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Non-Reactive Working Fluids for Reliably Sensing Nanoparticles in Automotive Exhaust Gases

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Abstract

Nanoparticles in the exhausts of automotive internal combustion engines are routinely measured using condensation nuclei counting (CNC) sensors. Traditionally, n-butanol is used as working fluid for sensing combustion aerosols. However, when used on combustion engines burning modern, (partly) biogenic fuels, strong system drifts and reduced saturator lifetimes occur. This effect could be traced to non-volatile reaction products of acidic exhaust components with the alcoholic working fluid that poison the sensor, creating an immediate need for alternatives. Following fundamental theoretical considerations of the CNC principles, n-alkanes were identified as a new, advantageous class of working fluids. The materials have favourable thermal and diffusion properties, are chemically inert and condense efficiently on the carbonaceous nanoparticles of combustion aerosols and can be used with standard CNCs under standard conditions. Subsequent tests with linear alkanes in the C_9 - C_{14} range proved their practical applicability as well as the validity of the underlying models.

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Keywords: nanoparticle sensor; condensation nucleus counter; automotive exhaust analysis; working fluid; system stability

1. Introduction

Condensation nucleus counters (CNC) quantify the number concentration of nanometer-scaled aerosol particles by passing them through a region super-saturated with a working fluid (Fig. 1) [1]. The presence of a nanoparticle in

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such a super-saturated zone (inset in Fig. 1) causes the working fluid to condense onto the nanoparticle [2], thus increasing them to sizes that are optically detectable. This principle is in wide use in atmospheric studies into cloud and rain formation, but also for the determination of the number concentration of nanoparticles in the exhaust of internal combustion engines [3]. Using n-butanol as working fluid, such sensors have proven efficient and reliable for the accurate detection of the number of soot nanoparticles emitted when combusting classical fuels.

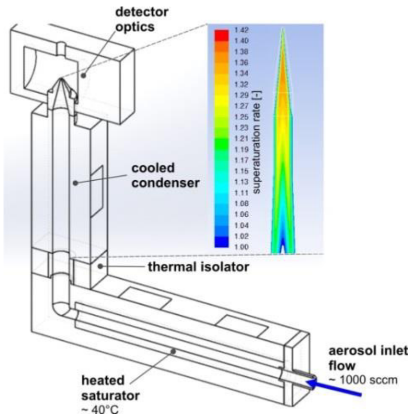

Fig 1: Fundamental CNC sensor layout.

Things, however, have changed with the increased use of bio-fuels, in particular bio-diesel. CNC sensors have been observed to drift in particular in their cut-on point, i.e. the minimal nanoparticle size that can be detected, and the signal strength at the optical detector already after a short time of use. Detailed studies showed that this effect increases with the biogenic content and can only be completely reversed by exchanging the saturator elements and cleaning the CNC. As the share of biogenic fuels is expected to increase further, the two key objectives of this work were *i*) to identify the exact nature of this sensor aging and *ii*) research suitable countermeasures.

2. Sensor Ageing Analysis

The most plausible reason for the shift in the detectable particle size is a change in the super-saturation. Since the temperatures of saturator and condenser, i.e. the primary control parameter for this, are precisely controlled, this indicates a lesser saturation of the aerosol stream in the saturator section of the CNC. To validate this assumption of an ageing of the saturator element(s), the concentration of n-butanol vapour was measured with a gas sensor at various points over the life-time of a CNC. It could be shown that the equilibrium concentration of n-butanol decreases over time when exposing the sensor to exhaust gases comprising biogenic components.

A visual inspection of saturator elements extracted from several CNCs showed the evaporation surfaces that were visibly discoloured, with the colour intensity typically increasing in the direction of the gas flow. Sections cut from these surfaces were chemically extracted and the extracts analysed using laboratory methods, in particular GC-MS and ATR/FTIR, finding substantial amounts of medium- to long-chain carboxylic acid butanol esters in saturator elements exposed to exhaust gases of engines burning (partly) biogenic fuels. Since biodiesel typically consists of fatty acid mono alkyl esters with C_1 – C_3-substituents, these findings led to the conclusion that partially combusted biogenic components, i.e. various organic acids and esters, react with the working fluid n-butanol in esterification or transesterification reactions. As in CNCs working fluid condensed on the walls of the condenser section flows back into the saturator section and is re-evaporated, butyl esters dissolved in the n-butanol follow that flow and enter the saturator element. Due to their low volatility, however, they then remain at the evaporation surfaces of the saturator, hindering the efficient evaporation of the fresh working fluid and thus irreversibly altering the sensor characteristics.

To reliably prevent this from happening, the next task became identifying and implementing alternative working fluids that work efficiently in a standard-type CNC but do not react with other substances in the exhaust gas.