Particulate Emissions Control by Advanced Filtration Systems for GDI Engines (ANL/Corning/Hyundai CRADA)

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Office of Vehicle Technologies

Project ID: ACE024

Overview

Timeline

- Start: Oct. 2011
  - Contract signed: Sept. 2012
- End: Sept. 2015
- 50% finished

Budget

- Total project funding
  - DOE share: $1.8M
  - Contractor share: $1.79M
- Funding received in FY13
  - DOE: $500K
  - Corning: $300K (in-kind)
  - Hyundai: $110K (in-kind) & $90K (fund-in)

Barriers

- Insufficient information about properties of GDI PM emissions
- Lack of understanding about filtration and regeneration mechanisms
- Increased back pressure by GPF

Partners

- Corning and Hyundai Motor
- University of Wisconsin – Madison
- Tokyo Institute of Technology

Relevance

- PM emissions standards (US Tier-3①; Euro-6②)
  - Mass: 0.003 g/mi (2017)① ; 0.005 g/km (2014)②
  - Number (2017)② : 6×10^{11} #/km for $23nm \leq \emptyset \leq 1\mu m$
  - PN emissions from GDI engines exceed those from PFI engines by more than O(1) of magnitude [SAE 2007-01-0209].
- GDI soot
  - Oxidation rate: 2 – 5 times higher than that of diesel soot [Konieczny et al., 6th Int'l Exhaust Gas and Particulate Emissions Forum (2010)].
  - Thus, insignificant soot loading, continuous oxidation, no extreme heat release in GPF, and a low GPF volume needed (avg. GPF to engine volume ratio = 0.7).
  - Most of PM emissions are formed in cold start and during warm-up [Health Effects Institute. Communication 16 (2011)].
  - Information about detailed properties of GDI soot is lacking.
- GDI ash
  - Relatively higher ash accumulation is expected in gasoline engines due to the higher engine speed [Mayer et al., SAE 2010-01-0792].
  - More comprehensive studies are needed.

Relevance (continued) and Research Plan

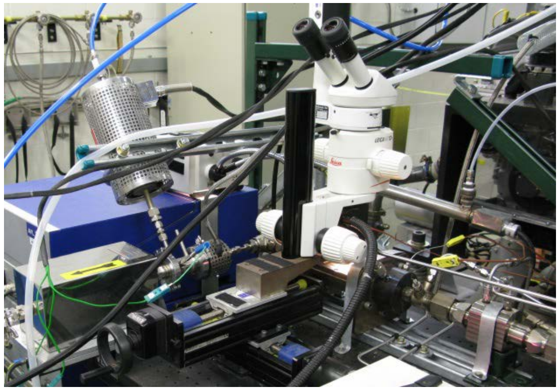
- Filtration and Regeneration
  - Filtration and regeneration mechanisms in GPFs, which continuously oxidizing loaded soot, have not been clearly understood.
  - Understanding of interactions of PM with catalysts is lacking.
  - GDI engines particularly for passenger vehicles need low back-pressure filters to be developed.

- Research Plan (FY13 – 14)
  - Characterize the detailed properties of soot, ash, and other chemicals in PM emissions at cold operations and various injection times.
  - Evaluate oxidation reactivity of soot in consideration of ash and soot nanostructures.
  - Clarify the effects of TWC on PM and ash compositions.
  - Clarify the filtration mechanisms of soot in a GPF.
  - Evaluate filtration efficiencies based on PN measurements.
  - Propose guidelines of nanoparticle control for GDI engines using filter systems.

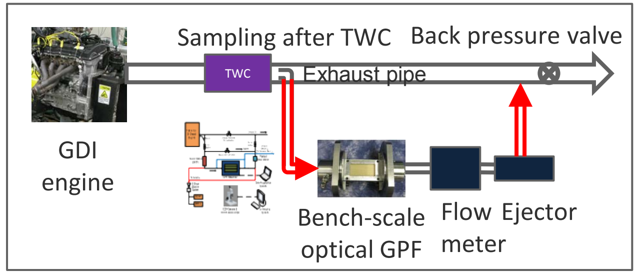
Project Milestone (FY13-14)

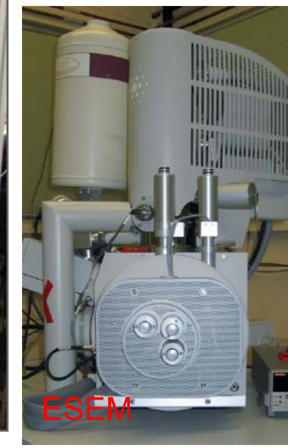
Month-Year	Milestone Description	Status
Apr – Sept, 2013	Characterize properties of GDI engine-out PM – Size, morphology, crystalline structures	Completed
Jun – Sept, 2013	Measure baseline PM emissions at different engine operating conditions and across the TWC – PM mass, PN	Completed
Oct – Dec, 2013	Evaluate effects of TWC on chemical compositions in PM – Soot, VOF, ash	Completed
Oct, 2013 – Feb, 2014	Evaluate oxidation reactivity of soot for PM samples collected at different engine conditions, using TGA	Completed
Mar – Jun, 2014	Evaluate filtration efficiency for different filter models	25% completed (to be continued)
Apr – Sept, 2014	Perform regeneration with visualization and find regeneration mechanisms, using both catalyzed and bare filters	Heating units being installed on emissions bypassing line (to be continued in FY14)
Sept – Dec, 2014	Examine ash properties and microstructures of aged filters; evaluate filtration/regeneration performance	25% completed (to be continued in FY14)

Approach



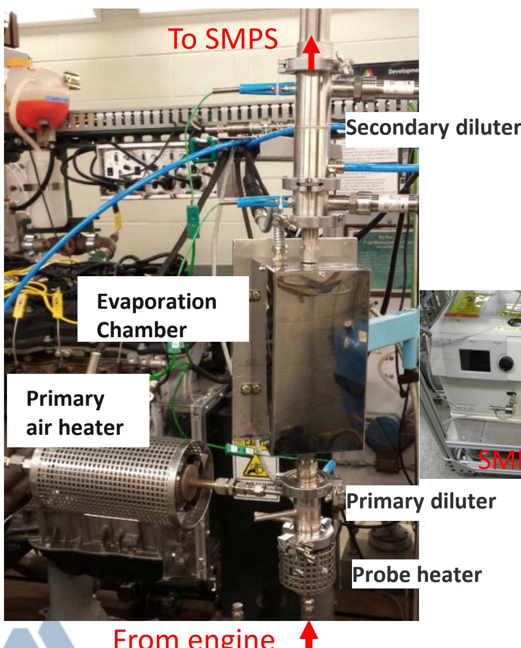
GPF test bench with dilution & μ-imaging systems

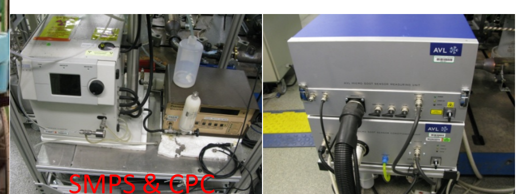




Soot oxidation experiments with TGA and ESEM

2.4L GDI Engine





Particle number/mass measurements

X-ray analysis of GDI soot and filter substrates (APS)

Approach (2) and Strategy

2.4L GDI engine

Analysis of Particulate Properties

Analyze important properties of GDI particulates at various engine conditions in comparison with diesel particulates to optimize GPF operations.

- Morphology, nanostructures: TEM

Filtration

Investigate filtration processes during cold and warm-up periods

- Evaluation of mass, number, size: AVL micro soot sensor, SMPS with dilution
- Visualization of filtration process at cold start and warm-up
- Evaluation of PN-based filtration efficiency of clean GPF along with visualization

Regeneration

Analyze compositions and oxidation reactivity of Engine-out and TWC-out soot

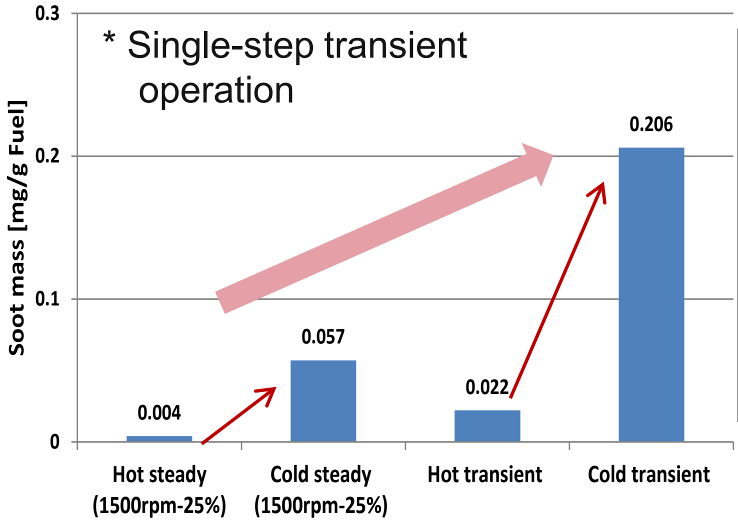
- Soot oxidation reactivity and compositions: TGA, SEM-EDS
- Comprehensive analysis of soot crystalline structures: Raman spectroscopy, PDF

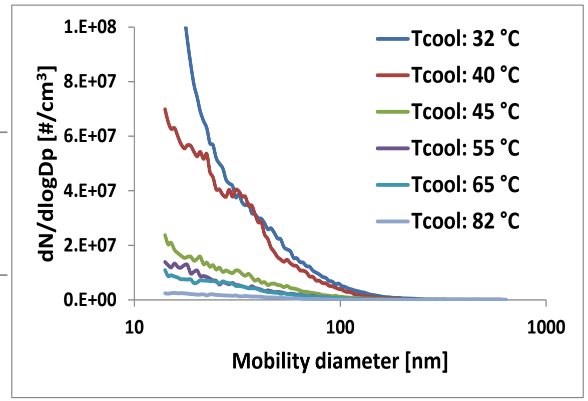
Visualize GPF regeneration at λ=1, steady-state engine condition

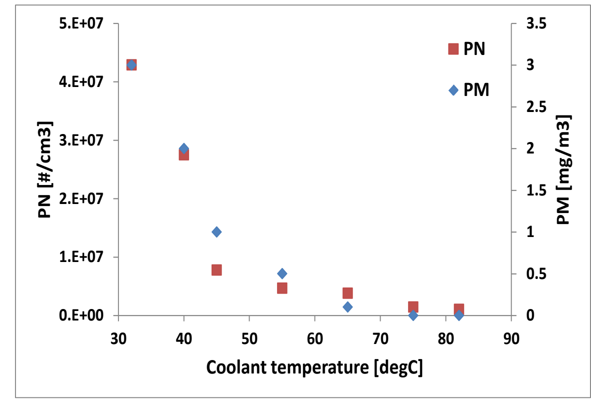
Ash effects on aged GPF

- Examine ash layers in aged GPF: SEM
- Examine soot oxidation behaviors: E-SEM

Cold operating conditions significantly increase PM mass and number, resulting in filling filter micropores

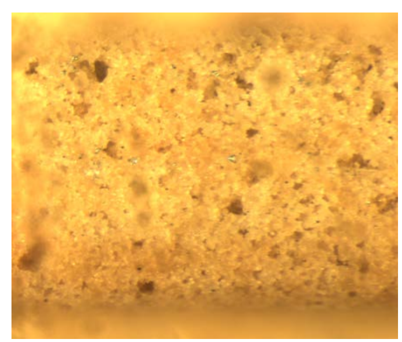






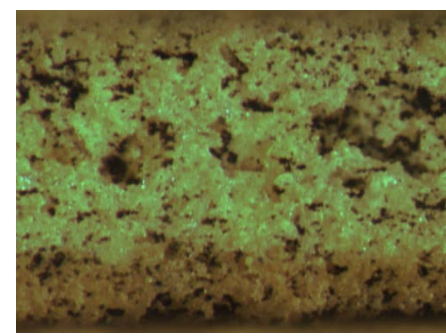
- Cold transient increase PM mass by **max 50 times**.
  - Cold vs. hot-steady: **10 – 15 times**
  - Transient vs. steady: **4 – 5 times**
- Cold-start conditions also increase PN significantly, particularly small nanoparticles.
- Fuel wetting and insufficient fuel mixing are responsible for the increased PM emissions.

Hot steady for 90 sec (1500rpm-50%)



<Soot Conc.: 1 mg/m³>

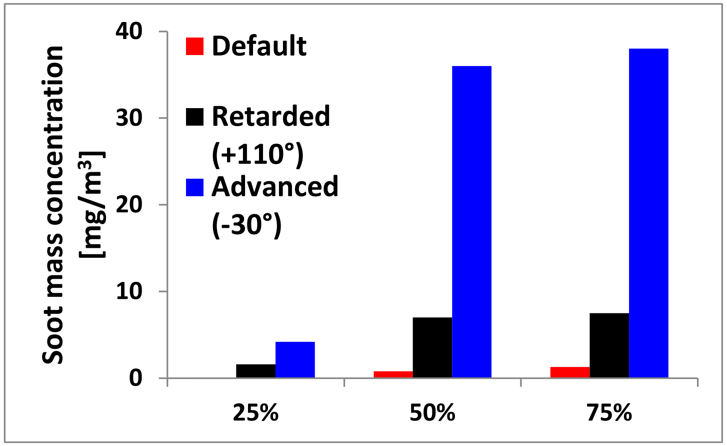
Cold start and rapid accel. (Start→idle→1500rpm/25%)

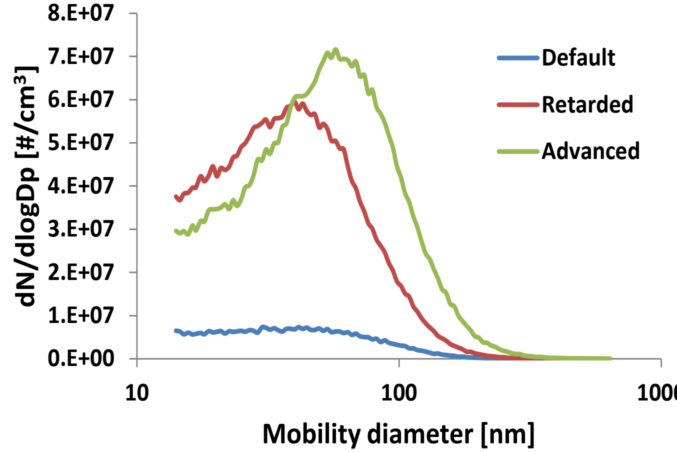


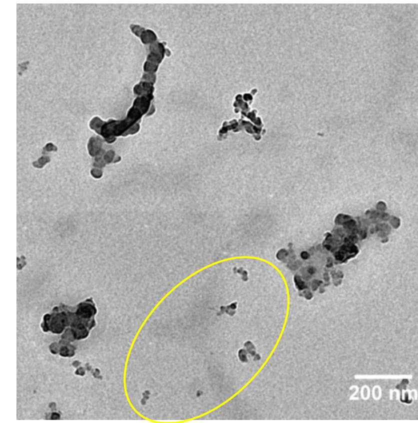
<Soot Conc.: 0 – 120 mg/m³ for 30 seconds>

Wall wetting (advanced) and insufficient mixing (retarded) are another important factors to increase PM emissions

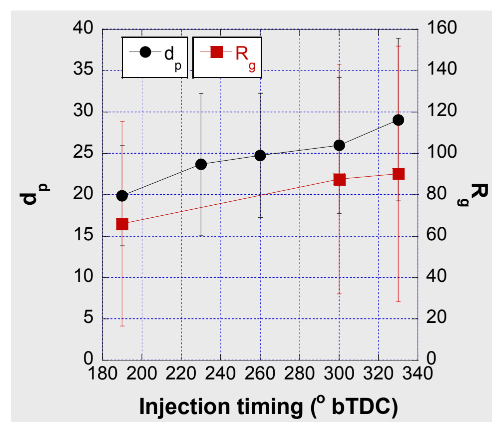
1500 rpm – 50% load

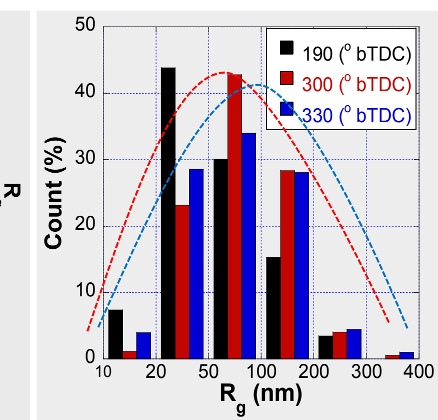




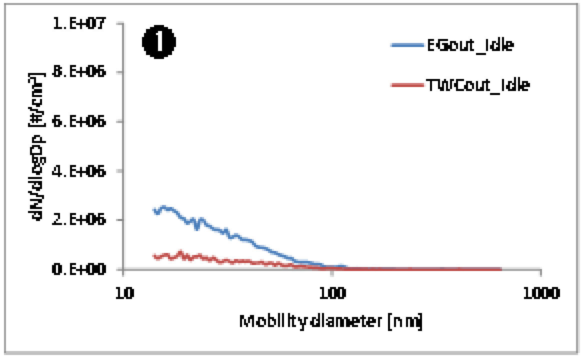


- GDI engine produced a wide range of nanoparticles.
- Both advanced- and retarded-injection timing (IT) increased PM mass and number.
  - Advanced IT: wall wetting increased # of relatively larger particles (sufficient residence time for particle growth)
  - Retarded IT: insufficient fuel-air mixing increased # of smaller particles

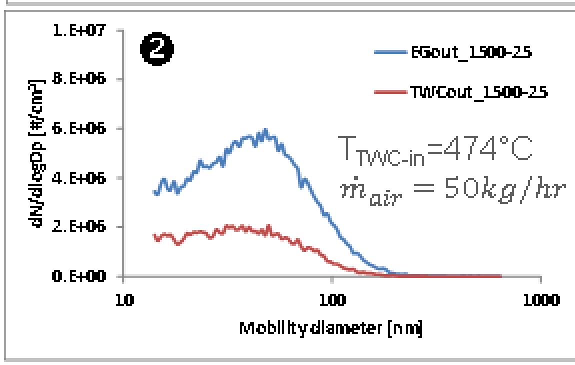


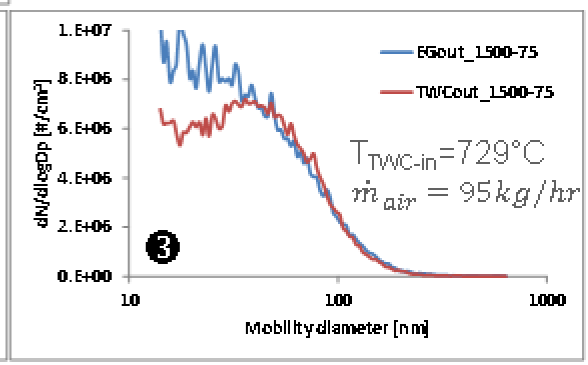


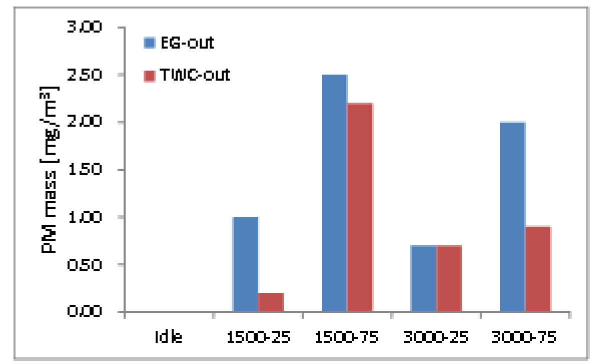
TWC effects are quite noticeable for PN and PM mass, particularly at lower engine speed/load conditions

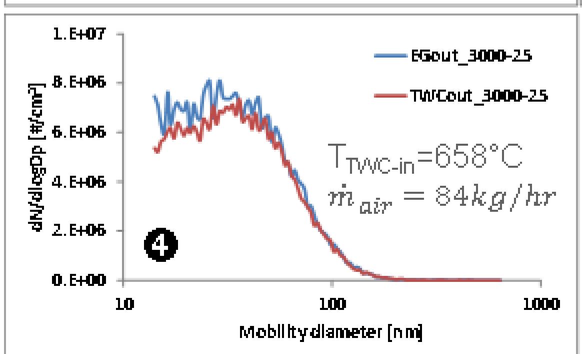


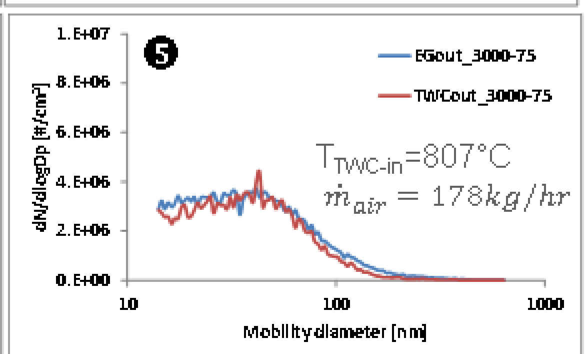
- PN measurements employed PMP method with VOFs removal.
- Low spatial velocity (❶❷): PN is effectively removed by both attachment (diffusion or impact) and oxidation of soot.
- Medium SV (❸❹): PN is removed by diffusion of small particles.
- High SV (❺): PN removal of large particles by impacts contributed to the significant reduction of PM mass.
- Indeed, practical TWCs remove both VOFs and soot (see page 20).

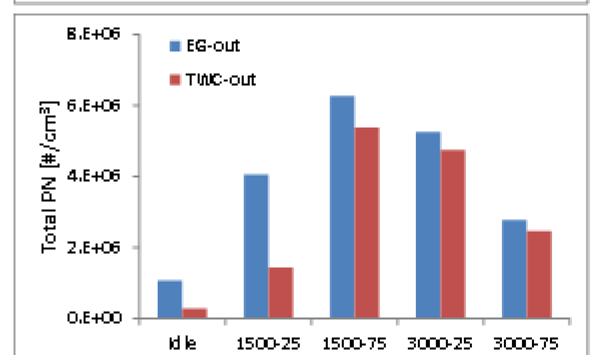




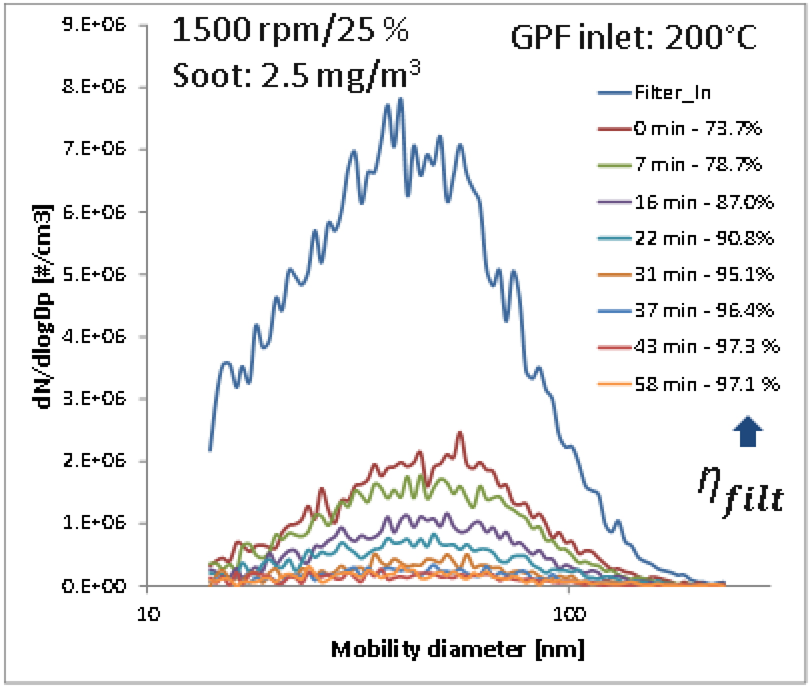


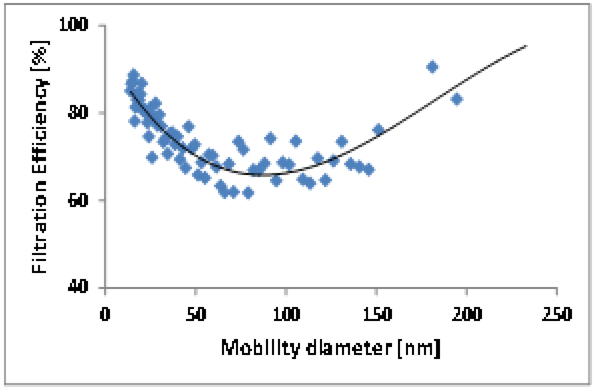




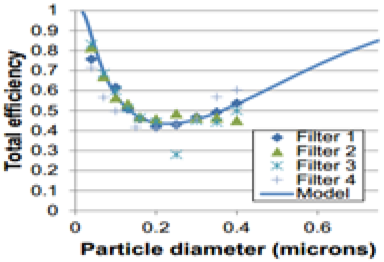


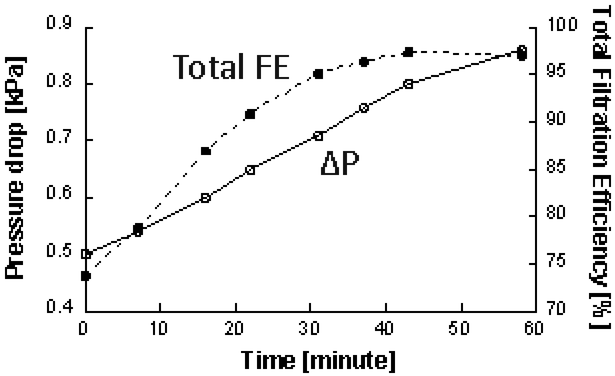
Filtration efficiency reaches 97% with 63 mg/l soot loading; η_{filt} changes from 70% to 90% depending on particle size

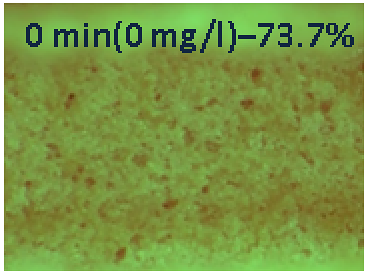


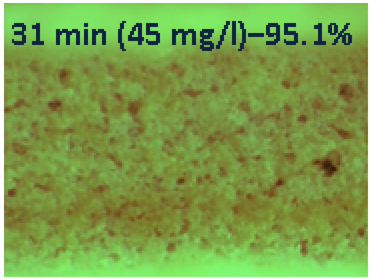


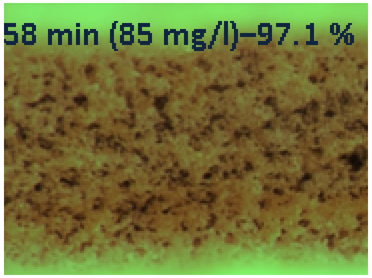
<PNNL data from aerosol>

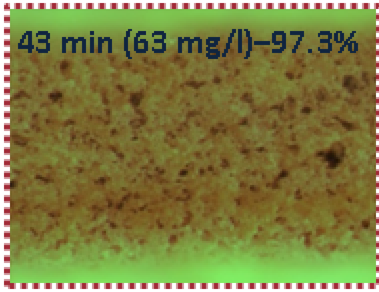








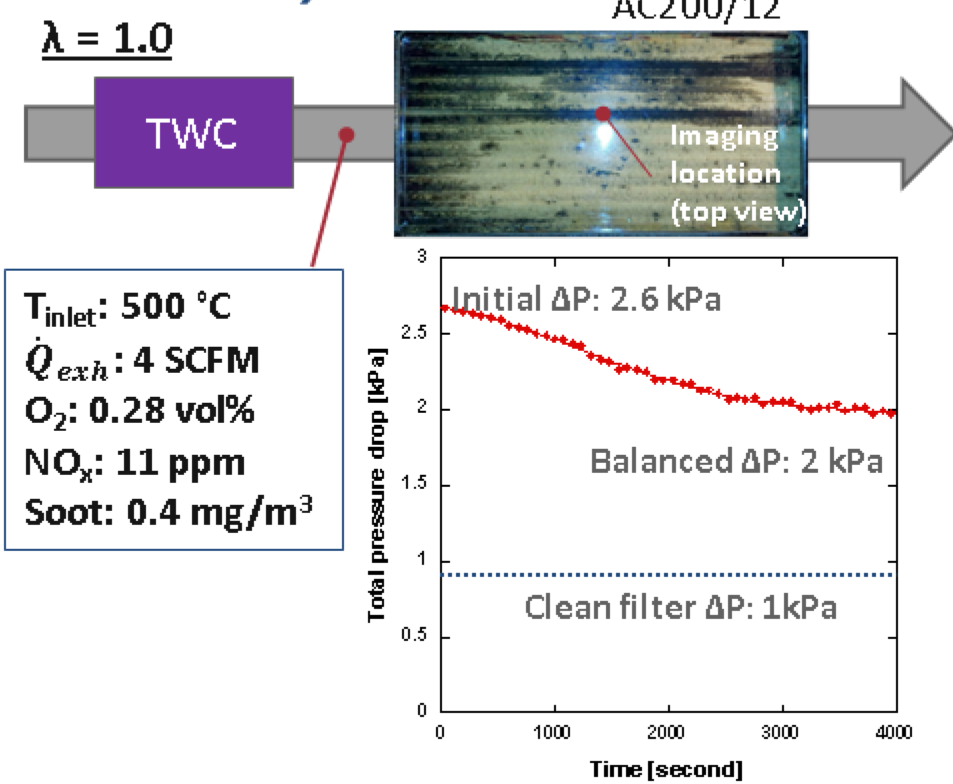




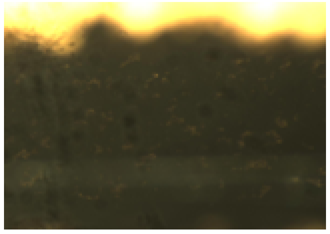
- AC 200/12 bare filter used.
- Greenfield gap: a size range of most penetrating particles
  - Mid-sized particles (60 – 100 nm) escape the filter at the most (*smaller than in modeling*).
  - Depending on filter geometry, spatial velocity, soot concentration, and soot morphology.

Continuous regeneration still occurs at the extremely low oxygen concentration in the exhaust stream (stoichiometric hot-steady condition)

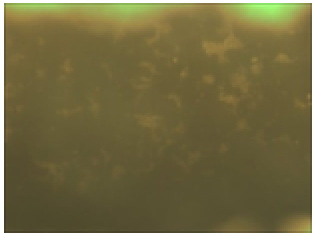
- Soot loading was accelerated to observe regeneration process.
- Pressure drop across the GPF gradually decreased with soot regeneration at 0.28 vol% oxygen concentration.
  - Different from active regeneration in DPF where a high concentration of oxygen is supplied.
- Pressure drop across the GPF reached a constant value of 2 kPa, which indicates a balance point between soot oxidation and loading.
  - The balance point depends on soot oxidation reactivity, exhaust gas composition and temperature, and soot concentration.



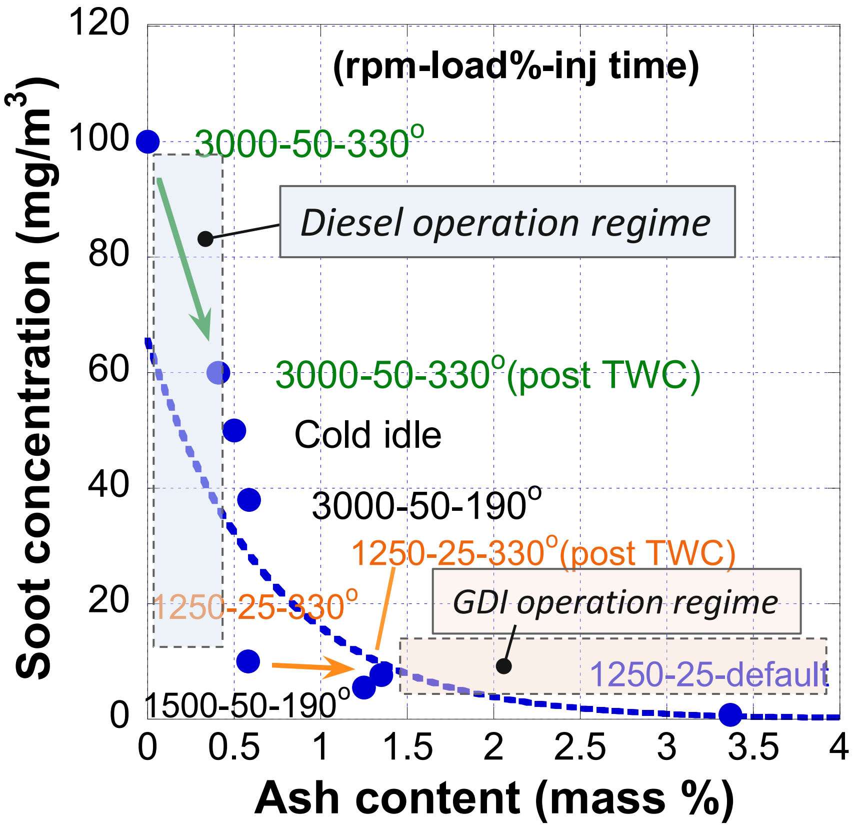
Initial: 0.5 g/L

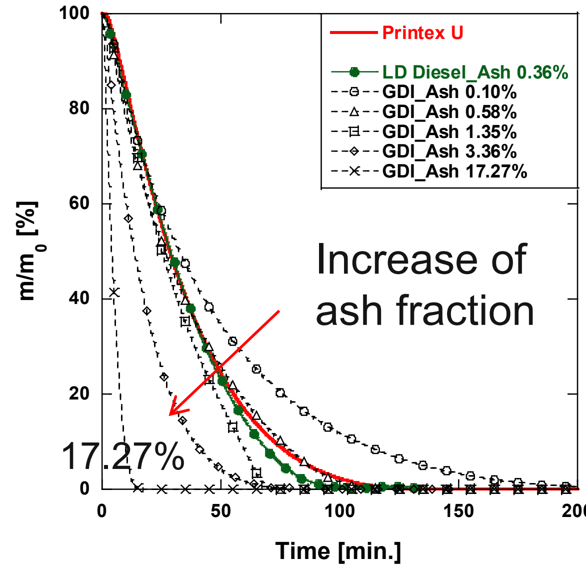


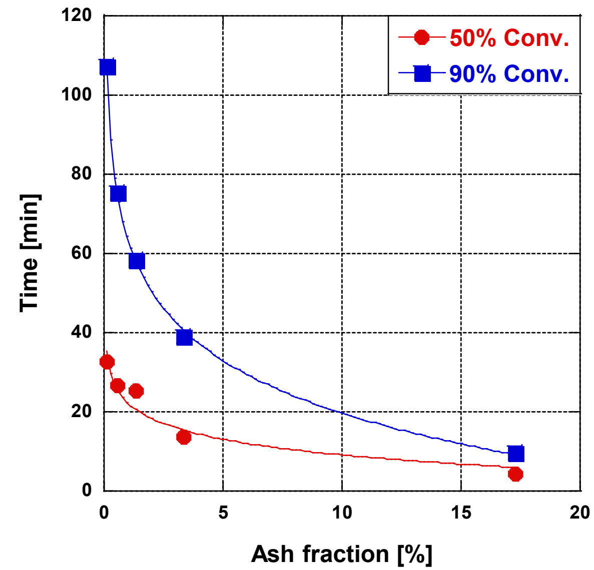
Final



Ash fraction, increased with decrease of soot concentration, enhances soot oxidation significantly





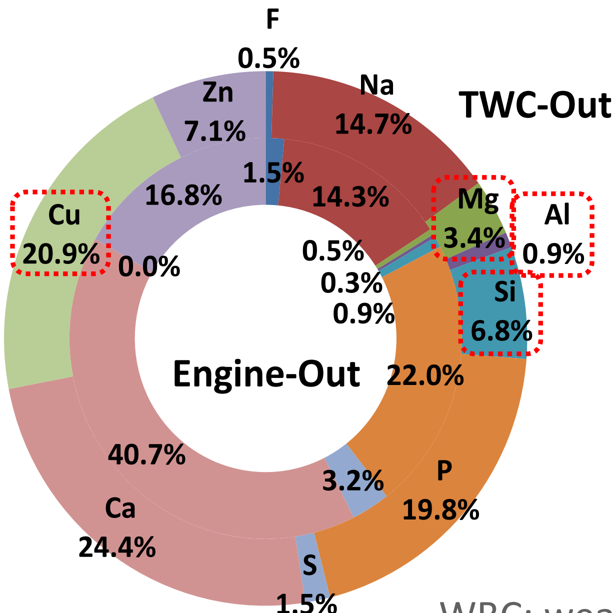


- GDI ash fraction higher than diesel by O(1).
- TWC reduces soot and adds ash amount.
- Ash fraction at cold idle is relatively low due to a high concentration of soot.
- Oxidation reactivity increases with ash fraction
- $Ash\ fraction \equiv f(soot\ mass, lube\ consumption)$

TWC contributes to ash fraction in PM emissions, ultimately enhancing soot oxidation

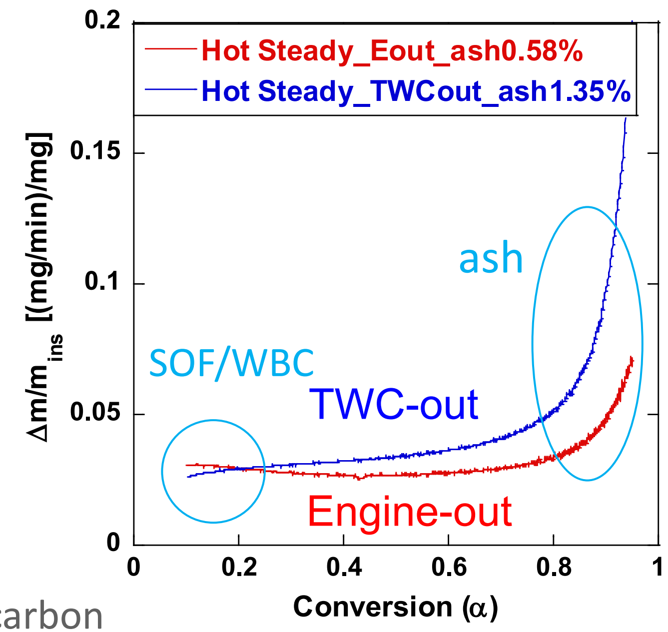
- Chemistry analysis by EDS revealed compositions of ash residues from TGA oxidation (Inner circle: Engine-out ; Outer circle: TWC-out).
- Higher fractions of Cu, Mg, Al, and Si were measured from TWC-out ashes.
  - Catalyst supporting materials separated from the TWC.
  - Lube oil-derived ashes: Ca, Zn, P, S, Na
- Oxidation reactivity of TWC-out PM increased mainly by the ash contribution.

Compositions of engine-out and TWC-out ashes



WBC: weakly bonded carbon

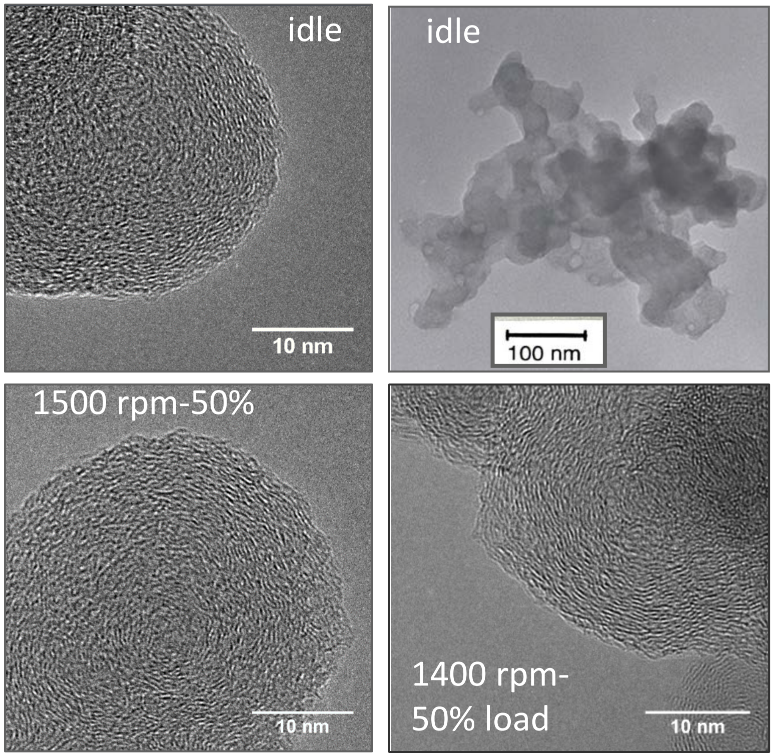
Instantaneous soot oxidation rates



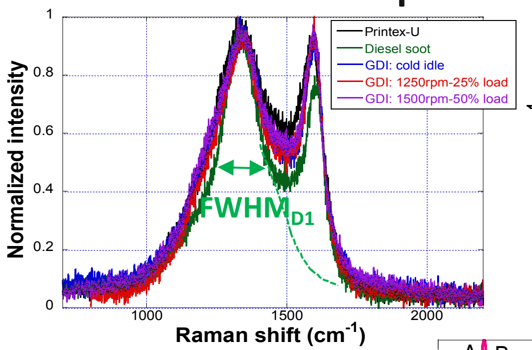
Gasoline soot represents well-defined crystalline structure in the entire engine operating range, including cold idling

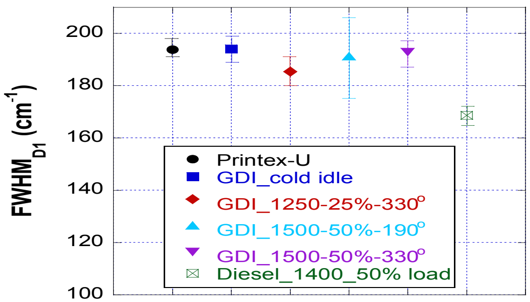
GDI

Diesel

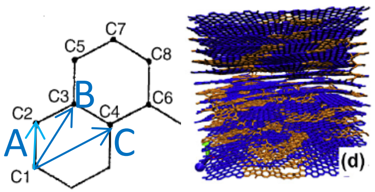


Raman Spectroscopic Analysis

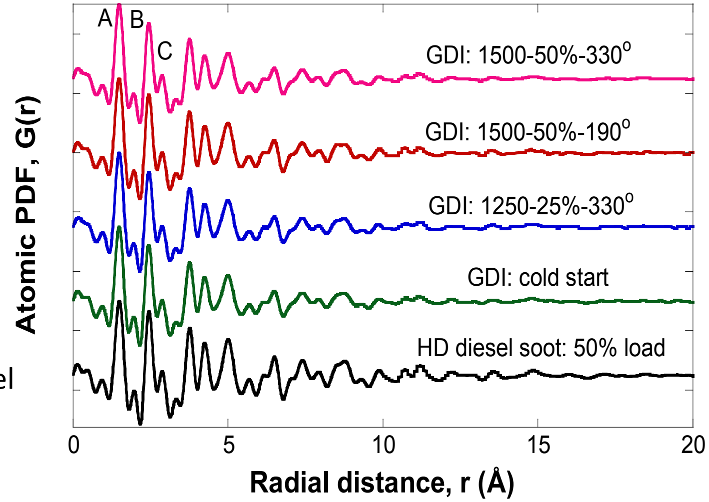




X-Ray PDF Analysis



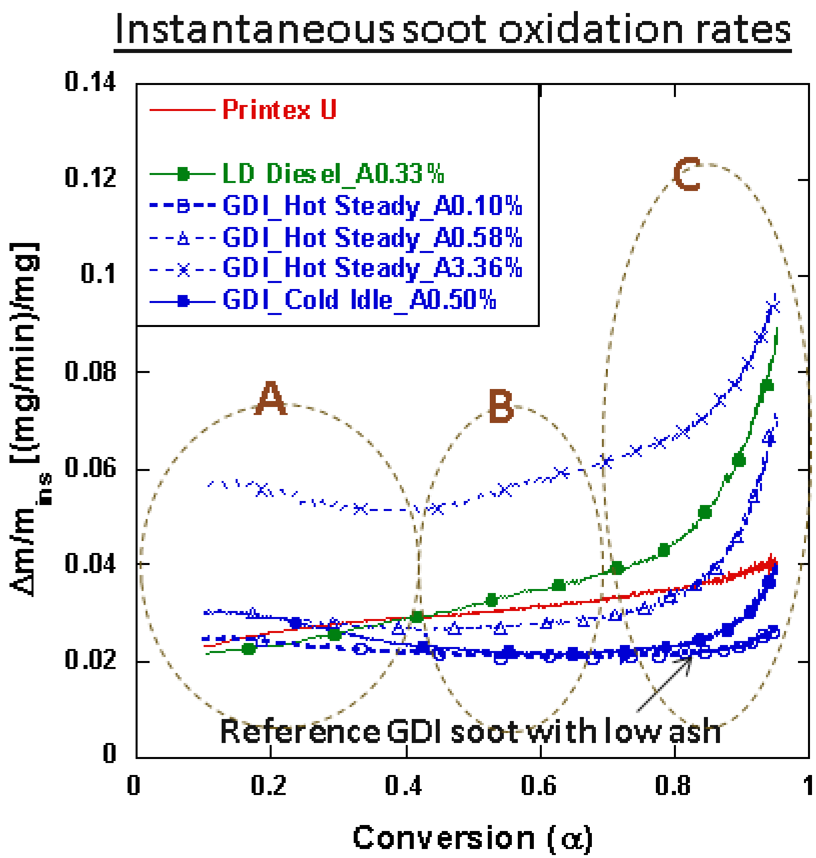
Pyrocarbon model (Carbon, 2012)

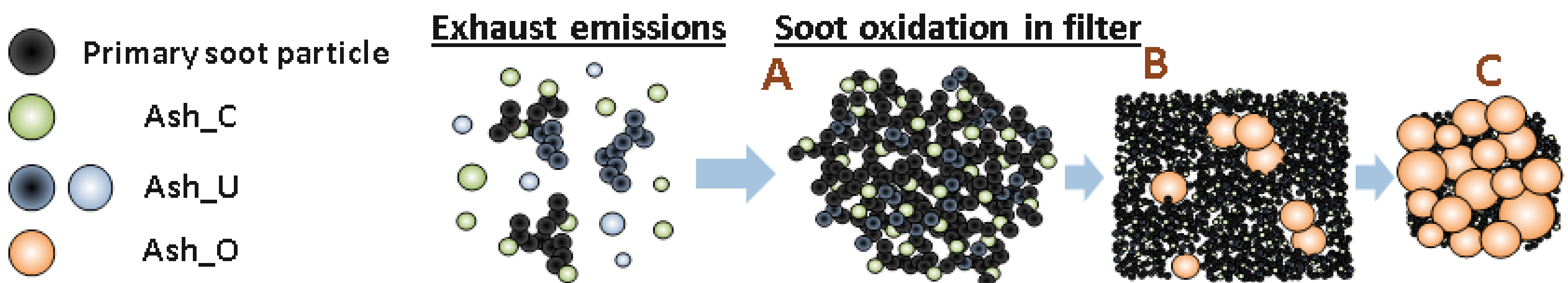


- Gasoline particulates show well-defined graphitic structures even in cold idling, different from diesel soot.
- This crystalline structures of GDI soot do not change much with engine speed/load.
  - Raman spectroscopic analysis revealed differences in crystalline structures.
    - Disorder of crystalline is proportional to $FWHM_{D1}$.
  - Pair distribution function (PDF) analysis validate the Raman data more accurately.
- *Therefore, intrinsic behaviors of soot oxidation reactivity should be similar among different GDI soot samples.*

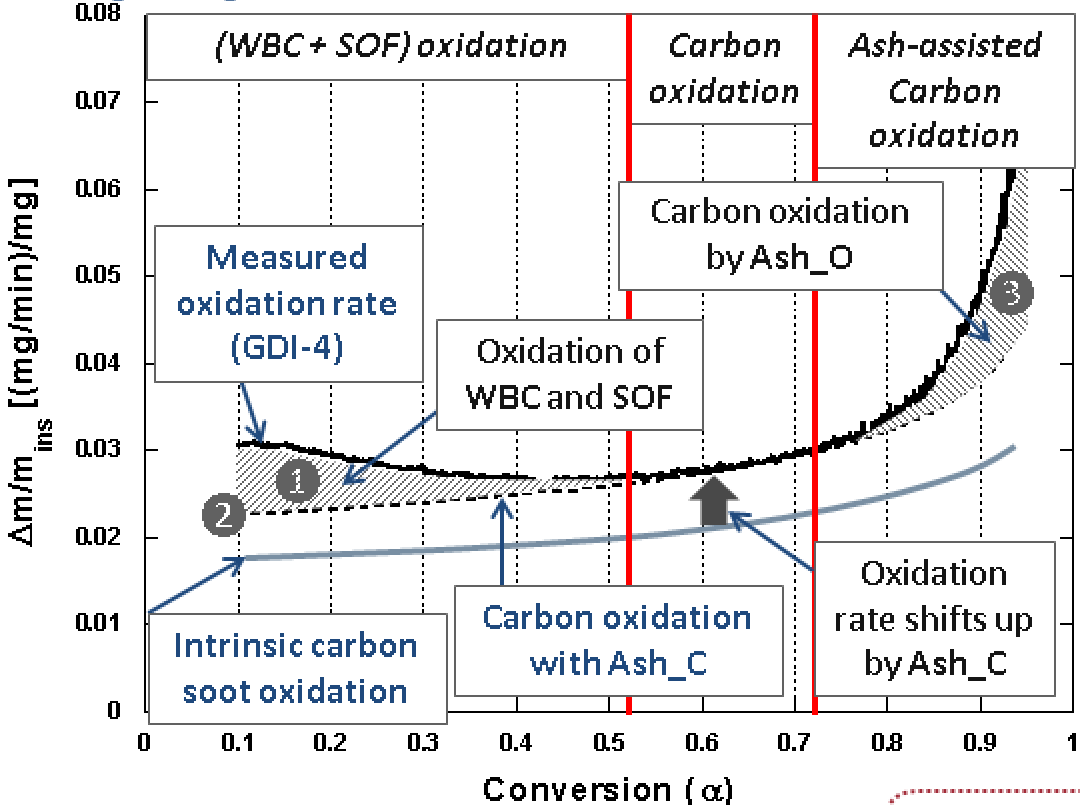
GDI soot exhibits unique oxidation behaviors most prominent in the highest ash-fraction stage (C), different from diesel soot or P-U

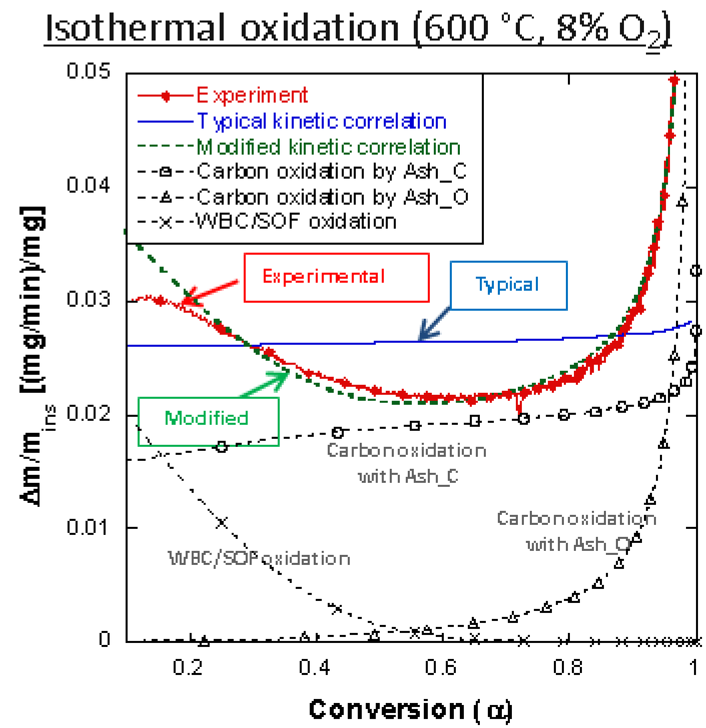
- Overall oxidation reactivity increases with ash.
- Oxidation characteristics in three different stages:
  - *Initial stage* (**A**): higher than diesel or P-U due to oxidation of SOFs and weakly bonded carbons (WBCs).
  - *Intermediate stage* (**B**): oxidation of carbon soot only
  - *Later stage* (**C**): soot oxidation at a high ash-to-soot ratio.
- Reactivity of intrinsic carbon soot
  - Similar oxidation reactivity between hot-steady low-ash soot (●) and cold idle soot (**O**).
- Different types of ash will involve in soot oxidation at the different oxidation stages:
  - Combustion-derived ash precursors (Ash_C)
  - Unburned oil-derived ash precursors (Ash_U)
  - Oxidation-derived ashes (Ash_O)





GDI-soot oxidation mechanisms and kinetic correlations are proposed in validation with experimental data





- The proposed kinetic model predicted soot oxidation rates accurately.
- Subscripts:
  - W-S: WBC-SOF, C: carbon

$$r = \frac{d\alpha}{dt} = (m_{W-S,0}/m_{soot,0}) \cdot r_{W-S} + (m_{C,0}/m_{soot,0}) \cdot r_C$$

1

$$r_{W-S} = \frac{d\alpha_{W-S}}{dt} = A_{W-S} \times e^{-E_{a,W-S}/RT} \times (1-\alpha_{W-S})^{n_{W-S}}$$

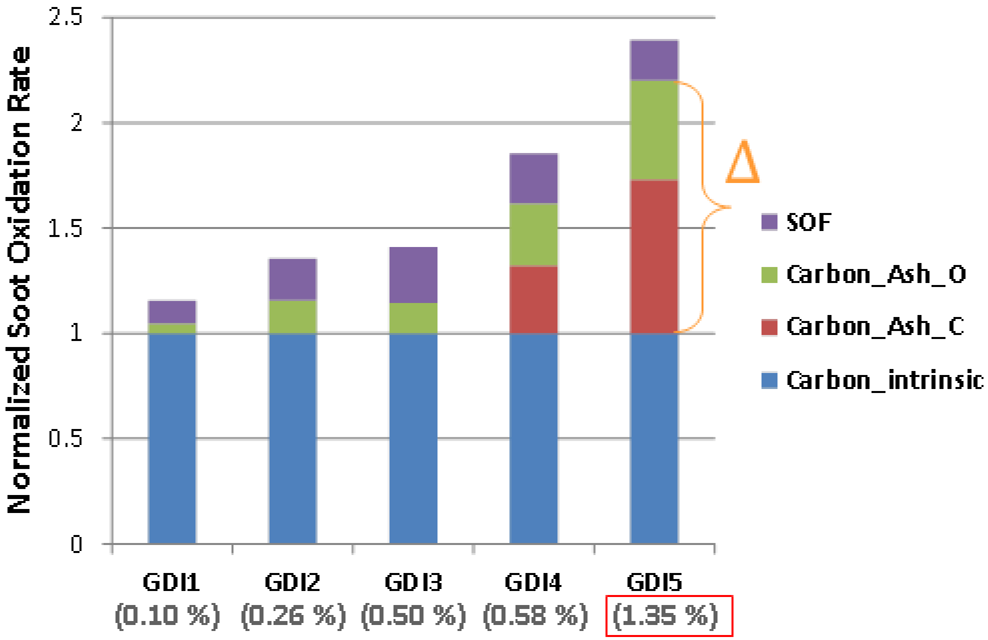
2 3

$$r_C = \frac{d\alpha_C}{dt} = A_C \times e^{-E_{a,C}/RT} \times (1-\alpha_C)^{n_C} + [Ash\_O\ assisted]$$

$$[Ash\_O\ assisted] = \frac{d\alpha_{Ash\_O\ assisted}}{dt} = (1-\alpha_C) \cdot (a \cdot \exp(b \cdot T)) \cdot f_{Ash\_O,i}$$

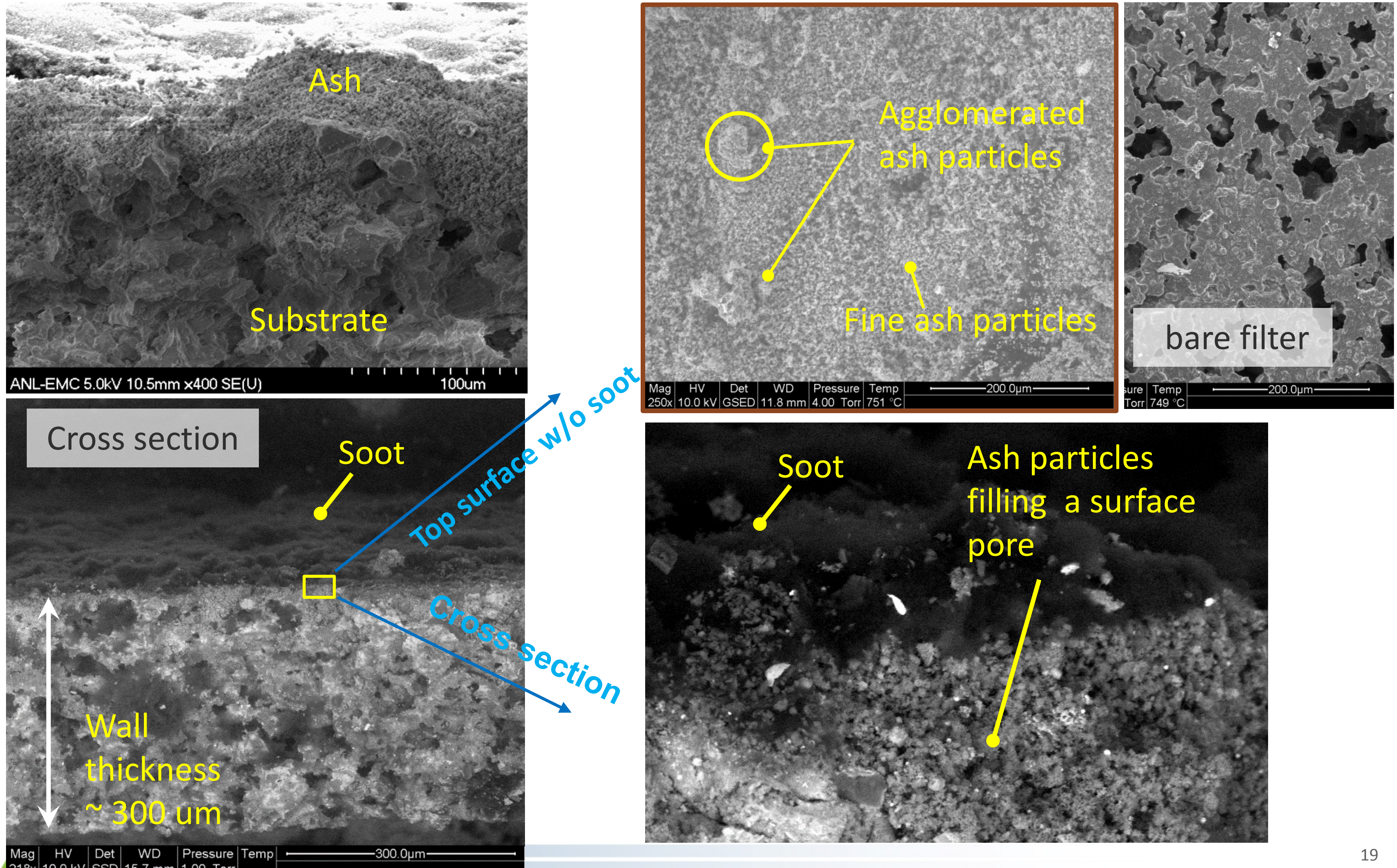
1% initial ash fraction in GDI soot enhanced the soot oxidation rate by a factor of two (2)

- Contributions of ash to soot oxidation rate:
  - High soot/low ash sample (GDI-1): 4.7% improved by the ash
  - Fuel-cut (GDI-2) and cold-idle (GDI-3) samples with higher SOF and ash: 15% improved by the ash
  - Engine-out low soot sample with further increased ashes (GDI-4): 62 % improved by the ashes
  - TWC-out low soot sample with increased ashes (GDI-5): 120% improved by the ashes

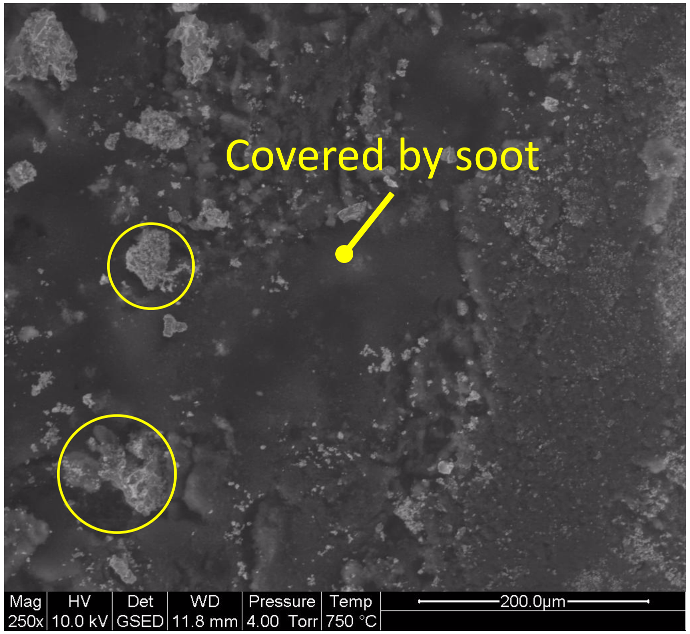


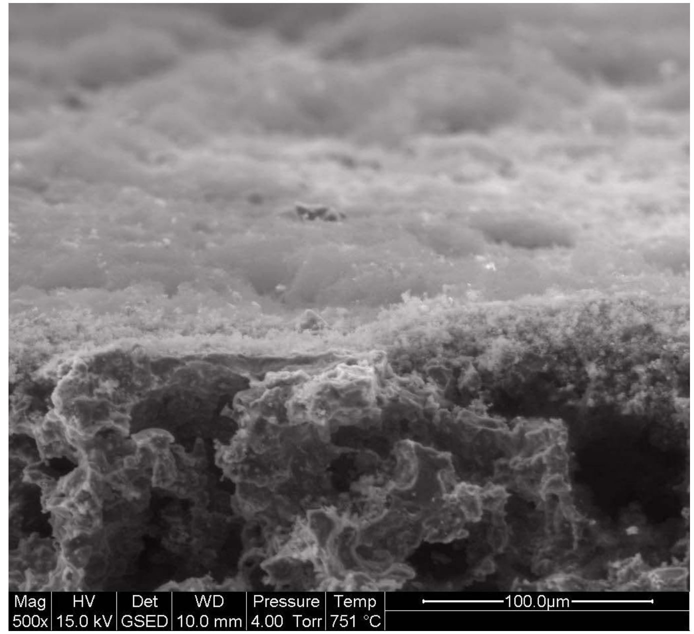
- Ash effects on soot oxidation are prominent in GDI engines, because the ash fractions are typically larger by an order of magnitude than those from diesel engines.
  - Ash effects on diesel soot oxidation are almost negligible, because of high soot and low ash concentrations.

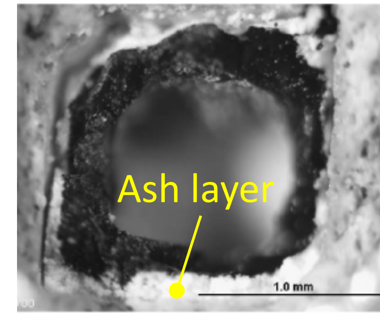
Micron-sized ash particles covered the filter surface and filled surface micropores (100K mi vehicle run)

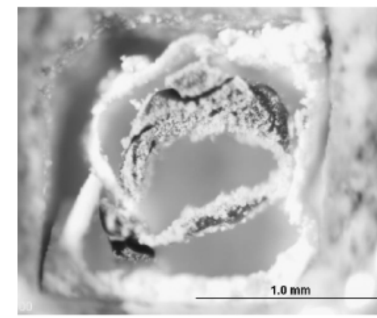


Aged filter loaded with actual GDI engine soot was tested for real-time observation of oxidation in ESEM.









- Ashes connected to the ash layer in a 100K mile-aged filter are not deformed during oxidation.

Oxygen pressure	4.0 Torr (533 Pa)
Reactant	O_2 at 750° C
Movie rate	4 fps

- *Oxidation with no reactant flows at 600° C (ash loading accelerated)*
- *Ash layers peel off from channel surfaces.*
  (SAE Int. J. Fuels Lube, 6:2, 2013)

Responses to FY13 Reviewers' Comments

- Many data showed for DPFs.
  - All FY14 data have been obtained from a GDI engine and GPFs.
  - The GPF test bench was ready to use June 1, 2013.
- No filtration efficiency and PN data were demonstrated.
  - Filtration efficiencies have been evaluated in basis of PN measurements with a PMP-compatible dilution system in FY14.
- How different are gasoline particulates from diesel particulates?
  - Comprehensive analyses of GDI particulates have been performed for a stock GDI engine in terms of morphology, fractal geometry, and crystalline structure, using TEM, Raman spectroscope, and X-ray PDF techniques.
- Goals and directions irrelevant to GPF work
  - Appropriate goals and directions relevant to GPFs have been set for FY14 work and new discoveries have been reported.
- Communications with industry partners needed.
  - The working group has had several technical meetings to discuss directions in approach and progress in result.
  - Corning Inc. has delivered 5 different models of filter substrates (total more than 50 samples), including the most recent models, and aged filters from its branch in Europe, and Hyundai has delivered catalyst-coated filters, aged filters, and technical information.

Collaborations with Other Institutions

- *University of Wisconsin*
  - Collaborated on characterizing PM emissions from a spark-ignited single-cylinder GDI engine.
  - Used gasoline and ethanol blend E20.
  - Found that the GDI engine generates numerous sub-23nm particles and PM emissions from E20 combustion contain a significant amount of soluble organics.
- *Tokyo Institute of Technology*
  - Tokyo Tech performs soot oxidation studies of particulate filters in micro-scale.
  - ESEM measurement technique has been transferred to Argonne for real-time evaluation of GPF regeneration.
- *Argonne hosted the 2nd International Joint Workshop (July 11 – 12, 2013)*
  - Discussed results about engine emissions and DPF research.
  - A total of about 60 participants from 27 different organizations.
    - 30 participants from national laboratories, 15 from universities, and 18 from industry.
    - 17 organizations from U.S., 7 from Korea, and 3 from Japan
  - 14 oral presentations and 16 poster presentations, including an invited speech by Prof. Kittelson from the University of Minnesota.
  - 3rd Joint Workshop will be hosted by Tokyo Tech in Japan, 2014.

Future Work (FY15)

- Chemical analysis of GDI PM in terms of soluble organics and oxygen functional groups, and find their effects on soot oxidation.
- Effects of ash in a GPF
  - Oxidation behaviors of ash-contacted soot
  - Interactions between soot, ash and catalyst
  - Ash sintering effects
- Evaluation of filtration efficiencies
  - Different filter substrate models
  - Catalyzed filters
- Evaluation of regeneration efficiencies
  - Different filter substrate models
  - Catalyzed filters
- Evaluation of aged GPF in terms of filtration/regeneration efficiencies.

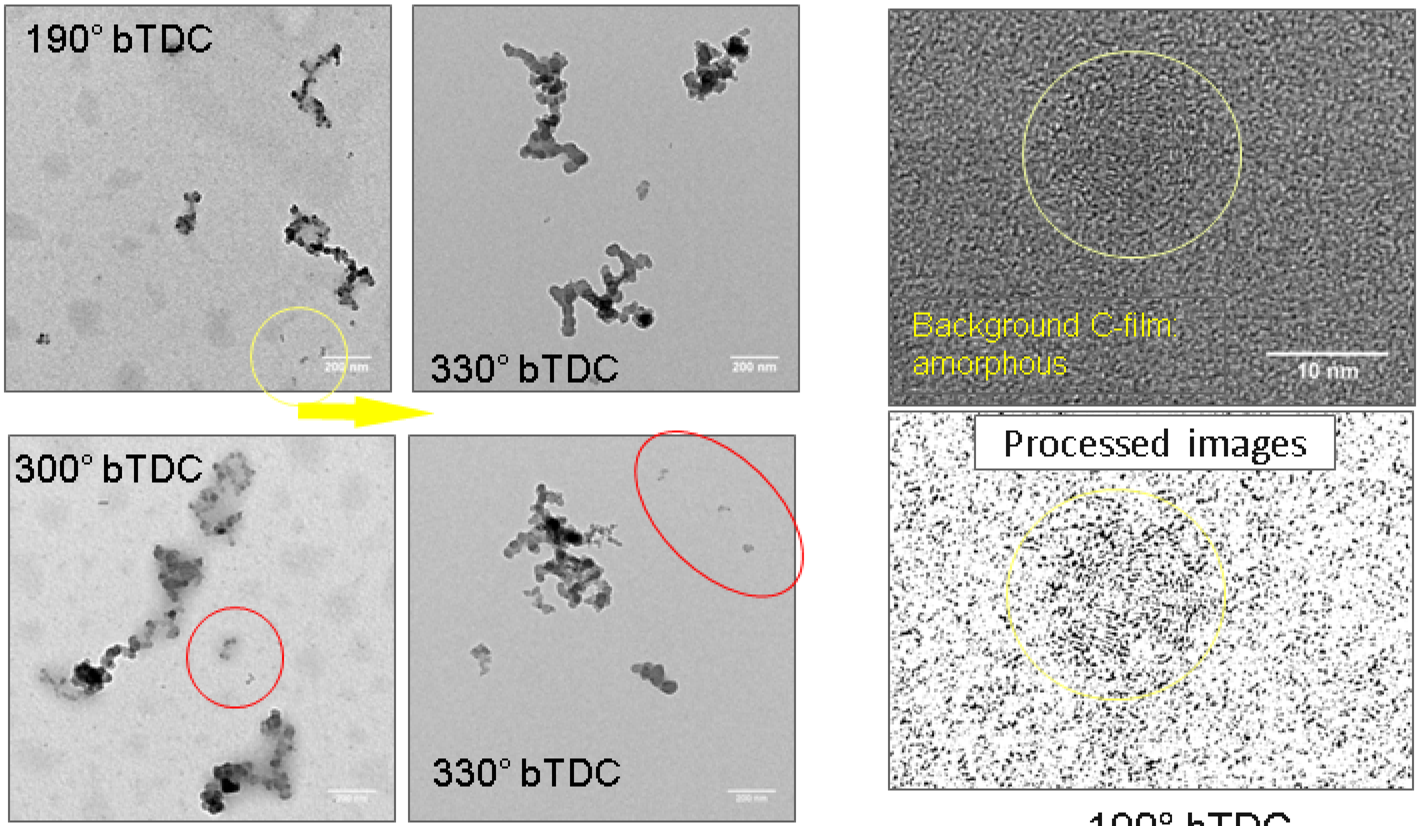
Summary

- **Cold start** operations and **wall wetting** are major sources of PM emissions from GDI engines, increased in both number and mass.
- **TWC** was found to be an important component that reduces PM emissions (volatile organics and soot) and adds chemicals to PM emissions in a form of ashes, resulting in enhancement of soot oxidation.
- **Filtration efficiency** of a fresh bare filter in this study reached over 97% with 63 mg/l in 43 minutes with no substantial regeneration, starting with an initial filtration efficiency of over 70%.
- **Increased ash fractions**, due to relatively low soot concentration and separation of catalytic materials in GDI engines, are responsible for **higher oxidation reactivity** of GDI soot than that of diesel soot.
- **Crystalline structures** of GDI soot are slightly less ordered than those of diesel soot, except for the idling condition, and do not change significantly with engine operating conditions. **Chemistry** (**SOFs, WBC, and ashes)** is a major component for the enhanced oxidation of GDI soot.
- In consideration of the effects of those chemical components, **a kinetic model of GDI soot oxidation** has been proposed, resulting in a good agreement with experimental data.
- Initial observation of an **aged GPF** revealed a significant amount of **ash build-up** in both filter channels and micropores, which aroused strong interest in studies on interactions among ash, soot, and catalyst materials.

Technical Back-up

Many sub-23nm soot particles are emitted from the GDI engine, caused by advanced fuel injection

1500 rpm
& 50% load



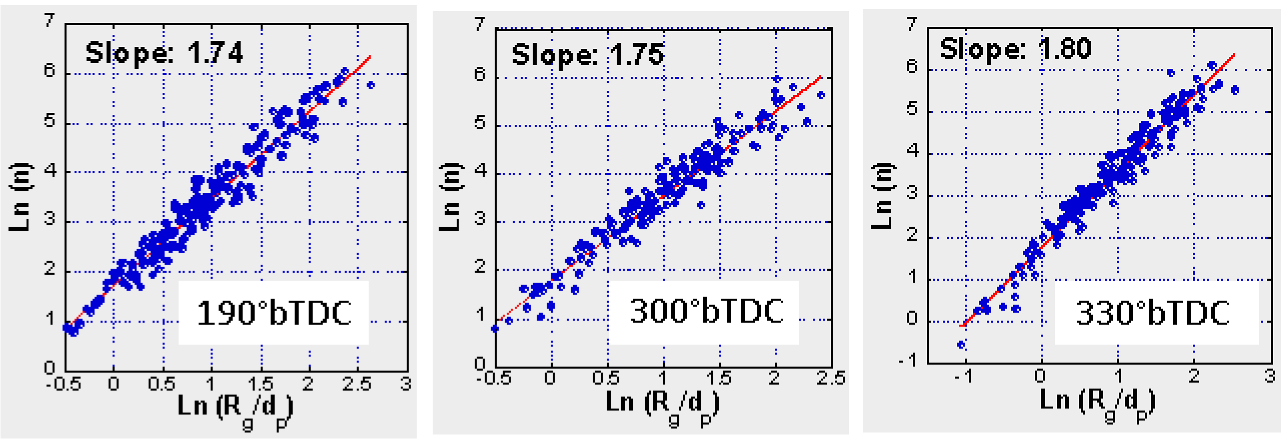
15,000X

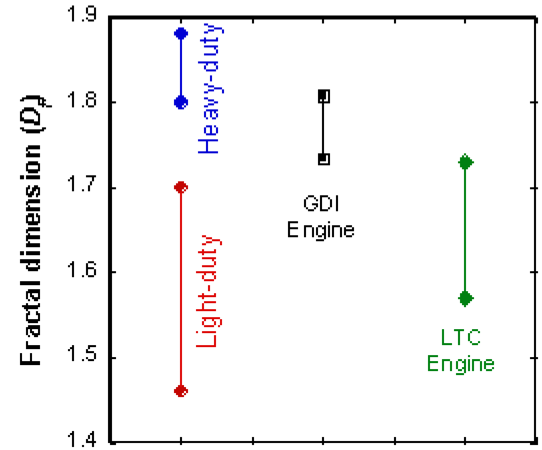
500,000X

190° bTDC

- Tested in the ranges of 1500–3000 rpm, 0–75% load, and 190–330° bTDC inj. time
- As reported last year, a number of sub-23nm nanoparticles were observed at various engine operating conditions.
- These nanoparticles exhibited graphitic structures represented by a distinct pattern of dark concentric fringes (in yellow circles), which indicate a solid soot particle.

GDI soot turns out to be more compact/spherical than light-duty diesel soot in terms of fractal geometry



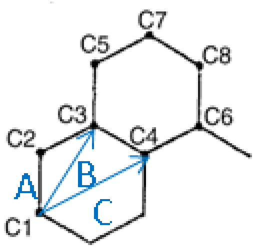


$$n = k_f \left(\frac{R_g}{d_p}\right)^{D_f} \longrightarrow Ln(n) = D_f \cdot Ln\left(\frac{R_g}{d_p}\right) + Ln(k_f)$$

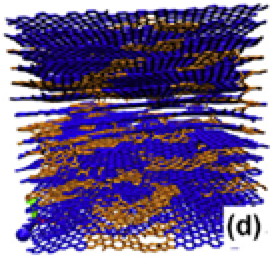
D_f: *fractal dimension*, n: *number of primay per aggregate*, k_f: *prefactor*

- Gasoline particles become slightly more compact with advancing injection timing, but its impacts are insignificant (1.74 → 1.75 → 1.81).
- The fractal geometry of particulates from the GDI engine turned out to be similar to that of heavy-duty diesel particulates, but more compact and spherical than those from light-duty diesel or LTC engines.

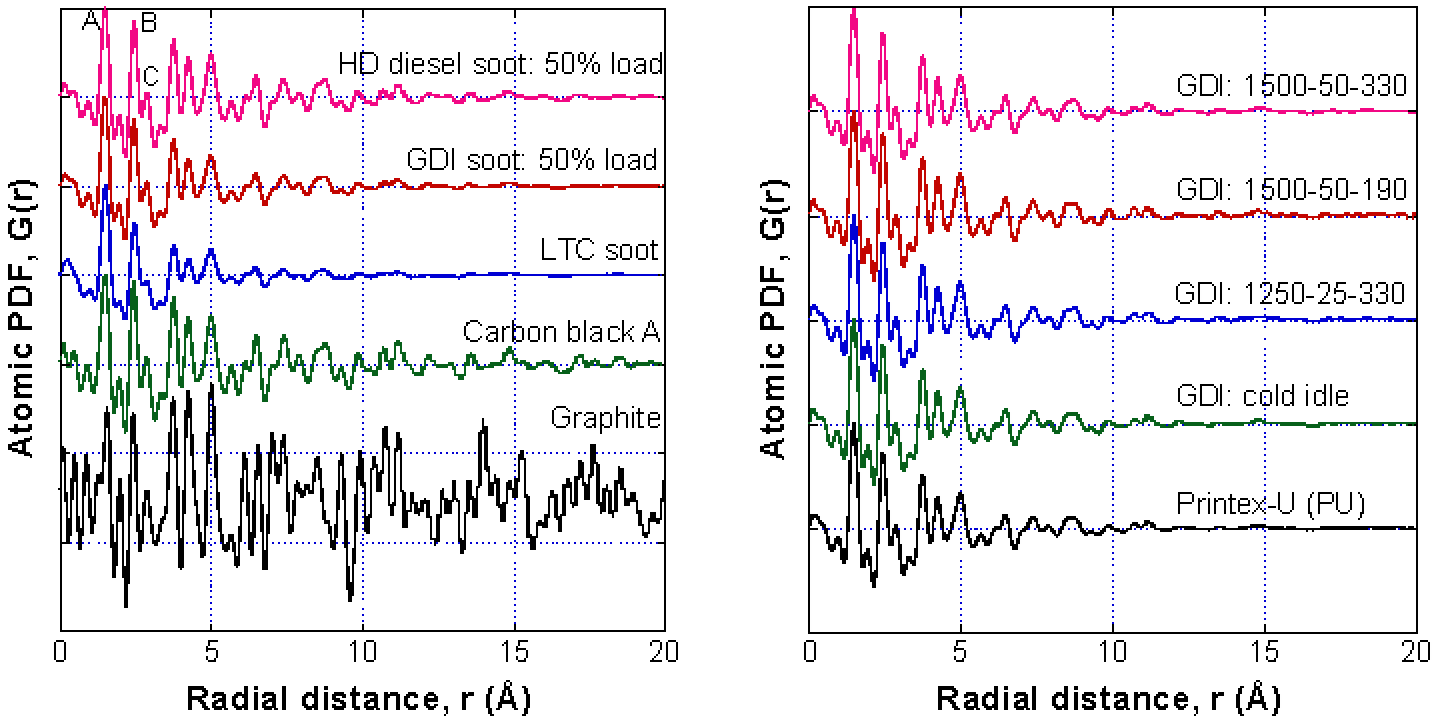
X-Ray PDF analysis was first used to validate the degree of crystalline structures of engine soot and similarity in reactivity among different GDI soot samples



< 1Å: artifacts
≤7 Å: intra-molecular
≥7 Å: inter-molecular

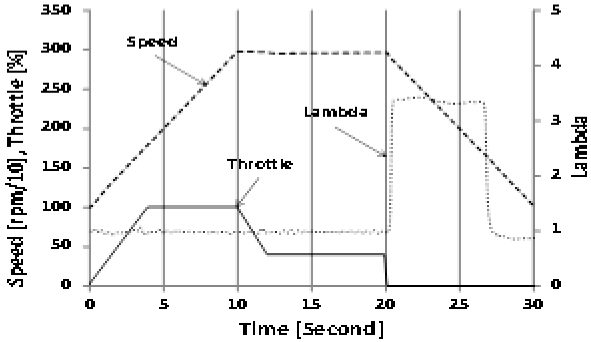


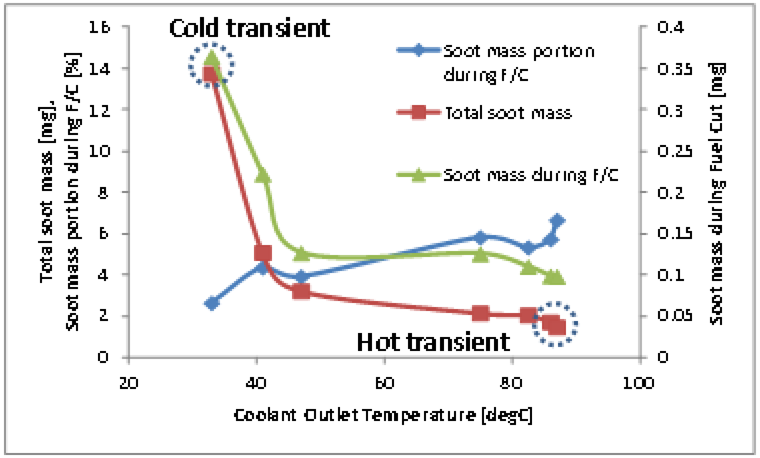
Pyrocarbon model
(Carbon, 2012)



- Pair distribution function (PDF) analysis by high energy X-ray enabled accurate evaluation of local and medium-range structures of various engine soot samples.
  - Higher peak-intensities below r≈7Å imply more ordered local atomic structures of soot.
  - Higher peak-intensities above r≈7Å indicate bigger crystallite domains with lateral and stacking coherence.
- PDF results verified the Raman results:
  - The crystalline structure of GDI soot is less ordered than that of diesel soot.
  - GDI soot is nearly identical to Printex-U in physical nanostructures.

Fuel-cuts also produce quite significant PM emissions in the initial cold operations





These PM emissions are ascribed to separation of deposits on the piston top land by blow-by at the low in-cylinder pressure.