

# Soot Oxidation in Periphery of Diesel Spray Flame via High-Speed Sampling and HR-TEM Observation

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## ABSTRACT

In order to better understand in-flame diesel soot oxidation processes, soot particles at the oxidation-dominant periphery of diesel spray flame were sampled by a newly developed “suck” type soot sampler employing a high-speed solenoid valve and their morphology and nanostructure were observed via high-resolution transmission electron microscopy (HR-TEM). A single-shot diesel spray flame for the soot sampling experiment was achieved in a constant-volume vessel under a diesel-like condition. The sampler instantaneously sucks out a small portion of soot laden gases from the flame. A TEM grid holds inside the flow passage close to its entrance is immediately exposed to the gas flow induced by the suction at the upstream of the solenoid valve, so that the quick thermophoretic soot deposition onto the grid surface can effectively freeze morphology variation of soot particles during the sampling processes. The morphology of soot particles sampled by the novel suck sampler and a conventionally used “skim” sampler directly exposing a TEM grid to the flame was compared and did not show notable qualitative differences. The on-grid concentration of soot sampled by the suck sampler was lower than the ones by the skim sampler, while the repeatability of the sampled on-grid soot concentration was improved especially at downstream in-flame sampling locations. The HR-TEM observations of soot particles sampled from the oxidation-dominant periphery of diesel spray flame showed that the outer layers of the soot particles exhibit lumpy surfaces which is possibly due to stripping and disintegration of the layers by rapid oxidation and makes it difficult to identify boundaries of primary particles within the aggregates. High-resolution images of the whole aggregates produced by stitching of multiple HR-TEM images showed that these nano-structural features are only partially seen in the aggregates sampled from the core regions of diesel spray flame especially at the perimeters of the aggregates, while the aggregates sampled from the flame periphery mostly exhibits wholly collapsed outer layers.

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## INTRODUCTION

Diesel engines are expected to play an important role as an effective and practical measure against the global warming problems because of their high thermal efficiency. On the other hand, diesel engines suffer from the tradeoff between soot and NO<sub>x</sub> emissions due to the high-temperature diffusion combustion nature. Recent diesel combustion models are able to predict NO<sub>x</sub> emission at an acceptable accuracy, while the prediction of soot emission, including the particle mass (PM) and the particle number (PN), remains to be improved because of the lack of the fundamental understanding of in-cylinder or in-flame soot formation and oxidation processes. Most of the soot particles formed in the cylinder disappear due to the rapid oxidation, and only 0.1% order of the peak soot mass remain unburned through the oxidation phase and are finally emitted as engine-out soot. This means even small fraction of error in soot oxidation prediction might results in the significant error in the soot emission prediction, as discussed by Kamimoto et al. [1]. For this reason, detailed understanding of diesel in-flame soot oxidation process is essential for accurate prediction of soot emission.

Unfortunately, there are many fundamental unknowns about diesel in-flame soot oxidation processes such as the applicability of currently available diesel soot oxidation models based on classical low pressure burner experiments by NSC [2] and Neoh [3], to the high pressure and high temperature in-flame conditions equivalent to modern diesel engines. As reviewed by Stanmore et al. in 2001 [4], the high-temperature soot oxidation in laminar burners and shock tubes have been studied and somewhat reflected to engine equivalent models. However, those classical models are still widely used in recent simulation studies [e. g. 5, 6 and 7] with bold assumptions like soot oxidation rates are proportional to the surface area of sphere-represented soot particles with arbitrarily adjustable coefficients. Additionally, our current understanding is severely lacking even on whether the oxidation process is homogeneous or heterogeneous within the scale of particle or aggregate sizes, which part of the soot particles or aggregates the oxidation starts from and how the oxidation affects separation or collapse of soot aggregates. Such fundamental unknowns on soot oxidation models and processes should be discussed based not on coarse comparisons between predicted and measured engine

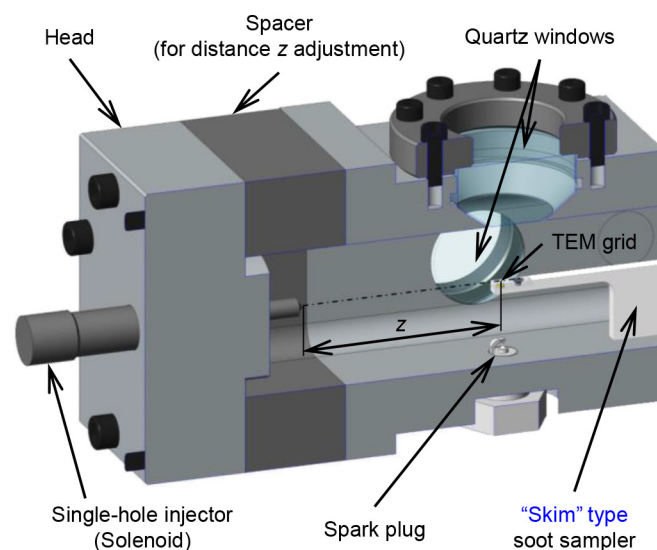
emissions, but should start from phenomenological and microscopic understanding of the diesel in-flame soot oxidation process itself under engine equivalent conditions.

Soot nanostructure, which refers to physical structure of oriented carbons graphene layers i.e. polycyclic aromatic hydrocarbons (PAHs) within the soot particles, is known to be related to oxidative reactivity [8, 9, 10, 11, 12]. Therefore, several researchers have used electron microscopy to observe the inner structure of particles and reveal the details of soot oxidation processes [13, 14, 15, 16, 17, 18]. Ishiguro et al. investigated nano-structural changes within the engine-exhaust soot during its oxidation in an electric furnace at 500°C air atmosphere via TEM observation and FT-IR spectroscopy [14]. It has been observed that, in the early stage of oxidation, void structure is formed by release of soluble organic fraction (SOF), and then, carbon layer planes within the soot particles are re-arranged towards more graphitic. Finally, the outermost shell within the soot is stripped and their primary particle diameter is decreased. Similar oxidation behavior has also been observed in different oxidation systems such as thermogravimetric analyzer (TGA) [11, 12] and laboratory flow reactor [13]. However, these preceding studies are mainly focusing on the soot oxidation by  $O_2$  at relatively low temperature corresponding to the regeneration of diesel particulate filters (DPF). The diesel in-flame soot oxidation, which is expected to be rapid, heterogeneous and known to be predominated by OH radicals [4, 19, 20, 21] at relatively high temperature around the diesel flame periphery [22, 23, 24, 25], can be significantly different from the ones observed in the preceding studies. Therefore, in order to understand the details of the diesel in-flame soot oxidation process, nano-structural TEM observation of soot particles directly sampled from the oxidation-dominant diesel flame periphery is important.

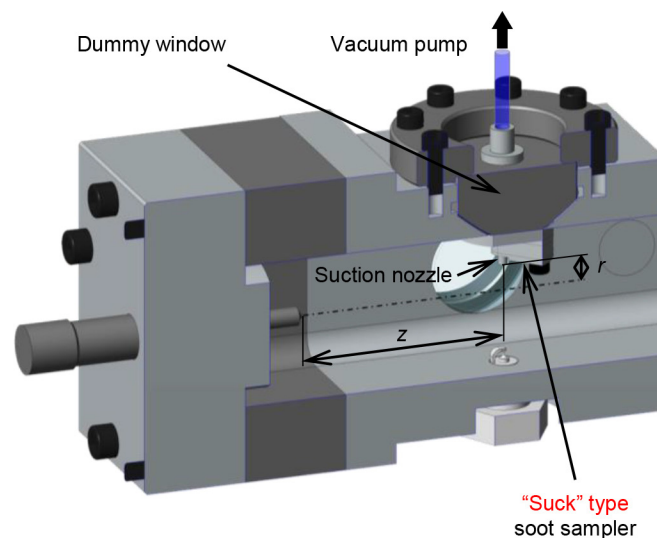
The authors have been conducting direct sampling of diesel in-flame soot particles in a constant-volume vessel and TEM analyses of their morphology and nanostructure variation along different spray axial locations [26, 27, 28] with several different fuels [29, 30, 31, 32, 33]. These studies revealed that the soot aggregate and primary particle sizes notably vary with in-flame locations, fuels and oxygen concentrations. However, the nanostructure of the in-flame soot exhibited only small variation with these parameters. These results seem contradictory to the ones of engine in-cylinder soot sampling and TEM analyses by Song et al. which reports significant changes in nanostructure from the in-cylinder to the exhaust soot [15, 34]. One possible reason for this discrepancy is that the in-flame sampling locations in the authors' previous studies had been limited to the spray flame core regions. In these spray flame core regions, temperature [35] and concentration of oxidants such as OH [22, 23, 24, 25] are expected to be too low for the soot oxidation to proceed and exhibit notable changes in soot nanostructure. For better understanding of in-flame soot oxidation, sampling of soot particles from diesel spray flame periphery and TEM analyses of their nanostructure are necessary.

Although the authors had been aware of this importance of the peripheral soot sampling and TEM analyses, the authors' experience difficulties to directly sample soot from diesel flame downstream and periphery. The in-flame soot sampling technique in the authors' previous studies employed a "skim" type soot sampler as shown in

Figure 1a, by which a TEM grid is directly exposed to a high temperature diesel spray flame. The primary mechanism of this soot sampling process is the thermophoresis caused by the temperature gradient within the thermal boundary layer formed on the relatively low temperature TEM grid surface. This sampling mechanism works well in the spray flame core where relatively high and constant spray axial velocity helps to maintain the steep temperature gradient within a thin boundary layer. However, in the downstream and periphery of diesel spray flame, lower and fluctuating spray velocity results in a thicker and unsteady boundary layer, making the soot sampling poorly repeatable or impossible. The present study firstly aims to enable repeatable soot sampling from diesel flame periphery while keeping the advantage of the simple and effective thermophoretic soot sampling.



a. Conventionally used "skim" type



b. Newly developed "suck" type

Figure 1. Cross-section view of a constant-volume combustion vessel with two different types of soot samplers: (a) conventionally used "skim" type and (b) newly developed "suck" type soot sampler.

In the present study, a novel soot sampler referred to as “suck” type sampler employing a high-speed solenoid valve was developed for the robust soot sampling in the periphery of the diesel spray flame. Firstly, in order to evaluate the usefulness and the reliability of the suck type sampler, the morphology of soot particles in the flame core sampled by the suck type and conventional skim type samplers was compared. Secondly, the suck type soot sampler was applied to the sampling of soot particles in the oxidation-dominant flame periphery and their morphology and nanostructure were compared with the ones of flame core soot.

## EXPERIMENTAL METHOD

### Constant Volume Combustion Vessel

The soot sampling from a single-shot diesel spray flames was conducted in an optically-accessible constant-volume combustion vessel using two different types of soot samplers as shown in Figure 1. The constant-volume vessel employs three quartz windows, which have effective view field of  $\phi 35$  mm in diameter. The in-flame soot behavior during the sampling process was visualized via a high-speed visible laser shadowgraphy. A common-rail fuel injector with a single-hole nozzle was mounted on the head center and the single-shot fuel spray is injected in a horizontal direction in the combustion vessel. The soot samplers for collecting in-flame soot particles were placed in the vessel with a TEM grid held in a cavity at the sampler tip. The detailed explanation for the samplers is described in the next section, “Soot Samplers”. In order to investigate the in-flame sooting tendency, the distance  $z$  from the injector nozzle orifice to the soot sampling locations was adjusted by selecting different thickness spacers between the combustion vessel and the head. The displacement of the constant volume vessel varies depending on the thickness of the spacer and is 560 cc for the standard case without the spacers. The combustion vessel, the TEM grid and the soot sampler were electrically pre-heated to 373 K to prevent water condensation.

### Soot Samplers

This section describes two different soot samplers. One is the “skim” type soot sampler as shown in Figure 1a, which has been conventionally used in the previous studies by the authors. The skim sampler was designed to fix a  $\phi 3$  mm-diameter TEM grid parallel to the spray axis. The TEM grid is exposed directly to the diesel spray flame, which forms a temperature gradient between the flame and the grid surface. The soot particles trapped in the velocity boundary layer are conveyed and deposited onto the grid surface by the thermophoretic force generated from the temperature gradient. The sufficiently low temperature of grid (373 K) enables to instantly freeze reactions on the sampled soot particles and keep the in-flame soot morphology after the deposition. As explained above, this sampling mechanism works well in the spray flame core, but not in the downstream and periphery of diesel spray flame. For the robust thermophoretic soot sampling regardless of the in-flame sampling locations, it is desirable to hold the TEM grid as close to the sampling location as possible while inducing a flow of soot-laden gas parallel to the grid surface to maintain a relatively thin boundary layer.

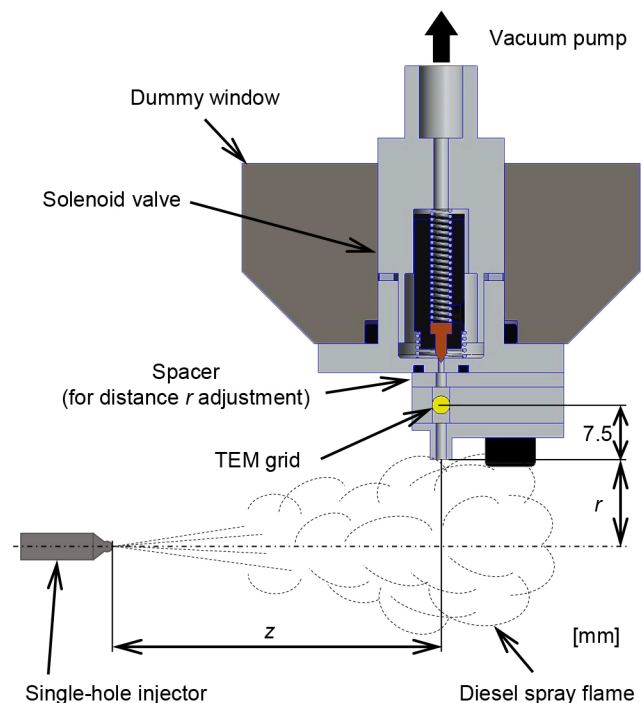


Figure 2. Cross-section view of newly developed “suck” type soot sampler.

In order to achieve this, the “suck” type soot sampler (Figure 1b) was newly designed to rapidly draw out a small portion of soot laden gas from the flame and induces the flow along the surface of a TEM grid hold inside the flow passage close to its entrance. The novel suck sampler is mounted to the combustion vessel by replacing the top quartz window with the sampler assembly. As shown in the cross-section view Figure 2, the suck sampler consists of a high-speed solenoid valve connected to a vacuum pump, a TEM grid holder and an inlet port of the soot laden gases. The solenoid valve (Parker Hannifin, Series 9 Pulse Valve) can operate under high ambient pressure (up to 8.5 MPa) and the shortest valve opening duration is 160  $\mu$ s by a driver for the exclusive use (Parker Hannifin, IOTA-ONE). This sampler is able to suck out a very small portion of the soot laden gases from the flame instantly. The grids were located close to its entrance as indicated by yellow circle and then exposed to the sucked soot laden gas flow. Potential drawbacks of this sampler are continued soot growth in the suction flow path and soot intrusion to the grid through the open flow path upstream of the solenoid valve at undesired timings. To balance these concerns, the TEM grid was located at 7.5 mm upstream from the inlet port tip. The preliminary study confirmed that the effects of the continued soot growth and soot intrusion are negligible at this location under the condition of the present study [36]. The diameter of sucking flow passage was set to  $\phi 1.5$  mm for the sufficient spatial resolution of the soot sampling locations. For morphology and nanostructure observation of the inflame sampled soot particles [29], two different types of TEM grid, carbon coated copper and molybdenum micro grids, were used respectively and simultaneously exposed to the sucked gas flow. The radial distance  $r$  from the spray axis to the inlet port tip was adjusted by changing a spacer between the solenoid valve and the TEM grid holder.

## Experimental Conditions

Table 1 summarizes the experimental conditions. A diesel-like high-pressure and high-temperature ambient gas condition ( $\rho_a=9.5$  kg/m<sup>3</sup>,  $P_a=2.5$  MPa,  $T_a=1,070$  K, 21%O<sub>2</sub>) was simulated by a spark-ignited combustion of a mixture composed of acetylene (C<sub>2</sub>H<sub>2</sub>), oxygen (O<sub>2</sub>) and nitrogen (N<sub>2</sub>). The ambient gas density and pressure were set below a typical modern diesel in-cylinder condition, mainly due to the safety limitations of the experimental devices used in the present study. However, the TEM based morphology analysis of inflame soot particles sampled under a higher density and pressure condition ( $\rho_a=22.8$  kg/m<sup>3</sup>,  $P_a=6.7$  MPa,  $T_a=1000$  K) [32, 33] did not show notable differences in an absolute value of the primary soot diameter and the general trend of the soot formation and oxidation processes on the spray axis, compared with the previous studies conducted under the identical conditions. Therefore, the obtained results in the present study are considered to be useful for discussing the in-flame diesel soot oxidation processes. JIS#2 Japanese conventional diesel fuel was used as the test fuel. Figure 3 shows the examples of time-sequence and time-integrated high-speed laser shadowgraphs of this spray flame without the sampler under the identical ambient conditions with the sampling cases. The liquid core length of the spray has been measured to be around 20mm at the present condition and the shadow in Figure 3 is mainly attributed to soot cloud. The horizontal arrows in the figure indicates the TEM grid exposing duration of the conventional skim type sampler and the solenoid valve opening duration of the novel suck type sampler. The dots plotted on the time-integrated shadowgraphs indicates the soot sampling locations in this spray flame by each types of the sampler. Note that the sampler intrusion to the spray flame indeed has a significant influence on the spray and flame propagation in the upstream of the spray flame beyond the sampler intrusion location. However, for the downstream from the nozzle to the sampler intrusion locations, notable differences of the

spray and flame propagation have not been experimentally observed between the cases with and without the sampler. Therefore, the sampled soot is reasonably considered equivalent to the ones from the original spray flame. In addition, the soot sampling experiments had been carried out only at the mid- to downstream locations where the sampler intrusion does not affect the ignition. Regarding the suck sampling, the solenoid valve was kept open for 2.5 ms in all sampling locations, which corresponds to the duration from the spray tip arrival to the tail passage.

Table 1. Experimental conditions

| Surrounding conditions               |                                                    |
|--------------------------------------|----------------------------------------------------|
| Ambient gas density $\rho_a$         | 9.5 kg/m <sup>3</sup>                              |
| Ambient pressure $P_a$               | 2.5 MPa                                            |
| Ambient temperature $T_a$            | 1070 K                                             |
| O <sub>2</sub> concentration         | 21%                                                |
| Injection conditions                 |                                                    |
| Injector type                        | G2S (Solenoid)                                     |
| Nozzle orifice                       | $\phi$ 0.14 mm×1                                   |
| Fuel                                 | JIS#2                                              |
| Injection pressure $\Delta P_{inj}$  | 80 MPa                                             |
| Injection duration $\Delta t_{inj}$  | 2.3 ms                                             |
| Injection amount $Q_{inj}$           | 10.3 mg                                            |
| Soot sampling conditions             |                                                    |
| Sampler types                        | Skim and Suck                                      |
| Distance from nozzle tip $z$         | 60, 80, 100 and 120 mm                             |
| Distance from spray axis $r$         | 0, 6 and 12 mm                                     |
| TEM grid types                       | Carbon-coated copper grid<br>Molybdenum micro-grid |
| Temperature of sampler $T_{sampler}$ | 373 K                                              |

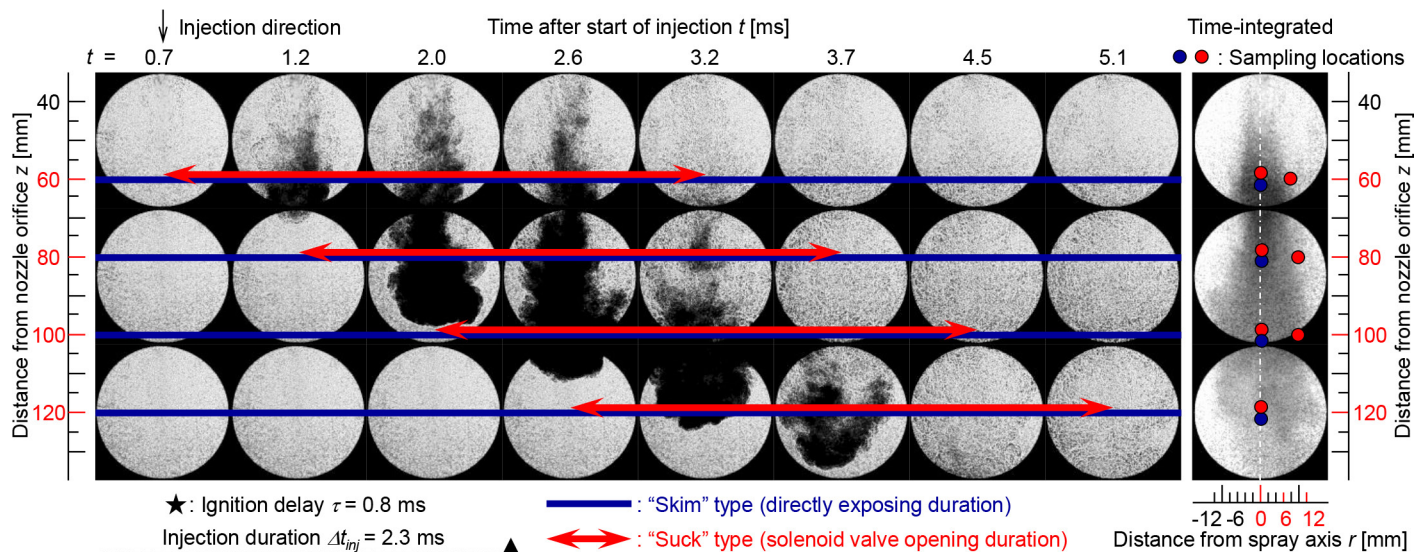


Figure 3. Time-sequence (left) and time-integrated (right) high-speed visible laser shadowgraphs of a diesel spray flame without the soot sampler under the identical ambient conditions with the sampling cases. The horizontal arrows in the left figure shows exposing duration of the conventional “skim” type sampler and solenoid valve opening duration of the novel “suck” type sampler, respectively. The dots in the right figure indicate soot sampling locations by each types of the sampler.