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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