Fuel 128 (2014) 260–267

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Effect of rapeseed methylester blending on diesel passenger car emissions – Part 2: Unregulated emissions and oxidation activity

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HIGHLIGHTS

- Highest biodiesel blends result in increased SOF's percentage to the DPM.
- O-D SOF and inorganic ions seen not to be affected by the fuel change.
- F-D SOF was the major constituent comprising 70–90% of total SOF.
- DPF equipped vehicles exhibited lower oxidation activity per km compared to V2.

ARTICLE INFO

Article history:
Received 15 September 2013
Received in revised form 27 January 2014
Accepted 11 March 2014
Available online 21 March 2014

Keywords:
RME
SOF
Redox activity
Unregulated emissions
n-Alkanes

ABSTRACT

The use of biofuels as automotive fuels is gradually increasing in order to meet the legislation targets for the use of renewable products in road fuels. Many types of bio-blending components are already used for this purpose throughout Europe with Fatty Acid Methyl Esters (FAMEs) being the most common. The objective of the present study was to evaluate the impact of Rapeseed Methyl Ester (RME) application on unregulated particulate emissions of modern diesel passenger vehicles, and specifically on exhaust particles' most important chemical constituents. Particle emissions were analyzed for their soluble organic fraction (SOF) and its constituents (fuel-derived SOF and lube oil-derived SOF), as well as for major inorganic ions (nitrate, sulfate, ammonium). Furthermore, the impact of RME on SOF's redox activity was investigated. A hydrocarbon-only diesel fuel (B0) and three blends of RME at 10%, 30% and 50% v/v were tested with three Euro 4 + compliant vehicles, one equipped with an oxidation catalyst and two others with different type of Diesel Particulate Filters (DPF), over the NEDC and Artemis Urban driving cycles. The use of higher biodiesel blends seem to result in increased SOF percentage to the total PM emitted. The same trend was also observed for fuel-derived SOF, while lube oil-derived SOF and major ion percentages to total PM were not significantly affected by the fuel change. Fuel-derived SOF was the major constituent comprising from 70% to 90% of the total SOF emitted. Additionally, in the non-DPF equipped vehicle the increase of biodiesel blend resulted in increased *n*-alkanes emissions (μg/km) without, however, the differences being statistically significant. Although the non-DPF equipped vehicle exhibited slightly higher sulfate than nitrate emissions, in DPF equipped vehicles sulfate were not detected at all. Higher RME contents resulted in elevated DTT-redox activity per mass in all tested vehicles, while on the other hand, the DTT-redox activity per unit of distance driven was not affected by the fuel change. Both DPF equipped vehicles exhibited 2–3 times higher DTT-redox activity per mass of emitted SOF when compared to the non-DPF equipped vehicle, however they exhibited 3–6 times lower oxidation activity per km, regardless the fuel. This is an indication that a significant amount of potentially more toxic organic compounds are trapped and oxidized in the DPF resulting thus in potentially less toxic organic emissions compared to the non-DPF equipped vehicle.

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http://dx.doi.org/10.1016/j.fuel.2014.03.018
0016-2361/

1. Introduction

Road transportation is a major source of particulate matter in the atmosphere of urban metropolitan areas. Especially, diesel vehicles are a great contributor holding a high percentage of particulate emissions among all means of transportation. Diesel particulate matter (DPM) is emitted as a result of incomplete fuel combustion and lubricant volatilization during the combustion procedure. Exhaust emissions mainly depend on the engine combustion concept and operating conditions, the fuel and lubricant, as well as the state of maintenance [1]. Despite the improvements introduced the last decade in diesel engines and aftertreatment technologies, DPM emissions are still of high concern due to their connection to many adverse health impacts, such as cardiopulmonary diseases, lung problems and various types of cancers [2–5]. On the other hand, DPM is also connected to a wide series of environmental problems, including visibility degradation, global warming and acid rain [6].

Despite their higher NOx and PM emissions when compared to gasoline vehicles, diesel vehicles are becoming more popular in Europe due to their superior fuel economy and lower CO_2 emissions [7]. As a result the EU has introduced more stringent diesel emission standards and emphasized on diesel's substitution by alternative fuels. For this purpose the 2009/28/EC Directive was introduced, requiring that 10% renewable energy must be used in road fuels by 2020. Many types of bio-blending components are being considered to achieve this requirement but in the near term fatty acid methyl esters (FAME), also known as biodiesel, are most likely to be used as diesel substitutes. Different FAME types are in use throughout the world depending on the raw material used in the production procedure with rapeseed methyl ester (RME) currently being the most common.

Taking into consideration that in some countries vehicles have been specially adapted to operate on biodiesel blends in the range 20–30% v/v, any potential impact of FAME on vehicle emissions is already affecting vehicle fleet pollutant emission levels and air quality. Regarding regulated emissions, biodiesel fuels have been widely investigated with most authors reporting an increase in NOx emissions with the introduction of biodiesel [8–11]. On the other hand, CO and HC emissions seem to decrease when biodiesel is used [12]. In case of PM things are not that clear since their emissions depend on factors like the vehicle, engine's technology and the test driving protocol selected [7,13]. As far as unregulated particle emissions are concerned, it is necessary to further investigate the effect of biodiesel on them since there is still a lack of data particularly when modern vehicles equipped with DPFs are considered. In this context, the present study aimed to evaluate the impact of higher RME levels on the unregulated particulate emissions of three Euro 4-compliant light-duty diesel vehicles.

This is the second part of an experimental study sponsored by the oil companies' European association for environment, health and safety (CONCAWE), which aimed to address the effect of RME application on modern diesel passenger car fuel consumption and emissions. The main objectives of the present study was the collection in a systematic way of emissions experimental data from diesel passenger cars operating with RME/diesel blends, as well as the evaluation of the impact of higher RME levels on unregulated particulate exhaust emissions of modern passenger cars. For this reason collected DPM samples were analyzed for their SOF emissions, the fuel and lube contributions to the soluble organic fraction, and also for their *n*-alkanes and major inorganic ion (NO_3^-, SO_4^{2-}, NH_4^+) emissions. Furthermore, the DTT assay was applied in order to determine the influence of higher biodiesel levels on the redox activity of the emitted SOF, due to its link with the production of reactive oxygen species and consequent generation of oxidative stress [14]. Finally, the influence of the DPF on these parameters was investigated. Overall, this work attempts to provide insight regarding pollutants, such as SOF and inorganic ions, that are not commonly reported in literature.

2. Methodology

Details concerning vehicles, fuels and the driving cycles tested are provided in the first part of the present study [15]. In brief, PM sampling was performed following the specifications of the PMP protocol [16]. A separate weighed PTFE-coated glass fiber filter was used for each driving cycle. Filters were conditioned for 24 h under controlled temperature and humidity before and after samplings. Filters were then weighed and PM emissions were calculated. In addition to the vehicle tests, six additional blank tests were performed for determining background levels for PM. The filter papers were folded in half with the side containing the PM deposit on the inside and wrapped in aluminum foil. Afterwards the foil-wrapped filters were placed in a suitably-sized self-sealing plastic bag which was stored in the chilled area of a refrigerator until PM speciation analyses.

2.1. SOF determination and SOF breakdown analysis

Total SOF in the DPM of the tailpipe emissions was determined according to the IP 443/99 standard [17]. Before the analysis filters were conditioned for 24 h under standard conditions (20 ± 1 °C and 50 ± 5% RH). Afterwards they were cut in two and each half was weighed on a balance of 1 μg readability. Them the first halves underwent Soxhlet extraction with 100 ml of dichloromethane for 13 cycles and were oven dried for 30 min at 50 ± 2 °C. After drying the filters were reconditioned for 24 h under controlled temperature and humidity and weighed again in order to determine SOF as the difference of the evaluated masses. Blank filters underwent the same procedure and samples were corrected with respect to background emissions.

In order to perform the SOF breakdown to the fuel (F-D SOF) and lube oil-derived hydrocarbons (O-D SOF), dichloromethane extracts were placed in a rotary evaporator at 36 °C at a final volume of approximately 1 ml. The concentrated extracts were then taken up in carbon disulfide, placed in a labeled sealed container and stored at the freezer at below −15 °C. SOF breakdown was performed by means of gas chromatography coupled with a flame ionization detector (GC-FID) according to the method described in detail at the IP 442/99 standard [18]. The following temperature program was applied:

(a) Injector and detector temperatures, 380 °C.
(b) Initial column temperature, 40 °C.
(c) Final column temperature, 360 °C.
(d) Ramp rate (linear), 8 °C/min.
(e) Isothermal time (at final temperature), 10 min.
(f) Carrier gas, helium.

According to [18] all SOF comes either from unburned fuel or unburned lubricant oil. All samples chromatograms were corrected with respect to background emissions using the corresponding averaged data obtained from the blank filters. The method's LODs were 0.197 and 0.199 $\mu g\,ml^{-1}$ for F-D SOF and O-D SOF, respectively. The overall precision of the analysis was estimated to lie between 5.4% (F-D SOF) and 16% (O-D SOF). Finally, even carbon *n*-alkanes from C14 to C36 in the DPM were determined simultaneously with SOF breakdown following the temperature programme described. The method's LODs varied between