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UNIVERSITY OF CALIFORNIA  
RIVERSIDE

Emissions Benefits From Renewable Fuels and Other Alternatives for Heavy-Duty Vehicles

A Dissertation submitted in partial satisfaction  
of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Maryam Hajbabaei

August 2013

Dissertation Committee:

Dr. David R. Cocker III, Chairperson  
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Dr. Marko Princevac  
Dr. Akua Asa-Awuku

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The Dissertation of Maryam Hajbabaei is approved:

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Committee Chairperson

University of California, Riverside

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The text of Chapter two of this dissertation, in part or in full, is a reprint of the material as it appears in Environmental Science and Technology, Volume 46, Issue 16, Maryam Hajbabaei, Kent C. Johnson, Robert A. Okamoto, Alexander Mitchell, Marcie Pullman, and Thomas D. Durbin, Evaluation of the Impacts of Biodiesel and Second Generation Biofuels on NO<sub>x</sub> Emissions for CARB Diesel Fuels, Pages 9163–9173, Copyright (2012), with permissions from ACS Publications. The text of Chapter three of this dissertation, in part or in full, is a reprint of the material as it appears in SAE International Journal of Fuels and Lubricants, Volume 6, Issue 2, Maryam Hajbabaei, Kent C. Johnson, Robert A. Okamoto, ,

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## **Dedication**

I dedicate this work to my parents Ms. Ashrafalsadat Tabatabaei and Mr. Mahmood Hajbabaei, and my husband Dr. Seyedehsan Hosseini for their endless love, encouragement, and support.

## ABSTRACT OF THE DISSERTATION

Emissions Benefits From Renewable Fuels and Other Alternatives for Heavy-Duty Vehicles  
by

Maryam Hajbabaei

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering  
University of California, Riverside, August 2013  
Dr. David R. Cocker III, Chairperson

There is a global effort to expand the use of alternative fuels due to their several benefits such as improving air quality with reducing some criteria emissions, reducing dependency on fossil fuels, and reducing greenhouse gases such as carbon dioxide. This dissertation is focused on investigating the impact of two popular alternative fuels, biodiesel and natural gas (NG), on emissions from heavy-duty engines.

Biodiesel is one of the most popular renewable fuels with diesel applications. Although biodiesel blends are reported to reduce particulate matter, carbon monoxide, and total hydrocarbon emissions; there is uncertainty on their impact on nitrogen oxides ( $\text{NO}_x$ ) emissions. This dissertation evaluated the effect of biodiesel feedstock, biodiesel blend level, engine technology, and driving conditions on  $\text{NO}_x$  emissions. The results showed that  $\text{NO}_x$  emissions increase with 20% and higher biodiesel blends. Also, in this study some strategies were proposed and some fuel formulations were found for mitigating  $\text{NO}_x$  emissions increases with biodiesel. The impact of 5% biodiesel on criteria emissions specifically  $\text{NO}_x$  was also fully studied in this thesis. As a part of the results of this study, 5% animal-based biodiesel was certified for use in California based on California Air Resources Board emissions equivalent procedure.

NG is one of the most prominent alternative fuels with larger reserves compared to crude oil. However, the quality of NG depends on both its source and the degree to which it is processed. The current study explored the impact of various NG fuels, ranging from low methane/high energy gases to high methane/low energy gases, on criteria and toxic emissions from NG engines with different combustion and aftertreatment technologies. The results showed stronger fuel effects for the lean-burn technology bus.

Finally, this thesis investigated the impact of changing diesel fuel composition on the criteria emissions from a variety of heavy-duty engine technologies. Emissions from an average diesel fuel used throughout the U.S. were compared with a 10% aromatic, ultra-low sulfur diesel fuel used in California with more stringent air quality regulations. The results showed that the emerging aftertreatment technologies eventually eliminate the benefits of the lower aromatic content/higher cetane number diesel fuels.

## Table of Contents

Chapter One: Introduction .....	1
1.1. Chapter 2, 3, and 4: Comprehensive Study of Emissions from Biodiesel Blends .....	3
1.2. Chapter 5: Comprehensive Emissions Study from Natural Gas.....	9
1.3. Chapter 6: Comparison of Emissions from California Air Resources Board Qualified Diesel Fuels and Federal Diesel Fuels .....	10
1.4. References .....	13
Chapter Two: Evaluation of the Impacts of Biodiesel and Second Generation Biofuels on NO <sub>x</sub> Emissions for CARB Diesel Fuels .....	20
2.1. Abstract.....	20
2.2. Introduction .....	21
2.3. Experimental Procedures .....	25
2.3.1. Test Fuels.....	25
2.3.2. Engine Selection .....	26
2.3.3. Test Cycles.....	27
2.3.4. Test Matrix.....	28
2.4. Emissions Testing .....	29
2.5. Results .....	30
2.5.1. NO <sub>x</sub> Emissions.....	32

2.5.2. NO <sub>x</sub> Mitigation Results.....	37
2.6. Discussion .....	43
2.7. Acknowledgements.....	48
2.8. Disclaimer.....	48
2.9. References .....	49
Chapter Three: Evaluation of the Impacts of Biofuels on Emissions for a California Certified Diesel Fuel from Heavy-Duty Engines .....	57
3.1. Abstract.....	57
3.2. Introduction .....	58
3.3. Experimental Methods .....	61
3.4. Results and Discussion .....	65
3.4.1. PM Emissions .....	65
3.4.2. THC Emissions.....	70
3.4.3. CO Emissions .....	73
3.4.4. CO <sub>2</sub> Emissions.....	75
3.4.5. BSFC.....	78
3.5. Summary/Conclusions .....	84
3.6. Acknowledgements.....	85
3.7. References .....	86

Chapter Four: Impacts of Biodiesel Feedstock and Additives on Criteria Emissions from a Heavy-Duty Engine .....	90
4.1. Abstract.....	90
4.2. Introduction .....	91
4.3. Experimental Methods .....	96
4.3.1. Test Fuels and Test Engine.....	96
4.3.2. Test Cycle and Test Matrix .....	99
4.3.3. Emissions Testing.....	99
4.4. Results and Discussion .....	100
4.4.1. NO <sub>x</sub> Emissions .....	105
4.4.2. PM and SOF Emissions .....	109
4.4.3. THC Emissions.....	113
4.4.4. CO Emissions .....	116
4.4.5. CO <sub>2</sub> Emissions.....	119
4.4.6. Brake Specific Fuel Consumption.....	120
4.5. Conclusion.....	123
4.6. Acknowledgements.....	124
4.7. Disclaimer.....	125
4.8. References .....	126

Chapter Five: Impact of Natural Gas Fuel Composition on Criteria, Toxic, and Particle Emissions from Transit Buses Equipped with Lean Burn and Stoichiometric Engines.....	132
5.1. Abstract.....	132
5.2. Introduction .....	133
5.3. Experimental Procedures .....	138
5.3.1. Fuels.....	138
5.3.2. Test vehicles .....	139
5.3.3. Test Cycles and Measurement Protocol.....	141
5.3.4. Emission Testing and Analysis .....	141
5.4. Results and Discussion .....	143
5.4.1. NO <sub>x</sub> Emissions .....	143
5.4.2. THC, NMHC, and CH <sub>4</sub> Emissions .....	145
5.4.3. CO Emissions .....	151
5.4.4. Fuel Economy and CO <sub>2</sub> Emissions .....	152
5.4.5. PM Mass, Particle Number and Particle Size Distributions.....	155
5.4.6. NH <sub>3</sub> Emissions .....	161
5.4.7. Carbonyl Emissions.....	162
5.5. Conclusion.....	165
5.6. Acknowledgments.....	166

5.7. References .....	167
Chapter Six: Assessment of the Emissions from the Use of California Air Resources Board	
Qualified Diesel Fuels in Comparison with Federal Diesel Fuels.....	172
6.1. Abstract.....	172
6.2. Introduction .....	173
6.3. Experimental Procedures .....	175
6.3.1. Test Fuels.....	175
6.3.2. Engine and Vehicle Selection.....	176
6.3.3. Test Cycles and Test Matrix.....	178
6.3.4. Emissions Testing.....	179
6.4. Results .....	180
6.4.1. NO <sub>x</sub> Emissions .....	183
6.4.2. PM Emissions .....	186
6.4.3. THC Emissions.....	189
6.4.4. CO Emissions .....	191
6.4.5. CO <sub>2</sub> Emission.....	194
6.4.6. Fuel Consumption and Fuel Economy.....	196
6.5. Discussions and Conclusion .....	198
6.6. Acknowledgements .....	207

6.7. Funding Acknowledgement.....	207
6.8. Disclaimer.....	207
6.9. Reference .....	208
Chapter Seven: Conclusions .....	212
Appendix A.....	217
Appendix B.....	224
Appendix C.....	232

## List of Figures

Figure 2-1. NO <sub>x</sub> emissions results of biodiesel, renewable, and GTL diesel fuel blends, and CARB diesel fuel for 2006 Cummins ISM. Note: Since B5 testing was run out of the test sequence and CARB diesel was provided separately for B5 testing. CARB diesel emissions are presented in a different column (CARB diesel-B5) .....	31
Figure 2-2. NO <sub>x</sub> emissions results of biodiesel, renewable, and GTL diesel fuel blends, and CARB diesel fuel for 2007 MBE4000. Note: Since B5 testing was run out of the test sequence and CARB diesel was provided separately for B5 testing. CARB diesel emissions are presented in a different column (CARB diesel-B5) .....	32
Figure 2-3. Correlation between NO <sub>x</sub> emissions and density and cetane number of different fuel blends tested over the mitigation part of the study .....	42
Figure 3-1. PM emission results for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle for 2006 Cummins ISM .....	69
Figure 3-2. THC emission results for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle for 2006 Cummins ISM .....	72
Figure 3-3. CO <sub>2</sub> emission results for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle 2006 Cummins ISM engine .....	77

Figure 3-4. BSFC for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle 2006 Cummins ISM engine .....	80
Figure 4-1. Average NO <sub>x</sub> emission results for the preliminary and certification testing A) B5, B) B20 with additives.....	106
Figure 4-2. Average PM and SOF emission results for the preliminary and certification testing A) and B) B5, C) B20 with additives.....	112
Figure 4-3. Average THC emission results for the preliminary and certification testing A) B5 , B) B20 with additives.....	115
Figure 4-4. Average CO emission results for the preliminary and certification testing A) B5 , B) B20 with additives.....	118
Figure 4-5. Average CO <sub>2</sub> emission and BSFC results for the preliminary and certification testing A) B5, B) B20 with additives .....	122
Figure 5-1. Average NO <sub>x</sub> emissions from NG buses over the CBD .....	144
Figure 5-2(a-c). Average THC, NMHC, and CH <sub>4</sub> emissions from NG buses over the CBD .....	150
Figure 5-3. Average CO emissions from NG buses over the CBD .....	152
Figure 5-4(a-c). Average volumetric (a) and carbon balanced (b) fuel economy, and CO <sub>2</sub> emissions from NG buses over the CBD.....	154
Figure 5-5(a-b). Average PM mass and particle number emissions from NG buses over the CBD .....	158
Figure 5-6(a-d). Average particle size distributions from NG buses over the CBD .....	160
Figure 5-7. Average NH <sub>3</sub> emissions from NG buses over the CBD .....	162

Figure 5-8(a-b). Average formaldehyde and acetaldehyde emissions from NG buses over the CBD .....	164
Figure 6-1. Average NO <sub>x</sub> emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle.....	184
Figure 6-2. Average NO <sub>x</sub> emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle.....	186
Figure 6-3. Average PM emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle .....	188
Figure 6-4. Average PM emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle.....	189
Figure 6-5. Average THC emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle.....	190
Figure 6-6. Average THC emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle.....	191
Figure 6-7. Average CO emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle .....	192
Figure 6-8. Average CO emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle.....	193
Figure 6-9. Average CO <sub>2</sub> emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle .....	194
Figure 6-10. Average CO <sub>2</sub> emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle.....	196

Figure 6-11. Average BSFC results for all the engines over both the FTP cycle and 50-mph Cruise cycle.....	197
Figure 6-12. Average fuel economy for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle.....	198

## List of Tables

Table 2-1. Selected fuel properties.....	27
Table 2-2. Percentages changes form mitigation study blends relative to CARB and associated statistical p-values for 2006 Cummins ISM and 2007 MBE4000 .....	38
Table 3-1. Comparison of the results of several review studies on biodiesel emissions.....	60
Table 3-2. Selected fuel properties.....	62
Table 3-3. Test engines specification.....	63
Table 3-4. Percentages changes for biodiesel/renewable/GTL blends relative to CARB and associated statistical p-values for 2007 MBE4000 engine for different cycles.....	81
Table 3-5. Percentages changes for biodiesel/renewable/GTL blends relative to CARB and associated statistical p-values for 2006 Cummins ISM engine for different cycles .....	82
Table 4-1. Fuel properties of pure animal, WVO, and soy-based biodiesel, CARB reference fuel, B5-Animal, B5-WVO, and B20- Soy.....	98
Table 4-2. Emissions (g/bhp-hr) and BSFC (gal/bhp-hr) percentage differences between the B5 biodiesel blends and the CARB reference fuel for the preliminary and certification testing .....	102
Table 4-3. Emissions (g/bhp-hr) and BSFC (gal/bhp-hr) percentage differences between the B20 additive biodiesel blends and the CARB reference fuel for the preliminary and certification testing.....	103
Table 5-1. Main properties of the fuel gas blends .....	140
Table 6-1. Selected fuel properties.....	176

Table 6-2. Percentages changes for Federal Diesel blends relative to CARB for both engine/chassis dynamometer studies .....	182
Table 6-3. Emission factors and vehicle population in California .....	205

## List of Abbreviations

2-EHN	2-ethyl hexyl nitrate
ACES	Advanced Collaborative Emissions Study
BSFC	Brake Specific Fuel Consumption
CARB	California Air Resources Board
CBD	Central Business District
CCR	California Code of Regulations
CE-CERT	Center for Environmental Research and Technology
CFR	Code of Federal Regulations
CH <sub>4</sub>	Methane
CNG	Compressed Natural Gas
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
CPC	Condensation Particle Counter
CRC	Coordinating Research Council
CRTs	Continuously Regenerating Traps
DDC	Diesel Detroit Corporation
DMA	Differential Mobility Analyzer
DNPH	2,4-dinitrophenylhydrazine
DPF	Diesel Particulate Filter
DRI	Desert Research Institute
DTBP	di-tert-butyl peroxide
ECM	Engine Control Module
EEPS	Engine Exhaust Particle Sizer
EGR	Exhaust Gas Recirculation
EIA	Energy Information Administration
EMFAC	CARB Emissions FACTors
EPA	Environmental Protection Agency
EU	European Union
FAME	Fatty Acid Methyl Esters
FTP	Federal Testing Procedure
g/bhp-hr	grams per brake horsepower hour
gals/bhp-hr	gallons per brake horsepower hour
GGE	Gasoline Gallon Equivalent
GTL	Gas-to-Liquid
HC	Hydrocarbons

HD	Heavy Duty
HHDT	Heavy Heavy-duty Diesel Truck
HHV	High Heating Value
HPLC	High Performance Liquid Chromatograph
LCFS	Low Carbon Fuel Standard
LTC	Low Temperature Combustion
MCP	Maximum Combustion Potential
MEL	Mobile Emissions Laboratory
MN	Methane Number
NAAQS	National Ambient Air Quality Standards
NDRC	National Development Reform Commission
NExBTL	Neste Oil biomass-to-liquid
NG	Natural Gas
NGL	Natural Gas Liquids
NGV	Natural Gas Vehicle
NH <sub>3</sub>	Ammonia
NMHC	Non-methane Hydrocarbon
NO <sub>x</sub>	Nitrogen Oxides
NREL	National Renewable Energy Laboratory
NYB	New York Bus
OC	Oxidation Catalysts
OEM	Original Equipment Manufacturer
PAHs	Polycyclic Aromatic Hydrocarbons
PM	Particulate Matter
PN	Particle Number
SIP	State Implementation Plan
SMPS	Scanning Mobility Particle Sizer
SOF	Soluble Organic Fraction
TAC	Toxic Air Contaminant
TBHQ	tert-butyl hydroquinone
tcf	trillion cubic feet
TDL	Tunable Diode Laser
THC	Total Hydrocarbons
TWC	Three-way Catalyst
U.S.	United States
UC	University of California
UCTC	University of California Transportation Center
UDDS	Urban Dynamometer Driving Schedule

ULSD	Ultra Low Diesel Fuel
WN	Wobbe Number
WVO	Waste Vegetable Oil

## Chapter One: Introduction

The demand for energy continues to increase worldwide creating a need to diversify from conventional fossil fuels. The global energy demand is expected to increase approximately 30% in the decades between 2010 and 2030.<sup>1</sup> In recent years there has been an increased emphasis on expanding the use of alternative fuels. Apart from reducing dependency on fossil fuels, much of the effort to increase the use of alternative fuels has been motivated by the importance of reducing greenhouse gases emissions, such as carbon dioxide, in response to the increasing threat of global warming. In particular, studies has suggested that the global temperature rise through the end of the century will lead to changes in systems related to snow, ice, glacier, and frozen ground, hydrological system, water resources, coastal zones, and oceans.<sup>2</sup> Regulations to expand the use of alternative fuels have been implemented at the local, national, and regional levels to address these issues, including the European Union (EU) Renewable Energy Directive (2009/28/EC) in Europe,<sup>3</sup> the Energy Policy Act in the United States (U.S.),<sup>4</sup> and Low Carbon Fuel Standard (LCFS) in California<sup>5</sup>.

An important element of bringing vast quantities of new fuels to the marketplace is understanding their impacts on emissions and air quality. On-road vehicles make a significant contribution to local, national, and global emissions inventories.<sup>6-8</sup> Diesel engines are the primary contributors to the emissions inventory for both particulate matter (PM) and oxides of nitrogen ( $\text{NO}_x$ ) and have been the target of regulations for a number of years.<sup>9</sup>  $\text{NO}_x$  can contribute to ground level ozone and secondary PM formation, and it can also have direct health impacts. Associations between ambient PM and adverse health effects have also been well documented in numerous studies.<sup>10,11</sup> Although alternative fuels, such as

natural gas (NG) and biodiesel, are generally thought to reduce vehicle emissions, as these fuels start to represent a larger fraction of the fuels market, further study is needed to evaluate if there are situations where these fuels could create emissions disbenefits. For example, while biodiesel generally reduces PM, total hydrocarbons (THC), and carbon monoxide (CO), it has shown a tendency to increase NO<sub>x</sub> emissions.<sup>12-16</sup> Similarly, while many studies have shown reductions in emissions for natural gas vehicles (NGVs), emissions for NGVs can sometimes be higher than those from conventional vehicles if the vehicle is not operating correctly or if NG with a widely varying composition is used.<sup>17-21</sup> In recent years, more advanced diesel engine aftertreatment technologies have also been introduced and newer NG engine technologies,<sup>17,22</sup> so it is also important to understand how emissions inventories will change as these new technologies become implemented into the on-road fleet along with higher levels of alternative fuels.

This dissertation is focused on investigating the impact of using two alternative fuels, biodiesel and NG, and varying conventional diesel fuel formulation in improving air quality by reducing exhaust emissions from heavy-duty engines and vehicles that comprise a large portion of on-road vehicles. The first three chapters (chapter two, chapter three, and chapter four) of this thesis are a summary of the results of one of the most comprehensive emissions study of biodiesel blends to date. This study was performed in two separate test campaigns. Chapter five is a summary of the results of a study that was conducted to investigate the impact of NG fuel composition on emissions from transit buses with several lean burn engines with oxidation catalysts and one stoichiometric combustion engine with a three way catalyst. Chapter six is a summary of a study that was performed to compare the regulated

emissions of a variety of diesel engine technologies from two different diesel fuels, including one regular diesel fuel used throughout U.S., and one equivalent 10% aromatic ultra-low sulfur diesel fuel used in California.

### **1.1. Chapter 2, 3, and 4: Comprehensive Study of Emissions from Biodiesel Blends**

In recent years, governmental agencies around the world have implemented legislation that targets increasing the use of renewable fuels in the transportation sector. In the U.S., the energy independence and security act of 2007 targets the production of 36 billion gallons of biofuels in the U.S. (mostly ethanol) by 2022.<sup>4</sup> The EU has implemented several government mandates, such as the EU Renewable Energy Directive (2009/28/EC), which requires at least 10% of each Member State's transport fuel use come from renewable sources (including biofuels).<sup>3</sup> In Asia, several regulations have recently been approved and implemented. In Japan, the government announced a target to increase the annual production of biofuels from 175,000 cubic meters in 2010 to 500,000 cubic meters in 2017.<sup>23</sup> In China, in August 2007, the National and Development Reform Commission (NDRC) announced a Medium and Long Term Development Plan for Renewable Energy. In India, a National Policy on Biofuels was approved in September 2008, which mandates a 20% share of biodiesel and bioethanol should be blended with diesel and gasoline by 2017.<sup>24</sup> On a more regional level, California, has implemented the LCFS in 2011 to promote the reduction of greenhouse gas emissions by targeting a reduction in carbon intensity in the transportation sector by 10% by 2020.<sup>5</sup>

Biodiesel, composed of Fatty Acid Methyl Esters (FAME), is the most widely used renewable fuel for diesel engines. Commercially, biodiesel is produced by transesterification of triglycerides, the main constituent of vegetable oils, animal fats, and waste cooking oils, with an alcohol in the presence of an alkaline liquid catalyst, usually sodium or potassium methoxide.<sup>25</sup> Biodiesel has several significant benefits aside from its value as a renewable fuel. For instance, biodiesel, either in its pure form or when blended with regular diesel fuel, can be used in existing diesel engines with no or minor engine modifications.<sup>16,26–28</sup> Biodiesel is currently used at a 7% level in diesel fuel throughout Europe.<sup>29</sup> Biodiesel use and production in the U.S. has also expanded considerably over the past decade, from 2 million gallons in 2000 to 1.1 billion gallons in 2011.<sup>30</sup> Several studies have shown that biodiesel blends reduce PM, CO, and total unburned hydrocarbon (THC) emissions compared to diesel fuel.<sup>12,13,25,31–34</sup> Biodiesel blends have been shown to reduce the overall life cycle emissions of CO<sub>2</sub>, when evaluated using a total carbon life cycle analysis.<sup>16,26,34</sup> A drawback in using biodiesel blends, however, is the potential to increase NO<sub>x</sub> emissions compared to ultra-low sulfur diesel fuel (ULSD).<sup>12,13,28,31,33–35</sup>

Although the impacts of biodiesel on NO<sub>x</sub> emissions may be small on a percentage basis, and difficult to quantify, this remains an important issue in regions and cities when poor air quality is a persistent problem. In California, for example, many of the urban areas do not meet the National Ambient Air Quality Standards (NAAQS) and have some of the worst pollution levels in the country for ozone and PM.<sup>36</sup> In order to meet the NAAQS standards, California has developed a State Implementation Plan (SIP) that specifies the baseline emissions levels and the impacts of control strategies that will be used to reduce emissions

over different periods of time.<sup>37</sup> The majority of diesel fuel use and diesel pollution production in California is from heavy-duty trucks for goods movement and transport, and for this reason, reductions of emissions from heavy-duty engines have been a focus. In an effort to address air quality concerns, California has developed diesel fuel requirements that are much more stringent than those in other parts of the U.S. Similar requirements are also in place in Texas, which also has a large population of people living in areas that do not meet the NAAQS.<sup>38,39</sup> Although biodiesel tends to increase NO<sub>x</sub> emissions and decrease emissions of other pollutants such as PM, THC, and CO, CARB regulatory efforts are structured such that any new fuels must not increase emissions of any criteria pollutants, even if there is a decrease in emissions of other pollutants. This is due in part to maintaining the provisions set forth in the SIP, as well as to ensure there is no “back sliding” of emissions reductions already put into place.

In recent years, many researchers have studied the impact of biodiesel blends on NO<sub>x</sub> emissions.<sup>15,16,40,41</sup> Many of these studies have shown increases in NO<sub>x</sub> emissions, although this trend is not consistent over all studies and all conditions.<sup>12–14,16,35</sup> Researchers have identified a variety of factors that could contribute to increased NO<sub>x</sub> emissions for biodiesel.<sup>25,27,28</sup> Recent studies have suggested that the impacts of biodiesel on NO<sub>x</sub> emissions is probably best explained by a combination of factors that couple together differently under different conditions. Eckerle et al. suggested that both fundamental combustion effects, driven by fuel chemistry and fluid dynamics, and the effects of operating on lower energy content biodiesel must be considered to understand the impact of biodiesel on NO<sub>x</sub>. They separated the combustion effect into flame temperature effects and ignition delay effects.<sup>42</sup>

For the fundamental combustion effects, they emphasized importance of the double bonds in biodiesel correlating with higher adiabatic flame temperatures, which can enhance  $\text{NO}_x$  formation through thermal (Zeldovich)  $\text{NO}_x$  formation mechanism had previously been suggested by Banweiss et al.<sup>43,44</sup> For the engine control effects, they evaluated the impact of increasing fuel volumetric flow rate needed for lower energy biodiesel on air-fuel ratio controls, exhaust gas recirculation (EGR) rate, and injection pressure and timing. Mueller et al. suggested that the presence of oxygen in biodiesel can also contribute to charge-gas mixtures that are closer to stoichiometric at ignition and in the standing premixed autoignition zone near the flame lift-off length. This in turn can lead to higher local and average in-cylinder temperatures, lower radiative heat losses, and a shorter, more advanced combustion event, which would all contribute to increased thermal  $\text{NO}_x$  emissions.<sup>44,45</sup> The importance of reduced radiant heat losses during combustion due to a reduction of PM emissions with biodiesel, and the corresponding higher combustion temperatures and higher  $\text{NO}_x$  emissions, has also been suggested previously by Cheng et al.<sup>45,46</sup> Mueller et al. also found that although adiabatic flame temperature differences may contribute to  $\text{NO}_x$  differences, it did not appear to play a primary role in this regard.<sup>45</sup> In older engine technologies with pump line fuel injection systems,  $\text{NO}_x$  increases have been associated with the higher bulk modulus of biodiesel, which leads to a more advanced injection timing, which in turn increases fuel residence time and heat release near top dead center and raises the combustion temperature.<sup>47</sup> While studies investigating the impact of biodiesel blends on emissions, and specifically  $\text{NO}_x$ , are extensive and diverse, such studies have often been limited in terms of the number of engines and test replicates, with many of these studies focusing mainly on diesel fuels with relatively high sulfur and aromatic contents compared to

the ones used in areas with more stringent air quality regulations, such as California and Texas.<sup>12,15,16</sup>

The chapter two and three of this thesis is part of a larger program that was conducted by California Air Resource Board, as a part of its effort to identify the need for additional regulations to facilitate the introduction of larger volumes of renewable fuels into use. This is one of the largest studies to date on biodiesel emissions impacts. One of the main focuses of this larger research study was on understanding and mitigating any impact that biodiesel has on NO<sub>x</sub> emissions from diesel engines for CARB-like diesel fuels, or diesel fuels with properties consistent with those needed to meet CARB diesel fuel requirements. The focus of chapters two and three of this thesis is on the most extensive part of the engine dynamometer testing, which was conducted on two on-road, heavy-duty diesel engines. This included a test matrix incorporating hundreds of tests and long term replication. The test fuels included a baseline CARB-certified diesel fuel, biodiesel blends produced from two different feedstocks (one soy-based and one animal-based), and a gas-to-liquid (GTL) and a renewable diesel fuel, with blend levels from 5% to 100%. Chapters two and three review the results from this heavy-duty engine dynamometer study, and discuss these results and their implications in the broader context of research on emissions from biofuels. Chapter two focuses on the impacts of biodiesel on NO<sub>x</sub> emissions. In this chapter, a range of strategies were also evaluated for the mitigation of any potential NO<sub>x</sub> impacts in this chapter. Chapter three summarizes the results of the other emission components, including PM, THC, CO, and CO<sub>2</sub>, and brake specific fuel consumption (BSFC), from the same study.

Chapter four expands upon the work described in chapter two and three to more extensively study emissions from low level biodiesels blends and additives. This study explores the emissions impacts of different B5 biodiesel blends and B20 with additive blends under CARB's procedures for qualifying emissions equivalent diesel fuel formulations. The results from chapters two and three showed that B20 and higher biodiesel blends would likely increase NO<sub>x</sub> emissions in CARB diesel fuels. However, the results were less definitive at lower blend levels such as B5. These results also showed that the impacts of NO<sub>x</sub> increases with biodiesel could be mitigated with combinations of blends with renewable and gas-to-liquid (GTL) diesel fuels, or with additives, such as di-tert-butyl peroxide (DTBP). The use of additives, in particular, has also shown some success in other studies, and could represent a viable and cost effective pathway to achieving NO<sub>x</sub> neutral biodiesel blends.<sup>48,49</sup> The emissions equivalent diesel certification procedure is robust in that it requires at least twenty replicate tests on the reference and candidate fuels, providing the ability to differentiate small differences in emissions. For this study, preliminary tests were performed on biodiesel blends at a 5% concentration by volume (B5) prepared from three different methyl esters, including an animal fat methyl ester, a soybean oil methyl ester, and a waste vegetable oil (WVO) methyl ester. In addition, higher biodiesel blends made at a 20% concentration by volume (B20) with soybean oil methyl ester and treated with five different additive combinations were evaluated. Full certification tests were then performed on two of the B5 fuels, the B5-animal and B5-WVO, and one of the B20-soy with additive blends.

## **1.2. Chapter 5: Comprehensive Emissions Study from Natural Gas**

NG is one of the most prominent alternative fuels with significantly larger reserves than crude oil, and also the potential for air quality benefits in vehicles.<sup>50</sup> In recent years, there have been dramatic changes in the NG market due to the rapid development of horizontal drilling and hydraulic fracturing. Such advanced techniques have unlocked vast reserves of oil and gas trapped underneath sedimentary rocks or shales. The U.S. Energy Information Administration (EIA) anticipates U.S. NG production to continue to expand into the future, growing from levels of 23.5 quadrillion Btu in 2011 to a projected 33.9 quadrillion Btu in 2040, representing a sizable 44% increase.<sup>51</sup> Shale gas production, which already accounted for 23% of total U.S. NG production in 2010, is expected to be the primary driver of this expansion, with shale gas production going from 6.8 trillion cubic feet (tcf) in 2011 to 13.6 tcf in 203.<sup>52</sup>

The quality of NG depends on both its source and the degree to which it is processed. Natural gas can be produced from oil fields (termed associated gas) or from gas fields (termed non-associated gas). Associated gas is typically higher in heavier hydrocarbons, which gives the gas a higher Wobbe Number (WN) and a lower Methane Number (MN). Associated gas is often processed using techniques such as refrigeration, lean oil absorption, and cryogenic extraction to recover valuable natural gas liquids (NGLs), such as ethane, propane, butanes, pentanes and hexanes plus, for other uses.<sup>53,54</sup> Traditional North American gas from Texas, for example, is often processed to recover feedstock for chemical plants. This process lowers the WN and increases the MN of the resulting NG stream. As NG production continues to increase, it is likely that a wider range of NG compositions could be

introduced into the marketplace, either due to different sources of production or perhaps a reduced emphasis on recovering NGLs from NG if the economics for these secondary products change. This could lead to NG with higher WNs and lower MNs being fed into the pipeline, which would likewise result in a pipeline gas with a higher WN and lower MN.

The objective of the chapter five of this thesis is to evaluate the impact of NG composition on the exhaust emissions of heavy-duty NG vehicles. This study focuses on transit buses, a category of heavy-duty vehicles that warrants attention for controlling NO<sub>x</sub> and PM emissions due to the fact that they operate primarily in populated urban and suburban settings. For this study, three NG transit buses were tested on a range of six different test gases over the CBD cycle. In addition to the regulated emissions and fuel economy, ammonia (NH<sub>3</sub>), carbonyl compounds, and particle number emissions were also evaluated. Information from this study on the impact of changing NG composition on emissions can be used for regulatory development, to ensure new NG compositions do not have an adverse impact on air quality, and to evaluate the viability of using a broader mixture of NG blends in transportation applications.

### **1.3. Chapter 6: Comparison of Emissions from California Air Resources Board Qualified Diesel Fuels and Federal Diesel Fuels**

Regulations to control diesel emissions have targeted both the engine technology as well as the diesel fuels used in the engines. California has a number of metropolitan areas that remain in nonattainment status for ozone and particulate matter, and the importance of improving air quality throughout California is well documented.<sup>55</sup> In California, diesel fuel

regulations mandate that fuels sold in the state must meet the requirement of 10% or less aromatic hydrocarbon content, or show emissions that are equivalent to a 10% aromatic reference fuel.<sup>56</sup> The development of the California diesel fuel regulations was based on several earlier studies that showed that certain fuel parameters such as aromatics, cetane number, and sulfur content can have an important impact on diesel emission levels. This included the Coordinating Research Council Project VE-1,<sup>57,58</sup> which was the main focus of this earlier analysis, as well as other studies, such as those from Chevron and Caterpillar/Mobil.<sup>59,60</sup> The California diesel fuel regulations are the most stringent in the United States, and CARB has estimated that implementing these regulations has resulted in emissions reductions of 7% for NO<sub>x</sub> and 25% for PM relative to pre-regulatory diesel fuel.<sup>61</sup> Air toxics, such as polyaromatic hydrocarbons and benzene, are also reduced.

Over the period of time since the California diesel fuel regulation was put in place, diesel engine technology has evolved considerably. Major studies have been conducted within the U.S.<sup>62–66</sup> Japan<sup>67,68</sup> and Europe<sup>69</sup> to examine the impacts fuel properties on emissions with changing engine technology, and several reviews have been conducted by different authors.<sup>34,70–74</sup> Based on his analysis, Hochhauser suggested that reductions in density and polyaromatic compounds, as opposed to total aromatics, lead to reductions in NO<sub>x</sub> and/or PM, although the existing data is complicated by a lack of orthogonality among variables, a small number of engines/vehicles, and differences in test cycles in many studies.<sup>75</sup> The actual impact of CARB diesel fuels on in-use diesel emissions has not been extensively studied, however. New engines are also now equipped with exhaust gas recirculation (EGR); diesel particulate filters (DPFs) to control PM, as of 2007; and, as of 2010, additional

aftertreatment to further control NO<sub>x</sub> emissions. Additionally, Federal diesel fuels have also changed, as ultralow sulfur levels (15 ppmw) have now been implemented nationwide to facilitate the use of these aftertreatment devices. As technology for diesel engines and fuels continue to evolve, it is important to understand and quantify the continuing and future impact that CARB diesel fuel has on controlling diesel emissions.

The chapter six of this thesis is an evaluation between California and federal diesel fuels to provide a better understanding of the impact of CARB diesel fuel in-use in the California heavy-duty truck fleet. The test program includes both engine dynamometer testing and heavy-duty chassis dynamometer testing. The engine dynamometer testing provides a comparison between the different fuels under more controlled conditions. Engine dynamometer testing was conducted on 3 engines over the Federal Test Procedure (FTP) and CARB 50-mph cruise cycles. The heavy-duty chassis dynamometer testing better characterizes in-use conditions, and included a wider range of engine technologies, from the latest technologies with aftertreatment for either PM and/or NO<sub>x</sub> to older technologies, where the fuel benefits would likely be more significant. Ten vehicles were tested over the CARB 50-mph cruise cycle for the chassis dynamometer testing. A total of 3 fuels were tested, including a CARB-certified diesel fuel and 2 federal diesel fuels. This chapter summarizes the results of this program.

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## **Chapter Two: Evaluation of the Impacts of Biodiesel and Second Generation Biofuels on NO<sub>x</sub> Emissions for CARB Diesel Fuels**

### **2.1. Abstract**

The impact of biodiesel and second generation biofuels on nitrogen oxides (NO<sub>x</sub>) emissions from heavy-duty engines was investigated using a California Air Resources Board (CARB) certified diesel fuel. Two heavy-duty engines, a 2006 engine with no exhaust aftertreatment, and a 2007 engine with a diesel particle filter (DPF), were tested on an engine dynamometer over four different test cycles. Emissions from soy- and animal-based biodiesels, a hydrotreated renewable diesel, and a gas to liquid (GTL) fuel were evaluated at blend levels from 5 to 100%. NO<sub>x</sub> emissions consistently increased with increasing biodiesel blend level, while increasing renewable diesel and GTL blends showed NO<sub>x</sub> emissions reductions with blend level. NO<sub>x</sub> increases ranged from 1.5% to 6.9% for B20, 6.4% to 18.2% for B50, and 14.1% to 47.1% for B100. The soy-biodiesel showed higher NO<sub>x</sub> emissions increases compared to the animal-biodiesel. NO<sub>x</sub> emissions neutrality with the CARB diesel was achieved by blending GTL or renewable diesel fuels with various levels of biodiesel or by using di-tert-butyl peroxide (DTBP). It appears that the impact of biodiesel on NO<sub>x</sub> emissions might be a more important consideration when blended with CARB diesel or similar fuels, and that some form of NO<sub>x</sub> mitigation might be needed for biodiesel blends with such fuels.

## 2.2. Introduction

The development and implementation of renewable and sustainable fuels for transportation applications is a critical element in meeting a number of different environmental and other challenges. The transportation sector is one of the largest sources of manmade carbon dioxide (CO<sub>2</sub>) emissions, which comprise the largest component of greenhouse gas inventories and can lead to global climate change.<sup>1</sup> There is also a need to diversify from fossil fuel resources, which will not be sustainable as a long term source of energy. The importance of these issues is further emphasized by the continuing expansion of transportation fuel use in less developed countries and areas, and associated projections that the use of transportation fuels will continue to increase going into the foreseeable future.<sup>2</sup> In the face of these issues, governmental regulations have been, and are being developed, worldwide to promote the use of increasing levels of biofuels, which can be produced from sustainable sources and can reduce CO<sub>2</sub> emissions when a complete carbon life cycle is considered. These regulations are being developed on a multinational level, such as the European regulations,<sup>3</sup> on a national level, such as the United States (U.S.) Energy Independence Act of 2007 and the associated renewable fuels standard,<sup>4</sup> and on a regional or state level, such as the California Air Resources Board's (CARB) Low Carbon Fuel Standard (LCFS)<sup>5</sup>.

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 a 7% level in diesel fuel throughout Europe.<sup>6</sup> Biodiesel use and production in the U.S. has expanded considerably over the past decade,<sup>7</sup> from 2 million gallons in 2000

to 1.1 billion gallons in 2011.<sup>8</sup> Studies have shown that biodiesel generally reduces carbon monoxide (CO), particulate matter (PM), and total hydrocarbons (THC) emissions compared to conventional diesel fuel.<sup>9-13</sup> It has also been reported in many studies, however, that average nitrogen oxides (NO<sub>x</sub>) emissions from biodiesel blends can increase with increasing biodiesel content. Although the impact of biodiesel on NO<sub>x</sub> emissions has been studied for many years, there is still uncertainty as to how prevalent this effect is, and the specific factors that might be contributing to biodiesel NO<sub>x</sub> increases, especially with newer engines.<sup>9,11,12,14-19</sup> The U.S. Environmental Protection Agency (EPA) conducted two comprehensive assessments of the impacts of biodiesel on emissions.<sup>9,20</sup> In their initial analysis, they estimated that a soy-based biodiesel at a B20 level would increase NO<sub>x</sub> emissions 2.0% compared to an average Federal base fuel, although there was considerable scatter in the data.<sup>9</sup> They found a similar increase of 2.2% in their follow up study.<sup>20</sup> McCormick et al. and Hoekman et al. also conducted reviews of biodiesel NO<sub>x</sub> impacts.<sup>10-12,21</sup> McCormick et al. found that on average there was either no net effect for B20, or there was at most a very small effect.<sup>11,21</sup> Hoekman et al. looked at a number of heavy/medium-duty and light-duty engine and chassis dynamometer studies and found biodiesel NO<sub>x</sub> impacts to be small, and inconsistent across all engine types, operating modes, fuel compositions, and other parameters.<sup>10,12</sup>

Although the impacts of biodiesel on NO<sub>x</sub> emissions may be small on a percentage basis, and difficult to quantify, this remains an important issue in regions and cities when poor air quality is a persistent problem. In California, for example, many of the urban areas do not meet the National Ambient Air Quality Standards (NAAQS) and have some of the worst

pollution levels in the country for ozone and PM.<sup>22</sup> In order to meet the NAAQS standards, California has developed a State Implementation Plan (SIP) that specifies the baseline emissions levels and the impacts of control strategies that will be used to reduce emissions over different periods of time.<sup>23</sup> The majority of diesel fuel use and diesel pollution production in California is from heavy-duty trucks for goods movement and transport, and for this reason, reductions of emissions from heavy-duty engines have been a focus. In an effort to address air quality concerns, California has developed diesel fuel requirements that are much more stringent than those in other parts of the U.S. Similar requirements are also in place in Texas, which also has a large population of people living in areas that do not meet the NAAQS.<sup>24,25</sup> Although biodiesel tends to increase NO<sub>x</sub> emissions and decrease emissions of other pollutants such as PM, THC, and CO, CARB regulatory efforts are structured such that any new fuels must not increase emissions of any criteria pollutants, even if there is a decrease in emissions of other pollutants. This is due in part to maintaining the provisions set forth in the SIP, as well as to ensure there is no “back sliding” of emissions reductions already put into place.

The impacts of biodiesel on NO<sub>x</sub> emissions for diesel fuels that are stringently regulated, such as CARB diesel, have not been as extensively studied as for other fuels used throughout the United States. The EPA analysis did include some information on “cleaner” base fuel diesels, which the EPA defined as diesel fuels meeting the CARB requirements for sale in California, or diesel fuels with cetane numbers greater than 52, aromatic contents less than 25 vol.%, and specific gravities less than 0.84. The EPA analysis indicated that the NO<sub>x</sub> impacts could be greater for “clean” diesel fuels than those for the average U.S. Federal

diesel fuel, but data were more limited in this area.<sup>9</sup> To date, information on biodiesel impacts for CARB-like diesel fuels has generally been isolated to studies conducted on small numbers of engines/vehicles, engines that are not representative of in-use engines, e.g., single cylinder engines, or with insufficient replication/precision to accurately quantify the true impact of biodiesel on NO<sub>x</sub> emissions. The importance of understanding the true emissions impacts of biodiesel for a full range of base fuels will likely become even more important, as the EPA is currently planning further tightening of ambient air quality standards, which will place increased emphasis on urban air quality and also increase the number of urban areas failing to meet the NAAQS.<sup>26</sup>

This study is a part of a larger program that was conducted by CARB, in conjunction with the University of California (UC) at Riverside, UC Davis, and others, as a part of its effort to identify the need for additional regulations to facilitate the introduction of larger volumes of renewable fuels into use.<sup>27</sup> This is one of the largest studies to date on biodiesel emissions impacts. The focus of this larger research study was on understanding and mitigating any impact that biodiesel has on NO<sub>x</sub> emissions from diesel engines for CARB-like diesel fuels, or diesel fuels with properties consistent with those needed to meet CARB diesel fuel requirements, and understanding the potential impacts of biodiesel on toxic emissions and health effects. The larger study included engine dynamometer testing, chassis dynamometer testing, and testing of off-road engines on a range of biodiesel and renewable diesel fuels. The focus of this paper is on the most extensive part of the engine dynamometer testing, which was conducted on two on-highway, heavy-duty diesel engines, with a primary focus on understanding biodiesel NO<sub>x</sub> impacts. This included a test matrix incorporating hundreds

of tests and long term replication. The test fuels included a baseline CARB-certified diesel fuel, biodiesel blends produced from two different feedstocks (one soy-based and one animal-based), and a gas-to-liquid (GTL) and a renewable diesel fuel, with blend levels from 5% to 100%. A range of strategies were also evaluated for the mitigation of any potential  $\text{NO}_x$  impacts. This paper reviews the results from this heavy-duty engine dynamometer study, and discusses these results and their implications in the broader context of research on emissions from biofuels.

## **2.3. Experimental Procedures**

### **2.3.1. Test Fuels**

Five primary fuels including a California Air Resources Board (CARB)-certified diesel fuel as the baseline fuel, biodiesels made from two feedstocks (one soy-based and one animal-based), a renewable diesel fuel, and a GTL diesel were used. The biodiesel fuels were selected to provide a range of properties that are representative of typical feedstocks, but also representing different characteristics of biodiesel in terms of cetane number and degree of saturation. Soy-based biodiesel is typically composed of ~17% saturated compounds, while animal or tallow-based biodiesel is typically composed of ~48% saturated compounds.<sup>28</sup> The degree of saturation is typically characterized by iodine number. Although iodine number was not measured for the biodiesel feedstocks in this study, previous studies have shown typical iodine values of 65.9 mg  $\text{I}_2$ /100 g FAME for animal-based or tallow biodiesel and 125.5 mg  $\text{I}_2$ /100 g FAME for soy-based biodiesel.<sup>28</sup> The renewable diesel was a Neste Oil biomass-to-liquid (NExBTL) diesel fuel.<sup>29–34</sup> This fuel is produced from renewable

biomass sources, such as fatty acids from vegetable oils and animal fats, via a hydro-treating process. The biomass source used for the renewable diesel in this study was primarily palm oil. The GTL diesel fuel was a Fischer-Tropsch diesel provided by a petroleum company. A summary of selected properties for the neat fuels is provided in Table 2-1, with a more detailed listing of the fuel properties provided in Table A-1 of the Appendix A. The soy-based and animal-based biodiesels were blended with the CARB diesel at levels of B5, B20, B50, as well as using the straight B100. The renewable and GTL diesel fuels were used as neat fuels (R100/GTL100) and blended with CARB diesel at 20% and 50% levels. Additional blends with various combinations of these fuels, as well as additives, were also made for the NO<sub>x</sub> mitigation portion of the study.

### **2.3.2. Engine Selection**

The engines for the heavy-duty engine testing were selected from 2 model year categories; 2002-2006 and 2007-2009. The 2002-2006 engine was selected since emissions inventory modeling using the CARB Emissions FACTors (EMFAC) model showed that these engines will represent an important contribution to the California emissions inventory from the present through 2017. The 2007 engine model year represents the latest technology that was available at the time of testing. The 2002-2006 engine was a 2006 model year, 10.8 L, Cummins ISM engine. The engine selected from the 2007-2009 model year category was a 2007, 12.8 L, Detroit Diesel MBE 4000, which was equipped with an original equipment manufacturer (OEM) diesel particulate filter (DPF). Both engines were equipped with exhaust gas recirculation (EGR) and common-rail fuel injection systems. The specifications of both engines are provided in Table A-2 in the Appendix A.

Table 2-1. Selected fuel properties

	Test Method	CARB diesel	Renewable diesel	GTL	Soy-biodiesel	Animal-biodiesel
API gravity (@ 60°F)	D287-82	39.3	51.3	48.4	29	28.5
Density (@ 60°F)		0.827	0.771	0.786	0.881	0.881
Aromatics, mass %	D5186-96	18.7	0.4	0.5	NA	NA
PAHs, mass %	D5186-96	1.5	0.1	<0.27	NA	NA
Cetane number	D613-94	55.8	72.3	74.8	47.7	57.9
Sulfur, ppm	D5453-93	4.7	0.3	0.9	0.7	2
Carbon, % Wt.		86.1	84.83	NA	76.72	75.89
Hydrogen, %Wt.		13.67	15.14	NA	11.97	12.22
Oxygen, % Wt.		0.23	0.03	NA	11.31	11.89
C/H Ratio		6.3	5.6	NA	6.4	6.2
Cloud Point, °C	D2500	-6.6	-27.1	-1	0	12.5
Pour Point, °C	D-97	-12	-47	-6	NA	NA
Distillation, °F	D86-96					
ibp		337	326	419	NA	NA
10%		408	426	482	NA	NA
50%		519	521	568	NA	NA
90%		612	547	648	NA	NA
ep		659	568	673	NA	NA
Distillation, T90 AET, °C	D1160	NA	NA	NA	350	347.5

NA = either Not Available or Applicable

IQT = ignition quality test derived cetane numbe

### 2.3.3. Test Cycles

The test cycles included the standard Federal Testing Procedure (FTP) for heavy-duty engines and three other cycles derived from chassis dynamometer data. The other cycles included a lightly loaded Urban Dynamometer Driving Schedule (UDDS) cycle, a 40 mile per hour (mph) CARB heavy heavy-duty diesel truck (HHDDT) cruise cycle, and a 50 mph CARB HHDDT cruise cycle. The different cycles were selected to provide a range of operating conditions and operational loads. The engine dynamometer cycles were developed from engine operating parameters that were obtained by operating a vehicle with the specific

test engine on a chassis dynamometer while recording the engine's operational parameters (e.g. engine speed and torque) from the Engine Control Module (ECM), or from previous studies in the literature. The development of these engine dynamometer cycles is discussed in greater detail by Durbin et al.<sup>27</sup>

#### **2.3.4. Test Matrix**

A randomized test matrix with long range replication over the course of testing was developed for this program. The detailed test matrix is included in the Appendix A (see Tables A-3 and A-4). The randomization included changing various blends and cycles every day throughout the testing and replicate tests of the CARB base fuel in between testing of other fuel blends. The base number of tests on each fuel/cycle combination was six. Analyses obtained from EPA indicated that seven replicates would be needed to detect a significant difference 90% of the time between the Base and B20 fuels at the 0.05 significance level, based on an expected percentage difference of 2% in NO<sub>x</sub> emissions and a coefficient of variation for the NO<sub>x</sub> measurement of 1%.<sup>35,36</sup> Preliminary testing showed that 6 iterations were more than sufficient to see the differences between the CARB diesel and the soy-based B20 blend. In some cases, for the testing of the soy-based biodiesel on the Cummins engine, fewer than six tests were obtained due to issues with the temperature of the water controlling the turbocharger inlet air temperature.<sup>27</sup> For the 2007 MBE4000 engine with a DPF, a regeneration was performed with each fuel change. This engine goes into a regeneration enable mode after 10,000 seconds of operation that could cause random regenerations to occur over the course of the testing, which would have interfered with the consistent operation needed for fuels testing. The regenerations were set up manually with a

Cummins software package to simulate an idle regeneration. It should be noted that while the elimination of regenerations from the test matrix creates some limitations in extrapolating the results to in-use emissions, the complexity of designing a study to characterize fuel effects under regeneration conditions was beyond the scope of this study.<sup>37</sup> In general, the soy-based, animal-based and renewable diesel fuels were tested over UDDS, FTP and 50 mph Cruise cycles, while the GTL fuel was only tested on the FTP. The 40 mph cruise cycle was only utilized for the soy-based biodiesel on the 2006 Cummins engine. Also, we have excluded the 50 mph cruise results for the 2006 Cummins engine from this paper since this engine did not show stable operation on this test cycle. This phenomena is discussed in greater detail in Durbin et al.<sup>27</sup> Since the expected NO<sub>x</sub> impact for the B5 should be less than that of B20, and hence more difficult to statistically differentiate from the testing variability, the B5 blend was run outside the main sequence in a more consolidated sequence. The B5 tests were run over the 40 mph Cruise cycle for the soy-based biodiesel for the 2006 Cummins engine, the FTP for the animal-based biodiesel for the 2006 Cummins engine, and the FTP for both B5 blends for the 2007 MBE4000 engine.

## **2.4. Emissions Testing**

The engine emissions testing was performed at the University of California at Riverside's College of Engineering-Center for Environmental Research and Technology's (CE-CERT) heavy-duty engine dynamometer laboratory. This engine dynamometer test laboratory is equipped with a 600 hp General Electric DC electric engine dynamometer. The emissions measurements were made from a dilution tunnel in CE-CERT's heavy-duty Mobile Emissions Laboratory (MEL) trailer.<sup>38,39</sup> Standard emissions measurements of NO<sub>x</sub>

emissions were measured using a chemiluminescent analyzer. The intake air humidity and temperature were controlled to provide a humidity correction near 1 for all tests. THC, CO, PM, and CO<sub>2</sub> were also measured using the standard analyzers.<sup>38,39</sup>

## **2.5. Results**

The emissions results for biodiesel, renewable diesel and GTL diesel fuel blends on a gram per brake horsepower hour (g/bhp-hr) basis are presented for NO<sub>x</sub> emissions in Figure 2-1 for the 2006 Cummins engine and Figure 2-2 for the 2007 MBE4000 engine. Renewable diesel and GTL diesel fuel blends were only tested on the 2006 Cummins ISM engine. PM, THC, CO, CO<sub>2</sub> and brake specific fuel consumption (BSFC) are not discussed in the main text, since the focus of this chapter is on NO<sub>x</sub> emissions, but these data are included in chapter 3 of this dissertation.

The percentage differences for different feedstocks, blend levels, and test cycles along with the associated p-values for statistical comparisons between the CARB diesel and different blends are provided in chapter three. The primary statistical analyses were conducted using a 2-tailed, 2 sample equal variance t-test. In some cases, additional statistical analyses were conducted using a bootstrapping methodology.<sup>41</sup> The R statistical software pack was used for the bootstrapping analyses.<sup>42</sup> The results of the bootstrapping analyses are provided in Table A-5 of the Appendix A.

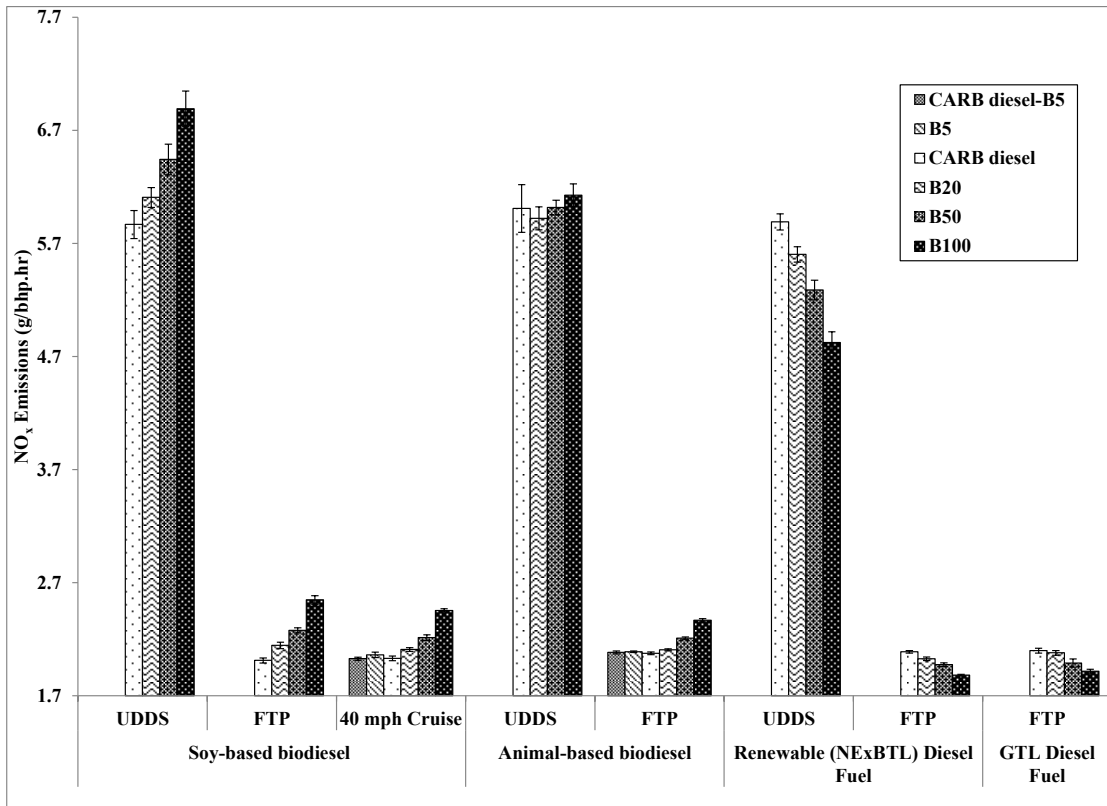


Figure 2-1. NO<sub>x</sub> emissions results of biodiesel, renewable, and GTL diesel fuel blends, and CARB diesel fuel for 2006 Cummins ISM. Note: Since B5 testing was run out of the test sequence and CARB diesel was provided separately for B5 testing, CARB diesel emissions are presented in a different column (CARB diesel-B5)

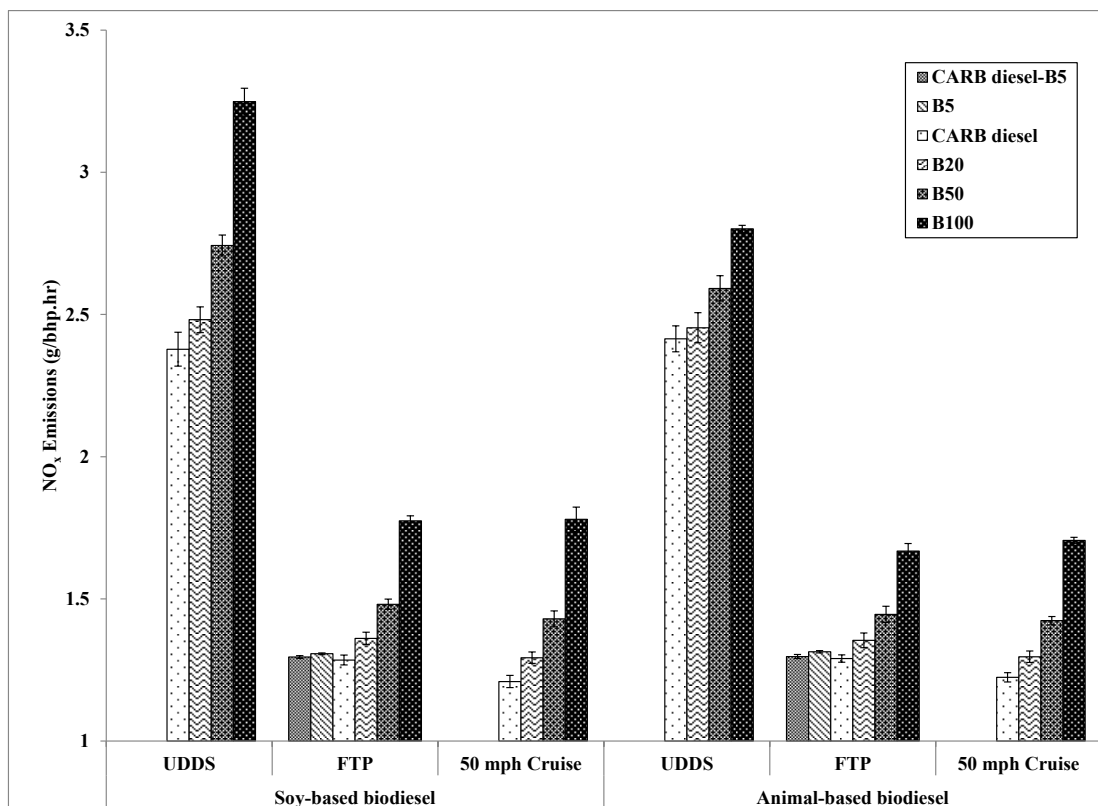


Figure 2-2. NO<sub>x</sub> emissions results of biodiesel, renewable, and GTL diesel fuel blends, and CARB diesel fuel for 2007 MBE4000. Note: Since B5 testing was run out of the test sequence and CARB diesel was provided separately for B5 testing. CARB diesel emissions are presented in a different column (CARB diesel-B5)

### 2.5.1. NO<sub>x</sub> Emissions

The results of this study showed that the average NO<sub>x</sub> emissions were higher at a statistically significant level for the B20 and higher biodiesel blends compared to the CARB diesel for all the test cycle/engine combinations, with the exception of the animal-based biodiesel on the UDDS cycle for the 2006 Cummins engine. From the graphs, it can be seen that the average NO<sub>x</sub> emissions for both engines show trends of increasing NO<sub>x</sub> with increasing biodiesel blend level, but the magnitude of this effect differs for different feedstocks, engines, and cycles. The soy-based B20 and higher biodiesel blends showed higher increases in NO<sub>x</sub>

emissions for the different blend levels, test cycles, and engines, in comparison with the animal-based biodiesel blends. The NO<sub>x</sub> emissions increases with the soy-based biodiesel blends ranged from 3.9%-6.9% for B20, 9.1%-18.2% for B50, and 17.4%-47.1% for B100 over all the engines and cycles. The NO<sub>x</sub> increases with the animal-based biodiesel blends ranged from 1.5%-5.9% for B20, 6.4%-16.3% for B50, and 14.1%-39.4% for B100 over the range of engines and cycles studied, excluding the UDDS on the 2006 Cummins engine. Results from the bootstrapping analysis showed that the differences between the NO<sub>x</sub> percentage increases for the soy-based and animal-based biodiesel were statistically significant for each of the cycle/blend level combinations on both engines (see Table A-5). The results of this study are consistent with those of previous studies, which have shown that NO<sub>x</sub> emissions tend to be higher for biodiesels with a higher degree of unsaturation and lower cetane numbers.<sup>43</sup>

In comparing the two engines, absolute NO<sub>x</sub> emissions were higher for the 2006 Cummins ISM compared to 2007 MBE 4000, which can be attributed to differences in the certification levels of the two engines. The magnitudes of the NO<sub>x</sub> emission increases with the biodiesel, however, were greater on a percentage basis for the 2007 MBE 4000 for all blend level/cycle combinations, except the soy-based B20 blend for the FTP. This included percentage increases in NO<sub>x</sub> emissions for some of the higher level blends (i.e., B50 and B100) combinations for the 2007 engine that were approximately twice those for the corresponding combinations on the 2006 engine. The bootstrapping analysis results showed that the differences in the NO<sub>x</sub> percentage increases between the different engines were statistically significant for the B50 and B100 blends, but not for the B20 blends (see Table A-5).

The differences between the NO<sub>x</sub> impact for the two engines could be due to differences in the engine calibration or how the engine ECM responds to fuels with different physical properties.<sup>19,44,45</sup> McCormick et al. also found greater increases in NO<sub>x</sub> emissions on a percentage basis with biodiesel for two engines meeting 2004 emission standards with EGR technology over an FTP cycle compared with their previous work performed on a 1991 DDC series 60 engine.<sup>43,46</sup> Nuskowski et al. found greater percentage NO<sub>x</sub> increases for progressively newer engines in comparing a 1992 DDC series 60 engine, a 1999 Cummins ISM, and a 2004 Cummins ISM.<sup>47</sup> Williams et al. tested a 2008 Cummins ISB 340 and an International MaxxForce 10 engine. In their study at a B20 level, they suggested the NO<sub>x</sub> increases for biodiesel with the 2008 Cummins ISB 340 were greater than those found in the broader literature, but they found no significant increases in biodiesel NO<sub>x</sub> emissions for the International MaxxForce engine.<sup>37</sup> Further study may be needed to see how prevalent or consistent these trends would be over a wider range of engine technologies.

NO<sub>x</sub> emissions also differed as a function of cycle power for both engines. In comparing different cycles, the highest percentage NO<sub>x</sub> increases for the 2007 MBE4000 were seen for the 50 mph Cruise for both the soy-based and animal-based biodiesel blends. The FTP NO<sub>x</sub> increases for the 2007 MBE4000 also tended to be higher than those for the UDDS cycle for the animal-based biodiesel, but this trend was not seen for the soy-based biodiesel. For the 2007 MBE4000 engine, the NO<sub>x</sub> emissions increases for the soy-based biodiesel in going from the lower load UDDS to the highest load 50 mph cruise ranged from 4.4%-6.9% for B20, 15.3%-18.2% for B50, and 36.6%-47.1% for B100. For the animal-based biodiesel for 2007 MBE4000 engine, the NO<sub>x</sub> increases from the lowest to the highest load cycle ranged from 1.6%-5.9% for B20, 7.3%-16.3% for B50, and 16.0%-39.4% for B100. For the 2006

Cummins ISM, the FTP cycle showed the largest percentage increases in NO<sub>x</sub> emissions in comparison with the lightly loaded UDDS and 40 mph cruise for both the soy- and animal-based feedstocks. The NO<sub>x</sub> increases for the Cummins engine for the soy-based blends were 4.1%, 9.8%, and 17.4% for the B20, B50, and B100 blends, respectively, for the UDDS and 6.6%, 13.2%, and 26.6% for the B20, B50, and B100 blends, respectively, for the FTP. Comparisons with the highest load 50 mph cruise were not available for the 2006 Cummins engine.

A trend of greater NO<sub>x</sub> increases for higher loads has been seen in other studies in the literature. Sze et al. observed larger increases in NO<sub>x</sub> with biodiesel as a function of increasing engine load and soy-based biodiesel blend level for a 2006 Cummins ISB engine. The NO<sub>x</sub> increases they found in going from light to high load cycles were comparable to, but were somewhat greater than, those seen in this study for similar blend levels for the 2007 MBE4000 engine, and ranged from 0.9-6.6% for B20 and 2.2-17.2% for B50.<sup>48</sup> In their 2009 study, the EPA conducted further analyses of NO<sub>x</sub> emissions as a function of load and found this to be an important factor in understanding biodiesel NO<sub>x</sub> impacts.<sup>20</sup> Eckerle et al. also reported that test cycle/load has an impact on NO<sub>x</sub> emissions increases. They estimated the NO<sub>x</sub> impact for B20 at a higher load, as represented by a high speed highway cruise speed cycle, to be a 4-5% increase, while the change in NO<sub>x</sub> at low loads for their higher cetane fuel was estimated to be a net decrease in NO<sub>x</sub> of 5%. The increase in NO<sub>x</sub> emissions for the FTP for a B20 blend with the high cetane fuel in that study was found to be 3.6%.<sup>19</sup> In the initial EPA review, NO<sub>x</sub> differences were also found in the biodiesel impacts for

steady-state and transient cycles, although the data for these comparisons were more limited.<sup>9</sup>

The impact of biodiesel on NO<sub>x</sub> emissions at levels lower than B20 can also be examined. For the soy-based B10, the results did show a statistically significant increase in NO<sub>x</sub> of 2.6% although this was based on a single test matrix point. The impact of B5 is less clear, however. As discussed above, the B5 comparisons were run outside the main sequence, so the CARB diesel tests used for these comparisons are labeled “CARB diesel-B5” in the Figures. For the present study, the soy-based and the animal-based biodiesels showed statistically significant increases of 0.9% and 1.3%, respectively, over the FTP for the MBE4000. The soy-based B5 also showed a statistically significant increase over the FTP of 2.2% for the Cummins engine during the NO<sub>x</sub> mitigation testing. Additionally, in the NO<sub>x</sub> mitigation testing, as discussed below, typically some combination of DTBP, renewable diesel or GTL diesel was needed to achieve NO<sub>x</sub> emissions neutrality with CARB diesel when blending with B5. The B5 soy-blend for the 40 mph cruise cycle and B5 animal-based biodiesel for the FTP for the 2006 Cummins engine, on the other hand, did not show statistically significant differences compared to the CARB diesel. Only two replicates of the B5 soy blend were available for the 40 mph cruise cycle, however.

The results for the renewable diesel and GTL diesel fuels show a steady decrease in NO<sub>x</sub> emissions with increasing blend level. NO<sub>x</sub> reductions with the renewable diesel fuel ranged from 2.9%-4.9% for R20, 5.4%-10.2% for R50, and 9.9%-18.1% for R100 over all the cycles. The reduction of NO<sub>x</sub> emissions with the renewable diesel fuel is consistent with previous investigations done on the NExBTL renewable diesel fuel.<sup>30,32,34</sup> Although these studies were

done on different heavy-duty engines and with different base fuels, in general, they report a 5-10% reduction of NO<sub>x</sub> emissions with neat NExBTL renewable diesel fuel, consistent with the present study. Rantanen et al. did not see a clear NO<sub>x</sub> reduction with the NExBTL renewable fuel, but this was for testing of light-duty vehicles on a chassis dynamometer rather than a heavy-duty engine dynamometer test.<sup>31</sup> The GTL diesel fuel showed reductions of 5.2% for the GTL50 and 8.7% for the GTL100. Over the FTP cycle, the NO<sub>x</sub> reductions for the renewable and GTL diesels were comparable for the 50% and 100% fuels, but the GTL fuel did not show statistically significant reductions at the 20% blend.

### **2.5.2. NO<sub>x</sub> Mitigation Results**

A range of different strategies were investigated for the purpose of NO<sub>x</sub> mitigation, especially for the 2006 Cummins ISM engine. The strategies investigated included blending with renewable diesel and GTL diesel fuels and cetane improver additives. Previous studies have shown that cetane improver additives can mitigate NO<sub>x</sub> emissions.<sup>49,50</sup> Renewable diesel and GTL diesel fuels have also shown the potential to decrease NO<sub>x</sub> emissions in this study and others.<sup>29-34</sup> The results of the NO<sub>x</sub> mitigation study for various successful and unsuccessful fuel formulations for both engines are provided in Table 2-2. Successful formulations are those that have NO<sub>x</sub> emissions that are either lower than or are not higher at a statistically significant level compared to the CARB diesel, as denoted with the grey shading in the table. Note that the primary focus of the NO<sub>x</sub> mitigation testing was on soy-based blends, since larger NO<sub>x</sub> increases were found for the soy-based biodiesel.

Table 2-2. Percentages changes form mitigation study blends relative to CARB and associated statistical p-values for 2006 Cummins ISM and 2007 MBE4000

Engine	Fuel Blend	Density	Cetane number	NO <sub>x</sub>	
				% diff	P value
2006 Cummins ISM	B5 - S	0.83	56	2.2%	0.000
	B10 - S	0.833	54.7	2.6%	0.000
	B20 - S*	0.838	55.4	6.6%	0.000
	B20-S 1% DTBP	0.838	71.4	0.0%	0.959
	B10-S 1% DTBP	0.832	74.2	-1.1%	0.002
	B20-S 1% 2-EHN	0.840	73.0	6.3%	0.000
	B5-S 1% 2-EHN	0.831	71.5	3.1%	0.000
	R80/B20-soy	0.797	64.8	-3.0%	0.000
	C25/R55/B20-S	0.810	62.9	-0.8%	0.029
	C70/R20/B10-S	0.823	58.3	0.9%	0.014
	C75/R20/B5-S	0.820	60.2	0.2%	0.674
	C80/B10-S/B10-A	0.837	55.3	3.9%	0.000
	C80/R15/B5-S	0.822	57.1	0.7%	0.117
	C80/R13/B3-S/B4-A	0.824	57.5	-0.3%	0.501
	C53/G27/B20-S	NA	NA	2.1%	0.000
	C80/G10/B10-S	NA	NA	2.4%	0.000
	C80/G15/B5-S	NA	NA	-0.7%	0.068
	C80/R10/B10-S 0.25% DTBP	NA	NA	-1.3%	0.002
2007 MBE4000	CARB80/R15/B5-S	NA	NA	1.1%	0.029
	B5-S 0.25% DTBP	NA	NA	0.4%	0.175

Notes: C = CARB diesel; R = renewable, G = GTL; Bxx = biodiesel blend level; S = soy biodiesel; A = animal biodiesel; \* From testing with the soy-biodiesel feedstock, NA= Not available, Grey shaded: NO<sub>x</sub> emissions that were either lower or were not higher at a statistically significant level from the CARB diesel fuel.

In developing NO<sub>x</sub> mitigation formulations with renewable diesel and GTL diesel fuels, it was noted that the levels of NO<sub>x</sub> reduction for the renewable diesel and GTL diesel fuels are less than the corresponding increases in NO<sub>x</sub> seen for the soy-based biodiesel at different blend levels, but are more comparable to the increases seen for the animal-based biodiesel blends. Thus, for soy-based biodiesel blends, the renewable diesel and GTL diesel fuels needed to be blended at higher levels than the corresponding biodiesel in order to mitigate the associated NO<sub>x</sub> increase. Blends of relatively high levels of renewable diesel or GTL diesel fuels with B20 soy-based biodiesels produced formulations that were NO<sub>x</sub> emissions neutral with CARB diesel. This included formulations with 80% and 55% renewable diesel

with a B20-soy biodiesel, which resulted in, respectively, 3% and 0.8% reductions in NO<sub>x</sub> emissions. NO<sub>x</sub> neutrality was also shown for other blends, including a CARB75/R20/B5-soy blend, a CARB80/R15/B5-soy blend, a CARB80/R13/B3-soy/B4-animal blend, and a CARB80/GTL15/B5-soy blend. These blends were designed to be more comparable to those that could potentially be used to meet CARB's low carbon fuel standard. Overall, the renewable and GTL diesels provided comparable levels of reductions for NO<sub>x</sub> neutrality over a range of blend levels.

Two additives, 2-ethyl hexyl nitrate (2-EHN) and di-tert-butyl peroxide (DTBP), were also tested for NO<sub>x</sub> mitigation over the 2006 Cummins engine. These additives have been reported to mitigate NO<sub>x</sub> emissions increases in some studies, but seemed to be less effective in newer engine technologies.<sup>46,49,50</sup> Of the two additives, only the DTBP was effective at mitigating the NO<sub>x</sub> increase of biodiesel in the current study. A 1% DTBP additive blend was found to fully mitigate the NO<sub>x</sub> impacts for B20 and B10 soy-based biodiesels. The 2-EHN was tested at a 1% level in both B20-soy and B5-soy blend and did not provide any significant NO<sub>x</sub> reductions. McCormick et al. tested the same percentages of these two additives in biodiesel blends in a 1991 DDC series engine, and showed that both of these cetane improvers were effective in mitigating increases in NO<sub>x</sub> emissions from biodiesel.<sup>50</sup> These additives were less effective in mitigating increases in NO<sub>x</sub> emissions from biodiesel in newer engine technologies in a later study, however.<sup>46</sup> The reduced effectiveness of additives in newer engines is consistent with the results of this study for the 2-EHN, although DTBP was found to be effective in the newer engine technologies used in this study. The differences in the additive effectiveness between DTBP and 2-EHN could be due to

differences in combustion or radical chemistry, or perhaps differences in NO<sub>x</sub> precursor species formed by the additives.<sup>51–53</sup>

Some combinations of different biodiesel types were also tested to see if the addition of a biodiesel with a lower tendency to increase NO<sub>x</sub> (such as the animal-based biodiesel) could be used to reduce the impact of a biodiesel with a greater tendency to form NO<sub>x</sub> (such as the soy-based biodiesel). Several blends of soy- and animal-based biodiesels showed that the NO<sub>x</sub> impact of biodiesels blended with two different feedstocks is intermediate between that for the two primary biodiesel feedstocks. A blend composed of 10% soy-biodiesel and 10% animal-based biodiesel with 80% CARB diesel was tested, for example. This blend showed an increase of approximately 3.9% in NO<sub>x</sub>, which is intermediate between the increases for the B20-soy (+6.6%) and the B20-animal (+1.5%). This indicates that the NO<sub>x</sub> impact for a particular biodiesel feedstock can be mitigated, in part, by blending with another biodiesel feedstock with a lower tendency for increasing NO<sub>x</sub>.

Since this study examined a wide range of fuels and fuel blends with different fundamental properties, such as cetane number and density, it is useful to examine the correlations between NO<sub>x</sub> emissions and fuel properties. This can also provide some insight into developing fuel formulations to mitigate biodiesel NO<sub>x</sub> impacts. Cetane number, which is a measure of ignition delay in the combustion process, is one property that could impact NO<sub>x</sub> emissions. Fuels with lower cetane numbers, and corresponding longer ignition delay times, can contribute to higher NO<sub>x</sub> emissions by contributing to greater preheating of the reactants in the combustion chamber and higher flame temperatures, or higher premix burn heat release due to the injection of more fuel prior to autoignition.<sup>54</sup> Previous studies have

shown trends of decreasing NO<sub>x</sub> emissions with increasing cetane number for both diesel fuels and biodiesel.<sup>43,54,55</sup> Cetane number is also often correlated with other fuel properties, however, such as density or aromatics for diesel fuel, or carbon chain length, number of double bonds or degree of unsaturation, and density for biodiesel fuels. In an analysis of cetane number effects, the EPA also found that the impact of cetane improvers on improving NO<sub>x</sub> emissions generally declines at natural cetane number levels above 50.<sup>56</sup> In the present study, the linear regression of cetane number and NO<sub>x</sub> emissions showed a slightly negative slope, or inverse relationship, as shown in Figure 2-3, but a poor correlation of R<sup>2</sup>=0.201. As such, cetane number effects, or correspondingly ignition delay effects, do not appear to be the most prevalent factor contributing to the biodiesel NO<sub>x</sub> increases seen in this study.

Density is another fuel property that has been shown to impact NO<sub>x</sub> emissions.<sup>43,57</sup> Higher densities have been correlated with higher NO<sub>x</sub> emissions for both diesel fuels and biodiesel fuels.<sup>43,57</sup> In this study, NO<sub>x</sub> emissions and density showed a much stronger correlation (R<sup>2</sup>=0.827) compared to cetane number across the fuels tested, as shown in Figure 2-3. Although some NO<sub>x</sub> correlations have been identified in this study, these correlations cannot be used to identify a single mechanism for NO<sub>x</sub> emissions increasing with biodiesel due to the complex interactions between fuel properties, and their associated impacts on the combustion process, combustion chemistry and stoichiometry, and engine calibration, as discussed by others.<sup>9,11,14,15,19,54,55,58–60</sup>

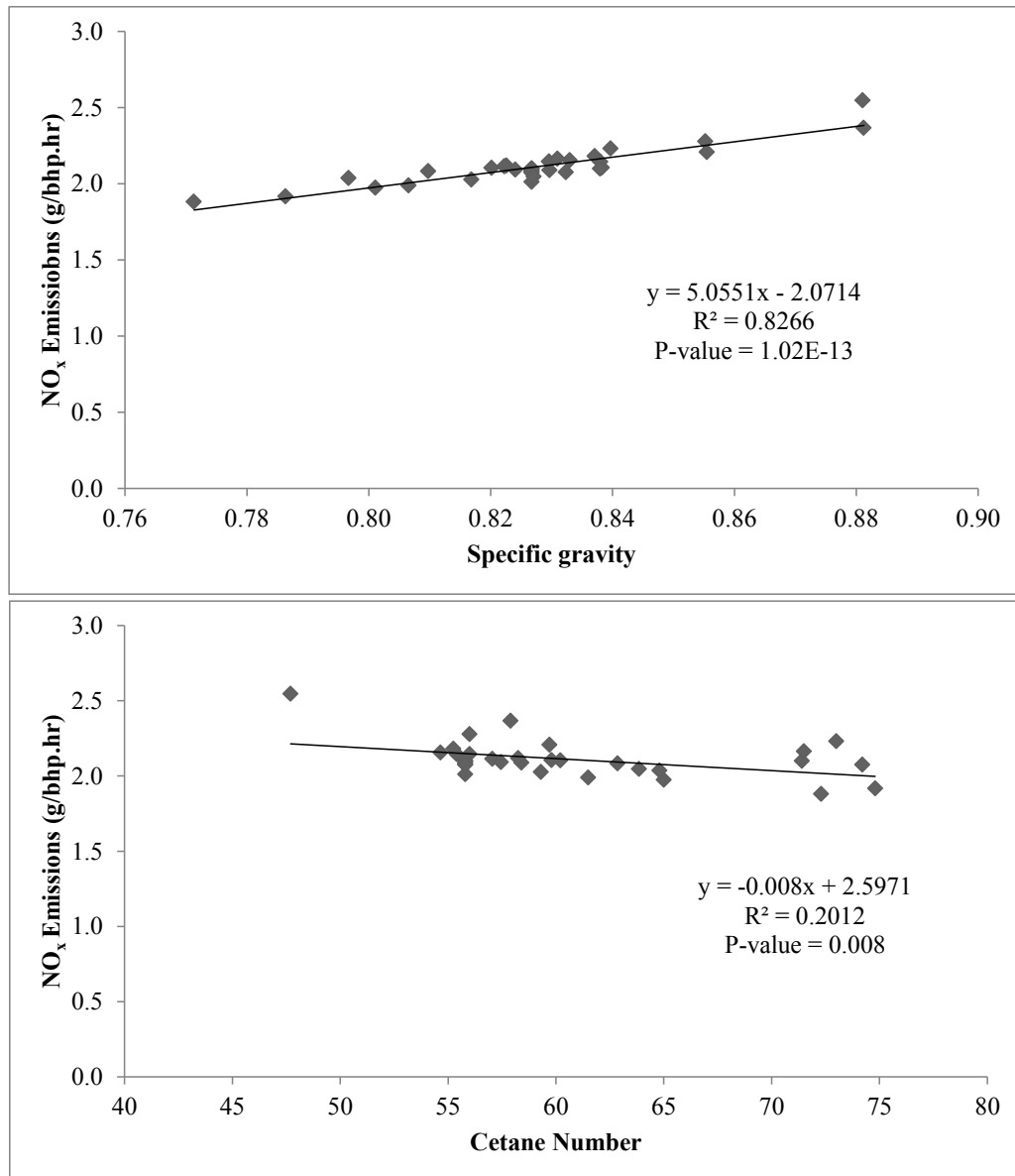


Figure 2-3. Correlation between NO<sub>x</sub> emissions and density and cetane number of different fuel blends tested over the mitigation part of the study

It is worth noting that engine modifications can also be used to control NO<sub>x</sub> emissions.<sup>16,55,61</sup>

Several studies have shown that NO<sub>x</sub> emissions increases can be reduced by techniques which retard and/or split fuel injection.<sup>62–66</sup> Using high EGR has also been shown to mitigate NO<sub>x</sub> emissions increases with biodiesel.<sup>67–72</sup> Some researchers have utilized both EGR and retarding injection strategies to reduce NO<sub>x</sub> emissions.<sup>61,73–75</sup> Recently, some

researchers have also successfully used a low temperature combustion (LTC) method to reduce NO<sub>x</sub>, which is a mixture of high EGR, and a combination of several modified fuel injections methods.<sup>76–78</sup> It should be noted, however, that these strategies are not being considered in the context of the development of fuels regulations, which would largely be implemented into unmodified engines.

## 2.6. Discussion

The potential and the nature of the impact of biodiesel on the formation of NO<sub>x</sub> emissions is still being debated in the literature, especially at lower blend levels. This will be the focus of this discussion. The complexity of understanding how and under what conditions biodiesel impacts NO<sub>x</sub> emissions can be seen from an overview of the literature. Several studies have analyzed a broader range of studies in the literature to try to better address this issue. In the EPA analysis of pre-2002 engine dynamometer data, a 2.0% increase in NO<sub>x</sub> emissions for soy-based B20 and a 10% increase in NO<sub>x</sub> emissions for B100 were estimated for a baseline fuel typical of the Federal average diesel in the U.S. While nearly all studies reviewed by EPA showed increases in NO<sub>x</sub> at the B100 level, the NO<sub>x</sub> impacts at the B20 level showed a much wider range of results, with percentage changes in NO<sub>x</sub> emissions varying from -7 to +7%.<sup>9</sup> McCormick et al. evaluated more engine dynamometer studies that were conducted subsequent to the EPA study and found an average change of  $-0.6\% \pm 2.0\%$  at a 95% confidence level. They concluded that while individual engines show NO<sub>x</sub> increasing or decreasing, on average, there was either no net effect for B20, or there was at most a very small effect, on the order of  $\pm 0.5\%$ , depending on the engine manufacturer and design.<sup>11</sup> In a related study, Yanowitz and McCormick found that if the results for pre-1992

two-cycle engines were removed from their database that there were no statistically significant differences between B20 and diesel fuel.<sup>21</sup> In a follow up study, the EPA found NO<sub>x</sub> increases of 2.2% for soy-based B20, consistent with the results of their original analysis. They also found that the results for the heavy-duty chassis and engine dynamometer tests were statistically indistinguishable, as were comparisons between different engine types. The EPA suggested that cycle load might be an important consideration in reconciling differences between different studies.<sup>20</sup> Hoekman et al. in their broad literature review and associated analysis found changes in NO<sub>x</sub> emissions for B20 of +1.8% for heavy/medium-duty engine dynamometer studies and -0.5% for heavy/medium-duty chassis dynamometer studies, and for B100 of +9.0% for heavy/medium-duty engine dynamometer studies and -4.9% for heavy/medium-duty chassis dynamometer studies.<sup>10,12</sup> A comparison of results from these broader studies with the results of our work is provided in chapter 3.

Although a broad overview of the biodiesel literature does not show consistent trends for NO<sub>x</sub> emissions, to understand the results of this study in the larger context of biodiesel emissions studies, it is important to do a more focused review. Specifically, the most critical element of this study is the impact of biodiesel in CARB-like base diesel fuels, which have been used in a much more limited range of studies. In the 2002 EPA analysis, some examination of “clean” diesel fuel data suggested that increases in NO<sub>x</sub> emissions might be more prevalent for clean diesel fuels than Federal average diesel fuel. Clean diesel fuels in the EPA study were defined as diesel fuels meeting the CARB requirements for sale in California, or diesel fuels with cetane numbers greater than 52, aromatic contents less than 25 vol.%, and specific gravities less than 0.84. EPA estimates showed increases in NO<sub>x</sub> of

5% for the clean base fuel at the B20 level (vs. 2% for the average base fuel), of 13% for the clean base fuel at the B50 level (vs. 5% for the average base fuel), and of 28% for the clean base fuel at the B100 level (vs. 10% for the average base fuel). This is very similar to our results for the soy-based B20 on the FTP for the Cummins engine. Results for clean/CARB-like diesel fuels were still relatively limited, however, at the time of that initial EPA study.<sup>9</sup> Hoekman et al. also did some evaluations of studies with CARB diesel. Their analyses showed average percentage changes relative to CARB diesel of 0.57% for B20 for heavy/medium-duty engine and chassis dynamometer studies and of 3.29% for B20 for light-duty chassis dynamometer studies.<sup>10,12</sup>

A listing of results of heavy-duty transient engine dynamometer tests for CARB-like diesel base fuels is provided in Table A-6 in Appendix A. For Table A-6, the list was limited to those using fuels with cetane numbers higher than 49. These studies provide the most direct comparison point to the present work, and are also important from a regulatory standpoint, since both California and Texas utilize heavy-duty engine dynamometer testing requirements in order to certify fuels for use in their respective states. Although it is not certain that all of these fuels would meet the CARB diesel fuel requirements, since the full range of fuel properties was not necessarily available for each fuel, it was felt that fuels with cetane numbers of at least 49 would be similar to CARB diesel fuels, and thus could be considered CARB-like, while providing for a sufficient number of studies for a more robust comparison with other studies in the literature. A total of 12 different engines are included in this listing. The number of replicates in these studies was generally two or three, with a few studies including some testing with more replicates. These transient heavy-duty engine

dynamometer studies all showed higher emissions on a soy-based biodiesel at a B20 level, with the increases ranging from 0.3 to 9.3%, with an average increase of 4.2%. Studies with other feedstocks, such as yellow grease and animal tallow, also showed predominantly increases, with most of the average increases ranging from approximately 2-3%. Overall, the results of these studies show a consistent trend of increasing NO<sub>x</sub> at the B20 level for heavy-duty engine dynamometer tests in comparison with CARB-like diesel, and in a range that is consistent with the results of this study. Some additional studies for multi-mode steady state tests and chassis dynamometer tests with CARB diesel and B20 blends are also available, but a detailed comparison with those results is beyond the scope of this study.<sup>79-84</sup>

It is also important to consider the impact of biodiesel on NO<sub>x</sub> at levels lower than B20, since these lower levels represent more practical levels for widespread implementation, especially in the initial years of renewable fuels regulations. The single test matrix point for the B10 blend level in this study showed a statistically significant increase in NO<sub>x</sub> of 2.6%. This increase is somewhat confirmed, however, by the fact that the addition of 10% GTL and 20% renewable diesel did not fully mitigate a B10-soy NO<sub>x</sub> increase during the NO<sub>x</sub> mitigation testing. In other transient heavy-duty engine dynamometer testing with a CARB-like diesel, Thompson et al. showed 2-3% increases for a B10 soy-based blend, consistent with the results of this study.<sup>85</sup> Few other studies of B5 in a CARB-like diesel fuel are available in the literature. In one such study, Nikanjam et al. showed no change to decreasing NO<sub>x</sub> for a B5 blend. Only two replicates were used in that study though.<sup>86</sup> In our study, the B5 results were mixed depending on the engine and biodiesel type, as discussed above, although some form of mitigation was needed to achieve NO<sub>x</sub> neutrality for the B5 soy-

based blends in the NO<sub>x</sub> mitigation testing. We are planning a more comprehensive study of the NO<sub>x</sub> impacts for B5 blends relative to CARB diesel in the near future.

In summary, the results of this study showed a relatively clear trend of increasing NO<sub>x</sub> emissions with increasing biodiesel blend level at levels of B20 and above for CARB-like/high cetane diesel fuels. The magnitude of the impact of biodiesel on NO<sub>x</sub> at these levels appears to depend on several different factors including the specific test engine technology and certification level, the feedstock from which the biodiesel is produced, and the test cycle or operating condition. Taking these results in conjunction with other literature studies of CARB-like diesel fuels, it appears that biodiesel likely has a more prominent impact on NO<sub>x</sub> when used with CARB-like diesels compared to more conventional US average diesels, at least at B20 or higher levels. For low level B5-B10 blends, that are most likely to be implemented in the near term in meeting regulatory requirements, it is still unclear if or what level of mitigation might be needed in regions such as California that have stringent provisions against any increases in NO<sub>x</sub> emissions. Potentially NO<sub>x</sub> neutral blends for such regions could include a B5 blend with a highly saturated biodiesel base stock, or combinations of B5 or lower blends with renewable diesel or GTL-like fuels, or with an additive. For biodiesels with a greater propensity for increasing NO<sub>x</sub>, such as soy-based biodiesel, further modification to the base fuel might also be possible to offset any potential biodiesel NO<sub>x</sub> increases.

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## **2.8. Disclaimer**

The statements and conclusions in this report are those of the contractor and not necessarily those of California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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## **Chapter Three: Evaluation of the Impacts of Biofuels on Emissions for a California Certified Diesel Fuel from Heavy-Duty Engines**

### **3.1. Abstract**

The impact of biodiesel and new generation biofuels on emissions from heavy-duty diesel engines was investigated using a California Air Resources Board (CARB) certified diesel fuel as a base fuel. This study was performed on two heavy-duty diesel engines, a 2006 engine and a diesel particle filter (DPF) equipped 2007 engine, on an engine dynamometer over four different test cycles. Emissions from soy-based and animal-based biodiesel, renewable diesel fuel, and gas to liquid (GTL) diesel fuel were evaluated at blend levels ranging from 5 to 100%. Consistent with previous studies, particulate matter (PM), hydrocarbons (HC), and carbon monoxide (CO) emissions generally showed increasing reductions with increasing biodiesel and renewable/GTL diesel fuel blend levels for the non-DPF equipped engine. The levels of these reductions were generally comparable to those found in previous studies performed using more typical Federal diesel fuels. The DPF-equipped engine THC, CO, and PM emission levels were very low and did not show significant fuel impacts. Carbon dioxide (CO<sub>2</sub>) emissions were slightly higher for biodiesel blends, and slightly lower for the renewable/GTL blends. Brake Specific Fuel Consumption (BSFC) was slightly higher for biodiesel and renewable/GTL blends, consistent with their lower energy density.

### 3.2. Introduction

There is a global effort to expand the use of renewable fuels in the transportation section. This can have several potential benefits, such as improving air quality, reducing emissions of some of the criteria air pollutants and carbon dioxide (CO<sub>2</sub>), which is a greenhouse gas, and reducing dependency on fossil fuels. A number of regulations have been implemented on a multinational, national, and regional level to increase the use of renewable fuels.<sup>1-3</sup>

Biodiesel is the most popular biofuel for diesel applications. Biodiesel blends can be used in existing diesel engine technologies with no or minor engine modifications.<sup>4,5</sup> Currently, 7% biodiesel is used in diesel fuel throughout Europe.<sup>6</sup> Biodiesel production in U.S has also increased substantially over the past decades and reached 1.1 billion gallons in 2011.<sup>7</sup> From an air quality perspective, the major benefit of biodiesel blends is that they can reduce the emissions of some of the primary air pollutants.<sup>4</sup> It has also been reported that biodiesel blends can reduce CO<sub>2</sub> emissions when a complete carbon life cycle analysis is performed.<sup>8</sup>

Numerous studies of biodiesel emissions have been conducted over the years. In order to better quantify average or typical biodiesel effects, several researchers have done quantitative evaluations in conjunction with comprehensive literature reviews. The U.S. Environmental Protection Agency (EPA) conducted an early assessment of the impact of biodiesel on pre-2002 engines, and more recently updated this study.<sup>9,10</sup> The National Renewable Energy Laboratory (NREL) also published several studies evaluating the biodiesel emissions literature from different perspectives to examine differences between engine technologies, between engine and chassis dynamometer tests, and other factors.<sup>11</sup> As part of the

Coordinating Research Council's (CRC's) AVFL-17 project, Hoekman et al. also did an evaluation of the literature looking at differences between different engine types (light-, medium-, and heavy-duty) and also between engine and chassis dynamometer studies, as well as other factors.<sup>8</sup> Table 3-1 shows a comparison between the percentage differences for these different studies. As shown in this table, PM, THC, and CO emissions showed reductions on average for biodiesel for nearly all comparison categories.<sup>8-12</sup> Most of the studies included in these reviews were performed using typical Federal diesel fuels as the baseline test fuel, over a limited number of driving cycles/feedstocks/blend levels, or with older engine technologies without aftertreatment. Therefore, the studies to date have some limitations with respect to their application in California, where more stringent diesel fuel standards are in place. Additionally, although most studies have shown reductions in PM, THC, and CO emissions with biodiesel, some studies have shown less prevalent reductions over some testing conditions, such as low loads, or light/medium duty chassis dynamometer studies.<sup>13-17</sup>

Table 3-1. Comparison of the results of several review studies on biodiesel emissions

		EPA, 2002 & 2009 <sup>24,25</sup>			McCormick et al., 2006 <sup>34</sup>	Yanowitz and McCormick, 2009 <sup>35</sup>	Hoekman et al., 2011 <sup>****26</sup>
		“Average” Base Fuel, 2002	“Clean” Base Fuel, 2002	“Average” Base Fuel, 2009			
PM	B20	-12%	-8%	-15.6%	0- -31%* Average -12.6%	-14% (SD=13%)** -17% (SD=13%)***	-17.2, -10.5, 1.7
	B50	-26%	-20%				
	B100	-46%	-35%				-44.3, 3.8, 7.9
THC	B20	-21%	-13%	-14.1%	0- -30% Average -10.3%	-16% (SD=18%)** -16% (SD=18%)***	-17.4, -13.3, -7.6
	B50	-45%	-30%				
	B100	-69%	-51%				-48.3, -59.5, -20.1
CO	B20	-12%	-9%	-13.8%	0—38% Average -12.9%	-15% (SD=10%)** -16% (SD=9%)***	-14.1, -17.3, 1.1
	B50	-27%	-20%				
	B100	-47%	-37%				-34.3, -39, 14.9
CO <sub>2</sub>	B100		1-3%				

\*Non-DPF equipped engines

\*\* Including new studies to EPA study

\*\*\* Including new studies but not two-stroke engine data to EPA study

\*\*\*\* Percentage differences are reported, respectively, over HD/MD engine dynamometer, HD/MD chassis dynamometer, LD Chassis dynamometer

The California Air Resources Board (CARB) has conducted one of the most comprehensive studies of biodiesel emissions impacts to date, in conjunction with researchers at the University of California (UC) at Riverside, UC Davis, and others. The focus of this larger study was to evaluate regulated and toxic emissions from biodiesel and renewable diesel fuels blended with CARB certified diesel fuel. This study is part of CARB efforts to identify the need for additional regulations to facilitate the introduction of larger volumes of renewable fuels into use. The larger program included engine dynamometer testing, chassis dynamometer testing, and testing of off-road engines on several biodiesel and renewable diesel fuels.<sup>18</sup> The importance of this study is that it provides a very robust set of data using CARB certified and CARB-like diesel fuels, which are produced to more stringent standards than other diesel fuels throughout the United States, and for which there is more limited data in the literature. This paper summarizes the results of the PM, THC, CO, and CO<sub>2</sub> emissions from the heavy-duty engine dynamometer part of this larger study. This is a companion paper to another article that focused on the nitrogen oxides (NO<sub>x</sub>) emissions results for the heavy-duty engine dynamometer testing.<sup>19</sup>

### **3.3. Experimental Methods**

Five primary fuels were blended at various levels from B5 to straight B100. These fuels include, a commercially available CARB-certified diesel fuel, soy-based and animal-based biodiesel fuels, a renewable diesel fuel produced from renewable biomass sources, such as fatty acids from vegetable oils and animal fats, via a hydro-treating process<sup>20-22</sup>, and a gas to liquid (GTL) diesel fuel produced via Fisher-Tropsch procedure. The biodiesel feedstocks were selected to provide a range of properties of the typical biodiesel feedstocks such as

cetane number and degree of saturation (iodine number). The renewable diesel fuel was the Neste Oil biomass-to-liquid (NExBTL) diesel fuel. Six tests were nominally performed for every fuel/cycle combination. A summary of selected properties for the neat fuels is provided in Table 3-2.

Table 3-2. Selected fuel properties

	CARB	Renewable	GTL	Soy	Animal
API gravity (@ 60°F)	39.3	51.3	48.4	28.5	28.5
Aromatics, vol. %	18.7	0.4	0.5	NA	NA
PNAs, wt. %	1.5	0.1	<0.27	NA	NA
Cetane number, D613	55.8	72.3	>74.8	47.7	57.9
Cetane number, IQT		74.7			
Sulfur, ppm	4.7	0.3	0.9	0.7	2
Carbon, % Wt.	86.1	84.83	84.6	76.72	75.89
Hydrogen, %Wt.	13.67	15.14		11.97	12.22
Oxygen, % Wt.	0.23	0.03		11.31	11.89
C/H Ratio	6.3	5.6		6.4	6.2
Cloud Point, °C	-6.6	-27.1	-1	0	12.5
Pour Point, °C	-12	-47	-6	NA	NA
Distillation, °F					
ibp	337	326	419	NA	NA
10%	408	426	482	NA	NA
50%	519	521	568	NA	NA
90%	612	547	648	NA	NA
ep	659	568	673	NA	NA
Distillation, T90 AET, °C	NA	NA	NA	350	347.5
Acid Number	NA	NA	NA	0.20	0.26
Free Glycerin%	NA	NA	NA	0.001	0.008
Total glycerin%	NA	NA	NA	0.080	0.069
Oxidation Stability				6.7	3.9

Two engines selected from 2 model year categories: 2002-2006 and 2007-2009 were tested on a 600 hp General Electric DC electric heavy-duty engine dynamometer located at the University of California at Riverside's College of Engineering-Center for Environmental Research and Technology's (CE-CERT). The 2002-2006 engines are estimated to represent an important contribution to the emissions inventory from the present through 2017. The 2007-2009 model year engine represents the latest technology that was available at the time of testing. The 2002-2006 engine was a 2006 model year, 10.8 L, Cummins ISM engine, and the 2007-2009 engine was a 2007, 12.8 L, Detroit Diesel MBE 4000. The Detroit Diesel MBE 4000 was equipped with an original equipment manufacturer (OEM) diesel particulate filter (DPF). Both engines were equipped with exhaust gas recirculation (EGR). More specifications of the engines are provided in Table 3-3.

Table 3-3. Test engines specification

Engine Manufacturer	Cummins, Inc.	Detroit Diesel Corp.
Engine Model	ISM 370	MBE4000
Model Year	2006	2007
Engine Family Name	6CEXH0661MAT	7DDXH12.8DJA
Displacement (liter)	10.8	12.8
Power Rating (hp)	385 @ 1800 rpm	Varies, 350-450 hp @ 1900 rpm
After-treatment	EGR	EGR & DPF

For every fuel/engine combination, different cycles representing different load and driving conditions were used. These cycles include: lightly loaded Urban Dynamometer Driving Schedule (UDDS), standard Federal Testing Procedure (FTP) for heavy-duty engines, 40 mile per hour (mph) CARB heavy heavy-duty diesel truck (HHDDT) Cruise, and a 50 mph CARB HHDDT Cruise. From a load perspective, the UDDS represents lowest load, the FTP and 40 mph Cruise represent the medium loads, and the 50 mph Cruise represents the

highest load. A randomized test matrix, including interspersed testing of the base fuel after a specific number of tests on other fuel blends and performing different cycles during each test day, was used for this study. After the initial round of testing on the soy-based biodiesel for the 2006 Cummins ISM, it was determined that the loads for the FTP and the 40 mph CARB Cruise cycle were very similar, and hence did not provide a sufficient load range to meet the study goals. Therefore, it was decided that an additional higher load cycle was needed to provide a larger range of load conditions. The cycle that was selected was the 50 mph CARB HHDDT Cruise cycle, with an average speed of 50 mph instead of 40 mph. This cycle was used for some further testing on the Cummins engine, but it did not provide stable enough operation to provide valid fuel comparisons for this engine. It was then also used in place of the 40 mph Cruise cycle for the MBE4000, where it provided more stable operation. The GTL diesel fuel was tested primarily for inclusion in another separate, but related, study on NO<sub>x</sub> mitigation, which was performed over the FTP cycle and mainly for the 2006 Cummins ISM engine. Therefore, the GTL blends emissions were only characterized over the FTP cycle.

For all tests, standard emissions measurements of THC, CO, PM, and CO<sub>2</sub> were performed from a dilution tunnel using the standard analyzers in CE-CERT's heavy-duty Mobile Emissions Laboratory (MEL) trailer.<sup>23,24</sup> PM mass in the diluted exhaust were collected over a 47 mm Teflon filters and measured gravimetrically with a Mettler Toledo, UMX 2 microbalance.

### **3.4. Results and Discussion**

The results of the average PM, THC, CO, CO<sub>2</sub> emissions and brake specific fuel consumption (BSFC) from soy-based and animal-based biodiesel blends, renewable and GTL diesel fuel for the 2006 Cummins ISM are shown in Figure 3-1 to Figure 3-4, respectively, on a gram per brake horse power hour (g/bhp-hr) and gallons per brake horse power hour (gals/bhp-hr) basis for the three different cycles. Since B5 was tested outside of the test matrix sequence, the average emissions for B5 were only compared to the average of CARB emissions for tests immediately before and immediately after the B5 was tested (CARB diesel-B5 in the figures). Table 3-4 and Table 3-5 show the emissions averages and the percentage differences for different feedstocks and blend levels for different cycles and for the 2006 Cummins and 2007 MBE4000, respectively, along with the associated p-values for statistical comparisons between the CARB diesel and different biodiesel/renewable/GTL diesel blends using a 2-tailed, 2-sample, equal variance t-test. These statistical analyses provide information on the statistical significance of the different findings. For this study, the results were considered to be statistically significant for p-values below 0.05, which represents a 95% confidence level.

#### **3.4.1. PM Emissions**

PM emissions, for 2006 Cummins ISM engine, showed consistent and significant reductions for biodiesel blends and renewable/GTL diesel fuels, with greater reductions with increasing blend level. For this engine, the PM percentage reductions for the biodiesel blends compared to CARB diesel over all cycles were 10 to 26% for B20 and 31 to 69% for B100, and 9% for

B5 for the FTP on the animal-based biodiesel. There also appears to be a trend of greater reduction in PM with increasing cycle load for both biodiesel fuels.

The PM emission results for biodiesel blends are consistent with the majority of previous studies, reporting PM emissions reductions from biodiesel blends. The 2006 Cummins ISM results showed reductions comparable to, but generally higher than those found in the broader biodiesel emissions analyses discussed above. The 2006 Cummins engine is newer than the engines used in most previous studies up to this time. McCormick et al. did find PM emissions reductions for 2003 vintage heavy-duty engines were larger than those found for older engines.<sup>25</sup> In a review over a wider range of studies, however, Yanowitz and McCormick did not find a correlation between emissions trends for engines with different model years.<sup>12</sup>

The reduction of PM with biodiesel is due to its ability to lower soot formation during combustion, which can be attributed to a number of different factors. The presence of oxygen in the biodiesel can reduce local fuel-rich regions during combustion, limiting the formation of soot.<sup>8,9,11,26</sup> In a study focusing primarily on NO<sub>x</sub> emissions, Mueller et al. emphasized that charge-gas mixtures that are closer to stoichiometric for biodiesel blends at ignition and in the standing premixed autoignition zone near the flame lift-off length would lead to a higher local and average in-cylinder temperatures, lower radiative heat losses, and a shorter, more advanced combustion event, all of which could contribute to lower PM.<sup>27</sup> Cheung et al. suggested that greater heat release in premixed combustion and higher heat radiation are other factors that promote more complete combustion and favor lower soot formation for biodiesel.<sup>28</sup> There are other factors that have been reported to reduce PM

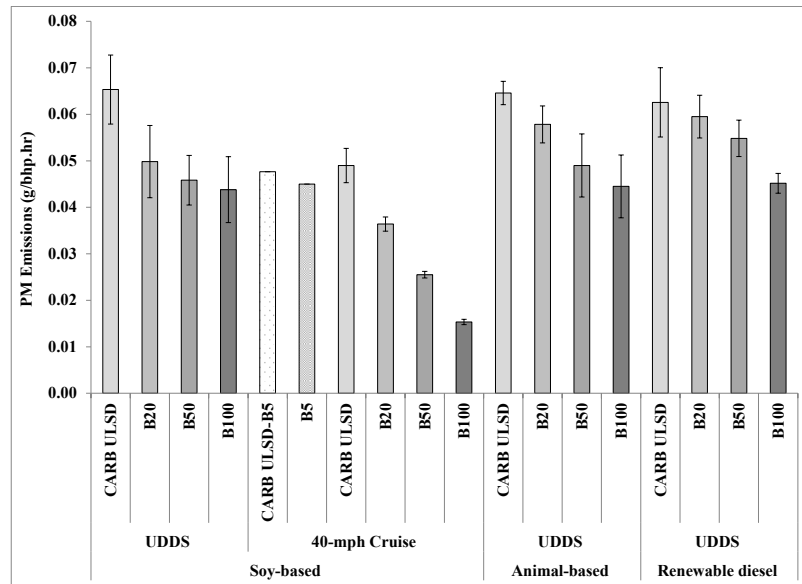
emissions with biodiesel blends. These include the absence in biodiesel of aromatics that are soot precursors, advanced injection timing in older engine technologies with in-line/mechanical pump systems with biodiesel blends that increases the residence time of soot particles in higher temperature conditions, a different structure for biodiesel and diesel soot that affects the oxidation of soot, and finally, a lower boiling point for biodiesel, in general, despite its higher average distillation temperature, which reduces the probability of soot formation from heavier hydrocarbons.<sup>4,29–34</sup>

It should be noted some previous studies have also shown conditions where the PM emissions benefits for biodiesel are not as prevalent, but many of these studies were conducted under different conditions, such as at light loads or chassis dynamometer tests of light- or medium-duty vehicles.<sup>13–17</sup>

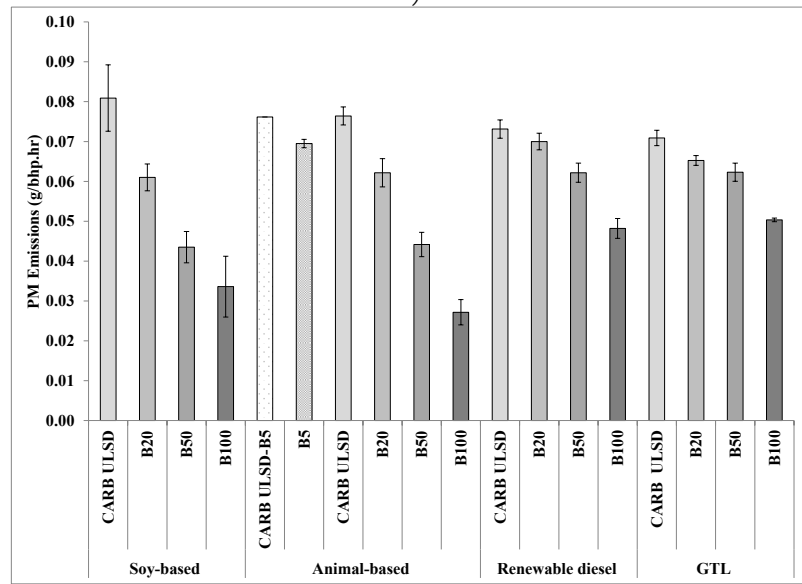
For the 2007 MBE4000 engine, the PM emissions values were well below the 0.01 g/bhp-hr emissions standard, and were essentially at the measurement detection limit. For this engine, the differences in PM emissions between various biodiesel blends and CARB diesel were not statistically significant. This is not unexpected due to the efficiency of the DPF in removing particles from the exhaust, which minimizes any fuel differences. Williams et al. similarly found that the traditional emissions benefits of biodiesel become immeasurable for engines equipped with DPFs.<sup>35</sup>

The PM percentage reductions of renewable/GTL diesel compared to CARB diesel for all the cycles were 4% for R20 and 28 to 34% for R100, and 8% for GTL20 and 29% for GTL100. The PM emissions reductions for the renewable diesel fuel were also consistent with the results of previous studies that found reductions in PM or smoke of 28-35% for

heavy-duty engine dynamometer tests with neat NExBTL.<sup>20,22</sup> Some studies of light-duty vehicles showed some tendency of PM reductions for different NExBTL blends, but also greater testing variability.<sup>21</sup> The PM emissions reductions for the renewable fuels can be attributed to their lower density and aromatic content compared to diesel fuel. The more paraffinic nature of renewable diesel fuel also increases the fuel cetane number and boiling point, which are reported to reduce PM emissions.<sup>36</sup>



a)



b)

\* Since B5 was tested outside of the test matrix sequence, the average emissions for B5 were only compared to the average of CARB emissions for tests immediately before and immediately after the B5 was tested (CARB diesel-B5 in the figures).

Figure 3-1. PM emission results for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle for 2006 Cummins ISM

### 3.4.2. THC Emissions

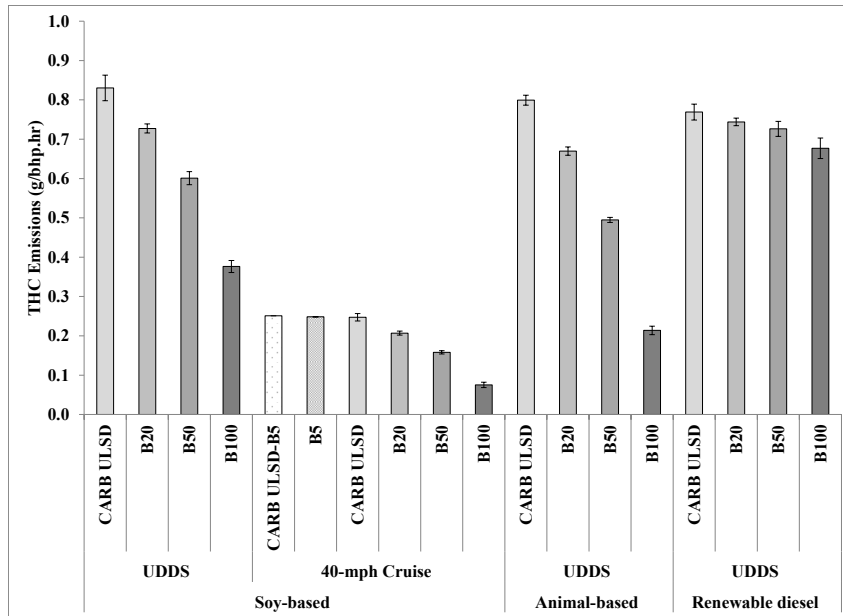
THC emissions for the 2006 Cummins ISM engine showed consistent and significant reductions for the biodiesel blends, renewable, and GTL diesel fuel, with greater reductions increasing with increasing blend level. The THC percentage reductions for the biodiesel blends compared to CARB diesel over all cycles were 11 to 16% for B20 and 55 to 73% for B100 for biodiesel blends, and 3% for B5 for the FTP on the animal-based biodiesel. There also appears to be a trend of greater reductions in THC with increasing cycle load for soy-based biodiesels.

The results of the 2006 Cummins engine were consistent with those of previous studies. Overall, the reductions obtained for both biodiesel fuels for the 2006 Cummins ISM for THC show reasonably good comparisons with the results for various heavy-duty engine biodiesel studies in the literature. The reductions of unburned hydrocarbons with biodiesel can be attributed to the presence of oxygen in the biodiesel fuel and its impact on more complete combustion of the unburned fuel, similar to the discussion provided above for PM emissions. Other parameters that are reported to decrease THC emissions when using biodiesel include advanced injection timing in older engine technologies and combustion timing.<sup>29</sup>

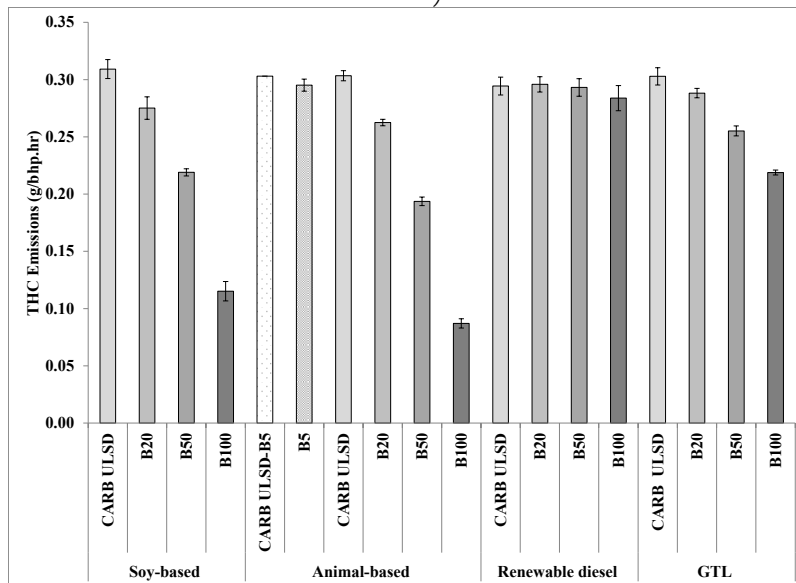
For the 2007 MBE4000, the THC emissions did not show consistent trends, which can be attributed to the efficiency of the DPF. Interestingly, this engine showed some statistically significant increases of THC emissions for the soy-based biodiesel, but these were small on

an absolute level. Additional testing would be needed to further clarify this trend for the 2007 MBE4000 engine.

The renewable diesel fuel showed statistically significant percentage reductions of 3% for R20 and 12% for R100 for only the UDDS cycle. The GTL diesel fuel also showed reductions in THC emissions of 5% for GTL20 and 28% for GTL 100 over the FTP. The renewable diesel fuel did not show any consistent THC trends over the FTP, however. Previous studies have reported reductions in THC with neat NExBTL in the range of 30-50%.<sup>20,22</sup> The differences between these studies and the present study might be related to different distillation properties of the fuels used in the studies. In the European studies, a summer grade NExBTL was used, while here a winter grade was used. The summer grade NExBTL had higher  $T_{10}$  and  $T_{50}$  distillation temperatures, which are important parameters with respect to hydrocarbon emissions in the EPA's Unified Model,<sup>37</sup> and tend to produce lower THC emissions.



a)



b)

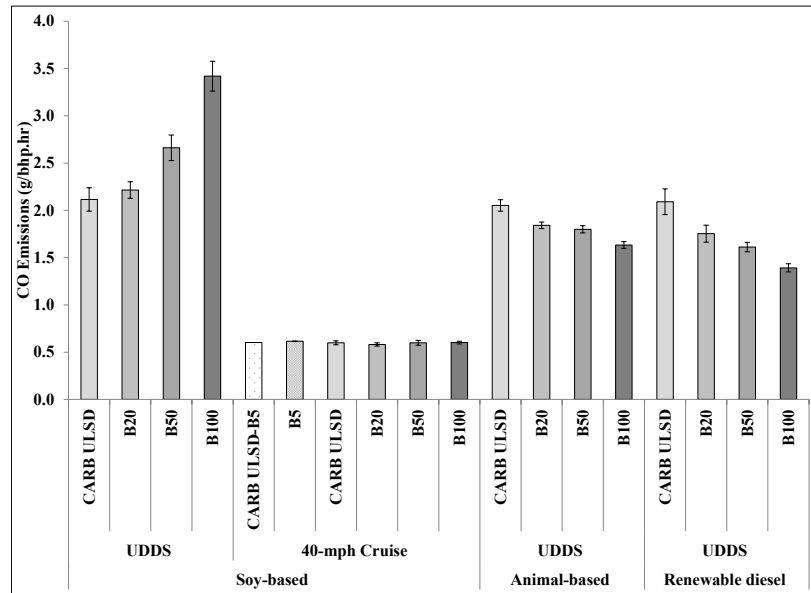
\* Since B5 was tested outside of the test matrix sequence, the average emissions for B5 were only compared to the average of CARB emissions for tests immediately before and immediately after the B5 was tested (CARB diesel-B5 in the figures).

Figure 3-2. THC emission results for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle for 2006 Cummins ISM

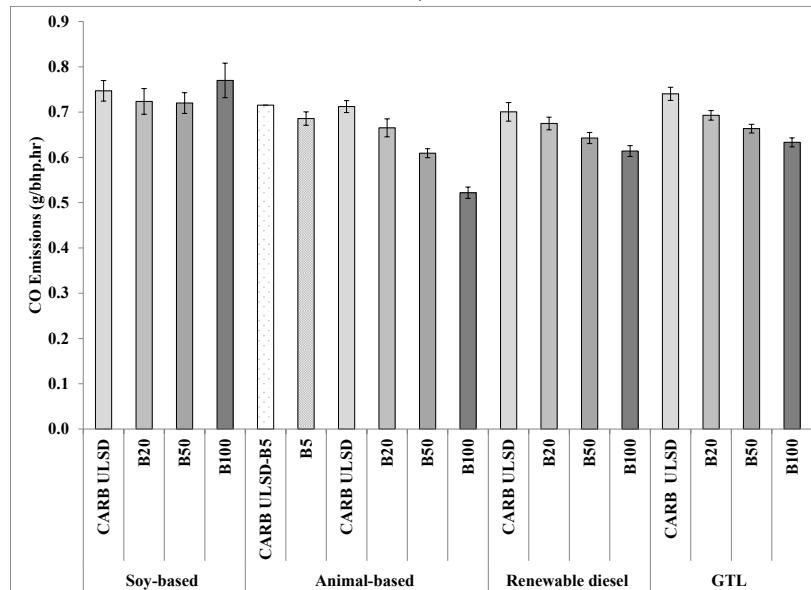
### 3.4.3. CO Emissions

CO emissions for the 2006 Cummins ISM engine showed consistent and significant reductions for the animal-based biodiesel blends and renewable/GTL diesel fuels. The percentage reductions for all cycles ranged from 4% for B5, 7 to 10% for B20, and 20 to 27% for B100 for the animal-based biodiesel, 4 to 16% for R20 and 12 to 33% for R100 for the renewable diesel fuel, and 6% for GTL20 and 14% for GTL100. The soy-based biodiesel blends did not show any strong fuel trends relative to the CARB diesel over the FTP and 40-mph Cruise cycle, with only the B50 over FTP showing a statistically significant 4% CO emissions reduction. For the UDDS cycle, on the other hand, the B50 and B100 soy-based biodiesel blends, respectively, showed statistically significant 26% and 62% CO emissions increases. Interestingly, statistically significant reductions in CO for the 2007 MBE4000 were found for both the B50 and B100 blend levels in comparison with the CARB diesel, but these were small on an absolute level due to the DPF.

The results for CO emissions for the animal-based biodiesel and renewable diesel for the 2006 Cummins ISM were also in good agreement with the previous studies. The reductions of CO emissions with biodiesel can be attributed to the oxygen in the biodiesel fuel and more complete combustion, as discussed above in relation to PM emissions. For the renewable blends, the observation of reduced CO emissions is consistent with the results seen in previous studies, although previous heavy-duty engine studies showed reductions closer to 30% for a neat NExBTL fuel.<sup>20,22</sup>



a)



b)

\* Since B5 was tested outside of the test matrix sequence, the average emissions for B5 were only compared to the average of CARB emissions for tests immediately before and immediately after the B5 was tested (CARB diesel-B5 in the figures).

Figure 3 3. CO emission results for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle 2006 Cummins ISM engine

The reason for the lack of CO reductions for the soy-based biodiesel for the 2006 Cummins is not readily apparent, especially given that consistent reductions are seen for both THC and PM on this engine, and for CO for the animal-based biodiesel. Some other studies have shown a lack of strong trends for CO emissions for biodiesel for different types of tests/vehicles/engines ranging from steady state tests to chassis dynamometer tests.<sup>13,17,38</sup> Overall, the CO emissions results for the soy-based biodiesel blends could be impacted by a number of different factors, including the engine load or cycle, differences in the base fuels, or differences between different engines or engines certified to different emissions standards. Additional testing would likely be needed to better understand the nature of these results.

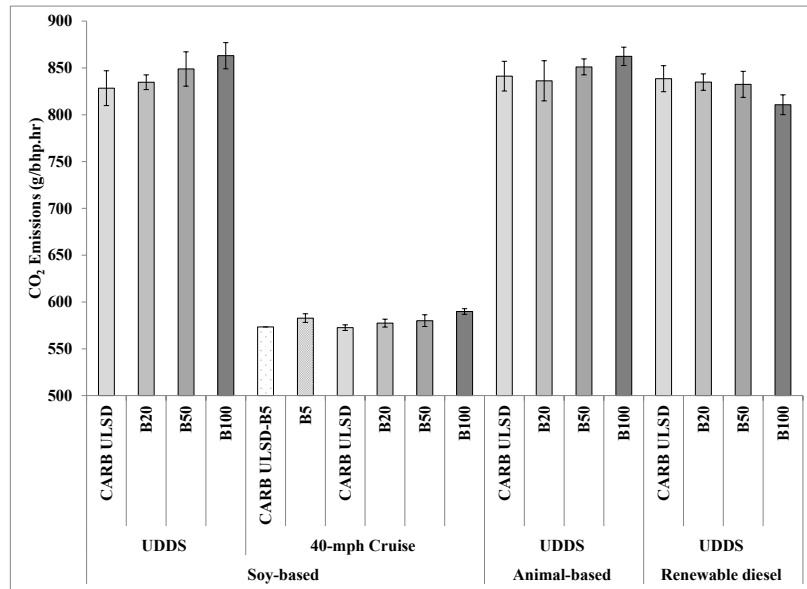
#### **3.4.4. CO<sub>2</sub> Emissions**

CO<sub>2</sub> emissions showed a slight increase for the higher biodiesel blends and a slight decrease for the renewable/GTL diesel fuel. The increases were statistically significant largely only for B100, and showed a range at that level from 0.7% to 4.2% for the 2006 Cummins engine and from 1.6 to 5.0% for the 2007 MBE4000 engine. The renewable diesel fuel showed a statistically significant reduction of 3.3 to 3.4% in CO<sub>2</sub> for the R100. GTL diesel fuel showed a statistically significant reduction of 1.9% for GTL50 and 3.5% for GTL100.

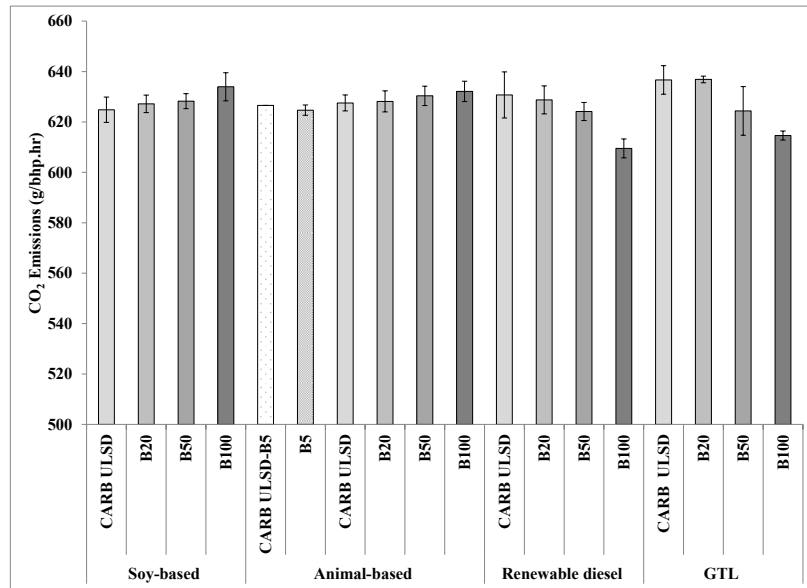
The CO<sub>2</sub> emissions results for the biodiesel blends were in qualitative agreement with the previous studies. EPA 2002 study reported an increase of 1-3% for B20 to B100 biodiesel blends for their “clean” base fuel. In their study, EPA compared fuels as a function of carbon content per energy of the fuel. In the 2002 EPA study, the average carbon content

per energy of the fuel (lb. carbon/million Btu) for typical biodiesel was 48.1 compared to 47.5 for the conventional diesel fuel. Given that the lower heating value of biodiesel is approximately 10-11% lower for neat biodiesel compared to typical diesel fuel on a mass basis <sup>4,8</sup> and the carbon contents for the present study are similar to those reported by EPA, similar differences in carbon content per energy of the fuel should be expected for this study between the CARB diesel and the biodiesel fuels. Thus, for a given amount of work, one would expect higher carbon consumption, and correspondingly higher CO<sub>2</sub> emissions for the biodiesel. It must be emphasized that an increase in tailpipe CO<sub>2</sub> emissions for biodiesel, does not imply that the use of biodiesel has a negative impact on greenhouse gas emissions. The actual contribution of different fuels towards total greenhouse gas emissions would need to be assessed through a full lifecycle analysis, which would account for the emissions attributed to harvesting, extracting, producing, associated land use changes for the various fuels.<sup>39</sup>

The CO<sub>2</sub> emissions results for renewable diesel fuel were consistent with previous studies for both engine and chassis dynamometer testing. Aatola et al. reported CO<sub>2</sub> emissions decreased with increasing renewable diesel fuel content, with the highest reductions for the R100.<sup>22</sup> In the current study, the reductions in CO<sub>2</sub> emissions for the renewable diesel can probably be attributed to the lower carbon weight fraction for the renewable diesel (84.8%), due to its paraffinic nature, compared to the CARB diesel (86.1%). Rantanen et al. also suggested that combustion improves for NExBTL due its paraffinic composition and chemical properties, but they found CO<sub>2</sub> emissions relatively unchanged over three light-duty passenger cars.<sup>21</sup>



a)



b)

\* Since B5 was tested outside of the test matrix sequence, the average emissions for B5 were only compared to the average of CARB emissions for tests immediately before and immediately after the B5 was tested (CARB diesel-B5 in the figures).

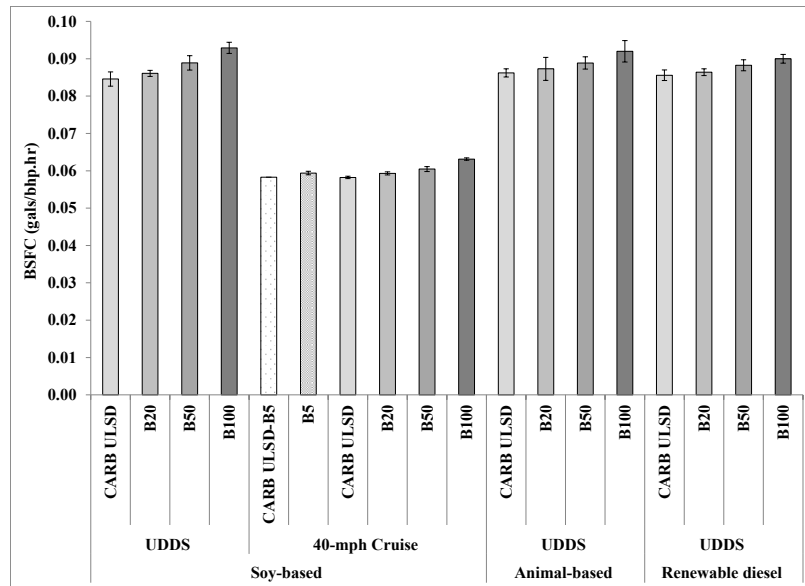
Figure 3-3. CO<sub>2</sub> emission results for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle 2006 Cummins ISM engine

### 3.4.5. BSFC

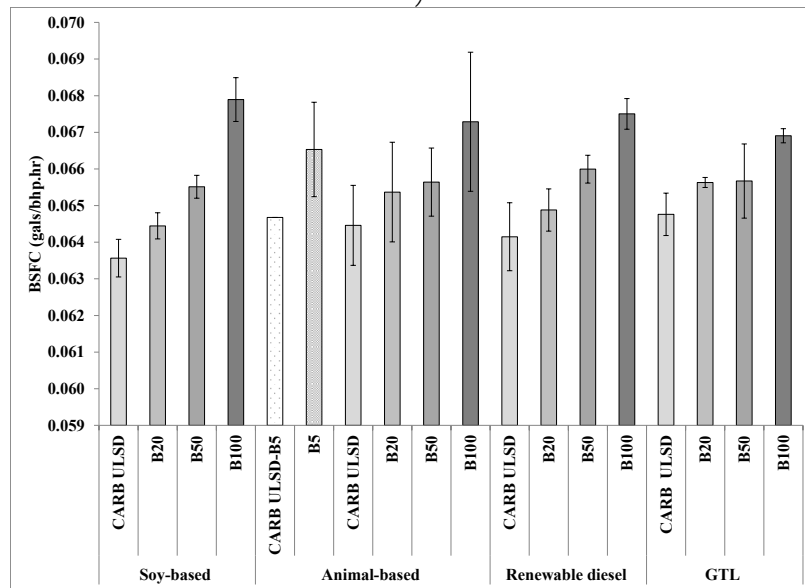
The biodiesel blends and renewable/GTL diesel fuel blends showed an increase in fuel consumption with increasing blend level. The increases in fuel consumption for the 2006 Cummins engine were 3.1 to 5.1% for B50, and 6.8 to 9.8% for B100 for the soy-based biodiesel, 1.8 to 3.1% for B50, 4.4 to 6.7% for B100 for the animal-based biodiesel, 2.9 to 3.1% for R50, and 5.1 to 5.2% for R100 for the renewable diesel fuel, and 1.3% for GTL20, 1.4% for GTL50, and 3.3% for GTL100. At the B20 level, the biodiesel fuel consumption increases were statistically significant for some cycle/feedstock combinations, but not for others. For the 2007 MBE4000 engine, the differences in fuel consumption ranged from 1 to 1.5% for B20, and 5.6-8.3% for B100 for the soy-based biodiesel. For the animal-based biodiesel fuel on the 2007 MBE4000 engine, the differences in fuel consumption ranged from 0.5% for B5, 0.2% for B20, and 7.8-8.1% for B100 for the soy-based biodiesel.

The increase in BSFC for biodiesel is due to its lower heating value compared to diesel fuel. Biodiesel is approximately 10-11% lower in heating value compared to typical diesel fuel on a mass basis, with this difference being slightly less on a volumetric basis due to biodiesel's higher density.<sup>4,8</sup> In general, studies have shown reductions in fuel economy proportional to the correspondingly lower heating value for biodiesel, although the magnitude of the increase in BSFC for biodiesel differs from study to study depending on the biodiesel feedstock and the engine used.<sup>4,39,40</sup> The 2002 EPA study found average increases of 9% in BSFC for neat biodiesel for the studies they reviewed. In typical in-use operation at B20 and lower blend levels, however, these differences may not be noticeable. Results of renewable diesel fuel are also consistent with those of other studies. Rothe et al. reported a 5% increase

in BSFC with R100 in a heavy-duty engine dynamometer study. This was attributed to the lower density and energy content for the renewable diesel.<sup>20</sup> Rantanen et al. did not find measureable differences in BSFC for a chassis dynamometer study of light-duty vehicles, however.<sup>21</sup>



a)



b)

\* Since B5 was tested outside of the test matrix sequence, the average emissions for B5 were only compared to the average of CARB emissions for tests immediately before and immediately after the B5 was tested (CARB diesel-B5 in the figures).

Figure 3-4. BSFC for the soy-based, animal-based biodiesel fuels, GTL, renewable, and CARB diesel fuels for a) UDDS and 40mph Cruise cycles, b) FTP cycle 2006 Cummins ISM engine

Table 3-4. Percentages changes for biodiesel/renewable/GTL blends relative to CARB and associated statistical p-values for 2007 MBE4000 engine for different cycles

Fuel Type	Cycle	Blend level	THC			CO			PM			CO <sub>2</sub>			BSFC		
			Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value
Soy-based	UDDS	CARB	0.023			0.022			0.0035			730.0			0.074		
		B20	0.021	-11%	0.770	0.008	-62%	0.453	0.0002	-94%	0.187	730.2	0.0%	0.971	0.075	1.0%	0.121
		B50	0.030	27%	0.400	-0.003	-111%	0.154	0.0038	9%	0.874	736.8	0.9%	0.334	0.076	2.5%	0.083
		B100	0.019	-18%	0.683	0.007	-67%	0.491	0.0022	-37%	0.470	766.2	5.0%	0.000	0.080	8.3%	0.000
	FTP	CARB-B5	0.004			0.076			0.0005			580.0			0.059		
		B5	0.006	38%	0.005	0.061	-20%	0.135	0.0002	-61%	0.096	580.3	0.0%	0.398	0.059	0.3%	0.113
		CARB	0.004			0.081			0.0006			578.9			0.059		
		B20	0.006	33%	0.005	0.091	13%	0.534	0.0006	-4%	0.944	578.7	0.0%	0.909	0.059	1.0%	0.016
		B50	0.006	25%	0.018	0.040	-50%	0.031	0.0010	58%	0.216	579.9	0.2%	0.722	0.060	1.7%	0.034
		B100	0.005	20%	0.081	0.021	-74%	0.002	0.0008	64%	0.403	592.6	2.4%	0.000	0.062	5.6%	0.000
	50 mph Cruise	CARB	0.003			0.015			0.0006			505.8			0.051		
		B20	0.003	-5%	0.801	0.014	-6%	0.809	0.0005	-19%	0.746	508.0	0.4%	0.249	0.052	1.5%	0.002
		B50	0.003	-20%	0.430	0.010	-33%	0.302	0.0006	2%	0.970	507.5	0.4%	0.548	0.052	1.9%	0.081
		B100	0.003	-13%	0.594	0.012	-21%	0.508	0.0005	-100%	0.704	518.9	2.6%	0.000	0.054	5.9%	0.000
Animal-based	UDDS	CARB	0.026			0.013			0.0004			733.6			0.074		
		B20	0.034	33%	0.000	0.016	18%	0.003	0.0012	224%	0.779	733.9	0.0%	0.000	0.075	0.2%	0.000
		B50	0.028	8%	0.695	0.011	-16%	0.875	0.0015	285%	0.219	740.7	1.0%	0.024	0.075	1.2%	0.008
		B100	0.027	6%	0.755	0.028	109%	0.238	0.0044	1043%	0.000	745.0	1.5%	0.009	0.080	8.1%	0.000
	FTP	CARB-B5	0.005			0.081			0.0005			583.1			0.059		
		B5	0.006	13%	0.612	0.072	-11%	0.202	0.0003	-32%	0.553	584.7	0.3%	0.007	0.059	0.5%	0.001
		CARB	0.005			0.084			0.0005			581.3			0.059		
		B20	0.006	13%	0.376	0.082	-3%	0.841	0.0003	-40%	0.341	581.7	0.1%	0.743	0.059	0.3%	0.182
		B50	0.005	-13%	0.568	0.052	-39%	0.040	0.0005	15%	0.757	582.4	0.2%	0.391	0.059	0.4%	0.069
		B100	0.006	5%	0.756	0.023	-73%	0.000	0.0003	-24%	0.611	590.9	1.6%	0.000	0.064	8%	0.000
	50 mph Cruise	CARB	0.003			0.018			0.0007			508.1			0.052		
		B20	0.004	17%	0.425	0.017	-7%	0.733	0.0004	-49%	0.143	508.4	0.0%	0.837	0.052	0.2%	0.301
		B50	0.003	-13%	0.448	0.012	-36%	0.144	0.0003	-58%	0.103	510.2	0.4%	0.150	0.052	0.6%	0.036
		B100	0.003	3%	0.905	0.008	-55%	0.027	0.0004	-39%	0.237	514.6	1.3%	0.002	0.056	7.8%	0.000

Table 3-5. Percentages changes for biodiesel/renewable/GTL blends relative to CARB and associated statistical p-values for 2006 Cummins ISM engine for different cycles

Fuel Type	Cycle	Blend level	THC			CO			PM			CO <sub>2</sub>			BSFC		
			Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value
Soy-based	UDDS	CARB	0.830			2.116			0.065			828.4			0.085		
		B20	0.727	-12%	0.000	2.215	5%	0.115	0.050	-24%	0.002	834.7	0.8%	0.448	0.086	1.8%	0.093
		B50	0.601	-28%	0.000	2.662	26%	0.000	0.046	-30%	0.000	848.9	2.5%	0.055	0.089	5.1%	0.001
		B100	0.376	-55%	0.000	3.419	62%	0.000	0.044	-33%	0.000	863.1	4.2%	0.003	0.093	9.8%	0.000
	FTP	CARB	0.309			0.747			0.081			624.9			0.064		
		B20	0.275	-11%	0.000	0.724	-3%	0.078	0.061	-25%	0.000	627.2	0.4%	0.309	0.064	1.4%	0.001
		B50	0.219	-29%	0.000	0.720	-4%	0.038	0.044	-46%	0.000	628.2	0.5%	0.159	0.066	3.1%	0.000
		B100	0.115	-63%	0.000	0.770	3%	0.163	0.034	-58%	0.000	634.0	1.5%	0.007	0.068	6.8%	0.000
	40 mph Cruise	CARB-B5	0.251			0.602			0.048			573.3			0.058		
		B5	0.249	-1%	0.573	0.615	2%	0.427	0.045	-6%	0.101	582.8	1.7%	0.085	0.059	1.9%	0.065
		CARB	0.247			0.599			0.049			572.6			0.058		
		B20	0.207	-16%	0.000	0.582	-3%	0.160	0.036	-26%	0.000	577.4	0.8%	0.056	0.059	1.8%	0.001
		B50	0.158	-36%	0.000	0.599	0%	0.986	0.026	-48%	0.000	580.0	1.3%	0.053	0.060	3.8%	0.000
		B100	0.075	-70%	0.000	0.602	0%	0.868	0.015	-69%	0.000	589.9	3.0%	0.000	0.063	8.4%	0.000
Animal-based	UDDS	CARB	0.799			2.052			0.065			841.3			0.086		
		B20	0.670	-16%	0.000	1.842	-10%	0.000	0.058	-10%	0.009	836.3	-0.6%	0.640	0.087	1.2%	0.404
		B50	0.495	-38%	0.000	1.800	-12%	0.000	0.049	-24%	0.001	851.1	1.2%	0.201	0.089	3.1%	0.005
		B100	0.214	-73%	0.000	1.634	-20%	0.000	0.045	-31%	0.000	862.4	2.5%	0.016	0.092	6.7%	0.000
	FTP	CARB-B5	0.303			0.715			0.076			626.5			0.065		
		B5	0.295	-3%	0.011	0.686	-4%	0.008	0.070	-9%	0.000	624.7	-0.3%	0.191	0.067	2.9%	0.031
		CARB	0.303			0.712			0.076			627.5			0.064		
		B20	0.263	-13%	0.000	0.665	-7%	0.000	0.062	-19%	0.000	628.2	0.1%	0.733	0.065	1.4%	0.145
		B50	0.194	-36%	0.000	0.609	-14%	0.000	0.044	-42%	0.000	630.4	0.4%	0.117	0.066	1.8%	0.038
		B100	0.087	-71%	0.000	0.522	-27%	0.000	0.027	-64%	0.000	632.1	0.7%	0.018	0.067	4.4%	0.001
Renewable diesel fuel	UDDS	CARB	0.769			2.091			0.063			838.5			0.086		
		R20	0.744	-3%	0.018	1.753	-16%	0.000	0.060	-5%	0.401	834.9	-0.4%	0.595	0.086	1.0%	0.255

Fuel Type	Cycle	Blend level	THC			CO			PM			CO <sub>2</sub>			BSFC		
			Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value	Ave.	% diff	P value
		R50	0.726	-6%	0.002	1.612	-23%	0.000	0.055	-12%	0.044	832.5	-0.7%	0.448	0.088	3.1%	0.007
		R100	0.677	-12%	0.000	1.392	-33%	0.000	0.045	-28%	0.000	810.7	-3.3%	0.002	0.090	5.1%	0.000
	FTP	CARB	0.294			0.701			0.073			630.7			0.064		
		R20	0.296	0%	0.719	0.675	-4%	0.022	0.070	-4%	0.023	628.8	-0.3%	0.652	0.065	1.1%	0.117
		R50	0.293	0%	0.777	0.643	-8%	0.000	0.062	-15%	0.000	624.2	-1.0%	0.124	0.066	2.9%	0.001
		R100	0.284	-4%	0.057	0.614	-12%	0.000	0.048	-34%	0.000	609.5	-3.4%	0.000	0.068	5.2%	0.000
GTL diesel Fuel	FTP	CARB	0.303			0.740			0.071			636.7			0.065		
		GTL20	0.288	-5%	0.000	0.693	-6%	0.000	0.065	-8%	0.000	636.9	0.0%	0.933	0.066	1.3%	0.001
		GTL50	0.255	-16%	0.000	0.664	-10%	0.000	0.062	-12%	0.000	624.4	-1.9%	0.001	0.066	1.4%	0.008
		GTL100	0.219	-28%	0.000	0.633	-14%	0.000	0.050	-29%	0.000	614.6	-3.5%	0.000	0.067	3.3%	0.000

### 3.5. Summary/Conclusions

In this study, the impact of different biodiesel feedstocks and renewable/GTL diesel fuel blends on criteria emissions was investigated using a CARB diesel fuel as the baseline. An important element of this study was the use of CARB diesel fuel as the baseline diesel, since it has a lower aromatic content and a relatively high cetane number compared to other Federal diesel fuels used throughout the country. For this study, two different engine technologies (one non-DPF and one DPF equipped engine) and four different engine test cycles were used. This study was one of the most comprehensive biodiesel emissions studies in terms of number of tests, testing replication and long term repeatability, and number of blend levels and types.

In general, PM, THC, and CO emissions showed reductions for biodiesel and renewable/GTL fuel blends with CARB diesel. The levels of these reductions were generally comparable to those found in previous studies performed using more typical Federal diesel fuels. For the non-DPF equipped engine, the 2006 Cummins ISM, PM and THC emissions decreased with increasing levels of different biodiesels. The reductions ranged from 10% to 26% for B20 blends and from 31% to 69% for B100 blends for PM, and from 13% to 16% for B20 blends and from 55% to 73% for B100 blends for THC. For the 2006 Cummins ISM, CO emissions decreased from 7% to 10% for B20 blends and from 20% to 27% for B100 blends for the animal-based biodiesel, but CO emissions for the soy-based biodiesel on this engine did not show any clear reduction trends, and even showed increases for the B50 and B100 blends over the UDDS. For this same engine, PM, THC, and CO emissions showed reductions with increasing renewable/GTL blend level, with the exception of THC

emissions for the renewable blends over the FTP cycle. For the DPF-equipped engine, the 2007 MBE4000, THC, CO, and PM emission levels were very low due to the DPF and did not show significant fuel impacts.

For both engines, CO<sub>2</sub> emissions showed slight increases of 1-5% for the pure biodiesels and a slight decrease of 3% for pure renewable/GLT diesel fuels, which is likely due to differences in average carbon content per unit of energy between the different fuels. BSFC showed slight increases of 1.4-9.8% with increasing biodiesel fuel and slight increases of 1.3-5.2% with increasing renewable/GTL diesel fuel, which is due to the lower heating value of these fuels compared to the CARB diesel.

### **3.6. Acknowledgements**

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## **Chapter Four: Impacts of Biodiesel Feedstock and Additives on Criteria Emissions from a Heavy-Duty Engine**

### **4.1. Abstract**

The reduction of emissions from diesel engines has been one of the primary elements in obtaining air quality and greenhouse gas reduction goals. Biodiesel is an important alternative fuel for diesel applications, but there is a tendency for biodiesel to increase nitrogen oxides ( $\text{NO}_x$ ) emissions, which remains an important issue in nonattainment areas for ozone and particulate matter (PM). This study investigated the effect of using low blend level biodiesels and fuel additives on emissions. Emissions from three B5 biodiesel fuels and six B20-soy with additive blends were evaluated as potential emissions equivalent biodiesel formulations for California. B5-soy and B5-Waste Vegetable Oil (WVO) both showed measurable increases in  $\text{NO}_x$  emissions, while a B5-animal showed a slight reduction or no change in  $\text{NO}_x$  emissions compared to the CARB reference diesel. The B5-animal blend also passed the criteria of the CARB diesel emissions equivalent certification test. Of the additives tested, only one provided reductions in  $\text{NO}_x$  emissions for the B20-soy blends, but the reductions were not significant enough to pass the CARB diesel emissions equivalent certification test at the B20 level. Biodiesel blends generally showed either reductions or no significant changes in PM, total hydrocarbon (THC), and carbon monoxide (CO) emissions.

## 4.2. Introduction

There is a global interest in expanding the long term use of renewable fuels in transportation applications. The transportation sector represents one of the largest contributions to greenhouse gas and criteria emission inventories. One of the primary drivers for increasing the use of renewable fuels is the potential to reduce greenhouse gas emissions, such as carbon dioxide (CO<sub>2</sub>), which contribute to global warming and climate change.<sup>1</sup> Studies have shown that the application of renewable fuels in the transportation sector can also decrease emissions of some criteria pollutants, such as particulate matter (PM) and carbon monoxide (CO), and help to improve air quality.<sup>2</sup> Increasing consumption of renewable fuels also reduces dependency on conventional fossil fuels, which ultimately have limited reserves.

In recent years, governmental agencies around the world have implemented legislation that targets growing the use of renewable fuels in the transportation sector. In the United States (U.S.), the energy independence and security act of 2007 targets the production of 36 billion gallons of biofuels in the U.S. (mostly ethanol) by 2022.<sup>3</sup> The European Union (EU) has implemented several government mandates, such as the EU Renewable Energy Directive (2009/28/EC), which requires at least 10% of each Member State's transport fuel use to come from renewable sources (including biofuels).<sup>4</sup> In Asia, recently several regulations have been approved and implemented. In Japan, the government announced a target to increase the annual production of biofuels from 175,000 cubic meters in 2010 to 500,000 cubic meters in 2017.<sup>5</sup> In China, in August 2007, the National Development Reform Commission (NDRC) announced a Medium and Long Term Development Plan for Renewable Energy. In India, a National Policy on Biofuels was approved in September 2008, which mandates a

20% share of biodiesel and bioethanol shall be blended with diesel and gasoline by 2017.<sup>6</sup>

On a more regional level, California implemented the low carbon fuel standard (LCFS) in 2011 to promote the reduction of greenhouse gas emissions by targeting a reduction in the carbon intensity of transportation fuels by 10% by 2020.<sup>7</sup>

Fatty acid alkyl esters – most commonly Fatty Acid Methyl Esters (FAME) often referred to as biodiesel, are one of the most widespread renewable fuels. Commercially, biodiesel is produced by transesterification of triglycerides, the main constituent of vegetable oils, animal fats, and waste cooking oils. Transesterification occurs when triglycerides are mixed with an alcohol in the presence of an alkaline liquid catalyst, usually sodium or potassium methoxide. Biodiesel has several significant benefits aside from its value as a renewable fuel. For instance, biodiesel, either in its pure form or when blended with regular diesel fuel, can be used in existing diesel engines with no or minor engine modifications.<sup>1,8,9</sup> Several studies have shown that biodiesel blends reduce PM, CO, and total unburned hydrocarbon (THC) emissions compared to diesel fuel.<sup>1,10–14</sup> Biodiesel blends have been shown to have the ability to reduce the overall life cycle emissions of CO<sub>2</sub>, when evaluated using a total carbon life cycle analysis<sup>1,15,16</sup>, although this can depend on a variety of factors, such as land use change, transportation, etc.<sup>17,18</sup> A drawback in using biodiesel blends, however, is the potential to increase NO<sub>x</sub> emissions compared to ultra-low sulfur diesel fuel (ULSD).<sup>10–12,15,19</sup>

NO<sub>x</sub> is one of the primary precursors of ground-level ozone and secondary ambient PM formation. Over the years, increasingly more stringent regulations on diesel engines have been put in place, culminating with the U.S. EPA 2010 on-road heavy-duty engine standards that essentially require exhaust aftertreatment to reduce NO<sub>x</sub> emissions. In states where a

number of urban areas do not meet the national ambient air quality standards (NAAQS), such as California or Texas, further regulations of diesel fuel quality have also been put into place. These regulations require diesel fuel to meet a more stringent set of properties, or show emissions equivalence to a 10% aromatic-hydrocarbon reference diesel fuel. As such, the California Air Resources Board (CARB) sets fuel specifications to ensure that fuels introduced into the state on a widespread basis do not adversely affect the State's air quality.

In recent years, many researchers have studied the impact of biodiesel blends on NO<sub>x</sub> emissions.<sup>12,15,16,20–22</sup> Many of these studies have shown increases in NO<sub>x</sub> emissions, although this trend is not consistent over all studies and all conditions.<sup>2,12,13,19,23,24</sup> Researchers have identified a variety of factors that could contribute to increased NO<sub>x</sub> emissions for biodiesel.<sup>8,9,14</sup> Recent studies have suggested that the impacts of biodiesel on NO<sub>x</sub> emissions is probably best explained by a combination of factors that couple together differently under different conditions. Eckerle et al. suggested that both fundamental combustion effects, driven by fuel chemistry and fluid dynamics, and the effects of operating on lower energy content biodiesel must be considered to understand the impact of biodiesel on NO<sub>x</sub>. They separated the combustion effect into flame temperature effects and ignition delay effects.<sup>25</sup> For the fundamental combustion effects, they emphasized importance of the double bonds in biodiesel correlating with higher adiabatic flame temperatures, which can enhance NO<sub>x</sub> formation through the thermal (Zeldovich) NO<sub>x</sub> formation mechanism, as had previously been suggested by Banweiss et al.<sup>26,27</sup> For the engine control effects, they evaluated the impact of increasing fuel volumetric flow rate needed for lower energy biodiesel on air-fuel ratio controls, exhaust gas recirculation (EGR) rate, and injection pressure and timing.

Mueller et al. suggested that the presence of oxygen in biodiesel can also contribute to charge-gas mixtures that are closer to stoichiometric at ignition and in the standing premixed autoignition zone near the flame lift-off length. This in turn can lead to higher local and average in-cylinder temperatures and a shorter, more advanced combustion event, which would all contribute to increased thermal  $\text{NO}_x$  emissions.<sup>27,28</sup> This could also contribute to reduced radiant heat losses during combustion due to a reduction of PM emissions with biodiesel, and the corresponding higher combustion temperatures and higher  $\text{NO}_x$  emissions, as has also been suggested previously by Cheng et al.<sup>29</sup> The Mueller et al. work did also find that although adiabatic flame temperature differences may contribute to  $\text{NO}_x$  differences, it did not appear to play a primary role in this regard.<sup>28</sup> In older engine technologies with pump line fuel injection systems,  $\text{NO}_x$  increases have been associated with the higher bulk modulus of biodiesel, which leads to a more advanced injection timing, which in turn increases fuel residence time and heat release near top dead center and raises the combustion temperature.<sup>30</sup>

While studies investigating the impact of biodiesel blends on emissions, and specifically  $\text{NO}_x$ , are extensive and diverse, such studies have often been limited in terms of the number of engines and test replicates, with many of these studies focusing mainly on diesel fuels with relatively high sulfur and aromatic contents compared to the ones used in areas with more stringent air quality regulations, such as California and Texas.<sup>1,11–13,23</sup> Durbin et al. recently performed a comprehensive biofuels emissions study focusing mainly on  $\text{NO}_x$  emissions.<sup>10,11</sup> They investigated the impact of biodiesel blends with diesel fuels meeting California Air Resources Board (CARB) requirements, which are characterized with low aromatic contents

and relatively high cetane numbers. The results of their study showed that B20 and higher biodiesel blends would likely increase NO<sub>x</sub> emissions in CARB diesel fuels. However, the results were less definitive at lower blend levels such as B5. The results also showed that the impacts of NO<sub>x</sub> increases with biodiesel could be mitigated with combinations of blends with renewable and gas-to-liquid (GTL) diesel fuels, or with additives, such as di-tert-butyl peroxide (DTBP).<sup>10,11</sup> The use of additives, in particular, has also shown some success in other studies, and could represent a viable and cost effective pathway to achieving NO<sub>x</sub> neutral biodiesel blends.<sup>19,22,31</sup>

The present study expands upon the earlier Durbin et al. work to more extensively study low level biodiesels blends and additives.<sup>10,11,32</sup> This study explores the emissions impacts of different B5 biodiesel blends and B20 with additive blends under CARB's procedures for qualifying emissions equivalent diesel fuel formulations. The emissions equivalent diesel certification procedure is robust in that it requires at least twenty replicate tests on the reference and candidate fuels, providing the ability to differentiate small differences in emissions. For this study, preliminary tests were performed on biodiesel blends at a 5% concentration by volume (B5) prepared from three different methyl esters, including an animal fat methyl ester, a soybean oil methyl ester, and a waste vegetable oil (WVO) methyl ester. In addition, higher biodiesel blends made at a 20% concentration by volume (B20) with soybean oil methyl ester and treated with five different additive combinations were evaluated. Full certification tests were then performed on two of the B5 fuels, the B5-animal and B5-WVO, and one of the B20-soy with additive blends.

### **4.3. Experimental Methods**

#### **4.3.1. Test Fuels and Test Engine**

Nine different biodiesel blends were tested in this study. The biodiesel fuels were blended volumetrically at 5% and 20% levels, and are denoted as B5 and B20 throughout this paper. Additives were also added to the B20 blends. A CARB reference fuel was used as the baseline fuel to which the candidate fuels emissions were compared, and the base fuel with which the biodiesel was blended to produce the candidate fuels. The reference fuel was a 10% aromatic hydrocarbon diesel fuel meeting the CARB reference fuel specifications under title 13, California Code of Regulations (CCR), section 2282(g)(3). The testing was conducted in two different segments for both the B5 and B20 fuels. First, preliminary or scoping testing was conducted on selected biodiesel blends for comparison. Full certification testing was then performed on the candidate fuels from the preliminary testing that showed the most promise.

Three B5 biodiesel blends were tested in the first phase of this study, one with a soy-based biodiesel, one with an animal tallow biodiesel, one with a WVO biodiesel, and one with a soy-based biodiesel. The B5 blends are denoted B5-soy, B5-animal, and B5-WVO throughout this paper.

Six soy-based B20 biodiesel blends were tested in the second phase of the study, including five with additives and one without an additive. The soy-based biodiesel, denoted as B20-soy, was used as the base fuel for all the B20 testing. The additives are denoted by the company that produces them, including Kern Fuels Research LLC (Kern), Viscon USA LLC

(Viscon), Octcet Inc. (Octcet), and Innospec Inc. (Innospec), along with the concentration of additive used. For Innospec, two different additives were used during the preliminary testing, as noted in the paper by adding numbers to the end of the name of the company. The two Innospec additives represented different combinations and concentrations of similar additive formulations.

Table 4-1 shows some key properties of the CARB reference fuels, the neat biodiesels, and the biodiesel blends. Note that two different batches of reference fuel from the same supplier were used in this study. One was used during the B5 testing and preliminary testing of the Kern and Octcet B20-soy blends, and the other was used for the rest of B20-soy blend preliminary and certification testing. It should be noted that the properties provided for the B20-soy and B5-soy blends are arithmetic averages of the corresponding properties for the CARB reference fuel and the pure soy-based biodiesel based on their relative volume, mass, or energy fractions. More detailed listings of all the properties of the CARB reference fuels, the neat biodiesel fuels, and the biodiesel blends are also provided in the Appendix B.

The engine that was used in this study was a 10.8L 2006 model year Cummins ISM engine with a turbocharger with a charge air cooler and exhaust gas recirculation (EGR). The specifications of the engine are provided in the Appendix B.

Table 4-1. Fuel properties of pure animal, WVO, and soy-based biodiesel, CARB reference fuel., B5-Animal, B5-WVO, and B20-Soy

Property	Test Method	Units	Animal	WVO	Soy	CARB Batch 1	CARB Batch 2	B5- Animal	B5-WVO	B5-Soy*	B20-Soy*
Sulfur	ASTM D5453	ppm	6.5	11.1	1.1	4.7	None Detected	4.5	5.3	NA	NA
Cetane Number	ASTM D613		61.1	54.6	49.2	53.1	48.4	61	52.2	NA	NA
Heating value	ASTM D240	BTU/lb	17133	17076	17140	19689	19689	19661	19649	19568	19200
API Gravity@60°F	ASTM D4052		30.20	28.40	28.43	37.2	38	38.5	38.2	36.76	35.4
Specific Gravity @60°F	ASTM D4052		0.8750	0.8851	0.8848	0.839	0.836	0.8326	0.8339	0.841	0.85
Carbon	ASTM D5291	wt%	76.19	76.67	77.10	85.80	85.80	85.78	85.85	85.4	84.1
Hydrogen	ASTM D5291	wt%	12.28	11.98	11.85	13.61	13.61	13.8	13.82	13.5	13.3
Carbon Unit per Energy		lbs. Carbon/BTU	$4.45 \times 10^{-5}$	$4.49 \times 10^{-5}$	$4.50 \times 10^{-5}$	$4.36 \times 10^{-5}$	$4.36 \times 10^{-5}$	$4.36 \times 10^{-5}$	$4.37 \times 10^{-5}$	$4.37 \times 10^{-5}$	$4.39 \times 10^{-5}$

- B5-soy and B20-soy properties are the arithmetic averages of B100-soy and CARB reference fuel

#### **4.3.2. Test Cycle and Test Matrix**

All testing was conducted in accordance with the Federal Test Procedure (FTP) for heavy-duty engines.<sup>33</sup> The testing for the preliminary and certification emissions testing was conducted using one of the hot start sequences described under 13 CCR 2282(g)(4)(C)1.b Alternative 1. The daily test sequence was performed as RC CR RC CR, where "R" is the reference fuel and "C" is the candidate fuel. For the preliminary testing, only a single day using this sequence was conducted for each of the candidate fuels. For the certification testing, this sequence was continued for a period of at least 5 days until a minimum of twenty individual hot start exhaust emission tests with an equal number of morning and afternoon tests were completed with each fuel. The test sequence for the certification testing is presented in the Appendix B. An engine map was conducted at the beginning of each test day on the reference fuel. This provided consistent preconditioning for each test day. The engine map on the reference fuel for the first day for a given test sequence was used for all subsequent emissions testing on both the reference and candidate fuels.

#### **4.3.3. Emissions Testing**

The engine emissions testing was performed in the University of California, Riverside's (UCR's) College of Engineering-Center for Environmental Research and Technology's (CE-CERT's) heavy-duty engine dynamometer laboratory. This laboratory is equipped with a 600-hp General Electric DC electric engine dynamometer.

For all tests, standard emissions measurements of THC, CO, NO<sub>x</sub>, PM, and CO<sub>2</sub> were made. The emissions measurements were made using the standard analyzers in CE-CERT's heavy-

duty Mobile Emissions Laboratory (MEL) trailer.<sup>34,35</sup> Fuel consumption was determined from these emissions measurements via the carbon balance method using the densities and carbon weight fractions from the fuel analysis.

As a part of the certification testing procedure, soluble organic fraction (SOF) analysis was performed on PM filters collected during the B5-animal and B5-WVO certification testing. For the B5-animal testing, PM filters from each test were analyzed for SOF. For the B5-WVO testing, only 3 SOF analyses were performed for both the CARB reference fuel and the B5-WVO since this blend did not pass the NO<sub>x</sub> certification criteria. For these three analyses on each fuel, filters from 12 different tests were aggregated into 3 different groups.

For SOF analysis, the filters were weighed prior to extraction with a Mettler Toledo MT5 electro microbalance with  $\pm 0.001$  mg sensitivity. The polyethylene ring was carefully removed from the exposed Teflon-membrane filters (47 mm) prior to weighing. The filters were subsequently extracted with dichloromethane followed by hexane in an Accelerated Solvent Extractor (Dionex 3000), dried, reconditioned and re-weighted to determine the SOF. A combination of dichloromethane with hexane was used for the extraction, since it gives good recovery for aliphatic hydrocarbons, cycloalkanes, PAH, hopanes, and steranes, i.e., the classes of compounds that are prevalent in motor vehicle emissions.

#### **4.4. Results and Discussion**

The results of the preliminary and certification testing for each emission component are presented in Figure 4-1 to Figure 4-5. These figures represent the average of all test runs done on a particular fuel for a specific test segment. The error bars represent one standard

deviation on the average value. The CARB reference fuel results are presented separately for the different test days for the preliminary testing and for the different test periods for the certification testing, and are shown with different bars in the figures, denoted as CARB vs. the blend name. Table 4-2 and Table 4-3 show the average emission values, the percentage differences for the different biodiesel fuels compared to the CARB reference fuel, and the associated p-values for statistical comparisons using a 2-tailed, 2-sample, equal-variance t-test. The results of this study were considered to be statistically significant for p-values  $\leq 0.05$ , and marginally statistically significant for  $0.05 \leq \text{p-values} < 0.1$ . The pass/fail criteria for the certification testing is based on additional statistical analysis for NO<sub>x</sub>, PM, and SOF. More detailed results for the NO<sub>x</sub>, PM, and SOF for the certification testing, and the corresponding statistical analysis for the certification test criteria, are provided in the Appendix B.

Table 4-2. Emissions (g/bhp-hr) and BSFC (gal/bhp-hr) percentage differences between the B5 biodiesel blends and the CARB reference fuel for the preliminary and certification testing

		NO <sub>x</sub> Emissions			PM Emissions			SOF Emissions			THC Emissions		
	Fuel Type	Ave. (g/bhp.hr)	% Diff vs. CARB	P- values	Ave. (g/bhp.hr)	% Diff vs. CARB	P- values	Ave. (g/bhp.hr)	% Diff vs. CARB	P- values	Ave. (g/bhp.hr)	%Diff vs CARB	P- values
	CARB	2.04			0.065						0.32		
	B5-Animal	2.05	0.1%	0.844	0.063	-5.9%	<b>0.003</b>				0.33	2.4%	0.367
	B5-WVO	2.07	1.2%	<b>0.020</b>	0.062	-3.8%	<b>0.000</b>				0.29	-8.8%	<b>0.000</b>
	B5-Soy	2.07	1.3%	<b>0.001</b>	0.063	-4.2%	<b>0.001</b>				0.33	4.3%	<b>0.001</b>
Certification Testing	CARB	2.04			0.067			0.0105			0.33		
	B5-Animal	2.03	-0.5%	<b>0.006</b>	0.065	-4.2%	<b>0.000</b>	0.0091	-13.6%	<b>0.036</b>	0.31	-4.8%	<b>0.001</b>
	CARB	2.05			0.068			0.0143			0.33		
	B5-WVO	2.08	1.0%	<b>0.0001</b>	0.063	-7.0%	<b>0.000</b>	0.0142	-0.2%	0.990	0.32	-2.1%	0.330
		CO Emissions			CO <sub>2</sub> Emissions			BSFC					
	Fuel Type	Ave. (g/bhp.hr)	% Diff vs. CARB	P- values	Ave. (g/bhp.hr)	% Diff vs. CARB	P- values	Ave. (g/bhp.hr)	% Diff vs. CARB	P- values			
Preliminary Testing	CARB	0.80			632.30			0.064					
	B5-Animal	0.80	-0.3%	0.761	637.21	0.8%	<b>0.000</b>	0.065	2.0%	<b>0.000</b>			
	B5-WVO	0.83	3.8%	<b>0.011</b>	638.08	0.9%	<b>0.000</b>	0.065	1.4%	<b>0.000</b>			
	B5-Soy	0.81	1.1%	0.272	636.45	0.7%	<b>0.002</b>	0.064	0.6%	<b>0.000</b>			
Certification Testing	CARB	0.78			634.88			0.064					
	B5-Animal	0.74	-5.9%	<b>0.000</b>	636.58	0.3%	<u>0.077</u>	0.065	1.0%	<b>0.000</b>			
	CARB	0.78			638.2			0.064					
	B5-WVO	0.77	-1.8%	<b>0.002</b>	638.9	0.1%	0.464	0.065	0.6%	<b>0.000</b>			

- Bold : Statistically significant; Underline : Marginally statistically significant

Table 4-3. Emissions (g/bhp-hr) and BSFC (gal/bhp-hr) percentage differences between the B20 additive biodiesel blends and the CARB reference fuel for the preliminary and certification testing

		NO <sub>x</sub>			PM Emissions			THC Emissions		
	Fuel Type	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values
Preliminary Testing 1	CARB vs. B20- soy 0.01% KERN	2.05			0.046			0.34		
	B20-soy 0.01% KERN	2.11	3.1%	<b>0.000</b>	0.036	-21.3%	<b>0.000</b>	0.30	-12.3%	<b>0.012</b>
	CARB vs. B20-soy 0.03% VISCON	2.06			0.045			0.35		
	B20-soy 0.03% VISCON	2.14	3.8%	<b>0.000</b>	0.048	-23.3%	<b>0.000</b>	0.31	-9.9%	<b>0.028</b>
	CARB vs. B20-soy 0.25% OCTCET	2.03			0.049			0.35		
	B20-soy 0.25% OCTCET	2.13	5.1%	<b>0.000</b>	0.037	-24.7%	<b>0.000</b>	0.31	-13.7%	<b>0.002</b>
	CARB vs. B20-soy 1% INNOSPEC 1	2.06			0.053			0.34		
	B20-soy 1% INNOSPEC 1	2.08	1.2%	<u>0.100</u>	0.038	-18.0%	<b>0.000</b>	0.29	-15.5%	<b>0.000</b>
	CARB vs. B20-soy	2.07			0.050			0.35		
	B20-soy	2.14	3.3%	<b>0.016</b>	0.039	-20.7%	<b>0.001</b>	0.31	-10.8%	<b>0.008</b>
Preliminary Testing 2	CARB vs. B20-soy 1.5% INNOSPEC 2	2.05			0.064			0.31		
	B20-soy 1.5% INNOSPEC 2	2.10	2.5%	<b>0.000</b>	0.054	-15.7%	<b>0.000</b>	0.28	-10.9%	0.337
Certification Testing	CARB vs. B20-soy 1% INNOSPEC 1	2.07			0.066			0.33		
	B20-soy 1% INNOSPEC 1	2.12	2.5%	<b>0.000</b>	0.052	-20.6%	<b>0.000</b>	0.28	-16.8%	<b>0.000</b>
		CO Emissions			CO <sub>2</sub> Emissions			BSFC		
	Fuel Type	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values
Preliminary Testing 1	CARB vs. B20- soy 0.01% KERN	0.78			622.0			0.063		
	B20-soy 0.01% KERN	0.73	-6.9%	<b>0.019</b>	624.6	0.4%	0.895	0.063	1.0%	0.103
	CARB vs. B20-soy 0.03% VISCON	0.79			619.7			0.062		
	B20-soy 0.03% VISCON	0.72	-8.9%	<b>0.009</b>	621.4	0.3%	0.156	0.063	1.2%	<b>0.001</b>
	CARB vs. B20-soy 0.25% OCTCET	0.81			629.2			0.063		
	B20-soy 0.25% OCTCET	0.72	-12.0%	<b>0.000</b>	630.6	0.2%	0.502	0.064	1.1%	<b>0.013</b>
	CARB vs. B20-soy 1% INNOSPEC 1	0.79			630.0			0.063		
	B20-soy 1% INNOSPEC 1	0.68	-14.5%	<b>0.000</b>	633.5	0.6%	<u>0.091</u>	0.064	1.5%	<b>0.002</b>
	CARB vs. B20-soy	0.78			620.4			0.062		
	B20-soy	0.76	-3.1%	0.278	623.9	0.6%	<b>0.008</b>	0.063	1.5%	<b>0.000</b>

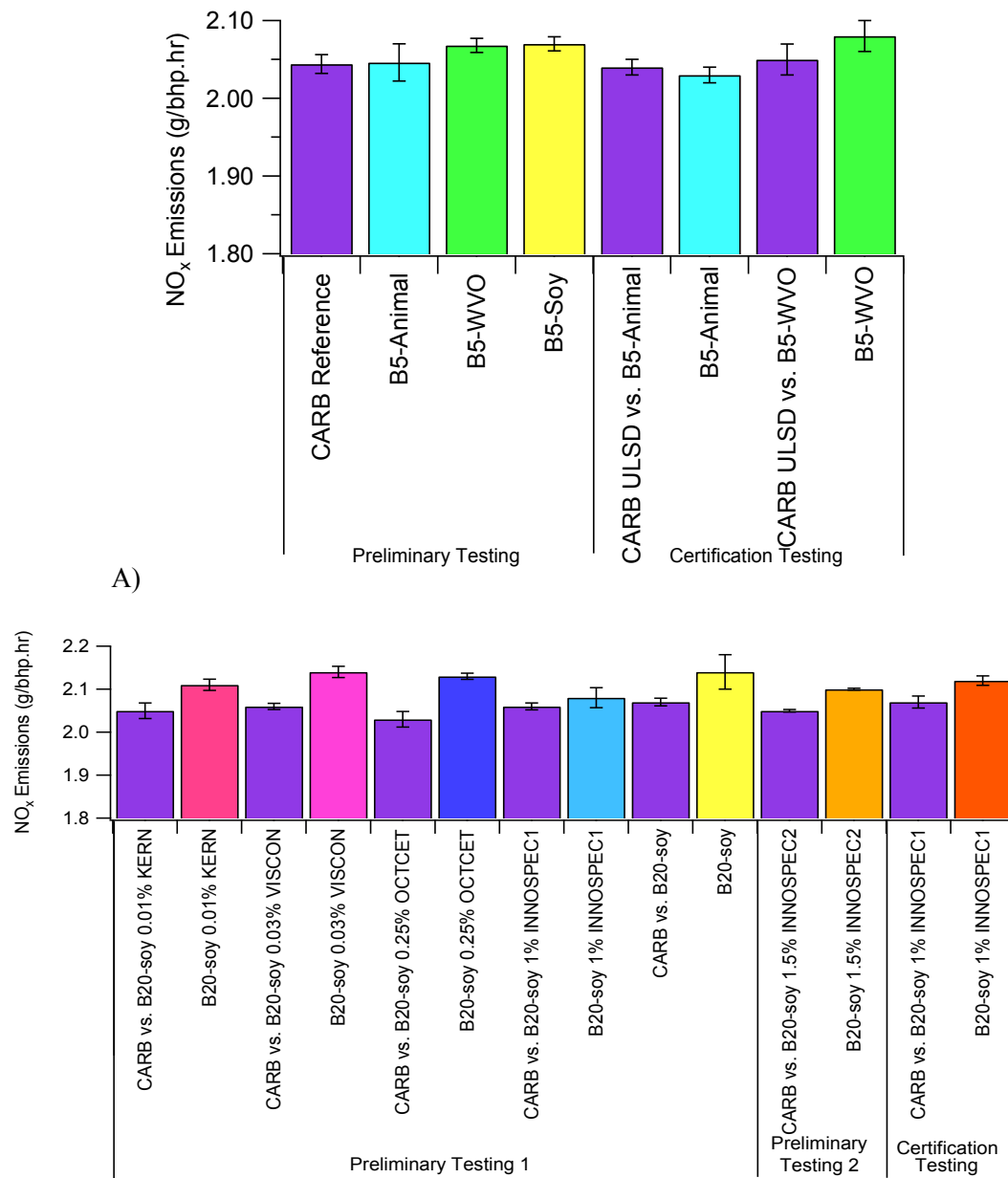
		NO <sub>x</sub>			PM Emissions			THC Emissions		
	Fuel Type	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values	Ave. (g/bhp.hr)	% Diff vs. CARB	P-values
Preliminary Testing 2	CARB vs. B20-soy 1.5% INNOSPEC 2	0.76			623.4			0.063		
Certification Testing	B20-soy 1.5% INNOSPEC 2	0.66	-14.2%	<b>0.002</b>	630.7	1.2%	<b>0.047</b>	0.064	2.1%	<b>0.011</b>
	CARB vs. B20-soy 1% INNOSPEC 1	0.80			624.6			0.063		
	B20-soy 1% INNOSPEC 1	0.67	-15.9%	<b>0.000</b>	626.5	0.3%	<u>0.062</u>	0.064	1.2%	<b>0.000</b>

- Bold : Statistically significant; Underline : Marginally statistically significant

#### **4.4.1. NO<sub>x</sub> Emissions**

The NO<sub>x</sub> emissions results for the B5 and B20 are presented in Figure 4-1 on a gram per brake horsepower hour (g/bhp-hr) basis. The preliminary B5 testing showed statistically significant 1.2-1.3% increases with the B5-soy and B5-WVO biodiesel blends compared to the CARB reference fuel. The preliminary B5-animal emissions results, on the other hand, did not show any statistical differences in NO<sub>x</sub> compared to the CARB reference fuel. Therefore, this fuel blend was considered the most viable candidate fuel for the actual certification testing.

The emissions equivalent B5 certification testing was performed on B5-animal and B5-WVO blends. The B5-animal emissions results of the certification testing showed a statistically significant 0.5% reduction in NO<sub>x</sub> emissions compared to the CARB reference fuel. The B5-WVO emissions results, on the other hand, showed a statistically significant 1.0% increase in NO<sub>x</sub> emissions compared to the CARB reference fuel. Based on the certification testing results, the B5-animal passed the certification criteria for NO<sub>x</sub> emissions, while the B5-WVO failed.



B)  
Figure 4-1. Average NO<sub>x</sub> emission results for the preliminary and certification testing A) B5,  
B) B20 with additives

The results of the B5 testing are consistent with previous studies showing that the magnitude of NO<sub>x</sub> emissions increases can change with the biodiesel feedstock, with more saturated feedstocks, such as animal tallow, often showing smaller increases.<sup>11,14,16</sup> It is worth noting that while candidate fuels must pass certification criteria for NO<sub>x</sub>, PM, and SOF, for biodiesel blends NO<sub>x</sub> emissions were considered the most important pollutant for this testing, since other pollutants generally tend to decrease for biodiesel blends.

NO<sub>x</sub> emissions results for the B20 preliminary testing showed a statistically significant 1.2-5.1% increase with B20-soy with additive blends compared to the CARB reference fuel. In comparison, NO<sub>x</sub> emissions results for the B20 soy blend without additives showed an increase of approximately 3.3%. The B20-soy 1% INNOSPEC 1 blend from the preliminary testing showed the lowest increase in NO<sub>x</sub> emissions (1.2%) compared to the other B20-soy with additive blends. The B20-soy 1% INNOSPEC 1 blend was also the only additive blend that showed a marginally statistically significant reduction in NO<sub>x</sub> emissions compared to the B20-soy based biodiesel without additives. It should be noted that there was a range of approximately 2% in the daily average NO<sub>x</sub> emissions for the CARB reference fuel between the days with the highest and lowest NO<sub>x</sub> emissions, so these data cannot be taken as a definitive comparison of the performance between the individual additives themselves. The B20-soy 1% INNOSPEC 1 blend was selected for the actual certification testing on the basis of the preliminary test results. The more comprehensive certification emissions testing results for the B20-soy 1.0% INNOSPEC 1 blend showed a 2.5% statistically significant increase in NO<sub>x</sub> emissions over the CARB reference fuel. Therefore, the B20-soy 1% INNOSPEC 1 blend did not pass NO<sub>x</sub> emissions criteria of the certification testing.

Although many studies have shown NO<sub>x</sub> increases with biodiesel, there are still questions as to the actual impact of biodiesel on NO<sub>x</sub> emissions at B20 and lower levels. Broad based literature reviews have shown there is considerable variability between studies, making it difficult to definitely conclude that biodiesel increases NO<sub>x</sub> emissions at B20 and lower levels.<sup>10-12,15</sup> Evaluating a more limited subset of studies using CARB-like diesel fuels shows a stronger tendency for NO<sub>x</sub> increases at the B20 level. In evaluating a range of heavy-duty engine dynamometer studies with B20 soy-based biodiesel in CARB-like diesel fuel, Hajbabaei et al. found average increases of 4.2% for B20-soy, comparable to values seen in this study.<sup>11</sup>

Studies characterizing the emissions impacts of biodiesel at levels lower than B20 have been even more limited. Hajbabaei et al. showed mixed results for B5 blends with CARB diesel depending on the engine type, biodiesel type, and number of replicates. For soy-based B5 blends, however, it was found that some type of mitigation, either in the form of an additive or blending with another renewable diesel, was needed to achieve NO<sub>x</sub> neutrality compared to CARB diesel.<sup>11</sup> Nikanjam et al. did not show significant differences in NO<sub>x</sub> with B5, although more limited replicates were used in that study.<sup>36</sup> At the B10 level, data are even more limited, with a few studies showing increases for B10 compared to CARB diesel.<sup>10,11,37</sup> The results of this study suggest that small but detectable increases can be seen for B5 blends with CARB diesel when a sufficiently robust test matrix is used, although increases were not seen for the animal-based B5 blend. This is consistent with other studies showing that more saturated biodiesels, such as animal-based biodiesel, show smaller increases in NO<sub>x</sub> emissions.<sup>2,12,19,24</sup>

Several previous studies have shown that NO<sub>x</sub> neutral biodiesel blends can be obtained using additive blends with either DTBP or 2-EHN. Some of these earlier studies used older engines or non-CARB-like base fuels, however, which would make them less comparable with the present study.<sup>19,22,31,38,39</sup> McCormick et al. investigated the effect of using cetane improver additives, such as DTBP, 2-EHN, and the antioxidant additive tert-butyl hydroquinone (TBHQ). They showed that these additives can reduce NO<sub>x</sub> emissions increases to some extent, however, the magnitude of the reductions was dependent on the base fuel aromatic content.<sup>39</sup> Several other authors have tested DTBP and 2-EHN additives and observed some potential for mitigating NO<sub>x</sub> increases with biodiesel blends.<sup>40-45</sup> The effect of cetane improvers tends to be less or negligible in newer engine technologies.<sup>2,40</sup> The results of a study performed by Durbin et al. were mixed for different additives tested on a different 2006 Cummins ISM engine, with a 1% DTBP additive blend showing NO<sub>x</sub> neutrality for B20 and lower blends, while other tests using an 2-EHN additive blend were not successful at mitigating NO<sub>x</sub> emissions even at blend levels as low as 5%.<sup>10,11</sup> Some of the specific additives used in this study have also shown more substantial reductions in other studies of a more limited scope.<sup>46,47</sup>

#### **4.4.2. PM and SOF Emissions**

The PM emission results for the B5 and B20 testing and SOF emissions results for the B5 certification testing are presented in Figure 4-2 on a g/bhp-hr basis. PM emissions showed consistent, statistically significant reductions for both the B5 and B20 blends. For the B5 blends, the reductions ranged from 4-7% over the preliminary and certification testing. Larger reductions ranging from 15.7-24.7% were found for the B20 with additive blends and

B20-soy compared to CARB reference fuel for preliminary and certification testing. No statistical differences were found between PM emissions of B20 with or without additives, indicating the additives did not appear to provide additional PM benefits beyond that obtained for the biodiesel itself. For the certification test, the reduction in PM emissions was 20.6% for the B20-soy 1.0% INNOSPEC 1 blend. The B20-soy 1% INNOSPEC 1 blend and both the B5 blends passed the PM emissions criteria of the certification testing.

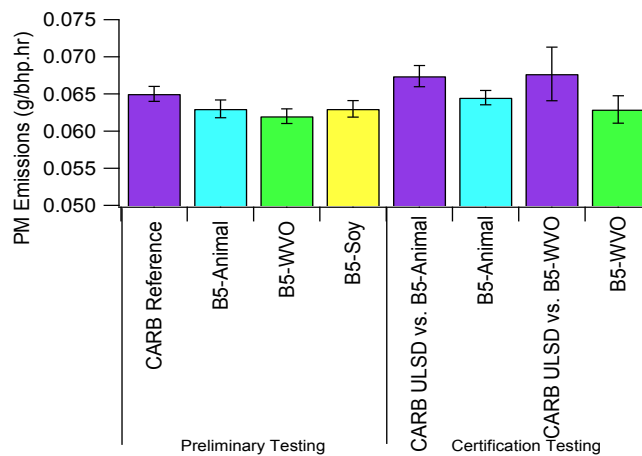
SOF overall represented a relatively small fraction of the total PM mass, ranging from 14-23%. The B5-animal emissions results showed a statistically significant reduction in SOF compared to the CARB reference fuel. The decrease in SOF emissions for the B5-animal was actually greater on a percentage basis than the reduction in total PM mass for the certification test. Based on the certification testing results, the B5-animal passed the certification criteria for SOF. The B5-WVO emissions results showed no difference compared to the CARB reference fuel for SOF. The greater variability for the B5-WVO results is probably due to the limited number of SOF analyses conducted for the B5-WVO certification test, or the fact that the samples were aggregated from several individual tests. Since the B5-WVO results were not analyzed for all of the samples, these results were not analyzed in terms of pass/fail for the certification test. SOF results were not analyzed for the B20 certification test since it did not pass the certification criteria for NO<sub>x</sub> emissions.

Consistent with many previous studies, PM emissions decreased with increasing biodiesel levels.<sup>11-14,21</sup> PM reductions with biodiesel blends are generally attributed to the presence of oxygen in the biodiesel and its impact on reducing excessively rich zones during combustion.

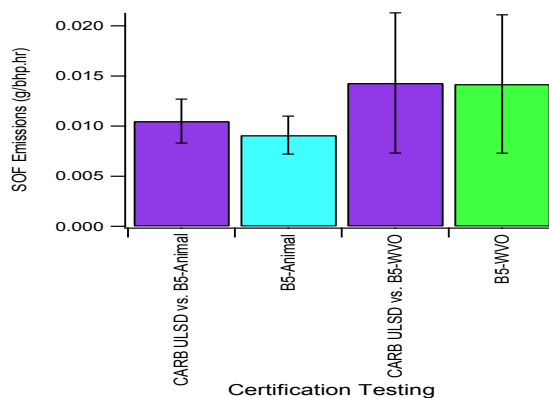
<sup>11-14,21,22,31,48,49</sup> In other studies, adding additives to biodiesel blends has generally not shown

significant additional benefits with respect to PM, similar to the present study<sup>10,22,31,48,49</sup>, with the exception of some tests that appear to be outliers.<sup>46,47</sup>

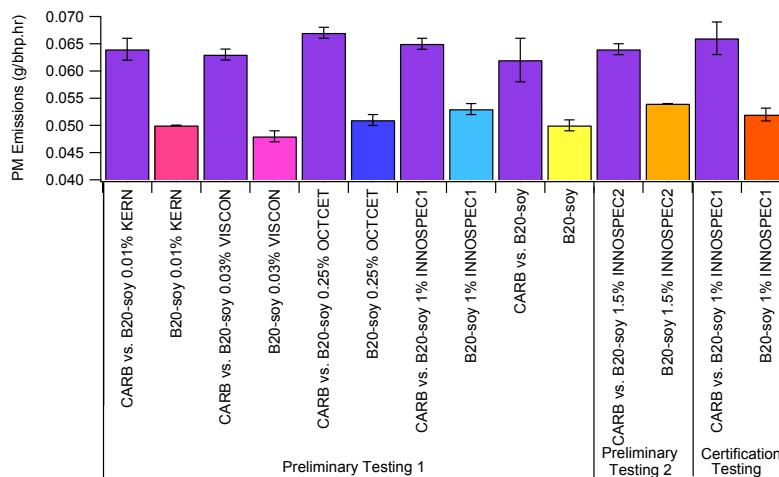
Previous studies have generally shown higher SOF emissions for biodiesel blends compared to either regular diesel fuel or low sulfur diesel fuel. However, most of these studies were performed on U.S. Federal diesel fuels as the base fuel, as opposed to a lower aromatic CARB diesel, and typically were characterized for higher biodiesel blend levels.<sup>8,50</sup> The increase in SOF emissions with biodiesel has been attributed to the higher boiling point or lower volatility of biodiesel fuel, which contributes to increased condensation of unburned hydrocarbons on the particle's surface.<sup>51,52</sup> This observation might vary from study to study due to testing conditions and methods for PM sampling.<sup>53</sup> Karavalakis et al. categorized the SOF emissions from biodiesel blends in four groups including methyl esters (mainly biodiesel components), oxygenated chemicals (chemicals with oxygen but not methyl esters), alkanes and alkenes, and aromatic species. Based on their study, SOF from B5 blends primarily consist of straight-chain alkanes, aromatic hydrocarbons, and aliphatic hydrocarbons like the regular diesel fuel.<sup>54</sup> This is consistent with the results of this study which showed a comparable level of SOF for both CARB low aromatic reference fuel and B5 biodiesel blends.



A)



B)



C)

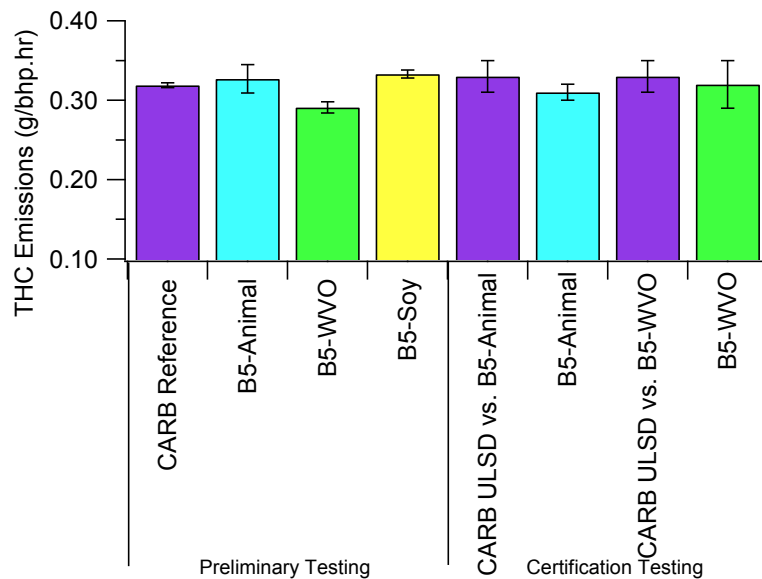
Figure 4-2. Average PM and SOF emission results for the preliminary and certification testing A) and B) B5, C) B20 with additives

#### 4.4.3. THC Emissions

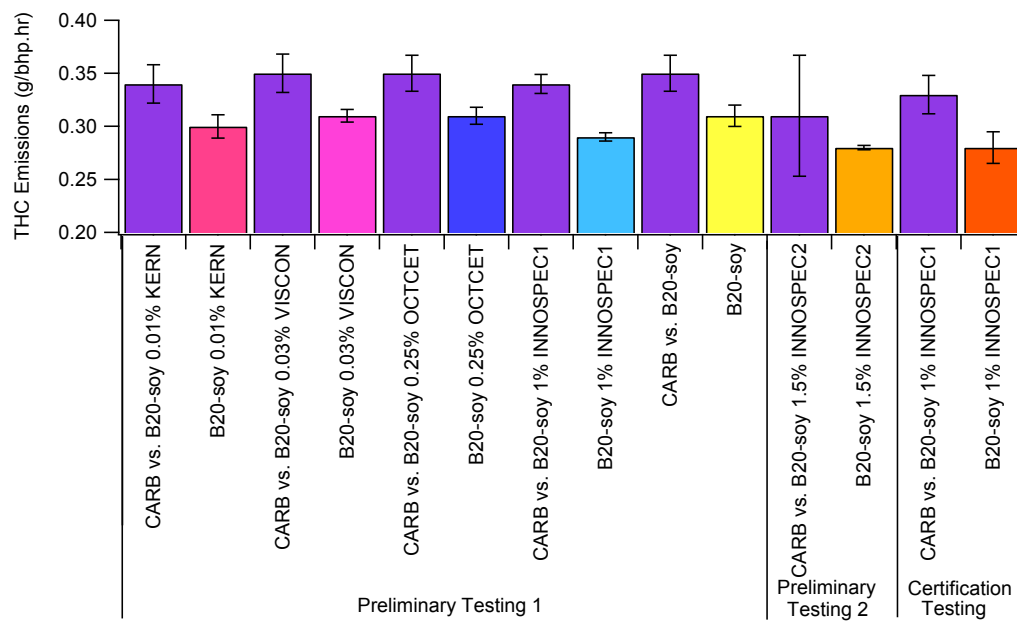
The THC emission results for the B5 and B20 testing are presented in Figure 4-3 on a g/bhp-hr basis. For the B5 certification testing, the emissions testing results for both blends showed reductions in THC compared to the CARB reference fuel. The reduction seen for B5-WVO was not statistically significant, however. THC results were mixed for the preliminary testing, with the B5-WVO emissions results showing a statistically significant 8.8% reduction in THC, while the B5-soy emissions results showed a slight statistically significant increase in THC compared to the CARB reference fuel. This observation is opposite to that seen in other studies<sup>2,10,12,13,23,24</sup> and might be due to the low values of THC emissions over all the fuel blends or limited number of tests done in the preliminary testing. The B5-soy preliminary testing results may have been an anomaly for that particular day. The stronger THC trends for the certification tests compared to preliminary tests is probably due to the more robust test matrix and the greater number of test replicates. It should be noted that THC emissions are not part of the pass/fail criteria for the full certification test.

THC emissions results for both the preliminary and certification testing of B20 blends showed consistent statistically significant 10.8-16.8% reductions for the B20 and B20 additive blends. Only the reduction in THC emissions results for B20-soy 1.5% INNOSPEC 2 compared to CARB reference fuel was not statistically significant, which might be due to the limited number of tests that were performed for this specific blend. For the certification test, the reduction in THC emissions was 16.8% for the B20-soy 1.0% INNOSPEC 1 blend.

The trends of reduced THC emissions for biodiesel and biodiesel additive blends is consistent with the results seen in other studies.<sup>2,10,12,14,23,24</sup> This can be attributed to the presence of oxygen in the biodiesel, which contributes to more complete combustion when biodiesel blends are used.<sup>12-15,25</sup> Durbin et al. showed that additives in conjunction with B20 blends provided greater reductions in THC emissions compared to the B20-soy baseline fuel alone.<sup>10</sup> The same trend was also seen for the B20-soy additive blends for the present study, with either equal or greater reductions in THC emissions seen for the B20-soy additive blends compared to the B20-soy blend. In other studies, adding additives to biodiesel blends has generally either shown modest additional benefits or no significant additional benefits with respect to THC<sup>10,22,31,48,49</sup>, with the exception of some studies with a more limited scope.<sup>46</sup>



A)



B)

Figure 4-3. Average THC emission results for the preliminary and certification testing A) B5 , B) B20 with additives

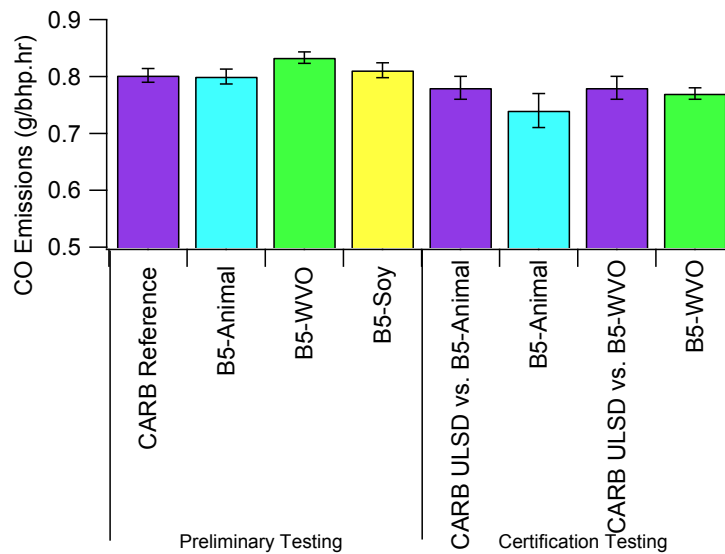
#### 4.4.4. CO Emissions

The CO emission results for the B5 and B20 testing are presented Figure 4-4 on a g/bhp-hr basis. The results for both B5 blends for the certification testing showed statistically significant reductions in CO emissions compared to the CARB reference fuel in the range of 2-6%. It should be noted that CO emissions are not part of the pass/fail criteria for the full certification test. The results of the B5 preliminary testing did not show consistent trends for CO emissions over all the biodiesel fuel blends. Interestingly, emissions testing results showed a statistically significant increase of 3.8% in CO emissions for B5-WVO compared to the CARB reference fuel in the preliminary testing. This is contrary to most studies in the literature, which generally show CO reductions with biodiesel.<sup>12,14,15,55</sup> This suggests that B5-WVO preliminary testing results may have been an anomaly for that particular day.

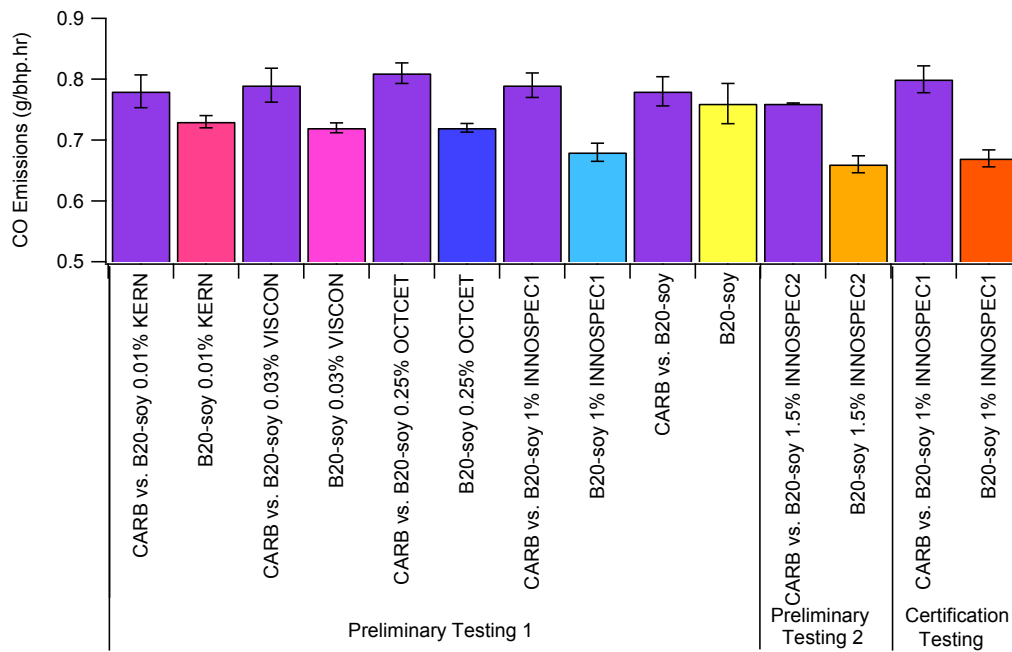
CO emissions results for B20 testing showed consistent trends of reductions over all the B20 additive fuel blends. These reductions ranged from 6.9-15.9% compared to CARB reference fuel for both the preliminary and certification testing. The B20-soy blend CO emissions results did not show statistically significant differences compared to the CARB reference fuel, however. For the certification test, the reduction in CO emissions was 15.9% for the B20-soy 1.0% INNOSPEC 1 blend.

Previous studies have generally showed reductions in CO for biodiesel blends, with greater reductions found for higher level blends.<sup>12,14,15,55</sup> CO reductions for biodiesel are generally attributed to the oxygen content in the biodiesel that promotes more complete combustion. Similar testing on another 2006 Cummins ISM, however, did not show strong effects for soy

based biodiesel blends ranging up to 100%, although CO emissions benefits were seen for biodiesel blends with an animal-based feedstock.<sup>10</sup> Durbin et al. found that additives can provide additional benefits in CO emissions beyond what would otherwise be achieved by biodiesel alone, although this was only studied for a soy-based blend.<sup>10</sup> In other studies, adding additives to biodiesel blends has generally either shown modest additional benefits or no significant additional benefits with respect to CO <sup>10,22,31,48,49</sup>, with the exception of some studies with a more limited scope.<sup>46</sup>



A)



B)

Figure 4-4. Average CO emission results for the preliminary and certification testing A) B5 ,  
B) B20 with additives

#### 4.4.5. CO<sub>2</sub> Emissions

The CO<sub>2</sub> emission results for the B5 and B20 testing are presented in Figure 4-5 on a g/bhp-hr basis. The preliminary testing results for all the B5 blends showed statistically significant 0.7-0.9% increases of CO<sub>2</sub> emissions compared to the CARB reference fuel. The differences in the CO<sub>2</sub> increases for the more robust B5 certification testing were smaller and less statistically significant. CO<sub>2</sub> emissions results showed increases for some of the B20 additive blends, but not for others. These increases were in the range of 0.2-1.2%. It should be noted that since the day to day variability in CO<sub>2</sub> emissions for the CARB reference fuel was approximately 1.5% over the course of the testing, these results should not be considered as a definitive comparison between the performance of specific additives. CO<sub>2</sub> emissions are not part of the emissions considered in the pass/fail criteria for the certification test.

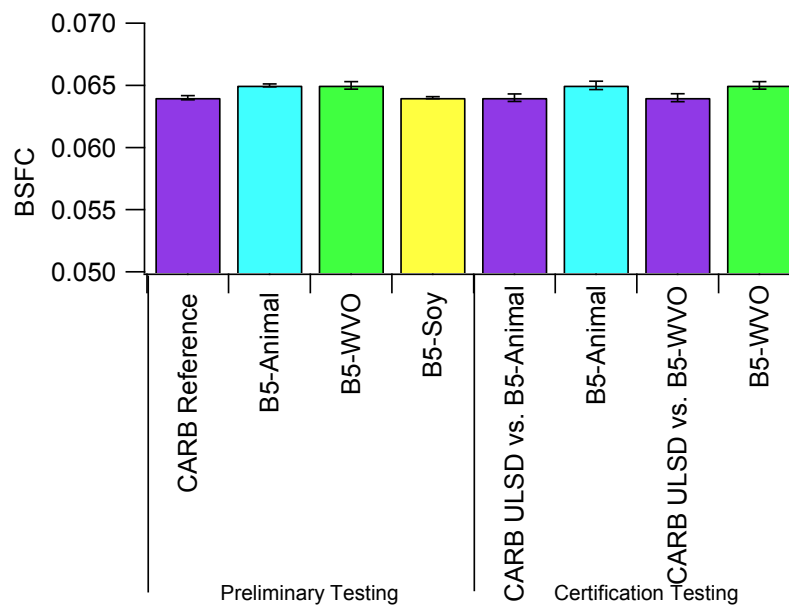
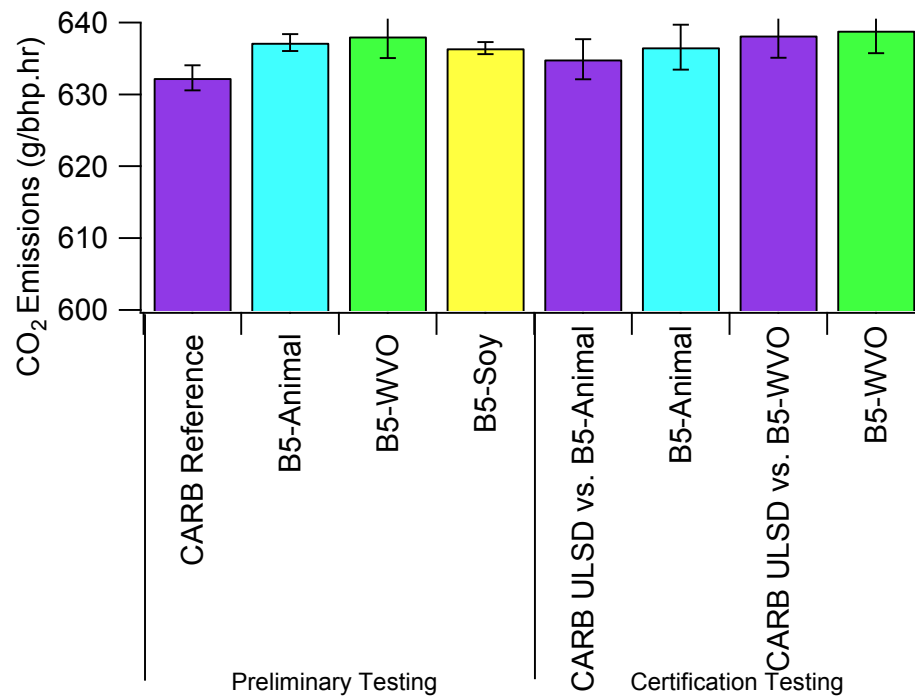
Previous studies have shown increases in exhaust CO<sub>2</sub> emissions with biodiesel, but this has generally been seen for higher biodiesel blend levels.<sup>12,14,15,55-57</sup> The increases in CO<sub>2</sub> emissions could be related to the generally higher carbon content per unit of energy for biodiesel compared to typical diesel fuel. As shown in Table 4-1 the neat biodiesel fuels for the present study had higher carbon contents per unit of energy than the CARB reference fuel. There was approximately a 0.46% difference in the carbon content per unit energy between the CARB reference fuel and the B20-soy, as shown in Table 4-1. This is comparable to the marginally statistically significant difference in CO<sub>2</sub> emissions seen for the B20-additive certification test. There were essentially no differences in the carbon contents per unit of energy for the B5 blends compared to the reference fuel, however. It should be emphasized that an increase in exhaust CO<sub>2</sub> emissions for biodiesel does not imply that the

use of biodiesel has a negative impact on greenhouse gas emissions. The actual contribution of different fuels towards total greenhouse gas emissions would need to be assessed through a full lifecycle analysis, which would account for the emissions attributed to harvesting, extracting, producing, and associated land use changes for the various fuels.<sup>8</sup>

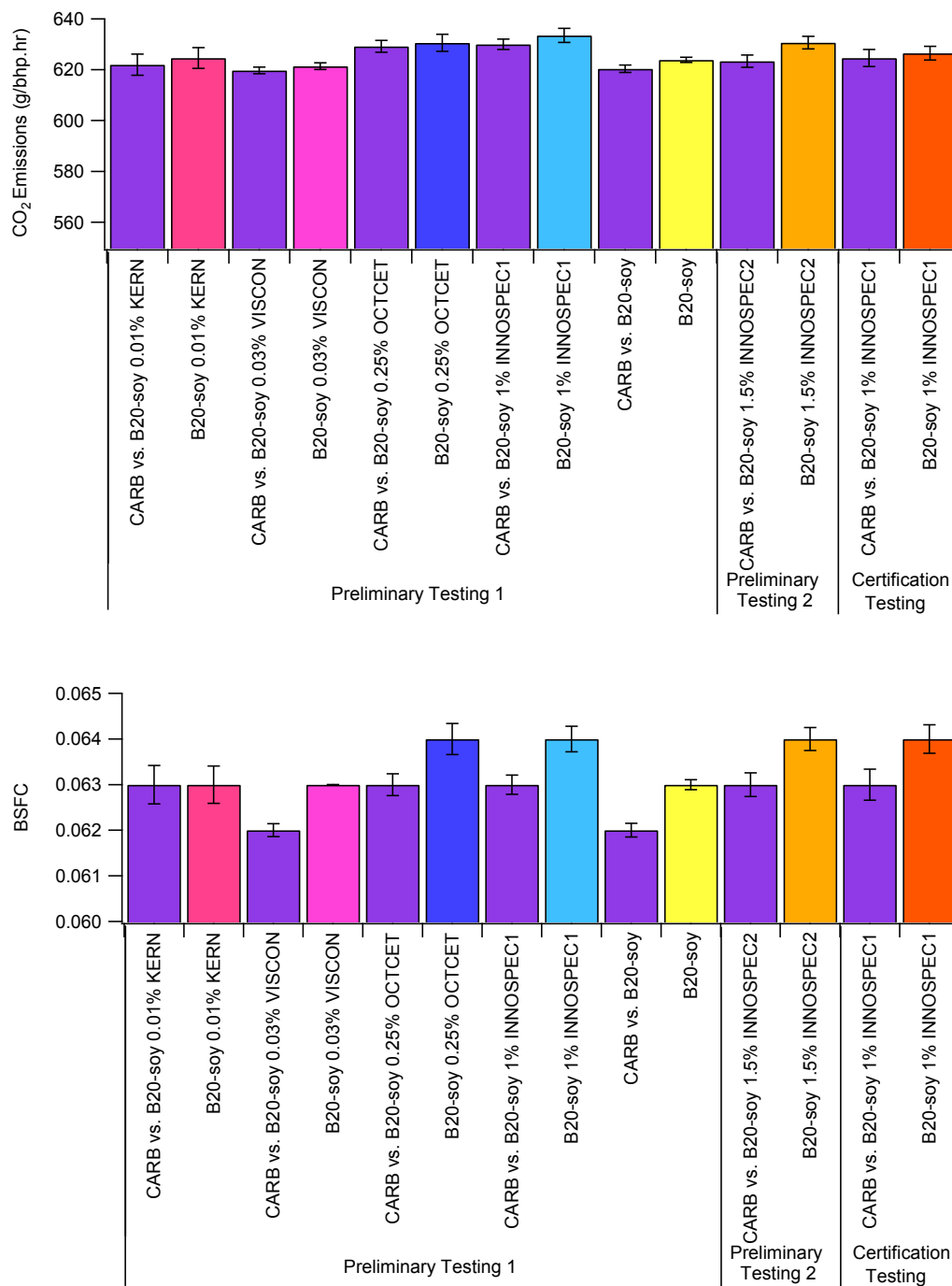
#### **4.4.6. Brake Specific Fuel Consumption**

The brake specific fuel consumption (BSFC) results for the B5 and B20 testing are presented in Figure 4-5 on a gal /bhp-hr basis. The BSFC results for both B5 blends tested during certification testing showed 0.6-1.0% increases in fuel consumption compared to the CARB reference fuel that were statistically significant. BSFC for the B5 blends was 0.6-2.0% higher in the preliminary testing compared to the CARB reference fuel. The B20 soy and B20-soy with additive blends of both preliminary and certification testing showed 1.0-2.1% higher BSFC compared to the CARB reference fuel. For the B20 certification test, the increase in BSFC emissions was 1.2% for the B20-soy 1.0% INNOSPEC 1 blend. Note that BSFC is not a pass/fail criteria consideration for the certification test.

The BSFC result is directionally consistent with the results of previous studies, although BSFC impacts are usually more readily apparent at higher blend levels.<sup>12,14,15,55–57</sup> In the present study, although there are differences in the energy contents of the pure biodiesel compared to the CARB reference as shown in Table 4-1, the differences in the energy contents of the B5 blends and the CARB reference fuel are very minor. For the B20-soy, the increases in BSFC for the testing were slightly less than the 2.6% difference in the energy content between the CARB reference fuel and B20-soy used in this fuel.



A)



B)

Figure 4-5. Average CO<sub>2</sub> emission and BSFC results for the preliminary and certification testing A) B5, B) B20 with additives

## 4.5. Conclusion

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. Currently, biofuels are being integrated into diesel fuel markets at levels of typically B20 and lower. The impacts of biodiesel at such levels on NO<sub>x</sub> emissions and emissions inventories have not been definitively characterized to date. In this study, the impacts of B20 and lower blends were evaluated for a 2006 Cummins ISM engine on a heavy-duty engine dynamometer over a relatively robust test matrix designed to distinguish small differences in NO<sub>x</sub> emissions. Overall, the results are consistent with our previous work and the work of others that the impact of biodiesel on NO<sub>x</sub> emissions might be a more important consideration when blended with CARB diesel or similar fuels, and that some form of NO<sub>x</sub> mitigation might be needed for biodiesel blends with such fuels.<sup>2,10-13,23,24</sup> The results showed definitive NO<sub>x</sub> increases at the B20 level, as well as increases at the B5 level, depending on the biodiesel feedstock type. For the B5 blends tested, B5-soy and B5-WVO both showed measurable increases in NO<sub>x</sub> emissions, while the B5-animal showed a slight reduction or no change in NO<sub>x</sub> emissions compared to the CARB reference diesel fuel. The B5-animal blend also passed the criteria of the CARB emissions equivalent certification test. The results also showed that certain additives can provide some benefits in NO<sub>x</sub> reduction, but that the benefits of the additives tested in this study were not sufficient to provide NO<sub>x</sub> neutrality at the B20 level. Overall, these additives showed less success than what was seen previously for a 1% DTBP additive blend, which showed NO<sub>x</sub> neutrality at the B20 level. Additional

testing is currently being planned to more comprehensively investigate the impacts of biodiesel at B5 and B10 levels in CARB diesel.

From a broader perspective on air quality, the potential for increased NO<sub>x</sub> emissions would need to be evaluated in a larger context of potential reductions in other emissions, such as PM, lifecycle analyses for GHGs, and full urban air shed modeling. Previous studies by the National Renewable Energy Laboratory have shown that NO<sub>x</sub> increases even for widespread use of B20 level would result in relatively minor impacts in ozone in urban areas.<sup>58</sup> For ambient PM, tradeoffs between reductions in primary PM emissions compared to the potential for NO<sub>x</sub> to form secondary PM would need to be evaluated. Further evaluation of a number of these issues is ongoing in California, where biodiesel penetration into the diesel market is still only about 0.5% of the total fuel volume used.<sup>59</sup> In Europe, where diesel fuel typically has lower aromatics and higher cetane numbers, greater impacts may be seen, since diesel fuel has a greater share of the transportation market and since biodiesel represents closer to 7% of the overall diesel fuel market. In countries or urban areas using less refined, higher aromatic diesel fuels, there would likely be reduced tendency for NO<sub>x</sub> to increase with biodiesel compared with that found in this study, especially at the with B5 level.

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#### **4.7. Disclaimer**

The statements and conclusions in this chapter are those of the contractor and not necessarily those of California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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## **Chapter Five: Impact of Natural Gas Fuel Composition on Criteria, Toxic, and Particle Emissions from Transit Buses Equipped with Lean Burn and Stoichiometric Engines**

### **5.1. Abstract**

This study investigated the impacts of varying natural gas composition on the exhaust emissions from different technology transit buses. For this study, two compressed natural gas (CNG) buses equipped with lean burn combustion and oxidation catalysts (OCs), and one stoichiometric CNG bus equipped with a three-way catalyst (TWC) and exhaust gas recirculation (EGR) were tested on a chassis dynamometer over the Central Business District (CBD) cycle on six different gas blends each. The gases represented a range of compositions from gases with high levels of methane and correspondingly lower energy contents/Wobbe number (WN) to gases with higher levels of heavier hydrocarbons and correspondingly higher energy contents/WN. For the lean burn buses, gases with low methane contents exhibited higher nitrogen oxides ( $\text{NO}_x$ ) and non-methane hydrocarbon (NMHC) emissions, but lower emissions of total hydrocarbon (THC), methane ( $\text{CH}_4$ ), and formaldehyde emissions. The stoichiometric engine bus with a TWC showed significantly reduced  $\text{NO}_x$  and THC emissions compared to the lean burn buses, but did show higher levels of carbon monoxide (CO) and ammonia ( $\text{NH}_3$ ). Particulate matter (PM) mass emissions did not show any fuel effects, while particle number (PN) emissions exhibited some reductions for the higher WN gases.

## 5.2. Introduction

In an effort to improve air quality, reduce greenhouse gas emissions, and reduce dependency on fossil fuels, regulatory agencies have implemented a variety of legislative measures to increase the use of alternative fuels. Natural gas (NG) is one of the most prominent alternative fuels with significantly larger reserves compared to crude oil, and also the potential for air quality benefits in vehicles.<sup>1</sup> In recent years, there have been dramatic changes in the NG market due to the rapid development of horizontal drilling and hydraulic fracturing. Such advanced techniques have unlocked vast reserves of oil and gas trapped underneath sedimentary rocks or shales. The United State (U.S.) Energy Information Administration (EIA) anticipates U.S. NG production to continue to expand into the future, growing from levels of 23.5 quadrillion Btu in 2011 to a projected 33.9 quadrillion Btu in 2040, representing a sizable 44% increase.<sup>2</sup> Shale gas production, which already accounted for 23% of total U.S. natural gas production in 2010, is expected to be the primary driver of this expansion, with shale gas production going from 6.8 trillion cubic feet (tcf) in 2011 to 13.6 tcf in 2035.<sup>3</sup>

The quality of natural gas depends on both its source and the degree to which it is processed. Natural gas can be produced from oil fields (termed associated gas) or from gas fields (termed non-associated gas). Associated gas is typically higher in heavier hydrocarbons, which gives the gas a higher Wobbe Number (WN) and a lower Methane Number (MN). Associated gas is often processed using techniques such as refrigeration, lean oil absorption, and cryogenic extraction to recover valuable natural gas liquids (NGLs), such as ethane, propane, butanes, pentanes and hexanes plus, for other uses.<sup>4,5</sup> Traditional North American

gas from Texas, for example, is often processed to recover feedstock for chemical plants. This process lowers the WN and increases the MN of the resulting NG stream. As NG production continues to increase, it is likely that a wider range of NG compositions could be introduced into the marketplace, either due to different sources of production or perhaps a reduced emphasis on recovering NGLs from NG if the economics for these secondary products change. This could lead to NG with higher WNs and lower MNs being fed into the pipeline, which would likewise result in a pipeline gas with a higher WN and lower MN.

A number of studies have compared the emissions of NGVs with diesel powered heavy-duty (HD) vehicles over a wide range of engine and aftertreatment configurations.<sup>6–11</sup> For the pre-2008 lean burn technologies, NG engines show reductions in particulate matter (PM) relative to diesel engine, and also slight reductions in carbon dioxide (CO<sub>2</sub>) emissions.<sup>6,7,9,10,12,13</sup> Emissions comparisons between NG and diesel for carbon monoxide (CO) and hydrocarbons (HCs) showed different trends over a range of studies depending on the specific technology tested, the condition of the vehicles, if the HCs were measured as total hydrocarbons (THC) or non-methane hydrocarbon (NMHC), and other factors.<sup>6,7,9,10,12–16</sup> The lean burn NG engines produced prior to the introduction of the Cummins Westport ISL-G could achieve reductions in nitrogen oxides (NO<sub>x</sub>) emissions relative to diesel engines without aftertreatment, but their NO<sub>x</sub> emissions were sometimes more variable in practice.<sup>6,10,17</sup> The use of stoichiometric combustion engines and improved three way catalyst (TWC) exhaust aftertreatment, as employed with the Cummins Westport ISL-G, is the primary technology being used with NG engines to achieve the current NO<sub>x</sub> standards.<sup>18–20</sup> The low levels of carbon-carbon bonds in NG and the absence of aromatics compared to

diesel fuel also reduces soot formation in NGVs.<sup>21</sup> NGVs have generally higher methane ( $\text{CH}_4$ ) emissions, which is a greenhouse gas.  $\text{CH}_4$  is less of a concern in the photochemical smog cycle, however, since it is less reactive compared to other hydrocarbons.

With the growing expansion of natural gas production and the potential change for natural gas fuel composition from source to source, it is crucial to investigate the effect of natural gas fuel composition on the performance and operation of natural gas heavy-duty vehicles, especially since limited comprehensive studies have been conducted in this area. In an earlier chassis dynamometer study, Graboski et al.<sup>22</sup> tested five different NG compositions in a bus equipped with a heavy-duty Cummins B5.9G lean-burn engine at high altitude. They found that THC emissions increased with increasing levels of inert gases and  $\text{NO}_x$  emissions increased with increasing fuel heating value, while CO and PM emissions were unaffected by fuel gas composition due to their low values. In a recent study, Karavalakis et al.<sup>23</sup> tested a refuse hauler with a Cummins Westport lean-burn spark ignited engine and an OC over the William H. Martin Refuse Truck Cycle on seven different gases. They found that  $\text{NO}_x$  and NMHC emissions increased for gases with higher levels of heavier hydrocarbons/higher WN, while THC, and  $\text{CH}_4$  emissions increased for gases with higher levels of  $\text{CH}_4$ . They also reported reductions in PM mass for gases with more heavier hydrocarbons and reductions in particle number emissions for some gases with more heavier hydrocarbons, but not for others. Feist et al.<sup>8,24</sup> also investigated the impact of several NG fuels for three different 1998-2006 HD lean burn NG engines with oxidation catalysts (OCs) and one 2008 HD stoichiometric NG engine with a TWC on an engine dynamometer. They observed that all lean-burn engines showed increased  $\text{NO}_x$  and HC emissions with higher WN fuels, while the

stoichiometric engine showed no clear trends for NO<sub>x</sub> or HC emissions with varying NG composition. They also found that PM and CO emissions did not show strong trends with MN or WN, and that low WN fuels resulted in increased fuel consumption. A number of other studies have also investigated the impact of NG composition on emissions, although most of these studies have focused on other applications, such as light-duty vehicles and engines, generators, and compressors.<sup>25–31</sup>

Limited information is available on the unregulated emissions from NGVs, including gaseous toxic pollutants and polycyclic aromatic hydrocarbons (PAHs). Kado et al.<sup>13</sup> found that the carbonyl emissions from compressed natural gas (CNG) buses were primarily formaldehyde. Formaldehyde emissions from these buses were much greater than those of diesel buses fitted with OCs, and continuously regenerating traps (CRTs). Ayala et al.<sup>6</sup> also found that formaldehyde emissions were reduced by OCs on CNG buses by over 95% over the Central Business District (CBD) cycle. Okamoto et al.<sup>15</sup> and Kado et al.<sup>13</sup> performed mutagenic tests on the exhaust from transit buses operating on CNG. They both reported lower mutagenic activity for CNG buses equipped with OCs, compared to buses without OCs. Kado et al.<sup>13</sup> also found that mutagenic activity using the TA98NR test strain decreased, indicating the possible presence of nitro-PAH in the PM emissions. Turrio-Baldassarri et al.<sup>32</sup> showed that a spark ignition heavy-duty urban bus NG engine with a TWC produced 20 times lower formaldehyde, more than 30 times lower PM emissions, and 50 times lower PAH emissions, compared to a diesel engine without aftertreatment.

Particle number (PN) emissions and particle size distributions are also of importance for NGVs. Particle emissions from NGVs are smaller in size than those from diesel engines.

This can be an issue since nano-sized particles have adverse human health effects. They are carcinogenic and can be transported easily to human organs, such as the lungs and brain.<sup>9,12,13</sup> Jayaratne et al.<sup>33</sup> tested particle emissions from four CNG and four diesel buses. They found that PN emissions were significantly lower for the CNG buses. They also reported that all the particles emitted from the CNG buses were in the nanoparticle size range and composed mostly of ash from lubricating oil. Similar results were reported by Holmen and Ayala<sup>34</sup> when they monitored the PN emissions from buses equipped with diesel engines with an OEM catalyzed muffler and with a DPF, and with a CNG engine without aftertreatment. They found that PN emissions in the accumulation mode were 10 to 100 times lower for the CNG engine compared to the diesel engine with the catalyzed muffler. Lanni et al.<sup>35</sup> tested two diesel buses with DPFs and three CNG buses without aftertreatment over the CBD and New York Bus (NYB) cycles and found the particle size distributions ranged from 10 to 30 nm, with an apparent shift towards smaller diameters for the CNG buses.

The objective of the present study is to evaluate the impact of NG composition on the exhaust emissions of heavy-duty NG vehicles. This study focuses on transit buses, a category of heavy-duty vehicles that warrants attention for controlling NO<sub>x</sub> and PM emissions due to the fact that they operate primarily in populated urban and suburban settings. For this study, three NG transit buses were tested on a range of six different test gases over the CBD cycle. In addition to the regulated emissions and fuel economy, ammonia (NH<sub>3</sub>), carbonyl compounds, and PN emissions were also evaluated. Information from this study on the impact of changing NG composition on emissions can be used for regulatory development,

to ensure new NG compositions do not have an adverse impact on air quality, and to evaluate the viability of using a broader mixture of NG blends in transportation applications.

### **5.3. Experimental Procedures**

#### **5.3.1. Fuels**

For this study six NG blends were used. Gases H1 and H2 are representative of historical Texas and Rocky Mountain Pipeline Gases and serve as the baseline fuels. The four other test gases all have lower methane contents and MNs, and corresponding higher WNs and HHVs. These gases are labeled ‘LM’ and are denoted as low methane gases throughout this paper. Gas LM3 is representative of Peruvian LNG that has been modified to meet a WN of 1385 and a MN of 75. Gas LM4 is representative of Untreated Middle East LNG with a high WN (above 1400). Gas LM5 is a high ethane gas with a WN of 1385 and a MN of 75. Gas LM6 is a high propane, high butane gas with a WN of 1385 and a MN of 75. Gases LM5 and LM6 are hypothetical gases designed to investigate whether two fuels with the same WN and MN, but different compositions, would produce different exhaust emissions. Gases with higher propane and butane than pipeline gas are found in the South Central Coast region oil and gas fields, while gases with high ethane are found in San Joaquin Valley oil and gas fields. Gases LM5 and LM6 are both at the extremes for WN and MN, so the typical local gas in the pipeline in these areas will have lower WNs and higher MNs. A wide range of scenarios were examined in this study to evaluate the viability of permitting the use of a broader mixture of NG blends in transportation applications. The test fuels properties are presented in Table 5-1.

### **5.3.2. Test vehicles**

Three buses were used in this study, including a bus equipped with a 2009 stoichiometric spark ignited Cummins Westport ISL-G 8.9 L engine with a three-way catalyst (TWC) and a cooled exhaust gas recirculation (EGR) system, a bus equipped with a 2004 John Deere 8.1L 6081H lean burn engine, and a bus equipped with a 2003 8.3L C-Gas Plus lean burn engine. Both the 2004 John Deere and 2003 C-Gas Plus lean burn vehicles were fitted with OCs for controlling THC and CO emissions. It should be noted that the John Deere bus was tested on two separate occasions, once before and again after a mechanical issue was discovered. Specifically, the bus lost compression in one of its combustion cylinders during the initial round of testing. The retesting on the repaired vehicle was done approximately one year after the initial testing.

Table 5-1. Main properties of the fuel gas blends

Gas #	Description	Methane	Ethane	Propane	I-butane	N <sub>2</sub>	CO <sub>2</sub>	MN	Wobbe number	HHV	H/C ratio	MON
H1	Texas Pipeline	96	1.8	0.4	0.15	0.7	0.95	99	1339	1021	3.94	135.1
H2	Rocky Mountain Pipeline	94.5	3.5	0.6	0.3	0.35	0.75	95	1361	1046	3.89	131.2
LM3	Peruvian LNG	88.3	10.5	0	0	1.2	0	84	1385	1083	3.81	125.7
LM4	Middle East, LNG-Untreated	89.3	6.8	2.6	1.3	0	0	80	1428	1136	3.73	121
LM5	Associated High Ethane	83.65	10.75	2.7	0.2	2.7	0	75.3	1385	1115	3.71	119.9
LM6	Associated High Propane	87.2	4.5	4.4	1.2	2.7	0	75.1	1385	1116	3.70	119.3

Gas composition is reported on a Mole percent basis; MN = Methane Number determined via California Air Resources Board (CARB) calculations <sup>36</sup>; Wobbe Number = HHV/square root of the specific gravity of gas blends with respect to air; HHV = Higher Heating Value; H/C = ratio of hydrogen to carbon atoms in the hydrocarbon portion of the gas blend; MON = Motor Octane Number derived via mathematical relation, which was developed in <sup>36</sup>

### **5.3.3. Test Cycles and Measurement Protocol**

Testing was performed over a specially developed CBD cycle. The driving pattern for the CBD cycle was developed as a general representation of transit bus operation in a downtown business district.<sup>10</sup> The cycle used in this study consisted of a single CBD cycle as a warm-up, followed by two iterations (i.e., a double) CBD cycle to provide a sufficient particle sample for analysis. The CBD cycle is characterized by an average speed of 20.23 km/h (13 mph), a maximum speed of 32.18 km/h (20 mph), an average acceleration of 0.89 m/s<sup>2</sup>, and a maximum acceleration of 1.79 m/s<sup>2</sup>. The driving distance for a single CBD cycle is 3.22 km, or 9.66 km for the full cycle, including the warm-up. A speed-time trace profile for the extended CBD can be found elsewhere.<sup>10</sup> Six tests were run on each vehicle/fuel combination for all vehicles, with a limited number of exceptions. The test matrix was randomized to allow some measure of the experimental reproducibility. Note that LM4 was not tested on the Cummins Westport C-Gas Plus bus.

### **5.3.4. Emission Testing and Analysis**

The chassis dynamometer testing was conducted at the University of California, Riverside (UCR) Center for Environmental Research and Technology's (CE-CERT's) heavy-duty chassis dynamometer facility. The emissions measurements were obtained using CE-CERT's Mobile Emissions Laboratory (MEL). For all tests, standard emissions measurements of THC, NMHC, CH<sub>4</sub>, CO, NO<sub>x</sub>, CO<sub>2</sub>, and PM mass, were performed according to Code of Federal Regulations (CFR) Title 40 (40 CFR) 1065 requirements. Total PM mass determinations were collected using 47 mm Teflon<sup>®</sup> filters and measured with a 40 CFR Part 1065-compliant microbalance in a temperature and humidity controlled clean chamber.

Total PN counts and particle size distributions were also measured. PN was measured using a TSI 3776 ultrafine-Condensation Particle Counter (CPC). This is a butanol-based CPC that has the ability to count particles down to 2.5 nm. This instrument can sample particles of about 300,000 per second, making the ultrafine CPC ideal for an accurate total PN measurement. Particle size distributions were measured using two different instruments due to the availability of different instruments at different times over the course of testing. A nano scanning mobility particle sizer (nano-SMPS) with 3085 TSI Differential Mobility Analyzer (DMA) column was used for the 2009 Cummins Westport ISL-G8.9 bus and the John Deere bus tests. The size range of the nano-SMPS was 4 to 70 nm with a scan time of 118 seconds. For the C-Gas Plus bus testing, an Engine Exhaust Particle Sizer (EEPS) was used for both particle size distributions and PN measurement. The EEPS had a faster scan time of one second and a wider size range from 6 to 423 nm compared to the nano-SMPS. The faster scan time allows the EEPS to more accurately capture the size distributions under transient operating conditions. Measurements of ammonia ( $\text{NH}_3$ ) were obtained on a real-time basis using a tunable diode laser near infrared absorption spectrometer (TDL). The TDL system was used because it provides significant advantages for the measurement of exhaust  $\text{NH}_3$  in sensitivity, response time, and the ability to measure in situ in raw exhaust.<sup>37</sup>

Testing and analysis of carbonyl compounds were performed in accordance with protocols developed as part of the Auto/Oil Air Quality Improvement Research Program.<sup>38</sup> Samples for carbonyl analysis were collected through a heated line onto 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA). Sampled cartridges were extracted using 5 mL of acetonitrile and analyzed with an Agilent 1200 series high

performance liquid chromatograph (HPLC) equipped with a diode array detector using the HPLC sample injection and operating conditions as specified in the SAE [930142HP] protocol. Three carbonyl samples were typically collected for each vehicle/fuel combination.

## **5.4. Results and Discussion**

The figures for each pollutant show the results for each vehicle/fuel combination based on the average of the tests conducted on that particular test combination. The error bars on the figures are the standard deviation over all tests for each test combination. The statistical analyses were conducted using a 2-tailed, 2 sample equal variance t-test. For the statistical analyses, results are considered to be statistically significant for  $p \leq 0.05$ , or marginally statistically significant for  $0.05 < p \leq 0.1$  in this analysis. The John Deere results are shown separately for the initial and post-repair testing.

### **5.4.1. NO<sub>x</sub> Emissions**

NO<sub>x</sub> emission results are shown in Figure 5-1. NO<sub>x</sub> emission levels for the stoichiometric Cummins Westport ISL-G8.9 bus fitted with a TWC were significantly lower than those of the lean-burn John Deere and C-Gas Plus buses with OCs, noting that the emissions for the Cummins Westport ISL-G8.9 bus are multiplied by 50 in the figure. Similar results, showing that stoichiometric engines equipped with cooled EGR and TWC significantly reduce NO<sub>x</sub> emissions, have been reported by other authors.<sup>14,16</sup> The effectiveness of the TWC in reducing NO<sub>x</sub> emissions is a key to achieving the NO<sub>x</sub> reductions seen for the ISL-G bus<sup>39</sup> coupled with the stoichiometric combustion needed to provide the conditions needed for the TWC to work optimally. In contrast, the OC does not provide catalytic reduction of

NO<sub>x</sub>. For the stoichiometric ISL-G8.9 Cummins bus, EGR also decreases NO<sub>x</sub> emissions by introducing inert exhaust gas back into the combustion cylinder, which reduces the combustion temperature.<sup>20</sup>

For the John Deere and C-Gas Plus buses, the NO<sub>x</sub> emissions generally showed trends of higher NO<sub>x</sub> emissions for the low methane gases. The C-Gas Plus bus showed statistically significant increases of 38%, 53%, and 32%, respectively, for LM3, LM5, and LM6 compared to H1. For the post-repair John Deere results, these increases were statistically significant for LM6 compared to H1 (+49%), while for the initial John Deere testing a statistically significant increase was found for LM4 fuel compared to H1 (+18.8%). The stoichiometric Cummins Westport ISL-G8.9 did not show significant differences between fuels for NO<sub>x</sub> emissions.

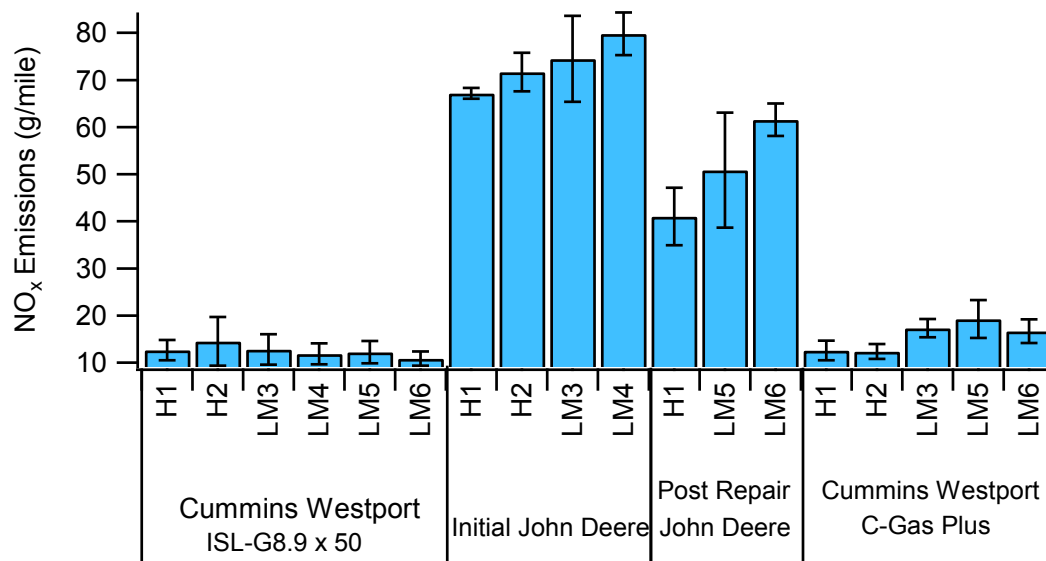


Figure 5-1. Average NO<sub>x</sub> emissions from NG buses over the CBD

The increases in NO<sub>x</sub> emissions with LM3, LM4, LM5, and LM6 gases for the lean burn engines could be attributed to the presence of higher molecular-weight hydrocarbons in these gases. The addition of higher hydrocarbons (ethane and propane) can increase the adiabatic flame speed. As flame speed increases at constant ignition timing, peak pressure occurs earlier, at smaller cylinder volumes, and thus higher temperatures. Peak combustion temperatures are therefore higher due to the advanced location of the peak pressure and higher adiabatic flame temperature<sup>8,24</sup>, which would result in higher NO<sub>x</sub> emissions, as NO<sub>x</sub> is generated predominantly through the strongly temperature-dependent thermal NO mechanism.<sup>31,40</sup> Previous studies have also shown that lean-burn engines run richer as MN is decreased.<sup>25</sup> This can lead to the oxidation of more fuel, higher combustion temperatures, and increased cylinder pressures. It is also possible that the higher hydrocarbons promote the formation of reactive radicals, which result in increased formation of prompt NO<sub>x</sub>.

#### **5.4.2. THC, NMHC, and CH<sub>4</sub> Emissions**

THC emissions results are shown in Figure 5-2a. THC emissions were significantly lower for the Cummins Westport ISL-G8.9 bus than the older John Deere and C-Gas Plus buses, noting that the emissions for the Cummins Westport ISL-G8.9 bus are multiplied by 10 in the figure. This can be attributed to the differences in the engine and aftertreatment technologies, since the older engines are all lean-burn engines fitted with OCs designed to meet an earlier certification standard, and the ISL-G is a stoichiometric engine with a TWC that is designed to meet a more recent and more stringent certification standard. Most of THC emissions reductions are due to the greater conversion efficiency of the TWC, which is larger in size and has higher loadings of precious metals compared to the OCs.<sup>41</sup> Also, the

conversion efficiency of  $\text{CH}_4$ , the predominate component of THC, can also be increased with different precious metals and under stoichiometric conditions.<sup>42</sup> Similar reductions have been seen in other studies.<sup>8,16,18</sup> Einewall et al.<sup>18</sup> found that catalyst efficiency was considerably higher for stoichiometric operation with a TWC compared to lean burn operation with an OC. Lean burn engines are typically characterized by cooler and slower combustion, which can lead to higher exhaust temperatures. Wit et al.<sup>43</sup> observed higher exhaust temperature in stoichiometric engines which increased the temperature of TWC and improved  $\text{CH}_4$  conversion efficiency compared to the lean burn engines. The cooler combustion temperatures for the lean burn engines and operation near the lean burn limit for HC formation, could also lead to higher levels of engine-out THC compared to stoichiometric engines.

The John Deere and C-Gas Plus buses showed trends of higher THC emissions for the gases with higher methane contents. For the C-Gas Plus bus, statistically significant reductions in THC emissions of 15%, 24%, and 21%, respectively, for LM3, LM5, and LM6 were found compared to H1. For the post-repair John Deere bus testing, LM5 and LM6 showed statistically significant reductions of 16.9% and 13.3%, respectively, in THC emissions compared to H1. For the initial testing on the John Deere bus, LM3 and LM4 showed statistically significant reductions of 11.8% and 8.8%, respectively, in THC emissions compared to H1. For the Cummins Westport ISL-G bus, THC emissions were very low, and did not show strong fuel trends. Although LM4 showed a slight increase in THC emissions compared to the baseline H1, the higher emission levels for LM4 are still on

same the order as the background levels of the system, and as such appear to be simply an artifact of measuring at such low levels.

This trend of higher THC emissions for the gases with higher methane contents for the lean burn engines is consistent with results previously reported by other authors.<sup>8,10,23</sup> This is probably due to the fact that the THC emissions were predominately methane with lower levels of heavier hydrocarbons. CH<sub>4</sub> is also less reactive than higher hydrocarbons and a considerably more stable molecule, so it is more likely to go through the combustion process unburned and more difficult to oxidize with the catalyst.<sup>44</sup> The reductions in THC emissions for the low methane gases could also be due to more complete oxidation of the fuel as the adiabatic flame speeds and combustion temperatures increased, as discussed under the NO<sub>x</sub> emissions section. The higher combustion temperatures could also lead to higher exhaust temperatures than the baseline gases, which could also result in higher conversion rates with the OC. A NO<sub>x</sub>/THC tradeoff, possibly caused by changes in peak flame temperature or speed, was observed. THC emissions decreased with low MN fuels, while NO<sub>x</sub> emissions increased with low MN and high WN fuels. These phenomena are in agreement with the results previously reported by Graboski et al.<sup>22</sup> and Karavalakis et al.<sup>23</sup>.

All the NG buses emitted substantially lower levels of NMHC emissions compared to THC emissions, as shown in Figure 5-2b, with the NMHC emissions for the stoichiometric Cummins Westport bus being at the background levels. This is consistent with expectations and indicates that the THC emissions from these vehicles are predominantly methane with little NMHC emissions. The very low NMHC emissions for the stoichiometric engine with a TWC are in agreement with other studies showing very low NMHC emissions for such

engines.<sup>14,16,45</sup> The significantly lower levels of NMHC emissions from the stoichiometric bus engine were predominately due to the higher conversion efficiency for the TWC compared to the OC.

The lean burn buses all showed trends of higher NMHC emissions for the gases containing higher levels of NMHCs (i.e., ethane, propane, and butane, as shown in Table 5-1). Previous studies have also shown that NMHC emissions increased with decreasing methane number of the fuel gases.<sup>8,23</sup> THC emissions from natural gas engines are predominately unburned fuel, therefore, the non-methane hydrocarbon fraction of THC exhaust emissions typically trends with the percentage of NMHC in the test fuel. The C-Gas Plus bus showed statistically significant increases in NMHC emissions for H2, LM3, LM5, and LM6 of 22%, 62%, 62%, and 39%, respectively, compared to H1. For the post-repair John Deere testing, LM5 and LM6 had statistically significant increases in NMHC emissions of 88% and 71%, respectively, compared to the H1. For the initial John Deere bus testing, the LM3 and LM4 gases showed statistically significant NMHC emissions increases of 78% and 39%, respectively, compared to H1, and of 102% and 57%, respectively, compared to H2.

Methane is the major hydrocarbon in NG. It is non-reactive and does not participate in photochemical smog generating reactions, and is unregulated in the U.S. Figure 5-2c shows the CH<sub>4</sub> emissions over the CBD cycle. The results showed that CH<sub>4</sub> emissions for the stoichiometric Cummins Westport ISL-G bus were about 95% lower than for the lean burn John Deere and C-Gas Plus buses, noting that the CH<sub>4</sub> emissions for the ISL-G are multiplied by 10 in the figure. The lower CH<sub>4</sub> emissions for the stoichiometric engine bus with the TWC, was primarily due to the larger size and higher precious metal loadings for

the TWC. The different precious metals and stoichiometric combustion for the TWC can also promote the CH<sub>4</sub> conversion, resulting in lower CH<sub>4</sub> emissions.<sup>42</sup>

The lean burn buses all showed a trend of higher CH<sub>4</sub> emissions for gases with higher methane contents, including H1 and H2. The C-Gas Plus bus showed the highest CH<sub>4</sub> emissions for H1 and H2, with reductions in CH<sub>4</sub> emissions of 4.3%, 23%, 33%, and 27%, respectively, for H2, LM3, LM5, and LM6 compared to H1, with most of the reductions being statistically significant. For the post-repair John Deere bus testing, H1 showed the highest CH<sub>4</sub> emissions, with statistically significant reductions in CH<sub>4</sub> emissions of 32% and 25%, respectively, for LM5 and LM6 compared to H1. For the initial John Deere test, H1 and H2 produced higher CH<sub>4</sub> emissions than those of LM3 and LM4. The stoichiometric Cummins Westport ISL-G showed slightly higher CH<sub>4</sub> emissions for gases LM3 and LM4, but similar to THC, the differences in CH<sub>4</sub> between gases are comparable to the background levels of the system, and hence, are probably an artifact of measuring at such low levels rather than real fuel effects.

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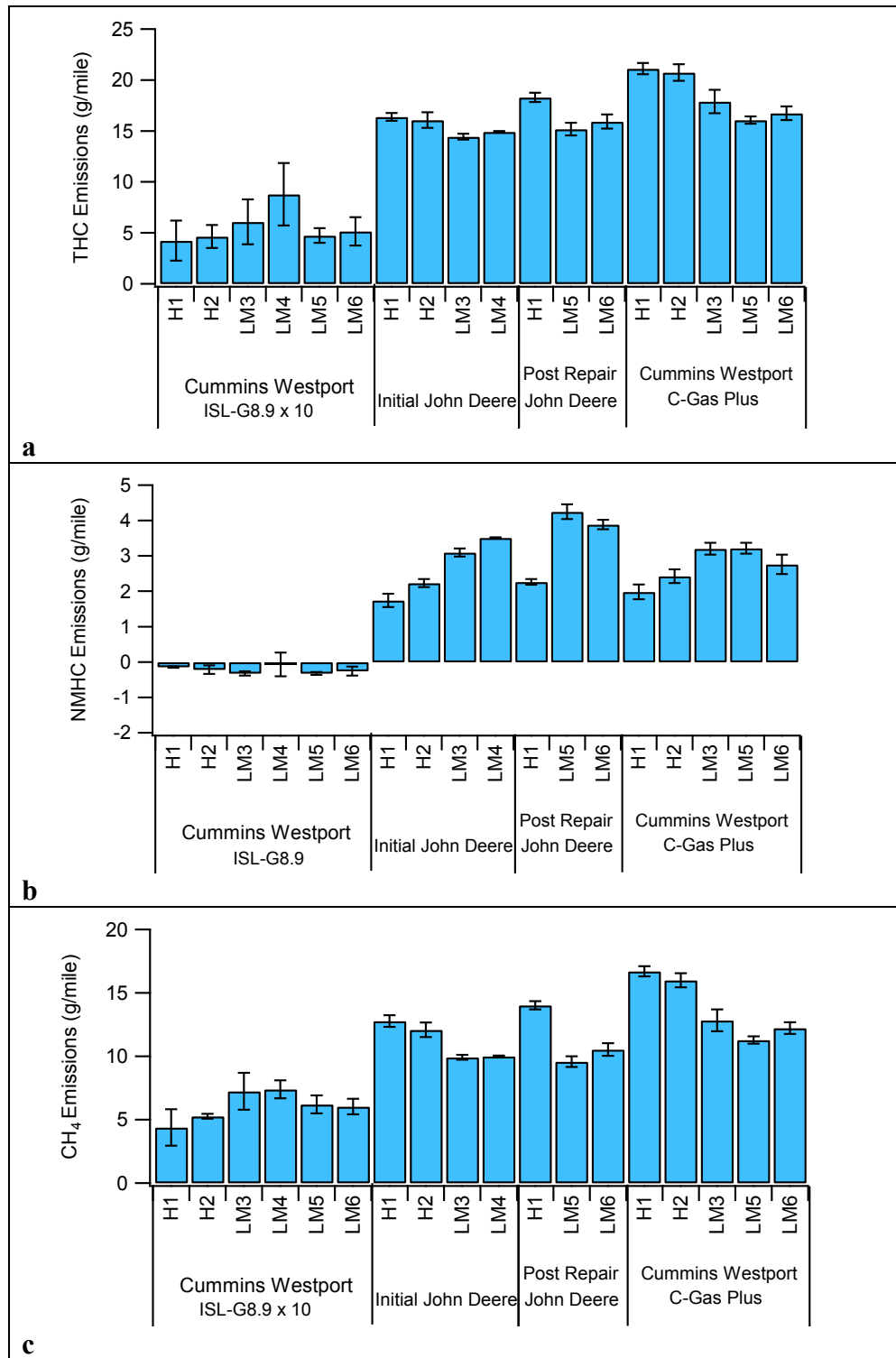


Figure 5-2(a-c). Average THC, NMHC, and CH<sub>4</sub> emissions from NG buses over the CBD

### 5.4.3. CO Emissions

CO emissions are shown in Figure 5-3. It is evident that CO emissions for the stoichiometric Cummins Westport ISL-G 8.9 vehicle were significantly higher than those emitted for the lean burn John Deere bus and for the lean burn C-Gas Plus bus. This can be attributed to the richer operating conditions of the stoichiometric combustion compared to lean burn combustion. Thus, less oxygen is available to oxidize CO to CO<sub>2</sub> during combustion or over the catalyst for the stoichiometric engine compared to the lean burn engine. This observation is consistent with the results of previous studies showing higher CO emissions for the stoichiometric Cummins Westport ISL-G engine compared to lean burn engines.<sup>16,45</sup> Although higher CO emissions were seen for the stoichiometric engine, the emissions are still relatively low compared to the certification limits. If a conversion factor of 4 bhp-hr/mile<sup>16</sup> is applied, the CO emissions levels are on the order of 2 g/bhp-hr, which is well below the certification standard of 15.5 g/bhp-hr.<sup>46</sup> CO emissions for the initial John Deere testing were higher than those for the post-repair testing, but were still about 74% lower than those for the Cummins ISL bus. The higher CO emissions for the initial John Deere testing compared to post-repair testing might be due to its mechanical issue. For the Cummins Westport ISL-G and John Deere buses, no statistically significant differences in CO emissions between fuels were found. The C-Gas Plus bus showed some increases in CO emissions of 78%, 185% and 103%, respectively, for the low methane LM3, LM5 and LM6 gases compared to H1 that were statistically significant. Higher MN fuels also have higher octane ratings, which could contribute to more efficient combustion, thereby reducing CO emissions. The CO emissions for H2 were comparable to those of LM3 and LM6, however.

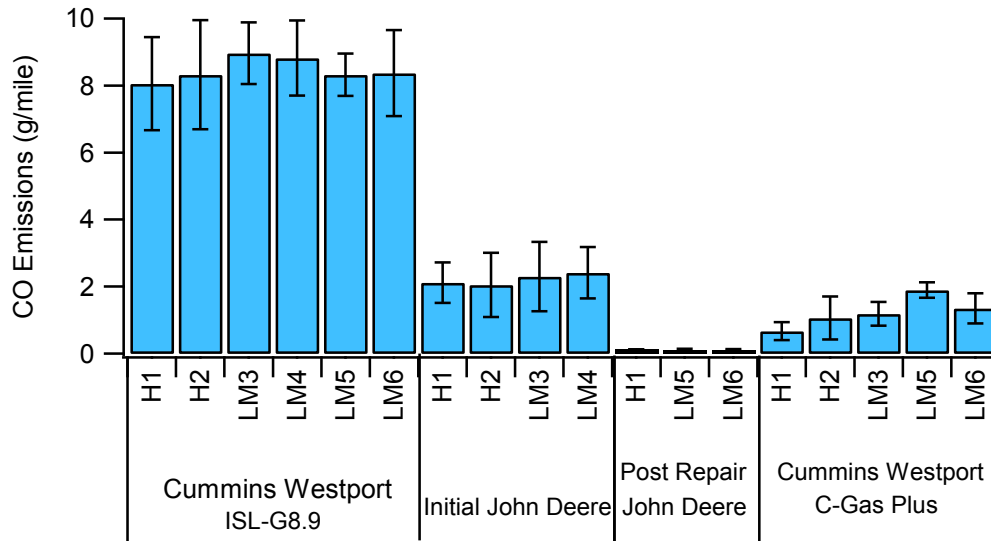


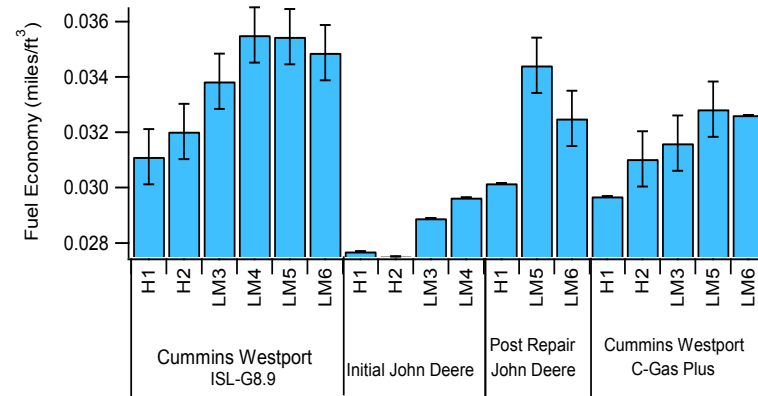
Figure 5-3. Average CO emissions from NG buses over the CBD

#### 5.4.4. Fuel Economy and CO<sub>2</sub> Emissions

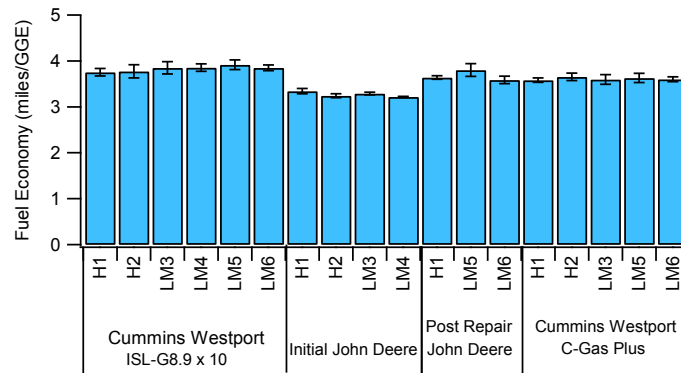
Fuel economy was determined using the EPA carbon balance method. Fuel economy is plotted on a volumetric basis in Figure 5-4a. This is the most important metric for the NG consumer since fuel is purchased on a volumetric basis. For all the buses, the low methane gases with the higher heating values, i.e., LM3, LM4, LM5, and LM6, showed slightly higher fuel economy on a volumetric basis compared to H1 and H2. Fuel economy can also be examined on an energy equivalent basis, as shown in Figure 5-4b. On this basis, the energy differences between the fuels are normalized so that the differences in fuels are more related to efficiency differences. Overall, the three buses showed comparable fuel economy results between fuels on an energy equivalent basis. The C-Gas Plus bus did not show any fuel effects, with the exception of H2 showing a statistically significant 2% increase compared to H1. The energy equivalent fuel economy differences for the post-repair John Deere were only marginally statistically significant for LM5, but were not statistically significant for LM6.

Interestingly, the stoichiometric Cummins Westport ISL-G bus fuel economy results generally showed a trend of higher energy equivalent fuel economy for LM3, LM4, LM5, and LM6, which are the low methane gases with higher energy contents. The initial testing results for energy equivalent fuel economy on the John Deere, on the other hand, showed statistically significant decreases in fuel economy for the low methane gases with higher energy contents (LM3 and LM4), but this could be related to the mechanical failure.

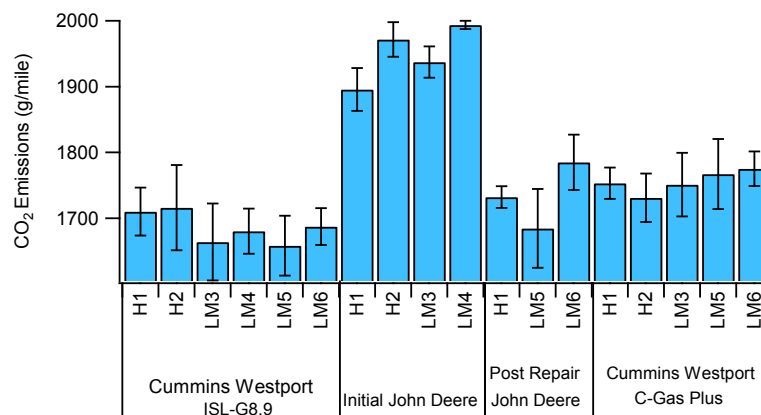
CO<sub>2</sub> emissions from the three buses were comparable, as shown in Figure 5-4c. The initial testing on the John Deere bus showed slightly higher CO<sub>2</sub> emissions, which could be related to its mechanical issues. The Cummins Westport ISL-G8.9, post-repair John Deere, and C-Gas Plus buses did not show strong trends in CO<sub>2</sub> emissions between the fuels. The initial testing of the John Deere bus showed slight, but statistically significant, increases in CO<sub>2</sub> emissions for H2 and LM4 compared to H1 and LM3. These differences could be related to the mechanical issue, however.



**a**



**b**



**c**

Figure 5-4(a-c). Average volumetric (a) and carbon balanced (b) fuel economy, and CO<sub>2</sub> emissions from NG buses over the CBD

#### 5.4.5. PM Mass, Particle Number and Particle Size Distributions

The results presented in Figure 5-5a, indicated that total PM mass emissions were low for all three buses on an absolute level, and are around the tunnel background levels. Although some differences were seen between fuels, these differences were all within the range of the tunnel background levels. The very low levels of PM mass emissions can be attributed to the fact that natural gas is primarily comprised of  $\text{CH}_4$ , which is the lowest molecular weight HC and has a simpler structure compared to diesel or gasoline fuels.<sup>47</sup> NG has a reduced tendency to form localized areas of rich combustion and generates unburned and partially oxidized hydrocarbons with lower molecular sizes in the exhaust, resulting in very low PM mass emission levels. Thus, the main source of PM in natural gas engines is considered to be the entry of engine lubricating oil into the combustion chamber.<sup>47</sup> It is worth noting that the stoichiometric bus produced somewhat higher PM emissions than the lean burn buses. This finding is not consistent with the results reported by Yoon et al.<sup>16</sup>, but is in agreement with the results from Feist et al.<sup>8,24</sup> and Nylund et al.<sup>45</sup>. Under the present test conditions, it is possible that the OC was also more effective in removing and oxidizing volatile and semi-volatile hydrocarbons that are usually adsorbed onto carbon particles, than the TWC aftertreatment. The observed results also could indicate higher lubrication oil consumption for the bus with the stoichiometric fueling than the lean burn buses.

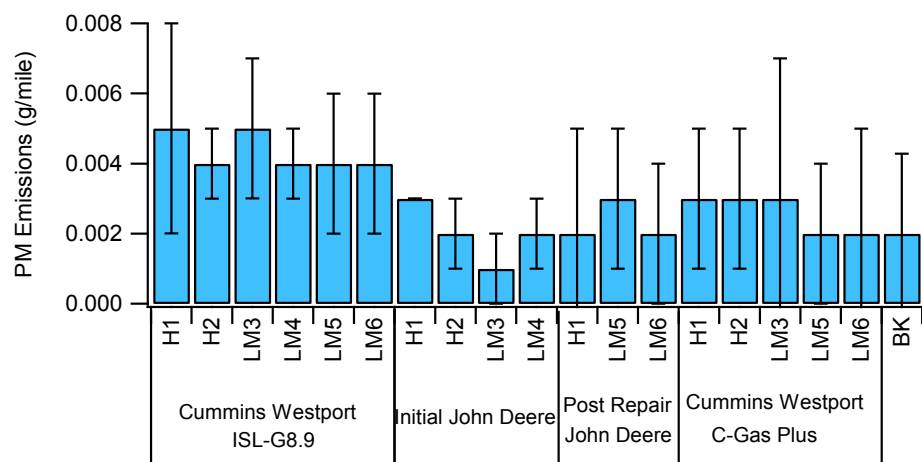
PN counts are presented in Figure 5-5b for all cases except for the post-repair John Deere bus testing. PN counts were not measured for the post repair vehicle because of issues with the data acquisition system for the CPC. For the C-Gas Plus testing, the EEPS was used for the PN measurements. The C-Gas Plus PN measurements with EEPS showed somewhat

greater variability than the other vehicles. For the initial John Deere bus testing, all test gases exhibited a statistically significant reduction in PN emissions compared to the baseline H1, with LM3 and LM4 showing the largest reductions. For the C-Gas Plus bus, H2 and LM3 showed PN emissions that were higher than H1, but these differences were not statistically significant. The greater variability for the C-Gas Plus bus PN measurements with the EEPS may also have made it more difficult to identify statistical trends, however. For the Cummins Westport ISL-G bus, some PN differences were seen between different fuels, but these differences were not statistically significant. The observed trends of lower PN emissions with the higher WN and higher flame speed gases for the initial John Deere bus testing could be due to higher temperature or more efficient combustion. Although the reduction of volatile and semi-volatile organics that are components of particles is not the primary function of the OC, the higher temperature combustion could lead to higher exhaust temperatures that could result in higher conversion efficiencies over the OC.<sup>43</sup>

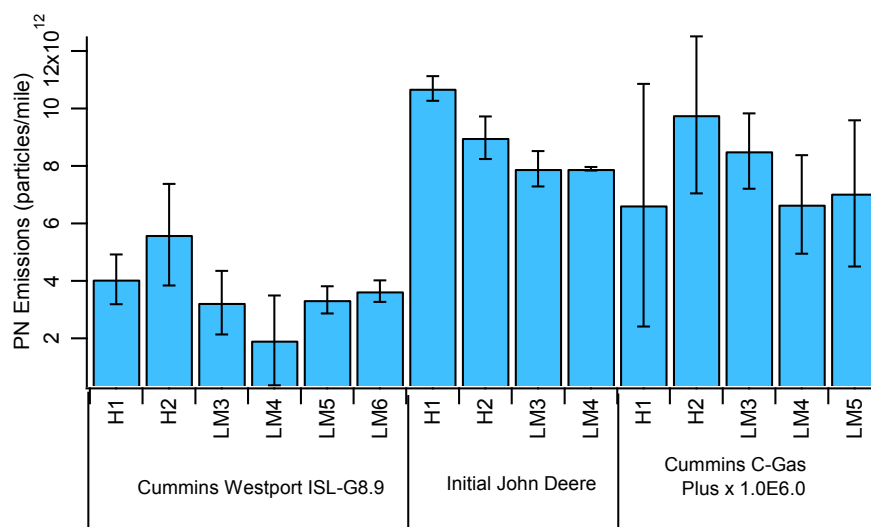
Measurements of the particle size distributions performed over the CBD cycle are displayed in Figure 5-6(a-d). Particle size distributions for all buses/fuel combinations exhibited a consistent unimodal in nature nucleation mode, with peak particle diameters at around 4-10.8 nm. The findings of this study are in strong agreement with previous studies reporting that the majority of particles from CNG buses were in the nucleation mode.<sup>12,35,48</sup> The very low PM mass for the CNG blends indicates that the level of agglomeration to form larger carbonaceous particles and gas phase adsorption and condensation was relatively limited. Due to the absence of these larger particles, nucleation is the prevalent mode of particle formation. It should be noted that although the measurements with the nano-SMPS provide

a good overall perspective of the particle sizes for the initial pre-repair John Deere bus testing and for the Cummins Westport ISL-G, the comparisons between fuels and the actual quantification of the PN concentrations are complicated by the relatively long scan time for the nano-SMPS instrument, which means this instrument samples only a small segment of its size range at any given time.

The C-Gas Plus bus produced unimodal distributions with a peak particle concentration at a diameter of 10.8 nm and with number concentrations ranging from  $\sim 8,000$  to  $9,700$  particles/cm<sup>3</sup>. For the C-Gas Plus bus, the formation of a second nucleation mode at 30-50 nm size range was also observed. The Cummins Westport ISL-G bus produced unimodal distributions with a peak concentration at a diameter of 5.5 nm and with PN concentrations ranging from  $\sim 8,000$  to  $22,000$  particles/cm<sup>3</sup>. For the initial John Deere testing, particle distributions exhibited a peak concentration at a diameter of 5.5 nm and PN concentrations ranged from  $\sim 90,000$  to  $270,000$  particles/cm<sup>3</sup>, while for the post repair John Deere bus particle sizes peaked at 8 nm and PN concentrations significantly decreased, and ranged from  $\sim 2,200$  to  $2,300$  particles/cm<sup>3</sup>. Under the present test conditions, consistent trends between fuels were not seen in the particle size distributions. Although there are differences in the fuels for different vehicles, they are not consistent between the different vehicles. For example, LM4 produced the highest level of nucleation particles for the initial John Deere bus, but the lowest for the Cummins Westport ISL-G bus. LM3 showed the highest emissions for the C-Gas Plus bus, but the lowest for the initial John Deere bus. Also, LM5 and LM6 showed the highest concentrations on the Cummins Westport ISL-G bus and the post-repair John Deere, but the lowest concentrations for the C-Gas Plus bus.

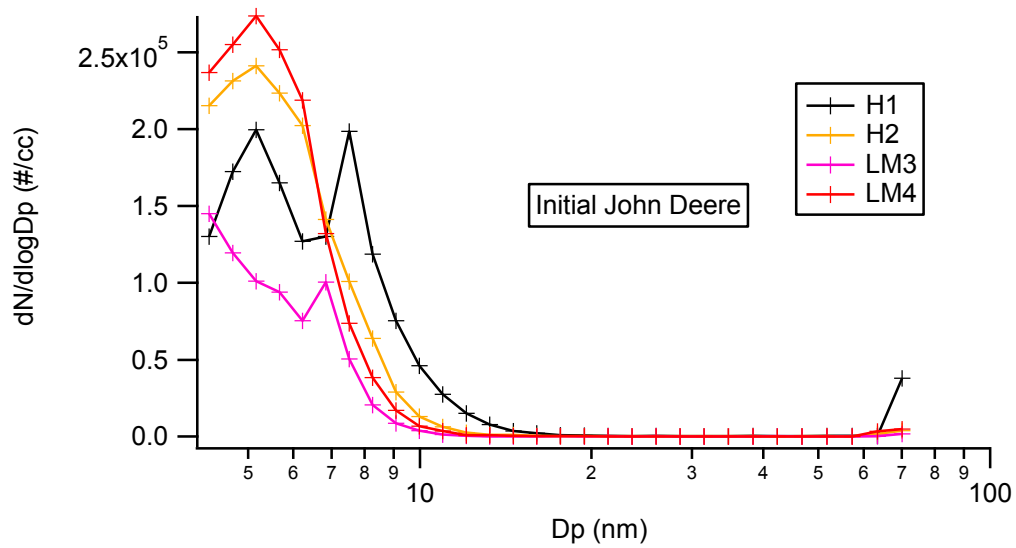
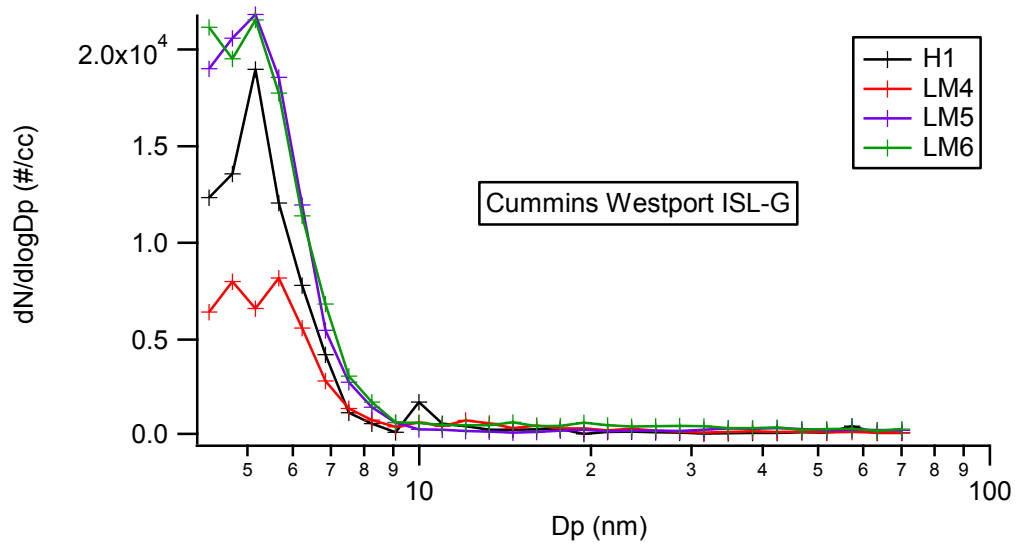


**a**



**b**

Figure 5-5(a-b). Average PM mass and particle number emissions from NG buses over the CBD



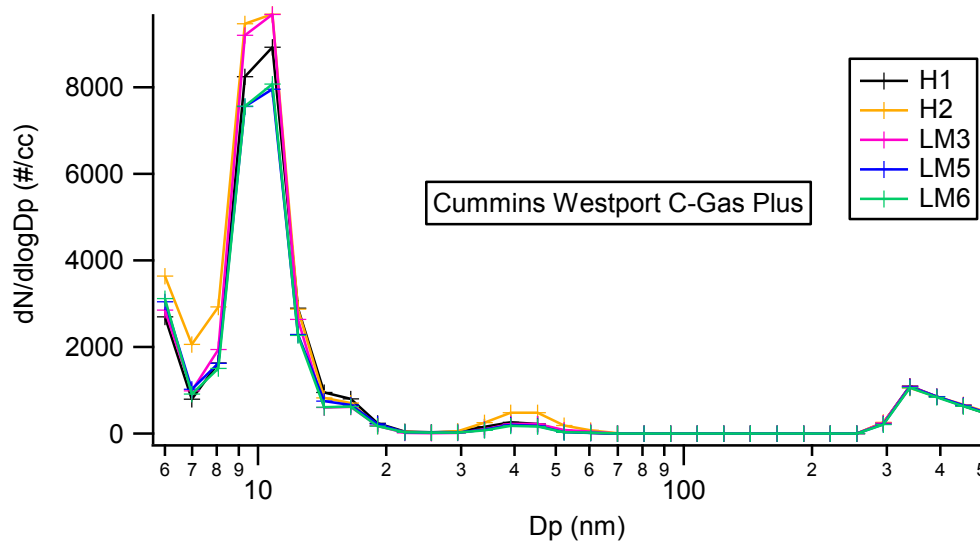
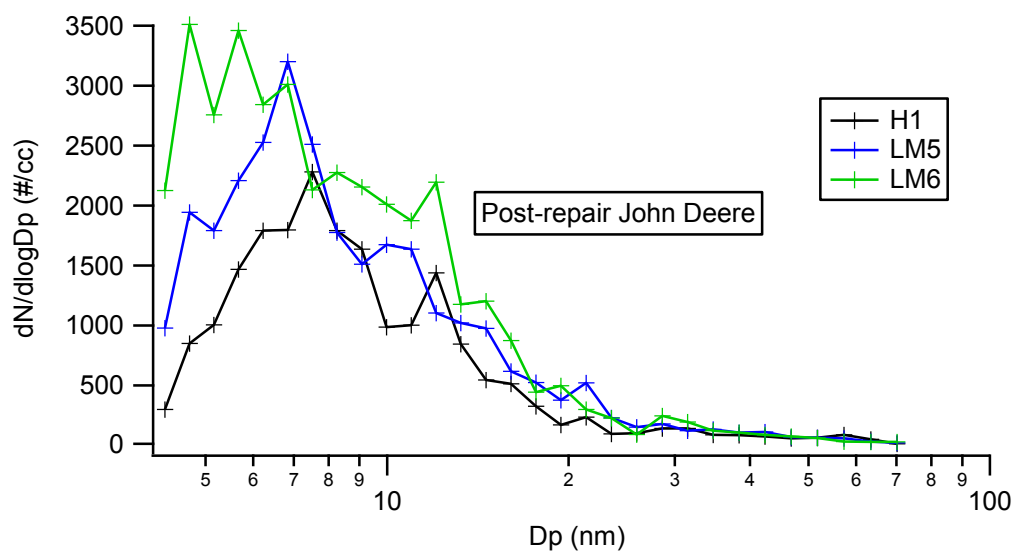


Figure 5-6(a-d). Average particle size distributions from NG buses over the CBD

#### 5.4.6. NH<sub>3</sub> Emissions

Figure 5-7 shows the ammonia emissions for the three buses over the CBD cycle. The results revealed that the stoichiometric Cummins Westport ISL-G bus produced substantially higher NH<sub>3</sub> emissions compared to the lean burn John Deere and Cummins C-Gas Plus buses. It has been documented that NH<sub>3</sub> is a secondary pollutant formed during the NO<sub>x</sub> reduction process over the TWC, with its formation to be dependent to the presence of both nitrogen oxide (NO) and hydrogen (H<sub>2</sub>) in the exhaust stream.<sup>19,49</sup> For TWC equipped stoichiometric natural gas engines, the production of NH<sub>3</sub> takes place in the presence of hydrogen molecules, which in turn are produced during periods of rich air-fuel mixtures.<sup>19</sup> Hydrogen could be either formed due to a water gas shift reaction involving CO and water or steam reforming reactions involving CH<sub>4</sub> and water in the exhaust.<sup>50,51</sup> The NH<sub>3</sub> emissions for the John Deere bus (for both initial and post-repair tests) were very low by comparison with the stoichiometric ISL-G bus. The NH<sub>3</sub> emissions for the C-Gas Plus bus were higher than those for the John Deere bus, but were still much lower than those for the stoichiometric ISL-G bus.

In general, no specific fuel effects were observed for the buses, and none of the emissions differences were statistically significant compared to H1. A weak trend towards higher NH<sub>3</sub> emissions was seen for the stoichiometric fueling bus for the higher WN/higher flame speed/lower MN gases, but not at a statistically significant level. Since the higher WN gases can produce higher exhaust temperatures and possibly slightly richer air-fuel ratios, the conditions for the formation of hydrogen as a precursor and NH<sub>3</sub> as reaction product could be enhanced for the higher WN gases.

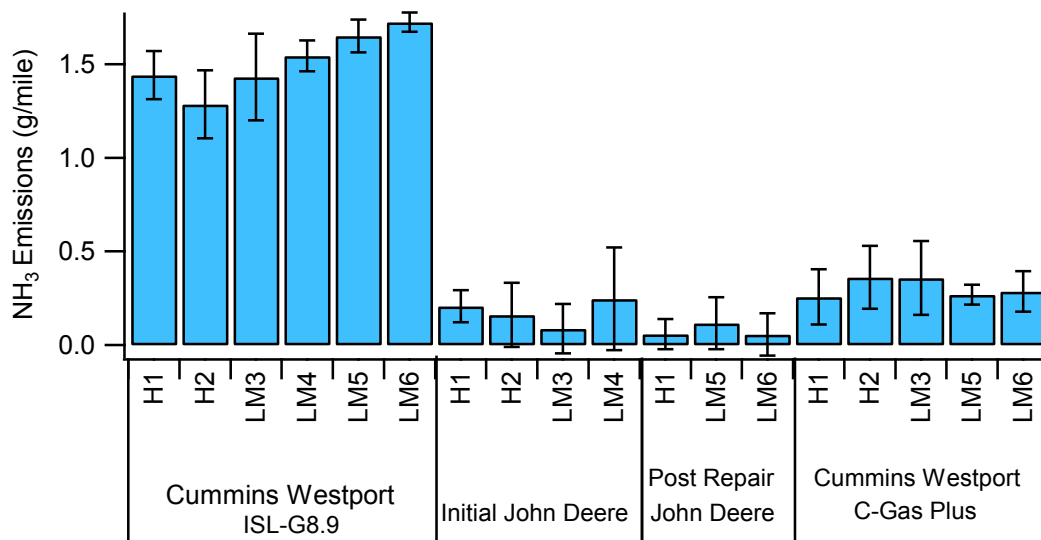


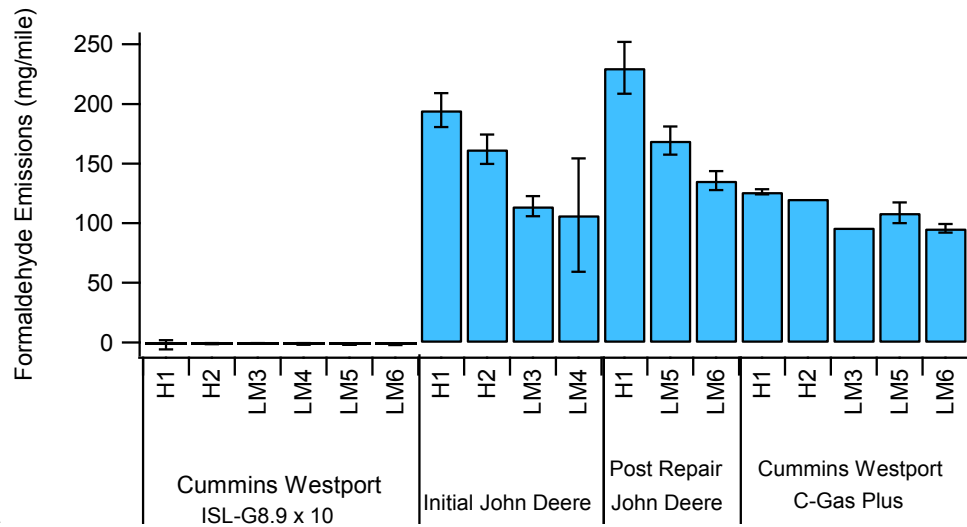
Figure 5-7. Average NH<sub>3</sub> emissions from NG buses over the CBD

#### 5.4.7. Carbonyl Emissions

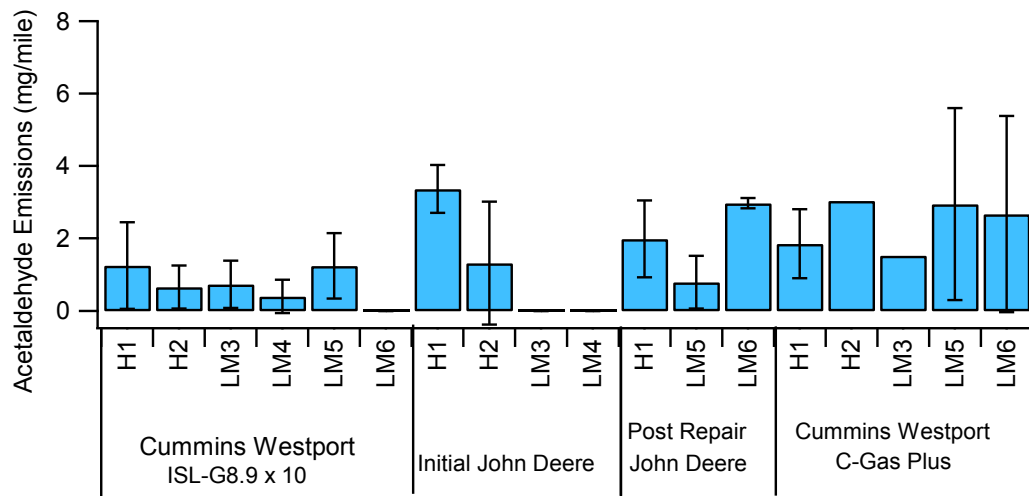
The emission levels for formaldehyde and acetaldehyde are shown in Figure 5-8(a-b). Formaldehyde and acetaldehyde emissions were the most prominent measured aldehydes in the tailpipe, with formaldehyde being the dominant compound. Note that formaldehyde and acetaldehyde are the lowest molecular weight aldehydes, having one and two carbons, respectively. Our results are in agreement with previous studies showing that the most abundant aldehyde emissions from CNG vehicles come from the lowest molecular weight compounds.<sup>13,32,52,53</sup> The magnitudes of formaldehyde and acetaldehyde emissions were at the measurement limits for the stoichiometric Cummins Westport ISL-G bus, and did not show any fuel trends. It appeared that the TWC was effective in reducing both aldehydes to close to background levels. This result is consistent with previous studies documented that stoichiometric fueled NG vehicles fitted with TWC produce lower formaldehyde emissions than lean-burn NG vehicles.<sup>14,45</sup>

For both the initial and post-repair John Deere bus tests, H1 and H2 showed the highest formaldehyde emissions compared to the other gases. For the post-repair John Deere testing, statistically significant reductions in formaldehyde emissions of 27% for LM5 and 41% for LM6 compared to H1 were found. For the initial John Deere testing, statistically significant reductions in formaldehyde of 16.9% for H2, 41% for LM3, and 45% for LM4 compared to H1 were found. For the John Deere bus, the formaldehyde results follow the same trends as the THC emissions, with gases with higher methane contents producing higher levels of formaldehyde. The same trend of higher formaldehyde emissions with the high methane gases was seen for the C-Gas Plus bus, although the trend was not as strong as for the John Deere. For the C-Gas Plus bus, H1 and H2 showed the highest formaldehyde emissions. Statistically significant reductions in formaldehyde emissions of 14% for LM5 and 24% for LM6 were found compared to H1 gas. For the acetaldehyde emissions, the buses did not show consistent fuel trends. However, for the initial John Deere bus testing, a statistically significant reduction of acetaldehyde emissions was seen for LM3 and LM4 compared to H1. H2 showed a marginally statistically significant reduction in acetaldehyde emissions compared to H1.

The higher formaldehyde emissions for the gases with higher methane contents is consistent with previous studies, since formaldehyde is an intermediate step in the oxidation of methane under high temperature conditions and across the catalyst.<sup>52</sup> The reductions in formaldehyde emissions for the low methane content gases may also be attributed to their higher adiabatic flame speeds, and ultimately to higher combustion temperature increases, which resulted in more complete oxidation of the fuel hydrocarbon fractions.



**a**



**b**

Figure 5-8(a-b). Average formaldehyde and acetaldehyde emissions from NG buses over the CBD

## 5.5. Conclusion

As the production of NG throughout the U.S. expands, there is potential for a wider range of natural gas compositions to be used in NGVs. It is important to evaluate whether changing compositions of NG will have adverse impacts on regional and global air quality. In this study, six blends of natural gas with different fuel compositions were tested. The gases represent a range of compositions from gases with high levels of methane and correspondingly lower energy contents and WNs to gases with higher levels of heavier hydrocarbons and correspondingly higher energy contents and WNs. Emissions testing was performed on three transit buses, a bus with a 2009 stoichiometric combustion, spark-ignited engine with cooled EGR and a TWC, and two buses with older 2002 and 2004 lean burn engines, fitted with OC over the CBD driving cycle.

The results showed that fuel composition influenced the formation of exhaust emissions from the older lean burn buses. Gases with low methane contents showed higher  $\text{NO}_x$  and NMHC emissions and improved fuel economy on a volumetric basis, but lower emissions of THC,  $\text{CH}_4$ , and formaldehyde emissions. The trends for the other emissions were not as consistent. The newest technology bus with the stoichiometric combustion engine and the TWC did not show any specific fuel effects. .

The results show that NG fuel composition can have an impact on emissions for older technology heavy-duty vehicles even for gases within pipeline specifications, albeit at the extreme ranges of what might be found in the pipeline. This suggests that control of the NG specifications is still needed for older technology heavy-duty NGVs. It appears that newer

technology heavy-duty natural gas engines can run on a wider range of NG fuels with varying composition without impacting emissions. Further study of the impact of NG composition for post-2007 engine is also planned for other applications, such as refuse trucks. Further studies also should be performed related to newer technology stoichiometric fueled NG engines and their associated  $\text{NH}_3$  emissions to better understand the  $\text{NH}_3$  formation mechanism and its possible contribution to secondary PM formation.

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## **Chapter Six: Assessment of the Emissions from the Use of California Air Resources Board Qualified Diesel Fuels in Comparison with Federal Diesel Fuels**

### **6.1. Abstract**

The California Air Resources Board (CARB) has regulated the properties of diesel fuel sold in California since 1988 to lower emissions of particulate matter (PM) and oxides of nitrogen ( $\text{NO}_x$ ). Although many studies have shown that reduced levels of aromatics and higher cetane numbers can improve emissions, the actual impact of CARB diesel fuels on in-use diesel emissions has not yet been extensively studied, especially as diesel engine and aftertreatment technology has evolved over the years. This study evaluates the differences between California and Federal diesel fuels with heavy-duty engine and chassis dynamometer tests. The engine dynamometer results showed that  $\text{NO}_x$  emissions for the federal fuels ranged from 4.7 to 9.5% higher than the CARB diesel. These  $\text{NO}_x$  reductions are similar to the estimates being used in the latest regulations. The chassis dynamometer test results did not show as consistent trends for  $\text{NO}_x$  as those seen for the engine dynamometer testing. For the chassis dynamometer testing, 4 of 10 vehicles showed consistent reductions in  $\text{NO}_x$ , with emissions for the federal fuels ranging from 3.3 to 9.9% higher than the CARB diesel, while the other 6 vehicles did not show any consistent fuel impacts. On an absolute level, the  $\text{NO}_x$  benefit for CARB diesel shows a decline with continuing advances in engine technology. The results also showed that CARB diesel did not show strong benefits for PM. The results also showed that the introduction of aftertreatment systems for PM and  $\text{NO}_x$  will, over time, largely eliminate any potential benefits that might be obtained through the use of CARB diesel, although  $\text{NO}_x$  benefits will persist through 2020.

## 6.2. Introduction

Diesel engines are primary contributors to the emissions inventory for both particulate matter (PM) and oxides of nitrogen ( $\text{NO}_x$ ) and have been the target of regulations for a number of years.  $\text{NO}_x$  can contribute to ozone and secondary PM formation, and it can have direct health impacts. Associations between ambient PM and adverse health effects have also been well documented in numerous studies.<sup>1,2</sup> The California Air Resources Board (CARB) designated PM emitted from diesel engines as a Toxic Air Contaminant (TAC) in 1998.<sup>3</sup>

Regulations to control diesel emissions have targeted both the engine technology as well as the diesel fuels used in the engines. California has a number of metropolitan areas that remain in nonattainment status for ozone and particulate matter, and the importance of improving air quality throughout California is well documented.<sup>4</sup> In California, diesel fuel regulations mandate that fuels sold in the state must meet the requirement of 10% or less aromatic hydrocarbon content, or show emissions that are equivalent to a 10% aromatic reference fuel.<sup>5</sup> The development of the California diesel fuel regulations was based on several earlier studies that showed that certain fuel parameters such as aromatics, cetane number, and sulfur content can have an important impact on diesel emission levels. This included the Coordinating Research Council Project VE-1,<sup>6,7</sup> which was the main focus of this earlier analysis, as well as other studies, such as those from Chevron and Caterpillar/Mobil.<sup>8,9</sup> The California diesel fuel regulations are the most stringent in the United States, and CARB has estimated that implementing these regulations has resulted in emissions reductions of 7% for  $\text{NO}_x$  and 25% for PM relative to pre-regulatory diesel fuel.<sup>10</sup> Air toxics, such as poly aromatic hydrocarbons and benzene, were also reduced.

Over the period of time since the California diesel fuel regulation was put in place, diesel engine technology has evolved considerably. Major studies have been conducted within the U.S.<sup>11–15</sup> Japan<sup>16,17</sup> and Europe<sup>18</sup> to examine the impacts fuel properties on emissions with changing engine technology, and several reviews have been conducted by different authors.<sup>19–24</sup> Based on his analysis, Hochhauser suggested that reductions in density and polyaromatic compounds, as opposed to total aromatics, lead to reductions in NO<sub>x</sub> and/or PM, although the existing data is complicated by a lack of orthogonality among variables, a small number of engines/vehicles, and differences in test cycles in many studies.<sup>25</sup> The actual impact of CARB diesel fuels on in-use diesel emissions has not been extensively studied, however. New engines are also now equipped with exhaust gas recirculation (EGR); diesel particulate filters (DPFs) to control PM, as of 2007; and, as of 2010, additional aftertreatment to further control NO<sub>x</sub> emissions. Additionally, Federal diesel fuels have also changed, as ultralow sulfur levels (15 ppmw) have now been implemented nationwide to facilitate the use of these aftertreatment devices. As technology for diesel engines and fuels continue to evolve, it is important to understand and quantify the continuing and future impact that CARB diesel fuel has on controlling diesel emissions.

This study is an evaluation between California and federal diesel fuels to provide a better understanding of the impact of CARB diesel fuel in-use in the California heavy-duty truck fleet. The test program includes both engine dynamometer testing and heavy-duty chassis dynamometer testing. The engine dynamometer testing provides a comparison between the different fuels under more controlled conditions. Engine dynamometer testing was conducted on 3 engines over the Federal Test Procedure (FTP) and CARB 50-mph cruise

cycles. The heavy-duty chassis dynamometer testing better characterizes in-use conditions, and included a wider range of engine technologies, from the latest technologies with aftertreatment for either PM and/or NO<sub>x</sub> to older technologies, where the fuel benefits would likely be more significant. Ten vehicles were tested over the CARB 50-mph cruise cycle for the chassis dynamometer testing. A total of 3 fuels were tested, including a CARB-certified diesel fuel and 2 federal diesel fuels. This chapter summarizes the results of this program.

### **6.3. Experimental Procedures**

#### **6.3.1. Test Fuels**

The test fuels included a commercially available CARB ultralow sulfur (CARB) diesel fuel as the baseline fuel and two Federal highway ultralow sulfur diesel (ULSD) fuels. One of the Federal diesel fuels, referred to as “Federal A”, was a certification diesel fuel selected to represent an average Federal ULSD. This fuel more closely represents the fuels found in states bordering California. The second, referred to as “Federal B”, was a commercially available Federal ultralow sulfur diesel fuel that, due to its properties, may contribute to higher exhaust emissions. The Federal B fuel was selected to have properties for aromatics, cetane number, density, and other parameters that were at the 85<sup>th</sup> percentile limits of Federal fuels in the marketplace, based on market surveys. The properties of the test fuels are provided in Table 6-1. It should be noted that these fuels do not contain any biodiesel. The Federal A fuel was not tested on the 2007 MBE 4000 for the engine dynamometer tests

since the 2007 MBE 4000 had to be reinstalled in its truck chassis for another test program before Fuel A was acquired.

Table 6-1. Selected fuel properties

	Units	Test Method	CARB ULSD	Federal A Diesel	Federal B Diesel
<b>Sulfur Content</b>	Mass ppm	D5453-93	7.4	13.3	5.3
<b>Total Aromatic Content</b>	Vol.%	D5186-96	19.1	30.6	36.0
<b>Total Aromatic Content</b>	mass%	D5186-96	19.4	32.0	37.8
<b>PAH</b>	mass%	D5186-96	1.6	11.6	5.8
<b>Nitrogen Content</b>	Mass ppm	D4629-96	115	4	84
<b>Cetane No.</b>	Rating	D613-94	50.4	45.5	44.1
<b>Density</b>	g/mL	D4052	0.8407	0.8488	0.8552
<b>Carbon Mass fraction</b>	%	D3343	86.56	86.97	87.15
<b>Distillation</b>		D86-96			
<b>10%</b>	°F		384.1	410.9	394.8
<b>50%</b>	°F		477.0	486.4	493.5
<b>90%</b>	°F		606.1	580.8	618.1
<b>Net Heat of Combustion</b>	Btu/gal	D3338	129815	130467	131161
<b>Carbon per Unit of Energy</b>	g Carbon/Btu		0.02124	0.02142	0.02153

### 6.3.2. Engine and Vehicle Selection

For the engine dynamometer testing of the program, three different engines were selected from 3 model year categories, 1991-1993, 2002-2006 and 2007-2009 that are representative of different engine certification level technologies. The 1991-1993 engine was an 11 liter, 1991 Detroit Diesel Corporation (DDC) Series 60 engine. This is the same engine model

used for the certification of alternative CARB diesel formulations, and thus it serves as a baseline for comparison of this data to the newer engine technologies. The 2002-2006 engine was an 11 liter, 2006 Cummins ISM engine. The engine from the 2007-2009 model year category was a 13 liter, 2007 DDC MBE4000. The 2007 MBE4000 engine was equipped with an original equipment manufacturer (OEM) DPF. This was the latest model year technology category available at the time of testing. The other engines were not equipped with diesel aftertreatment, while both the 2006 and 2007 engines were equipped with exhaust gas recirculation (EGR) technology. Descriptions of these engines are provided in Table C-1 of the Appendix C.

For the chassis dynamometer testing, ten vehicles were selected from different technology and model year categories for testing. Vehicles were selected to represent a range of different model years, certification levels and technologies. The vehicles were equipped with engines from several manufacturers, including DDC, Caterpillar, Cummins, and Navistar, with the model years ranging from 1994 to 2009 that are representative of different engine certification level technologies over that time period. Of the 10 test vehicles, 5 were equipped with aftertreatment, including 3 2007-2009 engines equipped with DPFs from the OEM, a 2000 DDC series 60 engine equipped with a Claire Longview aftertreatment device, and a 1998 DDC series 60 engine equipped with a Johnson Matthey Selective Catalytic Reduction with Continuously Regenerating Trap (SCRT). Both the Claire Longview and the SCRT aftertreatment devices incorporate a DPF for the reduction of CO, HC, and PM, and an aftertreatment system designed to reduce NO<sub>x</sub>. The Claire and SCRT systems are designed to reduce NO<sub>x</sub> by 25% and 60-80%, respectively. The five newest

vehicles were equipped with EGR. Descriptions of these vehicles are provided in Table C-2 of the Appendix C.

### **6.3.3. Test Cycles and Test Matrix**

Two test cycles were used for engine dynamometer testing, including the standard Federal Testing Procedure (FTP) and a cycle based on the CARB 50-miles-per-hour (50-mph), heavy-heavy-duty diesel truck (HHDDT) cruise cycle, which was selected to provide a higher load, highway driving test condition. For all the chassis dynamometer testing, only the CARB 50-mph, heavy-heavy-duty diesel truck (HHDDT) cruise cycle was used to allow for a greater number of replicates to be done at each test matrix.

For the 1991 DDC series and 2006 Cummins ISM engines, an engine dynamometer test cycle version of the 50-mph cruise cycle developed for the Advanced Collaborative Emissions Study (ACES) program was utilized.<sup>26</sup> For the 2007 MBE4000 engine, the 50 mph-cruise cycle was developed based on engine speed and torque data collected while running the vehicle from which the engine was pulled on a chassis dynamometer prior to the engine being removed.

The test matrix was developed to provide a sufficient number of replicates and a randomization throughout the testing on both engine dynamotor and chassis dynamometer part of the study. For the engine dynamometer testing, for each fuel type and cycle six replicates were tested. Table C-3 in the Appendix C provides the randomized test matrix designed for the engine dynamometer testing. Similar strategy was implemented in designing the chassis dynamometer test matrix, which is provided in Table C-4 of Appendix C, only

with 12 replicates for each vehicle/fuel combination. Note that for the chassis dynamometer testing there were some variations in the test matrix due to testing issues such as, for one vehicle, the 1994 CAT/3176, a change in the operation of the vehicle was observed for the final approximately day and 1/3 of testing. The cause for this change in operation was not identified or evaluated extensively, although the owner did report that he had the clutch adjusted after the vehicle was returned. Nevertheless, these data were removed from the final data set since the associated changes between tests would not be representative of fuel effects. In another case a vehicle was not able to complete the testing. For most breaks in testing, the testing would resume at the same point where testing had stopped to maintain the degree of randomization in the test matrix.

The 2007 and newer vehicles were all equipped with aftertreatment systems with active regeneration. For these vehicles, the testing sequence was conducted as normal. Once a regeneration event was observed to be starting, the test was stopped and the vehicle was manually triggered to regenerate. Once the regeneration was complete, testing was reinitiated at the same point in the test matrix when testing was stopped. No special conditioning has been performed for the passive systems which regenerate on a more continuous basis.

#### **6.3.4. Emissions Testing**

The engine dynamometer testing was performed at the University of California at Riverside's College of Engineering-Center for Environmental Research and Technology (CE-CERT's) heavy-duty engine dynamometer laboratory. This engine dynamometer test laboratory is

equipped with a 600-hp General Electric DC electric engine dynamometer and is designed to meet Code of Federal Regulations (CFR) requirements.

Chassis dynamometer testing was performed at CE-CERT's heavy-duty chassis dynamometer facility. The chassis dynamometer is an electric AC chassis dynamometer with dual 48" rolls, directly connected to 300-hp AC motors (model MD-AC/AC-300.48/300.48-45,000lb-HD-TANDEM). The dynamometer is capable of simulating road load and inertia forces of a vehicle operating over a range of different driving conditions, including highway cruise, urban driving, and other typical on-road driving conditions. The dynamometer can continuously absorb motor loads in excess of 600 hp from 45 to 80 mph, and intermittently absorb motor loads in a range up to 1,200 hp. The dynamometer can provide vehicle inertia simulation across a vehicle weight range of 10,000 to 80,000 lbs, over a broad range of different drive cycles.

For all tests, standard emissions measurements of total hydrocarbons (THC), carbon monoxide (CO), NO<sub>x</sub>, PM, and carbon dioxide (CO<sub>2</sub>) were performed. Fuel consumption was determined based on carbon balance using the carbon-based emissions results, the density, and the carbon mass fraction of each fuel. The emissions measurements were made using the standard analyzers in CE-CERT's heavy-duty Mobile Emissions Laboratory (MEL) trailer.<sup>27,28</sup>

## **6.4. Results**

The average results for regulated emissions and fuel consumption or fuel economy for both engine and chassis dynamometer testing are presented in Figure 6-1 to Figure 6-12. The

engine dynamometer testing results are reported in grams per brake horsepower hour (g/bhp-hr) or gallons per brake horsepower hour units, respectively. The chassis dynamometer testing results are reported in grams per mile or miles per gallon units. The results for each test cycle/fuel combination represent the average of all test runs done on that particular combination. The error bars represent one standard deviation on the average value. The Federal A diesel fuel was not tested for 2007 MBE4000, as discussed above.

Table 6-2 listed percentage differences for the different fuels on the different engines. Table C-5 and Table C-6 in the Appendix C show the average emissions rates, standard deviations, and percentage differences for the different fuels on the different engines, vehicles and test cycles, along with the associated p-values for statistical comparisons using a 2-tailed, 2-sample, equal-variance t-test. The statistical analyses provide information on the statistical significance of the different findings. For the engine dynamometer data, results were considered to be statistically significant for p-values below 0.05. For the chassis dynamometer data, a wider range in classifying statistical significance was used due to the greater variability of this type of testing with p-values below 0.05 considered statistically significant and p-values between 0.05-0.1 being considered marginally statistically significant. These p-values indicate that the probability that the compared emissions are the same is less than 5 to 10 percent.

Table 6-2. Percentages changes for Federal Diesel blends relative to CARB for both engine/chassis dynamometer studies

		THC	CO	NO <sub>x</sub>	PM	CO <sub>2</sub>	BSFC/MPG
<b>Engine Dynamometer</b>							
<b>2007 MBE 4000</b>							
<b>FTP</b>	<b>FED B</b>	27%	51%	7.3%	53%	1.4%	-0.9%
<b>Cruise</b>	<b>FED B</b>	-14%	31%	4.7%	109%	2.0%	-0.4%
<b>2006 Cummins</b>							
<b>FTP</b>	<b>FED A</b>	-1%	17%	6.7%	5%	1.3%	-0.1%
	<b>FED B</b>	12%	23%	7.9%	8%	1.3%	-1.0%
<b>Cruise</b>	<b>FED A</b>	-13%	5%	9.5%	0%	0.9%	-0.5%
	<b>FED B</b>	0%	9%	8.1%	3%	2.0%	-0.4%
<b>1991 DDC 60</b>							
<b>FTP</b>	<b>FED A</b>	14%	9%	7.5%	2%	1.7%	0.3%
	<b>FED B</b>	30%	12%	9.3%	3%	1.2%	-1.2%
<b>Cruise</b>	<b>FED A</b>	1%	5%	5.3%	7%	1.4%	-0.1%
	<b>FED B</b>	14%	3%	7.3%	2%	1.7%	-0.7%
<b>Chassis Dynamometer</b>							
<b>CAT/3176/1994</b>							
<b>FED A</b>		-11%	7%	0.7%	6%	1.2%	0.2%
<b>FED B</b>		-4%	10%	1.4%	12%	1.9%	0.5%
<b>DDC/S60/1998</b>							
<b>FED A</b>		9%	23%	-0.3%	-31%	-0.6%	1.9%
<b>FED B</b>		-39%	9%	0.3%	10%	2.6%	-0.2%
<b>DDC/S60/1999</b>							
<b>FED A</b>		3%	4%	-3.6%	13%	3.4%	-1.9%
<b>FED B</b>		3%	11%	-7.1%	20%	3.7%	-1.3%
<b>CAT/C15/2000</b>							
<b>FED A</b>		-8%	6%	3.3%	4%	1.3%	0.2%
<b>FED B</b>		2%	5%	5.3%	3%	1.9%	0.6%
<b>DDC/S60/2000</b>							
<b>FED A</b>		21%	-17%	5.4%	20%	-0.1%	1.5%
<b>FED B</b>		51%	-1%	9.4%	-13%	1.9%	0.5%
<b>CAT/C15/2005</b>							
<b>FED A</b>		-12%	-3%	-1.0%	-7%	0.3%	0.7%
<b>FED B</b>		-4%	27%	1.4%	11%	1.7%	0.7%
<b>Cummins/ISM/2006</b>							
<b>FED A</b>		9%	-0.4%	4.1%	-1%	1.5%	0.6%
<b>FED B</b>		1%	-0.2%	9.9%	9%	4.4%	-2.4%
<b>MBE/OEM/2007</b>							
<b>FED A</b>		17%	1%	4.8%	14%	1.3%	0.1%
<b>FED B</b>		-12%	24%	4.0%	-17%	2.2%	-0.03%
<b>CUM/ISX/2008</b>							

<b>FED A</b>	-261%	<b>-42%</b>	1.5%	0%	<b>3.6%</b>	<b>-2.1%</b>
<b>FED B</b>	-1080%	<u>-37%</u>	2.8%	-9%	0.1%	<b>2.3%</b>
Navistar /2009						
<b>FED A</b>	-59%	-14%	<b>-4.5%</b>	-26%	0.1%	1.3%
<b>FED B</b>	-3%	-31%	<b>8.7%</b>	-7%	<u>2.3%</u>	0.2%

**Bold: Statistically significant; Underline: Marginally statistically significant**

#### 6.4.1. NO<sub>x</sub> Emissions

For the engine dynamometer testing, NO<sub>x</sub> emissions for the Federal A and Federal B fuels were higher than those for the CARB fuel for all the engines and cycles. The NO<sub>x</sub> increases compared to CARB for the different engines ranged from 4.7 to 9.5% for the two Federal fuels, and were statistically significant for all cases. These differences were similar on a percentage basis between the different test engines, although the magnitude of the absolute emissions differences between fuels decreased for the newer engine technologies. For the 2006 Cummins ISM and the 1991 DDC 60 engines, the emissions for the Federal B fuel were higher than those for the Federal A fuel for most cycle combinations. For the 2006 Cummins engine, a marginally statistically significant difference (p=0.073) was found between the NO<sub>x</sub> emissions for the FTP for the Federal A and Federal B fuels, with the emissions for the Federal B fuel being approximately 1.2% higher than for Federal A. The differences between the NO<sub>x</sub> emissions for the Federal A and B fuels over the 50-mph cruise was not statistically significant (p=0.523). For the 1991 DDC 60, the NO<sub>x</sub> emissions were about 1.8 to 2.0% higher for the Federal B diesel fuel compared with Federal A diesel fuel over the two cycles, with all the differences being statistically significant.

The impacts of test cycle on the emissions differences between fuels over the three engines can be evaluated. For 2007 MBE 4000 and 1991 DDC 60, the observed emissions impacts

were greater for the FTP than the 50-mph cruise. The opposite trend was seen for the Federal A fuel for 2006 Cummins engine, although this can be attributed in part to stability issues seen with the 50-mph cruise on that engine. In particular, for some tests with the Federal B and CARB fuels NO<sub>x</sub> emissions were approximately 0.1 to 0.2 g/bhp-hr lower than other comparable tests. These differences were not fuel related and can be attributed to differences in operation that were observed between approximately 300 to 450 seconds into the cycle. The changes in engine operation were also observed with various engine parameters, including the fueling rate and boost pressure.

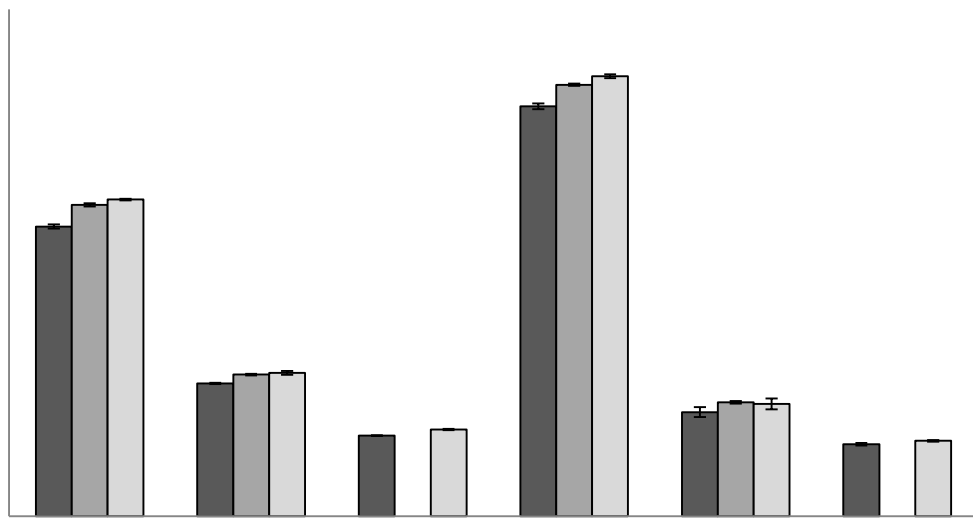


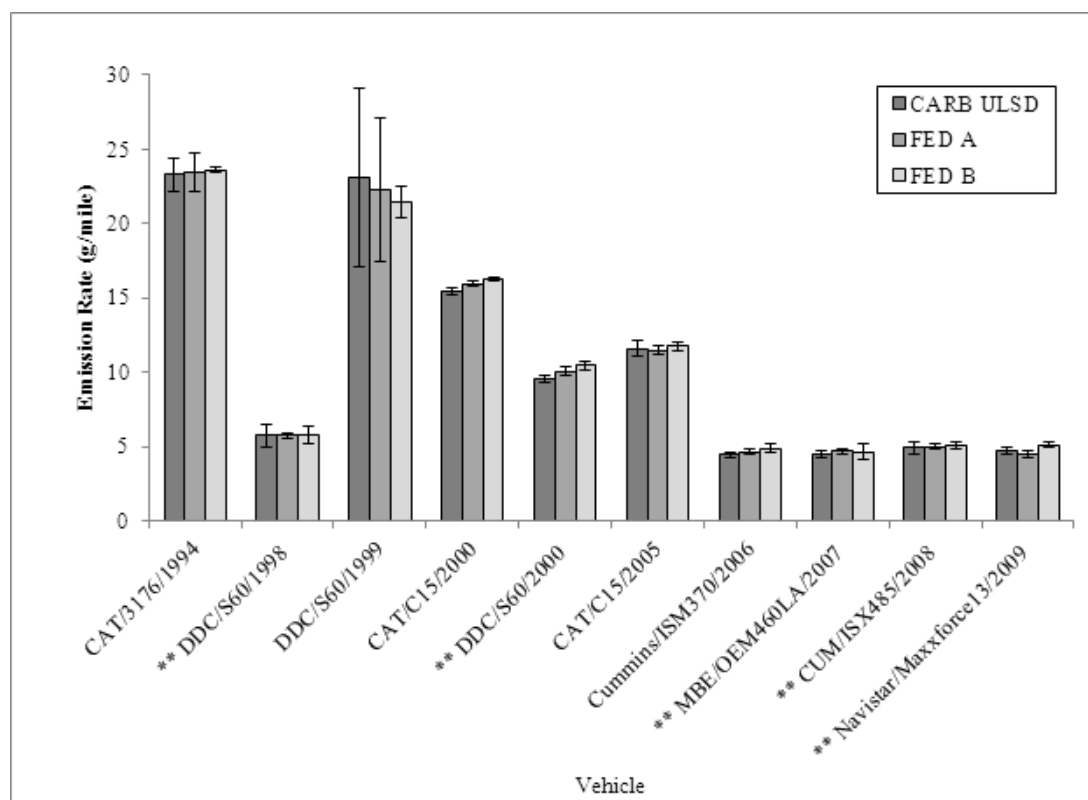
Figure 6-1. Average NO<sub>x</sub> emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle

For the chassis dynamometer, the average NO<sub>x</sub> emissions results showed a general trend of lower emissions for newer vehicles and for vehicles equipped with NO<sub>x</sub> retrofit aftertreatment devices. The retrofit vehicles included the 1998 DDC series 60 and 2000

DDC series 60. The retrofitted vehicles showed NO<sub>x</sub> reductions consistent with the different technologies employed on the vehicles, with the SCRT-equipped vehicle (1998 DDC series 60) showing greater reductions than the vehicle equipped with the Cleaire Longview (2000 DDC series 60). The trends in NO<sub>x</sub> emissions between the different fuels were not as consistent as for the engine testing. Four of the 10 vehicles, the 2000 CAT C15, the 2000 DDC series 60, the 2006 Cummins ISM, and the 2007 MBE4000 engines, showed statistically significant or marginally statistically significant increases in NO<sub>x</sub> for both the Federal A & B fuels, ranging from 3.3% to 9.9%. The 2009 Navistar engine showed a statistically significant increase for Federal B, but a decrease for Federal A. For the five vehicles that showed some increase in NO<sub>x</sub> emissions, the magnitude of the increase in NO<sub>x</sub> emissions was generally higher for Federal B compared to Federal A. For these vehicles, the magnitudes of the increases for the Federal A/B fuels were slightly less than those found for the engine testing.

For five of the 10 vehicles, no statistically significant differences in NO<sub>x</sub> emissions between fuels were found. For one of these vehicles, the 1999 DDC Series 60, operational issues during testing may have masked any fuel effects for the CARB and Federal A fuels. For this vehicle, there were clear indications that the engine timing changed for a subset of 4 tests. This change in engine operation could be seen from significant increases in NO<sub>x</sub> emissions, coupled with large decreases in PM emissions, as well as in the engine parameters obtained from the engine's ECM. The impact of these tests on the testing variability is shown by the large error bars for the CARB and Federal A fuels. For the 1998 DDC Series 60 engine, the effect of the NO<sub>x</sub> aftertreatment may have dampened potential fuel differences, although

fuel differences were seen for the other vehicle that was equipped with a less efficient NO<sub>x</sub> aftertreatment system, the 2000 DDC Series 60 engine.



\*\* Vehicles equipped with aftertreatment technologies

Figure 6-2. Average NO<sub>x</sub> emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle

#### 6.4.2. PM Emissions

For the engine testing, PM emissions showed statistically significant increases on the Federal A and B fuels for the Cummins engine over the FTP, but not over the 50-mph cruise cycle. PM emissions did not show any consistent trends for the 1991 DDC 60, with only the Fed A fuel for the 50-mph cruise showing statistically significant differences. For the 2007 MBE4000, the PM emissions were very low due to the DPF, and show the significant

reductions that are obtained with PM aftertreatment technology. The fuel differences were within the measurement error at these levels, and did not show any significant differences between fuels on either cycle.

For the chassis dynamometer testing, average PM emission results were very low for the vehicles equipped with retrofit or OEM/DPFs. The retrofit vehicles included the 1998 DDC series 60 and 2000 DDC series 60. The 2007 and newer vehicles with OEM-DPF technologies and retrofit vehicles had PM emissions that were lower by a hundred times or more compared to the PM emissions for the other five vehicles with no aftertreatment. For the DPF equipped vehicles, there were no statistically significant differences between fuels.

For the non-DPF equipped vehicles, only two vehicles (the 1999 DDC Series 60 & the 2006 Cummins ISM) showed statistically significant or marginally statistically significant increases for PM for the Federal B fuel. One other vehicle showed statistically significant increases for PM for the Federal A fuel (2000 CAT/C15). As discussed above, some of the variability in the PM emissions for the CARB and Federal A fuels for the 1999 DDC series 60 could be attributed to changes in engine operation/timing for a subset of 4 tests. This change is evidenced by the large error bars for the PM seen for this vehicle for the CARB and Federal A fuels. Overall, the chassis dynamometer results showed trends similar to the engine dynamometer testing, with only a small number of engine/cycle configurations showing statistically significant increases in PM for the Federal fuels, and with most cases showing no statistically significant differences between fuels.

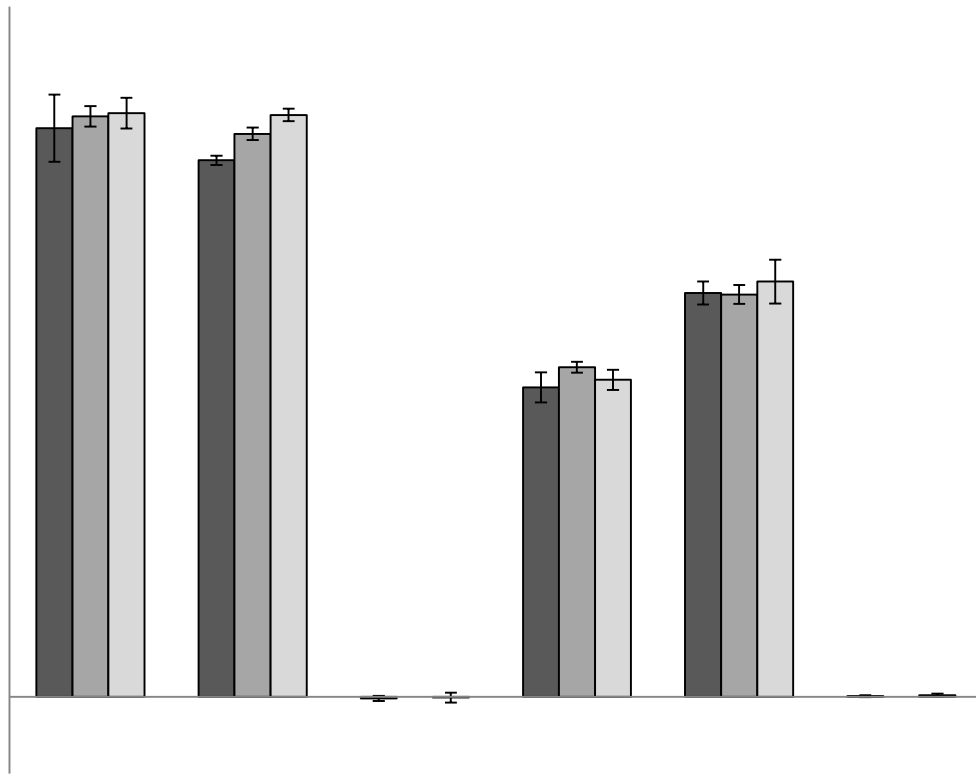
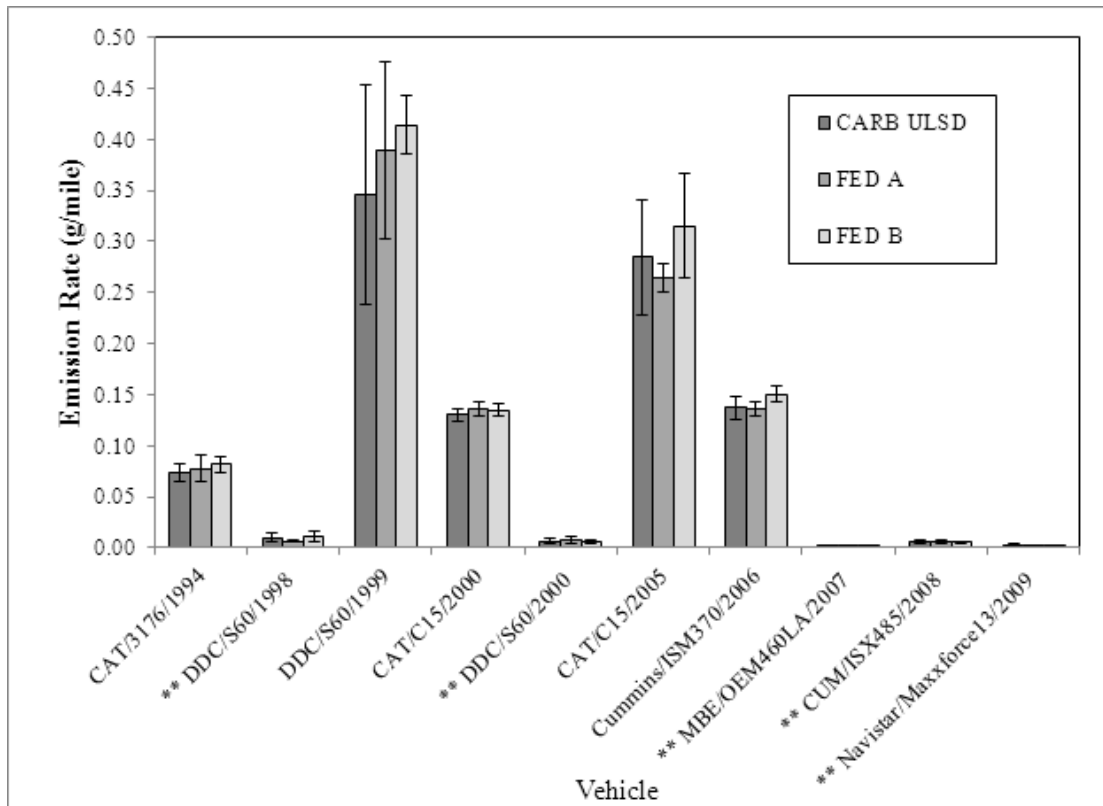


Figure 6-3. Average PM emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle



\*\* Vehicles equipped with aftertreatment technologies

Figure 6-4. Average PM emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle

#### 6.4.3. THC Emissions

For the engine dynamometer testing, THC emissions on 1991 DDC 60 showed statistically significant increases with Federal diesel fuels ranging from a 14 to 30%, while no consistent trends for 2007 MBE4000 and 2006 Cummins ISM were observed between the fuels over all the cycles. The THC emissions for the DPF equipped 2007 MBE4000 were considerably lower than those for the 2006 Cummins ISM or the 1991 DDC 60. This shows the significant reductions achieved due to the DPF.

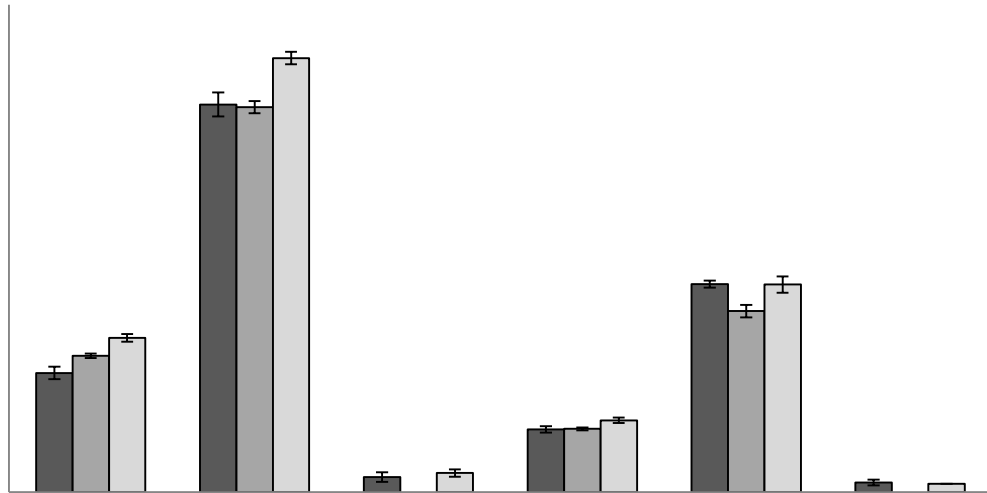
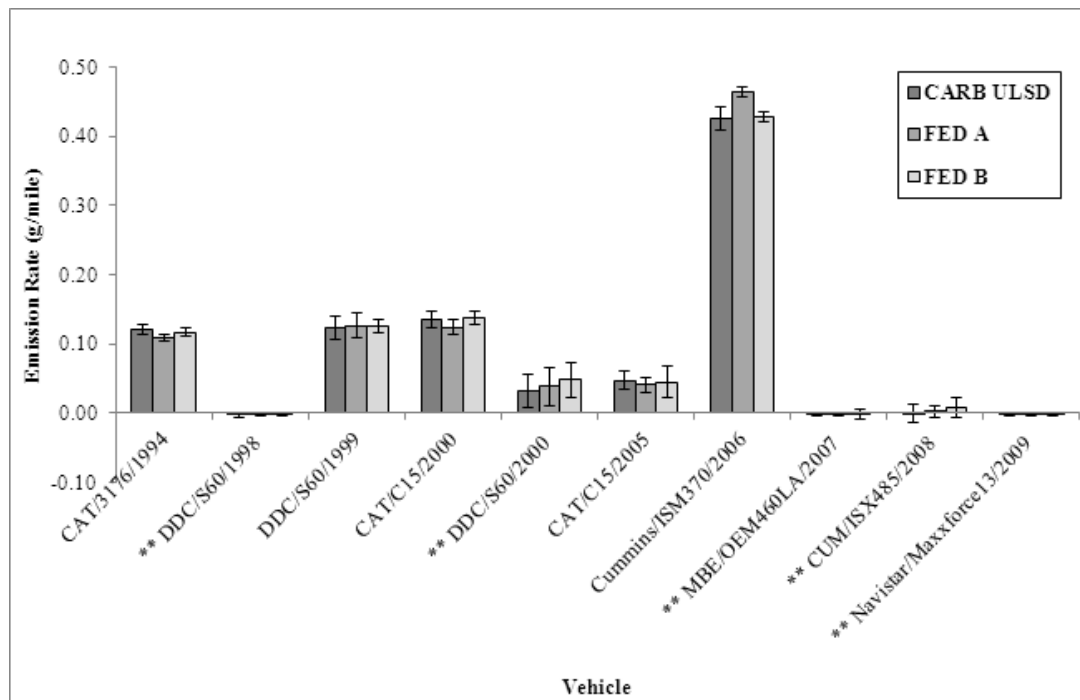


Figure 6-5. Average THC emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle

For the chassis dynamometer testing, the average THC emission results were very low for the vehicles equipped with retrofit or OEM/DPFs. For almost all of the vehicles, no statistically significant differences in THC emissions between fuels were found. The only statistically significant differences between fuels were for the CARB and Federal A fuels for three non-DPF equipped vehicles. The trends were not consistent, however, even between those vehicles, since two vehicles showed reductions in THC with the Federal A fuel (1994 CAT/3176 and 2000 CAT/C15) and one vehicle showed an increase with the Federal A fuel (2006 Cummins ISM).



\*\* Vehicles equipped with aftertreatment technologies

Figure 6-6. Average THC emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle

#### 6.4.4. CO Emissions

For the engine testing study, CO emissions for all the three engines showed higher emissions for both federal diesel fuels and both test cycles compared to the CARB ULSD. The CO emissions increases ranged from 9% to 51% over the different engine/fuel/cycle combinations. The emissions differences between CARB diesel and the federal diesels for the 2006 Cummins and the 1991 DDC 60 varied from approximately 5 to 23%. For 3 of the 4 test cycle combinations with these two engines, the emissions for Federal B were higher than those for Federal A. Although larger CO emissions changes were found on a percentage basis for the 2007 MBE4000, these changes were very small on an absolute basis. For 50-mph cruise for 2006 Cummins, the comparison was probably impacted by the issues

observed in running that cycle. The CO emissions for the DPF equipped MBE4000 were considerably lower than those for the 2006 Cummins or the 1991 DDC 60, showing the significant reductions that are achieved with DPFs.

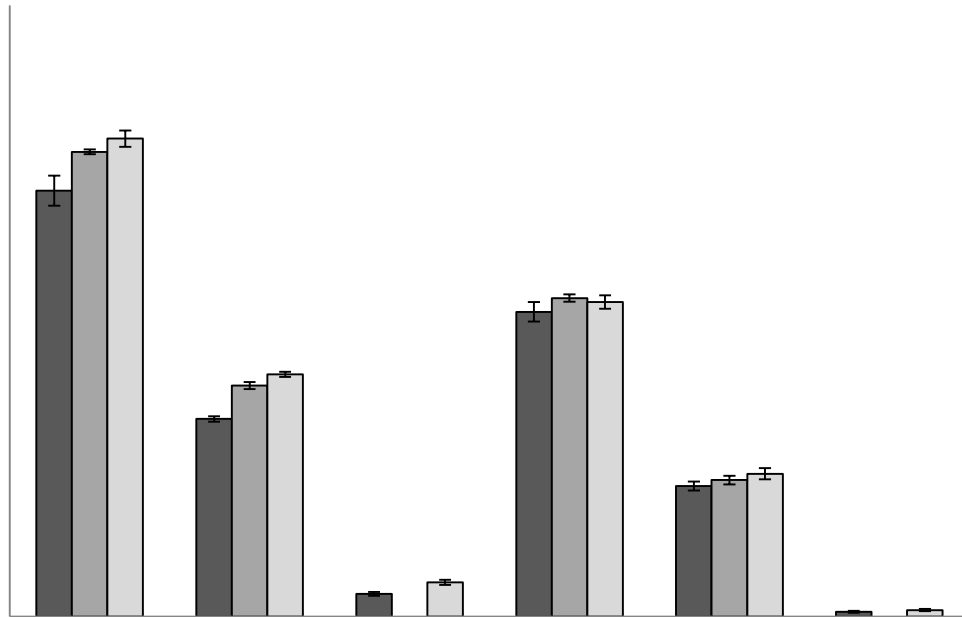
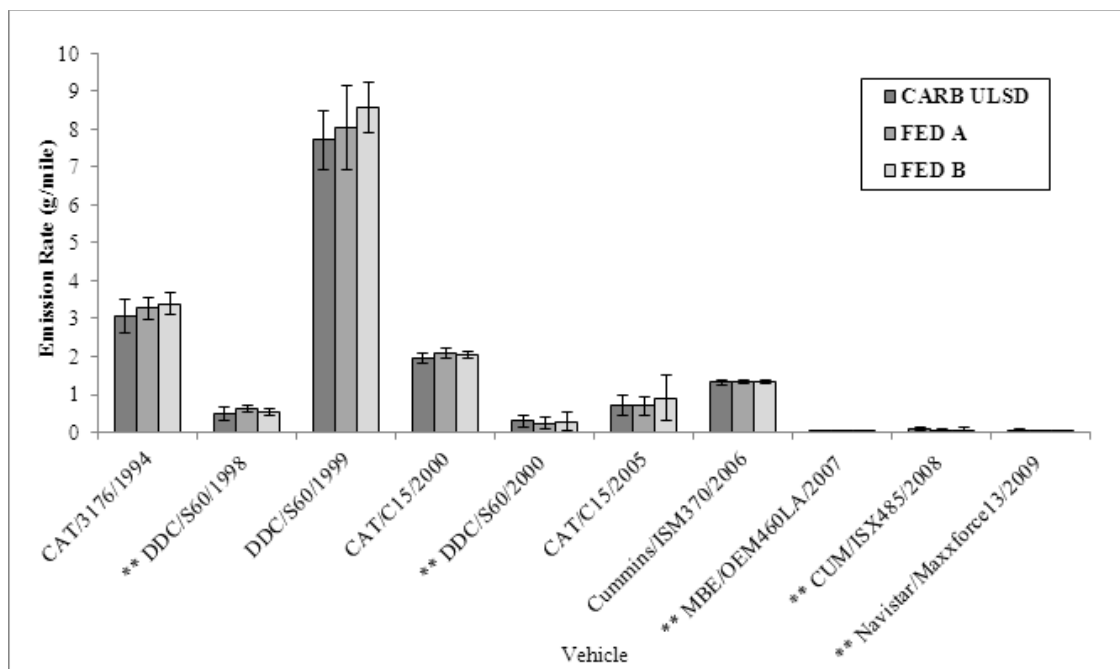


Figure 6-7. Average CO emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle

CO emissions of the chassis dynamometer study were at or below 3 g/mile for all vehicles except the 1999 DDC series 60, which had emissions in the 7 to 9 g/mile range. The 2007+ vehicles with OEM and DPFs and the retrofitted vehicles had the lowest CO emissions. CO emissions did not show consistent fuel trends over the test fleet. For seven of the ten vehicles, no statistically significant differences were found between fuels. For the vehicles with OEM or retrofit DPFs, it is expected that fuel differences would not be significant for

CO emissions. Only the 2000 CAT C15 showed statistically significant or marginally statistically significant increases in CO emissions for both the Federal A and B fuels. Interestingly, the DPF-equipped, 2008 Cummins ISM showed statistically significant or marginally statistically significant reductions of CO emissions for the Federal fuels compared to CARB ULSD. The differences in CO emissions between fuels for the 2008 Cummins ISX were very small on an absolute basis, however. The chassis dynamometer results differ from the results of the engine dynamometer testing, where statistically significant increases in CO emissions were found for both federal fuels for essentially all the engine/cycle combinations.



\*\* Vehicles equipped with aftertreatment technologies

Figure 6-8. Average CO emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle

#### 6.4.5. CO<sub>2</sub> Emission

CO<sub>2</sub> emissions showed slightly higher emissions for both federal diesel fuels and all three engines. The CO<sub>2</sub> emissions increases were relatively consistent between the three engines and ranged from 1 to 2%, with the Federal B fuel showing slightly higher increases than the Federal A fuel on the Cummins and DDC 60 engines for the 50-mph cruise cycle.

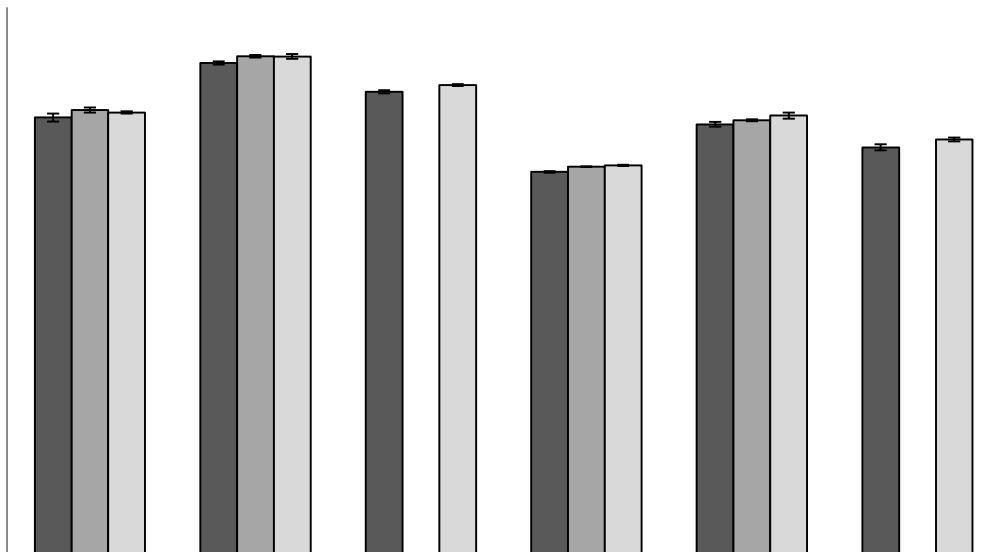
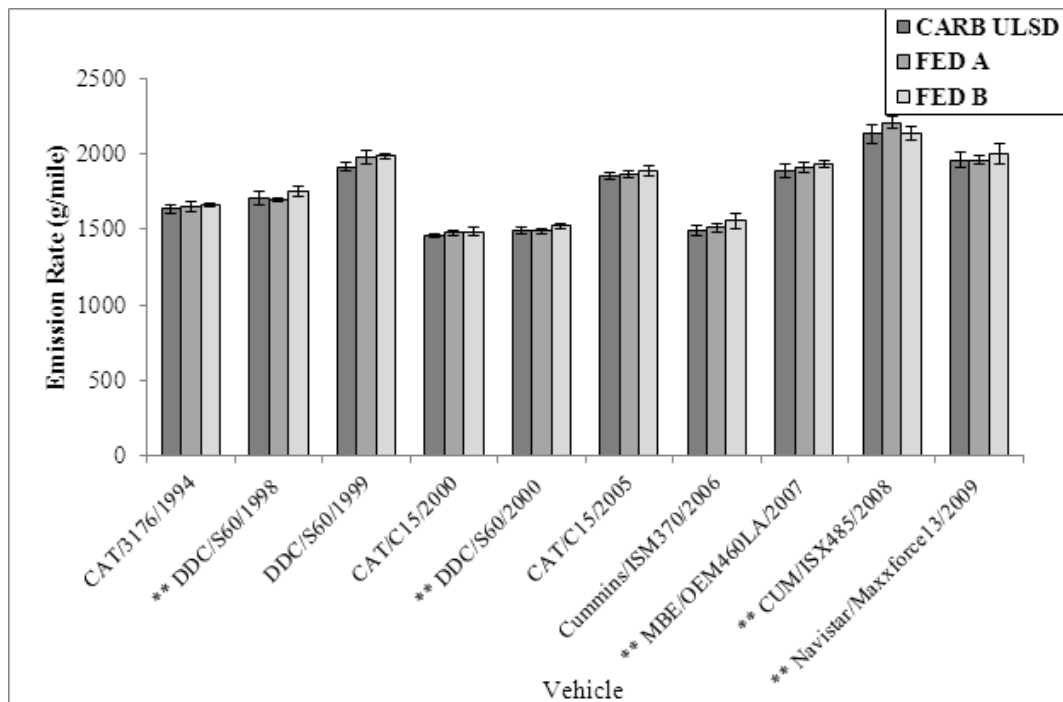


Figure 6-9. Average CO<sub>2</sub> emission results for all the engines over both the FTP cycle and 50-mph Cruise cycle

For the chassis dynamometer testing, CO<sub>2</sub> emissions showed statistically significant or marginally statistically significant increases for the Federal B fuel for 8 of the 10 vehicles. The Federal A fuel also had higher CO<sub>2</sub> emissions than CARB for 4 out of the 10 vehicles. In comparing between Federal A and B fuels, statistically significant differences in CO<sub>2</sub> emissions were seen for four out of ten vehicles (1998 DDC series 60, 2000 DDC series 60,

2006 Cummins ISM and 2008 Cummins ISX), with three out of four vehicles showing higher CO<sub>2</sub> emissions for the Federal B fuel. The magnitude of the increases in CO<sub>2</sub> emissions for the Federal fuels was approximately 1 to 4%, which is similar to the magnitude of the differences seen for the engine testing. The magnitude of these increases ranged from 1.3 to 3.6% for the Federal A fuel and from 1.7 to 4.4% for the Federal B fuel.

For CO<sub>2</sub>, the engine results showed more consistent trends with all engine cycle combinations showing increases in CO<sub>2</sub> emissions for the Federal fuels, while the chassis results showed some tests where statistically significant differences were not seen between fuels, and other cases where the increases in CO<sub>2</sub> emissions for the Federal fuels were larger than those seen for the engine dynamometer testing. The higher CO<sub>2</sub> emissions for the Federal A and Federal B fuels can be attributed to the fact that they have a higher carbon mass per unit of energy content compared to the CARB diesel, as shown in Table 6-1. The Federal A and Federal B fuels have carbon mass per unit of energy contents that are 0.85% and 1.4%, respectively, higher than the CARB fuel. This is comparable to the percentage increases in CO<sub>2</sub> emissions for the engine dynamometer testing but generally less than the percentage increases in CO<sub>2</sub> emissions for the chassis dynamometer testing.



\*\* Vehicles equipped with aftertreatment technologies

Figure 6-10. Average CO<sub>2</sub> emission results for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle

#### 6.4.6. Fuel Consumption and Fuel Economy

For the engine dynamometer testing of the program, some trends of lower brake specific volumetric fuel consumption were seen for the Federal B fuel. The differences between Federal B and CARB ULSD over the FTP cycle for all three engines were statistically significant. For 1991 DDC 60 the differences between the CARB ULSD and Federal B were also statistically significant over the 50-mph cruise. The lower fuel consumption for the Federal B fuel is not unexpected, given that this fuel has higher energy content or net heat of combustion than the other test fuels, as shown in Table 6-1. The CARB and Federal A fuels did not show any differences in fuel consumption for any of the engines.

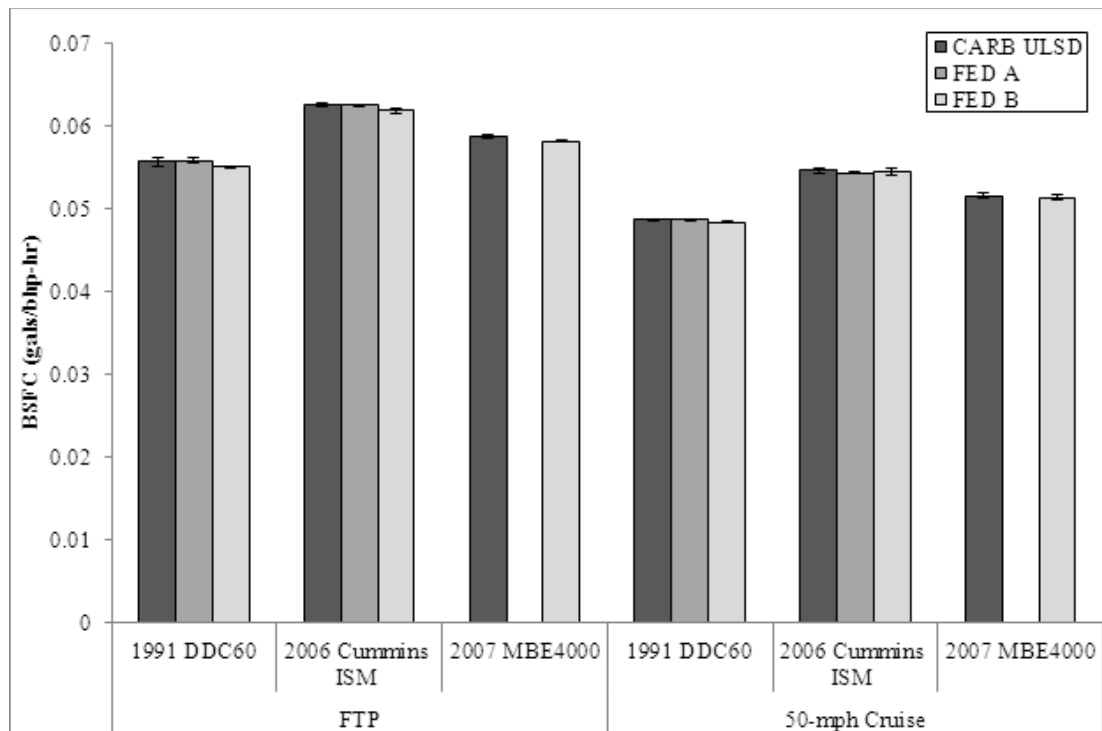
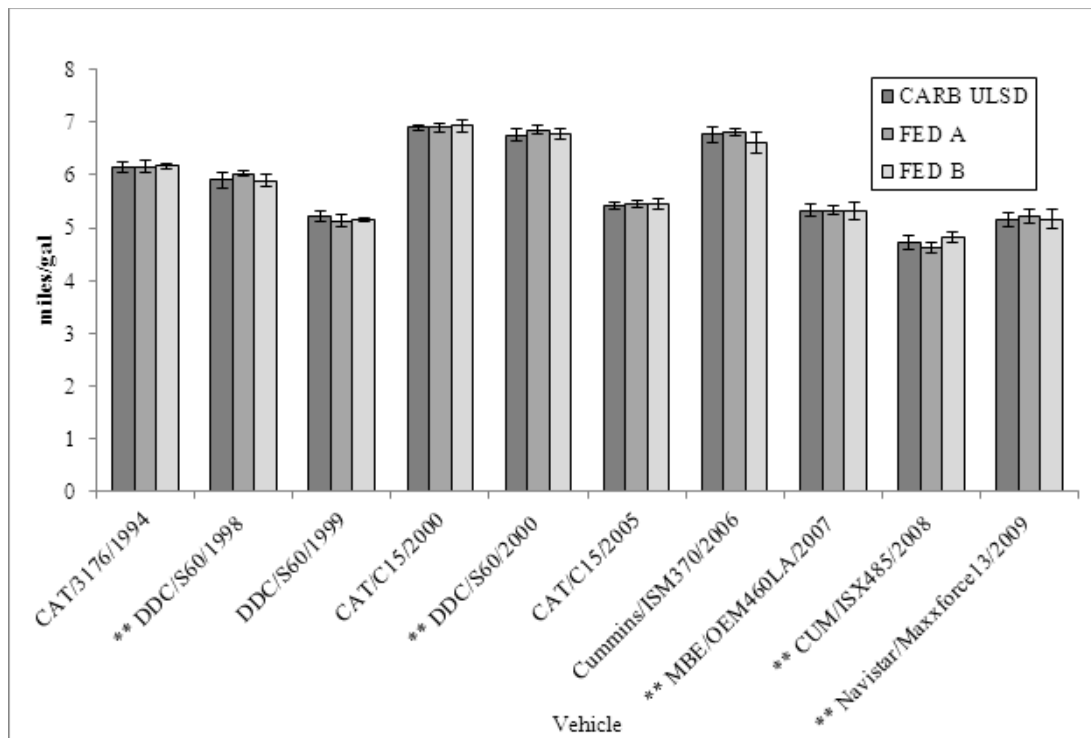


Figure 6-11. Average BSFC results for all the engines over both the FTP cycle and 50-mph Cruise cycle

For the vehicles as shown, average fuel economy ranged from about 4.6 to 6.9 miles per gallon for the ten test vehicles. Overall, there were no strong trends in fuel economy between the different fuels. Although 5 of the ten vehicles showed either statistically significant or marginally statistically significant differences between the CARB and either the Federal A or B fuels, these differences were inconsistent, with some showing increases and others showing decreases.



\*\* Vehicles equipped with aftertreatment technologies

Figure 6-12. Average fuel economy for Federal ULSD Fuels and CARB ULSD for ten test vehicles on 50-mph Cruise cycle

## 6.5. Discussions and Conclusion

It is useful to evaluate these results in the context of the CARB diesel fuel regulation that was originally approved in 1988,<sup>23</sup> and revised in 2003.<sup>2</sup> The 1988 regulation was primarily targeted at reducing  $\text{NO}_x$  and PM emissions, so these emissions will be the focus of our discussion. It is also worth noting that while the primary regulation focused on aromatics and sulfur content, the regulation allowed flexibility for fuels that could be shown to have emissions equivalent to those of a 10% aromatic diesel fuel. Thus, in reality, the fuels on the market typically show aromatic levels higher than 10%, with other fuel properties, such as cetane number or density, used to compensate for the higher aromatic levels.

For NO<sub>x</sub> emissions, it appears that CARB diesel fuel continues to provide some benefits. The engine dynamometer test results show consistent benefits in NO<sub>x</sub> for CARB ULSD for all engine combinations, with the Federal A and Federal B fuels ranging from 4.7 to 9.5% higher than the CARB diesel. The chassis dynamometer test results also showed some benefits in NO<sub>x</sub> for CARB ULSD, but the benefits are not as consistent as those seen for the engine dynamometer testing, with only 4 of 10 vehicles showing reductions in NO<sub>x</sub> for both the Federal A and B fuels, with emissions for the federal fuels ranging from 3.3 to 9.9% higher than the CARB diesel. The benefits with CARB diesel were also generally less compared with the average Federal A diesel than those for the Federal B fuel. In comparison, the most recent estimates of the benefits of the CARB diesel fuel regulation are a 6-7 percent improvement for 2009 (pre-NO<sub>x</sub>-aftertreatment) and older engines, with no benefits assumed for post-2009 engines.<sup>25</sup> On a percentage basis, the engine dynamometer test results are similar to those estimated in the latest version of the regulations. Based on the FTP-engine dynamometer results of the current study, CARB estimated NO<sub>x</sub> benefits of 6% and 8%, respectively, for the Federal A and Federal B fuels. The benefits of the NO<sub>x</sub> emissions in-use may also depend on the vehicle, however, as seen in the chassis dynamometer results, and perhaps the application. Additionally, on an absolute level, the NO<sub>x</sub> benefit shows a decline with continuing advances in engine technology. This trend will become more significant with the introduction of new engines with NO<sub>x</sub> aftertreatment, as of 2010, as well as for vehicles equipped with NO<sub>x</sub> retrofit aftertreatment devices.

The results of this study are consistent with those of previous studies for heavy-duty engines, which have shown that fuel properties such as density, aromatic content and cetane number

can affect NO<sub>x</sub> emissions. The results of other studies are hard to generalize due to a lack of orthogonality among the fuel properties and limitations on the number of tested engines for most studies, and differences in test cycles between studies.<sup>25</sup> A majority of studies have shown that a reduction of aromatic content leads to reductions of NO<sub>x</sub> emissions.<sup>29–33</sup> A few studies have reported either very small or no impacts of aromatic content on NO<sub>x</sub> emissions, however.<sup>34–38</sup> Some studies have shown that reducing density reduces NO<sub>x</sub> emissions.<sup>29–31</sup> In most studies, however, there are intercorrelations between density and aromatic content, so it is difficult to distinguish between the effects of these two variables.<sup>33,39</sup> Consistent fuel effects have not been found for the impact of cetane number on NO<sub>x</sub> emissions; however, the use of cetane number improvement additives has been shown to reduce NO<sub>x</sub> emissions.<sup>29–32,34,39,40</sup> The results of the engine dynamometer part of this study are in general agreement with the literature, although since the CARB diesel fuel has a combination of a lower density, aromatics content, and PAH content, and a higher cetane number compared to Federal diesel fuels, the individual effects of these different variables could not be distinguished.

For PM emissions, the primary reductions anticipated in the initial and subsequent regulatory development were due to the reductions in fuel sulfur level. In the most recent estimates of PM benefits, CARB diesel fuel was estimated to provide a 25% reduction in PM emissions for calendar years up to 2006, using a base sulfur level of 2800 ppmw for comparison. Since the level of sulfur in diesel fuels throughout the country has now been mandated to 15 ppmw levels, it is expected that the PM benefits of the CARB fuel would be significantly reduced. This is consistent with the experimental results, which showed PM benefits for only

a limited subset of fuel/engine combinations for the engine dynamometer testing, and no real PM benefit for the chassis dynamometer testing. Based on the FTP-engine dynamometer results of the current study, CARB estimated PM benefits of 3% and 5%, respectively, for the Federal A and Federal B fuels. The data also show that the implementation of PM aftertreatment on diesel engines will largely eliminate any potential benefits that might be obtained through the use of CARB ULSD for PM.

For heavy-duty engines, previous studies have not shown strong trends for aromatics, density, and cetane number impacts of PM emissions.<sup>25</sup> Some previous studies have shown PM effects for aromatics,<sup>16,20,34,35</sup> while others have not shown an effect.<sup>38</sup> In reviewing previous studies of fuel effects, Hochhauser suggested that the PAH content, rather than total aromatics, could have a more significant impact on PM emissions.<sup>25</sup> A few studies have shown the impacts of density on PM,<sup>39</sup> but this trend is not consistent over a wider range of studies.<sup>25</sup> Most studies have shown cetane number generally does not have a significant influence on PM emissions.<sup>25,29,32,36,38</sup>

For the other pollutant emissions, which were not evaluated as part of the initial CARB diesel fuel regulation, it appears that the CARB diesel will not provide significant benefits for THC, with THC benefits seen for only a limited subset of the engine dynamometer testing, and not at all for the chassis dynamometer testing. CO emissions showed mixed trends, with consistent benefits seen for the CARB diesel for the engine dynamometer testing, but not the chassis dynamometer testing. Any CO benefit for CARB diesel would also be eliminated for DPF-equipped vehicles. Previous studies have shown that cetane number seems to have the strongest impact on lowering THC and CO emissions.<sup>25</sup> The more paraffinic nature and

lower carbon per unit of energy for the CARB diesel was shown to provide reductions in tailpipe CO<sub>2</sub> emissions, although this is not necessarily indicative of total lifecycle greenhouse gas emissions. It is also likely that in-use, the CARB fuel would have a minimal impact on fuel economy, since a fuel economy disbenefit was only observed experimentally for the engine dynamometer testing in comparison with the more aromatic Federal B diesel.

The impact of CARB diesel fuel on the emissions inventory over time can also be evaluated. Table 6-3 lists the population of all diesel vehicles and NO<sub>x</sub>/PM emission inventories in California based on vehicle model year categories for calendar years 2010, 2015, and 2020. These emission inventories were obtained from CARB's online mobile source emissions inventory database.<sup>41</sup> The benefits of the CARB diesel fuel were determined for each calendar year for two cases, corresponding to the Federal A and Federal B diesel fuels, on both a tons per day and percentage basis. The emissions benefits on a percentage basis are calculated relative to what the emissions inventories would be if the CARB diesel had not been implemented.

For the emissions benefits, reductions of 6% for NO<sub>x</sub> and 3% for PM for the Federal A fuel, and 8% for NO<sub>x</sub> and 5% for PM for the Federal B fuel were used, based on CARB staff estimates from the FTP engine dynamometer tests from this study. The benefits of CARB relative to Federal A and Federal B were estimated as (the mean of the percent increases of Federal A relative to CARB)/(100% + the mean of the percent increases of Federal A relative to CARB) and (the mean of the percent increases of Federal B relative to CARB)/(100% + the mean of the percent increases of Federal B relative to CARB), respectively. In the mean of the percent NO<sub>x</sub> increases of Federal A relative to CARB, the

CARB staff included an estimated percent NO<sub>x</sub> increase of Federal A relative to CARB for the MBE4000 engine, calculated by using the ratio of the Federal A to Federal B average relative emissions from the other two engines to scale the Federal B relative emissions from the MBE4000 engine. These benefits were only applied to vehicles not equipped with DPFs or NO<sub>x</sub> aftertreatment systems or advanced PM and NO<sub>x</sub> controls. It was assumed that the 2007 and newer vehicles are equipped with DPFs and the 2010 and newer vehicles are equipped with NO<sub>x</sub> aftertreatment or other advanced NO<sub>x</sub> reduction technologies. It should also be noted that all 1996 and newer vehicles are expected to be retrofitted with DPFs by 2014 in California. Thus, the emissions benefits of CARB diesel fuel were only applied to 2009 and older vehicles for NO<sub>x</sub>, and to 2006 and older vehicles for the 2010 calendar year and to 1995 and older vehicles for the 2015/2020 calendar year for PM

The impacts of incorporating larger fractions of vehicles with advanced PM and NO<sub>x</sub> control strategies can be seen from both the changes in population and the emissions inventories over the three different calendar years. The percentage of vehicles that will have advanced PM controls goes from 19% in 2010 to 96% in 2020. Estimates for PM emissions benefits range from 2.8% to 4.7% in 2010 to 0.2 to 0.3% in 2020, indicating that PM benefits from CARB diesel fuel will be largely gone by 2015/2020. CARB diesel will likely provide a more long lasting benefit for NO<sub>x</sub> emissions, since the portion of the fleet with advanced NO<sub>x</sub> controls goes from 5% of the fleet in 2010 to 56% of the fleet in 2020. For NO<sub>x</sub> emissions, the benefit of CARB diesel for NO<sub>x</sub> emissions ranged from 5.9%, 5.3% and 4.1% for Federal A, and 7.9%, 7.1%, and 5.5% for Federal B, respectively, for the calendar years, 2010, 2015, and 2020. On an absolute basis, however, the NO<sub>x</sub> benefit will decline

from 44.7 to 60.8 tons per day in 2015 to 14.9 to 20.3 tons per day in 2020. It should be noted that the benefits of CARB diesel relative to the Federal A fuel are probably more representative of the real CARB diesel benefits, since this fuel more closely represents diesel fuel found in the states bordering California. On the other hand, the shipment of fuels from California refineries to bordering locations probably improves the overall properties of those fuels relative to what might be found if the California Diesel fuel regulation was not in place. It should also emphasize that the emissions inventory benefits calculated here were based on engine dynamometer test results, while the chassis dynamometer results, which may be representative of in-use conditions, showed generally lower/less consistent benefits.

Table 6-3. Emission factors and vehicle population in California

Calendar Year	Model Year	Vehicles Population	Vehicle Percentage	NO <sub>x</sub> (tons/day)	PM <sub>2.5</sub> (tons/day)
2010	...-1995	186293	20%	113.00	5.16
	1996-2006	589891	62%	519.15	17.80
	2007-2009	130145	14%	67.45	1.29
	2010-2011	43568	5%	7.36	0.36
	Total Emissions		949898	706.95	24.61
	Total Emissions without DPF & NO <sub>x</sub> after-treatment			699.60	22.96
	Emission Benefit with CARB diesel Fuel			44.66	0.71
	Emission Benefit Percentage Difference			60.83	1.21
2015	...-1995	99255	9%	50.80	1.62
	1996-2006	505452	46%	316.70	5.62
	2007-2009	149207	14%	91.39	1.83
	2010-2016	334545	31%	63.13	3.37
	Total Emissions		1088458	522.03	12.44
	Total Emissions without DPF & NO <sub>x</sub> after-treatment			458.89	1.62
	Emission Benefit with CARB diesel Fuel			29.29	0.05
	Emission Benefit Percentage Difference			39.90	0.09
2020	...-1995	49233	4%	24.32	0.67
	1996-2006	336136	29%	146.72	2.37

Calendar Year	Model Year	Vehicles Population	Vehicle Percentage	NO <sub>x</sub> (tons/day)	PM <sub>2.5</sub> (tons/day)
	2007-2009	123470	11%	62.86	1.29
	2010-2020	659744	56%	118.68	6.35
	<b>Total Emissions</b>	<b>1168583</b>		<b>352.59</b>	<b>10.69</b>
	<b>Total Emissions without DPF &amp; NO<sub>x</sub> after-treatment</b>			<b>233.91</b>	<b>0.67</b>
	<b>Emission Benefit with CARB diesel Fuel</b>			<b>14.9</b>	<b>0.02</b>
				<b>20.3</b>	<b>0.04</b>
	<b>Emission Benefit Percentage Difference</b>			<b>4.1%</b>	<b>0.2%</b>
				<b>5.5%</b>	<b>0.3%</b>

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## **6.8. Disclaimer**

The statements and conclusions in this chapter are those of the contractor and not necessarily those of California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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## Chapter Seven: Conclusions

This dissertation focused on investigating the impact of different alternative fuels, such as biodiesel and natural gas, on exhaust emissions from heavy-duty engines. Chapters two to four of this thesis explored the effect of different biodiesel and renewable/GTL blends on regulated emissions from various engine technologies. In chapter five, the impact of natural gas fuel composition on exhaust emissions from different technology buses was evaluated. Finally, chapter six is a summary of a comparison between the emissions of an average Federal diesel fuel and a diesel fuel meeting California's more stringent fuel quality standards.

In chapters two and three, the impact of different biodiesel feedstocks and renewable/GTL diesel fuel blends on criteria emissions was investigated using a CARB diesel fuel as the baseline. An important element of this study was the use of CARB diesel fuel as the baseline diesel, since it has a lower aromatic content and a relatively high cetane number compared to other Federal diesel fuels used throughout the U.S. For this study, two different engine technologies (one non-DPF and one DPF equipped engine) and four different engine test cycles were used. This study was one of the most comprehensive biodiesel emissions studies in terms of number of tests, testing replication and long term repeatability, and number of blend levels and types.

The results of chapter two of this dissertation showed a relatively clear trend of increasing  $\text{NO}_x$  emissions with increasing biodiesel blend level at levels of B20 and above for CARB-like/high cetane diesel fuels. The magnitude of the impact of biodiesel on  $\text{NO}_x$  at these levels appears to depend on several different factors including the specific test engine technology and certification level, the feedstock from which the biodiesel is produced, and

the test cycle or operating condition. Taking these results in conjunction with other literature studies of CARB-like diesel fuels, it appears that biodiesel likely has a more significant impact on  $\text{NO}_x$  when used with CARB-like diesels compared to more conventional US average diesels, at least at B20 or higher levels. For low level B5-B10 blends, that are the most likely to be implemented in the near term in meeting regulatory requirements, it is still unclear if or what level of mitigation might be needed in regions such as California that have stringent provisions against any increases in  $\text{NO}_x$  emissions. Potentially  $\text{NO}_x$  neutral blends for such regions could include a B5 blend with a highly saturated biodiesel base stock, such as an animal-based biodiesel, combinations of B5 or lower blends with renewable diesel or GTL-like fuels, or the addition of additives. For biodiesels with a greater propensity for increasing  $\text{NO}_x$ , such as soy-based biodiesel, further modification to the base fuel might also be possible to offset any potential biodiesel  $\text{NO}_x$  increases.

Chapter three is a summary of the other regulated emissions from this biodiesel study. In general, PM, THC, and CO emissions showed reductions for biodiesel and renewable/GTL fuel blends with CARB diesel. The levels of these reductions were generally comparable to those found in previous studies performed using more typical Federal diesel fuels. For the non-DPF equipped engine, the 2006 Cummins ISM, PM and THC emissions decreased with increasing levels of different biodiesels. The reductions ranged from 10% to 26% for B20 blends and from 31% to 69% for B100 blends for PM, and from 13% to 16% for B20 blends and from 55% to 73% for B100 blends for THC. For the 2006 Cummins ISM, CO emissions decreased from 7% to 10% for B20 blends and from 20% to 27% for B100 blends for the animal-based biodiesel, but CO emissions for the soy-based biodiesel on this engine

did not show any clear reduction trends, and even showed increases for the B50 and B100 blends over the UDDS. For this same engine, PM, THC, and CO emissions showed reductions with increasing renewable/GTL blend level, with the exception of THC emissions for the renewable blends over the FTP cycle. For the DPF-equipped engine, the 2007 MBE4000, THC, CO, and PM emission levels were very low due to the DPF and did not show significant fuel impacts. For both engines, CO<sub>2</sub> emissions showed slight increases of 1-5% for the pure biodiesels and a slight decrease of 3% for pure renewable/GLT diesel fuels, which is likely due to differences in average carbon content per unit of energy between the different fuels. BSFC showed slight increases of 1.4-9.8% with increasing biodiesel fuel and slight increases of 1.3-5.2% with increasing renewable/GTL diesel fuel, which is due to the lower heating value of these fuels compared to the CARB diesel.

Chapter four evaluated the impact of biodiesel feedstock at a B5 blend level and using additives with B20 biodiesel blends on regulated emission from a heavy-duty diesel engine. This chapter is a summary of the results of a study that has been done in compliment to the comprehensive biodiesel study. The results showed definitive NO<sub>x</sub> increases at the B20 level, as well as increases at the B5 level, depending on the biodiesel feedstock type. For the B5 blends tested B5-soy and B5-WVO both showed measurable increases in NO<sub>x</sub> emissions, while the B5-animal showed a slight reduction or no change in NO<sub>x</sub> emissions compared to the CARB reference diesel fuel. The B5-animal blend also passed the criteria of the CARB emissions equivalent certification test. The results also showed that certain additives can provide some benefits in NO<sub>x</sub> reduction, but that the benefits of the additives tested in this study were not sufficient to provide NO<sub>x</sub> neutrality at the B20 level. Overall, these additives

showed less success than what was seen previously for a 1% DTBP additive blend, which showed NO<sub>x</sub> neutrality at the B20 level. Additional testing is currently being planned to more comprehensively investigate the impacts of biodiesel at B5 and B10 levels in CARB diesel.

Chapter five evaluates whether changing compositions of NG will have adverse impacts on regional and global air quality. In this study, six blends of natural gas with different fuel compositions were tested. The gases represent a range of compositions from gases with high levels of methane and correspondingly lower energy contents and WNs to gases with higher levels of heavier hydrocarbons and correspondingly higher energy contents and WNs. Emissions testing was performed on three transit buses, a bus with a 2009 stoichiometric combustion, spark-ignited engine with cooled EGR and a TWC, and two buses with older 2002 and 2004 lean burn engines fitted with OCs, over the CBD driving cycle. The results showed that fuel composition influenced the formation of exhaust emissions from the older lean burn buses. Gases with low methane contents showed higher NO<sub>x</sub> and NMHC emissions and improved fuel economy on a volumetric basis, but lower emissions of THC, CH<sub>4</sub>, and formaldehyde emissions. The trends for the other emissions were not as consistent. The newest technology bus with the stoichiometric combustion engine and the TWC did not show any specific fuel effects.

The results show that NG fuel composition can have an impact on emissions for older technology heavy-duty vehicles even for gases within pipeline specifications, albeit at the extreme ranges of what might be found in the pipeline. This suggests that control of the NG specifications is still needed for older technology heavy-duty NGVs. It appears that newer

technology heavy-duty natural gas engines can run on a wider range of NG fuels with varying composition without impacting emissions. Further study of the impact of NG composition for post-2007 engines is also planned for other applications, such as refuse trucks. Further studies also should be performed related to newer technology stoichiometric fueled NG engines and their associated  $\text{NH}_3$  emissions to better understand the  $\text{NH}_3$  formation mechanism and its possible contribution to secondary PM formation.

The chapter six of this study evaluates the differences between California and Federal diesel fuels with heavy-duty engine and chassis dynamometer tests. The engine dynamometer results showed that  $\text{NO}_x$  emissions for the federal fuels ranged from 4.7 to 9.5% higher than the CARB diesel. These  $\text{NO}_x$  reductions are similar to the estimates being used in the latest regulations. The chassis dynamometer test results did not show as consistent trends for  $\text{NO}_x$  as those seen for the engine dynamometer testing. For the chassis dynamometer testing, 4 of 10 vehicles showed consistent reductions in  $\text{NO}_x$ , with emissions for the federal fuels ranging from 3.3 to 9.9% higher than the CARB diesel, while the other 6 vehicles did not show any consistent fuel impacts. On an absolute level, the  $\text{NO}_x$  benefit for CARB diesel shows a decline with continuing advances in engine technology. The results also showed that CARB diesel did not show strong benefits for PM. The results also showed that the introduction of aftertreatment systems for PM and  $\text{NO}_x$  will, over time, largely eliminate any potential benefits that might be obtained through the use of CARB diesel, although  $\text{NO}_x$  benefits will persist through 2020.

## Appendix A

Table A-1. Neat fuel and blends selected specifications

	Units	Test Method	S5	S20	S50	S100	A5	A20	A50	A100	CARB	R20	R50	R100
Physical Distillation, T90	°C-max	D86	624.1	635.1	641.1		627.5	633.6	637.4					
Cetane Number	min	D613	56	55.4	56	47.7	58.4	59.8	59.7	57.9	55.8	59.3	65.0	72.3
Derived Cetane #	Index	IQT*												74.7
Free Glycerin		D6854				0.001%				0.008%				
Total glycerin		D6874				0.080%				0.069%				
Distillation, T90 AET		D1160				350				347.5				
API Gravity		D1298/D287				29				28.5	39.3	41.7	45.1	51.3
Sp.Gr	@ 60°F	D4052s										0.82	0.80	
FAME Content (IR)		EN 14078	5.3	20.8	52.5		5.4	21.2	52.8					
Oxidation Stability	Hours -min	EN14112	12	12	12	6.7	12	12	12	3.9				
Total Aromatic Content	Mass-%	D5186-96									18.7	15.2	10.2	0.4
PAH	Mass-%	D5186-96									1.5	1.2	0.9	0.1
Nitrogen Content	Mass-ppm	D4629-96									0.8	<1.0	<1.0	1.3
Viscosity	@ 40 °C	D445	2.828	2.969	3.384	4.2	2.855	3.038	3.508	4.41	2.7	2.7	2.8	2.5
Flash Point	°C-min	D93	67.2	67.2	78.9	76.3	66.1	67.2	89.4	73.5	64.4	67.4	63.2	63.3
Cloud Point	°C	D2500	-16	-15	-1	0	-15	-14	2	12.5	-6.6	-15	-18	-27.1

\*Ignition Quality Test \*\*Free of un-dissolved water, sediment and suspended matter

Table A-2.. Test engines specification

<b>Engine Manufacturer</b>	<b>Cummins, Inc.</b>	<b>Detroit Diesel Corp.</b>
<b>Engine Model</b>	ISM 370	MBE4000
<b>Model Year</b>	2006	2007
<b>Engine Family Name</b>	6CEXH0661MAT	7DDXH12.8DJA
<b>Displacement (liter)</b>	10.8	12.8
<b>Power Rating (hp)</b>	385 @ 1800 rpm	Varies, 350-450 hp @ 1900 rpm
<b>After-treatment</b>	EGR	EGR & DPF

Table A-3. Engine 1-2006 Cummins ISM test matrix

A = Lght. UDDS B = FTP C1 = ARB 40 mph Cruise C = ARB 50 mph Cruise

**Engine 1-2006 cummins ISM**

**Soy based biodiesel**

Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
CARB	A	B20	B	B50	A	CARB	A	B100	A	CARB	A	B100	C1
	C1		A		B		B		C1		B		C1
	B		C1		A		C1		B		C1		B
B20	C1	B50	B	CARB	C1	B100	A	CARB	B	B20	A	CARB	C1
	B		A		B		B20		C1		B		C1
	A		A		C1		C1		A		A		B
Day 16	Day 17	Day 18	Day 19	Day 20	Day 21								
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
CARB	C	CARB	A	CARB	A	CARB	C	B50	A				
	A		C		B		C		B				
	B		C		C		C		A				
B20	A	B50	A	B100	A	B5	C	B20	C	B100	C		
	C		C		C		C		C		C		
B20	B	B50	B	B100	C	B5	C		C		C		
	A		A		C		C		C		C		
	C		C		C		C		C		C		
CARB	C	CARB	A	CARB	B		C		C		C		
	B		C		C		C		C		C		
	A		A		C		C		C		C		

A = Lght. UDDS B = FTP C1 = ARB 40 mph Cruise C = ARB 50 mph Cruise

**Engine 1-2006 cummins ISM**

**Animal based BDSL**

Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
CARB	A	B50	A	B100	A	B100	B5
	C		B		C		
	B		C		A		
B20	A	CARB	B	B20	B	CARB	CARB
	C		C		A		
B20	C	CARB	B	B20	A	CARB	
	A		A		B		
	B		C		C		
B50	A	B100	A	B50	B		
	B		C		C		
	C		B		A		

**Renewable Diesel**

Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel
CARB	A	R50	C	CARB	B	R100
	B		A		C	
	C		B		A	
R20	C	CARB	A	R50	C	CARB
	A		A		B	
	B		B		A	
R20	C	CARB	A	R50	C	
	A		A		B	
	B		B		A	
	C		C		C	
R50	B	R100	C	R100	R20	
	C		C		C	
	A		B		A	

**GTL Diesel**

Day 1	Day 2	Day 3
Fuel	Cycle	Fuel
CARB	B	G50
	B	
	B	
G20	B	CARB
	B	
	B	
G20	B	
	B	
	B	
G50	B	G100
	B	
	B	

Table A-4. Engine 2-2007 MBE4000 test matrix

A = light UDDS B = FTP C = 50 mph Cruise

**Soy-based biodiesel**

Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8		Day 9	
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
CARB	A	B50	A	CARB	C	B20	B	CARB	C	B100	B	CARB	B	CARB	B	CARB	B
	C		B		A		A		A		A		C		B		B
	B		C		B		C		B		C		A		B		B
B20	C	CARB	C	B100	B	A	A	B50	B	B	B	B20	C	B5	B		B
	A		B		A		B		C		C		B		B		
	B		A		C		C		A		A		A		B		
	C		B		C		A		C		CARB		A		B		
	A		C		A		C		B		C		A		B		
	B		A		B		B		A		B		B		B		

**Animal-based biodiesel**

Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8		Day 9	
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
CARB	B	B50	C	CARB	C	B20	C	CARB	A	B100	A	CARB	B	CARB	B	CARB	B
	C		B		A		A		C		B		C		B		B
	A		A		B		B		B		C		A		B		B
B20	C	CARB	A	B100	B	A	A	B50	C	B	B	B20	A	B5	B		B
	A		C		C		B		A		C		B		B		
	B		B		A		A		B		A		C		B		
	B		A		A		C		C		CARB		B		B		
	A		C		C		B		A		A		A		B		
	C		B		B		A		B		C		C		B		

**NOx Mitigation**

Day 1		Day 2	
Fuel	Cycle	Fuel	Cycle
ARB	B	Blend 2	B
	B		B
	B		B
Blend 1	B		B
	B		B
	B		B
	B		B
	B	CARB	B

Table A-5. Results of bootstrapping statistical analysis

Effect of feedstock			
2007 MB4000	FTP	B20	0.035
		B50	0.001
		B100	0.000
	UDDS	B20	0.000
		B50	0.000
		B100	0.000
	50-mph Cruise	B20	0.047
		B50	0.014
		B100	0.000
2006 Cummins ISM	FTP	B20	0.000
		B50	0.000
		B100	0.000
	UDDS	B20	0.000
		B50	0.000
		B100	0.000
Effect of Engine Technology			
Soy-based	FTP	B20	0.107
		B50	0.013
		B100	0.000
	UDDS	B20	0.499
		B50	0.001
		B100	0.000
Animal-based	FTP	B20	0.477
		B50	0.021
		B100	0.000
	UDDS	B20	0.487
		B50	0.014
		B100	0.000

Table A-6. List of results of heavy-duty transient engine dynamometer tests for the “clean” diesel base fuels

Data Label	Feedstock	Base Fuel Type	Blend Level	Engine	Duty Cycle	Test Cycle	Number of replicates	NO <sub>x</sub> base fuel	Blend NO <sub>x</sub>	% Δ
McCormick,2005 (Tallow-1) <sup>33</sup>	A	BP15	20	2002 ISM Cummins 6L	H-D	FTP	3 hot starts or more	2.063	2.120	2.8%
McCormick, 2005 (Tallow-2)	A	BP15	20	2003 DDC 60 14L	H-D	FTP	3 hot starts	2.110	2.180	3.3%
McCormick, 2005 (YG-1)	A	BP15	20	2003 DDC s 60 14L	H-D	FTP	3 hot starts	2.113	2.100	- 0.6%
McCormick, 2005 (YG-2)	A	BP15	20	2002 ISM Cummins 6L	H-D	FTP	3 hot starts or more	2.063	2.120	2.8%
McCormick,2002 <sup>43</sup>	A	CARB-like	20	1991 DDC series 60	H-D	FTP	3	4.478	4.586	2.4%
McCormick, 2005 (Canola-1)	C	BP15	20	2002 ISM Cummins 6L	H-D	FTP	3 hot starts or more	2.063	2.110	2.3%
McCormick,2005 (Soy-1)	S	BP15	20	2003 DDC 60 14L	H-D	FTP	3 hot starts	2.113	2.240	6.0%
McCormick, 2005 (Soy-2)	S	BP15	20	2002 ISM Cummins 6L	H-D	FTP	3 hot starts or more	2.060	2.220	7.8%
Clark, 1999 <sup>206</sup>	S	CARB-like	20	1994 Navistar T444E	H-D	FTP	3 hot	5.552	5.645	1.7%
Nuzkowski, 2009 <sup>90</sup>	S	CARB-like	20	1992 DDC series 60	H-D	FTP	3 starts	6.880	6.900	0.3%
Nuzkowski, 2009	S	CARB-like	20	1999 Cummins ISM 370	H-D	FTP	3 starts	5.410	5.530	2.2%
Nuzkowski, 2009	S	CARB-like	20	2004 Cummins ISM 370	H-D	FTP	3 starts	3.150	3.320	5.4%
Eckerle <sup>36</sup>	S	CARB-like	20	Cummins ISB	H-D	FTP	3	2.220	2.300	3.6%
McCormick, 2002	S	CARB-like	20	1991 DDC series 60	H-D	FTP	3	4.478	4.606	2.9%

Thompson <sup>123</sup>	S	CARB-like	20	1992 DDC series 60	H-D	FTP	2 starts	5.860	6.170	5.3%
Thompson	S	CARB-like	20	1992 DDC series 60	H-D	ESC	2 starts	10.051	10.592	5.4%
Nikanjam	S	CARB	20	1991 DDC series 60	H-D	FTP	2	4.596	4.691	2.1%
Nikanjam	S	CARB	20	1991 DDC series 60	H-D	ESC	2	7.532	7.714	2.4%
Starr <sup>219</sup>	S	CARB-like	20	1991-1993 DDC series 60	H-D	FTP	3 hot starts	4.18	4.57	9.3%
Thompson	S	CARB-like	10	1992 DDC series 60	H-D	FTP	2 starts	5.860	6.030	2.9%
Thompson	S	CARB-like	10	1992 DDC series 60	H-D	ESC	2 starts	10.051	10.304	2.5%
Nikanjam <sup>124</sup>	S	CARB	5	1991 DDC series 60	H-D	FTP	2	4.596	4.514	- 1.8%
Nikanjam	S	CARB	5	1991 DDC series 60	H-D	ESC	2	7.532	7.528	- 0.1%

Note: YG: Yellow Grease; A: Animal-based; C: Canola; S: Soy-based; H-D: Heavy-Duty

## Appendix B

Table B-1. Properties of CARB reference fuel

Property	ASTM Test Method	Units	Specification		Batch 1 Results	Batch 2 Results
Distillation, IBP	D 86	°F	340	420	354	359
5%					404	400
10%			400	490	416	414
20%					440	438
30%					464	460
40%					483	478
50%			470	560	497	493
60%					509	508
70%					523	524
80%					541	543
90%			550	610	565	568
95%					587	588
Distillation ep			580	660	608	605
Recovery		vol%			98.0	98.3
Residue					1.3	1.3
Loss					0.7	0.4
Gravity	ASTM D4052	API	33	39	37.2	38
Specific Gravity	ASTM D4052		0.83	0.86	0.839	0.836
Cloud Point	ASTM D2500	°F			-26	-22
Flash Point	ASTM D93	°F	130		172	172
Viscosity, 40 °C	ASTM D445	cSt	2.0	4.1	2.5	2.5
Sulfur	ASTM D5453	ppm wt		15	4.7	None Detected
Nitrogen	ASTM D4629	ppm		10	None Detected	None Detected
Total Aromatics	ASTM D5186	vol%		10	9	9
Polycyclic Aromatics	ASTM D5186	vol%		1.4	None Detected	0.3
Cetane number	ASTM D613		48		53.1	48.4
High Frequency Recip. Rig	ASTM D6079	microns		520	290	210
Carbon	ASTM D5291	wt%			85.80	85.80
Hydrogen	ASTM D5291	wt%			13.61	13.61
Heating Value	ASTM D240	BTU/lb			19689	19689
Carbon Unit per Energy		Carbon lbs. /BTU			4.36x10 <sup>-5</sup>	4.36x10 <sup>-5</sup>

Table B-2 Properties of biodiesel fuels

Property	ASTM Test Method	Units	Specification	Animal	WVO	Soy
Flash Point	ASTM D93	°C	130 min.	144.0	>150*	159
Water and Sediment	ASTM D2709	% Vol.	0.05 max.	<0.005	0.000	0.000
Kinematic Viscosity, 40°C	ASTM D445	mm <sup>2</sup> /s	1.9 – 6.0	4.691	4.2*	4.220*
Sulfated Ash	ASTM D874	% mass	0.02	<0.005	<0.01*	<0.01*
Sulfur	ASTM D5453	Ppm	15 max.	6.5	11.1	1.1
Copper Strip Corrosion	ASTM D130		No. 3 max.	1b	1a*	1a*
Cetane Number	ASTM D613		47 min.	61.1	54.6	49.2
Cloud Point	ASTM D2500	°C	Report	15	4	0
Carbon Residue	ASTM D4530	% mass	0.05 max.	<0.05	<0.02*	<0.02*
Acid Number	ASTM D664	Mg KOH/g	0.5 max.	0.42	0.29	0.26
Free Glycerin	ASTM D6584	% mass	0.02 max.	<0.005	0.000	0.003
Total Glycerin	ASTM D6584	% mass	0.240 max.	0.109	0.197	0.106
Monoglycerides	ASTM D6584	% mass	Report	0.417	0.634	0.342
Diglycerides	ASTM D6584	% mass	Report	0.051	0.154	0.124
Triglycerides	ASTM D6584	% mass	0.050 max.	<0.05	0.093	0.000
Visual inspection	ASTM D4176	1-6	2 max.	1	1	1
Phosphorous content	ASTM D4951	% mass	0.001 max.	<0.0001	<.0001*	<0.0001*
Distillation at 90% Recovered	ASTM D1160	°C	360 max.	352	325*	341*
Sodium/Potassium, combined	EN14538	ppm (µg/g)	5 max.	<1.0	<5.0*	<5.0*
Calcium/Magnesium, combined	EN14538	ppm (µg/g)	5 max.	<1.0	<2.0*	<2.0*
Oxidation Stability	EN15751	Hours	3 min.	13.0	6.1	4
Cold Soak Filtration	ASTM D7501	Seconds	360 max.	135	301	72
Moisture	ASTM D6304	%mass		0.024	370	190
Methanol Content	EN14110	%mass	0.2 max.		0.00	
Heating value	ASTM D240	BTU/lb		17133	17076	17140
API Gravity@60°F	ASTM D4052			30.20	28.40	28.43
Specific Gravity @60°F	ASTM D4052			0.8750	0.8851	0.8848

Carbon	ASTM D5291	wt%		76.19	76.67	77.10
Hydrogen	ASTM D5291	wt%		12.28	11.98	11.85
Carbon Unit per Energy		Lbs. Carbon/BTU		$4.45 \times 10^{-5}$	$4.49 \times 10^{-5}$	$4.50 \times 10^{-5}$

Table B-3. Test engine specifications

Engine Manufacturer	Cummins, Inc.
Engine Model	ISM 370
Model Year	2006
Engine Family Name	6CEXH0661MAT
Engine Type	In-line 6 cylinder, 4 stroke
Displacement (liter)	10.8
Power Rating (hp)	370 @ 2100 rpm
Fuel Type	Diesel
Induction/exhaust	Turbocharger with charge air cooler with EGR

Table B-4. Testing protocol for certification procedure

Day	Fuel Test Sequence
1	RC CR RC CR
2	RC CR RC CR
3	RC CR RC CR
4	RC CR RC CR
5	RC CR RC CR

## Statistical calculations for B20 with additive certification testing

The certification pass/fail criteria is determined as per 13 CCR 2282(g)(5). The criteria is evaluated for NO<sub>x</sub> and PM emissions. The statistical criteria includes a tolerance of 1% and 2%, respectively, for NO<sub>x</sub> and PM emissions. The tolerance is reduced by pooled variance term that increases with the variability in the data.

[illegible]

### Statistical calculations for B5 certification testing

The certification pass/fail criteria is determined as per 13 CCR 2282(g)(5). The criteria is evaluated for NO<sub>x</sub>, PM, and SOF emissions. The statistical criteria includes a tolerance of 1%, 2%, and 6%, respectively, for NO<sub>x</sub>, PM, and SOF emissions. The tolerance is reduced by pooled variance term that increases with the variability in the data.

B5 Animal-based, NO <sub>x</sub>									
	R	C	C	R	R	C	C	R	
Day 1					2.044	2.054	2.059	2.040	
Day 2	2.044	2.035	2.024	2.036	2.033	2.023	2.022	2.046	
Day 3	2.051	2.028	2.019	2.049					
Day 4	2.046	2.030	2.047	2.044	2.043	2.036	2.032	2.043	
Day 5	2.031	2.014	2.049	2.056	2.051	2.035	2.022	2.044	
Day 6	2.037	2.039	2.031	2.033	2.046	2.030	2.056	2.069	
n	t	x <sub>R</sub>	x <sub>c</sub>	(x <sub>c</sub> -x <sub>R</sub> )/x <sub>R</sub>	S <sub>R</sub>	S <sub>c</sub>	S <sub>p</sub>	S <sub>p</sub> (2/n) <sup>0.5</sup> t/x <sub>R</sub>	
20	1.0507721	2.044	2.034	-0.4916%	0.0087	0.0129	0.0110	0.1787%	-0.3129%
									CANDIDATE FUEL PASSES
B5 Animal-based, PM									
	R	C	C	R	R	C	C	R	
Day 1					0.068	0.064	0.064	0.069	
Day 2	0.067	0.062	0.066	0.067	0.067	0.064	0.065	0.067	0.067
Day 3	0.065	0.065	0.063	0.067					0.065
Day 4	0.064	0.064	0.064	0.068	0.068	0.065	0.065	0.071	0.064
Day 5	0.067	0.064	0.067	0.067	0.070	0.065	0.064	0.069	0.067
Day 6	0.066	0.064	0.064	0.067	0.067	0.064	0.065	0.068	0.066
n	t	x <sub>R</sub>	x <sub>c</sub>	(x <sub>c</sub> -x <sub>R</sub> )/x <sub>R</sub>	S <sub>R</sub>	S <sub>c</sub>	S <sub>p</sub>	S <sub>p</sub> (2/n) <sup>0.5</sup> t/x <sub>R</sub>	
20	1.0507721	0.067	0.065	-4.1997%	0.0014	0.0010	0.0012	0.6021%	-3.5977%

									CANDIDATE FUEL PASSES
B5 Animal-based, SOF									
	R	C	C	R	R	C	C	R	
Day 1					0.0110	0.0126	0.0088	0.0124	
Day 2	0.0091	0.0088	0.0081	0.0100	0.0128	0.0108	0.0089	0.0139	
Day 3	0.0101	0.0075	0.0089	0.0078					
Day 4	0.0159	0.0089	0.0080	0.0115	0.0077	0.0113	0.0134	0.0084	
Day 5	0.0075	0.0095	0.0090	0.0103	0.0084	0.0070	0.0061	0.0102	
Day 6	0.0106	0.0105	0.0090	0.0085	0.0120	0.0078	0.0061	0.0116	
n	t	x <sub>R</sub>	x <sub>c</sub>	(x <sub>c</sub> -x <sub>R</sub> )/x <sub>R</sub>	S <sub>R</sub>	S <sub>c</sub>	S <sub>p</sub>	S <sub>p</sub> (2/n) <sup>0.5</sup> t/x <sub>R</sub>	
20	1.0507721	0.010	0.009	-13.5901%	0.0022	0.0019	0.0021	6.5797%	-7.0104%
									CANDIDATE FUEL PASSES
B5 WVO, NO <sub>x</sub>									
	R	C	C	R	R	C	C	R	
Day 1	2.056	2.070	2.071	2.062	2.058	2.065	2.070	2.018	
Day 2	2.053	2.062	2.067	2.053	2.043	2.084	2.093	2.074	
Day 3	2.036	2.046	2.065	2.056	2.052	2.081	2.108	2.079	
Day 4	2.063	2.045	2.111	2.036	2.029	2.068	2.061	2.049	
Day 5	2.044	2.065	2.048	2.047	2.049	2.085	2.079	2.073	
Day 6	2.064	2.096	2.091	2.083	2.053	2.093	2.080	2.076	
n	t	x <sub>R</sub>	x <sub>c</sub>	(x <sub>c</sub> -x <sub>R</sub> )/x <sub>R</sub>	S <sub>R</sub>	S <sub>c</sub>	S <sub>p</sub>	S <sub>p</sub> (2/n) <sup>0.5</sup> t/x <sub>R</sub>	
24	1.04825	2.054	2.075	1.0100%	0.0160	0.0178	0.0169	0.2493%	1.2593%
									CANDIDATE FUEL FAILS
B5 WVO, PM									

	R	C	C	R	R	C	C	R	
Day 1	0.065	0.064	0.064	0.068	0.067	0.064	0.065	0.070	
Day 2	0.066	0.062	0.063	0.068	0.068	0.065	0.065	0.069	
Day 3	0.066	0.062	0.062	0.066	0.069	0.064	0.068	0.068	
Day 4	0.083	0.061	0.061	0.067	0.068	0.062	0.063	0.068	
Day 5	0.065	0.062	0.060	0.066	0.067	0.062	0.062	0.067	
Day 6	0.064	0.062	0.060	0.067	0.066	0.062	0.062	0.067	
n	t	$x_R$	$x_c$	$(x_c - x_R)/x_R$	$S_R$	$S_c$	$S_p$	$S_p(2/n)^{0.5}t/x_R$	
24	1.0482501	0.068	0.063	-6.9951%	0.0036	0.0018	0.0029	1.2801%	-5.7150%
									CANDIDATE FUEL PASSES

## Appendix C

Table C-1. Specifications for the engine dynamometer test engines

<b>Engine Manufacturer</b>	Detroit Diesel Corp.	Cummins, Inc.	Detroit Diesel Corp.
<b>Engine Model</b>	MBE4000	ISM 370	Series 60
<b>Model Year</b>	2007	2006	1991
<b>Engine Family Name</b>	7DDXH12.8DJA	6CEXH0661MAT	MDD11.1FZA2
<b>Displacement (liter)</b>	12.8	10.8	11.1
<b>Power Rating (hp)</b>	410 hp @ 1900 rpm	385 @ 1800 rpm	360 @ 1800 rpm
<b>EGR</b>	Yes	Yes	No
<b>After-Treatment</b>	DOC/DPF	None	None

Table C-2. Test vehicle/engine specifications

<b>Engine Manufacturer</b>	Caterpillar	Detroit Diesel	Detroit Diesel	Caterpillar	Detroit	Caterpillar	Cummins, Inc.	-Detroit Diesel	Cummins, Inc.	Navistar
<b>Engine Model</b>	3176	DDC Series 60	S60	C-15	DDC Series 60	C-15	ISM 370	MBE4000	ISX 485	“MAXXFORCE”13
<b>Model Year</b>	1994	1998	1999	2000	2000	2005	2006	2007	2008	2009
<b>Test Weight</b>	50000	61250	62154	58744	68460	58600	57300	61250	60260	61200
<b>Chassis Model</b>	1994 Freightliner	1998 Sterling	1999 Freightliner	2001 Freightliner	2001 Freightliner	2006 Peterbilt	2006 International 9200i	2008 Freightliner	2008 Peterbilt	2011 Transtar
<b>Engine Family Name</b>	RCP629EZDARA	WDDXH12.7EGD	XPOXH12.7 EGL	XH0893ERK	YDDXH12.7 EGL	5CPXH0928EBK	6CEXH0661MAT	7DDXH12.8DJA	8CEXH0912XAL	Maxforce
<b>Odometer Mileage</b>	53,460	84,229	103,429	32,407	705,222	133,049	92,624	9,524	67,727	3,339
<b>EGR</b>	No	No	No	No	No	Yes	Yes	Yes	Yes	Yes
<b>Displacement (liter)</b>	10.3	12.7	12.7	14.6	12.7	15.2	10.8	12.8		12.4
<b>Power Rating (hp)</b>	325 hp @ 1800	470 (peak)	470 hp @ 2100	475 hp @ 2100	470 hp @ 2100	475 hp @ 1800	385 @ 1800 rpm	420 hp @ 1750 rpm	485 (peak) 1650 (continuous)	430 hp(peak)
<b>After-Treatment</b>		Johnson Matthey SCRT			Cleaire Long View			OEM DPF	OEM DPF	OEM DPF
<b>Fuel Tested First</b>	Fed A	Fed B	Fed A	Fed A	Fed B	Fed B	Fed A	Fed B	Fed B	Fed A

\*\* Note odometer mileage is based on the mileage as read from the odometer – the actual mileage accumulated on the vehicle/engine may differ due to odometer roll over, rebuilding of the engine, or other circumstances.

Table C-3. Engine dynamometer test matrix for each test engine

Test Day				
Heavy-Duty FTP Test Cycle				
Day 1	CCC	AAA	AAA	BBB
Day 2	BBB	CCC		
CARB HHDDT Cruise Test Cycle				
Day 2			CCC	AAA
Day 3	AAA	BBB	BBB	CCC

C = CARB diesel fuel, A = Federal A diesel fuel, B = Federal B diesel fuel

Table C-4. Chassis dynamometer test matrix for each test vehicle

Test Day	Morning Schedule (assumes 6 replicates)	Afternoon Schedule (assumes 6 replicates)
<b>ARB HHDDT Cruise Test Cycle</b>		
Day 1	CCC AAA	AAA CCC
Day 2	CCC BBB	BBB CCC
Day 3	AAA CCC	CCC BBB

C = CARB diesel, A = Federal A diesel, B = Federal B diesel

For further randomization of the test matrix, the sequence used in testing fuels A and B was reversed for different vehicles within the same or similar technology categories. This helped to ensure that any impacts of testing on Federal A fuel right before the Federal B fuel would be minimized.

Table C-5. Percentages changes for Federal Diesel blends relative to CARB and associated statistical p-values for three tested engines

		THC				CO				NO <sub>x</sub>				PM				CO <sub>2</sub>				BSFC			
		Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P
MBE4000																									
FTP	CARB	0.006	0.002			0.093	0.008			1.275	0.004			-0.00018	0.0003			591.62	1.97			0.059	0.0002		
	FED B	0.007	0.001	27%	0.135	0.141	0.011	51%	0.000	1.368	0.011	7.3%	0.000	-0.00009	0.0007	53%	0.752	600.145	1.22	1.4%	0.000	0.058	0.0001	-0.9%	0.000
Cruise	CARB	0.004	0.001			0.021	0.004			1.137	0.019			0.00011	0.0001			520.339	3.98			0.052	0.0004		
	FED B	0.003	0.000	-14%	0.270	0.027	0.004	31%	0.024	1.190	0.011	4.7%	0.000	0.00022	0.0002	109%	0.297	530.551	2.53	2.0%	0.000	0.051	0.0002	-0.4%	0.255
2006 Cummins																									
FTP	CARB	0.143	0.004			0.809	0.011			2.096	0.010			0.070	0.001			628.574	2.00			0.063	0.0002		
	FED A	0.142	0.002	-1%	0.633	0.945	0.014	17%	0.000	2.236	0.014	6.7%	0.000	0.073	0.001	5%	0.000	636.977	1.65	1.3%	0.000	0.062	0.0002	-0.1%	0.667
	FED B	0.160	0.002	12%	0.000	0.991	0.011	23%	0.000	2.263	0.029	7.9%	0.000	0.076	0.001	8%	0.000	636.855	3.15	1.3%	0.000	0.062	0.0003	-1.0%	0.002
Cruise	CARB	0.077	0.001			0.534	0.019			1.643	0.079			0.053	0.002			549.941	3.19			0.055	0.0003		
	FED A	0.067	0.002	-13%	0.000	0.559	0.017	5%	0.041	1.799	0.020	9.5%	0.001	0.052	0.001	0%	0.831	555.102	1.26	0.9%	0.004	0.054	0.0001	-0.5%	0.080
	FED B	0.077	0.003	0%	0.904	0.585	0.023	9%	0.002	1.775	0.086	8.1%	0.020	0.054	0.003	3%	0.278	561.112	3.96	2.0%	0.000	0.054	0.0004	-0.4%	0.348
1991 DDC 60																									
FTP	CARB	0.044	0.002			1.742	0.061			4.572	0.032			0.074	0.004			558.584	5.11			0.0557	0.0005		
	FED A	0.050	0.001	14%	0.000	1.901	0.010	9%	0.000	4.913	0.027	7.5%	0.000	0.076	0.001	2%	0.425	568.080	3.25	1.7%	0.003	0.0559	0.0003	0.3%	0.524
	FED B	0.057	0.001	30%	0.000	1.955	0.033	12%	0.000	4.997	0.012	9.3%	0.000	0.076	0.002	3%	0.341	565.055	1.36	1.2%	0.013	0.055	0.0001	-1.2%	0.014
Cruise	CARB	0.023	0.001			1.247	0.040			6.470	0.045			0.040	0.002			489.017	1.01			0.049	0.0001		
	FED A	0.023	0.001	1%		1.303	0.015	5%	0.009	6.810	0.017	5.3%	0.000	0.043	0.001	7%	0.011	495.740	0.51	1.4%	0.000	0.049	0.0000	-0.1%	0.589
	FED B	0.027	0.001	14%	0.000	1.287	0.027	3%	0.070	6.945	0.030	7.3%	0.000	0.041	0.001	2%	0.330	497.295	0.92	1.7%	0.000	0.048	0.0001	-0.7%	0.000

Ave. = Average, SD= Standard Deviation, %=Percentage Difference, P= P-value

Table C-6. Percentages changes for Federal Diesel blends relative to CARB and associated statistical p-values for ten tested vehicles

	THC				CO				NO <sub>x</sub>				PM				CO <sub>2</sub>				MPG			
	Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P	Ave.	SD	%	P
<b>CAT-1994</b>																								
<b>CARB</b>	0.122	0.007			3.068	0.464			23.27	1.096			0.073	0.008			1635.55	29.25			6.15	0.111		
<b>FED A</b>	0.108	0.005	-11%	0.001	3.269	0.288	7%	0.357	23.44	1.339	0.7%	0.792	0.078	0.013	6%	0.418	1654.95	31.88	1.2%	0.234	6.16	0.120	0.2%	0.805
<b>FED B</b>	0.117	0.005	-4%	0.292	3.385	0.288	10%	0.294	23.61	0.134	1.4%	0.619	0.082	0.008	12%	0.141	1666.60	11.77	1.9%	0.108	6.17	0.042	0.5%	0.681
<b>DDC-1998</b>																								
<b>CARB</b>	-0.002	0.003			0.495	0.178			5.75	0.743			0.010	0.005			1707.03	43.22			5.91	-0.153		
<b>FED A</b>	-0.003	0.002	9%	0.879	0.607	0.091	23%	0.158	5.74	0.170	-0.3%	0.959	0.007	0.001	-31%	0.121	1697.50	14.03	-0.6%	0.606	6.02	0.050	1.9%	0.089
<b>FED B</b>	-0.002	0.002	-39%	0.461	0.541	0.076	9%	0.486	5.77	0.558	0.3%	0.956	0.011	0.005	10%	0.639	1751.08	33.35	2.6%	0.018	5.90	0.112	-0.2%	0.854
<b>DDC-1999</b>																								
<b>CARB</b>	0.123	0.017			7.709	0.759			23.05	6.022			0.345	0.108			1917.35	32.21			5.22	0.088		
<b>FED A</b>	0.126	0.018	3%	0.644	8.046	1.118	4%	0.358	22.22	4.828	-3.6%	0.712	0.389	0.087	13%	0.283	1982.43	44.04	3.4%	0.000	5.13	0.117	-1.9%	0.020
<b>FED B</b>	0.126	0.010	3%	0.592	8.566	0.664	11%	0.009	21.42	1.058	-7.1%	0.431	0.414	0.029	20%	0.074	1988.03	13.74	3.7%	0.000	5.16	0.036	-1.3%	0.038
<b>CAT-2000</b>																								
<b>CARB</b>	0.135	0.012			1.963	0.129			15.45	0.275			0.130	0.006			1458.41	10.44			6.90	0.050		
<b>FED A</b>	0.124	0.011	-8%	0.031	2.088	0.117	6%	0.022	15.96	0.202	3.3%	0.000	0.136	0.008	4%	0.040	1477.14	18.47	1.3%	0.002	6.91	0.086	0.2%	0.681
<b>FED B</b>	0.138	0.009	2%	0.454	2.052	0.074	5%	0.089	16.26	0.116	5.3%	0.000	0.135	0.006	3%	0.122	1485.53	27.45	1.9%	0.001	6.94	0.125	0.6%	0.262
<b>DDC-2000</b>																								
<b>CARB</b>	0.032	0.025			0.293	0.166			9.55	0.277			0.007	0.002			1493.58	26.52			6.75	0.118		
<b>FED A</b>	0.038	0.028	21%	0.550	0.243	0.142	-17%	0.460	10.07	0.287	5.4%	0.000	0.008	0.003	20%	0.215	1492.53	17.48	-0.1%	0.920	6.85	0.081	1.5%	0.039
<b>FED B</b>	0.048	0.025	51%	0.139	0.289	0.242	-1%	0.961	10.45	0.278	9.4%	0.000	0.006	0.002	-13%	0.336	1522.24	20.19	1.9%	0.012	6.78	0.089	0.5%	0.503
<b>CAT-2005</b>																								
<b>CARB</b>	0.047	0.013			0.714	0.264			11.60	0.560			0.285	0.056			1859.50	23.72			5.42	0.069		
<b>FED A</b>	0.041	0.011	-12%	0.351	0.694	0.253	-3%	0.855	11.48	0.282	-1.0%	0.577	0.265	0.014	-7%	0.307	1865.22	24.17	0.3%	0.567	5.46	0.064	0.7%	0.196
<b>FED B</b>	0.045	0.023	-4%	0.796	0.905	0.591	27%	0.264	11.76	0.516	1.4%	0.475	0.316	0.051	11%	0.180	1890.86	37.84	1.7%	0.016	5.46	0.108	0.7%	0.268
<b>CUM-2006</b>																								
<b>CARB</b>	0.426	0.017			1.319	0.066			4.45	0.141			0.138	0.011			1493.04	32.70			6.77	0.149		
<b>FED A</b>	0.464	0.007	9%	0.001	1.314	0.044	-0.4%	0.822	4.63	0.180	4.1%	0.006	0.136	0.007	-1%	0.749	1514.72	26.86	1.5%	0.086	6.81	0.066	0.6%	0.610
<b>FED B</b>	0.429	0.014	1%	0.696	1.317	0.048	-0.2%	0.919	4.89	0.214	9.9%	0.000	0.151	0.009	9%	0.006	1559.12	48.89	4.4%	0.000	6.61	0.207	-2.4%	0.054
<b>MBE-2007</b>																								
<b>CARB</b>	-0.002	0.002			0.037	0.013			4.46	0.227			0.001	0.001			1892.97	43.81			5.33	0.122		
<b>FED A</b>	-0.002	0.002	17%	0.766	0.038	0.005	1%	0.920	4.67	0.161	4.8%	0.025	0.002	0.001	14%	0.581	1917.57	33.63	1.3%	0.175	5.33	0.093	0.1%	0.899
<b>FED B</b>	-0.001	0.002	-12%	0.833	0.046	0.017	24%	0.163	4.64	0.140	4.0%	0.052	0.001	0.001	-17%	0.543	1934.39	26.88	2.2%	0.022	5.33	0.076	-0.03%	0.830

CUM-/2008																								
CARB	-0.001	0.012			0.103	0.047			4.92	0.429			0.006	0.002			2133.38	58.63			4.73	0.131		
FED A	0.001	0.008	-261%	0.628	0.060	0.025	-42%	0.011	5.00	0.205	1.5%	0.605	0.006	0.001	0%	0.998	2210.64	42.10	3.6%	0.001	4.63	0.087	-2.1%	0.038
FED B	0.008	0.019	-1080%	0.149	0.065	0.059	-37%	0.073	5.06	0.440	2.8%	0.446	0.005	0.001	-9%	0.464	2136.17	44.41	0.1%	0.901	4.83	0.101	2.3%	0.042
Navi-2009																								
CARB	-0.003	0.003			0.045	0.027			4.71	0.203			0.002	0.003			1959.13	49.83			5.15	0.130		
FED A	-0.001	0.002	-59%	0.132	0.039	0.016	-14%	0.532	4.50	0.225	-4.5%	0.021	0.001	0.001	-26%	0.615	1960.56	30.07	0.1%	0.938	5.22	0.080	1.3%	0.162
FED B	-0.003	0.002	-3%	0.925	0.031	0.026	-31%	0.223	5.12	0.242	8.7%	0.000	0.002	0.001	-7%	0.893	2003.34	71.68	2.3%	0.072	5.16	0.181	0.2%	0.860

Ave. = Average, SD= Standard Deviation, %=Percentage Difference, P= P-value