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The evaluation of fuel borne catalyst (FBC's) for DPF regeneration

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HIGHLIGHTS

- FBC additives containing iron, cerium zinc, potassium and cobalt were evaluated.
- Bench test for the evaluation of the FBC additives effectiveness was evaluated.
- Based on the tests results, the two most effective additives were manufactured.

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ABSTRACT

Even though diesel particulate filters (DPFs) have been in commercial production for many years, there is still much optimisation activity, especially in the field of the regeneration strategy of these filters.

A method for obtaining organosoluble substances with an iron content of 10–15 wt% and composition containing iron additives and other selected substances has been developed. These organosoluble substances form the basis for the development of various additives of the fuel borne catalyst (FBC) type for passive regeneration of DPF's.

To test and evaluate the effectiveness of the regeneration process supported by the developed FBC additives, a novel multistage procedure consisting of three separate engine tests, which allow a comprehensive examination of additives, has been implemented. Each additive had been rated in this engine procedure at different dosage levels in a specified order. This rating allowed reliable assessment of the operational properties of the additives under the conditions of dynamometer engine testing.

As a result, from a wide range of FBC-type additives developed and then rated in the engine bench test procedure, the best two additives were selected. These additives achieved a much better operational performance than the commercial additives from two of the reputed manufacturers.

The studies that we have performed present evidence of the high operational performance potential of FBC additives in the effective passive regeneration supporting of DPF's.

1. Introduction

For several years, quantitative and qualitative emissions of particulate matter (PM) in the exhaust gases of internal combustion piston engines (especially compression ignition (CI)) have attracted considerable attention as well as concern. This attention is reflected in a worldwide progressively increasing number of scientific investigations concerning the harmfulness of PM as well as ways to reduce PM emissions. Since the second half of the 1980s, regulations all over the world limiting the mass emissions of harmful PM into the atmosphere have been introduced and systematically tightened.

In the research work carried out to date, the form of PM that is most dangerous to human health has been found to be ultrafine particles with dimensions below 50 nm (nanoparticles), which are measured as particle numbers PN. Due to the small dimensions of these particles, they can penetrate into the alveoli, where the particles are perceived by the macrophages as foreign bodies, which can induce the immune defence in the lungs, leading to inflammation and cell injury. Some hypotheses postulate that in the case of genotoxic particles, strong defences can lead to oxidative DNA damage and cell mutation.

Abbreviations: CI, compression ignition; DPF, diesel particulate filter; DLS, dynamic light scattering; DNA, deoxyribonucleic acid; DOC, diesel oxidation catalyst; DF, diesel fuel; EU, European Union; FAME, fatty acid methyl esters; FBC, fuel borne catalyst; HD, heavy duty; ICP-AES, inductively coupled plasma-atomic emission spectrometry; PM, particulate matter; PN, particulate number; SCR, selective catalyst reduction; SiC, silicon carbide; TEM, transmission electron microscopy.

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On the basis of current knowledge, continually tightened performance limits to reduce PM & PN emissions will not be achievable only on the basis of structural and technological development of internal combustion engines and the newly introduced technologies for the production of fuels and lubricating engine oils. It is therefore necessary to use methods other than engine development such as exhaust gas after-treatment. One of elements of exhaust gas after-treatment is the use of a DPF as the most effective means for PM & PN emission reduction [1–4]. From the point of view of current knowledge, referring to future emission regulations, SCR in combination with a DPF offers a unique and global solution for compliance with the most severe regulations.

Modern DPF's using ceramic filter monoliths (Cordierit, SiC or Sintermetal) have efficiencies in the range of 95–99% of the total amount of captured PN and approximately 90–95% of the total weight of captured PM, including a 95–99.9% reduction of elemental carbon particles (soot), a 60–90% reduction in the range of the SOF (soluble organic fraction) emissions and a 50–70% reduction of PAH emissions [2–9]. However, particle filters such as "wall-flow", removing particle from the exhaust gas by utilising spatial filtration and/or layers, are subjected to rapid gradual clogging, manifested by increasing backpressure of exhaust gas flow. After exceeding the allowable value for the backpressure before DPF, a rapid decrease in engine efficiency and deterioration of the operational parameters of the engine follow. As a result, at least periodic regeneration of DPF must be carried out. Taking into account that primary components of PM are organic products (mainly soot and incompletely burned hydrocarbons), a very effective method of the DPF regeneration is burning off products accumulated in the filter monolith. However, to be able to initiate and conduct the thermal regeneration under the operating conditions of the engine, at least two fundamental conditions must be met, namely the temperature of the exhaust gases flowing through the DPF must attain at least 600–650 °C (required to initiate and support the soot oxidation process) and the residual oxygen content in the exhaust gases in the vicinity of oxidised PM should not be less than 5%. For CI engines, the exhaust gas temperature mentioned above under common operating conditions is achieved very rarely and only within a very narrow range of engine operating parameters, which is a key issue in the design of any system of DPF regeneration. Generally, there are four characteristic temperatures for DPF operation:

- The temperature at which a process of DPF "charging" occurs by increasing the mass of captured particulate matter during filter exploitation ($dM/dt > 0$).
- The initialisation (ignition) temperature of soot oxidation. At this temperature, the regeneration process is very slow.
- Equilibrium temperature of soot oxidation, at which the entire amount (weight) of soot flowing into the DPF is continuously oxidised (burned off) ($dM/dt = 0$).
- Regeneration temperature, at which "real-time" intercepted soot in the DPF is oxidised, with previously deposited (captured) material in the monolith filter, leading to total regeneration ($dM/dt < 0$).

In the case of supporting the regeneration process by the application of FBC-type additives, the temperature of the activation process can be reduced to approximately 300–350 °C, which is the exhaust gas temperature range often reached during the operation of Diesel engines. For the passive regeneration of DPF, FBC-type additives containing metals as catalysts for the soot oxidation are used [3,7–12,14,15]. Studies on the chemistry of soot formation and oxidation carried out to date suggest that the metals of the first and second groups of the Periodic Table can prevent the formation of the soot nucleus. Metals of the transition groups act at a later stage in the soot formation process, catalysing the burning of the soot in the DPF.

2. FBC's composition

The catalytic effect of ash additives (particularly organometallic) on oxidation (afterburning) of PM is well documented in the literature [13,14]. During the disintegration of the additive in the engine combustion chambers, metals or metal oxides with different structures are created. Next, these metals or metal oxides are incorporated into the particles generated by the combustion of fuel. The components of PM are, in this case, in close contact with oxidation catalysts and at a sufficiently high temperature, the exhaust gases may be subjected to afterburning. This process leads to the reduction of PM emissions. Examples of metals that have been or are used in additives of this type are cerium, iron, copper, manganese, sodium, strontium and calcium. Some of them are not allowed currently for secondary emissions reasons. The second issue is the regeneration of the DPF. Often additives that reduce PM emissions are at the same time catalysts supporting the regeneration of the DPF, relying on the continuous or stochastic (random) burning off of soot deposits captured in the filter.

The additives containing metal compounds, where the highest energy electrons are in the basic state in the "d" orbitals (appear in many oxidation stages), are mainly used in the DPF regeneration process. Compounds constructed from elements that can be present in various oxidation states have the ability to form complex compositions and readily undergo redox reactions, which are particularly important in the case of combustion improvement.

Inorganic metal compounds are components of the catalyst core of the FBC, with a more complex structure. FBC metallic additives are typically complex compounds in which the core is surrounded by long-chain molecules able to coordinate metals by using free electron pairs or double bonds.

The core of the catalyst is composed of particles that are insoluble in diesel fuel, so it is necessary to disperse complex compounds that have been formed by using organic dispersant to allow the additive to dissolve in the fuel. FBC catalysts are characterized by high chemical stability, and the FBC's cannot change the physicochemical and operating properties of the fuel into which they are doped.

Until recent years, FBC additives consisted mainly of compounds containing metals such as Na, K, Mg, Ca, V, Cr, Co, Pb, Sb, Ce, Cu, Mn, Fe, Pt, Zn and Sr [16–20]. These substances were generally dosed in amounts to ensure that the concentration of the metal in the fuel ranged from 1.5 to 10 mg per kg of fuel. Most of the above-mentioned additives containing metals have been withdrawn from use, e.g., for reasons of toxicity (additives containing manganese, chromium and lead) or secondary gaseous emissions behind the DPF. Despite the well-known beneficial effects of the interaction of iron with copper in FBC additives, on account of the proved effect of copper supporting the creation of dioxins in exhaust gases, all chemical compounds containing copper are also banned as FBC additives.

FBC-type catalyst systems consisting of two different interacting metals have also been used. In this type of additives, one of the metals constitutes only a small dopant. Doping substances are compounds of divalent or trivalent metals, rare earth elements, transition group metals and precious metals. Additives consisting of the main metal and the dopant metal compounds are generally in the form of complex metal oxides [20,21].

Currently, practical applications can be found mainly for iron, cerium and iron-cerium additives, and these elements are present mostly in the form of oxides, hydroxides, naphthenates,