



Surface functional groups and sp^3/sp^2 hybridization ratios of in-cylinder soot from a diesel engine fueled with *n*-heptane and *n*-heptane/toluene



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HIGHLIGHTS

- In-cylinder soot from *n*-heptane and *n*-heptane/toluene fueled-diesel engine was studied.
- Surface functional groups (SFGs) and sp^3/sp^2 hybridization ratios were assessed.
- Adding toluene to *n*-heptane increased the concentrations of SFGs.
- The sp^3/sp^2 hybridization ratio was obviously increased by toluene addition.
- Aliphatic C–H groups had a correlation with sp^3/sp^2 hybridization ratios.

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ABSTRACT

This work compared the surface functional group (SFG) types and concentrations and sp^3/sp^2 hybridization ratios of in-cylinder soot samples generated by a heavy-duty diesel engine when employing *n*-heptane and a toluene/*n*-heptane mixture (20% toluene by volume) as the fuels. In-cylinder soot samples were obtained from a total cylinder sampling system, and the SFGs and sp^3/sp^2 hybridization ratios were analyzed using Fourier transform infrared and X-ray photoelectron spectroscopy. Despite the differences in fuel formulation, both *n*-heptane and *n*-heptane/toluene soot exhibited similar trends in terms of changes in the SFGs concentrations and sp^3/sp^2 hybridization ratios during the combustion process. However, the addition of toluene to the *n*-heptane was found to increase the concentrations of all SFGs as well as the sp^3/sp^2 hybridization ratio. The C–OH and C=O group concentrations exhibited a bimodal distribution for both the *n*-heptane and *n*-heptane/toluene soot throughout the combustion process, with the concentrations peaking in the premixed and diffusion combustion phases, respectively. In contrast, the relative amounts of aliphatic C–H groups decreased in the premixed combustion phase, increased in the early diffusion combustion phase, and then decreased in the subsequent combustion phase. The sp^3/sp^2 hybridization ratios obtained from both fuel soot were observed to initially decrease, then to increase before a decrease during the combustion process. There was a definite correlation between the sp^3/sp^2 hybridization ratio and the relative concentration of aliphatic C–H groups.

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1. Introduction

Functional groups on soot surface are produced as intermediates during soot formation and oxidation [1–5], and play an important role in both these processes. For example, the thermal decomposition of surface functional groups (SFGs) can physically and chemically reduce the barriers to lamella realignment, thus mediating the reorganization of carbon lamella [6] and altering the soot structure. During soot oxidation, C–H and oxygenated

functional groups attached to non-six-membered carbon rings behave as highly reactive edges, providing a greater number of the reactive sites for the facile oxidation of soot [7–11]. Moreover, sp^3 and sp^2 hybridizations are the main chemical states of carbon in soot, and the amounts and spatial relationships of the carbon atoms in these two states are intimately linked to soot formation [12]. Thus, it is important to gain insights into the SFGs and sp^3/sp^2 hybridization ratio of soot to understand the soot formation and oxidation mechanisms.

Within the combustion history, the initial fuel composition plays a key role in the types and concentrations of SFGs and sp^3/sp^2 hybridization ratio of soot. Alfè et al. [13] reported that

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the soot produced from benzene and cyclohexane premixed flames contained relatively fewer C–H SFGs compared with the soot obtained from methane and ethylene premixed flames, and thus concluded that the amount of C–H groups on the soot surface was dependent upon the fuel nature. After examining the soot generating from several emission sources, Vander Wal et al. [12] found that the fuel oxygen content had a marked effect on the sp^2/sp^3 hybridization ratio. In the case of diesel-generated soot, it is very difficult to determine the impact of fuel composition on the SFGs and sp^3/sp^2 hybridization ratios because of the component complexity of conventional diesel fuel. For this reason, the alkane hydrocarbon *n*-heptane, which has a cetane number close to that of diesel fuel and for which the oxidation chemistry is very well known, has been widely employed as a surrogate for hydrocarbon fuels in diesel engines [14,15]. Aromatics account for a large fraction of conventional diesel fuels (about 25–35% by weight on average) [16,17] and toluene is representative of many of these aromatic compounds [18]. Thus, the *n*-heptane/toluene mixture has been proposed as a more suitable surrogate for the alkanes and aromatics in diesel fuel in experimental and numerical studies [15,19].

To date, the studies on the SFG and sp^3/sp^2 hybridization ratio have focused almost exclusively on the soot generated from laboratory flames [20–22] or diesel exhausts [8–11,23]. Due to the high pressure and temperature environment for the diesel combustion, there have been few reports on the SFGs and sp^3/sp^2 hybridization ratio of diesel in-cylinder soot. The properties of SFGs and sp^3/sp^2 hybridization ratio for the soot generated from laboratory flame differ substantially from those for the diesel in-cylinder soot due to differences in combustion processes, combustion temperature and gas pressure, all of which play an important role in the formation and decomposition of SFGs and the sp^3/sp^2 hybridization ratio [8,12]. Furthermore, the information obtained from exhaust soot can only provide the features of the SFGs and sp^3/sp^2 hybridization ratio of the mature diesel soot. In this context, this paper provided comprehensive characterization of the SFGs and sp^3/sp^2 hybridization ratio of diesel in-cylinder soot when *n*-heptane and an *n*-heptane/toluene mixture as fuels were burned in a diesel engine. A total cylinder sampling system was employed to obtain the in-cylinder soot samples. The aliphatic C–H functional groups on the obtained in-cylinder soot surface were measured using Fourier transform infrared (FT-IR) spectroscopy, while the oxygenated functional groups and sp^3/sp^2 hybridization ratios were assessed by X-ray photoelectron spectroscopy (XPS). In addition, an attempt was made to obtain a correlation between the SFGs and the sp^3/sp^2 hybridization ratios.

2. Materials and methods

A 5.79 L heavy-duty, direct-injection diesel engine was used in this study. This engine was equipped with a high-pressure, common-rail fuel injection system and a turbocharged/inter-cooled air intake system and powered up to 132 kW at a maximum speed of 2600 rpm. The sixth cylinder was modified as a total cylinder sampling system to allow the sampling of soot directly from the combustion chamber. During sampling, an aluminum alloy diaphragm was used to seal the engine cylinder head, acting

as a sampling valve. At a pre-set crank angle during a sampling cycle, this diaphragm was instantaneously cut by an electromagnet-actuated tube cutter, following which the cylinder contents were discharged from the cylinder into a sampling bag. The samples were immediately quenched and diluted by mixing with high pressure nitrogen to obtain a temperature below 52 °C, to prevent any additional reactions during the sampling process. A detailed description of this apparatus and sampling procedure has previously been reported in the literature [17,24–26].

The engine operating conditions are provided in Table 1. Two diesel fuel surrogates were used: *n*-heptane and a mixture of 80 vol.% *n*-heptane and 20 vol.% toluene (termed *n*-heptane/toluene). The relevant properties of both fuels have been described in the literature [25]. Different injection time intervals were employed to ensure the same equivalence ratios for the *n*-heptane and *n*-heptane/toluene fuels. Because the content of toluene in the *n*-heptane/toluene mixture was only 20%, the ignition delay when using the *n*-heptane/toluene was almost the same as when using the *n*-heptane fuel at the same equivalence ratio. Both fuels exhibited almost the same behavior in terms of the apparent heat release rates, in-cylinder pressures and average temperatures (see Fig. 1). To characterize the in-cylinder soot during combustion process, five representative sampling points were chose to represent the different diesel combustion phases according to the plots of in-cylinder pressure and apparent heat release rate in Fig. 1. The determination of the diesel combustion phase followed the method suggested by Heywood [27]: in the premixed combustion phase, the heat release rate is generally very high and the period corresponds to the rapid cylinder pressure rise. The dif-

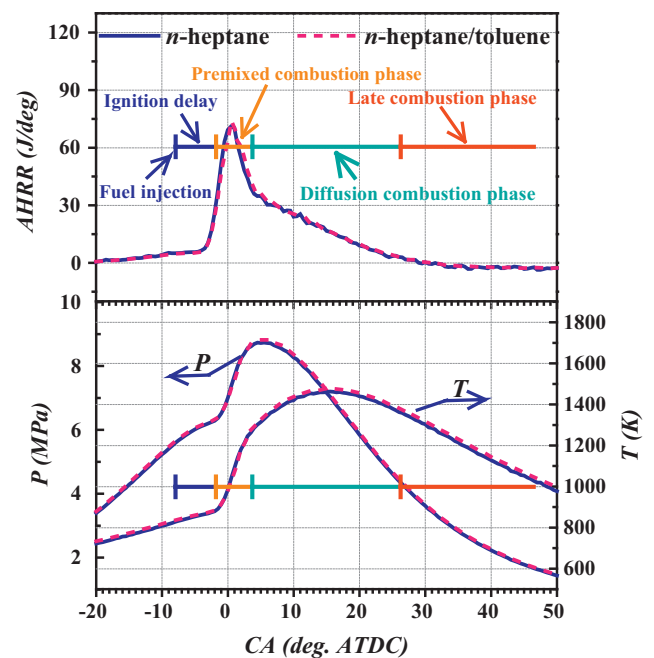


Fig. 1. Cylinder gas pressure (P), mean temperature (T) and apparent heat release rate (AHRR) as functions of crank angle (CA), identifying different diesel combustion phases.

Table 1
Diesel engine operating conditions.

Fuel	Engine speed (rpm)	Common rail pressure (MPa)	Start of injection (°CA ATDC)	Duration of injection (ms)	Fuel–air equivalence ratio (Φ)	Intake temperature (K)
<i>n</i> -Heptane	1000	60	–8	0.800	0.267	318
<i>n</i> -Heptane/toluene	1000	60	–8	0.832	0.264	318

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