Lube Oil-Dependent Ash Chemistry on Soot Oxidation Reactivity in a Gasoline Direct-Injection Engine

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ABSTRACT

Gasoline particulate filters (GPF) are considered an enabling technology to meet stringent particulate matter (PM) regulations for gasoline direct-injection (GDI) engines, which are known to produce significant PM emissions. While ash loading in filters has been recognized to be detrimental in filter performance by increasing back pressure, increased ash fractions in soot were observed to enhance soot oxidation. GDI soot samples derived from different gasoline/lube oil blends were evaluated to identify potential promoting factors when formulated lube oils were dosed into gasoline fuel. Ca-derived ash enhanced soot oxidation remarkably, while P- and ZDDP-derived ash deteriorated soot oxidation. It is apparent that the promoting effect of lube oil-derived ash is due mainly to the Ca component that is the most abundant among additive components in lube oil. Bulk and surface analyses of these ash compounds indicate that Ca-derived ash would be complex compounds, while the contribution of CaSO_4 , which is one of the most abundant ash compounds from diesel engines, is almost negligible. For the validation of the ash promoting impact in filters, the regeneration experiments were compared for a TWC-coated GPF in a GDI engine before and after ash loading was performed. The pressure drop of the ash-loaded GPF decreased noticeably in the initial regeneration stage and it increased gradually, whereas that of no ash-loaded GPF increased gradually without any reduction. So, it is concluded that the ash layer in the GPF assisted soot oxidation in the early regeneration stage when it was in close contact with soot.

KEYWORDS

Gasoline direct-injection (GDI) engine; Gasoline particulate filter (GPF); Soot oxidation reactivity; Lube oil additives; Ash

1. Introduction

Gasoline particulate filters (GPF) are expected to be widely spread for GDI engines in the future to meet the stringent particulate emissions standards of both mass and number. The particulate number (PN) emissions regulation of 6.0×10^{11} #/km will be phased-in with new type approvals called RDE (real driving emissions) testing from September 2017 in amended Euro-6 regulation [1]. The California Air Resources Board (CARB) proposed the LEV III standards, a phase-in schedule for particulate mass emissions of 3.0 mg/mile as of 2017 MY and 1.0 mg/mile as of 2025-2028 MY [2]. It has been reported that passive regeneration is sufficient for the GPF, due to low soot mass concentration and high temperatures of GDI engine emissions. Therefore, they may require relatively simple and cost-effective hardware and control systems than those used in diesel particulate filters (DPF) [3].

In our previous study [4], oxidation characteristics of GDI soot were examined at different engine operating conditions, and found that the metallic ash components in soot derived from lube oil, whose major components are Ca, P, Zn, and Na, strongly promoted soot oxidation. According to previous studies, Ca and Na compounds (oxide/hydroxide/carbonate) were reported to effectively lower soot oxidation temperatures as catalysts when they are in tight contact with soot, while Zn compounds showed relatively weaker activities than the former [5, 6]. P is known as an inhibitor of the graphite oxidation: thermal decomposition of the phosphorus compounds at 200-600 °C leaves a hydrophilic residue strongly adsorbed on the graphite surface at active sites where oxidation normally occurs [7]. It was also reported that the diesel soot surface thermal property is altered significantly after being treated by phosphoric acid and thio-phosphorous derivatives derived from ZDDPs by forming protection layer and physical barrier that prevents oxygen from diffusing effectively onto the carbon surface [8]. Although these studies provided valuable information about how each component impacted carbon oxidation, however, the mixing environment of carbon and each

chemical compound is different from actual combustion process in engine cylinder. Also, it is not apparent whether these metal compounds have the same effects as ash particles emitted from engines do. As a consequence, the incorporation of metallic compounds into carbon could lead to conclusions different from actual engine soot containing ash derived from lube-oil during the in-cylinder combustion.

In an effort to broaden our understanding of lube oil-derived ash effects on soot oxidation reactivity in GDI engines, gasoline fuel was burned in a light-duty GDI engine with designed lube oil formulations by a fuel doping method. Soot samples containing ash collected during the engine operation were analyzed in terms of soot oxidation reactivity and then, ash chemical compounds were investigated to find their roles influencing soot oxidation mechanisms. Finally, GPF experiments were performed in the GDI engine using a prototype bench-scale GPF to validate the effect of ash layer on soot oxidation during the regeneration process.

2. Experiment and analysis

2.1 Engine and GPF test setup

A 2.4 L 4-cylinder, naturally aspirated, GDI spark-ignition engine was used in this work. The engine geometry and specifications are given in Table 1. This engine basically operated at homogenous and stoichiometric charge conditions. The engine was mounted on a 112 kW blower-cooled AC dynamometer for speed control and torque measurements. In this work, the certified Tier 2 EEE gasoline fuel and commercially available ILSAC GF-5 conventional motor oil which is API SN rated with an SAE grade of 5W-20 were used.

Table 1.

A partial flow exhaust system was built to test prototype bench-scale GPFs (2" in diameter and 6" in length) at a wide range of flow rates (0 – 40 kg/hr) at the same steady state engine condition. Fig. 1 shows the schematic of the partial flow GPF setup. The flow rate into the GPF setup is controlled by two flow control valves located at the main exhaust pipe and the partial flow exhaust pipe. The pressure drop and temperatures across the filter were measured, and the particulate number and mass filtration efficiencies were calculated by measuring the particulate number and mass of upstream and downstream of the filter. The compressed air and air heater (6 kW) were connected to the partial flow exhaust pipe at the GPF inlet, which allows cold air and hot air (max. 600 °C @ filter inlet) test for pressure drop measurement and perform soot oxidation. For accelerated ash loading, lube oil was injected into the fuel supply line at a controlled rate to achieve 2 wt. % of the lube oil in gasoline fuel, which allows about 1 g/L of ash loading in 1 hour at 1250 rpm – 25% with 1 % sulfated ash lube oil. Soot mass concentration was measured before and after the GPF setup to evaluate filtration efficiencies and soot mass remaining in the filters using a high-sensitivity photo-acoustic sensor (AVL 483 micro soot sensor).

Fig. 1

2.2 Characterization tools

Thermogravimetric analysis (TGA)

The compositions and oxidation reactivity of GDI soot were measured using TGA (TA Instruments Q50). Raw PM from exhaust streams was sampled on a Teflon[®] filter. The PM sample scraped from the filter was thermally treated under nitrogen at 600 °C for 30 min to remove volatile fractions. Isothermal oxidation experiments were subsequently conducted under 8% of oxygen in nitrogen. The volatile organic fractions (VOF) were measured by the

mass removed during thermal treatment under nitrogen, and the ash fraction was measured using the mass that remained after completion of oxidation. And, instantaneous reaction rates were calculated over conversion based on TGA results.

Powder X-ray diffraction (PXRD)

Synchrotron PXRD patterns of ash samples were collected for the identification of ash compounds from the 11-BM beamline of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The samples loaded in Kapton tubes (inner diameter of 0.80 mm) were scanned at room temperature in the 2θ range of 0.5° to 50° and the wavelength was calibrated at $0.414169 \text{ \AA}$.

X-ray photoelectron spectroscopy (XPS)

XPS spectra were recorded in a Kratos Axis Ultra and post-processed by using CasaXPS software in order to measure surface elements in soot. Atomic percentages of elements were calculated based upon the spectra with Shirley background from survey scans, and high resolution Ca 2p, P 2p_{1/2}, Zn 2p and S 2p were examined to identify possible chemical compounds. All the spectra were calibrated with respect to the C 1s peak at 284.6 eV.

Scanning electron microscopy (SEM)

Soot and ash samples loaded onto an SEM sample holder were examined in JEOL field-emissions SEM 7500F. The electron dispersion X-ray spectroscopy (EDS) analysis was performed at 20 keV for elemental information.

3. Results and discussion

3.1 Ash impact on GDI soot oxidation reactivity

Engine tests were conducted with gasoline only (without lube oil dosing) at three engine speed-load sets, 1250rpm-25%, 1500rpm-50% and 3000rpm-50%. Two injection timings, base (300° CA BTDC) and advanced (330° CA BTDC), were applied at each set to evaluate

different soot emissions levels. With advanced injection timings, soot mass emissions significantly increased due to fuel wetting on the piston surface. Fig. 2a shows the ash fraction in soot with the variation of soot mass emissions under the three test conditions. Since lube oil consumption is anticipated similar at the same speed-load condition, the increased ash fractions in soot under base injection timings are ascribed to low soot mass emissions. TGA results in Fig. 2b indicated that soot oxidation was always promoted for low soot cases (solid lines), compared with high soot cases (dotted lines). Also, soot oxidation reactivity was in good agreement with ash fraction in soot as described in 90 % soot oxidation time (T90) over ash fraction (Fig. 2c), which validated our previous result [4]. This result may imply that low engine-out soot mass emissions from GDI engines contribute to enhanced soot oxidation due to high ash fraction in soot. In this light, low engine-out soot mass levels will achieve efficient regeneration of GPF.

Fig. 2.

3.2 Formulated additive-specific engine oils

It is clear that the ash derived from lube oil additives promoted soot oxidation, so the effect of each additive component was of interest to identify ash promoting effects. Elemental analyses were performed by inductively coupled plasma (ICP) for several lube oil products commercially available in the market as shown in Fig. 3. The metal components in gasoline lube oils were lower than in diesel engine oil, ranged between 4000 and 5000 ppm depending on the base stock and targeted functions. A conventional 5W20 oil (box in red line) used for this work contains 4659 ppm of metal components, Na, Ca, Zn, and P. Ca, Zn and P were analyzed to be major components in common and other metallic additives were present with low levels. Ca, P and Zn-P additives are typically sourced from calcium sulfonate, phosphite

and zinc dithiophosphate (ZDDP) compounds, respectively. Accordingly, calcium dodecylbenzene sulfonate, triethyl phosphite and ZDDP were chosen to formulate Ca-, P- and P-Zn-specific lube oils, respectively, by mixing with non-detergent lube oil that contains least amounts of additive compounds. Finally, the blends of 1 wt. % of each additive specific lube oil and 99 wt. % of gasoline were burned in the engine under the same operating condition (1250 rpm-25% load condition and fuel injection timing of 330° CA BTDC) for the fair comparison, while exhaust emissions were measured as below. Then, their impacts were compared to those of gasoline only, non-detergent oil (1 wt. %) + gasoline (99 wt. %), and conventional lube oil (1 – 2 wt. %) + gasoline (98 – 99 wt. %). Ca-, P- and P-Zn-specific particulate samples were collected on Teflon[®] filters by drawing raw exhaust streams from the engine and they were scraped off from the filters for characterization as explained below. The prepared samples and additive contents are listed in Table 2.

Fig. 3

Table 2.

3.3 Investigation of soot oxidation reactivity

TGA experiments were performed for additive-specific soot samples to better understand the effect of each metal additive on soot oxidation reactivity, as presented in Fig. 4a. The conventional oil-derived soot samples showed enhanced soot oxidation with increased ash fraction, when they were compared to the baseline non-detergent oil-derived sample. In comparison, the Ca-derived soot samples offered oxidation trends comparable to the conventional oil-derived soot samples. When ash fractions are concerned, however, the promoting effects of Ca additive appeared to be greater than metal additives from

conventional lube oil. On the contrary, the P- and P-Zn-specific soot samples presented oxidation trends opposite to the Ca- and conventional lube oil-derived samples: soot oxidation was retarded in the presence of P and P-Zn, indicating these metal additives deactivated soot oxidation. Based on TGA results, T90 was plotted against ash fraction as shown in Fig. 4b. There found a good linear relation between ash fraction and T90 with respect to T90 of the non-detergent oil-derived sample as a baseline.

Fig. 4

Accordingly, linear lines were drawn from the baseline T90 to T90 of each additive, and T90 changes were calculated for ash fraction of 1.0 wt. % in soot for each case (Table 3). As explained above, T90 changes clearly showed that soot oxidation was advanced in the order of $\text{Ca} > \text{conventional oil-derived ash mixture} > \text{P \& Zn} > \text{P}$. Since Ca is the most abundant additive component in lube oil, the promotion in soot oxidation with oil-derived ash mixture seems to be attributed to the dominant Ca presence in ash components despite adverse effects of P and P-Zn. Previously the Ca-enhancing effect on soot oxidation was also observed [5, 6, 9, 10], so this Ca-dominant ash formed during the combustion process seems to play a similar catalytic role in soot oxidation. This promoting effect of Ca-derived ash is assumed to be comparable to fuel-borne catalysts which lower oxidation temperatures [11, 12]: our previous work from [4] indicates that oxidation temperatures appreciably decreased when ash content was high. Interestingly, the activation energy of soot oxidation was invariant with ash present, like Ce-additives [11].

Table 3

In this work, the Zn effect on soot oxidation was not isolated from P, because one Zn element is always present in ZDDP with two P elements. Since one Zn element is heavier than two P elements, the Zn fraction in lube oil is always higher than P fraction, as indicated in Fig. 3. Therefore, the results suggest that Zn contribution to soot oxidation is minor, if it can be separated from P contribution. According to Neeft et al. [5, 6], ZnO is a mild soot oxidation enhancer. Also, P compounds have been known to retard soot oxidation reactivity, because when P blocks active sites of carbon materials, carbon oxidation is interfered [7, 13]. Since these results were taken from certain chemicals other than ash compounds, however, it is not clear whether our results from actual ash samples can be explained in the same manner as others. Indeed sulfated ash compounds and other chemical compounds are typically formed among different additive compounds [14–16]. Based on TGA results, instantaneous soot oxidation rates were calculated as shown in Fig. 5. Soot oxidation rates were promoted by more than 5 times with increased conversion, when the conventional oil-derived sample was analyzed, compared with no ash case (the non-detergent oil-derived sample). However, it is interesting to note that the Ca-derived sample showed quite a different rate pattern than the conventional oil-derived sample: the former had relatively high oxidation rates throughout the entire conversion range. It is yet unclear whether ash compounds and ash/soot distributions which can lead to different soot oxidation mechanisms have resulted in different rate patterns for both samples. On the contrary, both the P- and P-Zn-additives were found to present similar patterns in oxidation rate: significantly low rates from the early conversion stage. Although P inhibiting factors were typically examined when carbon materials were impregnated with P-containing compounds, our soot samples containing P and P-Zn compounds seem to follow oxidation mechanisms similar to P-impregnated carbon materials by others. Wu and Radovic reported that the strong inhibition of carbon oxidation was enabled with C-O-PO₃ formation, more specifically the bridge O atoms [13]. Under this

finding together with our results, the P- and ZDDP-derived cases can be hypothesized that organic P-only compounds and/or P_2O_5 produced from phosphite and ZDDP were utilized to create C-O-P bonds in carbon active sites, leading to delayed soot oxidation from the early oxidation stage. In this light, it is questionable why oxidation rates with lube oil-derived ash were high in the entire conversion range if organic P-only compounds or P_2O_5 could be formed during the combustion process. One possibility is that P-containing additive compounds react with other additive compounds during the combustion process to form inorganic compounds prior to C-O- PO_3 formation, so the negative function of P-containing compounds in soot oxidation would be extremely low. Therefore, it is of great interest whether or not ash formation and ash-soot interactions are influenced by additive types under different engine operating conditions.

Fig. 5

3.4 Characterization of ash compounds in soot

XRD is conventionally used to identify chemical compounds with crystalline structures. As ash samples available for the analysis were little, the synchrotron PXRD was used in this work. It was of great interest if $CaSO_4$ is a main ash compound from GDI engines, as it is proposed to be a major contributor in other cases [14, 16]. The Ca sulfonate-derived ash obtained from a muffle furnace (treated at 750 °C) showed the exactly identical peaks of $CaSO_4$ as shown in Fig. 6. However, there was no evidence found that the conventional engine oil-derived ash from the engine contained $CaSO_4$. Other than that, it was not possible to predict right chemical candidates from phase matching. Since the engine oil includes various additives, complex ash chemistries may have been involved among them during the combustion process.

Fig. 6

Since XPS is sensitive to surface elements, it was used to identify surface elements and their chemical compounds in soot to suggest potential soot oxidation mechanisms with additive specific engine oils. Table 4 shows atomic percentages of elements found in the examined soot samples, which tend to be appreciably lower than ash fractions from TGA tests.

Table 4

Since XPS detects the depth of around 10 nm only, much portions of metallic elements may not be exposed to surface. Interestingly the sulfur was not observed in these survey scans except the non-detergent oil-derived soot, although ZDDP and calcium sulfonate contain high amounts of sulfur, indicating sulfur was not preserved as compounds in this work. While no Zn was found in Ca-derived soot, the P contents were relatively high, probably sourced from non-detergent oil. Since P was not observed with the non-detergent oil case despite the same amount of non-detergent oil in gasoline (1%), somehow added calcium sulfonate may have played a certain role in increasing P contents only. Although the reason is not clear, this unexpected fining may suggest important ash formation process among ash precursor elements in lube oil. Although we tried to separate the Ca impact on soot oxidation from others, P might have counteracted soot oxidation reactivity with Ca-derived ash, in consideration of the role of P. Surprisingly Zn contents in ZDDP-derived soot were very low while P contents were relatively high, implying that surface-exposed Zn was extremely low compared with bulk Zn, or Zn itself was not much included in soot, which is consistent with the Ca-derived soot cases which did not show the Zn presence. The Ca 2p spectra of the Ca-

derived ash in soot indicated two characteristic peaks at 347.0 and 350.5 eV (Figure 7a). The Ca 2p of Ca compounds typically have the spin-orbit doublet at $2p_{1/2}$ and $2p_{3/2}$, in which the energy difference is 3.5 eV. It is difficult to compare the Ca 2p values of this work with others, unless C 1s information was given. According to the limited number of literatures (the energy shifts were corrected at the C 1s of 284.6 eV), the binding energy of the Ca $2p_{3/2}$ was reported to be 346.1 eV [17], 346.6 eV [18], 346.8 eV [19], 347.2 ± 0.2 eV [20] and 347.0 eV [21] for CaCO_3 , and 346.1 ± 0.2 eV [20] and 348.2 eV [22] for Ca(OH)_2 . In addition, the Ca $2p_{3/2}$ of CaO was shown to be around 346.6 eV [18], 346.5 eV [23] and lower than 346.1 eV [20, 22], and that of CaSO_4 was observed at 347.0 eV [24], 347.5 eV [18], 347.7 eV [25] and 347.8 eV [19]. Also, since the ratios of P to Ca in Table 4 were larger than 0.5, the Ca-derived ash could be contributed from Ca-P compounds such as $\text{Ca}_3(\text{PO}_4)_2$. The Ca $2p_{3/2}$ of various $\text{Ca}_3(\text{PO}_4)_2$ was also found at around 347.0 eV [26]. Since all these Ca compounds could have the Ca $2p_{3/2}$ at 347.0 eV, unfortunately, it is not possible to assign the Ca-derived ash to any specific Ca compounds. As evidenced in Figure 7b, however, the S 2p peaks were almost negligible in soot with Ca, P and ZDDP-specific engine oils, although the two cases showed the presence of minor amounts of sulfur. Therefore, it is suggested that the contribution of CaSO_4 to Ca-derived ash compounds is negligible in this work. Somehow this finding is partly consistent with the work of Uy et al. [16]: the sulfur contents in soot extracted from drain oils were high, whereas those in exhaust soot were low. As a result, the soot from drain oils contained CaSO_4 as a major ash compound, while that from exhaust had CaCO_3 , implying that the combustion process in engine cylinder affected ash formation chemistry. As shown in Fig. 6, ash remained after burning calcium dodecyl-benzene sulfonate in the furnace was found to be CaSO_4 , indicating that SO_3^- and Ca^{2+} reacted to produce CaSO_4 possibly through their other forms after dodecyl-benzene was detached at this relatively mild burning condition. From the fact that ash in the exhaust has minor or

negligible amounts of CaSO_4 , Ca^{2+} seems to favor interactions with exhaust gases and chemicals dissociated from ZDDP and other ash precursors, when calcium sulfonate passed through hot and highly-pressurized engine cylinders. Based on this PXRD data as well as Uy et al.'s result, therefore, it is suggested that CaSO_4 formation from lube oil is related with combustion environments provided at different temperatures and pressures.

Fig. 7

The P 2p of the P- and P-Zn-derived ash was observed in the almost identical range of 134.0 eV to 134.2 eV (Figure 7c). In consideration of the low Zn contents discussed above, the contribution of P-Zn compounds such as $\text{Zn}_3(\text{PO}_4)_2$ and $\text{Zn}_2\text{P}_2\text{O}_7$ to P-Zn-derived ash would be low. While some ZDDP could escape from the engine without dissociation, H_2PO_4^- and P_2O_5 were observed in the exhaust [27, 28]. Since the P 2p of P_2O_5 , $-\text{PO}_4^{3-}$ and $-\text{PO}_3^-$ was reported in the range of 134.0 eV to 135.0 eV [25, 29, 30], it seems hard to identify specific P-compounds from this analysis. It is interesting to note that the P 2p peaks appeared in this energy range as well when P is associated with carbon surface by bonding to O atoms [13]. When taking into account the possible delayed soot oxidation mechanism with P present, our XPS result seems to support that C-O-P would be formed with both P- and ZDDP-derived ash as discussed above. The Zn 2p_{3/2} of the P-Zn-derived ash was shown at 1021.8 ± 0.2 eV (Fig. 7d). In comparison, the binding energy of the peak was reported to be 1022.4 eV [31] and 1023.1 eV [32] for $\text{Zn}_3(\text{PO}_4)_2$, 1021.3 eV [31] and 1022.0 eV [33] for ZnO, and 1021.9 – 1022.6 eV for zinc phosphate glasses [31]. ZnSO_4 is one of ash compounds from oil deposits in diesel engines [14], but it is not apparent as far as sulfur presence is concerned. Therefore, Zn compounds contributing to ZDDP-derived ash could be complex ZnO and Zn-P compounds. Although we could not identify the role of Zn compounds in soot oxidation, their

impacts on soot oxidation are expected to be minor as discussed above [5, 6]. Accordingly, the delayed soot oxidation with P-Zn-derived ash was attributed to P-containing compounds that interacted with carbon surface, whose process seems to be comparable to those formed during the combustion process from phosphite.

The elemental analyses of Ca-derived soot and ash were further performed using SEM-EDS as found in Fig. 8. As expected from the XPS result, P contents were relatively high in these bulk samples, indicating that P is also abundant in bulk state like on surface. While XPS did not show the presence of Zn and S, they were detected in the bulk samples although their fractions were low. Although minor amounts of Zn and S contributed to Ca-derived ash in bulk state, therefore, this result is in good agreement with the XPS analysis. While it is clear that CaSO_4 is not an active material that facilitates soot oxidation in this work, single or complex Ca compounds are responsible for enhanced soot oxidation as many Ca-related materials are known to be carbon oxidation catalysts [5, 6, 9, 10, 34].

Fig. 8

3.5 GPF tests using a bench-scale flow reactor

The results presented above clearly show that soot oxidation is promoted in the presence of ash derived from lube oil, due mainly to Ca detergent which is a major additive element among inorganic elements. Ash particles and soot are thought to be tightly or closely bound when they are collected as bulk samples as did in TGA experiments. Therefore, it was questionable whether enhanced soot oxidation could also be realized in GPF tests, because the interaction between ash layer and soot cake in filters is reduced. To examine the effect of ash loading in a GPF on soot oxidation, pressure drop changes were monitored across a three way catalyst (TWC)-coated GPF (TWC/GPF) before and after ash loading of 2.0 g/L. As

shown in Fig. 9a, the trends in pressure drop increase were different for no ash and ash-loaded filter: for the no ash-loaded filter, pressure drop increased steeply up to 0.2 g/L (in-depth filtration regime) and it increased slowly (soot cake regime) with increased soot loading. For the ash-loaded filter, however, the in-depth filtration regime was completed within soot loading of 0.2 g/L and the soot cake regime started in an early stage. These different trends in GPF with no ash and ash loading resemble those observed in diesel particulate filters (DPFs) [35]. In addition, the figure indicates that the filtration efficiency was significantly increased with ash loading of 2 g/L: while the fresh GPF reached the filtration efficiency of 87%, the ash-loaded GPF achieved that of 98% when there was no soot loaded. Since pores in wall were plugged with ash particles, soot penetration through wall was suppressed. Although ash loading is a serious burden for the filter with increased pressure-drop in the end, slight ash loading seems beneficial when pressure drop and filtration efficiency are concerned. When soot loading reached 0.45 g/L, the engine operation condition was switched from 1250 rpm-25% load to 2000 rpm-50% load to increase the GPF inlet temperature up to 550 °C. As shown in Fig. 9b, for the GPF with no ash loading, the pressure drop gradually increased up to 500 seconds and its increase slowed down since then. After 1500 seconds, the pressure drop increase appears to be negligible, implying that soot accumulation and oxidation were balanced out. On the contrary, the ash-loaded GPF experienced the decrease in pressure drop up to 500 seconds and then, its pressure drop pattern resembles that of no ash-loaded GPF. The decrease in the pressure drop with the increased inlet temperature was ascribed to the spontaneous oxidation of soot in close contact with ash layer. Since the contact was lost with soot oxidation, the pressure drop increased gradually like no ash-loaded GPF. Accordingly, it seems apparent that ash layer can be more effective in soot oxidation during the GPF regeneration process than the TWC, when the former is in close contact with soot cake. Since the TWC was coated inside the GPF wall, the

interaction between the TWC and soot is relatively low. Also, since oxygen was mostly used for the oxidation of CO and HCs in the TWC, its availability for soot oxidation was quite limited at the stoichiometric condition as exemplified in the GDI operating strategy. However, it is still unclear why ash layer could facilitate soot oxidation under this extremely low oxygen environment. The detailed soot oxidation mechanism in the presence of lube oil-derived ash and the nature of oxidation enhancer are under investigation.

Fig. 9

4. Conclusion

Our previous work showed that soot oxidative reactivity was enhanced with increased ash fraction in soot, which was further validated by low/high soot concentrations at different engine speed and load conditions in this work. Effects of Ca-, P- and ZDDP-derived ash were systematically examined as an extended work to better understand oxidation of GDI soot impacted by ash components. The TGA results confirmed that Ca-derived ash significantly enhanced soot oxidation, whereas P- and ZDDP-derived ash appreciably retarded soot oxidation. Since Ca additive is the most abundant among metal additives in lube oil, the promotion effect of lube oil-derived ash seems to be related to the dominance of Ca over other components. Based on synchrotron PXRD, SEM - EDS and XPS, complex Ca compounds seem to be responsible for the enhanced soot oxidation, although the contribution of CaSO_4 , a well-known ash compound, was almost negligible in this work. In consideration of reaction rate patterns and extremely-low Zn contents, the soot oxidation mechanism by ZDDP-derived ash is comparable with that by P-derived ash, in which the C-O-P formation would cause delayed soot oxidation. The GPF experiments presented that ash layer helped

facilitate soot oxidation by showing pressure drop decrease at a stoichiometric condition during the regeneration process, which validates our observation in the TGA experiments.

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References

- [1] European Commission, REGULATIONS - COMMISSION REGULATION (EU) 2016/427 of 10 March 2016, Official Journal of the European Union (2016) L 82/1–L 82/98.
- [2] California Air Research Board (CARB), The California Low-Emission Vehicle Regulations (With Amendments Effective January 1, 2016) (2016).
- [3] A. Mamakos, G. Martini, P. Dilara, Y. Drossinos, Feasibility of Introducing Particulate Filters on Gasoline Direct Injection Vehicles, Report No. EUR 25297 EN, JRC Scientific and Policy Report, EU Commission, 2011.

- [4] S. Choi and H. Seong, Oxidation characteristics of gasoline direct-injection (GDI) engine soot: Catalytic effects of ash and modified kinetic correlation, *Combust. Flame* 162 (6) (2015) 2371–2389.
- [5] J. Neeft, M. Makkee, J.A. Moulijn, Catalysts for the oxidation of soot from diesel exhaust gases. I. An exploratory study, *Appl. Cat. B: Environ.* 8 (1) (1996) 57–78.
- [6] J. Neeft, M. Makkee, J.A. Moulijn, Metal oxides as catalysts for the oxidation of soot, *Chem. Eng. J.* 64 (2) (1996) 295–302.
- [7] D. W. McKee, C. L. Spiro, and E. J. Lamby, The inhibition of graphite oxidation by phosphorus additives, *Carbon*, 22 (3) (1984) 285–290.
- [8] H. L. Fang and M. J. Lance, Influence of soot surface changes on DPF regeneration, *SAE Tech. Pap.* (2004) 2004-01-3043, doi:10.4271/2004-01-3043.
- [9] L. Castoldi, R. Matarrese, L. Lietti, P. Forzatti, Intrinsic reactivity of alkaline and alkaline-earth metal oxide catalysts for oxidation of soot, *Appl. Cat. B: Environ.* 90 (2009), 278–285.
- [10] H. Seong, A. Boehman, Impacts of intake oxygen enrichment on soot oxidative reactivity and soot properties of diesel soot, *Energy Fuels* 25 (2011), 602–616.
- [11] H. Jung, D.B. Kittelson, M.R. Zachariah, The influence of a cerium additive on ultrafine diesel particle emissions and kinetics of oxidation, *Combust. Flame* 142 (3) (2005) 276–288.
- [12] J. Song, J. Wang, A. L. Boehman, The role of fuel-borne catalyst in diesel particulate oxidation behavior, *Combust. Flame* 146 (1–2) (2006) 73–84.
- [13] X. Wu and L. R. Radovic, Inhibition of catalytic oxidation of carbon/carbon composites by phosphorus, *Carbon* 44 (1) (2006) 141–151.
- [14] M. Patel and P. B. Aswath, Morphology, structure and chemistry of extracted diesel soot–Part II: X-ray absorption near edge structure (xanes) spectroscopy and high resolution transmission electron microscopy, *Tribol. Int.* 52 (2012) 17–28.

- [15] A. Liati, A. Spiteri, P. D. Eggenschwiler and N. Vogel-Schäuble, Microscopic investigation of soot and ash particulate matter derived from biofuel and diesel: implications for the reactivity of soot, *J. Nanopart. Res.* 14 (2012) 1224.
- [16] D. Uy, M. A. Ford, D. T. Jayne, A. E. O'Neill, P. Haack, J. Hargas, M. J. Jagner, A. Sammut and A. K. Gangopadhyay, Characterization of gasoline soot and comparison to diesel soot: Morphology, chemistry, and wear, *Trib. Int.* 80 (2014) 198–209.
- [17] J. Baltrusaitis, C. R. Usher and V. H. Grassian, Reactions of sulfur dioxide on calcium carbonate single crystal and particle surfaces at the adsorbed water carbonate interface, *Phys. Chem. Chem. Phys.* 9 (2007) 3011–3024.
- [18] B. Demri and D. Muster, XPS study of some calcium compounds, *J. Mat. Proc. Tech.* 55 (1995) 311–314.
- [19] A. B. Christie, J. Lee, I. Sutherland and J. M. Walls, An XPS study of ion-induced compositional changes with group II and group IV compounds, *Appl. Surf. Sci.* 15 (1983) 224–237.
- [20] M. López Granados, M. D. Zafra Poves, D. Martín Alonso, R. Mariscal, F. Cabello Galisteo, R. Moreno-Tost, J. Santamaría, J. L. G. Fierro, Biodiesel from sunflower oil by using activated calcium oxide, *Appl. Cat. B: Environ.* 73 (2007) 317–326.
- [21] W. J. Landis and J. R. Martin, X-ray photoelectron spectroscopy applied to gold-decorated mineral standards of biological interest, *J. Vac. Sci. Tech. A*, 2 (1984) 1108–1111.
- [22] Y. Inoue and I. Yasumori, Catalysis by alkaline earth metal oxides. III. X-ray photoelectron spectroscopic study of catalytically active MgO, CaO, and BaO surfaces, *Bull. Chem. Soc. Jpn.* 54 (1981) 1505–1510.
- [23] H. Guo, S. Wang, C. Li, Y. Zhao, Q. Sun and X. Ma, Incorporation of Zr into calcium oxide for CO₂ capture by a simple and facile sol-gel method, *Ind. Eng. Chem. Res.* 55 (2016) 7873–7879.
- [24] R. L. Nyenge, H. C. Swart and O. M. Ntwaeaborwa, Luminescent properties, intensity degradation and X-ray photoelectron spectroscopy analysis of CaS:Eu²⁺ powder, *Opt. Mat.* 40 (2015) 68–75.
- [25] G. C. Smith, A. B. Hopwood and K. J. Titchener, Microcharacterization of heavy-duty diesel engine piston deposits, *Surf. Interface Anal.* 33 (2002) 259–268.

- [26] C. C. Chusuei, D. W. Goodman, M. J. Van Stipdonk, D. R. Justes and E. A. Schweikert, Calcium phosphate phase identification using xps and time-of-flight cluster sims, *Anal. Chem.* 71 (1999) 149–153.
- [27] B. G. Bunting, K. More, S. Lewis and T. Toops, Phosphorous poisoning and phosphorous exhaust chemistry with diesel oxidation catalysts, SAE paper, 2005-01-1758 (2005).
- [28] R. M. Heck, R. J. Farrauto and S. T. Gulati, Catalytic air pollution control: Commercial technology, 3rd edition, John Wiley & Sons, Inc., Hoboken, New Jersey (2009).
- [29] A. Majjane, A. Chahine, M. Et-tabirou, B. Echchahed, T. – O. Do and P. Mc Breen, X-ray photoelectron spectroscopy (XPS) and FTIR studies of vanadium barium phosphate glasses, *Mat. Chem. Phy.* 143 (2014) 779–787.
- [30] Y. Wang and P. M. A. Sherwood, Phosphorous pentoxide (P₂O₅) by XPS, *Surf. Sci. Spec.* 9 (2002) 159–165.
- [31] E. C. Onyiriuka, Zinc phosphate glass surfaces studied by xps, *J. Non-Crystalline Solids*, 163 (1993) 268–273.
- [32] D. L. Felker and P. M. A. Sherwood, Zinc phosphate (Zn₃(PO₄)₂) by XPS, *Surf. Sci. Spectra*, 9 (2002) 106–113.
- [33] D. Das and P. Mondal, Low temperature grown ZnO:Ga films with predominant c-axis orientation in wurtzite structure demonstrating high conductance, transmittance and photoluminescence, *RSC Adv.* 6 (2016) 6144–6153.
- [34] R. G. Herman, G. W. Simmons, D. A. Cole, V. Kuzmich and K. Klier, Catalytic action of minerals in the low temperature oxidation of coal, *Fuel*, 63 (1984) 673–678.
- [35] A. Sappok, R. Rodriguez, V. Wong, Characteristics and effects of lubricant additive chemistry on ash properties impacting diesel particulate filter service life, *SAE Int. J. Fuels Lubr.* 3 (1) (2010) 705–722.

Table captions

Table 1. GDI engine geometry and specifications

Table 2. Compositions of metal additives in gasoline/engine oil blends

Table 3. T90 changes against non-detergent oil-derived sample with ash fraction of 1.0 wt. % in soot

Table 4. Surface elemental analysis of soot from survey scans using XPS

Table 1. GDI engine geometry and specifications

Compression ratio	11.3
Bore (mm)	88
Stroke (mm)	97
Displacement (cm ³)	2,359
Number of cylinders	4
Rated power (kW)	147.8 @ 6300 rpm
Rated torque (Nm)	250 @ 4250 rpm

Table 2. Compositions of metal additives in gasoline/engine oil blends

Dosage in fuel (ppm)	Ca	Zn	P	Na	Total
Gasoline Only	0	0	0	0	0
Non-detergent oil 1.0%	0.4	3.3	2.7	0	6.4
Conv. Oil 1 – 2%	21.2 – 42.4	11.0 – 22.0	9.6 – 19.2	4.6 – 9.2	46.5 – 93
Calcium Sulfonate	8 – 24	0	0	0	8 – 24
Triethyl phosphite	0	0	18.2 – 54.7	0	18.2 – 54.7
ZDDP	0	8.1 – 191.25	7.5 – 206.55	0	15.6 – 397.8

Table 3. T90 changes against non-detergent oil-derived sample with ash fraction of 1.0 wt. % in soot

Additive type	Change ^a
Ca	+14.5%
P	-15.4%
ZDDP (Zn+P)	-13.7%
Conv. Oil	+11.1%

a: + indicates T90 decrease, while – does T90 increase

Table 4. Surface elemental analysis of soot from survey scans using XPS

Sample	Atomic %							
	O	C	Ca	P	Zn	S	N	total
Soot ^a	9.38	90.62	0	0	0	0	0	100.0
ND soot ^b	8.67	91.13	0	0	0	0.19	0	100.0
Ca soot (5.8%)	9.18	89.10	1.10	0.62	0	0	0	100.0
Ca soot (3.5%)	11.05	87.91	0.60	0.32	0	0	0	100.0
P soot (3.2%)	10.32	88.77	0	0.38	0	0	0.53	100.0
P soot (5.6%)	10.06	86.80	0	2.64	0	0	0.50	100.0
P-Zn soot (8.5%)	14.05	82.00	0	3.2	0.08	0	0.67	100.0
P-Zn soot (16.7%)	11.32	86.12	0	2.47	0.09	0	0	100.0

a: Soot with no oil addition, b: soot with non-detergent oil addition

Figure captions

Fig. 1. Schematic of GPF test setup

Fig. 2. Low and high soot calibrations of GDI engine and their TGA results: (a) ash fraction in soot over soot mass emission, (b) comparison of soot oxidation performed at isothermal condition, and (c) T90 with respect to ash fraction. The parenthesis in (b) legends indicates ash fraction in soot.

Fig. 3. Elemental analyses of commercial lube oils performed by ICP.

Fig. 4. TGA results of soot samples derived from various gasoline/lube oil blends: (a) soot remaining mass over time at 600 °C under 8% O₂ in N₂, and (b) T90 with respect to ash fraction.

Fig. 5. Instantaneous soot oxidation rates with respect to conversion with various additives present: (a) conventional oil and Ca additive, and (b) P and ZDDP additives.

Fig. 6. Synchrotron PXRD data of ash samples

Fig. 7. High-resolution XPS peaks of Ca-, P- and P-Zn-derived ash in soot. The parenthesis indicates ash fraction in soot.

Fig. 8. SEM analysis of Ca-derived samples: (a) SEM image of soot sample (400X), (b) XEDS at the position 1 of (a), (c) SEM image of ash sample (1000X), and (d) EDS at the position 2 of (c). The copper peak was originated from copper tapes.

Fig. 9. Comparison of pressure drop changes with and without ash loading using a TWC-coated GPF: (a) pressure drop increase and mass filtration efficiency with soot loading at 1250 rpm-25% load condition, and (b) pressure drop change over time at 2000 rpm-50% load condition.

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