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# LUBE EFFECT ON CATALYST AND GASOLINE PARTICULATE FILTER AGING: LITERATURE REVIEW

## Final Report

May 2023

COORDINATING RESEARCH COUNCIL, INC.
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# Lube Effect on Catalyst and Gasoline Particulate Filter Aging: Literature Review

**Final Report**

**SwRI® Project 03.27271**

**In response to:**

**CRC Project AVFL-39**

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**May 18, 2023**

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## List of Acronyms and Abbreviations

GPF: Gasoline particulate filter

TWC: Three-way catalyst

THC: Total Hydrocarbons

NMHC: Non-Methane Hydrocarbons

ZDDP: Zinc dialkyl dithiophosphate

NMOG: Non-methane organic gases

$NO_X$: Nitrogen oxides

PM: Particulate matter

FUL: Full useful life

PN: Particle number

SPD: Solid particle number

ASD: Aerosol synthesis deposition

PHEV: Plug-in hybrid electric vehicle

GDI: Gasoline direct injection

ECTO-Lab: Exhaust Composition Transient Operation Laboratory$^{TM}$

ICP-MS: Inductively coupled plasma mass spectrometry

MFC: Mass flow controller

P: Phosphorous

PEI: Phosphorus Emission Index

EDX: Energy Dispersive X-ray Spectroscopy

SOF: Soluble Organic Fraction

BO: Base Oil

DCT: Dual Clutch Transmission

EV: Electric Vehicle

HEV: Hybrid Electric Vehicle

CT: Computerized Tomography

SRC: Standard Road Cycle

TGA: Thermogravimetric Analysis

## 1.0 FOREWORD

The Commercial Vehicle Systems Department of Southwest Research Institute's (SwRI) Office of Automotive Engineering is pleased to submit this final report to the Coordinating Research Council (CRC) for the CRC project AVFL-39 titled "Lube Effect on Catalyst and Gasoline Particulate Filter aging - Literature Review." This work was performed under SwRI Project 03.27271 with funding from the CRC.

## 2.0 EXECUTIVE SUMMARY

This report summarizes the findings of an extensive literature review effort on the effect of lube phosphorus level on catalyst efficiency, the effect of lube additives on ash accumulation in Gasoline Particulate Filer (GPF), pressure drop across GPF and their effects on fuel economy. Additional reviewed literature includes testing methods for lube additive effects on catalyst and GPF, the combination of the effects of engine operating mode and lube additive effect on catalyst and GPF efficiency, and the effect of soot level, soot deposition rate, and soot morphology on ash deposition in catalyst and GPF. Summaries are provided for the areas being reviewed with more detailed information in the respective sections. Concluding remarks discusses future programs that could be of interest to stakeholders.

## 3.0 BACKGROUND

Regulators continue to impose strict limitations on emissions from vehicles. The 2021 MY fleet avg requirement is 0.058 g/mi (NMOG + $NO_X$). The limit is anticipated to decrease to 0.03 g/mi (NMOG + $NO_X$) by 2025. California regulations will decrease the particulate matter (PM) standard from the current to 3 mg/mi limit to 1 mg/mi by 2025. These updated standards may require the use of a Gasoline Particulate Filter (GPF) in addition to a three-way catalyst aftertreatment system. Engine oil contains phosphorous (P), a well-known catalyst poison, which can enter the exhaust system and affect the performance of aftertreatment systems. New lube oil formulations have been developed to reduce the primary P-containing compound, Zinc Dialkyl Dithiophosphate (ZDDP), using other antiwear and antioxidant addition compound(s). This review focuses on state-of-the-art as well as on-going research being conducted to investigate the impact of modern lube oil formulations on catalyst and GPF performance to full useful life (FUL).

## 4.0 APPROACH

This literature review includes publicly available material on technologies that have helped reduce PM from gasoline vehicles. Reviewed literatures were chosen based on the quality of the journal, the authors and their affiliations, and the scope of the work explored. The following topics are discussed:

1. Effect of lube oil formulation on catalyst efficiency
    - Lube oil formulation effects of interest include primarily those resulting from additive phosphorus level but may also include effects of additives not containing phosphorus, base oil, and viscosity.

- Efficiency effects include conversion efficiency of criteria pollutants (CO, hydrocarbon, NOx, Particulate Matter (PM), and Particle Number (PN)).
- Efficiency effects include changes of conversion efficiency as catalyst ages to the expected useful life of the emissions control system (150,000 miles).
- Efficiency effects include changes resulting from catalyst poisoning, ash deposits blocking active sites, and ash deposits increasing pressure drop.

2. Effect of lube additives on ash accumulation in the GPF

- Effect of lube additives on ash accumulation in the GPF, the effect of ash on pressure drop across the GPF, and the effect of pressure drop on fuel economy.
    - Do all lube additives deposit ash in a similar manner and produce similar pressure drop?
- Lube oil formulation effects of interest include primarily those resulting from additive phosphorus level but may also include effects of additives not containing phosphorus, base oil, and viscosity.
- Efficiency effects include conversion efficiency of criteria pollutants (CO, hydrocarbon, NOx, Particulate Matter (PM), and Particulate Number (PN)).
- Efficiency effects include changes of conversion efficiency as GPF ages to the expected useful life of the emissions control system (150,000 miles).
- Efficiency effects include changes resulting from catalyst poisoning, ash deposits blocking active sites, and ash deposits increasing pressure drop.

3. A comparison of various test methods for lube additive effects on catalyst and GPF

- Evaluate strengths and weaknesses of the various test methods.
- Assess level of development of various test methods.
- Examples of test methods for consideration:
    - Vehicle tests
    - Engine tests with oil-in-fuel doping
    - Engine tests with piston ring modification
    - Aerosol synthesis deposition (ASD) reactor
    - Burner with oil-in-fuel doping
    - Burner with separate oil injection (separate from fuel)
    - Burner with separate oil injection and independent control of catalyst temperature, oil injection rate, and oil droplet size
- Additional test methods not listed above may also be included.
- What types of test methods are available and what are the pros and cons thereof?
- What types of oil deposition methods are used in these tests and what are the pros and cons thereof?
- How realistic are the various accelerated test methods compared to emissions performance of real vehicles on the road?

4. Combination of the effects of engine operating mode and lube additive effect on catalyst/GPF efficiency.

  - Operating modes of particular interest include those associated with conventional vehicles verses Plug-in Hybrid Electric Vehicles (PHEV).
  - Do certain types of lube additives produce ash that is more challenging in PHEV operating modes than conventional modes or vice versa?

5. Effect of soot level, soot deposition rate, and soot morphology on ash deposition in catalyst and GPF

  - Does soot level, soot deposition rate, and soot morphology affect ash deposits which then affect catalyst/GPF efficiency and pressure drop?

## 5.0 RESULTS AND DISCUSSION

The following section discusses the reviewed literature in detail on the respective topics.

### 5.1 Effect of Lube Oil Formulation on Catalyst Efficiency

A study was conducted to investigate the effects of engine oil formulation types on the catalyst performance after 100,000 miles of taxi service [1]. Zinc dialkyl-dithio-phosphate (ZDDP) is a common anti-wear and corrosion inhibiting lubricant additive. The oil formulations considered in this study included a reference lower limit of no phosphorous with and without zinc and an upper limit of no detergents in the presence of ZDDP and variations in alkaline earth detergent metals. It was observed that the taxi service provided an adverse driving cycle for phosphorous contamination of catalysts at low average speed and associated operating conditions. Four different oil formulations were considered as follows –

- Baseline oil (Oil 32 and 36) that was formulated to meet GF-2 performance levels for wear protection, oxidation control, fuel efficiency, etc.
- Experimental oils (Oil 33, 34 and 35) blended for this study which would not pass GF2 requirements
  - Oil 33 that did not have detergents
  - Oil 34 and 35 that did not contain ZDDP
  - Oil 35 that had a non-phosphorous anti-wear additive

These oil formulations were tested in a fleet of 20 vehicles with four vehicles per oil formulation. The mileage accumulation was performed with Howell EEE grade gasoline and averaged about 7,000 miles per month (oil changed at 5,000-mile intervals) and totaled two million fleet miles at the end of the program. The aftertreatment system consists of a close-coupled catalyst followed by two underbody catalysts per bank (6 bricks total) and these catalysts were 42 in$^3$ ceramic ovals with a production Pd-only washcoat. Over the course of mileage accumulation, loss of phosphorous due to volatilization was observed and results suggested that the presence of alkaline-earth metallic detergents can somehow suppress the rate of phosphorous volatilization.

During an FTP cycle, it was observed that oil formulation had clear impact on HC emissions after the close-coupled catalyst. Highest HC emissions were observed on TWCs exposed to Oil 33 which contained Phosphorous but no detergent while lowest HC emissions observed on Oils 34 and 35 which had no Phosphorous. Interestingly, Oils 32 and 36 which differed in detergent-additive type, displayed relatively similar HC emissions. $NO_X$ emissions at the intermediate sample location followed a similar trend to HC over the FTP cycle, which indicated that the change in emissions is due to the contamination of catalyst by Phosphorous and lack of detergent. During the FTP, highest tailpipe HC emissions observed on TWCs exposed to Oil 33 which contained P but no detergent while non-Phosphorous oils had 75% less HC than Oil 33. It was also observed that the high calcium oil formulation – Oil 36 behaved similarly to the baseline oil formulation. Similar trends were observed on CO and $NO_X$ emissions where P containing oil with no detergents produced highest concentration of CO and $NO_X$ among the tested candidates. Elemental analysis of close coupled catalysts suggested that P loss from the oils was due to selective volatilization and was the major pathway for phosphorous contamination in this study. In general, the capture efficiency of volatilized P on close coupled catalyst ranged from 75 to 86% and a clear trend of increased emissions with higher P on catalyst was observed. Further, non-detergent test oil had higher oil consumption and higher contamination of P on TWCs.

Guevremont et al. [2] examined catalytic converters that have been tested in a novel engine-based catalytic converter poisoning test to track the phosphorus distribution in the TWC. The Afton Catalyst Test (ACT) is a 240-hour catalyst aging test that emphasized and accelerated the effects of chemical degradation of TWC activity through consumption of volatile engine oil fractions and components. P from ZDDP decomposition was released into the crankcase air space and combusted with the positive crankcase ventilation gases. The test engine was operated to maintain 150°C oil temperature and 122°C coolant temperature while maintaining catalyst inlet temperature at 550 °C with the engine oil being replaced every 24 hours. TWCs were sourced from the front brick in the left-bank of a MY2004 Ford Crown Victoria and are zone coated with first 50% of the catalyst (lengthwise) being coated with 130 g/ft$^3$ PGM (1:14:1 Pt:Pd:Rh) and second 50% with 15 g/ft$^3$ PGM (2:0:1 Pt:Pd:Rh). Anti-wear and detergent additives were varied based on Phosphorous Emission Index (PEI) and detergent component. Across the literature, several efforts were reported to develop an effective method to measure the amount of P escaping into the exhaust gas phase that ended up interacting with the catalysts. Phosphorus emission index (PEI) is one such index that is based on measuring the mass of P that escaped from engine oil at 250 °C or at 165 °C for 16 hours. Formulations used with catalysts 16, 17, and 18 were published as oil code 35, 32, and 33, respectively [1]. The results from this study revealed that both PEI and detergent play significant role in catalyst deactivation. Elemental analysis of surface scans of Mg, Ca and Zn distribution were consistent with detergents in the respective formulations and were primarily concentrated at the catalyst inlet. However, P was distributed further downstream in the catalysts and the significant buildup of P along the centerline of a catalyst brick correlated with the lack of detergent in the corresponding catalyst formulation. Energy Dispersive X-ray Spectroscopy (EDX) mapping and line scan results exhibited deeper penetration of P in washcoat while Zn is more concentrated at the surface. Furthermore, HC was observed to be more sensitive to surface P than CO and $NO_X$. Measurement of P was impractical for predicting catalyst activity loss due to lube oil. Overall, detergents played a critical role in P poisoning of catalytic converters. Surface and total P in catalysts has a large correlation to the activity of the catalyst. Selection of anti-wear additive was found to be more important for minimizing catalytic activity loss as catalyst ages due to chemical (lube oil) and thermal exposure.

In another study [3], the impact of lubricant oil additives on the performance of Pd- based TWCs was evaluated. ZDDP is classified as a primary-alkyl or secondary alkyl depending on the type of hydrocarbons used in the manufacturing process. In general, primary alkyl ZDDP are more thermally stable and used in diesel engines while more reactive secondary-alkyl ZDDP are used for gasoline engines. Novel Ionic Liquid (IL) based lubricant additives were also being explored as alternatives to ZDDP. These lubricant additives enabled reduced friction and wear while they do not contain Zn. The antiwear performance of Ionic Liquid - tetraoctylphosphonium bis(2ethylhexyl) phosphate ([P8888] [DEHP]) was compared against ZDDP and found that DEHP lowered both friction coefficient and wear volume by 30% compared to conventional ZDDP + base oil. The test matrix in this study included a) No additive in the fuel when aging the TWC (baseline), b) ZDDP added to fuel during TWC aging, c) Ionic Liquid alone mixed with fuel during TWC aging (this sample isolated any impact of the IL as well as Zn), and d) Blend of IL and ZDDP. Blend d) is the proposed use of IL in the lubricant and was evaluated to ensure compatibility with TWC. The catalysts were aged to Full Useful Life (FUL) using engine exhaust targeting a midbed catalyst temperature of 700°C. The lubricant additives were mixed with standard tier 3 gasoline and lubricant consumption rate was set to 90 mg/km. The simulated exhaust stream consisted of 850 ppm $C_3H_6$, 100 ppm $C_3H_8$, 0.5% CO, 0.167% $H_2$, 13% $H_2O$, 13% $CO_2$ and balance $N_2$. CO and HC light off temperatures increased after exposure to an additive in general. IL impact on light off suggested that P is the key element in catalyst deactivation while Zn does not impact reactivity. $NH_3$ formation increased with additive exposure while $N_2O$ formation decreased with additive exposure. Authors have no explanation for the underlying mechanisms. Overall, a decrease in oxygen storage capacity was observed for all P containing additives while the loss of water gas shift activity was consistent between the additives indicating that P content is the key contributing factor to the loss of catalyst activity. The consistent surface area loss in all aged catalysts suggested that the decrease is due to hydrothermal aging and not the additives. In conclusion, the impact of IL, ZDDP, and IL+ZDDP on TWC performance was found to be similar and the primary mode of deactivation was phosphorous deposition on the catalyst surface.

In a similar study [4], four different catalysts were explored as:

- FUL_AR: TWC thermally aged to full useful life, evaluated as received
- FUL_NA: FUL_AR further aged by neat gasoline with no additive
- FUL_ZDDP: FUL_AR further aged by gasoline mixed with ZDDP
- FUL_IL: FUL_AR further aged by gasoline mixed with IL

Catalysts were aged using engine exhaust at 900 to 950°C for about 24 hours. P penetration was detected in inlet samples extracted from the TWCs exposed to ZDDP and IL while this was not observed in the case of neat gasoline with no additive. P overlayer detected in the middle and outlet of ZDDP aged samples suggested less overall penetration of IL derived P. Significant P content was detected on both ZDDP and IL aged samples. ZDDP aged samples exhibited greater loss of activity compared to IL samples. Overall, ZDDP additive degraded TWC conversion efficiency of criteria emissions. IL aged samples exhibited less degradation of TWC conversion efficiency over FUL with overall P content on IL aged TWCs was 33% lower than ZDDP aged TWC.

In another study [5], primary (ZDDP1) and secondary (ZDDP2) zinc dialkyldithiophosphate along with different composition blends of ZDDP and IL were evaluated. ZDDP1 aged samples exhibited less TWC performance degradation due to lower S, Zn, and P content compared to ZDDP2. Overall, choice of ZDDP additive had greater influence on catalyst degradation compared to the presence of IL.

The influence of oil viscosity on the tail pipe total hydrocarbon (THC), non-methane hydrocarbon (NMHC), CO, $CH_4$, and $NO_X$ were evaluated [6]. Emission concentrations were influenced by factors such as volatilization of engine oil and the inevitable small amount of combustion products in the oil [7-9], evaporation, and viscosity- temperature characteristics of oil [10], base oil type and ash content in the oil [11], particulate mass and number, micromorphology characteristics of particulate [12], speed and acceleration of vehicles [13], engine temperature [14] and types of elements in fuel and lubricating oil [15]. To explore the influencing factors of different engine lubricants on exhaust emissions, four engine lubricants with varying viscosity were tested over a WLTC cycle. The influence of oil viscosity on automobile exhaust emission was not consistent. For example, low viscosity oils reduced CO emissions in the low-speed segment, however CO increased in the extra high-speed segment. Further, in the extra high-speed segment, the low viscosity oils can reduce $CH_4$ emissions to different degrees. Similar inconsistent trends were observed with $NO_X$ emissions. In general, no clear correlation observed between emissions and oil viscosity. However, CO emissions were highly negatively correlated with the ash content of the engine oil. It was observed that the higher the ash content in the oil, the lower the CO emissions were. The emissions of THC and NMHC were highly positively correlated with the content of Ga, and highly negatively correlated with the content of Mg and Mo. $CH_4$ was highly negatively correlated with the content of Zn. In conclusion, it was difficult to conclude general trend relating oil viscosity to tailpipe emissions beyond positive impact at low-speed start-up conditions. Low-viscosity oil can reduce CO, THC, and NMHC emissions at low speeds but may result in increased emissions at higher speeds.

Bardasz et al. [16] examined quantitative sets of results generated using various vehicle and exhaust catalyst testing methodologies designed to follow the path of lubricant-derived phosphorous transfer from oil sump to exhaust catalytic systems. Post-mortem analysis of aged catalysts was used to both quantify the level of phosphorus exposure from the oil as well as estimate the loss of performance resulting from phosphorus deposition within the catalyst. Results revealed a significant and beneficial impact of reduced lubricant-derived phosphorus exposure on the life and efficiency of various three-way catalyst technologies when utilized in numerous vehicle types and driving cycles. The overall environmental benefits of the specific motor oil formulations in this study with the novel ZDDP versus conventional ZDDP are clearly defined by means of the life cycle analysis (LCA). The tests were performed on four catalysts and two lubricant formulations – a) Conventional ZDDP, commercially available secondary ZDDP used for passenger car and heavy-duty diesel applications and b) Hyper ZDDP - secondary ZDDP with alcohol mixtures balanced to reduce phosphorous volatility while maintaining wear protection. It was found that the addition of alcohol mixture to reduce volatile P in HPR ZDDP resulted in less P exposure thereby reducing the impact on overall emissions performance of the TWC. It was interesting to find that alcohols capable of reducing P volatility is one method to improve catalyst performance through FUL.

In summary, Phosphorus deposition is a major cause of deactivation of three-way catalysts. Type of phosphorous species influence the rate of deactivation. Deposition of phosphates associated with Zn such as $Zn_2P_2O_4$ were found to be accumulated in but did not block the pores of the catalyst, while formation of $CePO_4$ resulted in irreversible deactivation due to destruction of Ce-Zr layer (layer used for oxygen storage). Reduction of volatile P species through addition of alcohols can mitigate P poisoning. Also, detergent additives can prevent volatile P species from depositing on catalyst. Lube oil viscosity did not clearly correlate to catalyst performance. Further, certain Ionic Liquids can replace or supplement ZDDP with improved antiwear performance and reduced catalyst poisoning.

## 5.2 Effect of Lube Additives on Ash Accumulation in the GPF

Shao et al. [17] investigated the effects of oil formulation compositions on GPF performance, chemistry and composition of particulates produced using a 2.4L gasoline direct injection (GDI) engine. Accelerated ash loading of the GPF was conducted by direct oil injection into the engine combustion chamber using eight different oils with varying levels of sulfated ash, phosphorus, and detergent metals. GPF performance evaluation included particle number and mass filtration efficiency measurements at steady state modes of engine operation. All experimental oil formulations were SAE 5W-20 viscosity grade and varying levels of sulfated ash, phosphorous from ZDDP and alkaline earth metal type from detergents. ZDDP and detergent treating levels were varied to target sulfated ash and P values while other components such as dispersant, antioxidant, friction modifier and viscosity modifier were treated at constant levels for all oils. Partial flow exhaust system was used to test bench-scale GPFs with a 2.4L 4-cylinder naturally aspirated GDI engine at rated power (147.8 kW @ 6300 rpm) and rated torque (250 Nm @ 4250 rpm). To accelerate ash loading, lube oil was introduced into the fuel supply line on a 2 wt.% basis of lube oil in fuel with a target of 61 g and 122 g of lube oil consumption for the corresponding test conditions. After ash loading, oxidation of soot was conducted by creating ‘regeneration’ type conditions and subsequently filtration efficiency and pressure drop were measured for each oil ash loading conditions. Filtration efficiency was measured using an AVL 483 Micro-soot sensor (MSS) and a scanning mobility particle sizer (SMPS, TSI model 3936). Thermogravimetric analysis (TGA) was used to determine volatile organic fraction (VOF) and oxidation reactivity of PM collected on Teflon filters from the engine out location. Transmission Electron Microscopy (TEM) was used to examine morphology of GDI exhaust particles. Test results revealed that high sulfated ash oils resulted in about twice the amount of ash loading as those of low sulfated ash oils. TGA results suggested that for the same metal type, higher concentration of detergent leads to lower soot production rate while yielding high total ash level. For the same ZDDP level, high sulfated ash oil produced less soot compared to low sulfated ash oil, regardless of the metal type. Further, for the same ZDDP and sulfated ash level, calcium-based oil produced less soot than magnesium-based oils. ZDDP is a conventional antioxidant additive and hence higher soot was observed with ZDDP due to hindrance of oxidation. TEM analysis showed that primary particles were less spherical with rough surface due to oil derived nano particles in the case of oil injection. Also soot aggregation degree was lower than the case where oil was not injected. The presence of oil combustion products assisted in suppressing soot formation and oxidation of soot aggregates. In general, GPFs resulted in significant reduction of particulate emissions independent of the oil formulation. However, there were noticeable differences in engine-out particulate emissions observed using different oils. With no ash, PN filtration efficiency ranges from 70 to 88%, and mass filtration efficiency ranges from 70 to 88%. With the addition of ash deposition within the GPF, both PN and PM filtration efficiency increases to above 95%. For low sulfated ash oils, it was observed that higher metal/ZDDP ratios resulted in elevated filtration efficiency compared to oils with lower metal/ZDDP ratios. GPF pressure drop was generally lower for low sulfated ash oils. In summary, oil formulation influences particulate composition, morphology, and emission rates. While Calcium based detergent promoted higher soot oxidation rates, the higher sulfated ash level increased GPF ash loading and negatively impacted engine backpressure. Further, the results revealed size dependent filtration efficiency at different ash loading levels. Smaller particles were in the diffusion regime and in constant contact with filter material driven by Brownian motion while large particles were in the regime of inertial impaction and interception, where particles were too large to follow the exhaust stream and therefore collected by the filter. In comparison, mid-sized particles were the most difficult to be collected since the filtration efficiency mechanism was a mixture of diffusion and interception. Additionally, authors observed that even a small amount of ash loading could improve GPF filtration efficiency.

Custer et al. [18] investigated the impact of ash deposition in GPFs using an accelerated aging system to accumulate oil-derived ash in GPF samples. Accelerated GPF aging was conducted using a spark ignited burner system with engine oil introduction into the combustion chamber simulating the extended on-vehicle operation up to full useful life of 150,000 miles. Five identical GPFs were loaded with ash deposits simulating 15,000 to 150,000 miles of operation. The ash loading cycle was designed to simulate an underbody GPF position where the GPF is exposed to a maximum temperature of ~ 650 °C and average ash loading temperature of 400 °C with a periodic regeneration strategy. Soot accumulated during loading phase of the cycle was oxidized by elevating the filter inlet temperature and maintaining high oxygen content in the exhaust to induce an active regeneration. At the end of each loading cycle, the filter was weighed ‘hot’ (~ 170 °C) to determine mass of ash loaded. This hot weight measurement eliminated the variability that can be observed for weights taken of GPFs at lower temperatures where they could absorb water mass from the atmosphere. Higher temperatures are also not recommended due to buoyancy effects that could create lifting currents on the ends of the GPF (resulting in a variable and inaccurate weight measurement). The impact of ash on filter pressure drop and sensitivity to soot accumulation were investigated at specific ash levels. Pressure drop tests were conducted after each ash loading cycle. For the pressure drop test, flow rate through the filter varied from 0-80 scfm in steps of 5-10 scfm at an ambient temperature ranging between 20 to 35 °C. The results suggested that there is a high degree of sensitivity in pressure drop to relatively low levels of ash accumulation in the GPFs. The GPF that was ash loaded to 150,000 miles was also soot loaded to understand the effect of changes in pressure drop across GPF due to soot loading across its service life. It was observed that the first 4 g/L of ash loading resulted in steep pressure drop increase for all filters. This is associated with deep bed filtration regime during which ash particles deposit in the pores of the filter wall reducing the overall porosity. For ash loads greater than 8g/L, linear pressure drop increase was observed. This represented the cake layer filtration regime in which ash builds up on the surface of the filter walls causing an increase in pressure drop proportional to the thickness in the ash deposit layer. The transition from deep bed to cake layer occurred between 4g/L and 8 g/L ash load. Ash deposits and interactions with the filter substrate were studied using X-ray microcomputer tomography (CT), focused ion beam milling (FIB), cross section ion milling (CSIM), scanning electron microscopy (SEM), and energy dispersive x-rays (EDX). From CT scans, it was observed that ash plug length increased with increasing ash load and plug length varied more with ash loadings of 12 g/L and higher. Analysis of SEM images revealed that ash transport mechanisms within the filter included flow induced ash transport and soot oxidation related transport. Shrinking of the soot cake during oxidation results in concentrates of ash particles in islands near filter surface pores. As ash loading increases, these islands coalesce forming a uniform layer. Cross sections of the filter wall indicate specific details about ash-substrate interactions such as ash penetration into the substrate. Ash cake layer grows in thickness and uniformity from 3.3 g/L to 12.2 g/L with the extent of ash penetration into the wall appears to remain constant at a maximum depth of ~ 50 µm. Meanwhile, 12.2 g/L sample exhibited characteristics consistent with the growth of smaller ash islands into uniform cake layer across the filter surface. Ash cake layer over the pore was thicker in the 20.3 g/L (~40 µm) filter than in the 3.3 g/L filter (5-10 µm). For both cases, ash accumulates within the pores but does not completely fill the pores. Large gaps were observed in the pores, and this was particularly important as deep bed filtration pressure drop response is related to the amount and extent of ash penetration into filter pores. In summary, transition from deep bed filtration to cake layer filtration of ash is critical and impacts the pressure drop performance of a GPF for the remainder of its service life. This is due to ash being unable to enter the filter pores after the transition. Ash plug length grows linearly with increased ash loading and ash islands were observed along the surface of the channel walls. Ash was observed to penetrate up to 50 µm into the filter wall but did not completely fill the pores.

Lambert et al. [19] focused on the backpressure and fuel economy of two high mileage GPFs aged on GDI vehicles. Post-mortem analyses of the aged GPFs were also completed in addition to compositional analysis of ash extracted from the GPFs. Two MY2010 production vehicles equipped with 3.5L turbo GDI engines were utilized for aging GPFs with mile accumulation of 130,000 miles and 150,000 miles, respectively. The GPFs were composed of cordierite wall flow substrate coated with 1 g/in$^3$ of TWC containing Pd and Rh. The porosity of the filter was 65% with mean pore size of 22 µm. US EPA Standard Road Cycle (SRC) was used for mile accumulation. Both vehicles utilized 5W-30 grade oil, however, vehicle 1 used GF5 whereas GF4 was used in vehicle 2. Oil changes were performed at 10,000-mile intervals. Vehicle 1 (23,000 miles/quart) consumed oil at a higher rate than vehicle 2 (30,000 miles/quart). The backpressure and fuel economy results showed that no significant decrease in fuel economy was observed as a function of mileage with backpressure increased steadily. For both GPFs, ash was observed at the back of the inlet channels and the distribution was not uniform. Ash thickness was nominally around 6 mm in the central region and extended to 12 mm at one end of the back of the inlet channels. X ray fluorescence (XRF) analysis and microscopic analysis revealed that large concentration of Ca, P and Zn (primarily derived from engine oil) are observed at the back of the inlet channels where ash plugs formed. Higher concentration of Fe was also observed, but authors attributed that to the corrosion of exhaust pipes, manifolds, and other components upstream of the GPFs. Ash density analysis was performed using optical microscopy images from 64 different locations; average ash thickness varied depending on where samples were extracted. The ash plugs at the back of the inlet channels had about 6 mm filled with bulk ash with ash density of 0.7 g/cm$^3$ while ash deposited on the walls had over twice the density (1.6 g/cm$^3$) compared to the ash plugs. Historically, diesel particulate filters (DPFs) studies have shown that wall ash was only 25% denser than end plug ash with density values around 0.17 to 0.30 g/cm$^3$. The higher densities observed in the GPF may be due to higher temperature regimes of gasoline vehicles and lack of soot cake layer that can alter ash porosity.

Hua et al. [20] focused on filtration efficiency, back pressure, and fuel consumption of a GPF at various ash loading levels utilizing a GDI engine platform with accelerated ash loading protocol. A H15T turbocharged 1.5L GDI engine was operated at a steady state condition of 3500 rpm and 110 Nm. Commercially available lube oil was blended in fuel to result in a mass ratio of 0.5%. After ash loading for a specific period. GPF was regenerated to remove soot using secondary air supply at a high temperature. GPF performance was evaluated at 0 g, 30 g, 60 g and 100 g ash loading. At each milestone mentioned above, GPF was installed on the vehicle for chassis dynamometer-based emissions testing. Ash loading level reached about 100 g after 140 hours of aging on the engine bench and ash collection rate (defined as the ratio of actual ash loading to theoretical ash production) was about 30% after 15 hours of aging. No significant impact on fuel consumption was observed across various ash load levels however, an increase in backpressure was observed as a function of ash loading. PN and PM emission measurements were conducted after soot removal from the GPF using the chassis dyno at different ash loading levels. Filtration efficiency showed some improvement with increase in ash loading level and similar PM and PN filtration efficiencies were observed between bare and coated GPFs.

Bharat Emission Standard Stage 6 (BS6) regulations require GDI vehicles to meet PN emissions below 6E11 #/km. Rose et al. [21] examined the performance of GPFs as a function of mileage due to collected ash/soot. A high porosity GPF integrated with TWC referred to as cGPF was evaluated over 160,000 km and emissions were regularly evaluated at different milestone using Modified Indian Driving Cycle (MIDC) and World Harmonized Test Cycle (WLTC). A 1L turbocharged GDI vehicle with rated power (75 kW @ 5500 rpm) and rated torque (150 Nm @ 1700 rpm) was operated under its stock engine calibrations without any modifications to accommodate for GPF control technologies. The vehicle was driven in specific routes in an Indian city with RDE speed bins as boundary conditions. cGPF was installed at a close coupled location for convenient packaging purposes. Tests were conducted on chassis dynamometer at specific intervals with BS6 reference fuel and gaseous emissions and PM/PN were sampled from the engine out (cGPF in) location and from cGPF out location. Gaseous emissions (CO/ THC /$NO_X$ /NMHC) gradually increased as a function of mileage while $CO_2$ was relatively constant. PM reduction was observed as a function of mileage. PN filtration efficiency was greater than 90% beyond 3000 km while a fresh GPF resulted in an efficiency of 81%. cGPF delivered greater than 92% catalyst efficiency for all gases throughout mileage accumulation despite sulfur poisoning (BS6 reference fuel has less than 10 ppm of Sulfur). Total oil consumption was observed to be 6.1 kg, with an average of 40 mg/km. Cumulative ash mass over 160,000 km was around 19 g (volume of cGPF was 1.4L). Soot load typically decreases for close-coupled GPFs due to higher temperatures resulting in passive regeneration of soot. CT scans suggested that ash was accumulated in the rear of the cGPF to form ash plugs. Ash accumulated on the cGPF resulted in an increase in pressure drop across the cGPF. No significant decrease in fuel economy was observed, although, exhaust backpressure increase was observed.

Liu et al. [22] evaluated the filtration efficiency and back pressure performance impact of artificial ash deposited on a bare filter substrate. Alumina aerosol particles were prepared by using a boehmite (AIOOH) suspension (1 wt.%) and used as artificial ash. An aerosol nebulizer was used to aerosolize alumina particles; uncoated blank cordierite filters with cell density of 300 cells per square inch, wall thickness of 300 µm and porosity of 65% were used. Additionally, a 2017 model year 2.3L turbocharged GDI engine was used to age the close coupled GPF with TWC washcoat. Tests were conducted using a blank filter, low artificial ash load and high artificial ash load. GPF filtration efficiency was measured using two Dekati Mass Monitors (DMM) measuring pre-GPF and post-GPF simultaneously. TSI Engine Exhaust Particle Sizer (EEPS) was alternated between upstream and downstream and solid particle number (>23 nm) was measured with an AVL particle counter (APC) from a CVS tunnel. The artificial ash, alumina aerosol particles, were sub-micron particles with spherical morphology ranging from 10 nm to 500 nm in size, with a mean around 80 nm. From the SEM images, larger particles were captured by impaction and were scattered across the surface of the cordierite filter. On the periphery of the pores, fine particles agglomerated with dendritic structures typical of diffusion-controlled particle aggregation. As ash loading increases, these structures grow and bridge with each other to fill the porous areas within the filter. The vehicle-based testing revealed that high temperature and low flowrate through a filter improves particle capture by diffusion. Pre-GPF emissions were comparable for the blank, low ash and high ash load cases, meaning backpressure caused by the GPF had negligible impact on engine performance. GPF helped to reduce tailpipe particle emissions significantly and increased ash loading resulted in lower tailpipe particle emissions. Filtration efficiency during the cold-start phase increased from 71% for the blank filter to 88% for the high ash load filter. In summary, filtration efficiency was significantly improved, and the improvement continued with increasing loading, particularly levels of 0.5 to 1.5 g/L were effective in improving filtration efficiency.

Yang et al. [23] investigated the influence of two different components of lubricating oil on filtration efficiency, ash accumulation rate, vehicle WLTC emissions, fuel consumption and ash plug formation. A 2 L turbocharged GDI engine used for ash accumulation and a PN counter was installed upstream and downstream of the GPF to measure filtration efficiency. National V emission standard fuel was utilized in their study with lubricating oils differing in their detergent composition. The aging cycle profile had three stages – first 1.5 hour to simulate ash accumulation; next 0.5 hours to simulate thermal aging and final 0.5 hour to simulate soot aging. The filtration efficiency increased rapidly from 83% to 96% after 10 hours for the lube oil containing full Ca detergent. The filtration efficiency of GPF exposed to the lube oil with Ca/Mg detergent appeared unstable despite high initial filtration efficiency. The author attributed the instability in filtration due to the Mg content. In general, tailpipe PM decreased as filtration mode transitions from deep bed filtration to cake filtration. The different detergent formulations do not appear to significantly impact fuel consumption after 200,000 km worth of ash accumulation. Average ash height in the GPF exposed to the lube oil with full Ca detergent is less than that of the GPF exposed to the lube oil with mixed Ca/Mg detergent, as indicated by the postmortem CT scans.

In another study, Caillaud et al. [24] employed lube oil at two levels - 1.2% and 0.85% of SAPS (Sulfated Ash, Phosphorous and Sulfur). Both oils have Zn and P at approximately similar concentration while Ca, Mg and Mo were varied. The compounds of interest were tracked with radioactive tracers – Zn-65 for Zn, Sr-85 for Ca and Mg and Mo-99 for Mo. Oil consumption, weight and radioactive detection were used to determine contribution of elements to ash and their distribution. The test results showed that the ash loading contribution of detergents (Ca+Ma) is much larger than that from the friction modifier (Mo) and even more than anti-wear (Zn). With oil consumption of 4.5 kg, ash loading had low impact on backpressure and little effect on performance of GPF. It is also suggested that lube oil was not the only source of ash. Engine wear and fuel impurities also contributed to the ash load.

Bernardoff et al. [25] aimed to measure the accumulation of ash residues during an engine endurance test with a focus on Zn and Ca, along with the impact of lubricant formulation on GPF clogging. Testing was performed on a commercially available ceramic GPF which was installed on the exhaust line of a Euro 5 GDI engine. Ash accumulation in the GPF and in the catalyst was measured using both the weight measurement method and the radiotracer method which detected gamma rays emitted by radiotracers. Radioactivity measurement was used to derive the mass of specific lubricant derived deposits (Ca and Zn). Two different radiotracers were used: Zn-65 to label the Zn based anti-wear additive (ZDDP) and Sr-85 to label the Ca based detergent. The soot loading rate during the test (4000 rpm, 75% and 100% load) was ~1.5-2 g/hr which increased back pressure at a rate of 30 mbar/hr. Supplemental air injection was utilized upstream of the GPF to add oxygen for regeneration. Soot removal via supplemental air injection occurred once every hour of engine operation. Results revealed that only 48% of expected ash was deposited on the GPF. One possible reason for the difference between expected and accumulated ash is that only a certain fraction of the total lubricant formulation passes into the exhaust stream. This fraction contained reduced levels of Ca, Zn etc. relative to the sump lubricant. Ash may be carried back to the sump by blow-by gases or by being re-absorbed via the oil film present on the cylinder walls. Some ash might have passed through the GPF due to lower filtration efficiencies required in GPF applications. Ash formed in the GPF may not be in the same chemical state as measured in the ASTM D874 test (where full sulfation or oxidation is assumed). Some deposits, such as Zn, can begin to accumulate in the exhaust line for reaching the GPF. At the end of the test, about 50% increase in concentration of Zn and Ca observed in the sump oil while P concentration increased by 30%. About 15 to 20 g of ash likely concentrated in sump instead of exiting via exhaust. Ash formed during combustion could be transported by the expanding gases to the oil film on the cylinder wall and scraped back into the sump by the piston rings during the intake stroke. Also, some ash formed during combustion was taken back to the sump by blow-by gases. Fuel typically contains low concentrations of ash forming elements but is consumed at several orders of magnitude higher rates than lubricants. Apart from Ca, no other elements were found in significant quantities in the fuel. Fuel derived ash contribution could range from 3.6% (based on elemental Ca) to 12.3% (based on sulphated ash mass) of total weighed GPF ash. Presence of significant amount of $Fe_2O_3$ and $Cr_2O_3$ confirms engine wear contribute to ash formation. Lubricant derived species (CaO, $P_2O_5$, $SO_3$, $MoO_3$, $SiO_2$ and ZnO) when summed account for approximately 50% of collected ash, which was consistent with radio-tracer results. In general, Zn tended to accumulate towards the outlet and Ca accumulated more uniformly but slightly more at both inlet and outlet of the GPF. Ash deposition had a negligible effect on fuel consumption and Ca was mainly captured by the GPF whereas Zn accumulated preferentially in the TWC, albeit in very low quantities.

In conclusion, GPFs helped reduce tailpipe PM/PN emissions significantly. As a vehicle equipped with a GPF accumulated mileage, the GPF accumulates ash largely derived from engine lube oil. Ash accumulation on the GPF results in an improvement in filtration efficiency and no significant impact on fuel economy. Ash accumulation can occur on the channel walls and towards the end plug region. Ash composition analysis suggests that ash particles are composed of Ca, P, Zn, S and Fe of which Fe is likely from the exhaust pipes and/or engine parts. Ash accumulation rate is directly proportional to SAPS level and accumulation of detergent and antiwear elements tracked linearly to oil formulation concentrations and oil consumption rates. Only a few quality studies directly comparing the influence of different lube additive formulations on ash accumulation rate, distribution in GPF, and impact on GPF performance were found in current existing literature.

### 5.3 Comparison of Various Test Methods for Lube Additive Effect on GPF

Shao et al. [26] developed an accelerated aging protocol using an engine platform for a catalyzed GPF through simulated thermal aging in addition to ash and soot loading to simulate full useful life. Two lubricant formulations were utilized during aging to determine the impact of formulation on GPF as the component ages. Evaluations included tailpipe emissions, backpressure, catalyst performance and post-mortem analysis. cGPF durability was evaluated by ash loading to amounts equivalent to various points between 0 and 200,000 km (FUL) followed by emissions performance test. Post-mortem analysis of cGPF after durability tests included thermogravimetric analysis (TGA) and computerized tomography (CT) scan. Test fuel was China Phase V fuel but with higher aromatics to assist with soot accumulation. Lubricant formulations utilized fully formulated 5W-30 with reduced SAPS formulations using Group III base stocks – full Ca detergent and Ca/Mg detergent. Oil in the engine crankcase was changed every 10 hours during accelerated aging. Accelerated aging protocol development consisted of three primary elements – Thermal aging, Chemical aging derived from ash loading (lube oil and engine wear derived) and Soot generation and regeneration. Standard Road Cycle (SRC) was used to collect temperature profiles of TWC and cGPF on vehicle. Arrhenius equation is used to derive equivalent thermal load and effective aging is calculated via high temperature cycles to accelerate exposure to thermal load. Each aging protocol was repeated 4 times over 10 hours of aging. cGPF was regenerated and weighed after each 10-hour period of aging until desired ash loading was achieved. Emissions testing occurred at each target ash loading point. Significant amount of ash was collected in deposits in the combustion chamber compared to the normal combustion using un-doped fuel. Percent of ash was 73.1%, 74.2%, and 83.0% in intake valve, cylinder top, and exhaust valve, respectively. Collection rate of ash in cGPF was only around 30% which was consistent with previous work utilizing oil-doped fuel for accelerated ash loading and aging. Filtration efficiency improved significantly during the first 2.5 hours of aging and rapid increase in efficiency followed by tapering is consistent with transition from bed filtration to cake filtration. Backpressure increased with aging time as ash load increased. The magnitude of backpressure increase observed during this study is unlikely to impact cGPF performance within the range of durability requirement. Accelerated aging and ash loading method employed in this study can be used to show the durability of cGPF out to FUL. Both oils tested in this study retain their durability and ability to meet emissions requirements at FUL. CT scans indicated no noticeable plugging after aging protocol at FUL.

Lambert et al. [27] analyzed the performance of a GPF through various stages and techniques of aging that included low mileage (3k miles), high mileage (150k miles), rapid aging (50 and 60 hours) and burner-based aging (low mileage equivalent). Post aging analysis included CT scan of ash distribution, filtration efficiency, backpressure, material characterization, permeability, porosity, pore size distribution, elemental composition (XRF), material morphology by SEM and EPMA. Results suggested that small ash loads of 1-2 g/L improves filtration efficiency with small increase in backpressure. After 3k miles of operation, ash forms a web-like structure on inlet walls. Most of ash particles only went up to 60 µm, even at 3k miles, which improves filtration efficiency. Small (2 µm) hydrated ash $CaSO_4 \cdot 2H_2O$ crystallites were found in 3k mile GPF, which are similar to the large (100 µm) ones found in FUL filter. Ash distribution depended on washcoat loading & distribution, temperature history & dopant. Authors stated that more work is needed to develop accelerated ash accumulation methods accompanied with accelerated thermal aging. The ash collected from accelerated methods in this study was only comparable to low-mileage (3000 km) real world aging.

Eakle et al. [28] developed an accelerated method for ash accumulation on the GPF and TWC-F under simulated real operating conditions through the following techniques as a) Ash loading using the oil doping method on a GDI engine, b) Ash loading using a flipped piston ring method on a GDI engine, c) Ash loading using a burner system – Exhaust Composition Transient

Operation laboratory (ECTO-Lab). This approach included setup of a GDI engine for accelerated ash accumulation, baseline characterization, cycle development, degreening, followed by engine test stand ash loading via oil doping method or flipped piston ring method and/ or burner-based ash loading method. Constant volume oil sump apparatus was utilized to maintain a constant oil level in the engine along with fin-tube heat exchanger to maintain target GPF inlet temperatures during ash loading. Engine was coupled to an eddy current dynamometer and was calibrated to operate in the absence of a vehicle. All cGPF Samples were degreened prior to any testing to facilitate stabilized catalyst performance and a degreened, non-ash accumulated cGPF was referenced as a gold standard to compare CT scan and pressure drop characterization. Unmodified engine was used for accelerated ash accumulation with a mass flow controller to dope the engine fuel supply with lubricating oil. The mass flow controller is fed by a pressurized vessel that contains the same lubricating oil used in the engine. With oil doping technique, natural ash loading rate of the engine with a standard ring orientation was found to be between 0.02 and 0.05 g/hr. A liquid flow controller was employed to add lube oil to the fuel supply at 11 g/hr and consequently the measured ash loading rate increased approximately to 0.079 g/hr. With flipped piston ring method, engine piston rings were inverted, and the inverted ring scraped oil on the cylinder wall up into the combustion chamber.  This accelerated ash loading approach did not use additional doping of lube oil into the fuel. After the lower compression ring was inverted, the new average ash loading rate was about 0.160 g/hr representing a 425% increase in ash loading rate over the non-inverted lower compression ring configuration. This is equivalent to approximately 28.9 g/hr of engine oil consumption rate on an unmodified engine. In burner-based approach, ECTO-Lab burner was used for the accelerated ash accumulation of cGPF where oil was introduced into the burner fuel supply and the engine bench ash loading cycle (exhaust flow rate and gas temperature) was replicated on the burner. The test sequence for all these three approaches included ash loading a GPF to 3, 6, 12, 20 and 30 g/L, then perform CT scan at each loading interval followed by backpressure measurements. The pressure drop characterization result suggested that ash alone had a minimal impact on pressure drop. The inverted ring method resulted in a 37% increase in pressure drop at 3g/L for 450 $m^3$/hr flow condition compared to only a 11% increase under the same condition for the oil doping method, and it was minimal for the burner-based method. The difference in pressure drop performance could stem from the amount of deep pore penetration of ash in the channel walls that occurs for the inverted rings method. In general, although the burner-based method was the most rapid approach, it produced the lowest density ash plugs with a parabolic deposition profile. The oil doping method provided a controllable oil consumption rate over the period of ash loading. When comparing each of the accelerated ash loading methods to a field returned TWC-F, ash did not appear to be as dense as the ash accumulated in the field returned TWC-F. The inverted rings method yielded a deposition profile that was both uniform across the inlet channel end plugs and highly dense. This method appeared to be superior in replicating ash deposition mechanisms observed in the field returned GPF.

In general, with vehicle-based ash loading, drive cycles can replicate real-world conditions experienced by aftertreatment systems in the field however they are not an accelerated method for ash loading.  Vehicle-based ash loading requires extensive operating costs, availability of dynamometer, and a dedicated vehicle. Further vehicle operation will vary depending on age, engine, etc., which makes test reproducibility more challenging. In fuel doping-based engine ash loading technique, relatively uniform deposition of ash can be achieved and is capable of achieving accelerated rates of ash deposition in conjunction with normal consumption of oil during engine operation. However, variable costs associated with set-up, engine stand modification, maintenance schedule, etc. pose logistical challenges. Further, less dense ash deposition compared to field aged parts, engine mapping to determine aging conditions and appropriate oil consumption rate and variable oil consumption over time as the ring pack of the piston wears over time are some of the challenges of adopting this technique. With inverted piston ring ash loading technique, ash density and uniform deposition are relatively consistent with field aged parts and accelerated ash loading up to 4 times can be achieved without supplemental oil doping compared to a conventional noninverted compression ring configuration. However, relatively higher setup and maintenance costs and potential impact on ash properties due to increase engine oil consumption would pose challenges in adopting this technique. With burner-based ash loading technique, highly controllable rate of ash deposition via fuel doping and new MFC-controlled introduction of oil into the burner can be achieved. No need of engine mapping and highly reproducible operating conditions and control of exhaust results in predictable process at a desired accelerated rate make burner-based approach as a competent candidate for accelerated ash loading. However, solely utilizing fuel-doped burner-based ash loading results in non-uniform ash profile that is less dense than field-derived ash. Also, this approach cannot replicate ash deposition typically derived from metal wear in engine. Further, MFC-controlled oil introduction into the burner is required to match field-derived ash deposition density and uniformity. With the alumina-based ash loading (artificial ash) technique, the dendritic structure of alumina-based ash resembles field-derived ash and highly controllable rate of ash deposition can be achieved. However, the ash composition does not match lube oil derived ash and the scope could be limited to evaluating impact of back pressure increase on GPF performance.

## 5.4 Combination of the Effects of Engine Operating Mode and Lube Additive Effect on Catalyst Efficiency

Chen et al. [29] conducted a detailed review of the available literature of lubricants for electric vehicles (EV) and hybrid electric vehicles (HEV). They also addressed the differences in requirements for lube oils for conventional ICE and EV / HEV vehicles along with desired properties and failure modes with lube oils for EV/HEV. Many versions of HEV exist whose designs can be classified by power flows, power levels, and operation. HEV can frequently shut of ICE when it can run off electric motors which results in cooling of the ICE. Battery costs about 45% of total cost and its energy density to hydrocarbon fuel is 1:80. Current logistic challenges include driving range, charging rate, cost, and accessibility while technical challenges include charging technology, supercapacitors, thermoelectric generators, regenerative braking, and photovoltaic cells. The failure rate of bearing is about 40% of failures in motors due to complex voltages in shafts & bearing currents and the lubricant design is difficult due to the range of current for bearings. Major concern for lubricating oil for EV/HEV includes copper corrosion and compatibility with polymers in the electronic components. Possible solutions have been nanotechnology based anti-wear and friction lube oil, vapor phase lubrication, ionic liquids, and low viscosity base oils. Initial research suggested increase in engine efficiency in EV mode with low viscosity oil. Nanotechnology, synthetic base oils and thickeners as grease result in better lubricity, higher service life & low friction torque. Other promising formulations include aluminum, urea, and bio-based lubricants though they have some concerns with their production. Further, the dispersants in the transmission fluids in HEV requires insulating properties to avoid short circuiting motor parts.

Lubricating oils provide lubrication, protection from wear for metal-to-metal contact, cooling, anti-corrosives, etc. Transmission fluid functions in a similar way to create hydraulic pressure, dissipate heat and protect metal components from wear and grease reduces frictional losses between moving components. HEV has both electrical motor with an ICE, though the size of the engine is smaller than those applications equipped with ICE alone for similar power demands. The size of engine is inversely proportional to the size of the electric battery. Dual Clutch Transmission (DCT) has the highest mechanical efficiency and most HEV applications use them. In this setup, the motor is directly integrated with DCT box and is cooled by transmission lubricant. Hence, it is required that the lubricant has high thermal conductivity, dielectric constant, and dielectric strength. If future HEV designs include electric motor in the unit housing, there would be higher contact of copper and lubricant, raising risk of higher copper corrosion. The high heat generated by motor windings will challenge the ability of the lubricant to transfer heat and its thermal stability. It is likely that DCT will be used for EV/HEV as it has higher efficiency & lower weight. Since DCT does not have torque converter loss, it does not require high pressure oil supplies. The design and controls of HEV had an impact on the crankcase lubricants with lower temperatures for HEV compared to combustion engine. An electronically powered continuous variable transmission (E-CVT) has advantages such as higher reliability from mechanical simplicity, higher efficiency from absence of torque converters, shift gears and clutch which also reduces size.

There are several desired properties for EV based lubricants. Firstly, Base Oil (BO) is the main component to which other compounds and additives are added. BOs are classified into five groups based on manufacturing methods, sulfur content, saturate level, and viscosity index. Groups I – III are from crude oil, Group IV is completely synthetic (polyalphaolefin, PAO). All the BOs which do not fall in the first four groups are classified in Group V. Generally, the thermal stability of BO groups improves with increasing group number. Group V BOs are used for creating lubricating additives. Since saturated molecules remain stable for longer durations, the higher the amount of saturates in BO, the higher the molecular bond strength and the better the resistance to viscosity loss. Crude oil BO contain lower saturated molecules and the synthetic BO contain higher. Hence synthetic BO are more durable. The higher the viscosity index, the more viscosity is with temperature change. It is higher for Group IV & V than the crude oil lubricants (Group I-III). BOs with higher thermal conductivity, specific heat capacity and density are better for cooling. Longer chain molecules in BO provides better cooling. Additives are used for three reasons – improve desired properties, suppress undesirable properties, and add new properties. EV/HEV vehicles operate at higher speeds and greater torque thus require lubricants that can handle those conditions. Hence, lower viscosity and longer drain intervals are required for these lubricants.

Overall, the lubricating oil is desired with thermal and electrical properties compatible with electrical components, elastomers / polymers, and resistance to copper corrosion. Friction and wear protection for seals and bearings at greater than 25k rpm will be required. Since the lubricating oil will be in contact with motors and batteries, it must be compatible with the explosive electrolytes. Lubricants would also have to transfer high heat generated by the batteries. Lubricants in EV/HEV will be subjected to flow of current through the lubricating bearings. Lubricants with poor electric properties will cause Electrical Discharge (ED) damage. The lube oil requires proper electric resistance and dielectric strength through its useful life period. Ionic liquid as a neat lubricant would provide low conductivity, low coefficient of friction and high wear resistance, but can cause tribo-corrosive effect when bearing current is high. Electrical conductivity can be modified by adding additives to BOs. Compounds with polar molecules like phospholipid and calcium salicylates can reduce conductivity. Ionic liquid as an additive is expensive but it could increase wear resistance and lower conductivity. The effectiveness of additives is still not well known, and, in some cases, they could cause more wear on the bearings. Common failure mechanisms are degradation, microbubble formation and electrowetting. BOs and thickeners undergo chemical oxidation to form carboxyl compounds and formation of highly viscous and acidic products and agglomeration of additives reduces lubricity. Local overheating under charged conditions causes microbubble formation around the lubricated contact. When these microbubbles move outward from the contact, they can coalesce, and these microbubbles can cause electrical breakdown and destabilize oil.

Similarly thermal properties play a key role in the design and optimization of EV based lubricants. Heat capacity of the BO is determined by its quantum states with higher number of rotational and vibrational quantum states giving higher heat capacity, as it takes higher energy to raise its temperature. Additives can be used to optimize the thermal properties though it is unproven that it would work as well with EV/HEV. Lubricating oils for EV/HEV are required to operate under higher acceleration rates with their electric motor and must endure higher shear stress. The critical function of lubricating oil is high load bearing in ICE and torque transferring in EV. Operating conditions for bearing lube oils include high speeds, high temperatures and highly fluctuating electric & magnetic fields. Some of the traditional wear additives like ZDDP and MoDTC are unsuitable for EV/HEV due to high electric resistance. Another failure mode would be lubricant film collapse under high electric charge, which would cause lubricant starvation. Hence the lubricant design considerations need to account for low viscosity oil that lowers film thickness which causes a higher operating temperature leading to lower useful life of the bearings.

Further EV/HEV lubricants should satisfy the requirements such as robustness to endure high-temperature fluctuations and high shear strength, long life, resistance to water, load-bearing capacity, resistance to corrosion and low temperature performance and further the EV lube oils cannot influence or alter electrical or mechanical properties of the engine and the motor. Some of the EV lubricating system design considerations include design for torque transfer instead of load bearing. Lube oils will need to be designed for noise, vibration, and harshness control. Lube system components and lubricants would need 10x longer life than the current systems to withstand bearing fatigue. Transmission fluids will require high heat transfer to cool the high-speed motor.

New coatings will be required to offset surface adhesion and effect of thin films forming by low viscosity lube oils. New oil monitoring systems required to monitor several parameters for oil degradation due to extended oil drain periods and new cooling systems would need to be designed for the future requirements of the EV/HEV.

Fan et al. [30] investigated the influence of oil viscosity on transient emissions in hybrid vehicles and conventional engine operation using two drive cycles. Emissions tests were conducted on a chassis dynamometer with a Horiba MEXA 7200 emissions analyzer and DMS500 PN detector. PHEV 1.5L turbo-charged direct injection engine used for both hybrid mode and conventional mode. In hybrid mode, engine starts when state of charge (SOC) is lower than 20% and vehicle speed is over 20 km/hr. In conventional mode, engine operates continuously after cold start in idle condition. Direct and bag collection methods were utilized for gaseous emissions analysis and a sample line for PN was installed before the TWC to remove impact of catalytic oxidation of particles. Fuel consumption was calculated based on a carbon balance calculation. Commercial gasoline and two lubricants – SAE 5W-30 and 0W-20 were employed in this study. WLTC and continuous ECE 15 (European Driving cycle) were utilized. Oil temperature in ECE 15 for hybrid mode was maintained above 85 °C to simulate low-temperature engine operation in the real driving for PHEV. The results suggested that PHEV driven in urban driving cycles during charge storing state will produce higher $NO_X$ when utilizing higher viscosity oils (5W-30) compared to low viscosity oils (0W-20). Frequent engine start/stop cycles and high viscosity oils will increase PN emissions compared to conventional engine modes (continuous engine operation) and compared to PHEV mode with low viscosity oils. Increasing oil temperature will cause particle size to increase in diameter and more particles to be produced. 5W-30 oil showed strong dependence of PN on oil temperature, oil dilution rate, and fuel amount in incomplete combustion. 0W-20 oil had a higher tolerance for gasoline dilution and maintained PN in a narrow range. 0W-20 oil use in PHEV can meet China 6a emissions requirements while higher viscosity oil (5W-30) exceeded the limits.

The emissions of regulated and unregulated pollutants such as THC, $NO_X$, CO, PN, $NH_3$ and $N_2O$ from two PHEV architectures were investigated at ambient temperatures of 23 °C and -7 °C [31]. Euro 6 PHEV with parallel configuration that utilizes both ICE and electric motor was employed in the study. The first candidate was a PHEV equipped with 1.4L 110 kW gasoline engine and Li-ion battery with a 25Ah capacity and a nominal voltage of 345V. The second candidate was a US range extending auxiliary power unit (APU) denoted as BEVx. This is a series configuration that utilized the APU as a generator to supply electricity to the electric motor which is the primary energy source for propelling the vehicle. It was equipped with Li-ion battery with a 60Ah capacity and a nominal voltage of 360V and a 0.65 L 25 kW gasoline engine. 23 °C is the reference temperature used during the Type 1 test of the emission type-approval of LDVs in Europe and -7°C is the temperature used during cold start procedures in different regions of the world. Low temperature testing was conducted both with (Aux-ON) and without the use of the air heater system. Emissions bag samples were analyzed using a Horiba MEXA-7400HTR-LE. A solid particle number measurement system (AVL APC 489), with particle diameter cut-off of 23 nm, was used to measure solid PN and unregulated pollutants ($NH_3$ and $N_2O$) were analyzed using an MKS 2030-HS FTIR. WLTC tests were utilized for the vehicle test cycle. Significant increase in emissions was observed during cold weather operation, particularly when the heater is utilized. Authors defined a parameter called Emission Factor which was calculated as the ratio of integrated mass flow (mg) to the total driving distance in km to compare various exhaust emission species concentration. The weighted emission factors of $NO_X$ at -7 °C are 103 (without heater) and 139 (with heater). Similarly, the weighted emission factor of THC -7 °C are 55 (without heater) and 89 (with heater). PN emissions from PHEV at ambient temperature were comparable to gasoline vehicles and well were above a DPF-equipped diesel vehicle. Cold weather has a negative impact on PN emissions, particularly when the heater is turned on. In summary, cold weather was demonstrated to have a measurably negative impact on gaseous and particulate emissions from PHEV and the cold weather impacted the range of batteries in both PHEV and BEV.

Zhang et al. [32] investigated GPF application for a traditional vehicle equipped with an IC engine and a plug-in hybrid vehicle. Both vehicles use a 2L turbocharged GDI engine that can meet China 6 PN limit and China 6b gaseous emission limits. PHEV weighs 500 kg more than ICE and the distance between turbo-out and GPF inlet was longer for PHEV due to the battery pack. Both vehicles used Corning's DuraTrap GC HP gasoline particulate filters. WLTC tests were conducted on a chassis dynamometer and measurements were conducted from a full flow CVS tunnel. For ICE vehicle, WLTC test was conducted with 1 WLTC cycle following a vehicle pre-conditioning. For the PHEV, multiple WLTC cycles were conducted to evaluate emissions from charge-depleting (CD) mode to charge-sustaining (CS) mode. Vehicle was in CD mode from the first cycle to the third cycle and engine started during the third cycle. Beyond the fourth WLTC, the PHEV was in CS mode. Results for vehicles with fresh TWC and GPF revealed that PHEV exhibited worse emissions on CS mode than ICE while weighted results for PHEV were relatively better. The PM seems to be much higher than expected, compared to Solid Particle Number (SPN). This suggested that most of the PM emissions was volatile/semi volatile in nature. The soot burning rate in a GPF is a function of soot load, filter bed temperature and oxygen presence. Simulated soot oxidation rates for the ICE and PHEV vehicles showed that soot burning rate was faster for the ICE as the distance between turbo-out and GPF inlet is shorter (leading to increased bed temperature).

## 5.5 Effect of Soot Characteristics on Ash Deposition in Catalyst and GPF

Soot formation in the combustion chamber is a complex process that involves fuel pyrolysis, precursor formation, nucleation, coalescence and surface growth, agglomeration of primary particles and oxidation of soot agglomerates. Stringent Euro 6 PN regulations led to the widespread deployment of GPFs for spark-ignited engines in the EU, and other major countries like China and India are following their suit. CARB 1 mg/mile PM regulation may also result in OEMs adopting GPFs in the US. Wang et al. [33] conducted an extensive literature review of key issues related to GPFs emphasizing on ash origin, accumulation, transport, evolution, as well as reviewing artificial acceleration methods for ash loading. The ash is primarily formed through the introduction of lubricant oil into the combustion cylinders in the form of an aerosol due to pressure build up in the piston ring areas. Oil droplets partially or fully oxidize during combustion and during that process metallic additives in the lube oil may be converted into gas phase constituents. During the exhaust stroke, as gases cool, gas phase metallic constituents condense on available carbon particles. When ratio of ash to carbon is high, lube additives may form standalone solid ash particles due to a lack of condensation surface. Studies have observed standalone ash particles in the sub 20 nm size range which may be derived from this mechanism. As exhaust exits the combustion chamber, heavy hydrocarbons condense on carbon particles or form Soluble Organic Fraction (SOF) particles when there is insufficient condensing surface. The presence of ash in soot particles have been observed and reported in several studies and ash related signals have also been observed in the elemental analysis of soot particles. Two possible theories have been discussed regarding the transport mechanism of ash via soot. The first one is ash embedded in soot particles during the formation process. The second mechanism is that ash solid nanoparticles are formed independently, and then attach to soot particles via collision/agglomeration. Metal nanoparticles from engine wear and corrosion have been found to be attached to soot particles. Ash is emitted from combustion engines either as nanoparticles or precursors. As a function of ash to soot ratio, there may be standalone ash particles, or ash on soot particles (condensed).

Large fraction of ash emissions come from lubricant oil derived species. Ca, Zn, P and Mg are metallic additives used to enhance oil performance. Sulfates and phosphates of Zn, Mg and Ca are the main components of ash deposits. Further engine abrasion and corrosion related ash formation can also occur. Ash levels are impacted by fuel type, oil formulation, engine abrasion and other factors and the resultant ash composition changes dependent on the case. Ash finding ratio is the actual accumulated ash in the GPF divided by the expected ash amount estimated by oil consumption. Ash finding ratio was observed to be higher at idle and light load conditions. Engine operation affects the contributions of oil consumption mechanisms and thereby impacts ash finding ratio. The ash transport within the filter channels could happen with the transportation of ash precursors along with detached soot aggregates. Soot transport is driven by reduced adhesion force between the soot layer and substrate wall due to oxidation of soot near the wall during passive/active regeneration. Soot cake layer may break up, transport, and form mid-channel soot plugs. Ash particles could also be detached from substrate wall when exposed to flow (flow induced transport). This may happen when there is no soot cake layer coverage, typically post regeneration. Ash is distributed within a filter via flow-induced and soot oxidation-induced transport. Ash accumulates in three general areas within a filter, including the substrate pore network (usually in the inlet channel surface pores), along channel walls and in the plug. Ash accumulation is a function of ash characteristics such as particle morphology, chemistry, density, and ash-substrate interactions.  Ash accumulation may also result in displacing soot and can alter soot density and porosity. There are four different ways of ash spatial distribution observed as ash completely fills the pores, partially fills the pores, bridges the pores or sinters where ash solidifies in the pores completely blocking flow. On a channel scale, ash spatial distribution is affected by redistribution of flow and soot oxidation. Small ash islands are left behind after the shrinking of soot layer post regeneration. These ash islands may be sheared off the channel wall and be transported to the plug. Ash adhesion is known to be stronger with soot particles than with wall substrate. These information about channel level ash helps to improve filter design and optimization based on filter pressure drop, cleaning, and regeneration strategy. Axial and radial ash variations depend on the packing density and composition of ash particles. Key challenges and issues in the management of ash include abnormal ash distribution, unknown ash density, ash/substrate sintering due to prolonged exposure to high temperatures which may result in decreased or hindered catalyst activity. More research on this aspect is required to develop knowledge data base on ash management. Some of the ash management strategies include reducing ash accumulation through low ash oil, improved piston ring design, and more durable and robust washcoat on TWC upstream of GPF. Management of abnormal ash distribution could be conducted by triggering regenerations during high flow conditions to ensure adequate transport and the high-rate pulse flow to push fractured soot aggregates to the rear end of the inlet channel. Management of ash plug density can be accomplished by triggering thermal treatment to target controlled sintering. Moreover, better understanding of the interactions of particle size with flow rate, heating temperature, and duration and frequency of active regeneration events are important factors in ash management.

Choi and Seong [34] investigated the effects of lube oil derived ash on soot oxidation reactivity in GDI engines. A 2.4 L 4-cylinder GDI spark-ignition engine was mounted on a 112-kW blower-cooled AC dynamometer and a partial flow exhaust system was built to test prototype bench-scale GPFs at wide range of flowrates (steady-state condition). Gasoline fuel was burned in the GDI engine with lube oil formulations by fuel doping. Soot samples containing ash collected during engine operation were analyzed in terms of soot oxidation reactivity, and ash chemical constituents were examined to understand their impact on soot oxidation mechanisms. For accelerated ash loading, lube oil was injected into the fuel supply line at a rate of 2 wt% of lube oil in gasoline fuel. Compositions and oxidation reactivity of GDI soot were evaluated using TGA. Ash compounds were identified using Powder X-ray Diffraction (PXRD). Soot and ash morphology analysis were performed using SEM and X-ray Photoelectron Spectroscopy (XPS) was used to analyze surface elements in soot. Engine tests were conducted with un-doped gasoline fuel at 3 engine speed/load conditions. Soot oxidation was always promoted for low soot cases compared to high soot cases. Soot oxidation reactivity was in good agreement with ash fraction in soot. Low engine-out soot mass emissions from GDI engines contribute to enhanced soot oxidation due to high ash fraction in soot. TGA experiments were conducted for additive-specific soot samples to better understand effect of each metal additive on soot oxidation reactivity. Conventional oil showed enhanced soot oxidation with increased ash fraction compared to a non-detergent oil derived. Ca-derived soot samples offered oxidation trends comparable to the conventional oil derived soot samples. Promoting effects of Ca additive appeared to be greater than metal additives from conventional lube oil. Ca dominant ash plays a catalytic role in soot oxidation wherein oxidation temperatures appreciably decrease when ash content is high. PXRD results revealed no evidence of $CaSO_4$ derived ash coming from conventional engine oil. XPS analysis revealed that no sulfur was observed in the scans, except for the non-detergent oil-derived soot. Zn was observed in the Ca-derived soot, however, P was relatively high. Zn content in ZDDP derived soot were low while P contents were high implying that surface exposed Zn was low compared with bulk Zn. Filtration efficiency of GPF was improved with ash loading of 2 g/L – ash loaded GPF reached 98% without any soot load. While ash loading is a burden, slight ash loading seems to be beneficial towards filtration efficiency. Ash was found to be effective in soot oxidation during GPF regeneration when it is in contact with soot cake layer.

Catalytic effects of ash and oxidation characteristics of engine soot from GDI engine were investigated [35]. A 2.4 L 4-cylinder GDI spark-ignition engine was used. Engine operated at homogenous and stoichiometric charge conditions with fuel injection occurred during intake stroke at 300 crank angle before top dead center. Engine was mounted on a 112-kW blower-cooled AC dynamometer and equipped with two pieces of TWCs. Gaseous emissions (Horiba MEXA 7100) and soot mass concentration (AVL MSS 483) were measured. PM samples were collected on Teflon membrane filters. TGAS, TGM and Raman spectroscopy were performed on test samples. TGA results of fractions of volatile organics, soot, and ash in the PM samples indicated that PM yielded a wide range of VOF (2 to 16%) and ash fractions (0.1 to 17%). An inverse relationship between ash fraction and the soot mass concentration was observed. Ash is mostly derived from lube oil; ash fraction is determined by the relative ratio of combustion generated soot and lube oil consumption in the combustion chamber. Ca, Zn and P were major components in the engine-out ash (~ 80%). Ash in engine-out PM is derived from lube oil additives such as ZDDP and calcium sulfonate. TWC-out ash included Mg, Al and Si which may be derived from support materials from the TWC. Oxidation reactivities of Printex U and six different GDI soot samples were compared by TGA experiments. Oxidation reactivity can vary greatly depending on how the engine operates. Ash fraction is the most dominant factor in enhancing soot oxidation; at 600°C isothermal, sample mass decreased faster as the ash fraction increased. The combustion derived ash precursors provide strong catalytic effect on soot oxidation. Unburned ash plays little catalytic role because of its composition which is mostly unburned oil additives such as ZDDP and calcium sulfonate. Oxidation-derived ash provides weaker catalytic effects than combustion-derived ash precursors as micron sized particles are not in good contact with soot particles. Ratio of combustion-derived ash to unburned ash in soot depends on engine operating conditions. During normal engine operation following warm-up, combustion-derived ash is typically dominant. Unburned ash precursor increases at cold-idle and fuel-cut operation where low in-cylinder pressure increases lube oil transport. In general, GDI soot was found to have relatively constant intrinsic carbon oxidation reactivity that does not change with engine operation (different from diesel soot). Ash in GDI soot can be categorized into 3 different types: combustion-derived ash, unburned ash, and oxidation-derived ash. While at hot steady-state engine conditions, the GDI soot oxidation reactivity was improved proportionally with ash fraction. Ash effects were diminished at cold-idle and fuel-cut operations when in-cylinder temperature and pressure were low. Typical kinematic expressions did not hold for GDI soot oxidation rate due to the catalytic effects of ash and the presence of SOF. Catalytic effect of ash is expected to dominate oxidation reactivity of soot – especially in advanced combustion engines where soot mass emission is low. In a GPF, low-reactive soot is initially captured during cold-engine operation, followed by high-reactive soot after warm up; however, overall oxidation reactivity will depend on the duration of the driving cycle.

Abreu Goes et al. [36] investigated soot accumulation effects on the TWC reactions on catalyzed GPFs. $Ce_{0.35}Zr_{0.65}O_2$ was prepared using a sol-gel technique where the gel was added to an $Al_2O_3$ support at a 20 wt% loading and a Pd (0.92 wt%) and Pd/Rh (80/20 ratio at 1.15 wt%) sample was prepared via incipient wetness impregnation of the CeZr/$Al_2O_3$ support. The final Pd/CeZr/$Al_2O_3$ and Pd/Rh/CeZr/$Al_2O_3$ catalyst powders were washcoated onto a commercial GPF substrate. The washcoated cGPF samples were aged using an accelerated method in a dedicated aging reactor for 20 hours at varying temperatures (650, 800, and 950°C) in 5% $H_2O$, 10% $O_2$ and balance Ar with a total flow rate of 3 L/min. cGPF channels were modified by alternatively plugging channels at each end with a slurry composed of 95 wt% θ-$Al_2O_3$ and 5 wt% boehmite Dispersal P2 (Sasol) followed by drying and calcination at 550°C. Modified cGPFs were installed in the underfloor position of a Volvo gasoline vehicle. Accelerated soot loading was conducted by running aggressive RDE cycles for 10 hours in a vehicle chassis dynamometer (RTS95 cycle). Surface area measurements (BET) were collected using a TriStar 3000 instrument to determine the thermal stability of the support after aging. Catalytic activity was evaluated utilizing a quartz tube continuous gas flow reactor with reactor effluent analyzed via FTIR spectrometer (MKS 2030 HS). Catalysts were pretreated at 550 °C in 4 L/min Ar for 1 hour. Steady-state activity measurements over soot-free samples were conducted from 200 to 500 °C in a CO/HC gas mixture with variable $O_2$, 12% $CO_2$, and 5% $H_2O$. Effect of NO was evaluated by feeding either 0 or 300 PPM NO. Soot-loaded samples were evaluated in CO/HC mixtures like soot-free samples but with a temperature range of 125 to 300 °C to avoid soot oxidation. Temperature-programmed reactions in 0.5% $O_2$ and 5% $H_2O$ were conducted from 100 to 700 °C with a ramp of 3 °C/min to evaluate soot oxidation. Initial steady-state activity measurement protocol (200-500 °C) was repeated to compare soot-free activity to soot-regenerated samples. Influence of soot on light-off can be observed from lower conversion efficiencies on soot loaded catalysts. Degradation of TWC activity is attributed to soot inhibiting mass transfer of reactants to catalyst surface. The tested sample of Pd/Rh catalyst at 950°C exhibited lower light-off temperatures post-soot loading due to local heat effects caused by exothermic soot oxidation. High temperature hydrothermal treatment improves mobility of lattice oxygen in Ce coupled with increased contact between soot and catalyst via lower catalyst surface area. Catalytic oxidation of soot began at ~ 265 °C with two major peaks observed at 550 °C and ~675 °C. Higher rate of soot oxidation observed over Rh-promoted catalysts which attributed to the formation of surface oxide layer on Rh that promotes oxidation. Samples aged at lower temperatures exhibited a larger recovery of activity compared to samples aged at 950 °C even though soot oxidation was not complete over 650 °C-aged samples. Rh-promoted catalysts exhibited greater recovery of catalytic activity due to improved soot oxidation activity. Monometallic Pd catalyst aged at 950 °C recovered the least amount of activity due to PGM sintering and incomplete removal of soot. In general, high temperature hydrothermal aging results in loss of washcoat surface area and sintering of PGM on TWC components in cGPF. The presence of soot decreases TWC activity due to blockage of active sites and inhibition of reactant mass transfer to catalyst surface. PdRh bimetallic formulations aged at 950 °C exhibited some promotion from soot presence due to exothermicity of soot oxidation and local heat effects. Soot oxidation and catalyst regeneration resulted in recovery of some catalyst activity. However, the presence of ash within soot was not explored in this study. It can be assumed that catalyst regeneration via soot oxidation will leave ash particles on the catalyst surface. Ash is expected to build up over time as more soot is deposited and removed via oxidation. Presence of ash residue will lead to permanent blockage of active sites on catalyst surface. Soot inhibition does not occur to the same extent or at the same rate as in standard TWC (non-cGPF) components due to their inherent low filtering efficiency.

## 6.0 SUMMARY AND CONCLUSIONS

- Relatively few quality studies were found in the literature that directly examine the influence of different lube oil additive formulations on ash accumulation rate, ash distribution within the GPF, and the impact on GPF performance.
- A detailed summary of the impacts of various detergents and anti-wear lubricant additives of the lubricating oil on the performance of GPF is presented in Table 1
- Catalytic effects of ash is an important future topic, especially in advanced combustion platforms where soot emissions are low, and hence, ash to soot ratio is high.
- A detailed summary and comparison of various accelerated aging (ash loading) platforms currently utilized in the literature is presented in Table 2.
- When using accelerated ash loading methods, it is important to study their impact on particle size distribution, and how it compares to the original particle size distribution produced by a particular engine platform.
    - That is rarely done in a lot of studies
    - That is critical to shed some light on whether the method used can simulate the real world from standpoint of physical and chemical particle characteristics.
    - It will also shed some light on the extent to which ash acceleration rate can be increased prior to altering real-world phenomenon.
- SwRI observed some important shortcomings in the literature regarding how PN/PM is measured. Two issues were identified:
    - In one case the PN measured is neither solid PN using the EU definition nor total PN using dilution at ambient temperature.
    - In another study, SwRI observed a huge divergence in the PN/PM relationship where PM was much higher than expected based on the SPN results. There are two possibilities:
        - PM is dominated by volatile/semi volatile compounds
        - PM is dominated by measurement artifacts

**Table 1. Summary impacts of various detergents and anti-wear lubricant additives of the lubricating oil on the performance of GPF**

| *Candidate* | *Lubricating Oil* | *Detergent* | *Additive* | *Catalyst* | *P observed on the catalyst* | *P deposition ratio* | *$O_2$ storage capacity* | *HC emissions* | *CO emissions* | *$NO_X$ emissions* |
|---|---|---|---|---|---|---|---|---|---|---|
| *a* | Group II Base Oil (SAE 5W-30) | Ca/Mg | ZDDP2 | Pd based TWC | candidate 'a' and 'e' are similar | 84 | not reported | candidate 'a' and 'e' are similar | candidate 'a' and 'e' are similar | candidate 'a' and 'e' are similar |
| *b* | Group II Base Oil (SAE 5W-30) | None | ZDDP2 | Pd based TWC | highest | 86 | not reported | highest | highest | highest |
| *c* | Group II Base Oil (SAE 5W-30) | Ca/Mg | No Additive | Pd based TWC | Not applicable | 0 | not reported | lowest | lowest | lowest |
| *d* | Group II Base Oil (SAE 5W-30) | Ca/Mg | Antiwear additive containing Zn but not P | Pd based TWC | Not applicable | 0 | not reported | lowest | lowest | lowest |
| *e* | Group II Base Oil (SAE 5W-30) | Ca Only | ZDDP2 | Pd based TWC | candidate 'a' and 'e' are similar | 75 | not reported | candidate 'a' and 'e' are similar | candidate 'a' and 'e' are similar | candidate 'a' and 'e' are similar |

[*] P deposition ratio is defined as the ratio of total amount of P found on the catalyst to the total amount of P lost from the oil and its additives (Higher the P deposition ratio higher is the amount of P found on the catalyst and higher impact on the performance of GPF)

[*] ZDDPs are classified as primary ZDDP1(high thermal stability used for diesel engines) or secondary ZDDP2 (more reactivity used for gasoline eingines) depending on the type of alcohol used in the manufacturing process [5]

Table. 1 Cont.

| *Candidate* | *Lubricating Oil* | *Detergent* | *Additive* | *Catalyst* | *P observed on the catalyst* | *P deposition ratio* | *$O_2$ storage capacity* | *HC emissions* | *CO emissions* | *$NO_X$ emissions* |
|---|---|---|---|---|---|---|---|---|---|---|
| *f* | Not reported | Not reported | ZDDP2 | Pd based TWC | candidate 'f' and 'g' are similar | Not reported | reduced compared to 'no additive' scenario | higher than 'no additive' scenario | higher than 'no additive' scenario | higher than 'no additive' scenario |
| *g* | Not reported | Not reported | Ionic Liquid (IL) - [P8888][DEHP] | Pd based TWC | candidate 'f' and 'g' are similar | Not reported | Similar to candidate 'f' and 'h' | Similar to candidate 'f' and 'h' | Similar to candidate 'f' and 'h' | Similar to candidate 'f' and 'h' |
| *h* | Not reported | Not reported | IL [P8888][DEHP] + ZDDP2 | Pd based TWC | Slightly higher than candidate 'f' and 'g' | Not reported | Similar to candidate 'f' and 'g' | Similar to candidate 'f' and 'g' | Similar to candidate 'f' and 'g' | Similar to candidate 'f' and 'g' |
| *i* | Not reported | Not reported | [P66614][DEHP] | Pd based TWC | lower P than 'ZDDP2 only' | Not reported | higher than 'ZDDP only' scenario but lower than 'No additive' case | lower than 'ZDDP only' scenario but higher than 'No additive' case | lower than 'ZDDP only' scenario but higher than 'No additive' case | lower than 'ZDDP only' scenario but higher than 'No additive' case |

Table. 1 Cont.

| *Candidate* | *Lubricating Oil* | *Detergent* | *Additive* | *Catalyst* | *P observed on the catalyst* | *P deposition ratio* | *$O_2$ storage capacity* | *HC emissions* | *CO emissions* | *$NO_X$ emissions* |
|---|---|---|---|---|---|---|---|---|---|---|
| *j* | Gas to Liquids base oil | Not reported | primary ZDDP - ZDDP1 | Pd based TWC | lower P than 'ZDDP2 only' and 'IL [P8888][DEHP] + ZDDP2' | Not reported | highest - similar to no additive scenario | lower than 'l' and 'm' but similar to 'k' | lower than 'l' and 'm' but similar to 'k' | lower than 'l' and 'm' but similar to 'k' |
| *k* | Gas to Liquids base oil | Not reported | IL [P8888][DEHP] + ZDDP1 | Pd based TWC | similar to 'j' - IL contribution is negligible | Not reported | highest - similar to no additive scenario | lower than 'l' and 'm' but similar to 'j' | lower than 'l' and 'm' but similar to 'j' | lower than 'l' and 'm' but similar to 'j' |
| *l* | Gas to Liquids base oil | Not reported | secondary ZDDP - ZDDP2 | Pd based TWC | higher P than 'ZDDP1 only' and 'IL [P8888][DEHP] + ZDDP1' | Not reported | lower than 'j' and 'k'; similar to 'm' | higher than 'j' and 'k' but similar to 'm' | higher than 'j' and 'k' but similar to 'm' | higher than 'j' and 'k' but similar to 'm' |
| *m* | Gas to Liquids base oil | Not reported | IL [P8888][DEHP] + ZDDP2 | Pd based TWC | highest P content between 'j' to 'm' | Not reported | lower than 'j' and 'k'; similar to 'l' | higher than 'j' and 'k' but similar to 'l' | higher than 'j' and 'k' but similar to 'l' | higher than 'j' and 'k' but similar to 'l' |
| *n* | Group II Base Oil (SAE 5W-30) | Not reported | Hyper ZDDP2 - patented catalyzed additive | Pd based TWC | Not reported | Not reported | Not reported | reported 18% reduction over 'ZDDP2 | reported 30% reduction over 'ZDDP2 | reported 19% reduction over 'ZDDP2 |

### Table 2. Summary of various ash loading platforms currently reported in literature

| **Parameters** | **Ash loading Platform** | | | |
|---|---|---|---|---|
| | *Vehicle based ash loading - Field loaded* | *Engine-Based Ash Loading with Oil Doping* | *Engine based - Inverted Piston Ring Ash Loading* | *Burner-Based Ash Loading* |
| *Deposition of ash* | most realistic - uniform ash plug layer | uniform deposition of ash | uniform deposition of ash | parabolic deposition profile |
| *Quality of ash* | highly dense (benchmark) | lesser dense than benchmark | highly dense - close to benchmark | lower density ash plug layer |
| *Back pressure of the GPF* | benchmark | slightly higher back pressure | significant increase in backpressure | comparable to benchmark |
| *Controllability of ash loading* | least controllable | higher control | somewhat controllable | highest control |
| *Acceleration rate of ash loading* | 1X | up to 2X | up to 5X | up to 10X |
| *Replication of real-world condition* | Most accurate (benchmark) | differences in quality of ash and its deposition profile | comparable to benchmark | differences in quality of ash and its deposition profile |
| *Capital/Operating/Maintenance costs* | highest | lesser compared to vehicle based | lesser compared to vehicle based | lowest |
| *Lead time for ash loading* | longest | shorter than benchmark | shorter than benchmark | shortest |

## 6.1 Suggested Topics for Future Testing

Based on the detailed literature review conducted, some topics that require additional research have been identified below.

- Impact of hybrid engine operation and lube oil formulations on aftertreatment system performance
  - In general, not much information was found in the literature, and it is an important topic that requires additional research
  - Low temperature engine operation and frequent start/stop events may impact ash and soot generation and transport to the aftertreatment system
    - May also impact distribution within the aftertreatment system
  - Specialty lube oil formulations for hybrid vehicles have not been investigated in detail
  - A test program could be developed to simulate hybrid vehicle operation (including lube oil temperature) in the real-world and examine its impact on aftertreatment performance
    - Such aging/ash loading activities could be conducted using a burner-based platform or an engine platform configured for aging and ash exposure
- Influence of lube oil formulation on aftertreatment system performance for gasoline vehicles
  - GPF performance may be influenced by specific lube oil components
  - A test program examining the impact of individual metallic additives on engine-out emissions, as well as GPF performance could be developed
    - It is critical that such a program examines details such as particle size distribution, ash concentration, ash size distribution, loading rate, catalyst poisoning rate, among other variables
- Aging methods used to investigate durability performance of aftertreatment systems
  - Three methods that have been commonly utilized include burner-based, engine-based, and vehicle-based aging platforms. Additional research is required to understand whether accelerated aging techniques are representative of real-world aging. Further, such programs should examine the following:
    - Influence of rate of accelerated aging on particle size distribution
    - Transport phenomena of ash deposition, profile and distribution on the aftertreatment system
    - Thresholds for transition to new particle regimes, that may or may not be characteristic of field-aged component
- Evaluation of the performance of a catalyzed GPF compared to that of an uncatalyzed GPF. Such a program could examine the following:
  - Influence of catalyzed GPF to improve regeneration capabilities at lower temperatures
  - Impact of ash constituents on catalyzed GPF
    - Promoter or poison?

## 6.2 Key Components for Future Test Programs

- The above section highlighted some of the areas with knowledge-gaps. When future programs are conducted, it is important that they include the following key components:
- Characterization/measurement techniques that include:
  - Particle characterization techniques such as:
    - Real-time particle number and size distribution measurement
    - GPF Filtration efficiency measurement using two identical devices such as micro-soot sensors
    - Real-time ash number concentration, and size distribution measurement
    - Elemental speciation of ash components via PM filter collection, and ICP-MS analysis of the filter
  - For programs involving ash loading of the aftertreatment system, CT scan of the GPF should be conducted to understand ash distribution and density. Likewise, pressure drop changes across the GPF should be monitored via controlled experiments. Further, for programs involving engine and/or vehicle platforms, fuel economy changes that may arise due to increase in pressure drop across the aftertreatment system should be monitored.
- Based on the literature survey, several oil ingestion methods (such as fuel doping or inverted piston ring in engine or oil injection in a burner-based platform) can be adopted to accelerate ash loading on an aftertreatment system. It is important that the method chosen for a particular program simulates the particle characteristics of real-world operation.

## 7.0 REFERENCES

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