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Impact of Aromatic Concentration in Marine Fuels on Particle Emissions

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Abstract: The fuel sulfur content in marine fuels has been regulated in Sulfur Emission Control Areas (SECAs) since January 2015. However, other fuel characteristics are also believed to have an impact on particle emissions, particularly on the number of particles emitted. This study investigates the impact of the content of aromatics in fuel. To achieve fuel blends with concentrations of aromatics similar to those found in marine fuel oils, i.e. 20%–30% by volume (%vol.), normal diesel oil (4%–5% vol. aromatics) is doped with a mixture of aromatics. Emission measurements are conducted in test-bed engine facilities and particle emissions over a wide size range are analyzed. Results show a decreased number of particles emitted (or not change) with an increase in the aromatic concentration in fuel. This is because there is a reduction in the cetane number of the fuel with an increased aromatic content, which effects the combustion process and results in decreased particle formation. However, when ignition improver is used to increase the cetane number, particle emissions remain at a lower level than for normal diesel oil; thereby emphasizing the presence of other factors in the formation of particles.

Keywords: aromatics, particle emission, ship emission, marine fuel, SECA

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1 Introduction

The emission of particles from different combustion sources has an adverse impact on human health, the climate, and the environment. One of these sources is the combustion of marine fuel oils in marine diesel engines installed on ships. These emissions occur close to coastal areas and are consequently a significant source of air pollution in such areas (Corbett *et al*., 2007) and mainly consist of small particles with a diameter below 150 nm (Kivekäs *et al*., 2014; Merico *et al*., 2016).

Particle emissions from ships have been shown to relate to the Fuel Sulfur Content (FSC) (Kasper *et al.,* 2007*;* Lack *et al*., 2011; Lack *et al*., 2009), and therefore a reduction in the FSC within marine fuel oils reduces particle emissions from ships. The FSC is now regulated through MARPOL Annex VI Regulation 14 (Svensson, 2011), with regulations considering both at global level and at regional level involving designated Sulfur Emission Control Areas (SECAs). At a global level, 3.5 wt% S is permissible, although from 2020 this amount will be limited to 0.5 wt% S. The percentage allowance of FSC in SECAs has been specified as 0.1 wt% S since 1 January, 2015 (IMO, 2013).

However, it appears evident that other fuel characteristics besides the FSC have an impact on particle formation and growth, and consequently emissions. Plume measurements have shown that sulfate particles represent 10%–22% of total particle mass. Furthermore, a correspondence with FSC has only been found for Particle Mass (PM) but not for Particle Number (PN) emissions (Beecken, 2015). Measurements conducted using a test-bed engine (Anderson *et al*., 2015) and in ship plumes (Lack *et al*., 2011) have emphasized that both the FSC and other fuel characteristics need to be considered when evaluating particle emissions from ship operations. For example, other factors influencing particle emissions such as engine type, engine load, and the exhaust system should also be considered (Diesch *et al*., 2013).

In this study, the relationship between particle emissions and the aromatic content of the fuel is investigated. Aromatics are a group of organic compounds containing one or more ring structures with conjugated double bonds, e.g. benzene or xylene. Polyaromatic Hydrocarbons (PAHs) consist of fused aromatic rings. Aromatics, for example benzene and its derivatives, are known compounds in crude oil and PAHs in diesel fuel oils (Stone, 2012). Some PAHs are carcinogenic and other aromatics (such as benzene) are toxic to humans (Hart *et al*., 1999). Aromatics are seen as precursors in soot formation in fuel-rich zones within the cylinders during combustion (Brem *et al*., 2015) and have a higher soot formation tendency than other hydrocarbons in fuels (Ladommatos *et al*., 1996). The impact on particle emissions has previously been investigated in several studies (Brem *et al*., 2015; Den Ouden *et al*., 1994; Fukuda *et al*., 1992; Kidoguchi *et al*., 2000; Neill *et al*., 2000; Tan *et al*., 2013; Tsurutani *et al*., 1995). However, few studies have considered particle size and number concentrations (Brem *et al*., 2015) and none have applied the maritime aspect.

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Furthermore, no consensus can be found in literature on the connection between fuel aromatic concentration and particle emissions (Tree and Svensson, 2007). This is likely due to the use of variations in the aromatic content in the studies while maintaining other fuel properties; however, inter-correlations are considered to provide more significant results (Lee *et al*., 1998; Miyamoto *et al*., 1991).

This study has a maritime perspective to investigate whether a higher content of aromatics in fuel influences particle emissions with respect to PN, mass, and size distribution. Engine bench experiments were conducted using fuels containing varying amounts of aromatics but which were otherwise similar. The impact of operational conditions (here engine load) were also studied to relate the particle emissions to operations of real ships and the impact on air quality in coastal areas.

2 Material and methods

The measurements in this study were made in two different test-bed engine labs; firstly, in the test-bed engine lab at the Department of Shipping and Marine Technology, Chalmers University of Technology (Campaigns 1 and 2). After analyzing results, additional measurements were conducted in the test-bed engine lab at the Department of Applied Mechanics at Chalmers University of Technology (Campaign 3). The aim of these measurements was to further investigate the impact of aromatics on combustion processes such as heat release, peak pressure, and temperature.

2.1 Test-bed engines, fuels, and test cycle

The first measurements were conducted in two separate Campaigns in the test-bed engine lab at the Department of Shipping and Marine Technology: Campaign 1 in November 2012 and Campaign 2 in March 2014. The engine lab is equipped with a 2.4 liter, 4-stroke, turbocharged, Volvo Penta D3-110 marine diesel engine with five cylinders, a crankshaft power of 81 kW, and a maximum engine speed of 3000 r/min. The engine has a common rail system and four separate heated fuel tanks, which gives the opportunity to change fuel during operation of the engine and control the viscosity of the fuel, although the engine was originally designed to operate using Swedish environmental class 1 diesel (MK1). The engine is connected to a hydraulic brake, which enables operation at different loads. During Campaign 1, the engine was restricted to operating at a maximum engine load of 35% at 1800 r/min, and for Campaign 2 the engine was operated at a maximum load of 50% at 2000–2010 r/min, after changes had been made to the hydraulic brake and cooling system.

Measurements conducted in the test-bed engine lab at the Department of Applied Mechanics (Campaign 3) were conducted in January 2016. This engine rig was equipped with a 2-liter single cylinder heavy-duty diesel engine (Volvo D12), providing possibilities for detailed cylinder pressure analysis (rate of heat release analysis). The engine has a common rail system and Exhaust Gas Recirculation (EGR) system, and the rail pressure (P_{inj}), start of injection, and duration of injection were controlled using ATI Vision software. The cylinder pressure was measured using a system from Osiris, and the rate of heat release was calculated using an in-house Matlab code. The engine and system are further described in Zhang *et al*., (2015) and Sjöblom (2015).

The reference fuel used in Campaigns 1 and 2, was MK1 with a viscosity of 2.0 cSt at 40°C, a flash point between 61–71°C, heating value of 43.1 MJ/kg, and density of 800–830 kg/m^3 at 15°C. The ash content for MK1 during Campaign 1 was <0.01 wt% and the fuel contained 5%–7% RME (Rapeseed methyl esters). MK1 used during Campaign 2 did not contain RME. The same type of lubrication oil was used during Campaigns 1 and 2, with major compounds of calcium (2 850 mg/kg fuel), zinc (1 150 mg/kg fuel), and iron (20 mg/kg fuel). In Campaign 3, a VSD10 diesel was used as the reference fuel; this diesel meets the EN590 standard and contains no biofuel. To increase the content of aromatics in the reference fuels, a fuel additive consisting of aromatics (mainly mono- and diaromatics, >93%, Caromax 28) was used and mixed into MK1 in tanks. During Campaign 1, fuel blends with aromatic concentrations of 23% and 30% by volume (%vol) were tested; for Campaign 2, measurements were repeated using a fuel-blend of 30%vol aromatics; and for Campaign 3 fuel blends with aromatic volumes of 20% and 30% were tested (i.e. the experiments conducted during Campaigns 1 and 2 were repeated). The properties of the reference fuels, fuel blends, and Caromax 28 are presented in Table 1. Furthermore, during Campaign 3, an ignition improver (Cepro 100, 2-ethylhexyl nitrate) was added to the fuel blends with aromatic volumes of 20% and 30% to achieve a cetane number (CN) close to that of the value of the reference fuel. The amount of Cepro 100 to be added was decided from results of CN analysis tests of fuel blends at the accredited laboratory, Saybolt, which also made the fuel analyses using standard SS115166-93 for content of aromatics, EN-ISO 8754 for sulfur content, and ASTM D 7111-11 for metals.

For Campaign 1, measurements were conducted at engine loads of 10%–12%, 27%–29%, and 38%–40% of the Maximum Continuous Rate (MCR), with engine speeds of 1780–1790 r/min and at idle with 700 r/min. For Campaign 2, measurements were conducted at engine loads of 10%, 26%–27%, and 50%–51% of MCR at 2010 r/min and at idle with 700 r/min. At each load, the engine worked for 30–40 minutes. Engine loads were selected to be representative of those used in coastal and port areas and when ships operate at sea and run more than one main engine.

Several operating conditions were investigated during Campaign 3. Only two operating conditions are presented here to demonstrate the effects of aromatics. These points are named A25 and C75. For A25 the torque was 78 N·m, engine speed 1200 r/min, injection pressure 1800 bar, injection duration 660 µs, start of injection 4.5° before to dead center and EGR was 29%. For C75 the torque was 186 Nm, engine speed 1800 r/min, injection pressure 1800 bar, injection duration 1300 µs, start of injection 4.5° before to dead center and EGR was 22%. These operating points have earlier been used for this test-bed engine (see Zhang *et al.*, 2015). Due to the difference in the size and number of cylinders (multi-cylinder vs. single-cylinder) between the test-bed engines used, it was not possible to use the same operating points during Campaign 3 as for Campaigns 1 and 2. The load profile used during Campaign 3 was part of that used for the European Stationary Test Cycle.

Table 1 Properties of reference fuels (MK1 and VSD10), fuel blends with higher content of aromatics (arom.), and aromatic mixture Caromax 28. (n.a = "not analyzed")

Fuel property	Campaign 1			Campaign 2		Campaign 3			Caromax 28
	MK1	23% arom.	30% arom.	MK1	29% arom.	VSD10 diesel	20% arom.	30% arom.	
Aromatics total /%vol	4.4	23.5	30.0	<4.8	29.0	5.2	25.3	31.9	93.9
Monoaromatics /%vol	n.a	9.6	11.7	n.a	11.1	5.0	9.6	11.1	24.2
Diaromatics /%vol	n.a	13.7	18.1	n.a	17.9	0.13	15.7	20.8	69.7
Polyaromatics /%vol	<0.02[a]	0.02	0.02	<0.02[a]	<0.02	0.04	0.02	0.04	<0.02
Cetane number	n.a	n.a	n.a	52.8	39	52	n.a	n.a	n.a
Sulfur /(mg·kg^{-1})	<3	12	3.4	<2	20	<10	n.a	n.a	n.a
Vanadium /(mg·kg^{-1})	<0.05	<0.05	<0.05	<0.05	<0.05	n.a	n.a	n.a	n.a
Nickel /(mg·kg^{-1})	<0.05	<0.05	<0.05	<0.05	<0.05	n.a	n.a	n.a	n.a
Iron /(mg·kg^{-1})	0.05	0.05	0.05	<0.05	<0.05	n.a	n.a	n.a	n.a
Calcium /(mg·kg^{-1})	0.05	0.05	0.05	<0.05	<0.05	n.a	n.a	n.a	n.a
Zinc /(mg·kg^{-1})	n.a	0.09	0.2	n.a	0.08	n.a	n.a	n.a	n.a

[a] Expressed as PAH in the analyses

2.2 Experimental set-up

Similar experimental set-up was used for Campaigns 1 and 2. The aerosol instruments used were an Engine Exhaust Particle Sizer (EEPS, Model 3090, TSI Inc.) that measures particles in a size range of 5.6–560 nm, and a Dust Monitor (Model 1.108, Grimm) that measures particles in a size range of 300 nm to over 20 µm in diameter. The EEPS classifies particles in relation to their differential electrical mobility (TSI, 2006). The Grimm, an optical instrument, uses light scattering to count the number of particles and classify them into different sizes (Grimm Aerosol Technik GmbH & Co KG, 2010). The instruments were simultaneously used to make the measurements. A thermodenuder (TD, Dekati) heated to 300°C was used to study thermal characteristics of emitted particles, and was coupled in a series before the EEPS and Grimm with a bypass option. Measurements at each load were made both with and without the TD. For Campaign 3, a DMS500 (Differential Mobility Spectrometer) from Cambustion was used to conduct particle measurements. This instrument measures particles in a size range of 4.87–1000 nm. Similar to the EEPS, this instrument also use the differential electrical mobility of particles to classify them into different sizes (Symonds, Reavell, Olfert, Campell, & Swift, 2007). A TD, developed at the Department of Chemistry and Molecular Biology, University of Gothenburg, was heated to 300°C and used to study the thermal characteristics of the emitted particles during these measurements. In addition, filter sampling using Teflon filters (PTFE filters) was conducted during Campaign 1 and 2 at the highest engine loads. These filters were used for subsequent gravimetric analyses of Total Suspended Particles (TSP) (conducted at an accredited lab); analysis of black carbon (BC) content using a visible light reflectometer (part of the beta gauge monitor FH62 I-N, ESM Emberline, Germany) (Pettersson *et al.*, 2011); and in elemental analyses using Energy Dispersive X-Ray Fluorescence (EDXRF) (Boman, 2009).

For all three Campaigns, a fine particle sampler (FPS, Model 4000, Dekati) was used as the dilution system and connected directly to the exhaust gas channel. The FPS extracted the aerosol samples via a fixed inlet (Apex instruments) in Campaigns 1 and 2, and via a perforated sampling pipe (6 mm in diameter) placed in a perpendicular position to the exhaust gas flow in Campaign 3. The FPS diluted the raw exhaust gas sample in two steps: the primary dilution step in a perforated tube with preheated, clean and dry air (240-300°C, *i.e.*, the temperature of the raw exhaust gas) and the second dilution step with clean air of ambient temperature. In addition, an ejector diluter drew the sample from the primary dilution section. Residence time in the system was below 0.5 seconds (Dekati, 2010). The dilution ratios used during Campaign 1 varied from 30 to 82 for the different tests and for Campaign 2 37-57. In Campaign 3 the dilution ratio during experiments with VSD10 diesel was 209-400, and for experiments with aromatics 133-184.

Measurements of standard gaseous emissions (NO, NO_x, SO_2, CO_2, CO, and O_2) were made in parallel with aerosol measurements (Fuji Electric Model ZRE NDIR-analyzer, Fuji Electric Systems Co, Ltd, Japan for Campaigns 1 and 2, and with an AVL AMA i60 exhaust measuring system for Campaign 3). To determine the correct dilution ratio, the concentration of NO and/or NO_x was measured both in raw exhaust and in the diluted exhaust gases; for the latter, a chemiluminescence instrument (TH42i, Thermo Scientific) with a low range of 0–20 ppm was used.

2.3 Data analysis

Data obtained from measurements were analyzed for stable conditions. Data were corrected for the dilution ratio used, and size-dependent particle losses within the TD were accounted for by following manufacturer instructions (Campaigns 1 and 2) or from experimental studies (Campaign 3). Particle emissions were analyzed with respect to Particle Number (PN) concentration, Particle Mass (PM) concentration, size distribution by number, volatility, and for Campaign 1 the content of BC and inorganic compounds. Emission Factors (EFs) were calculated for both PN, PM, and size-resolved PN of total particle emissions and non-volatile fraction. The EF_{PM} from online measurements was calculated with the assumption of spherical particles with unit density. However, the density of diesel-generated particles differs from unity and are dependent on particle size and content of condensable compounds (Ahlvik *et al*., 1998; Barone *et al*., 2011; Olfert *et al*., 2007; Park *et al*., 2003; Virtanen *et al*., 2002). Calculations were based on the IMO NO_x Technical Code (IMO, 2009), and were made using the flow through the exhaust gas channel and included values for engine load and fuel consumption from readings of data in the engine control system.

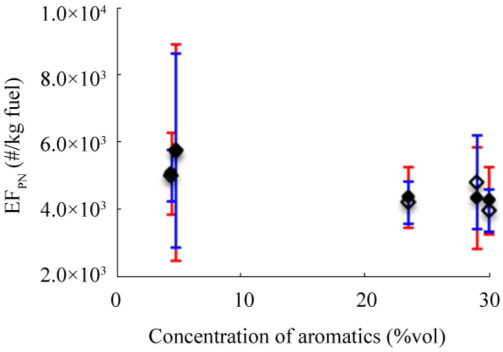
As mentioned in Section 2.2, different aerosol instruments were used to obtain measurements in the two separate test-bed engine labs. The absolute values of particle emissions measured using these three different instruments are not compared here (for example, the size distributions shown in Figs. 2 and 5); firstly, because measurements were based on the use of different technologies that measure different particle sizes, and secondly because they were made using two different test-bed engines. Results from measurements made with the EEPS and Grimm were used to calculate the EFs of PN and PM in Campaigns 1 and 2 (Section 3.1). Data from measurements made with the DMS500 in Campaign 3 are mainly used to discuss how the combination of various engine parameters with the content of aromatics in fuel effect particle emissions (Section 3.2).

3 Results and discussion

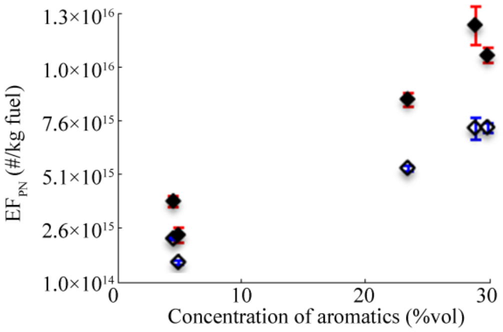
3.1 Particle emissions from marine test-bed engine

The measurements of particles (diameter (D_p) range 5.6–560 nm) show a higher PN emission tendency for MK1 than for the fuel blends with 23% or 30% aromatics (with respect to total particle number emissions and for the non-volatile fraction) for all engine loads (38%–51% (Fig. 1(a)), 26%–29%, and 10%–12%) except for idle. The same trend can be seen regardless of whether emissions are related to either engine load or fuel consumption (#/kWh vs. #/kg fuel). Furthermore, particle emissions consist mainly of a non-volatile fraction. Operation at idle resulted in the opposite trend: increased particle emissions with increased content of aromatics in the fuel, and a higher fraction of volatile compounds compared with at higher engine loads (Fig. 1(b)). For larger particles (in the size range 0.3 to >20 μm) measured at a 38%-50% engine load and at idle, similar trends can be seen as for particles in the size range 5.6-560 nm..

The trends seen for EF_{PN} are also seen for the size-resolved emission factors for PN presented in Fig. 2. Operation at the two higher engine loads (50% and 25%) using MK1 results in a higher emission of particles of all sizes between 5.6-560 nm; size distributions have a pronounced peak at 45-52 nm and a small peak at 10 nm (Fig. 2(a) and 2(b)). Fuel blends with a higher content of aromatics show a similar pattern. However, a decrease in engine load to 10% (Fig. 2c) or idle (Fig. 2d) changes the size distribution from that of a unimodal character to a more bimodal character, and an increased content of aromatics results in higher EFs for smaller particles, *i.e.*, D_p 5.6-22 nm for a 10% engine load with peak at 10 nm for total particle emissions. Furthermore, at a 10% engine load the combustion of MK1 results in higher emissions for particles with D_p>25 nm than the combustion of fuel blends. An increased content of aromatics at idle results in higher EFs for particles in the range 5.6-52 nm, with a peak at 19 nm for total particle emissions. A shift toward smaller particles can be seen for the non-volatile fraction, which shows a peak at 10 nm.



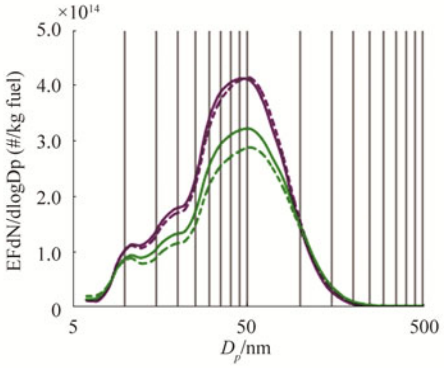
(a) 38%-51% engine load



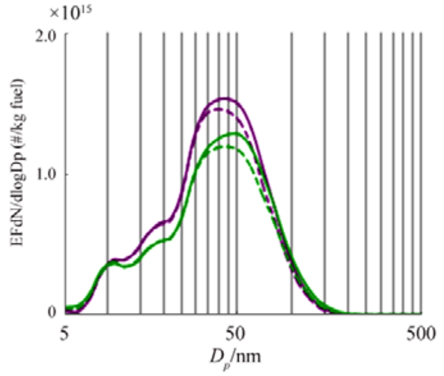
(b) Idle

The error bars represent one standard deviation (red for total emission and blue for non-volatile fraction). Note the scale on the *y*-axis

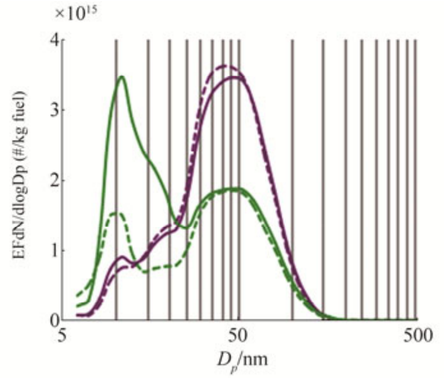
Fig. 1 Emission factors for PN (EEPS-measurements, 5.6–560 nm): total-PN (filled) and non-volatile fraction of PN, (unfilled) relate to content of aromatics at 38–51% engine load (a) and idle (b)



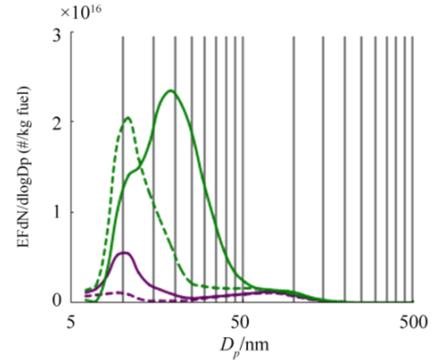
(a) 50%-51%



(b) 25%



(c) 10%

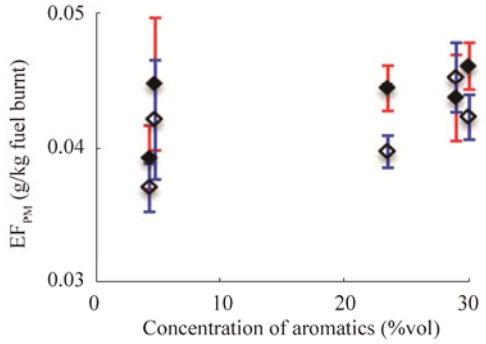


(d) Idle

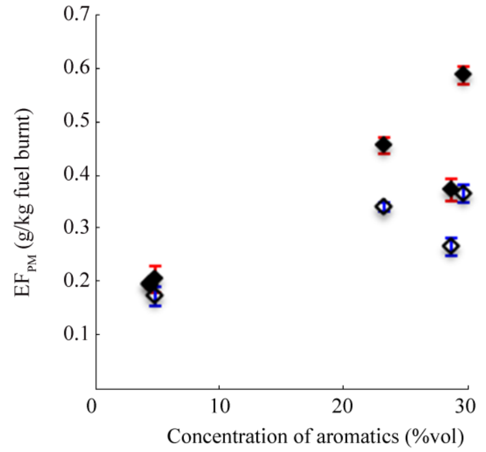
Solid lines represent total particle emissions
and dashed lines are non-volatile fraction

Fig. 2 Size-resolved emission factors for PN (EEPS-measurements, 5.6–560 nm) at: a) 50% engine load; b) 25% load; c) 10% load; and d) idle during Campaign 2 for MK1 (purple) and fuel-blend with 30% aromatics (green)

Operating at 38%–51% and 26%–29% engine loads results in no significant difference between EF_{PM} values for MK1 or the fuel blends. At higher engine loads the EF_{PM} values vary between 0.034–0.04 g/kg fuel for MK1 and 0.039-0.042 g/kg fuel for the fuel blends (Fig. 3(a)); corresponding values for engine loads of 26%–29% are 0.06-0.09 g/kg fuel for MK1 and 0.05-0.1 g/kg fuel for the fuel blends). EFs for TSP from filter sampling show a trend toward a lower mass of TSP for the fuel blends than for MK1 (0.06–0.08 g/kg fuel for fuel blends and 0.09–0.13 g/kg fuel for MK1).



(a) 38%-51% engine load



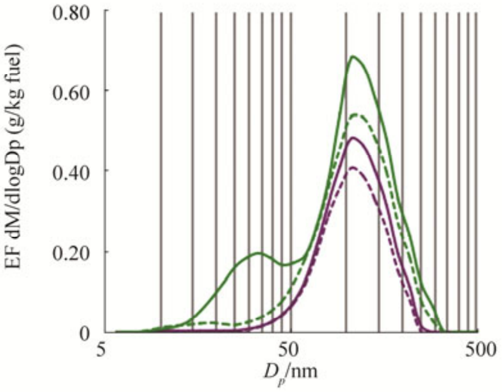
(b) Idle

The error bars represent one standard deviation (red for total emission and blue for non-volatile fraction). Note the scale on the *y*-axis

Fig. 3 Emission factors for PM (EEPS-measurements, 5.6 – 560), total-PM (filled) and non-volatile fraction of PM, (unfilled) related to content of aromatics for 38%–51% engine load (a) and idle (b)

At 10%–12% engine loads, there is a trend towards an increase in emissions for PM with a reduced content of aromatics (EF_{PM} for MK1 0.2 g/kg fuel and for fuel blends 0.1–0.14 g/kg fuel). An increase of EF_{PM}, both for total particle emissions and for the non-volatile fraction, with an increased content of aromatics is found while the engine is at idle (Fig. 3(b)); this is related to an increase in emissions of particles both with D_p 15–52 nm and around 100 nm (Fig. 4). The size distribution by mass for 50%, 25%, and 10%

engine loads shows the same pattern, with a peak at 90–110 nm, but there is no significant difference between the different fuels at the two higher engine loads. At a 10% engine load, MK1 results in higher emissions than the fuel-blend. There are small differences in EF_{PM} for the reference fuel. Small differences in EF_{PM} for the reference fuel and fuel-blends with a higher content of aromatics were reported from other studies as well (Den Ouden et al., 1994; Neill et al., 2000). Other studies, however, show a tendency of an increase in EF_{PM} for fuel blends with a higher content of aromatics (Kidoguchi et al., 2000; Tan et al., 2013; Tsurutani et al., 1995) as is seen in this study for idling (Fig. 3(b)).



Solid lines represent the total particle emission and dashed lines the non-volatile fraction

Fig. 4 Size-resolved emission factors for PM (EEPS-measurements, 5.6–560 nm) at idle during Campaign 2 for MK1 (purple) and fuel-blend with 30% aromatics (green)

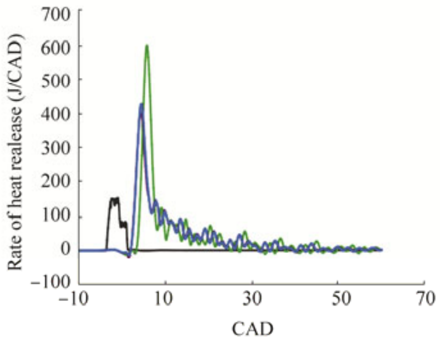
A higher content of aromatics does not result in higher emissions of BC (EF_{BC} for MK1 34 mg/kg fuel and for fuel blends 33–36 mg/kg fuel). Furthermore, similar levels of inorganic elements are found in the emitted particles using MK1 and the fuel blends (zinc 0.25-0.29 mg/kg fuel, iron 0.34-0.39 mg/kg fuel and nickel 0.40-0.53 mg/kg fuel). The exception was Ca, for which a higher content of Ca was found in the particles from the fuel-blend with an aromatic concentration of 30% vol (0.13 mg/kg fuel for fuel blend compared to below detection limit for reference fuel). However, there are no differences in the content of inorganic elements between MK1 and the fuel blends (Table 1), and the higher content of Ca is therefore probably related to the lubrication oil.

Both EF_{PN} and EF_{PM} increase with a reduced engine load, independently of the fuel or the aromatic content. However, higher EF_{PN} and EF_{PM} can be seen for the fuel blends than for MK1 at idle (Figs. 1(b) and 3(b)). Furthermore, there is an increase in the difference between total particle emissions and the non-volatile fraction with reduced engine load. It is considered that the changes in EFs and the amount of volatile compounds in emissions may be related to reduced temperatures in the exhaust gases and increased incomplete combustion (due to over-leaning) with a reduced engine load; the reduced temperatures in the exhaust gases and the increased incomplete combustion enhance the formation of new particles (nucleation) from the unburnt fuel and lubrication oil. In addition, volatile compounds, such as organic compounds, may also condense and adsorb onto the existing particles (Kittelson, 1998) and cause increased PM. It is also considered that a high concentration of aromatics in the fuel blends may contribute to higher nucleation and a greater number of volatile compounds, which can condense on existing particles when the engine load is reduced. This explains why EF_{PN} and EF_{PM} are higher for the fuel blends than for MK1 at idle. A rather low dilution ratio, both primary and totally, may also have an influence on the increased amount of volatile compounds during idle (see section 2.2).

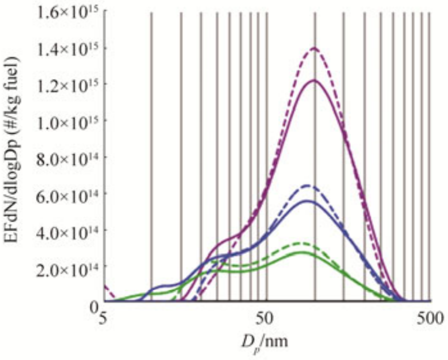
3.2 Campaign 3

The measurements conducted in Campaigns 1 and 2 show that an increase in the content of aromatics in fuel does not necessarily increase the emissions of particles, except for when the engine is operating at idle. One possible explanation for these results is that the increased content of aromatics reduces the CN of the fuel, which increases the ignition delay and leads to a longer amount of time for pre-mixing of the fuel and the air injected into the cylinder and a therefore reduce the formation of soot (Kidoguchi *et al*., 2000). Furthermore, this would increase the temperature and pressure in the cylinder and consequently also increase the oxidation of the soot formed. To follow-up measurements made using the marine engine and investigate the impact of aromatics and CN on the combustion process, additional measurements were conducted (Campaign 3). In addition to comparing fuels with different aromatic contents, an ignition improver was used with the aim of separating the effect of combustion timing from the effect of the fuel itself. Fig. 5 presents the results for two load points (A25, low speed and low load; C75, high load and high speed) for the reference fuel (VSD10 diesel), the fuel-blend with 30 %vol. aromatics, both with and without ignition improver added. In Figs. 5(b) and 5(d), emissions of the non-volatile fractions are higher than total particle emissions. This may be because the differences between these two emissions were low and there were low amounts of volatile compounds in the emissions. Furthermore, the compensation factors used in experiments with TD add uncertainty, and it is thus considered that the small difference lies within the range of uncertainty implicit in experiments.

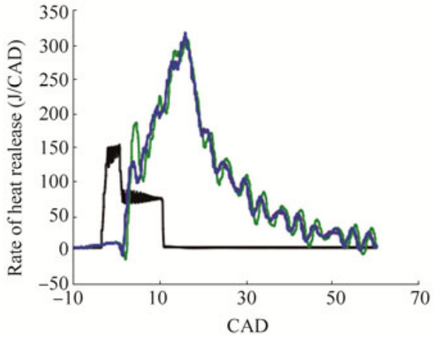
Measurements show a similar trend to those observed for the marine engine: combustion of reference fuel results in higher emissions of particles than fuel blends with a higher content of aromatics (Figs. 5(b) and 5(d)). The measurements confirm that an increased content of aromatics causes increased ignition delay, with a higher peak pressure in the cylinder during combustion and faster combustion (rate of heat release), which was also seen in a previous study (Fukuda *et al*., 1992) (Figs. 5(a) and 5(c)).



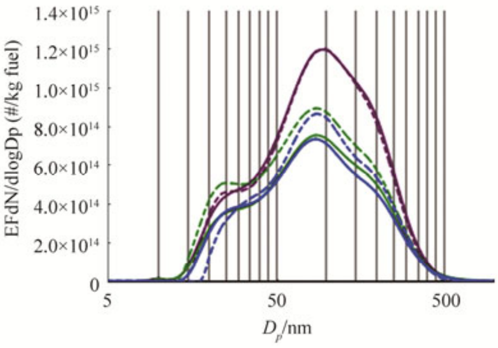
(a) A25



(b) A25



(c) C75



(d) C75

Solid lines in (b) and (d) represent total particle emissions; dashed lines represent non-volatile fraction; solid black line in (a) and (c) represent injection signal at that engine condition

Fig. 5 Rate of heat release (a, c) and size-resolved EF$_{PN}$ (b, d, DMS-measurements) during operation at load point A25 (a, b) and C75 (c, d) for reference fuel (purple), fuel-blend with 30% vol aromatics (green), and fuel-blend with 30% vol aromatics plus ignition improver (blue)

This effect is most evident at a low load (Fig. 5a); the low load case was dominated by pre-mixed combustion (injection ended before combustion began), and hence the effect of ignition delay (adjusted by addition of ignition improver) is evident.

The addition of an ignition improver to increase the CN to a similar level as that in the reference fuel (VSD10) results in a very similar pattern in the rate of heat release as with the reference fuel (Figs. 5(a) and 5(c)) (The graphs for reference fuel and fuel-blend with 30%vol aromatics plus ignition improver are quite similar in Figs. 5a and 5c and they are difficult to distinguish between.). However, there is not a similar increase in particle emissions as with the reference fuel (Figs. 5(b) and 5(d)). There is a low (or zero) impact on particle emissions when the ignition improver is added; as reported in an earlier study (Tsurutani *et al.*, 1995). For the high load case, there is a reduction in the difference in PN emissions between when ignition improver is added and when it is not (Fig. 5d). As seen in the injection trace (solid black line in Figs. 5(a) and 5(c)), a large quantity of fuel is injected during combustion (i.e. mixing controlled combustion), which explains why the effect of the ignition improver is reduced. These results emphasize the impact of a multitude of factors on particle emissions. In addition, the physical properties of fuel (viscosity, heat of vaporization/volatility) are evidently important factors for mixing air and fuel prior to ignition. Furthermore, the density of fuel, in combination with the gas density, may affect the spreading angle of the injected fuel (Siebers, 1999). It is also considered that the chemical properties of the fuel mixture, including the composition and molecular structure of the aromatics and other hydrocarbons in the fuel, may also be important (Brem *et al.*, 2015; Fukuda *et al.*, 1992; Zannis *et al.*, 2008).

4 Maritime implications and discussion

The objective of this study was to consider the results of above-described measurements from a maritime perspective. Therefore, it is necessary to draw firm conclusions from this study in relation to how aromatics in the fuel affect particle emissions from in-use marine diesel engines, and how such results depend on the engines and fuels used in this study. However, the two test-bed engines used do not represent main engines used on-board ocean-going ships, and the reference fuels used (MK1 or VSD10) are not typical marine fuels. Unfortunately, it is difficult to perform such experiments on-board actual ships due to safety concerns, and this necessitates the use of test-bed engine lab facilities. Furthermore, using marine fuel oil would increase the influence of other fuel characteristics on particle emissions, and would thus make it difficult to solely investigate the impact of aromatics. The use of MK1 as a reference fuel made the experiment possible, as it has a low fuel sulfur content and other compounds such as carbon residue that may influence the formation and growth of particles during and after combustion. The content of sulfur in marine fuel is at least 0.1 wt-%, compared to the amount (ppm) in MK1, and the carbon residue in a HFO can be around 7.00 wt-% (while it is below 0.20 wt-% for the MK1 used in the fuel-blend here).

The fuel blends investigated in this study have a comparable content of aromatics (total) to those in marine fuel oils, such as HFO and low-sulfur residual oils used on-board operating ships. The CN achieved in the fuel-blend with 29% aromatics is similar to that defined for marine diesel oil and marine gas oil, according to ISO 8217:2010 (Vermeire, 2012). However, for most cases it is unknown which types of aromatics are contained in marine fuel oils, and, as mentioned in Section 3.2, the molecular structure of the aromatics may affect the emissions. The aromatic solution used for the experiments in this study mainly consisted of mono and diaromatics. Although marine fuels have a considerable content of polyaromatics, which are thought to contribute to formation and growth of particles. However, the results from this study indicate that a higher content of aromatics does not necessarily result in increased particle emissions, and that other factors (such as engine operating parameters and other fuel characteristics) also need to be considered. For example, when ships change fuel upon entering or leaving a SECA, the engine operating parameters are not changed. This may affect the emissions, as different fuels result in different spray patterns (for example). A combination of all these parameters (the engine, its operating parameters, and fuels) make it difficult to provide an indication of how the combustion of marine fuel oils will affect particle emissions.

Table 2 Fuel properties for HFO, MDO, and the fuel-blend used in Campaign 2 and calculated emission factors for PN (total emissions (wo TD) and for non-volatile fraction (w TD)) for 35%-50% engine load and at idle

Fuel	Sulfur (wt-%)	Aromatics (%vol)		EF$_{PN}$ (10^{16} # kg^{-1} fuel)	
				35–50%	Idle
HFO	0.12	7.7	wo TD	0.68	133
			w TD	0.50	1.40
MDO	0.52	18.1	wo TD	0.32	1.5
			w TD	0.12	1.5
Fuel-blend	0.002	29	wo TD	0.021	1.2
			w TD	0.023	0.72

The validity of the results from this study is strengthened by the fact that measurements followed similar trends even though tests were conducted using two different test-bed engines. This trend can also be seen in earlier measurements conducted with marine fuel oils (HFO and MDO) using the same test-bed engine (with unchanged engine operating parameters between the fuels) as that used in Campaigns 1 and 2 in this study (Table 2) (Anderson *et al*., 2015). As shown in Table 2, the combustion of marine fuel oils with lower aromatic contents than a fuel-blend with 29 %vol. aromatics causes higher particle emissions. Furthermore, the combustion of HFO results in higher emissions of BC (112 mg/kg fuel for HFO, 10 mg/kg fuel for MDO and 33-36 mg/kg fuel for fuels included in these experiments). Consider the inorganic elements; combustion of HFO resulted in higher content of calcium, zinc, iron and vanadium in the particles than combustion of MK1 and the fuel blends used here. The content of nickel in the particles was on similar level independently of fuel type/blend (Anderson *et al*., 2015).

5 Conclusion

The objective of this study is to investigate whether an increased content of aromatics influenced the number of particles emitted. The impact of the aromatic content of fuel on particle emissions is investigated through experiments in two different test-bed engine lab facilities. Measurements performed under the above-described conditions show that combustion of fuel blends with a higher content of aromatics results in a lower (or an unchanged) particle emissions compared to the reference fuel, for all engine loads except at idle. This is in part a consequence of the reduced CN in the fuel blends, which increase the ignition delay and consequently increase the time involved in pre-mixing of injected fuel and air, thereby reducing the formation of particles in the cylinder. However, the addition of ignition improver to retain the CN present in fuel blends presented the same results, but to a smaller extent. Thus, the physical properties of aromatic fuel blends result in lower particle emissions at the engine operating conditions presented here.

When the aim is to understand the implications of one specific factor (in this case the aromatic content in the diesel fuel), it is important to consider the interdependencies of the various fuel properties and the internal combustion engine. In this study, the effect of ignition delay (degree of pre-mixing) and the rate of heat release are analyzed to improve understanding. However, the detailed underlying phenomena involved in explaining (and possibly also predicting) particle emissions from marine engines are still far from understood. It is considered that these types of experiments are important from academic, industrial, and regulatory perspectives. Furthermore, this study indicates the importance of considering the combustion process and other fuel characteristics when conducting future particle emission studies.

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