

INFLUENCE OF DIFFERENT BIOLOGICAL FUELS ON PARTICLE EMISSIONS OF DIESEL ENGINES

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Abstract

Fuels from renewable sources, i.e. from biological origin gain economical and ecological importance, particularly as fuel for diesel engines. This work investigates quantitatively the particulate matter emission of a diesel engine driven by different fuels of biological origin. Bio diesel (esterified rape seed oil), and the non-esterified rape seed oil, soy oil, sun flower oil and frying oil (used, filtered rape seed oil) have been investigated in comparison to traditional gasoil and "green diesel", a low sulfur gasoil.

The particle emission was measured on-line in the engine's hot raw exhaust at different load conditions by the 3-wavelength extinction technique (long path multi-wavelength extinction analyser LPME; Manufacturer: Wizard Zahoransky KG, D-79674 Todtnau; Fig. 1). LPME delivers the volume concentration and the mean particle size of the soot's primary particles. No exhaust gas conditioning or preparation is necessary. Two diesel engines are investigated on chassis-dynamometers. One heavy duty diesel engine, two cylinders, for steady state applications and one modern common rail TDI light duty diesel, four cylinders, for passenger cars. Only the results of the heavy duty diesel engine are presented in Figs. 2 and 3. The preliminary results of the common rail diesel need further experiments to prove them.

Appreciable differences could be found in the particle emissions of the different fuels, not only in the concentrations, but also in the particle sizes and composition of the emitted particles. The particles from gasoil, green diesel and bio diesel proved to be very similar, see Fig. 2: The primary particle size was in the range of 10 nm.

However, bio diesel had the lowest particle concentration in the exhaust (Fig. 3). Green diesel had somehow higher concentrations, but less than traditional diesel, as expected. The particles of the plant oils showed different optical properties with less absorption compared to normal diesel soot particles. These optical deviations have been sensitively detected by LPME. Oil fuels emitted larger mean particle sizes typically from 60 to 100 nm. However, the particle sizes are unexpectedly sensitive to the engine's load. A higher load reduced the mean particle size down to the 10 nm range.

The emitted particles from oil fuels are visualized by TEM pictures. The TEM investigation confirmed the differences found by the LPME on-line analysis. Furthermore, the particles from oil fuels showed small spots which seem to be inorganic material like calcium. The chemical analysis found much higher organic acids in the oil fuel particles compared to soot particles from traditional or green diesel. The unexpected results of the biological fuels need further investigations. The user-friendly LPME proved again to suit as a fast and reliable technique for detailed on-line aerosol analysis of engine particle emissions.

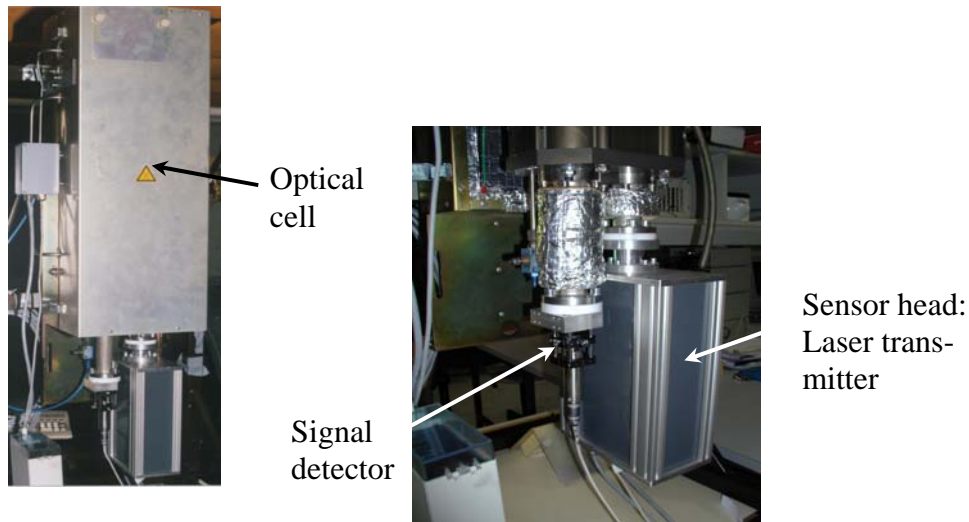


Fig. 1: On-line particle analyser LPME

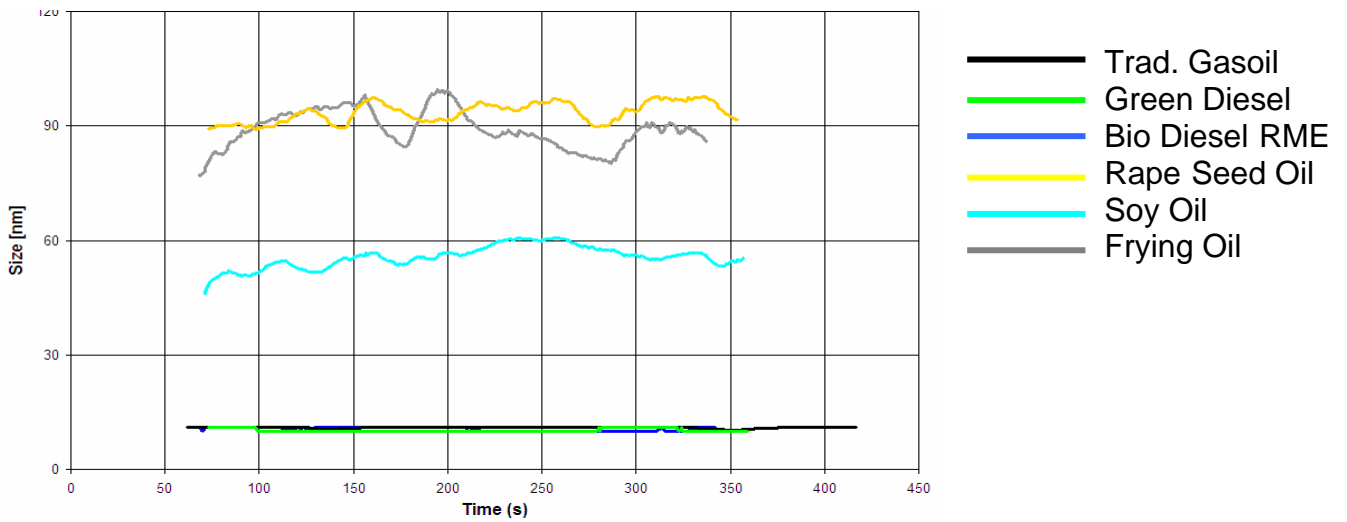


Fig. 2: Mean size of emitted primary particles. On-line graph of steady state condition.
Heavy duty engine conditions: Middle Load $P = 10.1$ kW, $n = 1,500$ rpm

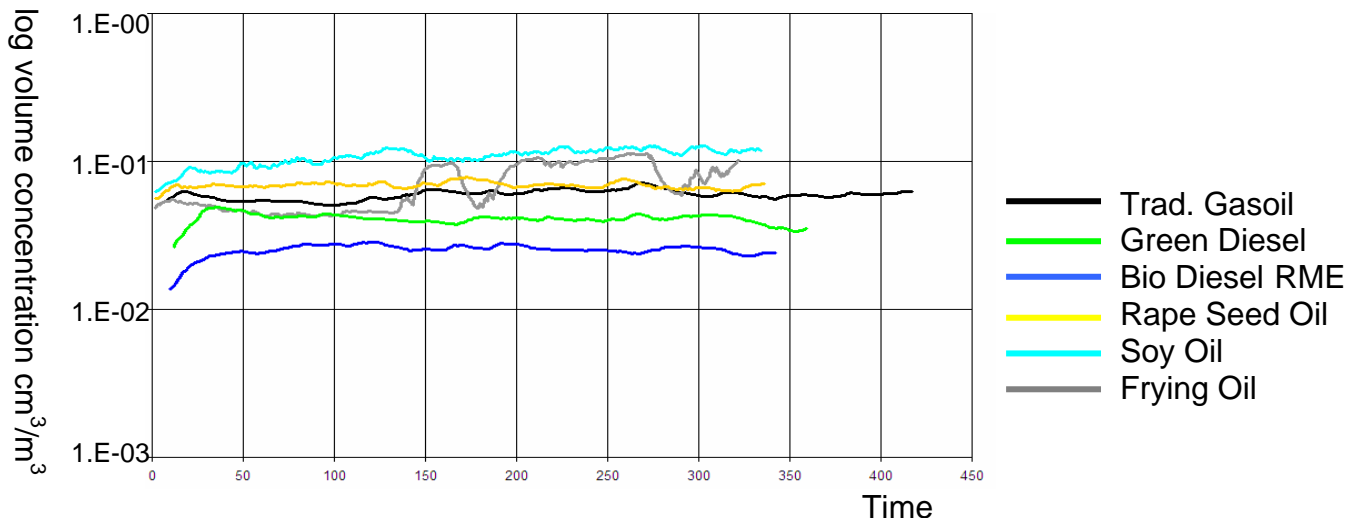


Fig. 3: Particle volume concentration. On-line graph of steady state condition.
Heavy duty engine conditions: Middle Load $P = 10.1$ kW, $n = 1,500$ rpm

9th ETH Conference on Combustion Generated Nanoparticles

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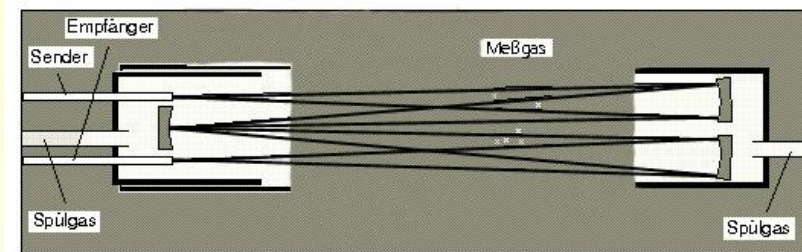
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Summary

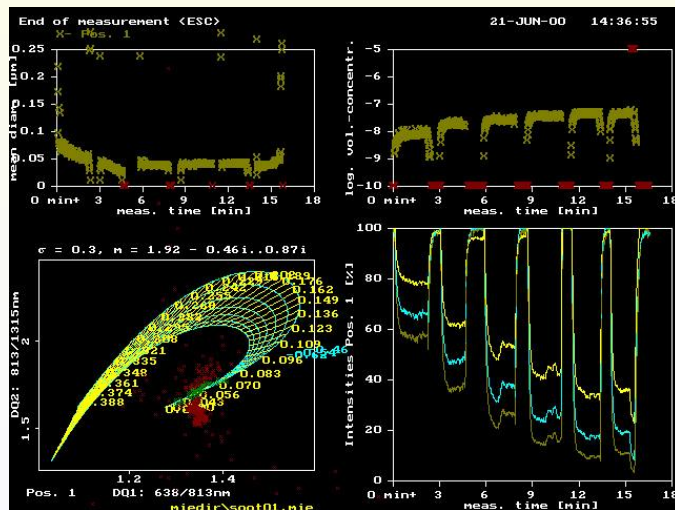
Fuels from renewable sources, i.e. from biological origin gain economical and ecological importance, particularly as fuel for diesel engines. This work investigates quantitatively the particulate matter emission of a diesel engine driven by different fuels of biological origin. Bio diesel (esterified rape seed oil), and the non-esterified rape seed oil, soy oil, sun flower oil and frying oil (used, filtered rape seed oil) have been investigated in comparison to traditional gasoil and “green diesel”, a low sulfur gasoil. The particle emission was measured on-line in the engine’s hot raw exhaust at different load conditions by the 3-wavelength extinction technique (long path multi-wavelength extinction analyser LPME). LPME delivers the volume concentration and the mean particle size of the soot’s primary particles. No exhaust gas conditioning or preparation was necessary. Two diesel engines are investigated on chassis-dynamometers. One heavy duty diesel engine, two cylinders, for steady state applications and one modern common rail TDI light duty diesel, four cylinders, for passenger cars. Only the results of the heavy duty diesel engine are presented. The preliminary results of the common rail diesel need further experiments to prove them.

Appreciable differences could be found in the particle emissions of the different fuels, not only in the concentrations, but also in the particle sizes and composition of the emitted particles. The particles from gasoil, green diesel and bio diesel proved to be very similar: The primary particle size was in the range of 10 nm. However, bio diesel had the lowest particle concentration in the exhaust. Green diesel had somehow higher concentrations, but less than traditional diesel, as expected. The particles of the plant oils showed different optical properties with less absorption compared to normal diesel soot particles. These optical deviations have been sensitively detected by LPME. Oil fuels emitted larger mean particle sizes typically from 60 to 100 nm. However, the particle sizes are unexpectedly sensitive to the engine’s load. A higher load reduced the mean particle size down to the 10 nm range. The emitted particles from oil fuels are visualized by TEM pictures. The TEM investigation confirmed the differences found by the LPME on-line analysis. Furthermore, the particles from oil fuels showed small spots which seem to be inorganic material like calcium. The chemical analysis found much higher organic acids in the oil fuel particles compared to soot particles from traditional or green diesel. The unexpected results of the biological fuels need further investigations. The user-friendly LPME proved again to suit as a fast and reliable technique for detailed on-line aerosol analysis of engine particle emissions.

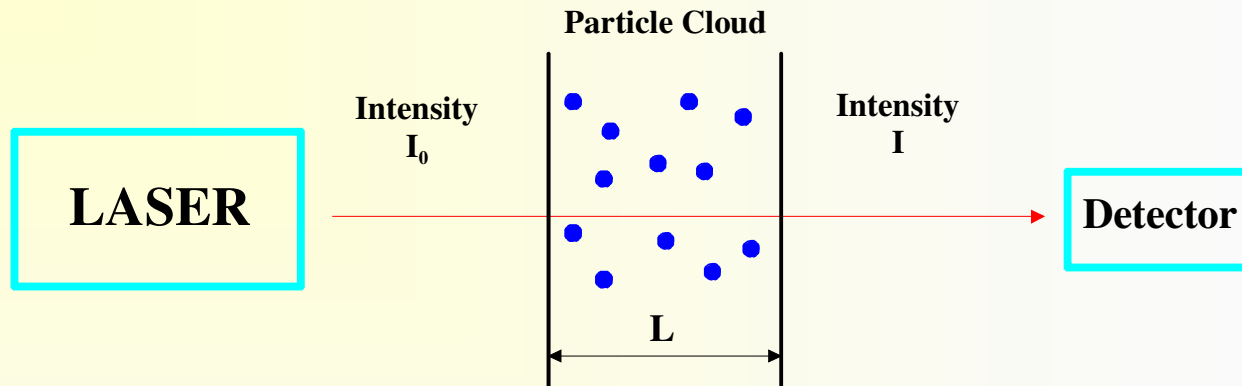
Content



- **Introduction**
- **Measurement System**
- **Investigated Fuels**
- **Measurement Results**
- **Conclusion**
- **Acknowledgments**



Principle of the Dispersion Quotient Technique (1)



monodisperse

$$I = I_0 \cdot \exp\{-N \cdot L \cdot \pi \cdot r^2 \cdot Q_{\text{ext}}(r, \lambda, n)\}$$

polydisperse

$$I = I_0 \cdot \exp\{-L \cdot N \cdot \pi \cdot \int r^2 \cdot Q_{\text{ext}}(\lambda, r, n) \cdot p(r) dr\}$$

with:

I = intensity

I_0 = initial intensity

N = particle concentration

L = optical path length

r = particle radius

Q_{ext} = extinction coefficient

λ = wavelength

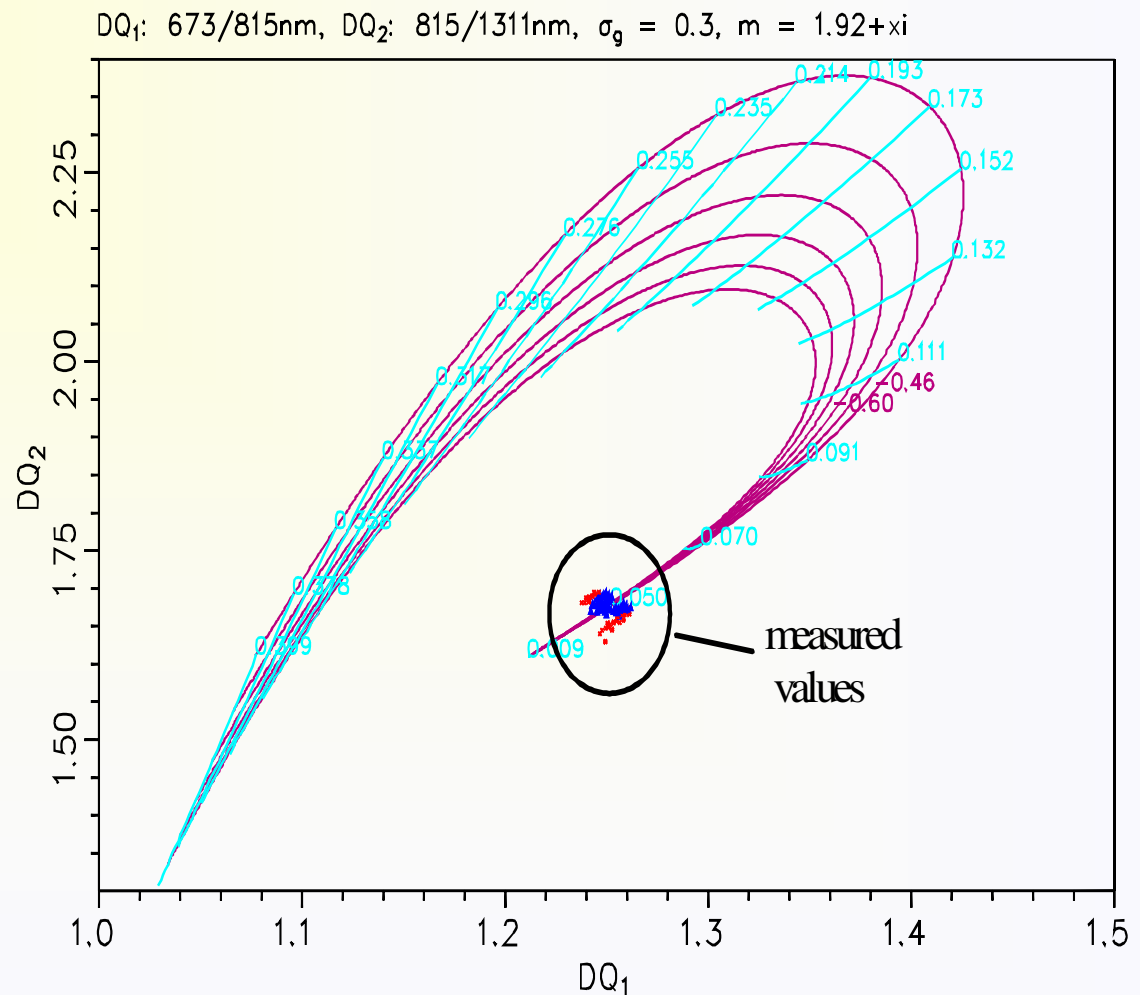
n = refractive index

$p(r)$ = number distribution

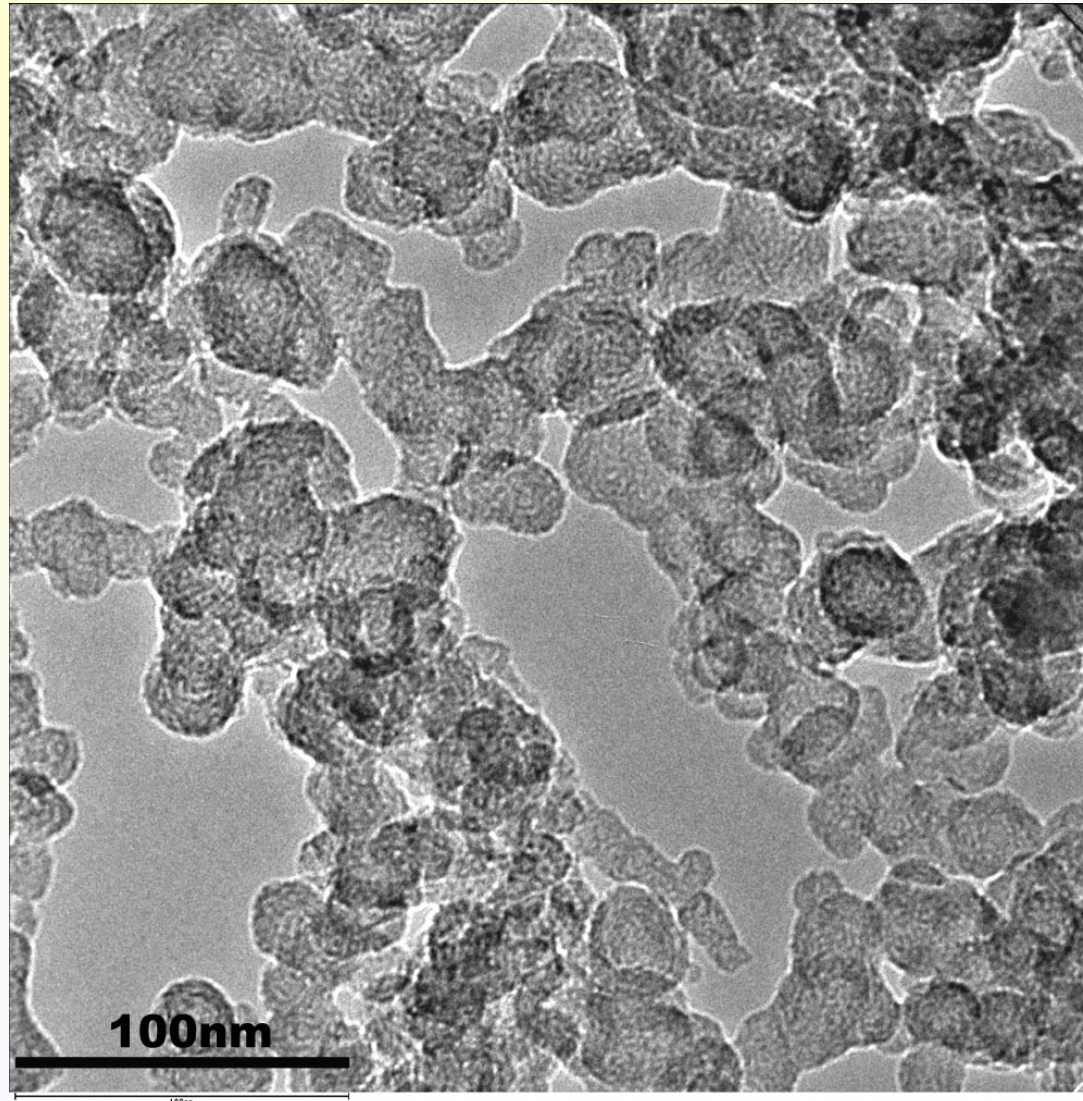
Principle of the Dispersion Quotient Technique (2)

$$DQ_1 = \frac{\ln\left(\frac{I}{I_0}\right)_{\lambda_1}}{\ln\left(\frac{I}{I_0}\right)_{\lambda_2}}$$

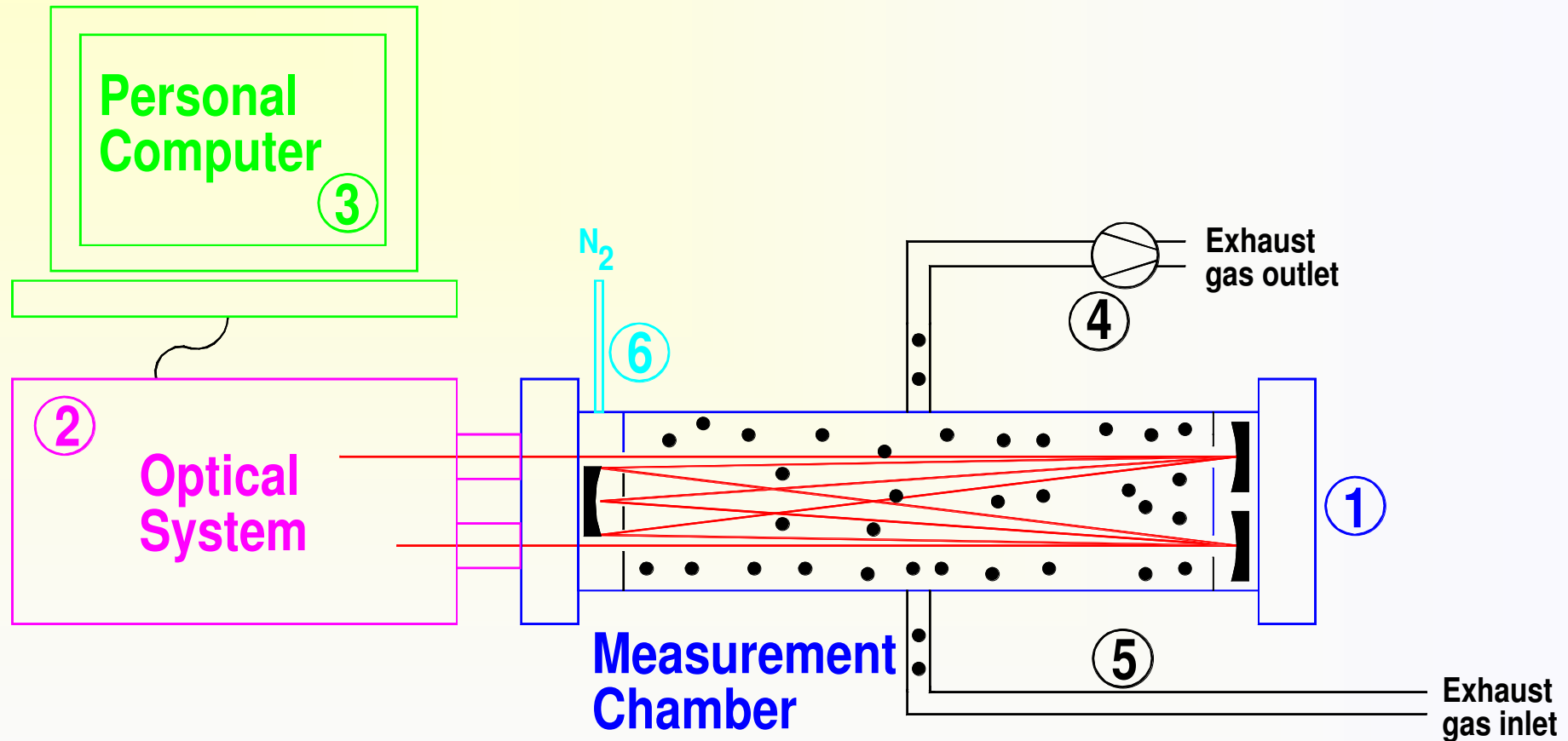
$$= \frac{-N \cdot L \cdot \pi \cdot r^2}{-N \cdot L \cdot \pi \cdot r^2} \cdot \frac{Q_{ext}(r, \lambda_1, n)}{Q_{ext}(r, \lambda_2, n)}$$



TEM picture of soot particle from traditional Diesel fuels: Chain of primary particles

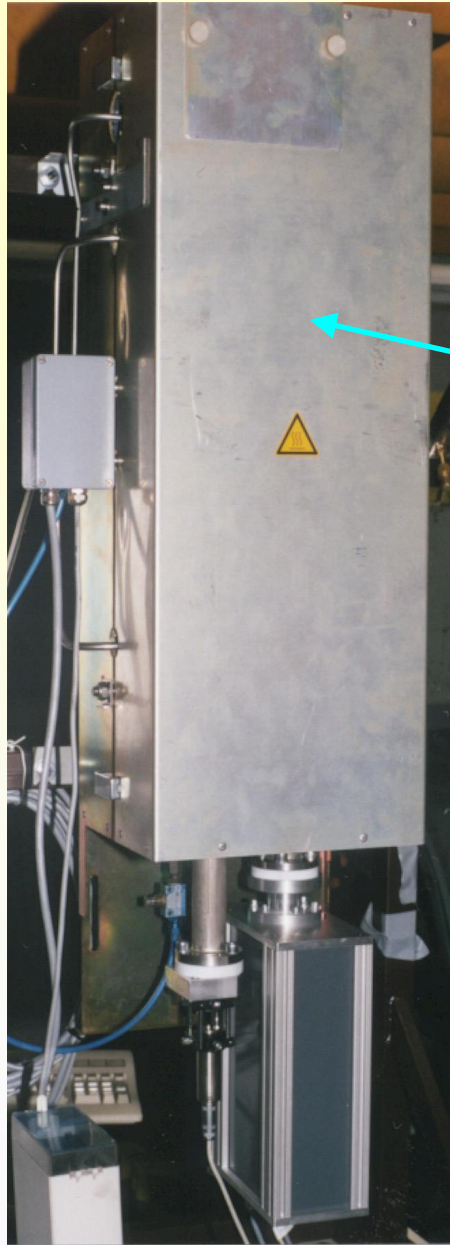


Schematic of the LPME technique



Long path multi-wavelength extinction technique LPME

Sensor at optical cell



Optical cell



**Sensor head:
Laser trans-
mitter**

Signal detector

Advantages of the LPME

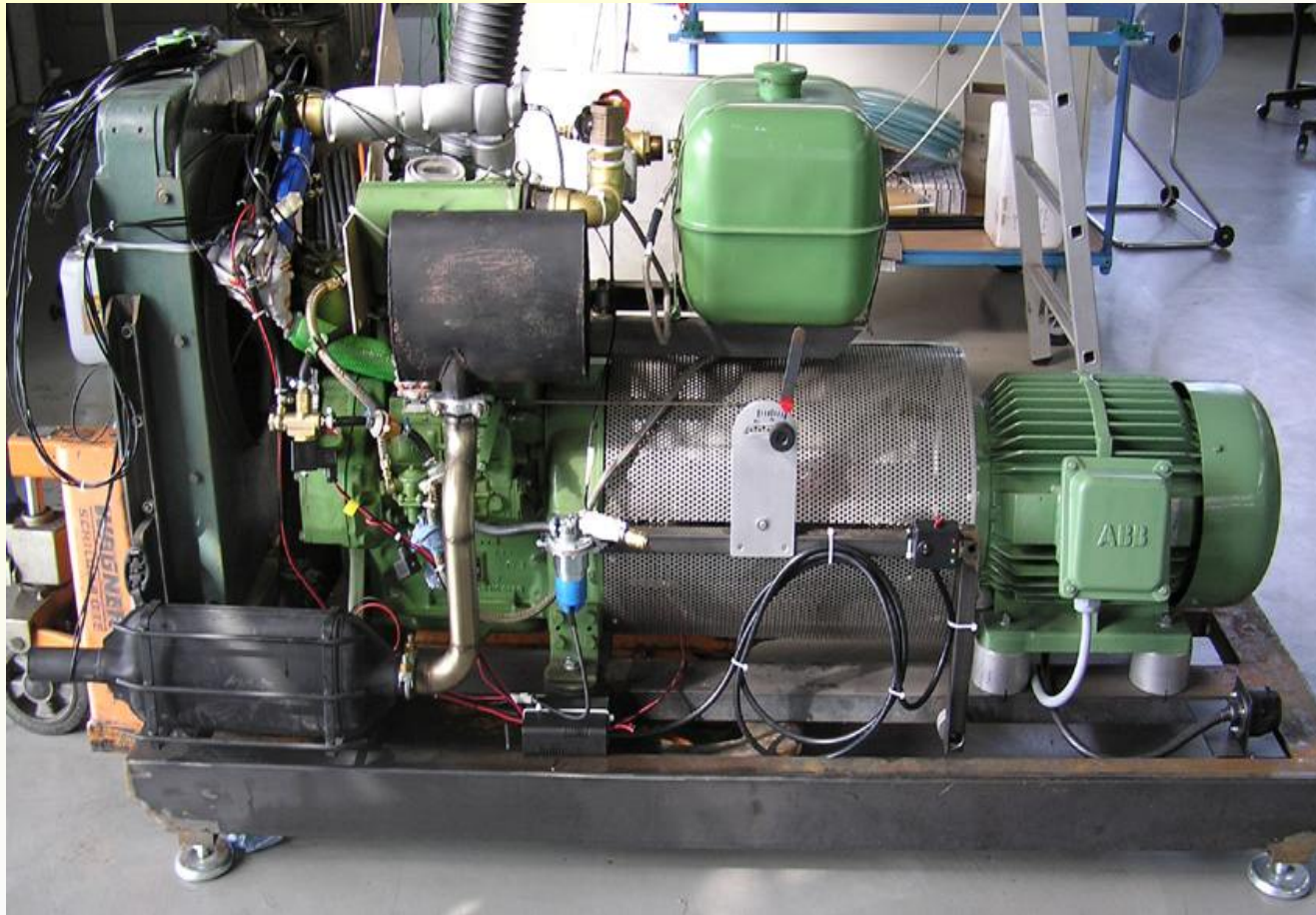
- ✓ Concentration and size information
- ✓ On-line system
- ✓ Accessibility to the raw, undiluted exhaust gas
- ✓ No sampling preparation
- ✓ Fast adaptation
- ✓ Direct measurements of stationary or transient engine conditions
- ✓ Comparable with gravimetric methods; $\rho = 2 \text{ kg/dm}^3$
- ✓ Correlation of particle size data with data of DMA measurements possible (fractal analysis)

Investigated Fuels

- **Fuels from mineral oil**
 - a. **Normal Diesel fuel (gasoil) S < 350 mg/kg**
 - b. **„Green Diesel“: Low sulfur gasoil S < 10 mg/kg**

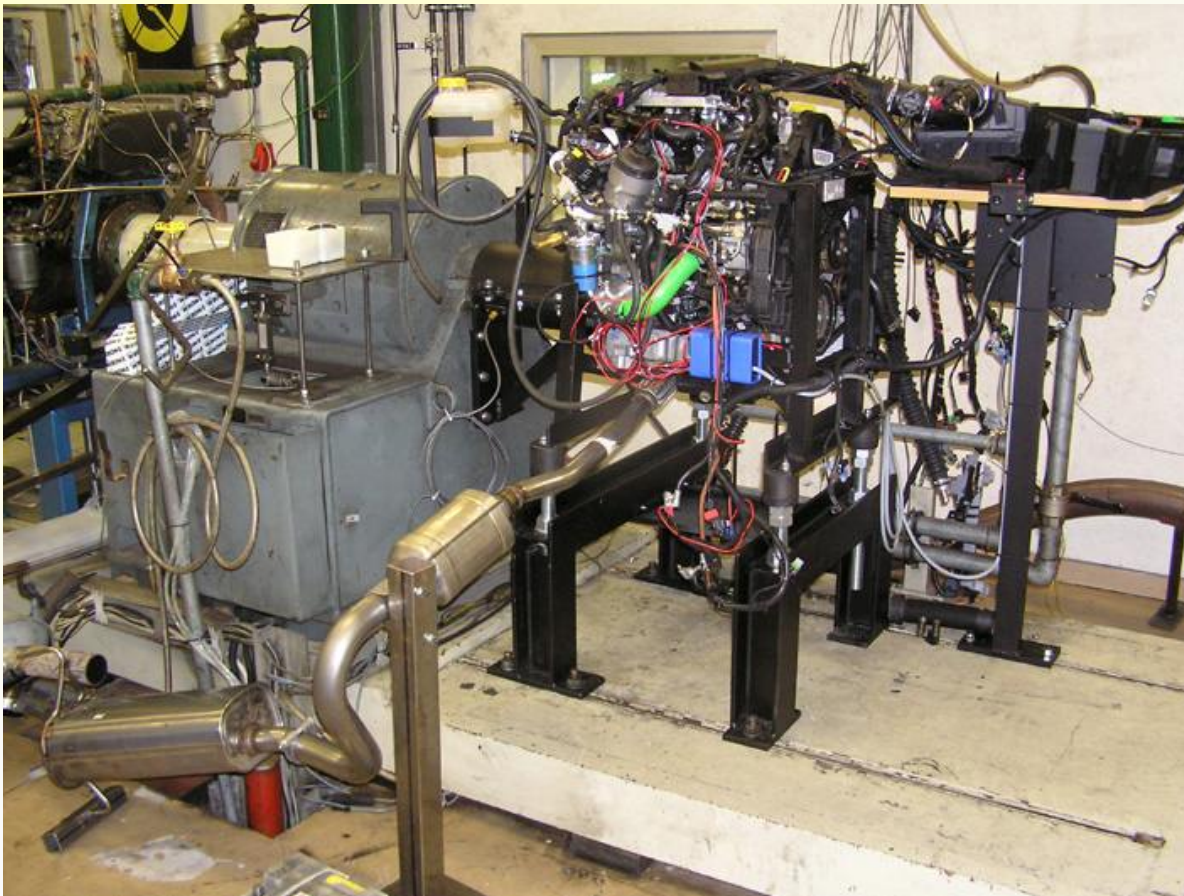
- **Fuels of biological origin**
 - a. **Bio Diesel (esterified rape seed oil, RME) S < 10 mg/kg**
 - b. **Rape seed oil (non-esterified); S < 20 mg/kg**
 - c. **Soy oil (non-esterified)**
 - d. **Frying oil (used, filtered rape seed oil)**

Heavy Duty Diesel Engine



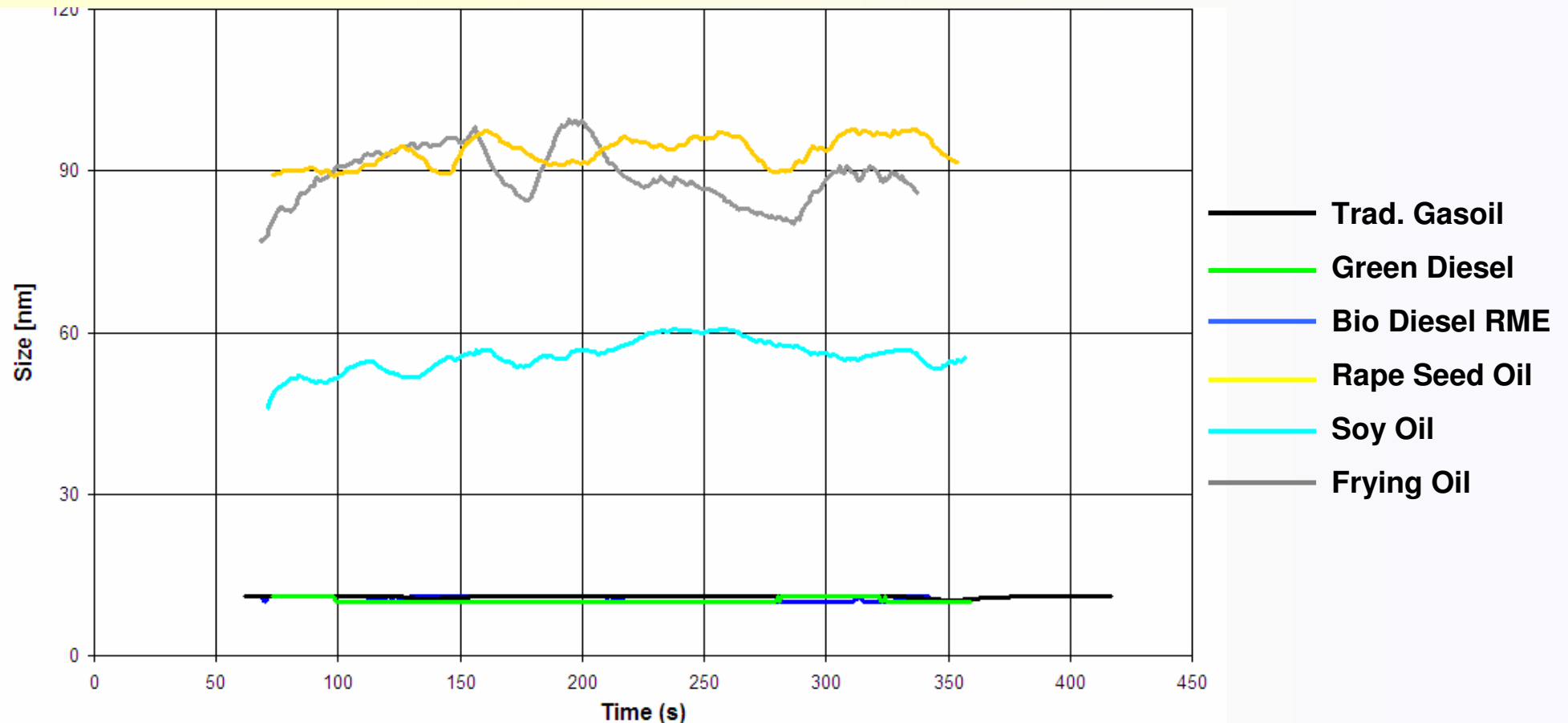
- Heavy Duty Diesel
- w/ Asynchr. Gen.
- Deutz Engine
- $p_{Inj.} = 200 \text{ bar}$

Passenger Diesel Engine



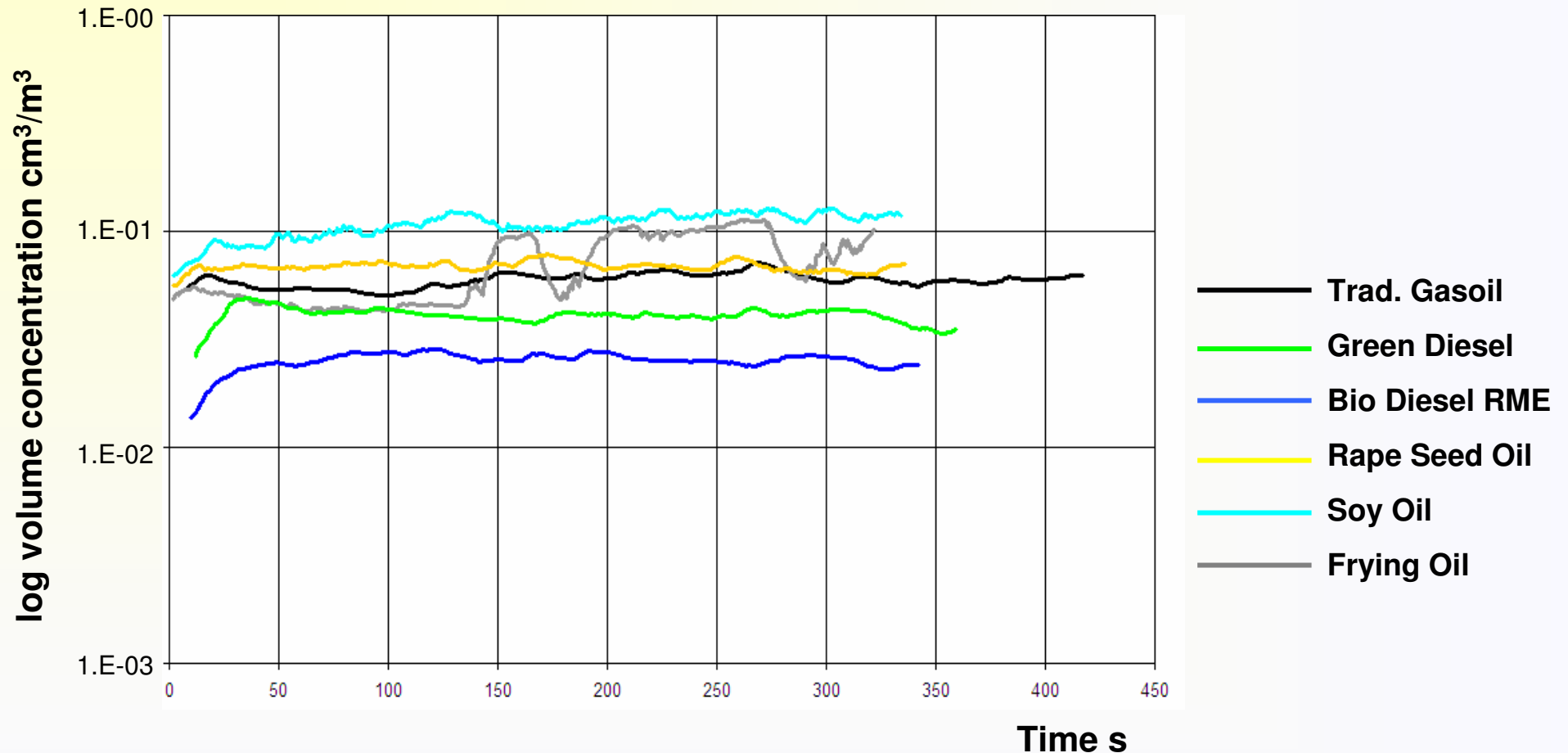
- Opel 1.7 I CDTi
- EURO 4
- Common Rail
- EGR
- $p_{\text{Inj.max}} = 1,800 \text{ bar}$

Mean particle size of different fuels: HD Eng.



Heavy duty engine conditions: Middle Load $P = 10.1$ kW, $n = 1,500$ rpm

Concentration of different fuels: HD Engine



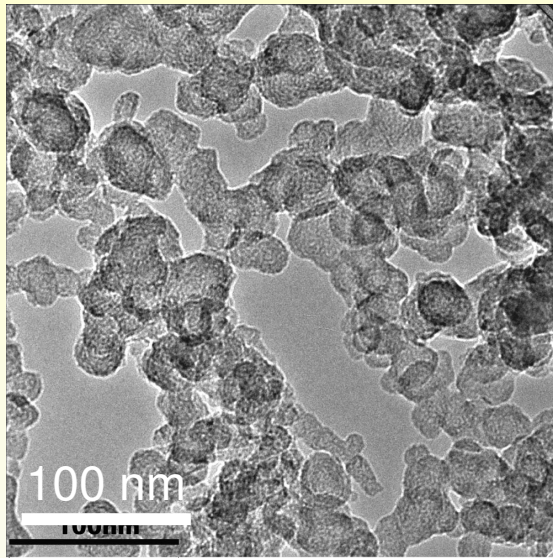
Heavy duty engine conditions: Middle Load $P = 10.1$ kW, $n = 1,500$ rpm

Concentration Values

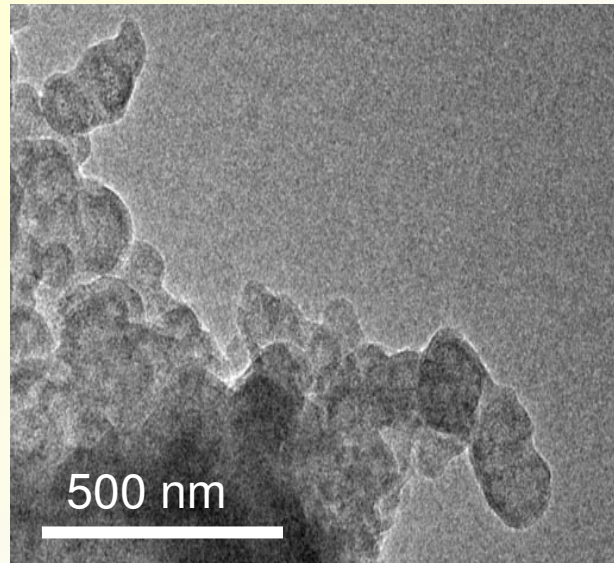
Fuel	Power kW	Volume Conc cm ³ /m ³	Mass Conc g/m ³	Mass/Work g/kWh	Primary Part. nm
Diesel	10.1	0.06	0.138	1.01	approx. 10
	10.4	0.10	0.230	1.58	approx. 10
	11.1	0.15	0.343	2.28	approx. 10
Green Diesel	10.1	0.042	0.096	0.70	approx. 10
	10.8	0.107	0.246	1.70	approx. 10
	11.1	0.135	0.309	2.05	approx. 10
Bio Diesel	10.1	0.026	0.0587	0.431	approx. 10
	10.4	0.057	0.1311	0.93	approx. 10
	10.8	0.081	0.1865	1.28	approx. 10
Rape Seed Oil	9,7	0.061	0.140	1.07	105
	10.1	0.069	0.159	1.17	90
	10.8	0.226	0.52	3.57	12
Soy Oil	10.1	0.108	0.248	1.83	55
	10.8	0.184	0.423	2.90	14



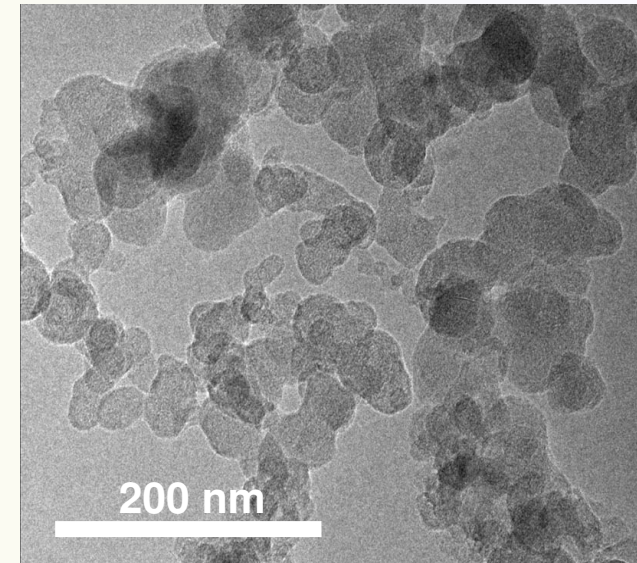
TEM Pictures of Soot Particles



**Traditional
Gas Oil**



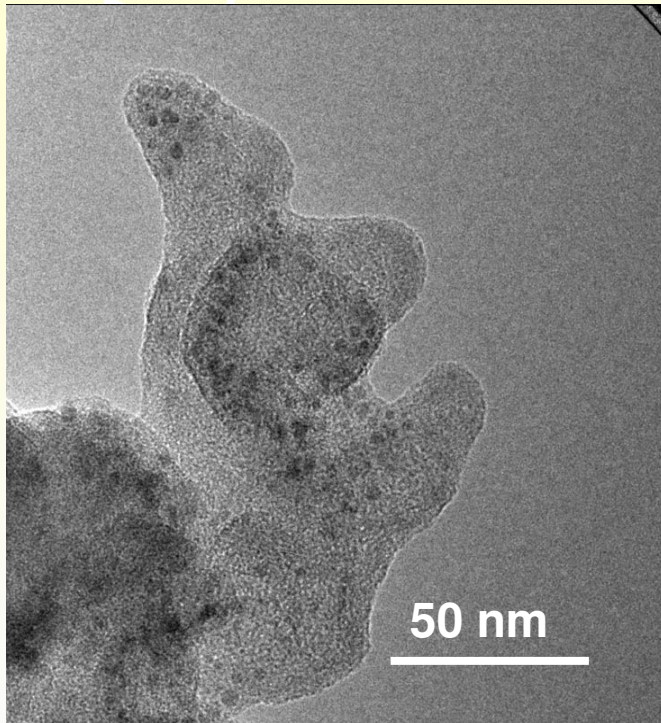
**Rape Seed
Middle Load**



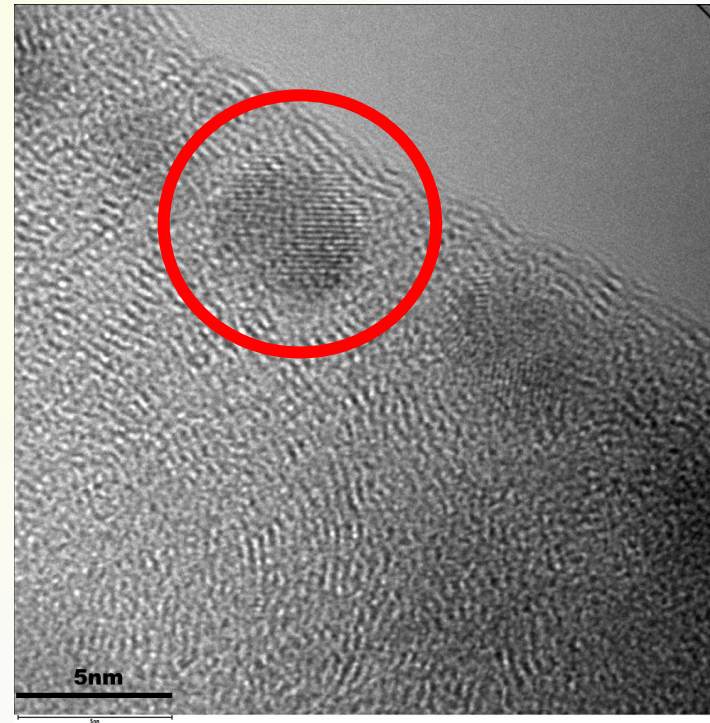
**Rape Seed
High Load**

TEM Pictures of Soot Particles

Particle from Bio Fuels (Example Bio-Diesel RME)



Inorganic Material
„Spots“ $2 < d_{sp} < 5 \text{ nm}$



Structure of
„Spots“

Preliminary Conclusions

Emitted Particle Size (primary particle size)

- Diesel, Green Diesel and Bio Diesel showed similar mean particle sizes of approx. 10 to 20 nm;
The particle size was rather insensitive to load conditions.
- Rape seed and soy oil had appreciably higher primary sizes of up to 100 nm for low load conditions;
Particle size proved to be very sensitive to load conditions: “Step like” behavior was detected at threshold power
- Big particles exhibited different optical properties:
Absorptive refractive index was lower; somehow whiter smoke:
First chemical analysis detected much higher contents of organic acids in particles
- TEM pictures proved these on-line measurements:
„Spots“ seem to be Ca and other inorganic components from plants

Preliminary Conclusions

Emitted Concentration

- Bio Diesel had lowest particle emission
 - Green Diesel provided less particle concentrations than traditional gasoil
 - Soy seed oil had highest particle emissions
 - Rape seed and frying oil had similar concentrations like traditional gasoil
 - The unesterified oils showed “step like” concentration changes in coincidence to the size changes
- ⇒ **Strange particle emission behaviour of the plant oils needs more investigations**

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Organic Acids in Soot Particles

	Molecule	Rape Seed Oil	Bio Diesel	Diesel	Green Diesel
	Glutar Acid	5,37	5,16	0,79	0,63
<i>Preliminary</i>	Adipin Acid	1,81	1,34	0,12	0,52
<i>Results</i>	Pimelin Acid	1,24	0,54	0,01	0,03
	Cork Acid	1,19	0,48	0,12	0,12
	Azelain Acid	1,67	0,52	0,10	0,12
	Sebazin Acid	0,50	0,09	0,03	0,04
	Undekandicarbon Acid	0,27	0,07	0,02	0,03
	Dodekandicarbon Acid	0,14	0,03	0,03	0,04
	Phtal Acid	13,24	11,56	3,36	1,78
	Total	25,42	19,79	4,58	3,31

Organic Acids in Soot Particles

	Molecule	Molec. weight	Structure
Linear	Glutar Acid	132	HOOC-(CH ₂) ₃ -COOH
Dicarbon	Adipin Acid	146	HOOC-(CH ₂) ₄ -COOH
Acids	Pimelin Acid	160	HOOC-(CH ₂) ₅ -COOH
	Cork Acid	174	HOOC-(CH ₂) ₆ -COOH
	Azelain Acid	188	HOOC-(CH ₂) ₇ -COOH
	Sebazin Acid	202	HOOC-(CH ₂) ₈ -COOH
	Undekandicarbon Acid	216	HOOC-(CH ₂) ₉ -COOH
	Dodekandicarbon Acid	230	HOOC-(CH ₂) ₁₀ -COOH
Aromatic Ac.	Phtal Acid	166	