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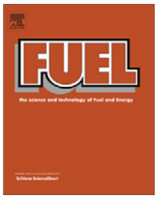

Performance of diesel particulate filter catalysts in the presence of biodiesel ash species

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HIGHLIGHTS

- Interaction of diesel particulate filter catalysts and biodiesel ash species.
- Catalytic conversion of soot in diesel particulate filters.
- Commercial catalyst (5:1 wt. ratio) decreased soot oxidation temperature.
- Biodiesel ash species (Na_2CO_3, K_2CO_3 or K_3PO_4) further decreased soot oxidation temperature.
- Engine oil ash species ($CaSO_4$, $Ca(H_2PO_4)_2$ and K_2SO_4) increased soot oxidation temperature.

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ABSTRACT

The utilization of bio-fuels, such as biodiesel, is expected to contribute significantly towards the planned 10% of renewable energy within the EU transport sector by 2020. Increased biodiesel blend percentages may change engine exit flue gas ash composition and affect the long-term performance of cleaning technologies, such as oxidation catalysts and diesel particulate filters. In this work the performance of a commercial catalyst has been studied for conversion of diesel particulate matter (SRM 2975) at 10% O_2, in the presence of salts simulating ash species derived from engine oil and biodiesel. Simultaneous thermal analysis experiments of the diesel particulate matter showed that it was dominated by soot with approximately 10 wt.% condensed hydrocarbons. The presence of a commercial catalyst (5:1 wt. ratio of catalyst to soot), in tight contact with the diesel particulate matter, decreased the temperature at which the oxidation rate peaked from 662 ± 1 °C to 526 ± 19 °C. The introduction of biodiesel ash species such as Na_2CO_3, K_2CO_3 or K_3PO_4 decreased the peak conversion temperature further (422 ± 12; 404 ± 4 and 423 ± 7 °C), with a limited dependence on ash concentration. A deterioration in catalytic conversion, i.e. increased peak conversion temperatures, was seen for two engine oil ash species and one mixed ash species (from engine oil and biodiesel) – $CaSO_4$ (569 ± 6 °C), $Ca(H_2PO_4)_2$ (699 ± 13 °C) and K_2SO_4 (581 ± 16 °C).

Kinetic parameters (A and E_a), obtained from Arrhenius plots of the data, showed a lower activation energy in the presence of the commercial catalyst ($E_a = 91 \pm 5$ kJ/mol) or CeO_2 ($E_a = 62 \pm 8$ kJ/mol) compared to pure SRM 2975 ($E_a = 220 \pm 3$ kJ/mol). The obtained kinetic data were able to describe the peak conversion temperature and the associated part of the mass loss curve, but an initial low-temperature gradual increase in conversion was not adequately described.

1. Introduction

Emissions from the transport sector and its contribution to global warming and detrimental effects on human health have become focus of growing concerns and awareness in recent years. This has caused the EU to aim for 10% renewable energy in the transport sector and 20% renewable energy overall by 2020 [1]. The introduction of bio-fuels (ethanol, biodiesel, etc.) into the transport sector is expected to contribute significantly to these goals. The introduction of new fuels or changes in fuel properties may affect engine performance, emissions, ash composition and long-term interactions with cleaning technologies such as the oxidation catalyst (DOC), the diesel particulate filter (DPF) and selective catalytic reduction of NO_x (SCR) [2]. Even a low concentration of catalyst poison in the exhaust may severely affect the performance of cleaning technologies as seen for power plants burning biomass [3–5].

Previous engine emission improvements were obtained by stricter fuel specifications and engine optimization, while after treatment systems, such as DPF and SCR, will likely be necessary

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Nomenclature

A	pre-exponential factor (frequency factor) (s^{-1})
a	cross sectional area (m^2)
C	concentration (mol m^{-3})
D	diffusion coefficient (m^2 s^{-1})
E_a	activation energy (kJ mol^{-1})
h	height (m)
k	reaction rate constant (s^{-1} Pa^{-1})
k^*	$k\ p_{O2}$ (s^{-1})
L	characteristic size (m)
M	molar mass (kg mol^{-1})
m	soot mass (kg)
p	partial pressure (Pa)
R	universal gas constant (m^3 Pa K^{-1} mol^{-1})
ρ	density [kg m^{-3}]
t	time (s)
T	temperature (°C)
Subscript	
b	bulk phase
e	effective
obs	observed
peak	peak in mass loss rate

to comply with the latest US and European legislation [6]. In the case of particulate emissions, a flow through DOC is capable of oxidising CO and gaseous hydrocarbons, that otherwise could condense and contribute to particle formation. The highly efficient DPF traps 95–99% PM by forcing the exhaust through a porous wall, thereby initially capturing PM in the pores followed by cake filtration on top of the channel walls [7,8]. To avoid excessive backpressure periodically DPF cleaning/regeneration by soot oxidation into CO_2 (reaction with O_2 or NO_2) is necessary. Two different regeneration strategies may be employed: Active regeneration at 500–800 °C (temperature increased by fuel injection) or passive regeneration down to 250–300 °C by either a catalytic fuel additive, a catalytic DPF coating for soot conversion or catalytic conversion of NO to NO_2 and subsequent low temperature soot oxidation by NO_2 [6,9]. Most modern system use noble metal based DOC and DPF formulations for indirect soot oxidation (through NO_2 formation), but direct catalytic soot oxidation by O_2 is expected to become increasingly important for future catalytic DPF's due to an increased focus on lower engine out NO_x (emission standards) and fuel economy (benefits from swifter and more frequent filter regeneration) [10,11]. A swift, cheap and energy efficient filter regeneration is desired, while maintaining filter integrity (no thermal run away or steep temperature gradients). Understanding the kinetics of filter regeneration is consequently of importance for filter optimization and regeneration strategies. The ash (incombustible residue) generated from engine oil, fuel, additives and engine/exhaust wear will accumulate in the DPF and eventually constitute the majority of trapped material. This influences catalytic DPF baseline pressure drop, pressure drop sensitivity and potentially affect regeneration frequency, heat release and performance [6,7,12]. The ash composition and properties will depend on fuel/oil origin, additives, DPF temperature history, etc. and the introduction of new fuels, such as bio-fuels, may change these.

The introduction of biodiesel has been reported to cause an increased reactivity of particulate matter [13,14] and some changes in ash composition [6,15]. The increased reactivity has been attributed to a more open structure of the de-volatilized biodiesel PM, allowing swifter O_2 diffusion to reactive sites, which is supported by the extraction of overall ultra low sulphur diesel (ULSD)/pure biodiesel (B100) kinetic data when normalising with the instantaneous surface area (E_a = 113 kJ/mol) [14]. Reported ash compositions from experiments with pure ULSD are dominated by species from the engine oil (~90%: Ca, Mg, Zn, P, S, B, Mo) in the form of: calcium sulphate, zinc phosphate, magnesium phosphate, magnesium sulphate and calcium phosphate [6,8,12]. Minor amounts of engine/exhaust wear components (Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Si, Sn, Ti, V), primarily as Fe_3O_4, are also present [6]. The utilisation of a 20% soybean methyl ester blend yielded ash similar in composition, except a somewhat higher content of engine/exhaust wear elements (~16 wt.%) and fuel alkali (~6 wt.% Na and K) [6]. This is supported by the presence of biodiesel alkali elements (4.2 wt.% Na and 2.1 wt.% K) in a survey of the particulate matter (ash + soot) collected after pneumatic cleaning of DPF/DOC on US vehicles [15]. The introduction of biodiesel may generally contribute with the elements Na, K, Ca, Mg and P, but the concentration of these elements is limited by standards such as the European EN14214 standard (Na + K $\leqslant$ 5 mg/kg, Ca + Mg $\leqslant$ 5 mg/kg and P $\leqslant$ 4 mg/kg). The ash obtained from experiments with an off-spec 100% canola methyl ester (Na + K and Ca + Mg exceeded specifications 10 times) yielded a significantly changed ash composition consisting of: calcium oxide, magnesium oxide, sodium phosphate, calcium phosphate and magnesium phosphate with 37 wt.%. Na + K [6].

Several studies of carbon oxidation (carbon black as well as automotive PM containing both soot and adsorbed hydrocarbons) and screening studies of various catalyst for soot/hydrocarbon conversion have been published in the literature [9,16–18] as has a few studies on the interaction between ash and DPF/after treatment systems [7–8,12,19]. Bardasz et al. [12] studied the influence of engine oil composition and ash content on continuously regenerating DPF, DOC and SCR performance on a 230 kW Euro IV prototype engine for simulated driving distance upto 115,000 km. No significant changes in DPF or DOC catalytic activity were found. Doping high ash oil into the fuel, a practice used for disposal or accelerated tests, did however cause rapid increases in DPF backpressure, changes in ash distribution and an increased ash density within the DPF. Sappok and Wong [7] studied the effect of ash on pressure drop and regeneration frequency by accelerated ash loading test with a 224 kW Cummins ISB engine. Ash was observed to accumulate and form end plugs in the inflow channels, thereby decreasing the effective filter volume, increasing pressure drop and causing changes in local soot concentration.

The aim of this work is to extend the present knowledge on the interaction between automotive ash species (especially from biodiesel) and catalytic DPF's in 10% O_2 by simulated filter regeneration experiments in lab-scale using simultaneous thermal analysis. This entails a detailed characterisation of non-catalytic and catalytic soot combustion in the presence of salts simulating different ash compositions. Direct catalytic soot oxidation by O_2 will likely become increasingly important for future catalytic DPF's due to focus on lower engine out NO_x (emission standards) and fuel economy (benefits from swifter and more frequent filter regeneration) [10].

2. Strategy of investigation

This investigation of soot reactivity, oxidation behaviour and the influence of catalytic materials and various salts (simulated