Biobased diesel fuels: particulate emissions and their inflammation response

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Lately there has been increasing pressure for the energy sector to find more environmentally friendly means of energy production. For diesel fuel production this trend means a shift from conventional fossil fuels to biobased alternatives. Very little is, however, known about the consequences of such a shift. One concern is how the differences between the fossil and the biobased fuels affect the physico-chemical characteristics and toxicity of the emissions.

The aim of this study was to investigate the effects of biobased diesel fuels on diesel engine emissions. We concentrated on the differences of particle mass emission, particle emission toxicity (inflammation) and chemical composition (organic and elemental carbon, OC/EC), particle number size distributions, and regulated gaseous emissions between different fuels. The measurements were carried out also with a catalytic converter (DOC+POC) to see, how a diesel oxidation catalyst (DOC) and a particle oxidation catalyst (POC) affect the emissions.

Biofuels used in this study were a 1st generation biodiesel rapeseed methyl ester (RME), and a hydro-treated vegetable oil (HVO). Conventional diesel (EN590) was used as a reference fuel. A non-road EURO II diesel engine coupled with an engine dynamometer was employed for this study and operated according to the international ISO standard (ISO 8178-4:1996, C1).

For the measurements of particle size distribution, OC/EC and particulate mass, a partial flow from the exhaust gas was diluted using a system consisting of a porous-tube diluter, an ageing chamber and an ejector-type diluter assembled accordingly. A similar dilution method has been previously used, for example in studies on diesel engine emissions by Lyyränen *et al.* (2004). Particle number size distributions were measured with a Fast Mobility Particle Sizer (FMPS), an Electrical Low Pressure Impactor (ELPI) with a filter stage, and a Scanning Mobility Particle Sizer (SMPS) with a long and nano Differential Mobility Analyzer (DMA). The OC/EC contents of the emitted particles were analyzed using a thermal-optical method (Sunset laboratory Inc).

Particulate samples for the toxicological analyses were collected from a Constant Volume Dilution tunnel (ISO 8178) with a High Volume Cascade Impactor (HVCI) (Sillanpää *et al.* 2003). They were collected and pooled together from four previously chosen steady states. Mouse macrophage cells (RAW264.7) were exposed for 24 hours to the particulate samples in a dose-related manner. The production of the proinflammatory cytokine TNFα was measured by Enzyme Linked Immunosorbent Assay (ELISA).

Results show that RME decreased the particle mass emission by 15% and HVO by 25%, compared to EN590 (Figure 1.). In contrast, the particle number emission increased by about 20% for RME. These findings were explained by a smaller geometric mean diameter of the emitted particles for RME. There was no clear difference in particle number emissions between HVO and EN590, but like with RME, the geometric mean diameter of particles was lower for HVO than for EN590.

With the catalytic converter, both the particle number concentration and the mass emission were notably decreased, as expected. For all the fuels studied, the geometric mean diameter of the emitted particles increased, when the catalytic converter was used;

most likely due to higher removal efficiency of the nanosized particles.

The elemental and organic carbon analysis of the particulate samples showed, that the elemental carbon decreased by 20% and 30% for HVO and RME, respectively, compared to EN590 (Figure 1.). The organic carbon emissions, on the other hand, reduced by about 30% and 20% for HVO and RME, respectively. When a catalytic converter was used, both the elemental and the organic carbon emissions dropped by about 50%.

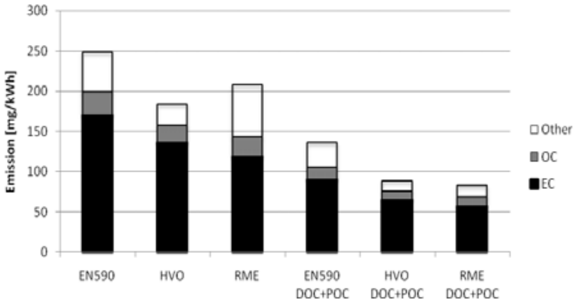


Fig 1. Organic and elemental carbon and total particulate mass emissions from fossil and biobased diesel fuelled engine, operated with and without catalytic converter.

The inflammatory (cytokine) response to the HVO particles was slightly higher than it was to the EN590 particles (fig. 2A). The responses to the EN590 and HVO particles also increased after a catalyst treatment of the emissions. The picture changed however, when the mass emission per kWh was taken into account (fig. 2B). The inflammatory potential of the particulate emission was assessed lower with the catalytic converter than without it and the inflammatory potential of the HVO particulate emission decreased below that of the EN590 particulate emission.

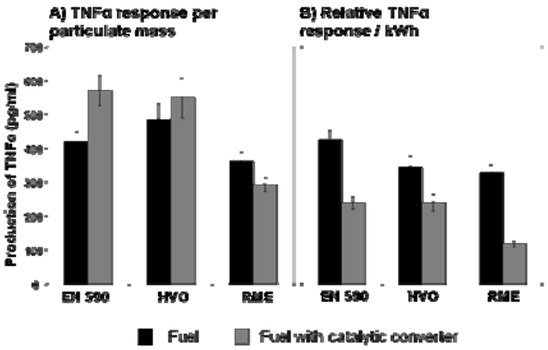
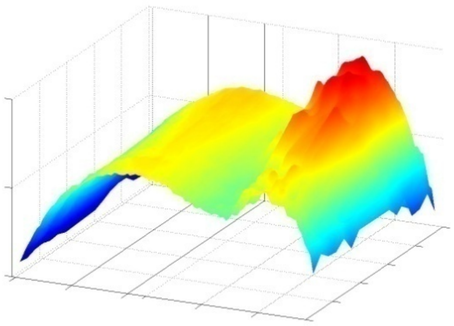


Fig 2. Production of the proinflammatory cytokine TNFα in macrophage cells by particles emitted from fossil and biobased diesel fuelled engine.

Lyyränen, J., Jokiniemi, J., Kauppinen, E.I., Backman, U. and Vesala, H. (2004). *Comparison of Different Dilution Methods for Measuring Diesel Particle Emissions.* Aerosol Sci. Technol., 38, 12-23.

Sillanpää, M., Hillamo, R., Mäkelä, T., Pennanen, A.S. and Salonen, R.O. (2003). *Field and laboratory tests of a high volume cascade impactor.* J. Aerosol. Sci. 34:485-500.



Biobased diesel fuels: particulate emissions and their inflammation response

Goals

- How do biobased diesel fuels affect emissions compared to the emissions of fossil diesel
  - Particulate
    - Physical
    - Chemical
    - Toxicological
  - Gaseous
- The effect of catalytic converter (DOC+POC)

Research team

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  The Fine Particle and Aerosol Technology Laboratory

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- National Institute for Health and Welfare,

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    Arto Pennanen

Fuels

EN 590

- Conventional fossil diesel
- Sulfur < 10ppm

HVO

(hydrotreated vegetable oil)

- Renewable biobased diesel
- Hydrotreatment --> paraffinic hydrocarbon
- Sulfur ~0ppm

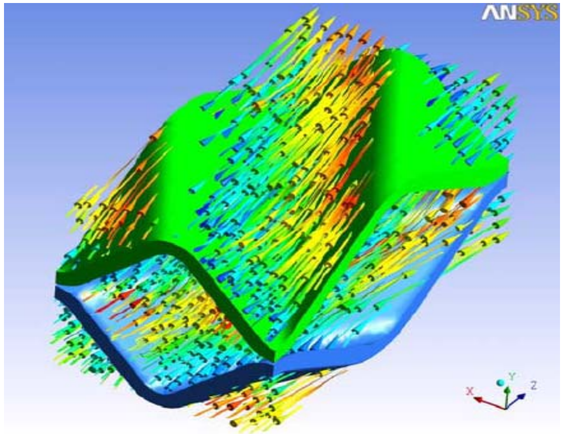
RME

(rapeseed methylester)

- Biodiesel
- Transesterification with methanol
- ~10% oxygen
- Sulfur < 10ppm

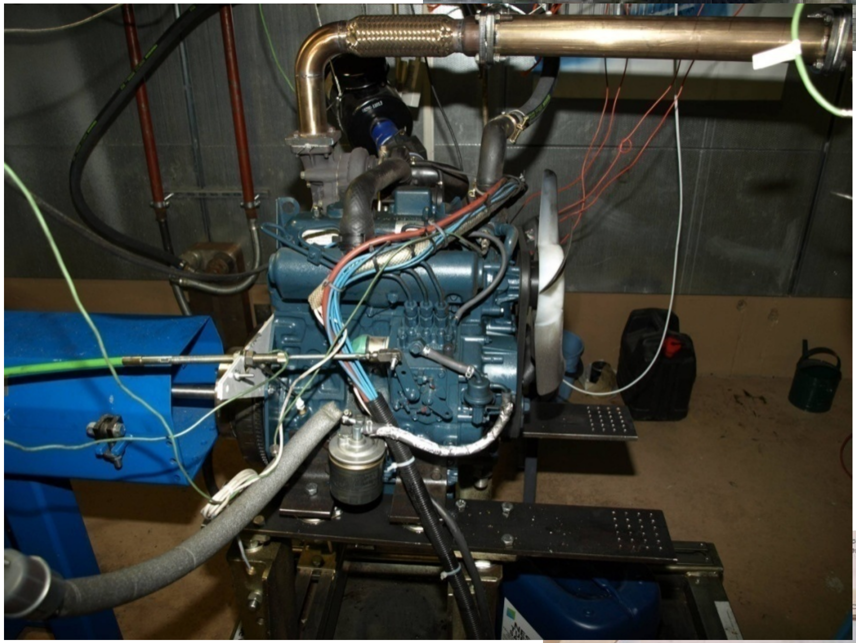
Catalytic converter (DOC+POC)

- Diesel oxidation catalyst (DOC)
  - Reduces HC, CO
  - Slight effect on PM
- Particle oxidation catalyst (POC)
  - Traps part of the soot particles
  - Continuous regeneration



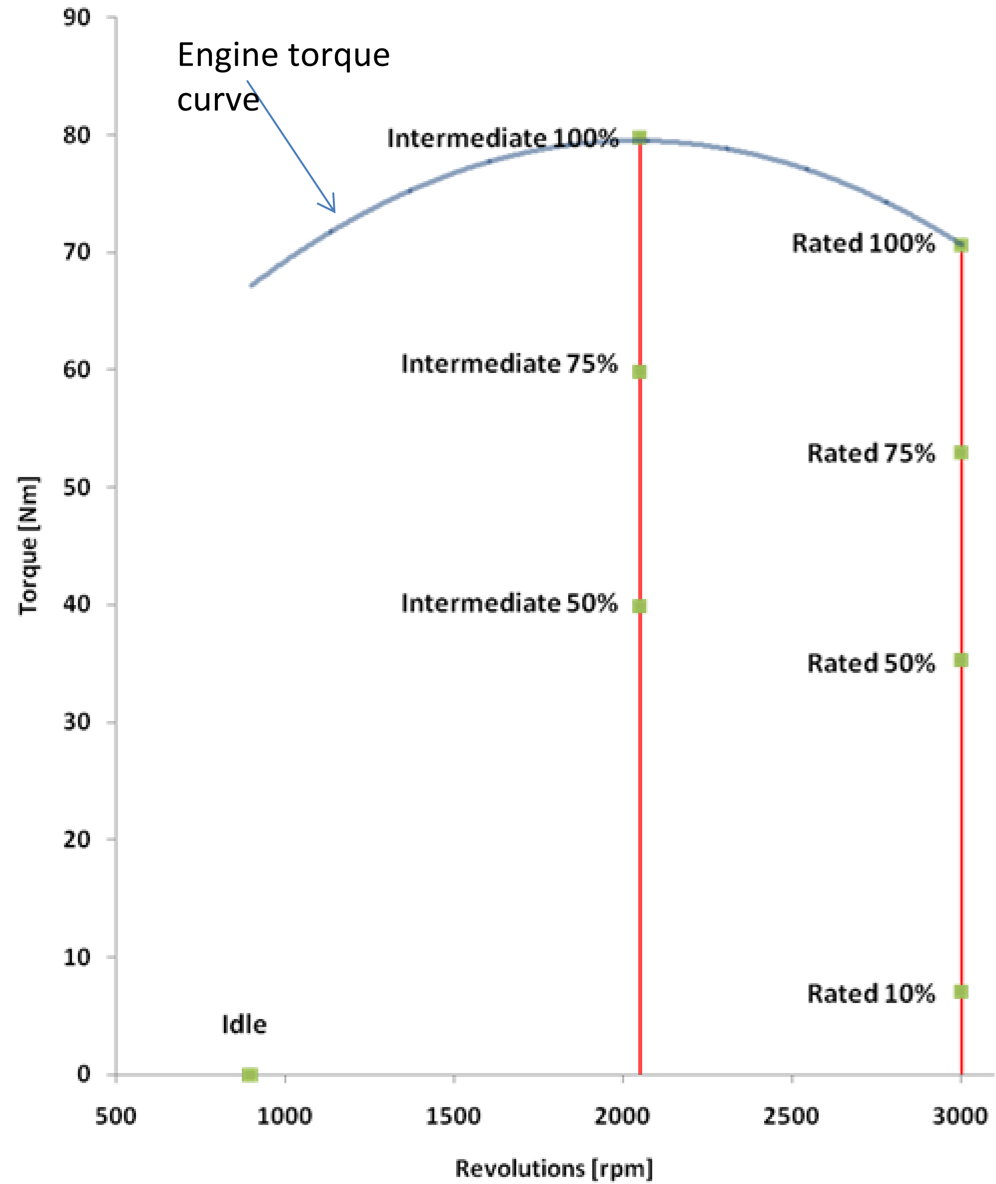
Engine

- Kubota turbo diesel engine 1.123 L
- Indirect fuel injection
- Power and torque
  - Max. torque 90 Nm @ 2050 rpm
  - Max. power 24 kW @ 3000 rpm



Engine modes

-Modes from the ISO standard for nonroad diesel engines, C1 (ISO 8178-4:1996)



Particulate measurement

Devices

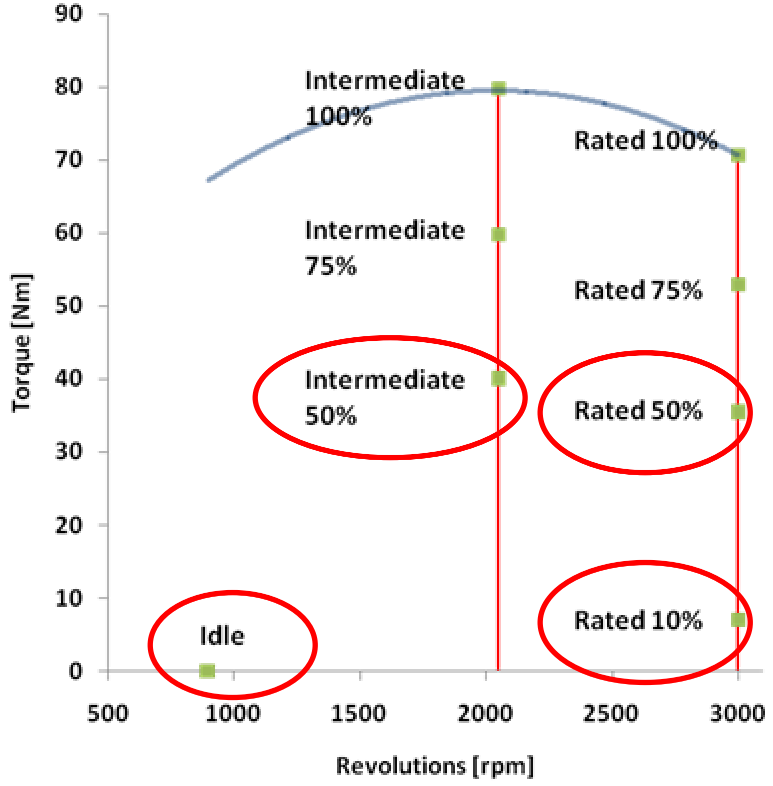
- FMPS
  - Fast Mobility Particle Sizer
  - 5.6nm – 560nm
- SMPS
  - Scanning Mobility Particle Sizer (3080), long and nano DMA
- Filter sampling
  - Mass and OC/EC analysis

Dilution

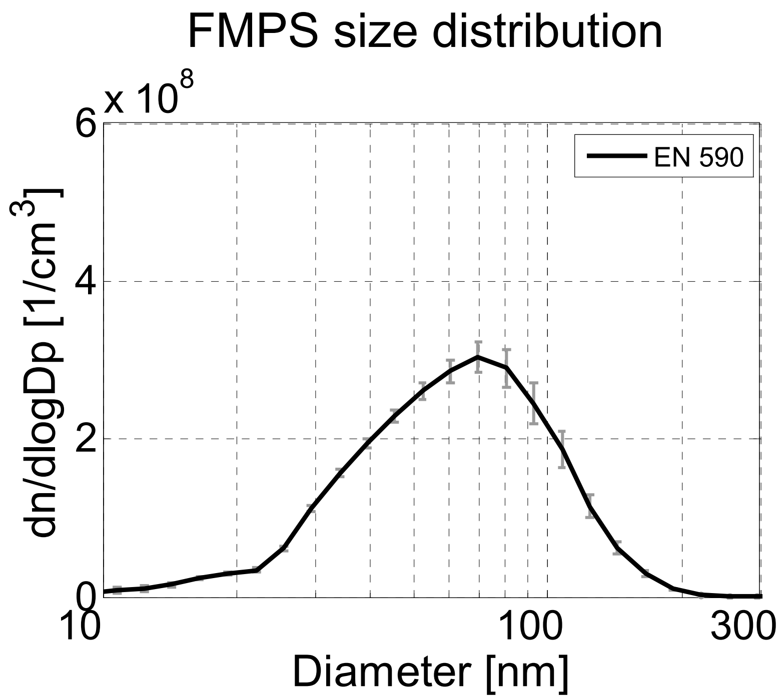
- Porous-tube diluter
  +ageing chamber
  +ejector diluter

Samples for the toxicological analyses

- HVCI - High Volume Cascade Impactor
- Dilution: constant volume dilution tunnel
- Samples from 4 steady states
- Expose cells: mouse macrophage cell line
- Exposure time: 24h
- Doses: 15, 50, 150, 300 µg/ml
- Indicators of: Inflammation, cytotoxicity, genotoxicity

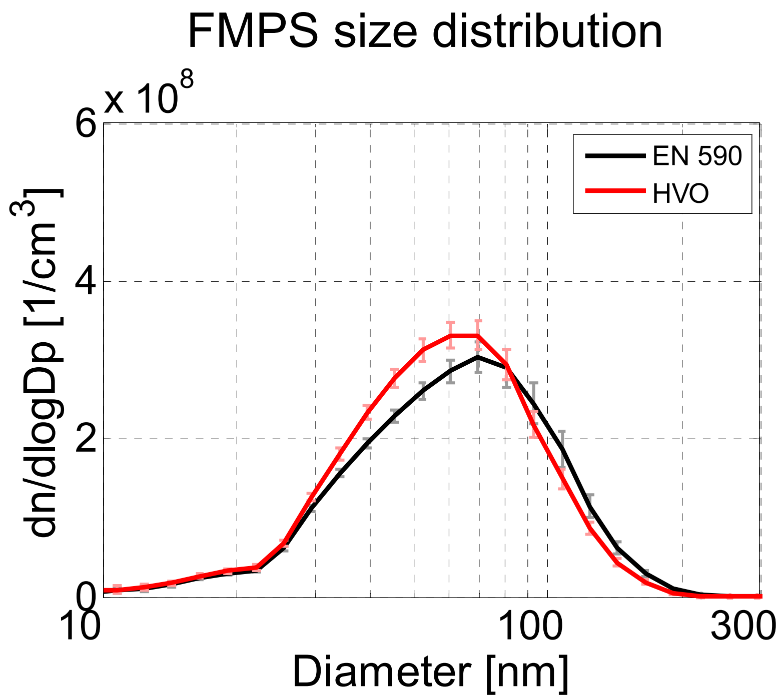


Effects of fuel on particulate emissions



- No catalytic converter
- Intermediate speed 75%

Effects of fuel on particulate emissions



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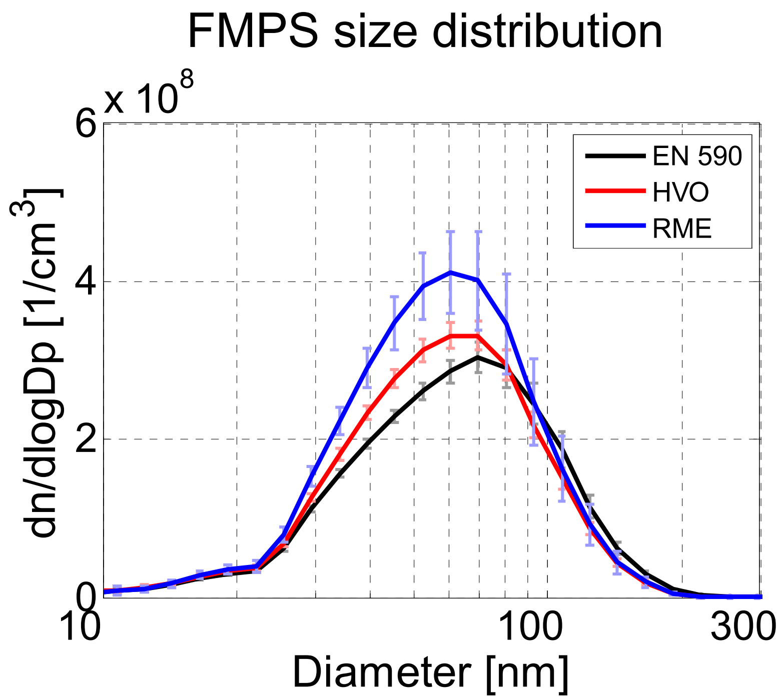

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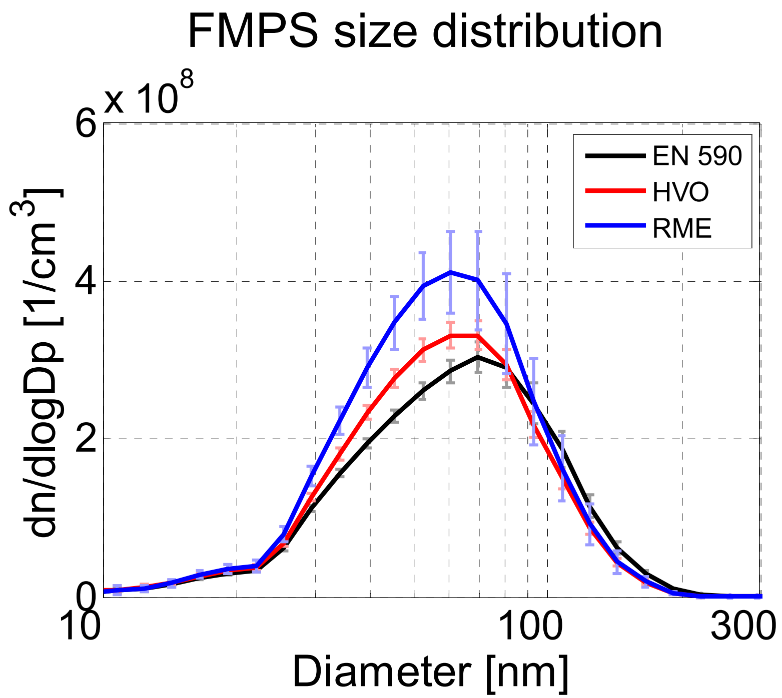
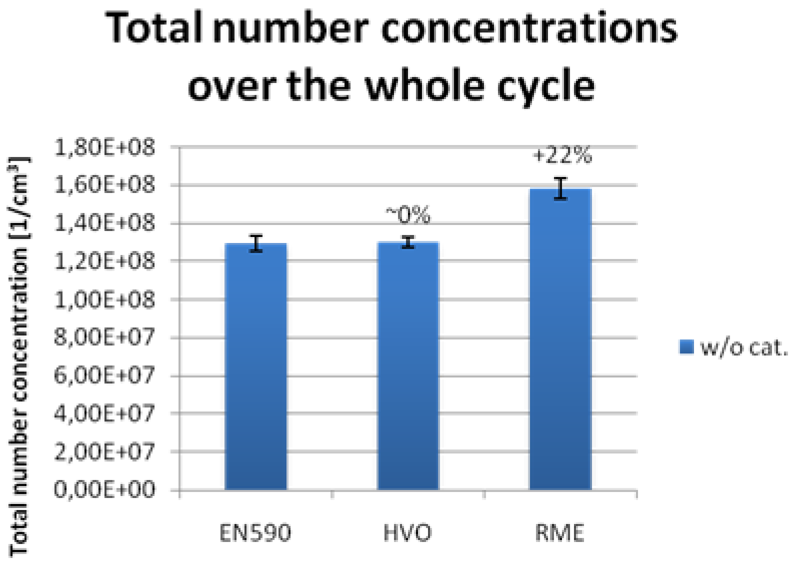
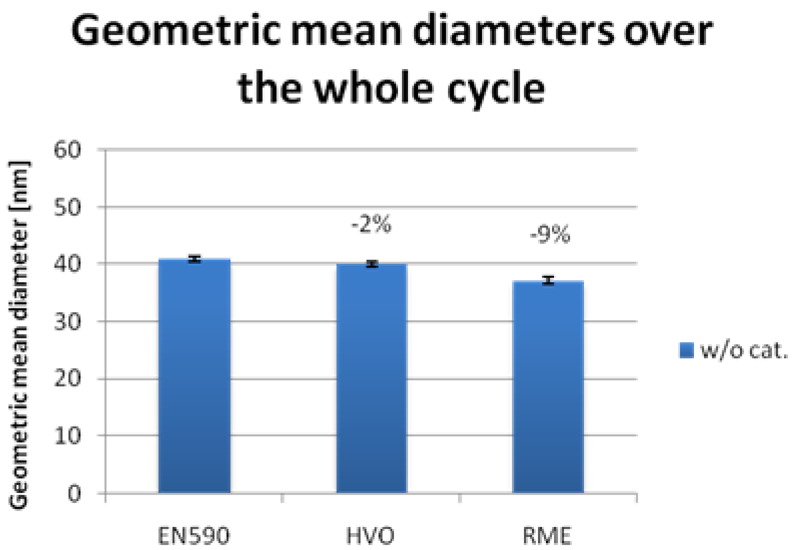
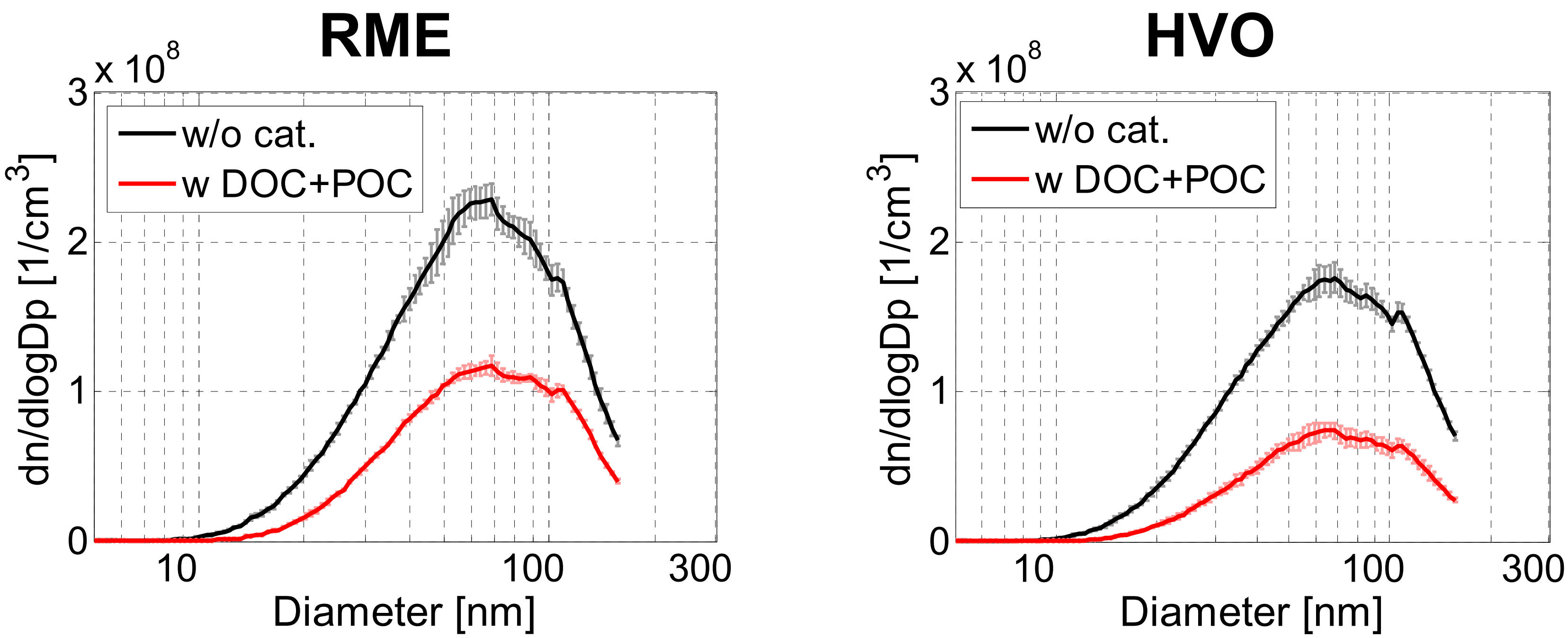


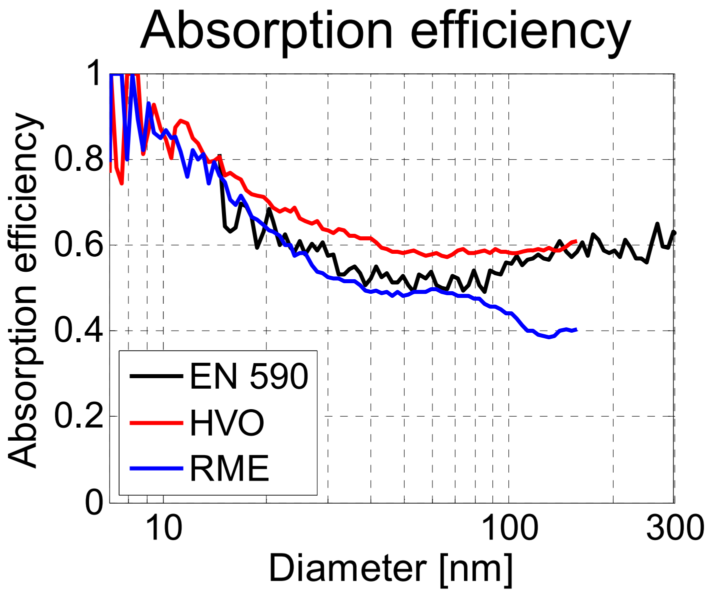


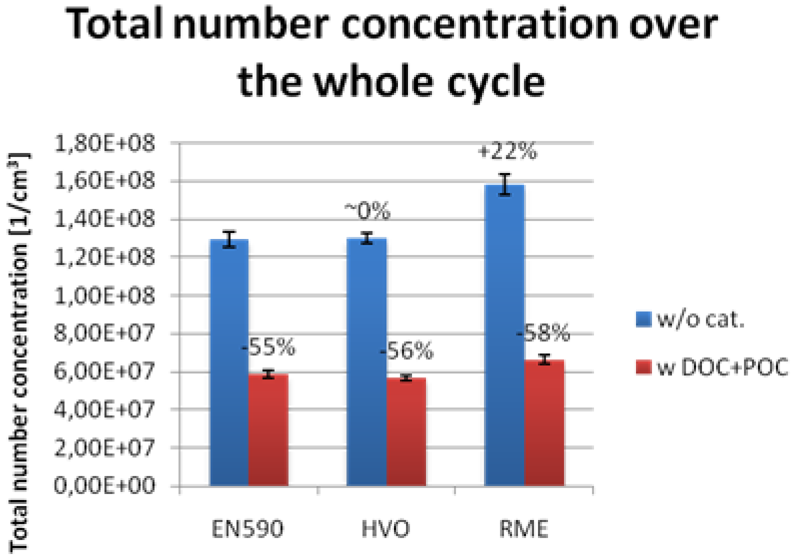


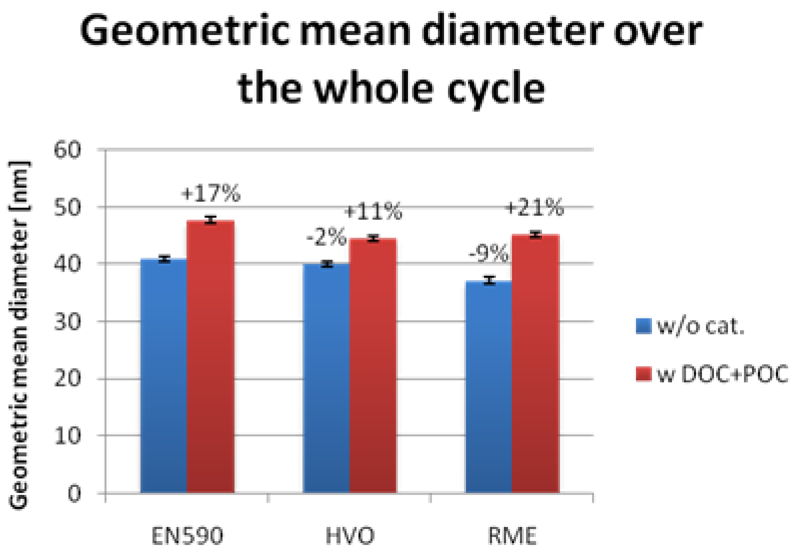
Effects of DOC+POC on particulate emissions



Effects of DOC+POC on particulate emissions

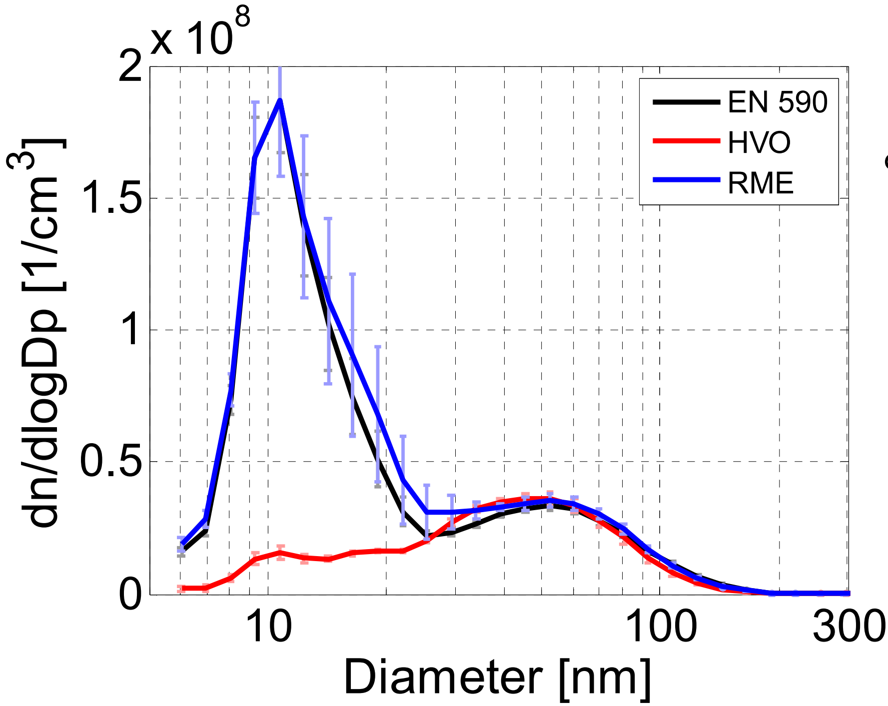




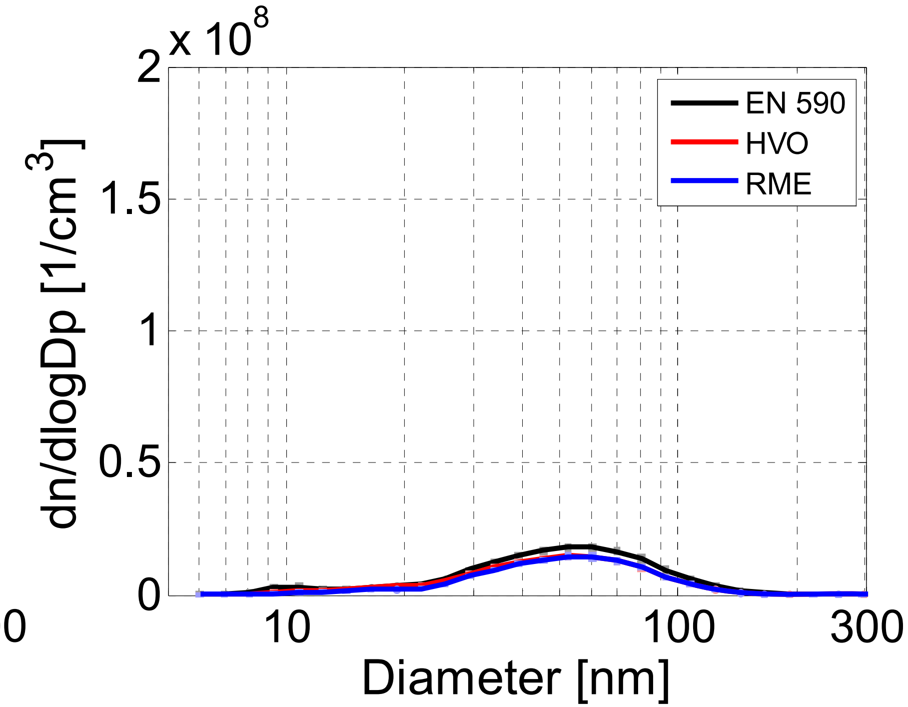


Nucleation mode, idle

No catalytic converter

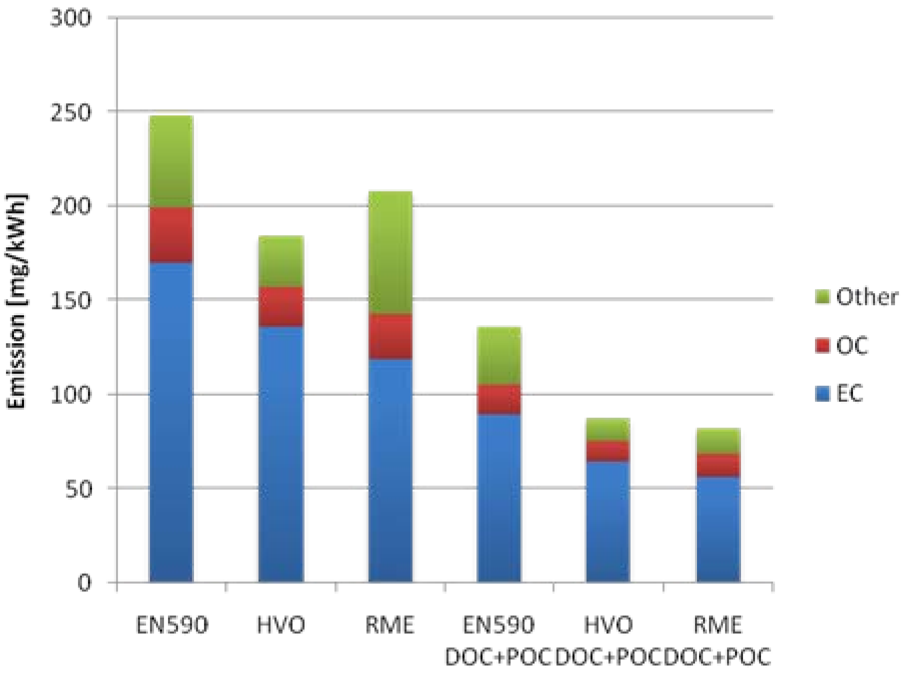


DOC+POC

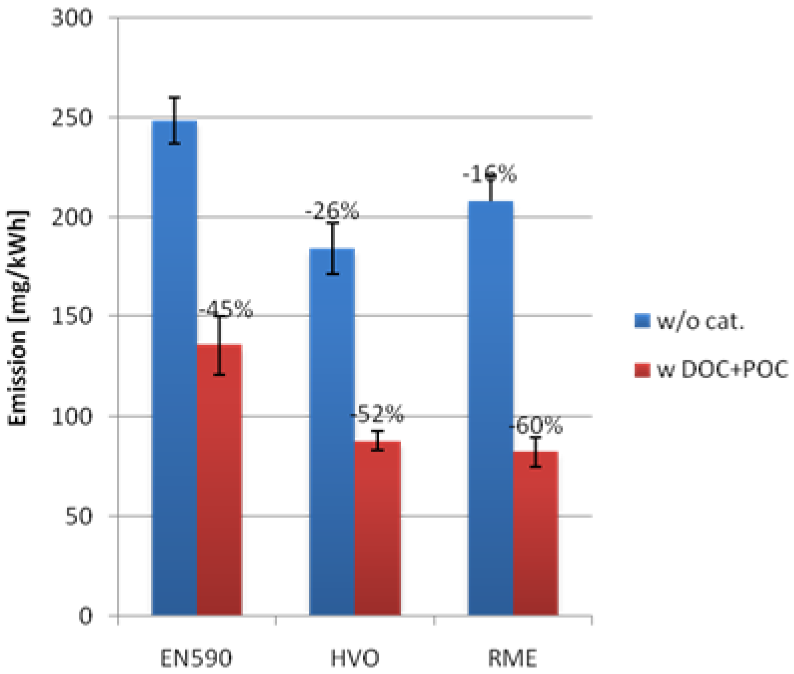


Particulate mass emissions

Total mass, OC and EC emissions



Total mass emission



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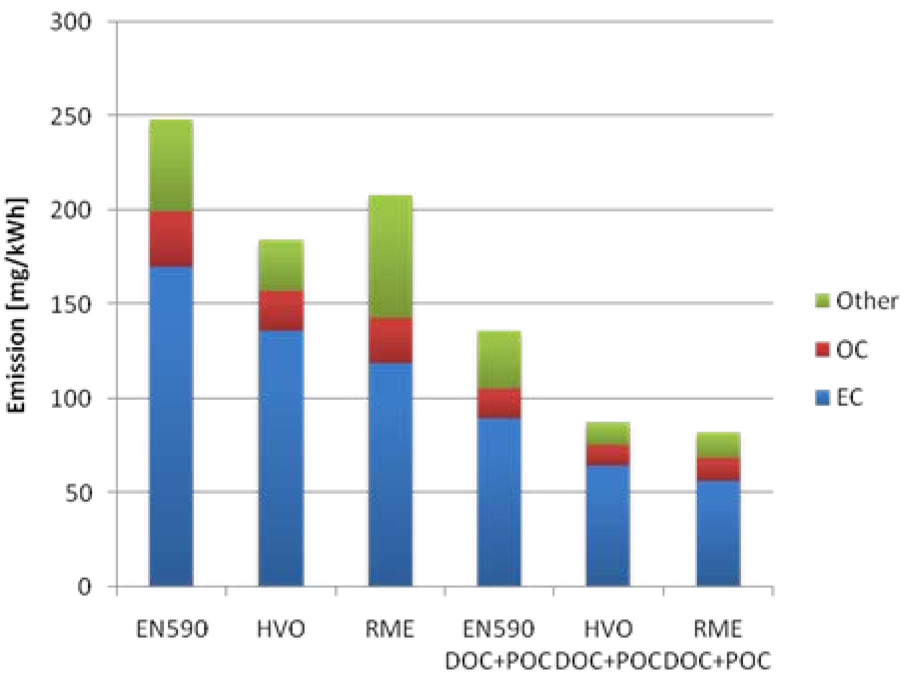
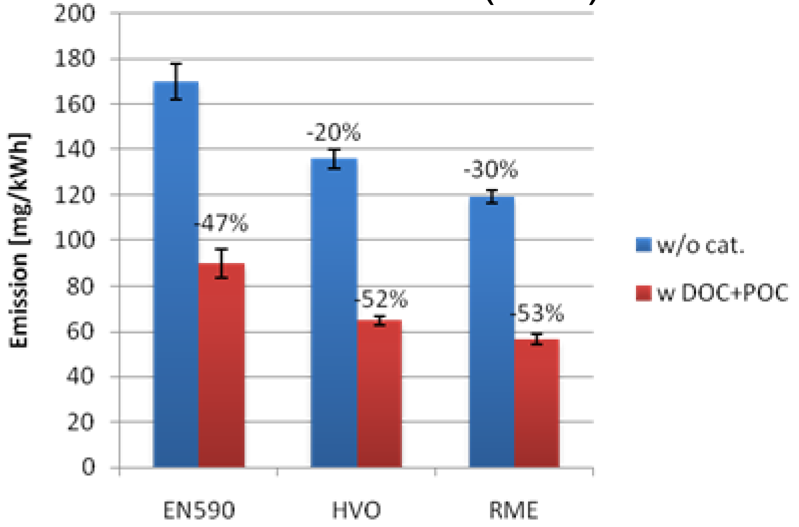
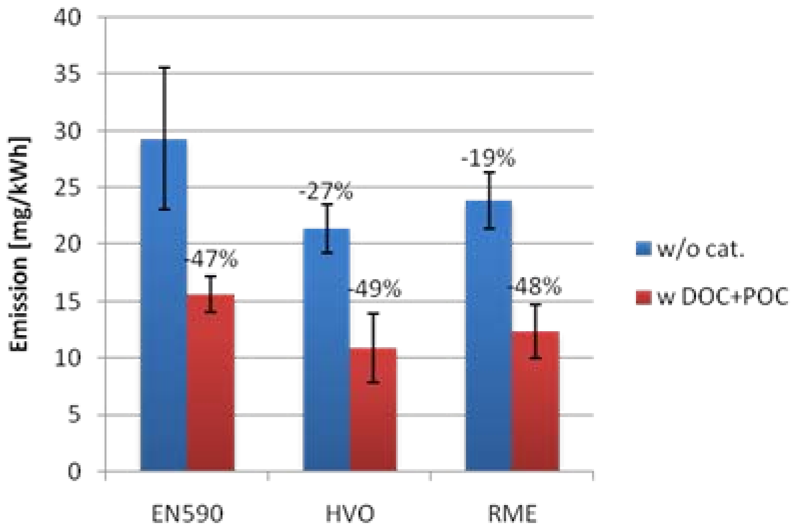


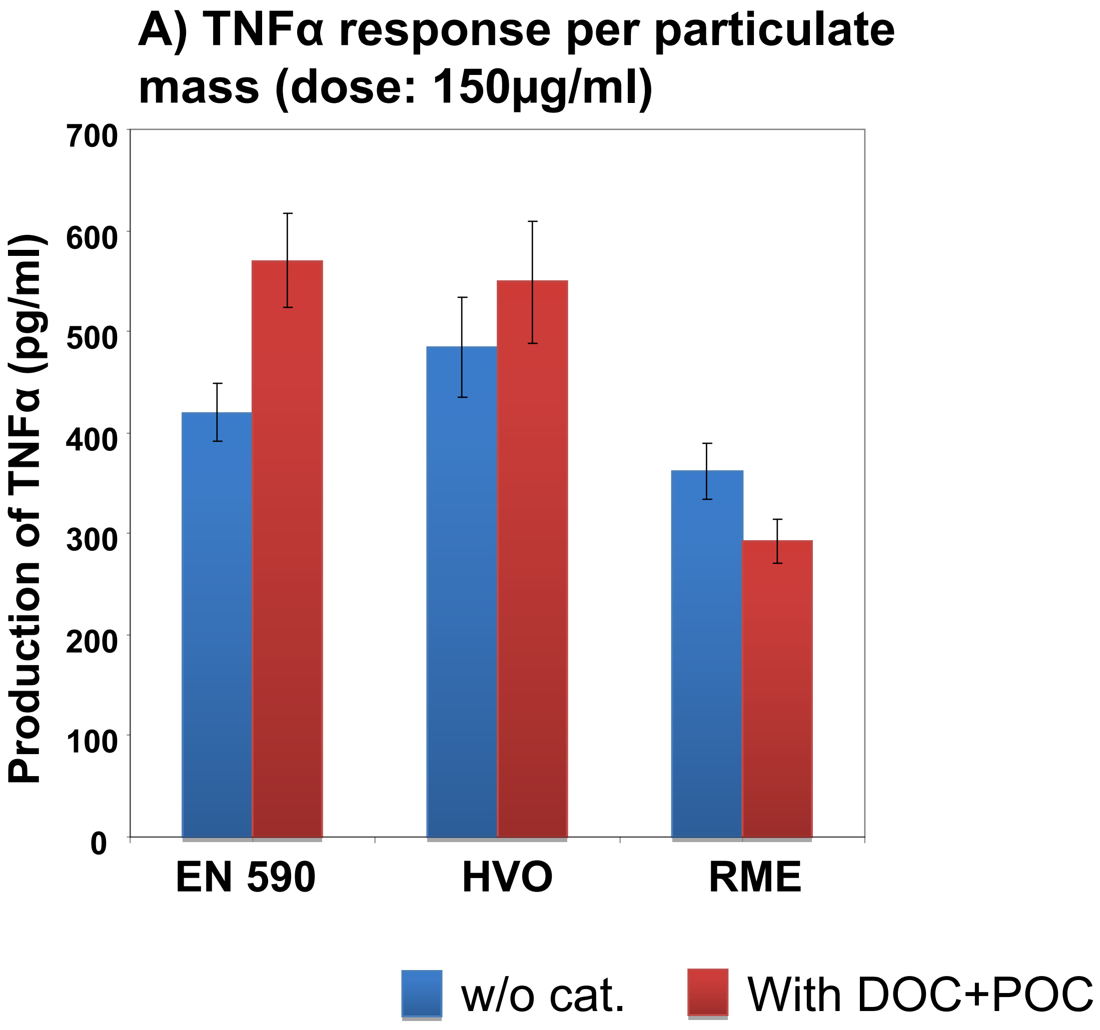
Elemental carbon (soot)



Organic carbon



Production of inflammatory cytokine TNFα (ELISA immunoassay)



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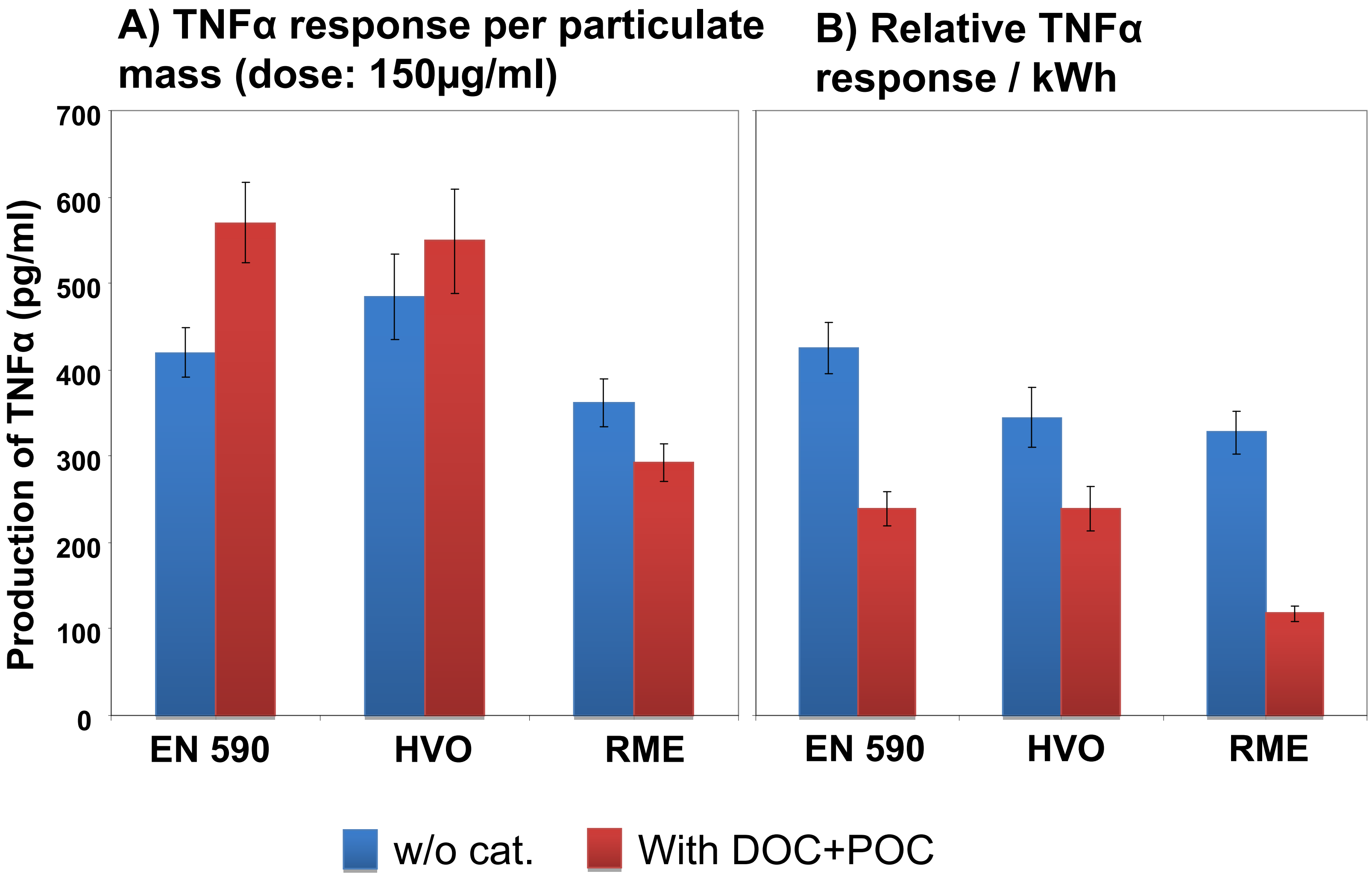

Conclusions

- Particulate emissions
  - RME and HVO decreased mass emissions when compared to EN590
  - RME produced more particles than EN590, but the particles were smaller.
  - Catalytic converter (DOC+POC) decreased mass emission (~-50%) and particle number concentrations (~-60%) on all fuels
  - There were a significant nucleation mode on low loads with EN590 and RME
  - Nucleation modes were suppressed by the catalytic converter (DOC+POC)

Conclusions

- Inflammation response
  - EN590 and HVO had largest inflammatory potency with equal mass dose
  - Catalytic converter (DOC+POC) increased the inflammatory responses per mass unit with EN590 and RME
  - Fuels and catalytic converter had an effect on particulate emissions → biobased fuels and catalytic converter reduced relative inflammation potency