

# Evaluating the Viability of Dimethyl Carbonate as an Alternative Fuel for the Transportation Sector

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A Research Report from the National Center for Sustainable Transportation

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# TABLE OF CONTENTS

EXECUTIVE SUMMARY .....	ii
Introduction .....	1
Literature Review .....	2
The Use of Oxygenates in the Diesel Fuel .....	3
DMC fuel properties.....	4
DMC Industrial Applications and Production .....	6
DMC Safety and Storage .....	7
DMC Combustion Research.....	9
DMC Emissions Research .....	11
Engine Dynamometer Testing .....	18
Experimental .....	18
Results and Discussion .....	19
Conclusions .....	35
Literature Review Conclusions .....	35
Engine Dynamometer Testing Conclusions .....	36
References.....	38

# Evaluating the Viability of Dimethyl Carbonate as an Alternative Fuel for the Transportation Sector

## EXECUTIVE SUMMARY

Some of the most important questions in the development of sustainable transportation are identify fuels that will reduce emissions, provide diversification from fossil fuels, reduce greenhouse gas emissions, be produced from renewable sources, and that can be produced in a sustainable manner. An alternative diesel fuel that could be used for particulate matter (PM) reductions and be produced from renewable sources could represent a key advance for the transportation sector in terms of sustainability, diversification for the marketplace for the alternative fuels, emissions reductions, and reductions in greenhouse gases. Dimethyl carbonate (DMC) is a potentially new fuel that could represent an important advance in the diesel fuel area. DMC can be produced from renewable sources such as grass, manure, or trees. Preliminary tests at the University of California at Riverside have also indicated PM reductions of about 76% at only a 20% blend with diesel fuel, which is about double or triple the reductions typically found for biodiesel at a comparable blend level, and comparable to the reductions found for diesel particulate filters (DPFs). Although these preliminary results indicate the promise of DMC as a PM mass reduction strategy, it is important to more completely characterize the emissions and viability of DMC before it can be more widely used in the fuel market or for in-field demonstrations.

The objective of this study was to conduct a preliminary evaluation of the viability of DMC as a transportation fuel for fleet and wider applications. This included a literature review to address questions related to air emissions, impact on vehicle system durability and parts, and any potential storage issues. This study also included some additional emissions testing to evaluate any emissions of toxic species, and to look at some optimization of blend level in terms of a full range of emissions components.

## Literature Review

DMC is an oxygenate that is miscible with diesel fuel, has a high oxygen content, and can provide reductions in PM and other emissions. DMC is currently being used as an industrial chemical in many applications, including polycarbonates and as a methylating agent. Although DMC has been lightly studied for vehicle/engine applications, it is attracting some attention as a potential renewable diesel fuel. The goal of this part of the study was to review some of the most important aspects of using DMC as a transportation fuel, including its fuel properties, its production, its safety and storage and the potential impact of air and liquid leaks, and its impact on combustion and emissions.

DMC differs in several key ways from diesel fuel, and it is these unique properties that can impact the performance and emissions when it is used in a diesel engine. DMC has a lower

cetane number (CN) compared to the diesel, which causes an increase in the engine ignition delay. It also has a lower boiling point which favors spray atomization and mixing. The instantaneous heat release rate for DMC added to diesel fuel is also higher than that of the diesel fuel itself during the initial combustion period, making the heat release process more concentrated. 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, which leads to an increase in the fuel consumed per mile for the DMC blended fuel.

The oxygen content also has important consequences on the difference emissions components. The most important impact is the relatively large reductions in PM that are found with the addition of DMC, which ranged up to 75% for the 20% blend in our initial studies. Along with a reduction in PM mass, a corresponding increase in particle number can be found, as particles show an increased tendency to form nucleation particles. Most studies have also shown reductions in carbon monoxide (CO) with the addition of DMC. For NO<sub>x</sub> emissions, DMC has shown mixed results, with some studies showing increases, while other studies have not. Similarly, hydrocarbons (HC) emissions have shown increases in some studies, while other studies have shown reductions.

The unique characteristics of DMC must also be considered in terms of the utilization of DMC within the existing petroleum infrastructure. DMC is a flammable liquid. It has a lower flashpoint than diesel fuel, but is safer than acetone, methyl acetate and methyl ethyl ketone from a flammability point of view. In terms of diesel-DMC mixtures, one issue is that these mixtures have a high critical solubility temperature value, which is the temperature where the two components of a mixture are no longer miscible and start to separate. This could cause problems in colder climates. DMC should be stored in a tight reservoir at a cool, dry, well-ventilated location away from moist air, plastics and resins. Carbonates are incompatible with cerium compounds, germanium, lead diacetate, magnesium, mercurous chloride, and silver nitrate. In terms of safety, DMC has a recommended industrial exposure (REL) limit of 100 ppm by inhalation over an 8-hour work day, which is similar to a number of common industrial solvents (Toluene, methyl ethyl ketone). DMC has also been exempted as a volatile organic compound (VOC) chemical.

Some additional information would be useful in order to perform a complete assessment of potential impacts of widespread use of DMC as a transportation fuel, such as the assessment that would be needed under the California Air Resources Board (CARB) multimedia procedure. This would include a more detailed characterization of the impacts of DMC leaks or spills on the atmosphere, as well as liquid release on surface soil and ground water. In storing, distributing, and utilizing DMC, it is also important to understand the impacts of DMC on fuel system components, such as gaskets, seals, or other materials that could be subject to swelling or degradation. Some additional studies of material compatibility would be useful in better understanding these potential impacts.

## Engine Dynamometer Emissions Testing

For this part of the study, the emissions performance of DMC when blended with typical on-road CARB ultralow sulfur diesel (ULSD) was assessed using a 1991 DDC Series 60 engine over the Federal Test Procedure (FTP) test cycle. For this study, emission measurements were performed on 5%, 12.5%, 20%, and 30% DMC blends by volume. 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. Particle number emissions followed opposite trends to the PM mass and showed increases with increasing DMC blending. The application of DMC also resulted in higher concentrations of smaller nucleation mode particles compared to CARB ULSD, consistent with the particle number (PN) results.

Emissions of  $\text{NO}_x$  and total hydrocarbons (THC) generally increased, especially for the higher DMC blends. As expected, BSFC showed increases with the DMC blends as a result to the lower energy content of DMC compared to diesel fuel. On the other hand, CO emissions showed clear reduction with the use of DMC blends. Overall, the use of DMC led to increases in some toxic hydrocarbon species.



## Introduction

Diesel vehicles and engines play a vital role in the transportation sector and the overall economy. Diesel engines have the advantages of better fuel economy and higher power output compared to gasoline engines. It is expected that the use of diesel engines and fuels will continue to expand into the foreseeable future, with some projections showing a 50% increase in the use of diesel fuel for heavy duty engines by 2040 compared to now (1). Despite the importance and benefits of using diesel engines, there are still issues with their use. One is the concern about the impact of diesel engine emissions on the environment. Most air quality issues in cities are associated with the burning of fossil fuels in internal combustion engines, including a large fraction of pollutants from diesel engines. Diesel engines generally have lower emissions of hydrocarbons (HC) and carbon monoxide (CO). However, diesel engines also have higher emissions of particulate matter (PM) and nitrogen oxides (NO<sub>x</sub>), and it is hard to reduce these pollutants simultaneously without exhaust aftertreatment (2-3). The other issue is related to fossil fuel sustainability and the carbon cycle of Greenhouse Gases (GHG), particularly in light of projections indicating that the use of fossil fuel will increase 28% by 2040 compared to now (1).

There is an increasing urgency in finding ways to control tailpipe emissions for diesel engines to meet the increasingly stringent emissions standards being implemented all over the world, while improving their fuel economy and maintaining costs at reasonable levels. In the United States (U.S.), this includes PM regulations for 2007 and newer on-highway diesel engines that essentially require Diesel Particulate Filters (DPF) and the NO<sub>x</sub> regulations for 2010 and newer on-highway diesel engines that are being met with Selective Catalytic Reduction (SCR) systems. In addition to exhaust aftertreatment devices like diesel oxidation catalysts (DOC), DPFs, and SCRs, diesel engines have adapted many other technical breakthroughs for reducing pollutant emissions and improving combustion efficiency including in-cylinder control techniques, like multi-stage injection, and emission gas recirculation (EGR) (4). These emission control technologies usually lead to cost increases or more fuel consumption. The cost of a DPF starts at \$8000 and ranges up to \$50,000 for very large applications and the cost of SCR ranges from \$10,000 to \$20,000 (5). The U.S. Environmental Protection Agency/National Highway Traffic Safety Administration (EPA/NHTSA) have also implemented Phase 2 fuel efficiency and GHG standards with a goal of a 20% increase in fleet fuel economy by 2040. Improvements in diesel engine technology that are expected to help meet this requirement include reduced friction, better air handling, better heat transfer, and improved aftertreatment, along with improved aerodynamics for the vehicles (6).

Alternative diesel fuels are another important option that offers the potential to reduce pollutant emissions, petroleum use, and GHGs (3,7). Alternative diesel fuels can be a lower cost option for reducing emissions compared to exhaust aftertreatment devices, especially in foreign countries with more severe air quality problems. Exxon Mobil (1) has projected that the use of renewables is expected to increase 183% to fulfill the energy demands by 2040. 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 (3,7-9). Investigations have shown that the oxygen inside the fuel can increase combustion efficiency (10), and it can also substantially reduce emissions of PM through more complete combustion. Some diesel-oxygenate blends can be used without large modifications of the diesel engine, providing wide applicability in currently used vehicles (8). Additionally, if you consider the Life Cycle Analysis (LCA) impact of CO<sub>2</sub> emissions, including production, extraction/harvesting, and transportation and distribution, there could be a significant reduction in GHG emissions using renewable oxygenated fuels (11).

There has been considerable research over the years about the characteristics of potential oxygenated fuel blends, including biodiesel and esters, ethers, and alcohols (7, 12-13). Carbonate esters (which consist of a carbonyl group connecting two alkyl groups) are promising fuels for use in compression ignition engines (14-15). Dimethyl carbonate [CH<sub>3</sub>OC(=O)OCH<sub>3</sub>, DMC] is a fuel that generates interest primarily due to its high oxygen content (53% by weight) (16). DMC is non-toxic, biodegradable, and highly miscible with diesel fuel. An additional benefit is that DMC can be produced from methanol and carbon dioxide (CO<sub>2</sub>) in the presence of a catalyst (usually potassium chloride) providing a sink for the GHG, CO<sub>2</sub> (17). 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 (18).

The objective of this study is to conduct a preliminary evaluation of the viability of DMC as a transportation fuel for fleet and wider applications. The methodology for this seed project included a two-pronged strategy. The first part of this study was a preliminary literature review to look at the environmental and system performance issues of using DMC as a transportation fuel. This included issues related to air emissions, impact on vehicle system durability and parts, and potential storage issues. The second part of this study was a small emissions testing program to evaluate potential increases in toxic species and to look at optimizing the blend level of the DMC for different emissions constituents. The results of this study provide valuable information that can be used in identifying and addressing barriers to the penetration DMC into the marketplace or for demonstrations.

## Literature Review

The goal of this literature review was to review some of the most important aspects of using DMC as a transportation fuel, including its fuel properties, its production, its safety and storage and the potential impact of air and liquid leaks, and its impact on combustion and emissions.

## The Use of Oxygenates in the Diesel Fuel

Biodiesel is the most widely used biofuel in diesel engines, and it is currently the main fuel being used or considered to meet renewable fuel requirements for diesel fuel. Biodiesel is currently used at up to a 7% level in diesel fuel throughout Europe (19). Biodiesel use and production in the U.S. has expanded considerably over the past decade (20), from 2 million gallons in 2000 to 1.8 billion gallons in 2013 (21). Biodiesel is biodegradable, nontoxic, and can significantly reduce toxic emissions and overall life cycle emissions of CO<sub>2</sub> from the engine when burned as a fuel. However, it can also lead to increases in NO<sub>x</sub> emissions (22-23).

Dimethyl ether (DME) (10, 13, 24) has also been investigated in diesel applications. DME is the simplest ether and it is used as a precursor to other organic compounds and as an aerosol propellant. The Global Dimethyl Ether Market was valued at US\$ 4.46 billion in 2013 and is likely to reach US\$ 8.37 billion in 2020, expanding at a compound annual growth rate (CAGR) of 9.4% between 2014 and 2020. The DME industry in China has also expanded considerably, since China has enormous coal reserves and coal is the primary feedstock used to produce DME. DME consumption in the China is estimated to grow at a CAGR of around 10.6% from 2013 to 2023, with the potential for this growth to increase over 20.0% after 2018 (25). Wang et al. (26) studied the effects of diesel/DME blends on emission characteristics and found that at high loads, the blends reduced PM significantly, and NO<sub>x</sub> emissions, with a small penalty on CO and HC emissions. However, the application of DME requires modifications to the engine.

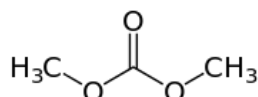
Besides Biodiesel and DME, alcohols have also been blended with diesel fuel. Studies of ethanol/diesel blends have shown reductions in PM, and increases THC, while CO and NO<sub>x</sub> could increase or decrease depending on the engine type and operating conditions (27-28). Methanol/diesel blends have been shown to reduce PM, CO, and total hydrocarbons (THC), while NO<sub>x</sub> emissions have shown increase (3, 29). Butanol has also been studied for blending with diesel fuel. Studies have shown that CO and NO<sub>x</sub> emissions can be reduced with the use of the butanol-diesel fuel blends with respect to those of the neat diesel fuel. HC emissions were observed to increase with the use of butanol-diesel blends, with this increase being higher for higher percentages of butanol in the blend (30).

Studies have also been conducted using 2-methoxyethyl acetate (MEA) as an oxygenated in diesel fuel in a single and a four-cylinder direct injection (DI) diesel engine (31-32). These studies have shown that MEA provided significant reductions in PM emissions. Reductions were also found in CO and HC emissions, whereas there was little effect on NO<sub>x</sub> emissions. Rakopoulos et al. (30) evaluated the performance and exhaust emission characteristics of diesel fuel blends with 8, 16, and 24% blends (by volume) of diethyl ether (DEE) in a single cylinder, high-speed DI diesel engine. Soot, NO<sub>x</sub>, and CO emitted by all DEE/diesel fuel blends were lower than the corresponding diesel fuel, while HC emissions were higher.

Dimethyl carbonate (DMC) is another oxygenate choice. It is non-toxic and highly miscible with diesel fuel. It also exists in liquid state at room temperature, which makes storage and

transportation convenient. DMC can be used as an oxygenated component to blend with diesel fuel to improve combustion and reduce pollutant emissions. It is difficult to fuel diesel engines directly with DMC due to its low cetane number (CN) and high latent heat of vaporization. However, Murayama et al. (33) suggested that DMC is a suitable oxygenated for blending with good blend fuel properties. Studies of DMC-diesel emissions have been conducted mostly with single (7, 9) and four (3, 34, 35) cylinder diesel engines. To date, little work has been done to evaluate emissions with diesel-DMC blends in heavy duty engines. This report provides a more in-depth review of the relevant aspects of using DMC as a transportation fuel, including its properties, storage and utilization considerations, and its impact on combustion and emissions.

### DMC fuel properties



Dimethyl carbonate (DMC) is an organic compound with the formula  $C_3H_6O_3$ . It is classified as a carbonate ester and a summary of its properties is provided in Table 1. It is insoluble in water. DMC is a colorless, transparent, and flammable liquid that has a flash point of  $17^\circ\text{C}$ . This is lower than the  $65^\circ\text{C}$  flash point for diesel liquid, but DMC is safer than acetone, methyl acetate and methyl ethyl ketone from a flammability point of view. The density of DMC at  $1.07\text{ g/ml}$  is slightly heavier than water. DMC also has advantages of solubility in diesel and a high oxygen content. DMC, as a nonpolar ester fuel, has a higher oxygen content and cetane number, but it has a higher critical solubility temperature than DME (31, 36-37). The lower boiling point of DMC favors spray atomization and mixing (38). With no carbon = carbon (C = C) bonds, the carbon in DMC can be readily oxidized, which contributes to reductions in PM emissions (39). Among the oxygenated fuels, DMC has attracted attention because of its market potential and favorable properties as fuel (35, 40-41).

**Table 1. DMC Fuel Properties**

DMC Properties	
Molecular formula	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>
Molar Mass	90.08 g/mol
Appearance	Clear Liquid
Density	1.069-1.073 g/ml
Flash Point	17 <sup>o</sup> C (63 <sup>o</sup> F)
Upper Explosive Limit (%)	12.87
Lower Explosive Limit (%)	4.22
Auto-ignition temperature	458 <sup>o</sup> C
Melting Point	2 <sup>o</sup> C (36 <sup>o</sup> F; 275K)
Boiling Point	90 <sup>o</sup> C (194 <sup>o</sup> F; 363K)
Heat of Combustion	3452 kcal/kg
Vaporization Latent Heat	8382 KJ/kmol
Solubility in Water	13.9 g/100
Relative Vapor Density	3.1 (vs Air)
Vapor Pressure	18 mmHg (21.1 <sup>o</sup> C)
Viscosity	0.664 mPa.s
Critical Pressure	4.57 Mpa
Critical Temperature	265.9 <sup>o</sup> C (510.5 <sup>o</sup> F; 539K)
Cetane Number	35
Color	APHA:<50

For fuels used in transportation applications, it is generally necessary to have a fuel specification for the fuel that is being used. There is not a specification for DMC as a transportation fuel. DMC will generally have a minimum 99.7% of DMC content and maximum 0.02% of moisture (42). The purity of DMC made using industrial production methods is generally able to hit or exceed 99.9% DMC. Based on the production method of methanol oxidative carbonylation, the impurity element is water.

In terms of diesel-DMC mixtures, one issue is that these mixtures have a high critical solubility temperature value (36), which is the temperature where the two components of a mixture are no longer miscible and start to separate. For complete solubility between diesel and DMC relative to the percentage of DMC, a temperature higher than 273.15 K is needed. At temperatures below this, depending on the DMC blend level, the mixture can separate into its different components. This can cause a decrease in the efficiency of the engine because it is fed with a nonhomogeneous charge. For these reasons, DMC cannot be used in cold temperature countries unless a blend pre-heater is added to the engine system. DMC-containing blends with low percentages of DMC can be used in warm regions where the risk of the two components in the mixture separating and the fuel supply becoming inhomogeneous is lower (43).

## DMC Industrial Applications and Production

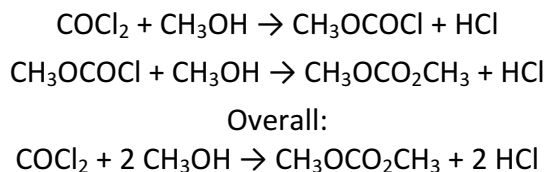
### *Industrial Applications*

DMC is an industrial chemical with many uses. It is primarily produced and polymerized to form polycarbonates, which are a type of plastic known for its optical transparency, impact resistance, and high dielectric strength. Polycarbonates are found in DVD and Blu-ray discs, safety goggles, eyeglass lenses, bullet-resistant windows, electrical insulators, aircraft, and missile components. By virtue of its unique molecular structure (CH<sub>3</sub>OCOOCH<sub>3</sub>), DMC is used as a reagent for methylation and carbonylation in the chemical industry. As a solvent, DMC has been exempted from classification as a volatile organic compound (VOC) in the U.S. In addition, owing to the active group, it has been widely used as a low toxicity solvent to replace phenyl or aldehyde solvents in industrial surface coatings (44-45). The use of DMC as a solvent includes being used as an electrolyte in lithium ion batteries. Dimethyl carbonate is often considered to be a green reagent (46). This abundance and variety of applications generates substantial demand for DMC and makes production a viable investment. DMC could also be an option for meeting the oxygenate specifications for gasoline and jet fuels due to its high oxygen content (53 wt%), good blending octane, freedom from phase separation, low toxicity and rapid biodegradability, and also as a means of converting natural gas (NG) to a liquid transportation fuel. With reductions in production costs, DMC has started to enter the energy market as a blend fuel in gasoline and diesel (9, 43).

### *DMC Production*

At present, the world DMC annual production capacity is approximately 170,000 to 200,000 ton/year, with the actual annual DMC output being less than 100,000 ton/year, mainly in Western Europe, the U.S., Japan and other countries. Among these countries, the U.S. is the largest producer, accounting for about 35% of the world's total capacity. In the U.S., DMC is mainly used for the production of furazolidone and pesticide chemicals, pharmaceutical intermediates, and a smaller percentage of polycarbonate production. In Japan, DMC is mainly used for the production of polycarbonate, pesticide chemicals and pharmaceutical intermediates (47).

Traditionally, DMC has been prepared by the reaction of phosgene with methanol via methyl chloroformate in the presence of a concentrated sodium hydroxide solution in a two-phase reaction in high yield and purity. This is generally done via a two-phase reaction that provides high yields and purity, as follows:



Other alcohols can also be phosgenated. DMC can also be produced via a process where methanol is reacted with CO and O<sub>2</sub> to form DMC. These production processes are both become less common, however, as phosgene is an extremely toxic and dangerous chemical (48), and as the second process incorporates the use of CO, which is a toxic gas (49). It is extremely unlikely that new plants will use either the phosgene or urea based process in the future (49-50).

Oxidative carbonylation of methanol has become the major process for manufacturing DMC (51-52). Two production schemes for DMC are close to full-scale commercial development. The first one is a process developed by ENIChem (Italy), which is a major scale-up process based on the oxidative carbonylation of methanol over a CuCl catalyst system. The second one was developed by UBE (Japan). It is an oxidative carbonylation process based technology they have been using for the past 10-12 years for the synthesis of dimethyl oxalate, for which DMC is a byproduct. Two other processes, while not commercially practiced, are close to commercial application. A scheme patented by Dow uses a catalyst system similar to the one used by ENIChem that is impregnated on an active carbon support. In another scheme developed by Texaco and others, a cyclic carbonate is formed from ethylene via an ethylene oxide and subsequently transesterified to form a mole of ethylene glycol for every mole of DMC produced (44).

Varieties of new metallic and nonmetallic materials have also been studied to provide inexpensive and high yield routes to synthesis of DMC, such as a polymer-complexed Cu(II) catalyst system with alkali that can be added to the methanol or a high selective catalyst CuCl/MCM-41 for oxidative carbonylation of methanol (53-54).

## **DMC Safety and Storage**

### *Human Exposure*

DMC has a recommended industrial exposure (REL) limit of 100 ppm by inhalation over an 8-hour work day, which is similar to a number of common industrial solvents (Toluene, methyl ethyl ketone). DMC is metabolized by the body to methanol and carbon dioxide, so accidental ingestion should be treated in the same manner as methanol poisoning. DMC is corrosive to the eyes and skin, and can cause serious or permanent injury (55). It is generally considered to be non-corrosive to all metals.

### *Atmospheric Activities Study and Non-Human Toxicological*

DMC received its Federal VOC exemption on January 13, 2009. As of March 1, 2011, it is exempt in 42 States. DMC was exempted as a VOC chemical because of its ultra-low Maximum Incremental Reactivity (MIR) values of 0.06 grams ozone/gram of VOC and 5.4 grams of ozone/mole of VOC, which were both below the EPA's benchmark MIR values for ethane (0.31 and 9.3, respectively). An MIR value is a measure of a chemicals ability to produce ozone due to photochemical degradation. The lower the MIR value, the less ozone generated by that



chemical in the atmosphere. The methodology and rating of MIR values was developed by Dr. William Carter of the University of California at Riverside.

Some animal studies have been done with exposures to DMC. Animal studies are sometimes used to provide an indication of what reactions could happen with chemical exposures in situations where direct human studies are not practical. The level of toxicity for a chemical is often characterized by its LD50 value. An LD50 is a standard measurement of acute toxicity that is stated in milligrams (mg) of pesticide per kilogram (kg) of body weight. An LD50 represents the individual dose required to kill 50 percent of a population of test animals (e.g., rats, fish, mice, cockroaches). Because LD50 values are standard measurements, it is possible to compare relative toxicities among pesticides. The lower the LD50 dose, the more toxic of the pesticide (56). Studies done by Bingham et al. (57) found that undiluted liquid DMC has an oral LD<sub>50</sub> in a rat and a mouse of between 6.4 and 12.8 g/kg and an intraperitoneal LD<sub>50</sub> in the range of 800 to 1600 mg/kg. Symptoms of exposures at these levels for a rat or mouse were weakness, ataxia with gasping, and unconsciousness. A dermal LD<sub>50</sub> in a guinea pig was found to be greater than 10 mL/kg. For the guinea pig, some weight loss was noted, and minimal skin absorption was suspected. However, the degree of irritation was relatively slight (58).

### *DMC Storage*

DMC can be stored in a tight reservoir at a cool, dry, well-ventilated location away from moist air, plastics and resins. Metal containers used in the transfer of DMC should be grounded and bounded. Outside or detached storage is preferred. DMC can freeze at the same temperatures as water. It can be thawed out with no loss of properties to itself or coatings based on DMC (59). Carbonates are incompatible with cerium compounds, germanium, lead diacetate, magnesium, mercurous chloride, and silver nitrate (60).

In storing, distributing, and utilizing DMC, it is also important to understand the impacts of DMC on fuel system components. This would include gaskets, seals, or other materials. The elastomers or plastics in these systems could be subject to swelling or degradation. To date, there is limited information on the compatibility of DMC with various system components. This information would likely require materials exposure studies.

### *DMC Vapor leaks/Airborne Release*

DMC is highly flammable, and is easily ignited by heat, sparks or flames. DMC vapors may form explosive mixtures with air. Vapors may travel to a source of ignition and flash back. Most vapors are heavier than air. They will spread along the ground and collect in low or confined areas (sewers, basements, tanks). Runoff to sewers may create a fire or explosion hazard. Containers may also explode when heated. Also, DMC needs to be separated from strong oxidants and stored in an area without drain or sewer access (61).

Exposure to vapor phase DMC can also contribute to different adverse health effects. If DMC is inhaled, the person should be removed to fresh air. If not breathing, the person should be given



artificial respiration. If breathing is difficult, the person should be given oxygen. For a more serious inhalation exposure, the victim should be evacuated to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult for the person, oxygen should be administered. If the victim is not breathing, mouth-to-mouth resuscitation should be performed. A person inhaling DMC should also get medical attention. The substance may be toxic to central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage.

### *DMC Liquid leaks/Liquid Phase Release*

DMC is can also be hazardous for contact with skin or the eyes. It is an irritant for skin contact or eye contact. It is slightly hazardous in case of skin contact (permeator), of ingestion, and of inhalation. If DMC contacts the eyes, check for and remove any contact lenses for the person. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. In case of skin contact, immediately flush the skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. If there is a more serious skin contact, wash the impacted skin with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. If DMC is injected, do NOT induce vomiting unless directed to do so by medical personnel. If the person becomes unconscious person do not give them anything by mouth. Loosen tight clothing such as a collar, tie, belt or waistband. For each of these cases, medical attention should be sought for the exposed person.

## **DMC Combustion Research**

### *Cetane Number and Engine Ignition Delay*

Cetane number (CN) is an indicator of the combustion speed of diesel fuel. CN is an inverse function of a fuel's ignition delay, and the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel. In a particular diesel engine, higher CN fuels will have shorter ignition delay periods than lower CN fuels (62). In short, the higher the CN the more easily the fuel will combust in a compression setting (such as a diesel engine). The characteristic diesel "knock" occurs when fuel that has been injected into the cylinder ignites after a delay causing a late shock wave. Minimizing this delay results in less unburned fuel in the cylinder and less intense knock. Therefore, higher CN fuels usually allow an engine to run more smoothly and quietly.

DMC has a lower CN compared to the diesel, which causes an increase in the engine ignition delay. Generally, the CN for DMC and a typical diesel fuel are 35 and 45, respectively. Several studies have found that the addition of DMC to diesel fuel increases the engine ignition delay for a variety of DMC blend levels (3, 8-9).

### Heat Release and Combustion Duration

The instantaneous heat release rate for DMC added to diesel fuel is higher than that of the diesel fuel itself during the initial combustion period, making the heat release process more concentrated. The high evaporability of DMC improves the mixing of fuel and air and boosts combustion (8-9). A higher amount of heat release has also been observed during premixed combustion. This shortens both the diffusive burning duration and the total combustion duration in a compression ignition diesel engine (3). Also, a relationship between combustion duration and oxygenated fractions in the blend has been found, with the combustion duration decreasing with an increase in the oxygenate fraction in the blends (8).

### Thermal Efficiency

Thermal efficiency is a dimensionless performance measure of a device that uses thermal energy, such as an internal combustion engine, a steam turbine or a steam engine, or a boiler. In other words, thermal efficiency indicates how well an energy conversion or transfer process is accomplished. Several Studies have shown slight improvements in thermal efficiency with DMC. Xiaolu et al. (7) found a 2-3% higher effective thermal efficiency than diesel fuel with pure DMC for an engine operated at moderate and high loads, partially due to its lower exhaust gas temperature. Cheung et al. (35) and Zhang et al. (37) found that with an increase of DMC in the blended fuel, the brake thermal efficiency of a diesel engine was slightly improved. In the light load zone, the brake thermal efficiency of a DMC fueled engine was slightly lower than that of a diesel fueled engine, owing to its higher HC emissions. It should be noted that the increase in thermal efficiency is relatively small compared to the differences in the fuels on a volumetric basis, as such overall fuel economy still decreases with the use of DMC compared to diesel fuel.

### DMC Spray

Xiaolu et al. (7) studied DMC sprays using an advanced digital particle image velocimetry (DPIV) measurement system, as shown in Figure 1 and Figure 2. A DMC spray is typically better than a diesel spray, providing smaller atomization particles and a more uniform distribution. This phenomenon could be related to their velocity vector distributions. The drop velocities in the core zone around the spray axes were higher than those in the spray periphery, which were hindered by the air. The DMC and diesel fuel was also found to entrain air in its spray periphery (7).

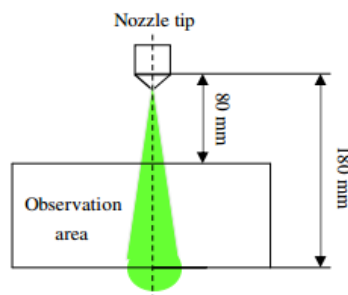
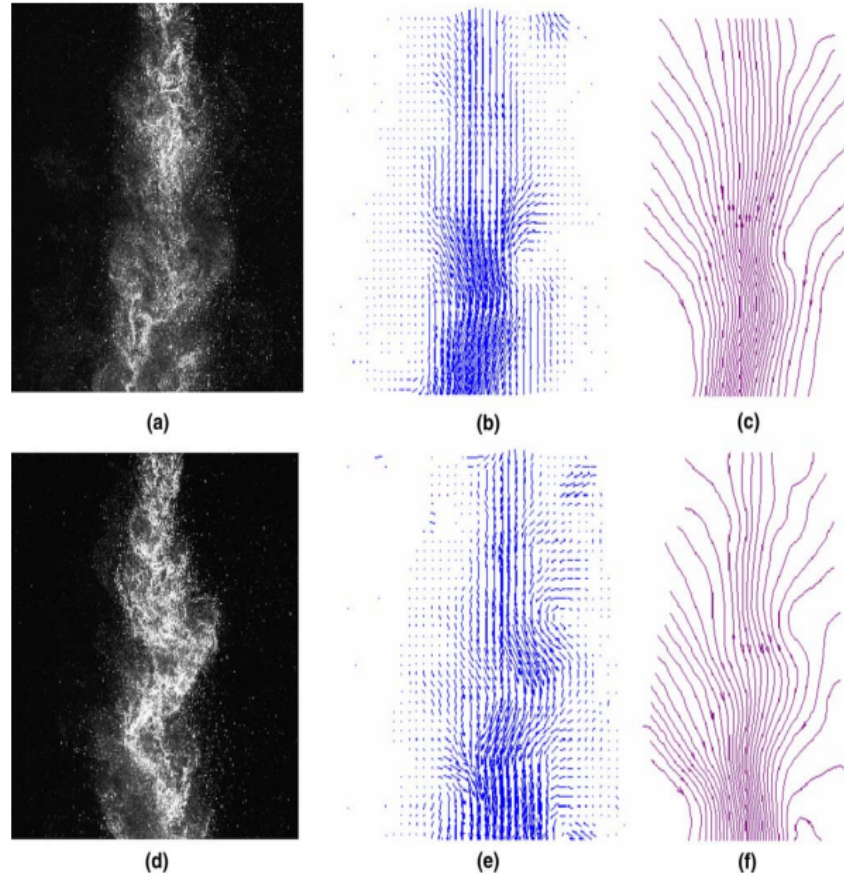


Figure 1. Schematic of photographic window



**Figure 2. Measurement results of DMC and diesel sprays: (a) particle image of DMC spray; (b) velocity vector distribution of DMC spray; (c) streamline distribution of DMC spray; (d) particle image of diesel spray; (e) velocity vector distribution of diesel spray; (f) streamline distribution of diesel spray.**

## DMC Emissions Research

### PM

The oxygen from blended fuel plays a key role in reducing PM emissions (40). There is a general consensus that fuel oxygen content provides reductions in soot formation and PM emissions (3, 7-9). A number of studies of DMC in particular have shown reductions in PM emissions. In our initial study, PM emissions decreased with increasing DMC blend levels, ranging from 30 to 78% for the DMC5 to DMC30 blends. For DMC blends from 4.5% to 18.6%, Zhu et al. (3) found PM mass emissions were reduced by 8–55%, 6–53%, 9–50%, 12–63%, and 17–59% for engine loads from 0.08 MPa to 0.70 MPa. Mei et al. (9) observed reductions in PM emissions for a 10% DMC blend for both loads tested and for most of the test conditions in terms of center of heat release and EGR rate. These emission reductions were quite large in some cases, for example,

under the high load engine mode (pmi  $\frac{1}{4}$  0.80 MPa, COHR  $\frac{1}{4}$  16°C, and EGR  $\frac{1}{4}$  36%), PM emissions decreased by 59.5%. Cheung et al. (35) found PM emission reductions of 5 to 17% for a 4.5% DMC blend up to 53 to 63% for a 18.6% DMC blend over a range of 5 engine loads. Zhang and Balasubramanian (63) found smaller reductions in PM of 7.8 and 15.4% for 5 and 10% DMC blends, respectively, in a single cylinder stationary diesel engine. In tests of a heavy-duty vehicle, Dillon and Iwamoto (64) and Kanne (65) found PM reductions from 0% at idle to 9% to 29% for speeds from 20 to 55 mph for a 5.3% DMC blend. Other researchers have also found reductions in other measures of PM, such as smoke level. Singh et al. (66) found reductions of up to 35% for 15 and 20% DMC blends. Ren et al. (8) showed reductions in smoke from slightly more than 15% to slightly more than 35% for DMC blends from 10 to 32.5%. Xiaolu et al. (7) found that smoke levels could be reduced to almost zero using a pure DMC fuel.

Some researchers have found that the PM mass reduction depends on the total oxygen mass fraction in the blend (67-68), while other researchers have reported that apart from the oxygen content, the chemical structure of the oxygenates also influenced the amount and toxicity of PM emissions (26, 37, 69-71). There are conflicting reports on the relative impacts of different oxygenated functional groups, however (26, 69-72).

Miyamoto et al. (67) found that the amount of PM reduction depended on the total oxygen mass fraction in the blends. Four different oxygenates were used in this study, including diethylene glycol dimethyl ether (DGM), ethylene glycol mono-n-butyl ether (ENB), 2-ethylhexyl acetate (EHA), and di-n-butyl ether (DBE), which have oxygen contents of 35.8%, 27.1%, 18.6%, and 12.3%. These four fuels and their blends showed a linear relationship between the emission reduction and the oxygen content, with PM reductions ranging from 52% to 100%, suggesting that the oxygen content, not the kind of oxygenate, was a dominant factor in PM emissions. Cheng et al. (68) investigated the effects of oxygenates blended with diesel fuel on PM emissions in a compression-ignition engine. They evaluated dimethoxy methane (DMM), diethyl ether (DEE), cetane (20% monoglyme and 80% diglyme), and ethanol, which have oxygen contents of 42.1%, 21.6%, 35.7%, and 34.7%. They found that PM reductions were correlated to the oxygen-content. Choi and Reitz (72) concluded that reductions in soot or PM mass were mainly dependent on the percentage of oxygen in the fuel blend.

Other researchers have found that chemical composition and other factors remain important in any PM reductions found for oxygenates. Stoner et al. (74) and Salvi et al. (75) found that different kinds of oxygenates have different thermophysical properties, which tend to affect not only the fuel injection and combustion processes, but also the PM emissions. In addition, even with the same oxygen content, the extent of soot and PM emissions reduction with oxygenated fuel blends may also be dependent on the engine types and operating conditions (72, 75).

It is also important to understand the composition of the PM. PM consists mostly of carbonaceous material (total carbon, TC), which is often classified as elemental carbon (EC) and organic carbon (OC). EC stems from fuel droplet pyrolysis in the fuel rich zone under high

pressures and temperatures, while OC originates from unburned fuels, lubricating oil, and combustion byproducts (76). Furthermore, from an environmental perspective, EC suspended in the atmosphere can effectively absorb solar radiation, thus affecting the energy redistribution and global climate (77), while some semi-volatile hydrocarbons in the OC fraction are suspected human carcinogens (78). Previous work mainly focused on studying the soot or PM mass emissions (67-73), with little investigation on the variation of EC and OC in response to the types and amounts of oxygenates used (79). Zhu et al. (3), however, did show DMC could significantly increase the soluble organic fraction (SOF) in the particulates. Changes in PM composition for biodiesel have been more extensively studied, with biodiesel tending to reduce EC. There remains a need to conduct a systematic investigation of changes in carbonaceous matter composition of PM emissions when different oxygenated diesel fuel blends are used in diesel engines, however, to improve our understanding of the environmental and health effects.

### *NO<sub>x</sub> emissions*

NO<sub>x</sub> is a generic term for the combination of mono-nitrogen oxides, nitric oxide (NO), and nitrogen dioxide (NO<sub>2</sub>). They are produced from the reaction of nitrogen and oxygen gases from the air used during combustion, especially at high temperatures. NO<sub>x</sub> contributes to the formation of fine particles and ground level ozone, both of which are associated with adverse health effects (80). NO<sub>x</sub> also impacts human respiratory conditions, causing inflammation of the airways at high levels. Long term exposure can decrease lung function, increase the risk of respiratory conditions and increase the response to allergens.

Studies of the emissions impacts of DMC on NO<sub>x</sub> emissions have shown varying results from one study to the next, with some researchers reporting that DMC blends can increase NO<sub>x</sub> emissions (9, 66), while others obtained different results (7, 35).

Singh et al. (66) showed slight increases in NO<sub>x</sub> emissions using 5% to 20% DMC. Mei et al. (9) showed some increases for a 10% DMC blend at a higher engine load, but no significant changes at a lower engine load. Our initial research at CE-CERT showed increases of 3.2% and 3.1%, respectively, for higher 20% and 30% DMC blends, but no statistically significant differences for 5% and 12.5% DMC blends.

Other studies have found different trends in NO<sub>x</sub> emissions, however. Xiaolu et al. (7) found that pure DMC produced lower NO<sub>x</sub> emissions for a wide range of engine loads, scavenging pressures, and fuel delivery advancement. Cheung et al. (35) found a flat NO<sub>x</sub> emission curve was found when operating on DMC-diesel blends. It was observed that NO<sub>x</sub> varied within 5% for 4.5% to 18.6% DMC blended fuels. This suggested the use of DMC-diesel blends does not increase NO<sub>x</sub> emissions. Cheung et al. did, however, find increases in NO<sub>2</sub> emissions with increasing DMC blend, which they suggested could be due to the greater oxygen content and the cooling effect of DMC. Yanxia and Yongqi (81) found that NO<sub>x</sub> emissions showed little change for blends of up to 10% DMC and ethylene glycol monoacetate (EGM). Ren et al. (8)

showed slight decreases in NO<sub>x</sub> emissions with increasing oxygen content for DMC and other oxygenates.

### *PN and Particle Size Distribution*

Particle Number (PN) is an accumulation of all the particles from all sizes. Fine and ultrafine particles are formed mostly by vehicular exhaust emissions. By contrast, coarse particles are generated mostly by mechanical processes that break down material from a variety of non-combustible sources into dust. Some particles, such as dust, dirt, soot, or smoke, are large or dark enough to be seen with the naked eye. Others are so small, they can only be detected using an electron microscope.

PM typically consists of fine particles (PM<sub>2.5</sub>) with a large number of ultrafine particles (UFP) and nanoparticles (NP) with aerodynamic diameters less than 100 nm and 50 nm, respectively. UFP and NP dominate the number concentration profiles of PM in diesel exhaust. UFP and NP have recently drawn considerable research attention due to their higher rate of pulmonary deposition, their ability to travel from the lung to systemic sites, their higher inflammation potential, and their greater biological activities compared to particles with larger sizes (78).

A number of studies have shown accumulation mode particles to be the predominant contribution to the particle size distributions (PSD). Zhang and Balasubramanian (63) measured particle size distributions at 25%, 50%, and 75% engine loads. They found that the PSDs consisted of only an accumulation mode at the 50 and 75% loads. At the 25% loads, the PSD was bimodal, but the accumulation modes 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, 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.

Zhu et al. (3) and Cheng et al. (68) measured size distributions from about 15 to 750 nm using a scanning mobility particle sizer. These studies did not show any evidence of nucleation mode particles, but did show a shift to smaller particles in the PSD curves. The use of oxygenates as blending agents has shown reductions in PM mass emissions, caused by a reduction in larger particles, while there might be an increase in UFP and NP sized particles. Studies by Zhu et al. (3) found that with the addition of DMC in diesel blends, the number concentrations of UFP and NP particles decrease, but the fraction of these smaller particles in comparison to the total number concentration increases. This is opposite to our initial results in terms of the overall number, but consistent with our result that the fraction of smaller particles increases. For Zhu et al. (3), at an engine load of 0.55 MPa, the percentage of nano and ultra-fine particles was 32.5% and 78.2% for Euro V diesel fuel, respectively, while the corresponding values for an 18.6% DMC diesel mixture were 42.5% and 85.4%. Similar trends were observed at each engine load. The results indicate that DMC can lead to a reduction of both groups of particles, but that greater reductions are found in the larger particles.



The literature results have generally shown a reduction in PN with increasing DMC blend levels. Zhang and Balasubramanian (63) showed a reduction in PN of 25.1 and 36.1% for 5 and 10% DMC blends, respectively, based on measurements with a fast mobility particle sizer with a size range from 5.6 to 560 nm. Zhu et al. (3) and Cheng et al. (68) also found reductions in PN emissions with DMC blends, but these researchers did not measure the smaller nucleation mode particles. Zhu et al. (3) found that total PN concentrations corresponding to the five different engine loads are reduced by 15–45%, 13–48%, 11–34%, 8–35%, and 9–24%, respectively, for DMC blends from 4.5 to 18.6%. Cheung et al. (35) also showed reductions on average of 21 and 37%, for 9.1 to 18.6% DMC blends, respectively.

For DMC-diesel fuel blends, PM emissions are generally found to be reduced, as discussed above, but this can cause a corresponding impact of increasing PN emissions. In particular, the formation of nucleation particles can be suppressed by a greater abundance of accumulation particles. Hence, as there is a reduction in the levels of accumulation mode particles, homogeneous nucleation can be enhanced. Desantes et al. (82) and Kittelson et al. (83) both reported the close relationship between the nucleation and accumulation modes for the particle formation. This is in consistent with Zhang and Balasubramanian's (63) study as well as our initial result, where an 80.6% increase in PN was found in conjunction with a 75.6% reduction in PM, which indicates the PM emissions are largely ultrafine particles.

In contrast, our initial studies with DMC blends from 5 to 30% showed a bimodal PSD, but dominated by nucleation mode particles as opposed to accumulation mode particles. Our initial results also showed increases in PN emissions with increasing DMC blend levels. This trend can be understood in the context of changes of the particle size distributions. In particular, the formation of nucleation particles can be suppressed by a greater abundance of accumulation particles. Hence, as there is a reduction in the levels of accumulation mode particles, homogeneous nucleation can be enhanced. Desantes et al. (82) and Kittelson et al. (83) both reported the close relationship between the nucleation and accumulation modes for the particle formation. The differences in the PSDs could be due to differences in the testing for the different studies, with our initial study being conducted over a transient test cycle, while the other studies were general conducted under steady state conditions. It should be noted that similar increases in PN and nucleation mode particles have also been seen in studies of DME (84).

The increased emissions of the sub-micron particles and the reduced emissions of larger size particles would change particle size distributions in ambient air as well as the characteristics of the inhalation exposure (78). For these reasons, the mass-based emission reduction from oxygenated fuels may not be as effective in mitigating their influence on the environment and human health. However, systematic studies and a comparative evaluation of the potential impacts of different oxygenated fuels on UFP and NP emission characteristics are currently lacking. Brown et al. (85) found some interesting results from a biological perspective. During a pollution episode, each lung acinus could receive on average 30-million particles and each alveolus about 1500 particles (for 24 h exposure), of which 50% are being deposited. Lung

airways and alveoli retain mostly PM<sub>2.5</sub> rather than PM<sub>10</sub>, a finding supported by various observations (86). Analytical electron microscopy measurements showed that 96% of effectively retained particles in the lung parenchyma were PM<sub>2.5</sub> and only 5% were ultrafine particles (0.1 μm) (87). Therefore, the size of PM and its retention in the lungs play an important role in the PM cytotoxic effects.

## HC

Studies done by Singh et al. (66), Mei et al. (9), Cheung et al. (35), and Ren et al. (8) have indicated that emissions of hydrocarbons were reduced by adding DMC to diesel fuel. Mei et al. (9) observed reductions of HC emissions with the addition of 10% DMC to the diesel fuel for both loads tested and for most of the test conditions in terms of center of heat release and EGR rate. Singh et al. (66) found HC emissions reductions for 5% to 20% DMC blends for 75% and 100% engine load conditions, but no significant changes in CO emissions at lower engine loads. Ren et al. (8) showed reductions in CO up to 30+% for DMC blends of up to 20%. Cheung et al. (35) found HC emissions decreased with increasing DMC for 4.5 to 18.6% blend levels for higher engine loads, but at lower loads the 4.5 and 9.1% blend levels. On the other hand, our initial study showed THC emissions increased with increasing DMC blend levels, ranging from 32.5 to 137% for the DMC5 to DMC30 blends. On the other hand, Xiaolu et al. (7) found that HC emissions of a DMC fueled engine were high compared to those of the engine using diesel fuel in the case of low and partial engine loads and small fuel delivery advance angles. The increases in HC emissions are more consistent with the results of our initial study, where THC emissions increased with increasing DMC blend levels, ranging from 32.5 to 137% for 5% to 30% DMC blends.

## CO

Singh et al. (66), Huang et al. (10), Mei et al. (9), and Ren et al. (8) have observed CO emissions reductions in their studies with DMC blends ranging from 5% to 20%. Singh et al. (66) found CO emissions reductions for 5% to 20% DMC blends for 75% and 100% engine load conditions, but no significant changes in CO emissions at lower engine loads. Mei et al. (9) observed for a DMC blend that CO emissions rise rapidly with an increase in the EGR rate at high engine load, however, because of the sensitivity to low excess air ratios. Ren et al. (8) showed reductions in HC for a wide range of oxygenates and blend levels. In our initial study, CO emissions decreased with increasing DMC blend levels, ranging from 26.3 to 60.9% for the DMC5 to DMC30 blends. Cheung et al. (35), on the other hand, showed increases in CO emissions for 4.5 to 18.6% DMC blends as lower engine loads, but slight decreases in CO emissions for the highest engine load tested. Xiaolu et al. (7) showed some increases in CO emissions at small fuel delivery advance angles and higher loads, while CO emissions decreased at lower scavenging pressures.

## *Fuel Consumption and Fuel Economy*

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 (9). Thus, the addition of DMC leads to a drop in the volumetric energy



density in the blended fuel, which leads to an increase in the fuel consumed per mile for the DMC blended fuel (3). Our initial study showed BSFC increased with increasing DMC blend levels, ranging from 4.5 to 14.6% for the DMC12.5 to DMC30 blends, although no statistically significant changes in BSFC were found for the DMC5 blend. Also, Cheung et al. (35) found that for a 4.5% to 18.6% DMC blend compared with straight diesel fuel, the brake specific fuel consumption increased from 14.4% for a 18.6% DMC blend under a 0.55 Mpa engine load, although the brake thermal efficiency is slightly improved. Ren et al. (8) also found increases in BSFC with increasing DMC blend levels/oxygen contents. These results are similar to the result from our initial study.

### *CO<sub>2</sub> Emissions and Greenhouse Gases*

CO<sub>2</sub> emissions are the predominant greenhouse gas (GHG) from diesel engines. Some studies of DMC have reported CO<sub>2</sub> emissions in addition to the emissions of the more standard pollutants. In our initial study, CO<sub>2</sub> emissions showed statistically significant increases for all of DMC blends except the DMC5. The CO<sub>2</sub> emissions increased with increasing DMC blend levels, ranging from 1.1 to 4.7% for the DMC12.5 to DMC30 blends. Singh et al. (66) found slight reductions in CO<sub>2</sub> emissions at high loads with 5 to 20% DMC diesel blends. The authors attributed this to the lower carbon percentages in the blends. The high load conditions represent the operating range where the engine produces the highest levels of CO<sub>2</sub> emissions for all fuels. CH<sub>4</sub> and N<sub>2</sub>O are other important GHG pollutants that are emitted in vehicle exhaust, but emissions of these pollutants were not mentioned in any of the studies reviewed for this study.

While tailpipe CO<sub>2</sub> emissions changes for different fuels are important, the impacts of different on greenhouse gases as a whole is generally done using a Life cycle analysis (LCA). LCA is the systematic approach of looking at a product's complete life cycle, from raw materials to final disposal of the product (88). It offers a "cradle to grave" look at a product or process, considering environmental aspects and other potential impacts (89). The only LCA study of DMC that was found in this literature review was an earlier study that was conducted by Aresta and Galatola (49). These researchers did a life cycle analysis for DMC fuel with six production pathways that had been developed at the time. Some of these processes have already been exploited on a commercial scale, while others are being implemented on different pilot-plant scales. They found that the traditional process via phosgene had a higher environmental impact compared to the oxidative carbonylation process. It is likely that an updated LCA analysis would be needed to provide a better estimate of the overall impact of DMC on GHGs.

## Engine Dynamometer Testing

The engine dynamometer testing portion of this study investigated the impact of DMC blending on the regulated emissions, mobile source air toxics (MSATs) that included 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 testing are discussed in the context of different DMC-diesel concentration and the influence of DMC properties on pollutant formation.

### Experimental

#### *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<sup>2</sup>/s, and calorific value of 15.8 MJ/kg (40). 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.

#### *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, 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.

#### *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 (50). For all tests, standard emissions measurements of THC, CO, NO<sub>x</sub>, carbon dioxide (CO<sub>2</sub>), and PM, were measured. CO and CO<sub>2</sub> 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<sub>x</sub> 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 to 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 (200cm x 4.6mm 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.

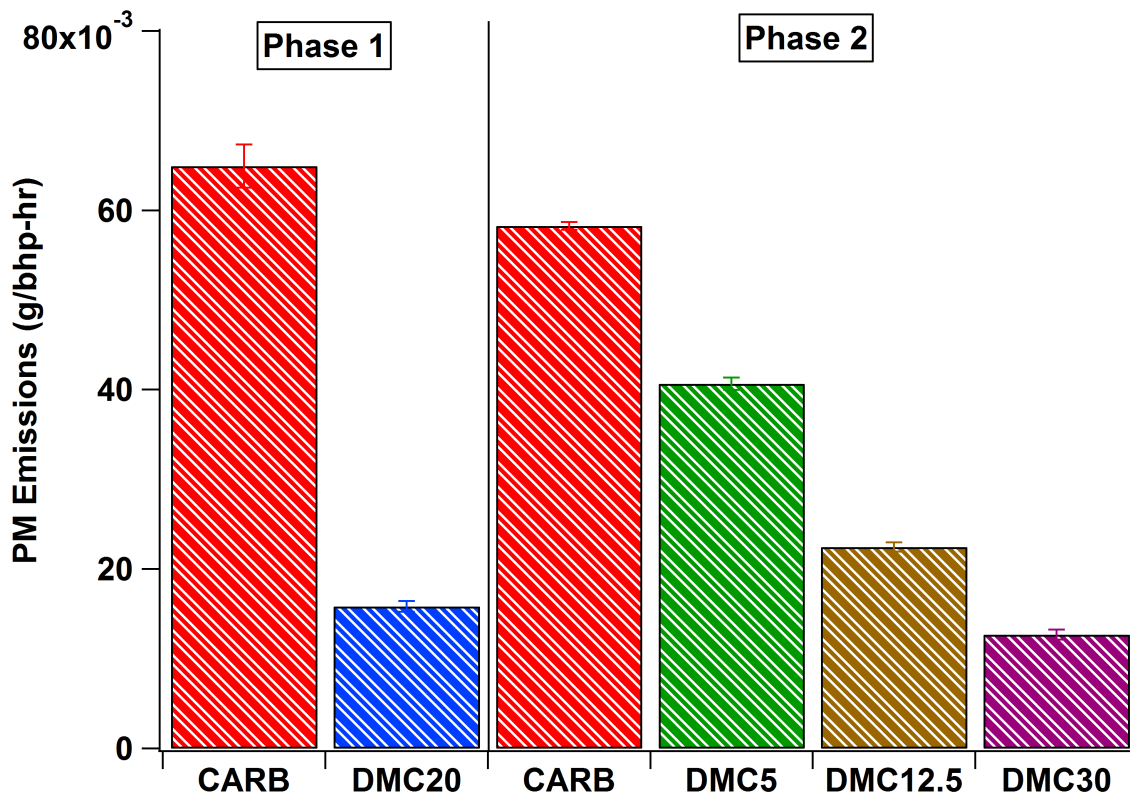
## Results and Discussion

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  $\leq 0.05$ . Results are considered marginally statistically significant for  $0.05 \leq p < 0.1$ . 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.

### *PM mass, particle number, and particle size distributions*

Emissions of PM mass, expressed on a gram per brake horsepower hour (g/bhp-hr) basis, for the different DMC blends tested over the two periods are shown in Figure 3.

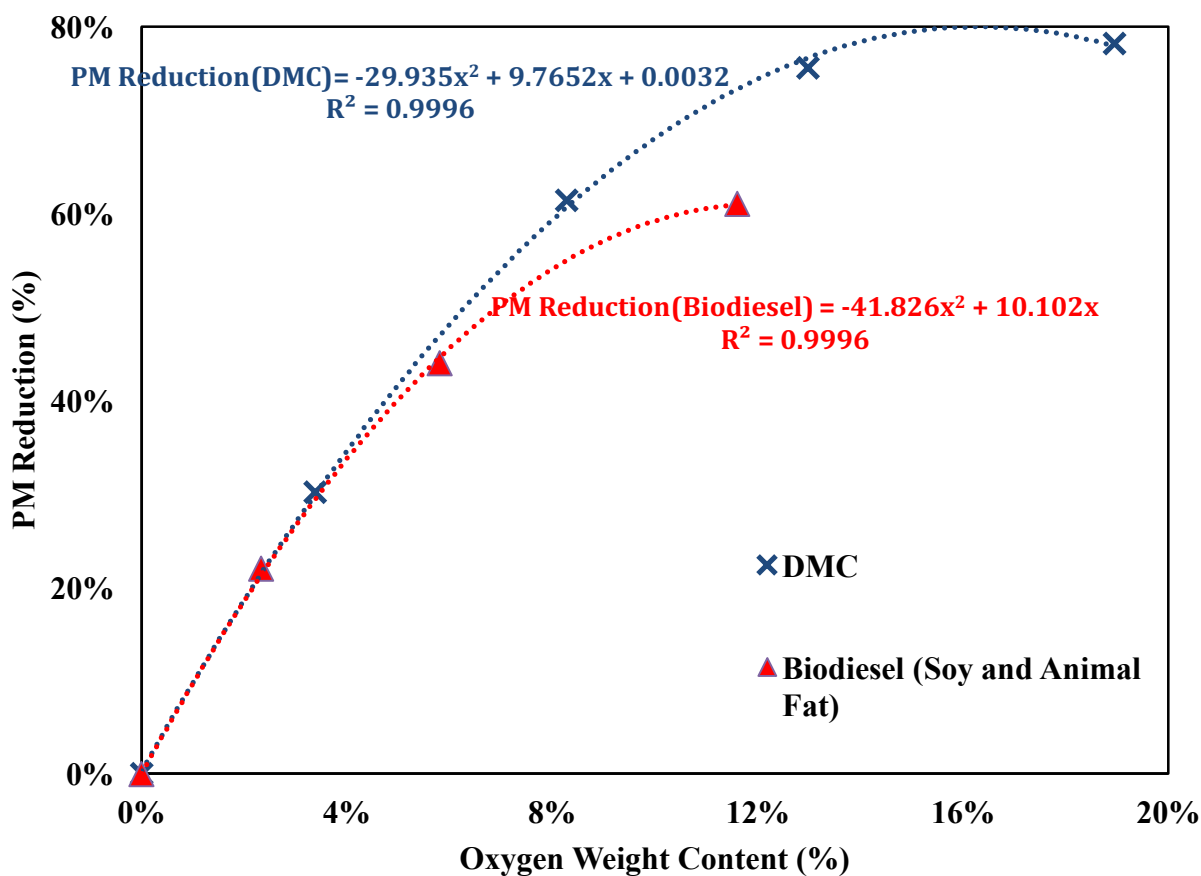


**Figure 3. Average PM mass emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.**

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 (38, 63, 90-91), as well as studies of other oxygenates such as biodiesel (23, 92-94). In comparison with biodiesel, however, the percentage reductions for the DMC are much larger than those seen for biodiesel for a comparable blend level.

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 Figure 4.



**Figure 4. Relationship between PM mass reduction (%) and oxygen content by weight (%)**

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 absence of C-C bonds in DMC could reduce the formation of the precursor soot species, such as acetylene ( $C_2H_2$ ) and benzene ( $C_6H_6$ ) (95). On the other hand, the production of free radicals ( $\bullet O$ ,  $\bullet OH$ , etc.) with

DMC combustion would promote the carbon oxidation to CO and CO<sub>2</sub> within the premixed flame zone, thus limiting the carbon available and modifying the path for the formation of soot (63, 68). 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 (3, 63, 67, 90, 96-97). 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 Figure 5.

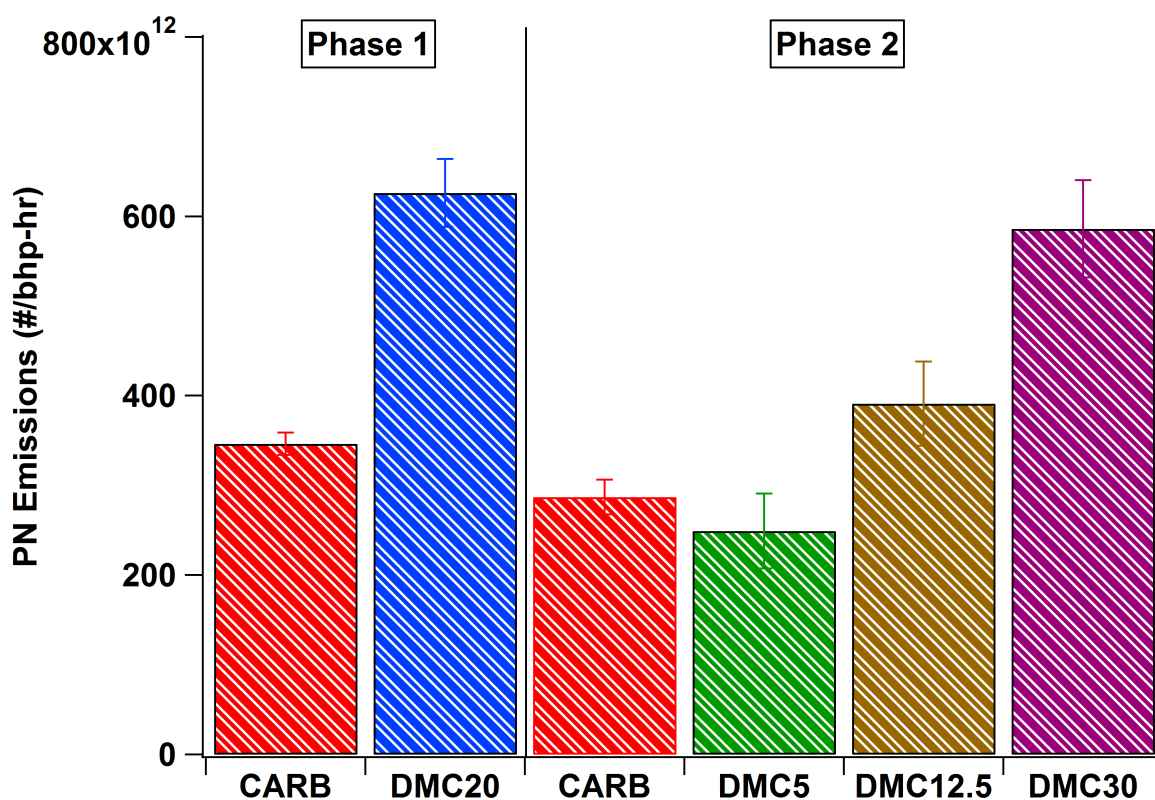


Figure 5. Average particle number emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

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 (3, 35, 61). Zhang and Balasubramanian (63) 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. (35) also showed reductions in particle number on average of 21% and 37%, for 9.1% to 18.6% DMC blends, respectively. On the other hand, similar increases in PN have also been seen in studies of DME (84). 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 (98). The corresponding decreased surface area of soot 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 (99).

The average particle size distributions for all test fuels are displayed in Figure 6 (a-b).



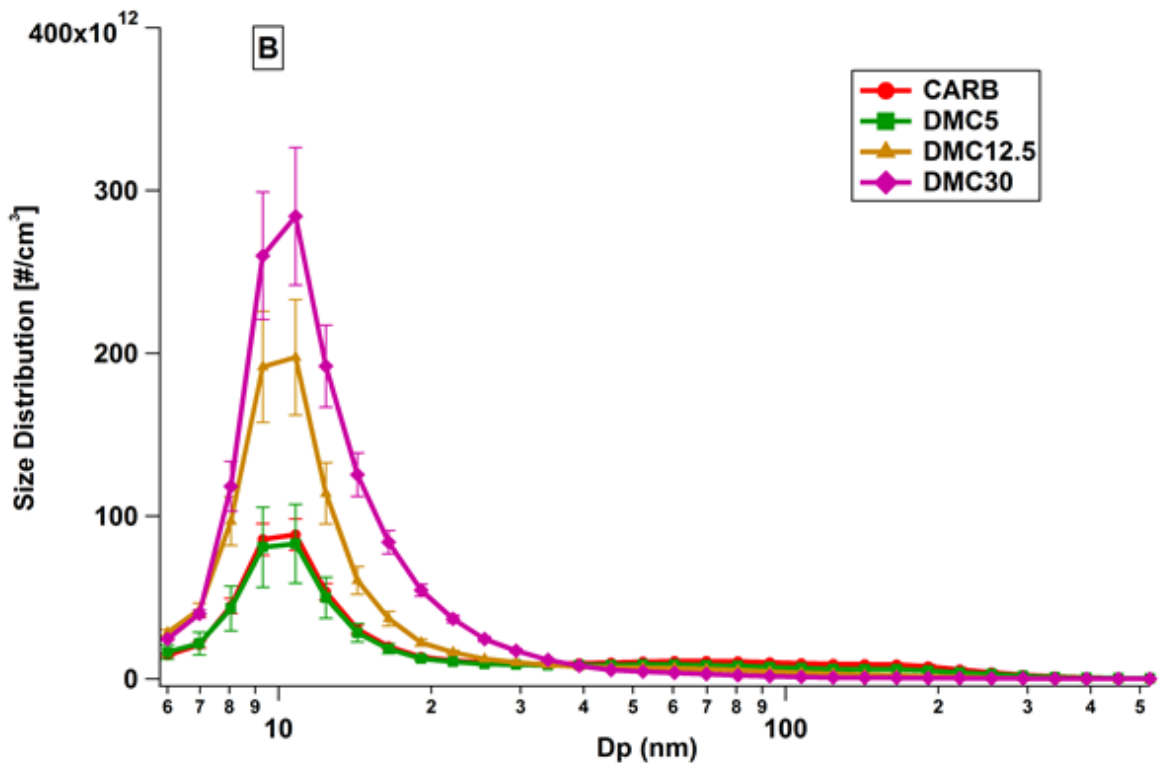
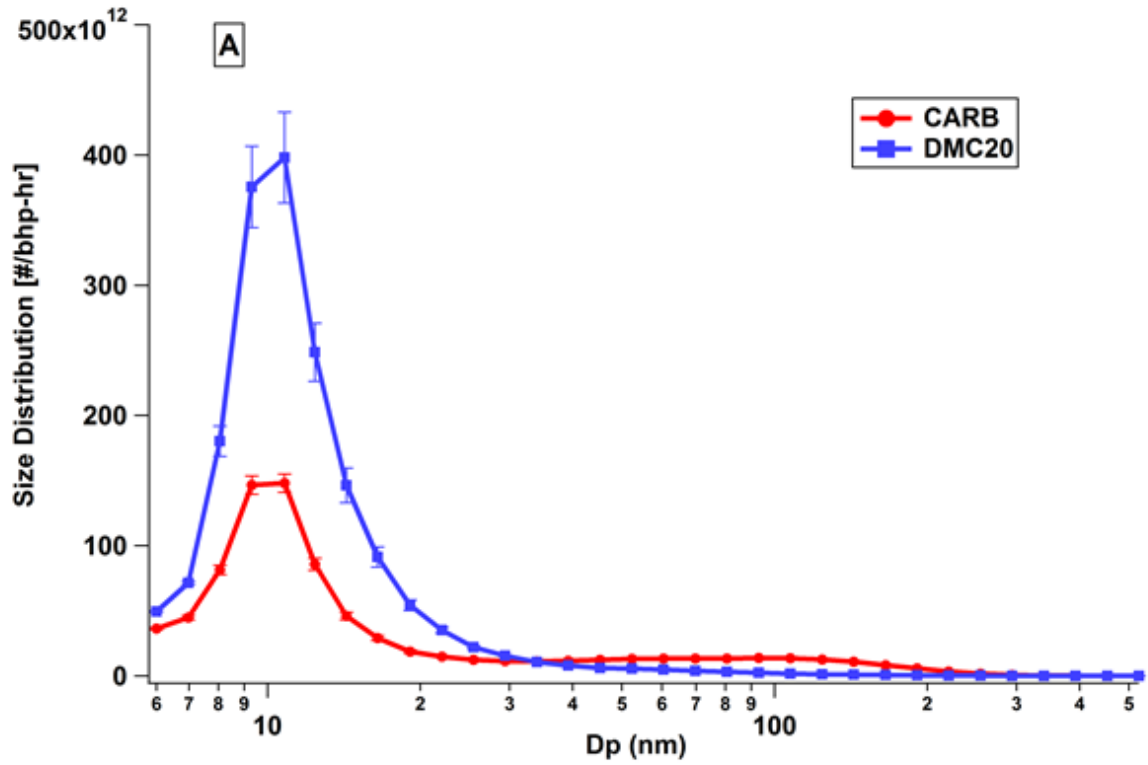


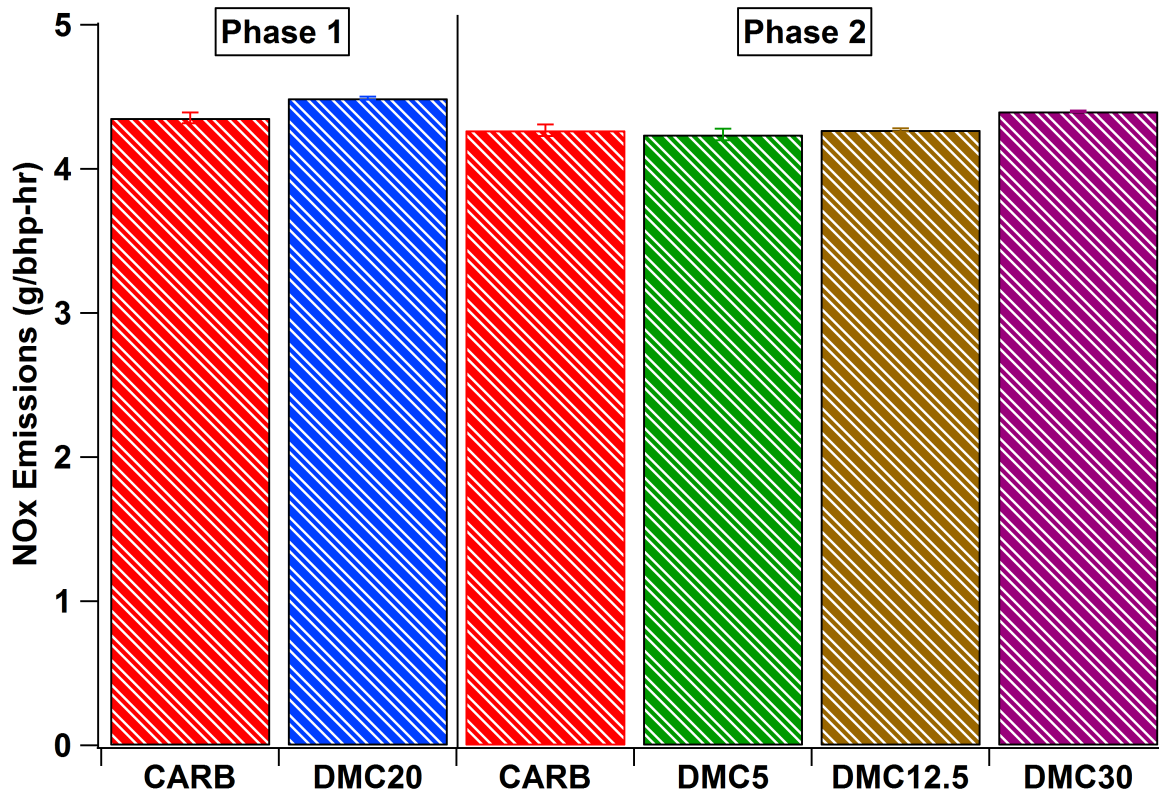
Figure 6 (a-b). Particle size distributions for CARB ULSD and the DMC blends



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 (3, 40). Increases in nucleation particles have also been seen in studies of DME (84). In a recent investigation, Zhang and Balasubramanian (63) 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.

## NO<sub>x</sub> emissions

The effect of DMC on NO<sub>x</sub> emissions is shown in Figure 7.



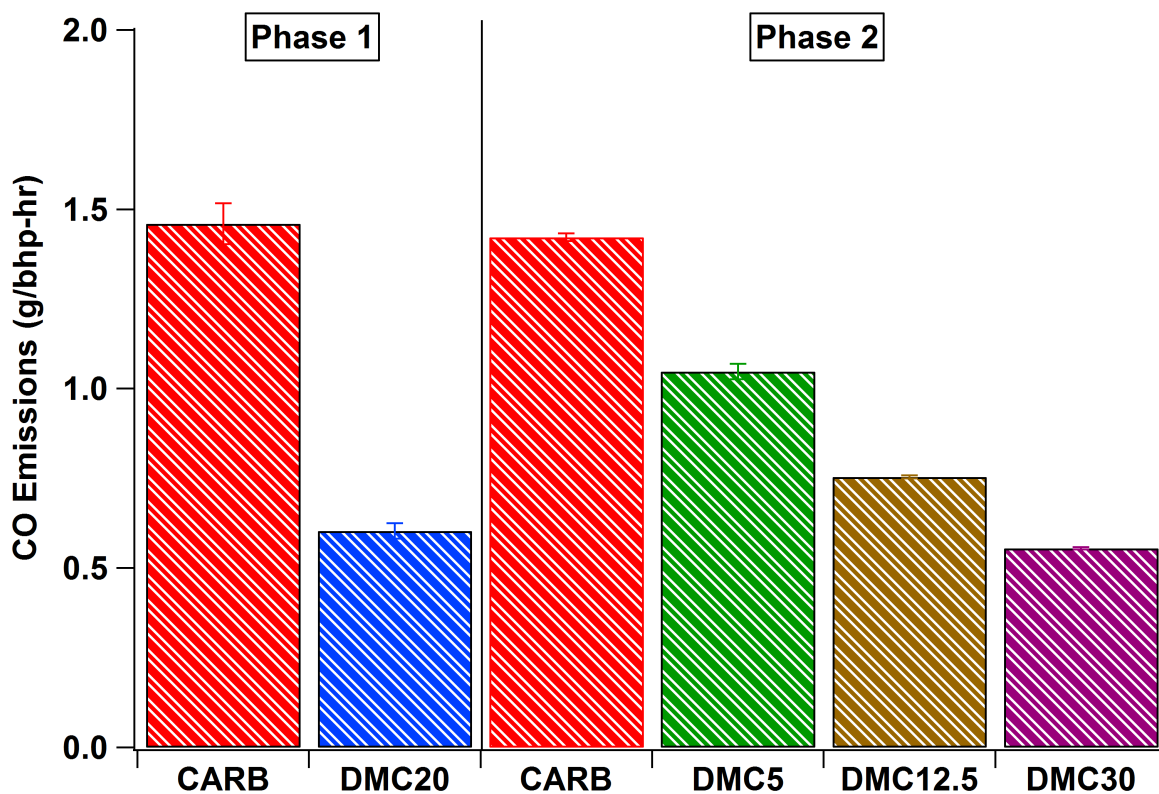
**Figure 7. Average NO<sub>x</sub> emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values**

NO<sub>x</sub> 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<sub>x</sub> emissions for the higher concentration DMC blends could be attributed to the increased oxygen content in the fuel blend, and NO<sub>x</sub> increases have been seen with other oxygenated fuels, such as biodiesel (23, 92, 94, 100-101). For biodiesel, Mueller et al. (101) 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<sub>x</sub> 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<sub>x</sub> emissions. A similar PM/NO<sub>x</sub> emissions trade-off was observed in a previous investigation (91). Previous studies have also shown that the application of DMC can increase NO<sub>x</sub> emissions (15, 40), whereas other studies have reported minimal changes in NO<sub>x</sub> emissions with DMC (35, 90).

Murayama and co-workers (33) have shown that  $\text{NO}_x$  increases were very significant with oxygen addition. However, they have also demonstrated the possibility of simultaneous reduction of PM and  $\text{NO}_x$  emissions when they applied a high EGR ratio in conjunction with oxygenated fuel combustion. Mei et al. (9) 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. (8) found slight decreases in  $\text{NO}_x$  emissions with increasing oxygen content for DMC and other oxygenates.

### CO and THC emissions

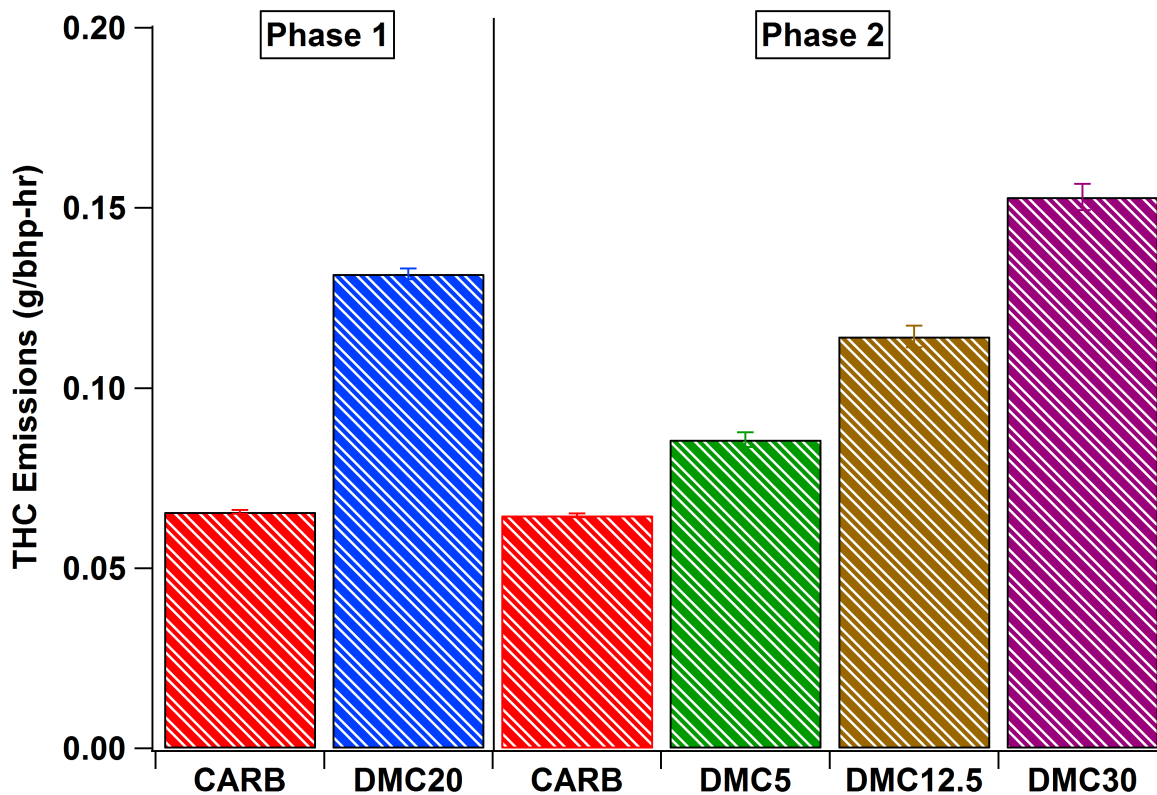
The CO emission results for the different DMC blends are shown in Figure 8 on a g/bhp-hr basis.



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

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 (8, 35, 90).

THC emissions showed systematic increases with the use of DMC blends, at a statistically significant level (Figure 9).

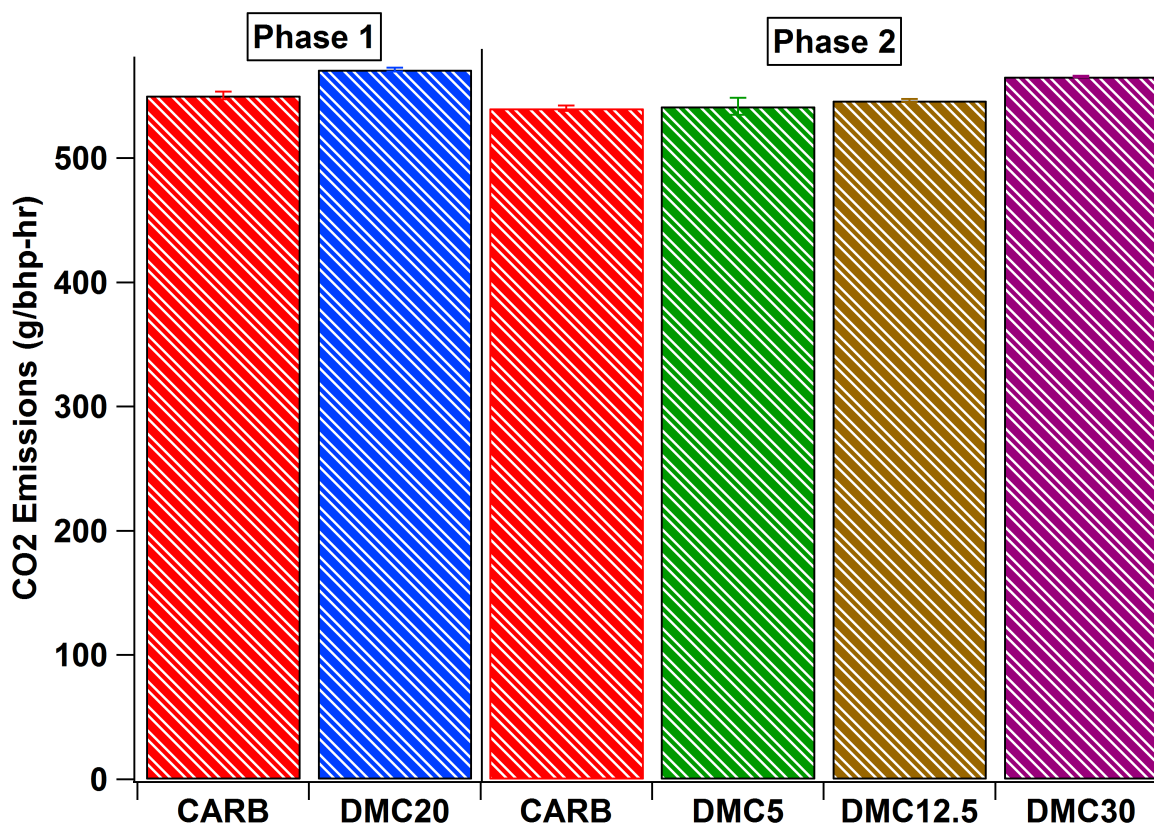


**Figure 9. Average THC emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.**

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. (102), 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 (8-9, 15, 40). A trend of increasing THC emissions has also been seen with other oxygenates in diesel fuel, such as ethanol-diesel blends (27-28). THC, a product of incomplete combustion, is formed where combustion is quenched (35). 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 (102).

## CO<sub>2</sub> emissions and brake specific fuel consumption

The CO<sub>2</sub> emission results are presented in Figure 10.

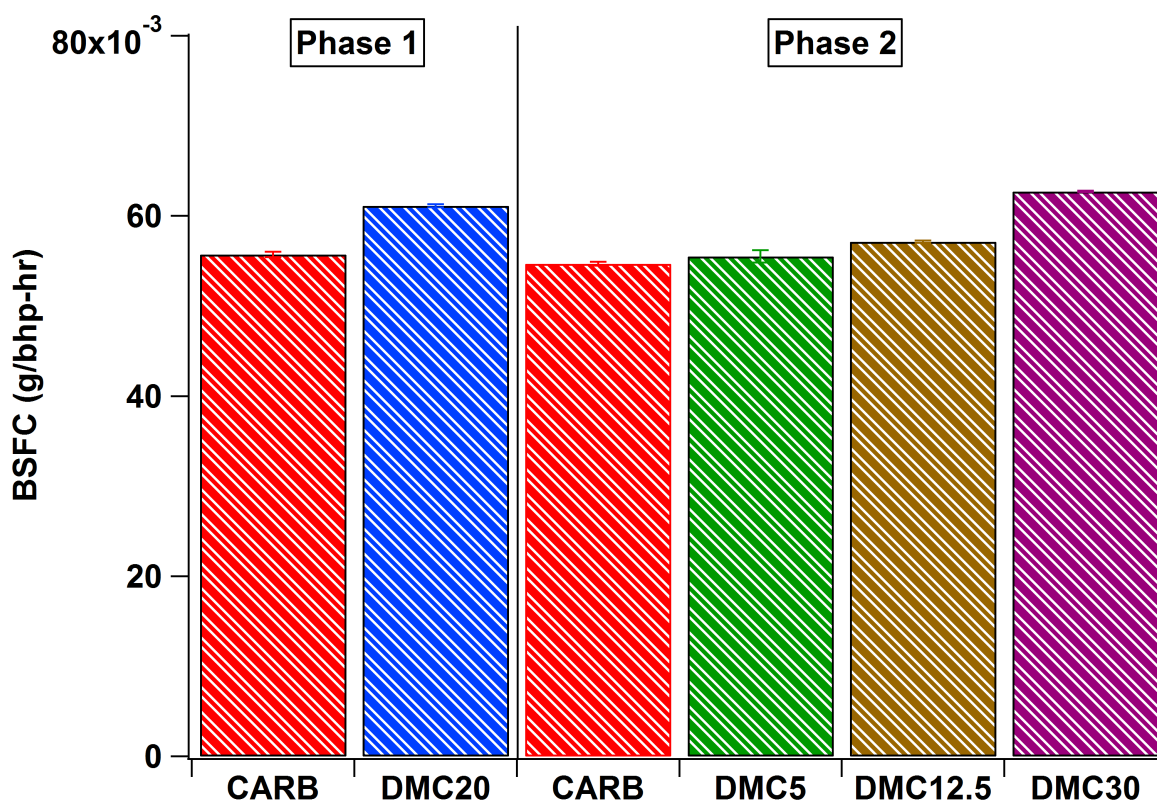


**Figure 10. Average CO<sub>2</sub> emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.**

CO<sub>2</sub> emissions showed statistically significant increases for the DMC blends compared to CARB ULSD, with the exception of DMC5. The increases in CO<sub>2</sub> emissions were in the range of 1.1%, 3.8%, and 4.7%, respectively, for DMC12.5, DMC20, and DMC30. The CO<sub>2</sub> 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<sub>2</sub> emissions that were observed in this study. Chemical kinetic modelling studies have also suggested that the DMC decomposition results in production of CO<sub>2</sub>, an alkyl radical, and an alkoxy radical (18, 103).

Figure 11 shows the brake specific fuel consumption (BSFC) for the DMC blends on a gal/bhp-hr basis.





**Figure 11. Average BSFC results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.**

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 (9). 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 fuel, which leads to an increase in the fuel consumed per unit or work for the DMC blended fuel.

### *Volatile organic compounds (VOCs) and carbonyl emissions*

Figure 12 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 2 shows all the VOC species quantified in the tailpipe.

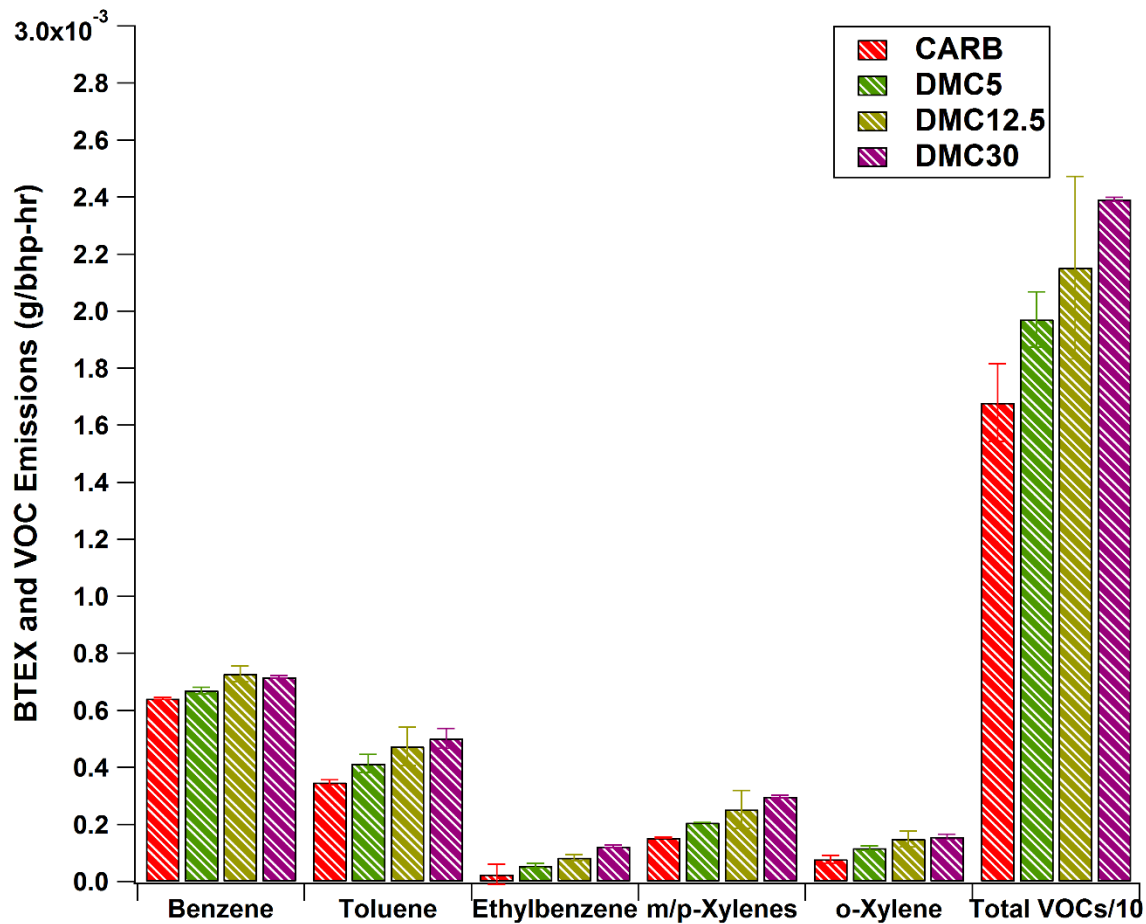


Figure 12. Average BTEX emissions and total VOCs for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.

**Table 2. Hydrocarbon emissions results for CARB ULSD and the DMC blends**

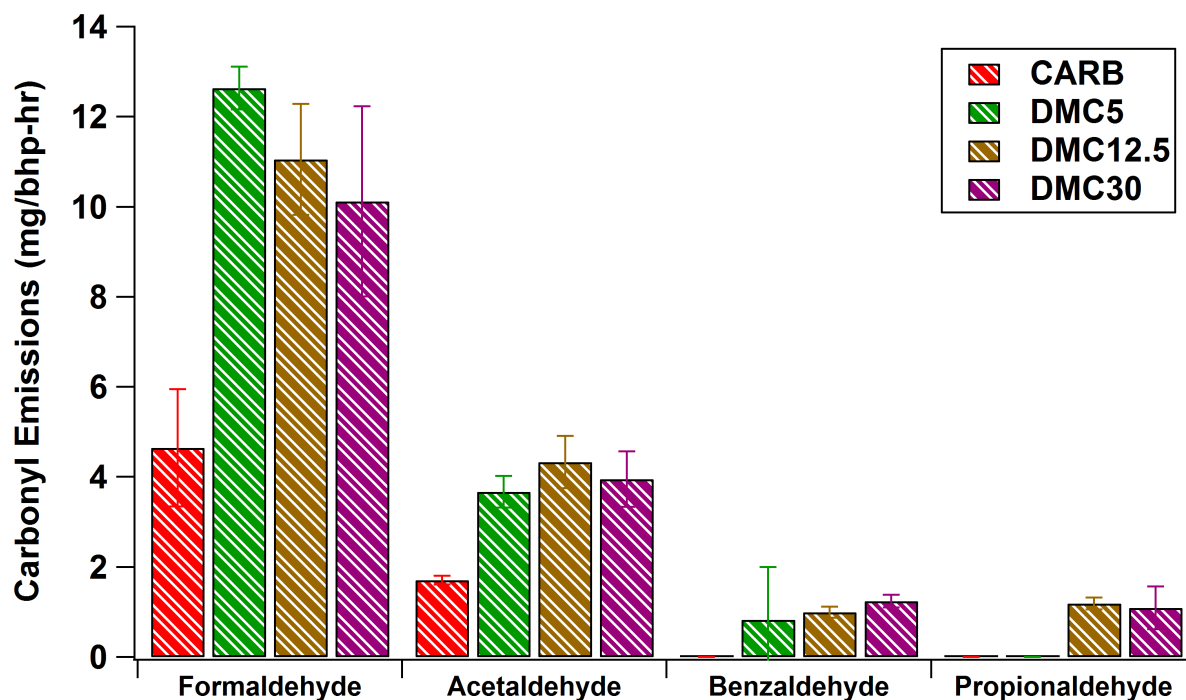
Hydrocarbon Species (g/bhp-hr)	CARB ULSD	DMC5	DMC12.5	DMC30
Ethylene	0.0067 ± 0.0003	0.0072 ± 0.0002	0.0076 ± 0.0004	0.0091 ± 0.0002
Acetylene	0.0012 ± 0.0000	0.0013 ± 0.0000	0.0013 ± 0.0001	0.0015 ± 0.0000
Ethane	0.0003 ± 0.0000	0.0006 ± 0.0001	0.0006 ± 0.0005	0.0005 ± 0.0000
Propylene	0.0024 ± 0.0001	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



Hydrocarbon Species (g/bhp-hr)	CARB ULSD	DMC5	DMC12.5	DMC30
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

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 (18, 38, 95, 103). 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, may also contribute to the enhancement of nucleation mode particles, as seen in the particle size distributions above.

The carbonyl emissions, expressed in mg/bhp-hr, are shown in Figure 13.



**Figure 13. Average carbonyl emission results for the DMC blends and CARB ULSD. The error bars represent one standard deviation of the average values.**

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 (99, 104-106). 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 ( $\text{CH}_3\text{OC}=\text{O}$ ) (18, 107-108). Acetaldehyde is primarily formed from reactions involving the  $\text{C}_2$  species (103).

## 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. DMC is an oxygenated fuel that could provide significantly greater reductions in PM compared to other liquid alternative diesel fuels, and can be made from renewable sources. The objective of this study was to assess the viability and potential advantages of using DMC in transportation applications. The study included a preliminary literature to look at the environmental and system performance issues of using DMC as a transportation fuel. This study also included a small emissions testing program to evaluate potential increases in toxic species and to look at optimizing the blend level of the DMC for different emissions constituents. The conclusions for the two different parts of the study are presented below.

### Literature Review Conclusions

DMC is an oxygenate that is miscible with diesel fuel, has a high oxygen content, and can provide reductions in PM and other emissions. DMC is currently being used as an industrial chemical in many applications, including polycarbonates and as a methylating agent. Although DMC has been lightly studied for vehicle/engine applications, it is attracting some attention as a potential renewable diesel fuel. The goal of this study was to review some of the most important aspects of using DMC as a transportation fuel, including its fuel properties, its production, its safety and storage and the potential impact of air and liquid leaks, and its impact on combustion and emissions.

DMC differs in several key ways from diesel fuel, and it is these unique properties that can impact the performance and emissions when it is used in a diesel engine. DMC has a lower CN compared to the diesel, which causes an increase in the engine ignition delay. It also has a lower boiling point which favors spray atomization and mixing. The instantaneous heat release rate for DMC added to diesel fuel is also higher than that of the diesel fuel itself during the initial combustion period, making the heat release process more concentrated. 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, which leads to an increase in the fuel consumed per mile for the DMC blended fuel.

The oxygen content also has important consequences on the difference emissions components. The most important impact is the relatively large reductions in PM that are found with the addition of DMC, which ranged up to 75% for the 20% blend in our initial studies. Along with a reduction in PM mass, a corresponding increase in particle number can be found, as particles show an increased tendency to form nucleation particles. Most studies have also shown reductions in CO with the addition of DMC. For NO<sub>x</sub> emissions, DMC has shown mixed results, with some studies showing increases, while other studies have not. Similarly, HC emissions have shown increases in some studies, while other studies have shown reductions.

The unique characteristics of DMC must also be considered in terms of the utilization of DMC within the existing petroleum infrastructure. DMC is very miscible and soluble in diesel fuel,

which facilitates blending. DMC is a flammable liquid. It has a lower flashpoint than diesel fuel, but is safer than acetone, methyl acetate and methyl ethyl ketone from a flammability point of view. In terms of diesel-DMC mixtures, one issue is that these mixtures have a high critical solubility temperature value, which is the temperature where the two components of a mixture are no longer miscible and start to separate. This could cause problems in colder climates. DMC should be stored in a tight reservoir at a cool, dry, well-ventilated location away from moist air, plastics and resins. Carbonates are incompatible with cerium compounds, germanium, lead diacetate, magnesium, mercurous chloride, and silver nitrate. In terms of safety, DMC has a recommended industrial exposure (REL) limit of 100 ppm by inhalation over an 8-hour work day, which is similar to a number of common industrial solvents (Toluene, methyl ethyl ketone). DMC has also been exempted as a VOC chemical.

Some additional information would be useful in order to perform a complete assessment of potential impacts of widespread use of DMC as a transportation fuel, such as the assessment that would be needed under the CARB multimedia procedure. This would include a more detailed characterization of the impacts of DMC leaks or spills on the atmosphere, as well as liquid release on surface soil and ground water. In storing, distributing, and utilizing DMC, it is also important to understand the impacts of DMC on fuel system components, such as gaskets, seals, or other materials that could be subject to swelling or degradation. Some additional studies of material compatibility would be useful in better understanding these potential impacts.

### **Engine Dynamometer Testing Conclusions**

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. For this study, emission measurements were performed on 5%, 12.5%, 20%, and 30% DMC blends by volume. 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<sub>x</sub> 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 showed increases with the

DMC blends as a result to the lower energy content of DMC compared to diesel fuel. On the other hand, CO emissions showed clear reduction 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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