Poster-Extended Abstract

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Title: Study of diesel soot structure and reactivity upon oxidation by Raman microspectroscopy

Introduction

Diesel soot is the product of incomplete combustion in diesel engines and can cause environmental and health effect problems. It is, therefore, essential to remove these particles from the exhaust and Diesel Particulate Filters (DPFs) are considered to be the most effective means for this purpose. However, DPFs have to be regenerated periodically by oxidation of the collected soot [1], in order to avoid undesirable backpressure in the engine and as a consequence the loss of engine power. In recent years several studies have appeared addressing how the morphology and microstructure of soot particles affect soot oxidation. Raman microspectroscopy is an analytical tool that can be used for a rapid determination of soot structure and has been the subject of several studies related to the soot reactivity [2-4].

In the present work, Raman microspectrosopy has been employed for the investigation of the structural changes of several diesel engine soot samples upon oxidation. The soot particles were acquired from filters exposed in diesel engine exhaust. The effect of engine type (common rail versus rotary pump engine), engine operating conditions (speed and load) and combustion mode (conventional versus Homogeneous Charge Compression Ignition, HCCI) were studied. For comparison purposes, the structural evolution of a carbon black (synthetic soot) sample and a graphite powder (representing the lower reactivity limits) were also studied. High-Resolution Transmission Electron Microscopy (HR-TEM), Elemental analysis and Thermogravimetric analysis (TGA) were also employed for the morphological characterization of untreated and partially oxidized soot samples, the quantification of C/H content and the determination of the oxidation rate, respectively. Correlation of the Raman spectral parameters with the soot oxidation rate was studied.

Experimental procedure

In Table 1 the soot samples employed for the present study are presented.

Table 1: Investigated soot samples

Soot samples	Combustion mode	Diesel Engine type	
Derived from Diesel Engine	Conventional	Common rail (CR) Euro III	CR1
		Common rail (CR) Euro IV	CR2
		Rotary pump (RP) Euro II	RP1
		Rotary pump (RP) Euro II	RP2
	Non-conventional	Euro IV	HCCI1
		Euro IV	HCCI2
Carbon Black	-	-	CB
Commercial Graphite	-	-	CG

Raman spectra were recorded on untreated soot samples as well as during the oxidation process with a Raman microscope system using a 514.5 nm laser line as an excitation source (delivering ~7.5 mW). The spectral parameters such as band position, band intensity (i.e. band height), band area (i.e. integrated area) and band width (i.e. Full Width at Half Maximum, FWHM) were determined using the Renishaw program Wire 2.0 and by curve fitting the spectra with five bands (G, D_1-D_4) [5]. The integrated intensity ratio I_{D1}/I_G of the D_1 and G bands was used to characterize the microstructure of soot samples. In particular, increase in this ratio is associated with an increased degree of structural disorganization. The soot oxidation experiments were performed under constant air-flow (100ml/min) and a temperature increase from 25 to 700^{o}C at a rate of 3^{o}C/min. Constant temperature oxidation of the soot samples under air was further performed at 600^{o}C. The goal of these experiments was to obtain partially oxidized (60% burn off) samples for sequential morphological characterization.

Results

Based on the acquired HRTEM pictures at ambient temperature, the CB and the conventional samples (collected either from a common rail or a rotary pump diesel engine and regardless of the engine operating conditions) exhibit the same shape of aggregates, which are composed of a number of near-spherical primary particles. The structure of the particles seems to be mainly amorphous with graphitic planes clearly visible in some of the amorphous domains. On the contrary, two types of aggregates & particles were observed in HCCI soot samples. In the first type, the aggregates and the particles resemble the ones of conventional samples. In the second type, particles with an amorphous inner core and a visible outer shell, consisting of crystal layers uniformly ordered and having equal distances between each other were observed. The results from the soot oxidation experiments performed up to 700^{o}C are presented in Figure 1. Evidently, in HCCI mode, the soot samples begin to burn at lower temperature and the reaction rates seem to be higher than the ones in conventional combustion, where the samples start to burn in higher temperatures. However, all diesel soot samples exhibit a maximum in the oxidation rate around 600^{o}C. Moreover, the elemental analysis of the samples revealed that the HCCI soot samples had higher hydrogen content (H/C: 0.0166 % w/w) toward the hydrogen content at the soot samples from conventional combustion (H/C: 0.0060% w/w).

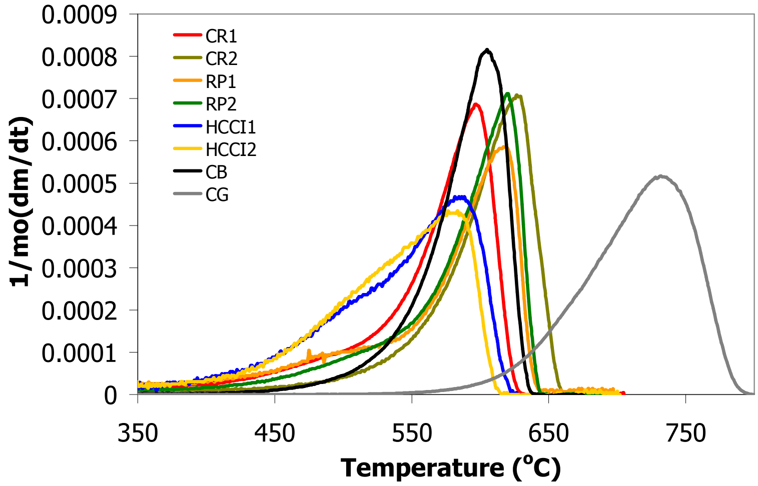
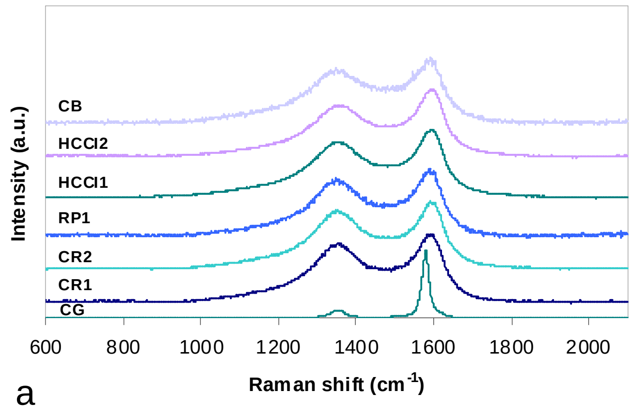


Figure 1: Evolution of the soot oxidation with increasing temperature for the soot samples.

Figure 2a shows exemplary first-order Raman spectra of all the investigated samples, while indicative I_{D1}/I_G ratios for the respective different soot samples are defined in Table 2. The spectrum of CG is characteristic of a mainly undisturbed graphitic lattice, exhibiting the lowest I_{D1}/I_G ratio, contrary to the other soot samples where an essentially equivalent degree of disorganization in the graphitic lattice is obvious.

Table 2: I_{D1}/I_G ratio for the different soot samples examined

Samples	I_{D1}/I_G
HCCI	4.6 ± 0.20
Conventional	4.4 ± 0.10
CB	4.5 ± 0.15
CG	0.2 ± 0.15



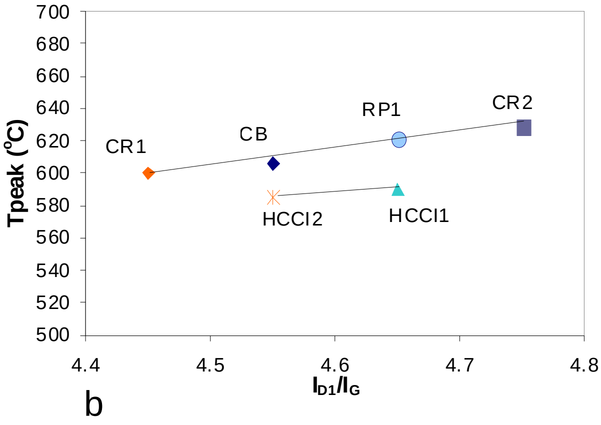


Figure 2: a) Raman spectra of different soot samples, b) Correlation of soot reactivity with I_{D1}/I_G Raman parameter at ambient temperature.

In Figure 2b, an attempt to correlate the reactivity of soot samples and their respective I_{D1}/I_G ratio is presented. It is obvious that there is a correlation between soot reactivity and this Raman parameter, however this correlation appears to be different for conventional and HCCI samples.

Based on the acquired HRTEM pictures of partially oxidized (60% burnoff) soot samples, obtained from the constant temperature oxidation experiments, no microstructural changes were identified for the conventional soot samples. The homogeneous amorphous structure hardly changed upon oxidation. On the other hand, the aggregates and the particles remained upon the oxidation of HCCI soot samples were just the ones that resemble the ones of the conventional samples. Partial oxidation seems to have eliminated the particles with the amorphous inner core and the visible outer shell. The Raman spectral parameters of soot samples changed slightly after this specific degree of oxidation.

Conclusions

In conclusion in the present study, μRaman spectroscopy was applied to analyze soot obtained from different diesel engine technologies (conventional and HCCI), while CB and CG samples were examined for reference. All conventional combustion soot samples exhibited similar degree of structural order on the primary particle scale, independently of the diesel engine type and the respective operating conditions, while upon oxidation slight changes were observed. Microscopic analysis showed that HCCI soot had different morphology on the primary particle scale, as well as higher reactivity towards oxidation than the other samples and the highest hydrogen content. A correlation between Raman parameter I_{D1}/I_G and reactivity was observed for conventional combustion soot samples, as well as for the HCCI samples. After a specific degree of burnoff, the morphology of HCCI sample changed, losing the outer shell of parallel graphitic planes and becoming more amorphous. The Raman spectral parameters of soot samples changed slightly after this specific degree of oxidation.

References

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Study of diesel soot structure and reactivity upon oxidation by Raman microspectroscopy

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ABSTRACT

Raman microspectroscopy is an analytical tool that can be used for a rapid determination of soot structure and has been the subject of several studies related to the soot reactivity [1]. Thus, in the present work, Raman microspectrosopy has been employed for the investigation of the structural changes of several diesel engine soot samples upon oxidation. The soot particles employed were acquired from filters exposed in diesel engine exhaust. The effect of engine type (common rail versus rotary pump engine), engine operating conditions (speed and load) and combustion mode (conventional versus Homogeneous Charge Compression Ignition, HCCI) were studied. For comparison purposes, the structural evolution of a carbon black (synthetic soot) sample and a graphite powder (representing the lower reactivity limits) were also studied. High-Resolution Transmission Electron Microscopy (HR-TEM), Elemental analysis and Thermogravimetric analysis (TGA) were also employed for the morphological characterization of untreated and partially oxidized soot samples, the quantification of C/H content and the determination of the oxidation rate, respectively. Correlation of the Raman spectral parameters with the soot oxidation rate was studied.

INVESTIGATED SOOT SAMPLES

Soot samples	Combustion mode	Diesel Engine type	
Derived from Diesel Engine	Conventional	Common rail (CR) Euro III	CR1
		Common rail (CR) Euro IV	CR2
		Rotary pump (RP) Euro II	RP1
		Rotary pump (RP) Euro II	RP2
	Non-conventional	Euro IV	HCCI1
		Euro IV	HCCI2
Carbon Black	-	-	CB
Commercial Graphite	-	-	CG

EXPERIMENTAL PROCEDURE

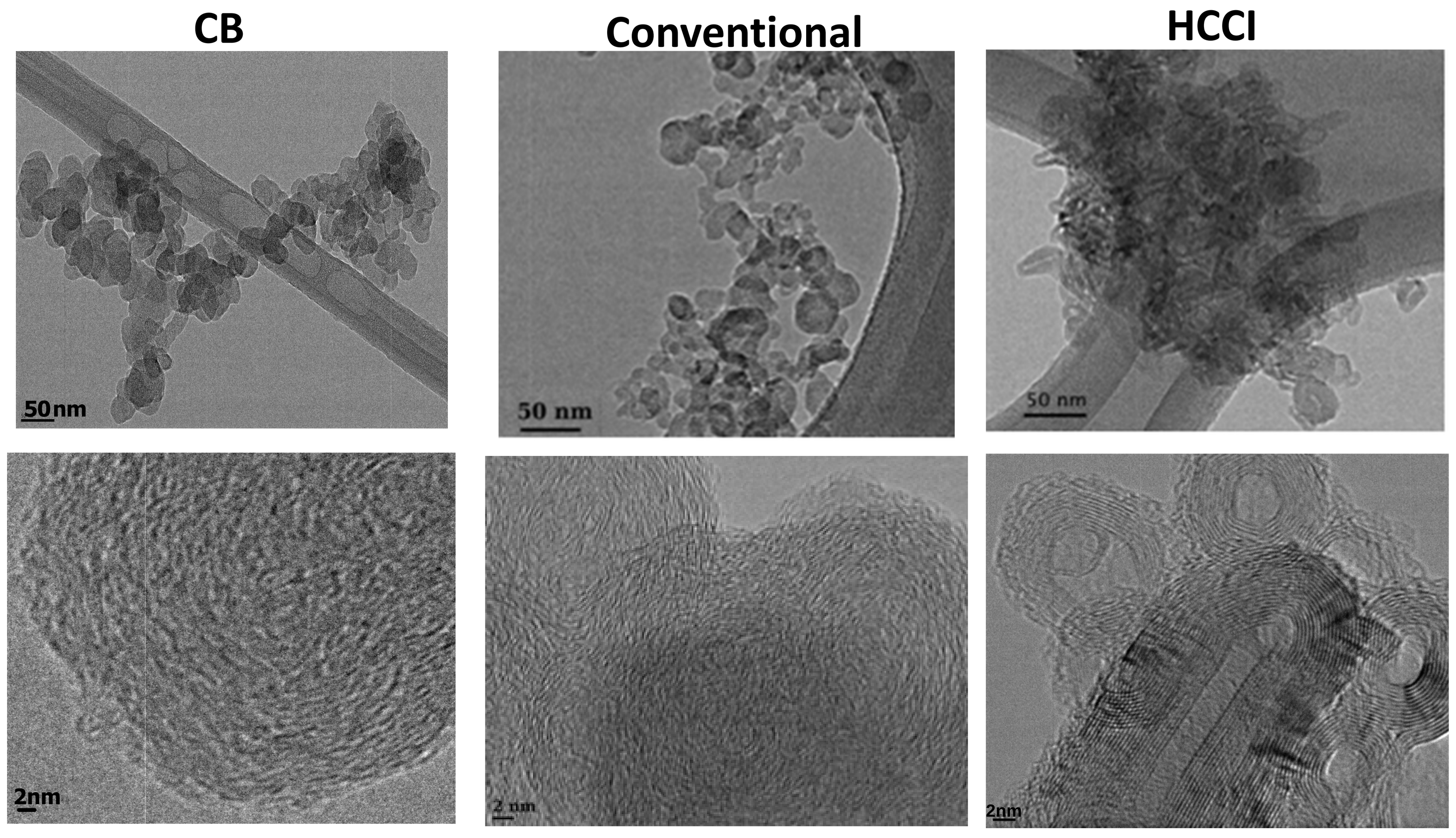
- A Raman microscope system using a 514nm laser as an excitation source (delivering ~7.5mW) was employed.
- The Raman spectral parameters were defined using the Renishaw program Wire 2.0 and by curve fitting the spectra with five bands (G, D_1-D_4) [2].
- Soot oxidation experiments were performed under constant air-flow (100ml/min):
  - at a temperature increase from 25 to 700ºC (3ºC/min) and
  - at 600ºC (constant oxidation temperature to obtain 60% burn off samples)

RESULTS

Morphological characterization

HR-TEM pictures of soot particles from different origins

CB **Conventional** **HCCI**

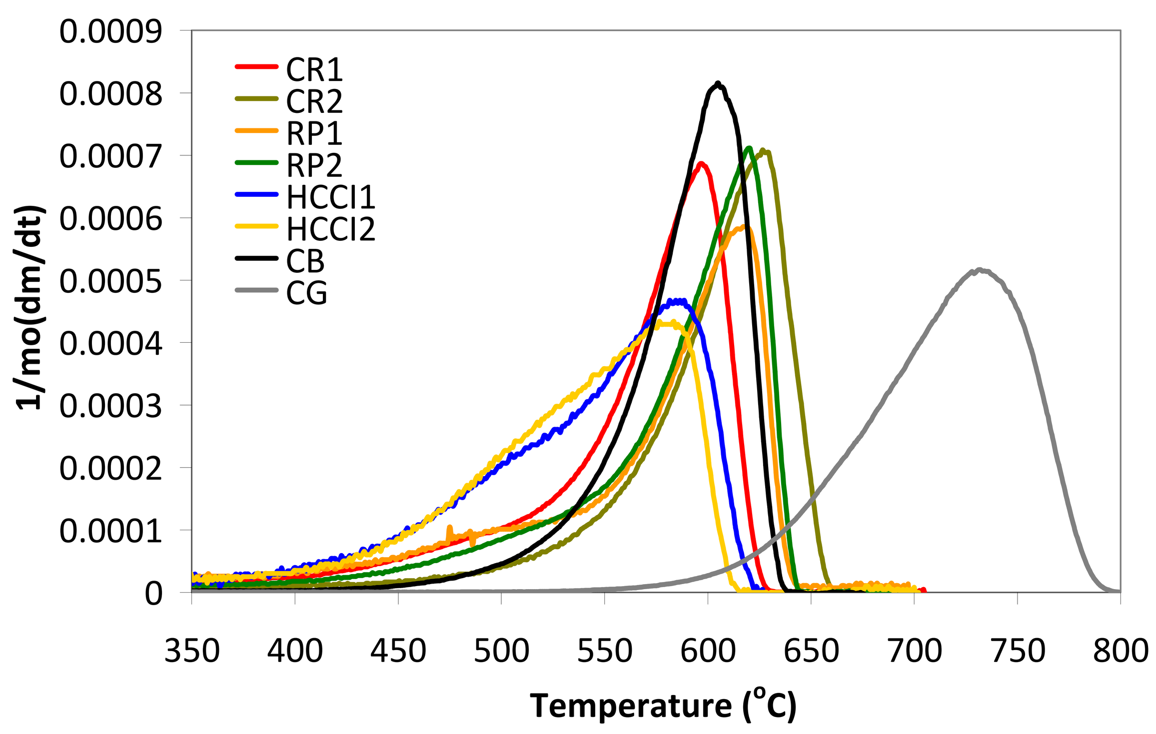


CB & Conventional samples
(collected either from a common rail or a rotary pump diesel engine and regardless of the engine operating conditions) exhibit the same shape of aggregates, which are composed of a number of near-spherical primary particles (mainly amorphous with graphitic planes clearly visible in some of the amorphous domains).

In **HCCI soot samples**
two types of aggregates and particles were observed. The aggregates and the particles resemble the ones of conventional samples and the particles with an amorphous inner core and a visible outer shell, consisting of crystal layers uniformly ordered and having equal distances between each other.

Thermogravimetric Analysis up to 700ºC

Evolution of the soot oxidation with increasing temperature for the soot samples.



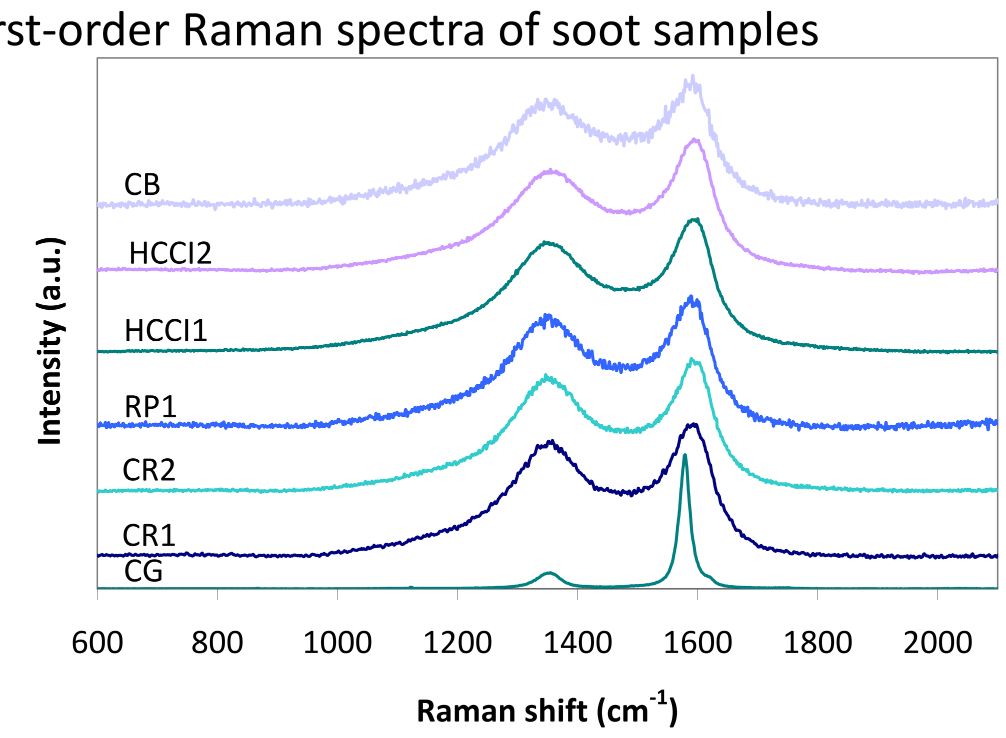
- In HCCI mode, the soot samples begin to burn at lower temperatures and the reaction rates seem to be higher than the ones in conventional combustion, where the samples start to burn in higher temperatures.
- All diesel soot samples exhibit a maximum in the oxidation rate around 600ºC.

Elemental Analysis

HCCI soot samples had higher hydrogen content (H/C: 0.0166 % w/w) toward the one of soot samples from conventional combustion (H/C: 0.0060% w/w).

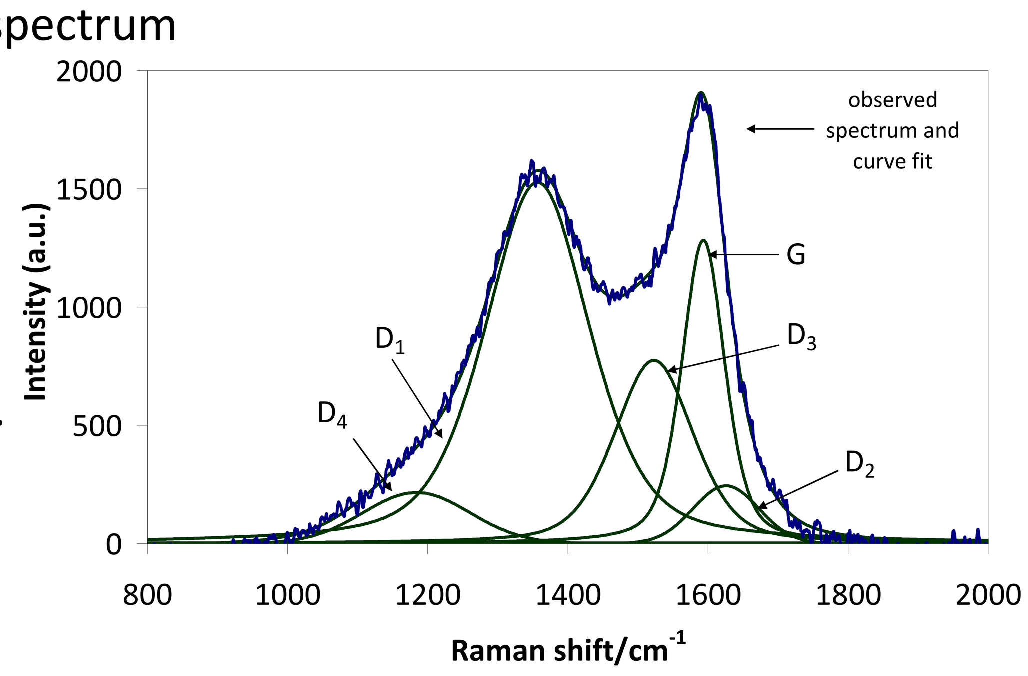
Raman microspectroscopy

Exemplary first-order Raman spectra of soot samples



Indicative curve fitting of Raman spectrum

- G band: ideal graphitic lattice.
- D1, D2 & D4 bands disordered
- graphitic lattice.
- D3 band: amorphous carbon
- (nongraphitic) content of soot.

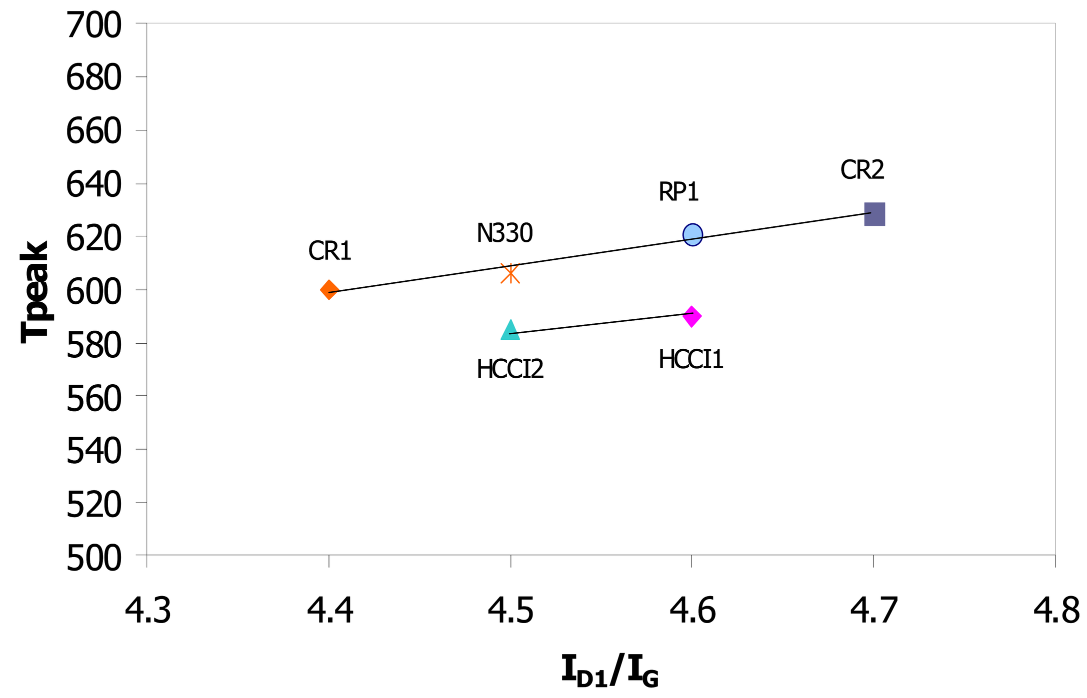


Samples	I_{D1}/I_G
HCCI	4.6 ± 0.20
Conventional	4.4 ± 0.10
CB	4.5 ± 0.15
CG	0.2 ± 0.15

The integrated area ratio I_{D1}/I_G is characteristic for the degree of structural organization.

- The spectrum of CG is characteristic of a mainly undisturbed graphitic lattice,
- exhibiting the lowest ID1/IG ratio.
- The spectra of Commercial and HCCI soot samples exhibit an equivalent degree of disorganization in the graphitic lattice.

Correlation of Soot Reactivity with Raman Parameter



- Discrimination between Conventional and HCCI soot samples.

After a 60% of burnoff, the morphology of HCCI sample changed, losing the outer shell of parallel graphitic planes and becoming more amorphous. The Raman parameters of soot samples changed slightly after this specific degree of oxidation.

CONCLUSIONS

- All conventional combustion soot samples exhibited similar degree of structural order on the primary particle scale, independently of the diesel engine type and respective operating conditions.
- HCCI soot had different morphology on the primary particle scale, higher reactivity towards oxidation and the highest Hydrogen content among the samples.
- A correlation between Raman parameter I_{D1}/I_G and reactivity was observed for conventional soot samples, as well as for HCCI samples.

REFERENCES

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