Oxidation Characteristics of Gasoline Direct-Injection (GDI) Engine Soot: Catalytic Effects of Ash and Modified Kinetic Correlation

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ABSTRACT

In this paper, experimental analyses are conducted into the GDI soot oxidation characteristics as dependent on engine operating conditions. Soot is sampled at various engine operating conditions of a commercial 2.4 L GDI engine with a naturally aspirated, homogeneous, and stoichiometric operation strategy. The oxidation reactivity, ash composition, and carbon nanostructure of the GDI soot samples are analyzed using thermogravimetric analysis (TGA), scanning electron microscope–energy-dispersive spectroscopy (SEM-EDS), high-resolution transmission electron microscopy (HR-TEM), and Raman spectroscopy. Based on the analyses, a global GDI soot oxidation mechanism is proposed which includes the effects of soluble organic fractions (SOF)/weakly bonded carbon (WBC), and three types of ash on GDI soot oxidation. The results show that GDI soot contains an order of magnitude higher ash fraction than does conventional diesel soot, and oxidation reactivity is significantly enhanced by the catalytic effects of ash, as a function of ash content in soot. A modified empirical kinetic correlation for GDI soot oxidation is suggested on the basis of the results, and the modified kinetic correlation predicts the GDI soot oxidation rate accurately for various engine operation points at wide ranges of soot conversion and temperature without modifying kinetic parameters. The kinetic parameters are determined from isothermal and non-isothermal thermogravimetric analysis (TGA) soot oxidation tests; the methods are elucidated in detail.

KEYWORDS

Gasoline direct-injection (GDI) engine, Soot oxidation reactivity, Ash, Thermogravimetric analysis (TGA), Reaction kinetics

1. Introduction

Gasoline direct-injection (GDI) engines have been reported to produce more particulate matter (PM) than conventional port-fuel-injection (PFI) gasoline spark-ignition engines, especially during engine warm-up and transient conditions [1-3]. Current Euro-5 emission standards for light-duty vehicles require an 80% reduction in PM mass emissions relative to 2005's Euro-4 standards, and the particulate number (PN) emissions regulation of 6.0×10^{11} particles/km will be effective from 2017 in Euro-6c for the both diesel and GDI passenger vehicles [4]. Gasoline particulate filter (GPF) systems have been considered to reduce particulate number emissions, and a comprehensive understanding of the physical and oxidation characteristics of GDI engine particulate emissions is needed [5].

The oxidation characteristics of engine-generated soot are quite different from flame (model) soot, because PM emissions from engines are a complex mixture of volatile/soluble organics, sulfate, nitrate, carbonaceous soot, and ash, whose composition and fractions vary depending on engine type, operating conditions, and fuel/lube oil composition [3]. The oxidation reactivity of diesel soot has been of interest to many researchers, and the studies have shown that soot oxidation reactivity is affected by the physical (primary particle size, carbon nanostructure) and chemical (organic fractions, surface functional groups) properties of soot. Boehman and coworkers have investigated the effects of fuel formulation [6-9] and engine operating conditions [10,11] on diesel soot oxidation reactivity in a series of papers. It has been reported that biodiesel fueling increases the soluble organic fractions (SOF) and makes nanostructure more amorphous, both of which combine to enhance the soot oxidation reactivity of soot [6,7]. The significant structural change of the outer band and a subsequent hollowing out of soot particle during the early stages of oxidation are one reason of the high oxidation reactivity of biodiesel soot [8]. The relatively high amount of initial oxygen groups is another important factor governing the oxidation rate [9]. Exhaust gas recirculation (EGR)

increases disorder of soot nanostructure and enhances soot oxidation reactivity with faster internal burning of primary particles [10]. With respect to engine speed and load effects, the impact of engine speed at constant torque is more pronounced than the impact of engine torque (equivalence ratio) at constant engine speed, in which higher engine speed is related to more reactive soot and higher volatile organic fraction (VOF) content. Diesel soot reactivity also increases as the injection timing is retarded [11]. Liu et al. [12] have shown that diesel engine soot has lower carbon content (65–74%) than model soot (Printex U, 92%) and that the oxidation reactivity of diesel engine soot depends on engine load, with higher reactivity occurring at lower engine load. Wang et al. [13] studied the oxidation reactivity of in-cylinder soot during the diesel combustion process, and found that the aliphatic C–H groups are more important in governing soot oxidation reactivity than oxygenated surface functional groups. It is well known that metal additives in fuel contribute to higher soot oxidation reactivity, due to the catalytic effects of metal oxides in particulate emissions [14–18]. The effects of lube oil-derived ash and metallic species on soot oxidation remain less clear because their fractions are typically low. Miyamoto et al. [19] performed oxidations of diesel soot containing catalytic metals such as Ca, Ba, Fe, or Ni, and observed two-staged oxidation, in which the first stage of oxidation is catalytically promoted by metal additives resulting in enhanced reaction rate and reduced activation energy. Jung et al. [20] tested 2% lube oil-dosed fuel and found that the light-off temperature was reduced about 150–200°C and the oxidation rate was increased significantly. Kim et al. [21] found that the presence of metallic additives in lube oil increases diesel soot reactivity by factors of two to five. Seong and Boehman [22] also discussed the catalytic role of lube oil-derived metallic species on soot oxidation reactivity from intake oxygen-enriched diesel engine tests.

Previous studies of the reaction kinetics of carbonaceous soot have reported that the Arrhenius-type equation in Eq. (1) is well accepted for the temperature dependence of soot oxidation by oxygen [23,24],

$$r = \frac{d\alpha}{dt} = A \times e^{-E_a/RT} \times (1 - \alpha)^n \quad (1)$$

where r is the rate of reaction (s^{-1}), A is a pre-exponential factor (s^{-1}), E_a is activation energy (kJ mol^{-1}), R is the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), α is the degree of conversion, and n is reaction order.

Much research has been conducted on the oxidation kinetics of diesel soot with respect to the regeneration of diesel particulate filters [25-30]. Diesel soot generally shows wider ranges of kinetic parameters than model soot, due to its complex chemical and physical properties depending on engine operating conditions. Models that predict surface reaction (Langmuir-Hinshelwood) and surface area-based oxidation rates have been applied with the Arrhenius-type equation; however, in most cases, the kinetics of diesel soot could not be generalized, because the kinetic parameters differed with respect to engine operation points and soot conversion.

The oxidation kinetics of diesel soot in the presence of catalytic effects has been studied extensively. Ciambelli et al. proposed a kinetic model for carbon catalytic oxidation with a copper-vanadium-potassium catalyst, based on the assumption that different carbon portions enter the reaction zone at different times, which can be applied for different carbon/catalyst initial mass ratios [31]. Darcy et al. proposed mechanisms for catalyzed (Pt/CeZrO₂ catalyst) and non-catalyzed diesel soot oxidation with oxygen from temperature programmed oxidations (TPO) of real diesel soot. Kinetic parameters for the catalyzed soot oxidation were measured as being lower than for non-catalyzed soot, in which the reaction order of oxygen dropped from 0.9 to 0.3 and the activation energy decreased from 164 kJ/mol to 114 kJ/mol [32]. Yezerets et al. developed a technique that decouples the effects due to soot sample

history, such as adsorbed hydrocarbons and initial high reactivity parts, showing that carbon oxidation of diesel soot by O_2 in the absence of H_2O can be well described by an unmodified simple Arrhenius equation [33]. Reichert et al. constructed a global kinetic model for catalytic soot/ NO_x/O_2 conversion into N_2 and CO_2 on Fe_2O_3 using C_3H_6/O_2 mixture diffusion flame soot. This kinetic model consists of a global rate law for COx formation and NO reduction, wherein both equations are coupled by the number of reactive carbon sites [34].

Several results have been reported for the influences of fuel and lube oil metallic additives on diesel soot oxidation kinetics. The cerium additives in fuel significantly lowered the ignition temperature of soot and enhanced the soot oxidation rate; in terms of kinetics, the pre-exponential factor tended to increase solely, while the activation energy was equivalent to that for undosed fuel [17,18]. Jung et al. measured the oxidation rate of lube oil-dosed diesel particles using the HTO-TDMA (High Temperature Oxidation-Tandem Differential Mobility Analyzer) technique. The pre-exponential factors increased by about a factor of two, whereas the activation energy was very close to that of undosed diesel particles (108 kJ/mol), suggesting that the presence of Ca increased the active sites [20].

There have been few studies about the oxidation characteristics and kinetics of soot from GDI engines. Recent studies have shown that GDI soot is more reactive than diesel soot [5, 35]; however, details of GDI soot oxidation characteristics remain unknown, and there is no clear understanding why GDI engine soot exhibits higher oxidation reactivity. The activation energies for O_2 - and NO_2 -based oxidation of GDI soot were estimated to be 146 and 71 kJ/mol, respectively, which is comparable to corresponding values reported for diesel and model soot [35].

In this study, the oxidation characteristics of GDI engine soot at different engine operating conditions were investigated using TGA, and the properties of GDI soot and ash were analyzed using SEM-EDS, HR-TEM, and Raman spectroscopy. A global GDI soot oxidation

mechanism was proposed based on the analyses, and finally a modified empirically kinetic correlation was developed. The details of the modified kinetic correlation are discussed, including the developmental process and the determination of kinetic parameters from the soot oxidation data for different GDI engine operation points.

2. Experiment and analysis

2.1 Engine setup and operations

A 2.4 L 4-cylinder, naturally aspirated, GDI spark-ignition engine was used in this research. The engine geometry and specifications are given in

Table 1. This engine basically operated at homogenous and stoichiometric charge conditions, and fuel injection started during intake stroke at about 300° crank angle before top dead center (CA BTDC). ETAS hardware and INCA software interfaces were used to access the engine electronic control unit (ECU) to adjust the injection timing. Two pieces of wall-through type three-way catalysts (TWC) were installed at about 4 ft downstream of exhaust manifold to convert regulatory gaseous emissions, CO, HC, and NO_x. The engine was mounted on a 112 kW blower-cooled AC dynamometer for speed control and torque measurements. Exhaust emissions were measured using an exhaust gas analyzer (Horiba MEXA 7100-DEGR), and soot mass concentration was measured using a high-sensitivity photo-acoustic sensor (AVL 483 micro soot sensor). In this work, the certified Tier 2 EEE gasoline fuel and commercially available ILSAC GF-5 motor oil that was API SN rated with an SAE grade of 5W-20 were used.

Table 1.

2.2 PM sampling conditions

PM from raw exhaust gas was sampled on a Teflon[®] filter and then scraped off the filter. To elucidate the differences among the soot oxidation characteristics under different engine operating conditions, six sampling conditions were chosen for PM analyses. The conditions are listed in Table 2; Injection timing was 30°CA advanced beyond the optimal injection timing to simulate the high level of PM caused by wall wetting. The GDI-1 sample was obtained at 1,500 rpm-50%, in which soot concentration is at a high of 36 mg/m³. For the GDI-2 sample, 20 times of fuel-cut operations were subsequently added after the sampling condition of GDI-1 to investigate the effect of fuel-cut on GDI PM. The GDI-3 sample was collected at the cold-idle condition, from the engine start. GDI-4 and GDI-5 samples were collected at the engine-out and TWC-out sampling positions, respectively, at 1,250 rpm-25%. For the GDI-6 sample, the engine was operated at 1,500 rpm-50% with a gasoline fuel dosed with 2% lube oil by mass to clarify the effects of lube oil on GDI PM. In addition, Printex U from Degussa AG was compared with GDI soot samples as a model soot, because its physical properties are quite comparable to those of GDI soot in terms of primary particle size, nanostructures and carbon crystalline structures (Raman results are included for comparison in Fig. 8).

Table 2.

2.3 Characterization tools

Thermogravimetric analysis (TGA)

The compositions and oxidation reactivity of GDI soot were measured using TGA (TA Instruments Q50). The samples were thermally treated under nitrogen at 600°C for 30 min to remove volatile fractions. Isothermal and non-isothermal oxidation experiments were subsequently conducted under 8% of oxygen in nitrogen. Isothermal tests were performed at wide range of temperatures: 500, 550, 600, and 650°C; for non-isothermal tests, the furnace

temperature was reduced to 250°C under nitrogen and 8% of oxygen was then introduced with a 1°C/min heating rate [24]. Details of the TGA instrument and experimental protocols are listed in Table 3. 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.

Table 3.

High-resolution transmission electron microscopy (HR-TEM)

For TEM analysis, approximately 1 mg of each raw GDI PM sample was dispersed in acetone by sonication, until the soot particles were homogeneously mixed with acetone. A drop of aqueous dispersion of PM was delivered to a lacey carbon-coated Cu TEM grid. The TEM grid was loaded in a single tilt holder and the TEM images were taken at 200 kV acceleration voltage by a JEOL JEM-2100 F electron microscope. The energy dispersive X-ray (EDX) spectra were examined with an INCA X-ray microanalysis system equipped on the microscope. Particles were investigated in a magnification range of 20,000 to 600,000X and the HR-TEM images shown were all obtained at the magnification of 600,000X.

Raman spectroscopy

Raman spectra of soot samples were obtained on a Renishaw Raman Microscope (In Via). Wavelength was automatically calibrated with an internal reference. Samples were spread on sticky tape on a pin mount, and the 50X objective lens of the microscope was used to focus and collect spectra at several different sample locations for each sample using 1% of laser power at 633 nm (He-Ne laser source) to avoid sample degradation. The spectra were obtained with a 30-second exposure time with three accumulations in a Raman shift range of

500 to 2,500 cm^{-1} . The spectra were curve-fitted via IGOR Pro 6.22A software (Wavemetrics Inc.), where three Lorentzian-shaped peaks, G ($\sim 1,580 \text{ cm}^{-1}$), D1 ($\sim 1,360 \text{ cm}^{-1}$), and D4 ($\sim 1,180 \text{ cm}^{-1}$), and one Gaussian-shaped peak, D3 ($\sim 1,500 \text{ cm}^{-1}$), were obtained with a linear baseline. The D1 full width at half maximum (D1 FWHM) was used as a Raman parameter to evaluate the degree of the carbon crystalline order. Raman spectra of ordered carbons such as polycrystalline graphite have two distinct characteristic peaks at D1 ($\sim 1,360 \text{ cm}^{-1}$) and G ($\sim 1,580 \text{ cm}^{-1}$), while disordered and amorphous carbons have additional peaks that generally increase the height of the valley between the D1 and G peaks [36]. The physical meaning of the D1 FWHM relates to the distribution of crystallite size, which increases as graphitic structural order in soot decreases [22].

3. GDI PM compositions

The fractions of volatile organics, soot, and ash in the GDI engine PM samples and Printex U were analyzed by TGA experiments at a 600°C isothermal condition, as shown in Fig. 1. The model soot contained 5.74% of VOF without ash. The GDI PM samples showed wide ranges of VOF (2.02–15.68%) and ash fractions (0.10–17.27%), depending on sampled engine conditions.

Fig. 1

Fig. 2

The ash fraction tends to increase as the soot mass concentration decreases as shown in Fig. 2. The ash fraction of GDI-4 increased by a factor of six relative to that of GDI-1, while the soot mass per cycle decreased to one-fifth. Since ash is mostly derived from lube oil [37], the

ash fraction is determined by the relative ratio of combustion-generated soot and lube oil consumption in the combustion chamber. Both fuel-cut operation (GDI-2) and the cold-idle condition (GDI-3) increase VOF and ash fraction in GDI PM relatively. Under both conditions, higher reverse gas flow can occur through the top piston ring gap due to low cylinder pressure, which subsequently causes high oil mist transport into the cylinder with the gas flow [38]. The oil mist can then be adsorbed and/or mixed with soot and increase the organic and ash fractions in the PM. TWC reduces VOF and increases the ash fraction in GDI PM. VOF reduced from 5.14% (GDI-4) to 2.02% (GDI-5) due to oxidation of organic components in the TWC. The increase in the ash fraction can be explained by two factors: first, the reduction of total mass of soot (10 mg/m^3 to 7.7 mg/m^3) by the catalytic oxidation of organic fractions and diffusive/thermophoretic losses of nanoparticles, and, secondly, the detachment of support materials in the catalytic converter. 2% oil-dosed fuel (GDI-6) increases both VOF and ash fraction. VOF was measured as 9.58%, which is about 3% higher than that of the base condition (GDI-1), and the ash fraction significantly increased to 17.27%. The results show that lube oil in the combustion chamber contributes to ash as well as organic components in GDI PM.

Further analysis on ash composition was conducted using ash residues that remained after the TGA experiments of the engine-out sample (GDI-4) and the TWC-out sample (GDI-5). The compositions of the two samples were analyzed by SEM-EDS, and the results are shown in Fig. 3. Ca, Zn, and P were three major components in the engine-out ash that occupied 80% of total weight for the engine-out sample (GDI-4). This means that the ash in the engine-out PM is mostly derived from lube oil additives, such as ZDDP and calcium sulfonate. However, the ash components in the TWC-out sample are different from those in the engine-out sample. Higher fractions of Mg, Al, and Si were detected than in the engine-out PM. This result implies detachment of some support materials from the catalytic converter.

Fig. 3

4. Oxidation characteristics of GDI soot

4.1 Ash effects on GDI soot oxidation reactivity

The oxidation reactivities of Printex U and six different GDI soot samples were compared by TGA experiments. Fig. 4 shows the TGA results at the isothermal condition (600°C) and the non-isothermal condition (heating rate 1°C/min). Note that soot mass in the plots only describes the reacting soot and does not account for volatile organics and ash. Thus soot oxidation starts at 100% of mass and ends at 0% for all samples, regardless of VOF and ash fraction. Previous studies have reported that GDI soot is more reactive than model soot and diesel soot [5, 35]. However, the results in this work show that the oxidation reactivity of GDI soot can vary significantly, depending on engine operating conditions, and that the ash fraction is one of the most dominant factors enhancing oxidation reactivity. At isothermal 600°C, the sample mass decreased faster (Fig. 4a) and the times for 50% and 90% conversion became shorter (Fig. 4b) as the ash fraction increased. And at the non-isothermal condition, the oxidation temperature window widened (Fig. 4c) to lower temperature and the temperature for 90% conversion decreased with an increase in the ash fraction (Fig. 4d). GDI-1 contains the smallest amount of ash (0.1% of ash fraction), and consequently exhibited the lowest oxidation reactivity among the samples. Due to the low ash fraction, GDI-1 can serve as a reference for the other samples, indicating the intrinsic GDI soot oxidation reactivity when ash has a negligible effect. Interestingly, the oxidation rate of GDI-1 was measured to be slower than that of Printex U, which proposes that the intrinsic oxidation reactivity of GDI soot would be lower than that of Printex U, possibly because of the differences in physico-chemical properties. It was found that the oxidation rate of GDI soot

becomes similar to that of Printex U when the ash fraction is 0.58% (GDI-4), and that samples with higher ash fractions (GDI-5 and GDI-6) exhibited even faster oxidation rates. Approximately a 1% increase in the ash fraction (GDI-5) shortened the 90% conversion time by a half at isothermal 600°C and reduced the 90% conversion temperature by 25°C at the non-isothermal condition. With an excessive amount of ash (GDI-6, 17.37%), the oxidation became an order of magnitude faster at isothermal 600°C, and the oxidation temperature window was widened significantly, in which the oxidation was initiated at a much lower temperature, approximately 350°C. However, the fuel-cut (GDI-2, 0.26% of ash) and cold-idle (GDI-3, 0.50% of ash) samples show oxidation rates similar to GDI-1, despite higher ash fractions. Please note that even though GDI-3 (0.50%) had an ash fraction comparable to GDI-4 (0.58%), the contribution of ash to oxidation reactivity was lower with GDI-3 than with GDI-4.

Fig. 4

As explained in the previous section, ash mostly consists of the metallic species Ca, Na, Mg, Zn, and Al (Fig. 3), which stem from lube oil additives, engine wear, and catalytic converter detachments. The catalytic effects of the metals and metal oxides on soot oxidation have been well understood from previous works [39-46]. Among the components of ash, Ca is known to have high catalytic activities with respect to soot oxidation, while Mg and Zn have relatively weaker activities. Na also has good catalytic activity in the hydroxide and carbonate forms. Al itself has weak catalytic activity, but enhances the effect of others when it is used at the same time. Catalytic activity with respect to soot oxidation strongly depends on the contact condition between the soot particles and catalytic materials. It is obvious that ash in GDI soot plays a catalytic role that enhances soot oxidation reactivity, and the effects

become dominant as the ash fraction in soot increases. For diesel engines, there have been few studies discussing the catalytic effects of oil-derived ash on soot oxidation [19-22], because the catalytic effects of ash on soot oxidation are less significant than other effects (i.e., crystalline structure, surface chemistry) due to the low ash fraction in the soot.

4.2 GDI soot oxidation characteristics at different engine conditions

GDI soot oxidation characteristics were compared in more detail by describing soot oxidation in terms of an instantaneous soot oxidation rate represented the reaction rate (dm/dt) divided by the actual soot mass present in the filter. These instantaneous soot oxidation rates typically increase at high conversion and can provide the actual soot oxidation rate by relating the reaction rate to the soot mass actually present in the filter [27]. The instantaneous soot oxidation rates of the Printex U and GDI soot samples are depicted in Fig. 5. Printex U followed the typical oxidation kinetics of soot, in which the oxidation rate linearly increases with conversion of soot mass. GDI soot exhibited oxidation characteristics different from Printex U, in which oxidation varied depending on engine conditions; specifically, three-stage oxidation appeared, with higher oxidation rates at the initial and final stages and a relatively low oxidation rate at the intermediate stage. Especially at the final stage ($\alpha > 0.7$), the soot oxidation rate increased rapidly with an increase in soot mass conversion. GDI-1, the reference soot sample that has the negligible ash fraction, exhibited a much slower oxidation rate than Printex U. The oxidation rate of GDI-1 was comparable to that of Printex U at the initial stage, but, it became much slower at the intermediate stage, which implies that the intrinsic oxidation reactivity of GDI soot is lower than that of Printex U.

The instantaneous soot oxidation rates of the hot steady-state soot samples are shown in Fig. 5a. GDI soot oxidation reactivity was significantly promoted with an increase in ash fraction. The oxidation rate of GDI-6 (2% oil-dosed) was much faster than that of the

reference (GDI-1) by a factor of 10 with an ash fraction of 17.3%. The oxidation reactivity of GDI-4 with an ash fraction of 0.58% was comparable to that of Printex U; however, the oxidation rate of the intermediate stage was still slower than that of Printex U. It was found that TWC influences the GDI soot oxidation characteristics significantly: GDI-5 collected after the TWC at the same engine condition as GDI-4, showed higher oxidation reactivity than did GDI-4, due to the increase in ash fraction (0.58% $\rightarrow$ 1.35%). Interestingly, the initial oxidation rate decreased compared to that of GDI-4. As the decrease in VOF of GDI-5 (5.14% in GDI-4 and 2.02% in GDI-5, see Fig. 1) has evidently shown, the reason could be that highly reactive components such as organic fractions and weakly bonded carbons (WBC) at the initial oxidation stage were reduced by the catalytic reaction in the TWC. At the hot steady-state condition, the contribution of ash to soot oxidation reactivity is obvious, in which the oxidation rates of the intermediate and final stages increased significantly. The rapid increase in the oxidation rate at the final stage is attributed to the additional catalytic effect of ash by the increase in ash-to-carbon ratio. Fig. 5b depicts the instantaneous soot oxidation rates of the fuel-cut (GDI-2) and cold-idle (GDI-3) soot samples in comparison to Printex U and the hot steady state soot samples (GDI-1 and GDI-4). As explained in section 3, the VOF and ash fraction increased under fuel-cut and cold-idle operation (Fig. 1) because oil mist transported to the combustion chamber and the exhaust system at low in-cylinder temperature and pressure; consequently, the soot oxidation rates at the initial and final stages were made faster by the increases in VOF and ash fraction, respectively. However, the contribution of ash to soot oxidation reactivity was much lower under these conditions than under hot steady-state conditions; cold-idle soot (GDI-3, 0.50% ash) showed a much slower oxidation rate than the hot steady-state soot (GDI-4, 0.58 % ash) in the intermediate and final stages even with similar ash fractions. Comparable soot oxidation rates were observed at the intermediate stage for the reference, the fuel-cut, and cold-idle samples, which implies that catalytic

effects of ash are almost negligible at the intermediate oxidation stage in the case of fuel-cut and cold-idle samples. The results implies that ash in GDI soot can exist in various forms that provide different levels of catalytic effects on soot oxidation depending on engine operating conditions as well as the conversion of soot oxidation.

Fig. 5

The kinetic parameters of the typical kinetic expression were obtained from TGA data by taking logarithm of Eq. (1) as follows [24]:

$$\ln\left(\frac{d\alpha}{dt}\right) - n \cdot \ln(1 - \alpha) = -\frac{E_a}{RT} + \ln A \quad (2)$$

GDI soot doesn't obey the typical kinetic expression in Eq. (1). For instance, correlations between $\ln(da/dt)$ and $\ln(1-\alpha)$, shown in Fig. 6, were not linear for GDI soot samples, and the slopes, which correspond to the reaction order (n), changed as function of the conversion of soot. In contrast, Printex U, a model soot without ash, clearly showed a linear relationship between them, which means a constant reaction order (n) throughout the conversion of soot.

Fig. 6

The kinetic parameters of the Printex U and GDI soot samples are listed in Table 4. The reaction order was obtained from the slope of the linear regression of $\ln(da/dt)$ and $\ln(1-\alpha)$ for 10–90% conversion. The confidence of the linear regression was 99.98% for Printex U, but it was down to 95–97% for GDI soot. The activation energy and the pre-exponential factor were then obtained from the slope and y-intercept of the linear regression of $\ln(da/dt) - n \cdot \ln(1-\alpha)$ and $1/T$, respectively. The kinetic parameters of the GDI soot samples varied in wide ranges, and no clear correlation with engine operating condition was found. The results

showed that the oxidation kinetics of GDI soot cannot be generalized using the typical carbonaceous soot oxidation kinetic expression, in which the parameters change depending on the engine operating condition, as does the conversion of soot due to the additional SOF/WBC and ash effects on GDI soot oxidation.

Table 4.

5. GDI soot oxidation mechanism

5.1 Intrinsic carbon oxidation reactivity: carbon nanostructure analysis

It was found in the previous section that ash plays a catalytic role in enhancing the oxidation reactivity of GDI soot. The carbon nanostructure of soot can be another factor that affects soot oxidation reactivity [47]. In diesel soot, significant changes in oxidation reactivity have been reported depending on injection parameters, EGR rate, and fuel types, for which variations in carbon nanostructure and surface functional groups in the soot are primarily responsible [6-13]. The effect of ash in diesel soot oxidation is relatively small or negligible due to the very low ash fraction in the soot, and consequently has not been the subject of much attention. As is evidently shown from the oxidation rates between the hot steady-state reference sample (GDI-1) and the cold-idle sample (GDI-3) for the almost same intermediate stage, the intrinsic carbon oxidation reactivity of GDI soot might have less variation than diesel soot, depending on engine conditions.

To support this idea, the carbon nanostructures of GDI soot samples at different engine conditions were analyzed using HR-TEM and Raman spectroscopy. Fig. 7 shows TEM images of carbon nanostructures of GDI soot primary particles at (a) cold-idle and two hot steady-state conditions: (b) 1,250 rpm-25%, and (c) 1,500 rpm-50%. It was found that GDI soot nanostructures are well-defined with clear concentric fringe patterns even at the cold-idle

condition. The apparent nanostructures of these soot samples were found to be similar, despite a wide range of engine operating condition. As visualized from skeletonized images of GDI soot in our previous work [48], GDI soot tends to contain irregularly patterned fringes and inter-connected fringes, compared to more ordered diesel soot and carbon black. However, Gaddam and Vander Wal [49] showed that GDI soot samples from rich-fuel and retarded fuel-injection condition have less ordered nanostructures than do those from lean-fuel and standard fuel-injection conditions. However, no such contrast nanostructures were observed for GDI soot samples from various engine operating conditions in this work.

Fig. 7

These HR-TEM images can be further analyzed using imaging processing software to inform tortuosity, interlayer spacing and fringe length distribution. However, since the limited number of samples analyzed is subject to homogeneity, Raman instrument was employed to validate TEM results by analyzing carbon crystalline structures of bulk samples. Fig. 8 presents (a) Raman spectra and (b) the D1 FWHM Raman parameters for Printex U and the three different GDI soot samples shown in Fig. 7. The three GDI soot samples exhibit almost identical Raman spectra, which implies similar orders of carbon crystalline structures among the GDI PM samples. The GDI soot samples might have slightly higher degrees of order than Printex U, with similar intensities of the D1 and G peaks and lower valley height, which corresponds to the fraction of amorphous carbon. The D1 FWHM parameters also indicate similar crystalline structure ordering for Printex U and the GDI soot, with similar values around 190 cm^{-1} . Indeed, a slightly higher degree of order was measured for the 1,250 rpm-25% GDI soot sample than for Printex U. As found in Raman studies, the degree of disorder of Printex U is quite similar to those of various GDI soot samples, which was also

validated by our synchrotron X-ray studies, which are not included in this work. Average primary particle size of Printex U is around 30 nm, which is comparable to those of various GDI soot samples. Our FTIR studies indicate that surface oxygen functional groups in Printex U are much less present than those remaining in GDI soot. As shown in Fig. 1, Printex U contains a slightly lower VOF than do GDI soot samples. Typically soot oxidation is known to be enhanced when the degree of disorder increases and the amounts of surface functional groups increase. So, the reason why Printex U is much more reactive than GDI soot containing a negligible amount of ash is still unclear, because GDI-1 contains more surface functional groups at a comparable degree of disorder in crystalline structure. According to others [49], the organic content exists as matrix-bound organics in GDI soot. In that sense, this unique GDI soot structure may be responsible for the delayed soot oxidation when the ash content is low. To verify this assumption, more comprehensive physico-chemical effects are under examination to better understand this oxidation difference between Printex U and GDI soot with low ash content.

Fig. 8

The nanostructure analyses of GDI soot have shown that the GDI soot samples have similar carbon nanostructures independent of engine operating conditions in this work. However, diesel soot was observed to develop into more ordered structure with increasing engine load [50, 51]. This result is understandable in light of the combustion phenomena in diesel and GDI engines. In contrast to the spray droplet combustion of a diesel engine in which heterogeneous soot formation and oxidation occur under wide ranges of fuel-air mixture and flame temperature conditions [52], flame propagation combustion in the homogeneous and stoichiometric GDI engine provides more consistent in-cylinder fuel-air mixture and flame

temperature conditions independent of engine operating conditions. Consequently, the carbonaceous part of GDI soot has an intrinsic oxidation reactivity that is almost constant, regardless of engine operating conditions. Therefore, the differences in GDI soot oxidation rates described in section 4 are primarily due to the changes in organic fractions and the ash fraction rather than the difference in the carbon nanostructure of soot.

5.2 Difference in ash catalytic effects depending on engine operating condition: classification of ash in GDI soot

The effects of ash on soot oxidation vary depending on the engine operating conditions and the soot conversion. As discussed previously, the soot oxidation rate was proportional to the ash fraction at hot steady-state conditions (Fig. 5a); however, at cold-idle and fuel-cut conditions, the oxidation rate changed little with an increase in ash, especially at the intermediate stage (Fig. 5b). Also, there is a trend for all the samples that, the soot oxidation rate of the final stage became faster as the ash fraction increased. From these results, it is hypothesized that the ash in the GDI soot can be categorized into three different types according to its formation conditions and catalytic effects on soot oxidation. If lube oil in the combustion chamber undergoes high-temperature chemical reactions, lube oil additives become decomposed and remaining metals are oxidized primarily to metallic oxides. This type of ash is named “combustion-derived ash precursor” in this study. The lube oil in the combustion chamber can also flow out to the exhaust system and be adsorbed on soot particles without experiencing significant chemical reactions when the in-cylinder temperature is low. This type of ash is named “unburned ash precursor” in this study. The combustion-derived ash precursor and the unburned ash precursor can exist in the exhaust emissions at the same time, as described in the conceptual drawing of soot and ash in the exhaust emissions (left image in Fig. 9). The combustion-derived ash precursor (green) can

be nano-sized particles that can exist independently, become agglomerated in soot aggregates, or embedded in soot primary particles. The unburned ash precursor (blue) can also be independent nano-sized aerosols and also adsorbed in the soot particles. Once the particulates are accumulated in the filter, the soot cake becomes a soup of these nano-sized particles, in which the two types of ash precursors are almost uniformly dispersed in the soot primary particles, as shown in the first image after the arrow in Fig. 9. As soot cake oxidation progresses, the organics and carbon in the soot are gasified, and remaining adjacent ash precursors mingle together to become larger ash particles. These ash particles are named “oxidation-derived ash” as illustrated in Fig. 9. After completion of oxidation, only the oxidation-derived ash particles are left, which are micron-sized particles. These micron-sized ash particles are not found in the engine-out soot by our TEM analyses of thermophoretically-collected GDI particulates. In terms of the catalytic effects, the combustion-derived ash precursor provides strong catalytic effects on soot oxidation from the initial stage, due to its metallic oxide composition and good nano-level contact with soot particles. On the other hand, the unburned ash precursor plays little catalytic role because of its composition, which is mostly unburned oil additives such as ZDDP and calcium sulfonate. The oxidation-derived ash provides weaker catalytic effects than the combustion-derived ash precursor, because the micron-sized ash particles are in poor contact with soot particles. The ratio of the combustion-derived ash precursor to the unburned ash precursor in soot depends on engine operating conditions. At normal engine operation after warm-up, most of the ash in soot becomes combustion-derived ash. The unburned ash precursor increases at cold-idle and fuel-cut operation, when the low in-cylinder pressure increases lube oil consumption by transport [38], and most transported oil droplets flow out to the exhaust system and become adsorbed on the soot particles without experiencing significant chemical reactions at the low in-cylinder temperature. The high unburned ash precursor in cold-idle soot (GDI-3) is

responsible for the lower oxidation reactivity of the cold-idle soot relative to that of hot steady-state soot with a similar ash fraction (GDI-4).

Fig. 9

5.3 GDI soot oxidation mechanism

A global GDI soot oxidation mechanism has been proposed based on the GDI soot oxidation characteristics, as shown in Fig. 10. The dash-dot line corresponds to the intrinsic GDI carbon oxidation rate, which obeys the typical carbonaceous soot oxidation kinetic expression, and is assumed to be constant at different GDI engine operating conditions. The oxidation rate is shifted up to the dot line by the catalytic effects of the combustion-derived ash precursor. The combustion-derived ash precursor is nano-sized metallic oxide particles, uniformly dispersed in soot cake, as shown in Fig. 9, and provides strong and consistent catalytic effects on soot oxidation throughout conversion. However, the unburned ash precursor is in the form of unburned oil mist and cannot play any catalytic role on soot oxidation. The dot line, the carbon oxidation rate assisted by combustion-derived ash precursor, is assumed to follow the typical carbonaceous soot oxidation kinetic expression in this study. The solid line is the measured GDI soot oxidation rate (GDI-4), and the difference between the solid line and the dot line, shown as slashed areas at the intermediate and final stages, corresponds to the additional SOF/WBC oxidation and the additional carbon oxidation due to oxidation-derived ash, respectively. The oxidation-derived ash consists of micron-sized ash particles converted from the two ash precursors during the soot oxidation (Fig. 9). Even though its catalytic effect is weaker than the combustion-derived ash precursor due to worse contact with soot particles, its contribution on carbon oxidation becomes significant at a later part of soot conversion due to an increase in the ash-to-soot ratio.

Fig. 10

6. Modified oxidation kinetic correlation for GDI engine soot

A new modified oxidation kinetic correlation for GDI engine soot was developed on the basis of the global GDI soot oxidation mechanism suggested in this study, in which the effects of SOF/WBC and ash were taken into account. The suggested correlation can predict the instantaneous GDI soot oxidation rates under wide engine operating conditions at a given SOF/WBC and ash fraction. The equations in the modified oxidation kinetic correlation were derived empirically from the soot oxidation experiment using TGA. The following are the key assumptions of the new correlation:

1. There are three types of GDI engine particulates: SOF/WBC, carbon, and ash.
2. The intrinsic oxidation rate of the carbon part of GDI soot is constant.
3. There are three types of ash in soot cake: combustion-derived ash precursor, unburned ash precursor, and oxidation-derived ash (Fig. 9).
4. Ash is initially in precursor forms (combustion-derived ash precursor and unburned ash precursor) and is converted to oxidation-derived ash particles at the same rate of soot conversion (Fig. 9).
5. The oxidation rates of SOF/WBC and carbon assisted by combustion-derived ash precursor obey the typical kinetic expression in Eq. (1), and the kinetic parameters do not depend on engine operating condition.

Details about the modified kinetic correlation are explained in this section, including how it was derived and how the kinetic parameters were obtained from the soot oxidation experiments.

6.1 Mass balance of GDI soot cake oxidation

GDI engine particulates consist of soot (gasifiable compositions) and ash. In this study, the components of soot were simply divided into SOF/WBC and carbon, and the ash was defined as three types: combustion-derived ash precursor (Ash_C), unburned ash precursor (Ash_U), and oxidation-derived ash (Ash_O). The mass balance of each component can be written as in Eq. (3),

$$m_{total} = m_{soot} + m_{ash} = (m_{S-W} + m_C) + (m_{ash_C} + m_{ash_U} + m_{ash_O}) \quad (3)$$

where, m_{total} is the total mass of the PM sample, m_{soot} is the mass of soot, m_{ash} is the mass of ash, m_{S-W} is the mass of SOF/WBC, m_{ash_C} is the mass of combustion-derived ash precursor, m_{ash_U} is the mass of unburned ash precursor, and m_{ash_O} is the mass of oxidation-derived ash. The total mass of the PM sample (m_{total}) and the mass of ash (m_{ash}) are measured, and the mass of the other components can be obtained from the oxidation mechanism and assumptions.

The conversion of soot (α) is defined in Eq. (4),

$$\alpha = \frac{m_{soot,0} - m_{soot,i}}{m_{soot,0}} = 1 - \frac{m_{soot,i}}{m_{soot,0}} \quad (4)$$

where, the subscripts 0 and i stand for initial and instantaneous mass, respectively.

In TGA tests, m_{soot} goes down to zero after completion of the soot oxidation ($\alpha = 1$), while m_{ash} remains unchanged throughout the soot conversion. Initially, the combustion-derived ash precursor and the unburned ash precursor exist in soot cake, and the two ash precursors are converted to oxidation-derived ash at a same rate as soot mass conversion, as explained earlier. So, the initial mass of oxidation-derived ash ($m_{ash_O,0}$) is zero. Since the initial ratio between those two ash precursors changes depending on engine operating condition, the initial mass ratio of combustion-derived ash precursor ($R_{ash_C,0}$) is defined in Eq. (5) to express the initial amounts of those two ash precursors.

$$R_{ash_C,0} = \frac{m_{ash_C,0}}{m_{ash}} \quad (5)$$

Then, the initial mass of the unburned ash precursor is written as Eq. (6) using $R_{ash_C,0}$.

$$m_{ash_U,0} = m_{ash} \cdot (1 - R_{ash_C,0}) \quad (6)$$

Under normal hot engine operation, $R_{ash_C,0}$ is close to 1 because most of ash is the combustion-derived ash precursor. The unburned ash precursor increases under cold and fuel-cut engine operation.

The initial overall ash fraction is defined as the mass of ash divided by the initial total mass of PM sample, as shown in Eq. (7).

$$f_{ash,0} = \frac{m_{ash}}{m_{total,0}} = \frac{m_{total,0} - m_{soot,0}}{m_{total,0}} = 1 - \frac{m_{soot,0}}{m_{total,0}} \quad (7)$$

The ash fraction increases with conversion of soot, and the overall ash fraction at a certain conversion of soot can be calculated as a function of α and $f_{ash,0}$ as in Eq. (8). Eq. (8) is derived during the discussion of Eq. (A4) and (A5) in Appendix A.

$$f_{ash,i} = \frac{m_{ash}}{m_{total,i}} = \frac{f_{ash,0}}{1 - \alpha + \alpha \cdot f_{ash,0}} \quad (8)$$

The fraction of the combustion-derived ash precursor is defined in Eq. (9), and the fraction is constant ($f_{ash_C,0} = f_{ash_C,i}$) throughout the conversion of soot because the ash precursor is converted to the oxidation-derived ash at a same rate as soot conversion, by assumption.

$$f_{ash_C,0} = f_{ash_C,i} = \frac{m_{ash_C,0}}{m_{soot,0} + m_{ash_C,0}} = \frac{f_{ash,0} \cdot R_{ash_C,0}}{1 - f_{ash,0} \cdot (1 - R_{ash_C,0})} \quad (9)$$

The fraction of the oxidation-derived ash at a certain conversion of soot is defined in Eq. (10) and can be expressed as a function of α and $f_{ash,0}$. Derivation details are given in Appendix A.

$$f_{ash_O,i} = \frac{m_{ash_O,i}}{m_{soot,i} + m_{ash_O,i}} = \frac{\alpha \cdot f_{ash,0}}{1 - \alpha - f_{ash,0} + 2\alpha \cdot f_{ash,0}} \quad (10)$$

The fraction of the oxidation-derived ash from Eq. (10) is plotted in Fig. 11 as function of the conversion of soot for three GDI soot samples with different total ash fractions.

Fig. 11

6.2 Structure of modified kinetic correlation

In the modified kinetic correlation, the reaction rates of SOF/WBC (r_{S-W}) and carbon (r_C) are calculated separately, on the basis of the global GDI soot mechanism in Fig. 10. The reaction rate of SOF/WBC is attributed to the slashed area of the intermediate stage in Fig. 10 and is written as Eq. (11) following the typical kinetics,

$$r_{S-W} = \frac{d\alpha_{S-W}}{dt} = A_{S-W} \times e^{-E_{a,S-W}/RT} \times (1 - \alpha_{S-W})^{n_{S-W}} \quad (11)$$

where, α_{S-W} is the degree of conversion of SOF/WBC, defined in Eq. (12), A_{S-W} is the pre-exponential factor of SOF/WBC oxidation (s^{-1}), $E_{a,S-W}$ is the activation energy of SOF/WBC oxidation ($kJ\ mol^{-1}$), and n_{S-W} is the reaction order of SOF/WBC oxidation.

$$\alpha_{S-W} = \frac{m_{S-W,0} - m_{S-W,i}}{m_{S-W,0}} = 1 - \frac{m_{S-W,i}}{m_{S-W,0}} \quad (12)$$

The reaction rate of carbon in Eq. (13) consists of two parts; one is carbon oxidation assisted by Ash_C, which corresponds to the area under the dot line in Fig. 10, and the other is additional carbon oxidation assisted by Ash_O, which is attributed to the slashed area of the final stage in Fig. 10,

$$r_C = \frac{d\alpha_C}{dt} = A_C \times e^{-E_{a,C}/RT} \times (1 - \alpha_C)^{n_C} + [Ash_O_assist] \quad (13)$$

where, α_C is degree of conversion of carbon, defined in Eq. (14), A_C is pre-exponential factor of carbon oxidation (s^{-1}), $E_{a,C}$ is the activation energy of carbon oxidation ($kJ\ mol^{-1}$), n_C is the reaction order of carbon oxidation, and $[Ash_O_assist]$ is the additional carbon oxidation rate assisted by Ash_O.

$$\alpha_C = \frac{m_{C,0} - m_{C,i}}{m_{C,0}} = 1 - \frac{m_{C,i}}{m_{C,0}} \quad (14)$$

[*Ash_O_assist*] was derived from the soot oxidation experiments, and details concerning [*Ash_O_assist*] are discussed in section 6.4. The *Ash_C*-assisted carbon oxidation was written in the typical kinetic expression, and the kinetic parameters, A_C , $E_{a,C}$, and n_C need to be varied as a function of the fraction of *Ash_C* (f_{ash_C}), so that the catalytic effects of *Ash_C* on carbon oxidation can be accounted for.

The overall reaction rate (r) is then obtained as the sum of the SOF/WBC (r_{S-W}) and carbon (r_C) reaction rates, as written in Eq. (15).

$$r = \frac{d\alpha}{dt} = (m_{S-W,0}/m_{soot,0}) \cdot r_{S-W} + (m_{C,0}/m_{soot,0}) \cdot r_C \quad (15)$$

6.3 Kinetics of intrinsic GDI carbon oxidation

It was found that GDI soot has a constant intrinsic carbon oxidation reactivity that is lower than Printex U. The kinetic behavior of intrinsic GDI carbon oxidation was obtained using the GDI-1 sample, which has the lowest ash fraction among the samples. The effect of the combustion-derived ash precursor was regarded as negligible with only 0.10% of f_{ash_C} . The effects of SOF/WBC and the oxidation-derived ash were eliminated by taking the intermediate stage, 60–70% of the conversion range, for calculating the kinetic parameters, in which oxidation of SOF/WBC was thought to be completed and f_{ash_O} was negligibly small with only 0.1016% at 60% of soot conversion. Fig. 12 shows the linear regressions of the soot oxidation data to obtain the kinetic parameters of the intrinsic GDI carbon oxidation. The reaction order was calculated to 0.985 by taking a linear regression between $\ln(da/dt)$ and $\ln(1-\alpha)$ in Eq. (2) from isothermal soot oxidation at 600°C, as shown in Fig. 12a. The activation energy and pre-exponential factor were obtained from isothermal soot oxidation tests at four different temperatures: 500, 550, 600, and 650°C. The average values of $\ln(da/dt) - n \cdot \ln(1-\alpha)$ at 60–70% of conversion were calculated, which showed a good linear correlation with $1,000/T$, as shown in Fig. 12b. The slope and y-intercept of the linear regression line

provided the activation energy of 152.5 kJ/mol, and the pre-exponential factor of $491,885 \text{ s}^{-1}$ for the intrinsic GDI carbon oxidation.

Fig. 12

6.4 Kinetics of SOF/WBC oxidation and oxidation-derived ash assisted carbon oxidation

The measured soot oxidation rates of the GDI-1 sample and the calculated intrinsic GDI carbon oxidation rates at four different temperatures are plotted together in Fig. 13. The measured soot oxidation rates (solid lines) were always greater than the intrinsic GDI carbon oxidation rates (dot lines) at the initial and final stages, while both oxidation rates were similar at the intermediate stage, as described by the GDI soot oxidation mechanism (Fig. 10). The difference between the measured GDI soot oxidation rate and the simulated intrinsic carbon oxidation rate at the initial stage corresponds to the SOF/WBC oxidation, and the degree of conversion of SOF/WBC (α_{S-W}) in Eq. (12) could be calculated by subtracting the simulated oxidation rate from the measured oxidation rate during the initial stage. The difference at the final stage is attributed to the additional carbon oxidation assisted by the oxidation-derived ash, and the mass of oxidation-derived ash-assisted carbon oxidation ($m_{C_ash_O_assist}$) could be calculated in the same way.

Fig. 13

The kinetic behavior of SOF/WBC oxidation was written in the typical expression in Eq. (11), and the kinetic parameters were obtained by the method explained in section 6.3. Fig. 14 shows the linear regressions of the measured data at 20–80% of the conversion range of α_{S-W} to obtain the reaction order (n_{S-W}), activation energy ($E_{a, S-W}$), and pre-exponential factor

(A_{S-W}) of SOF/WBC. All of the data showed good linear correlations, which means the kinetics of SOF/WBC oxidation obey the typical expression. The linear regressions of $\ln(d\alpha_{S-W}/dt)$ and $\ln(1-\alpha_{S-W})$ at 20–80% of SOF/WBC conversion at four different temperatures, in which the slopes are the reaction orders of SOF/WBC, are shown in Fig. 14a. The reaction order tended to decrease at higher temperature, and, in this study, the average value of the four temperatures ($n_{S-W}=1.00327$) was taken. The activation energy and pre-exponential factor were obtained from the slope and y-intercept of linear regression of $\ln(d\alpha_{S-W}/dt) - n_{S-W} \cdot \ln(1-\alpha_{S-W})$ and $1,000/T$ as shown in Fig. 14b. Each data point in the plot represents the $\ln(d\alpha_{S-W}/dt) - n_{S-W} \cdot \ln(1-\alpha_{S-W})$ value at each temperature averaged at 20–80% of SOF/WBC conversion. The obtained values of the activation energy and pre-exponential factor for SOF/WBC were 147.3 kJ/mol and $1,646,232 \text{ s}^{-1}$, respectively.

Fig. 14

The oxidation kinetics of carbon was written as Eq. (13); in which, the last expression, $[Ash_O_assist]$, stands for the additional carbon oxidation assisted by the oxidation-derived ash. A new correlation was derived for $[Ash_O_assist]$ from the experimental data in this study. The additional carbon oxidation is expected to be a function of the fraction of oxidation-derived ash (f_{ash_O}), and the catalytic effect of the oxidation-derived ash is likely to be proportional to temperature. A clear linear correlation was found between the instantaneous oxidation-derived ash-assisted carbon oxidation rate ($\Delta m_{C_ash_O_assist}/m_{C,i}$) and f_{ash_O} at various temperatures, as shown in Fig. 15a. All the y-intercepts of the linear regressions were very small and could be regarded as zero, which means that the additional carbon oxidation becomes zero without the oxidation-derived ash. The slopes of the linear

regressions increased as the temperature got higher, and, as shown in Fig. 15b, the slope exponentially increased with temperature.

Fig. 15

Since the y-intercept of the linear correlation between $(\Delta m_{C_ash_O_assist}/m_{C,i})$ and f_{ash_O} is zero, the relationship can be written as Eq. (16).

$$\frac{\frac{dm_{C_ash_O_assist}}{dt}}{m_{C,i}} = (Slope) \cdot f_{ash_O,i} \quad (16)$$

Again, from the exponential correlation between the slope and temperature, Eq. (16) can be derived as Eq. (17),

$$\frac{\frac{dm_{C_ash_O_assist}}{dt}}{m_{C,i}} = (a \cdot \exp(b \cdot T)) \cdot f_{ash_O,i} \quad (17)$$

where, a and b are the coefficients of the exponential curve fitting in Fig. 15b, $5.70E^{-11}$ and $2.555E^{-2}$, respectively.

After multiplying $(m_{C,i}/m_{C,0})$ to both sides of Eq. (17), the mass expression of the equation became fitted to the reaction rate of carbon (da_C/dt) in Eq. (13), as shown in Eq. (18).

$$\frac{\frac{dm_{C_ash_O_assist}}{dt}}{m_{C,0}} = \frac{m_{C,i}}{m_{C,0}} \cdot (a \cdot \exp(b \cdot T)) \cdot f_{ash_O,i} \quad (18)$$

Finally, by applying Eq. (13) in Eq. (18), $[Ash_O_assist]$ was derived as shown in Eq. (19).

$$[Ash_O_assist] = \frac{\frac{dm_{C_ash_O_assist}}{dt}}{m_{C,0}} = (1 - \alpha_C) \cdot (a \cdot \exp(b \cdot T)) \cdot f_{ash_O,i} \quad (19)$$

The coefficients a and b were defined as new kinetic parameters for the modified kinetic correlations.

6.5 Kinetics of combustion-derived ash precursor assisted carbon oxidation

As described in the global GDI soot oxidation mechanism, Ash_C promotes oxidation of the carbon part of GDI soot through conversion (attributed to the dot line in Fig. 10). Since the oxidation of carbonaceous soot obeys the typical kinetic expression, the kinetics were written as the first part of Eq. (13). In this study, the kinetic parameters A_C , $E_{a,C}$, and n_C were obtained as a function of f_{ash_C} , so that the catalytic effect of Ash_C can be taken into account. Those three kinetic parameters were determined from the isothermal oxidation tests (TGA) of three hot steady GDI soot samples (GDI-1, GDI-4, GDI-5) with different ash fractions, because all the ash in hot steady GDI soot is initially regarded as the combustion-derived ash precursor. To separate the oxidation rate only by Ash_C-assisted carbon from the measured soot oxidation rate, the SOF/WBC oxidation rate calculated using Eq. (11) (attributed to the slashed area at the initial stage of Fig. 10) and the Ash_O-assisted carbon oxidation rate calculated using Eq. (19) (attributed to the slashed area at the final stage of Fig. 10) were subtracted from the measured soot oxidation rate. The reaction order of Ash_C-assisted carbon oxidation could then be calculated by the slope of the linear regression of $\ln(d\alpha_C/dt - [Ash_O_assist])$ and $\ln(1 - \alpha_C)$ from Eq. (20), which was obtained by taking the logarithm of Eq. (13).

$$\ln\left(\frac{d\alpha_C}{dt} - (1 - \alpha_C) \cdot (a \cdot \exp(b \cdot T)) \cdot f_{ash_O,i}\right) = n_C \cdot \ln(1 - \alpha_C) - \frac{E_{a,C}}{RT} + \ln A_C \quad (20)$$

The linear regressions of Printex U and the four GDI soot samples (GDI-1, -3, -4, -5) are shown in Fig. 16, and all of the data showed good linear correlations, which evidently proves the exactness of the kinetic correlations. The reaction order (n_C) became smaller as the ash fraction in the soot sample increased for the three hot steady soot samples (GDI-1, -4, -5). The reaction order of cold-idle soot sample (GDI-3) was measured higher, 1.0465, than for GDI-1, even with its higher overall ash fraction (f_{ash}), 0.50%. This means that the Ash_C fraction (f_{ash_C}) of GDI-3 can be lower than for GDI-1, 0.10%, and initially there are large

amounts of Ash_U in soot cake at cold-idle engine operation, while the ash of hot steady soot samples is mostly Ash_C.

Fig. 16

The reaction orders of three hot steady GDI soot samples (GDI-1, -4, -5) showed good linear relations with Ash_C fraction (f_{ash_C}), as shown Fig. 17a. From the linear regression, the reaction order of Ash_C-assisted carbon oxidation (n_C) was expressed as a linear function of f_{ash_C} : $n_C = -0.1854 \times f_{ash_C} [\%] + 1.0047$. It was assumed that the pre-exponent factor (A_C) was not affected by ash, and the value of A_C was set to $491,885 \text{ s}^{-1}$, which is the A_C of intrinsic GDI carbon, for all GDI soot samples. The activation energy ($E_{a, C}$) could then be determined by matching the calculated and measured reaction rates of carbon at isothermal 600°C for each soot sample. The activation energy also tended to decrease as f_{ash_C} increased, but changed in a much smaller range than the reaction order, from 152.51 kJ/mol to 151.00 kJ/mol for 1.35% of Ash_C. The implication of this result is that 1% ash in GDI soot is too small to decrease the active temperature window significantly; however, ash may cause physical changes in carbon structure and soot cake during oxidation, such as an increase in surface area, which increases the reaction rate at higher conversion. The relation between $E_{a, C}$ and f_{ash_C} is given as $E_{a, C} [\text{kJ mol}^{-1}] = -1.169 \times f_{ash_C} [\%] + 152.5$, as shown in Fig. 17b.

Fig. 17

The kinetic parameters of Ash_C-assisted carbon oxidation for five GDI soot samples are listed in Table 5. The same kinetic parameters were used for the GDI-1 sample and the GDI-2 sample. f_{ash_C} of the GDI-2 sample is thought to be identical to that of the GDI-1 sample,

because the GDI-2 sample was prepared by adding 20 times of fuel-cut operation after sampling soot at the same engine operating condition as the GDI-1 sample.

Table 5.

6.6 Validation of modified kinetic correlation

The overall oxidation rates predicted by the modified kinetic correlation written as Eq. (15) were validated with measured oxidation rates for five GDI soot samples. The initial amounts (mass%) of SOF/WBC, f_{ash_C} , and f_{ash_U} are required inputs of the modified kinetic correlation; however, those inputs could not be measured directly. The amount of SOF/WBC was determined by integrating the difference between the measured oxidation rate and the calculated carbon oxidation rate given by Eq. (13) for each sample. The amounts (mass%) of SOF/WBC for the five soot samples showed a linear correlation with VOF measured by TGA as shown in Fig. 18, and the amount of SOF/WBC in the GDI soot sample can be determined from the VOF measured by TGA [28].

Fig. 18

Since no Ash_U was assumed in hot steady GDI soot, initial ashes in hot steady GDI soot samples were regarded as Ash_C. For fuel-cut (GDI-2) and cold-idle (GDI-3) soot samples, f_{ash_C} was assumed to be the same as for the GDI-1 sample, and the rest of the ashes became Ash_U. The initial amounts (mass%) of SOF/WBC, Ash_C, and Ash_U used for simulation of five GDI soot samples are listed in Table 6.

Table 6.

The formulas for the modified kinetic correlation for GDI soot are arrayed in Table 7, and the eight kinetic parameters are marked in red. The values of the eight kinetic parameters for the tested GDI engine, lube oil, and fuel are listed in Table 8. The oxidation rates of the different GDI soot samples were calculated using these formulas and kinetic parameters.

Table 7.

Table 8.

The soot oxidation rates measured by TGA and simulated by typical and modified kinetics for five GDI soot samples are plotted in Fig. 19 (isothermal at 600°C) and Fig. 20 (non-isothermal) for validation of the modified kinetic correlation. For each GDI soot sample, soot oxidation rates of measured ($\diamond$, solid line) and calculated typical (solid line) and modified (dot line) kinetics are overlapped in one plot. Calculated oxidation rates of each component by the modified kinetics, Ash_C-assisted carbon oxidation ($\square$), Ash_O-assisted carbon oxidation (Δ), and SOF/WBC oxidation ($\times$) (all in dot lines) are also shown in the same plot. In the typical kinetic expression, kinetic parameters obtained at 10–90% of conversion (Table 4) were used. As shown in the results for isothermal oxidation at 600°C (Fig. 19), the soot oxidation rates predicted by the typical kinetic expression did not match measured data, in which they underestimated soot oxidation rates of the initial and final stages and overestimated the intermediate stage soot oxidation. For non-isothermal oxidation (Fig. 20), the typical kinetic expression tended to overestimate the soot oxidation rates at 550–600°C and underestimate the soot oxidation rates at over 600°C, and the soot samples were

predicted to remain at higher temperature than the measurements. Because 500–800°C is the temperature range of interest in GPF, the inaccurate prediction by the typical kinetic expression may cause significant error in a soot cake oxidation simulation. The kinetic parameters for the typical kinetic expression are required to be changed in accordance with engine operating conditions, as well as conversion of soot. The modified kinetic correlation provided very accurate predictions of soot oxidation rates at wide ranges of conversion (Fig. 19) and temperature (Fig. 20) for various GDI engine operating conditions without changing the kinetic parameters. This means that once the eight kinetic parameters are determined for a target GDI engine from the methods suggested in previous sections, the soot oxidation rate of the target GDI engine can be predicted for any engine operating points using the modified kinetic correlation.

Fig. 19

Fig. 20

7. Conclusion

GDI soot oxidation characteristics of a naturally aspirated, homogenous, and stoichiometric GDI engine were analyzed in detail using TGA, SEM-EDS, HR-TEM, and Raman spectroscopy. The catalytic effects of ash that dominate the oxidation reactivity of GDI soot were clearly presented for the first time, and a mechanism and modified kinetic correlation of GDI soot oxidation were proposed.

As compared to Printex U, GDI soot had lower intrinsic carbon oxidation reactivity, but overall oxidation reactivity became higher due to the catalytic effects of ash in GDI soot, which is an order of magnitude higher fraction than in the diesel soot. Different from diesel

soot, GDI soot was found to have an almost constant intrinsic carbon oxidation reactivity, which does not change with engine operation conditions. Ash in GDI soot was categorized into three different types: combustion-derived ash precursor, unburned ash precursor, and oxidation-derived ash. The combustion-derived ash precursor is the product of combustion of oil additives, while the unburned ash precursor is oil mists discharged without major reactions. The oxidation-derived ash is micron-sized ash particles converted from the ash precursors during soot oxidation. At the hot steady-state engine conditions, the GDI soot oxidation reactivity was improved proportionally with ash fraction because most of ash is the combustion-derived ash precursor; however, the ash effects were diminished at cold-idle and fuel-cut operations where the in-cylinder temperature and pressure are low, because most of ash is unburned ash precursor. The GDI soot cake oxidation mechanism was proposed based on the series of analysis results, which can represent three-staged oxidation of the GDI soot by separating the effects of SOF/WBC and three different types of ash on soot oxidation.

The typical kinetic expression did not hold for the GDI soot oxidation rate primarily due to the SOF/WBC and catalytic effects of ash on GDI soot oxidation. The kinetic parameters in the typical expression had to be changed for different engine operation points, and the predicted soot oxidation rate did not agree with the measured data depending on the soot conversion and temperature ranges. Following the GDI soot oxidation mechanism, the modified empirical kinetic correlation was developed which includes separate formulas for SOF/WBC oxidation and the additional carbon oxidations by the catalytic effects of ashes (Table 7). The eight kinetic parameters in the modified correlation – three for SOF/WBC oxidation, three for carbon oxidation assisted by Ash_C, and two for carbon oxidation assisted by Ash_O – were obtained from the isothermal and non-isothermal TGA tests of GDI soot samples at various engine operating conditions (Table 8). Soot oxidation simulated

using the modified kinetic correlation showed good agreement with measured data for various engine conditions at wide ranges of temperature and soot conversion.

The initial amounts of SOF/WBC, Ash_C, and Ash_U remained uncertain for the modified kinetic correlation. SOF/WBC can be indirectly measured from VOF (Fig. 18), and ash fraction can be determined both by TGA test and/or by measuring soot concentration and lube oil consumption. The modified kinetic correlation can predict GDI soot oxidation accurately, if databases of the amounts of SOF/WBC, Ash_C, and Ash_U are prepared as functions of engine conditions. The suggested GDI soot oxidation mechanism and modified kinetic correlation may be valid for any naturally aspirated, homogenous, and stoichiometric GDI engine, but further validation may be necessary in the future for other types of GDI engines, such as boosted, external exhaust gas recirculation, and lean stratified GDI engines, in which changes in soot properties are expected to be significant.

The catalytic effect of ash is expected to dominate the oxidation reactivity of soot from advanced combustion engines such as low-temperature combustion, of which soot mass emission is low. And in the gasoline particulate filter, a large amount of low-reactive cold soot is initially captured during cold engine start and warm-up periods, and then high-reactive soot will accumulate on the cold soot after the engine is warmed up. Thus, the overall oxidation reactivity of soot in the filter will depend on the duration of the driving cycle.

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References

1. S. Daniel, K. Achim, S. Peter, F. Jan, D. Arndt, SAE Tech. Pap. (2011) 2011-01-0143, doi:10.4271/2011-01-0143.
2. O. Kannapin, T. Guske, MTZ 11 (2010) 16.
3. C.L. Myung, S. Park, Int. J. Automot. Tech. 13(1) (2012) 9–22.
4. DieselNet, Emission Standards European Union, Cars and Light Trucks, <http://www.dieselnet.com/standards/eu/ld.php>, Jan. 5, 2014.
5. A. Mamakos, G. Martini, P. Dilara, Y. Drossinos, Feasibility of Introducing Particulate Filters on Gasoline Direct Injection Vehicles, JRC Scientific and Policy Report, JRC68675, EUR 25297 EN, EU Commission, 2011, doi:10.2788/23375.
6. A.L. Boehman, J. Song, M. Alam, Energy Fuels 19(5) (2005) 1857–1864.

7. K. Yehliu, R.L. Vander Wal, O. Armas, A.L. Boehman, *Combust. Flame* 159 (2012) 3597–3606.
8. J. Song, M. Alam, A.L. Boehman, U. Kim, *Combust. Flame* 146(4) (2006) 589–604.
9. J. Song, M. Alam, A.L. Boehman, *Combust. Sci. Tech.* 179(9) (2007) 1991–2037.
10. K. Al-Qurashi, A.L. Boehman, *Combust. Flame* 155(4) (2008) 675–695.
11. K. Yehliu, O. Armas, R.L. Vander Wal, A.L. Boehman, *Combust. Flame* 160 (2013) 682–691.
12. J. Liu, Z. Zhao, C. Xu, A. Duan, G. Jiang, *Energy Fuels* 24(7) (2010) 3778–3783.
13. L. Wang, C. Song, J. Song, G. Lv, H. Pang, W. Zhang, *Proc. Combust. Inst.* 34 (2012) 3099–3106.
14. F. Bonnefoy, P. Gilot, B.R. Stanmore, G. Prado, *Carbon* 32(7) (1994) 1333–1340.
15. J. Lahaye, S. Boehm, P.H. Chambrion, P. Ehrburger, *Combust. Flame* 104(1) (1996) 199–207.
16. J.F. Brilhac, B. Stanmore, P. Gilot, *SAE Tech. Pap.* (1999) 1999-01-0115, doi: 10.4271/1999-01-0115.
17. G.A. Stratakis, A.M. Stamatelos, *Combust. Flame* 132(1) (2003) 157–169.
18. H. Jung, D.B. Kittelson, M.R. Zachariah, *Combust. Flame* 142(3) (2005) 276–288.
19. N. Miyamoto, H. Zhixin, O. Hideyuki, *SAE Tech. Pap.* (1988), 881224, doi: 10.4271/881224.

20. H. Jung, D.B. Kittelson, M.R. Zachariah, SAE Tech. Pap. (2003) 2003-01-3179, doi: 10.4271/2003-01-3179.
21. S.H. Kim, R.A. Fletcher, M.R. Zachariah Environ. Sci. Tech. 39(11) (2005) 4021–4026.
22. H.J. Seong, A.L. Boehman, Energy Fuels 25(2) (2011) 602–616.
23. B. R. Stanmore, J. F. Brilhac, P. Gilot, Carbon, 39(15) (2001) 2247-2268.
24. K.O. Lee, H. Seong, S.M. Choi, Proceed. Combust. Inst. 34 (2012) 3057–3065.
25. A. Fredrik Ahlström, C. U. Ingemar Odenbrand, Carbon, 27(3) (1989), 475-483.
26. J. Neeft, T. X. Nijhuis, E. Smakman, M. Makkee, J. A. Moulijn, Fuel, 76(12) (1997) 1129-1136.
27. A. Messerer, R. Niessner, U. Pöschl, Carbon 44(2) (2006) 307-324.
28. M. Lapuerta, R. Ballesteros, J. Rodríguez-Fernández, Measurement Science and Technology, 18(3) (2007) 650.
29. J. Rodríguez-Fernández, F. Oliva, R. A. Vazquez, Energy & Fuels, 25(5) (2011) 2039-2048.
30. H. S. Chong, S. K. Aggarwal, K. O. Lee, S. Y. Yang, H. Seong, Combustion Science and Technology, 185(1) (2013) 95-121.
31. P. Ciambelli, M. D'amore, V. Palma, S. Vaccaro, Symposium (International) on Combustion, 26(1) (1996) 1789-1796.

32. P. Darcy, P. Da Costa, H. Mellottée, J. M. Trichard, G. Djega-Mariadassou, *Catalysis Today*, 119(1) (2007) 252-256.
33. A. Yezerets, N. W. Currier, D. H. Kim, H. A. Eadler, W. S. Epling, C. H. Peden, *Applied Catalysis B: Environmental*, 61(1) (2005) 120-129.
34. D. Reichert, T. Finke, N. Atanassova, H. Bockhorn, S. Kureti, *Applied Catalysis B: Environmental*, 84(3) (2008) 803-812.
35. C. Wang-Hansen, P. Ericsson, B. Lundberg, M. Skoglundh, P.A. Carlsson, B. Andersson, *Topics Catalysis* 56 (2013) 446–451.
36. A. Soewono, S. Rogak, *Aerosol Sci. Tech.* 45(10) (2011) 1206–1216.
37. S.A.G. Watson, doctoral dissertation, Massachusetts Institute of Technology, 2010.
38. E. Yilmaz, T. Tian, V.W. Wong, J.B. Heywood, *SAE Tech. Pap.* (2004) 2004-01-2909, doi:10.4271/2004-01-2909.
39. D.W. McKee, *Carbon* 8(5) (1970) 623–635.
40. J. Neeft, M. Makkee, J.A. Moulijn, *Appl. Catalysis B: Environ.* 8(1) (1996) 57–78.
41. J. Neeft, M. Makkee, J.A. Moulijn, *Chem. Eng. J.* 64(2) (1996) 295–302.
42. G. Neri, L. Bonaccorsi, A. Donato, C. Milone, M.G. Musolino, A.M. Visco, *Appl. Catalysis B: Environ.* 11(2) (1997) 217–231.
43. C.A. Querini, M.A. Ulla, F. Requejo, J. Soria, U.A. Sedrán, E.E. Miró, *Appl. Catalysis B: Environ.* 15(1) (1998) 5–19.

44. M.N. Bokova, C. Decarne, E. Abi-Aad, A.N. Pryakhin, V.V. Lunin, A. Aboukais, *Thermochimica acta* 428(1) (2005) 165–171.
45. E. Saab, E. Abi-Aad, M.N. Bokova, E.A. Zhilinskaya, A. Aboukaïs, *Carbon* 45(3) (2007) 561–567.
46. F. Bin, C. Song, G. Lv, J. Song, K. Wang, X. Li, *Proceed. Combust. Inst.* 34 (2012) 2303–2311.
47. R.L. Vander Wal, A.J. Tomasek, *Combust. Flame* 134(1) (2003) 1–9.
48. H. Seong, K. Lee, S. Choi, *SAE Tech. Pap.* (2013) 2013-01-2574, doi:10.4271/2013-01-2574.
49. C. K. Gaddam, R. L. Vander Wal, *Combust. Flame* 160(11) (2013) 2517–2528.
50. A. Braun, N. Shah, F. E. Huggins, K. E. Kelly, A. Sarofim, C. Jacobsen, S. Wirick, H. Francis, J. Ilavsky, G.E. Thomas, G. P. Huffman, *Carbon*, 43(12) (2005) 2588–2599.
51. H. J. Seong, A. L. Boehman, *Energy & Fuels* 27(3) (2013) 1613–1624.
52. J.E. Dec, *SAE Tech. Pap.* (1997) 970873, doi:10.4271/970873.

Abbreviations

Ash_C Combustion-derived ash precursor

Ash_O Oxidation-derived ash

Ash_U Unburned ash precursor

BTDC Before top dead center

CA	Crank angle
GDI	Gasoline direct-injection
SOF	Soluble organic fractions
TGA	Thermogravimetric analysis
TWC	Three-way catalyst
VOF	Volatile organic fractions
WBC	Weakly bonded carbon
ZDDP	Zinc dialkyldithiophosphates

Nomenclature

A	Pre-exponential factor (s^{-1})
A_C	Pre-exponential factor of carbon oxidation (s^{-1})
A_{S-W}	Pre-exponential factor of SOF/WBC oxidation (s^{-1})
α	Degree of conversion
α_C	degree of conversion of carbon in soot
α_{S-W}	Degree of conversion of SOF/WBC in soot
E_a	Activation energy ($kJ\ mol^{-1}$)
$E_{a,C}$	Activation energy of carbon oxidation ($kJ\ mol^{-1}$)
$E_{a,S-W}$	Activation energy of SOF/WBC oxidation ($kJ\ mol^{-1}$)
f_{ash}	Overall ash fraction
f_{ash_C}	Fraction of combustion-derived ash precursor
f_{ash_O}	Fraction of oxidation-derived ash
f_{ash_U}	Fraction of unburned ash precursor
m	Instant soot mass (mg)
m_0	Initial soot mass (mg)
m_{ash}	Mass of ash (mg)
m_{ash_C}	Mass of combustion-derived ash precursor (mg)
m_{ash_O}	Mass of oxidation-derived ash (mg)

m_{ash_U}	Mass of unburned ash precursor (mg)
m_C	Mass of carbon (mg)
$m_{C_ash_O_assist}$	Mass of oxidation-derived ash assisted carbon oxidation (mg)
$m_{instant}$	Instantaneous soot mass (mg)
m_{S-W}	Mass of SOF/WBC (mg)
m_{soot}	Mass of soot (mg)
m_{total}	Total mass of PM sample (mg)
m_0	Initial soot mass (mg)
n	Reaction order
n_C	Reaction order of carbon oxidation
n_{S-W}	Reaction order of SOF/WBC oxidation
r	Overall reaction rate (s^{-1})
R	Universal gas constant ($kJ\ mol^{-1}\ K^{-1}$)
r_C	Reaction rate of carbon in soot (s^{-1})
r_{S-W}	Reaction rate of SOF/WBC in soot (s^{-1})
R_{ash_C}	Mass ratio of combustion-derived ash precursor
T	Temperature (K)
$[Ash_O_assist]$	Additional carbon oxidation rate assisted by Ash_O (s^{-1})

Subscripts

0	Initial value
i	Instantaneous value

Appendix A

The instantaneous fraction of oxidation-derived ash ($f_{ash,O,i}$) needs to be expressed as function of soot conversion (α) and the initial overall ash fraction ($f_{ash,0}$) for the convenient calculation of Ash_O-assisted carbon oxidation. The derivation process is introduced as follows.

The initial overall ash fraction can be written as Eq. (A1).

$$f_{ash,0} = \frac{m_{ash}}{m_{total,0}} = \frac{m_{ash}}{m_{soot,0} + m_{ash}} = \frac{m_{ash,C,0} + m_{ash,U,0}}{m_{soot,0} + m_{ash,C,0} + m_{ash,U,0}} \quad (A1)$$

By the assumption, “ash is initially in precursor forms (combustion-derived ash precursor and unburned ash precursor), and converted to oxidation-derived ash particles at the same rate of soot conversion,” Eq. (A1) can be written as Eq. (A2); thus Eq. (A3) is derived.

$$f_{ash,0} = \frac{m_{ash,C,0} + m_{ash,U,0}}{m_{soot,0} + m_{ash,C,0} + m_{ash,U,0}} = \frac{m_{ash,C,i} + m_{ash,U,i}}{m_{soot,i} + m_{ash,C,i} + m_{ash,U,i}} \quad (A2)$$

$$m_{ash,C,i} + m_{ash,U,i} = \frac{m_{soot,i} \cdot f_{ash,0}}{1 - f_{ash,0}} \quad (A3)$$

Since the mass of ash does not change during soot oxidation, the definition of instantaneous overall ash fraction ($f_{ash,i}$) can be written as Eq. (A4).

$$f_{ash,i} = \frac{m_{ash}}{m_{total,i}} = \frac{m_{ash}}{m_{soot,i} + m_{ash}} = \frac{m_{total,0} \cdot f_{ash,0}}{m_{soot,i} + m_{total,0} \cdot f_{ash,0}} = \frac{f_{ash,0}}{m_{soot,i}/m_{total,0} + f_{ash,0}} \quad (A4)$$

The first term of the denominator of Eq. (A4) can be expressed in terms of α and $f_{ash,0}$ as in Eq. (A5).

$$\frac{m_{soot,i}}{m_{total,0}} = \frac{m_{soot,i}}{m_{soot,0} + m_{ash}} = \frac{m_{soot,i}/m_{soot,0}}{1 + m_{ash}/m_{soot,0}} = \frac{1 - \alpha}{1 + m_{ash}/(m_{total,0} - m_{ash})} = (1 - \alpha) \cdot (1 - f_{ash,0}) \quad (A5)$$

By applying Eq. (A5) to Eq. (A4), $f_{ash,i}$ is finally expressed as function of α and $f_{ash,0}$, as in Eq. (8).

By definition, $f_{ash_O,i}$ is given as Eq. (A6).

$$f_{ash_O,i} = \frac{m_{ash_O,i}}{m_{soot,i} + m_{ash_O,i}} = \frac{m_{ash} - (m_{ash_C,i} + m_{ash_U,i})}{m_{soot,i} + m_{ash} - (m_{ash_C,i} + m_{ash_U,i})} \quad (A6)$$

By introducing Eq. (A3), Eq. (A6) becomes Eq. (A7).

$$f_{ash_O,i} = \frac{(1 - f_{ash,0}) - f_{ash,0} \cdot \left(\frac{m_{soot,i}}{m_{ash}}\right)}{\left(\frac{m_{soot,i}}{m_{ash}} + 1\right) \cdot (1 - f_{ash,0}) - f_{ash,0} \cdot \left(\frac{m_{soot,i}}{m_{ash}}\right)} \quad (A7)$$

The term $(m_{soot,i}/m_{ash})$ is written as in Eq. (A8) by dividing left-hand side of Eq. (A5) with

m_{ash} .

$$\frac{m_{soot,i}}{m_{ash}} = \frac{(1 - \alpha) \cdot (1 - f_{ash,0})}{f_{ash,0}} \quad (A8)$$

By replacing $(m_{soot,i}/m_{ash})$ with Eq. (A8), $f_{ash_O,i}$ is finally given as a function of α and $f_{ash,0}$, as in Eq. (A9).

$$f_{ash_O,i} = \frac{\alpha \cdot f_{ash,0}}{1 - \alpha - f_{ash,0} + 2\alpha \cdot f_{ash,0}} \quad (A9)$$

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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 @ 6,300 rpm
Rated torque (Nm)	250 @ 4,250 rpm

Table 2. GDI PM sampling conditions

	Description	Sampling position	Soot Conc. (mg/m ³)	Engine condition
GDI-1	High soot	Engine-out	36	1,500 rpm-50%, 30°C CA adv. inj. timing
GDI-2	Fuel-cut	Engine-out	36	1,500 rpm-50%, 30°C CA adv. inj. timing with subsequent 20 times of fuel-cut operation
GDI-3	Cold-idle	Engine-out	50	Idle (engine start ~1 min)
GDI-4	Low soot	Engine-out	10	1,250 rpm-25%, 30°C CA adv. inj. timing
GDI-5	Low soot	TWC-out	7.7	1,250 rpm-25%, 30°C CA adv. inj. timing
GDI-6	2% oil-dosed	Engine-out	39	1,500 rpm-50%, 30°C CA adv. inj. timing

Table 3. Details of TGA instrument and experiment protocols

TGA technical specification	
Maximum Sample Weight	1.0 g
Weighing Precision	$\pm 0.01\%$
Sensitivity	0.1 μg
Baseline Dynamic Drift	$< 50 \mu\text{g}$
Temperature Range	Ambient to 1 000°C
Isothermal Temp Accuracy	$\pm 1^\circ\text{C}$
Isothermal Temp Precision	$\pm 0.1^\circ\text{C}$
Controlled Heating Rate	0.1 to 100°C/min
Experimental protocol for non-isothermal tests	
1	Flow of nitrogen
2	Ramp 30.00 °C/min to 600.00 °C
3	Isothermal for 30.00 min
4	Ramp 50.00 °C/min to 150.00 °C
5	Isothermal for 10.00 min
6	Flow of oxygen (8%) with nitrogen
7	Ramp 1.00 °C/min to 900.00 °C
8	Flow of nitrogen
Experimental protocol for isothermal tests	
1	Flow of nitrogen
2	Ramp 10.00 °C/min to 600.00 °C
3	Isothermal for 30.00 min
4	Ramp 10.00 °C/min to $T_{\text{isothermal}}$
5	Flow of oxygen (8%) with nitrogen
6	Isothermal for 300.00 min
7	Flow of nitrogen

Table 4. Kinetic parameters of Printex U and GDI soot samples for a typical carbonaceous soot oxidation kinetic expression in Eq. (1)

	E_a [kJ mol ⁻¹]	A [s ⁻¹]	n
Printex U	152.94	672,663.1	0.768
GDI-1	141.57	126,880.4	1.011
GDI-2	126.80	15,582.4	0.976
GDI-3	126.73	16,594.1	0.982
GDI-4	125.32	13,503.4	0.778
GDI-5	132.20	34,234.9	0.512

Table 5. Kinetic parameters of carbon oxidation with combustion-derived ash precursor effects

	A_C [s ⁻¹]	$E_{a,C}$ [kJ mol ⁻¹]	n_C
GDI-1 (Reference)	491,885	152.51	0.985
GDI-2	491,885	152.51	0.985
GDI-3	491,885	152.51	1.047
GDI-4	491,885	151.60	0.898
GDI-5	491,885	151.00	0.754

Table 6. Initial amounts (mass%) of SOF/WBC, combustion-derived ash precursor, and unburned ash precursor used for simulation

	SOF/WBC (mass%)	$f_{ash,C}$ (mass%)	$f_{ash,U}$ (mass%)
GDI-1 (Reference)	10	0.10	0
GDI-2	13	0.10	0.16
GDI-3	19	0.10	0.40
GDI-4	10	0.58	0
GDI-5	6	1.35	0

Table 7. Modified kinetic correlation for GDI engine soot

Formula	
Overall reaction rate	$r = \frac{d\alpha}{dt} = (m_{S-W,0}/m_{soot,0}) \cdot r_{S-W} + (m_{C,0}/m_{soot,0}) \cdot r_C$
SOF/WBC reaction rate	$r_{S-W} = \frac{d\alpha_{S-W}}{dt} = A_{S-W} \times e^{-E_{a,S-W}/RT} \times (1 - \alpha_{S-W})^{n_{S-W}}$
Carbon reaction rate	$r_C = \frac{d\alpha_C}{dt} = A_C \times e^{-E_{a,C}/RT} \times (1 - \alpha_C)^{n_C} + (1 - \alpha_C) \cdot (a \cdot \exp(b \cdot T)) \cdot f_{ash_{O,i}}$

Table 8. Kinetic parameters of carbon oxidation with combustion-derived ash effects

Parameters	
A_{S-W}	1,646,232.7
$E_{a,S-W}$	147.26
n_{S-W}	1.0377
A_C	491,884.9
$E_{a,C}$	$E_{a,C} = -1.169 \times f_{ash_{C}} [\%] + 152.5$
n_C	$n_C = -0.1854 \times f_{ash_{C}} [\%] + 1.0047$
a	5.70069E-11
b	0.0255525

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(a)

(b)

(c)

(d)

Fig. 4 Normalized weight loss of Printex U and GDI soot samples at (a) isothermal 600°C, including (b) time to 50% and 90% conversion, and (c) non-isothermal with heating rate 1°C/min, with (d) temperatures to 20%, 50%, and 90% conversion

Fig. 5 Comparison of oxidation rates of GDI soot and Printex U (TGA, isothermal 600°C): (a) Soot oxidation rates of different hot steady-state engine conditions with effects of TWC; (b) Soot oxidation rates of hot steady-state, hot steady-state with fuel-cut, and cold-idle conditions

Fig. 6 Linear regression of $\ln(da/dt)$ and $\ln(1-\alpha)$ wherein the slope shows the reaction order of soot obtained during the overall oxidation period (10–90% conversion) for Printex U and GDI soot samples (600°C, isothermal)

Fig. 7 TEM images of engine-out GDI soot primary particles taken at different operating conditions: (a) cold-idle (GDI-3), (b) 1,250 rpm-25% (GDI-4), and (c) 1,500 rpm-50% (GDI-1)

Fig. 8 Comparison of (a) Raman spectra and (b) Raman parameters in terms of D1 FWHM parameters for Printex U and the GDI PM samples, Cold-idle (GDI-3), 1250 rpm-25% (GDI-4), and 1500 rpm-50% (GDI-1), in Fig. 7

Fig. 9 Conceptual drawings of soot and ash particles in the exhaust emissions (left) and changes in ash during soot cake oxidation (three figures after arrow)

Fig. 10 A global GDI soot oxidation mechanism

Fig. 11 Fraction of oxidation-derived ash as a function of conversion of soot for three GDI soot samples with different overall ash fraction

Fig. 12 Linear regressions of the intrinsic GDI carbon oxidation data to obtain kinetic parameters: (a) reaction order (60–70% conversion of soot, isothermal tests at 600°C), (b) activation energy and pre-exponential factor (isothermal tests at 500, 550, 600, and 650°C)

Fig. 13 Measured oxidation rates of GDI-1 sample (solid lines) and simulated oxidation rates of intrinsic GDI carbon (dot lines) at four different temperatures (isothermal tests at 500, 550, 600, and 650°C)

Fig. 14 Linear regressions of SOF/WBC oxidation data to obtain kinetic parameters: (a) reaction order, (b) activation energy and pre-exponential factor (20–80% of conversion of SOF/WBC, isothermal tests at 500, 550, 600, and 650°C)

Fig. 15 (a) Linear correlation between instantaneous oxidation-derived ash-assisted carbon oxidation rate ($\Delta m_{C_ash_O_assist}/m_{C,i}$) and fraction of oxidation-derived ash (f_{ash_O}), (b) exponential correlation between slopes of the linear regressions in left plot and temperature (isothermal tests at 500, 550, 600, and 650°C)

Fig. 16 Linear regressions of combustion-derived ash precursor-assisted carbon oxidation data for Printex U and four GDI soot samples (GDI-1, -3, -4, -5) to obtain the reaction order (n_C) (isothermal tests at 600°C)

Fig. 17 (a) Linear relations between Ash_C fraction (f_{ash_C}) and reaction order (n_C) given as $n_C = -0.1854 \times f_{ash_C} [\%] + 1.0047$, (b) f_{ash_C} and activation energy ($E_{a, C}$) given as $E_{a, C} [\text{kJ mol}^{-1}] = -1.169 \times f_{ash_C} [\%] + 152.5$

Fig. 18 Linear correlation of SOF/WBC with the VOF measured by TGA for five GDI soot samples

Fig. 19 Validation of modified kinetic correlation: instantaneous soot oxidation rates of measured ($\diamond$, solid line), typical kinetics (solid line), and modified kinetics (dot line), and oxidation rates of each component calculated by modified kinetics, Ash_C assisted carbon oxidation ($\square$), Ash_O assisted carbon oxidation (Δ), and SOF/WBC oxidation ($\times$) in dot lines for five GDI soot samples (isothermal at 600°C)

Fig. 20 Validation of modified kinetic correlation: specific soot oxidation rates of measured (◇, solid line), typical kinetics (solid line), and modified kinetics (dot line), and oxidation rates of each component calculated by modified kinetics, Ash_C-assisted carbon oxidation (□), Ash_O-assisted carbon oxidation (Δ), and SOF/WBC oxidation (x) in dot lines for five GDI soot samples (non-isothermal)