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Impacts of dimethyl carbonate blends on gaseous and particulate emissions from a heavy-duty diesel engine

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ABSTRACT

The reduction of emissions from diesel engines has been one of the primary elements in obtaining improvements in air quality and greenhouse gas reduction goals. Dimethyl carbonate (DMC) is an oxygenate fuel that can be used in petroleum diesel that is been lightly studied, but could provide significant reductions in particulate matter (PM) emissions from internal combustion engines. This study evaluated the emissions impacts of 5%, 12.5%, 20%, and 30% blends of DMC in a California diesel fuel. DMC showed PM reductions increased with increasing DMC blend levels, ranging from 30% to 78% for the DMC5 to DMC30 blends. In contrast, particle number emissions increased with increasing DMC levels, which could be attributed to the enhanced formation of small nucleation particles as the levels of larger accumulation particles were reduced. NO_x emissions showed increases of 3.2% and 3.1%, respectively, for the higher 20% and 30% blends, but no statistically significant differences for the 5% and 12.5% blends. Carbon monoxide (CO) emissions showed strong reductions from 26.3% to 60.9% with DMC blending, while total hydrocarbons (THC) emissions showed increases from 32.5% to 137% with DMC. Most of the hydrocarbon species showed increases with increasing DMC blend levels, including benzene and most mono-aromatic hydrocarbons. Similarly, formaldehyde and acetaldehyde showed statistically significant increases with DMC blending relative to diesel fuel. The carbon dioxide (CO_2) emissions and brake specific fuel consumption (BSFC) increased with increasing DMC blend levels compared to diesel fuel.

1. Introduction

Diesel exhaust and specific components within that exhaust continue to receive attention because of their adverse health effects and environmental impacts [1,2]. In California, diesel particulate matter (PM) has been classified as a toxic air pollutant since 1998 [3]. On a federal level, the United States Environmental Protection Agency (USEPA) enacted stringent 2007 emission standards for heavy-duty diesel engines to reduce PM on-road to 0.0134 g/kW h [4]. In addition to diesel PM, USEPA has been regulating nitrogen oxides (NO_x) emissions, a known pollutant that promotes secondary organic aerosol formation and enhances ozone in the presence of sunlight [5], from heavy-duty diesel engines with the aim to achieve a 95% reduction in NO_x emissions, effective as of 2010 [4]. To meet the USEPA standards, common approaches for PM and NO_x emissions reductions include the use of diesel particulate filters (DPFs) and selective catalytic reduction (SCR), respectively [4,6]. In addition to the implementation of sophisticated aftertreatment systems in automotive engines, new alternative fuel formulations are being introduced into the fuel market that are required to reach targets for renewable fuel use.

There is a growing interest in the use of renewable oxygenated fuels either as replacements of, or additives to, petroleum-based transportation fuels in internal combustion engines. Oxygenated biofuels, such as ethanol and fatty acid methyl esters, are attractive because they offer greenhouse gas (GHG) emission benefits, reduce the tendency to form soot and black carbon emissions, help address climate change, and reduce the dependence on fossil fuel resources [7–9]. Carbonate esters (which consist of a carbonyl group connecting two alkyl groups) are promising fuels for use in compression ignition engines [10,11]. Dimethyl carbonate [CH_3-OC(=O)OCH_3, DMC] is a fuel that generates interest primarily due to its high oxygen content (53% by weight) [12]. DMC is

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non-toxic, biodegradable, and highly miscible with diesel fuel. An additional benefit is that DMC can be produced from methanol and carbon dioxide (CO_2) in the presence of a catalyst (usually potassium chloride) providing a sink for the GHG, CO_2 [13]. The molecular structure of DMC includes oxygen atoms paired up with carbon atoms to form CO. Hence, the absence of carbon-carbon bonds in the fuel moiety will contribute to hydrocarbon oxidation rather than participation in soot growth reactions [14].

There have been studies of the combustion performance and emissions of diesel engines operating on DMC blends with petroleum diesel fuel [15–17]. Fundamental chemical kinetic studies have shown that when DMC is tested in a flame much of the oxygen in the dimethyl carbonate goes directly to CO_2, which reduces the effectiveness of DMC for soot reduction in diesel engines [14,15]. Rubino and Thomson [18] observed a marked reduction of soot precursors, such as acetylene and benzene, when using a counter-flow propene/air diffusion flame to study the inhibition of soot formation with DMC. This systematic tendency of DMC to reduce soot was also confirmed in older studies, where soot and smoke emissions declined almost linearly with increasing DMC content [19,20]. Cheung et al. [21] investigated DMC-diesel blends in a direct injection diesel engine and found small differences in gaseous emissions, with some increases in carbon monoxide (CO) and total hydrocarbons (THC), especially at lighter engine loads. They also found significant reductions in PM mass and particle number emissions with higher DMC concentrations, especially at higher engine loads. Huang et al. [22] studied the combustion and emissions characteristics of a diesel engine fueled with DMC-diesel blends and found that the engine's thermal efficiency increases and the emissions of PM, THC, and CO decrease. Similar reductions in PM emission were also seen in other studies with DMC-diesel blends, as well as the potential of reducing benzene and 1,3-butadiene emissions [23].

Motivated by previous studies published in the open literature, as well as by the concerns regarding global climate change caused by GHG emissions and the contribution of heavy-duty diesel engines to PM emissions, the present work investigates the impact of DMC blending on regulated emissions, mobile source air toxics (MSATs) that include some aromatics and carbonyl compounds, and particulate emissions. For this study, emission measurements were performed on 5%, 12.5%, 20%, and 30% DMC blends by volume. Testing was conducted on a 1991 Detroit Diesel Corporation (DDC) Series 60 engine over the standard Federal Test Procedure (FTP) cycle. The results of this work are discussed in the context of different DMC-diesel concentration and the influence of DMC properties on pollutant formation.

2. Experimental

2.1. Test fuels

A total of six fuels were employed in this study. The baseline fuel was a typical on-road CARB ultra-low sulfur diesel (ULSD). The DMC was provided by Yashentech Corporation of China. The DMC was produced using carbon dioxide and methanol as the only feedstock. Typical properties of DMC include a cetane number of 35.5, a viscosity (at 40 °C) of 0.6 mm^2/s, and calorific value of 15.8 MJ/kg [23]. The CARB ULSD was used to prepare blends with the DMC at proportions of 5% (denoted as DMC5), 12.5% (denoted as DMC12.5), 20% (denoted as DMC20), and 30% (denoted as DMC30) by volume. The blends were tested over two testing periods. The initial tests included a CARB ULSD and DMC20 blend. A second set of tests was then conducted on a CARB ULSD and a wider range of blends, including DMC5, DMC12.5, and DMC30. Although a different CARB ULSD was obtained for each of the two test periods, CARB diesel fuels are all certified to have emissions comparable to those of a 10% aromatic reference fuel, so it is expected that the two CARB ULSDs would have similar emissions characteristics.

2.2. Test engines, cycles, and test sequence

Testing was conducted on a 1991 model year Detroit Diesel Corporation (DDC) Series 60 engine. The engine had a displacement of 11.1 L, 6 cylinders in-line, and a rated horsepower of 360 hp at 1800 rpm, and was equipped with electronically controlled unit fuel injectors and a turbocharger with an aftercooler. The 1991 DDC Series 60 engine is the engine that has traditionally been used for the emissions equivalent diesel certification procedure in California, so it is one of the most widely tested engines in terms of studying CARB diesel fuels.

Emissions testing were conducted over the Federal Test Procedure (FTP) cycle for heavy-duty engines. The test matrix included 3 FTPs on each test fuel for each of the test periods. For each test period, an engine map was obtained for the CARB ULSD that was used for the testing on all fuels to provide a consistent basis for comparing the fuels.

2.3. Emissions testing

All tests were conducted in CE-CERT's heavy-duty engine dynamometer laboratory. This laboratory is equipped with a 600-hp General Electric DC electric engine dynamometer. Emissions measurements were obtained using the CE-CERT Mobile Emissions Laboratory (MEL). The facility and sampling setup have been described in detail previously and are only discussed briefly here [24]. For all tests, standard emissions measurements of THC, CO, NO_x, carbon dioxide (CO_2), and PM, were measured. CO and CO_2 emissions were measured with a 602P nondispersive infrared (NDIR) analyzer from California Analytical Instruments (CAI). THC emissions was measured with a 600HFID flame ionization detector (FID) from CAI. NO_x emissions were measured with a 600HPLC chemiluminescence analyzer from CAI. Fuel consumption was determined from these emissions measurements via carbon balance using the densities and carbon weight fractions from the fuel analysis. The mass concentrations of PM were obtained by analysis of particulates collected on 47 mm diameter 2 μm pore Teflon filters (Whatman brand). The filters were measured for net gains using a UMX2 ultra precision microbalance with buoyancy correction following the weighing procedure guidelines of the Code of Federal Regulations (CFR).

Particle number measurements were made with a TSI model 3776 ultrafine condensation particle counter (CPC), with a cut point of 2.5 nm. Particle size distributions were obtained using an Engine Exhaust Particle Sizer (EEPS) spectrometer. The EEPS (TSI 3090, MCU firmware version 3.05) was used to obtain real-time second-by-second size distributions between 5.6 and 560 nm. Particles were sampled at a flow rate of 10 L/min, which is considered to be high enough to minimize diffusional losses. The sample flow first went through a cyclone, which removes particles larger than 1 μm in diameter. Then, they were then charged with a corona charger and sized based on their electrical mobility in an electrical field. Concentrations were determined through the use of 22 ring-shaped electrometers. All the data were post-processed under the newly released 'soot' matrix from TSI.

Samples for carbonyl analysis were collected onto 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA). A critical flow orifice controlled the flow to 1.0 L/min through the cartridge. Sampled cartridges were extracted using 5 mL of acetonitrile and injected into an Agilent 1200 series high performance liquid chromatograph (HPLC) equipped with a variable wavelength detector. The column used was a 5 μm Deltabond AK resolution (200 cm × 4.6 mm ID) with an upstream guard column. The HPLC sample injection and operating conditions were set up according to the specifications of the SAE 930142HP protocol. Samples from the dilution air were collected for background corrections.

Hydrocarbon species were collected using a 6 L specially-prepared SUMMA passivated canister, which was connected to the CVS system. Analysis of the hydrocarbon species was conducted using a Gas Chromatography/Mass Spectrometry/Flame Ionization Detector (GC/MS/FID) analytical system with the standard PAMS Protocol Compendium Method TO-15.

3. Results and discussion

The following figures/tables present the results of this study. The results shown in the figures/tables represent the average of all test runs performed on that fuel for the specific test segment. The error bars represent one standard deviation on the average value. Statistical analyses were performed using a 2-tailed, 2-sample, equal-variance *t*-test. The statistical analyses provide information on the statistical significance of the different individual findings. The following discussion focuses predominantly on results that were found to be either statistically significant or marginally statistically significant. Results are considered to be statistically significant for p values $\leqslant 0.05$. Results are considered marginally statistically significant for $0.05 \leqslant p < 0.1$. It should be noted that the CARB ULSD results are presented separately for the different test periods, and are shown with different bars in the figures, denoted as CARB #1 and CARB #2.

3.1. PM mass, particle number, and particle size distributions

Emissions of PM mass, expressed on a gram per brake horsepower hour (g/bhp-h) basis, for the different DMC blends tested over the two periods are shown in Fig. 1. Overall, PM mass emissions showed substantial reductions with DMC application compared to CARB ULSD ranging from 30% to 78%, with these reductions being statistically significant. The results reported here are in good agreement with previous studies showing strong reductions in PM and soot emissions with DMC-diesel blends [16,17,25,26], as well as studies of other oxygenates such as biodiesel [27–30]. In comparison with biodiesel, however, the percentage reductions for the DMC are much larger than those seen for biodiesel for a comparable blend level.

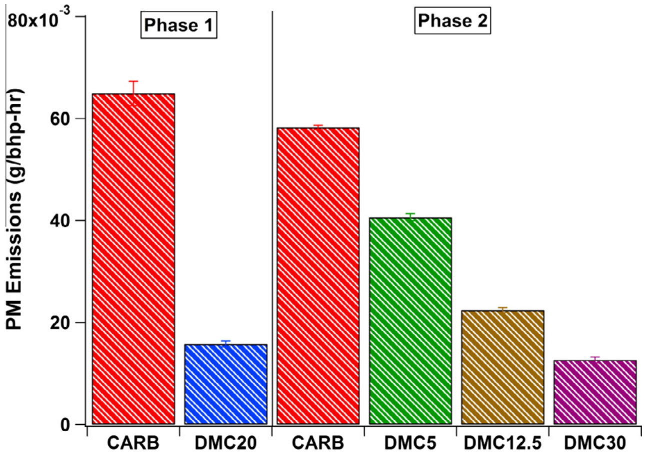

Fig. 1. Average PM mass emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

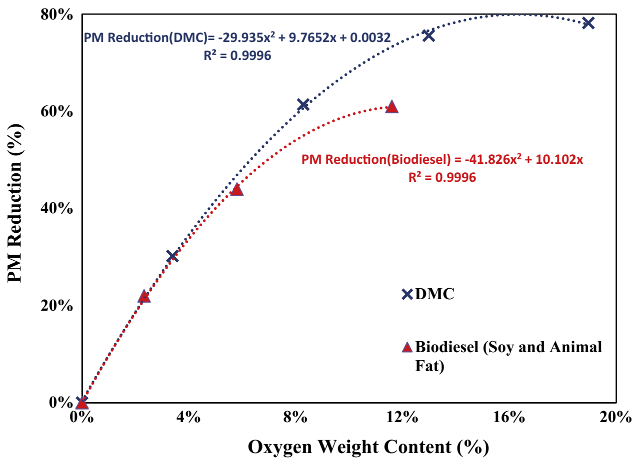

Fig. 2. Relationship between PM mass reduction (%) and oxygen content by weight (%).

There are several contributing factors that could be affecting the formation of PM with oxygenated fuels. The presence of oxygen in the fuel can lead to PM reductions due to its impact on reducing excessively rich zones during combustion. A comparison between the PM reductions as a function of oxygen content is provided in Fig. 2. This comparison shows that at lower blend levels the PM reductions for DMC and biodiesel both seem to be driven by the impact of oxygen on PM formation during combustion. For oxygen contents above 10%, however, the DMC shows slightly greater reductions on a per oxygen basis. This indicates that synergistic effects of DMC's chemical structure and physical properties may also be of importance at the higher oxygen levels. The absent of C—C bonds in DMC could reduce the formation of the precursor soot species, such as acetylene (C_2H_2) and benzene (C_6H_6) [18]. On the other hand, the production of free radicals ($^{\cdot}$O, $^{\cdot}$OH, etc.) with DMC combustion would promote the carbon oxidation to CO and CO_2 within the premixed flame zone, thus limiting the carbon available and modifying the path for the formation of soot [25,31]. DMC also has a lower viscosity and boiling point and a lower cetane number compared to diesel fuel. This may also lead to an increase in ignition delay together with an increase in the amount of fuel burned in the premixed combustion phase, since it was expected that the fuel atomized in smaller fuel droplets and at faster rates of vaporization and thus increasing the efficiency of fuel and air mixing prior to the start of combustion [16,19,25,32–34]. These phenomena would reduce the amount of fuel burned in the diffusion mode and hence suppress the formation of soot and subsequently PM emissions.

Particle number emissions are shown in Fig. 3. The use of DMC resulted in statistically significant increases in particle number emissions compared to CARB ULSD, ranging from 66% to 141%. Our results are in contrast with those seen in previous studies of DMC where particle number emissions showed reductions with higher concentrations of DMC in diesel fuel [21,25,33]. Zhang and Balasubramanian [25] found reductions in particle number emissions of 25.1% and 36.1% for 5% and 10% DMC blends, respectively, based on measurements with a fast mobility particle sizer (FMPS), while Cheung et al. [21] also showed reductions in particle number on average of 21% and 37%, for 9.1–18.6% DMC blends, respectively. On the other hand, similar increases in PN have also been seen in studies of DME [35]. Under the present test conditions, the increase in particle number emissions could be associated with the fuel's oxygen atoms through the formation of hydroxyl radicals that can consume the soot precursors, thus yielding a reduction in soot formation [36]. The corresponding decreased surface area of soot

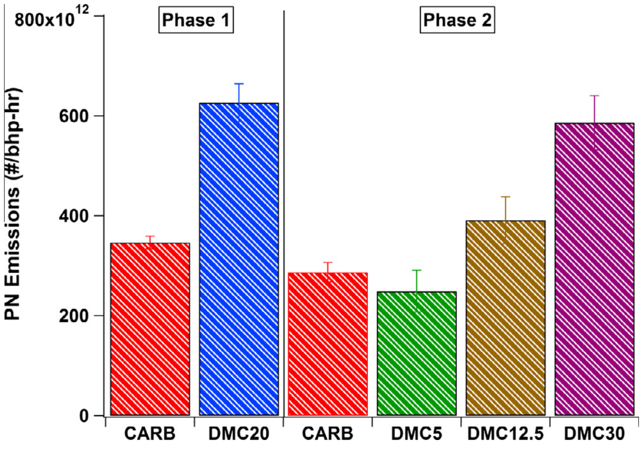

Fig. 3. Average particle number emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

particles, available for condensation of volatile and semi-volatile species would promote the formation of nanoparticles by homogenous nucleation. This phenomenon results in an increase in the total particle number population [37].

The average particle size distributions for all test fuels are displayed in Fig. 4(A and B). The results show, that for each DMC blend, there is a shift towards lower concentrations of accumulation mode particles and substantially higher concentrations of nucleation mode particles. The results reported here are consistent with those of the total particle number emissions. In particular, with a suppression of soot nuclei growth at the core of fuel droplets, homogeneous nucleation can be enhanced. It was also possible that condensed droplets of unburned and partially burned fuel account for a significant proportion of nucleation mode particles observed for the DMC blends. This could be a plausible explanation for the higher concentrations of nucleation mode particles with the DMC blends, since DMC possesses a lower boiling point than typical diesel fuel and emits higher levels of nucleation mode particles. Previous studies have shown a shift of the geometric mean diameter of particles towards smaller sizes in comparison to diesel fuel, primarily due to the fuel-borne oxygen [23,33]. Increases in nucleation particles have also been seen in studies of DME [35]. In a recent investigation, Zhang and Balasubramanian [25] found that particle size distributions consisted of only an accumulation mode at the 50% and 75% loads. At the 25% load, the particle size distribution was bimodal, but the accumulation mode particles were considerably higher in concentration compared to the nucleation mode particles. The nature of these differences could be due to differences in the testing conditions, as the testing in our study was done over a transient cycle while the testing in the other study was conducted at steady-state conditions.

3.2. NO_x emissions

The effect of DMC on NO_x emissions is shown in Fig. 5. NO_x emissions showed increases of 3.2% and 3.1%, respectively, for the higher DMC20 and DMC30 blends compared to CARB ULSD at a statistically significant level, but no statistically significant differences for DMC5 and DMC12.5 blends. The higher NO_x emissions for the higher concentration DMC blends could be attributed to the increased oxygen content in the fuel blend, and NO_x increases have been seen with other oxygenated fuels, such as biodiesel [8,27–30,38,39]. For biodiesel, Mueller et al. [39] showed that more oxygenated charge air mixtures that are closer to stoichiometric at ignition and in the standing premixed autoignition tend to produce higher local and average in-cylinder temperatures, lower radiative heat losses, and a shorter more advanced combustion, all factors that would be expected to increase thermal NO_x emissions. For DMC blends, the lower cetane number also leads to longer ignition delay and higher fraction of the premixed combustion phase, and hence higher NO_x emissions. A similar PM/NO_x emissions tradeoff was observed in a previous investigation [17]. Previous studies have also shown that the application of DMC can increase NO_x emissions [11,23], whereas other studies have reported minimal changes in NO_x emissions with DMC [16,21]. Murayama and coworkers [20] have shown that NO_x increases were very significant

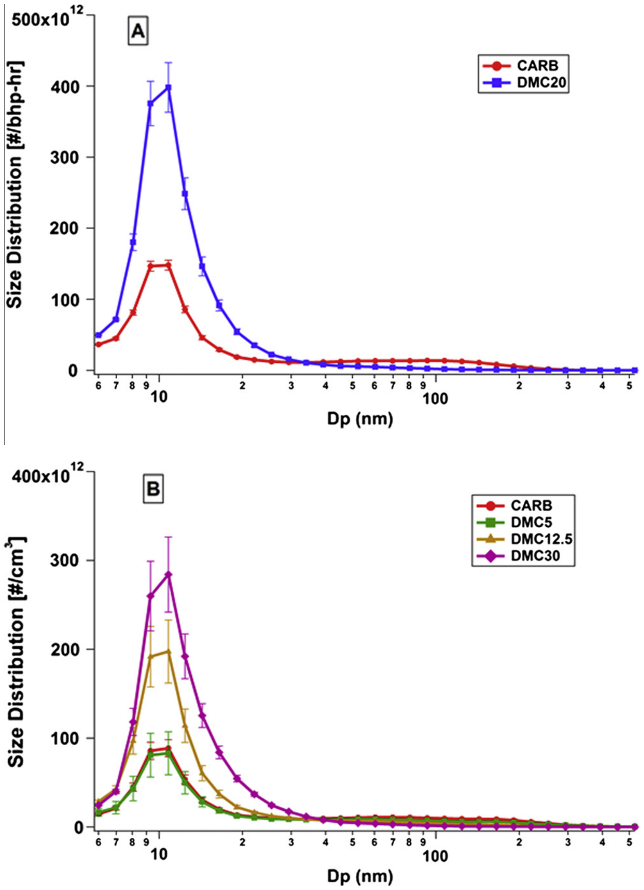

Fig. 4. (A and B): Particle size distributions for CARB ULSD and the DMC blends.

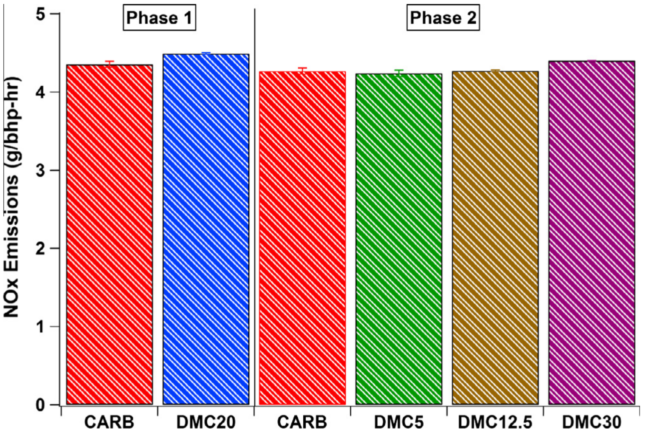

Fig. 5. Average NO_x emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

with oxygen addition. However, they have also demonstrated the possibility of simultaneous reduction of PM and NO_x emissions when they applied a high EGR ratio in conjunction with oxygenated fuel combustion. Mei et al. [40] reported some increases for a 10% DMC blend at a higher engine load, but no significant changes at a lower engine load. On the contrary, Ren et al. [41] found slight decreases in NO_x emissions with increasing oxygen content for DMC and other oxygenates.

3.3. CO and THC emissions

The CO emission results for the different DMC blends are shown in Fig. 6 on a g/bhp-h basis. CO emissions showed consistent, statistically significant reductions for all DMC blends compared to CARB ULSD, ranging from 26.3% to 61%. CO is a known product of incomplete combustion, arising under fuel rich conditions. Consistent with previous studies, our results attribute the reductions in CO emissions of DMC blends relative to CARB ULSD to the provision of oxygen in fuel rich zones and to more complete combustion [16,21,41].

THC emissions showed systematic increases with the use of DMC blends, at a statistically significant level (Fig. 7). The increases in THC emissions ranged from 33% to 137% for DMC5 to DMC30 relative to CARB ULSD. The findings of this study are in line with those of Lu et al. [42], but generally in contrast with the majority of studies where they reported lower THC emissions with the application of DMC-diesel blends as a consequence of the fuel-borne oxygen [11,23,40,41]. A trend of increasing THC emissions has also been seen with other oxygenates in diesel fuel, such as ethanol-diesel blends [43,44]. THC, a product of incomplete combustion, is formed where combustion is quenched [21]. It is theorized that the higher THC emissions for the DMC blends were likely produced due to quenching at the cylinder walls during the mixture formation as a result of the higher latent heat of evaporation of DMC relative to diesel fuel, which caused the oxygenated fuel in the blend to disperse to the crevice volumes of the combustion chamber and then discharge from the cylinder during the expanding stroke [42].

3.4. CO_2 emissions and brake specific fuel consumption

The CO_2 emission results are presented in Fig. 8. CO_2 emissions showed statistically significant increases for the DMC blends compared to CARB ULSD, with the exception of DMC5. The increases in CO_2 emissions were in the range of 1.1%, 3.8%, and 4.7%, respectively, for DMC12.5, DMC20, and DMC30. The CO_2 increases were as expected and could be related to the generally higher carbon content per unit of energy for DMC compared to typical diesel fuel. The increases in the grams of carbon per unit of energy are approximately 0.5%, 1.3%, 2.2%, and 3.5%, respectively, for DMC5, DMC12.5, DMC20, and DMC30 compared to diesel fuel. These values are comparable to the percentage increases in CO_2 emissions that were observed in this study. Chemical kinetic modelling studies have also suggested that the DMC decomposition results in production of CO_2, an alkyl radical, and an alkyoxy radical [14,15].

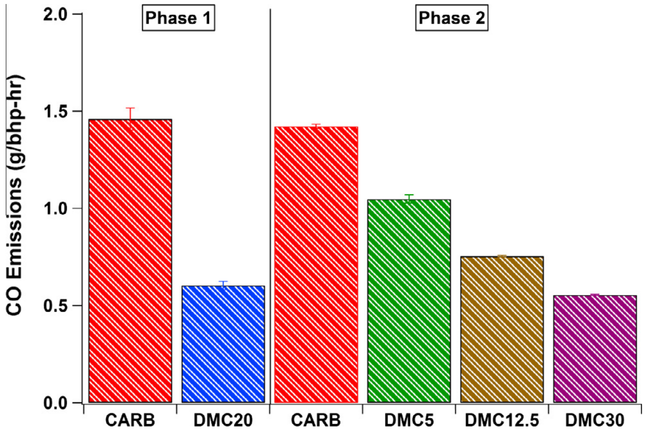

Fig. 6. Average CO emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

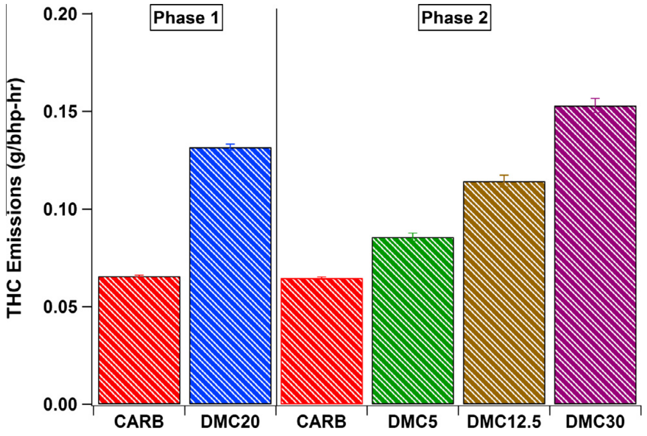

Fig. 7. Average THC emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

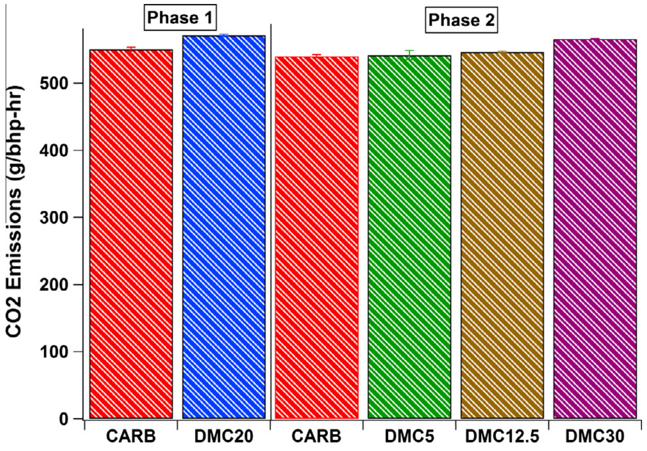

Fig. 8. Average CO_2 emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

Fig. 9 shows the brake specific fuel consumption (BSFC) for the DMC blends on a gal/bhp-h basis. BSFC showed statistically significant increases for all of the DMC blends relative to CARB ULSD, with the exception of DMC5. BSFC increased with increasing DMC levels in diesel fuel, with increases on the range of 4.5%, 9.7%, and 14.6%, respectively, for DMC12.5, DMC20, and DMC30. The higher BSFC with the application of DMC blends were as expected and can be attributed to the lower energy content of DMC compared to CARB ULSD. The heat value of DMC, at 15.78 MJ/kg, is considerably lower than that of diesel fuel, which is around 42.5 MJ/kg [40]. The reductions in the energy density per gallon are approximately 1.8%, 4.7%, 7.8%, and 12.2%, respectively, for DMC5, DMC12.5, DMC20, and DMC30 compared to diesel fuel. These values are comparable to the percentage increases in BSFC that were observed in this study. Thus, the addition of DMC leads to a drop in the volumetric energy density in the blended

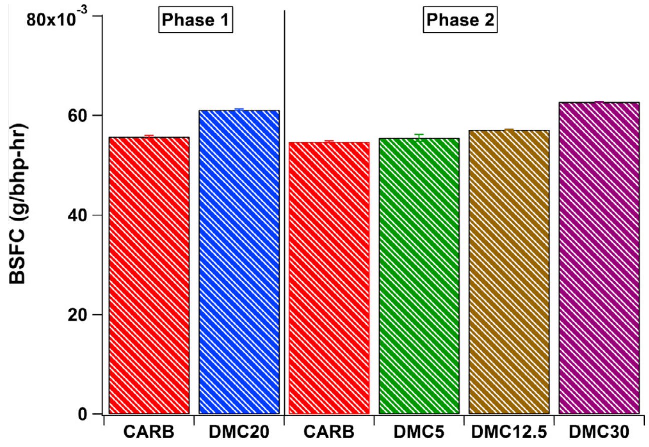

Fig. 9. Average BSFC results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

fuel, which leads to an increase in the fuel consumed per unit of work for the DMC blended fuel.

3.5. Volatile organic compounds (VOCs) and carbonyl emissions

Fig. 10 presents the benzene, toluene, ethylbenzene, *m*/*p*-xylene, and *o*-xylene compounds, collectively known as BTEX, and the sum of VOCs for each test fuel, while Table 1 shows all the VOC species quantified in the tailpipe. Benzene, a known carcinogen, was the dominant mono-aromatic hydrocarbon in the exhaust followed by toluene and xylenes. Overall, the polyunsaturated hydrocarbons (i.e., mono-aromatics and alkynes) increased with the use of DMC blends relative to CARB ULSD. Particularly, the increases for benzene and toluene emissions were statistically significant for DMC12.5 and DMC30 blends. For the DMC blends relative to CARB ULSD, increases for benzene emissions ranged from 4.4% to 13.6%, for toluene ranged from 19.5% to 35%, for ethylbenzene ranged from 126% to 399%, for *m*/*p*-xylene ranged from 35% to 94%, and for *o*-xylene ranged from 50% to 102%. Further increases for the DMC blends were also seen with the saturated hydrocarbons, including ethane and propane. Interestingly, the results reported here contradict those published in previous studies showing that the oxygen in DMC is the main driver for the reduction in the formation of soot precursors, such as benzene, acetylene, and other cyclization components [14,15,18,26]. In addition to BTEX species, ethylene, acetylene, propylene, butane, etc. were also found to increase with DMC blending. The higher emission levels of these compounds is consistent with the higher THC emissions observed for the DMC blends compared to CARB ULSD. The higher concentrations of these compounds could be due to quenching of the combustion flame, which could play a role in the early stages of particle formation, and particularly semi-volatile material that may also contribute to the enhancement of nucleation mode particles, as seen in the particle size distributions above.

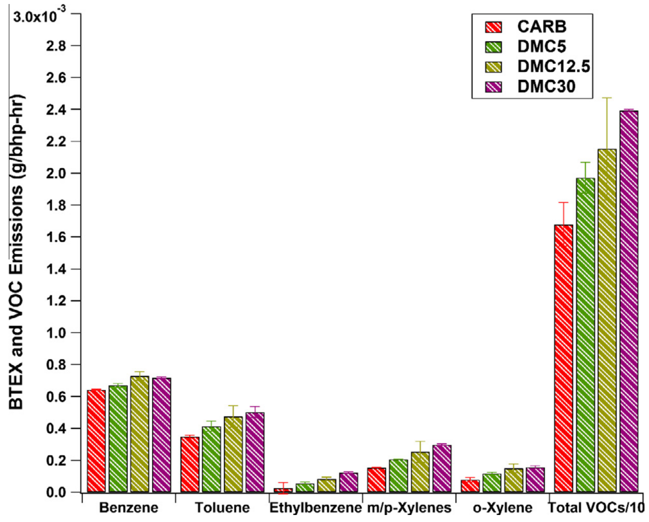

Fig. 10. Average BTEX emissions and total VOCs for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

The carbonyl emissions, expressed in mg/bhp-h, are shown in Fig. 11. Formaldehyde and acetaldehyde were the dominant aldehydes in the exhaust followed by benzaldehyde and propionaldehyde. Heavier aldehydes were also present, but in lesser amounts. These results are in reasonable agreement with other studies showing the predominance of low molecular aldehydes in the exhaust from oxygenated fuels [7,37,45,46]. The application of DMC blends led to statistically significant higher formaldehyde and acetaldehyde emissions relative to CARB ULSD, which could be a consequence of the oxygen content in the fuel molecule. For formaldehyde and acetaldehyde emissions, the increases for DMC blends relative to CARB ULSD ranged from 117% to 171% and from 115% to 154%, respectively. It should be noted that carbonyls are oxygenated hydrocarbons, and as such would have a reduced response for THC FID measurements, so in terms of overall organic material hydrocarbons, the increases with the DMC would be even greater than those found for the THC FID measurements. Previous studies have shown that formaldehyde is an important intermediate species in the DMC combustion, with H-atom abstraction from DMC leading to the formation of formaldehyde and methoxyl radical ($CH_3OC{=}O$) [14,47,48]. Acetaldehyde is primarily formed from reactions involving the C_2 species [15].

4. Conclusions

As the use of renewable fuels continues to expand in the transportation sector, it is important to continue to evaluate their overall impact on ambient air quality. Oxygenated fuels, and in particular DMC, has been shown to reduce soot emissions when blended with petroleum diesel fuel. The main goal of this study was to assess the emissions performance of DMC when blended with typical on-road CARB ULSD on a 1991 DDC Series 60 engine over the FTP test cycle. PM emissions showed consistent, statistically significant reductions for all of the DMC blends. PM emissions decreased with increasing DMC blend levels, ranging from 30 to 78% for the DMC5 to DMC30 blends. These reductions were significantly higher than those typically seen for biodiesel at a comparable blend level. This can be attributed to the higher oxygen content in the DMC molecule, with DMC's chemical structure and physical properties potentially also being of importance at the higher oxygen levels. Particle number emissions followed opposite trends to the PM mass and showed increases with increasing DMC blending. The increases in particle number emissions for the DMC blends were statistically significant, with the exception of DMC5. Consistent with the particle number emission results, the application of DMC resulted in higher concentrations of nucleation mode particles compared to CARB ULSD, suggesting a suppression of soot particles available for condensation of semi-volatile species and a promotion of nucleation mode particles.

Emissions of NO_x were generally increased, especially for the higher DMC blends. The same observation holds for the THC emissions, where the increases for the DMC blends relative to CARB ULSD were at a statistically significant level. As expected, BSFC

Table 1
Hydrocarbon emissions results for CARB ULSD and the DMC blends.

Hydrocarbon species (g/bhp-h)	CARB ULSD	DMC5	DMC12.5	DMC30
Ethylene	0.0067 ± 0.0003	0.0072 ± 0.0002	0.0076 ± 0.0004	0.0091 ± 0.0002
Acetylene	0.0012 ± 0.0000	0.0013 ± 0.0000	0.0013 ± 0.0001	0.0015 ± 0.0000
Ethane	0.0003 ± 0.0000	0.0006 ± 0.0001	0.0006 ± 0.0005	0.0005 ± 0.0000
Propylene	0.0024 ± 0.0001	0.0027 ± 0.0001	0.0029 ± 0.0001	0.0034 ± 0.0000
Propane	0.0002 ± 0.0000	0.0005 ± 0.0002	0.0004 ± 0.0003	0.0004 ± 0.0000
Isobutane	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0001	0.0001 ± 0.0000
1-Butene	0.0007 ± 0.0000	0.0007 ± 0.0000	0.0008 ± 0.0000	0.0010 ± 0.0000
n-Butane	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0002 ± 0.0001	0.0001 ± 0.0000
trans-2-Butene	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0002 ± 0.0000
cis-2-Butene	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0002 ± 0.0002	0.0001 ± 0.0000
Isopentane	0.0001 ± 0.0000	0.0002 ± 0.0001	0.0002 ± 0.0001	0.0002 ± 0.0000
1-Pentene	0.0003 ± 0.0000	0.0003 ± 0.0000	0.0004 ± 0.0000	0.0004 ± 0.0000
n-Pentene	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0001	0.0001 ± 0.0000
Isoprene	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0001 ± 0.0001	0.0000 ± 0.0000
trans-2-Pentene	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
1-Hexene	0.0002 ± 0.0000	0.0003 ± 0.0000	0.0003 ± 0.0000	0.0003 ± 0.0000
n-Hexene	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
Benzene	0.0006 ± 0.0000	0.0007 ± 0.0000	0.0007 ± 0.0000	0.0007 ± 0.0000
n-Heptane	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
Methylcyclohexane	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
Toluene	0.0003 ± 0.0000	0.0004 ± 0.0000	0.0005 ± 0.0001	0.0005 ± 0.0000
2-Methylheptane	0.0000 ± 0.0001	0.0000 ± 0.0001	0.0001 ± 0.0000	0.0001 ± 0.0000
n-Octane	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0003 ± 0.0000	0.0003 ± 0.0000
Ethylbenzene	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
m/*p*-Xylenes	0.0002 ± 0.0000	0.0002 ± 0.0000	0.0003 ± 0.0001	0.0003 ± 0.0000
o-Xylene	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0002 ± 0.0000
Nonane	0.0002 ± 0.0000	0.0003 ± 0.0000	0.0004 ± 0.0000	0.0004 ± 0.0000
Isopropylbenzene	0.0007 ± 0.0009	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000
m-Ethyltoluene	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
1,3,5-Trimethylbenzene	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
o-Ethyltoluene	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
1,2,4-Trimethylbenzene	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0003 ± 0.0000	0.0003 ± 0.0000
n-Decane	0.0004 ± 0.0000	0.0006 ± 0.0000	0.0007 ± 0.0001	0.0008 ± 0.0000
1,2,3-Trimethylbenzene	0.0000 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
m-Diethylbenzene	0.0001 ± 0.0001	0.0001 ± 0.0000	0.0001 ± 0.0001	0.0000 ± 0.0000
p-Diethylbenzene	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0001 ± 0.0001	0.0000 ± 0.0000
n-Undecane	0.0005 ± 0.0000	0.0007 ± 0.0000	0.0008 ± 0.0000	0.0009 ± 0.0000
n-Dodecane	0.0006 ± 0.0000	0.0009 ± 0.0000	0.0009 ± 0.0000	0.0011 ± 0.0000

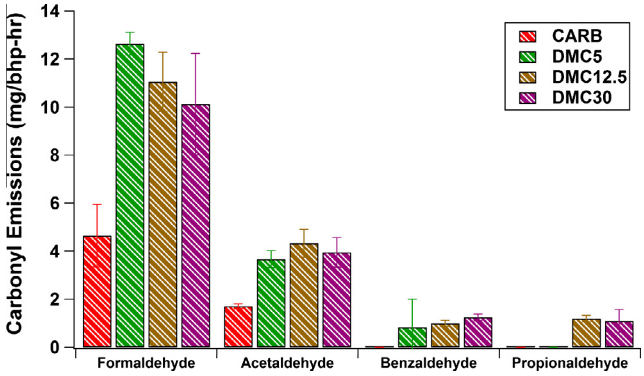

Fig. 11. Average carbonyl emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

showed increases with the DMC blends as a result of the lower energy content of DMC compared to diesel fuel. On the other hand, CO emissions showed clear reductions with the use of DMC blends at a statistically significant level. Overall, the use of DMC led to increases in BTEX emissions and most VOCs relative to CARB ULSD, including the carcinogenic benzene. It was observed that mono-aromatic and polyunsaturated hydrocarbons that are known soot precursors showed increases with increasing DMC blending. Formaldehyde and acetaldehyde were the predominant aldehydes in the exhaust, and the use of DMC resulted in higher aldehyde levels compared to CARB ULSD.

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