



APPENDIX AVAILABLE ON REQUEST

Special Report 17

Traffic-Related Air Pollution: A Critical Review of the Literature on Emissions, Exposure, and Health Effects

Chapter 2. Emissions from Motor Vehicles

HEI Panel on the Health Effects of Traffic-Related Air Pollution

Appendix B. Fuel Composition Changes Related To Emission Controls

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APPENDIX B. FUEL COMPOSITION CHANGES RELATED TO EMISSION CONTROLS

Gasoline Fuels

Gasoline is a complex mixture of volatile hydrocarbons used as a fuel in internal combustion engines. The pollutants of greatest concern from gasoline-fueled vehicles are CO, HC, NO_x, lead and certain toxic hydrocarbons such as benzene. Each of these can be influenced by the composition of the gasoline used by the vehicle. The most important characteristics of gasoline with regard to its impact on emissions are – lead content, sulfur concentration, volatility, aromatics, olefins, oxygenates, and benzene level.

The use of catalyst exhaust gas treatment requires the elimination of lead from gasoline. This change, which has occurred throughout most of the world, has resulted in a dramatic reduction of ambient lead levels. Other gasoline properties that can be adjusted to reduce emissions include, roughly in order of effectiveness, sulfur level, vapor pressure, distillation characteristics, light olefin content, and aromatic content. Sulfur impacts have been discussed previously but other fuel parameters will be reviewed below.

Vapor Pressure

Gasoline volatility is an indication of how readily a fuel evaporates. It is characterized by two measurements – vapor pressure and distillation.

Reid vapor pressure (RVP) is a measure of the volatility of gasoline at 100°F (37.8°C) in kilopascals (kPa). The RVP is largely governed by the fuel's butane content, whose average RVP is around 350 kPa. Pentanes, with an RVP of about 17 kPa, add volatility to a lesser extent. Butane content is partly a function of the nature of the crude, but occurs mostly as a result of the refining process.

Sufficient volatility of gasoline is critical to the operation and performance of spark ignition engines. At lower temperatures, higher vapor pressure is needed to allow easier start and warm up performance. Control of vapor pressure at high temperatures reduces the possibility of hot fuel handling problems such as vapor lock and carbon canister overloading. Vapor lock occurs when too much vapor forms in the fuel system and fuel flow decreases to the engine. This can result in loss of power, rough engine operation or engine stalls.

High gasoline vapor pressure causes high evaporative emissions from motor vehicles and is therefore a priority fuel quality issue. Evaporative emissions can comprise a large part of total hydrocarbon emissions. Their release may occur during the delivery and transfer of gasoline to storage, vehicle refueling, the diurnal breathing of vehicle fuel tanks (as they heat up and cool down with normal daily temperature variations), and the fugitive losses that occur from carburetor and other equipment during normal vehicle operation. Reductions in fuel volatility will significantly reduce evaporative emissions from vehicles. A reduction in vapor pressure is one of the more cost effective of the fuel-related approaches available to reduce hydrocarbon emissions.

Vapor pressure is most effectively managed on a regional and seasonal basis to allow for the different volatility needs of gasoline at different temperatures. The reduction of evaporative emissions is most effectively achieved when RVP is controlled when ambient temperatures are high – i.e. the summer period.

In the European Union, the Euro 3 gasoline specifications identify eight volatility classes. Each

class is based on seasonal temperature variations and specifies a range of RVP values. Class 1 is the most stringent situation, with the lowest RVP values, for the warmest climates; classes 7 and 8 applicable in very cold conditions where more volatile gasoline blends are required. The specifications also set a maximum summer (May to September) limit of 60 kPa. For member states with arctic conditions, summer is from 1 June to 31 August and the RVP is set higher at 70 kPa. In the USA and more especially in California where hot ambient conditions are prevalent, the levels of RVP set by the USEPA and California Air Resources Board are close to 50 kPa. In Asian countries where summer conditions are experienced throughout the year, the RVP limits at low levels are very critical. In one study for Thailand, reducing the RVP by 6.89 kPa was estimated to result in reductions in HC emissions of more than 100 tons per day.

Distillation

Distillation is a second method for measuring the volatility of gasoline. Distillation can be assessed in terms of 'T' points or 'E' points. For instance, T50 is the temperature at which 50% of the gasoline distills, while E100 is the percentage of gasoline distilled ('E' – evaporated) at 100°C.

Excessively high T50 point (low volatility) can lead to poor starting performance at moderate ambient temperatures. The measure of the Driveability Index (DI), which is derived from T10, T50, and T90 and oxygenate content, can be used as a control to facilitate cold start and warm-up performance. Use of a DI also helps to avoid inclusion of a high proportion of high density poor burning compounds, which contribute to carbon monoxide and NO_x emissions.

The European Programmes on Emissions, Fuels and Engine Technologies (EPEFE) study found that increasing E100 in gasoline reduces emissions of hydrocarbons but increases NO_x emissions. At E100, carbon monoxide emissions were at their lowest value of 50% by volume, for constant aromatics. Increasing E100 from 35% to 50% by volume showed a decrease in mass emissions of both formaldehyde and acetaldehyde. However, increasing E100 from 50% to 65% by volume showed no clear effect.

Limiting distillation temperatures and aromatic content appear to be the most important parameters for controlling emissions during the vehicle's 'cold cycle'.

Heavy end limits (and total aromatic limits) provide the best means to limit heavy aromatics, important in managing hydrocarbon and benzene emissions.

Research shows that combustion chamber deposits formation can relate to the heavy hydrocarbon molecules found, inter alia, in the T90-FBP portion of the gasoline. A major benefit of reduced combustion chamber deposits is a reduction in NO_x emissions.

In the European Union, the Euro 3 gasoline specification addresses distillation in terms of two E points: E100 – 46 % vol min, and E150 – 75 % vol min, and final boiling point (FBP) – 210°C max.

Olefins

Attention has been given in recent years to the specific make-up of the hydrocarbon content of gasoline. This is due both to the significant role hydrocarbon based vehicle emissions play in urban ozone (or photochemical smog) formation, and to the fact that there are significant adverse public health impacts from exposure to certain hydrocarbons. As a result, there has been a move towards setting content limits on the different hydrocarbon fractions within gasoline especially the aromatics and the olefins.

Olefins form a family of chemicals containing carbon-to-carbon double bonds. Olefins are unsaturated hydrocarbons (such as propylene and butylenes) and, in many cases, are also good octane components of gasoline. They can, however, lead to engine deposit formations and increased emissions of highly reactive ozone-forming hydrocarbons and toxic compounds. They tend to be chemically more reactive than other hydrocarbon types.

Olefins are oxidatively and thermally unstable and may lead to gum formation and deposits on the fuel injectors and in the engine's intake system. Combustion chamber deposits form from the heavy hydrocarbon molecules found, inter alia, in the olefin portion of gasoline. Combustion chamber deposits can increase tailpipe emissions, including carbon monoxide, hydrocarbons and NO_x.

Emission of olefins into the atmosphere as chemically reactive species contributes to ozone formation and toxic dienes. The US Auto/Oil Improvement Research Program (Coordinating Research Council 1997) concluded that reducing total olefins from 20% to 5% would significantly decrease ozone-forming potential.

Reduction of low molecular weight olefins accounts for about 70% of the ozone reduction effect. The ozone formation potential of olefins predominantly derive from the lighter volatile olefin fractions, which are typically removed where reductions of RVP to 48-50 kPa are required.

In addition, 1,3-butadiene, a known carcinogen, is formed during the combustion of olefin compounds in gasoline.

The European Union fuel specifications for Euro 3 set a maximum olefin content of 18% by volume.

Under both Phases of the US reformulated gasoline (RFG) program, the olefin specification is a maximum 8.5% by volume. The Californian RFG program (effective from 1996) provides several compliance options for meeting the refiner limits for olefins, one option being the utilization of a maximum (flat) limit of 6% by volume or an averaging limit of 4% by volume coupled with a cap of 10% by volume.

Aromatics

Aromatics are hydrocarbon fuel molecules based on the ringed six-carbon benzene series or related organic groups. They contain at least one benzene ring. Benzene (discussed separately below), toluene, ethylbenzene and xylene are the principal aromatics. They represent one of the heaviest fractions in gasoline.

Lower levels of aromatics enable a reduction in catalyst light-off time for all vehicles. Research indicates that combustion chamber deposits can form from the heavier hydrocarbon molecules found in the aromatic hydrocarbon portion of the gasoline. These deposits can increase tailpipe emissions, including carbon dioxide, hydrocarbons and NO_x.

The aromatic content of gasoline has a direct effect on tailpipe carbon dioxide (CO₂) emissions. The EPEFE study demonstrated a linear relationship between CO₂ emissions and aromatic content. A reduction of aromatics from 50 to 20% was found to decrease CO₂ emissions by 5%. This was considered to be due to their effect on the hydrocarbon ratio and hence carbon content of the gasoline – no clear effect of aromatics was found on calculated fuel consumption.

Combustion of aromatics can lead to the formation of toxic benzene in exhaust gas. Benzene is a proven human carcinogen that can cause leukemia in exposed persons. It is estimated that about 50%

of the benzene produced in the exhaust is the result of decomposition of aromatic hydrocarbons in the fuel. Both the Air Quality Improvement Research Program (AQIRP) and the EPEFE studies showed that lowering aromatic levels in gasoline significantly reduces toxic benzene emissions from vehicle exhausts. In the EPEFE study, benzene emissions were found to vary between 3.6% and 7.65 % of total volatile organic compounds for fuel aromatic contents ranging from 19.5% to 51.1% by volume. This is consistent with previous studies and can be explained by the dealkylation of substituted aromatics. The EPEFE study also found that emissions changes from changes to the aromatic content of fuel were influenced by other parameters such as distillation. Reducing the aromatic content of gasoline also contributes to the reduction of NO_x.

The European Union fuel specifications for Euro 3 and Euro 4 set maximum aromatic content limits of 42% and 35% by volume respectively.

The US specifications under the reformulated gasoline (RFG) program are maximum limits by volume of 27% for Phase 1 (January 1995) and 25% for Phase 2 (January 2000). The California specifications under the RFG program are maximum limits by volume of 32% for Phase 1 (January 1992) and 22% for Phase 2 (January 1996).

In Japan, the specifications for regular and premium grades set maximum aromatic content levels at 42% by volume. In South Korea they were set as maximum limits by volume at 45% in 1998, reducing to 35% in January 2000.

Benzene

Benzene is a six-carbon, colorless, clear liquid aromatic that occurs naturally in gasoline and is also a product of catalytic reforming used to boost octane levels. It is fairly stable chemically but highly volatile. It has a high octane rating – RON 106, MON 103.

Benzene in gasoline leads to both evaporative and exhaust emissions of benzene. The EPEFE study found that benzene exhaust emissions varied between 3.6% and 7.65% of total volatile organic compounds from gasoline containing benzene of 1.7% to 2.8% by volume. The control of benzene levels in gasoline is recognized by regulators as the most direct way to limit benzene evaporative and exhaust emissions and therefore human exposure to benzene. As a result, over the last decade there has been a steady move by regulators to lower the benzene content of gasoline.

As noted in the preceding section, the key health concern related to benzene exposure is leukemia. In the European Union, the Euro 3 and 4 gasoline specifications set maximum benzene limits of 1% by volume (the Euro 2 limit was 5%). The US set a flat limit of 0.8% benzene by volume from January 1995 and has continued with this limit under Phase 2 of the reformulated gasoline (RFG) program, effective from January 2000. It has recently proposed a national cap on benzene limits similar to those on reformulated gasoline. Japan introduced a maximum limit of 5% benzene by volume in 1996, which was reduced to 1% in 2000. In Singapore the current limit is 4%, and in Thailand it is 3.5% for all gasoline grades with a future target of 1%.

Oxygenates

Oxygen is added to gasoline to improve combustion, to limit emissions of ozone precursors and carbon monoxide, and/or to raise octane levels. The principal oxygenates which are used today are ethanol and MTBE. Where ethanol is used, evaporative HC emissions can increase significantly if the RVP of the fuel is allowed to increase. Increases in NO_x exhaust emissions can occur with either

oxygenate when the oxygen content is higher than 2 weight %. (There is some debate regarding the NO_x effect for newer technology vehicles.) The magnitude of the reductions in HC exhaust emissions depends upon the vehicle technology; while older (pre Euro 1) vehicles would experience some reductions in exhaust emissions, newer vehicles (Euro 1 and newer) with oxygen sensors and adaptive learning systems will experience little or no effects. HC emissions during storage and transportation depend upon the presence or absence of Stage I and Stage II vapor recovery systems. Carbon monoxide emissions can decrease by around 10% following an increase in gasoline oxygen content from 0 to 2% (by weight).

Other Additives

Certain other additives that are put into gasoline can also affect vehicle emissions. Methylcyclopentadienyl manganese tricarbonyl (MMT) when added to gasoline will increase manganese emissions from all categories of vehicles. Vehicle manufacturers have expressed concerns regarding catalyst plugging and oxygen sensor damage with MMT use, which could lead to higher in use vehicle emissions especially at higher mileage. The impact seems greatest with vehicles meeting tight emissions standards and using high cell density catalyst substrates (Alliance of Automobile Manufacturers 2002; ICCT 2004).

There is a growing body of literature on the health effects of manganese, and of MMT specifically, as well as an emerging literature of population studies of potential effects (Dobson et al 2004; Elder et al 2006; Mena et al 1969; Tjalve et al 1996; Zayed 2001). This literature (U.S. Environmental Protection Agency 2003) indicates that there are potential health risks of low levels of exposure, which require additional research. Based on the health concerns already identified, the Scientific Committee on Neurotoxicology and Psychophysiology and the Scientific Committee on the Toxicology of Metals of the International Commission on Occupational Health (ICOH) concluded that “The addition of organic manganese compounds to gasoline should be halted immediately in all nations” (Landrigan et al 2006). More information on the toxicology of MMT can be found in Chapter 5.

The Health Effects Institute recently summarized some of this science – in the context of its recent study by Yokel and Crossgrove (2004) – when it noted that, “[t]here is a large body of evidence that (1) under certain circumstances, manganese can accumulate in the brain, (2) chronic exposure can cause irreversible neurotoxic damage over a lifetime of exposure, (3) manganese may cause neurobehavioral effects at relatively low doses, and (4) these effects follow inhalation of manganese-containing particles (neurotoxic effect of dietary manganese are much more rare)”.

In the US, the Clean Air Act requires testing of motor fuels and additives. The US EPA has required the manufacturer of MMT to perform testing to help fill data gaps and potentially provide information that would result in a more definitive risk evaluation of MMT. This testing included three physiologically-based pharmacokinetic (PBPK) studies and one emission characterization study. In addition to the already completed tests, the manufacturer developed PBPK models for manganese derived from data generated from the completed testing. The manufacturer has submitted these PBPK to the US EPA for review. US EPA may then be able to refine its risk evaluation or may ask for further testing based upon the results of the submitted testing and resulting model now being developed, as well as any other available data. With funding from the manufacturer, the Research Triangle Institute (RTI) also completed a study of manganese exposures in Toronto, Canada where MMT was used. US EPA is also evaluating this study to determine what impact it might have on any evaluation of risk

associated with use of MMT. In the meantime, almost all gasoline sold in the US is MMT free; MMT was banned in California in 2008.

Due to the importance of this potential health risk at lower level exposures, literature on health impacts of manganese is currently also the subject of an extensive risk assessment of manganese at ambient levels that is being finalized by Health Canada and which is an update of a 1994 assessment (Wood and Egyed 1994). This study is expected to be completed soon and is expected to be the most current and comprehensive health assessment to date on potential effects of exposure to manganese at ambient levels from a variety of sources as well as identification of gaps in current understanding.

With a growing body of evidence, which indicates that metallic-based additives have negative health effects at very low levels, a report of the Asian Development Bank and the Clean Air Initiative commented that the environmentally responsible approach to metallic-based additives is to “apply the precautionary principle and to discourage their use until and unless the scientific and health studies show that they are safe” (Asian Development Bank and Clean Air Initiative 2008).

Impact of Gasoline Composition on Vehicle Emissions

Table B.1 summarizes the impacts of various diesel fuel qualities on emissions from light duty gasoline vehicles.

Table B.1. Impact of Gasoline Composition on Emissions from Light Duty Vehicles

Gasoline	Pre Ox Catalyst	Ox Catalyst	Comments
Lead ↑	Pb, HC↑	CO, HC, NOx all increase dramatically as catalyst destroyed	
Sulfur ↑ (50 to 450 ppm)	SO ₂ ↑	CO, HC, NOx all increase ~15-20% SO ₂ and SO ₃ increase	MIL light may come on incorrectly
Olefins ↑	Increased 1,3 butadiene, increased HC reactivity, NOx, small increases in HC for Euro 3 and cleaner		Potential deposit buildup
Aromatics ↑	Increased benzene in exhaust		Deposits on intake valves and combustion chamber tend to increase
	potential ↑ HC, NOx	HC, NOx, CO ↑	
Benzene ↑	Increased benzene exhaust and evaporative emissions		
Ethanol ↑ up to 3.5% O ₂	Lower CO, HC, slight NOx increase (when above 2% oxygen content), Higher aldehydes	Minimal effect with new vehicles equipped with oxygen sensors, adaptive learning systems	Increased evaporative emissions unless RVP adjusted, potential effects on fuel system components, potential deposit issues, small fuel economy penalty
MTBE ↑ up to 2.7% O ₂	Lower CO, HC, higher aldehydes	Minimal effect with new vehicles equipped with oxygen sensors, adaptive learning systems	Concerns over Water Contamination
Distillation Characteristics T50, T90↑	Probably HC↑	HC↑	
MMT ↑	Increased Manganese Emissions	Possible Catalyst Plugging	O ₂ sensor and OBD may be damaged, MIL light may come on incorrectly
RVP ↑	Increased evaporative HC Emissions		Most critical parameter for Asian countries because of high ambient Temperatures
Deposit control additives ↑		Potential HC, NOx emissions benefits	Help to reduce deposits on fuel injectors, carburetors, intake valves, combustion chamber

Diesel fuels

Diesel fuel is a complex mixture of hydrocarbons with the main groups being paraffins, naphthenes and aromatics. Organic sulfur is also naturally present. Additives are generally used to influence properties such as the flow, storage and combustion characteristics of diesel fuel. The actual properties of commercial automotive diesel depend on the refining practices employed and the nature of the crude oils from which the fuel is produced. The quality and composition of diesel fuel can significantly influence emissions from diesel engines.

As noted above, to reduce PM and NO_x emissions from a diesel engine, the most important fuel characteristic is sulfur because sulfur contributes directly to PM emissions and high sulfur levels preclude the use of or impair the performance of the most effective PM and NO_x control technologies. The required changes in diesel fuel parameters to achieve lower emissions are described below.

Cetane

Cetane number is a measure of auto-ignition quality. It is dependent on fuel composition, and relates to the delay between when fuel is injected into the cylinder and when ignition occurs. It influences cold startability, exhaust emissions and combustion noise. Rapidly igniting fuels have high cetane numbers (50 or above). Slowly igniting fuels have low cetane numbers (40 or below). Aromatic hydrocarbons are low in cetane number; paraffins are high, with naphthenes in between the two.

The cetane index provides an indication of the 'natural' cetane of the fuel. It is derived through a calculation process based on the fuel density and distillation parameters. It gives an estimation of the base auto-ignition quality of the fuel, but does not indicate the effects of cetane improver additives.

Experiments documented by the EPEFE study show that an increase in cetane number results in a decrease in carbon monoxide and hydrocarbon emissions (notably in light duty engines), nitrogen oxides emissions (notably in heavy duty engines), as well as benzene, 1,3 butadiene, formaldehyde and acetaldehyde emissions from light duty engines.

While the EPEFE study found that particle emissions increased from light duty vehicles as the cetane number increased (no significant effect was seen in heavy duty engines), other research has suggested that an increase in cetane number can lead to lowered particle emissions.

Cetane number requirements for diesel vehicles depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. High cetane number fuels enable an engine to be started more easily at lower air temperatures, reduce white smoke exhaust, and reduce diesel knock. With a low cetane number fuel, engine knock noise and white smoke can be observed during engine warm-up, especially in severe cold weather. If this condition is allowed to continue for any prolonged period, harmful fuel derived deposits will accumulate within the combustion chamber. While an engine may appear to operate satisfactorily on low cetane number fuel, after prolonged use, severe mechanical damage (e.g., piston erosion) can result.

An increase in natural cetane can contribute towards reduced fuel consumption. To avoid excessive dosage with cetane additives, the World Wide Fuel Charter (WWFC) recommends that the difference between the cetane index and the cetane number be no greater than 3. (Generally, large quantities of additive are not added for economic reasons, as the additive is expensive). This has also been general practice to prevent having the general character of the fuel too far from that implied by a certain cetane number.

Density

Density relates to the energy content of fuel in such a way that the higher the density of the fuel the higher its energy content per unit volume. The density of diesel fuel is largely dependent on its chemical composition – typically the aromatic content and distillation range. Higher density diesel fuel is frequently an indicator of high aromatic content of the fuel, for a given distillation range. Increased aromatic content is known to lead to increased particle emissions. Too high a fuel density for the engine calibration has the effect of over-fueling, increasing black smoke and other gaseous emissions.

The EPEFE study found that:

For light duty vehicles, reducing fuel density decreased emissions of particles, hydrocarbons, carbon monoxide, formaldehyde, acetaldehyde and benzene; increased emissions of NO_x; but had no impact on the composition of the particle load.

For heavy duty vehicles, reducing fuel density decreased emissions of NO_x; increased emissions of hydrocarbons and carbon monoxide; but had no impact on particle emissions or the composition of the particle load.

The EPEFE study also investigated the extent to which the observed density effects on emissions could be decreased by tuning the engine management system to fuel density. The test results indicated that the effect of density on engine emissions is, to a certain extent, caused by the physical interaction of fuel density with the fuel management system. Further density effects remained after engines were calibrated to specific fuels.

CONCAWE, CONservation of Clean Air and Water in Europe, investigations have shown that changes to engine calibration can considerably reduce the impact of changes in density (and viscosity) on emissions. Density effects could therefore be compensated for by changes in engine calibration.

Density levels are also influenced by T95 distillation maximum limits (discussed in more detail below) through their impact on the heavy fractions of the fuel. These limits could also be adjusted to compensate for density impacts.

Distillation Characteristics (Volatility)

Distillation is a reference to the volatility profile of diesel fuel. The distillation or boiling range of the fuel is a consequence of the chemical composition of the fuel meeting other fuel property requirements such as viscosity, flash point, cetane number and density, within a particular refinery's overall product slate.

Volatility can influence the amount and kind of exhaust smoke that is emitted. Correct distillation characteristics are therefore essential for efficient fuel combustion. This is achieved by the careful balancing of the light and heavy fuel fractions (parts) during the refining process. Heavy fractions have high energy content and improve fuel economy, but can cause harmful deposit formation inside engines. Light fractions reduce the overall viscosity to provide better fuel injection atomization, easier engine starting and more complete combustion under a variety of engine conditions, but they do not have as much energy per unit volume of fuel (i.e. density) as heavier fractions.

The distillation curve of diesel fuel indicates the amount of fuel that will boil off at a given temperature. The curve can be divided into three parts: the light end, which affects startability; the region around the 50% evaporated point, which is linked to other fuel parameters such as viscosity

and density; and the heavy end, characterized by the T90 (temperature at which 90% of the fuel will evaporate), T95 and final boiling points (FBP).

Investigations have shown that too much ‘heavy ends’ in the fuel’s distillation curve can result in heavier combustion chamber deposits and increased tailpipe emissions of soot, smoke and particulate matter. The effect of T95 on vehicle emissions was examined in the EPEFE study, which indicated that exhaust gas emissions from heavy duty diesel engines were not significantly influenced by T95-variations between 375°C and 320°C. However, a tendency for lower NO_x and higher hydrocarbon emissions with lower T95 was observed.

Polyaromatic Hydrocarbons (PAHs)

Crude oils contain a range of hydrocarbons including polyaromatic hydrocarbons (PAHs). They are heavy organic compounds found mostly in diesel particulate matter but can also be present in the gas phase. PAHs are also referred to as polynuclear aromatic hydrocarbons and polycyclic aromatic hydrocarbons.

A consequence of higher aromatic content in fuel is poorer auto-ignition quality, increased thermal cracking and peak flame temperatures – and delayed combustion processes. From a combustion perspective aromatics are, in general, a poor diesel fuel component.

PAHs are increasingly attracting special attention because many are known human carcinogens. Testing for the EPEFE study demonstrated that a reduction in the total aromatic content of diesel significantly lowers NO_x, PM, carbon monoxide, benzene, formaldehyde and acetaldehyde emissions. In summary the EPEFE study showed that:

For light duty vehicles reducing polyaromatics decreased NO_x, PM, formaldehyde and acetaldehyde emissions, but increased hydrocarbon, benzene and carbon monoxide emissions.

For heavy duty vehicles, reducing polyaromatics decreased NO_x, particles and hydrocarbon emissions.

Ash and Suspended Solids

Ash forming materials (incombustible mineral material) may be present in diesel fuel in two forms – as suspended solids or as hydrocarbon soluble organo-metallic compounds.

Ash forming materials present as suspended solids may contribute to fuel injector and fuel pump wear, which are critical issues in engines needed to meet tighter emission standards. Ash forming materials present as soluble organo-metallic compounds have little effect on wear of these components but, like suspended solids, can contribute to combustion chamber deposits, most critically on fuel injector tips, which can then influence emissions performance – specifically of fine particles.

While levels of suspended solids may be substantially reduced by engine fuel filters, dissolved organo-metallic compound levels are not reduced in this way, and require management by other means.

The issue of the use of recycled waste oil as diesel extender has the potential to increase the ash content of the fuel.

Viscosity

The viscosity of a fluid indicates its resistance to flow; the higher the viscosity, the greater the resistance. It is a property that, along with density and distillation range, is an important indicator of the fuel's overall character.

Viscosity of diesel fuel is important for the operation of the fuel injection equipment that is required to accurately measure small quantities of fuel prior to injection and to atomize the fuel in the injection process.

Fuel with low viscosity can result in excessive wear in some injection pumps and in power loss due to pump injector leakage. Spray may not atomize sufficiently, therefore, combustion is impaired and power output and fuel economy are decreased. This can have adverse effects on emissions performance.

Impact of Diesel Fuel Composition on Vehicle Emissions¹

Tables B.2 and B.3 summarize the impacts of various diesel fuel qualities on emissions from light and heavy duty diesel vehicles, respectively.

Table B.2 Impact of Fuels on Light Duty Diesel Vehicles

Diesel Fuel Characteristic	Pre Ox Catalyst	Post Ox Catalyst	PM Filter and NOx absorber	Comments
Sulfur↑	SO ₂ , PM↑	SO ₃ , SO ₂ , PM↑	PM↑ NOx↑;	Filter trap, requires <50 ppm , 10-15 ppm better; NOx adsorber requires near zero sulfur (<10 ppm) and the use of lubricity additives
Cetane↑	Lower CO, HC, benzene, 1,3 butadiene, formaldehyde & acetaldehyde			Higher white smoke with low cetane fuels
Density↓	PM, HC, CO, formaldehyde, acetaldehyde & benzene↓, NOx↑			
Volatility (T95 from 370 to 325 C)	NOx, HC↑ ; PM, CO↓			
Polyaromatics↓	NOx, PM, formaldehyde & acetaldehyde↓ but HC, benzene & CO ↑			Some studies show that total aromatics are important

Table B.3 Impact of Fuels on Heavy Duty Diesel Vehicles

Diesel	Pre-Ox Catalyst	Ox Catalyst and PM filters		Comments
Sulfur↑	SO ₂ , PM↑	If ox cat, SO ₃ , SO ₂ , PM↑	Filter requires <50 ppm , 10-15 ppm better	Filter trap requires <50ppm (10-15 ppm, better); NOx adsorber requires near zero sulfur (<10 ppm) and the use of lubricity additives
Cetane↑	Lower CO, HC, benzene, 1,3 butadiene, formaldehyde & acetaldehyde			Higher white smoke with low cetane fuels
Density↓	HC, CO ↑, NOx↓			
Volatility (T95 from 370 to 325 C)	Slightly lower NOx but increased HC			Too much heavy ends increases smoke and PM
Polyaromatics↓	NOx, PM, HC ↓			Some studies show that total aromatics are important

¹ Most Asian countries have linked their vehicle emissions control programs to the EU or ECE requirements so much of the discussion that follows will relate fuels parameters to different technologies meeting EU standards.

REFERENCES

- Alliance of Automobile Manufacturers. The Impact of MMT on Vehicle Emissions and Durability. Available from <http://www.autoalliance.org/files/mmt3.pdf>. Accessed October 15, 2008.
- Asian Development Bank and Clean Air Initiative. 2008. A Roadmap for Cleaner Fuels and Vehicles in Asia. Asian Development Bank. www.cleanairnet.org/caiasia/1412/articles-71194_roadmap.pdf.
- Coordinating Research Council. 1997. Auto/Oil Air Quality Improvement Research Program: Program Final Report, Alhambra CA
- Dobson AW, Erikson KM and Aschner M. 2004. Manganese neurotoxicity. *Ann NY Acad Sci* 1012:115-128.
- Elder A, Gelein R, Silva V, Feikert T, Opanashuk L, Carter J, Potter R, Maynard A, Finkelstein J and Oberdörster G. 2006. Translocation of inhaled ultrafine manganese oxide particles to the central nervous system. *Environ Health Perspect* 114:1172-1178.
- EPEFE. 1996 Outcome of the European Programme on Emissions, Fuels, and Engine Technologies (EPEFE). Society of Automotive Engineers, Int.
- ICCT. 2004. Status Report Concerning the Use of MMT in Gasoline. International Council on Clean Transportation.
- Landrigan P, Nordberg M, Lucchini R, Nordberg G, Grandjean P, Iregren A and Alessio L. 2006. The Declaration of Brescia on Prevention of the Neurotoxicity of Metals Brescia, Italia 17-18 June 2006. *Med Lav* 97.
- Mena I, Horiuchi K, Burke K and Cotzias GC. 1969. Chronic manganese poisoning. Individual susceptibility and absorption of iron. *Neurology* 19:1000-1006.
- Tjalve H, Henriksson J, Tallkvist J, Larsson BS and Lindquist NG. 1996. Uptake of manganese and cadmium from the nasal mucosa into the central nervous system via olfactory pathways in rats. *Pharmacol Toxicol* 79:347-356.
- UCED. 2007. Proceeding from the United Nations Conference on Environment and Development, Rio de Janeiro, Brazil.
- U.S. Environmental Protection Agency. 2003. Health Effects Support Document for Manganese. EPA 822-R-03-003. Office of Water, Health and Ecological Criteria Division. Washington, DC. Available from http://www.epa.gov/safewater/ccl/pdfs/reg_determine1/support_cc1_magnese_healtheffects.pdf.
- Wood G and Egyed M. 1994. Risk Assessment for the Combustion Products of Methylcyclopentadienyl Manganese Tricarbonyl (MMT) in Gasoline. Health Canada. Available from <http://www.hc-sc.gc.ca/ewh-semt/pubs/air/combustion-eng.php>.
- Yokel RA and Crossgrove JS. 2004. Manganese Toxicokinetics at the Blood–Brain Barrier. Research Report 119. Health Effects Institute, Boston MA.

Zayed J. 2001. Use of Mmt in Canadian Gasoline: Health and Environment Issues. Am J Ind Med 39.