Queensland University of Technology
Brisbane Australia

Pourkhesalian, A.M., Stevanovic, S., Salimi, F., Rahman, M.M., Wang, H., Pham, P.H., Bottle, S.E., Masri, A.R., Brown, R.J., & Ristovski, Z.D.
(2014)
Influence of fuel molecular structure on the volatility and oxidative potential of biodiesel particulate matter.
Environmental Science & Technology, *48*(21), pp. 12577-12585.

https://doi.org/10.1021/es503160m

Title: The influence of fuel molecular structure on the volatility and oxidative potential of biodiesel particulate matter

A.M. Pourkhesalian[1], S. Stevanovic[1], F. Salimi[1], M.M. Rahman[1], H. Wang[1], P.X. Pham[2], S.E. Bottle[1], A.R. Masri[2], R.J. Brown[1], Z.D. Ristovski[1]*

[1] ILAQH and BERF, Queensland University of Technology, Brisbane, QLD 4001, Australia

[2] Clean Combustion Research Group, The University of Sydney, NSW 2006, Australia

*Corresponding Author: Z.D. Ristovski,

Email: z.ristovski@qut.edu.au

Key words: Diesel exhaust nano-particles, ROS, Volatility, conventional diesel fuel, methyl ester biodiesel, carbon chain length, level of saturation

Abstract

We have studied the effect of chemical composition of biodiesel fuel on the physical (volatility) and chemical (reactive oxygenated species concentration) properties of nano particles emitted from a modern common-rail diesel engine. Particle emissions from the combustion of four biodiesels with controlled chemical compositions and different varying unsaturation degrees and carbon-chain lengths, together with a commercial diesel, were tested and compared in terms of volatility of particles and the amount of reactive oxygenated species carried by particles. Different blends of biodiesel and petro diesel were tested at several engine loads and speeds. We have observed that more saturated fuels

with shorter carbon chain lengths result in lower particle mass but produce particles that are more volatile and also have higher levels of Reactive Oxygen Species (ROS). This highlights the importance of taking into account metrics that are relevant from the health effects point of view when assessing emissions from new fuel types.

Introduction

Alternative and renewable sources of fuels draw a substantial amount of attention motivated by the constant movement towards more stringent regulation against diesel emissions, the rising price of crude oil, and the vulnerability of fossil fuel resources. Biodiesel is currently one of the most promising alternatives to fossil fuels, and depending on its chemical and physical properties, may be considered as a suitable choice for blending with diesel fuel to account for increasing fuel demand [1-3]. Biodiesel is a processed fuel which is derived from biological sources by transesterifying vegetable oils, animal fats or algae [3]. In terms of chemical composition, biodiesel fuels are mono-alkyl esters of fatty acids [3]. Most of the biodiesel fuels are composed of Fatty Acid Methyl Esters (FAMEs) [3]. The reasons that make biodiesels a suitable and practical fuel choice are numerous. They can be derived from a number of feed stocks such as rapeseed, soybean, palm, waste cooking oil, tallow, jatropha, algae etc [1-3].Biodiesels are renewable and degradable [2, 4]. Lack of polycyclic aromatic hydrocarbons reduces Hydro carbons (HC) and Carbon monoxide (CO) concentrations in the exhaust [5]. In addition, the oxygen content of biodiesel plays an important role in reducing black carbon (BC) formation when local oxygen concentration decreases due to a diffusion combustion [5-7]. The higher cetane number of biodiesel leads to a more complete combustion [8] which in turn results in higher levels of NOx concentration in the exhaust gas [9].

Recently, particulate matter (PM) produced by biodiesel combustion has become a popular research topic [10-15]. This is understandable considering that emissions from diesel engines have been recently declared as carcinogenic [16]. It is commonly seen that biodiesel causes less PM mass concentration in the exhaust gas [10, 17, 18]. However, some studies have reported an increase in the particle number concentration [11, 19, 20] as well as particle number per unit of particle mass [21]. An additional concern was the observation that non-petroleum diesel fuels emit excessive amounts of volatile compounds upon combustion, which potentially results in more toxic emissions[14, 22, 23]. It is also reported that combustion of biodiesel generates smaller particles that can penetrate deeper in lungs causing inflammation at the sites of deposition [12-14, 22].

The quality of combustion is a key factor that affects all the outputs of an engine. Viscosity, surface tension, density, cetane number, low-temperature properties (cloud point, pour point, etc.) [2, 8], heating value and lubricity [8] are amongst the physical parameters of the fuel affecting the combustion process. On the other hand, chemical properties such as carbon chain length, number of double bonds and the amount of oxygen borne by the fuel may also affect the aforementioned physical properties and in turn, the combustion process. There have been a growing number of publications that study the correlation between fuel composition and engine emission, especially diesel particulate matter (DPM) [9, 17, 24]. The relationship between biodiesel chemical properties and resulting emissions were investigated [2, 5, 8, 9, 24, 25],and it has been found that blends with higher oxygen content produce less PM but more volatile particles and increased levels of NO_x [5, 9, 25]; while biodiesel fuels with longer carbon chain length led to more PM [8, 24].

DPM is well known for its adverse effects on humans, animals and the environment [26-28]. Recently, based on the current body of knowledge, the International Agency for Research on Cancer (IARC) has labeled diesel exhaust as carcinogenic within class 1 [16]. While the mechanism by which DPM causes the adverse health effects are not known, a great deal of the harmful effects relate to its ability to cause oxidative stress [29-35]. Therefore, measurement of oxidative potential (OP), expressed through ROS concentration, can be used as a good estimate for its reactivity and toxicity. Based on the data provided in the literature so far, it remains unclear which chemical species contribute to the measured redox potential and the overall toxicity. Several studies in this area showed that [23, 29, 36] the organic fraction, more precisely semi-volatile component of PM, correlated well with the measured OP. Stevanovic et al. [29] further showed that the oxygenated fraction of the semi-volatile component of DPM was most responsible for the OP of DPM.

The primary objective of this work is to critically examine the influence of the carbon chain length and saturation levels of biodiesel fuel molecules on the overall volatility (OV) and OP of DPM. All the work has been undertaken by investigating particle emissions from a common-rail engine using four palm oil biodiesels and different blend percentages. All tested biodiesels were FAMEs with controlled fatty acid composition. This enabled us to assign the influence of a particular parameter more easily. This paper is an extension of a previous study[37] where the engine performance characteristics and emissions were investigated and presented, including some preliminary findings for the ROS emission, particularly for pure biodiesel. It should be noted that the results for B100 are reproduced here for comparison purposes. Furthermore, the paper elaborates on these findings and new analysis in terms of physico-chemical properties of the fuels and their blends.

Experimental setup and methodology

A schematic of the experimental setup is can be found in Figure S1 in supporting information. The test bed included a diesel engine coupled to a dynamometer and the accompanying instruments for PM and gas measurement. The specifications of the engine and dynamometer are shown in Supporting Information, Table S1. Raw diesel exhaust was sampled from the exhaust line and passed through a dilution tunnel and a Dekati ejector diluter both of which were fed with HEPA-filtered air. A TSI Dustrak (model 8530) measured the mass of particles. Gas analysers, consisting of a NDIR (Non-dispersive infra-red) CAI 600 series CO_2 and CO analyser and a CAI 600 series CLD (Chemiluminescence detector) NOx analyser, measured CO, CO_2 and NOx concentrations before the dilution system. Also, to determine the dilution ratio, a SABLE CA-10 CO_2 analyser was used to measure CO_2 concentrations after each dilution step. Real-time measurements of black carbon concentrations were performed by an Aethalometer (AE33, 7-Wavelength). A Scanning Mobility Particle Sizer (SMPS TSI 3080, with a 3022 CPC) measured the size distribution of diesel exhaust. A Volatility Tandem Differential Mobility Analyser (VTDMA) consisting of an electrostatic classifier, a thermo-denuder and an SMPS (in-house designed column with a 3010 CPC) measured the volatile content of particles. The VTDMA gave the change in particulate diameter for six pre-selected sizes: 30, 60, 90, 120, 150, 200 and 220 nm after they passed through the thermo-denuder with the temperature set at 300 °C. The flow rate through the thermo-denuder was kept constant at 1 lpm, which lead to a residence time of around 2 seconds. As the concentration of particles entering the thermo-denuder is rather small, there was no need to equip the thermo-denuder with a charcoal section. Absorption of the evaporated semivolatiles on the walls of the thermo-denuder was sufficient to reduce the vapour pressure and prevent them recondensing on to the existing nonvolaitle particles [38].

The volumetric volatile fraction (VVF) for each size was calculated from the difference in diameter of particles before and after the thermo-denuder[39].

This study approximates the fractal-like diesel aerosols by spherical particles with the corresponding electrical mobility diameter. Although the mentioned assumption is not accurate for larger agglomerates of diesel particles, it would not distract the results as this study aims at comparing various fuels and not at quantification of the amount of volatile material emitted by combustion of biodiesel.

The total amount of volatile matter is calculated for every sampling point and the parameter used for its quantification is the Overall Volatility (OV). This was previously introduced in the literature by Giechaskiel [40], where it was used for the calculation of the non-volatile fraction of PM. More details of the concept and the procedure used for calculation of OV can be found in the supplement material.

The BPEA molecular probe (bis(phenylethynyl) anthracene-nitroxide) was applied in-situ to assess the OP of different fuel stocks. Samples were collected by bubbling aerosol through an impinger which contains 20 mL of 4 µM BPEA solution (using an AR grade dimethylsulphoxide as a solvent). More details on the ROS sampling methodology, theory behind its application and proof of concept in the case of various combustion sources can be found in Miljevic et al. and Stevanovic et al. [41-45].

Fuel Selection

The present study investigates four biodiesels of controlled composition, differing in levels of unsaturation, carbon chain length and oxygen content. Commercial petro-diesel was used for blending. Some of the fuel properties were measured experimentally in a previous study [46], and others were estimated based on the chemical composition of methyl-esters which are shown in Supporting Information, Table S2. We labeled the tested FAMEs as C810, C1214, C1618 and C1875, based on the number of carbon atoms in the most abundant fatty acid in that particular biodiesel stock. The Iodine values of C810 and C1214 are very small, implying that they are almost fully saturated; but the large difference in saponification values shows that the carbon chain length of their molecules is quite different and, so is the oxygen content. The Iodine value is used in the literature as the indication of the unsaturation while Saponification value presents a measure of the average molecular weight or chain length [46]. Conversely, C1618 and C1875 have different iodine numbers but pretty close saponification values; which indicates that the carbon chain length of their molecules is close but with different levels of unsaturation. We chose these controlled fuels to be able to differentiate between the effect of unsaturation and carbon chain length.

The engine operated on blends of 100%, 50%, 20% and 0% of biodiesel and petro-diesel namely B100, B50 and B20 and B0, respectively. We conducted tests at idle, quarter (1500 and 2000 rpm) and full load (1500 rpm).

Results and discussion

Volatility measurements

To estimate the thermo-denuder temperature at which the volatile content of DPM is removed, measurements of the temperature dependent volatility were conducted for 30 and 150 nm particles using B0 at idle (Figure S2 in the Supporting Information). The temperature was ramped from room to

280°C in steps of 20°C. By 180°C the 30nm particles were almost completely evaporated and the larger 150nm particles reached a stable size. Therefore we can be confident that at the set temperature of 300°C all of the volatile material has been evaporated from the diesel particles and there will be no effect of the size and residence time of particles [47].

The VVF, calculated using Eq.1, for all the measured particle sizes and all the fuels and blends is shown in Figure S3 in the Supporting Information. Out of the 4 loads studied, the highest volatility was observed for particles produced during idling. This was valid for all the measured blends and fuels. In addition to the idling conditions, higher volatility was only observed at full load, while particles produced at quarter load and at both speeds did not show significant volatility. For almost all of the fuels and blends tested and for most of the loads, higher volatility was observed for smaller particles. This is the most obvious for idling conditions where 30nm particles were mainly volatile with a VVF of over 75%. Similar dependence on the volatility as a function of particle size has been observed previously [48, 49].

To get a better insight into the influence of the fuel type and blend on the VVF, from the data presented in Figure S3, we calculated the OV for each of the 3 fuel blends (B20, B50 and B100) and for all 4 tested modes being presented in Figure 1. Unfortunately the volatility for C1214 at B100 was not measured.

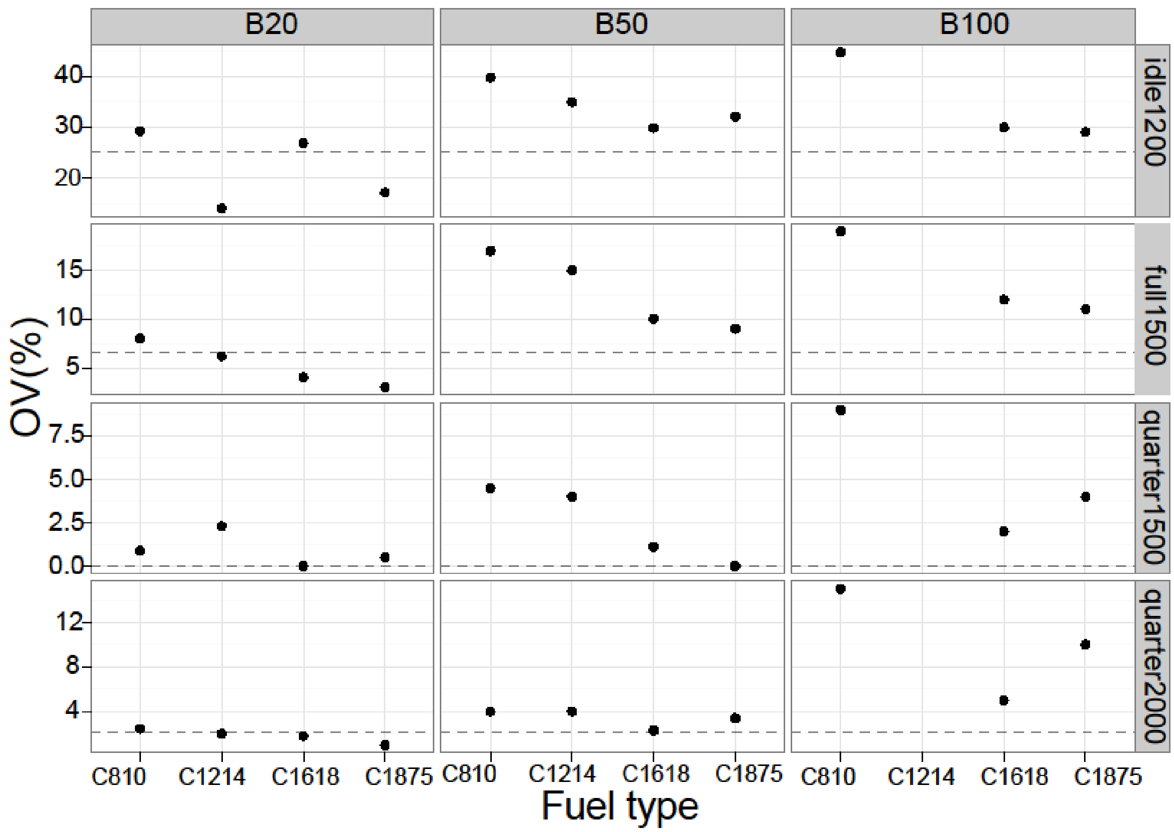

Figure 1, OV for all blends and modes tested. Rows present data measured at the same load, while columns data are measured at the same blend percentage. Different fuels are sorted along the x-axis according to their carbon chain length going from the shortest to the longest.

What is obvious from all of the graphs is that for all of the higher blends (B50 and B100) the measured volatility is larger than that of B0. Furthermore an increase in the volatility with the increase of the biodiesel blend percentage for the same fuel type can also be observed. While previously [23] have observed an increase in the volatility with increase in the blend percentage, the results did not show a stock dependency. In these measurements we do see a dependence on the feedstock, with the fuel with the shortest carbon chain length (C810) producing the most volatile particles for all the tests except one, B20 at quarter load and 2000 rpm. Although C810 did not produce particles with the largest OV the observed values were all within the measurement error. Also, in the case of the higher blend percentages B50 and B100, a decrease in the OV is followed by an increase in the carbon chain length. This refers to all the loads tested but is most significant at idle and full load where a larger OV was measured. This is in contrast with a previous observation [50] where an increase in the volatile organic fraction (VOF) was observed for an increase in the carbon chain length. It is worth mentioning that Pinzi et al. [50] have used a mechanical direct-injection engines, as compared to the common rail engine used in our case, for which the fuel physical properties have a significant influence on the spray pattern and therefore emissions.

Some previous measurements conducted for petro diesel point out that the volatile part of DPM is mainly due to the lubricating oil [51-53], and some recent measurements in the vicinity of busy roads also show that the main contributor to the primary organic aerosol (POA) is lubricating oil from both gasoline and diesel powered vehicles [54]. If that was the case, in our observations, the increase in the OV could be interpreted due to a decrease in the total non-volatile mass (volume) as the lubricating oil contribution would be the same for all of the different fuels and blends tested.

On the other side, measurements on biodiesel fuels show a large fraction of fuel derived organics contributing to the volatile part of DPM [55]. This contribution can be as large as 90% for B50 blends[56].

BC Emissions

The change in the OV could be either due to the change in the emission of primary organic aerosol (POA) or could be due to the change in the emission of the non-volatile soot component of DPM with the change of the carbon chain length. A good measure of the nonvolatile mass emitted from a diesel engine is the BC concentration. Figure 2 shows the BC emission factor (EF) for each of the 3 fuel blends (B20, B50 and B100) and for all 4 tested modes.

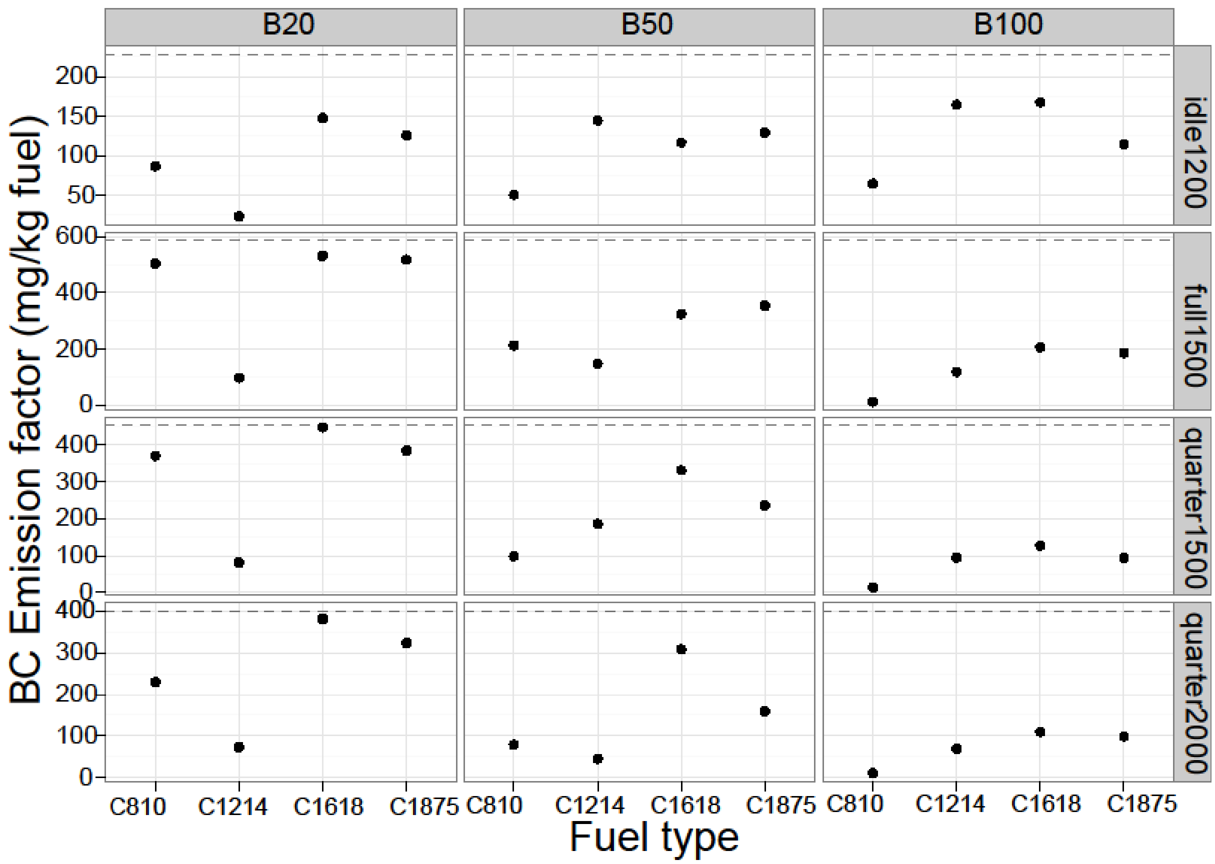

Figure 2, BC Emission factors for all blends and modes tested. The emission factor for B0 at each mode is shown as a dashed line. Rows present data measured at the same load, while columns data are measured at the same blend percentage. Different fuels are sorted along the x-axis according to their carbon chain length going from the shortest (C810) to the longest one (C1875).

We can see that all blends and all fuels reduce the BC emissions as compared to B0. Higher blend percentages of biodiesel (B50 and B100) show a clearer trend where the fuel with the shortest carbon chain length has the smallest BC emissions. An increase in BC emission is observed with the increase in carbon chain length up to C1618, afterwards a decrease is observed for C1875. While there is not a big difference in the carbon chain length of the FAMEs that make C1618 and C1875, as both fuels contain large fraction of oleic acid of 53 and 63.5% respectively, the later fuel contains additional 28.1% of FAMEs that are fully saturated (linoleic and linolenic acids). A similar increase in soot emission with the increase in carbon chain length and a decrease with the level of saturation was also observed by Pinzi et al. [50], although the later was not as obvious.

ROS measurements

OP measurement, expressed through ROS concentration of PM can be used as a good estimate for its reactivity and toxicity. An in-house developed profluorescent molecular probe BPEAnit was applied in an entirely novel, rapid and non-cell based way to assess particulate OP. Based on the data provided in the literature so far [45], there are some uncertainties related to the nature of chemical species responsible for the measured redox potential and overall toxicity. However, the majority of research in this field reported that organic fraction, more precisely semi-volatile organic content, is in a good correlation with ROS concentration [23, 36, 57].

Figure 3 illustrates the OP of particles for the same loads and blends as for the volatility measurements that were shown in Figure 1 (note logarithmic scale is used here). In idle mode, the ROS concentration is much higher than in the other cases. This may be a result of the additional combustion of lubricating oil, which would subsequently increase the overall organic content. Results do not show blend dependency in this mode, although it is clearly visible that combustion of C810 fuel generates the largest amount of ROS for all 3 blends and combustion of the fuel with the longest carbon chain length C1875 smallest amount of ROS. This could be a consequence of the way the OP is presented as the concentration of ROS per mass of emitted particles. As the fuels with the highest oxygen content have the lowest mass emission even for the same (or similar) ROS concentration they will exhibit the highest OP when calculated per unit mass of PM.

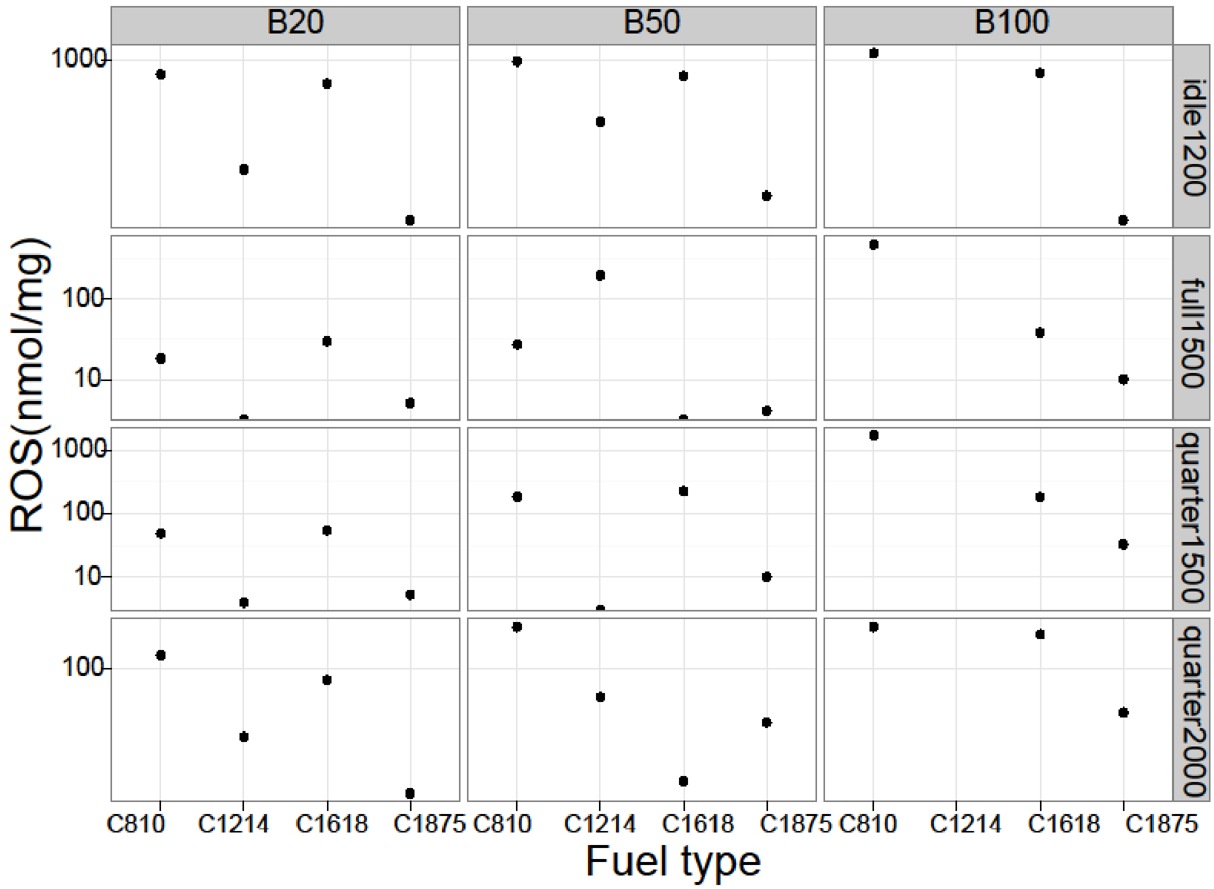

Figure 3, OP of PM for all four fuels, for all the blends and loads

For the other 3 loads and for most of the blends C810 produced higher ROS emissions. This is most apparent for B100, but it can also be observed even in 20 percent blends. While there is an increase in ROS emissions for 50 and 100 percent blends for all the tested fuels, C810 shows the largest increase of almost two orders of magnitude. This is a reasonable result as the C810 fuel molecules are of the shortest chain, fully saturated and with the largest oxygen content. These three parameters have synergetic effect in terms of prediction of resulting OP as have been seen previously as well [37].

Another important parameter that will influence resulting OP is the load on the engine. Generally, engine operating conditions significantly affect physicochemical properties of emitted PM and their subsequent toxicity that were demonstrated to change with varying engine loads and speeds. Also, OP tends to decrease with increasing engine load. This result can be explained by a more complete combustion that results from higher temperatures and lower air to fuel ratio at higher loads. In addition, at full load, the amount of lubricating oil that is available for combustion is minimal.

The role of oxygen content

As seen previously[58], out of all the fuel physical and chemical properties, oxygen content has the most significant influence on particle mass and number emissions. To further investigate the influence of the fuel oxygen content on particle volatility and ROS concentration, we have presented the dependence of the BC emission (Figure 4), ROS emissions (Figure 5a) and OV (Figure 5b) as a function of fuel oxygen content. This is done for each of the four modes tested. Oxygen content is calculated for all the fuels and blends assuming that oxygen content of base-line diesel fuel is considered to be zero. As all the fuels are methyl esters with varying carbon chain lengths, oxygen percentage increases with the decreasing carbon chain length in respective molecules. Consequently, C810 is the fuel with the highest oxygen content, followed by C1214, C1618 and finally C1875, as the fuel with the longest carbon chain length as well as the most unsaturated fuel.

The relationships between the variables were analyzed using the linear regression or generalized linear model with a log link function. The model assumptions were validated using the residuals versus fit values and QQ plots. The resulting fit functions, and their 95% condense intervals, indicate the relationship between the variables. Modeling and visualizations were performed using the ggplot2 package in R [59].

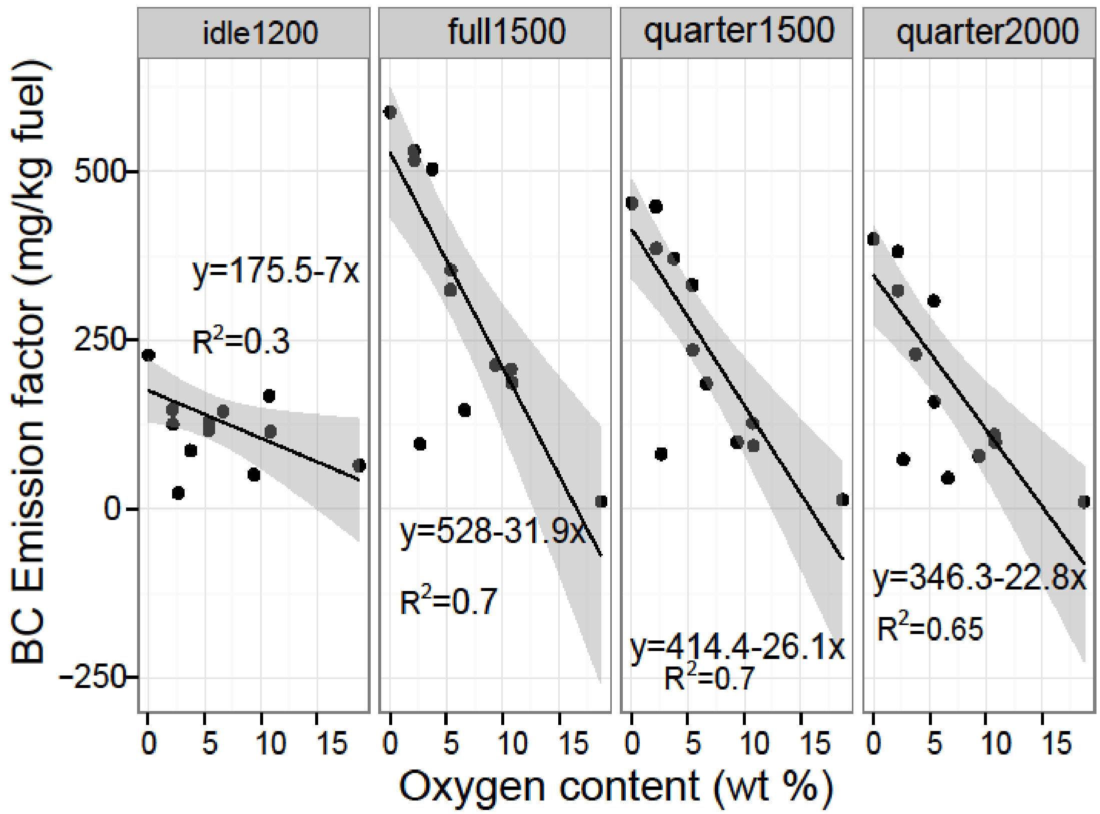

Figure 4, dependence of the BC emissions factor on fuel oxygen content for the four modes tested.

Figure 4 illustrates the decrease in the emitted BC mass with the increase of oxygen content in the fuels. The effect of oxygen content on BC formation and emissions was explained in the work of [60]Gill et al. [60] . It was suggested that oxygen present in the fuel molecule could promote the diffusion phase combustion, where soot is mainly produced, even though the diffusion phase is extended. Increased diffusion phase temperature will promote soot oxidation. Therefore the increase in oxygen content will result in a decrease in the soot or BC emissions. It is important to note that there was a linear relationship between the oxygen content and BC. Apart from idle, all other three modes showed very similar trends; so on the average, BC is reduced by 270 (mg/kg fuel) per every 10 percent of increase in oxygen content in the fuel.

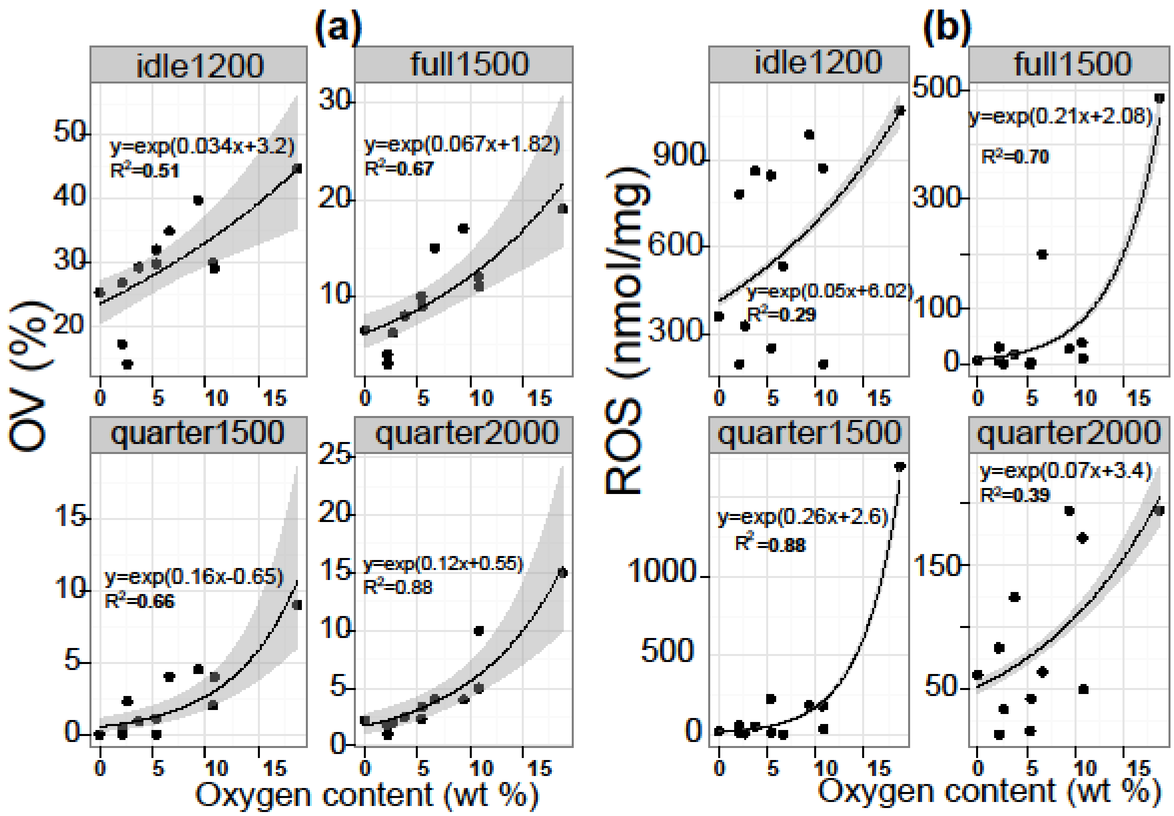

Figure 5, dependence of the a) Overall volatile content and b) ROS concentration on fuel oxygen content for the four modes tested. R^2 shown in the graphs are McFadden's pseudo R^2.

As can be seen from Figure 5 b) increasing the oxygen content leads to an increase in the ROS concentration, and therefore the OP of particles, for all of the modes tested. There is also an increase in the overall volatile content, or OV, as shown on Figure 5 a). It is interesting to observe that both the OP and OV do not seem to have a linear dependence on the oxygen content, as with BC, but exhibit a more complex behavior with an exponential dependency. The data also shows much more scattering for OP than the BC data and is strongly biased for the two 1500rpm modes (full and quarter) with the measurement of B100 C810 that had the highest oxygen content. Although not explicitly discussing the change in the volatile content with oxygen content, Pinzi et al. [50] saw an increase in the volatile content with an increase in the carbon chain length of the fuel. As fuels with longer carbon chain length have lower oxygen content they essentially observe an opposite effect. As mentioned previously, their trend could be due to the mechanical direct injection diesel engine that they have used whose emissions are more sensitive to the physical properties of the fuels as compared to a high-pressure common rail engine used in our case. In any case, as most of the new engines used today are common rail our test seems to be more relevant. The increase in the OV can be due to either the decrease in the available non-volatile soot onto which the volatiles condense or an actual increase in the amount of volatile material. If the trend displayed in Fig 7 a) was linear then one of the above effects would have been dominant. As the trend displayed on Fig 7 b) is non linear, in fact exponential, then one can assume that there is a combination of both effects: reduction in the mass of soot and increase in the fuel derived volatile (organic) material.

Similarly there are two processes that could lead to the increase in the OP. The first is the increase in the amount of ROS that is carried by the particles that could also be seen as the increase in the OV. The second is the decrease in the total mass of DPM as the OP is calculated per unit mass of particles. If the increase in the OP were due only to the decrease in the total mass then the dependence on oxygen content would be a reciprocal function and not an exponential. It is clear that the oxygen content plays a major role in the OP of DPM and most likely this is a combination of the decrease of the total DPM and an increase of the volatile organic fraction but also could be due to a change in the chemical composition of the organic fraction.

Figure 6 shows the dependence of the OP expressed through the ROS concentration as a function of the OV for all of the 4 modes tested. If the chemical composition of the volatile organic material that contributes to the OV was similar for the same mode than one would expect a linear dependence between the ROS concentration and OV. While this has been observed for the same wood combustion conditions [41] and in some cases even for the organic carbon in diesel exhaust [36] in general, various fuels and loads produce a VVF with significantly different OP [29].

As can be seen from Figure 6, it seems that idle mode and quarter2000 mode can also be modeled with linear fit. So, linear fit was also applied to those panels (i.e. idle1200 and quarter2000) to further explore the nature of this correlation. Calculated R^2 values for linear fit were 0.45 and 0.27 for idle1200 and quarter2000 respectively. This indicates the existence of an unspecific pattern (neither exponential nor linear). The explanation for this may be that for idle 1200 most of the volatile species contribute to the measured OP. However these compounds are not equally reactive but still very volatile. In the case of quarter load at 2000 rpm, as the consequence of an incomplete combustion, a number of unburnt hydrocarbons are expected to be present in the exhaust. These hydrocarbons will contribute to the OV values and do not necessarily need to carry measurable oxidative potential. This phenomenon would lead to an unspecific pattern (neither exponential nor linear).

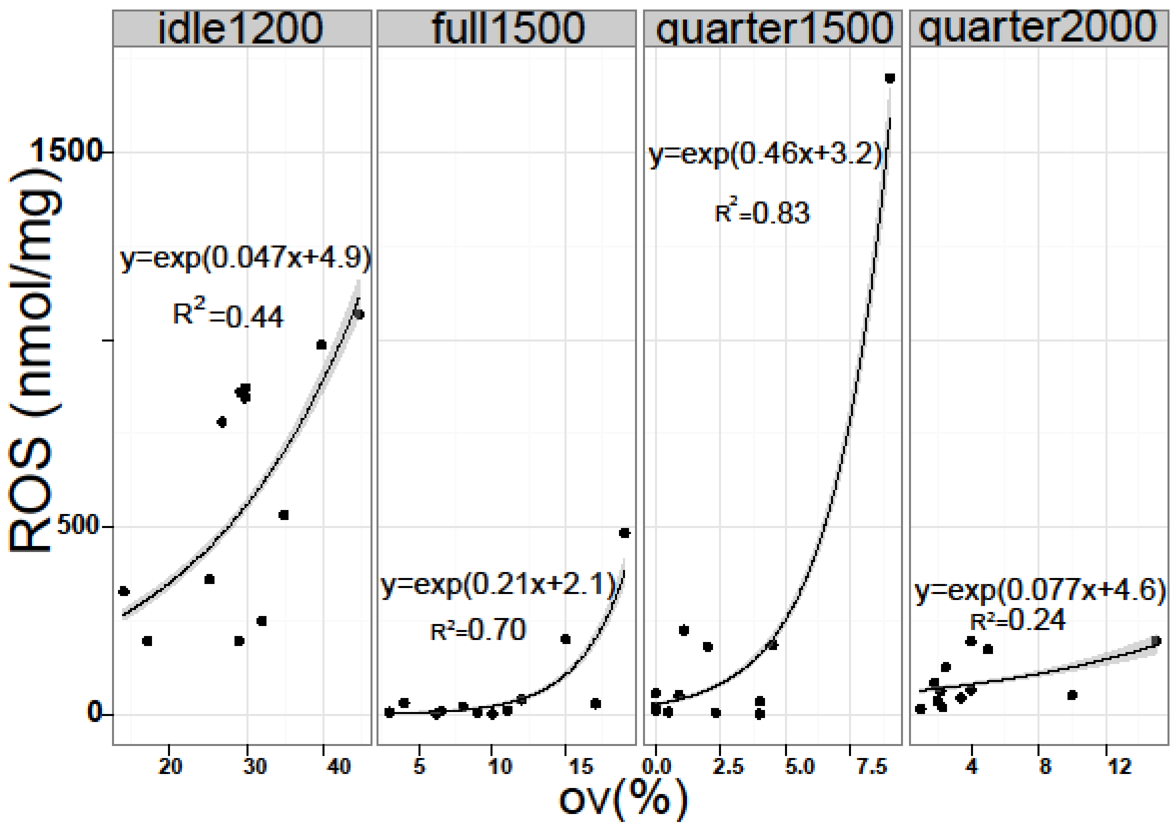

Figure 6 dependence of the ROS concentration on the overall volatile content (OV) for the 4 modes tested. R^2 shown in the graphs are McFadden's pseudo R^2.

The conclusion that follows the investigation of the fuel type on the OV and related OP is that generally, the OP is ultimately coupled to the structure of fuel molecules, especially its oxygen content, chain length and level of unsaturation. It also highlights the fact that this relationship is dependent on the chemical composition of volatile matter. Even though complete combustion can yield volatile paraffins, their OP is very low compared to oxygenated organic aerosols.

It appears that chemical composition of volatile matter, which contributes to high levels of ROS, is different in partial and full load and therefore a more detailed chemical analysis of the organic content of DPM is required to shed more light on the toxicity of DPM. The findings of this research show that the more saturated fuels caused more potentially toxic substances in the exhaust; and even though the more oxygenated fuels decreased PM, they also led to higher levels of ROS in the particles. It was established that the majority of the redox activity is due to the amount of organics in the PM. This highlights the fact that “less PM” does not necessarily mean less harmful effect for the environment or less toxicity for humans and that new metrics (taking into account the potentially toxic parts of DPM) should be considered.

Acknowledgments

The authors would like to acknowledge the support from the Australian Research Council under Grants LP110200158, DP1097125, DP130104904, DP110105535 and DP120100126. Laboratory assistance from Mr Noel Hartnett and Mr Scott Abbett were also appreciated.

Supporting Information Available

Engine specifications, fuels properties, schematic of experimental setup along with a VTDMA scan and explanation of VVF and OV concept and estimation procedure can be found in Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org/

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