Extended summary to the presentation

Detailed investigations of the influence of diesel engine operating parameters to the physicochemical properties of emitted soot

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In recent years, scientists have revealed the fact that emitted soot particles change with different engine types and different engine generations. This is not only true for a mass reduction according to emission regulations and for a reduction of the emitted particle number due to progress in combustion and exhaust gas aftertreatment devices, but also for the physical and chemical properties like BET surface area, reactivity or primary particle size of engine-out soot particles [1–3]. It has been shown by many research groups that these properties have an impact on health as well as an influence on the reactive behavior in catalytic aftertreatment devices [4–8]. Besides the influence of engine design and fuel properties, many of these changes in engine-out soot particle properties are influenced by the development in engine combustion [9,10]. For example in modern diesel engines the injection pressure has been raised up to over 2500 bar and the use of emission gas recirculation (EGR) is a common tool to control combustion and emissions. Therefore the main focus of our work is on the influence of changes in engine operating parameters on combustion and hence on the physical and chemical properties of emitted soot particles.

For this parameter study, both a light duty Euro 4 3.0L V6 TDI diesel engine on an engine test rig and an optically accessed single cylinder diesel engine are applied together with tailpipe soot sampling. With similar parameter variations in both engines the trends of SMPS and high resolution transmission electron microscopy (HR-TEM) results of soot emissions in the TDI engine are also seen for the single cylinder engine. This comparability is useful in order to take advantage of the different benefits of each engine. With the TDI engine satisfactory quantities of engine-out soot can be sampled for BET-surface measurements and thermogravimetric (TGA) analysis. Therefore, the intermittently fired optically accessed single cylinder engine can be used to visualize the in-cylinder processes of injection, mixture formation and combustion which mainly influence the soot formation and oxidation.

The results of the V6 TDI engine study were mainly presented on last year's conference and in one of our latest papers [10]. The most important results from this first part of the study were the influences of the injection pressure on different soot properties. SMPS and HR-TEM measurements revealed that the mobility diameter and the primary particle diameter of soot samples decreased with increasing injection pressure at different engine loads with varying Lambda ($\lambda = 1/\Phi$). For soot samples with a smaller average primary particle size, the temperature of the maximum oxidation rate in the TGA was decreased. These soot samples also revealed a higher ratio of sp^2/sp^3-hybridized carbon bindings in electron energy loss spectroscopy measurements for samples with a smaller average primary particle size and hence expressed a change in the elemental carbon (EC) structure of emitted soot.

In the single cylinder engine, the main study is conducted with a variation of injection pressure, injection timing, boost pressure, engine speed and emission gas recirculation (EGR). The measurement result of the most important parameter variations, injection pressure (p_{inj}) and boost pressure (p_{boost}), are presented in this paper. For the in-cylinder measurements the pressure indication is used besides the application of different high-speed imaging techniques:

- mie scattering for the measurement of liquid fuel penetration depth and distribution,
- laser induced exciplex fluorescence for the visualization of the mixture formation process and the determination of the Lambda before the start of combustion (SOI),
- combustion luminescence for the evaluation of the visible start of combustion, flame propagation and burn time,
- spectroscopy of the chemiluminescence of different combustion species, mainly OH* at 305 nm and soot at 490 nm,
- 2-color-pyrometry to measure the temperature development during combustion.

The produced engine-out soot is simultaneously sampled with a rotating disk diluter system with an extra thermodenuder for SMPS measurements and directly sampled in the tailpipe for HR-TEM measurements.

The measurement results revealed the following:

- p_{inj} and p_{boost} cause a homogenization of the fuel/air mixture before combustion and p_{boost} leads to leaner mixtures.
- With better homogenization and leaner mixtures, the ignition delay is decreased and the premixed combustion phase is intensified, thus leading to higher combustion temperatures and a reduced visible burn time.
- The homogenization of a mixture before combustion directly reduces the initially formed soot whereas additional oxygen and the increased combustion temperature in leaner mixtures develop increasing OH*/soot ratios with no initial reduction of soot, but with a faster oxidation process of in-cylinder soot due to increased OH*.
- The described effects of increasing p_{inj} and p_{boost} lead to a decreasing mobility diameter, mass and number as well as to a reduced mean primary particle size of the emitted soot.
- Soot samples with a decreasing mean primary particle size have an increasing ratio of sp^2/sp^3-hybridized carbon bindings.
- Effects of increasing p_{inj} and p_{boost} are also in correlation with a decreasing soot agglomerate size derived from HR-TEM images and with an intense reduction of the calculated fractal dimension of the soot agglomerates.

The results from the combination of different optical in-cylinder and emission measurements show a strong correlation of p_{inj} and p_{boost} with combustion and hence with the soot formation and oxidation processes thus strongly influencing physicochemical soot properties. The revealed changes in elemental carbon structure for primary particles of different average sizes could be a possible reason for the change in oxidation behavior.

Additional TG-FTIR-MS measurements and an upcoming statistical correlation of the results of this study will soon allow a more detailed evaluation of the most important processes responsible for the changes in soot properties.

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16th ETH-Conference on Combustion Generated Nanoparticles,
Zürich, 24th-27th June 2012

Ulrich Leidenberger, Wolfgang Mühlbauer, Sebastian Lorenz, Sebastian Lehmann, and Dieter Brüggemann

Detailed Investigations of the Influence of Diesel Engine Operating Parameters on Physicochemical Properties of Emitted Soot

UNIVERSITÄT BAYREUTH

Motivation

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Physicochemical properties of soot particle emissions change with engine operating conditions

- primary particle size
- oxidation behavior
- VOF / EC
- BET surface area
- morphology
- graphitization
- reactive groups
- toxic and inflammatory potential

Influence and consequences:

→ **catalytic aftertreatment**
→ **environmental impact**
→ **atmospheric processes**
→ **human health effects**

Motivation

Engine Sequence of Events

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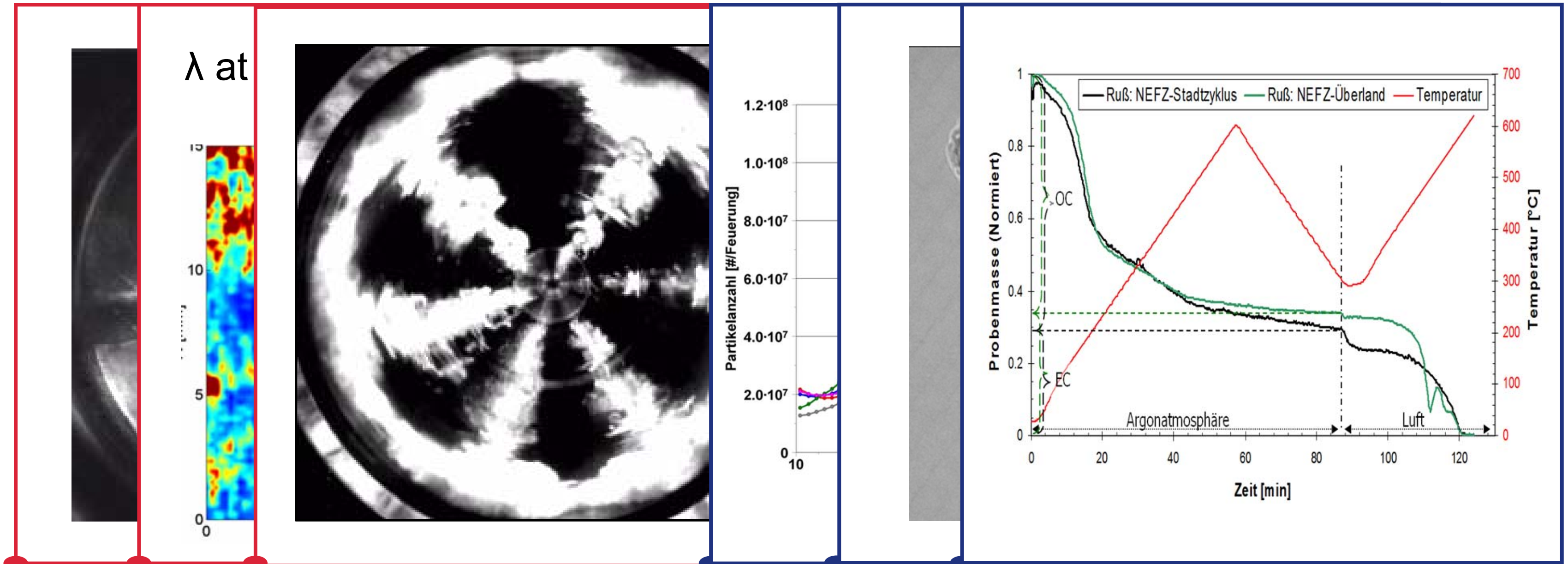
In-cylinder processes

Engine-out emissions



HS-spectroscopy, pressure indic.

TGA/BET-analysis

Laserinduced exciplex fluoresc. (LI

HR-TEM-imaging

Mie-scattering and HS-imaging

SMPS-measurement

Single Cylinder Engine

Variation of Operating Parameters

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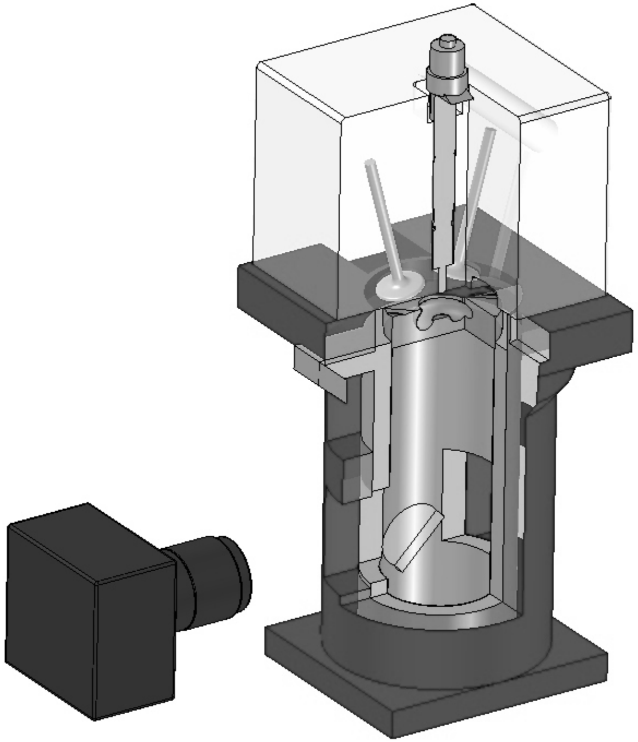
- Optical investigation of the in-cylinder processes
- Simultaneous sampling of the engine-out soot emissions



speed in min^{-1}	600; 800; 1000
injection pressure p_{inj} in MPa	80; 100; 130
star of injection in °CA BTDC	-10; -6; -3
boost pressure p_{boost} in MPa	0.105; 0.125; 0.145
EGR-rate in %	0; 25; 50
fueling rate in mg/stroke	17

Visualization of Combustion

Spectroscopy, LIEF, Thermometry

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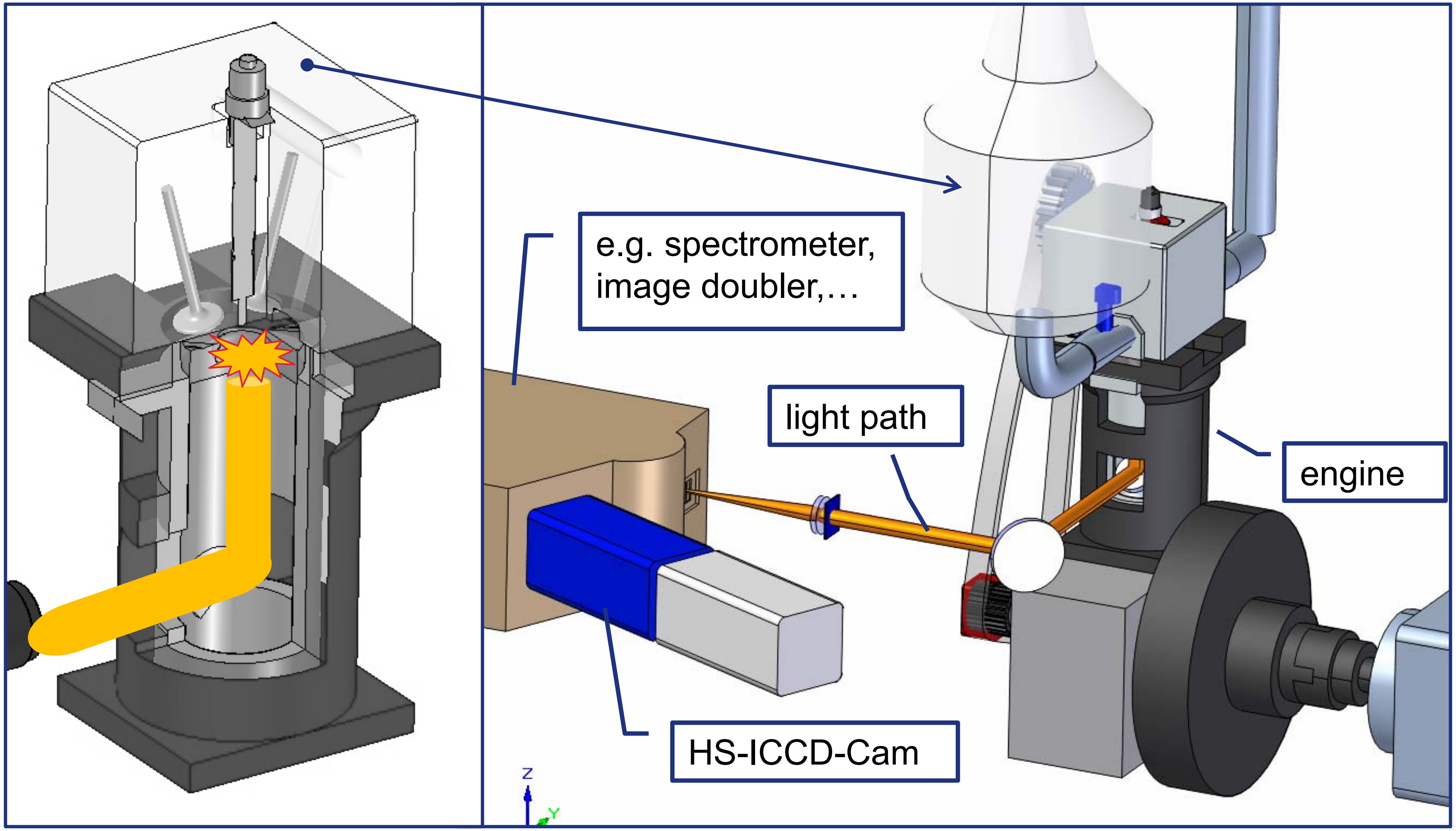

Summary of Intermediate Results From Last Year's Conference

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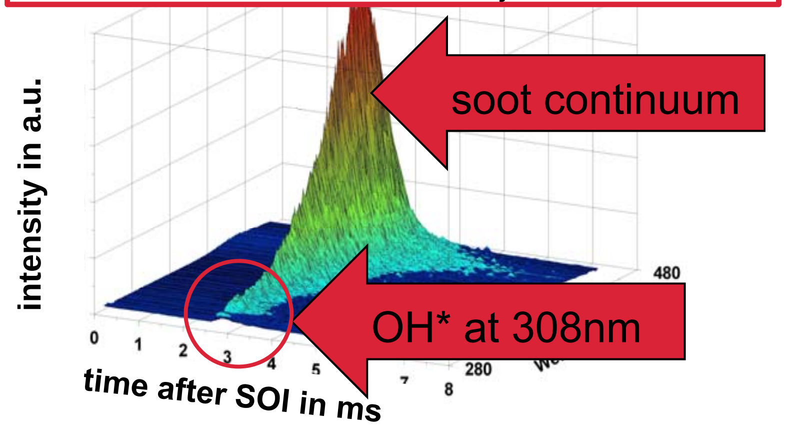
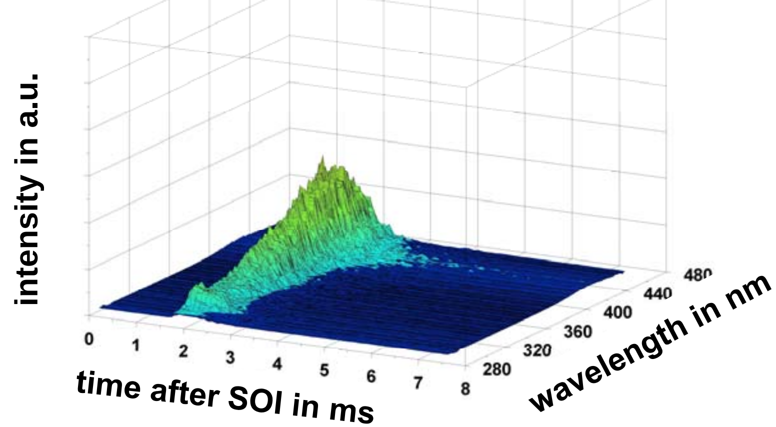
p_{boost} = 0.105 MPa, p_{inj} = 80 MPa



p_{boost} = 0.145 MPa, p_{inj} = 130 MPa



Results from a V6-TDI and an optically accessed single cylinder engine indicated:

- Increasing p_{boost} and p_{inj} caused higher spectral OH*/soot-ratio.
- Increasing p_{boost} and p_{inj} reduced emitted soot particle mass, mobility diameter, number and primary particle size.
- Smaller primary particles had lower oxidation temperatures in the TGA.
- Influence of p_{boost} and p_{inj} on soot agglomerate size and morphology was assumed by HR-TEM images.
- Mixing effects from p_{inj} and chemical effects from p_{boost} were assumed.

To do:
→ Clarify in-cylinder effects
→ Quantify influence on soot emissions
→ Correlate combustion to soot emissions

Laser Induced Exciplex Fluorescence

In-Cylinder Mixture Formation

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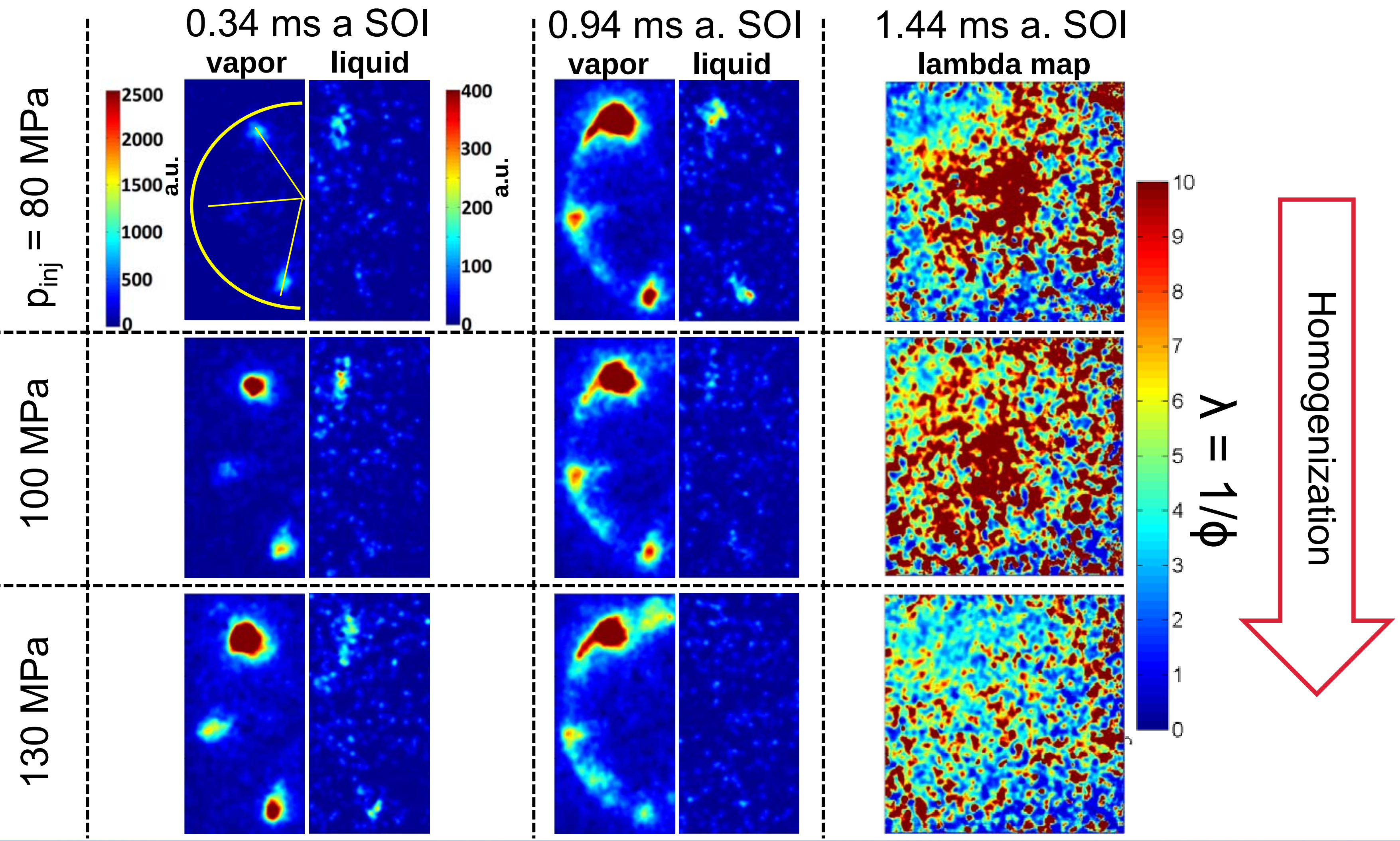

In-Cylinder Diagnostics
LIEF, 2-Color-Thermometry and OH* / Soot Chemiluminescence

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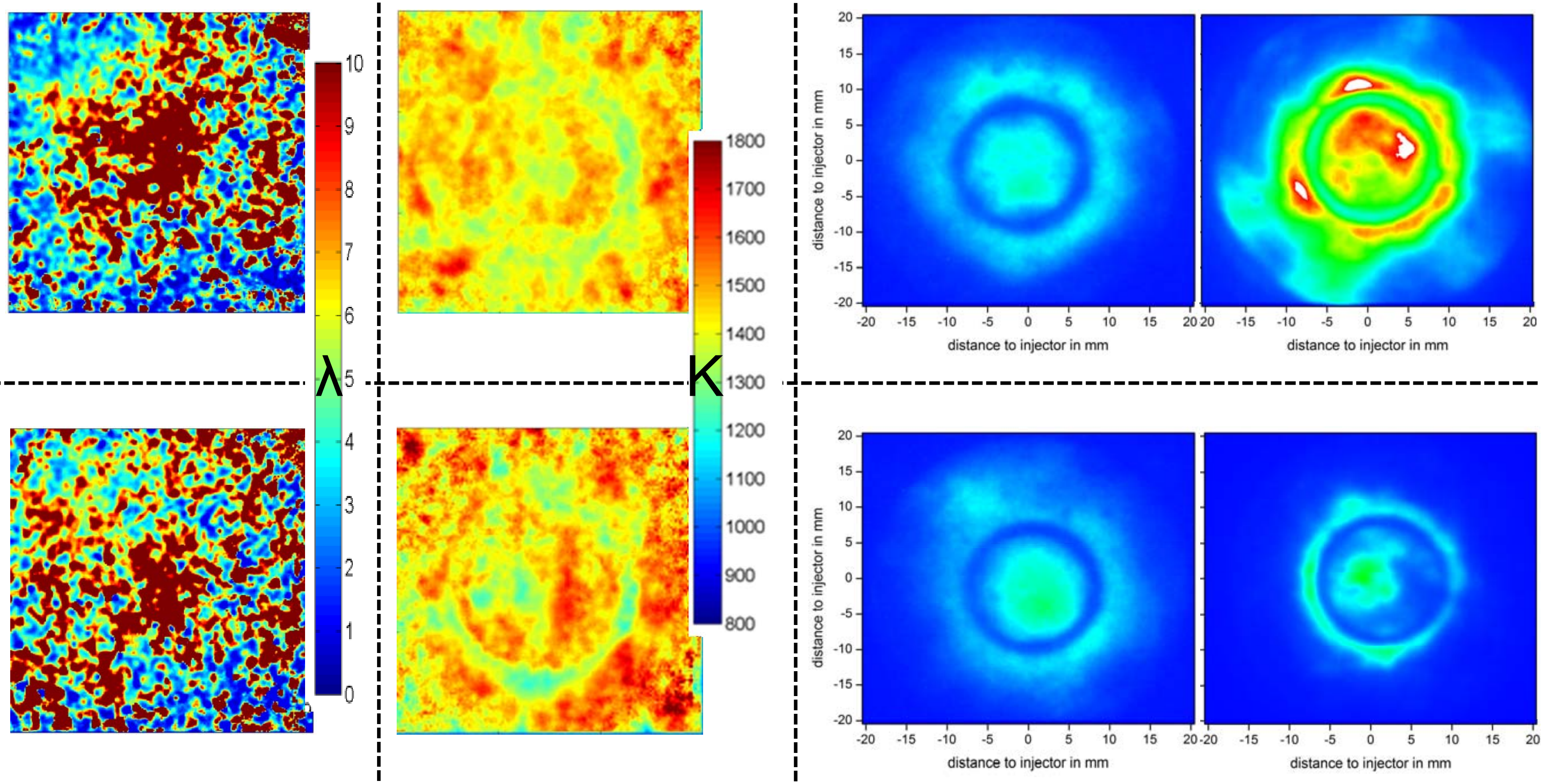
	Lambda (1/ϕ)	Temperature in K	OH* (308 nm)	Soot (490 nm)
p_{boost} = 0.105 MPa p_{inj} = 80 MPa				
p_{boost} = 0.145 MPa p_{inj} = 130 MPa				



Combustion Analysis
High Speed Luminescence Imaging, Pressure Indication

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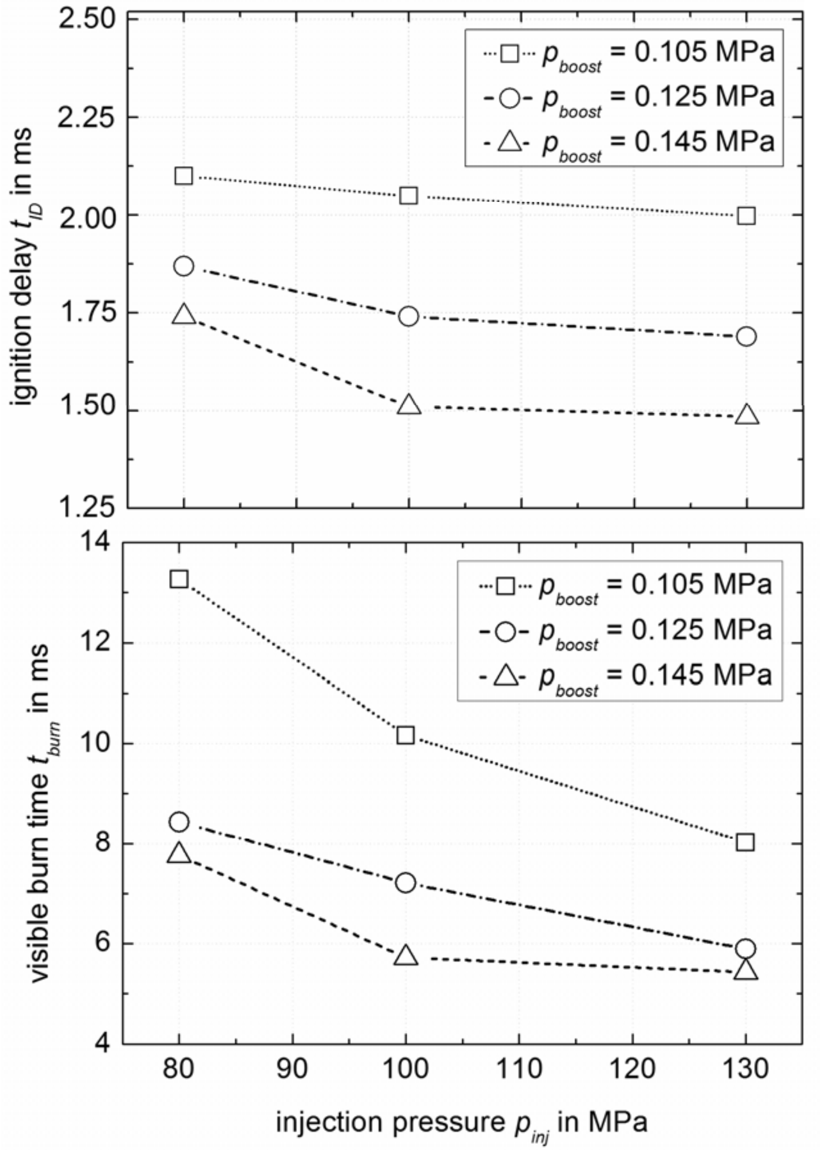
The ignition delay influences the position of the combustion phases.

The visible luminescence is equivalent to black body radiation of soot.

Short visible burn time:

→ Early oxidation of main in-cylinder soot concentration;

→ More time left for temperature dependent soot oxidation;



Visualization of Soot Emissions

HR-TEM Analysis

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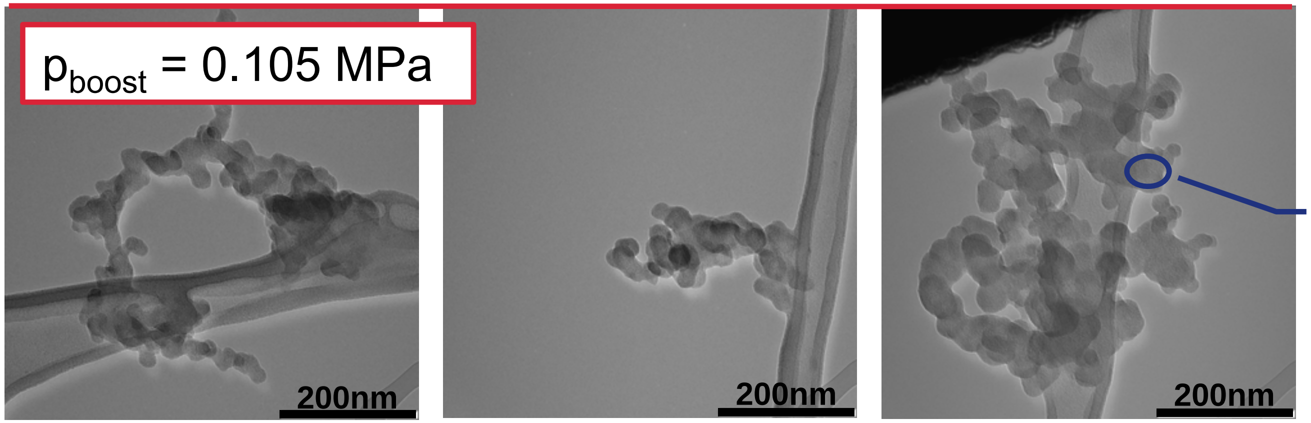
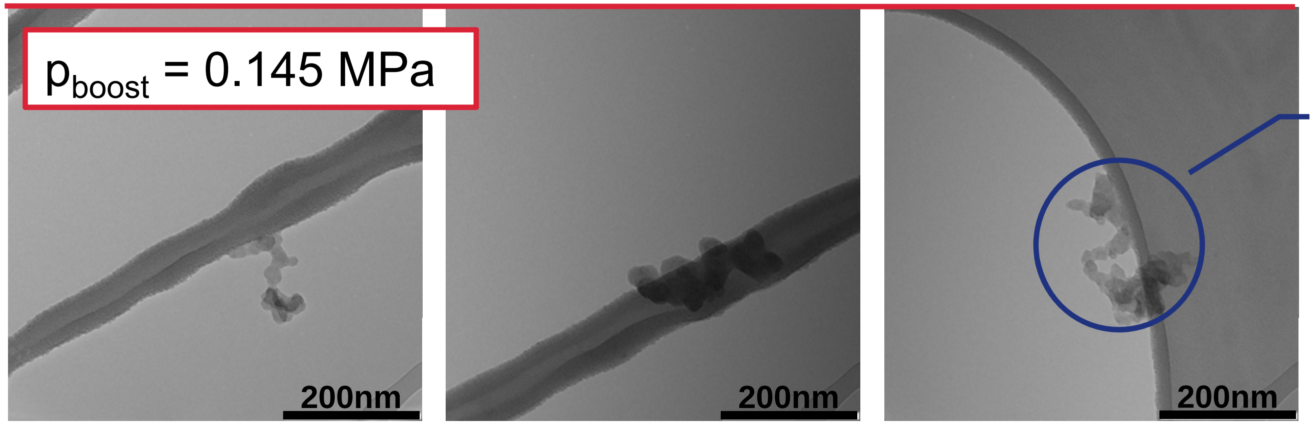


→Different properties change with operating parameters:



- Primary particle size
- Fractal dimension
- Carbon structure (EELS)
- Size of the agglomerate

HR-TEM: Geometric Measures

Agglomerate and Primary Particle Size

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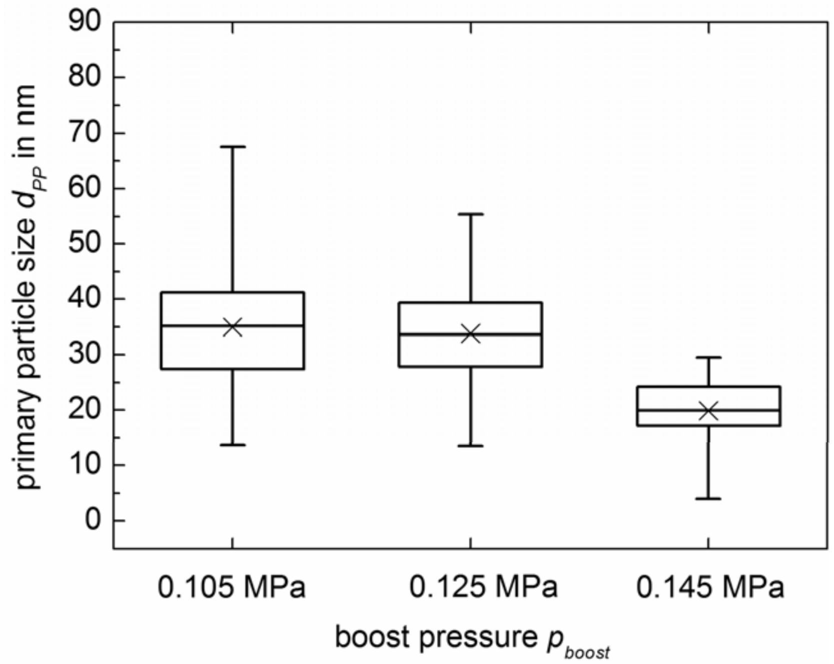
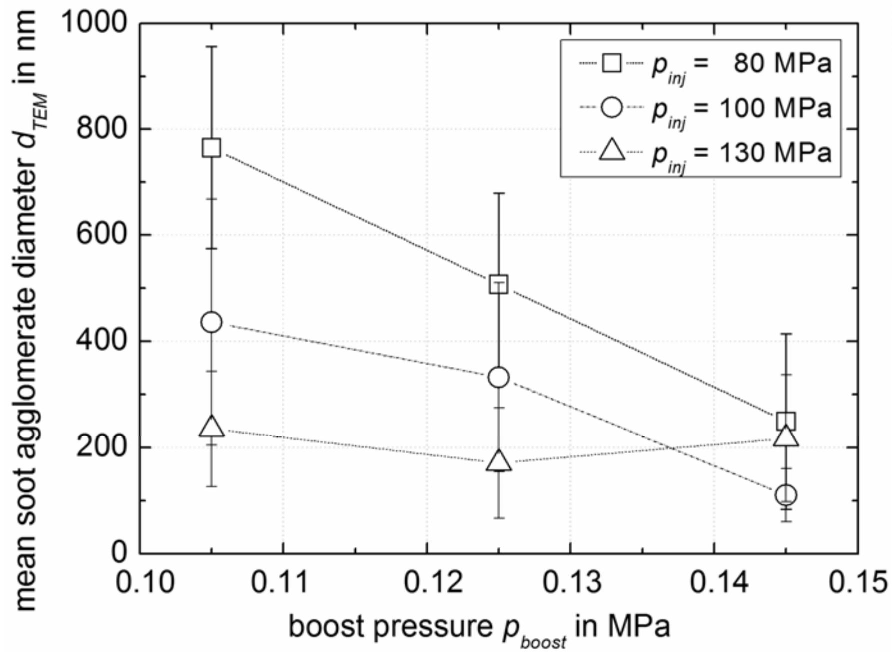
The primary particle size is reduced for increasing boost and injection pressure.

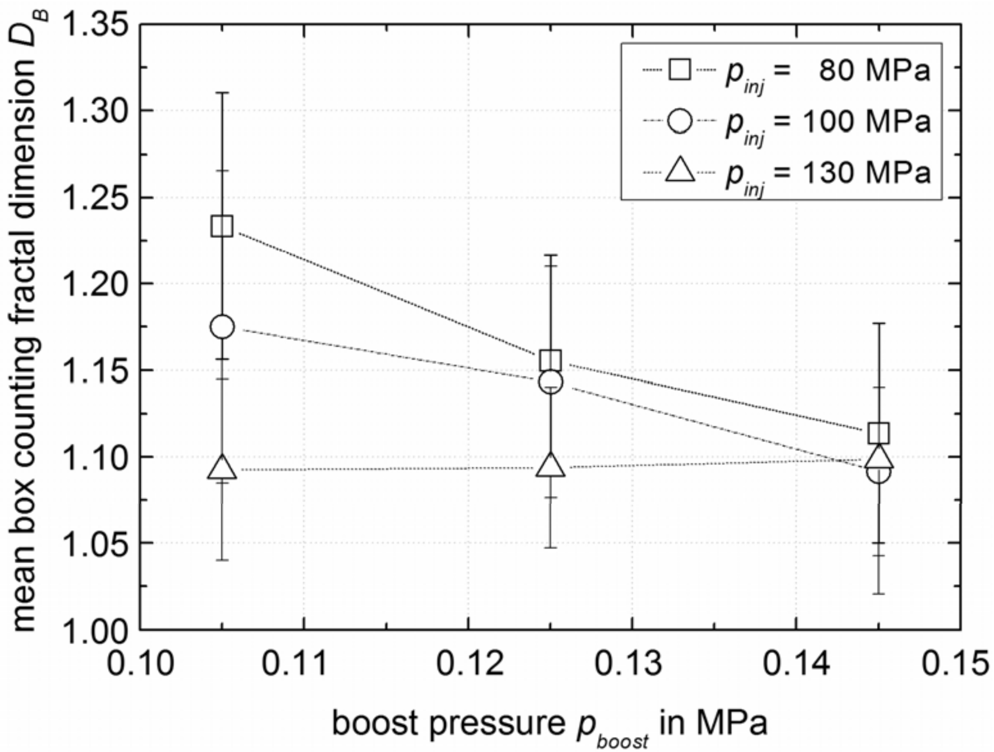


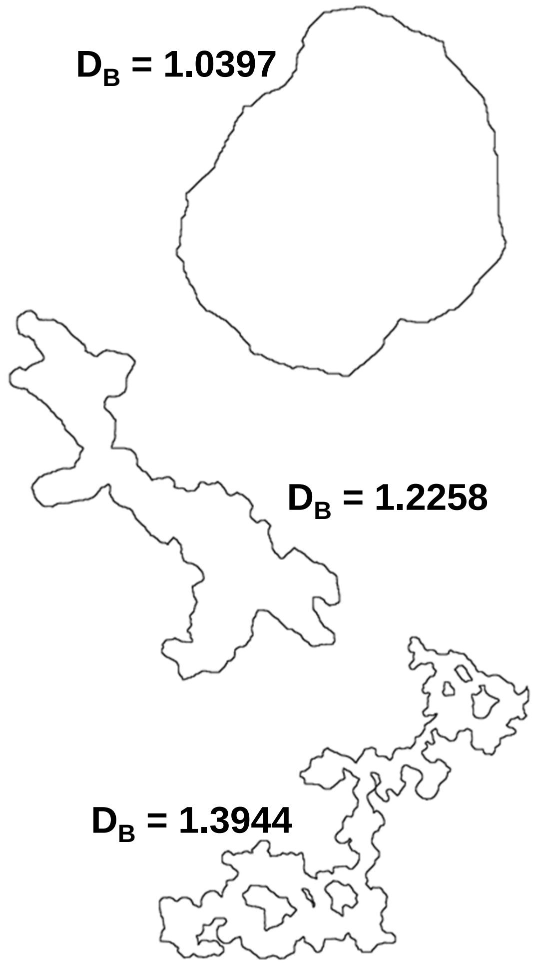


The mean of the maximum diameters concerning the visualized agglomerates is reduced for increasing boost and injection pressure.

HR-TEM: Soot Morphology

Box Counting Fractal Dimension





$$D_{B_i} = -lim\left(\frac{\log N_\varepsilon}{\log \varepsilon}\right)$$

N=Number of Boxes, ε=Scale of *i*

HR-TEM: Electron Energy Loss Spectroscopy
Information on the Carbon Structure

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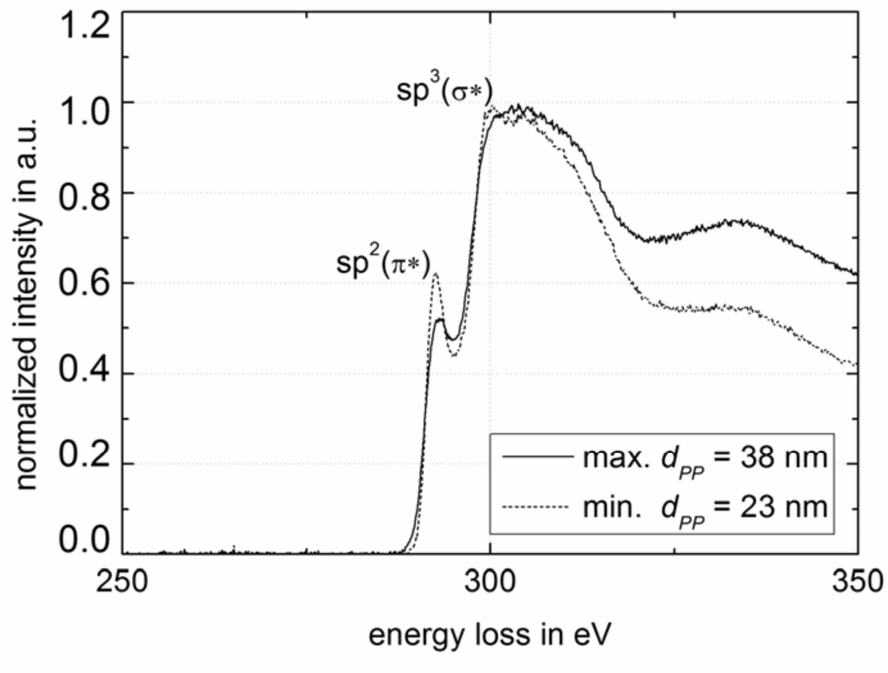
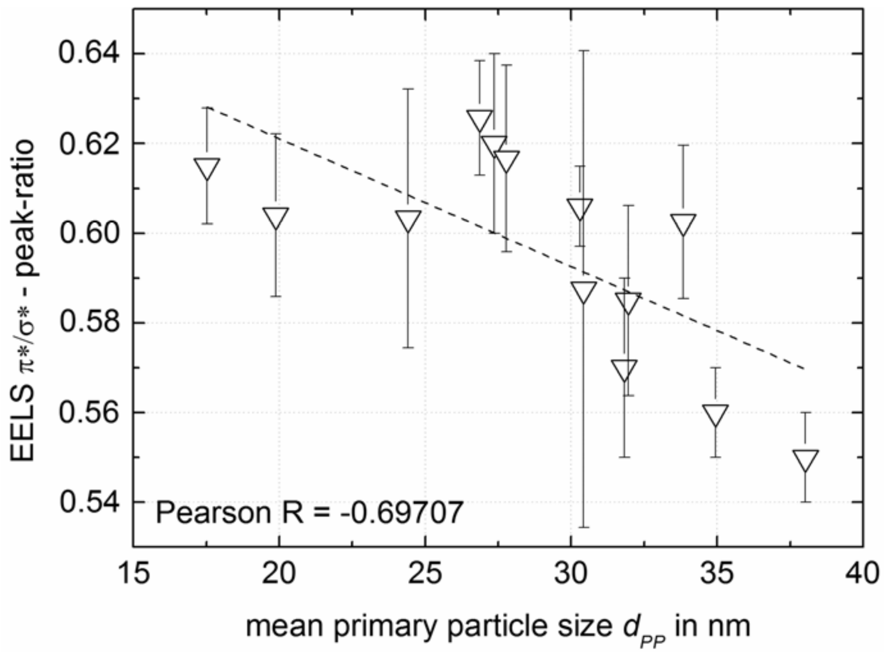
Absorption spectra of the carbon k edge reveals differences for soot from different operating points.





The characteristic π*/σ*-peak-ratio correlates well with the size of the primary particles.

Summary

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- Increasing p_{boost} and p_{inj} lead to
  - increasing homogenization of the fuel/air-mixture,
  - increasing combustion temperature and OH*/soot-ratio,
  - decreasing mean mobility diameter, particle mass and number,
  - decreasing soot agglomerate diameter and fractal dimension,
  - decreasing primary particle size.
- Smaller primary particles are correlated with
  - lower soot oxidation temperatures,
  - higher EELS π^*/σ^*-peak-ratio.
- p_{boost} has a stronger correlation with combustion derived results and emissions than p_{inj}.

Work in Progress

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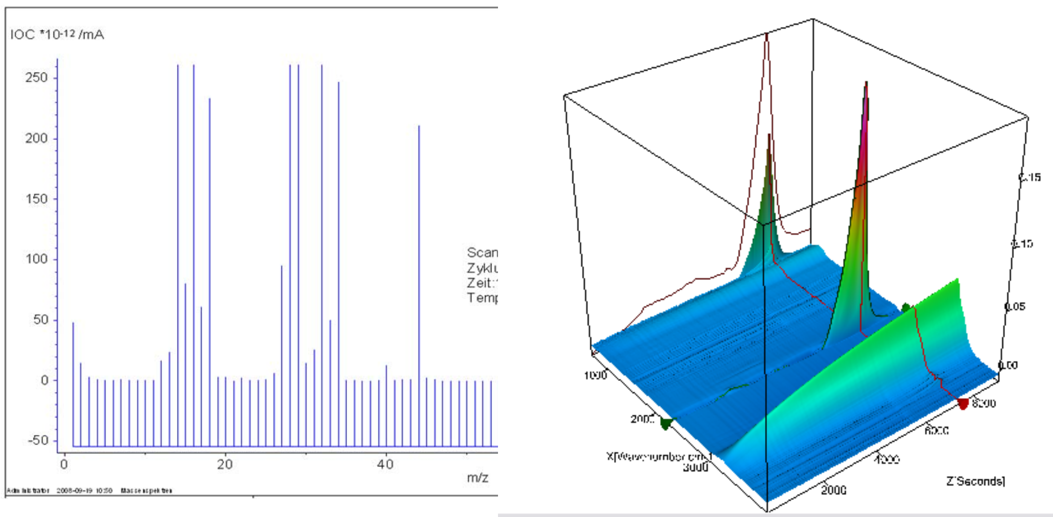
- Additional results from TGA-FTIR-MS analysis
- Statistical correlations between all results (operating parameters, combustion, emissions)
- Study with oxygenated fuels

TGA-FTIR-MS



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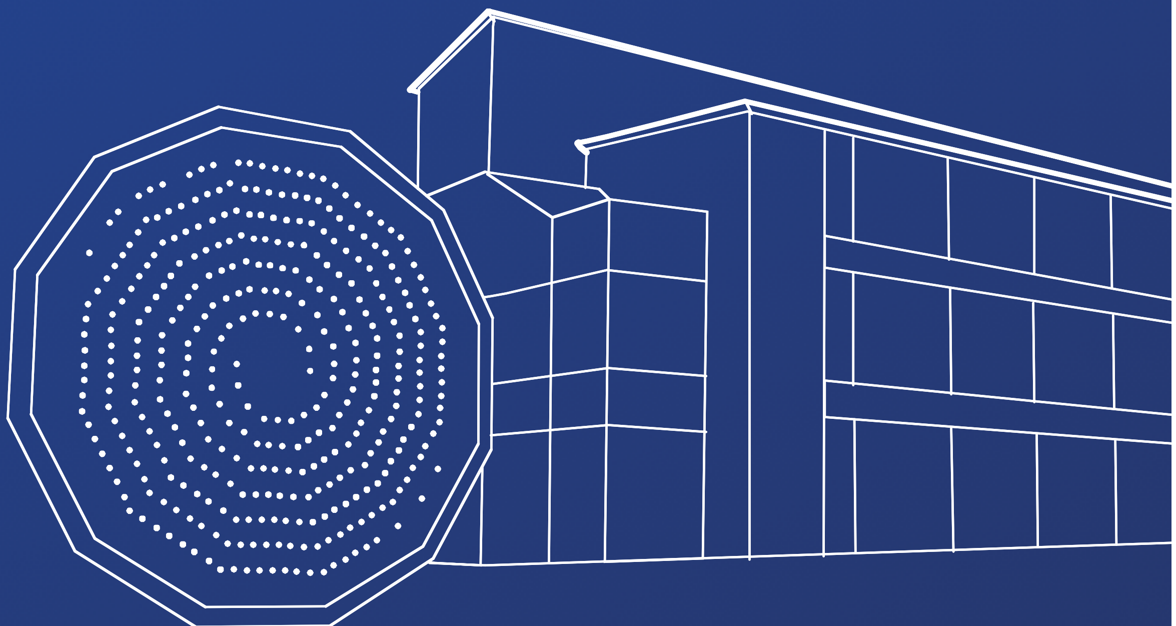

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