Individual effects of FAME biodiesel impurities on a diesel oxidation catalyst after full useful life operation in a heavy-duty truck

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Abstract: A DOC from a vehicle that had been in operation for a full useful lifetime in a biodiesel-powered heavy-duty truck was tested in a flow reactor. Consecutive selective contaminant removal procedures were used to remove catalyst poisons one by one. Catalyst activity was tested after each contaminant removal step to assess the effect of different poisons. Soot was found to negatively affect C_3H_6 oxidation, water-soluble contaminants (Na and Ca) were found to negatively affect NO oxidation activity, as did P. Thermal deactivation was found to cause decreased activity in CO, C_3H_6 and NO oxidation reactions.
Keywords: diesel oxidation catalyst, poisoning, biodiesel.

1. Introduction

Fatty acid methyl ester (FAME) has seen widespread adoption both as a pure biodiesel fuel (B100) and in blends with conventional diesel such as B20 (20% FAME, 80% conventional diesel). However, it may contain relatively high levels of contaminants, including Na, K, P, Ca and Mg, due to its production process. As an example, the European standard for FAME, EN14214, specifies that B100 may contain up to 4 ppm of P, up to 5 ppm combined of Na and K, and up to 5 ppm combined of Ca and Mg.[1] Such fuel impurities may deposit on the aftertreatment equipment and act as catalyst poisons. As the first aftertreatment component the exhaust gas encounters, the DOC is exposed to high concentration of impurities in the exhaust gas, and may therefore be susceptible to poisoning. The DOC helps generate NO_2, which is integral for effective operation of the rest of the aftertreatment system. Therefore, poisoning of the DOC may prevent the aftertreatment system from meeting pollutant abatement standards throughout the entirety of the vehicleôs lifetime.

Because several possible modes of catalyst deactivation may occur simultaneously in an aftertreatment system, isolating the individual effects of each is difficult. Several different fuel impurities may be present simultaneously, together with impurities originating from lubrication oils, while, at the same time, thermal deactivation may occur. One approach to isolate the effects of each of these simultaneously occurring deactivation routes is to selectively remove the catalyst poisons, one at a time, with catalyst activity measurements after each removal step.[2ï5] Such a method was employed here to study the effect of poisoning of a lifetimeôs operation with B100 FAME biodiesel on DOC activity

2. Experimental

Cylindrical Pt/Pd (mass ratio 3/1) on Al_2O_3 DOC samples (diameter: 20 mm, length 30 mm) were taken from the front of a DOC that had been in operation for over 700 000 km in a vehicle using B100 FAME biodiesel. The steps of the selective contaminant removal procedures are summarized in Table 1. The catalyst activity was tested before contaminant removal, and after each subsequent contaminant removal step, in a quartz flow reactor at a space velocity of 80 000 h^{-1}, at a nominal heating rate of 3.5 °C/min. The atmosphere contained 200 ppm CO, 200 ppm C_3H_6, 1000 ppm NO, 5% H_2O, 5% CO_2, 10% O_2, and balance N_2. The temperature was recorded with a type K thermocouple placed 3 mm in front of the catalyst inlet, at the radial centre of the reactor tube. Furthermore, a fresh DOC of the same type (which had experienced neither poisoning nor thermal deactivation) was tested for comparison.

Table 1. Description of selective contaminant removal procedures, methodology modified from Lance et al.[5]

Treatment	**Conditions**	**Purpose**
2 h at 400 °C	10% O_2, 7% H_2O + balance N_2 at a GHSV of 40000 h^{-1}	Removal of adsorbed hydrocarbons, soot and H_2O
Desulphation at 600 °C	Alternating between reductive and oxidative treatment, 5 minutes each, for a total of 12 reductive Ÿ oxidative sequences **Reductive:** 1% H_2 + 7% H_2O + balance N_2 **Oxidative:** 10% O_2 + 7% H_2O + balance N_2	Removal of S
De-ionized water leach	8*15 minutes of deionized water washing at 70 °C in ultrasound sonicator, followed by 2 h drying at 100 °C	Removal of water-soluble contaminants (primarily Na and Ca)
Acid leach	2*1 h treatment in aqueous solution of 5 wt% acetic acid and 5 wt% oxalic acid at 70 °C in ultrasound sonicator, followed by thorough washing with deionized water and 2h drying at 140 °C.	Removal of all remaining contaminants (mainly P)

3. Results and discussion

Catalyst activity after the different contaminant removal procedures are shown in Figure 1. None of the contaminant removal procedures had a significant effect on CO oxidation. The loss in low-temperature activity compared to a fresh sample is instead due to thermal deactivation. C_3H_6 oxidation activity recovered after oxidative soot removal, while subsequent contaminant removal steps had little effect. Aside from soot, thermal deactivation caused a significant activity drop in C_3H_6 oxidation activity. Finally, NO oxidation activity was considerably restored after water treatment and, later, acid treatment, indicating that water-soluble contaminants (Na and Ca) as well as P acted as poisons for the NO oxidation reaction. Comparison to a fresh catalyst again reveals a large effect of thermal deactivation. Surprisingly, the desulphurization procedure seems to have given rise to little catalyst activity recovery; that is, S seems to not have had an effect on catalyst activity. This could be explained by a previously observed phenomenon that long-term operation at moderate temperature (such as in diesel exhaust) causes S freshly deposited on active metal sites to migrate to the sulphating Al_2O_3 support, where it no longer appreciably affects catalyst activity.[6]

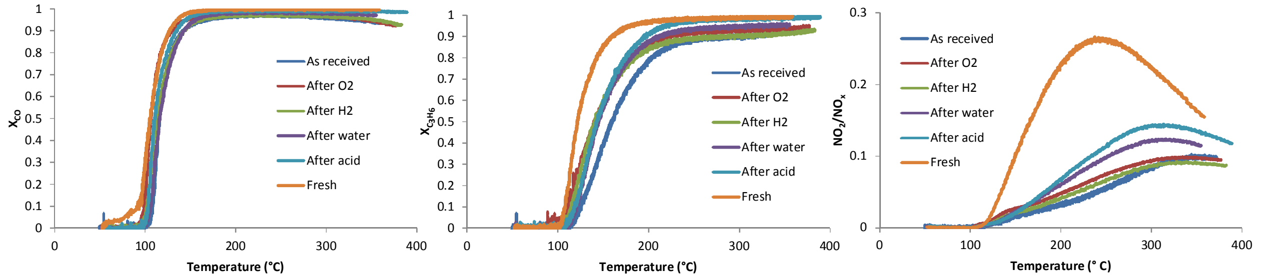

Figure 1. Catalyst activity in the CO, C_3H_6, and NO oxidation reactions after the different contaminant removal steps.

4. Conclusions

Activity testing of a DOC that had been used for a full lifetime in a FAME biodiesel truck revealed considerable deactivation compared to a fresh catalyst. Using selective contaminant removal procedures it was revealed that thermal deactivation, as well as poisoning by soot, P, and water-soluble contaminants (Na and Ca) were the causes of the activity loss. S seems to not have significantly affected DOC activity.

References

1. J. Granestrand, S. Dahlin, O. Immele, L. Schmalhorst, C. Lantto, M. Nilsson, R.S. París, F. Regali, L.J. Pettersson, Catalysis, in press (2018)
2. T. Beutel, J. Dettling, D. Hollobaugh, S. Kumar, T. Mueller, SAE 2005-26-021 (2005)
3. M.H. Wiebenga, C.H. Kim, S.J. Schmieg, S.H. Oh, D.B. Brown, D.H. Kim, J.-H. Lee, C.H.F. Peden, Catal. Today 184 (2012) 197
4. J. Li, T. Szailer, A. Watts, N. Currier, A. Yezerets, SAE 2012-01-1094 (2012)
5. M. Lance, A.A. Wereszczak, T.J. Toops, R. Ancimer, H. An, J. Li, L. Rogoski, P. Sindler, A. Williams, A. Ragatz, R.L. McCormick, SAE 2016-01-2322 (2016)
6. J. Li, A. Kumar, X. Chen, N. Currier, A. Yezerets, SAE 2013-01-0514 (2013)