Diesel fuel

Diesel vehicles emit significant quantities of both NO_x and particulate. Reducing PM emissions from diesel vehicles tends to be of highest priority because PM emissions in general are very hazardous and diesel PM especially is likely to cause cancer. Sulfur is the most important fuel characteristic to address in order to reduce PM and NO_x emissions from diesel engines. Sulfur contributes directly to PM emissions, and high levels of it in diesel preclude the use of the most effective PM and NO_x control technologies.

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Impact on emissions from heavy duty engines

A recent review addressed the impact of fuel composition changes on emissions from current heavy duty, direct-injection diesel engines. This was based only on studies where there were no significant correlations among germane fuel properties.[8] Conclusions from this review are summarized in Table 2. As shown, the compositional properties of at least some importance with respect to emissions are sulfur, aromatics, and oxygenate content; the physical properties identified are density and the T_{90} or T_{95} (the temperature at which 90% or 95% of diesel evaporates) distillation temperature. The cetane number/index was also identified as a factor with respect to emissions. The arrows in the first column of Table 2 show the directional changes in these fuel properties which will result in a "cleaner" fuel. The directional impact on NO_x, PM, HC, and CO emissions resulting from changes in each property in the direction indicated are also shown, along with an indication of the relative magnitude of the effect.

As shown in Table 2, emissions from engines with high base emission rates (generally older designs) tend to be more sensitive to changes in fuel composition than those from engines with lower base emissions rates (which tend to be newer designs). In addition, changes in all of the fuel properties have been found to have, at most, small impacts on emissions from engines with low base emission rates.

Table 2
Influence of Fuel Properties on Heavy Duty Diesel Emissions

Fuel Modification	NO_x	Particulates
Reduce Sulfur	0	⇓⇓[d]
Increase Cetane	⇓	0
Reduce Total Aromatics	⇓[c]	0
Reduce Density	⇓	0[a] / ⇓⇓[b]
Reduce Polyaromatics	⇓[c]	0[a] / ⇓⇓[b]
Reduce T_{90}/T_{95}	↓	0

⇓⇓/⇑⇑ = relatively large effect, ⇓/⇑ = small effect, ↑/↓ = very small effect, 0 = no effect
[a] Low emission emitting engine
[b] High emission emitting engine
[c] Polyaromatics are expected to produce a bigger reduction than mono-aromatics. Further studies (e.g., EPA Heavy duty engine working group) are investigating these parameters
[d] Reducing sulfur from 0.30% to 0.05% gives relatively large benefits; reducing sulfur from 0.05% to lower levels has minimal direct benefit, but is necessary to enable advanced technologies for engines without after-treatment systems

Impact on emissions from light duty vehicles

The most recent, comprehensive study of fuel composition impacts on light duty diesel emissions was performed as part of the EU Program on Emissions, Fuels and Engine Technologies.[9] The generalized results of this study are presented in Table 3. As shown, although there are some differences in terms of the magnitude of fuel composition effects on emissions from vehicles with indirect- and direct-injection engines, the directional impact on emissions is usually the same.

Table 3
Impact of Fuel Composition Changes on Emissions of Current Light Duty Diesel Vehicles

	NO_x Emissions		PM Emissions	
Change	IDI[a]	DI[b]	IDI	DI
⇑ Cetane (50 to 58)	↑	↓	None	⇑
⇓ Density (0.855 to 0.828 g/cm^3)	None	⇑	⇓⇓	⇓⇓
⇓ T_{95} (700 to 620°F)	↑	⇑	None	⇓
⇓ Polycyclics (8 to 1 vol %)	↓	↓	↓	⇓

⇑⇑/⇓⇓ = relatively large effects (10% or greater change in emissions), ⇑/⇓ = small effects (5 to 10% change), ↑/↓ = very small effects (~1 to 5% change), g/cm^3 = grams per cubic centimeter, none = no effect, T_{95} = temperature at which diesel evaporates
[a] Indirect-injection engines
[b] Direct-injection engines

A comparison of the heavy duty and light duty tables indicates that there are some instances where changing a given diesel fuel property is expected to have the opposite directional impact on emissions, depending on whether the fuel is being used in a heavy duty or light duty engine. Most notable is the increase in NO_x emissions from light duty direct-injection engines in response to a decrease in fuel density, and also the NO_x emission increases from both light duty indirect- and direct-injection engines in response to a decrease in the T_{95} temperature.[10]

Sulfur

Sulphate particulate and SO_x emissions, both harmful pollutants, are emitted in direct proportion to the amount of sulfur in diesel fuel. Sulphate PM contributes directly to PM_{10} and $PM_{2.5}$ emissions[11] and their associated adverse health and environmental effects. SO_2, one fraction of SO_x, is a criteria pollutant with associated adverse effects. The health and welfare effects of SO_2 emissions from diesel vehicles are probably much greater than those of an equivalent quantity emitted from a utility stack or industrial boiler, since diesel exhaust is emitted close to the ground level in the vicinity of roads, buildings, and concentrations of people. Further, some SO_x are also transformed in the atmosphere to sulphate PM with the associated adverse effects noted for PM.

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Diesel PM consists of three primary constituents—a carbonaceous core, a soluble organic fraction (SOF) which sits on the surface of this core, and a mixture of SO_x and water which also sits on the core's surface. Lowering the sulfur in fuel lowers the SO_x fraction of PM thus lowering the overall mass of PM emitted. Diesel fuel evaluations carried out in Europe show that reduced sulfur in diesel can lower particulate. For example, lowering the diesel sulfur level from 2000 ppm to 500 ppm reduced the overall particulate from light duty diesels by 2.4% and from heavy duty diesels by 13%.[12] The relationship between particulates and sulfur levels was found to be linear; for every 100-ppm reduction in sulfur there will be a 0.16% reduction in particulate from light duty vehicles, and a 0.87% reduction from heavy duty vehicles.

The technology-disabling effect of sulfur in diesel fuel is comparable to lead and sulfur in gasoline. Catalytic converters or NO_x adsorbers can eliminate much of the NO_x emissions from new diesel engines, but sulfur disables them in much the same way that lead poisons the three-way catalyst. Thus, the presence of sulfur in diesel fuel effectively bars the path to low emissions of conventional pollutants. As stated by a German government petition to the European Commission in support of low-sulfur fuel, "A sulphur content of 10 ppm compared to 50 ppm increases the performance and durability of oxidizing catalytic converters, DeNOx catalytic converters and particulate filters, and therefore decreases fuel consumption. There are also lower particulate emissions (due to lower sulphate emissions) with oxidizing catalytic converters. For certain continuously regenerating particulate filters, a sulphur content of 10 ppm is required for the simple reason that otherwise the sulphate particles alone (without any soot) would overstep the future [European] particulate value of 0.02 g/kWh." Figure 4 shows the current and proposed sulfur levels in diesel in Asia, Europe and the United States.

In addition to its role as a technology enabler, low-sulfur diesel fuel gives benefits in the form of reduced sulfur-induced corrosion and slower acidification of engine lubricating oil. This leads to longer vehicle maintenance intervals and lower maintenance costs. These benefits can offer significant cost savings to the vehicle owner without the need to purchase new technologies. Therefore, with regard to diesel fuel, the following policies are recommended:

	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Bangladesh							5000									
Cambodia					2000											
Hong Kong, China		500					50									
India	5000				2500					500					350	
Indonesia	5000															
Japan	500				100					50		10[a]				
Malaysia	5000		3000				500[b]									
Pakistan	10000						5000									
Philippines	5000					2000			500							
PRC	5000		2000													
Republic of Korea	500															
Singapore	3000		500													
Sri Lanka	10000							3000								
Taipei,China	3000			500			350					50				
Thailand	2500			500					350							
Viet Nam	10000							2000		500						
European Union					350					50				10		
United States	500														15	

> 500 ppm 51–500 ppm < 50 ppm

Figure 4
Current and Proposed Sulfur Levels in Diesel in Asia, European Union and United States

[a] Under consideration
[b] Marketed

- Emerging advanced PM and NO_x control technologies capable of achieving very low emissions will require a maximum of 50 ppm sulfur or less. A plan for introducing such fuel quality—frequently referred to as ULSD—should be adopted early in the development of a long-term vehicle pollution control strategy. Certain advanced diesel control technologies such as NO_x adsorbers cannot function properly even with 50-ppm fuel and will require a maximum of 10 ppm.
- While interim improvements in diesel fuel quality will benefit air quality, it is most efficient and cost effective for a refinery to go directly to ULSD rather than via several interim steps.

- When ULSD is introduced, strong consideration should be given to retrofitting existing vehicles with oxidation catalysts or diesel PM filters which can achieve significant and rapid PM reductions.
- An effective means of encouraging the rapid introduction of ULSD beyond traditional command-and-control regulations is to adopt a tax policy that results in higher-sulfur fuels costing more at the pump. Hong Kong, China has successfully implemented such a strategy.

Other diesel fuel properties

Volatility

Diesel fuel consists of a mixture of HC with different molecular weights and boiling points. As a result, as some of it boils away on heating, the boiling point of the remainder increases. This fact is used to characterize the range of HC in fuel in the form of a "distillation curve" specifying the temperature at which 10%, 20%, etc. of the HC have boiled away. A low 10% boiling point is associated with a significant content of relatively volatile HC. Fuels with this characteristic tend to exhibit somewhat higher HC emissions than others.

Aromatic hydrocarbon content

Aromatic hydrocarbons are HC compounds containing one or more "benzene-like" ring structures. They are distinguished from paraffins and napthenes, the other major HC constituents of diesel fuel, which lack such structures. Compared to these other components, aromatic hydrocarbons are denser, have poorer self-ignition qualities, and produce more soot in burning. Ordinarily, "straight run" diesel fuel produced by simple distillation of crude oil is fairly low in aromatic hydrocarbons. Catalytic cracking of residual oil to increase gasoline and diesel production, however, results in increased aromatic content. A typical straight run diesel might contain 20–25% aromatics by volume, while a diesel blended from catalytically cracked stocks could have 40–50% aromatics.

Aromatic hydrocarbons have poor self-ignition qualities, so that diesel fuels containing a high fraction of aromatics tend to have low cetane numbers. Typical cetane values for straight run diesel are in the range of 50–55; those for highly aromatic diesel fuels are typically 40–45, and may be even lower. This produces more difficulty in cold starting, and increased combustion noise, HC, and NO_x due to the increased ignition delay.

Increased aromatic content is also correlated with higher particulate emissions. Aromatic hydrocarbons have a greater tendency to form soot in burning, and the poorer combustion quality also appears to increase particulate SOF emissions. Increased aromatic content may also be correlated with increased SOF mutagenicity, possibly due to increased polynuclear aromatics (PNA) and nitro-PNA emissions. There is also some evidence that more highly aromatic fuels have a greater tendency to form deposits on fuel injectors and other critical components. Such deposits can interfere with proper fuel-air mixing, greatly increasing PM and HC emissions.

Polycyclic aromatic hydrocarbons (PAH) are included in the great number of compounds present in the group of unregulated pollutants emitted from vehicles. Exhaust emissions of PAH (here defined as three-ringed and larger) are distributed between particulate and semi-volatile phases. Some of these compounds in the PAH group are mutagenic in the Ames test and in some cases even cause cancer in animals after skin painting experiments. Because of this fact, it is important to limit PAH emissions from vehicles especially in densely populated high traffic urban areas.

An important factor affecting vehicle PAH emissions is the selection of fuel and fuel components. A linear relationship exists between fuel PAH input and PAH emissions. PAH emissions in exhaust consist of uncombusted through-fuel input PAH and PAH formed in the combustion process. Selection of diesel fuel quality with low PAH content [less than or equal to 4 mg/l, sum of PAH (i.e. individual PAH, phenanthrene to coronene, amounts added together)], will reduce PAH exhaust emissions by up to approximately 80% compared to diesel fuel with PAH contents larger than 1 g/l (sum of PAH). By reducing fuel PAH content in commercially available diesel fuel, PAH emissions to the environment will be reduced.[13]

Other

Other fuel properties may also have an effect on emissions. Fuel density, for instance, may affect the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. This is because fuel injection pumps meter fuel by volume not by mass, and a denser fuel contains a greater mass in the same volume. Fuel viscosity can also affect the fuel injection characteristics and thus, the mixing rate. Corrosiveness, cleanliness, and fuel lubricating properties can all affect the service life of fuel injection equipment, and possibly contribute to excessive in-use emissions if the equipment is worn out prematurely.

- While less critical, other diesel fuel properties such as cetane number, density, distillation and polyaromatic content can also have positive or negative impacts on emissions and should be carefully evaluated.
- To the extent that a long-term vehicle emissions standards strategy is to adopt Euro 4 standards for light duty vehicles and Euro 5 standards for heavy duty vehicles, the European diesel standards as summarized in Table 4 should be adopted in the same time frame.

Table 4
European Union Diesel Fuel Specification Limits

	2000	2005
Diesel Fuel Parameter	**Linked with Euro 3 Vehicle Standards**	**Linked with Euro 4 Vehicle Standards**
Cetane number, min.	51	51
Density 15°C kg/m³, max.	845	845
Distillation 95%, v/v °C, max.	360	360
Polyaromatics %v/v, max.	11	11
Sulfur ppm, max.	350	50

kg/m³ = kilogram per cubic meter, max = maximum, min = minimum, ppm = parts per million, % m/m = percent by mass, % v/v = percent by volume

Fuel additives

Several generic types of diesel fuel additives can have a significant effect on emissions. These include cetane enhancers, smoke suppressants, and detergent additives. In addition, some additive research has been directed specifically at emissions reduction in recent years.

Cetane enhancers are used to improve the self-ignition qualities of diesel fuel. These compounds (usually organic nitrates) are generally added to reduce the adverse impact of high aromatic fuels on cold starting and combustion noise. These compounds also appear to reduce the adverse impacts of aromatic hydrocarbons on HC and PM emissions, although PM emissions with the cetane improver are generally still somewhat higher than those from a higher quality fuel able to attain the same cetane rating without the additive.

Smoke suppressing additives are organic compounds of calcium, barium, or sometimes magnesium. Added to diesel, these compounds inhibit soot formation during the combustion process and thus, greatly reduce visible smoke emissions. However, they tend to significantly increase the number of very small ultrafine particles that are suspected of being even more hazardous to health. Their effects on the particulate SOF are not fully documented, but one study has shown a significant increase in PAH content and SOF mutagenicity with a barium additive. Particulate sulphate emissions are greatly increased with these additives, since all readily form stable solid metal sulphates, which are emitted in the exhaust. The overall effect of reducing soot and increasing metal sulphate emissions may be either an increase or decrease in the total particulate mass, depending on the soot emission level at the beginning and the amount of additive used.

- While smoke suppressing additives may appear attractive, their use is not recommended because of the potentially more hazardous ultrafine particle emissions and mutagenicity.

Detergent additives (often packaged in combination with a cetane enhancer) help to prevent and remove coke deposits on fuel injector tips and other vulnerable locations. By maintaining new engine injection and mixing characteristics, these deposits can help to decrease in-use PM and HC emissions. A study for the California Air Resources Board estimated the increase in PM emissions from in-use trucks due to fuel injector problems as being more than 50% of new vehicle emissions levels. A significant fraction of this excess is unquestionably due to fuel injector deposits.

- The use of detergent additives to reduce deposits on injector components is highly recommended, especially on more modern engines.

Alternative fuels

In addition to conventional gasoline and diesel fuels, many countries around the world have identified significant benefits associated with a shift to alternative fuels, especially CNG, LPG, and ethanol. Besides CNG (mainly composed of methane) and LPG (composed of propane or butane), alternative fuels include methanol, ethanol, hydrogen, electricity, vegetable oils (including biodiesel), synthetic liquid fuels derived from coal, and various fuel blends such as gasohol.

Natural gas

Natural gas (85-99% methane) is clean burning, cheap and abundant in many parts of the world. Because natural gas is mostly methane, natural gas vehicles (NGVs) have much lower non-methane HC emissions than gasoline vehicles, but higher methane emissions. Since the NGV fuel system is sealed, there are no evaporative emissions and refuelling emissions are negligible. Cold-start emissions from NGVs are also low, since cold-start enrichment is not required. In addition, this reduces both VOC and CO emissions. NO_x emissions from uncontrolled NGVs may be higher or