Fuel 179 (2016) 246–257

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Development of a soot particle model with PAHs as precursors through simulations and experiments

Yan-zhao An [a], Xiang Li [a], Sheng-ping Teng [a], Kun Wang [a], Yi-qiang Pei [a,*], Jing Qin [a,b], Hua Zhao [a]

[a] State Key Laboratory of Engines, Tianjin University, Tianjin 300072, PR China
[b] Internal Combustion Engine Research Institute, Tianjin University, Tianjin 300072, PR China

HIGHLIGHTS

- PAHs and soot particulates emitted from a GDI engine were sampled and analyzed.
- A gasoline surrogate fuels mechanism with PAHs formation has been developed.
- Validation including ignition delays and laminar flame speeds for gasoline.
- A soot model coupled with the TRF-PAH mechanism was developed.

ARTICLE INFO

Article history:
Received 3 January 2016
Received in revised form 27 March 2016
Accepted 28 March 2016
Available online 1 April 2016

Keywords:
GDI engine
PAHs mechanism
Soot particle model
CFD simulation

ABSTRACT

In the present study, the polycyclic aromatic hydrocarbons (PAHs) and soot particulates emitted from a gasoline direct injection (GDI) engine were sampled and analyzed. The results show that the vapor-phase PAHs and particulate-bound PAHs exist in GDI engine exhaust emissions. Soot particles are formed by the agglomeration of the quasi-spherical primary carbon particles, and the size of the PAH cluster is close to that of the core of the primary carbon particles. To predict soot particulates evolution in the engine cylinder, a reduced toluene reference fuel (TRF)-PAH chemical mechanism consisting of iso-octane, n-heptane and toluene as gasoline surrogate fuels for the GDI engine combustion simulation was developed. The reduced mechanism contains 232 reactions and 85 species, including 17 species and 40 elementary reactions, related to the PAH formation, which could well capture the oxidation characteristics of ignition delays and laminar flame speeds, as well as PAH emissions from the GDI engine. Then, a mathematical soot growth model coupled with the reduced TRF-PAH mechanism was developed based on the method of moment. The obtained experimental soot emissions were well predicted by this soot model. The distribution of particle number density was consistent with the distribution of A4 and C_2H_2, and the growth and distribution of soot mass was determined by the particle surface growth due to C_2H_2, the nuclear reaction of A4 and the particle surface oxidation reaction.

1. Introduction

In automotive engines, the diesel engine produces a higher level of soot particulate emissions, and the port fuel injection (PFI) gasoline engine produces a lower level of soot particulate emissions. The soot particulate emissions of a gasoline direct injection (GDI) engine are between those of the PFI engine and the diesel engine; however, the GDI engine produces a higher particle number and higher ultrafine particles ($d < 50$ nm). These ultrafine particles can adhere to the surface of soot particles and increase their toxicity [1–3]; they can also cause atmospheric photochemical smog and atmospheric two-particle generation. To gain a better understanding of the formation and change of soot particulates in the GDI engine combustion process, it is necessary to further study the chemical kinetics mechanism of the soot precursor and the particle dynamics mechanism of soot particles that are generated by the combustion of gasoline fuel in a GDI engine.

Sgro et al. [4] analyzed soot particles sampled from the exhaust of a GDI engine, and they reported that the solid core particles with a size of 1–5 nm might exist in the high-temperature region of the combustion chamber. The semi-volatile species condensed on the surface of the ultrafine particles as the exhaust cooled in the tail pipe. These ultrafine particles directly affected the surface growth of soot particles. Raj et al. [5] constructed a detailed soot particle

* Corresponding author. Tel./fax: +86 (0)22 2740 5807.
E-mail addresses: anyzh007phd@tju.edu.cn (Y.-z. An), peiyq@tju.edu.cn (Y.-q. Pei).

http://dx.doi.org/10.1016/j.fuel.2016.03.100

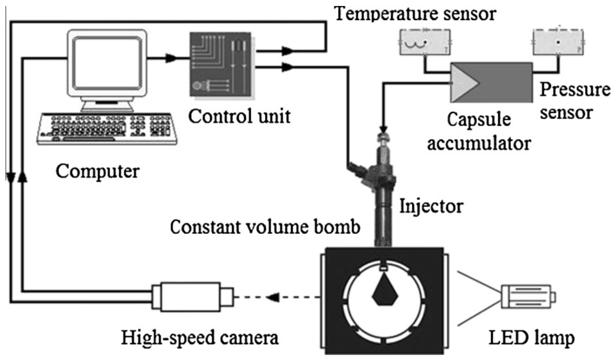

Fig. 1. Schematic diagram of spray visualization system.

growth model (KMC-ARS) with polycyclic aromatic hydrocarbons (PAHs) as the precursors. This model was verified for PAHs and the soot mole fraction in C_2H_2 and C_6H_6 flames, but it was not verified by an actual engine test. Jia et al. [6] developed the primary reference fuel (PRF)-PAH (isooctane/n-heptane) mechanism for diesel engine combustion; this mechanism was verified for the PAH mole fraction in laminar flames and diffusion flames. They developed a phenomenological soot model based on this mechanism and predicted the soot emissions from a diesel engine. Recently, the author developed a TRF-PAH (toluene reference fuel, TRF, composed of isooctane/n-heptane/toluene) semi-detailed reaction mechanism that contains 219 species and 1229 reactions [7]. This mechanism was verified for ignition delay times in a shock tube, laminar flame speeds in a flat flame adiabatic burner, small molecular species mole fraction and PAH mole fractions in isooctane/n-heptane flames. The predicted results were in good agreement with the measured results. In addition, the reaction pathways of PAH generation and consumption were determined by the species sensitivity analysis.

Soot precursors are the key species in the initial particle nucleation reaction and in the subsequent particle surface growth process, the prediction of soot particles should be based on the accurate prediction of the precursors. Therefore, the author developed the PAH formation mechanism and verified it for basic chemical experiment data and in an engine bench test; based on these results, the soot particle model for the GDI engine was constructed using the Converge code coupled with the reduced TRF-PAH chemical mechanism. Finally, the numerical simulations of the combustion and soot particle evolution process in a GDI engine were performed.

2. Experimental setup and calculation model

2.1. Spray test system and PAHs-soot particle sampling system

The spray test system is shown in Fig. 1. The experimental system was composed of a constant volume bomb, an image acquisition system, a fuel supply system, and a signal control system. In the experiment, an LED lamp was used as the background light source. Two coaxial viewing quartz windows of 100 mm in diameter were used to shoot the spray image. The capsule accumulator was used to provide a stable fuel supply pressure with an injection pressure adjustment range of 1–18 MPa. The shooting frequency of the high-speed camera was 10,000/s, and the resolution was 768 × 768. The obtained spray images were processed using Matlab to obtain the spray boundary. Each experimental case obtained five spray images performed with an average processing for reducing the experimental error. The injector and test conditions are shown in Table 1.

Table 1
Injector and test conditions.

Nozzle hole number	Symmetric 6 holes
Nozzle diameter (mm)	0.2
Injection pressure (MPa)	10
Injection pulse width (ms)	1.5
Test fuel	95# gasoline
Fuel temperature (K)	303
Ambient temperature (K)	298
Ambient pressure (MPa)	0.1

Table 2
Engine specifications.

Turbo GDI engine	
Bore × Stroke	82.5 × 92 mm
Injector	Multi-hole nozzle
Displacement/L	1.967
Air inlet mode	Turbocharged intercooled
Valve	Double VVT 16 valves
Maximum power/KW	160
Maximum torque/N m	320

A turbocharged, gasoline direct injection, inline four cylinders, double variable valve timing (VVT) engine was used in the current PAH and soot particle sampling experiments. By adjusting the open electronic control unit, the coefficient of variation (COV) was maintained below 3% during the measurement and sampling process. The engine specifications are shown in Table 2. The test fuel for the present experiment was commercial gasoline. The main combustion parameters, such as the in-cylinder pressure, pressure rise rate and in-cylinder temperature, were monitored by the self-developed combustion analyzer. The soot emissions were measured by AVL415; the air fuel ratio was detected by the LA4 oxygen sensor from the ETAS Company.

The red box[1] and blue box in Fig. 2 show the schematic diagram of the PAH and soot particulate sampling system. The detailed experimental instructions were described in the author's previous study [7]. The particulate-bounded PAHs were sampled using a fiber film (T60A20), and the vapor-phase PAHs were sampled using polyurethane foam (PUF), which contained 2.5-cm XAD-2 resin (Supelco). The sampling rate of the exhaust was 5 L/min, and the collection time was 45 min in the present experiment. The sampled PAHs were subjected to a classical Soxhlet extraction, and then, the extract concentration was determined using gas chromatography–mass spectroscopy (GC–MS) analysis. A standard solution containing 16 EPA-PAH compounds in acetonitrile solvent (PAHs Solution Mixture; J&K Scientific, Beijing, P.R. China) was used to calibrate the GC–MS. Table 3 shows the characteristic parameters and the retention time for the standard 16 PAH compounds. Soot particles were immobilized on a Quantifoil micro-machined holey carbon support film and were then suitably prepared for observations using a field-emission transmission electron microscope (FE-TEM). To avoid the accumulation of soot particles in the support film, the collection time was generally controlled at 8–10 s.

2.2. PAH formation mechanism

The soot particles formed in the GDI engine cylinder evolved from the soot precursors produced by the thermal cracking of the fuel injected into the cylinder. Because the coupling of a computational fluid dynamics (CFD) calculation required a substantial

[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.