

Aromatic Additive Effect on Soot Formation and Oxidation in Fischer-Tropsch Diesel (FTD) Spray Flame -Morphology and Nanostructure Analysis of In-Flame Soot Particles via HRTEM-

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ABSTRACT

In order to examine the effect of aromatic addition to Fischer-Tropsch Diesel (FTD) fuel on formation and oxidation processes of soot particles in diesel spray flame, small amount of naphthalene (0 to 65,000 ppm) was added to the FTD fuel and variation of soot morphology and nanostructure of primary soot particles directly sampled in a diesel spray flame were investigated via High-Resolution Transmission Electron Microscopy (HRTEM). A single-shot diesel spray flame was achieved in a constant volume combustion chamber under a diesel-like condition ($T_a=1000\text{K}$, $P_a=2.7\text{MPa}$) and a grid for HRTEM observation was directly exposed to the spray flame to thermophoretically sample soot particles onto the grid surface. The primary particle diameter, aggregate gyration radius, lattice fringe length, lattice fringe tortuosity and lattice fringe separation of soot particles sampled at different locations (from 60 to 90mm from nozzle tip) in the spray flame were analyzed. Naphthalene addition promoted soot formation process in the spray flame. The soot morphology analysis showed that the size of primary particles sampled in spray flames with and without naphthalene addition did not show significant difference, while the naphthalene addition increased size and the number of soot aggregates. These data suggest that naphthalene addition resulted in the increased total number of primary particles in the spray flame. The soot nanostructure analysis showed that the fringe separation became narrower from upstream to downstream for both cases with and without naphthalene, suggesting that the oxidation of soot particles progresses from up to downstream and thus the fringe layers get more crystallized. The change of the fringe separation from up to downstream was larger and faster in the naphthalene added case, suggesting that the naphthalene addition promoted faster formation of fluffier soot particles in the upstream and their faster oxidation.

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INTRODUCTION

Fischer-Tropsch Diesel (FTD) fuel is an alternative cleaner diesel fuel that has been expected to overcome ever-stringent emission regulations and depletion problems of fossil fuel. The FTD fuel does not contain aromatics and sulfur that are related to particulate matter (PM) emission and degeneration of after treatment catalysts. The FTD fuel is synthesized from natural gas, the production of which is estimated to last longer than that of crude oil, and thus stable and long-term supply of the FTD fuel is feasible. Moreover, the FTD fuel can be used with current diesel engines with minimum modification as blending stocks or unblended. Numerous reports on combustion and emission characteristics

of FTD-fuelled diesel engines, including performance improvements by engine optimization for the FTD fuel, had been published [1, 2, 3, 4, 5, 6, 7, 21].

Numerical analyses on the behavior of aromatics in soot formation process have also been conducted using detailed chemical reaction schemes [8, 9, 10, 11, 12]. However, the mechanism of PM reduction in FTD-fuelled diesel engines compared with conventional diesel fuel has not been clearly explained and validated through comprehensive experimental investigation.

Authors have been working on detailed optical diagnostics of the formation and growth processes of polycyclic aromatics hydrocarbons (PAHs) and soot particles in diesel spray flame. The in-flame soot processes with

conventional diesel fuel (JIS#2), aromatic-free FTD fuel and aromatic-added FTD, with small amount of naphthalene (21 to 13,000ppm) as a representative aromatic component, have been examined in detail via high-speed laser shadowgraphy, 2-color method and Excitation-Emission Matrix (EEM) spectroscopic technique using a multi-wavelength laser source[4, 5]. It was found that the aromatics originally contained in the JIS#2 fuel and added to the FTD fuel promote and advance soot formation as a seed to grow into larger PAHs and then soot particles in the spray flame. The addition of small amount of naphthalene also increased apparent flame temperature measured via 2-color method by up to 100K, which is likely due to accelerated soot oxidation in the flame periphery. It is, however, difficult to fully understand the mechanism for the promoted soot formation and oxidation solely by the optical measurements. For example, it is not clear from the optical measurement results mentioned above if the promoted soot formation is either by the increased number, the increased size, or both, of soot particles. The cause for the promoted soot oxidation may also be related to morphology and crystallic nano-structure of soot particles, which is difficult to be examined by optical diagnostics.

High-Resolution Transmission Electron Microscopy (HRTEM) is a powerful tool for investigation of morphology and nanostructure of soot particles which is known to reflect their formation and oxidation processes. There have been many studies on TEM observation of diesel soot particles sampled from the exhaust [19, 22]. In-flame soot sampling and TEM analysis provides more direct and detailed information on the formation and oxidation processes. Kook and Pickett pioneered the morphological analysis of soot particles directly sampled from a diesel spray flame in a constant volume vessel [19] and more recently in a diesel engine [20]. Authors extended this direct in-flame soot sampling and TEM analysis to include detailed examination along different in-flame axial locations [6, 7], fuel comparison among conventional diesel, biodiesel and FTD [8, 18], nanostructure analysis of primary particles [12], and relevant uncertainty analysis [14]. The present study employs this direct in-flame soot sampling and TEM analysis to examine the above mentioned aromatic addition effects on soot formation and oxidation processes in the FTD spray flame. Small amount of naphthalene (0 to 65,000 ppm) was added to the FTD fuel and variation of soot morphology and nanostructure of primary soot particles directly sampled in its spray flame were investigated via HRTEM. The primary particle diameter, aggregate gyration radius, primary particle nanostructures such as lattice fringe length, tortuosity and separation of soot particles sampled at different axial locations (from 60 to 90mm from nozzle tip) in the spray flame were analyzed.

EXPERIMENTAL METHOD

Soot Sampling

The experiments of direct soot sampling from a diesel spray flame were conducted in a constant volume combustion chamber with a soot sampler placed inside as shown in Fig. 1. The chamber is equipped with three quartz windows and its internal volume is 560cm³. The soot sampler is made of aluminum, 10mm-thick and equipped with a 3.1mm-diameter and 1.5mm-deep cavity at the tip on the top horizontal surface to hold a carbon-coated copper grid or a molybdenum micro-grid for HRTEM observation. The carbon-coated copper grid was used for lower magnifications of x6k and x20k, while the molybdenum micro-grid was used for a higher magnification of x500k. The sampler is placed parallel to the spray axis to skim the gas containing soot from the spray centerline while attempting to minimize flow disturbance at least to the upper half of the spray flame. The grid and the sampling probe were heated to 373K together with the combustion vessel. The grids are directly exposed to the diesel spray flame and the soot particles are deposited onto the cooler TEM grid via thermoporesis. The distance z between the injector nozzle tip and the center of TEM grid was adjusted by selecting different spacers for the combustion chamber. For all grid locations examined in the present study, liquid droplets are completely vaporized by upstream mixing with high temperature gas and combustion products. Only one grid sample for each experimental condition was analyzed because of the time-consuming and complex analysis procedure, while the uncertainty caused in the sampling, observation and analysis has been discussed elsewhere [14].

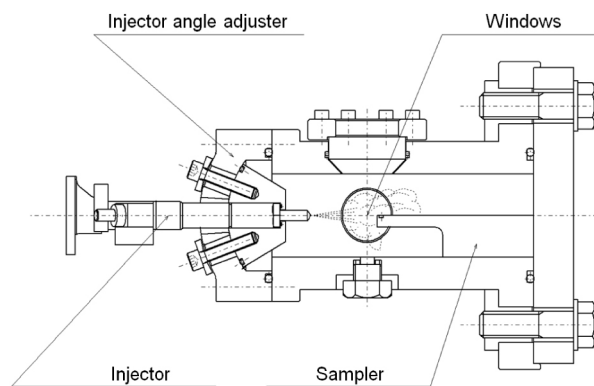


Fig. 1. Constant volume combustion chamber

Table 1 summarizes the experimental conditions. A high pressure and high temperature condition (2.7MPa, 1000K) was simulated by spark-ignited combustion of a premixture of acetylene, oxygen and nitrogen. A common-rail fuel injector with a single-hole nozzle was used for single-shot injection. The aromatic-free FTD fuel with and without seeded naphthalene (65,000ppm) were used as the test fuels. Soot particles were sampled on the spray axis at $z=60, 70$ and

90mm from the nozzle tip in the spray flame. 60 and 70mm correspond to soot formation regions in the spray flame, while at 90mm soot oxidation becomes more dominant. The soot nanostructure analysis was conducted all for the three sampling locations, while the soot morphology analysis was conducted only for 60 and 70mm. Soot has been sampled also for other axial locations, but the analysis is time-consuming and still in progress.

Table 1. Experimental conditions

Surrounding conditions	
Ambient gas density: ρ_a [kg/m ³]	9.5
Pressure: P_a [MPa]	2.7
Temperature: T_a [K]	1000
O ₂ concentration: X_{O_2} [%]	15
Injection conditions	
Injection pressure: F_{inj} [MPa]	80
Injection duration: ΔT_{inj} [ms]	2.5, 4.0
Nozzle	$\phi 0.14$ mm $\times$ 1
Fuel	FTD
Injection amount: M_f [mg]	10.3, 14.9
Naphthalene concentration: X_{naph} [ppm]	0, 65,000
Sampling conditions	
Distance from nozzle orifice: z [mm]	60, 70, 90
Grid type	Carbon coated copper grid Molybdenum micro-grid
Temperature of sampler: $T_{sampler}$ [K]	373

Table 2. FTD and conventional diesel (JIS#2) fuel specification

Parameter	JIS#2	FTD
Density at 15°C [kg/m ³]	834	758
Distillation [°C]		
Initial boiling point	166	156
10%	217	171
50%	286	204
90%	339	302
Final boiling point	360	320
Cetane number	54	69
Viscosity at 40°C [cSt]	3.926	1.773
Pour point [°C]	-12.5	-50
Lower calorific value [MJ/kg]	43.0	43.8
Sulphur [%mass]	6	0.1
Aromatics [%mass]		
Mono	15.8	—
Di	1.9	—
Tri	0.2	—
Total	17.9	—

Table 2 shows the specifications of the FTD fuel used in the present study compared with Japanese conventional JIS#2 diesel fuel [4]. The JIS#2 fuel contains 17.9 per cent of

aromatics, while the FTD does not contain aromatics. Naphthalene was chosen as a representative aromatic substance as a soot precursor because high concentration of naphthalene has been detected by gas sampling in a burner flame [13]. Furthermore, in our previous investigations, naphthalene was confirmed to be a useful marker of small PAHs easily distinguishable from combustion-generated larger PAHs via EEM multi-wavelength spectroscopic technique [3].

TEM Observation of Sampled Soot

Soot particles directly sampled onto the grid from a diesel spray flame were observed using a High-Resolution Transmission Electron Microscope (JEOL, JEM-2100F) with a specified maximum point resolution of 0.19nm. The acceleration voltage is 200keV. All images were digitally recorded with a CCD camera (Gatan Ultrascan 1000/FIRST LIGHT). The image resolution is 2048 $\times$ 2048 and physical pixel resolution is 14 μ m. The grid directly exposed to the diesel spray flame was observed without any thermal or chemical pre-treatments to maintain the original properties of soot particles in a diesel spray flame as much as possible. In the present study, the soot samples on the grids are highly vacuumed during the TEM observation and thus the existence and the effects of organic volatiles deposited on the soot samples cannot be observed or discussed. The time between the sampling experiment and the first TEM observation of the soot sample ranged from hours to months. Noticeable difference in the morphology, however, has not been observed in our general experience among samples with different storage duration up to years.

TEM observations were conducted at 3 different magnifications of x6k, x20k and 500k. The x6k was mainly used for the analysis of sampled soot concentration and aggregate morphology with larger number of aggregate samples for reliable analysis. The x20k was mainly used for the identification and size measurement of primary particles including separately existing ones and the ones within aggregates with reasonable resolution. The x500k was used for the high-resolution nanostructure analysis inside the primary particles. TEM images were taken at five different locations on each TEM grid as defined in Fig. 2 (a) with two different magnifications of x6k and x20k, resulting in more than 120 TEM images to be observed. For magnification of x500k, more than 60 TEM images were also taken at five different locations on each TEM micro-grid as defined in Fig. 2 (b). As reported by the authors, the fluctuation of sampled soot density among different on-grid locations is significant, while the fluctuation of morphology is relatively smaller [14]. In order to gain reliable analysis results, the number of on-grid observation locations and the number of soot samples have to be carefully decided. In the present study, however, the observed effects of in-flame axial locations and the fuel difference on the morphology and nanostructure of soot particles were more significant than the uncertainty caused by these fluctuation effects.