8nm Cerium Oxide as a Fuel Additive for Fuel Consumption and Emissions Reduction

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ABSTRACT

8nm cerium oxide is surface functionalised for diesel compatibility and added to fuel at a level of 5-8ppm. Static engine tests and large scale field trials show that engine fuel consumption is reduced by 3.5-8% and emissions, particularly of black carbon particulates and unburnt hydrocarbons are reduced by >15%. Cerium oxide acts as an oxygen donating catalyst which, as a refractory ceramic, survives the fuel burn and acts to improve engine performance in two ways. Firstly, the activation energy of cerium oxide is size related and as a consequence 8nm particles act to burn off carbon deposits within the engine cylinder at the wall temperature. The engine is progressively cleaned up by cerium oxide and performance improves. Secondly, the cerium oxide acts in the gas phase during fuel burning to reduce the deposition of non-polar compounds on the cylinder wall. This indicates oxidation of fuel during the burn which in turn results in a reduction of engine deposit build up and carbon based emissions.

Keywords: catalysis, fuel, cerium, oxidation, emissions

1 INTRODUCTION

The industrialization of the Western World has resulted in a huge increase in the use of fossil fuel combustion, approximately 50% of which is vehicular based. The overall combustion reaction is superficially simple, however it is one of the least understood widely used reactions. The basic equation, the release of CO_2 and H_2O from combustion of hydrocarbons with release of thermal energy, is [1]:

$$C_m H_n + \left(m + n/4\right) O_2 \rightarrow m.CO_2 + \left(n/2\right) H_2O$$

It is generally accepted that this is a free radical mediated reaction, and that the complex series of reaction pathways may lead to incomplete fuel burn, which leads to non-optimum engine performance and a variety of environmentally harmful pollutants, included unburnt hydrocarbons, carbon monoxide and black carbon or soot. The latter is a particular problem with diesel engines [2].

The source of the 12 million tonnes of soot emitted into the atmosphere every year is primarily combustion, from both fuel and biomass burning, and although sources are localized to urban environments in the main, the distribution in the atmosphere may range up to thousands of kilometers from the source. However, the atmospheric mass is concentrated in urban environments, with up to 45% sub-100nm atmospheric particles being soot [3, 4]. There are a variety of direct and indirect effects on climate from this atmospheric soot load, which have been considered in terms of the global mean energy budget of the planet – the "radiative forcing" (positive forces a mean warming, negative forces a mean cooling). Generally, studies indicate that soot has a positive radiative forcing up to about a third that of CO_2, making soot the second most important atmospheric contributor to global warming [5]. It has been suggested that a reduction in the emission of soot may be a relatively quick "win" in the battle against global warming [6].

Rare earth elements have been used for some decades as catalysts for a variety of processes in the field of environmental treatment of exhaust gases from vehicles [7]. More specifically, cerium oxide (CeO_2) is used to increase oxygen storage/release properties of three way catalysts used in vehicular exhaust systems [8]. The efficacy of cerium oxide as a catalyst is related to its ability to undergo a transformation from the stoichiometric CeO_2 (+4) state to the non-stoichiometric Ce_2O_3 (+3) valence state via a relatively (at least in comparison with other oxides) low energy reaction. This is in turn related to the general property of fluorite oxide structures to deviate strongly from stoichiometry. Even at a loss of considerable amounts of oxygen from the crystal lattice, and the formation of a large number of oxygen vacancies as a result, the fluorite structure is retained. Such sub-oxides may readily be reoxidised to CeO_2 in an oxidising environment. Because no crystal structure phase change is involved in the supply and re-absorption of oxygen from the CeO_2 lattice, CeO_2 may be used as an oxygen storage material in catalysis via the following reaction [9].

$$2CeO_2 \leftrightarrow CeO_2 + 0.5O_2$$

Cerium oxide has found an important application in exhaust catalytic converters where harmful emissions from

fuel burning are converted to harmless gases by the following series of reactions.

Hydrocarbon combustion:

$$(2x+y)CeO_2 + C_xH_y \rightarrow \left[(2x+y)/2\right]Ce_2O_3 + x/2\, CO_2 + y/2\, H_2O$$

Soot burning :

$$4CeO_2 + C_{soot} \rightarrow 2Ce_2O_3 + CO_2$$

NO_x reduction :

$$Ce_2O_3 + NO \rightarrow 2CeO_2 + 1/2\, N_2$$

Unburnt fuel, particulates and harmful gases are reduced when cerium oxide is used as an exhaust catalyst [10].

2. CeO_2 NANOPARTICLES AS A DIESEL FUEL ADDITIVE

Cerium oxide may also be used as a catalyst by addition of the material into the fuel itself. In the case of a dense inorganic oxide such as cerium oxide the material may only be additised effectively into the fuel when the particle size is nanocrystalline (8-10nm), as shown in Figure 1, and the surface is suitably modified such that the particles remain stable in the fuel medium. If such properties are obtained then the catalyst acts to promote lower emissions and a reduction in engine fuel consumption by two principal mechanisms, more complete fuel burning and carbon deposition destruction.

In order for a catalyst to be effective when additised into the fuel three principal properties are required. Firstly, complete hydrocarbon oxidation should be promoted, secondly formation of NO_x should not be favoured, and finally the catalyst should remain thermally stable [11,12].

As has been discussed, the ability of cerium oxide to donate oxygen allows complete hydrocarbon and soot burning in principle. In practice the activation energy of the cerium oxide, i.e. the lowest temperature at which oxygen donation occurs, is a crucial factor. Although the gas temperature of a diesel engine is high (approximately 1700ºC) [13], a low catalyst 'switch-on' temperature will clearly promote a more complete fuel burn in the milliseconds during which combustion occurs [14]. The high thermal stability of cerium oxide results in CeO_2 nanoparticles re-oxidising and remaining active after enhancing the initial combustion cycle. This is demonstrated in Figure 2, in which a thermogravimetric analysis (TGA) of a 5% w/v 8nm CeO_2 package is shown in comparison with two standard organic commercial additive packages. It is clear that all of the organic material is burnt by 400°C, whereas the CeO_2 based additive remains functional at temperatures >1000°C.

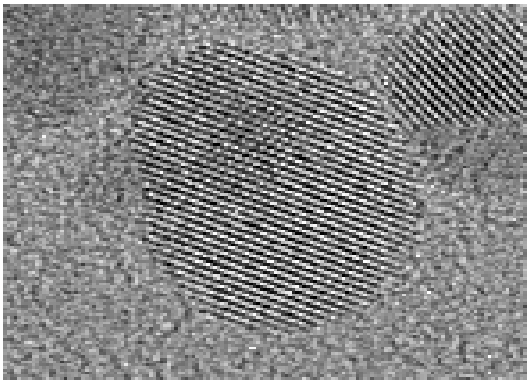

Figure 1. A TEM micrograph of 8nm CeO_2 fuel additive nanoparticles.

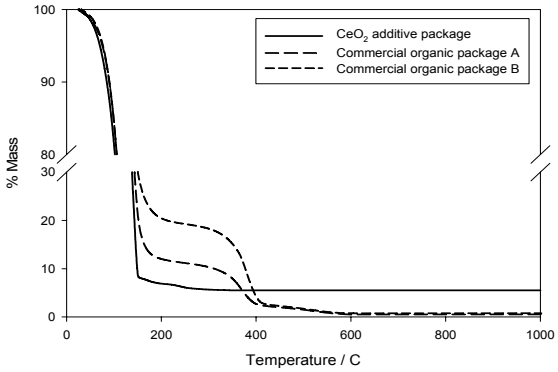

Figure 2.TGA analysis of 5% w/v CeO_2 additive package and two commercial organic additive packages.

3. EFFECT OF CeO_2 NANOPARTICLES ON INTERNAL CYLINDER DEPOSITS

CeO_2 nanoparticles are added to diesel fuel at between 5ppm and 8ppm in topical application. The effect on internal cylinder deposits is studied by analysis of deposits removed from the cylinder of a Kipor KDE2200E 2.8kW static diesel generator. The soluble fraction of the combustion chamber deposits (CCD) typically consists of a wide variety of low molecular weight hydrocarbons. Extraction of the soluble component into MeCN and subsequent separation by HPLC using a hydrophilic silica column allows a general distinction between polar and non-polar components.

A plot of the ratio of polar and non-polar soluble components is given in Figure 3. Addition of 5ppm CeO_2 to diesel fuel results in a reproducible decrease and increase of the non-polar/polar ratio as fuel is alternated between

additised and unadditised respectively. This variation indicates the effect of CeO_2 on the soluble fraction of the combustion chamber deposits is to convert non-polar to polar compounds. This results from the oxidative activity of ceria on non-polar compounds.

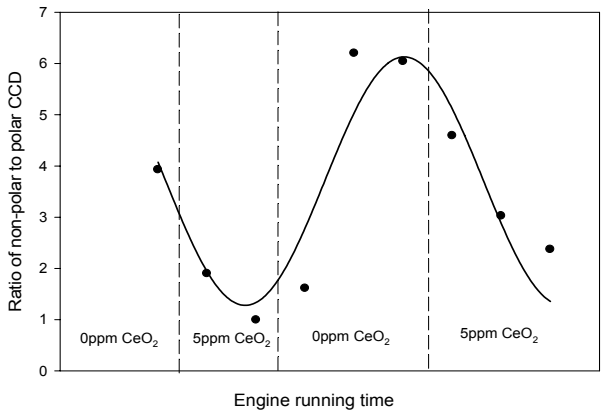

Figure 3. Variation of non-polar/polar ratio with CeO_2 additive level for 3 hour static engine cycles.

Studies of deposits formed prior to catalyst exposure show clear changes as a result of CeO_2 addition to fuel. All deposits in the cylinder are affected by the presence of ceria in the fuel. Deposits present on the head and piston surface area resulting from lubricant pyrolysis normally present in the engine as a shiny black material are converted to soft, matt black deposits easily removed by mild abrasion. Examination of areas close to the injector demonstrate that CeO_2 breaks up deposits with large grain structures being fragmented into smaller structures with some regions flaking away from the surface.

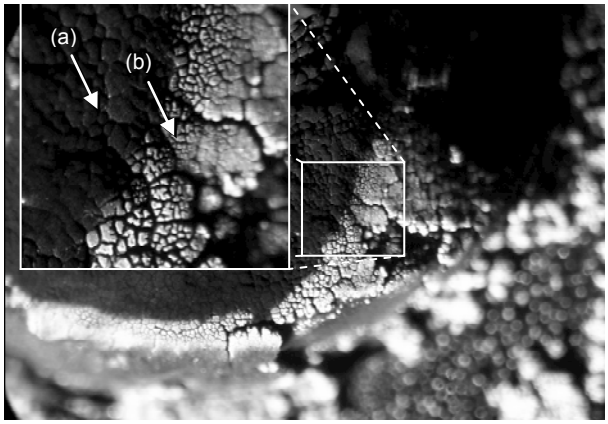

Figure 4. Injector body area after exposure to CeO_2 dosed fuel showing regions with (a) large grain deposit structures and (b) fragmented deposit structures exposed to flame

Deposits on intake and exhaust valves, shown in Figure 4, are typically present as a dense layer prior to CeO_2 exposure due to the rapid percussive movement of the valves removing loose deposits continuously during engine operation. The formation of deposits on injectors is well known to be detrimental to combustion characteristics.

4. EFFECT OF CeO_2 NANOPARTICLES ON FUEL CONSUMPTION

Accurate measurements of engine fuel consumption require an environmentally controlled engine test bed system. In these studies a Ricardo single cylinder E6 engine is used to monitor fuel consumption and emissions. Brake specific fuel consumption (BSFC) data from a single cylinder Ricardo E6 engine before and after CeO_2 addition is given in Figure 5. The engine has little carbonaceous deposit build up prior to exposure and hence the reduction in fuel consumption is primarily due to gas phase effects. Fuel consumption is reduced rapidly by 3.5% during the first two hours of exposure to 5ppm CeO_2 additive. Larger effects (7-8% fuel consumption reduction) have been demonstrated in engines following a suitable dirtying up period. Large scale field trails with up to 1000 additised public service vehicles have demonstrated fuel savings of 5-7%.

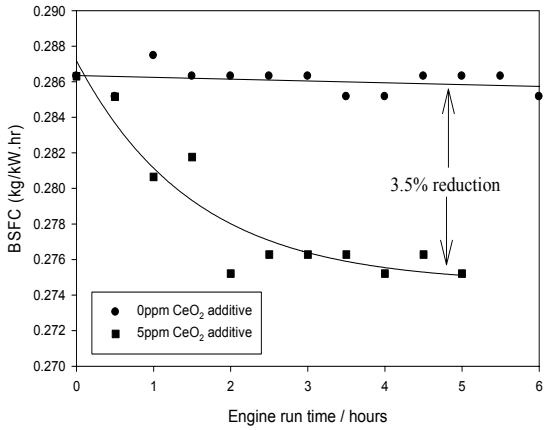

Figure 5. Fuel consumption reduction after 5ppm CeO_2 additised into diesel reference fuel

5. EFFECT OF CeO_2 NANOPARTICLES ON SOOT AND HYDROCARBON EMISSIONS

The fuel droplet is progressively vaporized once injected into the hot gases of the combustion chamber. As the fuel vaporizes from the droplet it mixes with air and spontaneously combusts. The rate of combustion during this stage – known as diffusive combustion – is limited by the rate of fuel vaporisation and oxygen mixing. If fuel vaporisation is not complete when the fuel temperature

reaches a critical level then fuel pyrolysis (non-oxidation decomposition of fuel without oxygen) occurs resulting in soot formation. The particles agglomerate and, particularly as the combustion temperature is lowered at the end of combustion, hydrocarbon condensation onto the soot particles signficantly increases particle mass.

Emissions testing has been carried out on a number of engines under a variety of operating conditions. The results are summarised in Table 1, the numbers correspond to % reduction in emissions upon switching from unadditised to additised fuel.

	Peugeot 306	Peugeot 406	Cummins M11
Soot particulates	-15.5%	-19.0%	-16.5%
Hydrocarbons	-9.8%	-7.4%	-9.5%
Carbon monoxide	-6.6%	0	-9.8%

Table 1.Emissions data from fuel containing 5ppm CeO_2 nanoparticles.

The operating conditions for the engines are: Peugeot 306, standard EU urban/extra urban cycle; Peugeot 406, steady state 70kph; Cummins M11, standard speed and load conditions on an engine dynometer.

It is clear from the data that the incorporation of CeO_2 nanoparticles into diesel fuel results in a reduction in hydrocarbon, soot and CO emissions resulting from the ability of CeO_2 to act as an oxygen storage catalyst and assist in the oxidation of species resultant from an incomplete fuel burn.

6. CONCLUSIONS

The addition of CeO_2 nanoparticles into fuel at low loading results in two main effects within the engine cylinder, the net result of which is reduced fuel consumption and reduced emissions. CeO_2 particles act to enhance fuel burn and remove engine deposits thereby reducing fuel consumption of the engine. The improvement in fuel burn leads to a reduction in emissions associated with an incomplete burn.

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