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On-road emissions evaluation of student-produced biodiesel

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To the Graduate Council:

I am submitting herewith a thesis written by Scott James Curran entitled "On-road emissions evaluation of student-produced biodiesel." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Mechanical Engineering.

David K. Irick, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Dr. Wayne T. Davis

Dr. Ke Nguyen

Dr. Robert M. Wagner

Accepted for the Council:

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On-Road Emissions Evaluation of Student-Produced Biodiesel

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Scott James Curran
May 2009

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ABSTRACT

UT Biodiesel is a small scale, student run Used Frying Oil (UFO) to biodiesel production program at the University of Tennessee, Knoxville. A single batch transesterification reaction using methanol and potassium hydroxide (KOH) as the catalyst is used to produce biodiesel from UFO collected from UT Dining Services. A warm deionized water wash is used to remove contaminants from the biodiesel. A heat and settle method is used to dry the biodiesel. The processor has been shown to be capable of producing fuel that meets the ASTM D6751 specification for biodiesel. The project uses in-house testing to ensure the quality of the fuel. In-house tests include methanol content, water content, total glycerin, and acid number. This study evaluates the on-road emissions of the student-produced biodiesel in a modern diesel vehicle. The test vehicle is powered by a GM 1.9 liter direct injected turbo diesel using cooled EGR. The vehicle is equipped with a diesel oxidation catalyst and a diesel particulate filter. An Autologic five gas analyzer was used to evaluate tailpipe emissions on a prescribed driving cycle. An Autologic heavy duty smoke meter was used to evaluate smoke opacity using a stationary test. Biodiesel blends of B20 and B50 were evaluated against ultra low sulfur diesel fuel (ULSD) and neat biodiesel, B100.

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NOMENCLATURE

AEA	AutoGas Emissions Analyzer
ASTM	American Society for Testing and Materials
BAR	Bureau of Automotive Repair
BEP	Break-Even Point
BPT	Balance Point Temperature
BXX	Biodiesel Blend (XX=% of Biodiesel)
CAN	Controller-Area Network
CARB	California Air Resource Board
CI	Compression Ignition
CLD	Chemiluminescent Detector
CNG	Compressed Natural Gas
CO	Carbon Monoxide
CRT	Continuously Regenerating Trap
DOC	Diesel Oxidation Catalyst
DOHC	Dual Over Head Camshafts
DOE	Department of Energy
DOT	Department Of Transportation
DPF	Diesel Particulate Filter
E85	85% Ethanol 15% Gasoline
EPA	Environmental Protection Agency
EGR	Exhaust Gas Recirculation
FAME	Fatty Acid Methyl Esters

FID	Flame Ionization Detector
GATE	Graduate Automotive Technology and Education
GM	General Motors
HCHO	Formaldehyde
HDPE	High Density Polyethylene
ICPAES	Inductively Coupled Plasma Atomic Emission Spectrometry
KOH	Potassium Hydroxide
LDPE	Low Density Polyethylene
LEV	Low Emission Vehicle
LNT	Lean NO_X Trap
mph	Miles Per Hour
NO_2	Nitrogen Dioxide
NaOH	Sodium Hydroxide
NDIR	Non-Dispersive Infra Red
NDUV	Non-Dispersive Ultra Violet
NiMH	Nickel Metal Hydride
NMOG	Non Methane Organic Gases
NO	Nitric Oxide
NO_X	Oxides of Nitrogen ($NO + NO_2$)
nPAH	Nitrated Polycyclic Aromatic Hydrocarbons
O_2	Oxygen
PAH	Polycyclic Aromatic Hydrocarbons
PEMS	Portable Emissions Measurement Systems

PM	Particulate Matter
PM_{XX}	Particulate Matter (XX = size of PM in micrometers)
ppm	Parts Per Million
SCR	Selective Catalytic Reduction
SI	Spark Ignition
SiC	Silicon Carbide
SOF	Solid Organic Fraction
SUV	Sport Utility Vehicle
TDEC	Tennessee Department of Environment and Conservation
THC	Total Hydrocarbons
UFO	Used Frying Oil
UFOME	Used Frying Oil Methyl Esters
ULEV	Ultra Low Emission Vehicle
ULSD	Ultra Low Sulfur Diesel
VGT	Variable Geometry Turbocharger
VOC	Volatile Organic Compounds

Symbols

σ_{ext}	Extension Coefficient

SECTION I

INTRODUCTION

Background

The UT Biodiesel project is a student run biodiesel production pilot plant that converts used frying oil (UFO) generated by UT Dining Services into biodiesel to be used by UT Facility Services in diesel vehicles and diesel equipment in a B20 blend (20% biodiesel, 80% D-2 diesel fuel). The pilot plant uses an open-sourced single-batch processor that is commonly used in “homebrewing” or microscale biodiesel production. As universities that have a large diesel fleet, and produce waste cooking oil, look to save money on fuel costs, save money on waste cooking oil disposal costs, improve air quality and reduce petroleum use on campus, producing biodiesel from waste cooking oil can appear very attractive. This research explores the emissions benefits from biodiesel produced in a university setting from used frying oil using the Appleseed processor.

The research leading to this thesis is the result of two grants that were awarded the UT Biodiesel Pilot Plant program headed by Dr. David Irick in the Department of Mechanical, Aerospace and Biomedical Engineering at the University of Tennessee. The first grant was administered through the Environmental Semester program through Student Services at UTK under the supervision of Mark Alexander which allowed the startup of the program. The second grant was provided by the Tennessee Department of Environment and Conservation (TDEC) under the Alternative Fuel Innovation grants program. The TDEC grant allowed for the evaluation of the open source processor to produce biodiesel at the university level and to study the on-road emissions benefits of using the fuel in various blends. The processor being evaluated is the “Appleseed Processor” popularized by Maria Alovert (1). The Appleseed processor plans are readily available on the internet (2) or in a self published guide (3). The use of an Appleseed processor and waste cooking oil has become a popular method of microscale biodiesel production for individuals and small co-ops. Recently, schools and businesses have also started looking into the open source plans to meet their microscale biodiesel production needs.

Biodiesel is the common name for mono-alkali methyl esters (methyl esters), an alternative diesel fuel made from plant oil or rendered animal fat that conforms to the standards set forth in ASTM D6751 (4). Biodiesel can also be referred to as Fatty Acid Methyl Esters (FAME) or methyl esters of the feedstock such as Used Frying Oil Methyl Esters (UFOME). Biodiesel is considered non-toxic and biodegradable. Biodiesel can be produced from a variety of chemical processes, the most common being a transesterification reaction using methanol with either sodium hydroxide (NaOH) or potassium hydroxide (KOH) as a catalyst. The fuel is then purified using a “washing” technique which removes the water soluble contaminants from the hydrophilic methyl esters. Biodiesel is most commonly used in blends which are referred to as BXX where the XX stands for the amount of biodiesel mixed in with traditional diesel fuel, for example B20 has 20 percent biodiesel and B100 is neat or pure biodiesel. The use of biodiesel in compression ignition engines does not require any major conversions to the engine or fueling system other then ensuring materials compatibility of those components that come into contact with the fuel.

Biodiesel is produced from renewable resources and can be produced from feedstocks grown in the United States. Biodiesel helps reduce the use of petroleum by directly replacing petroleum fuel in blends. Biodiesel reduces harmful emissions including those which are discussed fully in Section 3. Biodiesel is seeing increased use in personal diesel vehicles as well as in fleets. According to the National Biodiesel Board, the U.S. produced 450 million gallons of biodiesel from October 2006 to the end of September 2007 (5), which was less than one percent of the total ULSD consumed in the U.S. in the same period (6).

A number of factors including rising fuel prices, concerns about the environment, regional air quality, limited oil reserves and concerns about dependency on foreign oil have caused individuals, business, institutes of higher learning and other organizations to look at using biodiesel and even producing biodiesel themselves from local feedstocks or used frying oil. The single base transesterification reaction is a relatively simple reaction to carry out and can give the illusion that it is easy to make biodiesel. Biodiesel is defined as a fuel conforming to the ASTM D6751 standard which requires careful attention to the quality of the feedstock, the process, as well as storage and handling. A problem for microscale biodiesel production is the expense of ASTM D6751 testing which can range from $600 to well over $1000 per batch tested.

Internet sources for biodiesel recipes and plans for biodiesel processors along with a likeminded community looking to make their own fuel have caused homebrewing or microscale processing to rise in popularity. Waste cooking oil can be an appealing feedstock for both microscale producers as well as commercial producers. UFO is normally a waste product for restaurants and food producers that must be discarded at a cost. Used frying oil is an attractive feedstock since it is a waste product, can be obtained for free or inexpensively in certain areas and is normally easier to find than virgin oils.

Purpose

This study is the culminating test of the student-produced fuel from the UT Biodiesel project. One of the primary reasons to use biodiesel is that biodiesel blends are known to reduce regulated emissions including CO, NMOG and PM without severely compromising fuel economy or power. Many studies have shown that NO_X increases with the amount of biodiesel contained in the blend. Studies have shown that B20 blends can have a positive or negative effect on NO_X emissions but for the most part show that NO_X does go up slightly. This study will help further the understanding of the effects of biodiesel blends in modern diesel engines and will also demonstrate how to successfully apply biodiesel in diesel fleets and characterize the emissions advantages of using the alternative fuel in real world driving.

Statement of Problem

Biodiesel that meets ASTM quality standards does not differ greatly in engine performance or emissions regardless of which feedstock is used to produce the fuel. The type of testing used to evaluate the performance and emissions can, however, greatly affect emissions results. On-road emissions testing can provide an accurate evaluation of the emissions benefits of using various blends of biodiesel produced by a student-run project which meets ASTM D 6751 standards. Even though on-road testing loses some of the repeatability from chassis dynamometer testing or engine dynamometer testing, the results are more representative of real-world driving conditions and can provide a local picture of emissions benefit. Of particular interest is the change in NO_X levels in the B20 and B50 blends.

Scope

This study evaluates the tailpipe emissions for EPA regulated compounds except for formaldehyde (HCHO) using a drive cycle that is representative of daily driving in Knoxville, Tennessee. NO_X is evaluated without the application of any de-NO_X technologies. The test vehicle is fitted with a diesel oxidation catalyst and diesel particulate filter so PM, CO and NMOG emissions have been reduced from engine-out emissions. On-road emissions testing are conducted using the advanced diesel electric hybrid SUV from the Challenge X competition over an on-road driving cycle. PM emissions are evaluated indirectly using a stationary smoke opacity test. The engine utilizes a high pressure common rail direct injection with a variable geometry turbocharger and high rates of cooled exhaust gas recirculation (EGR). The exhaust aftertreatments include a diesel oxidation catalyst and a diesel particulate filter. A separate removable fuel tank was installed to ensure purity of the biodiesel blends being tested. An Autologic portable five gas emissions analyzer and an Autologic smoke meter were used to compare the emissions performance of B20, B50 and B100 blends to that of ULSD in the presence of a diesel oxidation catalyst and diesel particulate filter.

SECTION II

BIODIESEL PRODUCTION

Overview

Biodiesel is similar enough to ASTM D-2 diesel fuel that it can be used as a direct fuel substitute. The differences in chemical composition between biodiesel and petroleum derived diesel mean that the emissions profiles of the two fuels will be different. This section provides a brief overview of biodiesel production and fuel quality, as well as an overview of the UT Biodiesel project which produced the fuel used for this study. Understanding how biodiesel is made, what it is, and its properties will help us understand why biodiesel is known as clean burning alternative fuel.

Unlike other alternative fuels such as E85 or the gaseous fuels such as CNG, propane and hydrogen, using biodiesel in a diesel engine requires little to no modification to the engine or fueling system. The US biodiesel specification, ASTM D6751, as well as biodiesel specifications across the world, requires biodiesel to have a viscosity, a cetane value and flashpoint similar to D-2 diesel fuel. The heating value of biodiesel is nearly that of D-2 diesel fuel. This means that biodiesel auto ignites like diesel, flows like diesel, and has nearly the same energy content of diesel, allowing a diesel engine to run on biodiesel without modification.

Biodiesel is a strong solvent and as such a few issues are encountered in using biodiesel for the first time, especially in older diesel vehicles. Biodiesel is not compatible with natural rubber and will attack it readily (7). Compatible materials include stainless steel, Teflon®, Viton®, aluminum, fluorinated plastics and HDPE (8). Biodiesel will readily dissolve the buildup left over from years of running traditional diesel fuel. There are two common problems users experience using biodiesel for the first time. The first problem is clogging a few fuel filters from the dissolved buildup trapped in the filter. After this buildup is removed, the interval between fuel filter changes is prolonged. The second problem is with older vehicles built before approximately 1993, the natural rubber fuel lines should be replaced with a compatible fuel line if higher blends then B20 are used.

The transesterification reaction used to produce biodiesel is well understood (9) (10). Other methods can be used to make biodiesel including pyrolysis, but in this thesis the discussion is limited to the transesterification reaction. Transesterification takes place between a triglyceride and a short chained alcohol. The reaction is slow and reversible which is overcome by the use of excess alcohol and a catalyst.

The ideal amount of excess alcohol has been determined by various studies to be 1.6 times the stochiometric amount (11) which is a 3:1 molar ratio (10). The alcohol of choice for most commercial and microscale producers is methanol. Ethanol can be used to produce ethyl esters, but tends to form emulsions more readily than when using methanol (9). Methanol is also currently less expensive than ethanol (10). Other alcohols have been shown to work as well, but the process is more difficult and expensive (10).

Though both strong acids and strong bases can be used as a catalyst, acid catalysts are much slower and are only recommended for high fatty acid content feedstocks. The most common bases used are potassium hydroxide and sodium hydroxide. Though sodium hydroxide is a stronger base, potassium hydroxide is often the catalyst of choice for smaller producers since it is safer to work with, dissolves faster in methanol, and the products containing potassium can be used as the basic component of fertilizers (11). The amount of catalyst used is dependent on the amount of free fatty acids present in the feedstock. There is a stochiometric amount of catalyst that must be used for the reaction plus more catalyst to neutralize any free fatty acids present in the feedstock.

During transesterification, the triglyceride undergoes a number of successive reactions which take the molecule from a triglyceride to a diglyceride then a monoglyceride and finally to glycerol, producing a methyl ester during each step. The mechanisms and kinetics of this reaction have been reported in various studies (10) (12) (13). The transesterification reaction is represented in Figure 1 with a triglyceride molecule with fatty acid chains of various lengths represented by R_1, R_2, and R_3. The reaction requires heat to allow full conversion of triglycerides into methyl esters in a reasonable amount of time, usually reported as one hour at 60° C (11). This process creates the methyl esters along with soaps and glycerol.

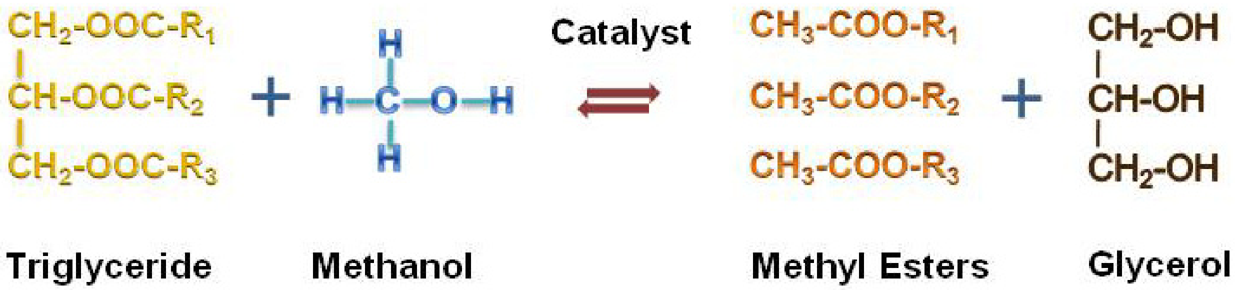


Figure 1. Transesterification Reaction (14)

The final methyl ester mixture contains these soaps, residual methanol and glycerol which all must be removed before the fuel can be safely used. The mixture may also contain trace amounts of un-reacted triglycerides as well as monoglycerides and diglycerides. Removal of these polar (hydrophilic) containments can be accomplished by the use of a water wash or by using a “dry wash” with an adsorbent such a calcium silicate or a resin bed.

Feedstocks

In the United States, biodiesel is primarily made from soybean oil (15) but as noted above, any triglyceride source can be used to produce biodiesel. The National Biodiesel Board (NBB) reports that in 2007, 460 million gallons of biodiesel were produced in America (16). In a recent report to the NBB (17) it was estimated that the feedstock represented around 83 percent of the total production costs which means biodiesel prices are tied ultimately to soybean prices. Other important feedstocks include canola oil, rapeseed oil, mustard seed oil, sunflower oil, corn oil and UFO.

There have been studies on the economics and the feasibility of large scale production of biodiesel from used frying oil (18). Biodiesel derived from UFO is competitive in terms of price and performance with other feedstocks (18) (19). Used frying oil offers a number of advantages over other plant oil based feedstocks including the fact that it is considered a waste product and is often available for lower costs than virgin oils. There are companies that will process used frying oil into commodities such as chicken feed or cosmetics. Most waste water treatment plants are not equipped to process oils so restaurants are often required to have grease traps installed in the drains. Microprocessors can still find restaurants that will donate their UFO or even pay a fee to have the producer take the UFO. As microscale processing has become more popular in certain areas, waste cooking oil has become a valuable commodity.

The principal difficulty with using UFO as a feedstock is that it can often contain too much free fatty acids for a base catalyzed reaction to be effective. Free fatty acids will consume the catalyst and often lead to soaps which can cause emulsion during water washing and can prevent the separation of glycerin after the reaction (9). When the oil is used for frying foods, it is exposed to heat and water and the oil will undergo hydrolysis causing the triglycerides breaking down (19). The breakdown of triglycerides results in the fatty acids breaking free from the triglyceride thereby becoming free fatty acids. There are ways to avoid forming emulsions (11), but for homebrewers and universities using the Appleseed processor, this limitation can prevent consistent outputs of high quality fuel.

Biodiesel properties are linked to the feedstock from which the fuel is produced. The lengths of the carbon chains that compose the esters remain unchanged when making biodiesel. The cetane number of the fuel is linked to the chain length and the number of double bonds in the molecule. There have been numerous studies that explore the performance and emissions profiles of biodiesel composed of various chain lengths and various feedstocks but that is outside the scope of this study (15)

UT Biodiesel Project

The UT Biodiesel project is entirely run by students at the University of Tennessee. Students collect the UFO from UT Dining services and test the collected oil for quality including water content, acid number and rancidity and then filter the oil in preparation for biodiesel production. The Appleseed processor has proven to be capable of producing ASTM quality biodiesel from UFO at UTK. The ASTM test performed on the fuel is presented in Appendix V. In-house fuel quality testing equipment is used to ensure that each batch produced meets key quality specifications. The ultimate goal of the UT Biodiesel program is to make enough biodiesel to allow UT Facility Services to fuel all diesel vehicles and equipment with a B20 blend using the student-produced fuel.

Appleseed Processor

The equipment used by UT Biodiesel allows a batch size of 150L (40 gallons). The Appleseed processor, shown in Figure 2, consists of a water heater as the main reactor with one HDPE tank used for methoxide mixing and another HDPE tank used for settling, glycerin separation and washing. The tanks are all connected using stainless steel pipes. An explosion proof recirculating pump is used to transfer fluids and circulate the methoxide into the heated vegetable oil inside the reactor. The reactor, methoxide and main tank are all set in an aluminum spill pallet which can contain the contents of any given tank in case of a catastrophic tank failure. This is the traditional Appleseed configuration as provided by the open-source plans (1).

Figure 2. UT Biodiesel's Appleseed Processor

All materials used in constructing the Appleseed are compatible with biodiesel, methanol, potassium hydroxide, and water. All the piping and valves are fabricated from 304 stainless steel and the heater elements for the hot water heaters have been replaced with stainless steel. All plastic parts are high density polyethylene (HDPE) except the transfer tubes which are reinforced vinyl which allows visual inspection during transfer. The reinforced vinyl tubing is replaced when it becomes hard to the touch.

Biodiesel Production

Students collect waste cooking oil from the HDPE UT Biodiesel bin provided by UT Dining Services. This bin allows only the best cooking oil to be used in biodiesel production which saves time and energy used in heating and filtering the oil.

The oil is transferred into 113L (30 gallon) HDPE drums for transporting back to the lab where the oil is tested for water content and acid number before filtering. The water content of the oil is tested to help avoid emulsions forming during the reaction. As the oil is heated and used to fry frozen food, micro-emulsions of water can form in the oil. The acid number determines the amount of catalyst needed to perform the transesterification reaction. The oil is filtered through a 10 micron filter to ensure compatibility with the nozzles used in modern diesel engines.

The filtered oil is transferred into the main reactor and is heated to 60° C. The correct amount of potassium hydroxide is measured out from 500 g bottles of KOH pellets. The correct amount of methanol is transferred into the methoxide tank and is recirculated using the pump. The KOH is quickly added to methanol to prevent the absorption of water by the pellets. A mesh screen is installed to prevent the pellets from clogging up the drain on the Methoxide tank and will allow the pellets to dissolve completely during the methoxide reaction. HPDE must be used since the exothermic methoxide reaction can produce temperatures near or above 71° C which is too high for LDPE. The methoxide mixture is recirculated for 20 minutes or until there are no visual signs of un-dissolved KOH, whichever comes later. During the methanol transfer and methoxide mixing, care must be taken to avoid breathing methanol vapors, and exhaust fume venting is used to minimize methanol vapor exposure.

Washing

All of the contaminants in the biodiesel -glycerin, potassium salts, methanol and soaps are all polar compounds and therefore water soluble, while biodiesel is hydrophobic. This feature allows biodiesel to be literally “washed” using water. A bed of

Siemens deionizers are used to produce highly purified dionized water which is feed into a smaller hot water heater used to heat the wash water. Warm water is more effective at removing containments than cold water and is also more effective at removing the trace amounts of monoglycerides and diglycerides (20). Dionized water is much more effective than using hard water and does not introduce extra sodium or potassium like many water softeners.

The main tank is fitted with a spray nozzle that is positioned to cover the surface of the fuel sitting in the tank. The main tank is also fitted with a HDPE aerator. The mister allows the biodiesel to be washed with a fine water spray over the surface which falls to the bottom, collecting water soluble material on the way down. The bubbler is used after water is filled one third of the way up on the tank were the bubbler resides to create air/water bubbles that float up to the top due to buoyancy forces. As the bubbles rise up, they collect water soluble material over the surface area of the bubbles then pop when they reach the top. As the water, with a greater density than biodiesel, falls due to gravity, it collects more water soluble material. With either process, or the two processes combined, the washing is repeated until the water is clear, then until the fuel meets the ASTM specification for total glycerin and flashpoint.

In house Testing

Fuel quality is of upmost importance for biodiesel to meet performance and emissions expectations. Fuel that does not meet ASTM specifications can cause problems ranging from degradation of fuel injection components to increased NO_X emissions. In-house testing equipment is used to ensure fuel quality from the UT Biodiesel program and includes tests for total glycerin, flash point, water content and acid number. Total glycerin is measured using the SafeTEST from MP Biomedicals. The test uses a proprietary enzymatic solution and spectroscopy to determine glycerin levels. The flash point is measured using a Pensky Martins closed cup apparatus. Water is tested using a water test kit from Sandy Brae laboratories and uses calcium hydride and a pressure vessel to determine the amount of water present in the fuel. Acid number is determined by titration with a reference solution against phenolphthalein.

Fuel Quality

In the U.S., biodiesel quality is defined by the ASTM specification D6751. ASTM D6751 describes all required properties of biodiesel sold in the US unless another agreement has been reached between purchaser and the supplier. State or local regulations that are more restrictive will replace any specification for that area. The most current revision in place is designation: D 6751 – 08. Some of the newer tests included in the most recent revisions are specifications for oxidative stability, alcohol control and, new to 2008, is cold soak filterability which will be discussed in the following section.

The fuel properties, test method and the limits prescribed by ASTM D6751 are presented in Table 1 (4). Each fuel property is described in depth in Appendix XII along with a description of the test method. Table 2 is a listing of why the fuel properties specified in ASTM D6751 are tested and how they can affect emissions.

Table 1. ASTM D6751 – Detailed Specifications For B100

Property	Method	Test Apparatus	Limits	Units
Calcium and Magnesium	EN 14538	Spectroscopy by ICPAES	5 max	ppm (µg/g)
Flash Point	D93	Pensky Martins Closed Cup Apparatus	93 min	^{o} C
Alcohol Control (1 or 2)				
1. Methanol Content	EN14100	Gas Chromatography	0.2 max	mass %
2. Flash Point Control	D 93	Pensky Martins Closed Cup Apparatus	130 min	^{o} C
Water and Sediment	D 2709	Centrifuge with a Precession Tube	0.050 max	% volume
Kinematic Viscosity	D445	Glass Capillary Viscometer	1.9 - 6.0	mm^2/s
Sulfated Ash	D 874	Evaporating Disk in a Furnace	0.020 max	% mass
Sulfur	D 5453	Ultraviolet Fluorescence	0.0015 max	% mass (ppm)
Copper Strip Corrosion	D 130	Copper Strip and a Corrosion Vessel	No. 3 max	-
Cetane	D 613	Variable Compression Ratio Test Engine	47 min	-
Cloud Point	D 2500	Special Jar in a Cooling Bath	Report	^{o} C
Carbon Residue	D 4530	Heated Glass Vial in an Inert Atmosphere	0.050 max	% mass
Acid Number	D 664	Potentiometric Titration	0.50 max	mg KOH/g
Free Glycerin	D 6584	Gas Chromatography	0.020 max	% mass
Total Glycerin	D 6584	Gas Chromatography	0.240 max	% mass
Phosphorus Content	D 4951	Spectroscopy by ICPAES	0.001 max	% mass
Distillation Temperature	D 1160	Vacuum Distillation Apparatus	360 max	^{o} C
Sodium and Potassium	EN 14538	Spectroscopy by ICPAES	5 max	ppm (µg/g)
Oxidation Stability	EN 14112	Rancimat	3 min	hours

Table 2. ASTM Properties And Reasons For Test (4), (21), (7)

Property	Reason for Test
Calcium and Magnesium	Abrasive solids can plug fuel filters and cause engine deposits and DPF deposits
Flash Point	Flash point limits the flammability of fuel and also limits methanol content Low flash point can cause premature ignition and irregular timing
Water and Sediment	Water can cause corrosion inside the engine Sediment can cause clogging of injectors, pumps or filters
Kinematic Viscosity	High - The fuel will not flow correctly – can cause injection timing increase Low - Power loss may occur due to injection pump or injector leakage.
Sulfur	Sulfur is known to poison catalysts and can lead to PM formation
Copper Strip Corrosion	Measures the fuel's tendency to corrode copper and brass components
Cetane	Cetane number is a measure of ignition quality of diesel fuels High cetane provides good cold start and reduce NOx
Cloud Point	Determines the temperature at which the fuel becomes cloudy from crystal formation
Carbon Residue	Approximation of the tendency to cause carbon deposits in the engine
Acid Number	High acid number can increase fueling system deposits and corrosion
Free Glycerin	High levels can cause injector deposits, clogged fueling systems
Total Glycerin	Helps ensure high conversion of feedstock into biodiesel
Phosphorus Content	Phosphorus can damage catalytic converters
Distillation Temperature	Ensures that the biodiesel has not been adulterated with high boiling containments Provides a measure of the ability of the fuel to evaporate for complete combustion
Sodium and Potassium	Abrasive solids can plug fuel filters and cause engine and DOC deposits
Oxidation Stability	Ability for long term storage

SECTION III

BIODIESEL EMISSIONS REVIEW

Overview

This section addresses the current research on the effect of biodiesel blends on regulated emissions including how biodiesel performs with diesel exhaust aftertreatments. Particular emphasis is placed on studies regarding light duty direct injection turbo diesels. The focus of the aftertreatment section will be on actively re-generated diesel particulate filters (DPF) and diesel oxidation catalysts (DOC). Diesel emissions in general, clean diesel technology and current emissions legislation in the United States are also discussed.

Transportation is responsible for a considerable portion of the air pollution generated in the United States. According to the EPA, motor vehicles are responsible for around 30 percent of all emissions of nitrogen oxides (NO_X) and volatile organic compounds (VOCs) which are the two primary pollutants that cause smog (22). The use of alternative fuels, advanced engine management and exhaust aftertreatments can help reduce EPA regulated emissions which vehicle manufactures are required to meet. The use of alternative fuels is also being legislated by the EPA renewable fuel standard which provides mandates for the amount of renewable fuels to be blended into transportation fuels (23).

Biodiesel is known as a clean burning alternative fuel produced from domestic resources (24) and does reduce some EPA regulated tailpipe emissions when compared to traditional petroleum based diesel fuel. The current EPA fifty state light duty diesel standard is the Tier 2 Bin 5 standard. Using biodiesel as an alternative diesel fuel addresses two of the important sustainability criteria; it is a renewable fuel produced from either plant oil or animal fat, reduces some EPA regulated emissions and can reduce lifecycle carbon emissions as well.

Emissions Legislation

In the United States, light duty diesel vehicles are subject to US Environmental Protection Agency (EPA) emission-control legislation or California Air Resources Board (CARB) legislation. Under EPA Title 2, states can adopt emission-control legislation that is stricter than that of the US EPA. This section focuses on the Federal EPA standard and points out major differences that are set forth in CARB legislation.

The Tier II standard applies to all cars, trucks and SUV's up to 8500 lbs Gross Vehicle Weight (GVWR). The Tier 2 standards apply to all vehicles sold in the United States regardless of fuel type, which means that diesel vehicles have to meet the same stringent emissions standards as gasoline vehicles, natural gas vehicles as well as all other transportation fuels (25). As of Model Year 2004, the phase-in of Tier 2 emissions standards for passenger vehicles sold in the US was started with final implementation taking place for Model Year 2007.

The EPA regulated tailpipe emissions include Non-Methane Organic Gases (NMOG), Carbon Monoxide (CO), Oxides of Nitrogen (NO_X), Particulate Matter (PM) and Formaldehyde (HCHO). NMOG includes VOCs and unburned hydrocarbons and can contribute to the formation of secondary air pollutants in the atmosphere (22). CO formation is the result of incomplete combustion of the fuel and is quite toxic to humans (26) as well as to the environment. CO inhibits the ability to transport oxygen in the blood and can lead to distress and even death. This condition may be reversible when exposure to CO is discontinued (22). NO_X is important for the formation of ground level ozone and plays an important role in atmospheric chemistry (22). NO_X has a Global Warming Potential (GWP) of almost 300 times that of CO_2 (27) and is known to be a precursor for acid rain (22), and as such, the control of NO_X is of great importance. NO_2 can also be hazardous to human health especially for populations with respiratory problems (26). PM_{10} includes all particulate matter 10 micrometers in diameter and smaller and is responsible for reducing visibility. $PM_{2.5}$ is very dangerous to human health and can cause severe respiratory problems (26). HCHO is dangerous to human health and also plays an important role in atmospheric chemistry (28).

The emission limit on each of the regulated pollutants is established in terms of fleet averages in grams of pollutant per mile over the FTP 75 Drive Cycle and Speed SFTP (Supplemental Federal Test Procedure).The addition of the SFTP takes into account aggressive, high speed driving with the US06, and the use of air-conditioning with the SC03 (29).

The FTP 75 shown in Figure 3 has a total length of 11.04 miles with a total duration of 1875 seconds with an average speed of 21.19 mph and a maximum speed of 56.68 mph (30). The SC03 shown in Figure 4 has total length of 3.58 miles lasting 598 seconds with an average speed of 21.55 mph. The US 06 driving cycle shown in Figure 5 has a total length of 8.01 miles with an average speed of 48.37 mph and a duration of 596 seconds.

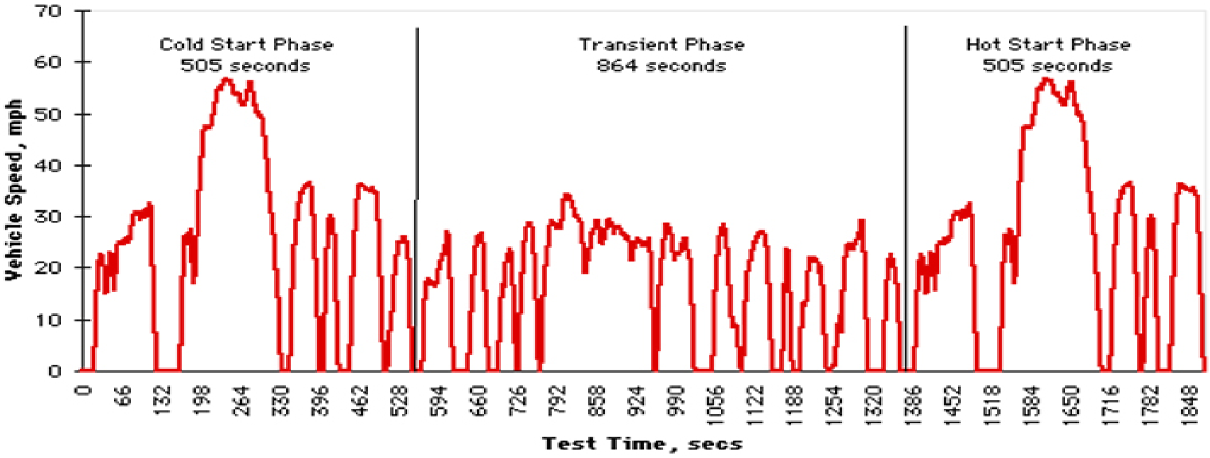


Figure 3. FTP 75 Drive Cycle with Phases Labeled (29)

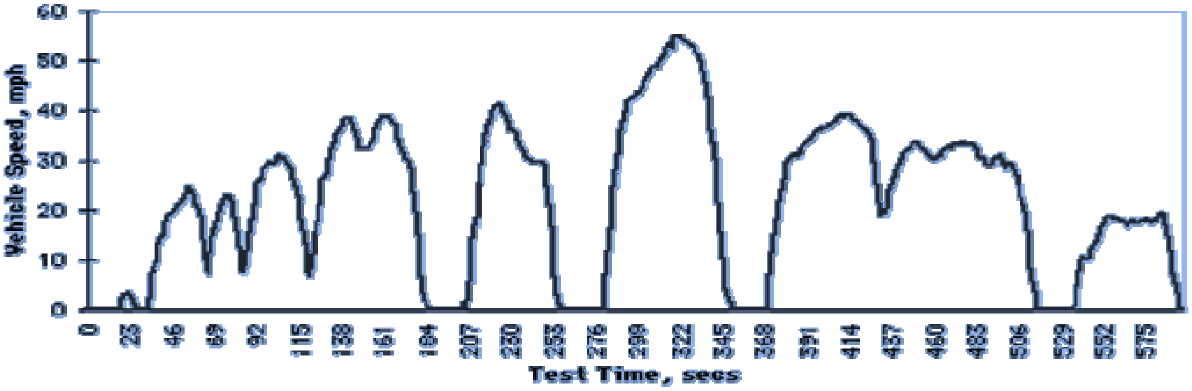


Figure 4. SCO3 – Speed Correction Driving Cycle (31)

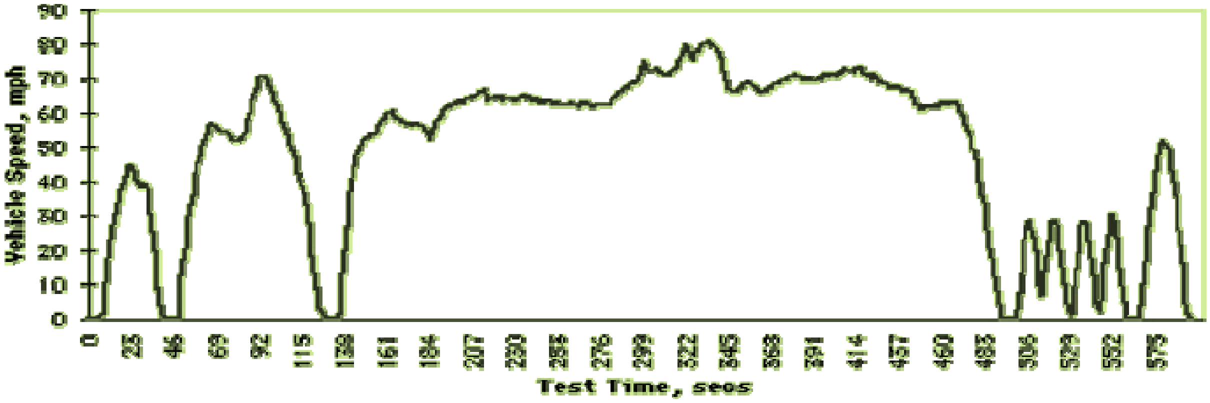


Figure 5. US 06 – Supplemental FTP Driving Cycle (31)

The Tier 2 emission standard is divided into ten bins, where Tier 2 Bin 5 is equivalent to the CARB LEV II standard (Low Emission Vehicle II) and is the current standard that light duty diesel vehicles must meet to be sold in all 50 states. To date, ten states have adopted the stricter CARB standards including Connecticut, Main, Massachusetts, New Jersey, New York, Pennsylvania, Oregon Rhode Island, Vermont and Washington (30).

The defining feature of Bin 5 is the fleet average limit of 0.07 grams of NO_X per mile over the full useful life of the vehicle and a limit of 0.05 grams of NO_X per mile for the first 50,000 miles. As shown in Table 3, the allowable emissions of NO_X and PM are both reduced by the previous CARB standard for ULEV certification (30).

As CO_2 standards loom for the USA (32) and Corporate Average Fuel Economy (CAFÉ) standards increase (33), OEMs will look to technologies such as hybrids and diesels to increase fuel economy compared to spark ignition engines. Modern diesel engines are typically 30 percent more fuel efficient than a similarly sized spark ignition engine (34). This increase in fuel economy comes at a price in terms of increased emissions of NO_X and PM. Tier 2 NO_X and PM limits for the various bins are shown in Figure 6.

Table 3. Tier 2 Permanent Emissions Bins Compared To ULEV Standard (30)

Emission	Tier 2 Bin 5 (g/mile)	ULEV (g/mile)	Decrease
PM	**0.01**	0.04	75 %
NOx	**0.05**	0.2	75 %
CO	**3.4**	1.7	-
NMOG	**0.075**	0.04	-
HCHO	**0.015**	0.008	-

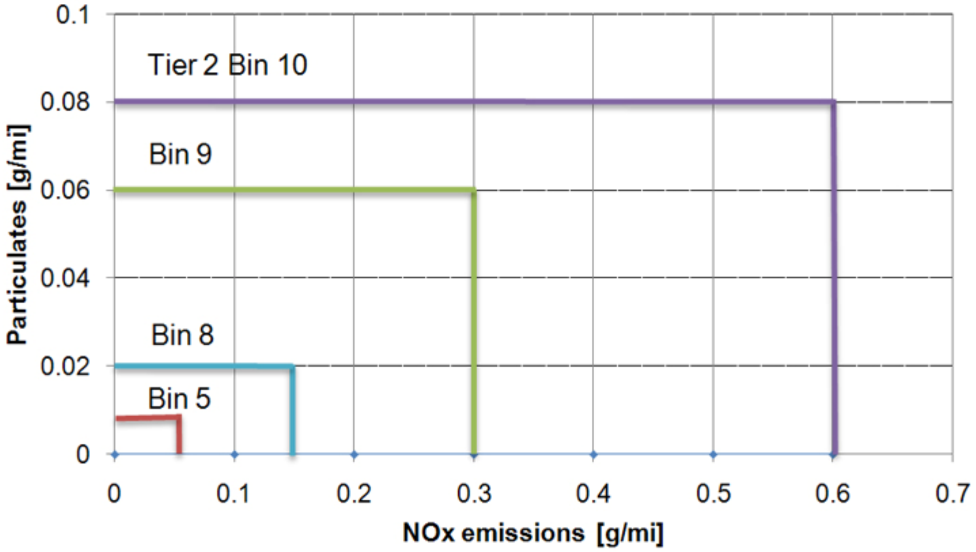


Figure 6. Tier 2 Emissions Levels For NO_X And PM (30)

Diesel Emissions

Diesel vehicles can conjure images of black smoke pouring from old passenger diesels or semi-trucks but modern diesel vehicles can meet the same emissions standards as gasoline vehicles. Of the EPA regulated emissions, compression ignition engines produce more NO_X and PM than SI engines. On the other hand, compression ignition engines do produce less CO than SI engines due to the amount of excess air present during the combustion cycle.

PM Emissions

PM consists of soot and adsorbed components resulting from incomplete combustion of the diesel fuel. Total particulate matter is characterized by three fractions; the solid fraction includes carbon particles and ash, the Soluble Organic Fraction (SOF) includes absorbed organic material from unburned fuel or lubricating oil, and the sulfate particles form from water and sulfur (28). The increased PM emissions are a byproduct of the compression ignition cycle. For both direct-injection and indirect-injection, fuel is injected as droplets of size depending on injection pressure which is mixed heterogeneously with the intake air. Larger droplets of fuel are not fully combusted in the combustion chamber and are the primary cause of PM (34).

NO_X Emissions

NO_X is the collective term for nitric oxide (NO) and nitrogen dioxide (NO_2). NO_X is formed during combustion as the oxidation of atmospheric N_2 with O_2 (22). NO_X formation occurs with the high temperatures from fuel combustion and is dependent on the availability of oxygen during combustion. The increase in NO_X with CI engines is due to higher in-cylinder temperatures during combustion in the presence of high levels of excess air. These conditions are perfect for the formation of NO_X with the primary component being NO (70-90%) (34). The principal reactions resulting in NO are shown in Equations 1, 2, and 3 (34).

$$\boldsymbol{O + N_2 = NO + N} \tag{1}$$

$$\boldsymbol{N + O_2 = NO + O} \tag{2}$$

$$\boldsymbol{N + OH = NO + H} \tag{3}$$

With the high in-cylinder temperatures and lean conditions, it is easy to look at the principal reactions and see why CI engines have such high levels of NO_X. NO_2 formation is only 10 to 30 percent of the total composition of NO_X (34). The mechanisms for NO_2 formation are also known, but are not presented here (34).

Clean Diesel Technology

The development of the current generation of diesel engines has been shaped by trying to maximize power density while keeping both engine out NO_X and PM to minimum. The current generation of diesel engines has been branded as “clean diesels” (35).

Modern diesel engines are defined by a number of advanced technologies including electronically controlled high-pressure common rail direct injection. High-pressure common rail injection systems allow injection pressure to be controlled independently of engine speed, load (36) and injected fuel amount (25). High-pressure common rail system can have maximum rail pressures of around 1600 bar (25) which provide the ability for more complete atomization of the fuel when combined with modern fuel injectors with smaller injection nozzle diameters. Current fuel injectors including solenoid and piezo-injectors minimize fuel leakage after injection and allow for better control over the mixture formation (25). Atomization of the fuel allows the fuel to evaporate and mix well with the charge air (34). The use of fuel injectors that abruptly and completely stop fuel flow along with evaporation from atomization account for much of the reduction in PM in modern diesel engines. Electronically controlled injection timing with these advanced injection technologies allows for significant control over emissions including NO_X and PM, noise, power and fuel consumption (36). Multiple-injections during each combustion event are used to reduce noise as well as PM and NO_X (37).

Clean diesels are also defined by the use of forced induction, namely turbochargers, which are used to increase the power density of the engine and provide increased oxygen for combustion. Current turbocharger technology such as variable geometry turbochargers (VGT) allows more control over boost especially at low speed, low torque conditions which traditionally results in more smoke (36). Intercoolers are often used to cool the high turbine outlet temperatures which can improve charge density and thereby volumetric efficiency.

NO_X can be controlled to a point by lowering cylinder temperatures by retarding the injection timing (22) and using Exhaust Gas Recirculation (EGR) as a diluent. Retarding the timing is effective in lowering the peak cylinder pressure which in turn lowers the cylinder temperature. EGR works on the principle that exhaust gas re-circulated back into the combustion chamber does not participate in combustion so it effectively adds thermal mass to absorb some of the combustion energy (25) and reduces the available oxygen which in turn lowers combustion temperature (34). Significant reductions in NO occur with EGR rates of only 10 to 25 percent (34). Cooled EGR is becoming more popular to further help reduce the flame temperature and increase charge density (37). High EGR rates during high engine loads can lead to increased PM emissions by reducing the amount of available oxygen (37).

Despite all of the these advanced technologies, modern diesel engines are not able to meet the current EPA emissions requirements without the use of exhaust aftertreatments to further reduce NOx, PM and NMOG. Though NO_X is proving to be the most technically difficult and cost prohibitive to reduce.

Diesel Aftertreatments

The stringent standards in Tier 2 Bin 5 require that exhaust aftertreatments be used to reduce tail pipe emissions of regulated pollutants. Exhaust aftertreatments such as Diesel Oxidation Catalysts (DOC), Diesel Particulate Filters (DPF) and de-NO_X technology such as Lean NO_X Traps (LNT) and Selective Catalytic Reduction (SCR) catalysts are now commonplace components of diesel exhaust and fuel management systems. The discussion in this section will be limited to the operation of DOCs and DPFs and biodiesel's effect on both aftertreatments.

Diesel Oxidation Catalysts

DOCs are honeycomb monoliths with a chemical washcoat that succeed in oxidizing hydrocarbons, CO and PM when the catalyst reaches its operating temperature, also known as the light-off temperature. DOCs are effective at removing the Soluble Organic Fraction (SOF) of PM (38). DOCs act similar to three-way catalysts in SI engines and are in fact sometimes called two way catalysts (25).

The main catalyst pathways are seen in Equations 4 and 5, and since diesel engines always operate lean; the main reaction is seen in Equation 5, where the hydrocarbons, represented by HC, are oxidized to carbon dioxide and water vapor.

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O}_2 -> CO_2 \tag{4}$$

$$HC + O_2 -> CO_2 + H_2O \tag{5}$$

Diesel Particulate Filters

PM emissions can be reduced by using porous ceramic blocks that trap particulate matter which are called Diesel Particulate Filters (DPF). DPFs filter out up to 90% of PM (25) by impaction, interception or diffusion (39). Exhaust enters the DPF in small channels made from the porous monolith material. The ends of each alternating channel are blocked forcing the particulate laden exhaust through the channel walls trapping the PM as shown in Figure 7. This type of DPF is known as a wall flow DPF (28). The channel walls are usually 300 – 400 micrometers thick and cell densities range from 100 to 300 cells per square inch and are often made of SiC or cordierite (25).

DPFs require replacement or regeneration as the channels become full; otherwise, dangerous amounts of backpressure can result in engine damage. Active regeneration occurs at temperatures above 600° C and is usually accomplished with engine management to increase exhaust temperature or by injecting excess fuel during the power stroke. Other methods of active regeneration are commercially available including electrical heating devices, and full flow burners (39).

The use of catalyzed DPFs for passive control is becoming more widespread (39) since they can help reduce the increased fuel consumption from regeneration by engine management. Fuel additives are also being investigated to lower the active regeneration temperature (25).

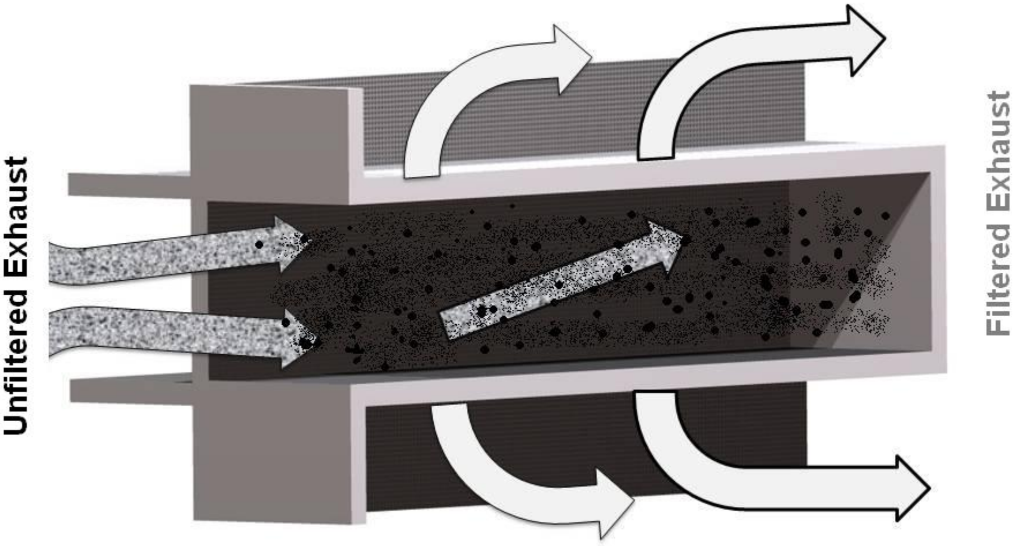


Figure 7. PM Filtration By Wall Flow DPF (39)

Biodiesel Emissions Studies

The increased use of biodiesel in the United States, along with growing interests in renewable fuels and emissions reductions, has fueled a wealth of studies on the emissions performance of biodiesel made from various feedstocks, in both light duty and heavy duty engines. A recent literature review of biodiesel emissions showed that biodiesel emissions studies have increased exponentially over the last fifteen years (40) which is shown in Figure 8 from the ISI Web of Knowledge. The number of studies on the subject of biodiesel has also increased exponentially as well. There have been many emissions reviews published as well as numerous book chapters devoted to the subject. The following section discusses the current thinking on why each regulated emission is different with biodiesel and biodiesel blends compared to petroleum diesel fuel.

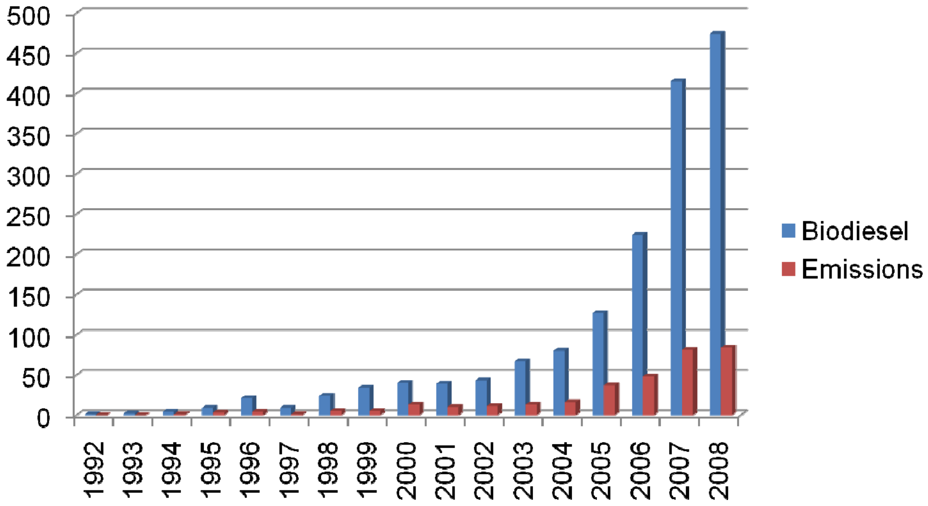


Figure 8. Number of Biodiesel Studies Per Year Since 1992

This section is not intended as a repeat of other literature reviews, but as a presentation of the research relevant to light duty, high pressure common rail turbocharged diesel engines. In general, research has shown that NMOG, PM and CO emissions decrease for B20 compared to petroleum diesel with roughly the same NO_X emissions. Higher blends show increasing reductions with the amount of biodiesel for all emissions but do show a significant increase in NO_X emissions as seen in Table 4 (41). The general trend of emissions with respect to the amount of biodiesel in the fuel from the 2002 EPA study (42) is presented in Figure 9. With such stringent emissions requirements and the ever apparent need for alternative fuels, the role biodiesel plays in engine out emissions and biodiesel effects on aftertreatments needs to be understood. Since HCHO emissions are not a problem for diesel engines and not evaluated in this study, the focus of the following discussion will be on NO_X, PM, NMOG and CO.

Table 4. Average Biodiesel Emissions Compared to Petroleum Diesel according to the EPA (24)

Emission	B100	B20
Total Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
NO_X	10%	+2% to -2%

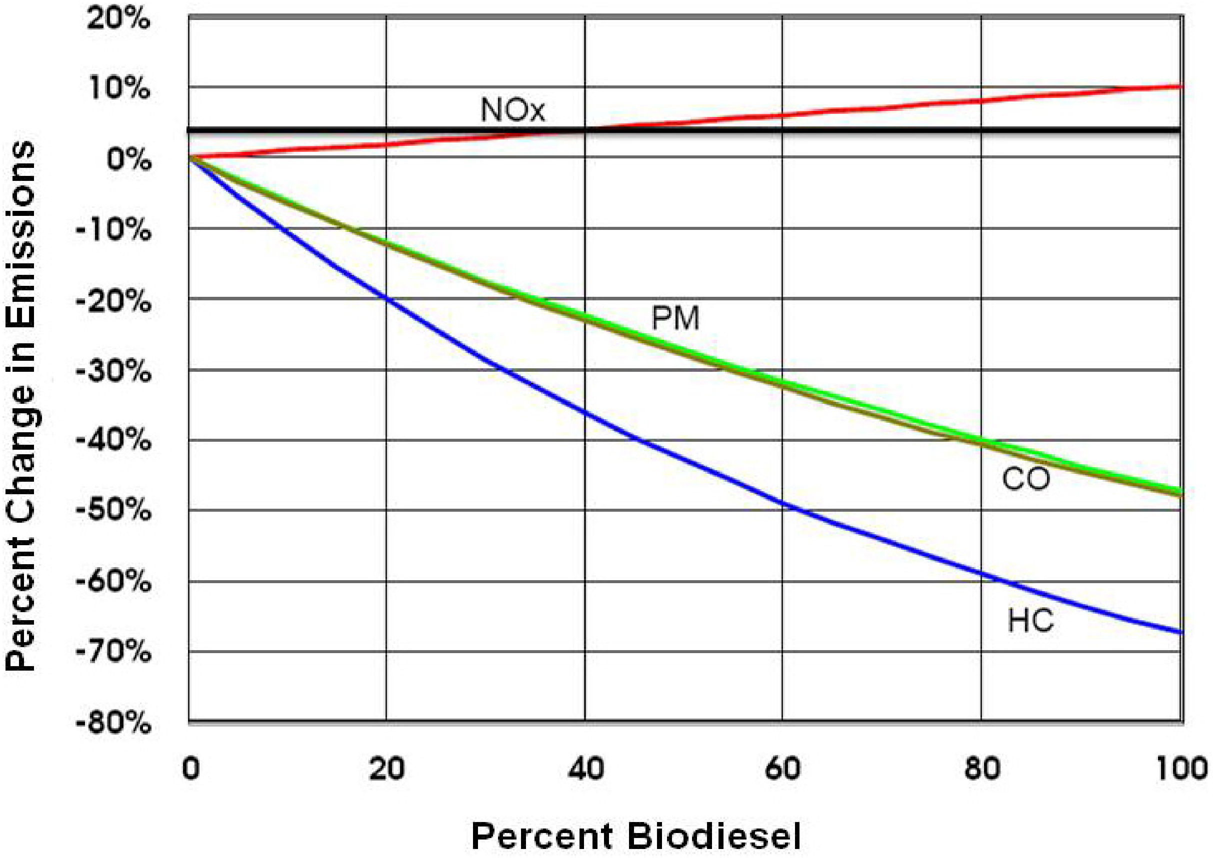


Figure 9. Change In Emissions With Change In Biodiesel (42)

Biodiesel and PM

The main reason biodiesel has been branded as a clean burning fuel is the obvious reduction in PM emissions. End users of biodiesel note that, even with lower blends, the exhaust has visibly less black smoke and also has been reported to smell better. Biodiesel has been shown to reduce total PM and smoke opacity (7). Smoke opacity is only loosely tied to PM emissions since opacity is affected more by black smoke than white smoke (7). In the literature review by Lapuerta et al., 95% of the studies examined showed a decrease in PM emissions (40). The study by McGill et al. found across the board PM reductions from 15% - 25% from a 1.9L VW TDI engine with blends of 30% and 100% biodiesel from rape seed oil, soy bean oil and used frying oil (43). Reductions were generally greater with B100 than B30 and also greater for higher loads and higher RPMs (43). PM emissions and smoke opacity have been found to increase at cold startup (40), which has been attributed to the higher distillation temperature of biodiesel initially lowering the amount of fuel that evaporates. It seems that this tendency is quickly eclipsed as the cylinder temperature increases.

Soot from biodiesel has been found to be more unstable than soot produced from D-2 diesel fuel and the instability increases with the amount of biodiesel in the fuel blend. This is important for the ability of biodiesel PM to be oxidized during combustion and in DOCs and catalyzed DPFs. The PM profile of biodiesel is different than that of D-2 diesel fuel. Biodiesel soot contains a higher portion of SOF compared to petroleum diesel fuel while the solid carbon portion is diminished (44). In terms of particle size distribution, studies have found that the number of smaller particles increased with biodiesel blends (40), but the total number of particles across all sizes decreased. The shift in particle size distribution towards the lower particles does have implications for the effect biodiesel emissions have on human health.

By only looking at the properties of biodiesel, it could be predicted that PM emissions would increase since higher density, kinematic viscosity and distillation temperature can all lead to poor fuel atomization and vaporization. The higher oxygen content however seems to overcome these properties, which results in reduced soot emissions. The amount of oxygen contained in biodiesel, 10 -11% by weight (45), has a dramatic effect on the formation of soot during combustion. PM reduction is generally attributed to the higher oxygen content of the fuel, which encourages more complete combustion and reduces the chance of fuel-rich regions in the combustion chamber, producing less PM (40). The lack of aromatics, which are known soot precursors, (7), near zero sulfur content, the lower boiling point and the more reactive soot produced all help PM oxidize in the combustions chamber. Biodiesel has also been shown to cause advances in injection timing which can lead to higher combustion temperatures leading to less PM. The injection advancing behavior is discussed more fully in the next section regarding NO_X. The PM reduction seems to be independent of chain length (40) and the type of alcohol used to produce the fuel, but is highly dependent on the amount of oxygen contained in the fuel.

Biodiesel and NO_X

In general it has been shown that for biodiesel blends higher than B20, NO_X emissions are increased. In the review by Lapuerta et al., the authors found that the vast majority of studies, 85%, showed an increase in NO_X (40). The McGill et al. study found that NO_X generally increased for biodiesel blends except for high speed conditions and some low load conditions (43). The highest increases were seen for lower speeds at high loads and were greater for B100 then B30 (43).

Research has shown that there are a number of reasons for the increase in NO_X emissions with higher blends of biodiesel. The increase in the amount of oxygen in biodiesel contributes to higher NO_X emissions. Schmidt and Van Gerpen found that a B20 blend can provide 4% more oxygen during the combustion process, leading to higher levels of NO_X (46), on the order of 1% to 3%. Recent research has also shown that biodiesel can cause an advance in fuel injection timing due to the higher bulk modulus of biodiesel (45) and higher density of the fuel. The higher density of the fuel can cause a faster increase in injection pressure causing an advance in injection timing of as much as 3 to 5 degrees (47). This feature has been also been attributed to the higher bulk modulus of biodiesel compared to D-2 diesel fuel. It has been noted that biodiesel advanced the timing to a greater extent at high loads than low loads (40). It is interesting to note that studies holding injection timing constant have also found an increase in NO_X output (40).

The higher cetane of biodiesel can help lead to NO_X reductions (7). The higher cetane of biodiesel can reduce the ignition delay (48) which can actually help reduce NO_X by reducing the duration that the fuel is exposed to the high combustion temperatures.

Biodiesel and NMOG

Biodiesel has been shown to generally decrease NMOG emissions. The majority of the studies reviewed by Lapuerta et al. (95%) showed a decrease in NMOG emissions (40). The McGill et al. study showed that biodiesel blends produced less hydrocarbon emissions (43). The Krahl study showed a 30% decrease in hydrocarbon emissions with B100 (49). In general NMOG emissions decreases are greater with the higher biodiesel blends (40)

From a properties standpoint, it may appear that the higher boiling temperature of biodiesel might lend itself to less fuel evaporating during combustion which would result in more unburned fuel in the exhaust. Studies have shown, however, that the increased oxygen content and cetane value for biodiesel actually help reduce NMOG emissions. The effects described in the NO_X section also tend to reduce NMOG emissions due to more complete combustion of the fuel in the same manner that PM emissions are reduced. The oxygen content of biodiesel leads to more complete combustion as do the higher cetane level and advanced timing. Decreases have been found up to 60%-70% compared to petroleum diesel (40). Load does not appear to be a factor in NMOG reduction unlike the other emissions reductions (40). The lower volatility of biodiesel can in turn increase NMOG. It has been noted that FIDs used to detect hydrocarbons are less sensitive to detecting oxygenated compounds which could skew the results and the sampling lines may not be designed to handle biodiesel which can condense in the line (40). Biodiesel with greater chain length and higher saturation levels both help reduce NMOG emissions (40).

Biodiesel and CO

Biodiesel use has been found to decrease CO emissions which are already small compared to spark ignition engines. The Krahl study found a CO reduction of 60% with FAME compared to D-2 diesel fuel using a six cylinder Mercedes engine (49). Senatore et al. found CO to decrease over all operating conditions with B100 using common rail turbocharged 1.9L Alfa Romeo engine (50). In addition, CO reductions have been found to be more effective at higher loads (40).

As was the case for other emissions, the increased oxygen content helps reduce CO as does a higher cetane and advanced injection timing. CO decreases are higher with more saturated feedstocks such as animal fat and also for fuels with longer carbon chains (40). It has been suggested that oxygen content in the biodiesel leads to a lower equivalence ratio which almost universally shows a decrease in CO emissions (40).

Unregulated Emissions

There have also been studies on the effects biodiesel blends have on unregulated emissions that have an effect on human health and on the environment. The NBB reports a reduction of PAH and nPAH (5). These results have been seen in other studies as well (51). A detailed discussion of these results is outside the scope of the study but important to note.

Biodiesel and Aftertreatments

Biodiesel is playing an important role not only in issues of sustainable mobility, but also in the ultra low sulfur diesel (ULSD) requirements in the U.S. and other countries. Many aftertreatment systems are susceptible to poisoning by sulfur compounds in the fuel, and the fact that biodiesel is essentially sulfur free means that biodiesel is a good lubricity additive candidate as well as diesel replacement. Biodiesel has been used as an additive for ULSD to meet lubricity requirements in ASTM D975, the on-road diesel fuel standard in the USA. Engine OEMs are driven in part to meet the stringent emissions requirements of EPA Tier II standard, and the effect that biodiesel has on aftertreatments is of utmost importance. The absolute need of aftertreatments for light duty diesel vehicles to meet EPA Tier 2 Bin 5 means that the performance of biodiesel with current aftertreatment technologies needs to be understood, and to that end, there have been a number of studies on this topic.

Biodiesel and DPFs

Biodiesel has been shown to lower PM emissions at all blends and the behavior of biodiesel with both active and passive DPFs has been explored in various studies. The availability of oxygen in biodiesel means that biodiesel will combust more thoroughly than petroleum diesel and it turns out the biodiesel soot behaves differently than petrol diesel.

There have been a number of studies that have evaluated the performance of catalyzed DPFs with different biodiesel blends. DPF regeneration depends on NO_2 which is a more aggressive oxidation agent at lower temperatures. This means that increases in NO from blends of B20 and higher can have a significant effect on the performance of the DPF (52). Another effect that biodiesel can have is by lowering the balance point temperature (BPT) also called break-even point (BET) of the DPF. The BPT is the temperature in which rate of deposition of particulate matter equals the rate of particulate matter oxidation on the filter (53).

Biodiesel and DOCs

The increased SOF with biodiesel blends means that DOCs should be more effective at reducing PM (7). PM reductions in excess of 50% can be obtained by the DOC alone, mainly due to the higher oxygen content of the fuel (7). It has been shown that DOCs perform well at reducing CO and HC from biodiesel (54) (55). In the McGill et al. study the DOC reduced PM more effectively with a B30 blend than with petroleum diesel (43). It has been shown that biodiesel blends increased formaldehyde emissions without a DOC installed (43).

Biodiesel and De-NO_X technologies

Though this study did not include the use of any de-NO_X technologies a brief mention is warranted for completeness of the discussion.

All light duty vehicles scheduled for sale in the US will require some form of de-NO_X technology, and the higher NO_X output from higher biodiesel blends must not render these aftertreatments ineffective. It has been shown that LNTs reduce NO_X more effectively with a B20 blend (56). Studies have also shown reduced performance with LNTs using B100 (54). This reduced performance was attributed to the inability of biodiesel to act as a reductant by created a rich spike over the catalyst. With SCR systems the ratio of NO_2 to NO makes a big difference in the performance of an SCR, which holds promise for biodiesel blends when an SCR and DPF are used in series. In this case the DPF can be used to control the NO/NO_2 ratio to promote SCR effectiveness (57).

SECTION IV

TEST EQUIPMENT AND METHODOLGY

Overview

On-road emissions were evaluated using an Autologic 5 gas analyzer and an Autologic Heavy Duty Smoke Meter. Stationary smoke opacity was evaluated using an Autologic Heavy Duty smoke meter. The test vehicle used was a custom built diesel electric hybrid with a 1.9 liter GM direct injected turbocharged diesel engine that is representative of modern clean diesel technology. The test vehicle was fitted with a diesel oxidation catalyst and diesel particulate filter. The emissions testing was performed over a drive cycle that is routed through the city of Knoxville, TN that mimics elements of the EPA drive cycles used for emissions evaluations.

Test Vehicle

The test vehicle used was a 2005 Chevrolet Equinox crossover sport utility vehicle (SUV) that had been modified to be a diesel electric hybrid vehicle through the Department of Energy and General Motors sponsored Challenge X competition. The Equinox had a 1.9 liter direct injection turbo diesel installed which is coupled to the front drive wheels through a GM F40 six speed manual transmission. The vehicle is pictured in Figure 10.

Figure 10. Test Vehicle Used For Emission Testing

The vehicle is a through-the-road parallel electric hybrid whose rear drive wheels are powered by 67kW Ballard integrated power transaxle connected to a 288 volt NiMH battery pack. The control system for the hybrid electric drive unit can be disabled rendering the vehicle a front wheel drive diesel SUV. The vehicle was effectively a non-hybrid front wheel drive SUV for the entire study.

The vehicle weight is 1950 kg (4300 lb) and the tires are low rolling resistance run-flat tires used for the Challenge X competition. The vehicle was fitted with a secondary fuel tank for emissions testing to allow for complete draining when switching blends. The secondary fuel tank is a five gallon racing cell from Summit racing that uses quick disconnect valves on the fuel lines for ease of removal. The tank was installed in the rear cargo area of the SUV.

Engine and Aftertreatments

The engine installed in the test vehicle is representative of the current clean diesel technology used to meet stringent EURO and EPA standards. The GM 1.9 liter turbocharged diesel engine was originally used in Opel, Fiat and Vauxhall passenger cars in Europe. The engine is rated at 320 Nm of torque at 2000 rpm and a peak power of 110 kW at 4000 rpm (150 HP, 315 ft-lb torque). The engine is a 16 valve DOHC 4 cylinder diesel with a compression ratio of 17.5 to 1. Forced induction is provided by a Garret variable geometry turbo charger (VGT) capable of 2.2 bar intake boost pressure. Table 5 shows the engine specifications for the GM 1.9 turbo diesel. A CAD image of the engine is presented in Figure 11. The intake air is cooled using an air to air intercooler that was custom built for the vehicle. The engine uses a Bosch high-pressure common rail injection system capable of a maximum rail pressure of 1600 bar. The injection system uses Bosch CRIP2-MI injectors with an included angle of 148° and seven injection holes. The injection system is capable of multiple injections for emissions and noise reduction as well as DPF regeneration.

The engine also uses water-cooled EGR for NO_X reduction with the maximum EGR rates being proprietary. The engine is mated to a pre-cat metal substrate DOC and combination DOC/DPF with a secondary DOC located at the inlet of the DPF. These are the aftertreatment devices that were mated to the engine in the Vauxhall configurations. The engine is designed to be EURO IV compliant with the use of the DOC and DPF. The vehicle is also fitted with an SCR catalyst that uses anhydrous ammonia as the reductant; The SCR system was disabled for the emissions testing.

Table 5. Engine Specifications

Component	**Specification**
Engine Power	110 kW @4000 rpm
Engine Torque	320 Nm @ 2000 rpm
Compression Ratio	17.5:1
Turbocharger	Garret VGT – 2.2 bar boost max
Intercooler	Air to Air - custom
Injection System	High Pressure Common Rail – 1600 bar max
Injectors	Seven hole, 148°, 440mm/s
EGR	Cooled - Electronic Controlled

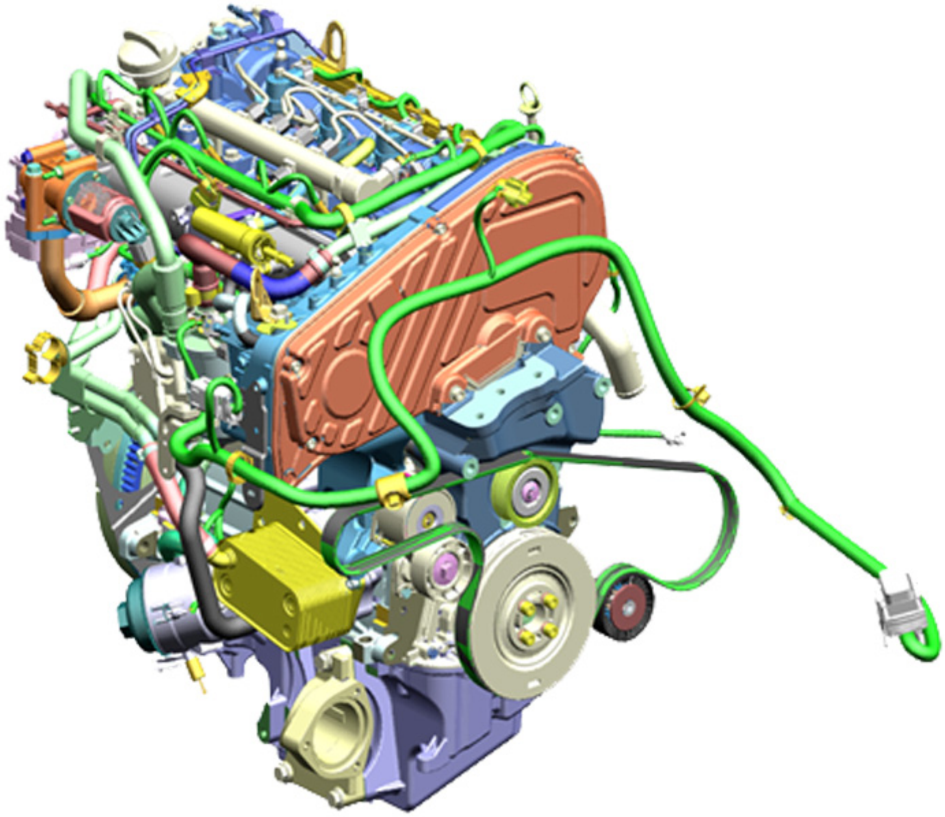


Figure 11. CAD Image Of GM 1.9 L Diesel Engine

On-Road Emissions Testing Equipment

The tailpipe emissions were evaluated using Autologic's AutoGas™ Emissions Analyzer. The AutoGas unit is a portable five gas analyzer that measures HC, CO, CO_2, O_2 and NO_X. The analyzer is designed to meet ASM/BAR 97, OIML and BAR 90 standards which are all vehicle inspection standards that states use to check exhaust for local emission requirements. The unit reads the 5 chemical species in percent or ppm by volume. The range and resolution for all chemical species is presented, along with product specifications, in Appendix I.

The AutoGas emissions analyzer (AEA) uses a nondispersive infrared sensor (NDIR) to measure HC, CO and CO_2 using fixed, non-scanning infrared light. The absorption of infrared light increases with the concentration of gas molecules in the light path. Separate infrared filters are used for each species (58). NO_X and O_2 are measured using chemical cell sensors, known as NO_X sensors and O_2 sensors respectively, which produce an output voltage proportional to the concentration in the sampled exhaust gas. The AEA uses an onboard pump to pull a sample of exhaust into the analyzer. Water and PM are removed using an inline paper filter and a fuel filter before the sampled gas is introduced into the analyzer cells.

The AEA is an inexpensive analyzer for on road emissions testing and for diagnostics. It is appropriate for measuring the differences in the emissions for the various biodiesel blends compared to each other on the same driving course. The analyzer does have limitations especially in the fact that it only reads in volume percent of species and does not have a measured volumetric flow rate. An example of an ideal mobile emissions analyzer is the SEMTECH-DS from Sensors Inc which has been used by the US EPA (59). The SEMTECH-DS uses a heated Flame Ionization Detector (FID) for NMOG, NDIR for CO and CO_2, and a proprietary Non-Dispersive Ultra Violet (NDUV) resonant absorption spectroscopy for simultaneous NO and NO_2 measurements. The SEMTECH unit uses an exhaust flowmeter to allow data to be presented in grams per mile. The SEMTECH-DS is cost prohibitive with units costing nearly $100,000 while the AutoGas unit is under $10,000.

The AEA does not meet EPA CFR Part 1065 for Test Procedures and Equipment. CFR 1065 requires that NDIR be used to measure CO and CO2, chemiluminescent detectors (CLD) for measuring NO_X, and a FID for hydrocarbon measurement.

The analyzer, shown in Figure 12 along with the sampling tube, measures hydrocarbons in the form of hexane and does not directly measure NMOG. The analyzer uses the Brettschneider equation to convert the ppm of HC as hexane to NMOG (60).

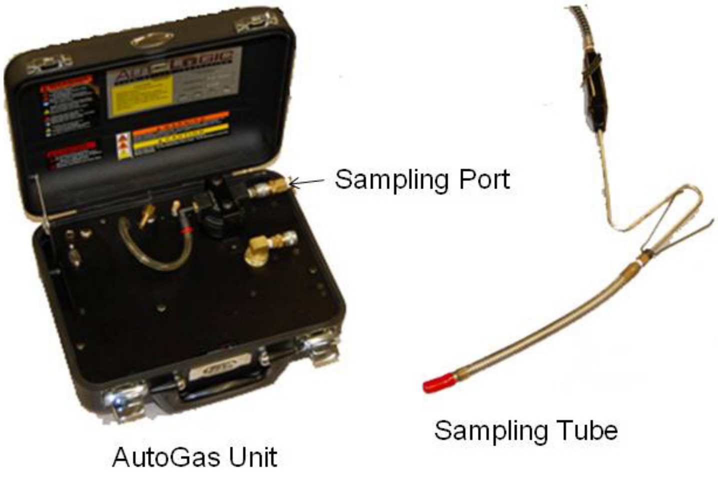


Figure 12. AutoGas Emissions Analyzer With Sampling Tube

Calibration and Time Response

The time response of the analyzer was tested by exposing the analyzer tip to the calibration gas and measuring the response time for all measured species. The time response of the unit found to be an average of 9 seconds which is just over the analyzer specifications of 8 seconds for the NDIR response. This response time is much greater than the amount of time the exhaust takes to travel down the tail pipe to where it is read by the sampling tube. Assuming plug flow, and that the exhaust has similar properties to air, it was calculated that the average exhaust flow rate was 8 meters per second (m/s) with a high of 20 m/s. This corresponds to a delay of around 0.375 seconds on average. The time response for the AEA is presented in Appendix II.

Smoke Meter

Exhaust PM was indirectly measured by an Autologic HeavyDuty J1667 diesel smoke meter. The smoke meter measures diesel smoke in percent opacity. The unit uses a stationary test method based on the SAE J 1667 standard. The smoke meter specifications are presented in Appendix III. Though as discussed earlier, smoke and PM are directly coupled, smoke opacity is a good representation of PM reductions, especially black smoke

The smoke head is placed in the exhaust pipe as shown in Figure 13 and routes the exhaust through the path of a green LED light of a known intensity.

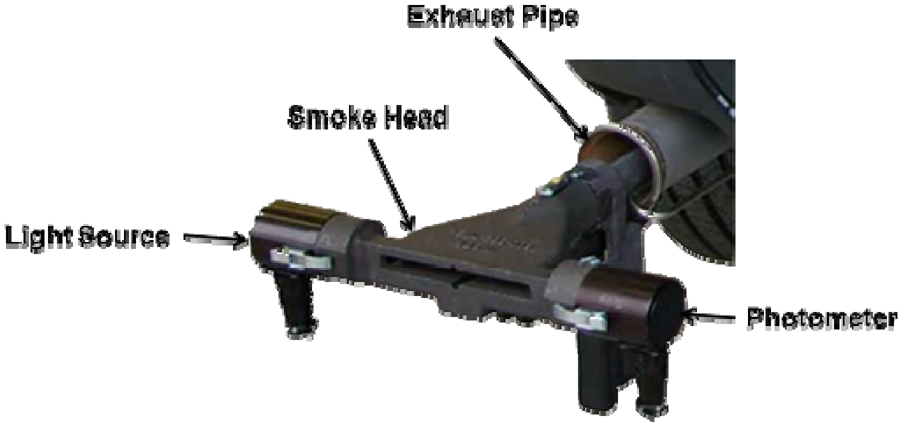


Figure 13. Smoke Head Diagram

The light intensity is measured by a photocell and is converted to percent opacity using the Beer-Lambert law. The Beer-Lambert law uses transmittance and optical path length to obtain opacity. This relationship is discussed in Appendix VI.

The test uses a cycle of idling followed by maximum engine speed after the engine is warmed up. The SAE J 1667 test is known as the Snap-Acceleration Smoke Test Procedure for Heavy-Duty Diesel Powered Vehicles (61). The SAE J1667 test is used for assessing smoke emissions for state and local regulations.

Drive Cycle

Driving cycles are used in EPA emissions testing to ensure a repeatable driving simulation for results that are comparable and repeatable for all vehicles. The EPA drive cycles are representations of realistic driving conditions seen on the roads in the U.S. The use of what is known as Portable Emission Measurement Systems (PEMS) is becoming important in monitoring heavy-duty vehicles in the US and in Europe (62), as well as in powertrain research and development (63). Recent research using PEMS has shown with appropriate driver training emissions measurements have been able to achieve repeatability levels of 6% error for CO_2 and NO_X (64). It has been shown that PEMS need to have appropriate response times and the ability to synchronize all data being logged (65). The data for this study is being synchronized against the know time delay of the NDIR for the five-gas analyzer.

Emissions measurements were conducted over an on-road drive cycle originally created for use in the Department of Energy advanced vehicle technology competition known as Challenge X. This on-road drive cycle is called the UTK drive cycle and provides a good representation of a mixture of city and highway driving in Knoxville.

The UTK drive cycle also represents a reasonable facsimile of both EPA driving cycles, as shown in Table 6, and provides values that are representative of real-world driving. There is value in using real-world emissions data for local outreach and education for clean diesels and biodiesel blends since the Federal drive cycles are known to not accurately represent real-conditions (65). It has also been shown that the drive cycle used can have an effect on both NO_X and PM emissions (66).

Table 6. Drive Cycle Comparison

Drive Cycle	**Duration (s)**	**Length (miles)**	**Average Speed (mph)**	**Max Speed (mph)**
FTP 75	1874	11.0	21.2	56.7
HWFET	765	10.3	48.1	59.9
UTK	2150	25.7	38.4	60.0

On-road emissions testing more accurately shows what the real-world emissions benefits or drawbacks are from using biodiesel produced by students at the University of Tennessee in a modern diesel. The UTK drive cycle was mapped using a DL1 data-logging GPS unit. Detailed instructions for following the drive cycle were created suing the GM proving ground drive cycle as a model. Landmarks are used to provide acceleration targets in which the driver must accelerate to the prescribed speed before reaching. In the case of stretches of road with multiple traffic lights, an acceleration time is prescribed. For example, during a portion of the course when driving on Middlebrook (a main thoroughfare in Knoxville), a constant speed of 50 mph must be reached within 22 seconds if an unscheduled traffic light is encountered. There are a number of scheduled stops over the drive cycle that were chosen such that the stop could be made independent of traffic lights. A simplified drive cycle instruction sheet is shown in Figure 14. The actual drive cycle instruction sheet has 60 instruction points and is presented in the Appendix X.

Figure 15 shows the drive cycle overlaid on a satellite map of the area with the speed indicated by a color scale. The DL1 was also used on the emissions testing runs to ensure that the drive cycle was followed and to record vehicle speed.

Marker	Instruction (mph)	Time (sec)
1	Enter on ramp to I40 West	0
2	Accel to 60	70
3	Decel from 60 to 45	106
4	Accel to 70	134
5	Brake to Stop	539
6	Accel to 40	604
7	Brake to stop	632
8	Idle for 45 seconds	655
9	Accel to 40	700
10	Brake to Stop	771
11	Accel to 50	776
12	Brake to stop	843
13	Accel to 30	876
14	Brake to Stop	915
15	Accel to 45	940
16	Brake to stop	1297
17	Idle for 30 Seconds	1338
18	Accel to 45	1400
19	Brake to stop	1713
20	Accel to 40	1747
21	Decel to 30	1805
22	Brake to stop	1860
23	Idle for 40 seconds	1873
24	Accel to 40	1930
25	Decel to 5	1955
26	Acell to 60	2000
27	Brake to top - END	2150

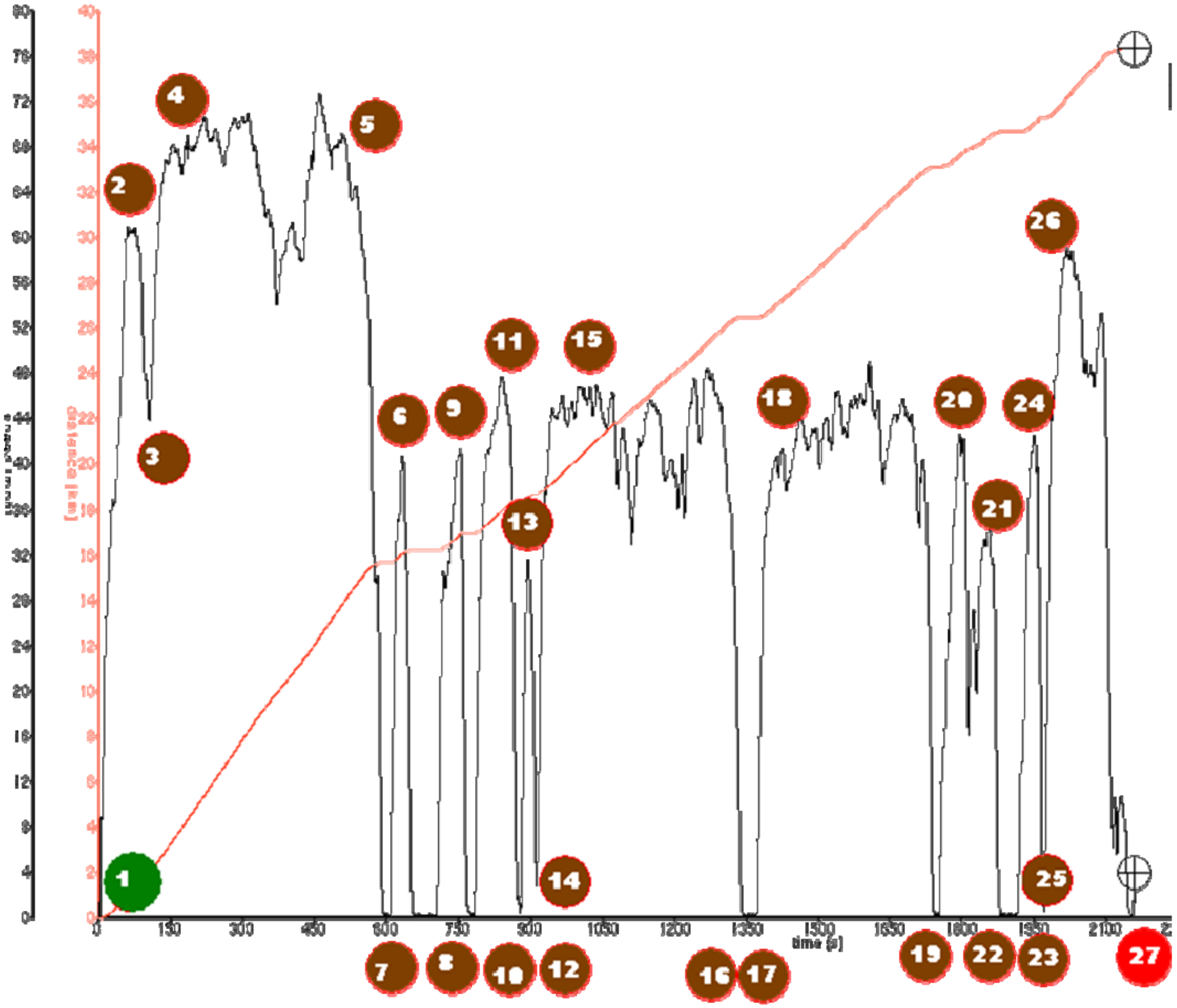


Figure 14 UTK Drive Cycle (Velocity Vs. Time) – Red line shows cumulative distance (miles)

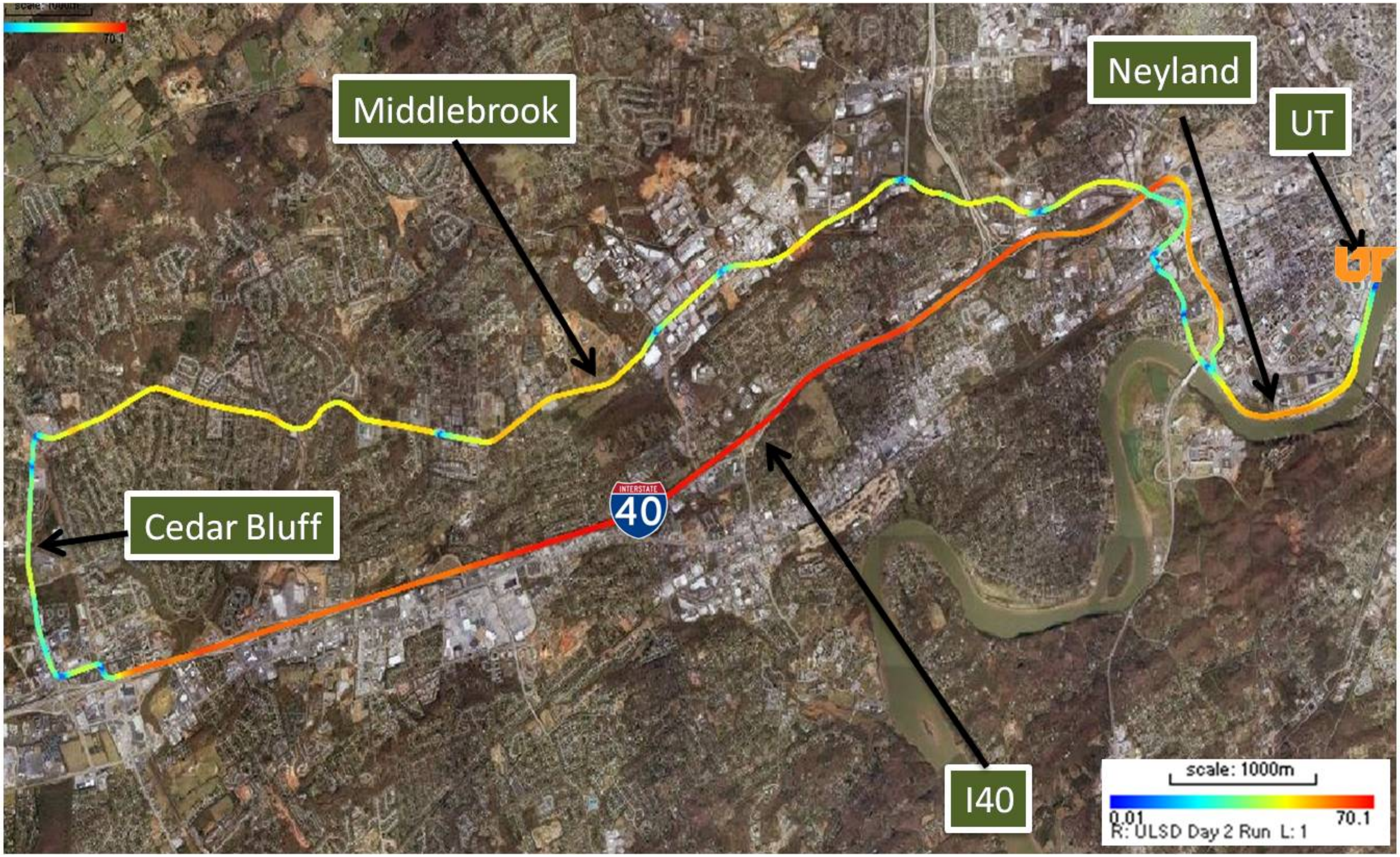


Figure 15. UTK Drive Cycle Route - Route colored based on speed

Fueling Procedure

All biodiesel used in this study was produced by the UT Biodiesel processor from used frying oil produced from a single batch whose properties are shown in Appendix V. All ULSD used was purchased from a single local retailer. To mix the biodiesel blends, a graduated cylinder was used to measure out the volumes needed to make each blend. The same 1 liter capacity graduated cylinder was used to make all volumetric fuel measurements. Each fuel was stored in new HDPE DOT approved fuel containers.

During each fuel change, the secondary fuel tank was completely drained. A half of a gallon of the fuel to be tested was then added to the tank, sloshed around and drained again. The low pressure fuel pump was then used to clear the fuel lines of the previous fuel. The fuel to be tested was then circulated through the fuel system using the low pressure pump. The fuel tank with the new fuel was then installed in the vehicle. A warm up cycle consisting of a 10 minute idle followed by a three minute high speed high load drive was used to clear the high pressure common rail system of all of the previous fuel.

Testing Procedure

On Road Emissions

For each new fuel tested, the fueling procedure was followed as prescribed in the Fueling Procedure section above. The AEA was installed and allowed to zero and warm up as the user instructions prescribed. Before each test the vehicle was started and allowed to idle for 10 minutes to allow engine operating temperature to stabilize and help bring the oxidation catalysts up to the operating temperature.

Initially the five- gas analyzer was calibrated using calibration gas supplied by the manufacturer of the analyzer. The specifications of the calibration gas are presented in Appendix VII. The water filter for the unit was replaced with a new filter originally supplied with the kit. The analyzer was then run through a leak test that the AEA performed automatically. The calibration and leak test both passed.

To run each test the 5 gas analyzer was turned on and allowed to warm up. The AEA would then zero the analyzer with the sampling port removed from the tailpipe. The sample tube was installed in the exhaust pipe and secured. The warm vehicle was driven to the start of the drive cycle. The emissions analyzer and the DL1 were put into data logging mode at the same time and allowed to log 10 seconds of idling and then the drive cycle was started. When the drive cycle ended both the analyzer and DL1 were stopped and the data were transferred to another computer. The vehicle was idled for 10 minutes before the second test was run.

The AEA can calculate humidity corrected NO_X values given the current temperature, humidity and barometric pressure. Before each run the local conditions were taken from weather.com and entered into the user interface. Corrected NOX values are required for the California BAR 97 test. It is well known that NO_X emissions decrease as humidity increases (67). The standard correction factor used for BAR 97 is shown in Appendix VIII.

The UTK drive cycle was followed with the air-conditioner always running to ensure a consistent load on the engine during all tests and to better represent real world driving. The shift schedule for driving was to drive at constant speeds at 2000 RPM, upshift at 2500 RPM and downshift at 2000 RPM. The engine was idled when coming to a stop when the engine speed reached 1000 RPM in second gear.

Tire pressure was maintained at 32 psi in each tire during the testing to ensure that the drag forces due to tire friction were constant during all tests. Tire pressure was monitored using a Smart Tire wireless tire pressure monitoring system used as part of Challenge X. To avoid heavy and unpredictable traffic conditions, tests were not performed during the morning commute, lunch or evening commute times.

Smoke Test

For the stationary smoke test, the fueling procedure was followed when changing test fuels. The engine was required to be warmed up using the previously described procedure. The smoke meter was calibrated using a neutral density filter provided as part of the smoke meter package. The smoke meter was turned on and the engine details such as idle speed, maximum governor speed, engine power and that the engine was turbocharged were entered into the dialog box of the user interface. The smoke meter resets the hardware before each test and zeros the smoke meter as well. After zeroing, the smoke head was installed into the exhaust and secured using the provided clamp.

The on-screen instructions tell the operator to either idle the engine or rev the engine to the maximum governor speed. A timer tells the operator how long each phase of the test should last. The test is repeated three times and the computer records average opacity to compare to the federal standards and provides the results of each run (60).

SECTION V

RESULTS

Overview

The results of the on-road emissions testing with the reference ULSD fuel and the biodiesel blends are presented here. The results for the smoke opacity tests are also presented. For the on-road emissions tests, the repeatability of each test was also examined and the plots comparing the runs are presented in Appendix XIII.

On Road Data

For the on-road emissions testing, two tests were conducted. The first test evaluated each of the biodiesel blends over two tests repeated back to back. The first test (Test 1) examined B100 first, B50 and then B20. The second test (Test 2) evaluated each fuel with one road test per fuel. The second test examined B20 first, B50, B100 and ULSD last. The same fueling procedure, warm up procedure and drive cycle instructions were used for both tests. Each test was performed over the span of a single day, but on different days.

The following section presents the emissions plots for both tests. The average and maximum values are also presented in graphical form and an interpretation of the results is provided. The results for Test 1 and Test 2 are presented independently in the following section.

Test 1 Summary

For each fuel, the on-road emissions testing was conducted twice to ensure that driver repeatability over the course and local traffic patterns do not overly affect the results. This also allowed the emissions results of the fuels to be compared to make sure that the data for each fuel matched for both runs. Test 1 only evaluated the biodiesel blends.

The hydrocarbon reading for this test was high during each fuel change and a gurgling sound was audible from the sample probe indicating condensation was building up in the line and sample probe. The humidity was high for the tests and fog was visible for the early tests. The first B20 test was conducted at the end of the evening commute and a stall on I-40 occurred. This will be discussed later.

The temperature, humidity, pressure and ambient hydrocarbon readings were taken before each test and are shown in Table 7. The residual hydrocarbon reading was recorded before each run since the AEA started reading higher ambient hydrocarbons than expected after zeroing. This phenomenon is explained further in this section and fully in Appendix XI.

Table 7. Ambient Weather Conditions For Test 1

Test	Time	Humidity (%)	Temp (°F)	Pressure (in Hg)	HC (ppm)
B100 Run 1	9:30 am	94	56	29.89	4
B100 Run 2	10:30 am	90	59	29.91	13
B50 Run 1	2:45 pm	84	63	29.85	21
B50 Run 2	3:30 pm	92	60	29.82	32
B20 Run 1	5:30 pm	93	59	29.81	17
B20 Run 2	6:15 pm	94	59	29.79	17

Test 1 NOx

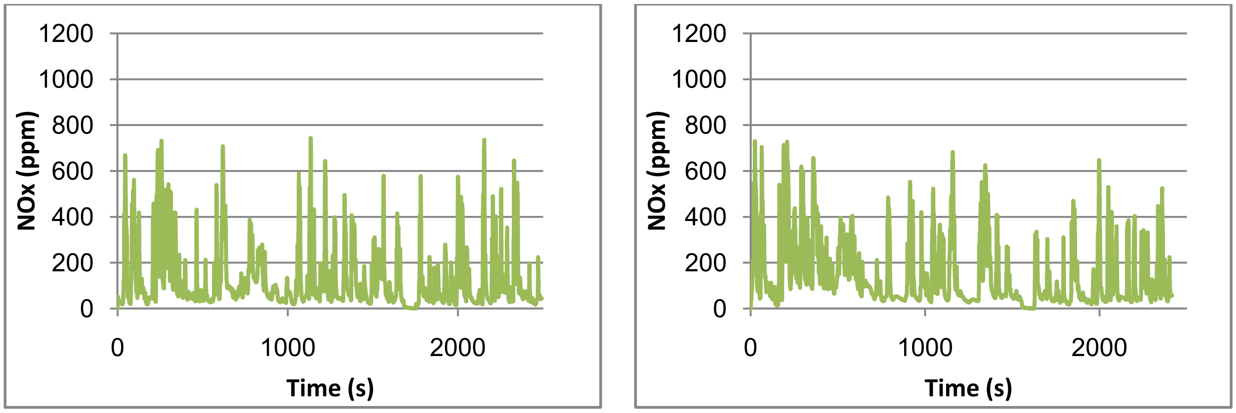
Since the normal measure of grams per mile is not used for comparison, other characteristics of the data can be used to compare the relative NO_X performance of each of the test fuels. The maximum and average values of NO_X emissions were examined. The number of peak values that were above a certain value was also evaluated. The plots of NO_X versus time are examined for trends. The values here are raw NO_X values that are not corrected for temperature and humidity as well as the humidity corrected NO_X values.

Figure 16 shows the plots of NO_X versus time for each of the runs and Figure 17 shows the humidity corrected NO_X results. The AEA software applies a correction factor to the NO_X results based on relative humidity and temperature of the ambient air (58).

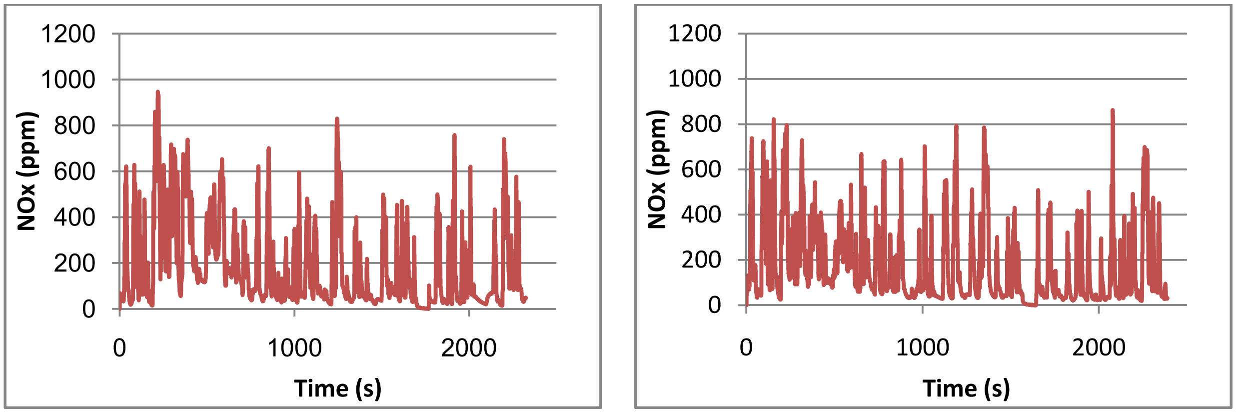
Figure 18 shows the absolute maximum NO_X values for each biodiesel blend. The uncorrected values are to the left and in color while the humidity corrected values appear on the right in grey. The average NO_X values for each run are presented in Figure 19 in the same format as the maximum values.

The number of peaks beyond each threshold ppm is presented in Figure 20 for NO_X and in Figure 21 for humidity corrected NO_X. Figures 20 and 21 show all of the fuels and each of the runs on the same plot.

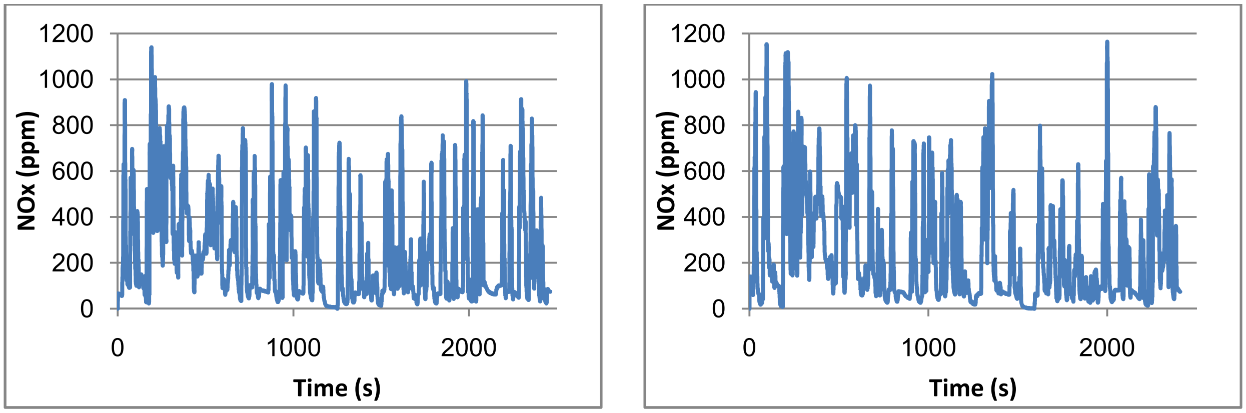
Test 1 NOx Plots



B20 Run 1 B20 Run 2



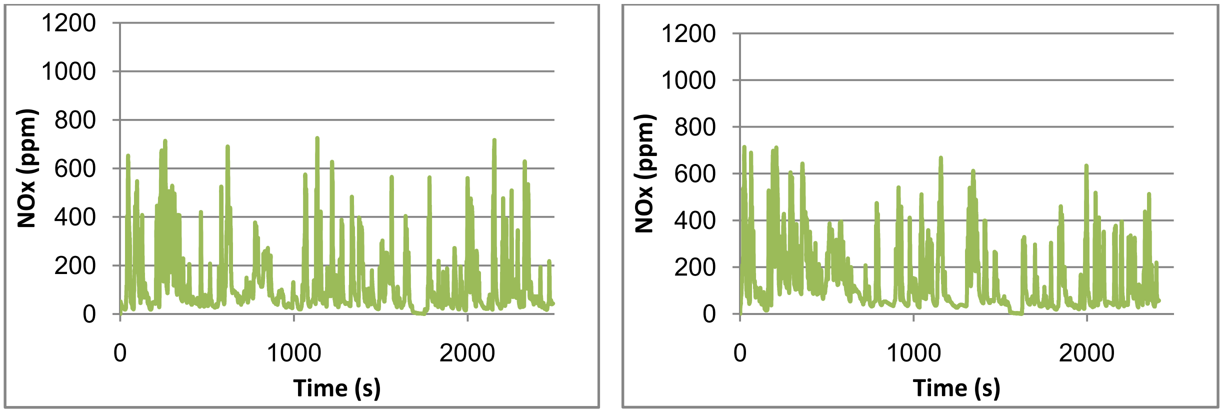
B50 Run 1 B50 Run 2



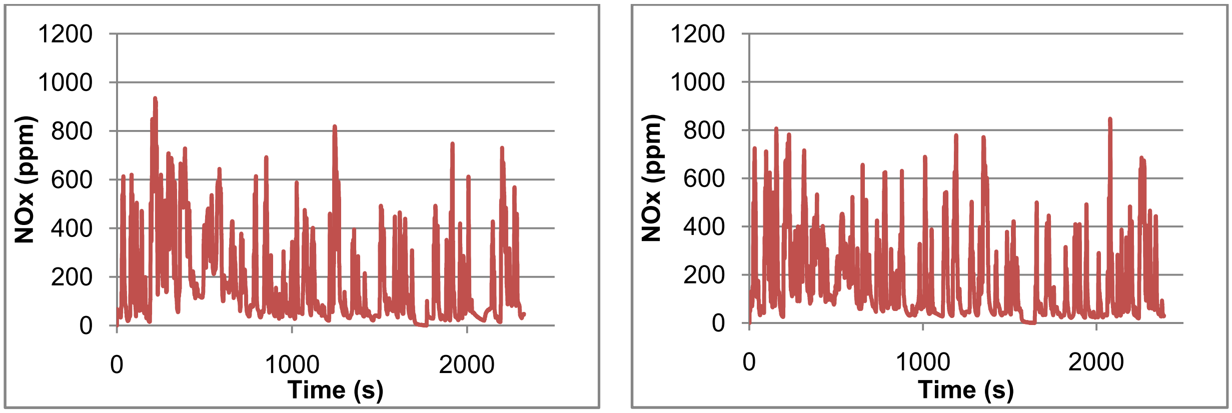
B100 Run 1 B100 Run 2

Figure 16. NOx Versus Time For Each Run In Test 1

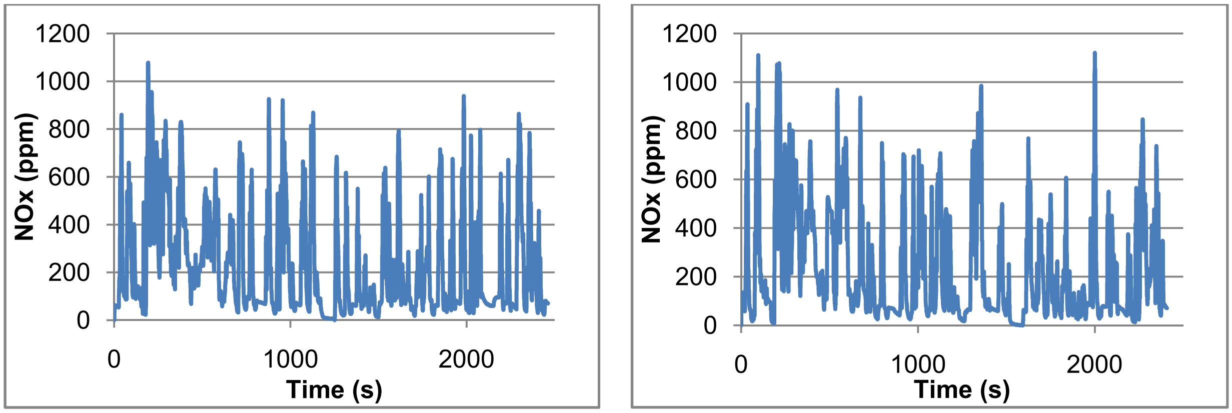
Test 1 Humidity Corrected NOx



B20 Run 1 B20 Run 2



B50 Run 1 B50 Run 2



B100 Run 1 B100 Run 2

Figure 17. Humidity Corrected NOx Versus Time For Test 1

Test 1 Maximum and Average NOx

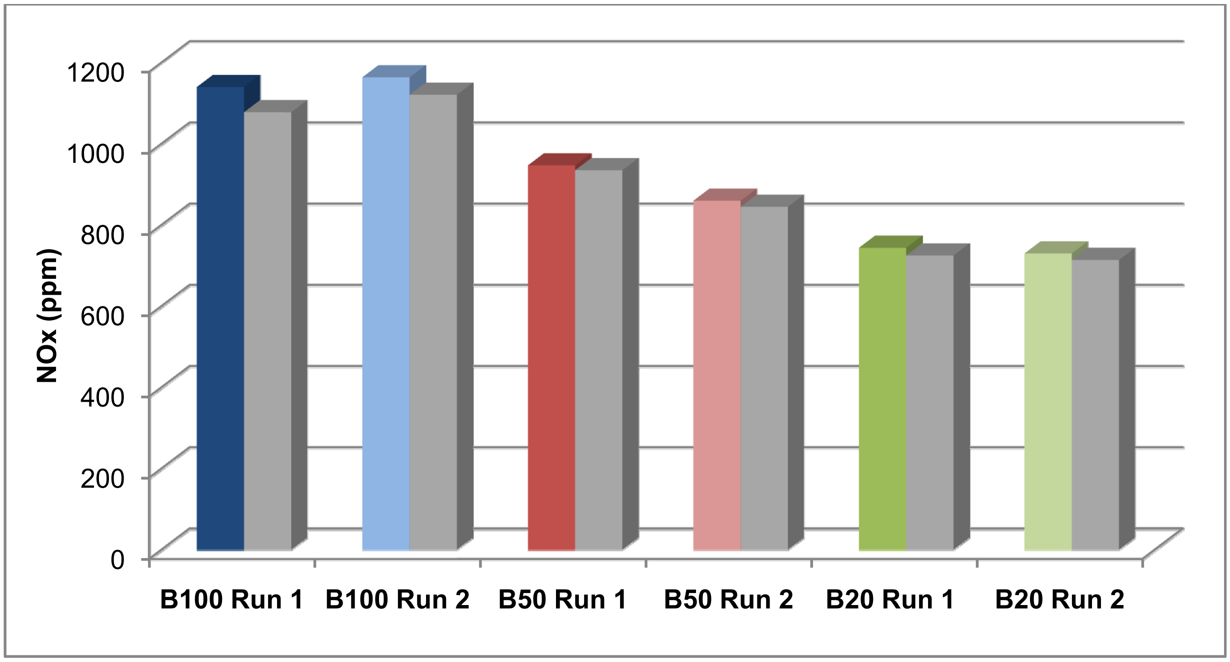


Figure 18. Maximum NOx For Test 1 (Humidity Corrected Values in Grey)

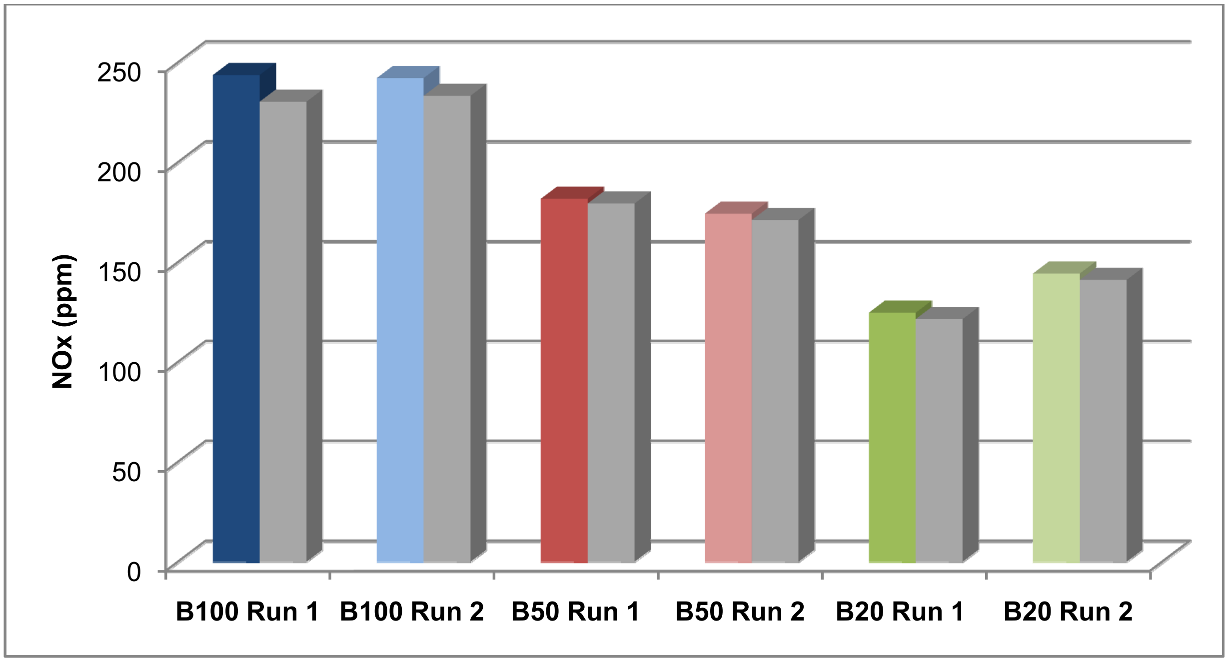


Figure 19. Average NOx For Test 1 (Humidity Corrected Values in Grey)

Test 1 NOx Frequency

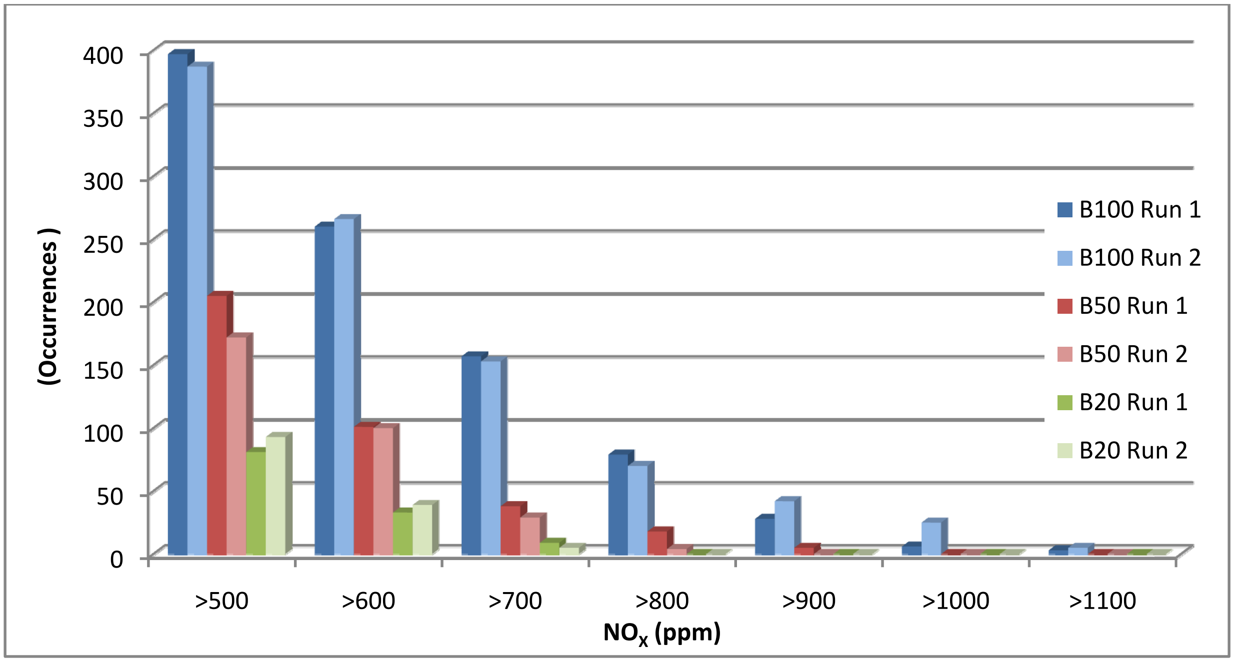


Figure 20. NOx Maximum Frequency For Test 1

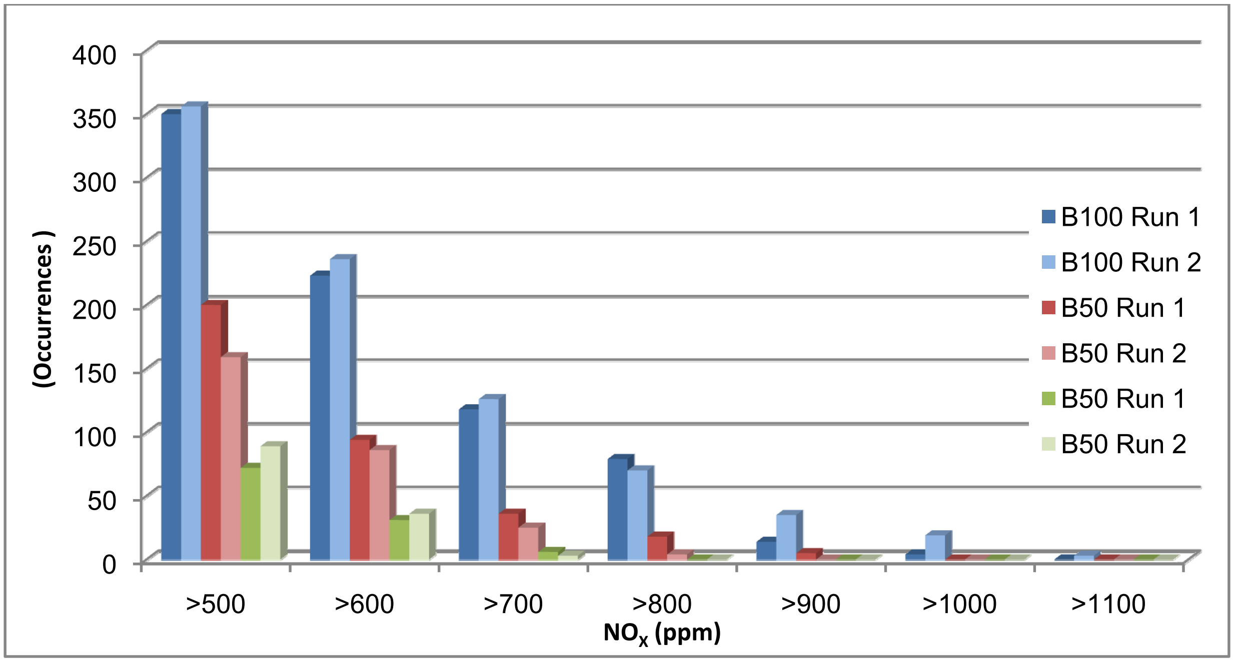


Figure 21. Humidity Corrected NOx Maximum Frequency For Test 1

The plots in Figures 15 and 16 show that as the biodiesel content is increased, the peak NO_X goes up which is in agreement with the general trend of previous studies. The difference between the B100 plots and the B50 and B20 plots is striking. The B50 plots and the B20 do not have as obvious of a difference. On a closer look the maximum NO_X values for the B100 runs were 1140 ppm and 1164 ppm while the maximum values for B50 were 947 ppm and 860 ppm and the for B20 the maximum values were 744 ppm and 730 ppm.

The same trend was seen for the humidity corrected NOX values. The average NOX and average humidity corrected NOX shown in Figures 18 and 19 show the same trend. The number of peaks that exceeded certain levels shows that B100 had more peaks in the higher ppm levels than B50 and B20.

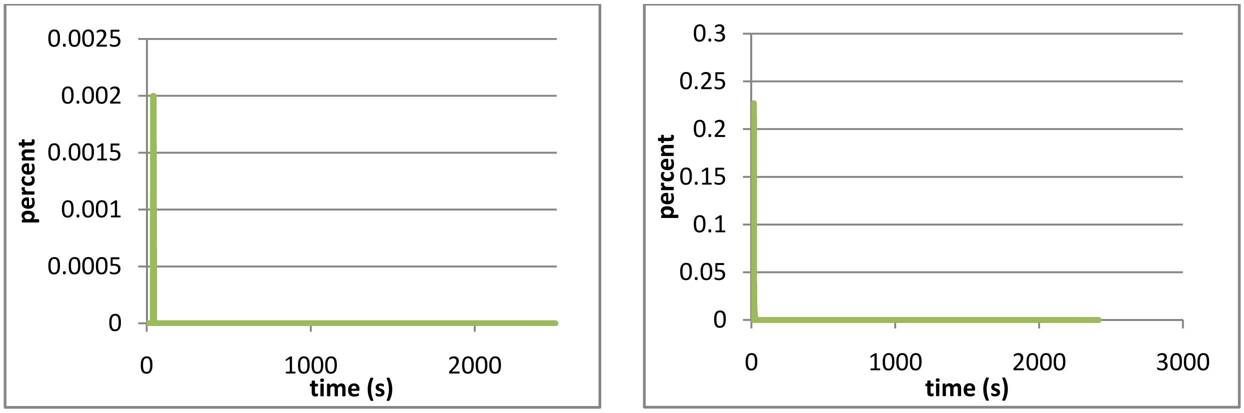
The runs for each fuel show good repeatability. The drop in NOX for B50 run 2 can be attributed to 8% increase in humidity and 3 degree drop in temperature. The lower average NOX in B20 run 1 can be attributed to the long period of traffic standstill on I-40. This is seen around the 500 second mark. The humidity was actually 1 % higher with the same temperature compared to the second B20 run.

Test 1 CO

The plots for CO are presented in Figure 22 in varying scales since the CO results varied greatly in magnitude. All plots show approximately zero CO with a few spikes which could be attributed to instrument error.

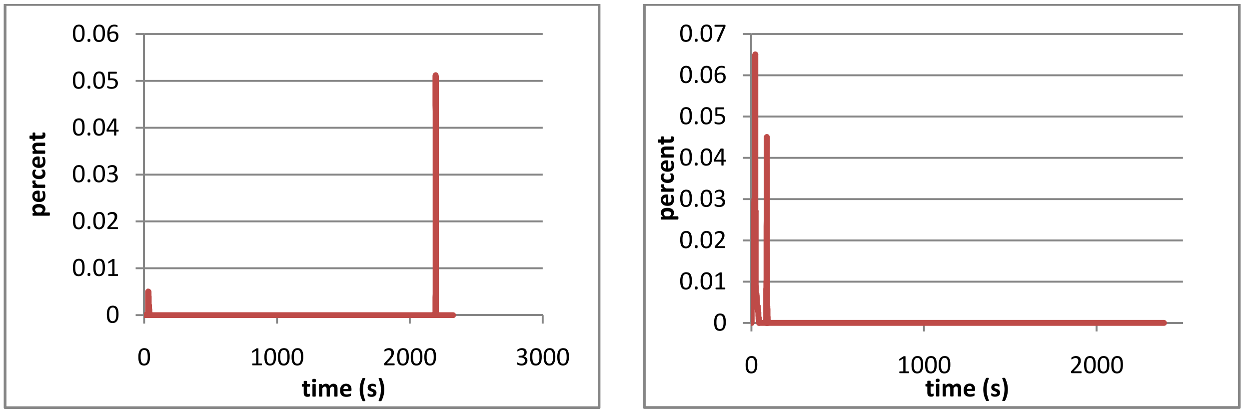
Maximum CO values are presented in Figure 23 and the averages are presented in Figure 24. The results show that CO production is insignificant for CI engines and it is difficult to show differences between the fuels with equipment used.

Test 1 CO Plots



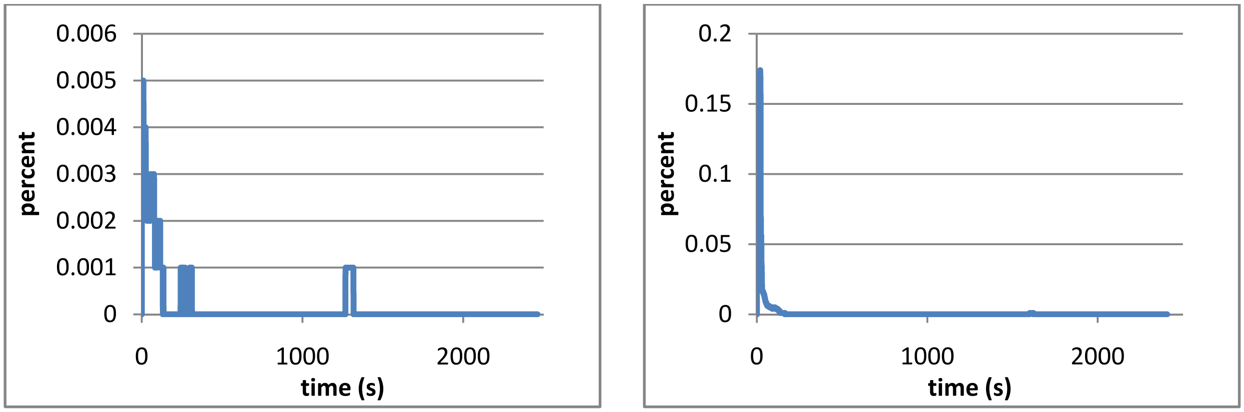
B20 Run 1

B20 Run 2



B50 Run 1

B50 Run 2



B100 Run 1

B100 Run 2

Figure 22. Carbon Monoxide Versus Time For Test 1 (Not on same axis scale)

Test 1 CO maximums and averages

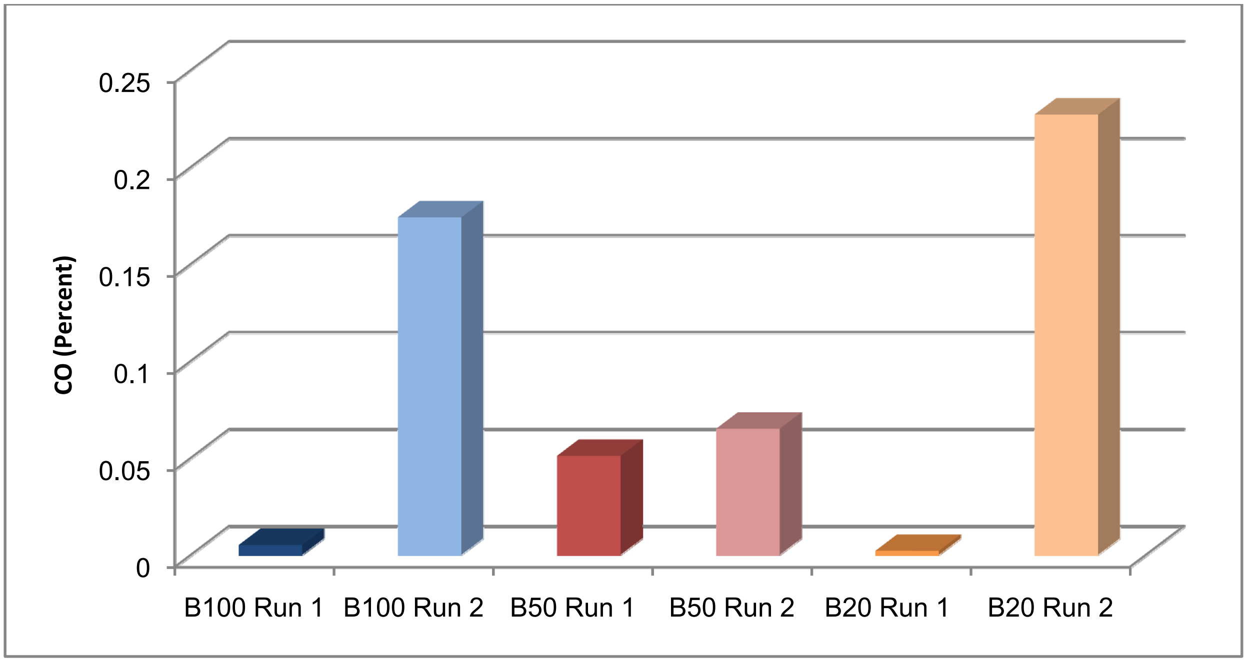


Figure 23. Maximum CO Values For Test 1

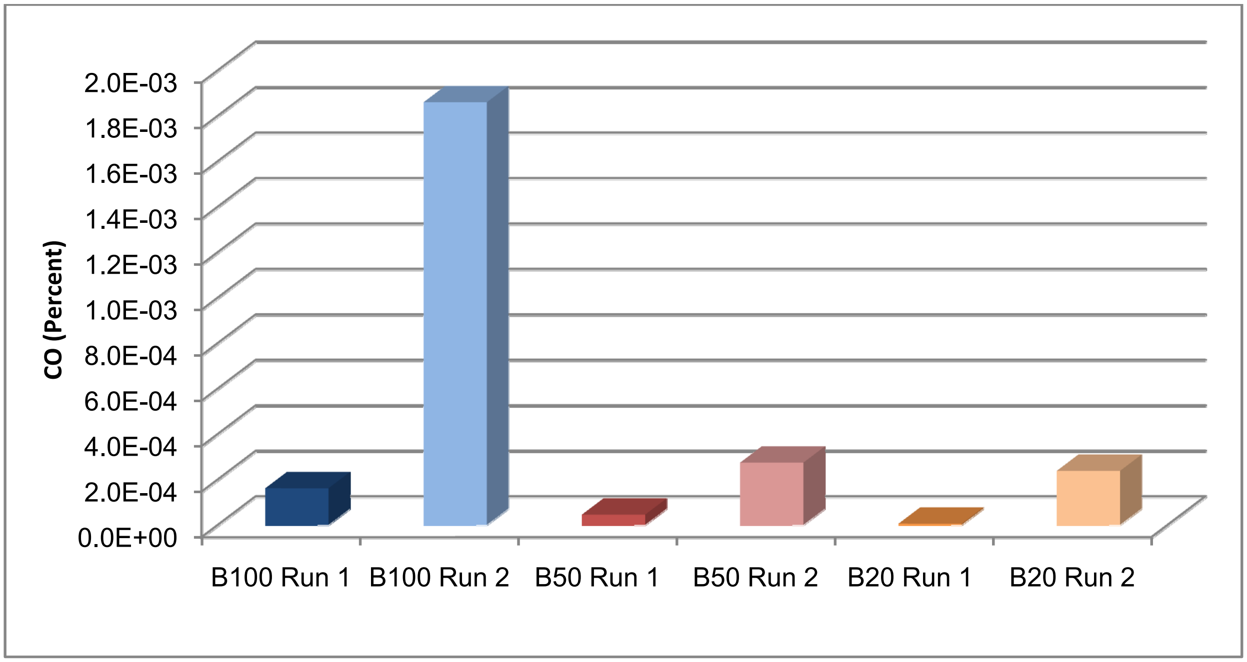


Figure 24. Average CO For Test 1

Test 1 HC

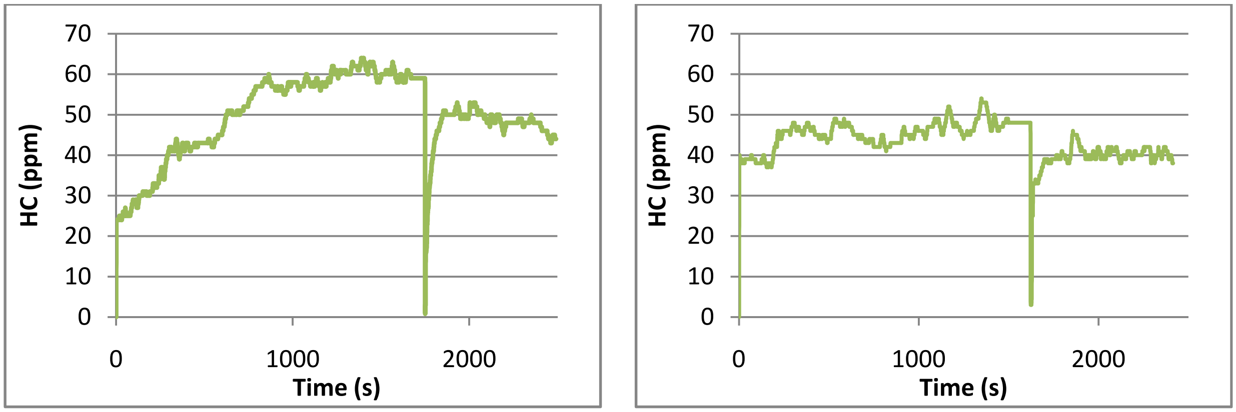
There were problems with residual hydrocarbon readings with test 1 which are discussed further in Appendix XI. Even though the sample probe was removed from the tail pipe at the end of each run and the AEA unit was zeroed, there were still high residual hydrocarbon readings. The residual hydrocarbon was highest for run 2 with B50 at 32 ppm.

Figure 25 shows all of the hydrocarbon plots for each run, Figures 26 and 27 show the maximum hydrocarbon readings and average hydrocarbon readings respectively. There is a point somewhere between 1000 and 2000 seconds where the AEA goes through an automatic zero during each run.

The hydrocarbon readings appear to have decreased with the amount of biodiesel in the first test. This result is expected from previous studies, but the effect of condensation in the sample line may mean that no conclusions are able to be drawn from the data. The fact that for both the B100 run and the B50 run, the second test showed higher max and average HC readings indicates that the residual hydrocarbon reading may have skewed the test. The residual hydrocarbon readings make these results somewhat suspect since the hydrocarbon readings went up as the day progressed, the order of tests was B100 first, B50 and then B20.

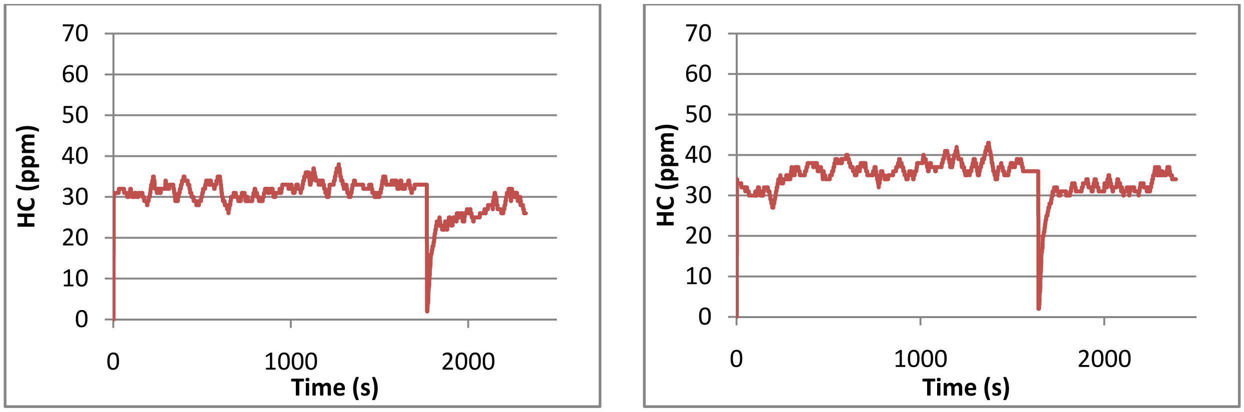
The residual HC reading for the B20 was 17 ppm for both tests but for B100 the residual hydrocarbon increased 225% for B100 from run 1 to run 2. For B50 the residual hydrocarbon reading increased 52% from 21 ppm to 32 ppm. The plot for the first B20 run shows a climbing hydrocarbon reading which makes the plot suspect. The plot is still presented for demonstration.

Test 1 HC Plots



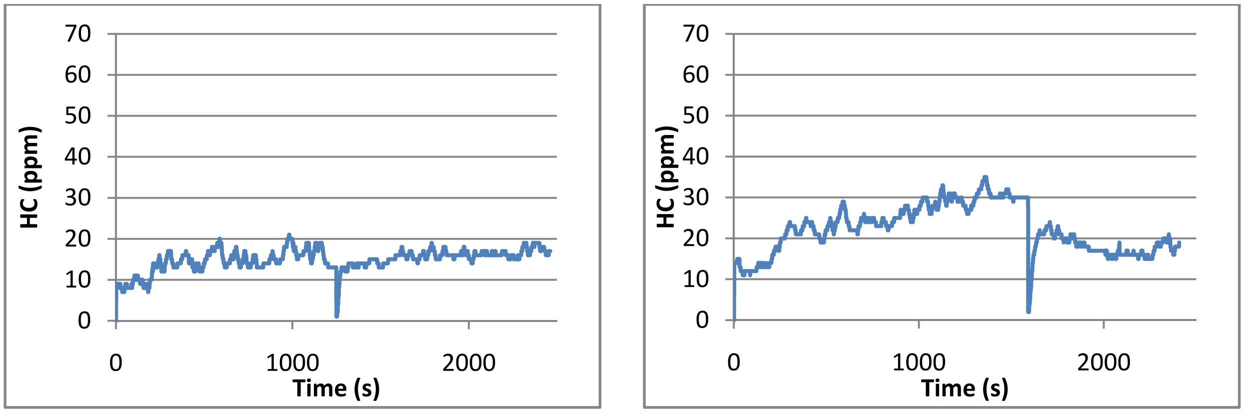
B20 Run 1

B20 Run 2



B50 Run 1

B50 Run 2



B100 Run 1

B100 Run 2

Figure 25. Hydrocarbons Versus Time For Test 1

Test 1 HC Maximum and Average

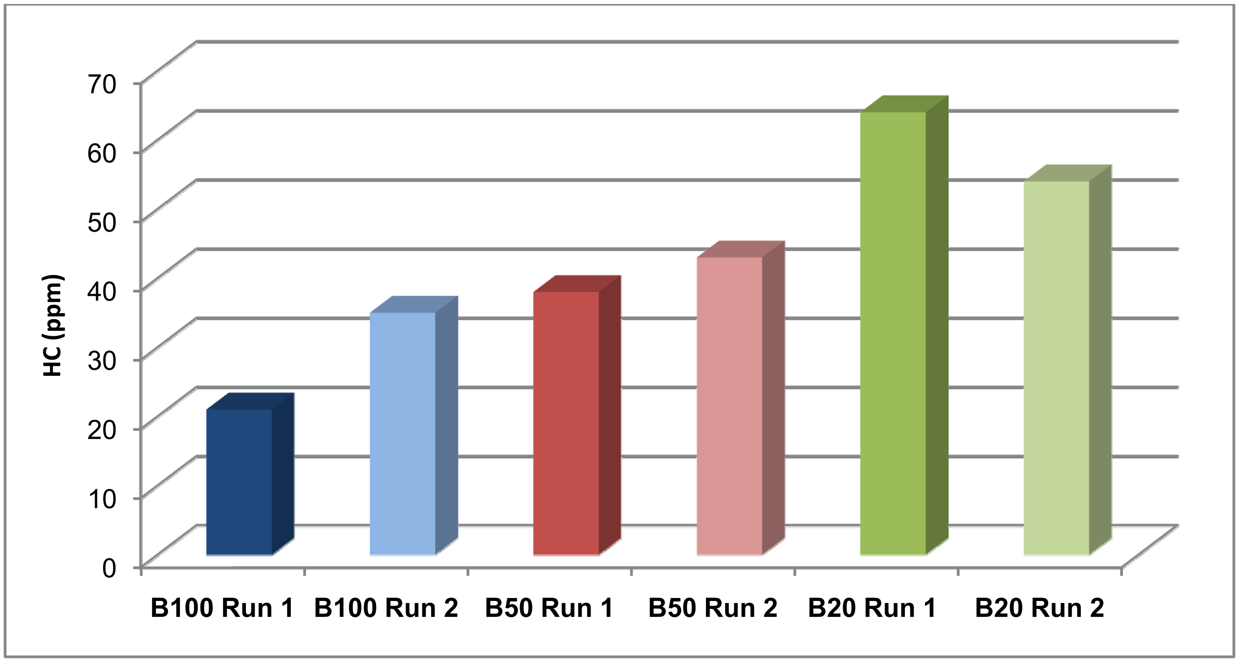


Figure 26. Maximum Hydrocarbon Emissions For Test 1

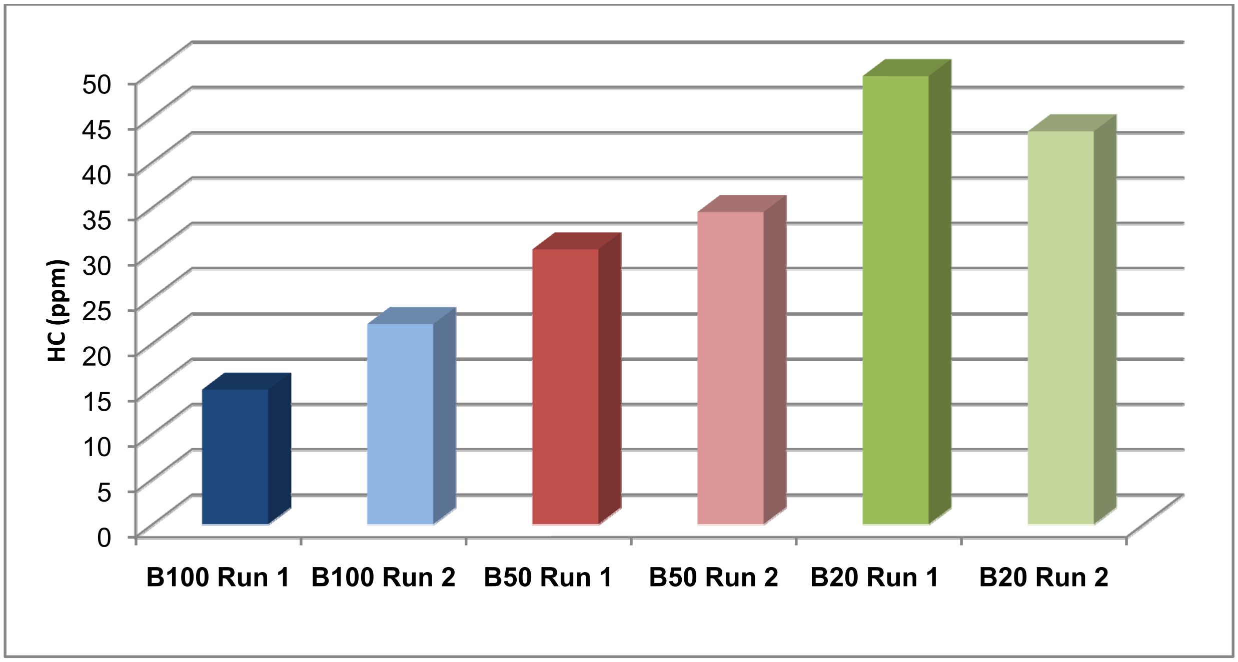


Figure 27. Average Hydrocarbon Emissions For Test 1

Test 2 Summary

The second test started with cleaning the AEA to eliminate the high residual hydrocarbon readings and the gurgling sound from the sample probe. There was a significant amount of liquid condensation in the sample probe, sample line and in the intake tubes in the AEA internals. The inline filters were changed and compressed air was used to remove the water. The sample probe was disassembled and cleared with compressed air before all runs except the B50 test. The results of the cleaning are discussed fully in Appendix XI. The temperature, humidity, pressure and hydrocarbon readings were taken before each test and are shown in Table 8.

It should be noted that the weather conditions for Test 2 were different than Test 1. The wind speeds during the second test were noticeable higher than the first test so the wind speed data was also recorded for the second test. High wind speeds could cause higher power requirements for the vehicle. The temperatures were colder than for the first test and the humidity was lower.

Table 8. Ambient Weather Conditions For Test 2

Test	Time	Humidity (%)	Temperature (°F)	Pressure (In Hg)	Wind speed (mph)	HC (ppm)
B100	3:40 pm	64	51	29.8	15	6
B50	2:08 pm	66	52	29.8	17	15
B20	12:42 pm	83	52	29.7	17	3
ULSD	5:20 pm	68	47	29.8	11	3

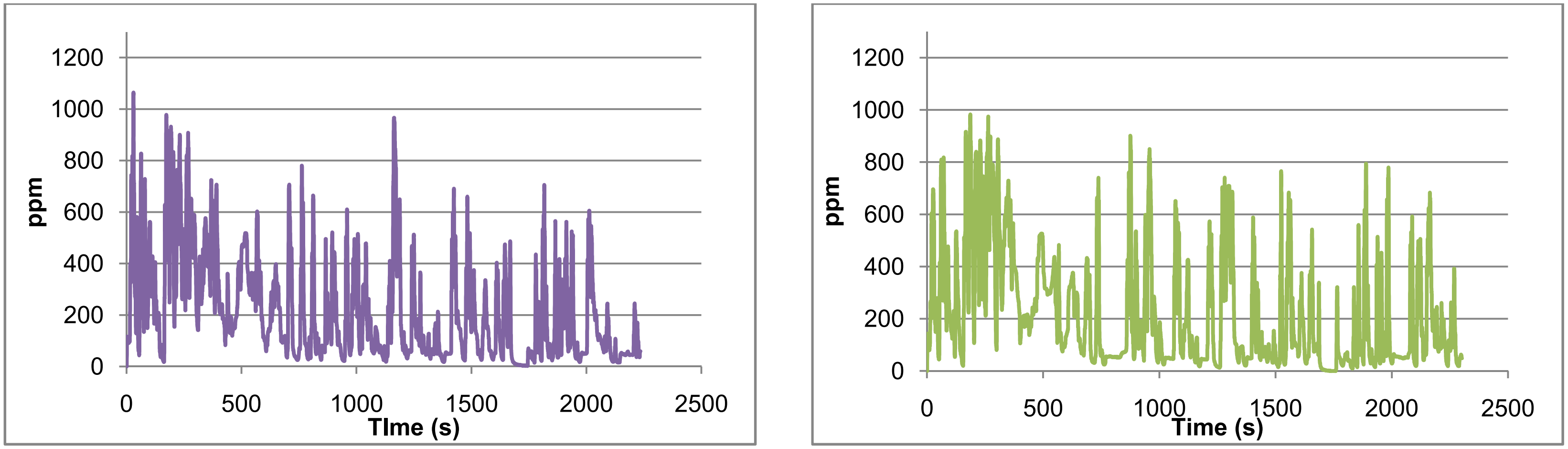
Test 2 NOx

Figure 28 shows the plots of NO_X versus time for each fuel in Test 2. Figure 29 presents the humidity corrected NO_X values over time. Figure 30 shows the maximum NO_X values for each biodiesel blend. The uncorrected values are to the left and in color while the humidity corrected values appear on the right in grey. The average NO_X values for runs are presented in Figure 31 which shows both NO_X and humidity corrected NO_X. The number of peaks beyond each threshold ppm is presented in Figure 32 for NO_X and in Figure 33 for humidity corrected NO_X.

The NO_X results are not so clear cut for the second test by looking at the maximum and average NO_X graphs in Figures 30 and 31 respectively. The maximum uncorrected NO_X for ULSD actually shows an increase compared to the biodiesel blends. This could be just an unexpected spike in NO_X, since the other measures show the expected trend. The average NO_X shows the expected trend of increasing NO_X with biodiesel content. The results for B50, B20 and ULSD are actually quite similar with the average for B50 only 6.2% higher than ULSD and 8.6% higher for humidity corrected NO_X. The average for B100 compared to ULSD was 40 % higher for NO_X and 41.2% for humidity corrected NO_X.

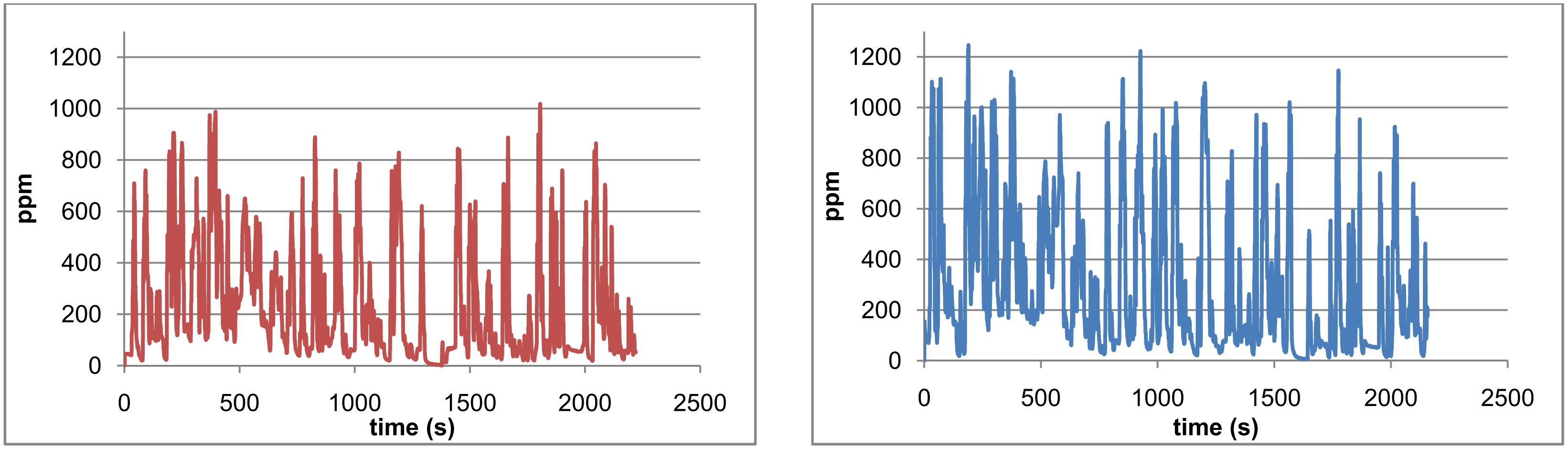
The frequency plots in Figures 32 and 33 show the expected trend of higher NO_X for increasing biodiesel content. The humidity corrected NO_X plot in Figure 33 shows an unexpected increase in NO_X for B20 compared to B50. The humidity for the B50 test had dropped 15% with no change in temperature. The plots also show that even though ULSD had a higher peak than B20, the frequency of high NO_X values was lower.

Test 2 NOx



ULSD NO_X

B20 NO_X

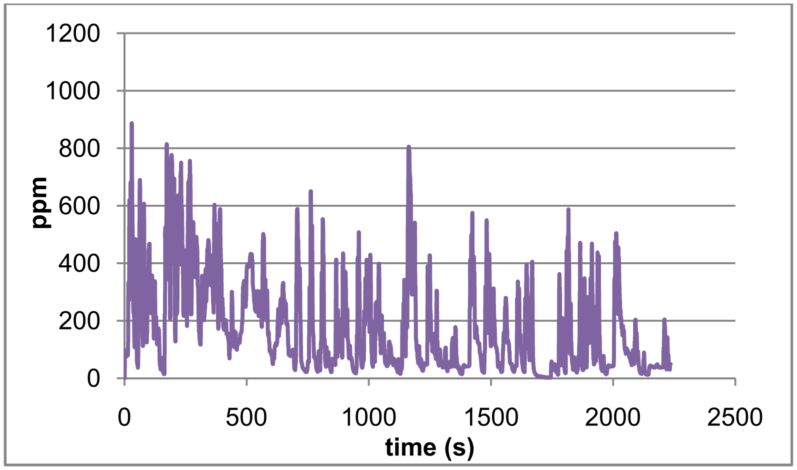


B50 NO_X

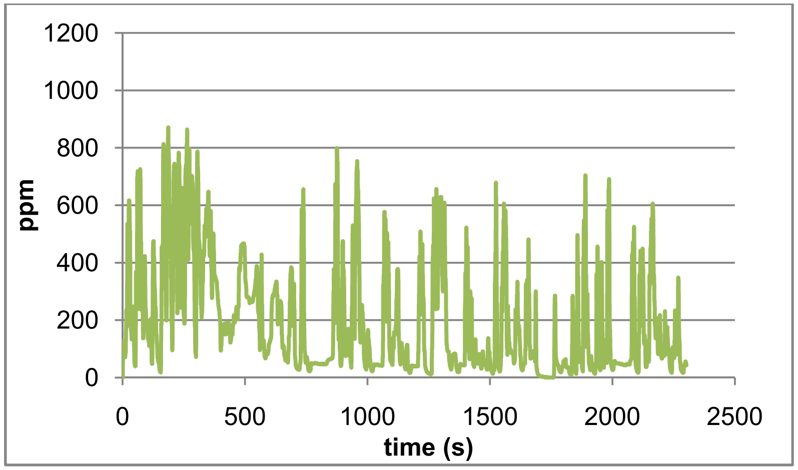
B100 NO_X

Figure 28. NO_X Versus Time For Each Fuel In Test 2

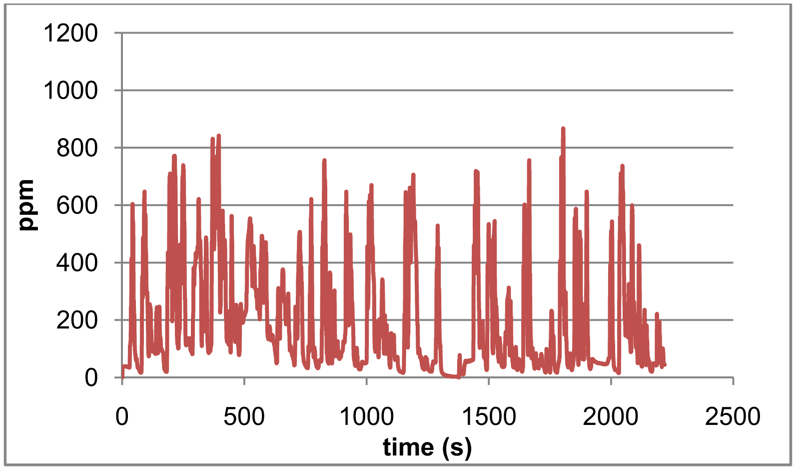
<u>Test 2 NOx Corrected</u>



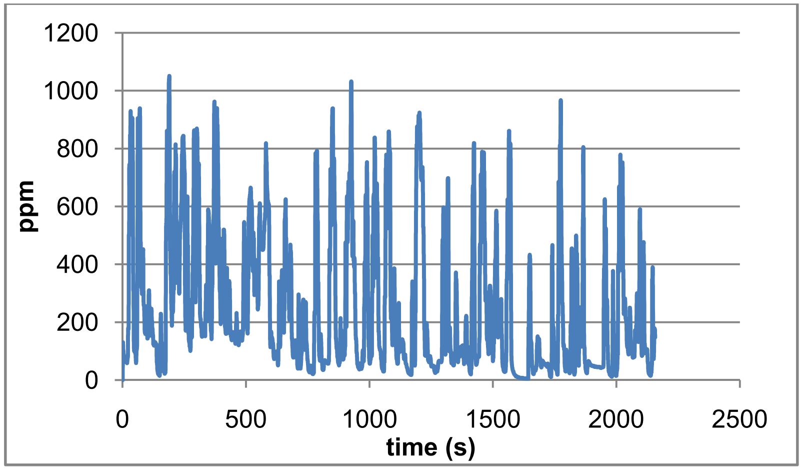
ULSD NO_X Corrected



B20 NO_X Corrected



B50 NO_X Corrected



B100 NO_X Corrected

Figure 29. Humidity Corrected NOx Versus Time For Each Run In Test 1

Test 2 Maximum and Average NOx

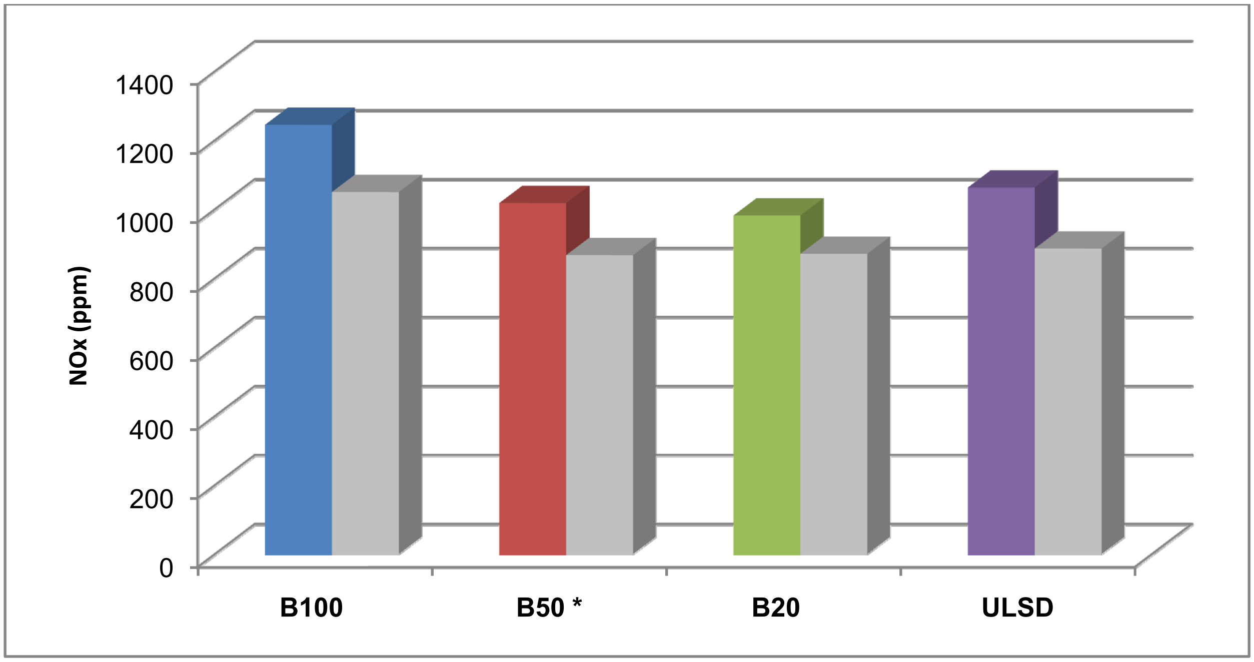


Figure 30. Maximum NOx Value For Each Fuel in Test 2 (Humidity Corrected Values in Grey)

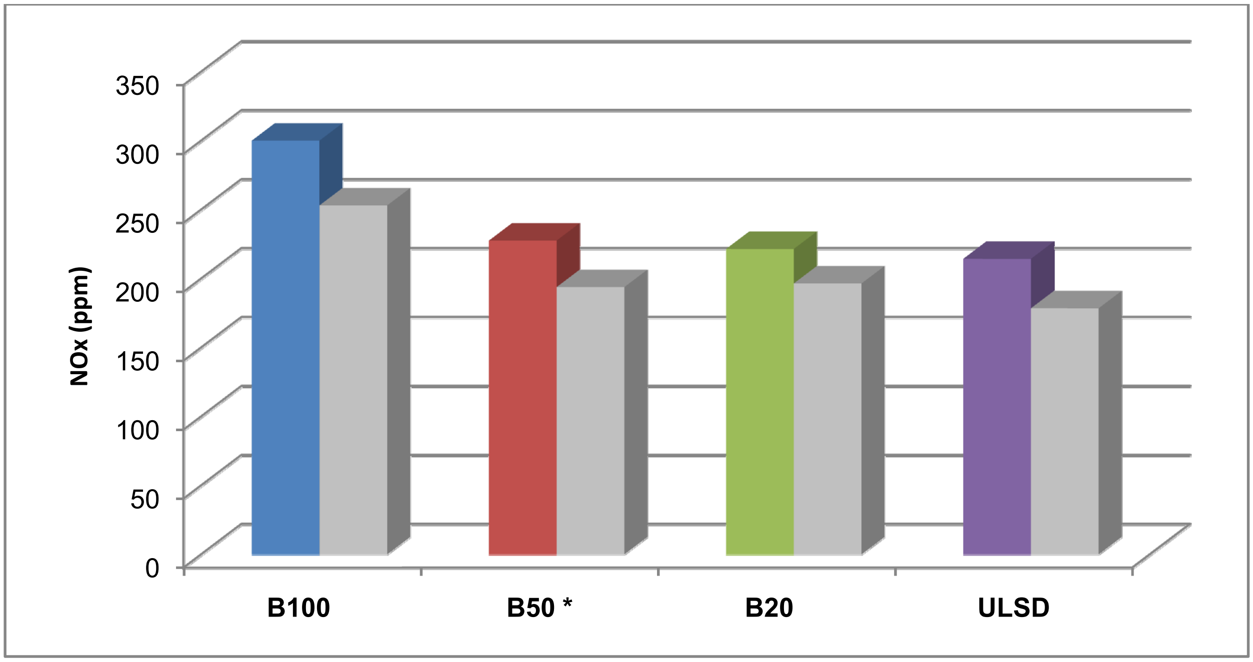


Figure 31. Average NOx For Each Fuel in Test 2 (Humidity Corrected Values in Grey)

Test 2 NOx Frequency

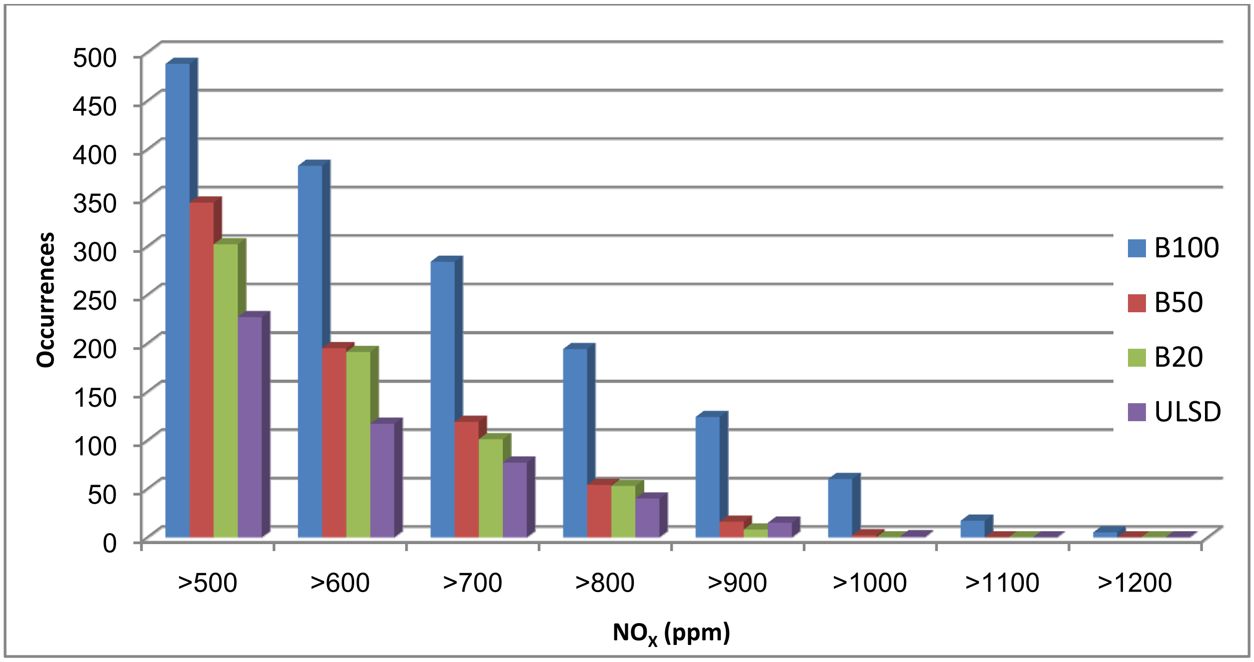


Figure 32. NOx Maximum Frequency For Test 2

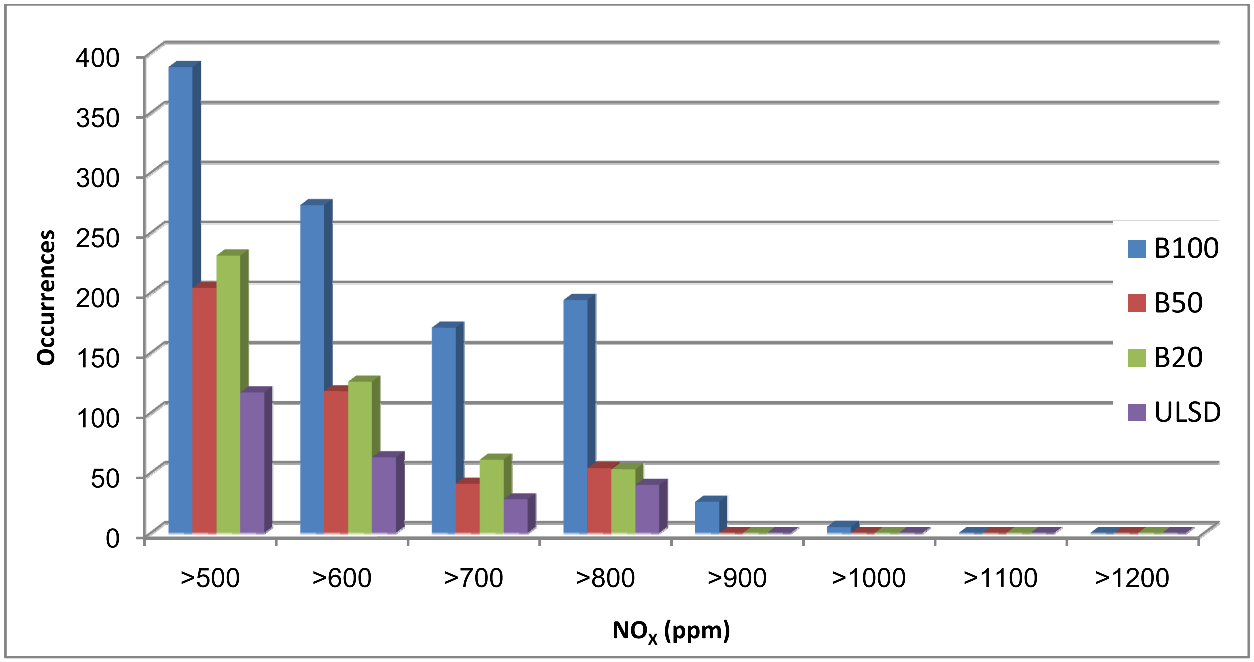


Figure 33. Humidity Corrected NOx Maximum Frequency For Test 2

Test 2 CO

The maximum CO emissions for Test 2 are shown in Figure 34. The average CO is so dominated by the maximum CO peaks that the relative emissions appear the same. The plots for CO for each fuel in Test 2 are shown in Figure 35.

The graph for the B50 peaks at 0.008 ppm which is most likely just noise. There was very little CO produced for any of the fuels. For the ULSD and B20 tests an expected spike in CO occurs when the test was begun. The test with B100 also had a large CO peak at the beginning of the test. As was the case for Test 1, it does appear that there are random peaks throughout the tests. These random peaks could just be characteristic of NDIR sensor in the AEA since the sensor has a very short path length.

As seen in Test 1, it is again obvious that CI engines produce insignificant amounts of CO. The low CO emissions along with the low sensitivity of the AEA's NDIR make CO comparison difficult.

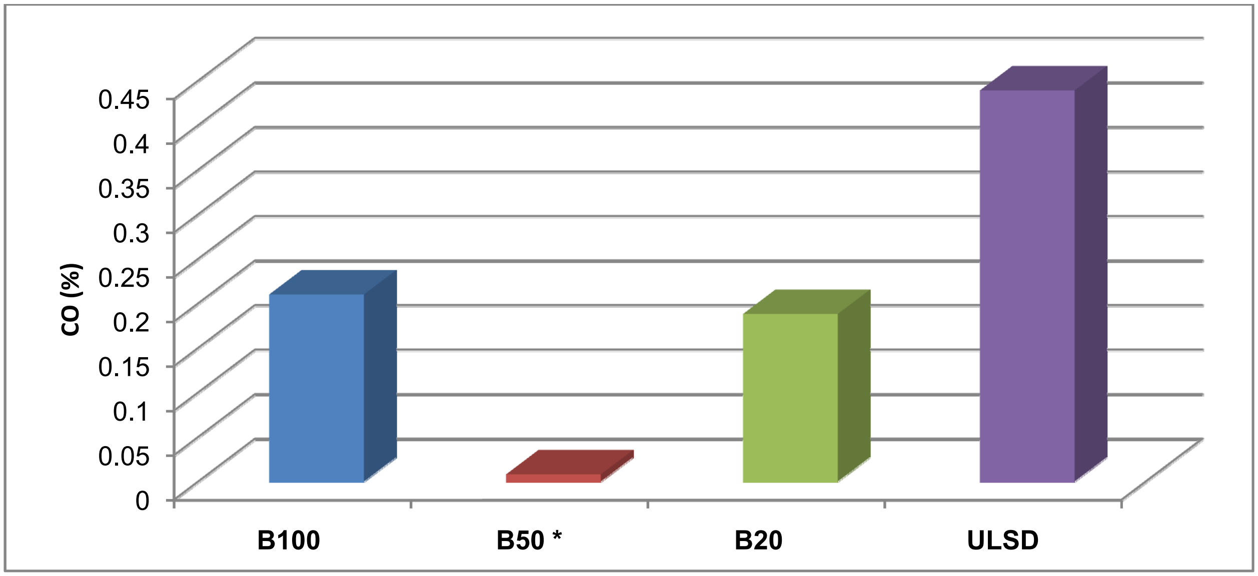
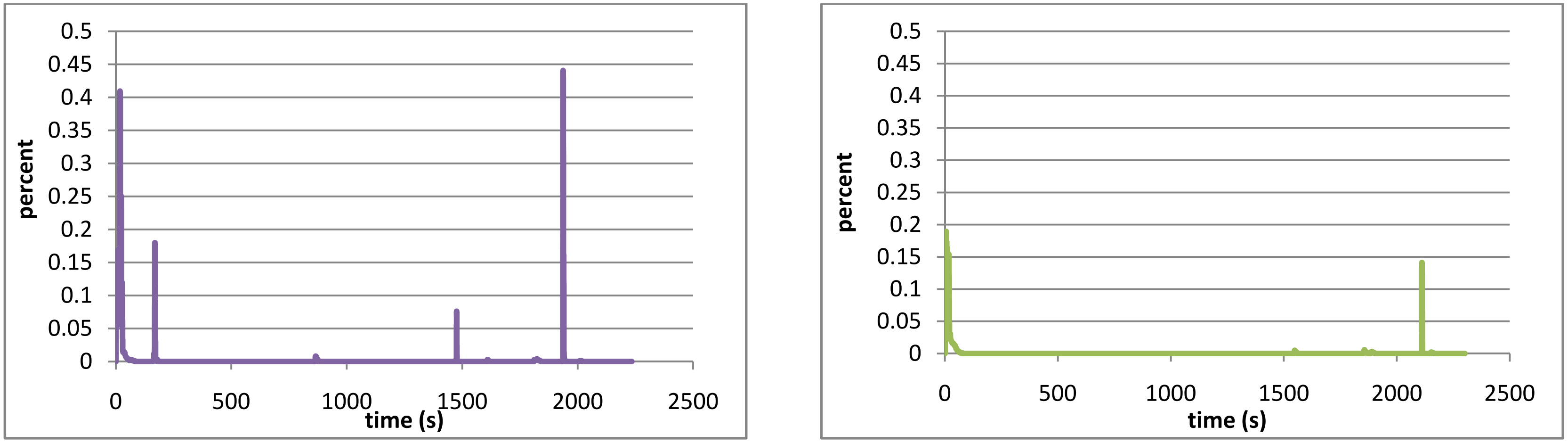


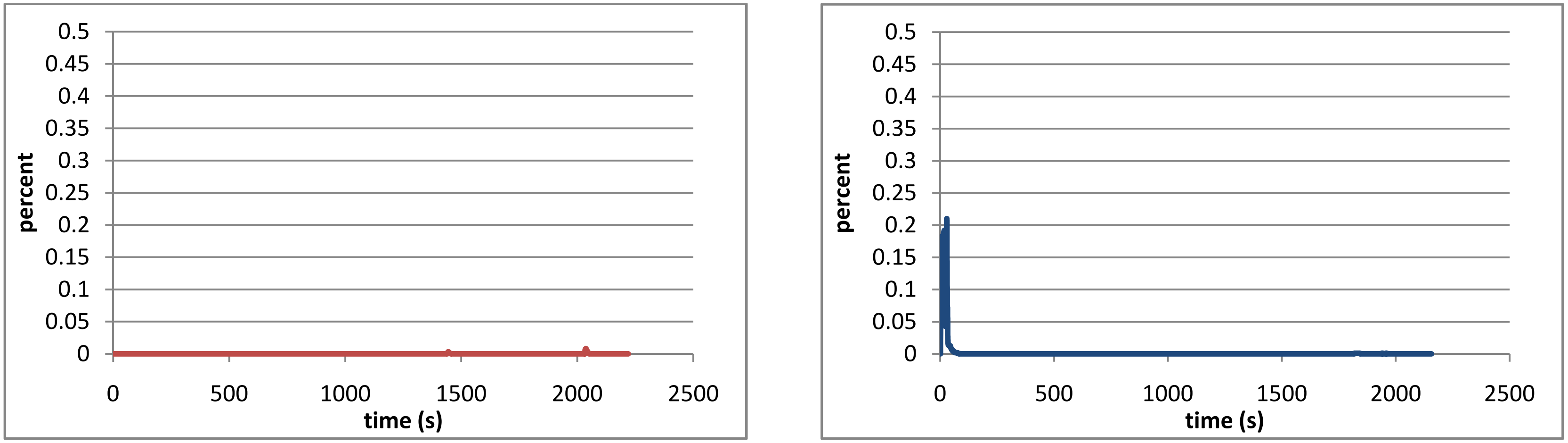
Figure 34. Maximum CO Emissions For Test 2

Test 2 CO Plots



ULSD CO

B20 CO



B50 CO

B100 CO

Figure 35. CO Versus Time For Test 2

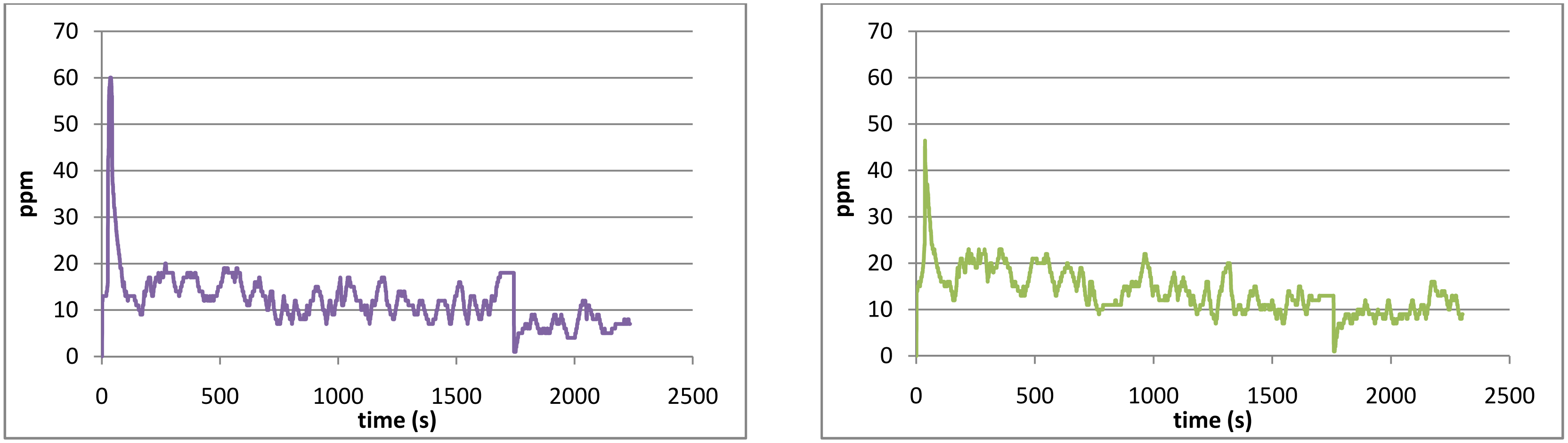
Test 2 HC

The maximum hydrocarbon emissions follow the same general trend of increasing hydrocarbon emissions with the amount of ULSD in the fuel. The plots in Figure 36 show that the average hydrocarbon emissions for ULSD were actually lower than the biodiesel blends, which is seen again the average hydrocarbon graph in Figure 37. Figure 38 shows the average hydrocarbons for each fuel which shows the opposite trend of what was expected. B50 hydrocarbon emissions were higher than B100 which could be attributed to the fact that the sample nozzle was not cleared before the B50 test. The hydrocarbon emissions decreased for B20 and further with ULSD compared to the higher biodiesel blends. The HC plots for ULSD and B20 also show a high peak reading at the beginning of the test which was not seen in Test 1.

For the second test B20 was tested first immediately after the AEA was cleaned. The sample line was not cleared for the B50 run but was cleared for the B100 and for the ULSD test which was ran last. There is a sharp drop in every plot between 1000 seconds and 2000 seconds where the AEA performs a zeroing operation.

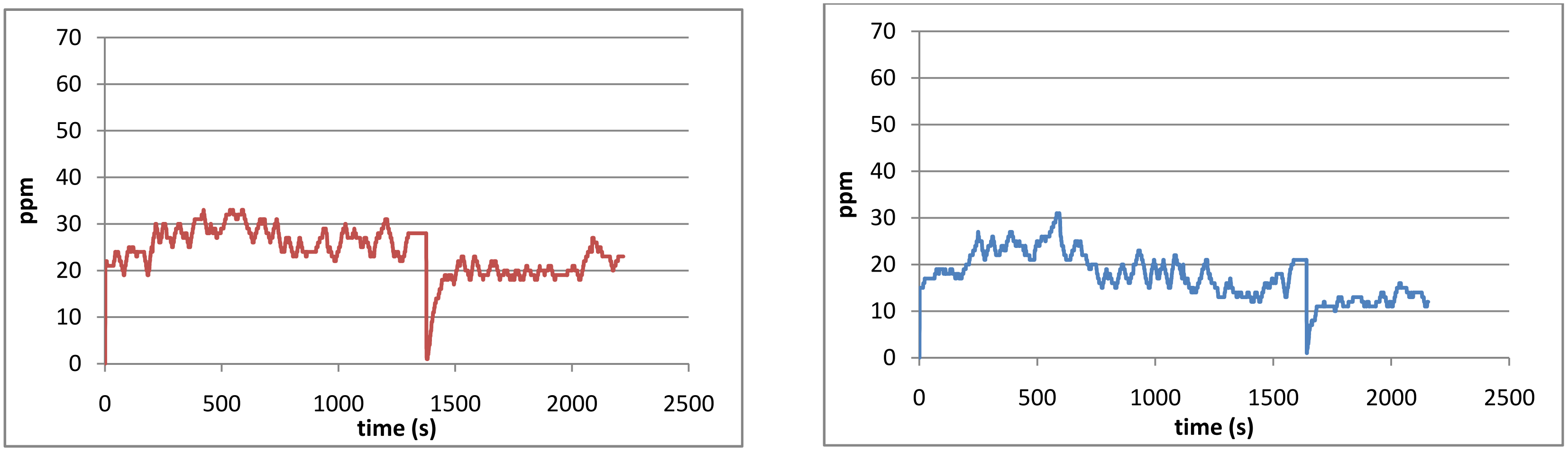
The residual hydrocarbon readings and the unexpected behavior in hydrocarbon emissions both call the accuracy and performance of the NDIR sensor to be able to read hydrocarbon emission in the presence of liquid condensation in the sample line into question. The standard test for reading hydrocarbons is a FID, which is how the SEMTECH measures hydrocarbons. The results are presented here for completeness but should not be viewed as meaningful.

Test 2 HC



ULSD HC

B20 HC



B50 HC

B100 HC

Figure 36. Hydrocarbon Emissions Versus Time For Test 2

Test 2 Maximum and average HC emissions

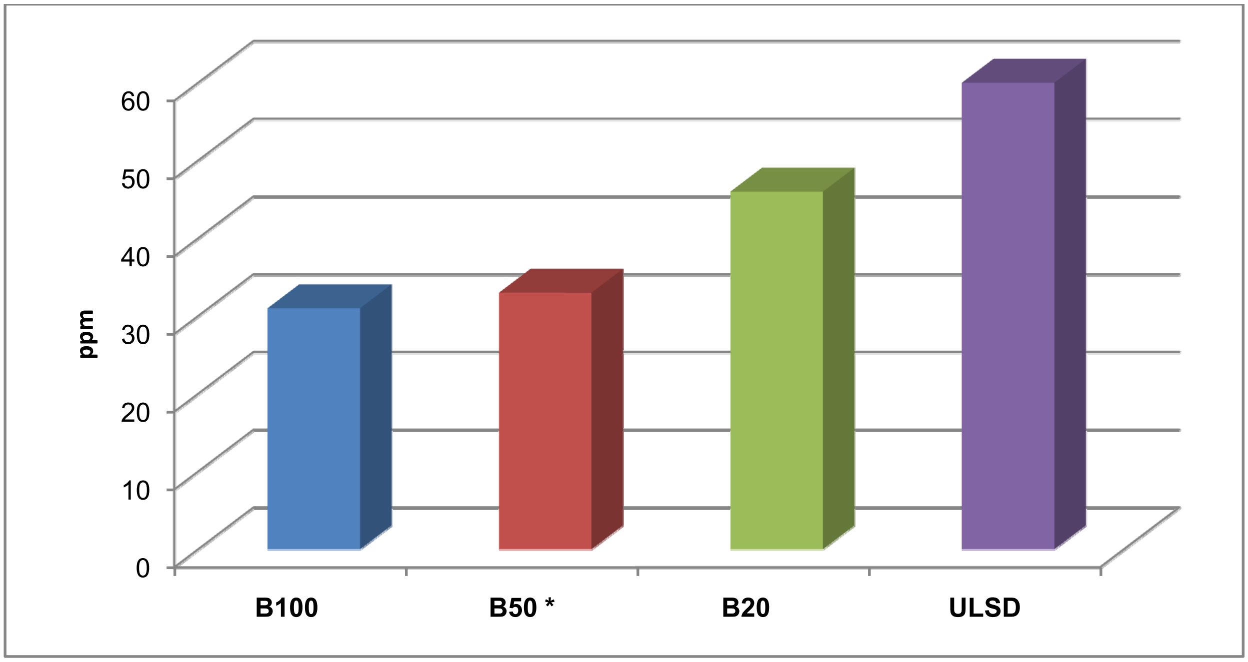


Figure 37. Maximum HC Values For Test 2

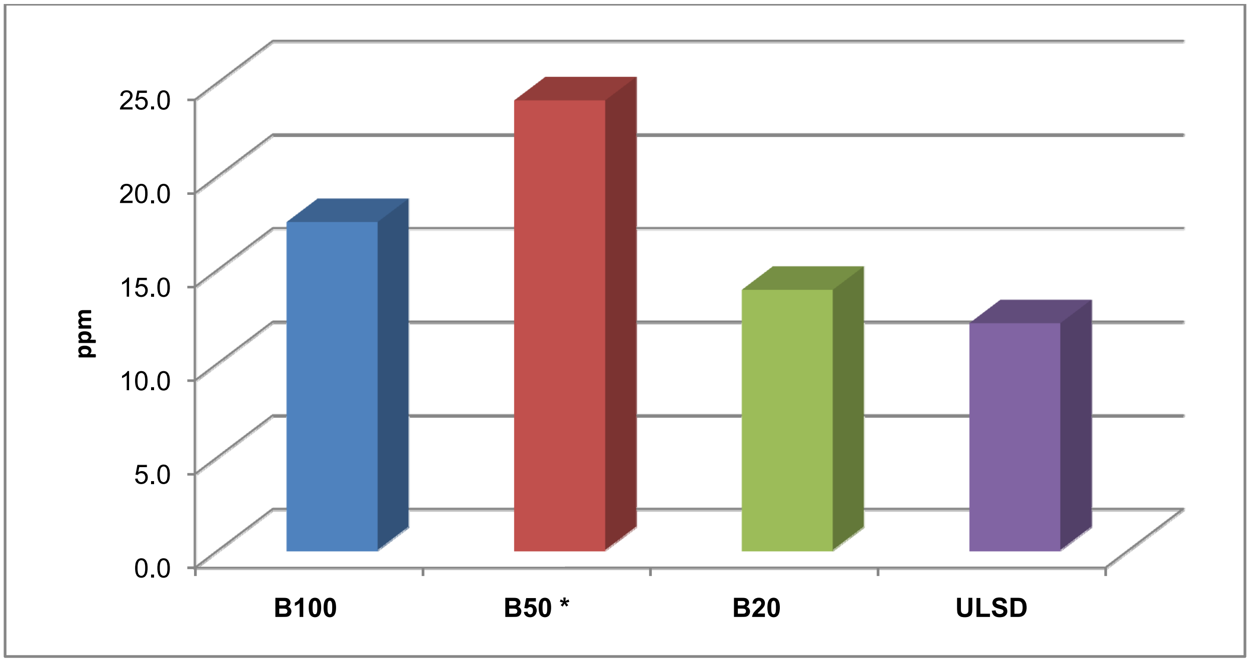


Figure 38. Average HC For Test 2

NO_X and Power

The DL1 records lateral and longitudinal accelerations and speed and can estimate drive wheel power given the vehicles coefficient of drag, coefficient of rolling resistance and vehicle weight. The graphs show that measured NO_X follows the expected trend of NO_X production as a function of drive wheel power. The following graphs are for the B100 in Test 2. The power relationship is shown in Appendix IX.

Looking at the graphs for NO_X and power in Figure 39 they are found to be visually similar. Both the peaks and the area under the curve appear almost identical. The areas in which they do not match up could be attributed to the DL1 not being able to log altitude. The relationship of NO_X makes sense in terms of higher loads will cause higher in cylinder temperatures leading to more $NO_{X.}$ This pattern was seen throughout the tests.

The values are normalized to their maximum value and are presented in Figure 40. The 8 second delay is not obvious on the 2500 second scale and the two plots line up remarkable well.

The results for each run are not presented here but the general observation is important to note.

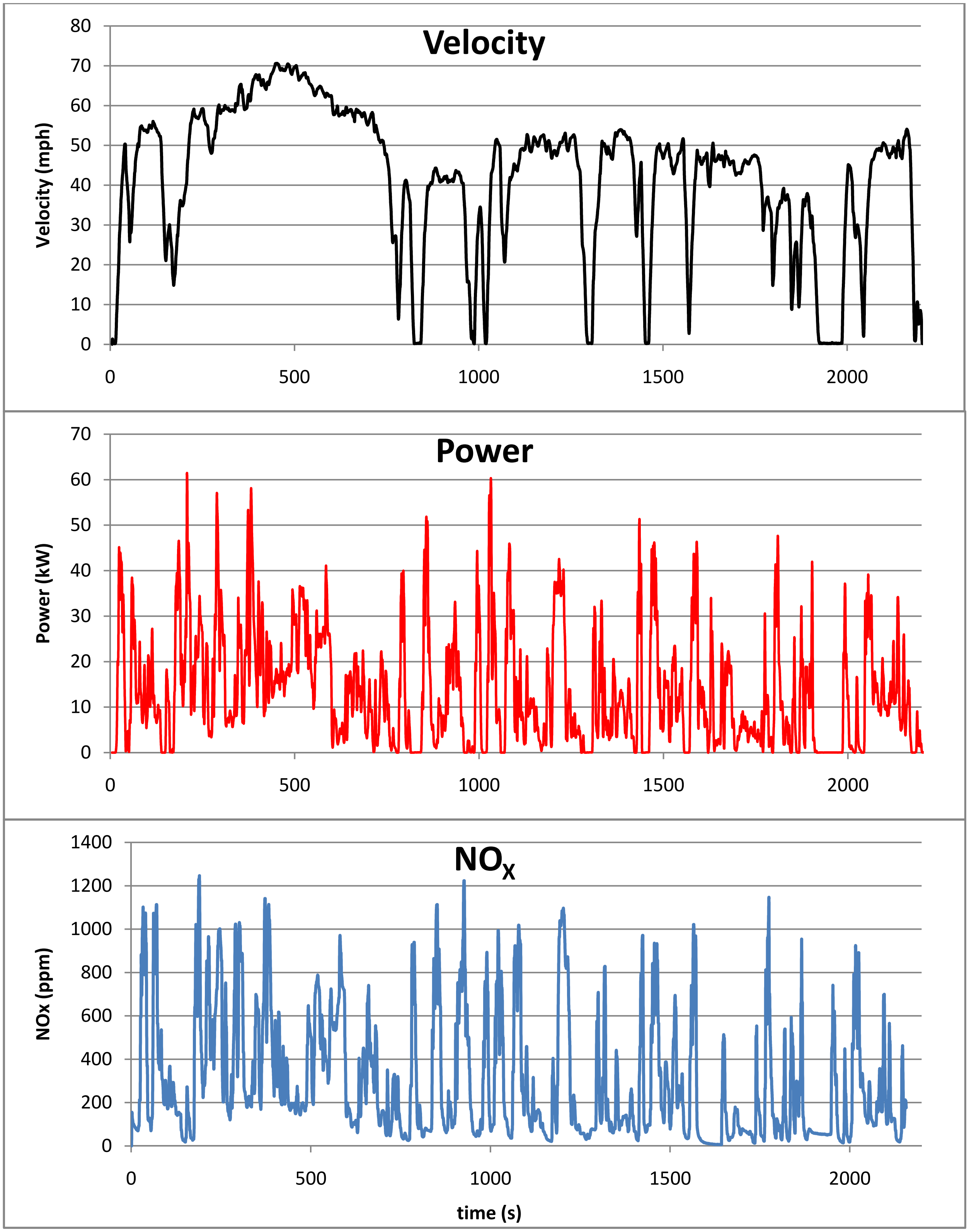


Figure 39. Velocity, power and NOx Versus Time For B100 In Test 2

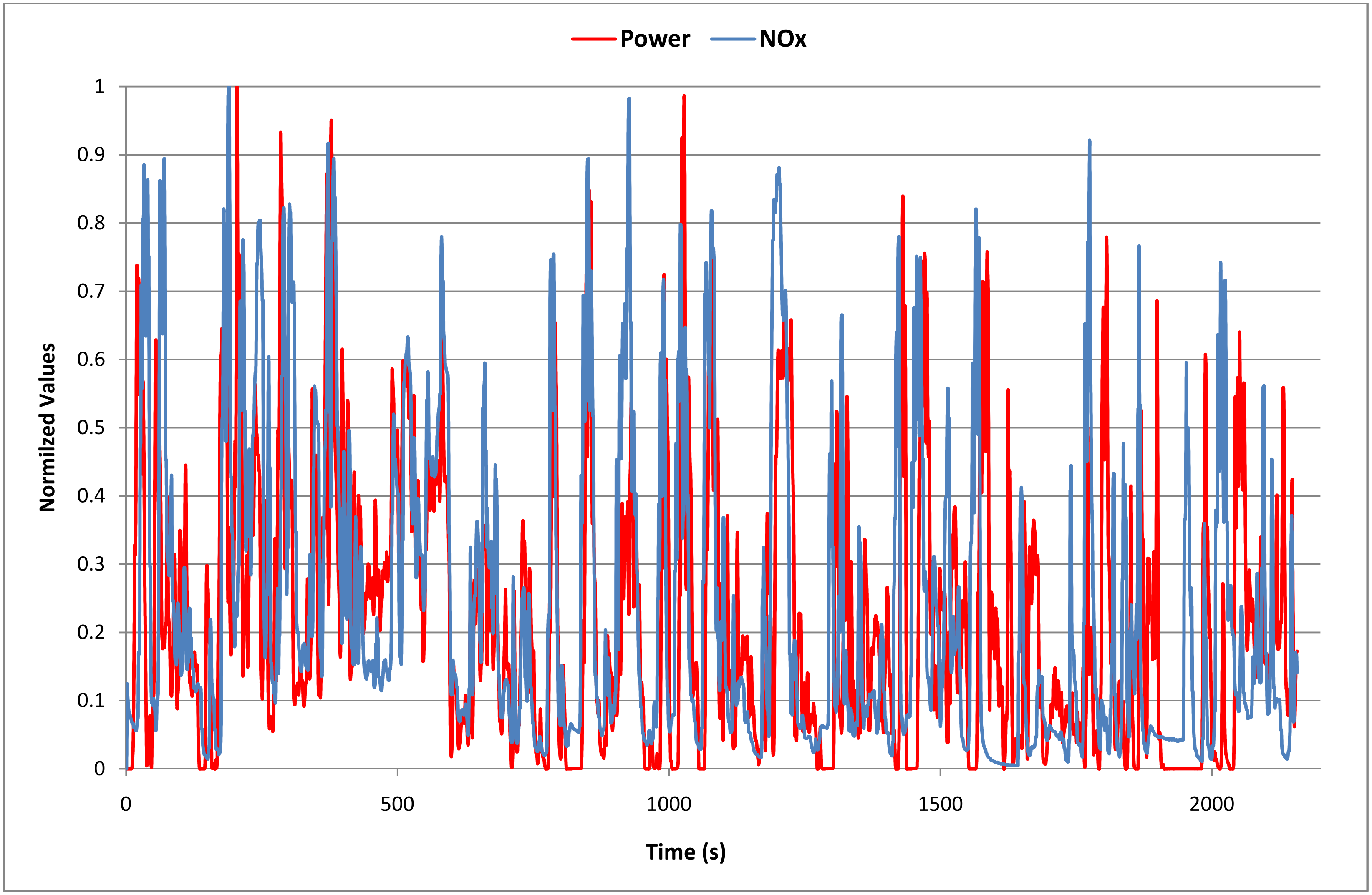


Figure 40. Overlaid Normalized Power and NOx for B100 During Test 2

Smoke Data

The smoke test was performed with ULSD and B20. The smoke meter does not have the capability to log data so the on-road effects of the various fuels could not be evaluated. Neither test produced enough PM to register an opacity change with the test equipment. The tests were performed a number of times with the same results.

The DPF and secondary catalyst unit were removed from the exhaust and the tests were performed again using ULSD. The test again did not show any change in opacity. The smoke meter can be operated in an instantaneous meter mode to see a graph or digital meter of opacity. At idle and max governor speed the meter showed 0.0 % opacity. The engine was then run through the entire RPM range at increments of 250 RPM. The only change in opacity observed was from the 2750 to 3250 rpm range where the % opacity averaged 5% with a maximum opacity of 16%. The smoke observed coming out of the exhaust was white with no visible traces of black smoke which has more of an effect on opacity.

Observations

When the DPF/DOC system was removed from the exhaust the effect of the exhaust on the operator was noticeable. The first observation was that exhaust's smell had a much stronger "diesel" smell during idle than when the DOC/DPF was in place. The second observation is that the exhaust had a dramatic effect on the operator's physical wellbeing. During the testing without the DPF/DOC the operator reported feeling light headed and woozy and had "bad" feeling from being exposed to the exhaust. The possible reasons for these observations are discussed in the conclusions.

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

Overview

The conclusions regarding the experiments are presented here along with a discussion regarding the possible sources of error in the testing. Recommendations are also given for future on-road emissions testing.

Conclusions

It is important to keep the conclusions regarding the results in the context of the scope of the experiment. The intention of the study was only to evaluate the relative emissions performance of various biodiesel blends produced by the UT Biodiesel project against ULSD and each of the other blends. The study examined the real-world performance of the various biodiesel blends over a drive cycle that was similar to, but not identical to the federal drive cycle. The emissions testing equipment was appropriate for comparison purposes considering budget and equipment limitations. The limitations of the equipment are understood and mean that the results can be used for comparing the relative performance of the fuels however the values of the emissions should not be used outside the context of this study. The nature of an on-road drive cycle over public roads makes absolute repeatability impossible, but through driver training and adherence to the driving schedule the tests can still be valid.

On Road Emissions

Despite the difficulty of reproducing exact conditions during an on-road drive, the drive cycles were found to be quite similar as were the repeated emissions results from Test 1. The AEA unit would always automatically zero as mentioned before. It is not clear if the zeroing had any effect on the data. There was no clear way to prevent the AEA from performing the zero.

The use of B100 does raise NO_X emissions noticeable. The frequency of high NO_X peaks increased significantly with the higher biodiesel blends as did the average NO_X emissions and peak NO_X emissions for both tests. Temperature and humidity can cause a big difference in NO_X values and should be recorded during all tests but especially for tests performed outside where temperature and humidity can vary greatly during the course of testing.

The AEA's NDIR was not sensitive enough to allow for meaningful comparisons between fuels. CI engines produce very little CO and when a DOC is present they produce insignificant amounts of CO.

No conclusions can be made regarding the HC results between fuels. The NDIR is not suited for measuring hydrocarbons from diesel fuels in the presence of water condensation.

NOx Emissions and Power

On-road NO_X emissions are dependent on drive wheel power which is dependent on acceleration for lower speeds and aerodynamic drag at higher speeds. Drivers have control over both the top speed driven and acceleration from stops. It is well known that fuel economy depends on load and it makes sense that emissions would depend on load as well. This observation also has implications on the design of traffic light systems to minimize the amount of stop and go traffic. This can be accomplished through traffic light synchronization.

Smoke

The PM emissions technology employed in the vehicle was too effective to allow any changes in opacity to be observed with the various fuels. The smoke test evaluates the exhaust at idle and at the maximum governor speed of the engine. These two operating conditions have been optimized to produce minimum PM. The only opacity change observed was in the 2750 – 3250 RPM range which most likely has less boost pressure then maximum throttle and higher EGR rates than idle or the maximum governor engine speed.

The effect on the operator could be explained by a larger portion of unburned hydrocarbons being present when the DPF/ DOC system was removed.

Sources of Error

Possible sources of error can be divided into driver error, drive cycle repeatability, variability due to ambient temperature and humidity, and equipment. Sources of error include:

- Local traffic
- Accelerations
- Stop light and stop sign variability
- Oxygenated hydrocarbon compounds with NDIR

- Chemical condensation in sample line
- High NO_2 levels could affect opacity measurement
- Humidity and temperature of ambient air effects NO_X readings

An analysis of repeatability and error is presented in Appendix IVX.

Recommendations

Though this study did provide valuable information regarding the emissions performance of each of the blends, the limitations of the study can guide future studies toward higher quality techniques and results. Improvements can be made to the on-road driving cycle; there are more appropriate emissions testing equipment available; and there are even opportunities for more in-depth studies on this platform.

On-road emissions testing offers valuable information and can be used for emissions evaluations when laboratory testing is not available. When constructing an on-road drive cycle, particular emphasis needs to be placed on a cycle that is representative of the driving in the area and does follow the general format of the federal test cycles. When designing the route, roads should be picked that have as few traffic lights as possible to limit the uncertainty of the length and number of stops on the cycle. If traffic lights are unavoidable, then traffic lights next to parking lots can offer the driver a way to pull off the road to execute the requisite idling time.

The emissions testing equipment used for this study was adequate but state of the art. Given sufficient time and resources, the AEA could be compared to higher quality equipment over the same drive cycle and the A could be used be used on a chassis dynamometer cycle to compare the results against known standards. The condensation problem that the AEA exhibits needs to be addressed. To counter the condensation problem, the sample line could be shortened and heated. The tests could be run again or compared to a known standard to see if this would allow the HC measurements to be useful

The PM testing could be performed under load for the normal exhaust configuration and with the DPF/DOC system removed to see the full effects of the various biodiesel blends. This would require equipment such as proportional particulate mass device developed by Sensors Inc (68). .

The test vehicle offers a lot of possibilities for future testing. The performance of the oxidation catalyst and diesel particulate filter mated to the engine could be evaluated on each of the fuel blends. The engine control unit has sensors to monitor the temperature of the DOC and the temperature and backpressure of the DPF. If reference voltages could be applied to the ECU, then the testing could be performed with and without the aftertreatments. Catalyst temperatures could be monitored during driving as well to see the effect of catalyst temperature on emissions reduction.

This study did not look at cold start emissions, but it is expected that emissions will be greater with a cold soaked engine and cold soaked DOC.

The new DL1 units have the ability to log elevation which would provide more information regarding the on road drive cycle. The addition of logging manifold pressure and engine speed would also provide more information regarding load. The load data could then be synchronized to the NO_X data to show the effect of load and engine speed.

LIST OF REFERENCES

1. Alovert, Maria "Mark". Biodiesel Appleseed Reactor Plans. *Biodiesel Community.* [Online] http://www.biodieselcommunity.org/appleseedprocessor/.

2. Addison, Kieth. Make your own biodiesel. *Journey to Forever.* [Online] http://journeytoforever.org/biodiesel_make.html.

3. Alovert, Maria. *Biodiesel Homebrew Guide.* : B100.org, 2005. 10th ed..

4. ASTM. *Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.* : ASTM International, 2008. ASTM D6751- 07b.

5. National Biodiesel Board. Fuel Fact Sheets. *National Biodiesel Board.* [Online] http://www.biodiesel.org/pdf_files/fuelfactsheets/CommonlyAsked.PDF.

6. Energy Information Administration. U.S. Product Supplied for Crude Oil and Petroleum Products. *EIA.* [Online] September 2008. http://tonto.eia.doe.gov/dnav/pet/pet_cons_psup_dc_nus_mbbl_m.htm.

7. *Composition of Fat and Vegetable Oil Derived Fuels in Diesel Engines.* Graboski, Michael S and McCormick, Robert L. 2, : Progress in Energy and Combustion Science, 1998, Vol. 24.

8. ADM. *Biodiesel Technical Manual.* Decatur : Archer Daniels Midland Company, 2007.

9. *Technical aspects of biodiesel production by transesterification—a review.* Meher, L.C., Sagar, D. Vidya and Naik, S.N. : Renewable and Sustainable Energy Reviews, 2004.

10. *Biodiesel production: a review.* Ma, Fangrui and Hanna, Milford A. : Bioresource Technology, 1999, Vol. 70.

11. *Biodiesel processing and production.* Van Gerpen, Jon. : Fuel Processing Technology, 2005, Vol. 86.

12. *Transesterification Kinetics of Soybean Oil.* Freedman, Bernard, Butterfield, Royden O. and Pryde, Evereff H. 10, : JAOCS, 1986, Vol. 63.

13. *Kinetics of Transesterification of Soybean Oil.* Noureddini, H. and Zhu, D. 11, : JAOCS, 1997, Vol. 74.

14. Van Gerpen, Jon and Knothe, Gerhard. Biodiesel Production. [book auth.] Gerhard Knothe, Jurgen Krahl and Jon Van Gerpen. *The Biodiesel Handbook.* Champaign : AOCS Press, 2005.

15. Knothe, Gerhard and Dunn, Robert. Biodiesel: An alternative fuel from vegetable oils or animal fats. [book auth.] Gerhard et al. Knothe. *The Biodiesel Handbook.* : AOCS, 2005.

16. NBB. US Biodiesel Capacity. *National Biodiesel Board.* [Online] September 2008. http://www.biodiesel.org/pdf_files/fuelfactsheets/Production%20Capacity_91708.pdf. Production Capacity_91708.pdf.

17. Urbanchuk, John M. Economic Contribution of the Biodiesel Industry. *National Biodiesel Board.* [Online] 2007. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/20071119_gen384.pdf. 20071119_gen384.pdf.

18. *Waste Cooking Oils, An Economical Source for Biodiesel: A Review.* Kulkarni, Mangesh G. and Dalai, Ajay K. 9, : Ind. Eng. Chem. Res, 2006, Vol. 45.

19. *The potential of restaurant waste lipids as biodiesel feedstocks.* Canacki, Mustafa. : Bioresource Technology, 2005.

20. *Investigation of the Refining Step of Biodiesel Production.* Karaosmanoglu, Filiz and al., et. : Energy and Fuels, 1996, Vol. 10.

21. Bently Tribology. *Biodiesel Testing and Analysis Labs.* [Online] http://www.biodieseltesting.com/tests.php.

22. Wark, Kenneth, Warner, Fecil F. and Davis, Wayne T. *Air Pollution - Its Origin and Control, 3rd ed.* : Addison Wesley Longman, 1998.

23. US EPA. Renewable fuel standard program. [Online] http://www.epa.gov/OMS/renewablefuels/.

24. National Biodiesel Board. Biodiesel Basics. *National Biodiesel Board.* [Online] 2008. http://www.biodiesel.org/resources/biodiesel_basics/.

25. Bosch. *Automotive Handbook.* Cambridge : Bentley Publishers, 2007. 7th ed. .

26. Hodgson, Jeffery W., Irick, David K. and Fussell, Lori M. Automotive Engines and Vehicles. [book auth.] Robert A. Meyers. *Encyclopedia of Environmental Analysis and Remediation.* : John Wiley & Sons, 1998.

27. Energy Information Administration. Voluntary Reporting of Greenhouse Gases Program. *Energy Information Administration.* [Online] EIA, 2001. http://www.eia.doe.gov/oiaf/1605/GWPs.html.

28. Majewski, W. Addy and Khair, Magdi K. *Diesel Emissions and Their Control.* Warrendale, Pa. : SAE International, 2006.

29. Diesel Net. Emission Test Cycles: FTP-75. *Diesel Net.* [Online] http://www.dieselnet.com/standards/cycles/ftp75.html.

30. Delphi. *Worldwide Emission Standards: Passenger Cars and Light Duty Trucks.* 2007.

31. EPA. *EPA's Program for Cleaner Vehicles and Cleaner Gasoline.* Ann Arbor : United States Environmental Protection Agency, 1999. Regulatory Announcment.

32. *Advances in Turbocharging Technology and its Impact on Meeting Proposed California GHG Emission Regulations.* Arnold, Steve, et al. : SAE International, 2006. 2005-01-1852.

33. US Environmental Protection Agency. *EPA's Fuel Economy and Emissions Programs.* : US EPA, 2004. EPA420-F-04-053.

34. Heywood, John B. *Internal Combustion Engine Fundamentals.* : McGraw-Hill, Inc, 1988.

35. Ricardo. Dual of the Eco-Champions. *Ricardo Quarterly Review.* Q3, 2007.

36. Charlton, Stephen J. Control Technologies for Compression-Ignition Engines. [book auth.] Eran Sher. *Handbook of Air Pollution from Internal Combustions Engines: Pollution Formation and Control.* San Diego : Academic Press, 1998.

37. Pundir, B.P. *Engine Emissions: Pollutant Formation and Advances in Control Technology.* Oxford : Alpha Science International, 2007.

38. Eaton, Scott J. *Accelerated Poisoning of Diesel Oxidation Catalysts by Zinc Dialkyldithiophosphate-Derived Phosphorus.* : Master's Thesis - The University of Tennessee, 2006.

39. *A Review of Diesel Particulate Filter Technologies.* Khair, Magdi K. : SAE International, 2003. 2003-01-2303.

40. *Effect of biodiesel fuels on diesel engine emissions.* Lapuerta, Magin, Armas, Octavio and Rodriquez-Fernandez, Jose. : Progress in Energy and Combustion Science, 2007, Vol. 34.

41. *Effects of Biodiesel, Biodiesel Blends, and a Synthetic Diesel on Emissions from Light Heavy-Duty Diesel Vehicles.* Durban, Thomas D., et al. 3, : Environmental Resource & Technology, 2000, Vol. 34.

42. US EPA. EPA. *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions.* [Online] 2002. http://www.epa.gov/otaq/models/analysis/biodsl/p02001.pdf.

43. *Emission Performance of Selected Biodiesel Fuels.* McGill, Ralph, et al. : SAE International, 2003. 2003-01-1866.

44. *Determination of Particulate and Unburned Hydrocarbon Emissions from Diesel Engines Fueled with Biodiesel.* Chang, David Y. and Van Gerpen, Jon H. : SAE International, 1998. 982527.

45. *NOx Emissions of Alternative Diesel Fuels: A Comparative Analysis of Biodiesel and FT Diesel.* James P. Szybist, Stephen R. Kirby, Andre´ L. Boehman. 4, : Energy & Fuels, 2005, Vol. 19.

46. *The Effect of Biodiesel Fuel Composition on Diesel Combustion and Emissions.* Schmidt, Kevin and Van Gerpen, Jon. : SAE International, 1996. 961086.

47. *A Comparative Analysis of Combustion Process in D. I. Diesel Engine Fueled with Biodiesel and Diesel Fuel.* Senatore, A., Rocco, A. and Prati, M.V. : SAE International, 2000. 2000-01-0691.

48. *An Experimental Investigation on Combustion and Emissions Characteristics of Turbocharged DI Engines Fueled with Blends of Biodiesel.* Xiaoming, Lu, et al. : SAE International, 2005. 2005-01-2199.

49. *The Influence of Fuel Design on the Exhaust Gas Emissions and Health Effects.* Krahl, J et al. : SAE International, 2005. 2005-01-3772.

50. *Experimental Characterization of a Common Rail Engine Fuelled with Different Biodiesel.* Senatore, A., Cardone, M. and al., et. : SAE International, 2005. 2005-01-2207.

51. *Chemical and Biological Characteristics of Exhaust Emissions from a DI Diesel Engine Fuelled With Rapeseed Oil Methyl Esters (RME).* Hansen, Ken Friis and Jensen, Michael Grouleff. : SAE International, 1997. 971689.

52. *Effect of Biodiesel Blends On Diesel Particulate Filter Performance.* Williams, Aaron, et al. : SAE International, 2006. 2006-01-3280.

53. *Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particulate Filters.* Boehman, Andre L, Song, Juhun and Alam, Mahabubul. : Energy and Fuels, 2005, Vol. 19.

54. *Application of Biodiesel Fuel to a Modern Diesel Engine.* Kawano, Daisuke, et al. : SAE International, 2006. 2006-01-0233.

55. *Effects of an Oxidation Catalytic Converter and a Biodiesel Fuel on the Chemical, Mutagenic, and Particle Size Characteristics of Emissions from a Diesel Engine.* Bagley, Susan T., et al. 9, : Environmental Science and Technology, 1998, Vol. 32.

56. *Effects of Biodiesel Operation Light-Duty Tier 2 Engine and Emission Control Systems.* Tatur, Marek, et al. : SAE International, 2008. 2008-01-0080.

57. *Fuel and System Interaction Effects of Urea-SCR Control of NOx in Diesel Exhaust Aftertreatment.* Acharya, R., Alam, M. and Boehman, A.L. : SAE International, 2005. 2006-01-0638.

58. AutoLogic. AutoGas 5 Gas Analyzer Manual.

59. Sensors Inc. *Semtech_DS.* [Online] http://www.sensors-inc.com/Semtech_DS.htm.

60. AutoLogic. Heavy Duty Diagnostic Center Manual. : Autologic LLC, 2006.

61. SAE International. *Snap-Acceleration Smoke Test Procedure for Heavy-Duty Diesel Powered Vehicles.* : SAE International, 1996. SAE J1667.

62. *Development of an official test method for on-board PM measurements from Heavy-Duty diesel engines in the European Union.* Rubino, L, et al. : SAE International, 2007. 2007-01-1046.

63. *Performance Test Results of a New On Board Emission Measurement System Conformed with CFR Part 1065.* Nakamura, Haroshi, et al. : SAE International, 2007. 2007-01-1326.

64. *Reproducibility and Accuracy of On-Board Emission Measurements Using the RAVEM System.* Weaver, Christopher S and Petty, Lawrence E. : SAE International, 2004. 2004-01-0965.

65. *Quality Assurance of Exhaust Emissions Test Data Measured Using Portable Emissions Measurement System.* Krishnamurthy, Mohan and Gautam, Mridul. : SAE International, 2005. 2005-01-3799.

66. *Impact of the Driving Cycle on the NOx and Particulate Matter Exhaust Emissions of Diesel Passenger Cars.* Zervas, Efthimios and Bikas, George. : Energy and Fuels, 2008, Vol. 22.

67. *The Effect of Ambient Temperature, Humidity, and Engine Speed on Idling Emissions from Heavy-Duty Diesel Trucks.* Pekula, N., et al. : SAE International, 2003. 2003-01-0290.

68. *Road Test of an On-Board Particulate Matter Mass Measurement System.* Brooker, D.R., Giannelli, R.A. and Hu, J. : SAE International, 2007. 2007-01-1116.

69. California Bureau of Automotive Repair. BAR-97 Software Specification. [Online] 2007. http://www.bar.ca.gov/80_BARResources/02_SmogCheck/Engineering/BAR97_Specifications_Sec3.html.

70. *Real-Time On-Board Measurement of Mass Emission of NOx, Fuel Consumption, Road Load, and Engine Output for Diesel Vehicles.* Kihara, Nobutaka, et al. : SAE International, 2000. 2000-01-1141.

71. ASTM. *Standard Test Method for Distillation of Petroleum Products at Reduced Pressure.* : ASTM , 2003. D 1160 – 03.

72. *The Influence of Antioxidants on the Oxidation Stability of Biodiesel.* Mittelbach, Martin and Schober, Sigurd. 8, : AOCS, 2003, Vol. 80.

73. *The effect of biodiesel oxidation on engine performance and emissions.* Monyem, Abdul and Van Gerpen, Jon H. : Biomass and Bioenergy, 2001, Vol. 20.

APPENDICES

Appendix I – AutoGas Emissions Analyzer Product Specifications

Model Number: 310-0020

Serial Number: 2408

Gas Analyzer Measurement Ranges

Species	Range	Resolution
HC	0 – 2000 ppm	1 ppm
CO	0 – 15 %	0.001 vol %
CO2	0 – 20 %	0.01 vol %
O2	0 – 25 %	0.01 vol %
NO_X	0 – 5000 ppm	1 ppm

Temperature: 0 – 50° C operation; -20 to 70°C storage

Humidity: Up to 95% non-condensing

Altitude: -300 to 2,500m

Vibration: 1.5 G sinusoidal 5-1000 Hz.

Shock: 1.22m drop to concrete floor (gas analyzer)

Response Time: 0-90% <= 8 seconds for NDIR measurements

Appendix II – AutoGas Emissions Analyzer Time Response

Time Response

Recordings Data						
Time (sec)	**CO_2 %**	**CO %**	**HC ppm**	**O_2 %**	**NO_X ppm**	**NO_X Cor ppm**
1	0.00	0.004	0	20.37	0	0
2	0.00	0.004	0	20.37	0	0
3	0.00	0.003	0	20.37	0	0
4	0.00	0.003	0	20.37	0	0
5	0.00	0.003	0	20.36	0	0
6	0.00	0.003	0	20.37	0	0
7	0.00	0.004	0	20.37	0	0
8	0.00	0.004	0	20.37	0	0
9	2.04	1.249	287	20.04	41	38
10	2.71	1.782	388	18.36	216	198
11	2.71	1.782	388	18.36	216	198
12	2.71	1.785	380	14.31	531	488
13	2.71	1.785	380	14.31	531	488
14	2.84	1.859	384	14.12	539	495
15	2.89	1.912	402	13.49	592	544
16	2.86	1.865	403	13.26	608	559

Appendix III – Autologic Smoke Meter Specifications

Model Number: 310-0322

Serial Number: 2474

Heavy Duty J1667	
Voltage:	12 VDC
Measurement Range:	-0.0% to +100.0%
Ambient Temp:	-2 to +55° C
Operating Temp:	+28 - +131° F
Resolution:	0.40%
Weight:	2.3 kg (5.0 lbs)
Path Length:	5 inches (variable to J1667 (61))

Appendix IV- DL1 Specifications

Model Number: Dl1-2G

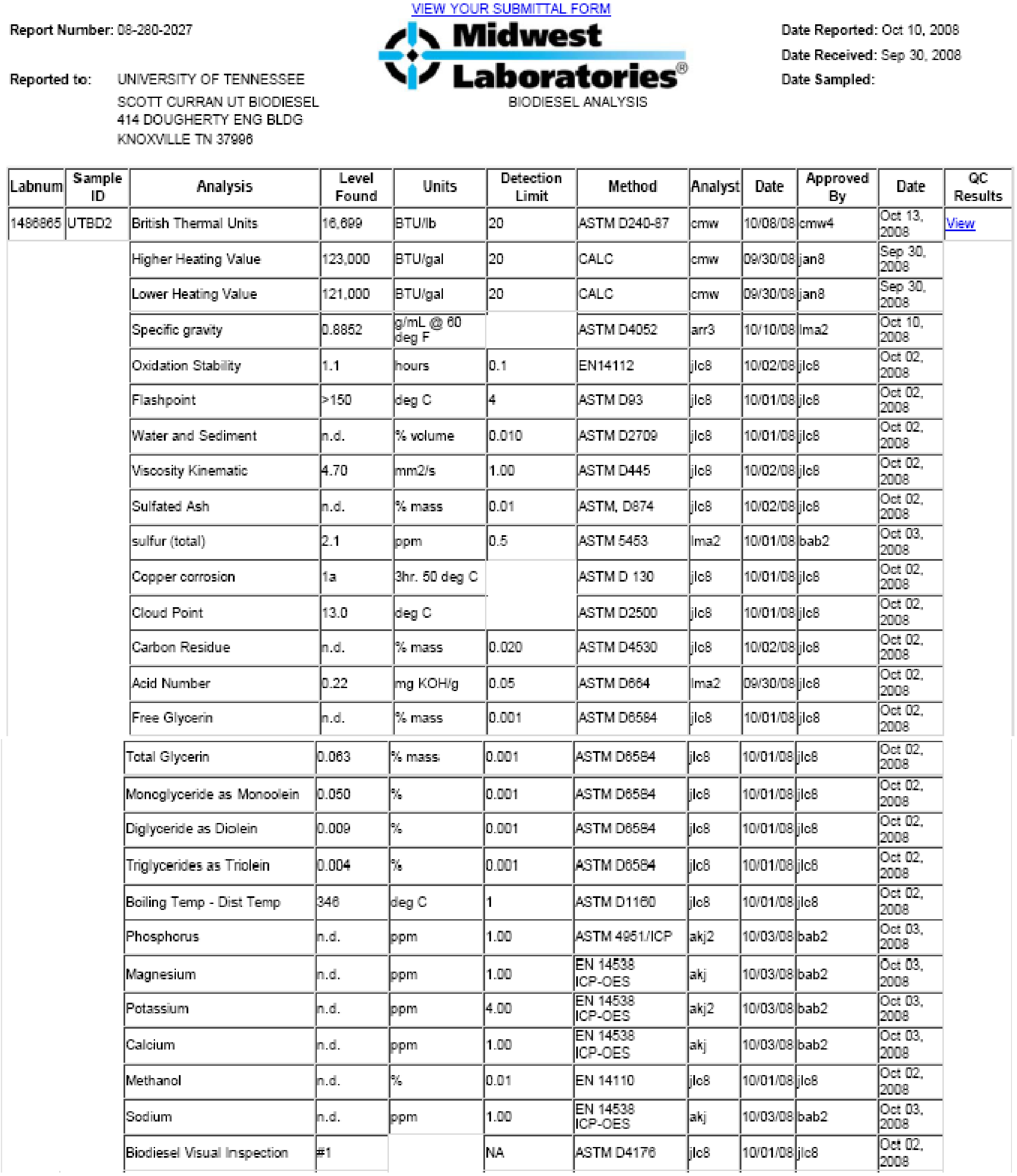
Serial Number: 2458

Software Version: 7.3.27

GPS: Outputs position, speed, position accuracy and speed accuracy every 100ms with no interpolation.

Accelerometers: 2-axis, resolution of 0.006g

Appendix V- ASTM Test Results for Test Fuel



VIEW YOUR SUBMITTAL FORM

Report Number: 08-280-2027

Reported to: UNIVERSITY OF TENNESSEE
SCOTT CURRAN UT BIODIESEL
414 DOUGHERTY ENG BLDG
KNOXVILLE TN 37996

Midwest Laboratories®
BIODIESEL ANALYSIS

Date Reported: Oct 10, 2008
Date Received: Sep 30, 2008
Date Sampled:

Labnum	Sample ID	Analysis	Level Found	Units	Detection Limit	Method	Analyst	Date	Approved By	Date	QC Results
1496865	UTBD2	British Thermal Units	16,699	BTU/lb	20	ASTM D240-87	cmw	10/08/08	cmw4	Oct 13, 2008	View
		Higher Heating Value	123,000	BTU/gal	20	CALC	cmw	09/30/08	jan8	Sep 30, 2008	
		Lower Heating Value	121,000	BTU/gal	20	CALC	cmw	09/30/08	jan8	Sep 30, 2008	
		Specific gravity	0.8852	g/mL @ 60 deg F		ASTM D4052	arr3	10/10/08	lma2	Oct 10, 2008	
		Oxidation Stability	1.1	hours	0.1	EN14112	jlc8	10/02/08	jlc8	Oct 02, 2008	
		Flashpoint	>150	deg C	4	ASTM D93	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Water and Sediment	n.d.	% volume	0.010	ASTM D2709	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Viscosity Kinematic	4.70	mm2/s	1.00	ASTM D445	jlc8	10/02/08	jlc8	Oct 02, 2008	
		Sulfated Ash	n.d.	% mass	0.01	ASTM, D874	jlc8	10/02/08	jlc8	Oct 02, 2008	
		sulfur (total)	2.1	ppm	0.5	ASTM 5453	lma2	10/01/08	bab2	Oct 03, 2008	
		Copper corrosion	1a	3hr. 50 deg C		ASTM D 130	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Cloud Point	13.0	deg C		ASTM D2500	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Carbon Residue	n.d.	% mass	0.020	ASTM D4530	jlc8	10/02/08	jlc8	Oct 02, 2008	
		Acid Number	0.22	mg KOH/g	0.05	ASTM D664	lma2	09/30/08	jlc8	Oct 02, 2008	
		Free Glycerin	n.d.	% mass	0.001	ASTM D6584	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Total Glycerin	0.063	% mass	0.001	ASTM D6584	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Monoglyceride as Monoolein	0.050	%	0.001	ASTM D6584	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Diglyceride as Diolein	0.009	%	0.001	ASTM D6584	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Triglycerides as Triolein	0.004	%	0.001	ASTM D6584	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Boiling Temp - Dist Temp	346	deg C	1	ASTM D1160	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Phosphorus	n.d.	ppm	1.00	ASTM 4951/ICP	akj2	10/03/08	bab2	Oct 03, 2008	
		Magnesium	n.d.	ppm	1.00	EN 14538 ICP-OES	akj	10/03/08	bab2	Oct 03, 2008	
		Potassium	n.d.	ppm	4.00	EN 14538 ICP-OES	akj2	10/03/08	bab2	Oct 03, 2008	
		Calcium	n.d.	ppm	1.00	EN 14538 ICP-OES	akj	10/03/08	bab2	Oct 03, 2008	
		Methanol	n.d.	%	0.01	EN 14110	jlc8	10/01/08	jlc8	Oct 02, 2008	
		Sodium	n.d.	ppm	1.00	EN 14538 ICP-OES	akj	10/03/08	bab2	Oct 03, 2008	
		Biodiesel Visual Inspection	#1		NA	ASTM D4176	jlc8	10/01/08	jlc8	Oct 02, 2008	

Appendix VI- Beer-Lambert Law and Opacity

The Beer-Lambert law is defined in terms of transmittance (T), smoke density (k) and effective optical path length (L).

$$T=e^{-kL}$$

This equation can also be written in terms of the intensity of the light source (I_o) the measured intensity from the light source (I), the effective optical path (L) and the extension coefficient of green light in diesel exhaust (σ_{ext} with a wavelength of 570 nm).

$$\frac{I}{I_0}=e^{-\sigma_{ext}L}$$

Opacity (N%) is then defined as

$$N(\%)= 100*(1-T)$$

Appendix VII- PRAXAIR Calibration Gas Specifications

PRAXAIR Blend Code 43 -97 MID2

BAR # PP06145416

LOT # 042120081

Filled: 4/21/2008

Expires: 4/21/2010

Species	**Concentration**
CO	4.83%
CO_2	7.2 %
NO	1816 ppm
C_3H_8	1936 ppm
N_2	Balance

Appendix VIII- NO Humidity Correction Factor

The NO Humidity Correction Factor from the BAR 97 test is used to minimize the effects humidity has on NO formation in compression ignition engines. The following is equation for the BAR 97 correction factor (Kh) (69).

$$Kh = e^{0.004977*(H-75)-0.004447*(T-75)}$$

where

Kh = NO humidity correction factor

H = Absolute humidity in grains of water per pound of dry air

T = Temperature in °F

The equation used for absolute humidity (H) uses saturated vapor pressure which must be looked up in a handbook.

$$H = \frac{(43.478)R_a P_d}{P_B - \left(P_d \frac{R_a}{100}\right)}$$

where

R_a = Relative humidity of the ambient air in percent

P_d = Saturated vapor pressure in mm Hg, at the ambient dry bulb temperature

P_B = Barometric pressure in mm Hg

Appendix IX – Drive Wheel Power

The DL1 estimates power using the acceleration data along with velocity given the coefficient of rolling resistance, drag coefficient and vehicle mass. The absolute value of power estimation was not important for this study but the values used are presented in the table. The equation for drive wheel power (in kW) is given by the following equation (25), (70).

$$P_{drive}=\left(F_{accel}+F_{roll}+F_{aero}+F_{grad}\right)^{*}v(t)$$

where:

P_{drive} = drive wheel power

F_{accel} = Acceleration Resistance

F_{roll} = Rolling Resistance

F_{aero} = Aerodynamic Drag

F_{grad} = Climbing Resistance

$v(t)$ = Vehicle Speed

The DL1 used in this study does not directly measure elevation, but the new versions do.

Appendix X – UTK Drive Cycle Instructions

Instruction	**Speed**	**Notes**
Exit Annex	0	10 Seconds of Idle after Data begins recording
Accel to 40 before Traffic Light	40	
Maintain 40	**40**	
At Light, Break to stop **(idle)**	0	Slow down to 20 mph or less if green light
Acel To 55 Before Water Treatment Plant	55	
Maintain 55 until exit ramp	**55**	
Decel to 20 to Enter on ramp to I40 West	20	
Accel to 40 by end of ramp	60	Up hill, requires hard acceleration
Accel to 55	55	
Maintain 55 until I40 Entrance	**55**	
Accel to 60 by end of Entrance ramp	60	
Maintain 60	**60**	
Accel to 70 by Clinton Highway exit	70	
Maintain 70	**70**	
Decel to 60 at West Hills Exit	60	Up hill, does not usually require breaking
Maintain 60 Unitl Cedar bluf exit	**60**	
Decel and stay right to Executive Park exit	15	
Brake to stop at Light	0	Usually able to stop even if light is green
Turn Left on Exec Park	0	If unable to stop go to first gear
Aceel to 40 before trafic light	40	
Maintain 40	**40**	
Brake to stop at Light **(Long Idle)**	0	
Turn Right On Cedar Bluff	0	If light is green come to stop before turn
Accel to 45 before Sherril	40	Up hill, requires hard acceleration
Maintain 45	**40**	Accel in 20 seconds if any red lights are hit
Brake to Stop at Middlebrook	0	
Turn right on Middlebrook	0	
Accel to 50 by Hidden Valley Sign	50	
Hold at 50	50	Accel in 22 seconds if any red lights are hit
Brake to Stop at Vanosdale Station **(idle)**	0	Pull over to gas station if light is green
Accel to 50 by Hidden Valley	50	
Maintain 50	**50**	
Brake to stop at Weisgarber **(Idle)**	0	Pull over to Excell entrance if green
Accel to 45 by Excell	45	
Maintain 45	**45**	
Decell to 30 at Ed Shoop	30	Almost never red light, can usually slow down
Accel to 45 Lonas	45	
Maintain 40	**45**	
Decel to 35 at Proctor	35	Hit breaks after train tracks
Maintain 35	**35**	
Decel to stop at Sutherland	0	Can usually come to stop before turning

Continued on Next Page

UTK Drive Cycle Continued

Instruction	Speed	Notes
Turn Right on Sutherland	0	
Accel to 35 by top of hill	35	Up hill - hard acceleration needed
Maintain 35	**35**	Try not to overshoot 35
Break to stop at light	0	Can always come to stop before turning
Turn Left at Concord	0	
Accel to 20 before tracks	20	
Decel to 5 mph 1st gear on tracks	5	Shift into first before accelerating
Aceel to 35 by cross walk	35	
Maintain 35	**35**	
Come to stop at stop light **(Long idle)**	0	Turn into Physical Therapy center if green light
Acell to 45 by light	45	
Maintain 45	45	
Break to stop at second light	0	Can usually slow down if neither light is red
Acell to 60 by End of UT Gardens	60	
Maintain 60 Until Turn off	**60**	
Brake to stop at turn lane to annex	10	Gives last spike in velocity
Turn Left into Annex	0	Pull in and come to complete stop
Come to stop - idle 10 seconds	0	Turn off both AEA and DL1 after 10 seconds

Appendix XI- AEA Cleaning

The AEA showed a reading of 4 -8 ppm of hydrocarbons even after the unit was zeroed. The hydrocarbons started to climb to 30ppm and finally reached a peak of 78 ppm in ambient air. The sample probe was brought outside into fresh air and the results did not change. On further inspection, the sample probe was making a gurgling sound while the pump ran. The residual hydrocarbon emissions could be a result of unburned hydrocarbons that have condensed in the sample line. Biodiesel has a higher distillation temperature then ULSD, and as such, some unburned fuel may have started condensing in the sample line. Hot air was blown into the sample port using a heat gun to try to evaporate whatever was in the line. After some time the gurgling sound disappeared but the residual HC reading did not disappear. The AEA manual suggests the operator change out the inline filters if there is a residual hydrocarbon reading. Both filters were changed per the manual but the analyzer still read a constant 5 – 8 ppm of HC.

At the end of day 1 testing condensation was seen in the intake tubes and exhaust tubes. The AEA pump was allowed to run for 15 minutes after the tests were completed to help drive out condensate.

At the beginning of day two testing, more condensate was seen in the intake tubes and when the AEA was turned on the gurgling sound from the sample tube was obviously louder than during the previous testing. The HC with the sample probe was 450 ppm. The reading without the probe went down to 130 ppm. The first filter was changed and the bowl had visual condensate in it, as did the inline tubing. The filter was soaked with liquid, but not dripping. The filter did not have any detectable diesel or biodiesel smell. The filter was dipped in distilled water and wrung out; the water was clear with no evidence of diesel or biodiesel contamination. The second inline filter was changed as well. All lines that had visual condensate were removed and blown out with compressed air. Some of the tubes had a significant amount of condensate. The sample probe was then disassembled and blown out with compressed air as well. There was a significant amount of water in both the probe and the sample line. The AEA was re-assembled and a leak test was performed. The leak test passed. The unit was zeroed and the HC reading without the sample probe fluctuated between 0 and 1 ppm. When the sample probe was installed the HC reading went to 32 ppm. The AEA was zeroed again and the HC reading went to a fluctuating reading between 0 and 1ppm.

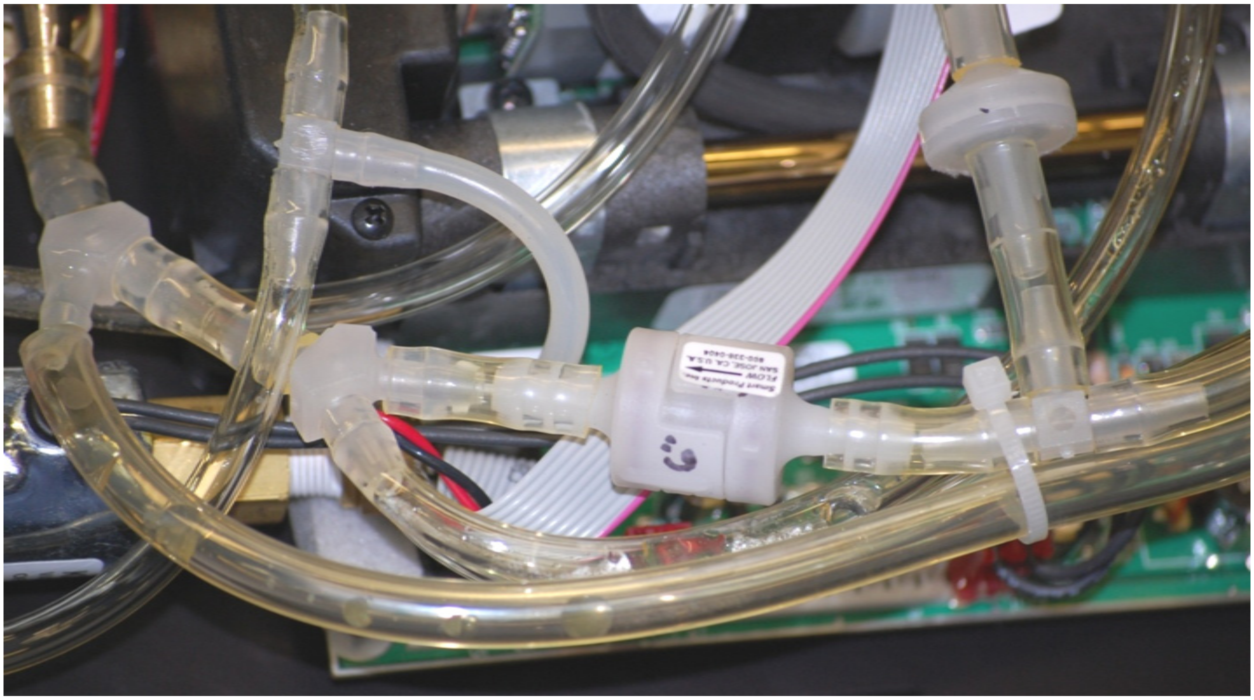
It appears that water condensate was building up in the unit which could trap and perhaps absorb hydrocarbons, which were giving the constant reading. The figures on the next page show the water buildup.

Day 2 testing

The sample probe was cleared of water for every run except the B50 run. When changing fuel to ULSD, care was taken to clear out the tank twice with ULSD, then the tank was filled full to minimize possible biodiesel contamination.

For day two tests, one run for each fuel was conducted after the AEA was cleaned. For the first fuel tested, B20, there were significant differences in the base HC and the NO_X results during the test compared to the first day. The NOX results can be attributed to humidity and temperature but the hydrocarbon readings were most likely due to the condensation.

Condensation in the line coming out of the first inline filter



Condensation seen inside the AEA

Appendix XII- ASTM D6751 Fuel Properties

The following is a brief discussion on the fuel properties specified by ASTM D6751 and the reference methods used to test each property (4).

Flash point

Though flashpoint is specified for petroleum diesel as well, the flash point for biodiesel also imposes an upper limit on the flammability of the fuel. Biodiesel is considered nonflammable and is much safer to transport and handle than gasoline or even petroleum diesel. Flash point also limits the amount of unreacted alcohol in the fuel, the higher the concentration of alcohol the lower the flash point. Tests have shown that 1% methanol present in the fuel can lower the flash point by 130° C (14). Flash point is measured using a Pensky Martins Closed Cup Apparatus. A brass test cup is filled with test specimen and fitted with a cover then heated. The specimen is stirred at a specified rate. A flame is directed into the test cup at regular intervals until a flash is detected.

Alcohol Control

One of the newer tests for ASTM D6751, the alcohol control parameter is a further step at controlling un-reacted alcohol present in the fuel. The amount of alcohol can be tested directly by measuring the amount of methanol present using gas chromatography, or indirectly by measuring flash point. This alcohol control flashpoint has a higher specification, of 130° C, then the flash point described above 90°C.

Water and sediment

Water can contribute to corrosion inside the engine and reduced power. Water can also damage fuel injectors and fuel pumps which rely on the viscosity of diesel fuel for correct operation. Water can also speed up oxidation processes especially when metal ions and UV light are also present. Sediment of course can cause clogging of injectors, pumps and filters. The ASTM test for both water and sediment uses a calibrated centrifuge tube to visually inspect the volume percent of water and sediment. A sample of the undiluted fuel is centrifuged at specified conditions in a centrifuge tube measurable to 0.01 ml. After centrifugation, the volume of water and sediment which has settled into the long graduated tip of the centrifuge tube can be read.

Kinematic viscosity

Upper and lower limits of viscosity are defined for biodiesel. If the viscosity is too high the fuel will not flow correctly and if a minimum viscosity is not met power loss may occur due to injection pump or injector leakage. Lowering the viscosity is one of the main reasons that biodiesel is preferred over straight vegetable oil (SVO). SVO must be heated considerable (to about 60°C) to obtain a suitable viscosity. The measurement is performed using a glass capillary viscometer to determine the flow time of the fuel using the calibration constant of the viscometer

Sulfated Ash

Testing for sulfated ash is important to prevent engine wear that can result from abrasive solids found in the fuel. These solids can also be responsible for engine deposits and fuel filter plugging. This test is rather complicated and involves a sample being burned in an electric furnace until only ash and carbon remain. The residue is treated with sulfuric acid and heated until oxidation of the carbon is complete. The ash is then re-treated with sulfuric acid, and heated to a constant weight.

Sulfur

B100 is essentially sulfur free which helps it obtain a better emissions profile then petroleum diesel. This also means that biodiesel is inherently safe to use with catalysts that experience sulfur poisoning. Sulfur in petroleum diesel fuel helps with lubricity, biodiesel is the preferred lubricity additive for ultra low sulfur diesel. The ASTM test for sulfur uses ultraviolet fluorescence. The test involves placing a fuel sample into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide ($SO_{2)}$ in an oxygen rich atmosphere and then exposed to ultraviolet light. The fluorescence emitted from the excited SO_2 as it returns to a stable state is detected by a photomultiplier tube.

Copper strip corrosion

The Copper strip corrosion test measures the fuel's tendency to corrode copper and brass components. If the fuel contains acids or sulfur compounds, the strip will show tarnishing, or in extreme cases, pitting. The test is performed by immersing a polished copper strip in a fuel sample and heated for a specified time at a specified temperature. The copper strip is removed and cleaned, and the color and tarnish level assessed against a visual guide.

Cetane Number

Cetane number is a measure of ignition quality of diesel fuels. It is a non-dimensional measure of delay from compression to explosion. Engines are designed to operate in a narrow range of cetane numbers. If the cetane number is too high, the fuel will not have enough time to mix. Higher cetane values are important for cold starting

(34). If the cetane number is too low the engine will be prone to misfire and experience excessive noise and vibration. Any alcohol present in the fuel will serve to lower the cetane number. The cetane number evaluation is one of the most expensive ASTM tests. The test uses a variable compression ratio test engine, Model CFR F-5 Cetane Method Diesel Fuel Rating Unit, from the Waukesha Engine Division. The compression ratio is variable from 8:1 to 36:1. The cetane number of the fuel is determined by comparing its combustion characteristics in the test engine against reference fuels under standard operating conditions (71).

Cloud point

The temperature at which the fuel becomes cloudy from crystal formation is known as cloud point. Biodiesel has a higher cloud point then petroleum diesel which means that in cold climates blending with winterizing agents is important. Feedstocks like palm oil which produce biodiesel with high cloud points are unsuitable for fuel in cold climates when better feedstocks are available. Though there is no specified limit for cloud point, it is reported and is important to fuel purchasers. The cloud point is measured by cooling a fuel sample in a special jar in a cooling bath at a specified rate and examining the sample to find when a cloud is first observed at the bottom of the test jar.

Carbon residue

This test gives an approximation of the tendency of the fuel to cause carbon deposits in the engine. As CI engines are becoming higher precision machines, deposits left by the evaporation of the fuel can do more damage to newer engines, for example causing coking of the fuel injectors. The test for carbon residue uses a special glass vial that is heated in an inert atmosphere. The sample undergoes coking reactions, and the carbonaceous-type residue remaining is reported.

Acid number

The acid number shows how much free fatty acids or remaining processing acids are present in the fuel. High acid number can increase fueling system deposits and may increase likelihood of corrosion. A high acid number is also an indicator of fuel that has started to undergo oxidation. Biodiesel should be close to a neutral acid number (8), and as the methyl esters break down acidic compounds can be formed. Acid number is measuring using potentiometric titration.

Free Glycerin

High levels of glycerin result in a higher viscosity of fuel. High levels of glycerin can also result in injector deposits, clogged fueling systems as well as an unwanted buildup in the bottom of fuel tanks and storage tanks. Free and total glycerin are both measured using a gas chromatograph.

Total Glycerin

Total glycerin determines the level of free glycerin as well as unreacted glycerin. Measuring total glycerin helps to ensure complete conversion of the triglycerides into methyl esters.

Phosphorus content

The main reason that phosphorus is tested for is that phosphorus can damage aftertreatment systems. Any phosphorus contained in the biodiesel is a result of the feedstock's chemical composition and must be taken into account when choosing a feedstock. Phosphorus content is measure using an Inductively Coupled Plasma Atomic

Emission Spectrometry (ICPAES). The ICPAES is used to compare emission intensities of the elements in the fuel sample with emission intensities measured with the calibration standards which allow the concentrations of elements in the sample to be calculated.

Distillation Temperature

This test helps insure that the biodiesel is similar to petroleum diesel. Biodiesel exhibits a boiling point instead of the traditional distillation curve of petroleum diesel fuel. The test came about to ensure that the biodiesel has not been adulterated with high boiling contaminants. The actual value of the boiling point also indicates how well the biodiesel will evaporate during combustion. The higher boiling point of biodiesel also has an effect on engine oil dilution. With petroleum diesel some of the blow-by fuel will evaporate back out of the crankcase, but this is not the case with biodiesel which will tend to dilute crankcase oil much faster. The test uses a vacuum distillation apparatus to distill a fuel sample at controlled conditions. The initial boiling point, the final boiling point, and a distillation curve relating volume percent distilled and atmospheric equivalent boiling point temperature are measured.

Sodium and Potassium

When present as abrasive solids either may cause injector, fuel pump, piston and ring wear as well as engine deposits. When present as soluble metallic soaps they may contribute to filter plugging and engine deposits. High levels of sodium or potassium compounds may be collected in exhaust particulate removal devices, which can cause increase engine back pressure an increased need for maintenance. The test is performed by optical emission spectral analysis with inductively coupled plasma

(ICPAES). Sodium and potassium can also deactivate aftertreatment devices such as DOC, LNT, SCR and others.

Calcium and Magnesium

Calcium and magnesium are monitored for the same reason as sodium and potassium. The test is the same spectral analysis test as mentioned before.

Oxidative Stability

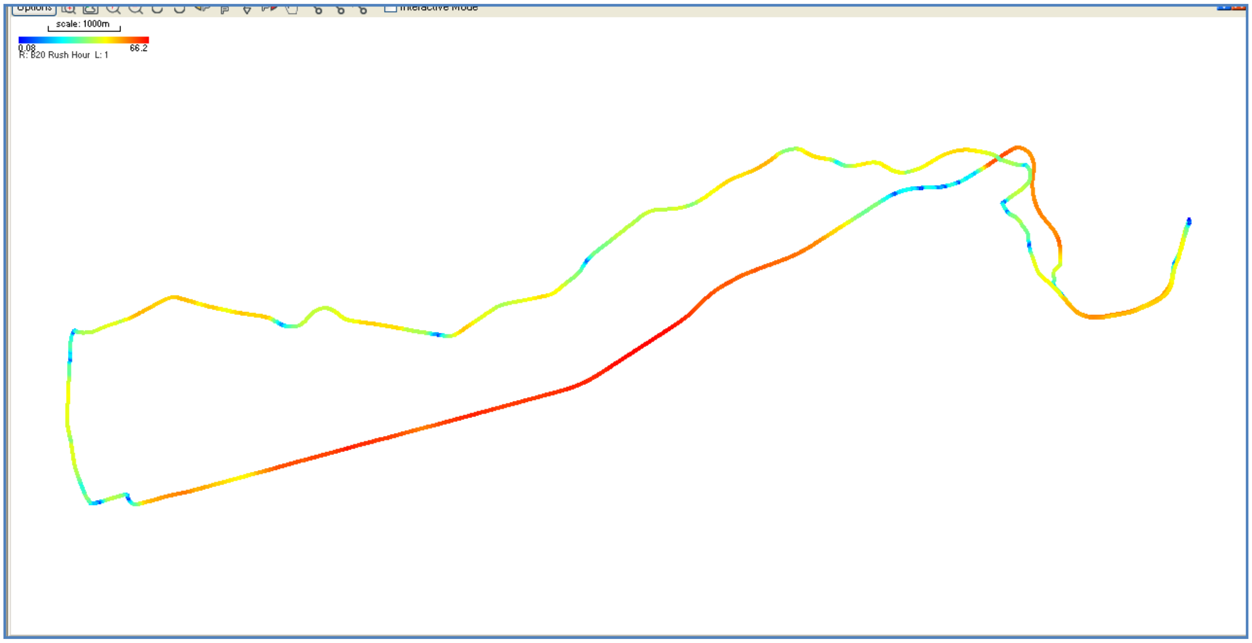
The long term storage of biodiesel is limited by the tendency of biodiesel to oxidize in the presence of metal ions, water, heat and UV. Since this specification has gone into effect many biodiesel producers have had to resort to the use of oxidative stability additives to meet the demands of the accelerated oxidative stability test (72). It has also been found that fuel that has undergone oxidation has been shown to increase fuel consumption but not significantly affect PM or NO_X levels with B20 blends (73).

Cold Soak Filterability

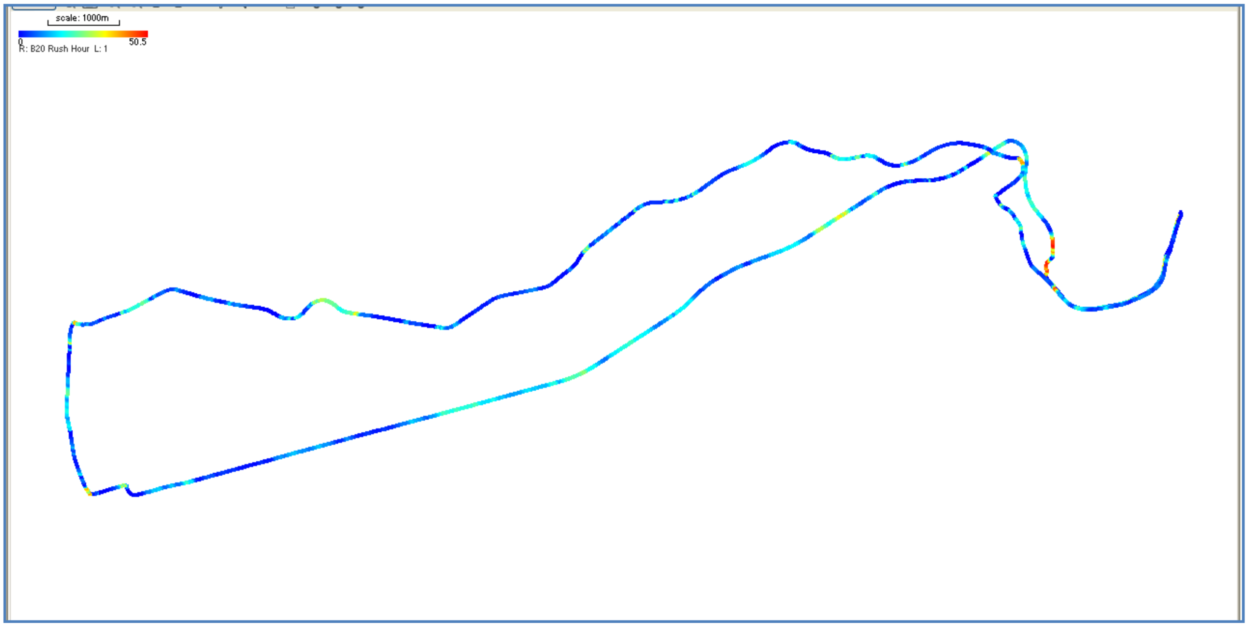
This specification has not gone into full effect yet and the test is still under development which means that it is currently just an agreed upon standard by industry (8). This test was found necessary to ensure cold weather performance from biodiesel and biodiesel blends. The test involves the chilling a sample of fuel which will encourage the growth of precipitates, the fuel is then warmed back up and filtered. The collection of precipitates is then indicative of cold weather performance. The time it takes to pass through the filter is measured along with the amount of material collected in the filter (21).

Appendix XIII- Drive Cycle Repeatability

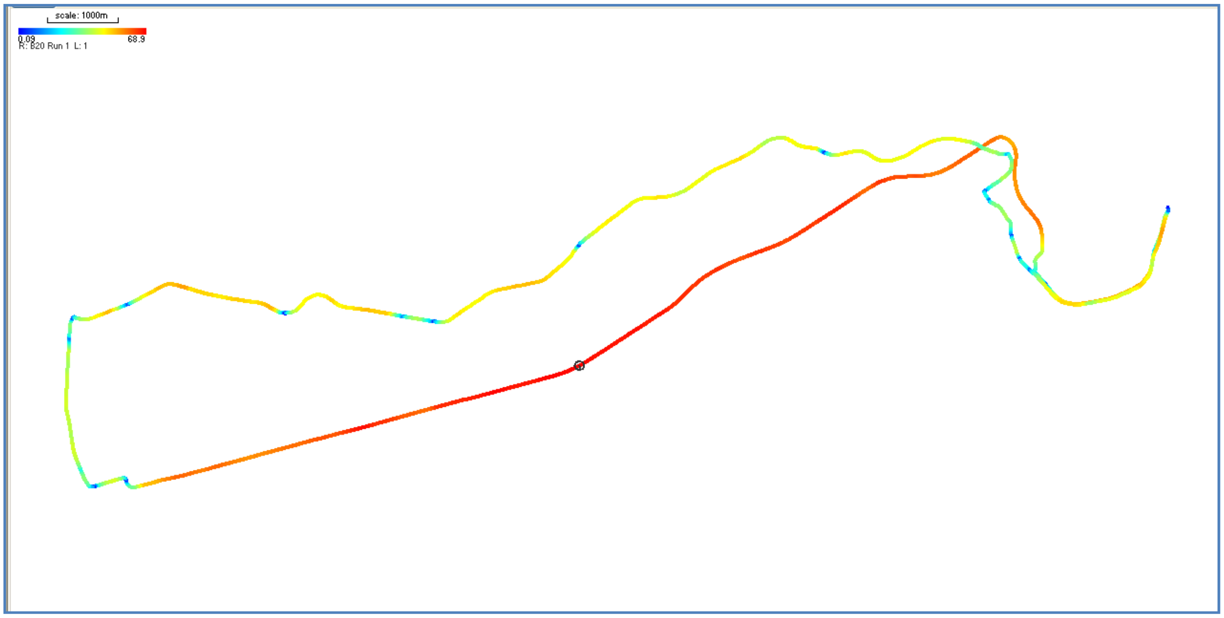
Test 1



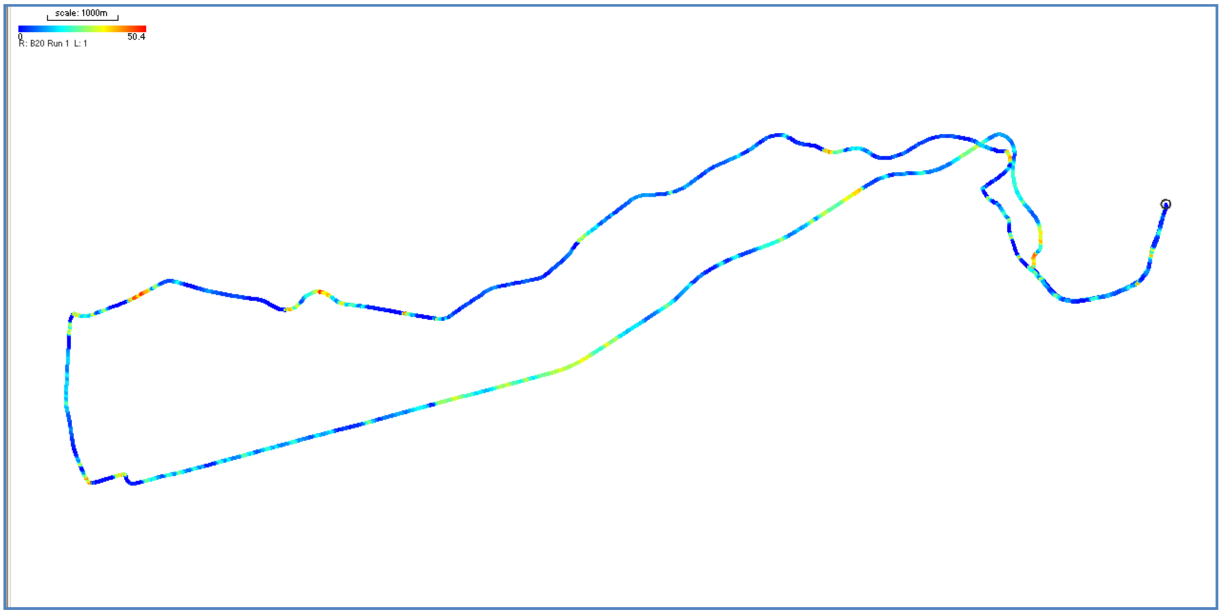
B20 Run 1 [speed]



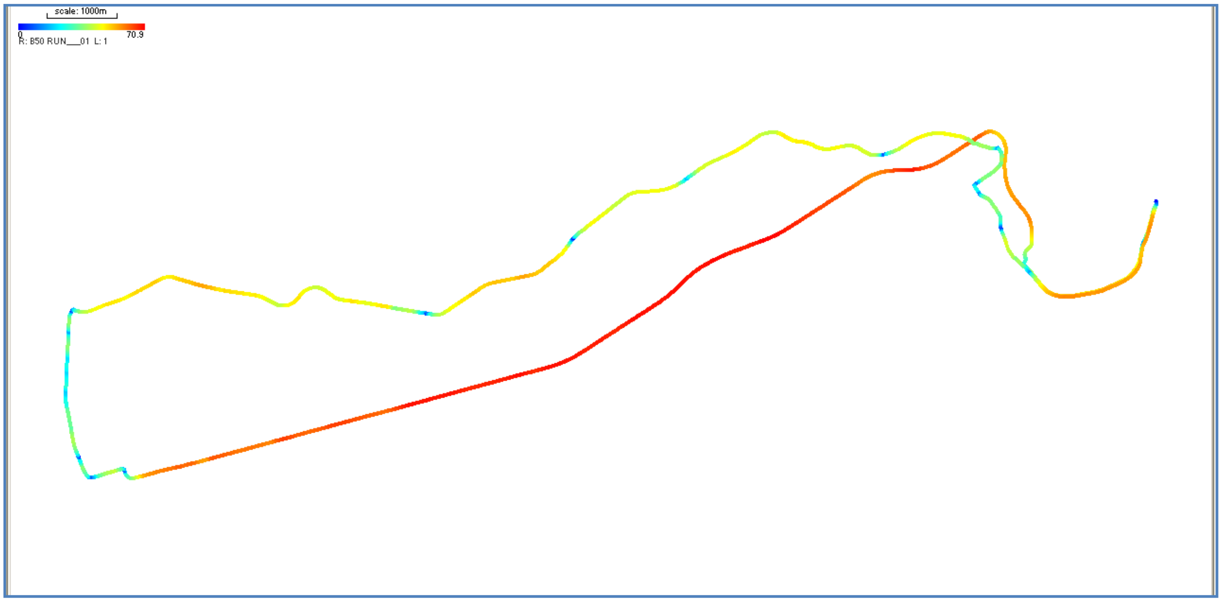
B20 Run 1 [power]



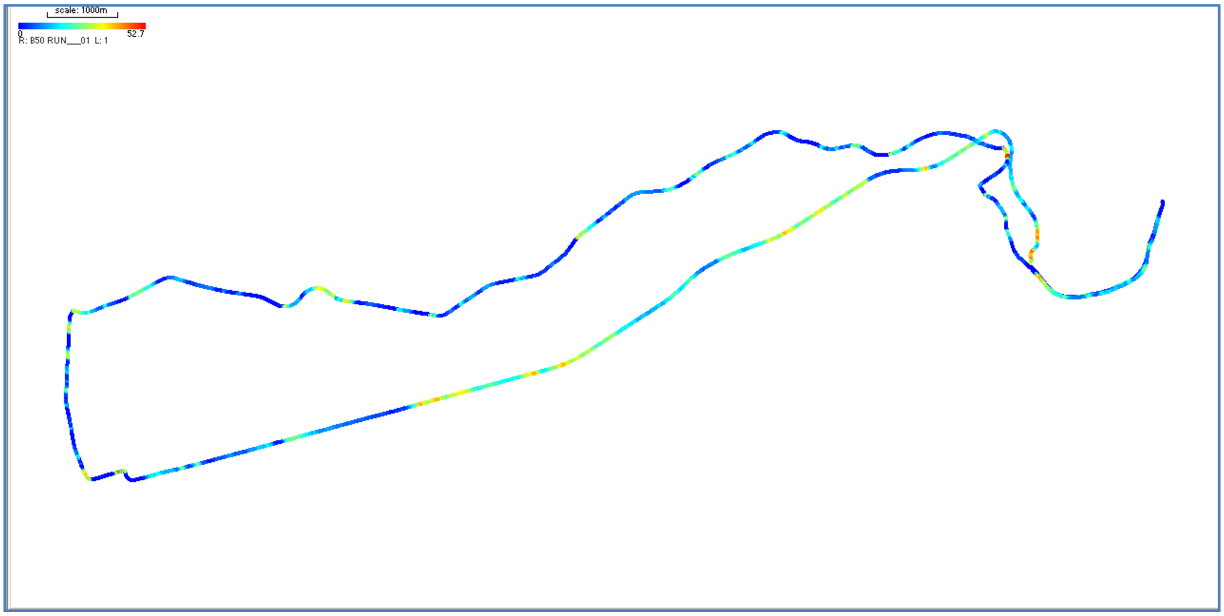
B20 Run 2 [speed]



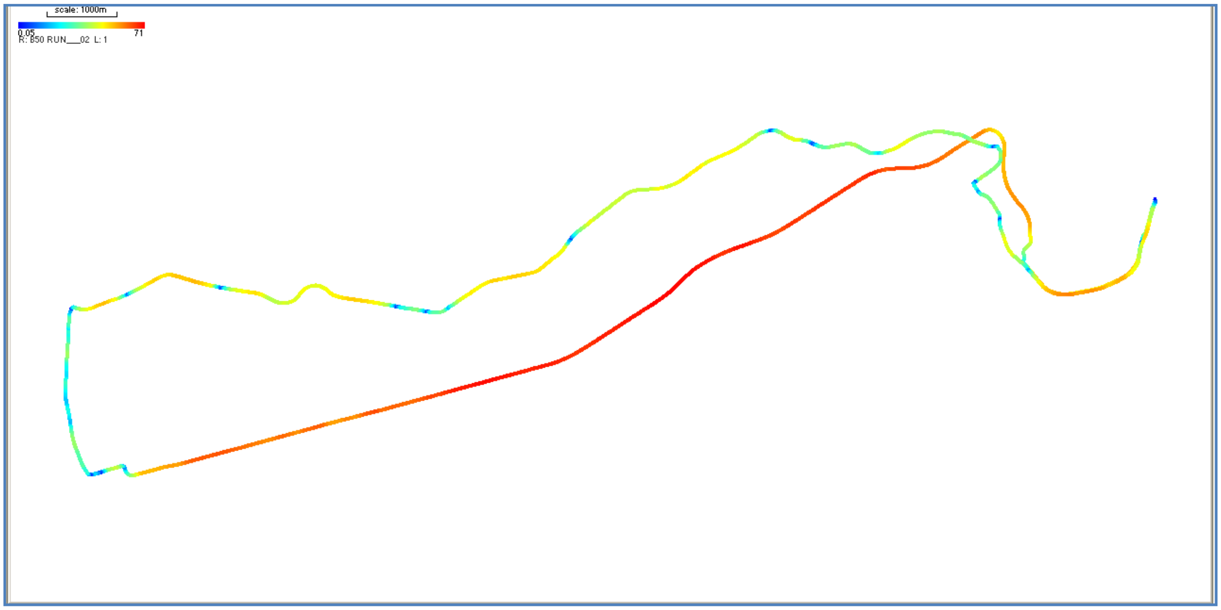
B20 Run 2 [power]



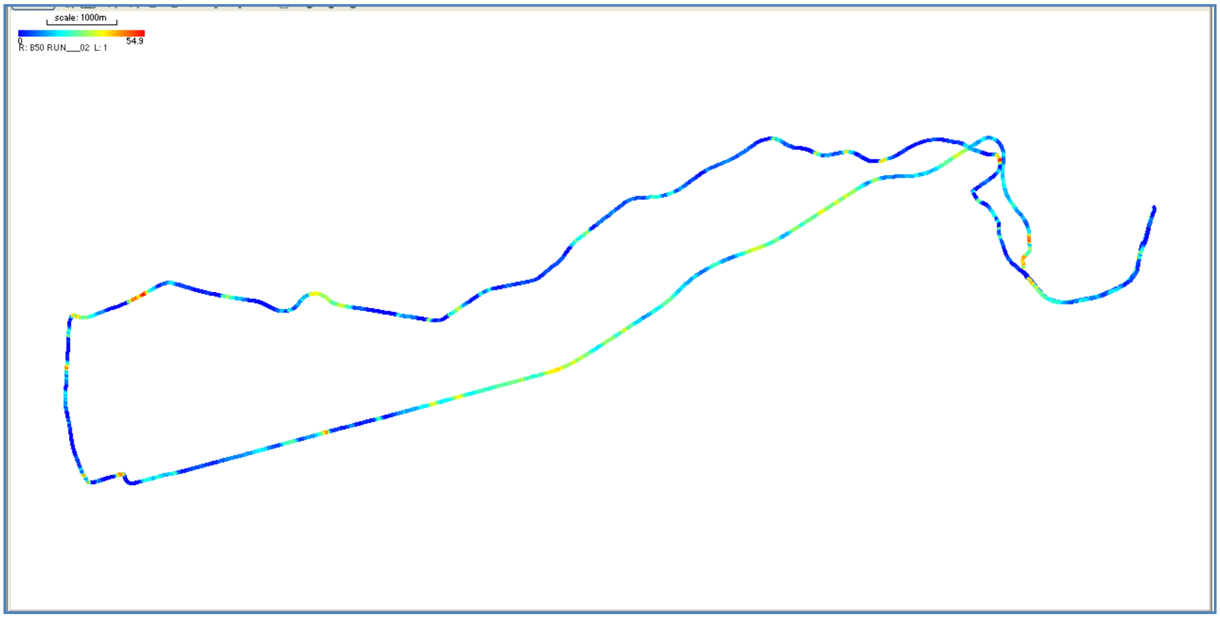
B50 Run1 [speed]



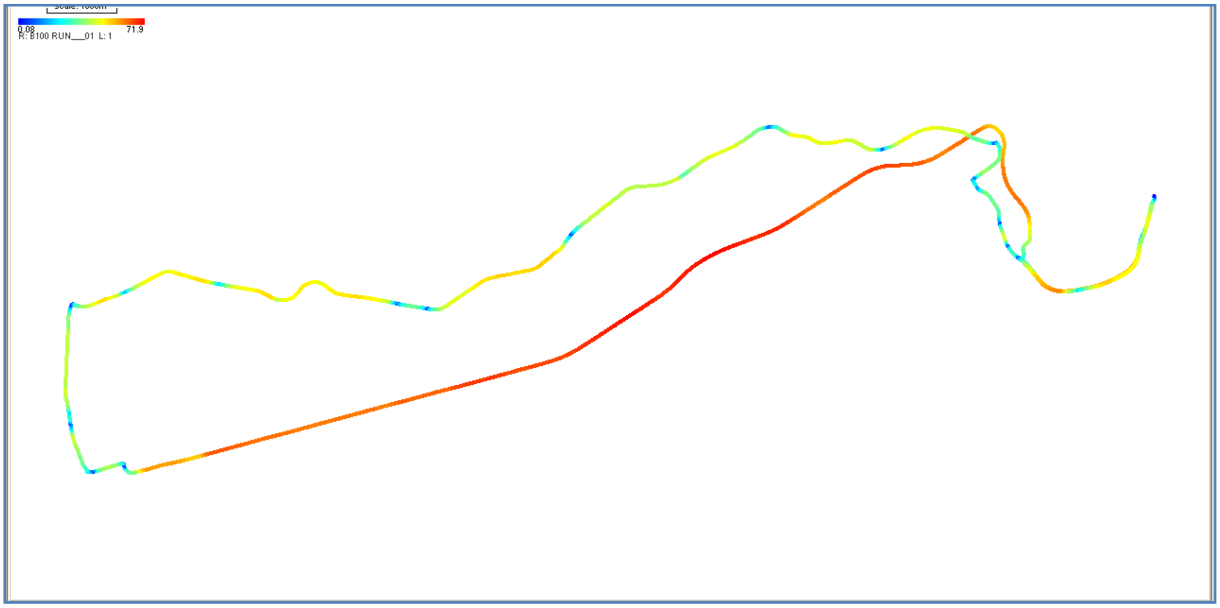
B50 Run1 [speed]



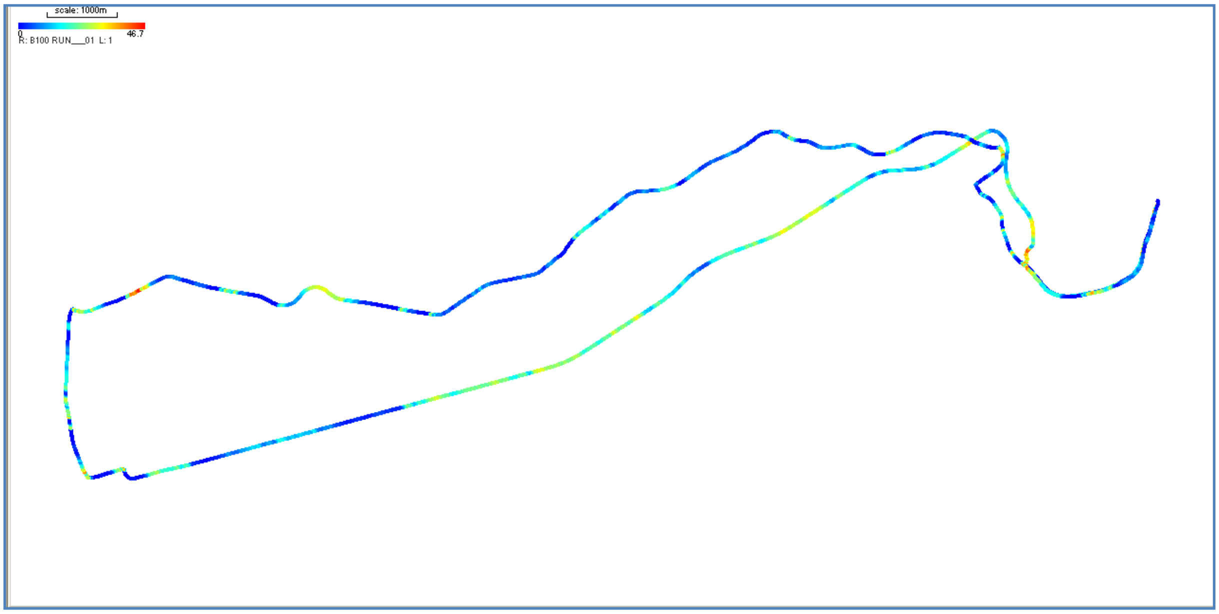
B50 Run 2 [speed]



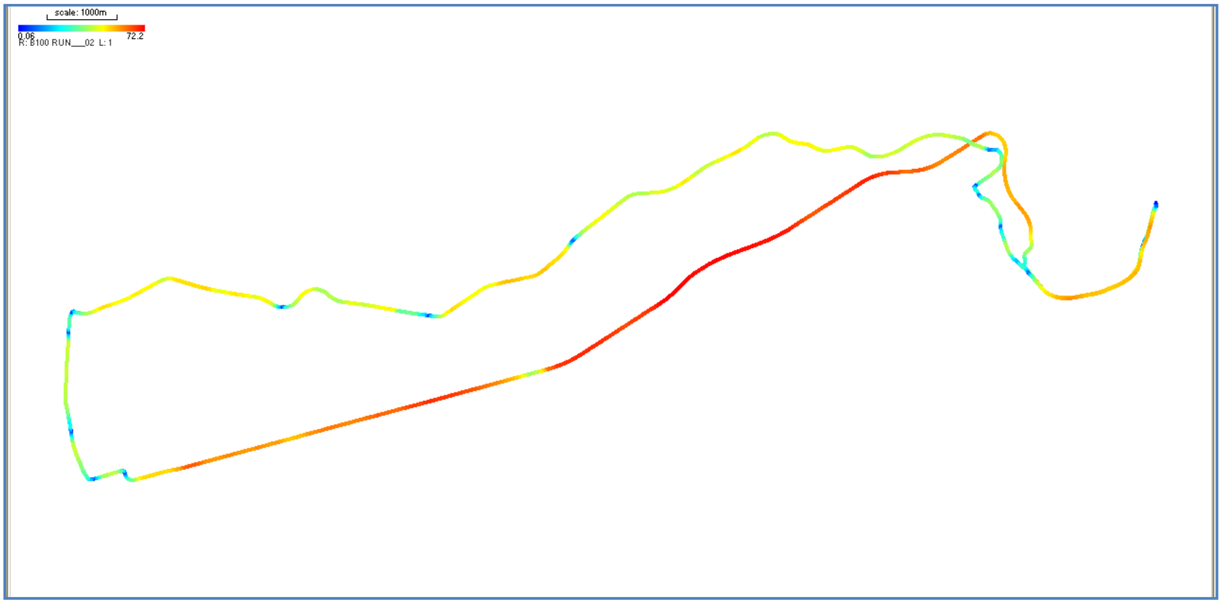
B50 Run 2 [power]



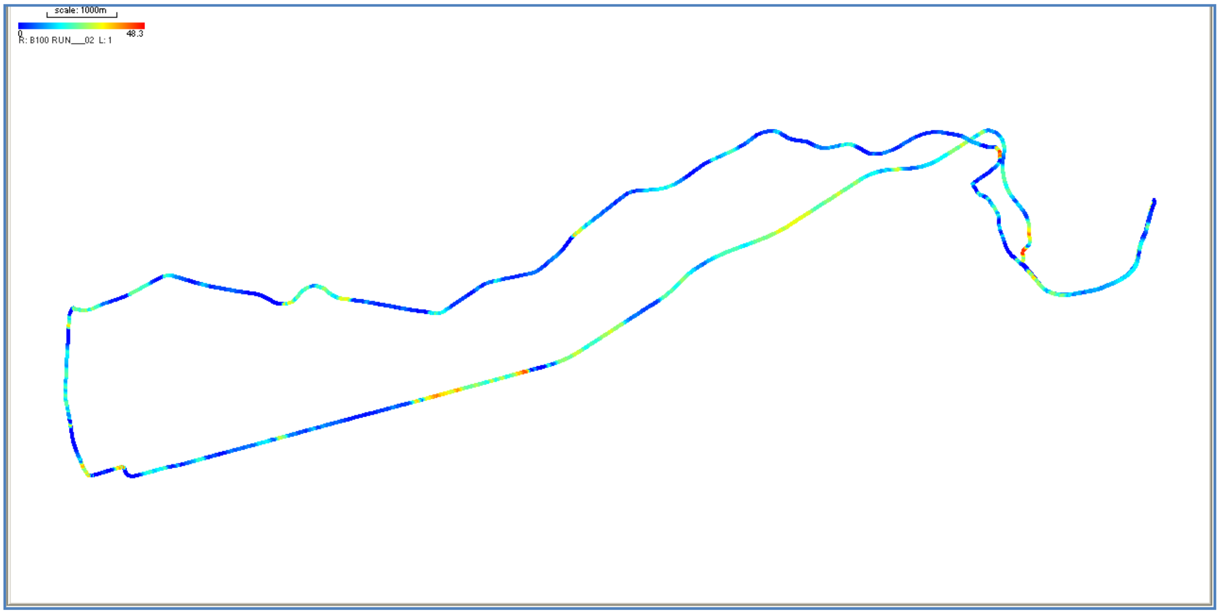
B100 Run 1 [speed]



B100 Run 2 [power]

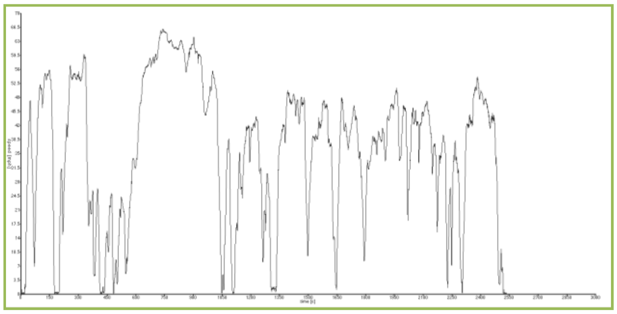


B100 Run 2 [speed]

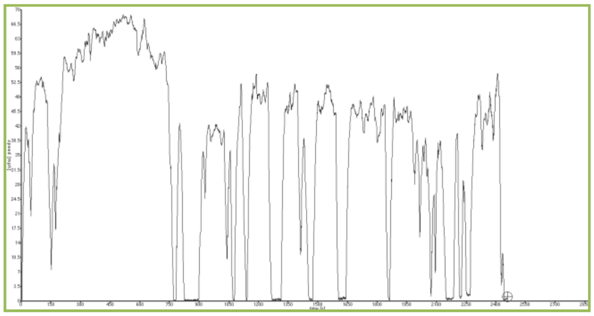


B100 Run 2 [power]

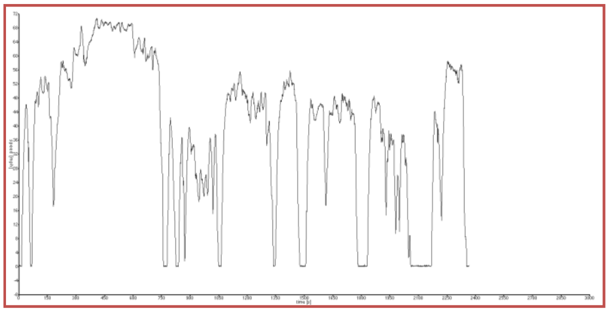
Velocity versus time plots for Test 1



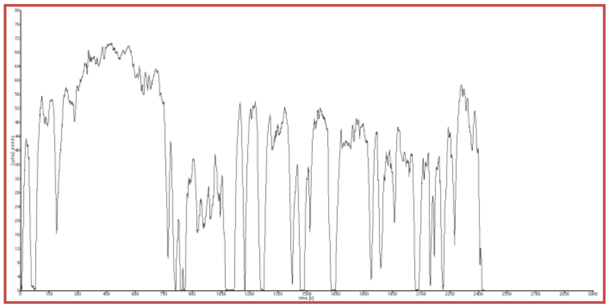
B20 Run 1



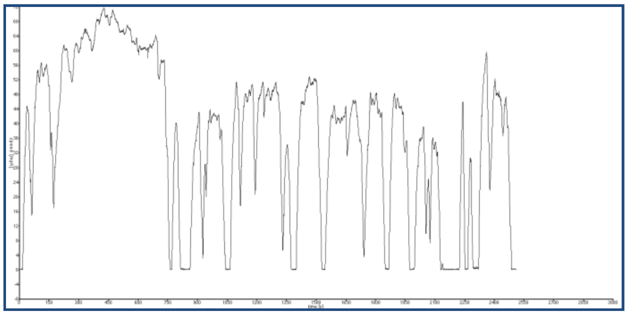
B20 Run 2



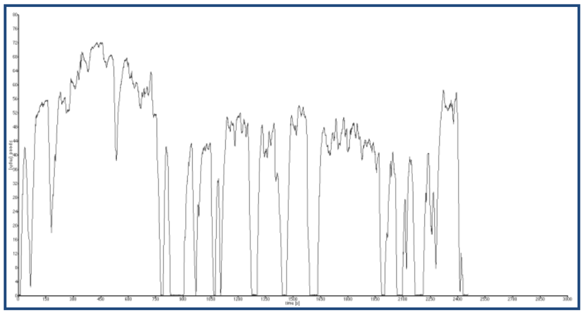
B50 Run 1



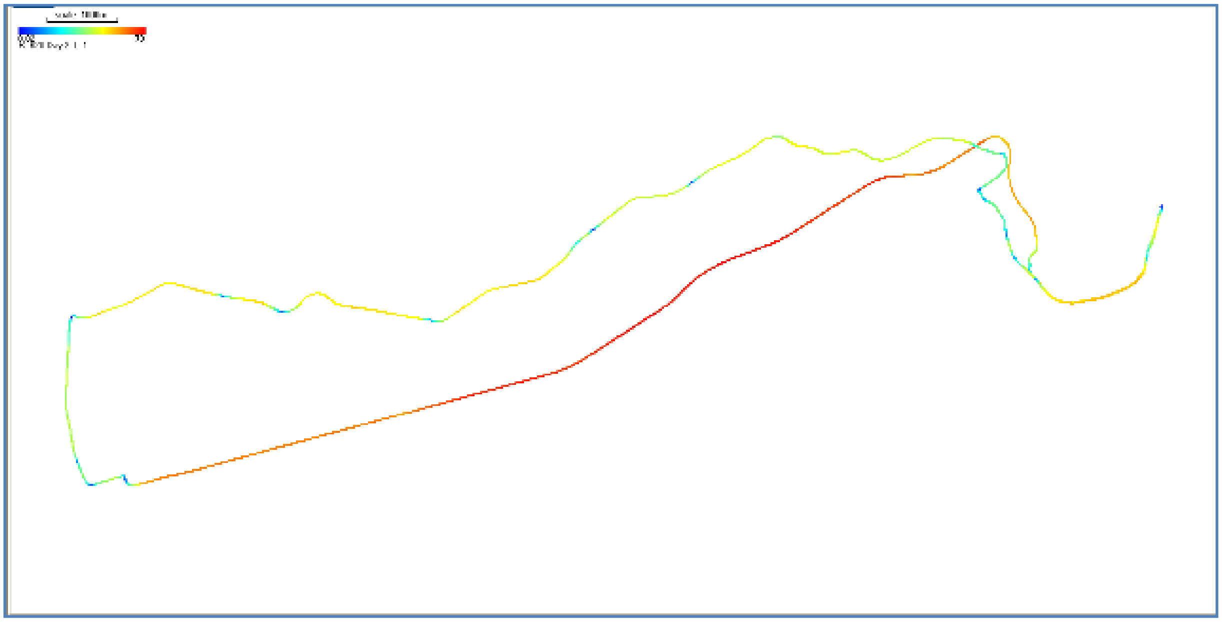
B50 Run 2



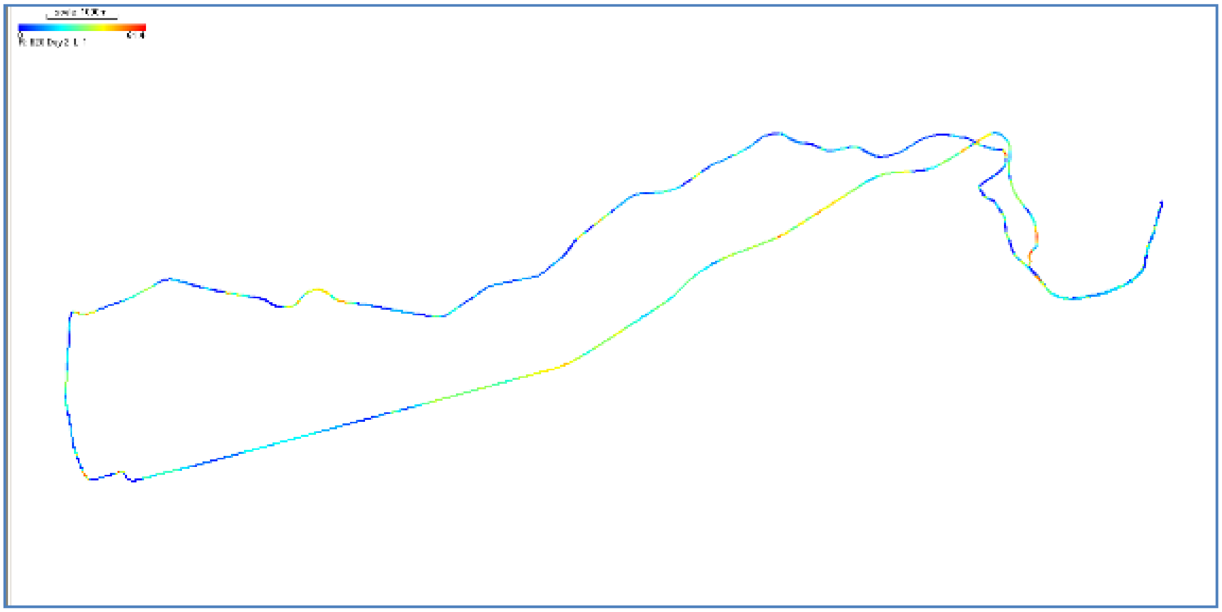
B100 Run 1



B100 Run 2

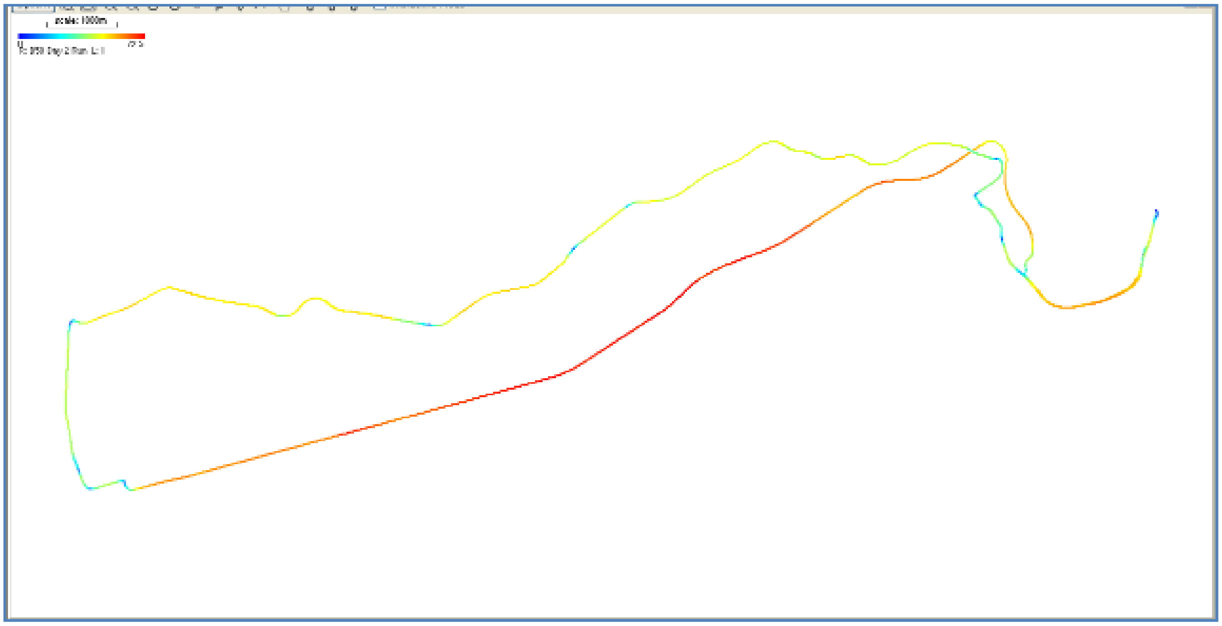


B20 Test 2 Run [Speed]

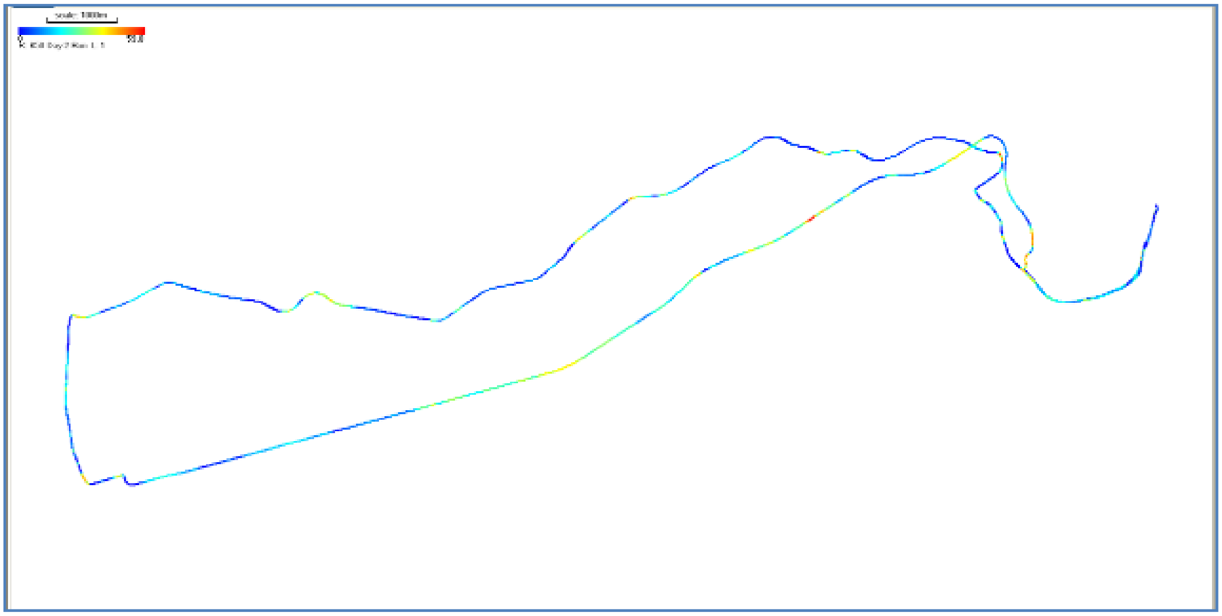


B20 Test 2 Run [Power]

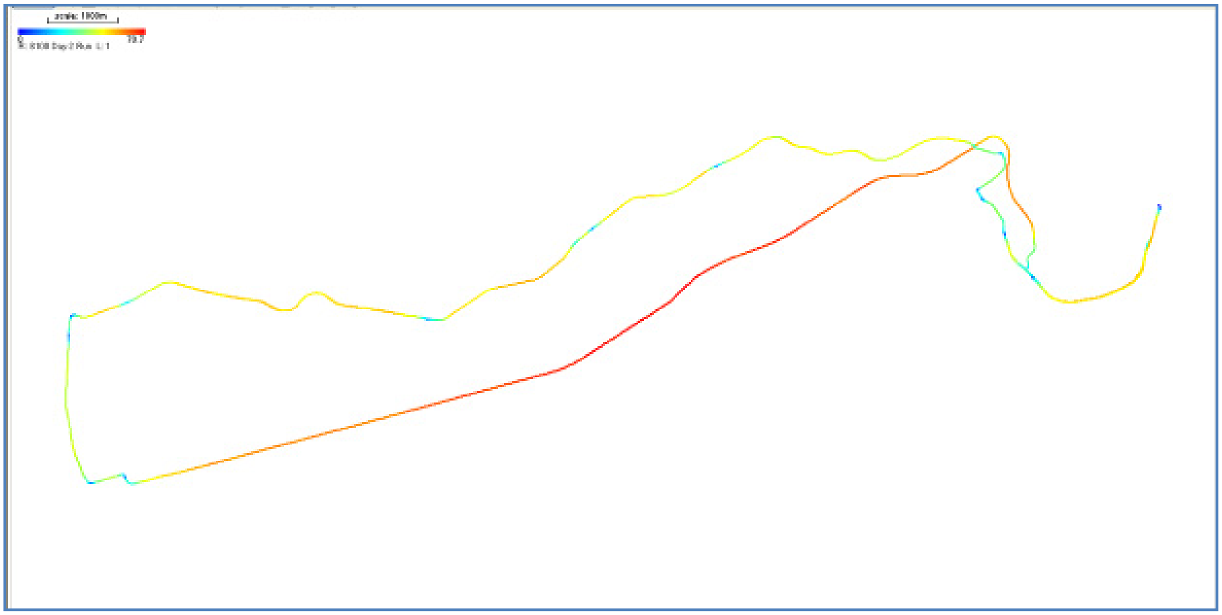
__Test 2 Speed and Power Maps__



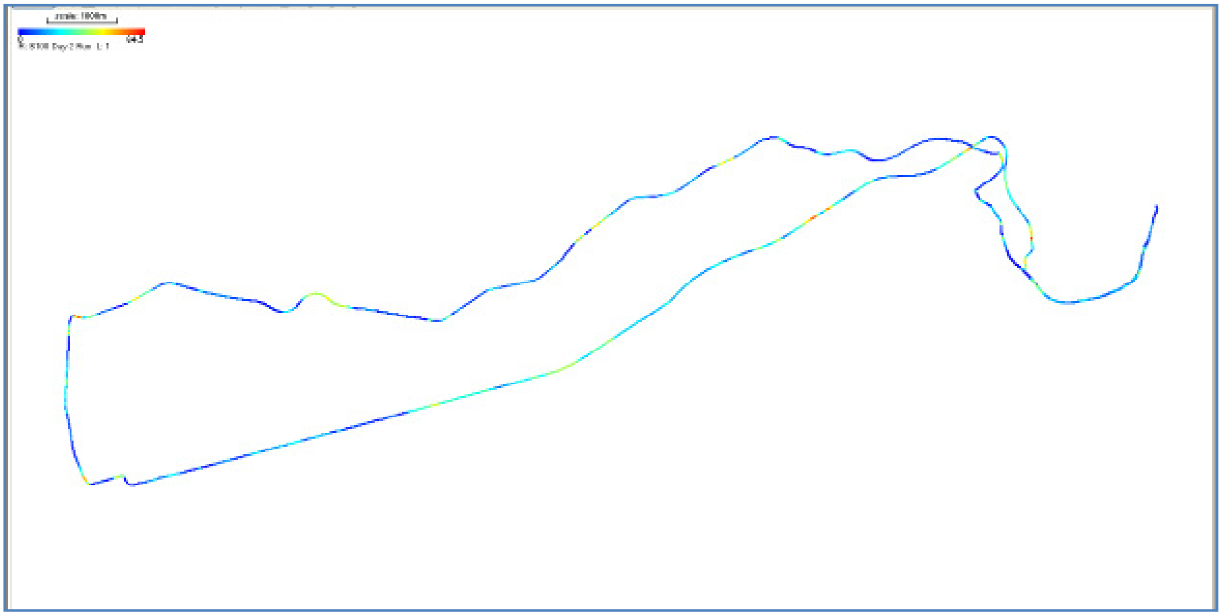
B50 Test 2 [Speed]



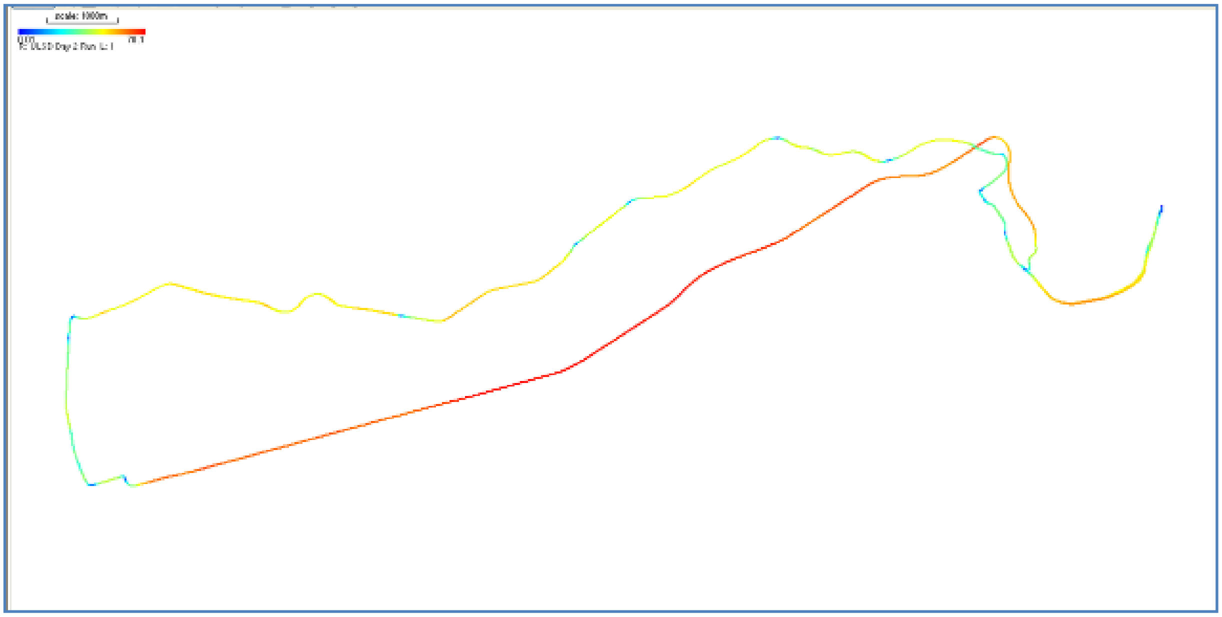
B50 Test 2 [Power]



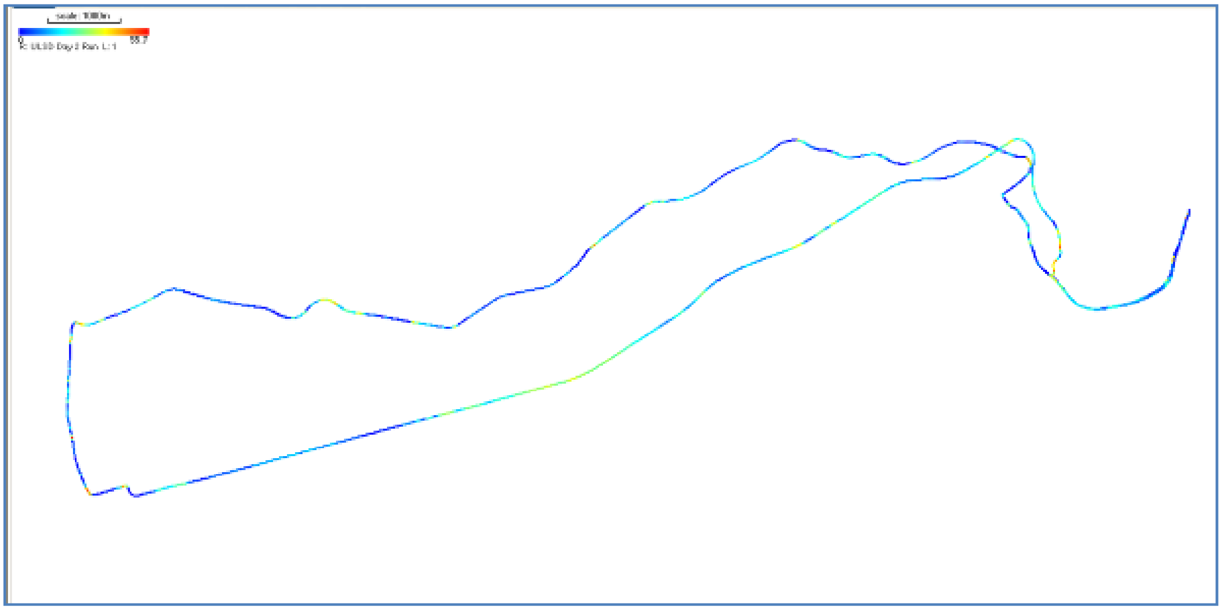
B100 Test 2 [speed]



B100 Test 2 [power]

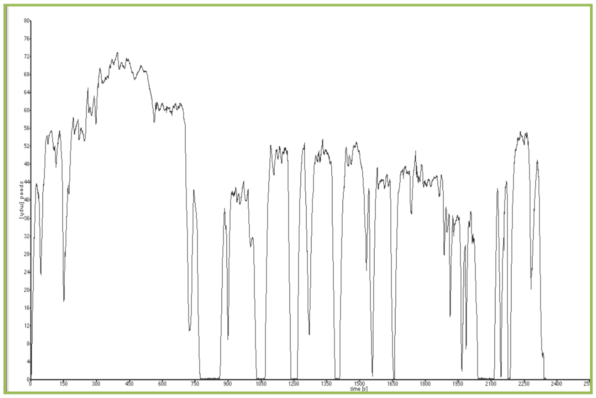


ULSD Test 2 [speed]

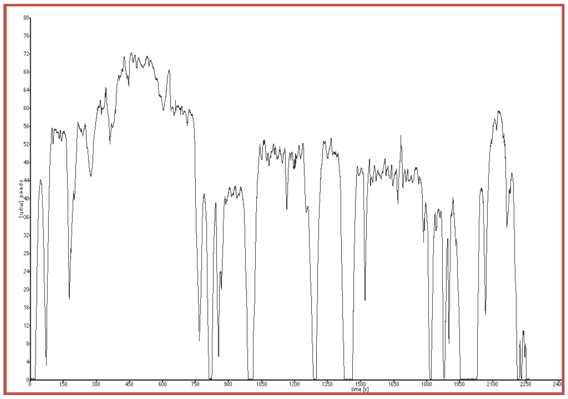


ULSD Test 2 [power]

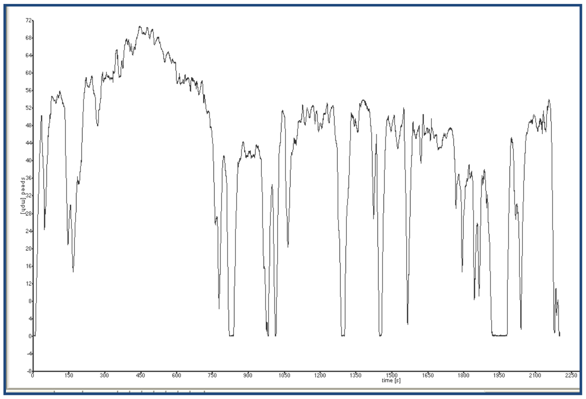
Test 2 Velocity Versus Time Plots



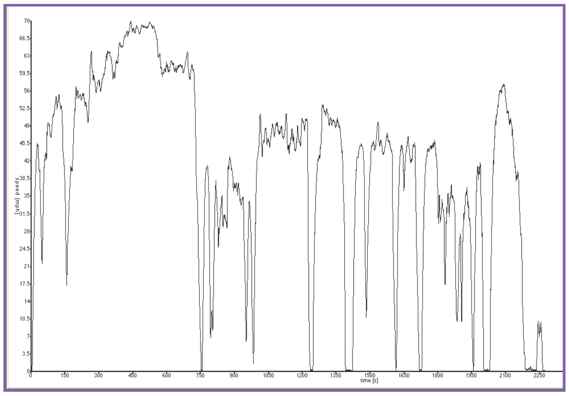
Test 2 B20



Test 2 B50



Test 2 B100



Test 2 ULSD

Appendix IVX – Error/Repeatability Analysis

Drive Cycle Repeatability

The repeatability of the drive cycles was analyzed for both Test 1 and Test 2 by looking at the average and maximum values of speed, power and longitude acceleration data. The standard deviation of these averages was then compared to the mean values.

Test 1	B20 Run 1	B20 Run2	B50 Run 1	B50 Run 2	B100 Run 1	B100 Run 2
Average Speed [mph]	36.3	37.5	38.9	37.9	36.7	37.6
Max Speed [mph]	66.1	68.9	70.7	70.8	71.8	72.1
Average Power [kW]	8.2	9.8	10.7	11.0	9.7	9.7
Max Power [kW]	49.1	49.4	51.0	54.0	46.6	48.0
Max Long Accel [g's]	0.261	0.286	0.345	0.300	0.242	0.272

Test 1	Median	Mean	SD	% SD/mean
Average Speed [mph]	37.5	37.5	0.923	2.46
Max Speed [mph]	70.80	70.08	2.28	3.22
Average Power [kW]	9.78	9.85	0.96	9.86
Max Power [kW]	49.24	49.67	2.59	5.25
Max Long Accel [g's]	0.2790	0.2842	0.0361	12.9

Test 2	ULSD	B20	B50	B100
Average Speed [mph]	40.5	39.2	40.7	41.8
Max Speed [mph]	70.0	71.0	72.3	70.63
Average Power [kW]	10.2	15.7	13.0	13.3
Max Power [kW]	39.0	61.32	58.7	61.2
Max Long Accel [g's]	0.312	0.349	0.289	0.314

Test 2	Median	Mean	SD	% SD/mean
Average Speed [mph]	40.6	40.6	1.06	2.61
Max Speed [mph]	71.5	71.5	1.40	1.96
Average Power [kW]	13.2	13.1	2.24	17.0
Max Power [kW]	59.9	55.1	10.7	17.9
Max Long Accel [g's]	0.313	0.316	0.024	7.85

For emissions error and repeatability the results from Test 1 were compared to each other for each fuel tested.

Standard Deviation
Max

	B100	% of Full	B50	% of Full	B20	% of Full
NOx	16.971	1.61	61.518	7.67	9.899	1.36
NOx Corr	30.406	2.96	63.640	8.11	7.778	1.09
CO2	0.997	8.41	0.127	1.10	0.431	3.64
CO	1.195E-01	106.22	9.899E-03	29.55	1.591E-01	70.09
HC	9.899	27.12	3.536	6.61	7.071	13.09
O2	0.042	0.20	0.035	0.17	0.099	0.47

Standard Deviation
Average

	B100	% of Full	B50	% of Full	B20	% of Full
NOx	1.043	0.49	5.283	3.53	13.857	9.60
NOx Corr	2.106	1.02	5.832	3.99	13.869	9.83
CO2	0.245	4.55	0.035	0.62	0.127	2.34
CO	1.201E-03	126.15	1.619E-04	116.26	1.644E-04	69.28
HC	5.119	19.51	2.920	6.95	4.311	9.94
O2	0.145	1.08	0.129	1.01	0.112	0.88

Standard Deviation
NOX Frequency

	B100	% of Full	B50	% of Full	B20	% of Full
>500	7.071	0.62	23.335	2.46	8.485	1.140495
>600	4.243	0.37	0.707	0.07	4.243	0.570247
>700	2.828	0.25	6.364	0.67	2.828	0.380165
>800	6.364	0.56	9.899	1.05		
>900	9.899	0.87	3.536	0.37		
>1000	13.435	1.18				
>1100	1.414	0.12				

Standard Deviation
NOX Corr Freq

	B100	% of Full	B50	% of Full	B20	% of Full
>500	4.243	0.38	28.991	3.06	12.021	1.62
>600	9.192	0.82	5.657	0.60	3.536	0.48
>700	5.657	0.50	7.778	0.82	2.121	0.29
>800	6.364	0.57	9.899	1.05		
>900	14.849	1.32	3.536	0.37		
>1000	10.607	0.95				
>1100	2.121	0.19				

VITA

Scott James Curran was born in Craig, Colorado in 1981 and moved to Oak Ridge, Tennessee in 1991. He attended Oak Ridge High School and started classes at Roane State Community College's Oak Ridge Branch Campus in the fall of 2001. At Roane State he tutored in algebra and in 2003 was nominated for the president's award for outstanding student achievement. In the fall of 2003 Scott transferred to The University of Tennessee to study Mechanical Engineering. Scott was awarded three Summer Undergraduate Research Internships from UTK, the first for the retrofit of a single cylinder engine to run E85, the second was to evaluate an E85 retrofitted engine on a small dynamometer and create an E85 powered race kart as a demonstration. He presented the E85 work at the ASME student conference's Old Guard Oral Presentation competition and published the work in the proceedings of the National Conference on Undergraduate Research. The last was to work on the UT Biodiesel project where he presented the final work at the 2007 Sustainable Biodiesel Summit. Scott also received the Boeing scholarship to work on the UT Biodiesel project. Scott graduated from UTK in the spring of 2007 with a B.S. in Mechanical Engineering, having worked on the Challenge X hybrid design project as his senior capstone design in which he worked on NO_X reduction with an ammonia SCR system and started graduate studies under Dr. David Irick in the fall of 2007. He was awarded the GATE fellowship to be a graduate team leader for the Tennessee Challenge X team and a graduate research assistantship to work on the UT Biodiesel research project. In the spring of 2008 he was awarded another research assistantship to work on a plug-in electric hybrid project.