Oxidation Characteristics of Soot from a Gasoline Direct-Injection (GDI) Engine

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Background and Objective

- **Background**
  - Higher PN of GDI engines: gasoline particulate filter (GPF)
  - Most of GDI particulate emissions are formed during cold start (warm-up) and transient periods.
    - For GPF regeneration, the oxidation characteristics of cold soot are important.
  - Soot oxidation reactivity: Printex U (flame soot) < Diesel soot < GDI soot
  - Diesel soot oxidation reactivity depends on engine conditions (speed, load, EGR, inj. timing): changes in carbon nanostructure and chemical properties (organic fractions, SFG)
  - Few studies about GDI soot oxidation characteristics.

- **Objectives**
  - Investigating GDI soot oxidation characteristics in relations to engine operating conditions and TWC effects.
  - Proposing a kinetic correlation relevant to GDI soot which can be used for simulation of GPF regeneration
Experimental setup with 2.4L 4-cylinder NA GDI engine - homogenous/stoichiometric charge strategy
Ash fraction is much higher in GDI soot than in diesel soot, primarily due to lower soot mass emissions of the GDI engine.

- Ash fraction (in mass %) in engine-out soot will vary as function of soot mass emission and lube oil consumption.
  - Ash fraction in soot tends to increase with lower soot mass calibration.
- GDI soot with default calibration contains over 3% of ash due to very low soot mass.
- GDI soot at advanced or retarded IT shows similar levels of soot mass and ash fraction (order of 0.1%) to diesel soot.
- TWC decreases total soot mass, but increases ash fraction in soot.
- At cold start, GDI soot lies in diesel-like regime with high soot mass and moves to the GDI engine regime as the engine warms up.
GDI soot oxidation reactivity is significantly enhanced with increased ash fraction in soot.

- Catalytic effect of ash is one of the driving factors that enhances oxidation reactivity of GDI soot.
GDI soot has unique oxidation characteristics different from flame or diesel soot

- The oxidation rates of GDI soot are significantly promoted with increase of ash fractions.
- Without ash, oxidation reactivity of GDI soot is lower than that of Printex U.
- GDI soot shows three-staged oxidation which differs from Printex U/diesel soot.
  - **Initial stage** (A): higher oxidation rate due to additional oxidation of soluble organics and weakly bonded carbons (WBC)
  - **Intermediate stage** (B): lower oxidation rate after completion of SOF and WBC oxidation (sole carbon oxidation)
  - **Final stage** (C): soot oxidation rate becomes higher, because of additional catalytic effects of ash by higher ash-to-soot ratio in the remaining sample.
TWC decreases SOF/WBC and increases the ash fraction in GDI soot, and improves oxidation reactivity in overall:

- **Three reasons of ash fraction increase after TWC**
  - Catalytic oxidation of organics, WBC, and carbon soot in the TWC
  - Physical loss (attachment on the TWC wall) of soot particles
    - Particles loss was measured by SMPS.
  - Separation of catalyst supporting materials: SEM-EDS data
    - Higher fractions of Mg, Al, and Si were measured from TWC-out ashes.

- Oxidation reactivity of TWC-out soot is enhanced by the increase in ash fraction.

### Specific soot oxidation rates

![Graph showing specific soot oxidation rates for Hot Steady_Eout_ash0.58% and Hot Steady_TWCout_ash1.35%]
Cold condition GDI soot: ash plays less catalytic roles, resulting in lower oxidation reactivity

- Low ash (0.1%) soot represents intrinsic GDI soot oxidation reactivity. (negligible ash effects)
- The oxidation rates of cold GDI soot in the intermediate stage is close to intrinsic GDI soot oxidation rate.
  → *Hypothesis 1*: GDI soot seems to have an “Intrinsic carbon oxidation reactivity” which is unchanged at different engine conditions.
- With similar ash fractions, the oxidation rate is much slower for cold idle soot than hot steady state soot.
  → *Hypothesis 2*: Ash in GDI soot may have different forms, offering different levels of catalytic effects, depending on hot and cold engine conditions.
Hypothesis 1: HR-TEM and Raman spectroscopy revealed that GDI soot nanostructures are well defined and unchanged by engine conditions: “Constant intrinsic carbon soot reactivity”

Conventional diesel engine: spray combustion

Flame structures and temperatures of diesel spray combustion strongly depend on ambient P & T at injection, dilution (EGR), and swirl.

Diesel soot nanostructures change significantly with engine conditions. → Different carbon soot reactivity

GDI engine (NA, λ=1): premixed flame propagation

Turbulence increases reaction surface area with highly wrinkled and convoluted flame sheet. Flame sheet structure (thickness) and temperature do not change much at different engine conditions.

GDI soot nanostructures do not depend on engine conditions. → Constant carbon soot reactivity

[TEM images: Yehliu, Combustion and Flame, 2013]
Hypothesis 2: Three different states of ashes are proposed for GDI soot oxidation

- **Combustion-derived ash precursor (Ash_C)**
  - Metallic oxide nano-particles generated during in-cylinder combustion and soot formation processes.
  - Tight-contact with soot particles in nano-scale, offering strong catalytic effects on soot cake oxidation.
  - Converted to oxidation-derived ash by sintering during soot cake oxidation.

- **Unburned oil-derived ash precursor (Ash_U)**
  - Unburned oil additives (e.g., ZDDP or calcium sulfonate) discharged to exhaust in cold engine condition.
    → Nearly no catalytic effects.
  - Converted to oxidation-derived ash by oxidation and sintering during soot cake oxidation.

- **Oxidation-derived ash (Ash_O)**
  - Metallic oxide micron-particles generated from the ash precursors with soot cake oxidation.
  - Loose-contact with soot particles, offering weak catalytic effects on soot cake oxidation.
  - Contribution increases at the final soot oxidation stage with increase in ash-to-soot ratio.
A global GDI soot oxidation mechanism is proposed which includes the effects of organics/WBC and ash.

- **Assumptions in mechanism**
  - Constant intrinsic carbon soot oxidation reactivity
  - Three states of ashes
  - Conversion of ash precursors to Ash_O at the same rate as soot conversion

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**Measured oxidation rate**

**Oxidation of SOF/WBC**

**Intrinsic carbon soot oxidation**

**Carbon oxidation assisted by Ash_C**

**Carbon oxidation shifted up by Ash_O**

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**Oxidation derived ash content [mass %]**

- 0.10%
- 0.58%
- 1.35%
- 17.3%

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**Conversion (α)**
A modified kinetic correlation for GDI soot is derived in consideration of SOF, WBC and ash effects

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

$$\alpha = \frac{m_{\text{conv}}}{m_0}$$

- The typical kinetic correlation doesn’t hold for GDI soot oxidation.
  - Activation energy ($E_a$) and reaction order ($n$) change with conversion, due to the effects of organics/WBC and ash.
- A modified kinetic correlation has been developed for accurate prediction of soot oxidation.
  - The effects of SOF/WBC and ash are taken into account.
  - Soot oxidation rates can be predicted at different engine conditions without changing kinetic parameters.

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

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

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

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

**Reaction order ($n$) of soot samples**

**GDI soot oxidation mechanism**
The modified kinetic correlation predicts accurate oxidation rate of GDI soot at a wide ranges of conversion and temperature.

 Isothermal oxidation (600 °C, 8% O₂)

 Non-isothermal oxidation (increased by 1°C/min, 8% O₂)
Summary

- Major characteristics of GDI soot oxidation
  - High ash fraction: an order of magnitude higher ash fraction than in diesel soot.
  - Catalytic effects of ash: dominantly enhances soot oxidation reactivity.
  - Three-staged oxidation: additional SOF/WBC oxidation at initial, and Ash_O assisted carbon oxidation at final.
  - Constant intrinsic carbon soot oxidation reactivity, independent to engine conditions.
  - TWC effect: enhances soot oxidation reactivity due to increased ash fraction.
  - Lower oxidation reactivity of cold condition soot: unburned oil-derived ash precursor.

- A general GDI soot oxidation mechanism and a modified kinetic correlation have been proposed.
  - The oxidation rates of GDI soot have been accurately predicted at wide ranges of conversion/temperature and engine conditions, without changing kinetic parameters.
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Thank you for your attention!

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Technical support pages
Significance of cold and transient condition soot in the GDI engine
Contributions of SOF/WBC and ashes on GDI soot oxidation of different engine conditions

Normalized Soot Oxidation Rate

- SOF
- Carbon_Ash_O
- Carbon_Ash_C
- Carbon_intrinsic
TWC effects on soot mass/particle size distribution and ash composition

MSS and SMPS
(Soot mass and particle size distribution)

**Soot mass:**
1.0 → 0.2 mg/m³

**Soot mass:**
2.5 → 2.2 mg/m³

SEM-EDS
(Compositions of ash)

**Engine-Out**
- Ca: 30.8%
- Si: 8.6%
- S: 2.0%
- P: 25.0%
- F: 0.6%
- Na: 18.5%
- Mg: 4.3%
- Al: 1.2%
- Zn: 9.0%
- P: 0.9%
- Mg: 0.3%
- Na: 14.3%
- Zn: 0.5%

**TWC-Out**
- Ca: 30.8%
- Si: 8.6%
- S: 2.0%
- P: 25.0%
- F: 0.6%
- Na: 18.5%
- Mg: 4.3%
- Al: 1.2%
- Zn: 9.0%
- P: 0.9%
- Mg: 0.3%
- Na: 14.3%
- Zn: 0.5%
Validation of the modified kinetic correlation - Isothermal 600 °C, 8% O₂

GDI-1

Experiment
Typical kinetic correlation (10-90% Param.)
Modified kinetic correlation
Carbon oxidation by Ash_C
Carbon oxidation by Ash_O
SOF/WBC oxidation

GDI-2

Conversion (α)

GDI-3

GDI-4

GDI-5
Validation of the modified kinetic correlation - Non-isothermal 1 °C/min, 8% O₂