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16. Abstract

The objective of this document is to summarize the available findings by Lubrizol and by third parties on the effects of PuriNOx on a variety of diesel engines operating over a variety of conditions. The information was obtained from the 19 documents provided by Lubrizol and additional documents obtained from the Engineering Library at the University of Texas. It is obvious from this synthesis that the available literature exhibits conflicting data, conclusions, and recommendations about the benefits of emulsified diesel fuels. However, it can be concluded with relative certainty that emulsified diesel fuels always provide benefits in terms of NOx and PM emissions when tested over any cycle. The magnitude of the advantage from using emulsified diesel fuels is, however, largely a function of the engine type, the operating conditions, the properties of the baseline diesel fuel, and the properties of the diesel fuel that is blended into the emulsion. In addition, it is known that emulsions offer a benefit in terms of thermal efficiency and lubricity. Questions relating to the cost effectiveness of using PuriNOx and engine durability were not adequately addressed in the available literature. The results from this synthesis will allow for an informed discussion of the scope of the current study.

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Emulsified Diesel Fuels: Literature Review and Consolidation of Lubrizol Recommendations

R. D. Matthews

Research Report 4576-1

Research Project 0-4576
Emulsified Diesel Emission Testing, Performance Evaluation, and Operational Assessment

Conducted for the
Texas Department of Transportation
in cooperation with
U.S. Department of Transportation
Federal Highway Administration
by the
Center for Transportation Research,
Bureau of Engineering Research,
The University of Texas at Austin

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Notice

The United States Government and the State of Texas do not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of this report.

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1. PuriNOx: Conversion and Handling

1.1 Consolidation of Lubrizol Recommendations for Converting Vehicles to PuriNOx

1. Verify the type of existing fuel filter(s) and water separator on the vehicle. PuriNOx fuel is only compatible with particulate-type diesel fuel filters. PuriNOx fuel is not compatible with water-absorbing-type fuel filters or turbine-type water separators. If necessary, change the fuel filter(s) and remove the turbine from the water separator. Continue the use of a water separator system that is gravity based---do NOT use a chemically-based water separator. Centrifugal style separators can be used if the turbine is removed.

   Four different types of filter media are acceptable, and are listed in order of preference:

   - Synthetic
   - Synthetic / cellulose combination
   - Resin-impregnated cellulose
   - Cellulose

   Media treatment that has been chemically treated to absorb water is not acceptable and must be avoided. Silicone is an example of a common media treatment that must be avoided.

2. Add PuriNOx to an empty or low fuel tank. An empty fuel tank is preferred; this provides the immediate emission benefits of PuriNOx.

3. After using the first tankful of PuriNOx or after approximately the first 24 hours of operation, replace the fuel filter.

   NOTE: Cleaning of the fuel system will occur due to the high-powered surfactant in PuriNOx fuel. This could cause premature filter plugging.

4. If any time during the first month of operation a power loss is experienced, the fuel filter should be replaced.

5. The vehicle can be changed back to diesel fuel at any time. However, it is recommended that this fuel mixture be consumed through ongoing vehicle operation. When operating on a mixture of diesel fuel and PuriNOx, a particulate-type diesel fuel filter must continue to be used.

1.2 Obtaining a PuriNOx Compatible Fuel Filter

1. The following major North American fuel filter manufacturers provide technical support for their filter product line. They may be called if there are questions related to the proper selection of fuel filters for PuriNOx fuel.

Baldwin	1-800-822-5394
Donaldson	1-800-374-1374
Fleetguard	1-800-223-4583
Fram	1-800-890-2075
Luber-finer	1-800-882-0890
NAPA	1-800-805-6272
Purolator	1-800-526-4250
Racor	1-800-272-7537
Wix	1-800-949-6698

2. Know your current filter part number so it can be cross-referenced for a replacement.

   If for any reason you are unable to get a replacement particulate-only filter, then contact Lubrizol Customer Service at 1-866-854-9669.

1.3 Spill Cleanup and Health Information

1.3.1 Spills and Cleanup of PuriNOx 20

The following was extracted from the Lubrizol paper "Recommended Procedures: Spills and Cleanup, PuriNOx Fuel (Summer Blend)."* A representative of Lubrizol said that the exact same procedure applies to winter-grade PuriNOx (Duncan, 2002). A similar report is available for the additive package (PuriNOx 1121A), but is not reviewed because TxDOT personnel will not be handling the additive except as a component within the PuriNOx 20 fuel.

	Recommended Handling					
Scenarios	**A**	**B**	**C**	**D**	**E**	**F**
Contaminated soils, rags, absorbents, etc. from spill cleanup	X					
Product pooling (created from a spill)	X		X			
Unused product		X				
Residual product in lines, fittings, packaging (drums, pails, etc.)		X	X			
Unusable product due to contamination or improper handling			X			
Contamination of surface water				X		
Spill to a municiple sewer system				X		
Cleaning of contaminated objects (cars, clothing, etc.)					X	
Disposal of packages: drums, pails, etc.						X

A. Material would be classified as a waste and all contaminated soil, debris, etc. must be properly handled/disposed of according to regulatory requirements. **PuriNOx summer blend can be handled in a similar manner to handling diesel fuel. PuriNOx summer blend is not an RCRA hazardous waste.**

B. Residual PuriNOx summer blend should be consumed as a fuel, if possible. Excess PuriNOx summer blend may be mixed with diesel fuel and consumed in an engine. Contact Lubrizol representatives for details.

C. Contaminated or otherwise unusable PuriNOx summer blend must be disposed of by a proper, licensed disposer (handled in a similar manner to diesel fuel). **Lubrizol cannot accept return of waste material.**

D. Immediately notify proper agencies (e.g., surface spills in U.S., contact Coast Guard). PuriNOx summer blend is lighter than water and is insoluble in water. Contain spill and recover using booms, vacuum, etc.

E. Lightly soiled clothing or objects (e.g., cars) can be washed with soap/detergent and water. Heavily contaminated articles may require use of a hydrocarbon solvent (e.g., diesel fuel), which must be collected during use and disposed of properly.

F. Empty drums, pails, etc. can be recycled or disposed of according to regulatory requirements. PuriNOx summer blend is classified as a combustible material; residual fuel, or exposure to heat or flame may cause a fire.

* Please refer to the most recent MSDS. Contact Lubrizol with further questions at 1-877- 787-4669. See disclaimer at the bottom of the original Lubrizol recommendations.

1.3.2 Health and Safety Information from the MSDS

<u>Distilled Diesel Fuel (distillate fuel oil, e.g., #2 diesel fuel)</u>

Principal Hazards:

- Harmful if inhaled.
- Combustible liquid.
- May cause chronic health effects.

Noteworthy Warnings:

- Toxic fumes, gases, or vapors may evolve on burning.
- Empty container retains residue. Do not cut, weld, braze, solder, drill, grind, or expose container to heat, flame, spark or other sources of ignition.
- No explosive properties in the liquid state, but vapors may form ignitable mixtures in air.
- On thermal decomposition, smoke, carbon monoxide, carbon dioxide, aldehydes, and other products of incomplete combustion are formed.

Acute Exposure:

- Accidental ingestion: the LD50 in rats is in the range of 2000–5000 mg/kg, based on actual data.
- Not expected to cause eye irritation, based on data from components or similar materials.
- Prolonged or repeated skin contact (e.g., from clothing wet with fuel) will cause dermatitis. Symptoms may include redness, edema, and drying and cracking of the skin.
- Dermal toxicity: the LD50 in rabbits is >2000 mg/kg, based on actual data.
- Inhalation toxicity: high concentrations may cause headaches, dizziness, fatigue, nausea, vomiting, drowsiness, stupor, and other central nervous system effects leading to visual impairment, respiratory failure, unconsciousness, and death.
- Respiratory irritation: no data are available to indicate whether product or components may cause respiratory irritation under normal workplace conditions and good industrial hygiene practices.

Chronic Exposure:

- Repeated and prolonged overexposure to diesel fuel may cause degenerative changes in the liver, kidneys, and bone marrow.

Ecological Information:

- No data are available to evaluate the bioconcentration potential of diesel fuel.

Waste Disposal:

- The material, if discarded, is a ***hazardous waste*** under RCRA Regulation 40 CFR 261. Waste management should be in compliance with federal, state, and local laws. Material, if discarded, is expected to be hazardous waste under RCRA due to ignitability (D001).

<u>**PuriNOx™ 20 SB-RO (Summer Grade)**</u>

Principal Hazards:

- Harmful if inhaled. (*Same as diesel fuel*.)
- Combustible liquid. (*Same as diesel fuel*.)
- May cause chronic health effects. (*Same as diesel fuel*.)

Noteworthy Warnings:

- Toxic fumes, gases, or vapors may evolve on burning. *(Same as diesel fuel.)*
- Empty container retains residue. Do not cut, weld, braze, solder, drill, grind, or expose container to heat, flame, spark or other sources of ignition. *(Same as diesel fuel.)*
- No explosive properties in the liquid state, but vapors may form ignitable mixtures in air. *(Same as diesel fuel.)*
- On thermal decomposition, smoke, carbon monoxide, carbon dioxide, aldehydes, and other products of incomplete combustion are formed. *(Same as diesel fuel.)*

Acute Exposure:

- Accidental ingestion: the LD50 in rats is >5000 mg/kg, based on data from components or similar materials. *(Less hazardous than diesel fuel.)*
- Not expected to cause eye irritation, based on data from components or similar materials. *(Same as diesel fuel.)*
- Prolonged or repeated skin contact (e.g., from clothing wet with fuel) will cause dermatitis. Symptoms may include redness, edema, drying, and cracking of the skin. *(Same as diesel fuel.)*
- Dermal toxicity: the LD50 in rabbits is >2000 mg/kg, based on data from components or similar materials. *(Same as diesel fuel.)*
- Inhalation toxicity: high concentrations may cause headaches, dizziness, fatigue, nausea, vomiting, drowsiness, stupor, and other central nervous system effects leading to visual impairment, respiratory failure, unconsciousness and death. *(Same as diesel fuel.)*
- Respiratory irritation: not expected to cause nose, throat, or lung irritation, based on data from components or similar materials. *(Similar to diesel fuel.)*

Chronic Exposure:

- Repeated and prolonged overexposure to diesel fuel may cause degenerative changes in the liver, kidneys, and bone marrow. *(Same as diesel fuel.)*

Ecological Information:

- Less than 1% of the components potentially bioconcentrate, based on octanol/water coefficients. *(No data available to evaluate the bioconcentration potential for diesel fuel.)*

Waste Disposal:

- The material, if discarded, is a ***hazardous waste*** under RCRA Regulation 40 CFR 261. Waste management should be in compliance with the federal, state, and local laws. Material, if discarded, is expected to be hazardous waste under RCRA due to ignitability (D001). *(Same as diesel fuel.)*

PuriNOx™ 20WB-CT (Winter Grade)

Principal Hazards:

- Flammable liquid, may create a flash fire hazard. (*Stronger wording than for diesel fuel and summer-grade PuriNOx.*)
- Harmful if inhaled. (*Same as diesel fuel and summer-grade PuriNOx*.)
- Component(s) known to cause chronic human health effects. (*Stronger wording than for diesel fuel and summer-grade PuriNOx*.)
- May be harmful if absorbed through skin. (*Not noted for diesel fuel or summer-grade PuriNOx*.)
- May cause eye irritation. (*Not noted for diesel fuel or summer-grade PuriNOx.*)

Noteworthy Warnings:

- Static ignition hazard can result from handling and use. Electrically bond and ground all containers and equipment before transfer or use of material. *(Not noted for diesel fuel or summer-grade PuriNOx.)*
- Vapors from spill may form explosive mixtures with air. Immediately evacuate all personnel from danger area. *(Not noted for diesel fuel or summer-grade PuriNOx.)*
- Empty container retains residue. Do not cut, weld, braze, solder, drill, grind or expose container to heat, flame, spark or other sources of ignition. *(Same as diesel fuel and summer-grade PuriNOx.)*
- Toxic fumes, gases or vapors may evolve on burning. *(Same as diesel fuel and summer-grade PuriNOx.)*

- On thermal decomposition, smoke, carbon monoxide, carbon dioxide, aldehydes, and other products of incomplete combustion are formed. *(Same as diesel fuel and summer-grade PuriNOx.)*

Acute Exposure:

- Accidental ingestion: the LD50 in rats is >5000 mg/kg, based on data from components or similar materials. *(Less hazardous than diesel fuel.)*
- Ingestion of methyl alcohol can affect the optic nerve and result in blindness. It can also cause gastrointestinal tract irritation, mental sluggishness, nausea, severe illness, and possible death. *(Not noted for diesel fuel or summer-grade PuriNOx.)*
- Weak to moderate eye irritant. Does not meet Canadian D2B or EU R36 criteria. *(Neither diesel fuel nor summer-grade PuriNOx is expected to cause eye irritation.)*
- Prolonged or repeated skin contact (e.g., from clothing wet with fuel) will cause dermatitis. Symptoms may include redness, edema, and drying and cracking of the skin. *(Same as diesel fuel and summer-grade PuriNOx.)*
- Dermal toxicity: the LD50 in rabbits is >2000 mg/kg, based on data from components or similar materials. (*Same as diesel fuel and summer-grade PuriNOx*.) Components of this material may be absorbed through the skin. *(Not noted for diesel fuel or summer-grade PuriNOx.)*
- Inhalation toxicity: high concentrations may cause headaches, dizziness, fatigue, nausea, vomiting, drowsiness, stupor, and other central nervous system effects leading to visual impairment, respiratory failure, unconsciousness, and death. *(Same as diesel fuel and summer-grade PuriNOx.*)
- Respiratory irritation: if material is misted or if vapors are generated from heating, exposure may cause irritation of mucous membranes and the upper respiratory tract, based on data from components or similar materials. *(Stronger respiratory irritation hazard than either diesel fuel or summer-grade PuriNOx.)*

Chronic Exposure:

- Repeated and prolonged overexposure to methanol can cause eye, lung, spleen, kidney, brain, and nervous system damage, and also liver abnormalities in laboratory animals. *(Not noted for diesel fuel or summer-grade PuriNOx, since these do not contain methanol.)*
- Repeated and prolonged overexposure to diesel fuel may cause degenerative changes in the liver, kidneys, and bone marrow. *(Same as diesel fuel and summer-grade PuriNOx.)*
- In-vitro tests on methanol indicate limited evidence of mutagenicity. No in-vivo information. *(Not noted for diesel fuel or summer-grade PuriNOx, since these do not contain methanol.)*

- Methanol has been reported to cause birth defects in rats exposed to very high levels of vapor: 20,000 ppm. *(Not noted for diesel fuel or summer-grade PuriNOx, since these do not contain methanol.*)

Ecological Information:

- Less than 1% of the components potentially bioconcentrate, based on octanol/water coefficients. (*Same as summer-grade PuriNOx; no data available to evaluate the bioconcentration potential for diesel fuel*.)

Waste Disposal:

- The material, if discarded, is a ***hazardous waste*** under RCRA Regulation 40 CFR 261. Waste management should be in compliance with the federal, state, and local laws. Material, if discarded, is expected to be hazardous waste under RCRA due to ignitability (D001). *(Same as diesel fuel and summer-grade PuriNOx.)*

2. Literature Review

2.1 Introduction

Lubrizol provided 19 reports that are reviewed in Section 2.2. Additional reports were obtained from the Engineering Library at the University of Texas. These reports are reviewed in Section 2.3. A summary and conclusions are presented in Section 3.

2.2 Reports Provided by Lubrizol

The first report provided by Lubrizol (Anon, undated) appears to be a copy of a PowerPoint presentation on PuriNOx, with comments added. As far as emissions and fuel consumption are concerned, few specifics are provided regarding engines, test cycles, etc. However, the summary they present for engine dyno tests of a variety of engines is of some interest. This summary is provided in Table 1.

Table 1. Lubrizol Summary of Engine Dyno Results

Application	NOx Reduction (%)	PM Reduction (%)
Construction eqpt.	-19	-25
Generator	-15	-51
On-highway truck	-9	-38
Truck/bus	-14	-63
Bus	-16	-55

It is not stated whether these are averages within each category, or maximum or minimum values. It is also not known whether the same test was performed for each and every engine or if this is a mix of types of tests. However, it is believed that the results in Table 1 were extracted from the reports discussed later in this section. Two conclusions can be extracted from this table. First, the effect on particulate matter (PM) is much larger than the effect on the emissions of the oxides of nitrogen (NOx). Because it appears that the State of Texas is only interested in NOx emissions–from the State Implementation Plan perspective–the larger PM benefit is only of mild interest. The second conclusion from Table 1 is that the benefit is variable. This may be due to a variety of factors, such as the type of test, the emissions standards that the engine was designed to meet (i.e., the engine and aftertreatment technology), and whether or not the engine was modified to recoup the torque loss that is associated with diluting the diesel fuel with water. In the present review, the effects of these factors will be analyzed.

The reports provided by Lubrizol can be divided into 9 categories: fundamental studies, steady state "mode" engine tests, transient cycle engine tests, European cycle vehicle tests, vehicle task tests, in-use tests, injector deposit tests, lubricity tests, and durability tests. Each of these is discussed below.

2.2.1 Fundamental Studies

Reports categorized as fundamental studies are those which are focused upon understanding the nature of the effects of emulsions on the combustion process in diesels.

An SAE paper by Lubrizol investigators (Langer et al., 2001) reports the results of three fundamental studies. The first involved use of an optically accessible Cummins diesel at the Combustion Research Facility of Sandia National Labs. This engine was used to image PM formation during the premixed phase of diesel combustion. It was shown that PuriNOx decreases PM formation more than would occur if the water served solely as a thermal diluent. From other studies (see Section 2.3), it is known that the presence of water in the fuel generates "microexplosions": because the water has a lower boiling point than most of the components in diesel fuel, it boils early, causing the relatively large diesel fuel droplets to "explode" into much smaller droplets. The second study reported in this paper reports the operation of a 1986 Caterpillar 3406B on the marine 4-mode cycle (ISO 8178-4). It was found that the brake specific emissions of NOx and PM (g/hp-hr) improve almost linearly with increasing mass percent water in the emulsion for all injection timings investigated, including retarded and advanced timings. However, the PM effect was weaker with the advanced injection timing. It is also shown that fuel consumption increases linearly with increasing water content for all injection timings, but the effect is nonlinear with injection timing. These results suggest that there is an optimum timing, given the trade-offs between NOx, PM, and fuel consumption. The final study in this report examines the effects of a PM oxidation catalyst in combination with an emulsified fuel. A 1988 Cummins LTA-10-300 six cylinder diesel was subjected to modes 9 and 11 of a 13-mode heavy duty diesel test procedure. It is shown that these two control techniques are complementary in controlling PM emissions.

The other fundamental study provided by Lubrizol is an interim report from Southwest Research Institute (SwRI) to Lubrizol (Ryan et al., 2001). SwRI found that ~98% of the water in PuriNOx ends up in the exhaust without reacting to form other species. SwRI also found that the consumption of diesel fuel was 0.7% lower when using PuriNOx than when using straight diesel for this operating condition (mode 4 of the AVL 8-mode test, which is a cycle that was developed to mimic the PM emissions from the heavy-duty diesel transient federal test procedure). Detailed analysis of the cylinder pressure histories revealed that the duration of combustion was shorter in spite of the necessarily longer duration of injection for PuriNOx. In turn, this produces increased thermal efficiency.

2.2.2 Steady State "Mode" Engine Tests

PuriNOx has been subjected to several "mode" tests. These consist of a sequence of steady state operating conditions (modes), with each mode specified by both percent torque and percent speed. Percentages are specified, rather than absolute values, so that a variety of engines with different torque and engine speed capabilities can be subjected to a common test sequence. A single emissions value for each species is calculated from the results for each mode as a specified weighted average.

Table 2A. Engines Subjected to Steady State Mode
Dyno Tests, from Air Improvement Resource, 2001

Engine	Model	Year	Standards	Application	Control	SS test	Baseline diesel fuel
Cat	3306	1990	none	off-road	mechanical	8-mode	CARB
DDC	6V92	1995	none	off-road	mechanical	8-mode	off-highway
Cat	3508	2000	6.9/0.45	off-road	mechanical	8-mode	diesel
Perkins	1004.4 T	1999	6.9/0.45	off-road	mechanical	8-mode	**high-S**
Perkins	1004.4 T	1999	6.9/0.45	off-road	mechanical	8-mode	**low-S**
Cat	C-12	1996	5.0/0.1	**on-hiway**	**electronic**	8-mode	CARB
Cat	3406B	1996	none	off-road	mechanical	**4-mode**	diesel

Standards: NOx/PM in g/hp-hr.

In a final report to Lubrizol by Air Improvement Resource Inc. (Air Improvement Resource, 2001), results from tests of 11 engines/vehicles operating over a variety of test cycles are reported. Of these, 6 engines were subjected to steady state tests. Two of these engines were then adjusted to compensate for the PuriNOx torque loss and retested. As shown in Table 2A, all were tested on the off-highway 8-mode cycle except the 1996 Cat 3406B, which was tested on an off-highway 4-mode cycle. All but one engine were for off-road applications with mechanical controls. The exception was a 1996 Cat C12, which is an electronically-controlled on-highway engine. Three of the six were designed to meet emissions standards, the C12, a 1995 Perkins 1004.4T, and a 2000 Cat 3508. Five different baseline diesel fuels were used, but in each case the PuriNOx was made from this baseline fuel. The “diesel” in Table 2A is claimed to be very similar to CARB certification diesel fuel.

The results of these steady state engine dyno tests are shown in Table 2B. Because the raw results for the Cat C12 are not provided in the AIR report, they were back-calculated from the 5-engine averages for this review and, thus, are not as accurate. This paper (Air Improvement Resource, 2001) reports averages over all of the tests and engines, in spite of different fuels and different tests, which is not scientifically rigorous. These authors also report the fuel consumption characteristics only for one of the test vehicles (discussed in Section 2.2.3). Because a fuel consumption penalty is expected from diluting diesel fuel with water, this failure to report the brake specific fuel consumption for the engine dyno tests is disconcerting, at the very least.

The largest NOx improvement was for the Detroit Diesel Corporation (DDC) 6V92, which had the highest NOx emissions with the baseline fuel and with PuriNOx, used off-road diesel as the baseline fuel, and was not designed to meet any emissions standards. For this engine, PM and CO emissions were not measured, but there was a 50% penalty in hydrocarbon (HC) emissions. The smallest NOx benefit, largest PM benefit, and smallest HC penalty all occurred for the Cat 3406B, but this was for a 4-mode test. This may reflect the importance of the test sequence, or operating conditions, on the emissions performance of PuriNOx. Compared to the results from the other 8-mode tests, the only electronically-controlled diesel in the test group had the fourth-best NOx benefit, the second-best PM benefit (only 5 of these 6 had PM measurements), but the second-worst HC penalty. Again, compared only to the other 8-mode tests, the newest engine in this group – the 2000 Cat 3508 – had the smallest NOx benefit, the highest PM benefit, and was the only engine (of the 6) that did not suffer a penalty in HC emissions. The most pronounced effects of decreasing the fuel-sulfur level was a decrease in the HC and CO penalties (for the 1999 Perkins).

Table 2B. Results of Steady State Mode Engine
Dyno Tests, from Air Improvement Resource, 2001

		Diesel Emissions (g/hp-hr)				PuriNOx Emissions (g/hp-hr)				Emissions Change (%)			
Engine	**No. tests avgd.**	**NOx**	**PM10**	**HC**	**CO**	**NOx**	**PM10**	**HC**	**CO**	**NOx**	**PM10**	**HC**	**CO**
Cat 3306	1	4.367	0.117	0.543	8.824	3.572	0.133	1.009	12.87	-18.2	**13.7**	**85.8**	**45.9**
DDC 6V92	2	11.470	na	0.06	na	8.125	na	0.09	na	-29.2	na	**50.0**	na
Cat 3508	1	6.080	0.184	0.245	0.491	5.170	0.091	0.211	0.449	-15.0	-50.5	-13.9	-8.6
Perkins	3	8.08	0.26	0.36	0.72	5.92	0.18	0.79	0.90	-26.7	-30.8	**119.4**	**25.0**
Perkins	3	7.77	0.22	0.36	0.71	5.91	0.15	0.71	0.81	-23.9	-31.8	**97.2**	**14.1**
Cat C12	1	7.4	0.248	0.318	0.7	5.75	0.155	0.675	0.7	-22.3	-37.5	**112.3**	0.0
Cat 3406B	1	5.940	0.460	0.120	1.360	5.480	0.080	0.130	0.940	-7.7	-82.6	**8.3**	-30.9

This report also presents results for the Cat 3306 and the Cat 3508 without engine adjustments ("fill-and-go") and with adjustments to recoup the torque loss ("repowering"). Unfortunately, they do not present raw results for the "repowered" tests, only percentage changes in emissions. Their results are presented in Table 2C. For the 1990 Cat 3306, repowering the engine (e.g., increasing the rack stop limit so the engine fueled with PuriNOx can produce the same torque as the unmodified engine operating on diesel fuel) had a small effect on the NOx benefit, changed the PM results from a penalty to a significant benefit, and decreased the HC and CO penalties. For the 2000 Cat 3508, repowering produced small but directionally beneficial effects on NOx and PM but somewhat larger beneficial effects on HCs and CO. Unfortunately, the authors do not report the test-to-test repeatability of these results, so it is impossible to say which of these results are statistically significant.

Table 2C. Effects of "Repowering" the Engine on PuriNOx Emissions Performance, Steady State Mode Engine Dyno Tests, from Air Improvement Resource (2001)

		Emissions Change (%)			
Engine	mod?	NOx	PM10	HC	CO
Cat 3306	no	-18.2	**13.7**	**85.8**	**45.9**
Cat 3306	yes	-19.1	-25.2	**12.8**	**36.7**
Cat 3508	no	-15.0	-50.5	-13.9	-8.6
Cat 3508	yes	-16.6	-52.3	-18.8	-17.1

In a 2000 SAE paper coauthored by Lubrizol investigators (Brown et al., 2000), the effects of repowering versus fill-and-go were also reported. Few specifics were given other than that a 34.5 liter 8 cylinder engine was subjected to an 8-mode test. Again, neither raw emissions (in g/hp-hr) nor fuel consumption were reported. The results they did provide are shown in Table 3. Obviously, this is the 2000 Cat 3508 from Table 2C, but the HC+NOx emissions are given (dominated by NOx) and the CO2 emissions are reported.

Table 3. Additional Cat 3508 "Repowering" Results, Steady State Engine Dyno Tests, from Brown et al. (2000)

		Emissions Change (%)					
Engine	mod?	NOx	PM10	HC	CO	HC+NOx	CO2
34.5L 8 cyl.	no	-15.0	-50.5	-13.9	-8.6	-15.0	-6.3
34.5L 8 cyl.	yes	-16.6	-52.3	-18.8	-17.1	-16.6	-4.4

The lower relative CO2 emissions for the repowered engine indicate that the engine is either more efficient or doing less work over the 8-mode test after repowering, compared to fill-and-go. However, the 8-mode off-highway test includes two modes that specify 100% torque. When operating on PuriNOx without adjusting the engine, it produces less torque for these two modes than when operating on diesel. The other modes also specify a percent torque. The authors do not state whether the percent torque used for these other modes were a percentage of the maximum torque they could obtain with PuriNOx, or whether they ran these other modes as close to the diesel torque values as possible. In either case, the engine does less work over the 8-mode test with PuriNOx than with diesel, the question is by how much. A CO_2 benefit is expected for the fill-and-go 8-mode test because the engine does less work than when operating on diesel. However, after repowering, the torque values when operating on PuriNOx are presumably the same as when operating on diesel. In this case, no benefit in CO_2 is expected unless the engine is more efficient when operating on PuriNOx. As reviewed in Section 2.2.1, the engine is, in fact, more efficient when operating on PuriNOx due to the decrease in the duration of combustion.

Southwest Research Institute performed 8-mode tests on a 1999 Detroit Diesel Series 50 engine (Sarlo, 2001). This is an 8.5 liter, 4 cylinder, 4 valves/cylinder, turbocharged engine that has electronically-controlled fuel injection and exhaust gas recirculation (EGR). Emissions for a Houston baseline diesel fuel were compared to PuriNOx made from this baseline fuel. The specified torque could not be attained for 3 of the 8 modes, and this will, by itself, affect emissions. Two tests on each fuel were performed, which is insufficient for statistical analysis. The results for each mode are provided in Figures 1–6.

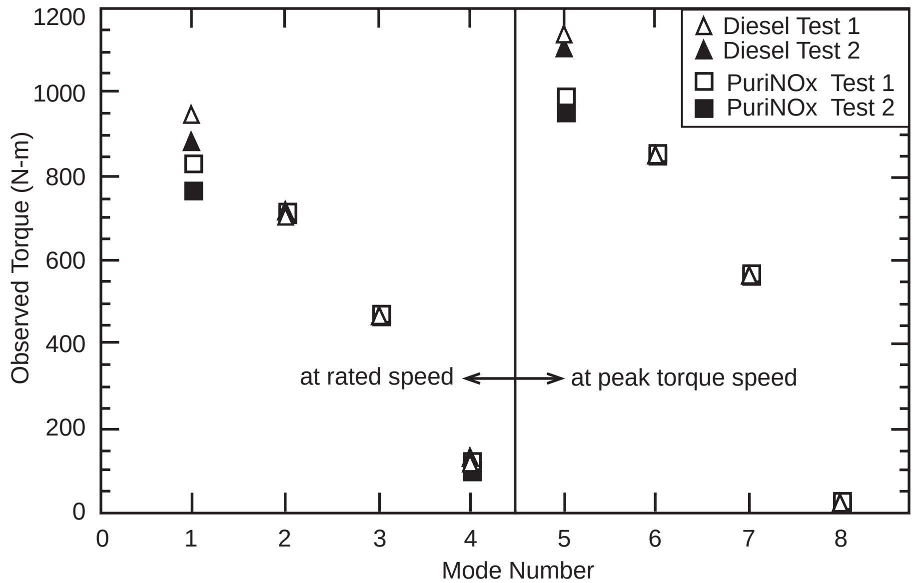

Figure 1. Observed torque versus mode for an 8-mode test of a 1999 DDC Series 50, from Sarlo (2001).

Figure 1 shows the torque as a function of mode number for the 8-mode test. Modes 1 and 5 are supposed to be at 100% torque (at rated speed and at peak torque speed, respectively), but the PuriNOx tests could not obtain this torque. The differences in torque for Mode 4 may not be as important. It should also be noted that the data for Test 1 for both fuels were acquired on the same day, as were the Test 2 data. However, these days were about two months apart. This is important because "observed torque" is reported, but observed torque is a complicated function of the state of the air inducted into the engine. Because the state of the ambient air probably differed between Test 1 and Test 2, it is not surprising that the full-load torque was not precisely the same for Test 1 as it was for Test 2. Thus, the results for the two initial tests should be compared with each other (Test 1, diesel vs. PuriNOx), but not with the data from the second test.

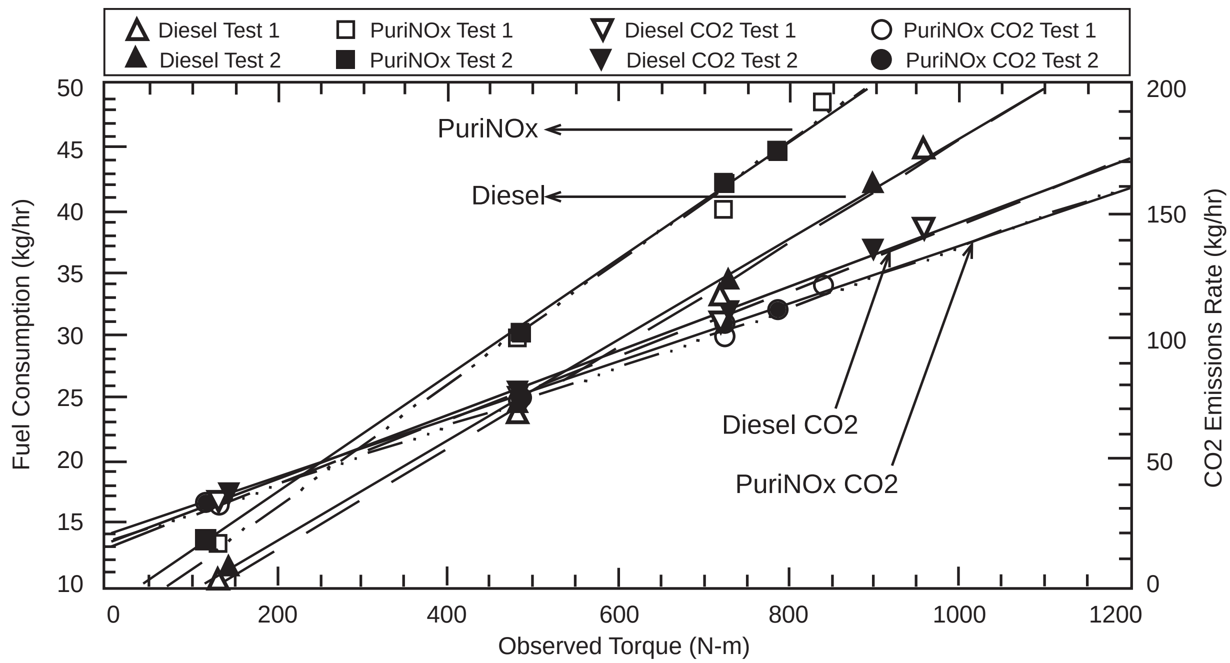

Figure 2A. Fuel consumption and CO_2 emissions versus observed torque at rated speed (2100 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

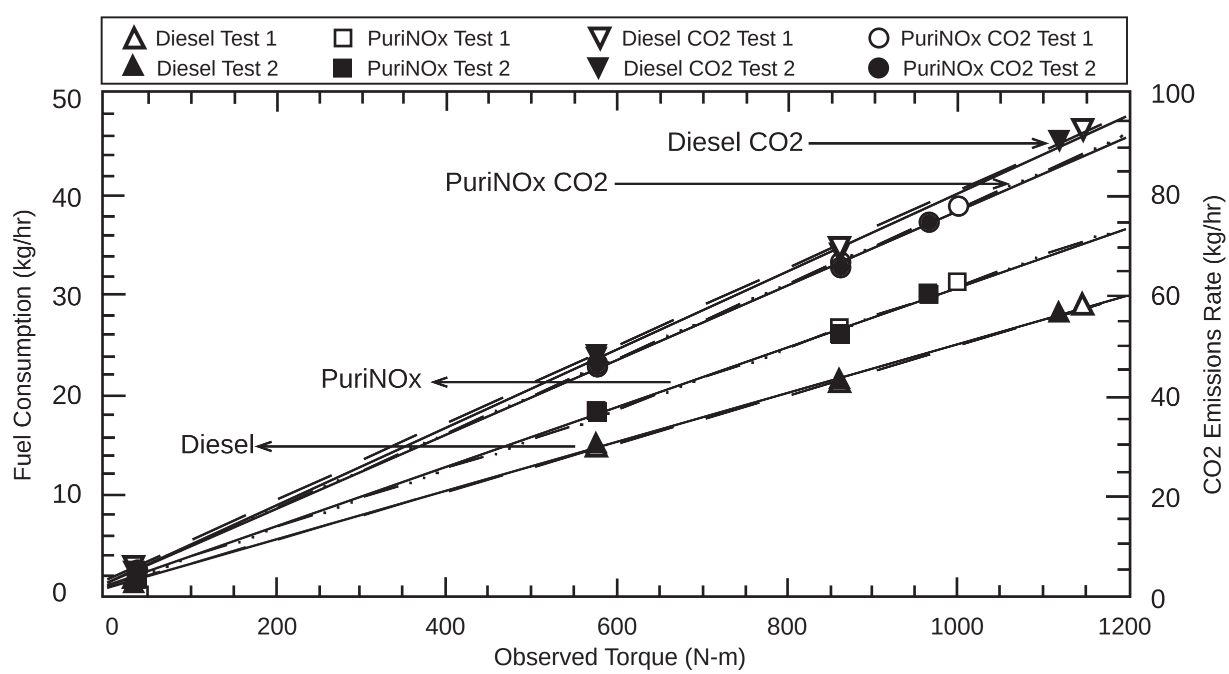

Figure 2B. Fuel consumption and CO_2 emissions versus observed torque at peak torque speed (1200 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

Figures 2a and 2b show the fuel consumption and CO_2 emissions rates. Figure 2a is for the rated speed of 2100 rpm (Modes 1–4) and Figure 2b shows the results at peak torque speed (1200 rpm, Modes 5–8). All of the data in Figures 2a and 2b are linear, with a correlation coefficient of ~0.99. Graphing the results against torque allows comparison at any given fixed torque value in spite of differences in peak torque attained. Figures 2a and 2b show that more fuel was consumed with PuriNOx, as expected, to provide the same chemical energy. However, somewhat less CO_2 was generated by PuriNOx at any given torque, due to improved thermal efficiency.

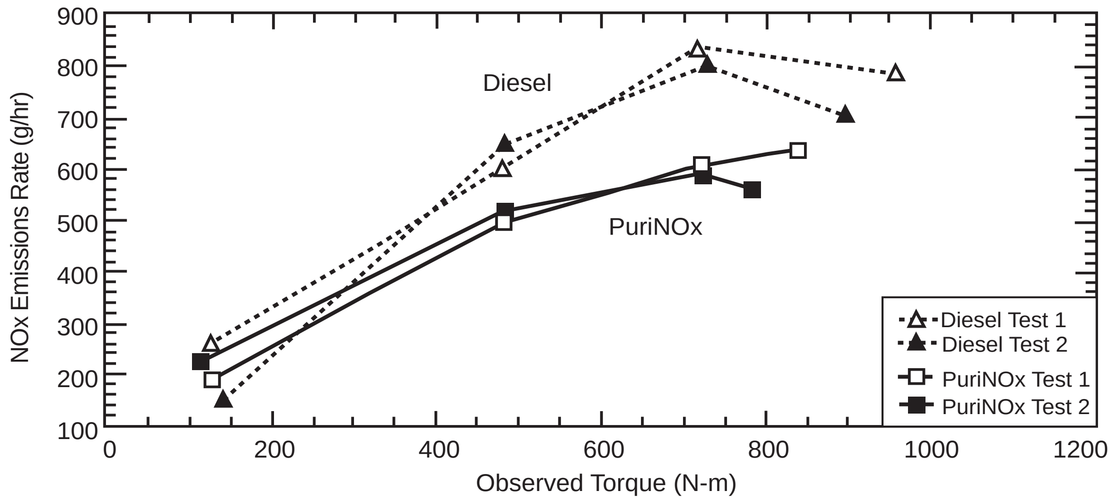

Figure 3A. NOx emissions versus observed torque at rated speed (2100 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

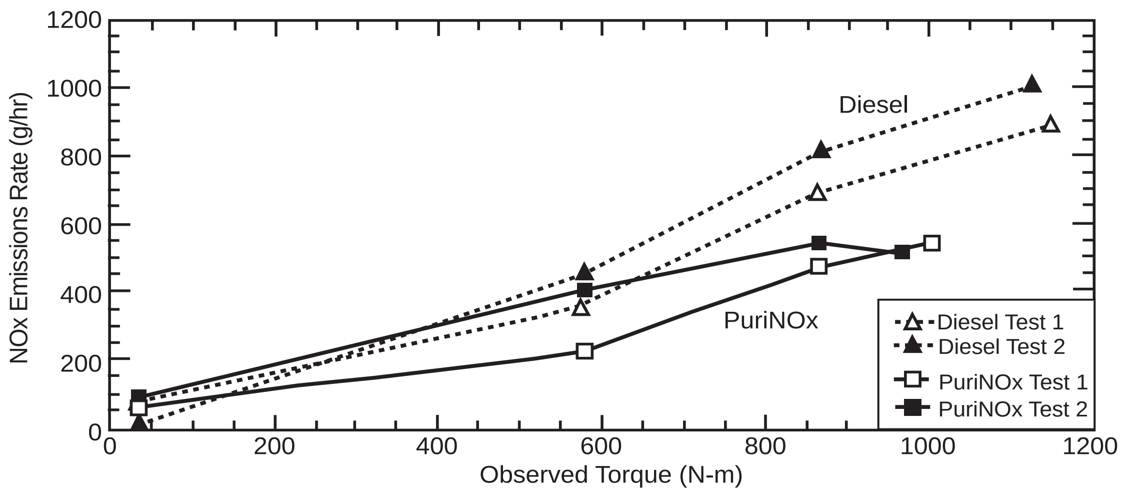

Figure 3B. NOx emissions versus observed torque at peak torque speed (1200 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

Figure 3a shows the NOx emissions rates at rated speed (2100 rpm) and Figure 3b shows them at peak torque speed (1200 rpm). As noted previously, the open symbols should be compared to each other and the filled symbols should be compared to each other, but comparisons between the tests on different days should not be done. At the higher speed, PuriNOx provided a NOx benefit at all loads except for the second test, for which PuriNOx produced somewhat higher NOx at the lowest load. At the lower speed, the PuriNOx benefit was marginal or absent up to about half load for the second test, but was more pronounced, except at the lowest load, for the first test.

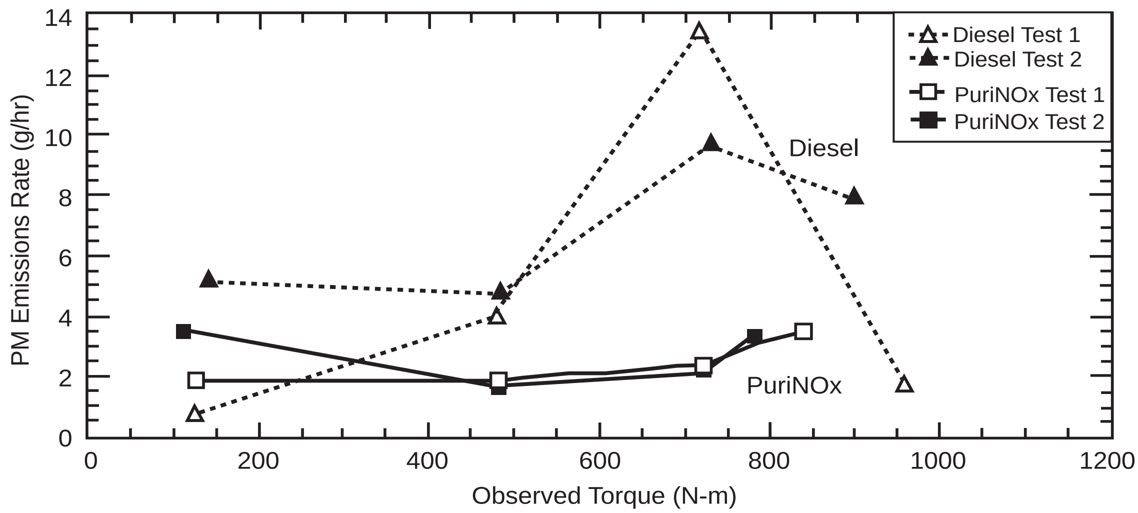

Figure 4A. PM emissions versus observed torque at rated speed (2100 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

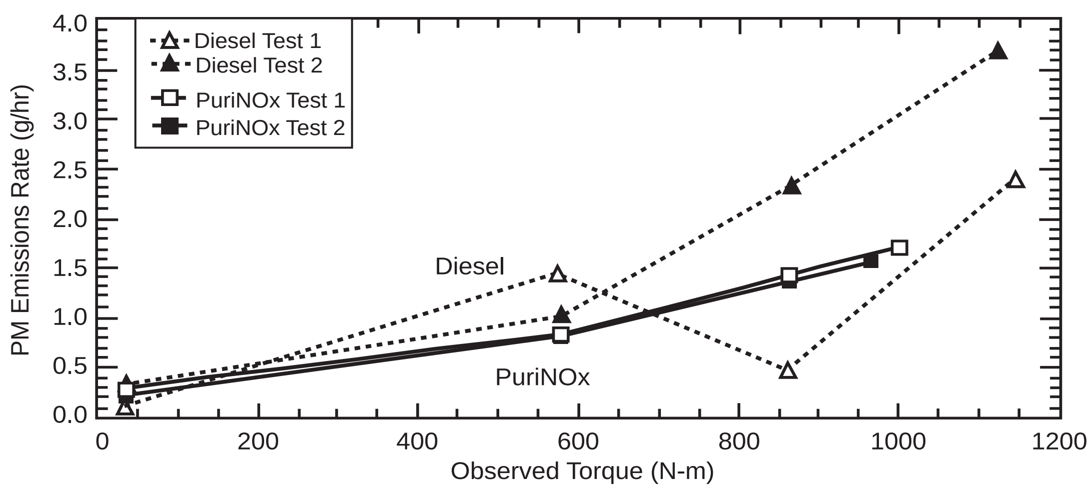

Figure 4B. PM emissions versus observed torque at peak torque speed (1200 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

Figures 4a and 4b show the particulate matter (PM) emissions rates. At the higher speed, PuriNOx provided a PM advantage for all loads except for the first test at the lowest load (10% torque). At the lower speed, the first test showed a PuriNOx advantage ONLY at half load, whereas the second test showed a significant PuriNOx advantage only above half load. The results show clear test-to-test differences in PM emissions on diesel fuel but small differences when using PuriNOx.

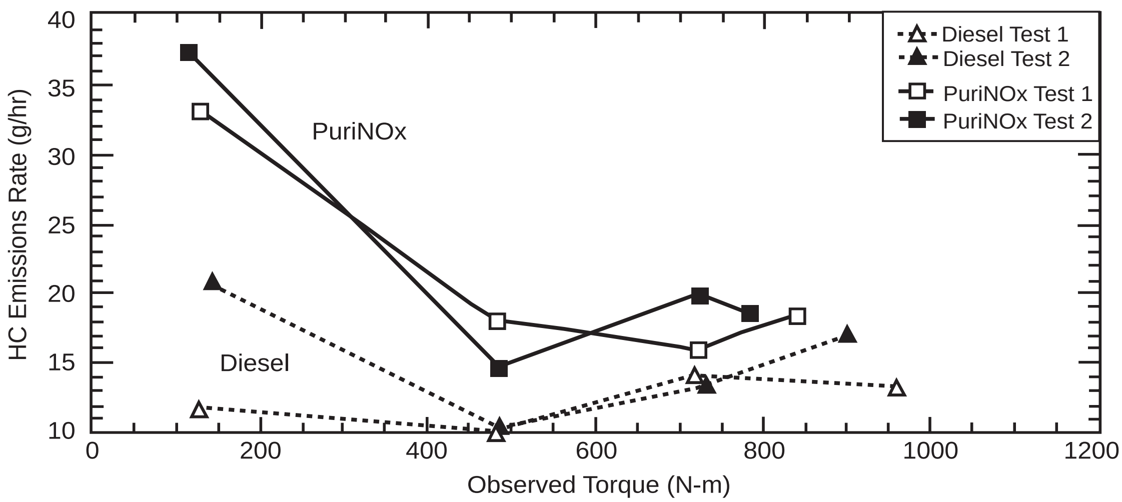

Figure 5A. HC emissions versus observed torque at rated speed (2100 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

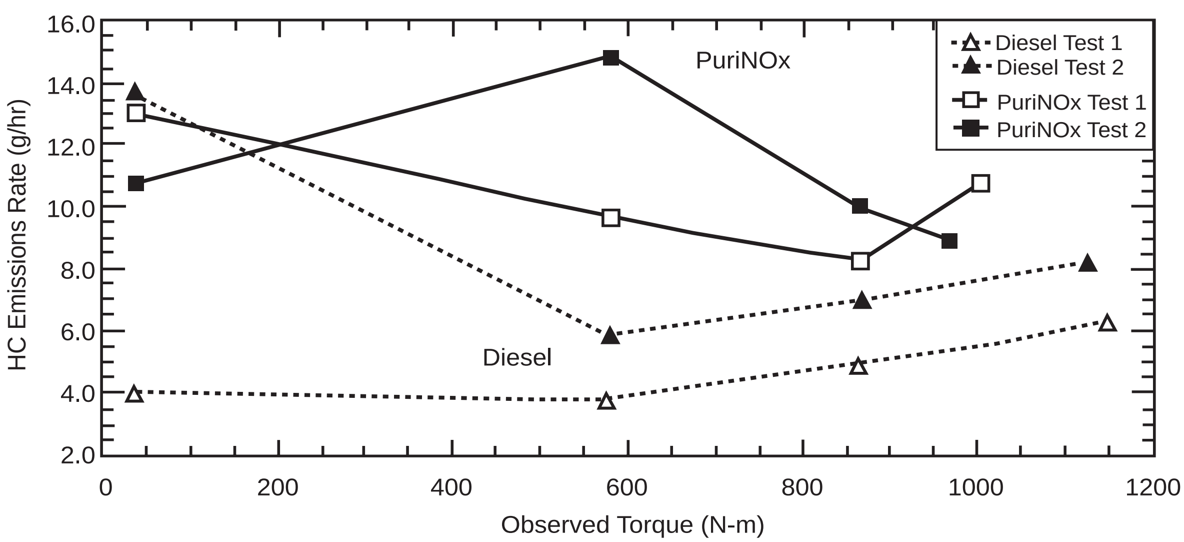

Figure 5B. HC emissions versus observed torque at peak torque speed (1200 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

The HC emissions rates are compared in Figure 5. At the higher speed, PuriNOx produced a hydrocarbon penalty at all loads, but especially the lowest load. At the lower speed, PuriNOx produced a penalty at all loads (except for the lowest load on Test 2) but it was most pronounced at half load.

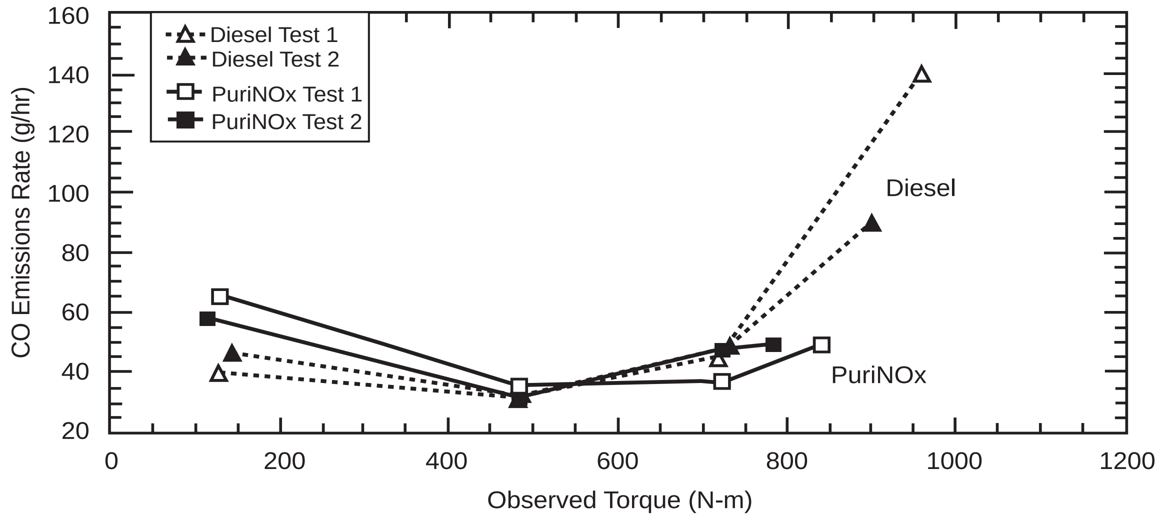

Figure 6A. CO emissions versus observed torque at rated speed (2100 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

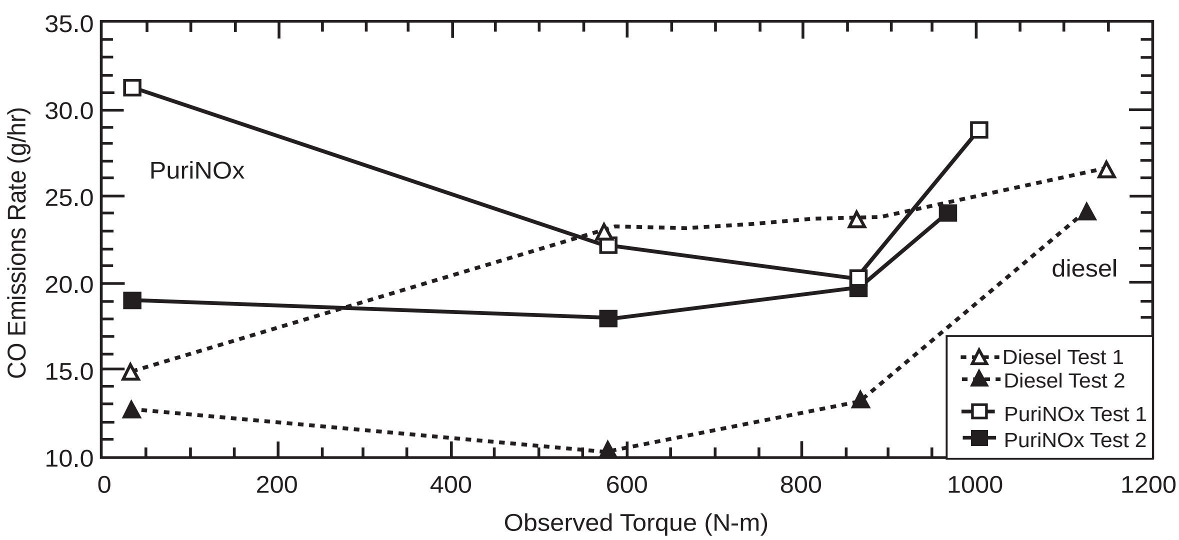

Figure 6B. CO emissions versus observed torque at peak torque speed (1200 rpm); 1999 DDC Series 50, from Sarlo (2001).
Test 2 for PuriNOx is filled squares and circles; Test 2 for diesel is filled triangles.

Figures 6a and 6b show the CO emissions rates. At the higher speed, there was a CO penalty at the lowest load (10% torque) but a benefit at the highest load. At the lower speed, the second test revealed a CO penalty at all loads but the first test showed about the same CO emissions for both fuels at half load, a PuriNOx advantage at 75% torque, and a penalty at the highest load.

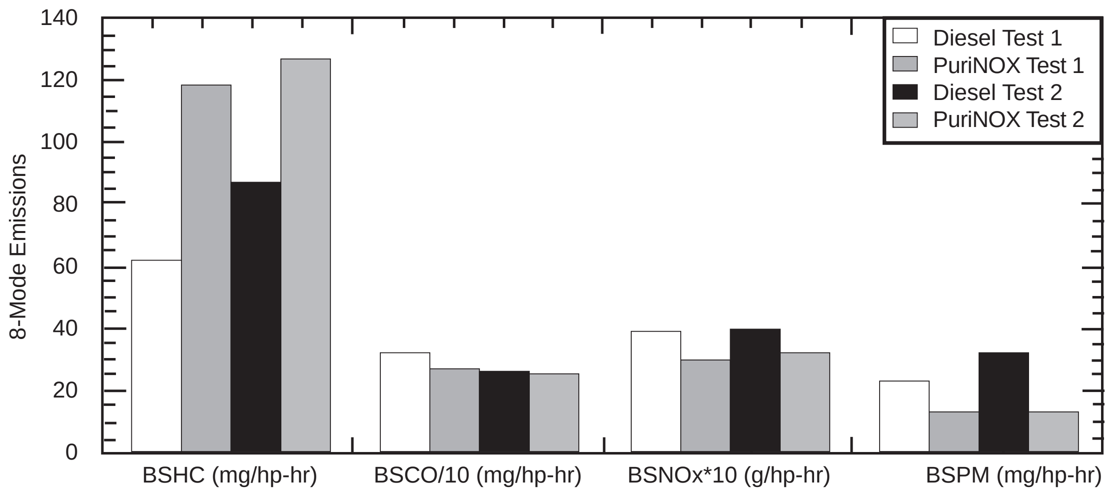

Figure 7. Results for the 8-mode test (weighted) emissions; 1999 DDC Series 50, from Sarlo (2001).

Figure 7 shows the weighted 8-mode results from the SwRI study (Sarlo, 2001). It should be recalled that PuriNOx could not attain the specified torque for Modes 1 and 5. In Figure 7, the brake specific CO emissions calculated for the tests was divided by 10 to provide a more convenient magnitude for the graph. Similarly, the brake specific NOx emissions were multiplied by 10. For the 8-mode tests of this electronically-controlled diesel, there is a NOx benefit, a PM benefit, a small CO benefit (that may or may not be statistically significant), and a penalty in HC emissions.

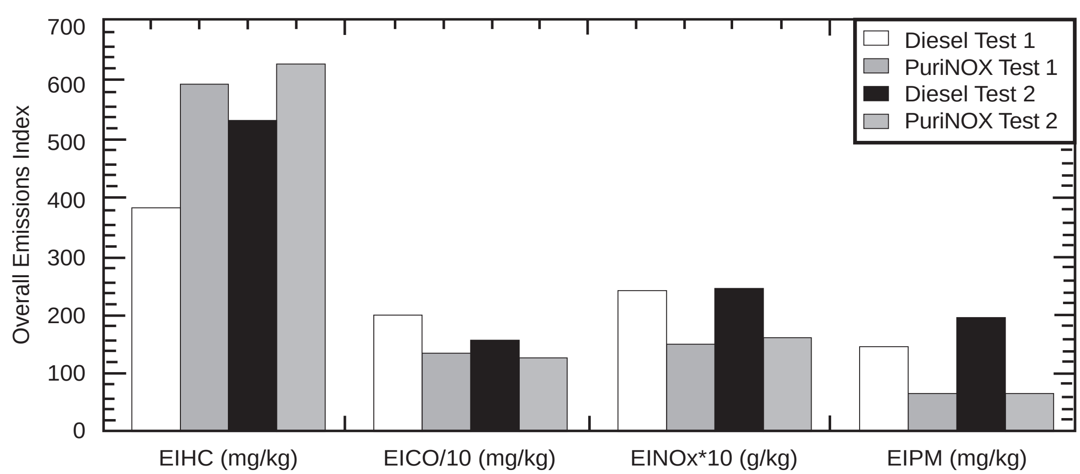

Figure 8A. Emissions Indices calculated from the 8-mode tests.
Here, the EI is based on the overall fuel (including water for the emulsions).

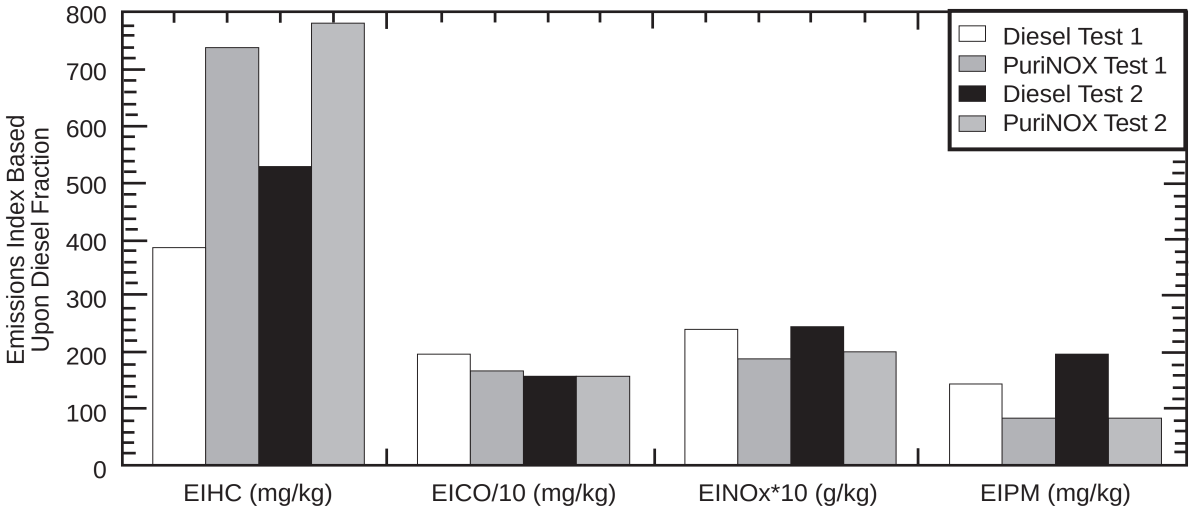

Figure 8B. Emissions Indices based upon the nonwater fraction of the fuel (excluding water for the emulsions).

Figures 8a and 8b present the results from SwRI's 8-mode tests on an Emissions Index basis. The EI is the ratio of the emissions rate to the fuel consumption rate. For Figure 8a, the overall fuel consumption rate is used. Figure 8b presents the Emissions Indices based upon the nonwater fraction of the fuel. This is convenient because the carbon in the HCs, CO, and PM are derived from the carbon in the nonwater fraction of the fuel and the NOx emissions result from the energy liberation by the fuel – and water does not have any chemical energy available for release by combustion. Figure 8b resembles Figure 7 but shows that, of the fuel carbon that does not end up in the preferred product (CO_2), most goes into CO (recall that the EICO value is divided by 10), the next most goes into HCs, and little ends up as PM. Figure 8b also shows that the mass of NOx formed per unit mass of diesel fuel burned is lower for the emulsion.

2.2.3 European Cycle Vehicle Tests

Investigators from Engine Control Systems and from Lubrizol report (Brown et al., 2000) the effects of a diesel oxidation catalyst, a diesel particulate trap, and two emulsified diesel fuels in a bus operating over the Millford London Transport Bus (MLTB) cycle. These results were also included in three other reports (Air Improvement Resource, 2001; Barnes et al., 2000; Rowlands et al., 1999). Speciated results (Hazardous Air Pollutants) from the bus tests are reported by Brown et al., 2000 and Bailey et al., 1999. The bus was a 1997 Olympian Double Decker with an automatic transmission. The engine was a Volvo B10A, a turbocharged 9.6 liter 6 cylinder with a rating of 183 kW at 2000 rpm and 1050 N-m at 1450 rpm. The system met Euro II emissions standards. A European ultra low sulfur (<50 ppm) diesel fuel was used as the baseline.

Results for PuriNOx 10E (~10% water by mass) are not discussed below because, as expected, this is not as effective as PuriNOx 20E (~20% water). Similarly, results for the catalyst and the trap are not discussed. As noted previously, the combined technologies (emulsified fuel plus either a catalyst or trap) are as or more effective than either technology alone. Neither of these are options for TxDOT: the emulsified fuel will contain the water content provided as standard, and no additional emissions control hardware will be added to that which came with the engine.

The MLTB cycle consisted of an "outer loop" (stop-and-go with a peak vehicle speed of ~30 mph) and an "inner loop" (stop-and-go with a peak vehicle speed of ~22 mph). For each of these two "phases," the emissions are presented in total grams emitted during that phase and the fuel consumption is presented in total volume consumed. Three runs were made on both the baseline diesel fuel and on PuriNOx 20E. Combined (or composite) results are presented for the two combined phases for each of the three test runs. In this case, the emissions are presented in g/km and the fuel consumption in L/100 km. The test-to-test repeatability was sufficiently good that the emissions and fuel consumption differences between the two fuels were statistically meaningful. However, because the emulsion produces a torque loss, it is also necessary to be concerned about whether the prescribed driving trace (vehicle speed versus time) was precisely followed when using the emulsified fuel. If the prescribed accelerations and peak speeds are not maintained, the tests with the emulsified fuel do not represent as much work, in which case the emissions and fuel consumption are expected to be different. Brown and coworkers (2000) only provide a graph comparing the engine speeds during a 200-second portion of the low speed phase of the overall 2281-second cycle. During this period, it appears that the accelerations and peak vehicle speeds were maintained the same between the fuels, but this does not guarantee that this was true for the entire MLTB cycle.

The emissions and fuel consumption changes – based upon the averages of the three tests for each fuel – are shown in Table 4A. As shown in this table, the differences between the inner and outer loop have an almost insignificant effect on the performance of PuriNOx. For the composite cycle, the NOx emissions decrease ~18%, PM10 emissions decrease ~44%, and HC emissions decrease ~12%, but CO increases ~5% (with all on a g/km basis). The increase in CO emissions is not important, especially from the perspective of Texas' ozone nonattainment areas. Also, on a L/100 km basis, the fuel consumption increases ~15%.

Table 4A. Effects of PuriNOx 20E on Emissions and Fuel Consumption for a London Bus

	Emissions or Fuel Consumption Change (%)				
	NOx	PM10	HC	CO	Fuel
Outer loop avg.	-19.1	-43.3	-13.5	4.0	14.1
Inner loop avg.	-18.0	-45.6	-10.3	3.9	14.3
Composite avg.	-18.1	-43.7	-11.5	4.8	15.0

This report was the second reviewed thus far that provided almost all of the data required for calculating the Emissions Index. The Emissions Index is a useful parameter for comparing the emissions resulting from the two fuels. It is defined as the grams of pollutant emitted per kilogram of fuel injected. This is especially useful for HC, PM, and CO emissions, since the carbon in these species comes from the fuel. Because the ideal end products are that the carbon in the fuel is entirely converted to CO_2 and the hydrogen in the fuel is entirely converted to H_2O, higher Emissions Indices for HC, PM, and CO are indicative of the incompleteness of combustion. Even though NOx does not derive directly from the fuel, it is a result of energy liberation by the fuel. Thus, the Emissions Index for NOx (EINOx) is also of interest. The Emissions Index can be calculated from the mass emissions rate divided by the mass consumption rate of the fuel. However, the reports on the bus tests only provided the volume consumption rate of the fuel. Thus, the densities of each fuel were needed, and were provided by one of the report authors (Duncan, 2002) as 0.835 g/cc for the baseline diesel and 0.855 g/cc for PuriNOx 20E. Additionally, because the fate of the fuel-carbon depends solely upon the components of the fuel which contain carbon (i.e., everything other than water), the Emissions Indices for the emulsified fuel should be calculated from the consumption rate of the diesel (or non-water) fraction of the fuel. For this calculation, the mass percentage of water in PuriNOx 20E is required (20%).

As shown in Table 4B, based upon the Emissions Indices the NOx, PM, and HC benefits of PuriNOx 20E are not quite as high and the CO penalty is higher than indicated in Table 4A. However, the fact that the NOx and PM benefits remain—even when the Emissions Index based upon the diesel fraction of the fuel is used for comparison—is additional proof that the emulsion has a substantial effect on the combustion process.

Table 4B. Results of the London Bus Tests on an Emissions Index Basis

	Diesel Emissions Index (g/kg fuel)				PuriNOx Emissions Index (g/kg diesel component)				Emissions Index Change: Diesel Component (%)			
	NOx	PM10	HC	CO	NOx	PM10	HC	CO	NOx	PM10	HC	CO
Composite avg.	30.95	0.40	1.45	3.35	27.0	0.2	1.4	3.7	-12.9	-40.2	-6.0	11.4

The size distributions of the particulate matter were also reported for the London bus tests (Brown et al., 2000). The narrative claims that PuriNOx 20E decreases the numbers of particles in the 0.1–1.0 μm size range but the corresponding graph appears to show a decrease for the high end of this range but an increase for the low end of this range. In spite of the much lower number densities of larger particles (1–10 μm) for both diesel and emulsified fuel, the total PM mass is dominated by these large particles. However, there is concern about the potential health effects of the small particles. The current regulations do not address this concern about ultrafine particles; currently the standards regulate total mass of particles less than 10 μm (PM10) and future standards decrease the upper cutoff to 2.5 μm (PM2.5). Since the mass (which is all that is regulated) is dominated by the larger particles, the change from PM10 to PM2.5 is more effectively a change in the allowed mass emissions rate than a reflection of concerns about the particle sizes that may impact the public health.

The volatile organic fraction of the PM was reported (Bailey et al., 1999) for one of the MLTB tests for each fuel. This experimental technique allows determination of how much of the particulate mass is due to engine oil, how much is due to unburned fuel, and how much is due to sulfates (derived from the sulfur impurity of the fuel). The remainder is primarily elemental carbon. Unfortunately, the sulfate analysis was not requested but would have been of interest due to the potential for the water in the emulsified fuel to react with the fuel sulfur to form sulfuric acid, which should have been captured on the particulate filter as a contributor to the sulfates. For both diesel fuel and PuriNOx 20E, unburned fuel was a small contributor to the PM mass. Surprisingly, both the percent oil contribution to the PM mass and the mass of condensed oil in the particulates increased substantially for the emulsified fuel, as shown in Table 5. The reason for this increase in condensed oil on the particulates is not obvious.

Table 5. Volatile Organic Fraction Results from the London Bus Tests

	Diesel		PuriNOx 20E	
	Phase 1	Phase 2	Phase 1	Phase 2
Total PM mass (g)	0.846	0.456	0.514	0.267
Mass % oil	15.96	8.95	37.62	28.54
Oil mass (g)	0.135	0.041	0.193	0.076
% increase in oil mass	-	-	43.21	86.7

The hydrocarbon speciation for the London bus tests was also reported (Bailey et al., 2000; Brown et al., 2000). Speciation allows quantification of the Hazardous Air Pollutants (HAPs) and the Ozone Forming Potential (OFP) of the exhaust HCs. EPA has identified 5 gas phase HAPs: formaldehyde, acetaldehyde, acrolein, 1,3-butadiene, and benzene. Millford used the CARB procedure for speciating the exhaust HCs. This involves gas chromatographic analysis of 157 C1-C12 hydrocarbons from bag samples, and 13 carbonyls (aldehydes and ketones) from cartridge samples. However, this procedure was generated for gasoline vehicles and does not measure many of the diesel fuel components that may appear in the exhaust as C13 and higher HCs. The result was that the total hydrocarbon measurements from the conventional "hot flame ionization detector" were more than 50% higher than the sum of the species measured using CARBs procedure. In turn, this leads to questions concerning the accuracy of the OFPs. The results of these tests indicated a decrease in OFP of ~25% for PuriNOx compared to diesel fuel. These tests also revealed a decrease in total HAPs and in 4 of the 5 individual HAPs in mg/km, with the exception being a 30% increase in the rate of benzene emissions. Table 6 provides these results on an Emissions Index basis.

Table 6. Hazardous Air Pollutant Emissions from the London Bus Tests, on an Emissions Index Basis

Diesel Emissions Index (mg/kg fuel)					PuriNOx Emissions Index (mg/kg diesel component)					Emissions Index Change: Diesel Component (%)				
form.	**acet.**	**acrol.**	**1,3-but.**	**benz.**	**form.**	**acet.**	**acrol.**	**1,3-but.**	**benz.**	**form.**	**acet.**	**acrol.**	**1,3-but.**	**benz.**
260.8	48.6	11.5	6.2	8.8	164.4	30.0	5.8	3.0	9.8	-37.0	-38.2	-49.4	-51.5	10.4

2.2.4 Heavy-Duty FTP Transient Cycle Engine Tests

Results from transient engine dyno testing over the Heavy-Duty Diesel Federal Test Procedure (HDD FTP) cycle are provided in a final report to Lubrizol by Air Improvement Resource (2001). The engines tested are listed in Table 7A. The results for the 1991 engine were extracted by AIR from a report from Southwest Research Institute (SwRI) to Lubrizol (Khalek et al., 2000). Emissions differences for the engine tested at SwRI were shown to be statistically significant for the SwRI study. All three engines in the AIR report were electronically controlled, were designed for on-road applications, and were certified to meet heavy-duty diesel emissions standards. For all three sets of tests, the baseline diesel fuel was a CARB certification diesel fuel.

Table 7A. Engines Tested Using the HDD FTP, from Air Improvement Resource (2001)

Engine	Model	Year	Standards	Application	Control	transient test	baseline diesel fuel
DDC	series 60	1991	5.0/0.25	on-highway	electronic	HDD FTP	CARB
DDC	series 50	1995	5.0/0.1	on-highway	electronic	HDD FTP	CARB
DDC	series 60	1999	4.0/0.1	on-highway	electronic	HDD FTP	CARB

Standards: NOx/PM in g/hp-hr

As shown in Table 7B, PuriNOx produced large PM emissions benefits, smaller NOx benefits, and HC penalties for all three engines. Interestingly, the smallest NOx and PM benefits and largest HC penalty were for the newest of the three DDC engines tested.

Table 7B. Results from the HDD FTP Engine Dyno Tests, from Air Improvement Resource (2001)

		Diesel Emissions (g/hp-hr)				PuriNOx Emissions (g/hp-hr)				Emissions Change (%)			
Engine	**No. tests averaged**	**NOx**	**PM10**	**HC**	**CO**	**NOx**	**PM10**	**HC**	**CO**	**NOx**	**PM10**	**HC**	**CO**
91 DDC Series	21	4.21	0.191	0.110	2.38	3.62	0.071	0.166	1.28	-14.0	-62.8	**50.9**	-46.2
95 DDC Series	2	5.593	0.065	0.063	1.087	4.677	0.029	0.193	1.457	-16.4	-55.4	**206.3**	**34.0**
99 DDC Series	6	3.410	0.090	0.044	0.877	3.090	0.055	0.146	0.758	-9.4	-38.9	**231.8**	-13.6

The SwRI report (Khalek et al., 2000) on the 1991 DDC tests provided much more detail than the AIR report (2001). A portion of these additional results is presented in Table 7C. The last column shows that ~4% less work was done on average over the 21 PuriNOx tests, compared to the 21 diesel tests, for which the average was 1.1% higher than the target value for the work (24.72 hp-hr). The small decrease in the work done during the PuriNOx tests will result in a small difference with respect to emissions. Overall fuel consumption increased ~22%, or about the same as the 20% water in the emulsion. However, if the BSFC is recalculated on the basis of the nonwater fraction of the emulsion, the brake specific diesel fuel consumption (BSDFC) improved by 2.3% for operation on PuriNOx. Also, the brake specific CO_2 emissions (BSCO2) decreased ~1%. The improvements in BSDFC and BSCO2 may be due to the fact that less work was done for the PuriNOx tests and/or due to the slight improvement in thermal efficiency noted previously. In spite of the water in the emulsion, which also contained the sulfur impurity in the diesel fuel, the sulfate (SO_4) emissions were 40% lower with PuriNOx. However, the soluble organic fraction (SOF) of the particulate matter increased ~19% with PuriNOx. This increase in SOF is similar to the 43–87% increase in oil condensed on the PM from the London bus study discussed in the previous section. That is, although the total PM decreased with PuriNOx, it appears that this was dominated by a large decrease in carbonaceous material which more than offset increases in condensed phases.

Table 7C. Additional Results for the 1991 DDC, from Khalek et al. (2000)

	Emissions and Fuel Consumption (g/hp-hr)				
	SOF	SO4	CO2	fuel consumption	act. work (hp-hr)
Diesel	0.047	0.0010	534.54	170.07	24.99
PuriNOx	0.056	0.0006	531.52	207.71	24.07
% change	19.1	-40.0	-0.6	22.1	-3.7

The SwRI report (Khalek et al., 2000) also provides results for the HAPs (formaldehyde, acetaldehyde, 1,3-butadiene, and benzene; acrolein not measured). As shown in Table 7D, the emissions of formaldehyde, acetaldehyde, and 1,3-butadiene all increased, whereas the emissions of benzene were not altered. This contrasts sharply with the results from the London bus tests discussed in the previous section, for which the emissions of all HAPs other than benzene decreased dramatically and the emissions of benzene increased ~10%. It is not known whether this difference is due to engine technology, base diesel fuel, or driving cycle. The three aromatics that were measured that are not on EPA's list of exhaust toxics were toluene; the sum of m-, o-, and p-xylene; and ethyl benzene. All three increased, and the sum of the three increased by almost a factor of two. Additionally, the emissions of 19 polyaromatic hydrocarbons (PAHs) were measured. The emissions of eight of these decreased, four increased, and the remainder stayed about the same for operation on PuriNOx.

Table 7D. HAP Emissions for the 1991 DDC, from Khalek et al. (2000)

Diesel Emissions (mg/hp-hr)				PuriNOx Emissions (mg/hp-hr)				Emissions Change (%)			
form.	acet.	1,3-but.	benz.	form.	acet.	1,3-but.	benz.	form.	acet.	1,3-but.	benz.
15.92	4.87	0.98	0.66	25.06	7.84	1.32	0.66	57.4	61.0	34.7	0.0

To allow an additional comparison of PuriNOx and diesel fuel, the Emissions Index was calculated for this review. The results are provided in Table 7E. On the basis of mass of pollutant per unit mass of diesel fuel injected, the NOx, PM, and CO benefits are more pronounced and the HC penalty is greatly reduced. Because the Emissions Index based upon the diesel fuel injected directly accounts for the fate of the carbon in the fuel, the small increase in CO_2 noted in Table 7E may reflect the fact that less of the carbon is emitted as CO and PM. Also, on this Emissions Index basis, the SO_4 benefit of PuriNOx is somewhat smaller while the penalties in SOF and the HAPs are somewhat larger.

Table 7E. Emissions Index Comparisons for the 1991 DDC

	Emissions Index (g/kg diesel)							Emissions Index (mg/kg diesel)			
	NOx	PM10	HC	CO	SOF	SO4	CO2	form.	acet.	1,3-but.	benz.
Diesel	24.75	1.12	0.65	13.99	0.28	0.01	3143.10	93.61	28.64	5.76	3.88
PuriNOx	21.79	0.43	1.00	7.70	0.34	0.00	3198.69	150.81	47.18	7.94	3.97
% change	-12.0	-62.0	**54.5**	-45.0	**21.9**	-38.6	**1.8**	**61.1**	**64.8**	**37.9**	**2.3**

2.2.5 Vehicle Task Tests

Lubrizol contracted Environment Canada (the Canadian counterpart to the U.S. EPA) to study in-use emissions – during specified tasks - at several facilities. These studies are reviewed in this section.

The first in-use test (Rosenblatt and Ainslie, 1999) was conducted at the Morton Salt Fairport Mine near Cleveland, Ohio. The vehicle tested was a Caterpillar 988F front-end loader, which is used to load trucks and ships with salt. The engine was a Caterpillar 3408 V8 diesel with mechanically-controlled injection. The engine year was not provided, and it is not known whether or not it was designed to meet emissions standards. A repetitive cycle consisting of 2 pickups and drops per lap and 5 laps per test was used for measuring the in-use emissions and fuel consumption. The use of a repetitive in-use test sequence assured that the vehicle performed the same job (task) for each fuel but not that the engine did the same amount of work. There were 5 tests using low sulfur #2 diesels followed by 5 with PuriNOx and then another 5 with PuriNOx after repowering the engine. However, when the technician repowered the engine, he found that there was a problem with the air/fuel ratio controller, which he refurbished. To this reviewer, that makes the repowered tests invalid, because the baseline diesel used the problematic controller, as did the unadjusted PuriNOx tests. Thus, only the unadjusted results will be discussed. For this comparison, it does not appear (the graphs are extremely difficult to read) that the same amount of work was done with PuriNOx, even though the same task was accomplished. The decreased work with PuriNOx will automatically result in different emissions. For this test, it does not appear that the PuriNOx was made from the baseline diesel fuel. This makes comparing the emissions – especially SOF – problematic.

Results for four tests on each fuel were presented as an Emissions Index (grams of pollutant per kilogram of fuel injected), along with a fuel rate in kg/hr. The Emissions Indices for the PuriNOx results were based upon the overall fuel (diesel fuel plus water plus additive package). The differences appeared to be statistically different. For this review, the Emissions Index was recalculated based upon the nonwater fraction of the emulsion. The results are presented in Table 8. Based upon both techniques for calculating the Emissions Index, PuriNOx provided benefits in NOx, PM, SOF, and CO but a penalty in HC emissions. The SOF benefit observed in this study contrasts with the SOF penalty in studies discussed previously (Brown et al., 2000; Khalek et al., 2000).

Table 8. Emissions Index Comparisons for the Caterpillar 3408 In-Use Test

		Emissions Index (g/kg diesel portion)				
Caterpillar 3408	Fuel cons. (kg diesel/hr)	**EICO**	**EINOx**	**EITHC**	**EIPM**	**EISOF**
Diesel	35.9	10.3	41.1	0.35	1.21	0.19
PuriNOx	31.4	6.3	23.6	0.47	0.42	0.12
% change	-12.5	-38.4	-42.4	**33.0**	-65.6	-34.2

The Port of Houston provided two yard haulers for the second test (Howes, 2000a). The Port of Houston uses yard haulers to move shipping containers around the dock area. One of the engines was a Cummins 6CT8.3 (8.3 liters) rated at 215 hp and the other engine was a 5.2 liter Detroit Diesel 6V53 rated at 210 hp. It is not known whether these engines were designed to meet any emissions standards. The PuriNOx was made from the baseline low sulfur diesel. The test sequence was intended to simulate normal operation, including a shipping container with four cement blocks, each weighing 12,880-13,200 lb. The test sequence consisted of 6 minutes of driving, 1 minute at idle, and a final 6 minutes of driving. Three tests on each fuel were performed. The emissions results are presented as an Emissions Index based upon the overall fuel.

For the Cummins, the fuel consumption and emissions for the two fuels appeared to be statistically different with the exceptions of CO_2 and SOF, which are not discussed further. For this review, the Emissions Indices and fuel consumption based upon the overall fuel were recalculated on the basis of the nonwater fraction of the emulsified fuel. The results are shown in Table 9A. The most important item of note is that the fuel consumption was significantly lower for the emulsified fuel, not only on the basis of the portion of the fuel that actually contains chemical energy (Table 9A), but also on the basis of the overall fuel. Conservation of energy dictates that the yard hauler did less work when using PuriNOx than when using diesel, even though the same task was performed. In other words, the accelerations and/or cruising speeds must have been lower when using PuriNOx. By itself, this affects the emissions when using PuriNOx. Nevertheless, as shown in Table 9A, for the same task the PM and NOx emissions benefits of PuriNOx were quite small compared to other studies.

Table 9A. Emissions Index Comparisons for the Cummins 6CT8.3 In-Use Test

		Emissions Index (g/kg diesel portion)			
Cummins 6CT8.3	Fuel cons. (kg diesel/hr)	**EICO**	**EINOx**	**EITHC**	**EIPM**
Diesel	4.53	7.09	34.82	1.78	1.41
PuriNOx	2.96	11.36	32.80	2.09	1.30
% change	-34.6	**60.2**	-5.8	**17.3**	-7.5

For the Detroit Diesel, as for the Cummins, differences in CO_2 and SOF emissions did not appear to be statistically different and will not be discussed. Again, the Emissions Indices and fuel consumption based upon the overall fuel were recalculated on the basis of the nonwater fraction of the emulsified fuel. The results are shown in Table 9B. As noted for the Cummins, the fuel consumption decreased significantly when using PuriNOx, showing that the Detroit Diesel did less work to perform this task during the PuriNOx tests (lower accelerations and/or cruising speeds). The NOx benefit for PuriNOx is much better for the Detroit Diesel than for the Cummins, and the PM benefit is better but still quite low compared to the reports discussed above.

Table 9B. Emissions Index Comparisons for the Detroit Diesel 6V53 In-Use Test.

		Emissions Index (g/kg diesel portion)			
DDC 6V53	fuel cons. (kg diesel/hr)	**EICO**	**EINOx**	**EITHC**	**EIPM**
diesel	5.34	17.35	47.62	2.05	4.20
PuriNOx	3.86	15.88	40.50	2.07	3.47
% change	-27.6	-8.5	-15.0	**0.8**	-17.3

The final report provided by Lubrizol on in-use testing involved a City of Houston municipal waste truck with a 7.3 liter Volvo VE-275 diesel rated at 275 hp. This was another study done by Environment Canada for Lubrizol (Howes, 2000b). Again, the report did not disclose the year of the engine, whether it was electronically or mechanically controlled, or what emissions standards it was designed to meet. As was done in the previous in-use tests discussed above, a test sequence was developed to simulate normal vehicle operations and three tests were done with each fuel. The PuriNOx was made from the baseline low sulfur diesel fuel. The results were presented as an Emissions Index based upon the overall fuel. Again, the CO_2 and SOF emissions did not appear to be statistically different. In contrast to the yard hauler study, the overall fuel consumption was not statistically different either. Emitting the same CO_2 with the same fuel consumption rate for a fuel that has a 20% lower mass of carbon is not reasonable and indicates some problem with the measurements, at least for CO_2. As for the other in-use tests discussed above, the Emissions Indices were recalculated based upon the portion of the fuel that contains carbon and chemical energy. The results are shown in Table 10. As for the yard hauler tests, the significant decrease in diesel consumption during the tests using PuriNOx dictates that the truck did less work to accomplish the same task when using PuriNOx (lower accelerations and/or cruising speeds). By itself, this affects emissions. As shown in Table 10, the NOx and PM benefits of PuriNOx are much better than for the yard haulers.

Table 10. Emissions Index Comparisons for the Volvo In-Use Test

		Emissions Index (g/kg diesel portion)			
Volvo VE-275	Fuel cons. (kg diesel/hr)	**EICO**	**EINOx**	**EITHC**	**EIPM**
Diesel	4.49	14.30	27.72	0.45	1.03
PuriNOx	3.56	8.69	22.85	0.87	0.38
% change	-20.7	-39.2	-17.6	**94.0**	-63.5

2.2.6 In-Use Tests

Two reports recently received from Lubrizol discuss in-use tests. The first (Dunfee and Carlson, 2001) was a report by Clayton Environmental Services and Lubrizol on the effects of PuriNOx on PM levels within a salt mine. Samples were collected at various locations within the mine before and after switching to PuriNOx. It was found that airborne PM concentrations decreased by ~32%, on average. The second paper was a report to Lubrizol by two occupational hygiene consultants (Robertson and Miles, 2002). They studied exposures to various exhaust products within two bus garages in London. PuriNOx was used by the buses in one garage and ultra low sulfur diesel was used in the other. Measurements were taken during the morning "run-out" period, which includes starting, warm-up, and eventually leaving the garage. The measurements included total inhalable dust, respirable dust, formaldehyde, acetaldehyde, acrylaldehyde, SO_2, CO, total HCs, and NOx as NO_2. It was found that exposures within the garage where PuriNOx was used were generally lower. However, the facilities were not identical and it was not stated whether or not the emissions controls on the buses were identical. Nevertheless, the most important points were that the exposure levels for all species were well below the guidelines and that bus operations, such as revving the engine to make it warm up faster, were predominately responsible for occasional short-term skin and respiratory irritation.

2.2.7 Deposit Tests

Engineering Test Services was contracted to run a standardized diesel injector deposit test for Lubrizol (Strete, 1998a). Two V6 diesel engines were used for this test, one operating on a reference diesel fuel and the other operating on PuriNOx that was made from the reference fuel. Due to the torque loss with PuriNOx, the engine using it could not attain the specified engine speed. Therefore, the engine speed for the other engine was decreased to that obtained using PuriNOx. Although this did not invalidate the tests, it meant that plunger rating pass/fail criteria were not available. Nevertheless, the flow losses and plunger ratings for the 6 PuriNOx injectors were superior to those for the 6 reference fuel injectors.

2.2.8 Lubricity Tests

Engineering Test Services was also contracted to run a standardized diesel fuel lubricity test for Lubrizol (Strete, 1998b). Two Stanadyne diesel fuel pumps were used for this test, one pumping 2D diesel and the other pumping PuriNOx made from the baseline 2D diesel. The pumps were run for 500 hours at 1100 rpm. The lubricity of the fuel was measured at the beginning and end of the test, and the pump was disassembled and inspected for wear at the end. Over the course of the test, the lubricity did not change for either fuel. It was found that the emulsion had superior lubricity from the perspective of pump wear and performance.

2.2.9 Durability Tests

Lubrizol has supplied reports for two engines that have been subjected to 1000 hour durability tests: a DDC Series 50 and a Caterpillar C12. The results for the DDC Series 50 are discussed initially, followed by a discussion of the tests of the C12.

Southwest Research Institute performed a 1000 hour durability study of PuriNOx (Sarlo, 2001). The engine was a 1999 DDC Series 50 with electronically controlled injection and EGR. This is an 8.5 liter turbocharged, 4 cylinder, 4 valves/cylinder engine. It is rated at 275 hp (205 kW) at 1800–2100 rpm and 890 ft-lb (1207 N-m) at 1200 rpm. A DDC-specified 20-step, 720 second EGR cycle was used for the durability study. A 1000 hour durability test was first performed using PC-9 diesel fuel. Modified 8-mode emissions tests were then conducted, comparing a Houston baseline diesel and PuriNOx made from this Houston diesel fuel. This was followed by a 1000 hour durability test with PuriNOx made from a CARB diesel base fuel. Problems with fuel dilution of the oil were encountered during the baseline durability run (up to 2.5% during the first 200 hours, typically ~1% during the remaining 800 hours). This resulted in replacement of injectors and, at the end of the test, an engine rebuild. These problems were obviously not related to PuriNOx. Fuel dilution of the oil was negligible during most of the PuriNOx durability test. However, at one point during the PuriNOx durability test, an injector eliminated from use initially was intentionally used during a portion of the PuriNOx test, and oil dilution by the fuel increased during this 200 hour period. There were other hardware problems during these tests as well, but the primary problem was the injectors. Furthermore, when fueled with PuriNOx the engine did not attain the same power as the base diesel fuel for any of the 20 steps, except the 4 idle points. The various problems with the injectors, the use of a faulty injector for 20% of the 1000 hour PuriNOx test, and the differences in horsepower during the tests make it difficult for this reviewer to draw firm conclusions from the durability tests. Nevertheless, some of the findings were: 1) less wear metals in the oil, 2) less soot in the oil, 3) much more oil sludge in the valve cover and oil pan, 4) lower ring wear for all three rings in all 4 cylinders, and 5) much less liner wear for PuriNOx compared to the baseline fuel. It seems possible that some of these differences may be due to the fuel dilution of the oil throughout the baseline tests.

PerkinElmer Automotive Research performed a 1000 hour durability test on a Caterpillar C12 in late 2001 (Zaiontz, 2002). A Caterpillar durability test procedure was used that represents a linehaul truck with 75% load. The 240 second cycle consists of four parts: low idle, high idle, rated power at rated speed, and full load at peak torque speed. The durability test consisted of running this cycle over and over. The injectors in the engine already had 525 hours of service using PuriNOx before the durability test began. All injectors were scheduled for replacement 500 hours into the 1000 hour durability test. One injector failed a diagnostic at hour 423 (948 hours of service), but the other 5 injectors operated to specifications the full 1,025 hours. After the scheduled replacement, all 6 injectors performed satisfactorily for the final 500 hours of the durability test. There was no loss of full load performance over the 1000 hour duration of the test, but there was a torque loss of ~17% compared to diesel fuel. Valve stem, piston ring, and liner wear were all within Caterpillar specifications, suggesting that PuriNOx is not adversely affecting the durability of these components. Via a private communication, Mark Dubois (2002) of Caterpillar said that they did not find the oil sludge problem observed in the DDC Series 50 durability test discussed above. He also said that Caterpillar has approved the use of PuriNOx in their older pump-line-nozzle group of engines (specifically the 3208, 3304, 3306, 3406B, 3406C, 3408B, 3408C, 3412B, and 3412C). However, Caterpillar has not approved the use of PuriNOx in their newer, electronically-injected engines. For these engines, they have found the same types of injector failures as when using diesel fuel, but with a higher failure rate when using PuriNOx. Caterpillar is still studying this issue.

2.3 Additional Reports on Emulsified Diesel Fuels

A literature survey was conducted to find additional reports on diesel-water fuel emulsions. Emulsions have been the subject of study for more than 20 years (e.g., Dryer, 1976; Jaques, 1977; Lasheras et. al., 1979; Law et al., 1980; and Coon, 1981). Because diesel engine technology has evolved over the past 2 decades, only the more recent papers are reviewed below. Additionally, some of the more recent papers have discussed studies of various waste oils to form biodiesel emulsions (e.g., Crookes et al., 1997; Yoshimoto et al., 1999; and Vu et al., 2001). Because biodiesel emulsions are not of interest to TxDOT, these studies are not reviewed. The studies identified may be divided into three categories, each of which is discussed below. The categories are: fundamental studies, engine and/or vehicle cycle tests, and web site material.

2.3.1 Fundamental Studies

Reports that are classified as fundamental studies include numerical models, non-engine tests, and engine tests at a few selected operating conditions to provide improved understanding of the performance of emulsions. Such studies are reviewed in this section. Many of these studies characterized the particulate emissions via the Bosch smoke number. Since this does not correlate with PM mass, such results are not discussed.

Tsukahara and Yoshimoto (1992) studied a 33% (by mass) emulsion blended from Japanese diesel fuel (Cetane Index = 57.5, which is significantly higher than for U.S. diesel fuels) in a single cylinder, water-cooled direct injection diesel. They varied the speed, load, injection timing, and compression ratio. They found that the injection timing that minimized the BSFC was different for the two fuels. This occurs because, for the emulsion, the ignition delay is longer for the emulsified fuel but the duration of combustion is shorter, more of the fuel burns during the premixed phase, the rate of pressure rise is higher, and the peak pressure is higher. Additionally, they found that they could use a lower compression ratio to achieve the same BSFC with lower NOx emissions for the emulsion compared to the baseline diesel. In a follow-on study (Yoshimoto, et al., 1996), they found that the rate of heat loss to the coolant was lower with the emulsified fuel resulting in higher indicated thermal efficiency.

Sheng and coworkers (1995) studied micro-explosions in a high pressure combustion bomb and also explored the effects of emulsions via a numerical model for diesel combustion and engine experiments. The bomb experiments showed that the droplets have an outer layer near the droplet surface that contains no water. As the droplet heats, the "micro-water dots" boil and superheat, tearing the droplets apart and ejecting the smaller droplets formed several millimeters. The ejection distance decreases with increasing gas density. The microexplosions decrease the duration of combustion and increase the rate of heat release. In turn, this improves thermal efficiency. However, the authors note that the efficiency may actually decrease "in newer engines" at high load (this was a 1995 study by the Chinese Academy of Sciences).

Samec and coworkers (2002) generated a chemical kinetics model and also performed engine experiments. The kinetics model was used to improve understanding of how an emulsion can simultaneously lower NOx and PM emissions, since virtually all other technologies yield a trade-off between PM and NOx. The dominant effect on NOx is the dilution of the flame zone by the water in the fuel. This dilution decreases the flame temperature (inhibiting formation of the N and O atoms that are crucial to NO formation). In absence of water in the fuel, this decrease in flame temperature would result in a decreased concentration of hydroxyl radicals (OH), which are essential to oxidation of particulates. However, the model shows that most of the water within the fuel decomposes to OH and molecular hydrogen, thereby increasing the OH radical pool and enhancing the oxidation of particulates. The authors note that this is a secondary beneficial effect, with the dominant effect being the micro-explosions. The model also predicts an increased Sauter mean diameter of the particulates. This finding appears to lend credence to this reviewer's interpretation of the size distribution data from the London bus tests (Brown et al., 2000) — a decrease in particle number density for sizes near 1 μm but an increase for sizes near 0.1 μm. These investigators also studied a diesel at various speed and load combinations, but do not present detailed data. Of significant interest is the authors' conclusion that diesel emulsions may have minimal effect on PM emissions for modern diesels that use very high injection pressures, since the droplets are already very small for these engines and the "secondary atomization" from micro-explosions may have little effect.

In 2001 Gonzales and coworkers examined micro-emulsions. A Cetane improver (additive) was used to compensate for the decrease in Cetane associated with the water. The authors note that their surfactant increased the viscosity and improved the lubricity compared to the base diesel fuel. As for PuriNOx, a decrease in torque was observed, as were decreases in NOx and PM. However, of the various engines they tested, for the 1994 Series 50 engine – which met 1994 EPA standards - the PM emissions for a range of steady-state operating conditions were not statistically different. Although details about this engine, such as injection pressure, were not provided, this finding may support the conclusion Samec and coworkers (2002) that the PM benefit may be small for modern engines with high injection pressures. On the other hand, the AIR report (2001) notes a significant reduction in PM for a 1995 DDC Series 50 over the transient HDD FTP cycle (but it is not stated whether this engine did the same work over the cycle for PuriNOx and diesel fuel).

Kegl and Pehan (2001) compared the emissions for an emulsion to those for water addition into the intake stream at several locations. They found that all decreased NOx but only the emulsion decreased PM, whereas water injection into the intake air stream increased PM emissions independent of where the water was injected. This is an example of the classic NOx-PM trade-off that is observed for virtually all diesel emissions control techniques other than use of emulsions.

Subramanian and Ramesh (2001) compared an emulsion with a diesel fuel from India. The emulsion was 29% water by mass and 1% surfactant. The properties of the diesel fuel were not provided. Tests were also performed when enrichening the intake air with oxygen, but these results will not be discussed because they are not relevant to the present purposes. An air-cooled, single cylinder DI diesel was used for the tests. The compression ratio was 17.5:1 and the rated power at 1500 rpm was 4.42 kW. All tests were conducted at rated power speed (1500 rpm) with the static injection timing at 22.8 CA^{o} BTDC, which was the optimum for operation on diesel fuel. For fixed speed and injection timing, diesel fuel produced a higher brake thermal efficiency up to about 90% load. The emulsion produced lower NOx but higher HCs for all loads. The CO emissions were higher for the emulsion for all loads except an 18% overload. As in other studies cited above, these investigators found that the ignition delay was longer, the peak pressure was higher, and the rate of pressure rise was higher for the emulsion for all loads. Although the results of this study are not directly relevant to PuriNOx, the results are similar to those from studies of PuriNOx.

Nazha and coworkers (2001) compared an emulsion, water induction, exhaust gas recirculation (EGR), and various combinations. The emulsion was made from a baseline English diesel fuel. No specifications for the diesel fuel were provided. A light-duty diesel was used for the tests (a 4 cylinder, direct injection 2.5 liter Ford). All tests were performed at 2500 rpm. The injection timing was advanced 3 CA^{o} from the factory setting to increase the NOx emissions so that changes would be more pronounced. The BSFC was approximately independent of the water fraction of the emulsion at constant load, whereas the NOx emissions decreased with increasing water. Use of EGR produced the best BSFC at intermediate loads and about the same BSFC as diesel alone at the lowest and highest loads. A 20% water emulsion by volume (~23% by mass) had the worst BSFC at the lowest load but about the same BSFC as diesel fuel at higher loads. The NOx benefit of the emulsion compared to diesel fuel decreased with increasing load. The report authors state: "It is accepted that the effects of emulsified fuel differ from one engine to the next and depend to a large extent on the operating conditions and the injection timing." They also cite a prior study (Storment and Coon, 1978) that reports that the benefits of emulsified fuels are more significant at low speeds and light loads. In this study (Nazha et al., 2001), it was found that EGR was more effective in suppressing NOx at lower loads but less effective at higher loads compared to the emulsion. Water induction, with a 1.5:1 water/fuel ratio (7 times the water in the emulsion), was most effective in suppressing NOx for all loads. This finding for water induction disagrees with the findings from Kegl and Pehan (2001). This discrepancy is not important because water induction is not practical. As also found in the studies cited above, these authors found that the emulsion increased the ignition delay but resulted in a higher peak pressure, in this case compared not only to the baseline diesel fuel tests but also to both EGR and water induction. Combining the emulsions with EGR produced the same BSFC as the baseline diesel tests and diesel plus EGR tests, decreased CO compared to both, increased HCs compared to both, and produced about the same NOx (in ppm) as diesel plus EGR.

Park and coworkers (2000) investigated the combustion characteristics of diesel/water mixtures in a rapid compression machine. Water volume fractions of 17% and 29% were investigated. Direct measurements were not made of NOx. Pressure traces and high-speed photography indicated that there was a lower rate of pressure rise and reduced flame luminosity with the emulsion. The decreased flame luminosity agrees with the results in Yoshimoto et al., (1996) of decreased heat rejection to the coolant. However, the lower rate of pressure rise disagrees with the studies discussed above where this was measured in a diesel engine rather than a rapid compression machine. In a related study, Park and coworkers (2001) examined emulsions in a 8 liter, 6 cylinder water-cooled diesel engine. A range of water contents in the emulsion was examined. All experiments were conducted at 80% load. At speeds below 1000 rpm, they found that the emulsion had little effect on NOx but improved NOx for 1400 rpm and higher. Recall that Storment and Coon (1978) found that emulsions are more beneficial at low speeds and loads than high and that Nazha and coworkers (2001) found that the emulsions were more effective at low load for constant speed tests. Thus, the high load used by Park and coworkers (2001) might explain the poor effect of the emulsion at low speeds. However, for a modern electronically-controlled diesel, Figure 3 revealed that PuriNOx is more effective (for NOx) at high speeds and loads. The Park et al., (2001) study also found that more of the fuel burns during the premixed phase, in agreement with Tsukahara and Yoshimoto (1992). They also found that, at 1400 rpm, 80% load, increasing the water fraction of the emulsion increased the HC and CO emissions but decreased the NOx emissions for all injection timings studied.

Song and coworkers (2000) conducted experiments similar to those of Park et al. (2000, 2001), but used an optically accessible DI diesel engine. They also used a laser extinction measurement to characterize the in-cylinder soot production. The results of the combustion imaging and heat release analysis showed a self-consistent ignition delay and reduction of soot as the amount of water was increased. The emulsion reduced soot during both the premixed and mixing controlled regimes of diesel combustion. They also conclude that the increase in the ignition delay with increasing water content appears to be an important factor in reducing soot during premixed combustion.

2.3.2 Engine and Vehicle Cycle Tests

Multimode steady state and transient engine and chassis dyno tests are discussed in this section.

ELF is a French petroleum company. They have developed an emulsified diesel fuel called Aquazole. It is 13±3% water, 85±3% diesel fuel, and 2–3% surfactant additive package. They reported the effects of its use in 2000 (Barnaud et al., 2000). A 9.8 liter I6 Renault diesel was tested in configurations meeting Euro 1 and Euro 2 emissions standards. The test cycles included the steady-state 13 mode R-49 cycle (Euro 1 and 2 cycle). The Euro 2 version of this engine was also tested against the new test procedure prescribed for Euro 3 certification. Chassis dyno tests were also performed using the Millford London Transport Bus Test cycle. Other vehicle tests were performed using other cycles, but only smoke opacity was measured. For the engine dyno tests, the injection pump was recalibrated to regain the lost torque. This was not done for the bus tests. They found reductions in NOx and PM, but the effect on HC and CO could vary between a 20% decrease and a 20% increase. Of course, these results do not relate directly to PuriNOx. However, the authors note that the emissions results depend on the type of engine, its age, its conditions of use, and the measurement cycle. This is expected to be true for PuriNOx as well.

Gonzales and coworkers (2001) performed the microemulsions study discussed in the prior section. That study also included examination of a Series 60 engine that was, apparently, operated over the HDD transient FTP. Decreases in NOx, PM, and CO were found, along with an HC penalty. Additionally, brake specific SOF and SO_4 increased, as did brake specific emissions of the gas phase "exhaust toxics": formaldehyde, acetaldehyde, 1,3-butadiene, and benzene. Again, because this is a microemulsion, whereas PuriNOx is a macroemulsion, the results may not be directly applicable. However, these results are similar to the trends for PuriNOx from other studies.

In a 2001 SAE paper (Basar et al., 2001), Lubrizol researchers report the marine 4-mode tests and the Mode 9 and Mode 11 tests discussed previously in Section 1.2.1 with regard to the work by Langer and coworkers (2001). They also discuss the Millford London bus tests again, which were covered in Section 1.2.3 with respect to Brown et al., (2000). This paper also reports the results of the in-use emissions tests that were discussed in Section 1.2.5 regarding References Rosenblatt and Ainslie (1999); Howes, (2000b). Results are provided for two additional tests that have not yet been reviewed. One engine was a naturally aspirated, air-cooled Deutz F8L 413FW indirect injection, 12.7 liter V8 rated at 129 kW. This engine was tested at full load. The other was a turbocharged, liquid-cooled Komatsu S6D140-1 direct injection, 15.2 liter I6 rated at 219 kW. This drill-rig engine was tested under the condition of "free acceleration" full load. The tests for these engines are included in the engine cycle category because both were tested in their normal operating mode. For both engines, the baseline fuel was ultra low sulfur diesel and the emulsion was 13% water. It is not stated whether or not the emulsion was made from the baseline diesel. Emissions of NOx decreased for both engines and CO decreased for the Duetz but was the same for both fuels for the Komatsu. These results are not directly relevant, since the PuriNOx to be used in Texas is 20% water by mass.

2.3.3 Web Site Material

Searching for "PuriNOx" on the Web reveals a large number of sites. The information available includes ongoing tests of PuriNOx (Hartsfield International Airport in Atlanta; Port of Houston; City of Sacramento; City of San Jose; Central Ohio Transit Authority; Port of Los Angeles; Port of Oakland; etc.) and recently completed tests (City of Houston; Golden Gate Ferry; Ramos Oil Co.; North Central Texas Council of Governments; State of Connecticut; Central Artery/Tunnel Project in Boston; Port of San Francisco; City of Cleveland; etc.). The completed projects generally provide emissions benefits/penalties, but without sufficient detail for evaluation.

3. Summary and Conclusions

The Material Safety Data Sheets for diesel fuel and summer-grade PuriNOx are essentially identical. The diesel fuel in the emulsion is diluted 20% by water (which imposes no safety or health risks by itself) and the 3% additive package is so diluted by both water and diesel fuel that it does not appear to pose any risks above those from the diesel fuel alone. The methanol in winter-grade PuriNOx does pose some additional risks.

The available literature on emulsified diesel fuels presents a lot of conflicting data. For some engines and test conditions, the HC and/or CO emissions decrease while other studies show increases. However, although some studies show increases in HC emissions by a factor of 2–3, no studies appear to show increases in HCs or CO that would fail the emissions standards. This is due to the very low HC and CO emissions from diesels, relative to the standards. Some studies conclude that emulsions are more beneficial at low speeds and low loads, whereas others maintain that they are more beneficial at high speeds and loads. Some studies show the soluble organic fraction of the particulate emissions decreasing while others show an increase (due to increased condensation of the lube oil in the combustion chamber on the particulates). Similarly, some studies show the emissions of Hazardous Air Pollutants increasing, whereas other studies show that HAPs decrease.

It is obvious that the results of using emulsified diesel fuels depend upon the engine, the test cycle, and probably upon the baseline diesel fuel used for comparison, whether or not the baseline diesel fuel was blended to make the emulsion, and the properties of the diesel fuel in the emulsion. This is made even more complicated by the torque loss due to the water in the emulsion. For both engine dyno tests and vehicle tests, there are usually conditions for which the peak torque is required, but the peak torque is lower for the emulsion. Performing the baseline test at higher torque than the test for the emulsified fuel affects emissions, in and of itself. “Repowered” tests and vehicle task tests address this problem. However, the results from the vehicle task tests make it obvious that less work was done with the emulsion than for the baseline. That is, even though the same task was accomplished, the emulsion must have resulted in lower accelerations and/or cruising speeds. Again, this affects emissions by itself. The repowered tests appear to be the only tests that have compensated for the lost torque. However, in practice, adjusting the engine to regain lost torque would probably void the warranty and might be viewed as tampering by the EPA. The problem occurs if the engine is switched back to diesel fuel: – the increased fuel injection rate allowed by the adjustment will result in more smoke, some of which will get into the lube oil, - decreasing durability. Perhaps the best solution to the predicament of how to compare the emulsion with diesel fuel has not yet been attempted. Specifically, for engine dyno tests the full load torque curve should be generated for operation on the emulsion, and this should serve as the reference for 100% torque for both the emulsified fuel and diesel fuel tests. The engine dyno tests to be conducted as part of the present project will be performed in this manner, to allow a straightforward comparison. Similarly, for chassis dyno tests a “route” should be specified rather than vehicle speed versus time. The speed-time specification is composed of “microtrips” for which each microtrip begins with idle followed by acceleration, then a cruise and deceleration back to idle. Each microtrip represents something akin to accelerating away from a stop sign, cruising down the road, and then decelerating to a stop at the next stop sign. If the vehicle cannot accelerate as hard and/or cruise as fast when using the emulsion, following a specified speed-time trace results, effectively, in stopping well before the next stop sign. In a route test, the cruise will be maintained longer with the emulsion, such that the vehicle does not begin the deceleration until it is time to begin slowing for the next stop sign. The route test technique guarantees that the same work is done with both conventional and emulsified diesel fuels. Such route tests have never been attempted in the past, but are planned for the present project.

It has also been shown that the optimum injection timing is different for an emulsion than for diesel fuel. Additionally, it has been shown that emulsions work in concert with exhaust aftertreatment (particulate traps, catalysts). However, neither of these are options for TxDOT. TxDOT will not alter injection timing and will stay with whatever emissions control devices came with the engine/vehicle.

In spite of all the confusion, some things are known with relative certainty. Emulsified diesel fuel always provides benefits in NOx and PM emissions when tested over any cycle. The magnitude of the advantage depends upon the engine, the operating conditions, the properties of the baseline diesel fuel, and the properties of the diesel fuel that is blended into the emulsion. The PM advantage should be especially engine dependent. The PM advantage stems primarily from the microexplosions and is augmented by generation of hydroxyl radicals from the water in the emulsion. For modern engines that have extremely high injection pressures, the fuel droplets are already quite small, so the microexplosions may not be as beneficial. However, the State of Texas appears to be interested only in NOx. The NOx benefit of emulsions is not nearly as strong as their effect on PM. Some data suggest that the NOx benefit is most pronounced at low speeds and loads, while other data show the opposite. The two primary theories about NOx formation in diesels disagree with each other. Therefore, it is impossible to explain the discrepancies in the data, or evaluate the NOx potential for various engines, from theory. Thus, data are required for the various engines in the TxDOT fleet – under operating conditions that simulate their actual use – to assess the NOx emissions benefits of PuriNOx.

It is also known that emulsions offer a benefit in thermal efficiency. This occurs due to a cascade of factors. The water in the fuel increases its "activation energy," resulting in a longer ignition delay. In turn, this results in more premixing during the longer delay and thus more fuel burning during the premixed phase of combustion in a diesel. Therefore, even though the duration of injection is longer to get the same chemical energy into the chamber, the duration of combustion is shorter with an emulsion. A shorter duration of combustion increases the thermal efficiency. Additionally, the reduced PM – as dominated by the microexplosions – results in lower flame luminosity and, therefore, less heat loss to the walls. This also increases thermal efficiency. Again, for modern diesels with extremely high injection pressures, the microexplosions may not have much impact, decreasing the thermal efficiency benefit. Even though diesel fuel consumption decreases, overall fuel consumption increases, and PuriNOx is more expensive than diesel at the present time. This means that the NOx benefit, once quantified for the TxDOT fleet, must be weighed against the increased operating cost. The effects of the torque loss on operations must also be weighed in decisions regarding adoption of emulsified diesel fuels.

Data from tests commissioned by Lubrizol, plus information from the literature, show that stabilized emulsions like PuriNOx have superior lubricity compared to diesel fuel, in spite of the large fraction of water in the emulsion. This indicates that injector pump durability might not be adversely affected by the water in the emulsion. The injector deposit tests also appear to be conclusive. At present there is no reason to doubt that the emulsion will decrease deposits on the injectors. The results from the two 1000 hour durability tests revealed less wear when using

PuriNOx, especially of piston rings and liners. However, concern remains over the durability of fuel injectors, and possibly fuel pumps, especially for engines that use very high fuel injection pressures. Additional study of this issue is recommended.

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