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

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DOE Annual Merit Review & Peer Evaluation Meeting

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DOE Project Managers: Ken Howden & Gurpreet Singh

Office of Vehicle Technologies

Project ID: ACE024

Overview

Timeline

- Start: Oct. 2011
  - Contract signed: Sept. 2012
- End: Sept. 2015
- 80% finished

Budget

- Total project funding
  - DOE share: $1.5M
  - Contractor share: $1.5M
- Funding for FY15
  - DOE: $500K
  - Project partners: $500K

  in-kind + fund-in $75K (Hyundai)

Barriers

- B. Lack of cost-effective emission control
- C. Lack of modeling for combustion and emission control
- E. Durability

Partners

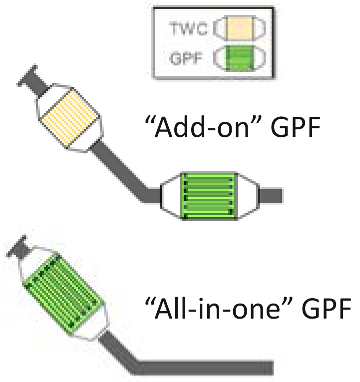
- Corning and Hyundai Motor
- University of Illinois at Urbana-Champaign
- University of Illinois at Chicago

Relevance and Objectives

- PM emissions from GDI engines are mandated to be reduced
  - Current GDI engine-out emissions cannot meet future PM regulations (mass & number)
  - Cold start and transient modes are recognized to produce high PM emissions
  - New test procedures reflecting real life drives require robust PM reduction technologies
- GPFs have been developed to meet stringent PM regulations
  - High PN efficiency & low pressure drop
  - Developing directions: “Add-on” GPF and “All-in-one” GPF

	"Add on" GPF	TWC Integrated GPF
Cell Density	200cpsi	200/300cpsi
Wall Thickness	8mil	Optimized
Material	Cordierite	Cordierite
Porosity	Medium	High

Corning, 2012 DEER Conference



Relevance and Objectives (Cont'd)

- Ash impact could be more appreciable with GDI engines than with diesel engines
  - Ash impact on DPF performance has been well characterized by MIT researchers. However, few reports on GPF performance with ash loading were disclosed.
  - Backpressure increase and TWC functionality are of great interest.
  - Increased ash fraction was observed to enhance soot oxidation (ANL, 2014 AMR).
- Objectives
  - Further validate ash enhancing effects on soot oxidation.
  - Understand filter performance in terms of pressure drop and filtration efficiency, related with filter geometry and pore structure.
  - Evaluate impact of ash loading on TWC-coated GPFs, based on backpressure increase, filtration efficiency and particle penetration with filter regeneration.

Project Milestone (FY14-15)

Quarter, Year	Milestone Description	Status
Q3, 2014	Detailed morphology data of particulates from a stock GDI engine with variation of injection parameters	Complete
Q4, 2014	Analytical data to optimize the filter design	MIP & X-ray microtomography, Ongoing
Q1, 2015	Complete development of GPF test protocol, installation of test system, and preliminary test	Complete
Q2, 2015	Complete tests for 4 bare filters	Complete
Q3,2015	Complete tests for 3 catalyzed filters and an aged filter	Ongoing

Overall Approach – soot & filter characterization

Characterization of GDI soot and filter substrates (APS, CNM, UIUC)

Gravimetric sampling

2.4L GDI Engine

Soot oxidation experiments and bench-scale filter tests (2”(D)x6”(L))

PM properties
- Operation-specific PM emissions source (# & mass)
- Morphology & physicochemical properties
- Oxidation reactivity

Filter geometry
- Mercury intrusion porosimetry (MIP)
  X-ray microtomography: 2D & 3D
- Impact on ΔP change and filtration performance
- Coating effects on filter geometry

Evaluation of filter performance
- Understanding soot oxidation mechanism
- Aging impact on filter performance using accelerated ash loading
- Physical & chemical effects with ash loading - ΔP change, filtration efficiency, TWC function

GPF Test Approach – targeting feasible GPF testing

- Corning provided advanced cordierite-based filters

Selected sample	% porosity	Medium diameter (d_{50}, µm)
AC 200/12	50.56	20.74
KEX 200/8	57.22	11.67
HP 300/8	64.60	20.38
HP 200/12	65.76	20.93

- Hyundai provided TWC-coating services on bare filters through OEM

- In-wall coating used in current TWC-coating technology

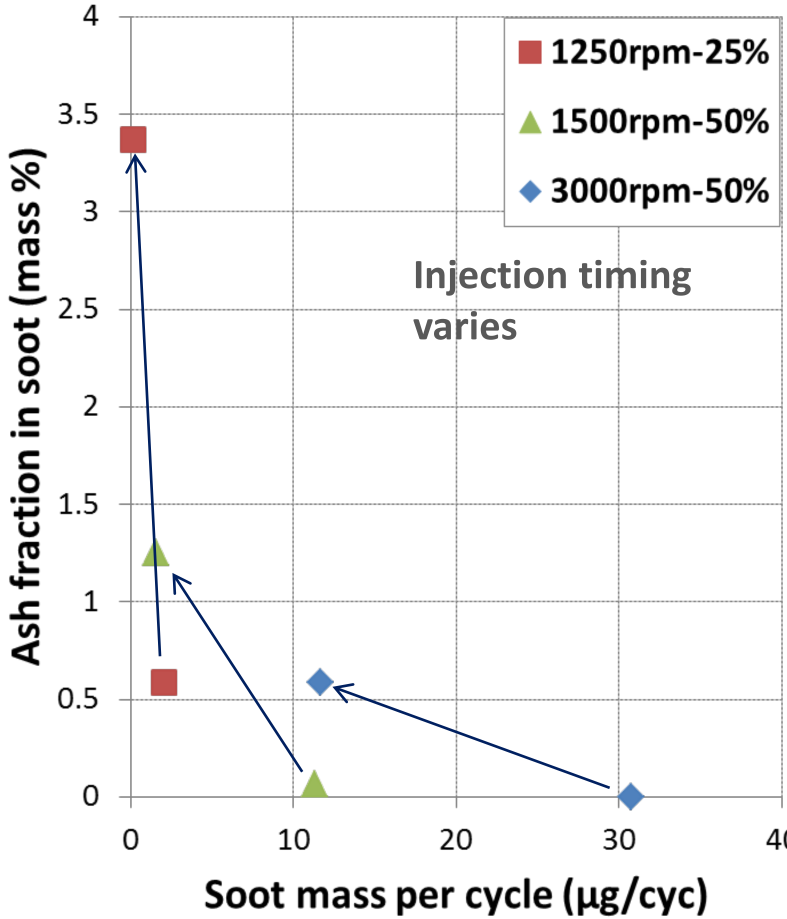
Selected Samples	Catalyst Coating	Loading (g/L)	PGM loading (g/ft^3)
AC 200/12	w/ PGM, OSC, PGM&OSC	50	0.5
KEM 300/8	w/ TWC	25, 50 and 100	0.5
HCW 200/12	w/ TWC	50	0.5

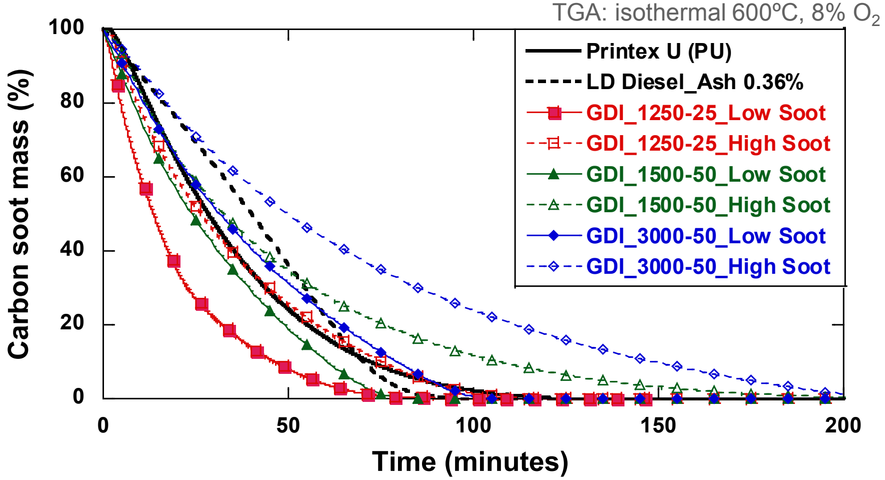
- Argonne evaluated different types of filters for fair comparison at real engine operating conditions using a bench-scale flow reactor under proposed test protocol.

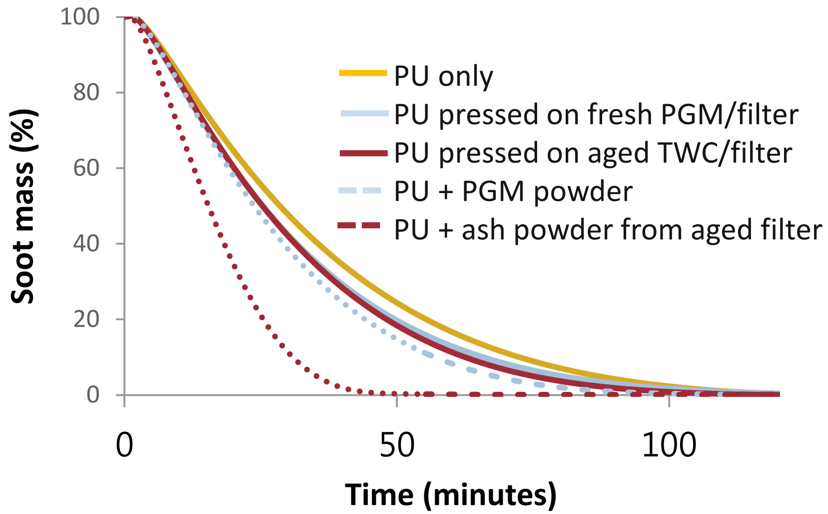
Summary of Technical Achievements in FY15

- Enhancement in soot oxidation was further validated by TGA experiments.
  - Different engine operating conditions and simulated tight & loose contact
  - Examinations of soot oxidation for three major inorganic additives (Ca, P & Zn) formulated by fuel doping
- Pore structures of filters were examined by X-ray tomography and mercury intrusion porosimetry (MIP) to understand catalyst coating effects.
  - Medium porosity filter (AC 200/12) vs high porosity filters (HP 200/12 & 300/8)
  - Catalyst loading: 25 g/L (1X), 50 g/L (2X) and 100 g/L (4X)
- TWC-coated GPF performance was evaluated in the 2.4L GDI engine using the newly installed bench-scale reactor.

Ash effect on soot oxidation is further validated



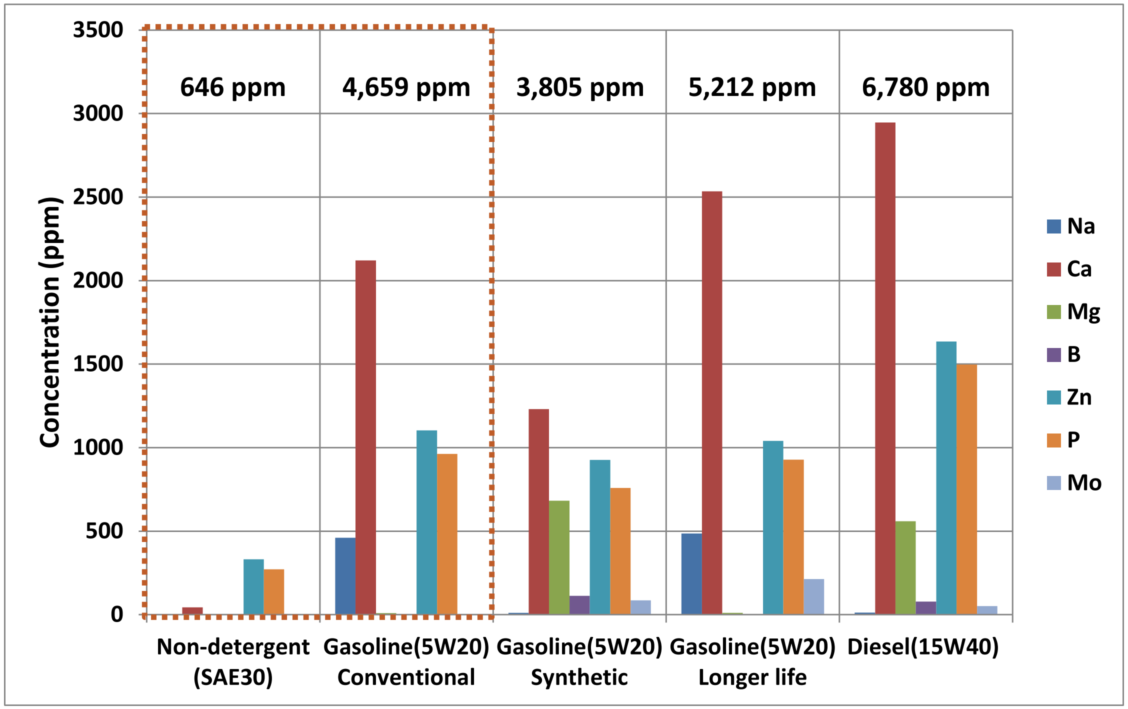


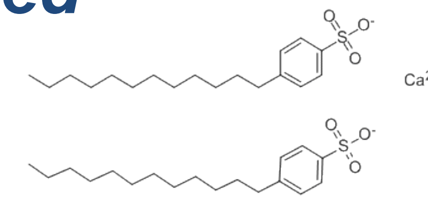


- Ash fraction and soot mass were inversely correlated under the same condition sets
- Low-mass soot was always found to be more reactive due to increased ash fraction
- Ash, taken from filters of 100,000 mile run vehicle, enhanced soot oxidation reactivity at simulated tight contact and loose contact conditions

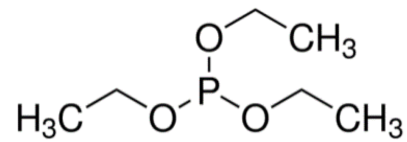
Based on major additive components, Ca-, P- & Zn-P-specific engine oils were formulated

ICP analysis: Proc-Rev 1158-3.9





Ca source: Calcium dodecyl-benzene sulfonate

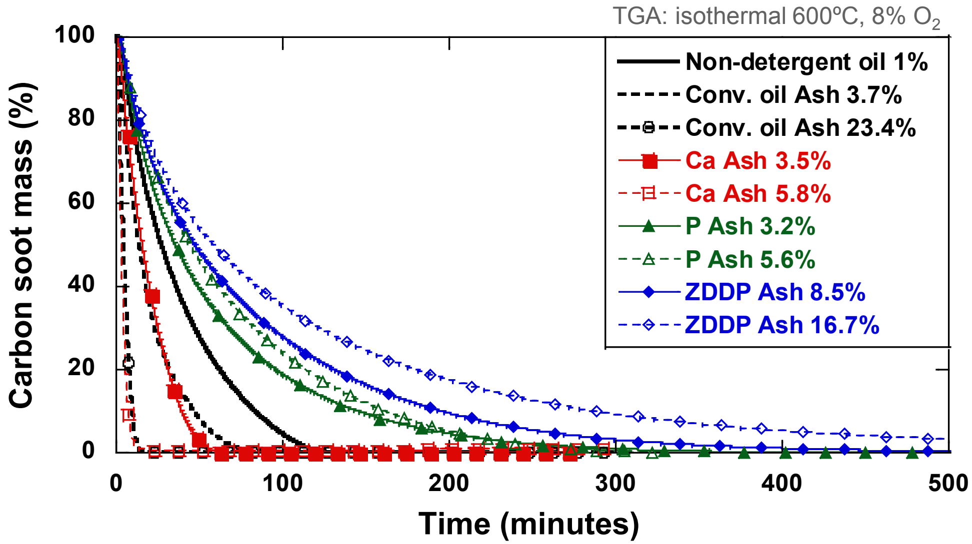


P source: Triethyl phosphite

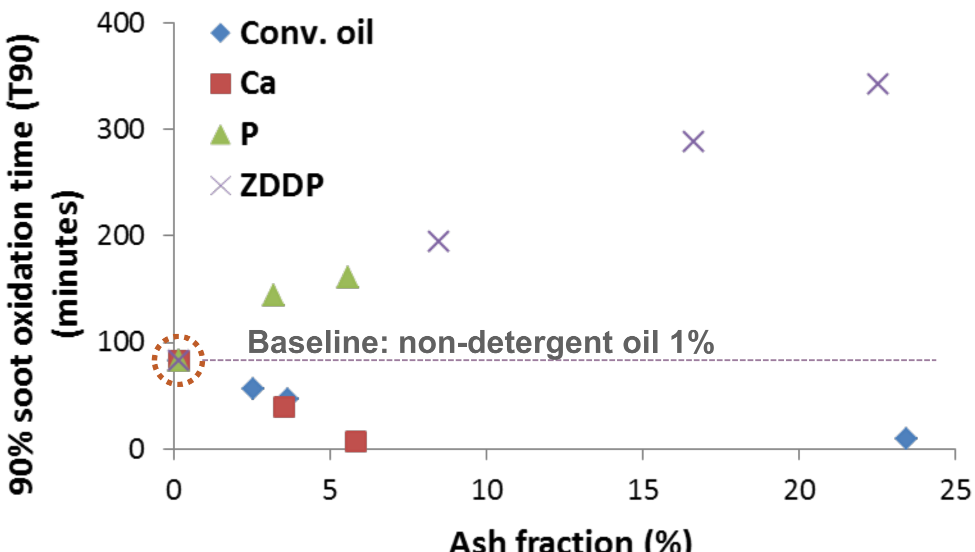
Zn & P: Zinc dithiophosphate (ZDDP)

Dosage in fuel (ppm)	Ca	Zn	P	Na	Total
Gasoline Only					0.0
1% Non-detergent oil	0.4	3.3	2.7		6.4
1% Conventional oil	21.2	11.0	9.6	4.6	46.5
Calcium Sulfonate in 1% non-detergent oil	4 – 24				4 – 24
Phosphite in 1% non-detergent oil			18 – 55		18 – 55
Zinc Dialkyl Dithiophosphate (ZDDP) in 1% non-detergent oil		8 – 206	8 – 191		16 – 397

Soot oxidation enhanced with Ca, while deteriorated with P

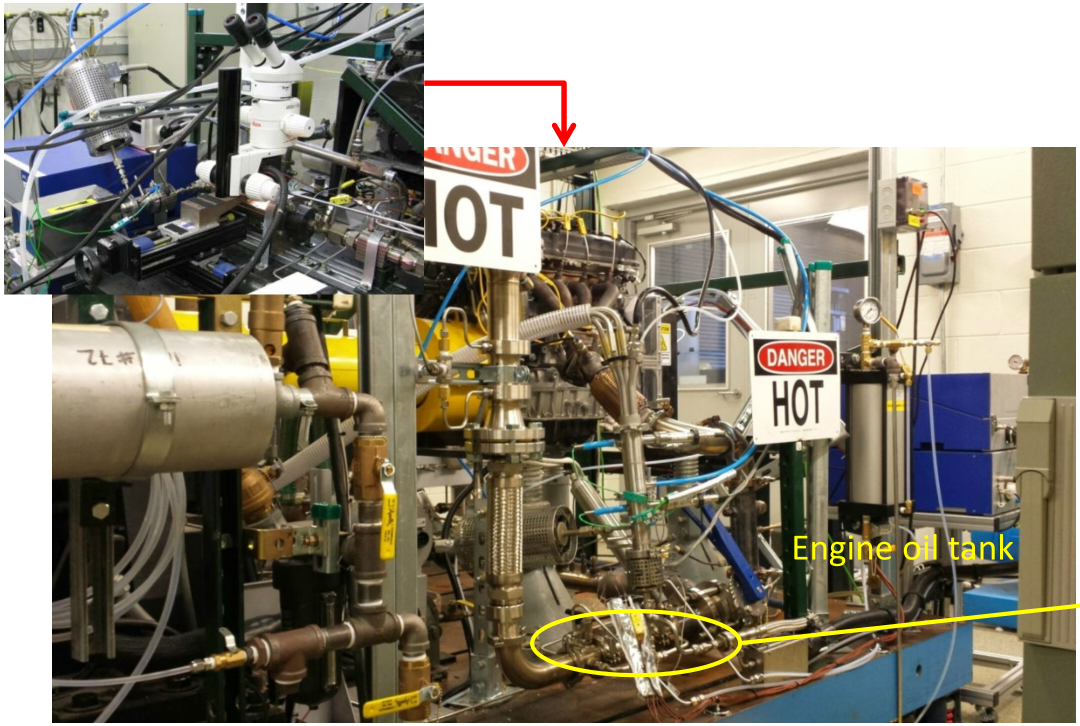


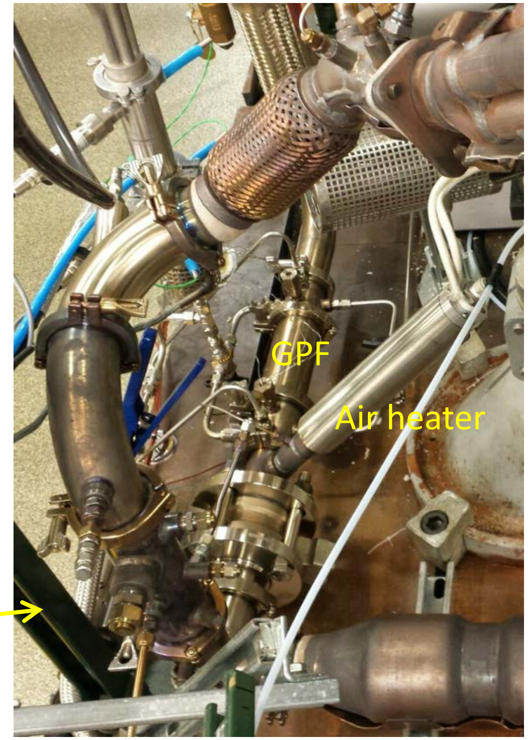
Impact on soot oxidation by 1.0 wt.% of ash fraction in soot	
Ca	+14.5%
P	-15.4%
ZDDP (Zn+P)	-13.7%
Conv. oil	+11.1%



- Ca-derived ash significantly improved soot oxidation reactivity, while P-derived ash impaired reactivity
- Impact of Zn-derived ash seems to be minor
- Enhanced soot oxidation by ash present is because Ca is a dominant component in ash

Testing set-up that enables aging test and realistic GPF conditions has been newly built

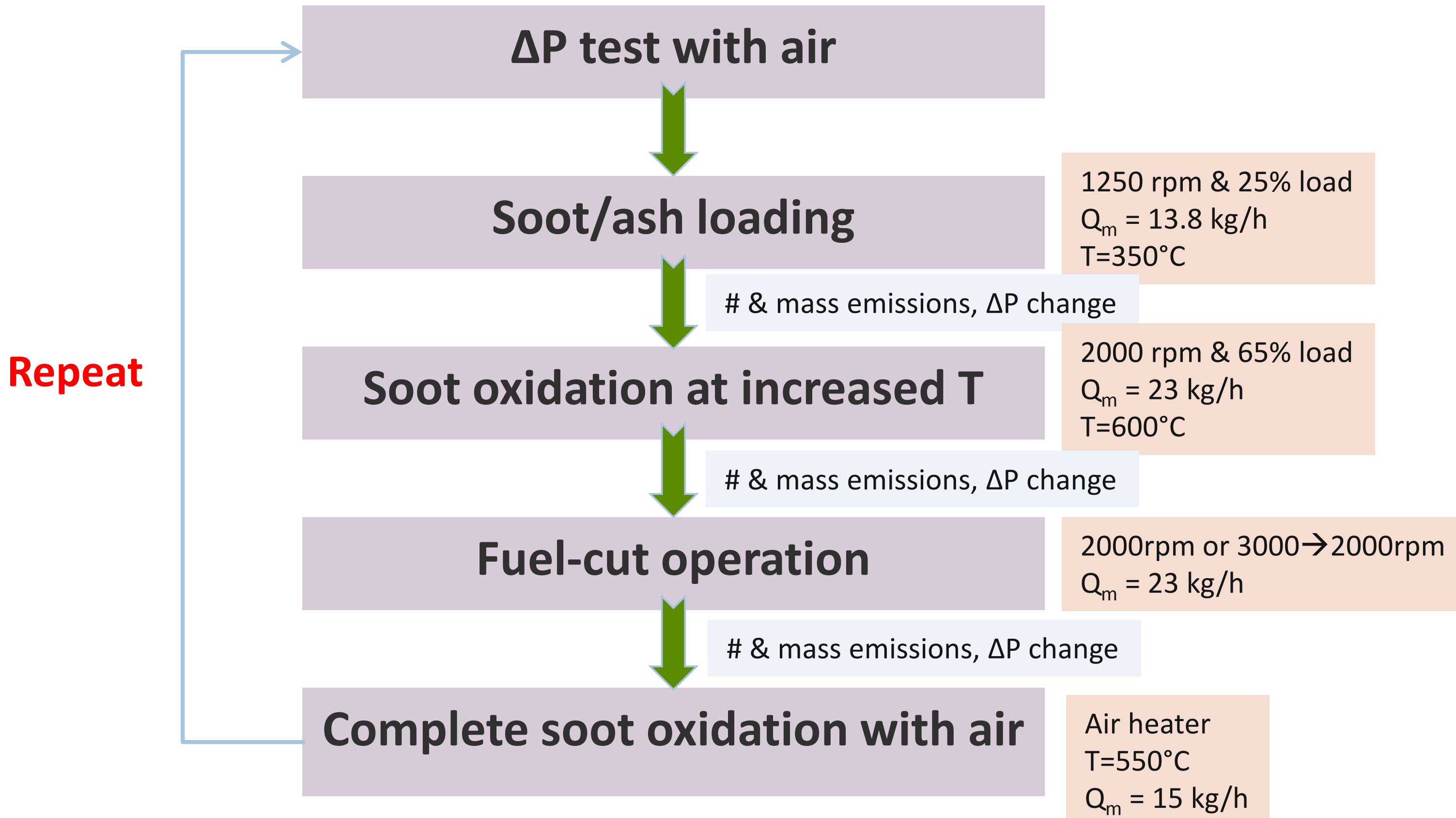




Previous system	Current system
Optical GPF setup (half cut 2"(D)x6"(L))	In-line GPF setup (2"(D)x6"(L))
- Visualization	- No visualization
- Low exhaust T with long line	- Hot exhaust T as actual test
- Sealing problem with quartz window	- No sealing problem
Dilution setup and emissions measurements	Dilution setup and emissions measurements
- Cumbersome handling for inlet & outlet	- Quick access: 3-way valve for fast measurements
No lube-oil injection system	Lube-oil injection system
-	- Aging test enabled

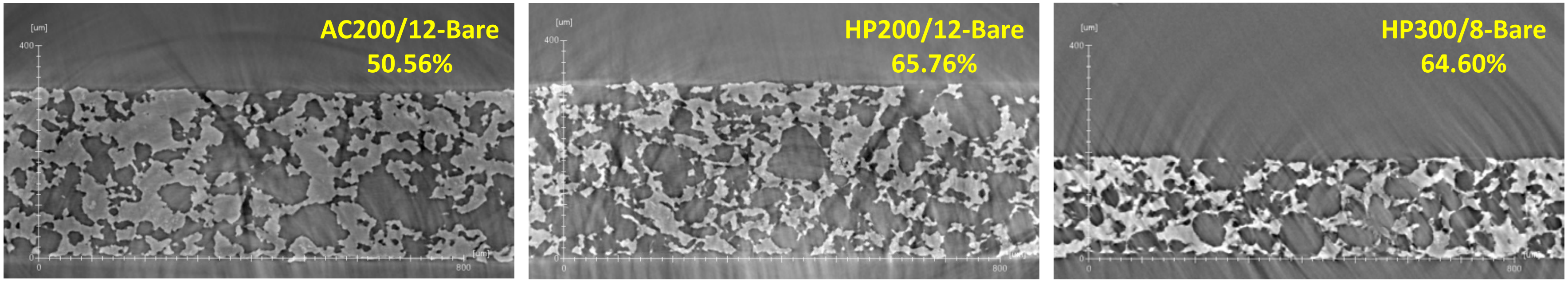
GPF test protocol was prepared to evaluate GPF performance for the bench-scale reactor

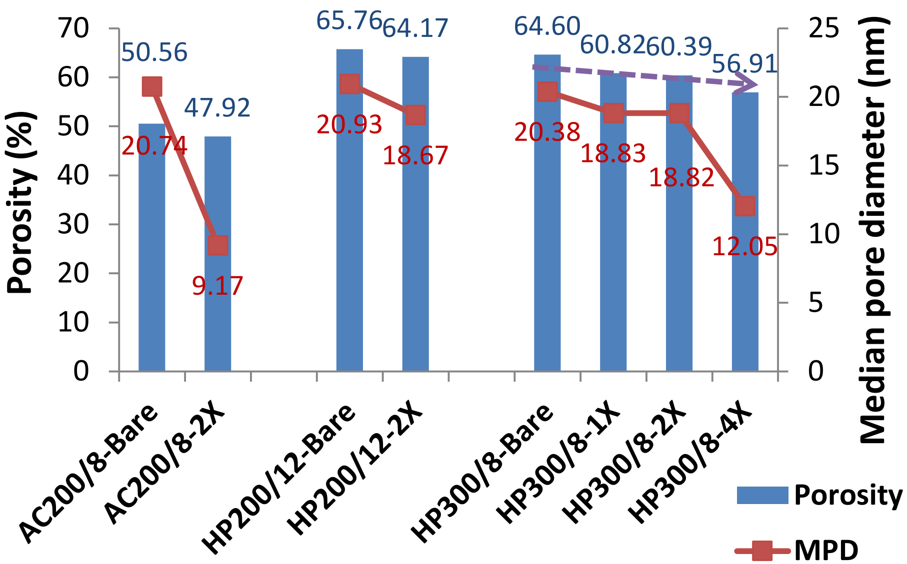
- Require test protocol that evaluate filter performance with ash loading
- Better understand GPF regeneration condition
- Need clean filter condition with no soot contained for fair comparison



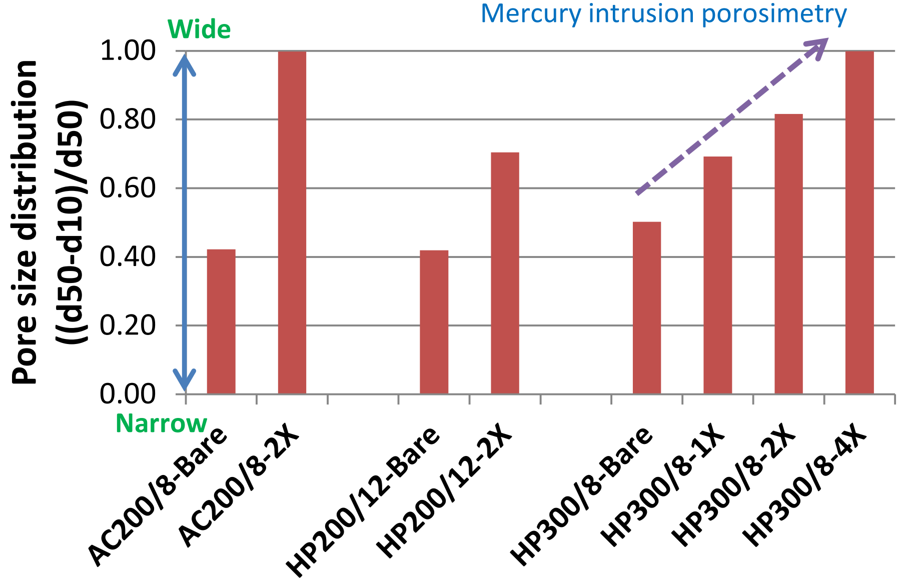
High porosity filter had relatively minor changes in pore structures with catalyst coating

2D images of X-ray microtomography from APS



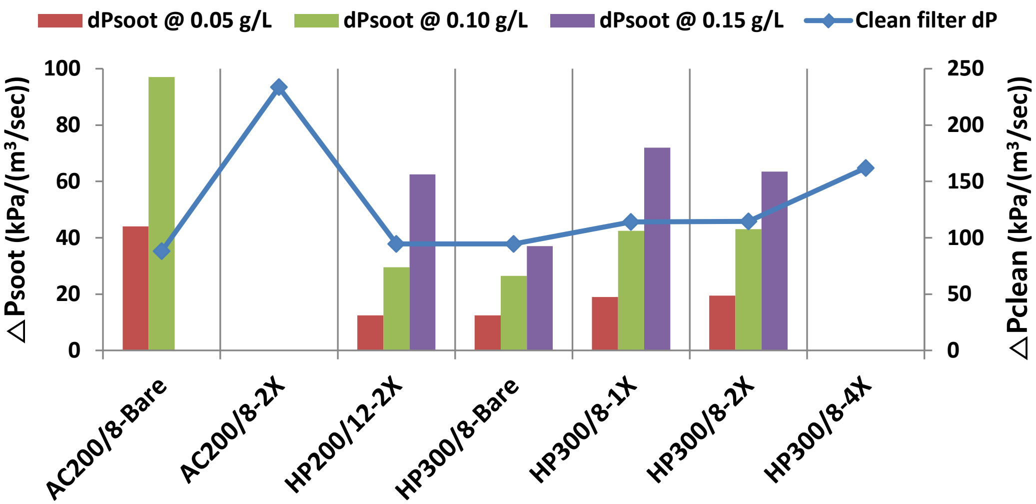


Mercury intrusion porosimetry

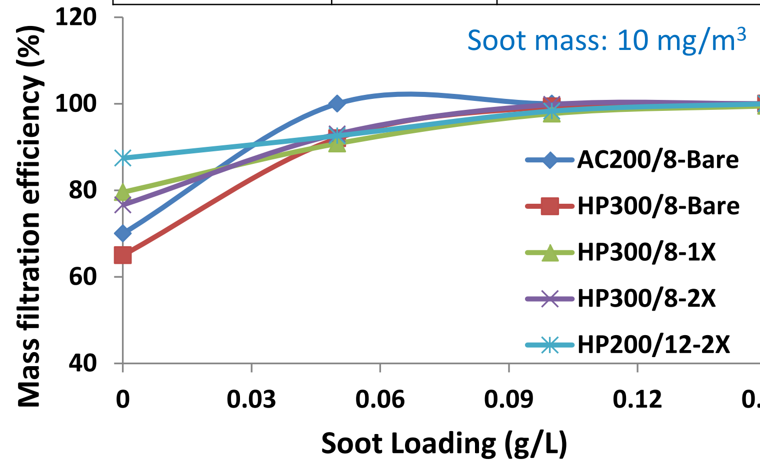


- High porosity filters have relatively big pores uniformly spread in filters
- Changes in total porosity were minor with catalyst coating, regardless of filter type. However, MPD decreased significantly with catalyst coating for medium porosity filter.
- With catalyst coating, PSD became wider for medium porosity filter than for high porosity filters.
- High porosity filter lost porosity benefits with high catalyst coating (4X).

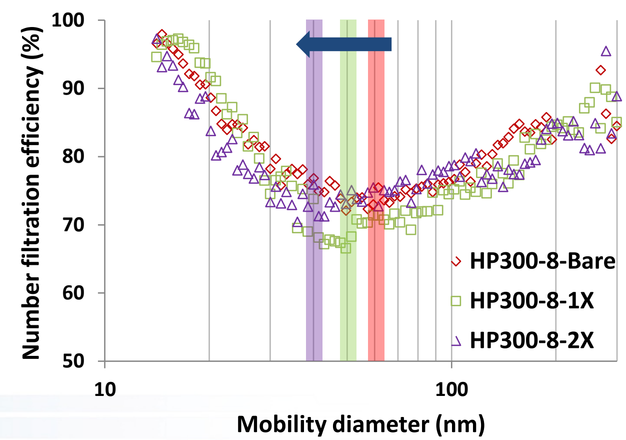
Low & medium catalyst loadings had minor impacts on ΔP, mass & # filtration efficiencies for HP filter



	Initial η_{mass} (%)	Soot loading (g/L) @ η_{mass} 100%
AC200/8-Bare	70.0	0.040
HP300/8-Bare	65.0	0.140
HP300/8-1X	79.5	0.120
HP300/8-2X	76.6	0.175
HP200/12-2X	87.4	0.110

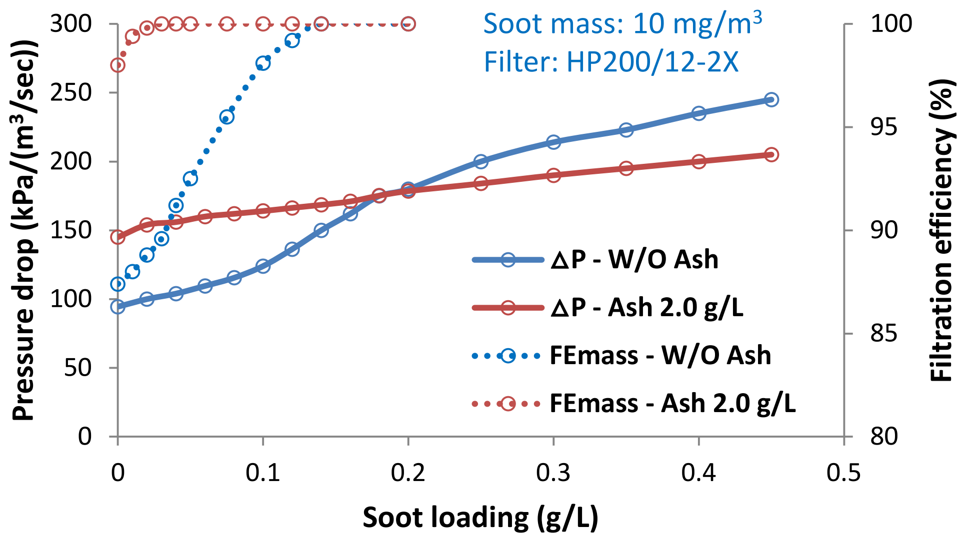


- High porosity filters had low ΔP increase and slow increase in filtration efficiency up to the max point with soot loading.
- High porosity filter (HP300/8) has comparable ΔP increase, mass & # filtration efficiencies with low (1X) and medium (2X) catalyst loadings.
- For high porosity filter, lowest # filtration efficiency was obtained for 40 – 60 nm particles, which are smaller than what others observed (100 – 150 nm).
  - Greenfield gap showing the most particle penetrating range tends to slightly shift to smaller size range with catalyst loading.

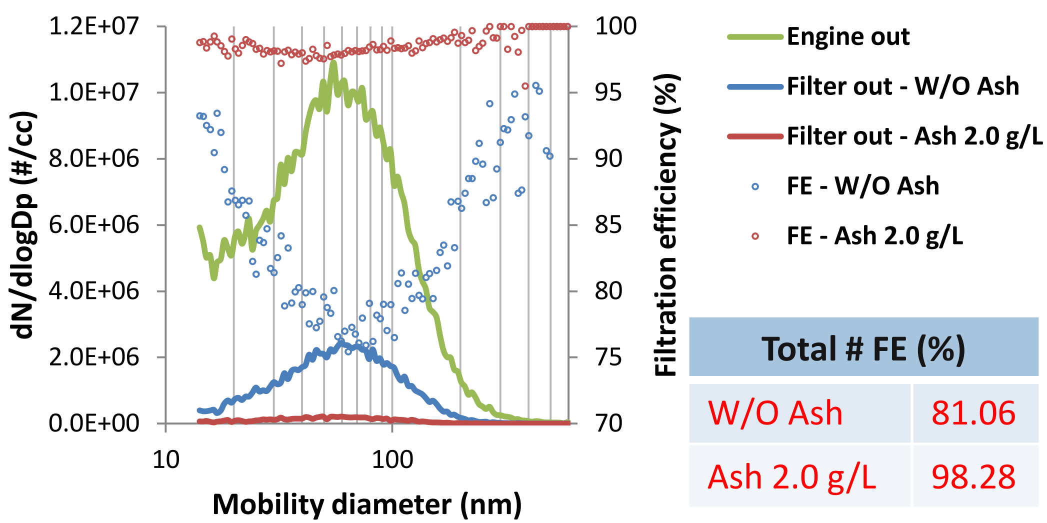


With pore plugging by ash loading, depth filtration duration significantly decreased, improving filter efficiencies

- Ash loading
  - Engine oil: 5W20 conventional (p.10)
  - Oil consumption rate: 2% in fuel
  - Ash loading of 2 g/L in 3 hrs
- Ash loading changed ΔP patterns as observed from previous DPF studies
  - Short depth filtration (0.02 vs 0.2 g/L of soot)
  - Lower ΔP slope (inverse point: 0.18g/L)
- Ash loading improved filtration efficiency
  - Initial mass η_{filt} (98 vs 87.4%)
  - Initial # η_{filt} (98.3 vs 81%)



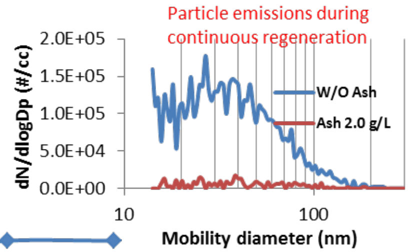
At the start of soot loading

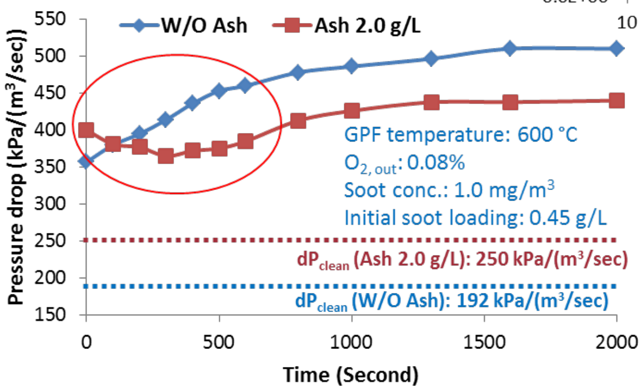


Total # FE (%)	
W/O Ash	81.06
Ash 2.0 g/L	98.28

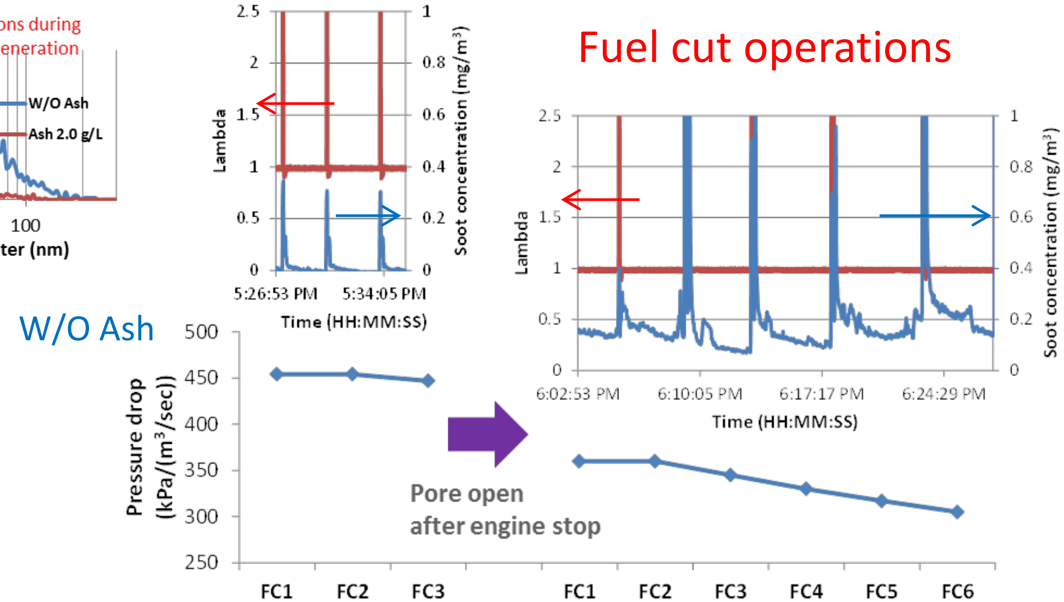
Ash induced continuous regeneration and suppressed particle penetration with pore plugging

Continuous operation

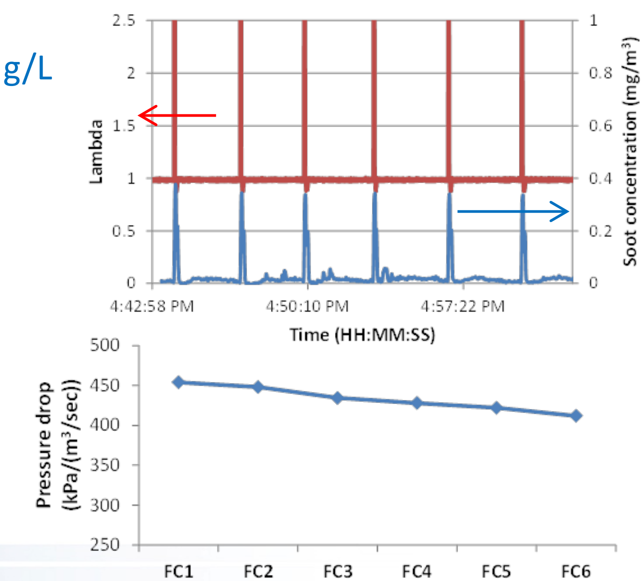




Fuel cut operations



Ash 2.0 g/L



- Continuous regeneration was observed at an initial stage with ash loading.
  - After soot burning at the initial stage, soot loading resumed
  - No or very slow soot oxidation with no ash even at 600°C due to the extremely low O_2 availability
- Particle emissions were relatively high during continuous regeneration with no ash loading.
- Right after fuel cut, particle penetration increased with pores opened, resulting from soot oxidation, when there was no ash loaded. With ash loading of 2 g/L, however, particle penetration was minor after fuel cut.

Responses to FY14 Reviewer Comments

- Ash effects were noteworthy, but they need more supportive data.
  - As examined in this work, enhancement in soot oxidation with ash present is due to Ca additive that is the most abundant in engine oil.
  - Continuous regeneration occurred at 600°C with ash loading without fuel cut. In comparison, soot oxidation is quite slow even at such a high T with very low O_2 availability when ash loading is negligible.
- There need studies on fundamentals of PM formation in GDI engines.
  - Based on this work as well as others, increased PM emissions from GDI engines are directly related with delayed fuel vaporization and resultant fuel-air mixing problems. Although deeper investigation is out of scope, several operating strategies such as increased injection pressure and fast warm-up are shown to decrease soot emissions.
- Integration with kinetics expertise is required
  - After more investigations on filter type, catalyst loading and filter position, kinetics research is recommended for the future.
- Collaborations with research partners are not clear.
  - Collaborations with other partners were not clearly defined (for instance, Tokyo Tech and workshop hosting). Clear roles of research partners are listed in the following page.

Collaborations

Collaborating Partners

- *Corning Incorporated*
  - Provided 8 different filter substrates including most advanced GPF filter substrates
  - Had several technical meetings for future directions
  - Performed MIP of uncatalyzed and catalyzed filters
- *Hyundai Motor Company*
  - Provided a 2.4 production GDI engine and open ECU for full control
  - Gave technical advice of GPF research direction and provided catalyst coating services for GPF substrates based on current state-of-the-art coating technology

Other Internal and Outside Partners

- *University of Illinois at Urbana-Champaign*
  - Performed XPS analysis
- *University of Illinois at Chicago*
  - Xiao Fu (Ph.D. student) helped to analyze X-ray tomography as a guest graduate
- *User Facilities at Argonne (Advanced Photon Source & Center for Nanoscale Materials)*
  - X-ray microtomography, TEM, Raman, FTIR and SEM

Remaining challenges and barriers

- Accelerated ash loading needs more investigation for qualification.
  - Rarely examined in GDI engines
  - Will be compared with aged filters from field tests
- Long-term TWC functionality in TWC-coated GPF has not much known with ash loading.
  - Ash loading challenges maintaining TWC performance as well as backpressure increase over time
  - Development of ash-durable catalyst and filter systems may be required
- Development of cost-effective and durable GPF system is complicated.
  - "Add-on" GPF vs "All-in-one" GPF
  - "All-in-one" GPF has cost benefit over "Add-on" GPF, but the former could be more vulnerable toward catalyst poisoning and backpressure increase

Future Work (to the end of FY15)

- Mechanisms of enhanced soot oxidation in the presence of Ca additive
- Long-term aging tests with catalyzed filters
  - High-porosity catalyzed filters (HP 300/8 & 200/12)
  - Targeted ash loading: 30g/L
  - Aging effects: pressure drop, filter regeneration and TWC performance
- Advancing X-ray micro-tomography and SEM analysis
  - 3-D image analyses of uncatalyzed, catalyzed and aged filters
  - Post-Mortem analysis: ash loading in filters

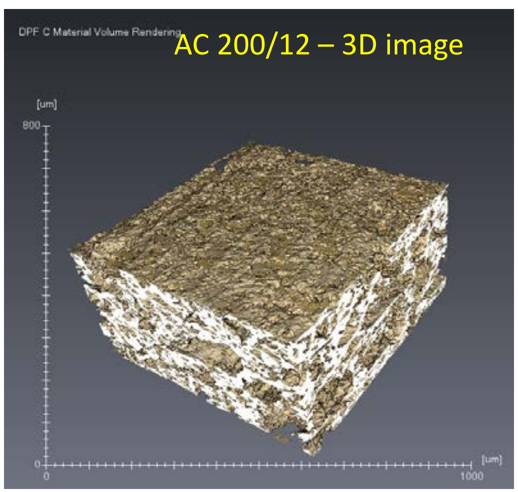
Summary

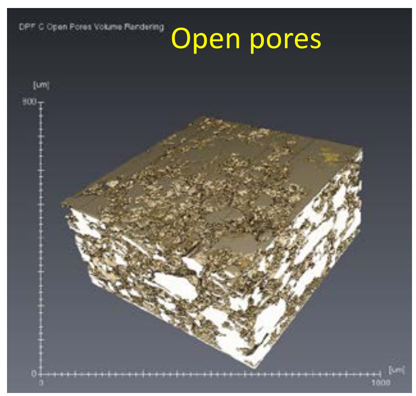
- Enhancement in soot oxidation by ash is due mainly to Ca additive that is a major component in engine oil additives.
- The newly-built in-line GPF system with an engine oil injection system enabled “TWC-coated GPF” tests with ash loading, in which TWC performance, pressure drop and soot oxidation performance are measured.
- High porosity filter had relatively minor changes in pore structure with catalyst coating, resulted in minor impact on ΔP, filtration efficiencies, in comparison with medium porosity filter.
  - However, high catalyst loading (100g/L) sacrificed high porosity benefits.
  - Greenfield gap was observed to be in small particle range of 40 - 60 nm in mobility diameter.
- Ash loading had significant impacts on ΔP and filtration efficiency.
  - Shorter depth filtration duration and increased mass & number filtration efficiencies.
  - Continuous regeneration occurred spontaneously at high T with ash loading.
  - Ash loading helped suppress particle penetration after soot oxidation.
- While continuous regeneration was interfered even at 600°C with extremely low O_2, fuel cut conditions induced continuous regeneration.

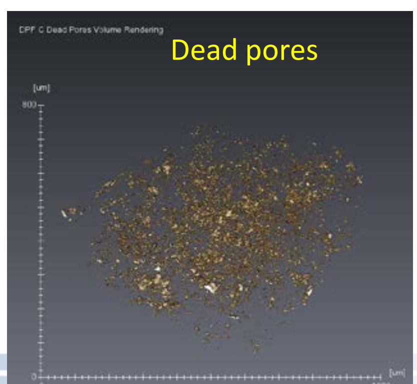
Technical Back-up

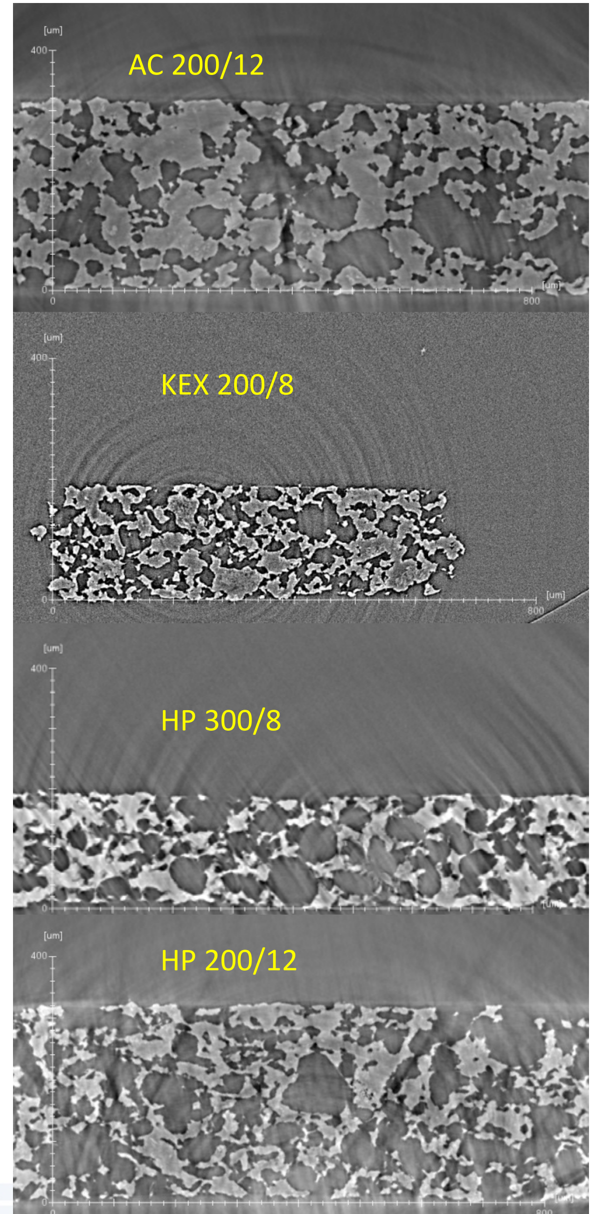
Developing micropore measurement capability using the X-ray microtomography facility at APS-Argonne

- APS facility provides high-fidelity micropore structures with a spatial resolution of 0.65 µm/voxel
- 3-D images reconstructed from ~2000 2-D images
- Will examine effects of catalyst coating and ash loading on detailed micropore structures









Porosity

50%

57%

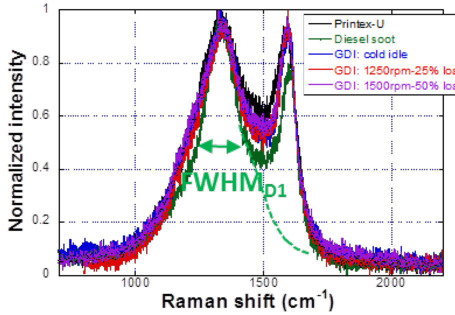
65%

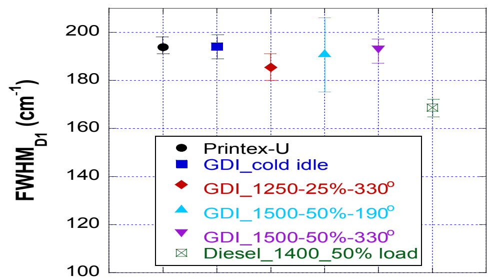
66%

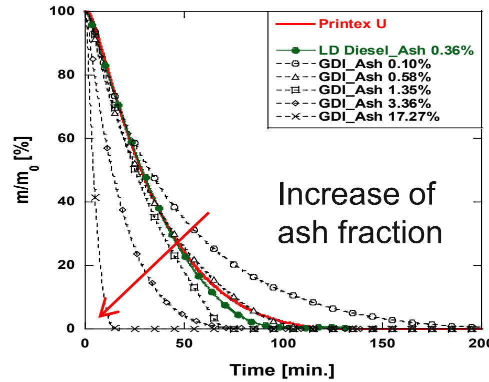
Despite similar crystalline structure, GDI soot shows different oxidation patterns, than Printex U

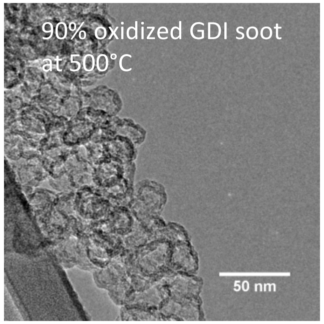
From 2014 AMR

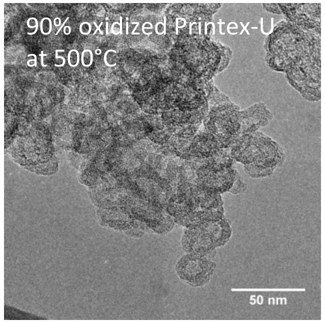
Raman Spectroscopic Analysis

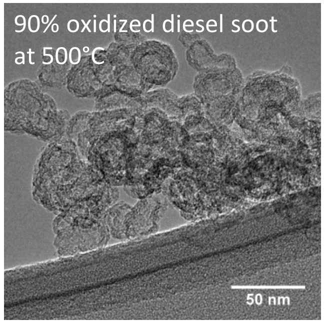


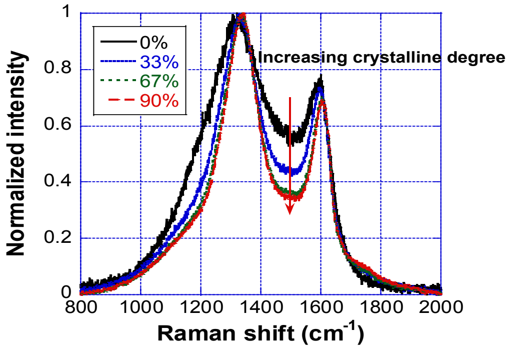


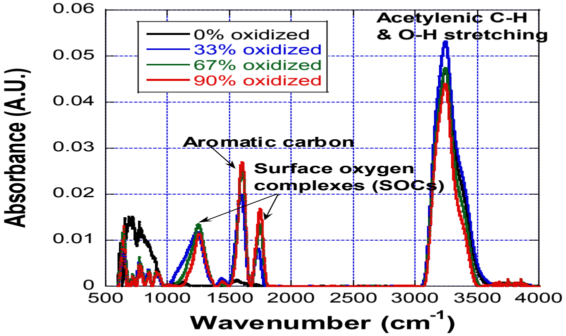


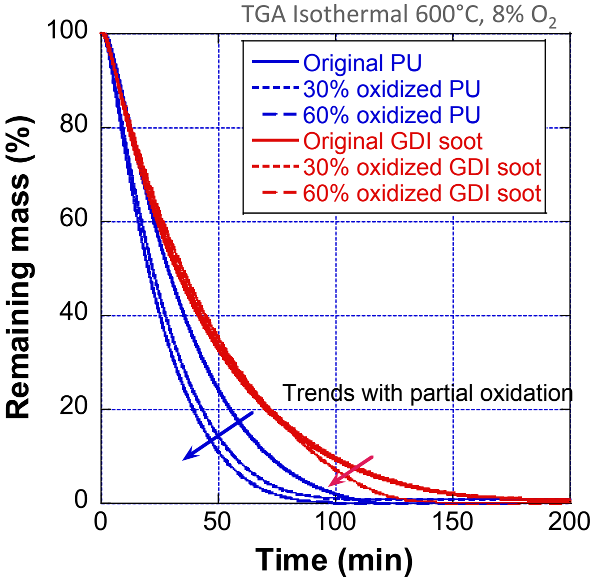








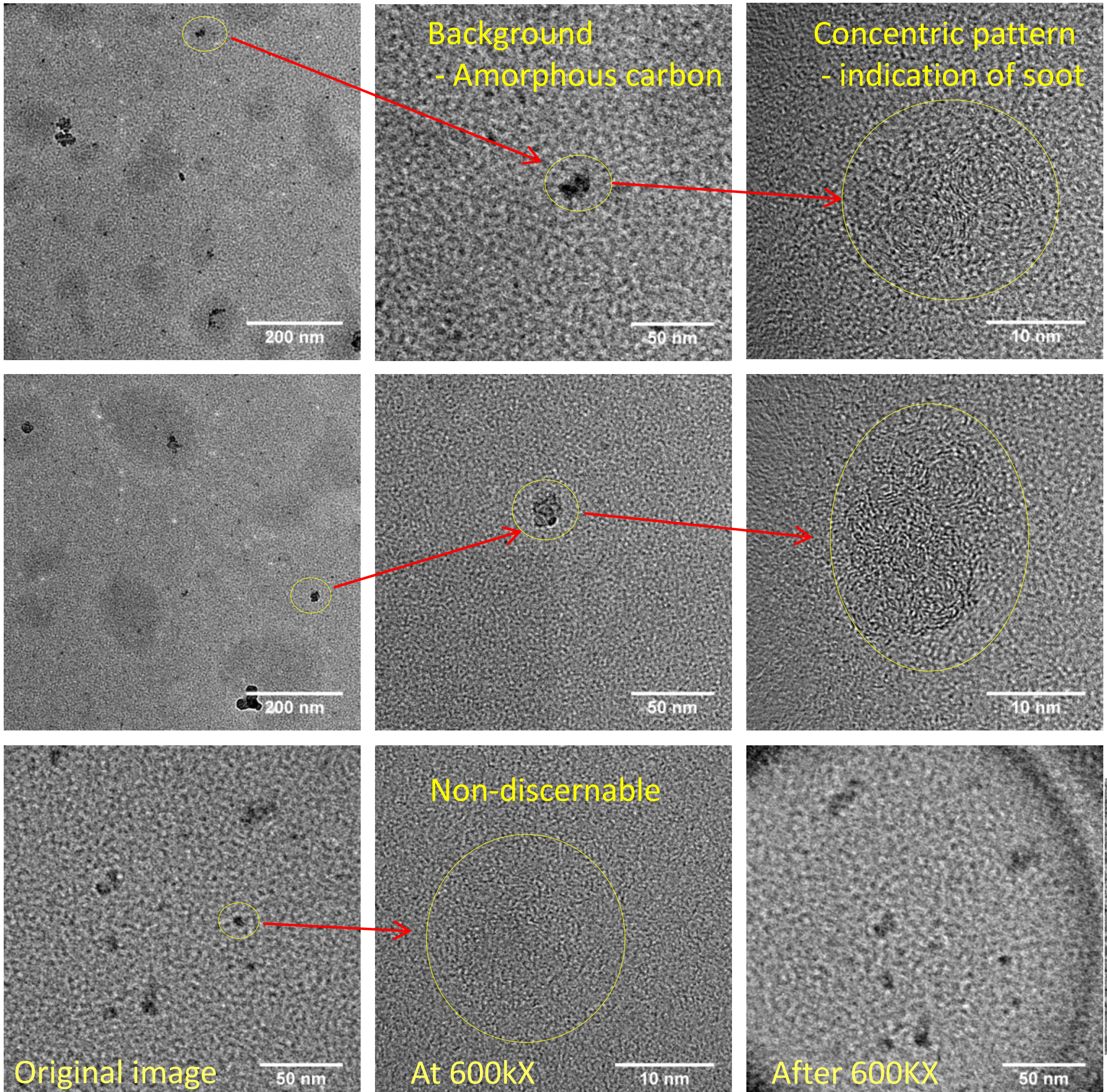




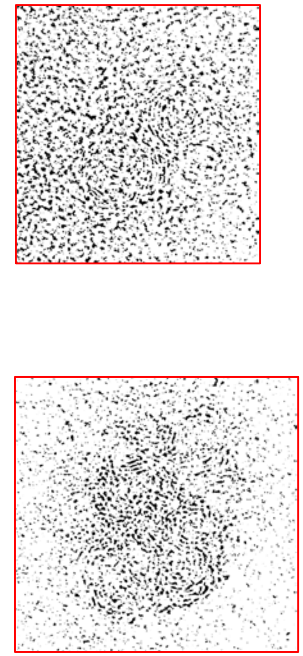
- With oxidation, GDI soot experienced internally burned-out process like Printex-U (PU)
- However, oxidation enhancement with partial oxidation is significant with PU, whereas it is minor with GDI soot ➔ need more investigation

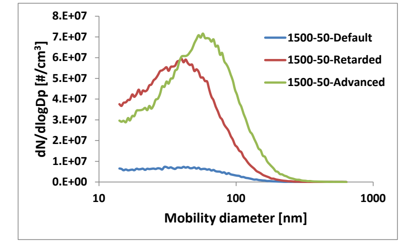
Technical Accomplishments

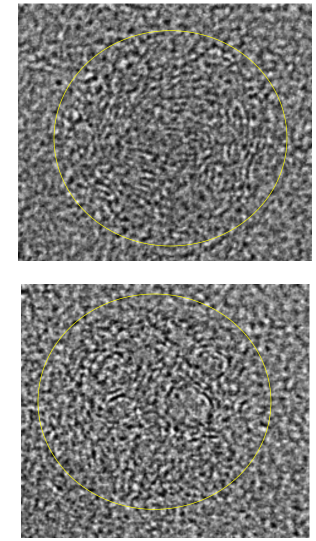
Many of sub-23-nm particles seem to be soot

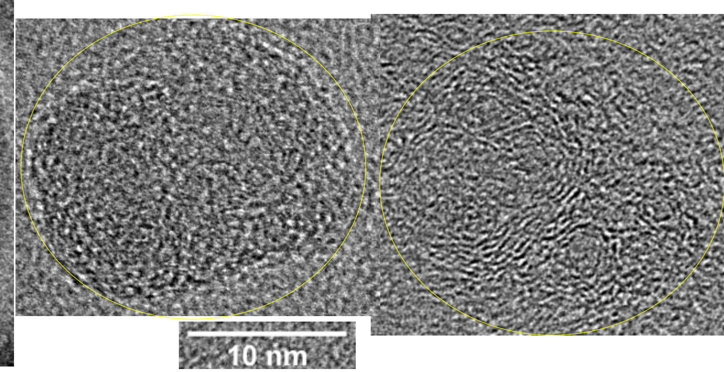


Images processed





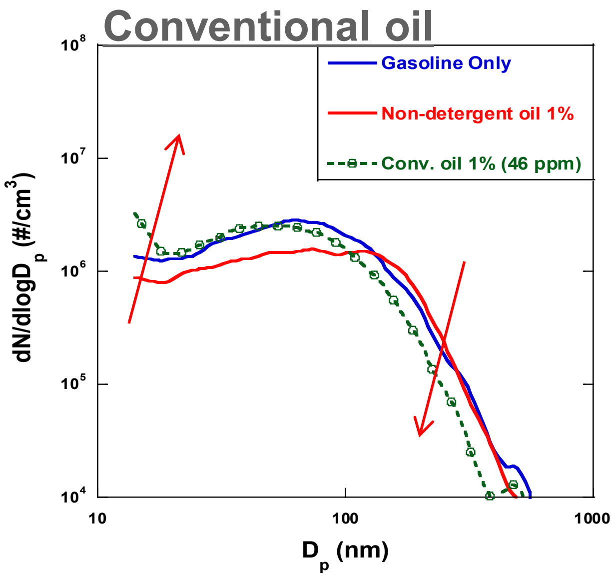


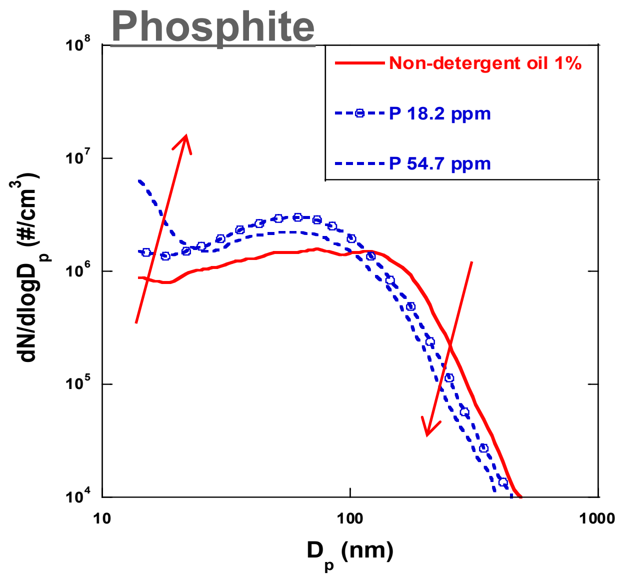


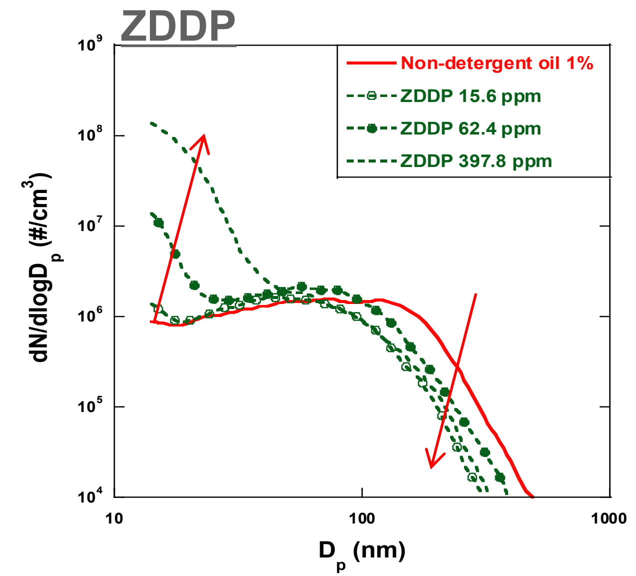
Most sub-15-nm particles are amorphous carbon

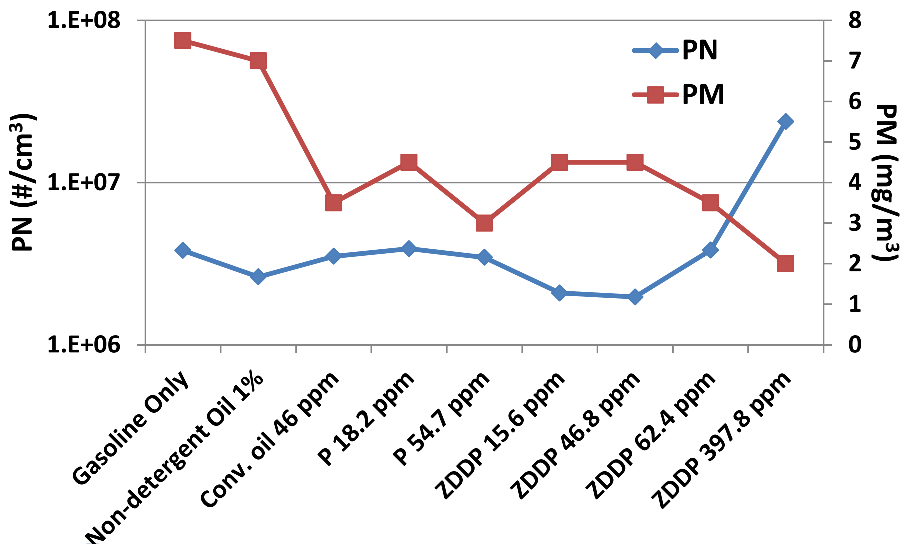
Particles still remained, despite high energy beam under high vac.

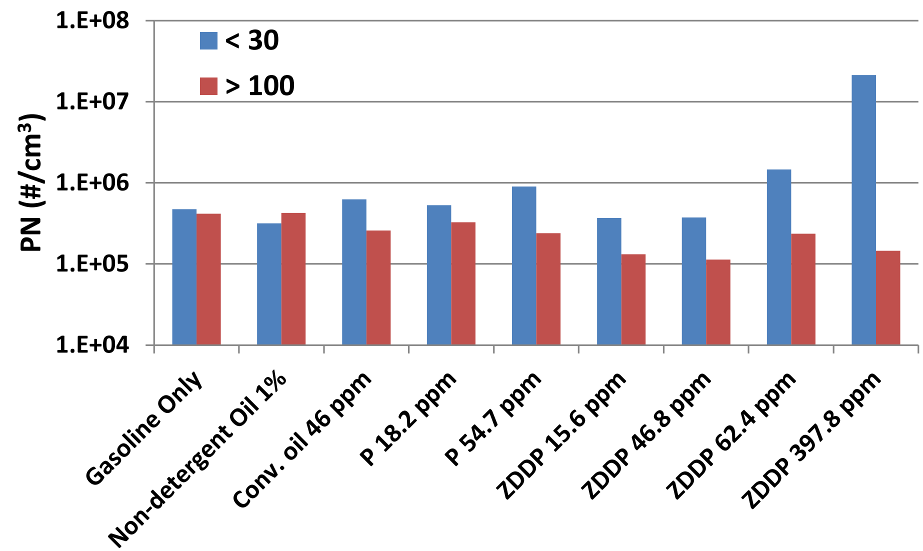
Lube oil additives increase the number of sub 30 nm particles and decrease number of large particles



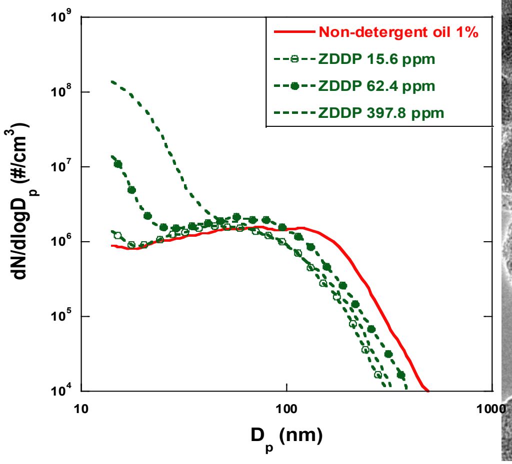


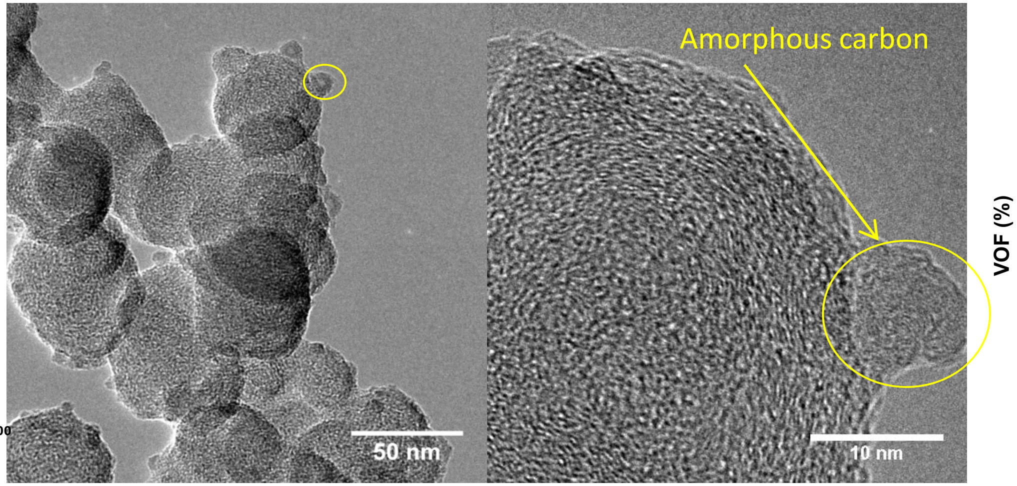


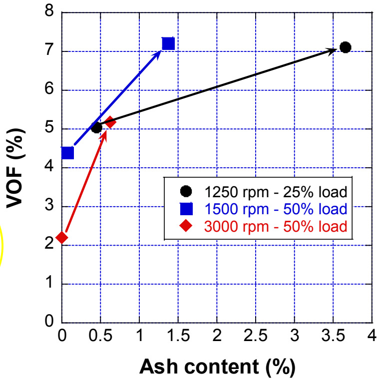


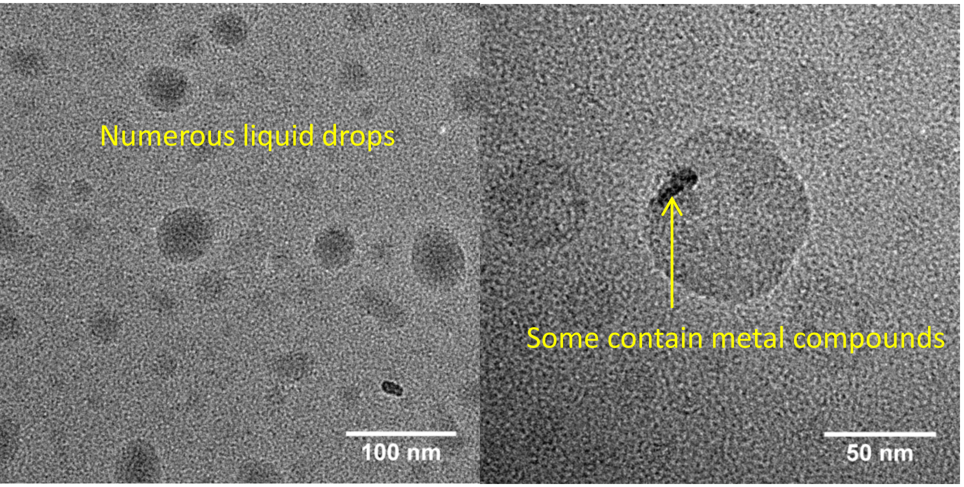


Engine oil may emit as liquid drops or less-ordered carbon without complete oxidation – Engine condition-dependent









Case	XPS, atomic %				From TGA (mass %)
	Ca	P	Zn	S	
Ca additive	1.23	0	0	0	5.8
P additive	0	2.83	0	0	5.6
ZDDP	0	2.88	0.08	0	16.7