{RT}) f(\alpha)$ ($\beta = \frac{dT}{dt}$: Heating rate)
  - $\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T} \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dT$
  - Integral method
    - $g(\alpha) = \frac{A}{\beta}\frac{E_a}{R} \cdot p(x)$ $[g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)}, p(x) = \int_x^{\infty} \frac{e^{-u}}{u^2} du, u = \frac{E_a}{RT}]$
    - Coats-Redfern's approximation, $p(x) = e^{-x}\frac{x-2}{x^2}$, and taking logarithm
    - $log\frac{g(\alpha)}{T^2} = log\left[\frac{AR}{\beta E_a}(1 - \frac{2RT}{E_a})\right] - \frac{E_a}{2.3RT}$ (A plot of $log\frac{g(\alpha)}{T^2}$ vs. $\frac{1}{T}$)

Theory (continued)

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

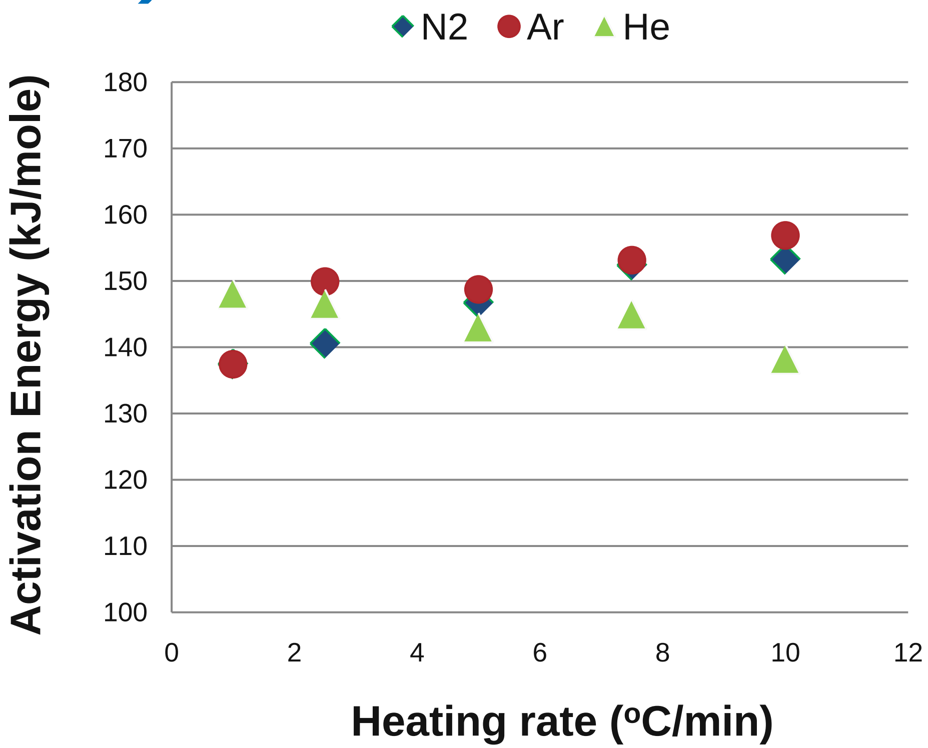
- Differential method (proposed)
  - $\frac{d\alpha}{dt}$ = $\mathrm{A}\exp(-\frac{E_a}{RT}) \cdot (1-\alpha)^n$, where $f(\alpha) = (1-\alpha)^n$
  - $log(\frac{d\alpha}{dt}) - nlog(1-\alpha) = -\frac{E_a}{RT} + logA$
  - E_a *and* A *can be found by plotting left-hand terms vs.* $1/T$ *with a variation of hypothesized* n.

Isothermal Method gives different activation energies depending on inert gases



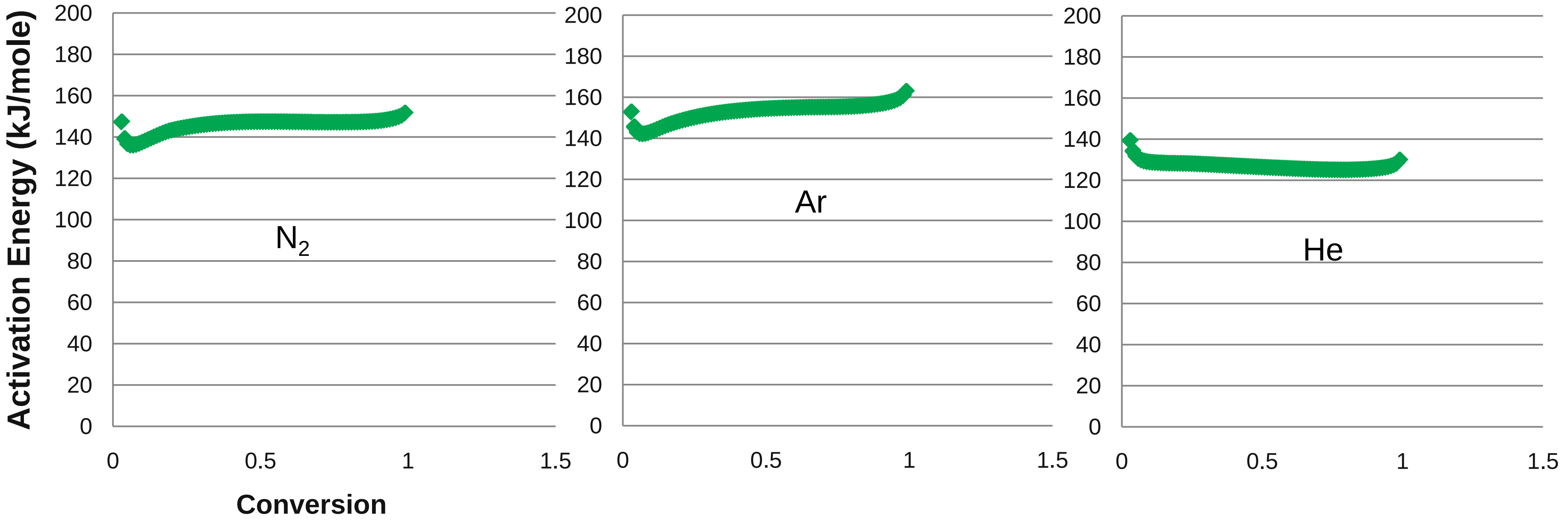
- Each data set was evaluated for three different isothermal conditions: 500, 550, and 600 °C.
- Average activation energy: 164.5 (N_2), 163.9 (Ar), and 149.5 kJ/mole (He)

Integral Method evaluated activation energies quite significantly changing with heating rate (Non-isothermal)



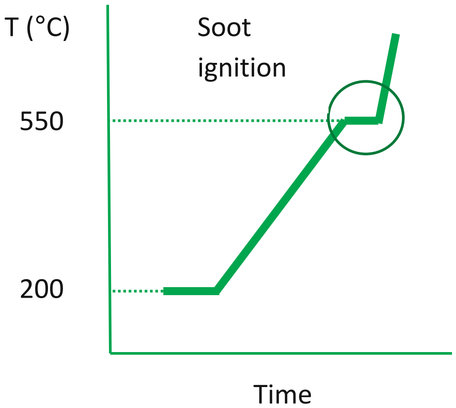
- Activation energy appears to be sensitive to the heating rate for all three inert gas-air mixtures.
- Data for N_2 and Ar show almost identical values.

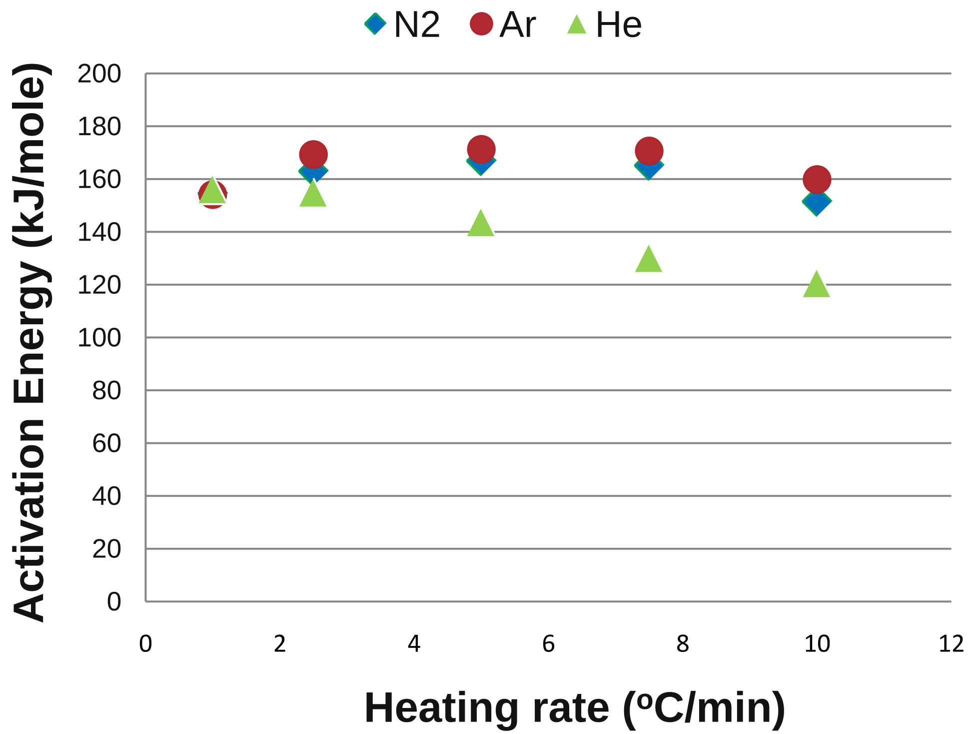
Iso-Conversional Method evaluated the activation energies depending on inert gas



- Average activation energy: 145.7 (N_2), 152.8 (Ar), and 127 kJ/mole (He)

Differential Method gives a single value of activation energy suitable for regeneration in DPF systems





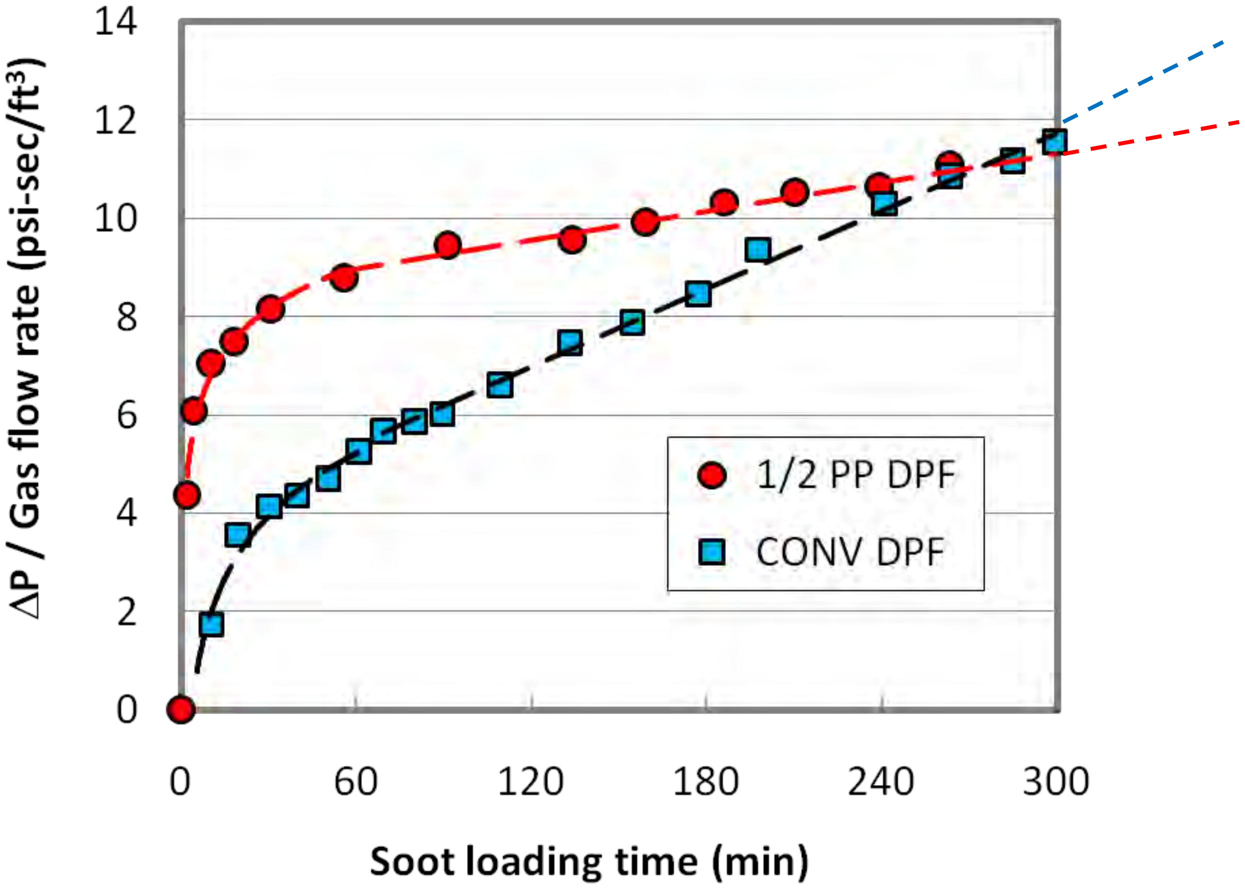
- Relatively even distributions with heating rate were evaluated for N_2 and Ar.
- Activation energy converges at the lowest heating rate, regardless of inert gas (155 kJ/mole).

Summary of activation energy values evaluated by different analytic methodologies

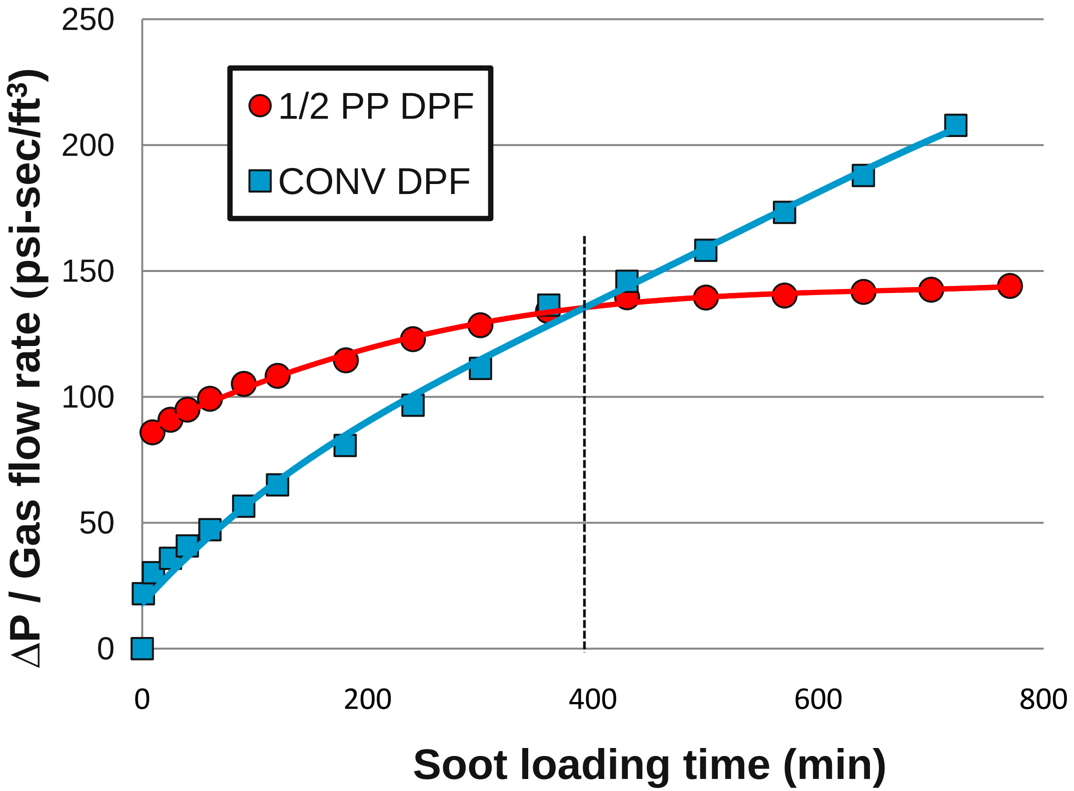
Methodology \ Inert gas		N_2 (kJ/mole)	Ar (kJ/mole)	He (kJ/mole)
Isothermal		164.5	163.9	149.5
Non-isothermal	Integral	138 – 155	← (Approx. same)	138 – 148
	Iso-coversional	145.7	152.8	127
	Differential	155 – 170 (Avg. ≅ 160)	← (Approx. same)	120 – 155

- Comparable molecular weights between N_2 (14) and Ar (18)
- Comparable mass diffusivity and thermal diffusivity between N_2 and Ar

Modified DPF membrane showed an improvement of pressure drop in a short soot loading period

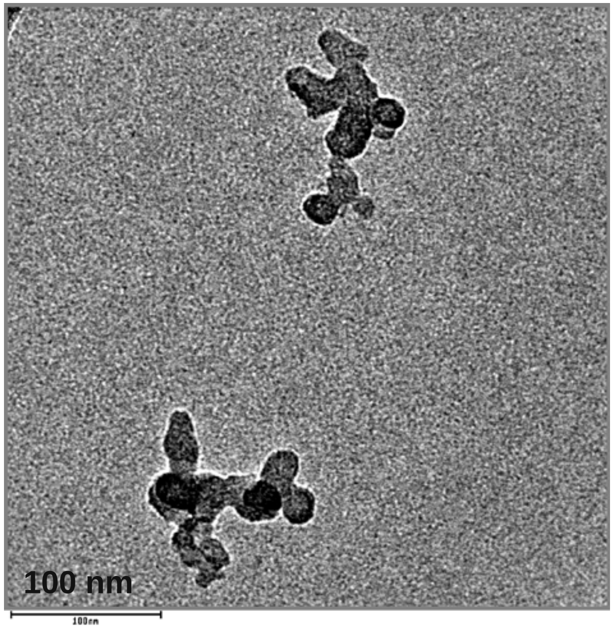


Extended soot loading revealed an apparent reduction of back pressure in modified membranes

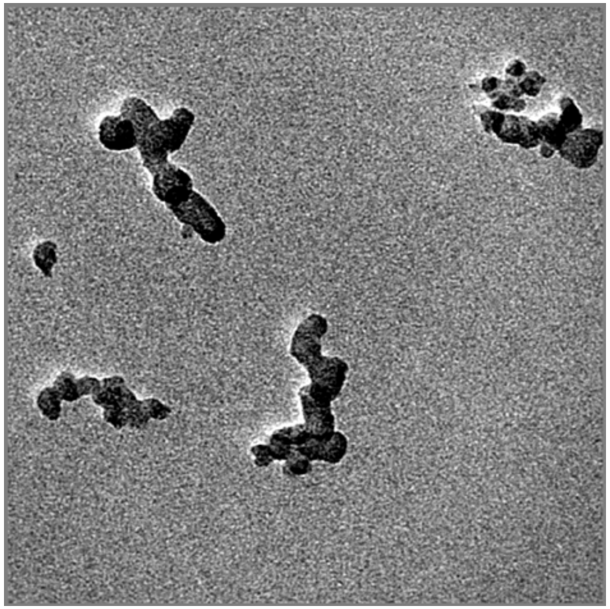


- A heavy-duty single cylinder has been used for soot loading.
- The modified filter allows a lower back pressure during more than 90% time period of a regeneration cycle.

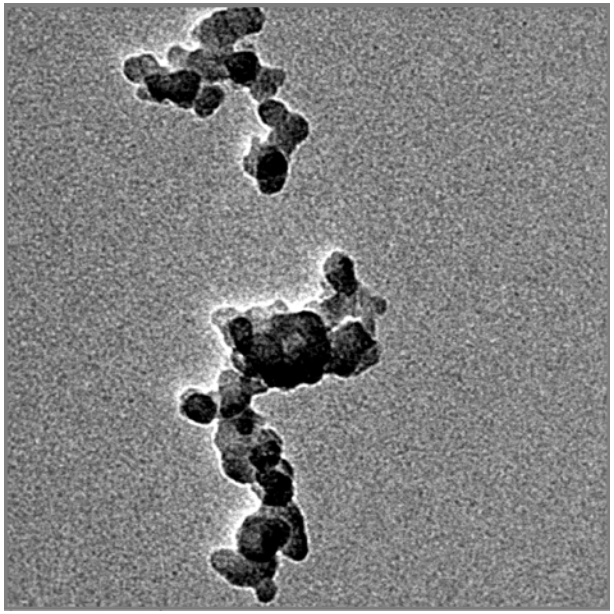
Particulates from LTC with bio fuels showed considerably different morphology



Soy bean B20



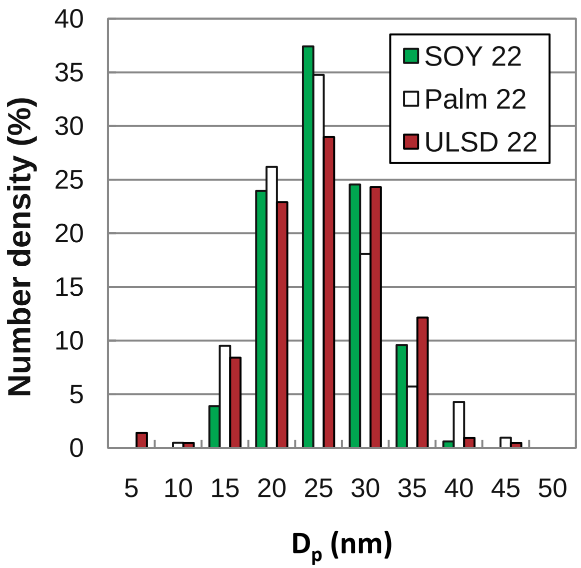
Palm oil B20

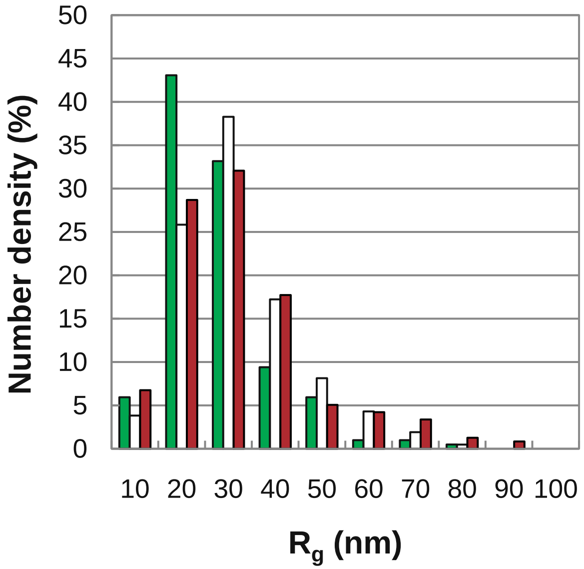


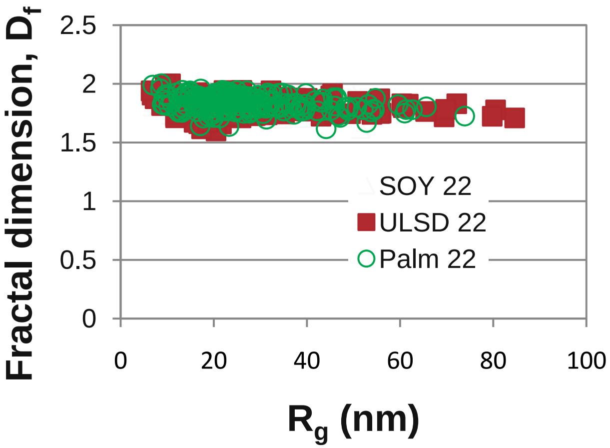
ULSD

- 1.9 L diesel; 2000 rpm/5.5 bar IMEP; 67% EGR; 9.5% O_2 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 nano-structures 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







Dimensions	Soy bean B20	Palm oil B20	ULSD
Avg. D_p (nm)	23.2	22.2	23.0
Avg. R_g (nm)	22.9	27.4	27.5
D_f	1.84	1.83	1.82

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_2O) 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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