Appendix IV

Fuels Report: Appendix to the Diesel Risk Reduction Plan

October 2000

TABLE OF CONTENTS

Contents | Page

TABLE OF CONTENTS (cont.)

Contents | Page

I. SUMMARY

This report addresses the need for and the appropriate degree of regulation of diesel-engine fuel for the control of diesel particulate matter (PM) from diesel-fueled engines. Diesel PM from diesel-fueled engines was identified by the Air Resources Board (ARB or Board) as a toxic air contaminant (TAC) in 1998.

All diesel fuel sold or supplied in California for motor-vehicle use (CARB Diesel) must have a sulfur content of 500 ppmw or less (13 CCR 2281). In addition, the average aromatic hydrocarbon content of CARB Diesel, except that produced by California small refiners, must not exceed 10 percent by volume, unless the fuel is produced as an ARB-certified alternative formulation (13 CCR 2282). The ARB has certified a total of 25 alternative formulations.

Reducing sulfur levels from the CARB Diesel average sulfur content of 141 ppmw to 15 ppmw in the absence of exhaust after-treatment, is expected to have an impact on diesel PM emissions equal to a FTP-cycle specific emission reduction of about 0.004 g/bhp-hr. More importantly, improved after-treatment control efficiency (to over 90 percent control of diesel PM emissions) has been consistently demonstrated with very low-sulfur diesel fuel. Very low-sulfur fuel would allow after-treatment manufacturers to use more highly active catalysts, which operate effectively at lower temperatures and have a broader range of vehicle applications.

In February of 2000, the ARB approved a Fleet Rule for Urban Transit Bus Operators (13 CCR 1956.2). Beginning July 1, 2002, transit agencies shall not operate diesel buses on diesel fuel with a sulfur content in excess of 15 ppmw. ARB staff has estimated an incremental refining cost of less than $0.05-per-gallon to produce this fuel.

The United States Environmental Protection Agency (U.S. EPA) has published proposed regulations which would require that all diesel fuel sold for use in on-road vehicles have a sulfur content no greater than 15 ppmw, beginning June 1, 2006. U.S. EPA estimates that the overall cost, associated with lowering the sulfur cap from the current level of 500 ppmw to the proposed level of 15 ppmw, would be approximately $0.03 to $0.04 per gallon.

Alternative diesel fuels, such as water-in-fuel emulsions, have demonstrated great promise for reducing diesel PM and other emissions from diesel engines. While there is uncertainty in the emission-reduction potential of these fuels versus CARB Diesel, diesel PM emission reductions of over 20 percent have been demonstrated in comparison testing with other diesel fuels. An appropriately optimized emulsion of water in CARB Diesel should result in significant diesel PM and other emission reductions versus CARB Diesel alone. The use of alternative diesel fuels to achieve emission reductions is best suited for application to fleets, stationary engines, and equipment, which have access to a centralized fueling station.

To be consistent with U.S. EPA and to enable after-treatment control technologies for off-road and stationary diesel engines; the ARB should adopt a regulation in 2001, which would require very low-sulfur ($\leq$ 15 ppmw S) CARB Diesel for all on-road, off-road, and stationary engines statewide, effective in 2006. In the regulatory development process, the ARB staff will investigate the feasibility of an earlier implementation date. Also, guidance on diesel fuel options and associated emission reductions should be developed to assist local districts in their permitting of fleets and equipment.

Summary of Recommendations

Recommendation	Emission Reduction (%)		Incremental Cost ($/gal)	Implementation or Issue Date
	Diesel PM	NOx		
Very low-sulfur ($\leq$ 15 ppmw S)	> 90 *	> 80 *	< 0.05	2006 ***
Diesel Fuel Guidance	20 **	10 **	< 0.18 **	2001 ****

* Emission reductions with after-treatment.
** Estimated for emulsions of water in CARB Diesel.
*** Very low-sulfur CARB Diesel to be considered at ARB hearing in 2001.
**** Guidance for districts' use to be approved and issued by ARB in 2001.

II. INTRODUCTION

A. Purpose

In 1998, diesel PM was identified by the Board as a TAC in accordance with Division 26, Part 2, Chapter 3.5, Article 3 (section 39660 et seq.) of the California Health and Safety Code (H&SC). Board Resolution 98-35, identifies an estimated range of lifetime excess lung-cancer risk, associated with diesel PM inhalation, of 1.3×10^{-4} to 2.4×10^{-3} per microgram diesel PM per cubic meter of air exposure (1.3 to $24 \times 10^{-4}\ \mu g^{-1}\text{-}m^{3}$). Resolution 98-35 also directs ARB staff to begin the risk management process for diesel PM and other potentially harmful pollutants from diesel-fueled engines.

Article 4 (H&SC section 39665) directs the executive officer of the ARB to prepare a report on the need and appropriate degree of regulation for each substance determined to be a TAC. H&SC section 39667 directs the ARB to consider the adoption of regulations specifying the content of motor vehicle fuel to achieve the maximum possible reduction in public exposure to TACs; and further provides that the regulations may include the modification, removal, or substitution of vehicle fuel or fuel additives. This report addresses the appropriate degree of regulation of diesel-engine fuel for the control of diesel PM.

B. Review of Adopted and Proposed Regulations

1. U.S. EPA Regulations

All diesel fuels, Grades 1-D and 2-D, and all fuel additives for on-road motor-vehicle use must be registered in accordance with 40 CFR Part 79 – Registration of Fuels and Fuel Additives. The registration requirements for diesel fuels apply to fuels composed of more than 50 percent diesel fuel by volume and their associated fuel additives. As provided in 40 CFR 79.56, manufacturers may enroll a fuel or fuel additive in a group of similar fuels and fuel additives through submission of jointly-sponsored testing and analysis, conducted on a product which is representative of all products in that group. The general grouping categories are baseline, non-baseline, and atypical.

The baseline diesel fuel category is comprised of a single group, represented by diesel base fuel specified in 40 CFR 79.55(c). Fuel additives are categorized as mixed with diesel base fuel. The baseline category is defined as fuels possessing the characteristics of diesel fuel as specified by ASTM D 975-93 and derived only from conventional petroleum, heavy oil deposits, coal, tar sands, or oil sands. Baseline category fuels may contain no elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur; and the oxygen content must be less than 1.0 percent by weight. Fuels and fuel groups in the non-baseline diesel fuel category are derived from sources other than those listed for the baseline category or contain 1.0 percent or more oxygen by weight, or both. Fuels and fuel groups in the atypical diesel fuel category contain one or more elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur.

U.S. EPA regulation (40 CFR 80.29) prohibits the sale or supply of diesel fuel for use in on-road motor vehicles, unless the diesel fuel has a sulfur content, by weight, no greater than 500 parts per million (ppmw). In addition, the regulation prohibits on-road motor-vehicle diesel fuel, unless the diesel fuel has a cetane index of at least 40 or has an aromatic hydrocarbon content of no greater than 35 percent by volume (vol. %). All on-road motor-vehicle diesel fuel sold or supplied in the United States, except in Alaska, must comply with these requirements. Diesel fuel, not intended for on-road motor-vehicle use, must contain dye solvent red 164.

On May 13, 1999, in anticipation of Tier 2 emission standards for passenger cars and light trucks, U.S. EPA published its Advance Notice of Proposed Rulemaking (ANPRM) – Control of Diesel Fuel Quality (Federal Register pp. 26142-26158).
The ANPRM solicited comment on all potentially beneficial diesel fuel quality changes, but pointed to fuel desulfurization for the purpose of enabling new engine and after-treatment technologies that are sensitive to sulfur compounds in the exhaust stream. For example, oxidation catalysts, which are a proven technology already in widespread use on diesel engines, promote the conversion of oxides of sulfur (SOx) to particulate sulfates. The recently developed continuously regenerating diesel PM filter has shown considerable promise for light-duty diesel applications due to its ability to regenerate even at fairly low exhaust temperatures. However, these systems are fairly intolerant of fuel sulfur and are effectively limited to use with diesel fuel of less than

50-ppmw sulfur. Diesel-engine after-treatment control technologies for oxides of nitrogen (NOx) may require fuel sulfur levels of five ppmw or less.

Any emission control technologies that prove effective in light-duty, on-road diesel applications are likely to be effective with heavy-duty, on-road engines as well. Eventually, these advanced technologies could also find application in off-road equipment. U.S. EPA is considering regulating off-road diesel fuel temporarily to a quality similar to that of current, on-road motor-vehicle diesel fuel. This would provide for the transfer of advanced on-road engine technologies already under development for use with that fuel.

In its notice of Proposed Rulemaking – Control of Air Pollution from New Motor Vehicles: Proposed Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements (Federal Register pp. 35430-35559; June 2, 2000), U.S. EPA proposes regulations which would require that all diesel fuel sold for use in on-road vehicles have a sulfur content no greater than 15 ppmw, beginning June 1, 2006. U.S. EPA estimates that the overall cost, associated with lowering the sulfur cap from the current level of 500 ppmw to the proposed level of 15 ppmw, would be approximately $0.03 to $0.04 per gallon.

2. ARB Regulations

All diesel fuel sold or supplied in California for motor-vehicle use must have a sulfur content of 500 ppmw or less (13 CCR 2281). In addition, the average aromatic hydrocarbon content of motor-vehicle diesel fuel produced for sale in California, except that produced by California small refiners, must not exceed 10 percent by volume, unless the fuel is produced as an ARB-certified alternative formulation (13 CCR 2282). The average aromatic hydrocarbon limit for small refiners is 20 percent by volume. About 90 percent of the diesel fuel sold or supplied in California meets these “CARB Diesel” requirements. Only marine vessels and locomotives are currently totally exempt from the requirements. Stationary engines are exempt from the state requirements, but may be required under local district rules to use CARB Diesel. Portable engines registered under a Statewide Portable Equipment Registration Program are also required to use CARB Diesel (13 CCR 2456(e)(2)).

About seven million gallons of CARB Diesel are consumed in California each day. The fuel is produced at 12 California refineries, operated by five major refining companies, two large independent refiners, and two small refiners. The ARB has certified a total of 25 alternative formulations, including six for small refiners, one for a small refiner which is no longer in business. Five of the alternative formulations have been authorized for full public disclosure. The specifications of the five public alternative formulations are tabulated on the next page. Also shown are some of the specifications of the general reference fuel, against which the alternative formulations must be emission-tested in order to demonstrate equivalency. The small refiner reference fuel has different specification limits for aromatic (20 vol. %), polycyclic aromatic (4 wt. %), and nitrogen (90 ppmw) contents, as well as natural cetane number (47). The reference fuels are produced from straight-run California diesel fuel by a hydrodearomatization process and contain no additives for cetane boosting.

Summary of Public Alternative Formulation and General Reference Fuel Specifications

ARB Executive Order No.	Fuel Id. Number	Max. Aromatic Content	Maximum Polycyclic Aromatics	Minimum Cetane No. w/ Additives	Max. Nitrogen Content	Max. Sulfur Content
G-714-001	Chevron D4781	19 wt. %	2.2 wt. %	58	484 ppmw	54 ppmw
G-714-003	Chevron D4922	19 wt. %	4.68 wt. %	59	466 ppmw	196 ppmw
G-714-006	Chevron D4988	15 wt. %	3.6 wt. %	55	340 ppmw	200 ppmw
G-714-007	ARCO D-25	21.7 vol. %	4.6 wt. %	55.2	20 ppmw	33 ppmw
G-714-008	ARCO D-26	24.7 vol. %	4.0 wt. %	56.2	40 ppmw	42 ppmw
Reference		10 vol. %	1.4 wt. %	48 (natural)	10 ppmw	500 ppmw
Average[1]		15.8 vol. %	2.5 wt. %	54	156 ppmw	141

[1] Volume-weighted average properties from California refiner survey taken by the California Energy Commission (CEC) in summer 1997.

In February of 2000, the ARB approved a Fleet Rule for Urban Transit Bus Operators (13 CCR 1956.2). To reduce public exposure to diesel PM, transit agencies and companies that lease buses to transit agencies must participate in a program to retrofit diesel buses in their fleets, and to operate their diesel buses on very low-sulfur diesel fuel. Beginning July 1, 2002, transit agencies shall not operate diesel buses on diesel fuel with a sulfur content in excess of 15 ppmw. ARB staff has estimated an incremental refining cost of less than $0.05-per-gallon to produce this fuel. In fact, compliance sampling and analysis indicates that diesel fuel meeting this requirement has already been marketed in California for general use. Three of the major refining companies, which produce over 70 percent of the CARB diesel, have expressed support for the Fleet Rule and its requirement for very low-sulfur diesel fuel. About 20 percent of the motor-vehicle diesel fuel currently produced in California meets the 15-ppmw sulfur limit.

In a February 18, 2000 letter to Mr. Robert Perciasepe, U.S. EPA’s Assistant Administrator for Air and Radiation; Chairman Alan Lloyd of the ARB urged U.S. EPA to “adopt a nationwide cap on sulfur in diesel fuel of no greater than 15 parts per million for on-road and off-road engines effective no later than 2006.”

C. Other Diesel Fuel Specifications and Properties

ASTM D 975, Standard Specification for Diesel Fuel Oils, covers five grades of diesel fuel oils suitable for various types of diesel engines. Grade No. 2-D is a general-purpose, middle distillate fuel for automotive diesel engines, which is also suitable for use in non-automotive applications, especially in conditions of frequently varying speed and load. Grade No. 1-D is a light distillate fuel for automotive applications requiring higher volatility; and Grade No. 4-D is a heavy distillate fuel for low- and medium-speed, non-automotive applications, involving predominantly constant speed and load. ASTM D 975 also covers Grade Low Sulfur No. 1-D and Grade Low Sulfur No. 2-D. The low-sulfur grades comply with the Clean Air Act and 40 CFR Part 80 – Regulation of Fuels and Fuel Additives: Fuel Quality Regulations for Highway Diesel Fuel Sold in 1993 and Later Calendar Years.

About 100 percent of the diesel fuel sold in California is Grade Low Sulfur No. 2-D. An abbreviated table of ASTM requirements for Grade Low Sulfur No. 2-D is presented on the next page. Grade Low Sulfur No. 1-D may become more prevalent in the future if cleaner burning diesel fuel is required. The table shows the specifications of Grade Low Sulfur No. 1-D which differ from the specifications of Grade Low Sulfur No. 2-D.

Flash point is the lowest fuel temperature, corrected to standard barometric pressure, at which application of an ignition source causes the fuel vapors to ignite. The flash point is not directly related to engine performance, but is important for legal requirements and safety precautions involved in fuel handling and storage, and is normally specified to meet insurance and fire regulations.

Cloud point is of importance in that it defines the highest temperature at which a cloud or haze of wax crystals appears in the fuel under prescribed test conditions. The temperature generally relates to the temperature at which wax crystals begin to precipitate from the fuel in use. See table note 1.

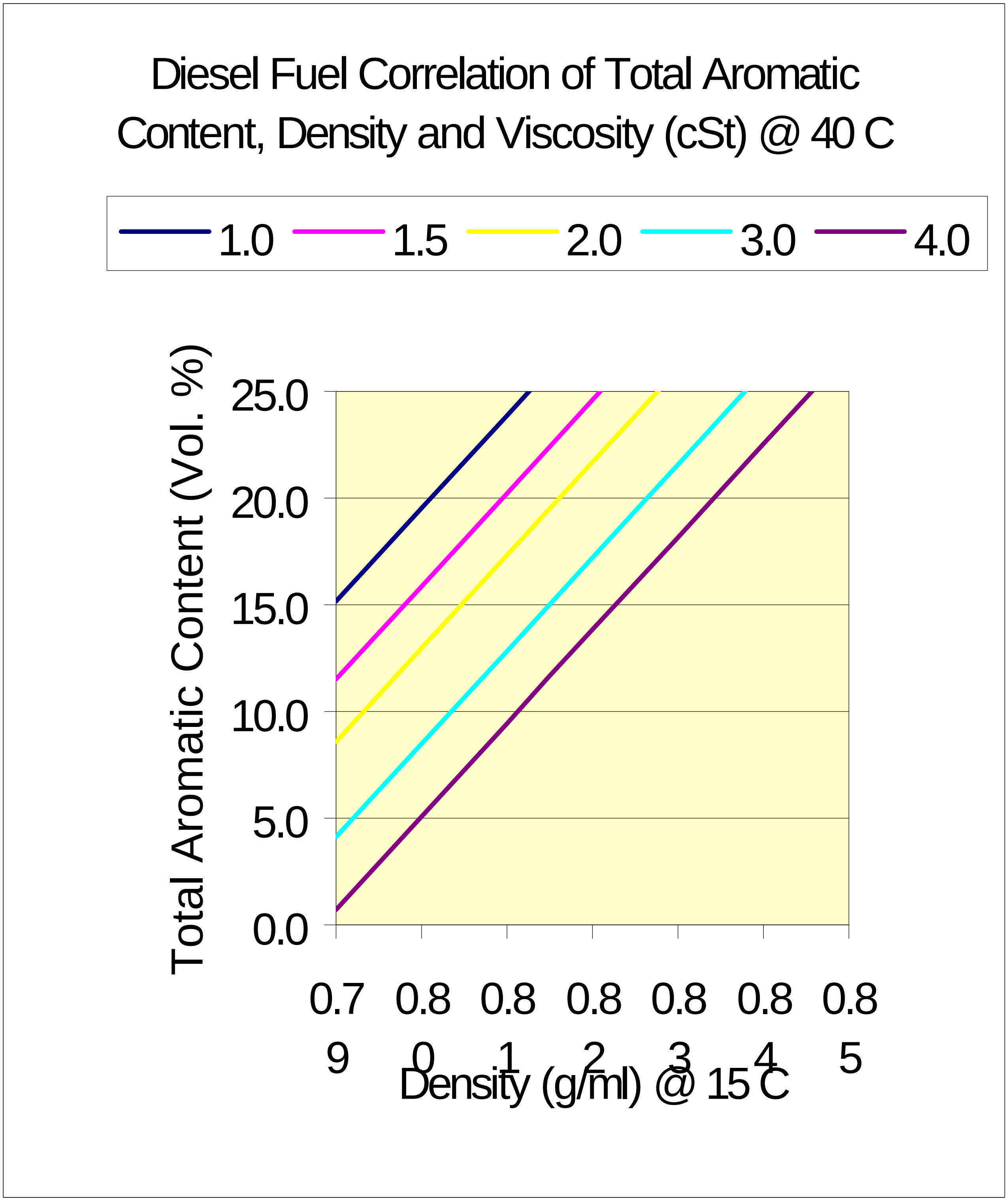
The distillation temperature at which 90 percent of volume is recovered (T_{90}) is a measure of fuel volatility; the lower the T_{90}, the more volatile the fuel. For engines in services involving rapidly fluctuating loads and speeds, as in bus and truck operation, the more volatile fuels generally provide better performance, particularly with respect to smoke and odor. However, better volumetric fuel economy (VFE) is generally obtained from the less volatile types of fuels because of their higher densities and higher volumetric energy contents.

Abbreviated Table of ASTM D 975 Requirements for Grade Low Sulfur Fuels

Property	ASTM Test Method	Grade Low Sulfur No. 2-D	Grade Low Sulfur No. 1-D
Flash Point, Minimum	D 93	52 °C (126 °F)	38 °C (100 °F)
Cloud Point, Maximum	D 2500	[1]	[2]
Distillation Temperature at 90 % Volume Recovered, Minimum / Maximum	D 86	282 °C (540 °F) / 338 °C (640 °F)	No Minimum / 288 °C (550 °F)
Kinematic Viscosity At 40 °C (104 °F), Minimum / Maximum	D 445	1.9 cSt (11 in^2/hr) / 4.1 cSt (23 in^2/hr)	1.3 cSt (7 in^2/hr) / 2.4 cSt (13 in^2/hr)
Cetane Number, Minimum	D 613	40	[2]
Cetane Index, Minimum, or Aromatic Hydrocarbon Content, Maximum	D 976 or D 1319	40 or 35 vol. %	[2]
Sulfur Content, Maximum	D 2622	0.05 wt. % (500 ppmw)	[2]

[1] Satisfactory operation should be achieved in most cases if the cloud point (or wax appearance point) is specified at 6 °C (11 °F) above the tenth percentile minimum ambient temperature for the area and calendar month. When a cloud point less than -12 °C (10 °F) is specified, the minimum flash point shall be 38 °C (100 °F), the minimum viscosity at 40 °C (104 °F) shall be 1.7 cSt (9.5 in^2/hr), and the minimum T_{90} shall be waived.
[2] Same as Grade Low Sulfur No. 2-D specification.

Viscosity is a measure of flow resistance; the higher the viscosity, the greater the resistance to flow. Fuel viscosity is also related to fuel density, generally the lighter fuels being less viscous and the heavier fuels being more viscous. Based on the properties of 52 finished diesel fuels and blending components, a correlation of viscosity, density, and total aromatic hydrocarbon content has been described (see figure on next page).


Diesel Fuel Correlation of Total Aromatic Content, Density and Viscosity (cSt) @ 40 C
1.0
1.5
2.0
3.0
4.0
Total Aromatic Content (Vol. %)
25.0
20.0
15.0
10.0
5.0
0.0
0.79
0.80
0.81
0.82
0.83
0.84
0.85
Density (g/ml) @ 15 C

Fuel viscosity requirements are pertinent to the design of fuel-metering and fuel-injection equipment, which must accurately meter and precisely inject a small quantity of fuel. Since viscosity is temperature-dependent, the fuel tolerance band between maximum and minimum viscosity should be kept as small as practicable to avoid loss of performance under extreme conditions. At low temperature, viscosity reduces fuel flow rates; and a high-viscosity fuel may result in incomplete filling of the metering chamber and an inadequate volume of fuel being injected. A low-viscosity fuel in high-temperature, low-speed operation could result in unacceptable clearance leakage from the pumping elements; making "hot restarting" impossible until the fuel system has cooled down. Fuel viscosity also affects injector-spray penetration rate, cone angle, and drop-size distribution.

Cetane number is a measure of the ignition quality of the fuel and influences combustion roughness. The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. A cetane number too low can result in poor combustion and high emissions under transient cycle operation. Cetane number can be increased through the use of ignition improvement additives such as 2-ethyl hexyl nitrate. Cetane index is an estimate of the natural cetane number of the fuel, and is calculated based on the fuel's density and mid-boiling temperature (T_{50}) (an updated ASTM method additionally uses the T_{10} and T_{90}).

The aromatic hydrocarbon content (aromaticity) of diesel fuel has a great influence on fuel quality. Aromatic compounds have high liquid densities. Monocyclic compounds have relatively low boiling points; polycyclic compounds have relatively high boiling points. Aromatic compounds are also relatively refractory to combustion. High aromaticity generally means high volumetric energy content, high combustion temperatures, poor combustion (ergo, low natural cetane number), and high emissions.

Fuel sulfur content can affect engine wear, deposit formation, and emission performance. Fuel sulfur that is not deposited within the fuel system, engine, or exhaust system is emitted as sulfurous compounds, such as gaseous sulfur dioxide (SO_2) and particulate sulfates (SO_4^{-2}). Sulfur compounds in engine exhaust can also reduce the effectiveness of emission control equipment.

ASTM D 975 also addresses fuel lubricity, but does not currently include a standard for fuel lubricity. Two fuel characteristics, which affect fuel lubricity and equipment wear, are fuel viscosity and the amounts of trace fuel components which have an affinity for metal surfaces. Fuel lubricity is a concern when fuels with lower viscosities than what is specified for a particular engine are used, or when fuels are used which have been processed in a manner that results in the elimination of the surface active species, which act as lubricating agents. Fuels, which have been shown to have lubricity problems, are fuels, which have been severely hydro-treated to remove sulfur and reduce aromaticity. This effect can be counteracted with the use of lubricity improvement additives.

Work in the area of diesel fuel lubricity has been ongoing by several organizations, such as the International Standard Organization (ISO) and the ASTM Diesel Fuel Lubricity Task Force. The charge of the ASTM task force is the recommendation of lubricity test methods and a fuel lubricity specification for D 975. Test Methods D 6078, a scuffing load ball-on-cylinder lubricity evaluator (SLBOCLE) method, and D 6079, a high frequency reciprocating rig (HFRR) method, were proposed and approved by the task force. Both methods in their current forms do not apply to all fuel-additive combinations.

Further research is required before the task force can recommend a lubricity specification. SAE Technical Paper 952369 indicates that fuels with scuffing load values below 2000 g in Test Method D 6078 will probably cause accelerated wear in fuel-lubricated, rotary-type fuel injection pumps. Work at ISO, documented in SAE Technical Paper 952372, indicates that fuels with Test Method D 6079 wear-scar diameters of 450-micron, or less, at 60 °F (380-micron, or less, at 25 °C) should protect all fuel injection equipment.

Unspecified properties of No. 2 diesel fuel include density, lower heating value (LHV), and volumetric energy content. A summary of composition and property ranges is tabulated below for No. 2-D. The ranges may be narrower for Grade Low Sulfur or other cleaner burning No. 2-D fuels.

Summary of Composition and Property Ranges for No. 2-D

Molecular Formula	C_8 to C_{25}
Carbon Content (wt. %)	84 to 87
Hydrogen Content (wt. %)	13 to 16
Boiling Temperature (°F)	370 to 650
API Gravity	27 to 43
Specific Gravity @ 60 °F/ 60 °F	0.81 to 0.89
Density (lb/gal) @ 60 °F	6.7 to 7.4
Lower Heating Value (Btu/lb)	18,000 to 19,000
Volumetric Energy Content (Btu/gal)	126,000 to 130,800

Fuel Density (g/ml) @ 15 °C ≈ Specific Gravity @ 60 °F/ 60 °F = 141.5 ÷ (131.5 + API Gravity)

III. FUEL OPTIONS

A review of engine emission testing programs for fuel property effects on heavy-duty diesel (HDD) emissions, based on both transient-cycle and steady-state testing, indicates that six properties of diesel fuel have some influence on HDD emissions. The properties studied were sulfur content, aromatic hydrocarbon content, polycyclic (or polynuclear) aromatic hydrocarbon (PAH) content, cetane number, density, and volatility. Another property, which may influence HDD emissions, is oxygen content. In this report we discuss this property effect under “Alternative Diesel Fuels,” as it may properly relate to the specific oxygenated component of the fuel.

A. Reformulated and Synthetic Diesel Fuels

Studies indicate generally that reducing sulfur, aromatic, and PAH contents; increasing cetane number and back-end volatility; and decreasing the density of diesel fuel causes reductions in diesel PM and NOx emissions. These property changes generally cause favorable or neutral behavior with respect to gaseous hydrocarbon (HC) and carbon monoxide (CO) emissions, with the exception that these emissions generally behave oppositely with respect to back-end volatility and fuel density. Overall, the fuel property effects on HDD emissions are generally more pronounced in higher-emitting engines. Also, the greatest absolute and relative emission reductions can of course be achieved relative to a fuel with high-emitting properties.

CARB diesel and its alternative formulations have low-emitting properties; except that volatility and density are essentially unregulated aspects of the basic property requirements or equivalency determinations. The T_{90} of the reference fuel may vary from 550 to 610°F (288 to 321°C) and the API gravity of the reference fuel may vary from 33 to 39 (0.83 to 0.86 g/ml). The specifications for alternative formulations are not required to include volatility or density specifications.

Swedish Urban Diesel and ARCO's Emission Control – Diesel (EC-D) are reformulated diesel fuels which are refined from crude. Syntroleum's ultra-low-aromatic synthetic diesel fuel is synthesized from natural gas by the Fischer-Tropsch (F-T) process. All of these fuels should perform similarly to ASTM Grade No. 1-D fuel. All of these fuels have properties which, when compared to CARB diesel, are consistent with the six property changes discussed previously, and which combined should reduce diesel PM, NOx, HC, and CO emissions overall.

Of the six fuel properties, which have been identified as influencing HDD emissions; only sulfur content, aromatic hydrocarbon and PAH contents, and fuel density significantly affect diesel PM emissions.

1. Very low-sulfur CARB Diesel

Sulfur in diesel fuel results in proportional amounts of engine-out SOx and particulate sulfate emissions. Reducing sulfur levels below the CARB Diesel average sulfur content of 141 ppmw in the absence of exhaust after-treatment, is expected to have an impact on diesel PM emissions. An U.S. EPA on-road emission model predicts that reducing sulfur content from 141 ppmw to 15 ppmw would reduce SOx emissions (as SO_2) by 0.11 grams per pound (g/lb) of fuel, and would reduce diesel PM emissions (as $H_2SO_4 : 7H_2O$) by 0.0080 g/lb of fuel. The SOx emission reductions would reduce atmospheric sulfate formation (as half NH_2SO_4 and half NH_4HSO_4) by 0.026 g/lb of fuel. These differences are approximately equal to FTP-cycle specific emission reductions of 0.016 grams per brake horsepower-hour (g/bhp-hr) for SOx, 0.0040 g/bhp-hr for diesel PM, and 0.013 g/bhp-hr for indirect sulfate. Based on the U.S. EPA model, reducing fuel sulfur from 141 ppmw to 15 ppmw would reduce diesel PM emissions by about 4 percent from engines with FTP-cycle specific emission rates of 0.1 g/bhp-hr. (A reduction from 500 ppmw to 5 ppmw would result in about a 16 percent reduction from 0.1 g/bhp-hr.) At 15-ppmw sulfur, the residual engine-out SOx and particulate sulfate emissions would be 0.013 g/lb of fuel and 0.0010 g/lb of fuel, respectively. These emission ratios are approximately equal to FTP-cycle specific emissions of 0.007 g/bhp-hr for SOx and 0.0005 g/bhp-hr for particulate sulfate (see table).

Fuel Sulfur Content, Predicted Engine-Out Sulfur Compound Emissions, and Predicted Atmospheric Sulfate Formation

Fuel Sulfur (ppmw)	SOx Emissions		Sulfate Emissions		Indirect Sulfate	
	(g/lb)[1]	(g/bhp-hr)[2]	(g/lb)[1]	(g/bhp-hr)[2]	(g/lb)[1]	(g/bhp-hr)[2]
500	0.44	0.22	0.032	0.016	0.10	0.051
368	0.33	0.16	0.023	0.012	0.075	0.038
141	0.13	0.063	0.0090	0.0045	0.029	0.014
54	0.048	0.024	0.0034	0.0017	0.011	0.0055
15	0.013	0.0067	0.0010	0.00048	0.0031	0.0015
5	0.0044	0.0022	0.0003	0.00016	0.0010	0.00051

[1] Predicted with U.S. EPA on-road emission model.
[2] FTP-cycle emissions if brake specific fuel consumption (BSFC) is 0.5 lb/bhp-hr.

2. Impact of Sulfur on After-Treatment Technology

a) MECA Demonstration Results

The impact of sulfur content on diesel PM emissions varies widely depending on whether exhaust after-treatment is used and what type of after-treatment is used. A 1999 Manufacturer of Emission Controls Association (MECA) report, *Demonstration of Advanced Emission Control Technologies Enabling Diesel-Powered Heavy-Duty Engines to Achieve Low Emission Levels*, compares emissions from a 1998-model, Detroit Diesel Corporation (DDC) series-60 engine with various after-treatments and for fuels with different sulfur contents. One of the fuels contained 368 ppmw sulfur and another contained 54 ppmw sulfur; other properties of the fuels were not the same. The lower-sulfur fuel yielded fuel-effect diesel PM emission reductions of approximately 14 percent with no after-treatment to 72 percent for after-treatment with a catalyst-coated diesel particulate filter (DPF-A). Some of the reduction in baseline (without after-treatment) emissions may have been due to other property differences of the fuels; however, the U.S. EPA on-road emission model predicts an emission difference of about 0.01 g/bhp-hr due to sulfur alone. Two medium-activity diesel oxidation catalysts (DOC-B and DOC-E) and one high-activity diesel oxidation catalyst (DOC-F) were also tested with the two fuels. Improved after-treatment control efficiency was consistently demonstrated with the lower-sulfur fuel (see table).

MECA Demonstration Results

After-Treatment	368 ppmw sulfur Fuel		54 ppmw sulfur Fuel		Fuel Effect
	g/bhp-hr[1]	% Reduction[2]	g/bhp-hr[1]	% Reduction[2]	% Reduction
Baseline	0.073	--	0.063	--	14
DOC-B	0.054	26	0.043	32	20
DOC-E	0.053	27	0.045	29	15
DOC-F	0.077	-5	0.053	16	31
DPF-A	0.022	70	0.0062	90	72

[1] Federal test procedure (FTP)-cycle diesel PM emissions.
[2] Reduction from baseline diesel PM emissions.

With catalytic after-treatment, SO_2 in the engine exhaust can be oxidized to SO_3, which condenses with water. The condensed SO_3 increases the particulate mass, offsetting the reduction of other particulate components. For this reason, reducing fuel sulfur improves after-treatment effectiveness and reduces diesel PM emissions. Very low-sulfur fuel would allow after-treatment manufacturers to use more highly active catalysts, which operate effectively at lower temperatures and have a broader range of vehicle applications.

b) DECSE Program's DPF Results

The United States Department of Energy (DOE), the Engine Manufacturers Association (EMA), and MECA have been conducting a joint test program to evaluate four levels of diesel sulfur (350, 151, 30, and 3.1 ppmw) with four types of after-treatment technologies. Tabulated below are some of the data from this Diesel Emission Control – Sulfur Effects (DECSE) Program's *Phase I Interim Data Report No. 4: Diesel Particulate Filters – Final Report*.

A Caterpillar model 3126 engine rated at 205 kW (275 horsepower) and equipped with electronic controls was used for the DPF tests. The 3126 engines are typically used for applications that result in relatively low-temperature exhaust (e.g, below 300 °C (572 °F)). Because fuel sulfur level is expected to affect the filter regeneration temperature, these low-temperature applications are an excellent test of the effects of fuel sulfur level. Two different DPFs were tested; one catalyzed (catalyst-coated) DPF (CDPF) and one continuously regenerating DPF (CR-DPF). The CR-DPF has an upstream oxidation catalyst, which generates NO_2 to oxidize the filter-collected diesel PM. Emissions were sampled for Organisation Interntionale des Constructeurs d'Automobiles (OICA) 13- mode, peak-torque, and "road-load" steady-state engine tests.

DECSE Program's DPF Results

Steady-State Test	After-treatment Device	Diesel PM Emissions (g/bhp-hr)			Efficiency (% Reduction)		Sulfur Effect (% Reduction)	
		151 ppmw	30 ppmw	3.1 ppmw	30 ppmw	3.1 ppmw	30 ppmw	3.1 ppmw
OICA 13-Mode	Eng.-out	0.0708	0.063	0.0613	--	--	11	13
	CDPF	0.0707	0.0166	0.0031	74	95	77	96
	CR-DPF	0.0729	0.0176	0.0032	72	95	76	96
Peak-Torque Mode	Eng.-out	0.0563	0.0489	0.043	--	--	13	24
	CDPF	0.046	0.0137	0.0031	72	93	70	93
	CR-DPF	0.0456	0.0133	0.0039	73	91	71	91
Road-Load Mode	Eng.-out	0.0459	0.0414	0.041	--	--	10	11
	CDPF	0.0574	0.0082	0.0026	80	94	86	95
	CR-DPF	0.0637	0.008	0.0012	81	97	87	98

We have assumed the 151-ppmw-sulfur data as the baseline for sulfur effects on diesel PM emissions. The DPF data for the 350-ppmw-sulfur fuel indicate significant diesel PM increases due to catalytic sulfate generation. Carbon monoxide emission reductions of 90 percent or more, and hydrocarbon emission reductions of over 50 percent, were achieved for all fuel sulfur levels and engine tests with both DPFs.

3. Other Reformulation Options

Aromatic-hydrocarbon-content, PAH-content, and fuel-density limits should help to control diesel PM emissions; however, more data on emission effects on the various engines and run cycles are needed to determine what the limits should be.

4. Swedish Urban Diesel Fuels

In 1991, Sweden introduced new environmental classifications for diesel fuels, with tax incentives to encourage their use. The revised specifications for Swedish Urban Diesel Fuels, issued in 1992, are tabulated here.

Revised Specifications for Swedish Urban Diesel Fuels

Property	Limit	Swedish Class 1	Swedish Class 2
Sulfur (ppmw)	Maximum	10	50
Aromatic Content (vol. %)	Maximum	5.0	20
PAH Content (vol. %)	Maximum	0.02	0.1
Initial Boiling Point (°C)	Minimum	180	180
T_{95} (°C)	Maximum	285	295
Density (g/ml)	Range	0.800 to 0.820	0.800 to 0.820
Cetane Index	Minimum	50	47

A concern was identified that Swedish Class 1 and Class 2 fuels may cause premature injection-pump wear due to their low lubricity characteristics; however, testing has shown that Class 1 fuel, enhanced with a lubricity additive, performs without problems.

5. ARCO's Emission Control – Diesel

ARCO has developed a diesel fuel called EC-D that results in substantially lower exhaust emissions compared to a CARB Diesel fuel blend. EC-D has a very low-sulfur content, low aromatic and PAH contents, a high natural cetane number, and low density. EC-D is produced from typical crude oil using a conventional refining process.

Three engines were tested in an emissions laboratory and six urban trucks and buses were tested on a heavy-duty vehicle chassis dynamometer. Initial test results indicate that EC-D reduces regulated emissions while maintaining fuel economy, compared to a CARB Diesel fuel blend. The initial test results that averaged the reductions on emissions and a summary of the fuel properties from the initial EC-D test program are tabulated below.

Averaged Results from Initial EC-D Test Program

Emission Reductions by Percentage	
Diesel PM	13
HC	13
CO	6
NOx	3

Summary of Initial EC-D Test Program Fuel Properties

Property	**EC-D**	**CARB Blend**
Sulfur Content (ppmw)	<2	120
Aromatic Content (vol. %)	8.8	18.9
PAH Content (wt. %)	0.5	2
Natural Cetane Number	61.7	53.2
Nitrogen Content (ppmw)	1	98
API Gravity	41.5	36.3
Specific Gravity	0.818	0.843
Cloud Point (°F)	32	10.4
Initial Boiling Point (°F)	386	358

As discussed previously, very low-sulfur fuels such as EC-D will enable the use of sulfur-sensitive emission control devices for even greater exhaust emission reductions. A technology validation program evaluating EC-D and regenerative DPF technology on urban diesel vehicles has been initiated. The fuel's impacts on engine durability, vehicle performance, and emissions will be evaluated in eight truck and bus fleets. Currently, 184 trucks and buses are participating in the test program, 74 (40 percent) of which will be retrofitted with regenerative DPFs. So far, no significant maintenance issues have been reported for school bus, tanker truck, and grocery truck fleets, which have been participating in the program for over six months. Preliminary test results indicate that the EC-D with DPFs reduces diesel PM emissions by over 90 percent. The properties of the program test fuels are tabulated below.

Summary of Current EC-D Test Program Fuel Properties

Property	EC-D	CARB Blend
Sulfur Content (ppmw)	7.4	121.1
Aromatic Content (vol. %)	10.9	22.5
PAH Content (wt. %)	0.9	4.1
Natural Cetane Number	64.7	54.1
API Gravity	42.8	36
Density @ 15 °C (g/ml)	0.8119	0.8445
Energy Content (Btu/gal)	126,300	130,000
Cloud Point (°F)	27	16
Initial Boiling Point (°F)	412.8	351.7
T_{10} (°F)	445.4	409.0
T_{50} (°F)	526.1	525.4
T_{90} (°F)	610.9	622.7
Final Boiling Point (°F)	656.2	664.9

The averaged preliminary emission test results for two school buses and two tanker trucks are tabulated below. The vehicles were tested on a heavy-duty chassis dynamometer over a City-Suburban Heavy Vehicle Route (CSHVR) driving schedule. Averaged results of testing, prior to DPF installation, indicate NOx and diesel PM emission reductions, due to EC-D alone, of 10 and 15 percent for the buses and 11 and 3 percent for the trucks. The VFE decrease observed with EC-D, approximately 3 percent, was about equal to the difference in volumetric energy contents between the EC-D test fuel and the CARB blend.

Averaged Preliminary Results from Current EC-D Test Program

Vehicle Type	Fuel/ DPF	NOx		CO		HC		Diesel PM		VFE	
		g/mi	%Δ	g/mi	%Δ	g/mi	%Δ	g/mi	%Δ	mpg	% Δ
Bus	CARB	20.19	--	2.51	--	0.55	--	0.218	--	4.70	--
Bus	EC-D	18.12	-10	2.25	-10	0.48	-13	0.186	-15	4.57	-2.8
Bus	w/ DPF	16.25	-20	0.15	-94	0.00	-99>	0.000	-99>	4.79	1.9
Truck	CARB	16.46	--	3.13	--	1.35	--	0.581	--	5.55	--
Truck	EC-D	14.66	-11	2.89	-8	1.24	-8	0.562	-3	5.36	-3.4
Truck	w/ DPF	13.93	-15	0.32	-90	0.11	-92	0.026	-96	5.24	-5.6

6. Ultra-Low-Aromatic Synthetic Diesel Fuel

Fischer-Tropsch is a gas-to-liquid chemical conversion process that is being successfully used to produce high quality gasoline and diesel fuel products from coal, natural gas, and biomass feedstocks. The process originates from Franz Fischer and Hans Tropsch, who patented the synthesis of petroleum at normal pressure using metal catalysts in 1926. In the Syntroleum Process, sulfur is first removed from natural gas. Then, the natural gas is reformed with air, producing a nitrogen-diluted synthesis gas containing mostly CO and H_2. A cobalt-based F-T catalyst is used to reassemble the synthesis gas molecules into highly saturated synthetic oil and by-product water. The principal products are iso- and normal paraffins, along with minor amounts of simple olefins and primary alcohols. These few olefins and alcohols are removed by mild hydrosaturation, leaving very-low-aromatic, super-very low-sulfur synthetic diesel fuel. Fischer-Tropsch fuels may require a lubricity additive to prevent undue fuel-injection system wear. A commercially available lubricity additive has been found to be effective.

Three different F-T diesel fuels have been tested against a CARB Diesel fuel with properties of the general reference fuel, following a procedure similar to the CARB procedure for evaluation of alternative formulations. On average, the testing showed emission reductions, compared to the CARB fuel, of 4 percent for NOx, 36 percent for CO, 20 percent for HC, and 26 percent for diesel PM (see table). Averaged properties of the three F-T fuels and the properties of the CARB fuel are also shown below.

Averaged Emission Reductions Due to Three F-T Test Fuels

Emission Reduction	
NOx	4 %
CO	36 %
HC	20 %
Diesel PM	26 %

Averaged Properties of Three F-T Test Fuels and Properties of CARB Test Fuel

Property	**F-T**	**CARB**
Sulfur Content (ppmw)	0	345
Aromatic Content (vol. %)	0	10
Cetane Number	74	50
Specific Gravity @ 60 °F/ 60 °F	0.769	0.842
Kinematic Viscosity @ 40 °C (cSt)	1.58	2.79
Cloud Point (°F)	-9	4
Flash Point (°F)	144	180

Four trucks, White-GMC WG64T class-8 tractors (80,000-lb gross vehicle weight), with 1996- and 1997-model Caterpillar 3176B, 350-hp diesel engines were tested with a F-T fuel and a CARB Diesel fuel on a heavy-duty chassis dynamometer. Emission reductions with the F-T fuel averaged 12 percent for NOx, 18 percent for CO, 40 percent for HC, and 24 percent for diesel PM (see table on next page). Based on the volumetric energy contents of the two fuels, a VFE reduction of about 3.4 percent was predicted for the F-T fuel. The test average reduction was 2.4 percent. Drivers could not detect a performance difference between trucks operating on the F-T fuel and the CARB Diesel. Properties of the two fuels are summarized below.

Summary of Chassis Dynamometer Emission Results for F-T and CARB Fuels

Average Values	CARB	F-T	% Reduction
NOx (g/mi)	13.4	11.7	12
CO (g/mi)	3.99	3.27	18
HC (g/mi)	0.67	0.40	40
Diesel PM (g/mi)	0.48	0.37	24
VFE (mpg)	5.95	5.81	2.4

Summary of F-T and CARB Test Fuel Properties

Property	**F-T**	**CARB**
Sulfur Content (ppmw)	< 5	100
Aromatic Content (vol. %)	0.1	17.9
Cetane Number (Index)	> 74	(53.7)
Specific Gravity @ 60 °F/ 60 °F	0.7845	0.8337
Volumetric Energy Content (Btu/gal)	123,600	127,900
Initial Boiling Point (°F)	410	347
T_{10} (°F)	500	415
T_{50} (°F)	572	514
T_{90} (°F)	628	630
Final Boiling Point (°F)	640	685

B. Alternative Diesel Fuels

The fuels discussed in this section contain oxygenated components or consist of oxygenated chemical compounds.

1. Fuel/water Emulsions

A-55, Incorporated, has patented diesel/water and naphtha/water emulsion fuels for use in compression ignition (CI or diesel) engines. The diesel/water fuel patented by A-55 consists of about 30 percent water and about 70 percent petroleum diesel. Small amounts (less than 1 percent) of a proprietary additive are included to maintain the emulsion, enhance the lubricity, inhibit corrosion, protect against freezing, and limit foaming potential. The diesel fraction of the emulsion can be either a naphtha cut or finished diesel fuel.

The presence of water in the emulsion reduces both diesel PM and NOx emissions in diesel engines. The water causes lower combustion temperatures, which reduces NOx emissions. The NOx emissions reductions increase as the water content of the emulsion increases. Also, for a given water content, the NOx reductions are greater for diesel/water emulsions than for diesel/naphtha emulsions. The water also produces a different combustion pattern, which causes the carbon in the fuel to burn more completely, producing lower diesel PM emissions. Tests in a transit bus showed NOx reductions of 53 percent and diesel PM reductions of 20 percent. More recent tests on a 1999 diesel pickup showed NOx reductions of 26 percent and diesel PM reductions of 22 percent.

There does not appear to be any loss in engine power or degradation in performance from the use of diesel/water or naphtha/water emulsions. Testing has shown that power and torque curves with the emulsions are comparable to those of No. 2-D fuel. Peak cylinder pressures are also comparable. Diesel/water emulsions appear to result in slightly greater thermal efficiency. The presence of water decreases the volumetric energy content, which is translated into a reduction in VFE (miles per gallon). However, there appears to be little difference, or perhaps a slight increase, in the fuel economy, on a miles-per-BTU basis with the emulsion. Because of the reduced volumetric fuel economy, the range is reduced. Also, on some applications, the volumetric flow rate to the engine is increased, necessitating modifications to the fuel metering system. The need for these modifications is an obstacle that has to be overcome before diesel/water emulsions could be considered feasible on a widespread basis for all diesel vehicles.

The use of diesel/water and naphtha/water emulsions has been demonstrated in some bus fleet applications. The regional transit agency in Reno had three urban transit buses operating on diesel/water and naphtha/water emulsions, and the Washoe County School District became the first school district to approve the use of the fuels in four school buses. More recently, two para-transit buses in Sacramento were operated on A-55.

The Lubrizol Corporation has also been developing diesel/water emulsions for use in diesel engines. Lubrizol calls its fuel PuriNOx Performance Systems fuel (PuriNOx). PuriNOx is a diesel/water emulsion in which the diesel fuel is the continuous phase and the water is emulsified. The water content of PuriNOx is about 20 percent and the diesel fuel content is about 80 percent. Surfactants and other additives make up less than 1 percent. Lubrizol has reported a NOx reduction of 15 percent, and a diesel PM reduction of 51 percent, in eight-mode emission testing of PuriNOx in an eight cylinder, 34.5-liter diesel engine. The table below summarizes the reported emission reductions.

Emission Reductions from Engine Testing of PuriNOx

Pollutant	Reduction (%)
NOx	15
THC	14
CO	9
Diesel PM	51

Lubrizol has also conducted a chassis dynamometer test on a Euro II Olympian bus in which PuriNOx was used in combination with a diesel oxidation catalyst. Over the Millbrook London Transport Bus (MLTB) Cycle, the combined use of the diesel oxidation catalyst and PuriNOx achieved a NOx reduction of 21 percent and a diesel PM reduction of 70 percent. The baseline diesel fuel and the emulsion-base diesel fuel were the same, and had a sulfur content of less than 50 ppmw and a T_{95} of less than 345 °C. The table below summarizes the observed emission reductions.

Emissions and Emission Reductions from Chassis Testing of a Bus with Diesel Oxidation Catalyst and PuriNOx

Pollutant	Baseline Emissions (g/km)	Emissions w/ DOC+PuriNOx (g/km)	Emission Reduction (%)
NOx	14.0	11.1	21
THC	0.654	0.055	92
CO	1.516	0.046	97
Diesel PM	0.182	0.055	70

In summary, diesel/water and naphtha/water emulsions have promise for applications where central fueling facilities exist. Fleet applications such as transit buses and school buses are examples of such applications.

2. Ethanol-Diesel Micro-Emulsions

Emulsions between ethanol and diesel recently have shown promise as an emission reduction technology for diesel engines. In ethanol-diesel emulsions, globules of ethanol are dispersed within the diesel fuel. Most of the research to date has focused on formulations with aqueous ethanol, that is, solutions of water and ethanol. The aqueous ethanol content of the emulsions is typically 12 to 24 percent by weight. A stable emulsion is maintained with the presence of surfactants, which contain polar and non-polar ends. The polar ends point towards the interior of the globules where the ethanol molecules are found, while the non-polar ends point to the area between the globules where the diesel compounds are found. The globules in ethanol-diesel emulsions tend to be smaller than those found in fuel/water emulsions. Hence they are referred to as micro-emulsions, as opposed to macro-emulsions. Micro-emulsions are clear, temperature-stable formulations that can be handled the same way as diesel fuel.

Ethanol-diesel emulsions are being developed as a strategy for diesel PM and NOx emission reductions. NOx reductions are achieved as a result of lower combustion temperatures. The combustion temperatures are reduced as a result of the high heats of vaporization of ethanol and water. The diesel PM emissions are reduced as a result of a phenomenon referred to as steam explosion. Steam explosion refers to the sudden vaporization and expansion of the water within the globules. This vaporization better atomizes the fuel, which promotes complete combustion. The emission reduction effects of water and ethanol are proportional to their concentration. So-called “first generation” formulations of ethanol-diesel emulsions reduced diesel PM emissions by approximately 40 percent and NOx emissions by approximately 10 percent. “Second generation” formulations incorporating several refinements increased the NOx reduction somewhat, but decreased the diesel PM reductions. Further work is being done to obtain the optimum formulation for combined NOx and diesel PM reductions. Some tests have shown that the use of ethanol-diesel emulsions increases emissions of some pollutants. Exhaust hydrocarbon emission increases of 20 to 50 percent have been measured. The presence of ethanol in the emulsion causes both formaldehyde and acetaldehyde to increase. The table below summarizes the emissions reductions from the use of ethanol-diesel emulsions.

Potential Emission Benefits of Ethanol-Diesel Fuel Emulsions

Pollutant	Percent Reduction
Diesel PM	30 to 40
NOx	10 to 20
CO	0 to 20
HC	-20 to -50
Formaldehyde	-170
Acetaldehyde	-75

Ethanol-diesel emulsions appear to have little effect on diesel-engine fuel economy. The volumetric energy content of ethanol-diesel emulsions is lower than that of diesel fuel. This would tend to reduce the fuel economy of ethanol-diesel emulsions. However, the thermal efficiency of an engine fueled with an ethanol-diesel emulsion is somewhat higher than with diesel fuel, and this offsets the effect of lower energy content. Consequently, the net VFEwith ethanol-diesel emulsions is about the same as with diesel fuel.

A number of companies are working to commercialize the ethanol-diesel emulsion technology. Pure Fuels USA, Incorporated, is working to find the optimum mix of ethanol, water, and diesel. They are also working to optimize the amount and type of emulsifier. The use of other additives to increase cetane number, improve NOx reductions, and lower cost is also being explored. Pure Energy Corporation has developed an additive package that allows the emulsion to be maintained at temperatures as low as -20 °F. Pure Energy Corporation participated in a demonstration program by the Chicago Transit Authority in which 15 buses were operated with an ethanol-diesel emulsion.

Further development work needs to be done before ethanol-diesel emulsions can be considered a viable alternative to conventional diesel. Currently, ethanol-diesel emulsions are not cost competitive with conventional diesel, costing about $0.07 to $0.15 more per gallon to produce. Ethanol-diesel emulsions require government subsidies in the form of tax breaks to approach cost competitiveness with conventional diesel. Further fleet testing is required to demonstrate the lack of adverse, long-term engine and fuel system effects. Specifically, more information is needed on long-term lubricity and corrosion effects. Also, further optimization of the emulsifier/additive package is required. In order to optimize the total emissions reductions from diesel engines, the integrated use of ethanol-diesel emulsions in engines using exhaust gas treatment technologies needs to be demonstrated.

3. Biodiesel and Blends

Biodiesel is a mono-alkyl ester-based oxygenated fuel, a fuel made from vegetable oil or animal fats. It can be produced from oilseed plants, such as soybeans and canola, or from used vegetable oil. It has similar properties to petroleum-based diesel fuel, and can be blended into petroleum-based diesel fuel at any ratio. It is most commonly blended into petroleum-based diesel fuel at 20 percent. This mixture is commonly referred to as "B20". Neat biodiesel is termed B100. The use of biodiesel, neat or in petroleum-based blends, does not require modifications to the engine or fuel system.

Biodiesel is registered as a fuel and fuel additive with the United States Environmental Protection Agency. It has gone through the U.S. EPA Tier I Health Effects Testing under the Clean Air Act section 211(b), which provides an inventory of environmental and human health effects attributes. Recently, B100 has been classified as an alternative fuel by the United States Department of Energy, and the United States Department of Transportation.

Biodiesel has similar properties to petroleum based diesel fuel; however, there are some significant differences. Biodiesel contains 11 percent oxygen by weight and contains no sulfur or aromatic hydrocarbons. On a transient test cycle, fuel economy and power are about 10 percent lower than conventional diesel fuel; with B20 the loss is about 2 percent. Biodiesel has favorable lubricity characteristics, but will soften and degrade certain types of elastomers and natural rubber compounds over time. Manufacturers recommend that natural or butyl rubbers not be allowed to come in contact with pure biodiesel. Biodiesel can be stored in the same tanks as petroleum based diesel, but it has a shorter shelf life, which makes it less suitable for use in emergency generators or engines that operate infrequently.

Emission data comparing biodiesel to CARB diesel are limited, but data comparing biodiesel to conventional diesel fuel are more readily available. Compared to CARB diesel or conventional diesel fuel, the use of B100 significantly reduces diesel PM, CO, and HC, but significantly increases NOx. Also, based on Ames mutagenicity studies, B100 may provide a 90-percent reduction in cancer risk compared to conventional diesel fuel. In comparing B20 to conventional diesel fuel, the changes in emissions are directionally the same, but smaller. The table on the next page provides a summary of emission test results from the use of B100 and B20 compared to conventional diesel fuel.

Potential Emission Benefits of Biodiesel and a 20-Percent Biodiesel Blend		
Pollutant	**B100 (%)**	**B20 (%)**
NOx	+13	+2
Carbon Monoxide	-50	-20
Hydrocarbons	-93	-30
Particulate Matter	-30	-22
Sulfates	-100	-20*
Polycyclic Aromatic Hydrocarbons**	-80	-13
Nitro-PAH's**	-90	-50***

* Estimated from B100 result

** Average reduction across all compounds measured

*** 2-nitroflourine results were within test method variability

Source: Biodiesel Emissions, Fact Sheet, National Biodiesel Board

Biodiesel reduces the health risks associated with conventional diesel fuel. Biodiesel emissions showed decreased levels of PAH and nitrited-PAH (nPAH) compounds, which have been identified as potential cancer causing compounds. In recent tests, PAH compounds were reduced by 75 to 85 percent, with the exception of benzo(a)anthracene, which was reduced by roughly 50 percent. Also nPAH compounds were reduced significantly. The 2-nitrofluorene and 1-nitropyrene emissions were reduced by 90 percent, and the rest of the nPAH compounds were reduced to only trace levels. These toxic emission differences are likely to be smaller when compared to CARB Diesel fuel, but may still be significant. More data comparing CARB Diesel to biodiesel are needed.

C. Diesel Fuel Additives

There are thousands of additives that have been registered with the U.S. EPA as injector cleaners, corrosion inhibitors, or lubricity enhancers; however, the focus of this section is to investigate existing additives and their effectiveness in reducing diesel PM emissions from diesel engines. Additive manufacturers have used different additives to improve combustion efficiency or to facilitate the post combustion reactions in a catalyst or particulate filter. However, in many cases very limited data is available regarding the use of these additives in California diesel fuels. The following is a description of information provided to the ARB staff with regard to additives and their potential ability to reduce diesel PM. Any additives with unsupported claims of emissions reductions were not included; however, the discussion of the following additives does not constitute an endorsement or confirmation of the results by the ARB staff.

1. Fuel-Borne Catalysts

Fuel-borne catalysts (FBCs) or regenerative additives can be used to improve the performance of diesel oxidation catalysts and particulate filters. A number of these types of additives have been registered with the U.S. EPA for on-highway use. In Europe certain FBCs have been approved for use with filters in mines, tunnels and construction vehicles; and Peugeot recently announced a new light-duty diesel vehicle using an on board reservoir of FBC and filter.

However, there is also growing concern about potential long-term health effect of the metals in these catalysts. In particular, concerns have been raised about the use of certain FBCs at high levels of treatment on vehicles not equipped with filters. This is generally related to the potential for high levels of metal emissions and an increase in ultra-fine particles when FBCs are used at high treatment rates without filters. Recently certain FBCs have demonstrated PM reductions at ultra-low levels of metal (4-8 ppm) with no increase in the number of ultra-fine particles emitted.

Limited emissions testing using fuel-borne metallic additives has shown varied emissions results. Diesel PM emissions increased slightly with some additives and decreased significantly with others. Diesel fuel tested in vehicles with and without diesel particulate filters, with metallic additives, showed from an 8 percent increase to a 30 percent reduction in diesel PM. HC emissions decreased, and CO emissions either did not change or decreased by about 10 percent. NOx emissions decreased from two to 10 percent, depending on the test additive. However, in combination with a four degree timing retard; some fuel-borne catalysts have been shown to reduce NOx by up to 30 percent, without affecting diesel PM emissions or increasing fuel consumption. Based on tests that were done to measure exhaust metal emissions, metal emissions do not appear to change substantially by using these metallic additives.

Additive manufacturers claim that the use of these additives also improves fuel efficiency, particularly at lower engine speeds, and can reduce the need for very low-sulfur diesel fuels.

In both 368-ppmw and 54-ppmw sulfur fuel, an EPA-registered FBC along with a low-activity DOC has been shown to reduce diesel PM emissions by about 43 percent in FTP testing of a 1998 DDC Series 60 engine. More recent testing of the bimetallic platinum/cerium fuel-borne catalyst, used alone at levels of 8 ppm in a CARB low-sulfur (50 ppm) market blend of diesel, demonstrated a 13 percent reduction in PM emissions. When FBC-treated CARB fuel was used with either an uncatalyzed DPF or lightly catalyzed DPF, PM emissions were reduced by over 80 percent to 0.01g/bhp-hr. Testing of this same FBC in a commercial grade of jet/kerosene fuel produced PM emissions 17 percent below the CARB blend with slightly lower NOx emissions. A combination of FBC-treated CARB fuel blended with 20 percent biodiesel, and used with engine timing changes and a lightly catalyzed filter, reduced PM by 82 percent to 0.011g/bhp-hr and lowered NOx by 8 percent versus the CARB fuel baseline.

1998 DDC SERIES 60-400hp CERTIFIED @ 0.1/4.0 PM/NOx
(Average of Triplicate Hot FTP Transient)

Fuel / Technology	PM	NOx
	(gbhp-hr)	
CARB Market Blend @ 50ppm S	0.060	3.73
CARB + FBC	0.052	3.76
CARB + FBC + DPFA	0.010	3.76
CARB + FBC + DPFD	0.011	3.76
CARB + FBC +DPFA +2 ^{o} TR	0.011	3.61
CARB + FBC +DPFA +4 ^{o} TR	0.026	3.33
CARB + FBC + BIO +4^{o} TR + DPFC	0.011	3.42
FBC + Jet/Kerosene @ 300ppm S	0.050	3.63

Testing in support of EPA registration and under the European VERT protocol has shown that at 8 ppm the level of metal emitted is 5 percent of that input to the engine and less than 1 percent is emitted after a filter. This is roughly equivalent to attrition from current autocatalysts. There is no increase in ultra-fine particle emissions with FBC-treated fuel at these low levels, and there was a 95 percent reduction in the number of ultra fines with the FBC and filter combination. Cost increases are estimated at $0.10/gal for the fuel borne catalyst alone and $0.15/gal for the FBC-jet/kerosene formulation over conventional highway diesel fuel.

2. Nonmetallic Additives

Chemecol developed a nonmetallic combustion-enhancing additive to reduce emissions. This additive technology is applicable to most diesel fuels and is comprised of mainly hydrocarbon species. It is not believed to be a health hazard because its combustion produces mainly carbon dioxide and water vapor. The additive is currently used in Europe and it has been used in variety of European vehicles for over 8 million miles with no compatibility problems.

The use of this additive has been shown to reduce diesel PM by ten to 20 percent, and to reduce other emissions, in both ECE15 + EUDC and R49 and FiGE transient test conditions. It also reduces PAH and nPAH levels and reduces the sub-2.5-micron particle numbers.

Additives containing esters have been shown to reduce opacity in snap idle tests, but data indicating particulate emission reductions are not available.

IV. RECOMMENDATIONS

A. Changes to Fuel Specifications and Applicability

Depending on technology, very low-sulfur ($\leq$ 15 ppmw S) CARB Diesel may need to be required for all engines to be manufactured or retrofitted with diesel PM after-treatment. To be consistent with U.S. EPA and to enable after-treatment control technologies for off-road and stationary diesel engines; the ARB should adopt a regulation in 2001, which would require very low-sulfur CARB Diesel for all on-road, off-road, and stationary engines statewide, effective in 2006. In the regulatory development process the ARB staff should investigate the feasibility of earlier implementation.

Also, directionally, lower aromatic hydrocarbon and PAH contents and lower fuel-density may help to reduce engine-out diesel PM emissions. These fuel specifications should be evaluated for further control.

Synthetic or alternative diesel fuels may cost more than reformulated very low-sulfur CARB Diesel, but should be considered if shown to be cost-effective for diesel PM and other emission reductions. As these alternatives may result in significant benefits for higher-emitting operational categories, such as off-road engines; consideration may need to be given to operational applicability.

B. Diesel Fuel Guidance for Districts

Guidance on diesel fuel options and associated emission reductions should be developed to assist local districts in their permitting of fleets and equipment. The guidance may be especially useful in cases where control equipment retrofitting is impractical.

V. RESEARCH NEEDS

A. Fuels

More information is needed on the emission effects of the aromatic hydrocarbon and PAH contents, and the density, of very low-sulfur CARB Diesel for various engines and run cycles. Also, more information is needed on the emissions from synthetic and alternative diesel fuels versus very low-sulfur CARB Diesel.

VI. IMPACTS OF RECOMMENDED MEASURES

A. Particulate Matter Emission Reduction

For engines manufactured or retrofitted with after-treatment, the emission reductions with very low-sulfur CARB Diesel would be included as a result of the after-treatment. Reductions from fuel reformulation, synthetic and alternative diesel fuels, and additive-enhanced fuel are uncertain at this time; but would probably range from about 5 percent to 30 percent for diesel PM emissions.

B. Other Emissions

For engines manufactured or retrofitted with after-treatment, the emission reductions with very low-sulfur CARB Diesel would be included as a result of the after-treatment. Reductions from fuel reformulation, synthetic and alternative diesel fuels, and additive-enhanced fuel are uncertain at this time; but would be fuel and emission specific.

C. Cost

We estimate an incremental cost of less than $0.05-per-gallon for production of very low-sulfur CARB Diesel. This cost should be added to the cost of after-treatment in considering the overall cost and cost-effectiveness of after-treatment.

Synthetic or alternative diesel fuels may cost more than reformulated very low-sulfur CARB Diesel, but should be considered if shown to be cost-effective for diesel PM and other emission reductions. Additive-enhanced, reformulated very low-sulfur CARB Diesel should also be considered.

D. Other Environmental Impacts

Any changes in CARB Diesel fuel requirements would require increased refinery operations. Decreased fuel density would require an increase in fuel distribution if VFE decreases. These changes are not expected to cause significant negative environmental impacts.

Impacts of these and other potential fuel changes, if proposed as future regulations, should be evaluated as required under regulatory development. The potential environmental impacts of fuel alternatives, considered in the future for equivalency, should be addressed under the equivalency demonstration and certification application process.

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