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The Impact of Fuel Parameters on Vehicle Emissions

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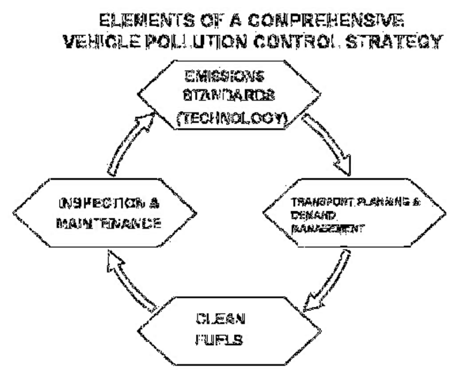
A Background Paper for the Oil Dialogue

Clean Air Initiative- Asia

Executive Summary

Motor vehicles emit large quantities of carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx), and such toxic substances as benzene, formaldehyde, acetylaldehyde, 1,3,butadiene, fine particles (PM), and lead (Pb). Each of these, along with secondary by-products such as ozone, can cause serious adverse effects on health and the environment. Because of the growing vehicle population in most Asian countries and the high emission rates from many of these vehicles, as well as emissions from other sources, serious air pollution and associated adverse health problems have been increasingly common phenomena in modern life.[1]

Reducing the pollution that comes from vehicles will usually require a comprehensive strategy that includes four key components: emissions standards for new vehicles, specifications for clean fuels, programs to assure proper maintenance of in-use vehicles, and transportation planning and demand management. One important lesson that has been learned is that vehicles and fuels should be treated as a system. These emission reduction goals should be achieved in the most cost effective manner available.



Over the last fifteen years, extensive studies have been carried out to better establish the linkages between fuels and vehicles and vehicle emissions. Relying heavily on these studies, the purpose of this paper is to summarize what is known about the impact of fuel quality on emissions.

Diesel Fuel

Diesel fuel is a complex mixture of hydrocarbons with the main groups being paraffins, napthenes 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.

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

[1] **Review of Studies of Health Effects of Outdoor Air Pollution in the Developing Countries of Asia,** Health Effects Institute, 2004

Impact of Diesel Fuel Composition on Asian Vehicle Emissions[2]

The following tables summarize the impacts of various diesel fuel qualities on emissions from light and heavy duty diesel vehicles, respectively.

Impact of Fuels on Light Duty Diesel Vehicles

Diesel Fuel Characteristic	Pre-Euro	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5[3]	Comments
Sulfur↑	SO_2, PM↑		If ox cat, SO_3, SO_2, PM↑		If Filter, 50 ppm maximum, 10-15 ppm better		If NOx adsorber used requires near zero sulfur (<10 ppm) With low S, use 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 increase, PM, CO decrease						
Polyaromatics↓	NOx, PM, formaldehyde & acetaldehyde↓ but HC, benzene & CO ↑						some studies show that total aromatics are important

Impact of Fuels on Heavy Duty Diesel Vehicles

Diesel	Pre-Euro	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5[4]	Comments
Sulfur↑	SO_2, PM↑		If ox cat, SO_3, SO_2, PM↑		If Filter, 50 ppm maximum, 10-15 ppm better		If NOx adsorber used requires near zero sulfur (<10 ppm) With low S, use lubricity additives
Cetane↑	Lower CO, HC, benzene, 1,3 butadiene,						Higher white smoke

[2] 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.

[3] Euro 5 emissions standards for light duty diesel vehicles have not yet been adopted by the EU. However, the EU Commission has indicated that it will propose these standards during 2005 and they will likely become mandatory during the period from 2008-2010. It seems likely that these standards will mandate the use of PM filters on all light duty diesel vehicles.

[4] The EU Commission has also indicated that it will propose Euro 6 emissions standards for heavy duty engines during 2005, likely mandating the use of PM filters on all heavy duty diesel vehicles from 2010 or 2012.

	formaldehyde & acetaldehyde	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

Higher **sulfur** content will tend to increase sulfur dioxide (SO2) and PM emissions from all vehicle categories, from the least controlled to the most controlled. Sulfur dioxide is an acidic irritant that also leads to acid rain and the formation of sulfate particulate matter. As vehicle emissions standards are tightened to Euro 2 and Euro 3 levels, oxidation catalysts will tend to be introduced to reduce PM emissions but these systems will also tend to convert some of the SO2 into more hazardous SO3 emissions which when combined with water vapor leads to sulfuric acid mist (H2SO4). Further tightening of vehicle emissions standards will tend to require the introduction of PM filters on many vehicles and while these systems can largely eliminate PM emissions they tend to be very sensitive to sulfur levels in fuel. It is generally recommended that maximum sulfur levels with these systems be reduced to 50 ppm or less; many of these systems give optimum performance with fuels having sulfur levels in the range of 10 to 15 ppm or less. NOx control systems for diesel vehicles are still evolving with the two major candidates for Euro 4 and Euro 5 vehicles being Selective Catalytic Reduction (SCR) Systems which are not especially sensitive to sulfur levels in fuel[5] and NOx adsorber systems which are extremely sensitive to sulfur and require levels in the range of 10 to 15 ppm or less.

Cetane number is a measure of auto-ignition quality. High cetane number fuels enable an engine to be started more easily at lower air temperatures, reduce white smoke exhaust, and reduce diesel knock. An increase in cetane number generally results in a decrease in carbon monoxide and hydrocarbon emissions, nitrogen oxides emissions (most notably in heavy duty engines), as well as benzene, 1,3 butadiene, formaldehyde and acetaldehyde emissions from light duty engines. For diesel vehicles equipped with oxidation catalysts or catalyzed PM filters, emissions of CO, HC and the toxics, benzene, 1,3 butadiene, formaldehyde and acetaldehyde, will tend to be less sensitive to cetane number. While one major study (the EU EPEFE[6] 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.

Density relates to the energy content of fuel; the higher the density of the fuel the higher its energy content per unit volume. Too high a fuel density for the engine calibration has the effect of over-fuelling, increasing black smoke and other gaseous emissions. The European EPEFE study found that:

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[5] While SCR systems are not particularly sensitive to sulfur levels, they tend to be combined with an oxidation catalyst to reduce ammonia slip and these oxidation catalysts are sensitive to sulfur levels. They will also tend to increase sulfate emissions levels.

[6] European Program on Emissions, Fuels and Engine technologies

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

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

CONCAWE 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.

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,[7] T95 and final boiling points. 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 NOx and higher hydrocarbon emissions with lower T95 was observed.

Polyaromatic hydrocarbons (PAHs) are increasingly attracting special attention because many are known human carcinogens. Testing for the EU EPEFE study showed that:

- For light duty vehicles reducing polyaromatics decreased NOx, particles, formaldehyde and acetaldehyde emissions, but increased hydrocarbon, benzene and carbon monoxide emissions.
- for heavy duty vehicles, reducing polyaromatics decreased NOx, particles and hydrocarbon emissions

Gasoline

Gasoline is a complex mixture of volatile hydrocarbons used as a fuel in internal combustion engines. The pollutants of greatest concern from gasoline-fuelled vehicles are CO, HC, NOx, 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.

Impact of Gasoline Composition on Asian Vehicle Emissions.

[7] The temperature at which 90% of the fuel will evaporate.

The following tables summarize the impacts of various diesel fuel qualities on emissions from light duty gasoline vehicles.

Impact of Gasoline Composition on Emissions from Light Duty Vehicles

Gasoline	No Catalyst	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5	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 increases in HC, NOx	HC↑, NOx↓, CO↑		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	Likely 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

Lead additives have been blended with gasoline, primarily to boost octane levels, since the 1920s but there is now a clear worldwide trend to eliminate their use and most Asian countries have done so. Lead emissions from all vehicles using leaded gasoline increase in direct proportion to the amount of lead consumed. This lead is toxic and has long been recognized as posing a serious health risk especially for children. In addition, vehicles using leaded gasoline cannot use a catalytic converter (required to comply with Euro 1 emissions standards or tighter) and therefore have much higher levels of CO, HC and NOx emissions.

Sulfur dioxide emissions increase from all categories of gasoline fueled vehicles in direct proportion to the amount of **sulfur** in fuel. Sulfur dioxide is an acidic irritant that also leads to acid rain and the formation of sulfate particulate matter. Its greatest impact, however, is in vehicles equipped with catalytic converter technology, required for compliance with Euro 1 or tighter vehicle emissions standards. Testing of catalysts has demonstrated reductions in efficiency resulting from higher sulfur levels across a full range of air/fuel ratios. The effect is greater in percentage for lower emission vehicles (Euro 3, 4 and 5) than for less controlled vehicles (Euro 1 or 2). The durability of catalysts is also impacted by sulfur levels in fuels as active catalyst sites tend to get coated with sulfur compounds. Studies have also shown that sulfur adversely affects heated exhaust gas oxygen sensors; slows the lean-to-rich transition, thereby introducing an unintended rich bias into the emission calibration; and may affect the durability of advanced on-board diagnostic (OBD) systems.

The lean-burn gasoline engine with direct fuel injection which is emerging makes possible a 15% decrease in fuel consumption compared with conventional gasoline engines thereby reducing greenhouse emissions. In Europe, there is a clear recognition that to be able to comply with future ‘severe emissions limit values’, the use of NOx accumulator DeNOx catalytic converters will be necessary. Even low levels of sulfur in fuel lead to deterioration in the accumulation capacity of this catalytic converter and make more frequent regeneration intervals necessary, which causes an increase in fuel consumption. A reduction of the fuel sulfur content from 50 to 10 ppm lowers the frequency of the regeneration intervals, and decreases fuel consumption; with sulfur levels above 50 ppm, DeNOx catalysts are not feasible.

The EU EPEFE study found that reducing sulfur from 382 to 18 ppm reduced exhaust emissions of HC, CO and NOx (the effects were generally linear at around 8-10% in urban driving and 20 to 50% in high speed driving). In the case of air toxins, benzene and C3-12 alkanes were in line with overall hydrocarbon reductions, with larger reductions (around 18%) for methane and ethane.

Gasoline **volatility** is an indication of how readily a fuel evaporates and is characterized by two measurements – vapor pressure and distillation. High gasoline **vapor pressure** causes high evaporative hydrocarbon emissions which 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 carburetors 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. Any associated cold weather driveability-related problems can be addressed by either restricting limits to the summer period, or by shortening the summer period and/or setting regional volatility limits to take into account both climatic and seasonal temperature profiles.

Distillation is a second method for measuring the volatility of gasoline. The EPEFE study found that increasing E100 in gasoline (the percentage of gasoline evaporated at 100°C) reduces emissions of hydrocarbons but increases NOx emissions. Increasing E100 from 35% to 50% by volume showed a decrease in mass emissions of both formaldehyde and acetaldehyde but increasing E100 from 50 % to 65 % by volume showed no clear effect.

Olefins are good high octane components of gasoline but they can lead to the build up of engine deposits and increased emissions of highly reactive ozone-forming hydrocarbons and toxic compounds. They tend to be chemically more reactive than other hydrocarbon types. A study by the US Auto/Oil program 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. In addition, 1,3-butadiene, a known carcinogen, is formed during the combustion of olefin compounds in gasoline and is therefore reduced by lowering the olefin fraction in gasoline.

Aromatics are hydrocarbon fuel molecules based on the ringed six-carbon benzene series or related organic groups. Combustion of aromatics can lead to the formation of benzene in exhaust gas, a human carcinogen that can cause leukemia in exposed persons. Lowering aromatic levels in gasoline significantly reduces toxic benzene emissions from vehicle exhausts. In the EU 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.

Benzene is a six-carbon, colorless aromatic that occurs naturally in gasoline and is also a product of catalytic reforming used to boost octane levels. Benzene in gasoline leads to both evaporative and exhaust emissions of benzene.

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 NOx exhaust emissions can occur with either oxygenate when the oxygen content is higher than 2 weight %. (There is some debate regarding the NOx 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).

Certain other **additives** which 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.

Deposit control additives can reduce the build up of deposits on various engine components including fuel injectors and carburetors thereby maintaining low emissions from vehicles.

Two and Three Wheeled Vehicles

Many countries and cities throughout Asia have much higher proportions of two and three wheeled vehicles than anywhere else in the world. While emissions from these vehicles are expected to be influenced by fuel characteristics, there has been very little study focused on the impacts of specific fuel parameters on these vehicles. However, based on the limited available data and the combustion similarities between these and other internal combustion engines, these impacts are estimated to be as shown in the table below.

Impact of Gasoline Composition on Emissions from Motorcycles

Gasoline	No Catalyst	India 2005	Euro 3	India 2008	Taipei,China Stage 4	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 SO_2 and SO_3 increase				
Olefins ↑	Increased 1,3 butadiene, HC reactivity and NOx					Potential deposit buildup
Aromatics ↑	Increased benzene exhaust					
Benzene ↑	Increased benzene exhaust and evaporative emissions					
Ethanol ↑ up to 3.5% O_2	Lower CO, HC, slight NOx increase	Minimal effect with oxygen sensor equipped vehicles				Increased evaporative emissions unless RVP adjusted, potential effects on fuel system components, potential deposit issues, small fuel economy penalty

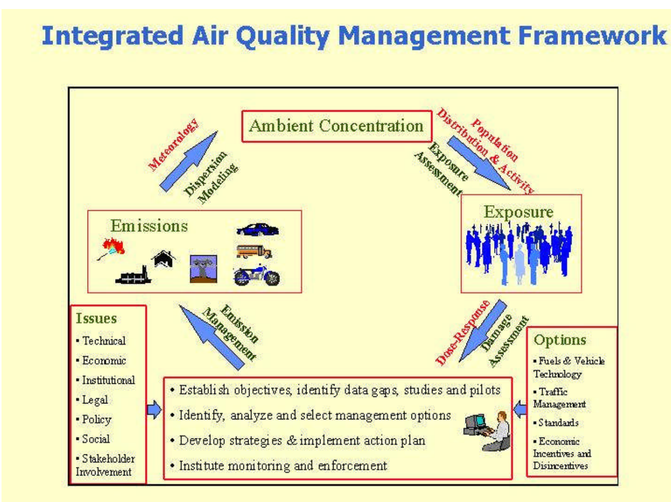
MTBE ↑ up to 2.7% O_2	Lower CO, HC	Minimal effect with ox. sensor equipped vehicles	Concerns over Water Contamination small fuel economy penalty
Distillation characteristics T50, T90 ↑	Probably HC↑	HC↑	Not as quantifiable as in passenger cars
MMT ↑	Increased Manganese Emissions	Possible Catalyst Plugging	With low cell density, catalyst plugging risk seems small but there are concerns regarding deposits on spark plugs and in the combustion chamber
RVP ↑	Increased evaporative HC Emissions		
Deposit control additives ↑		potential emissions benefits	Help to reduce deposits on fuel injectors, carburetors

Most two and three wheeled vehicles currently used throughout the region are not equipped with catalytic converters to control emissions. Therefore it would seem that the impact of the various fuels parameters will be similar to those from pre Euro 1 cars. Some catalysts are starting to enter the fleet as emissions standards are being tightened, especially in India, Taipei,China and Europe. These vehicles are anticipated to be impacted by sulfur and lead in a manner similar to Euro 1 and 2 gasoline fueled cars. For two and three wheeled vehicles equipped with 2-stroke engines, the amount and quality of the lubricating oil is probably more important than fuel quality.

I. Introduction

Motor vehicles emit large quantities of carbon monoxide, hydrocarbons, nitrogen oxides, and such toxic substances as benzene, formaldehyde, acetylaldehyde, 1,3,butadiene, fine particles, and lead. Each of these, along with secondary by-products such as ozone, can cause serious adverse effects on health and the environment. Because of the growing vehicle population and the high emission rates from many of these vehicles, serious air pollution and health effect problems have been increasingly common phenomena in modern life.

Over the course of the past 30 years, pollution control experts around the world have come to realize that cleaner fuels must be a critical component of an effective clean air strategy. In recent years, this understanding has grown and deepened and spread to most regions of the world. Fuel quality is now seen as not only necessary to **reduce or eliminate certain pollutants** (e.g., lead) directly but also a **precondition for the introduction of many important pollution control technologies (lead and sulfur)**. Further, one critical advantage of cleaner fuels has emerged - its **rapid impact on both new and existing vehicles**. (For example, tighter new car standards can take ten or more years to be fully effective whereas lowering lead in gasoline will reduce lead emissions from all vehicles immediately.)

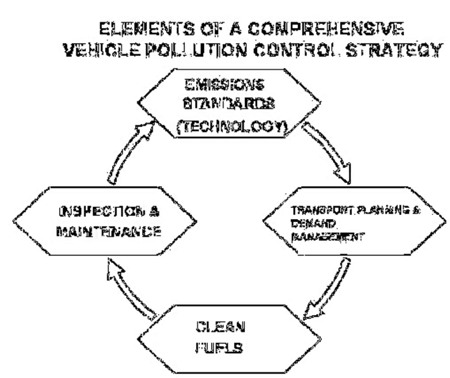


In developing strategies to clean up vehicles, it is necessary to start from a clear understanding of the emissions reductions from vehicles and other sources that will be necessary to achieve healthy air quality. Depending upon the air quality problem and the contribution from vehicles, the degree of control required will differ from location to location. As illustrated in the Figure regarding Integrated Air Quality Management Framework, one should start with a careful assessment of air quality and the sources that are contributing the most to the problem or problems.

Where vehicles are the major culprits, a broad based approach to the formulation and implementation of policies and actions aimed at reducing their pollution will be needed.

Reducing the pollution that comes from vehicles will usually require a comprehensive strategy that includes four key components: emissions standards for new vehicles, specifications for clean fuels, programs to assure proper maintenance of in-use vehicles, and transportation planning and demand management. One important lesson that has been learned is that vehicles and fuels should be treated as a system. These emission reduction goals should be achieved in the most cost effective manner available.

Over the last fifteen years, extensive studies have been carried out to better establish the linkages



between fuels and vehicles and vehicle emissions. One major study, the Auto/Oil Air Quality Improvement Research Program (AQIRP) was established in 1989 in the US and involved 14 oil companies, three domestic automakers and four associate members[8]. In 1992, the European Commission also initiated a vehicle emissions and air quality program. The motor industry (represented by ACEA) and the oil industry (EUROPIA) were invited to cooperate within a framework program, later known as "the tripartite activity" or European Auto/Oil Program. In June 1993, a contract was signed by the two industries to undertake a common test program, called the European Program on Emissions, Fuels and Engine Technologies (EPEFE).

Relying heavily on both of these studies as well as other more recent work, the purpose of this paper is to summarize what is known about the impact of fuel quality on emissions.

Most Asian countries have linked their vehicle emissions control programs to the EU or ECE requirements so it is useful to summarize the EU fuel quality specifications. These can usefully be described in terms of 3 classes (effectively Euro 2, 3 and 4). For the Euro 3 and 4 standards, specifications have been set with particular attention given to the 'environmental qualities' of the fuel. The specifications for these three classes for the key environmental diesel fuel parameters are presented in Table A. The only change in the specifications for Euro 4 diesel to date has been the establishment of the sulfur content at 50 ppm.[9]

Table A: EU diesel fuel quality specifications

Petrol/Gasoline	2000	2005		Diesel	2000	2005
RVP summer kPa, max.	60	60		Cetane number, min.	51	51
Aromatics, % by vol. max.	42	35		Density 15^{o}C kg/m^{3}, max.	845	845
Benzene, % by vol. max.	1	1		Distillation 95% by vol. ^{o}C, max.	360	360
Olefins, % by vol. max.	18	18		Polyaromatics, % by vol., max.	11	11
Oxygen, % by mass max.	2.7	2.7		Sulfur, ppm max.	350	50/10
Sulfur, parts per million	150	50/10				

NOTE: RVP = Reid Vapor Pressure; kPa = kilopascals [1 atmosphere of pressure equals about 100 kPa]

SOURCE: Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998, amending Council Directive 93/12/EEC.

II. Diesel Fuel

[8] "Auto/Oil Air Quality Improvement Research Program, Final Report", January 1997.

[9] A maximum limit of 50 parts per million applies for all diesel and gasoline sold in the EU in 2005 but fuels with a maximum limit of 10 ppm must be widely available by that year. All fuel must comply with a maximum limit of 10 ppm by 2009 at the latest.

A. Introduction

Diesel fuel is a complex mixture of hydrocarbons with the main groups being paraffins, napthenes and aromatics, the latter including alkyl benzenes, and polyaromatic (PAH) structures. 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 significantly influence emissions from diesel engines.

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

B. Environmental' Fuel Specifications

Key diesel fuel parameters which are known to have significant effects on emissions (either directly or indirectly because they affect emissions reduction technology) have been identified as sulfur, cetane, density, T95 distillation (volatility) and polyaromatic hydrocarbons (PAHs). Other parameters that are also considered significant in this respect are ash content and viscosity.

The emissions effects of fuel changes may vary (and in fact have opposing effects) between heavy and light duty diesel vehicles. In general, the emissions effects of fuel changes are much smaller for heavy duty (HD) engines than light duty (LD) engines, with light duty engines usually displaying a greater sensitivity to fuel changes. In addition, there can be substantial differences in response between individual vehicles and engines.

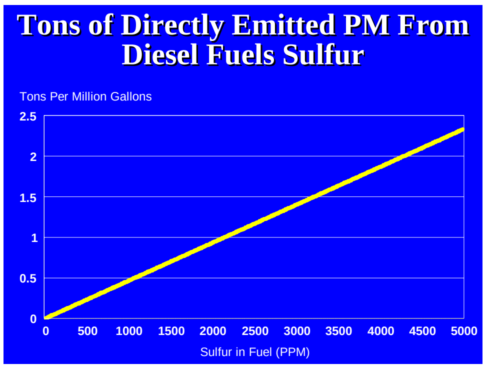
These effects can be further compounded by the intercorrelation of fuel parameters, emission test cycles and after treatment technologies. It has been noted that changing a few parameters in a diesel fuel may also lead to a change in other parameters. For instance, reducing aromatics in diesel will tend to increase the cetane number, which in turn improves the startability of the engine thereby decreasing the exhaust smoke opacity during cold starts. Diesel fuels containing high levels of aromatics are high in density but have low cetane numbers. Therefore, when considering the effects of reducing emissions by changing one parameter, it is important to look at the impact on other fuel quality parameters and emissions consequences.

1. Sulfur

Sulfur occurs naturally in crude oil, and the sulfur content of diesel fuel depends on both the source of the crude oil and the refining process.

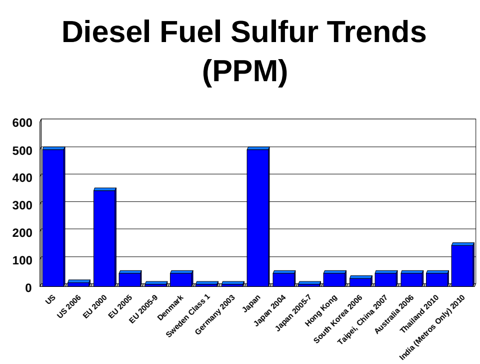
a) Impact

The contribution of the sulfur content of diesel fuel to exhaust particulate emissions has been well established with a general linear relationship between fuel sulfur levels and this regulated emission. Shown below is one estimate of this relationship provided by the US EPA. (This figure shows only the sulfur related PM not the total PM emitted from a diesel engine.) An indirect relationship also exists as some emissions of sulfur dioxide will eventually be converted in the atmosphere to sulfate PM.



Light duty diesel engines (<3.5 tons GVM) generally require oxidation catalysts to comply with Euro 2 vehicle emission standards. Oxidation catalysts lower hydrocarbons, carbon monoxide and particle emissions, and typically remove around 30% of total particle mass emissions through oxidation of a large proportion of the soluble organic fraction. The conversion of sulfur in the catalyst reduces the availability of active sites on the catalyst surface. This sulfur catalyst 'poisoning' is reversible through high temperature exposure - the sulfur compounds decompose and are released from the catalyst washcoat. However, due to generally low diesel exhaust temperatures, in many diesel engine applications the conditions needed for full catalyst regeneration may rarely be reached. High sulfur content in the fuel can also lead to the formation of sulfates in the converter which are then emitted as additional particles.

To enable compliance with tighter particle emission standards for diesel vehicles, tighter limits on the maximum sulfur content of commercial diesel fuel have been, or are being, introduced in many countries.(see figure below) While substantial reductions in particle emissions can be obtained without reducing sulfur levels, compliance with Euro 2 or tighter vehicle emission standards is not possible when fuel sulfur levels are greater than 500 ppm because of the relatively greater proportion of sulfates in the total mass of particle emissions.



In the case of Euro 3 and Euro 4 vehicle emission standards, even lower sulfur levels (350 ppm and 50 ppm respectively) in diesel fuel will be required to ensure compliance with the standards. Apart from contributing to the effective operation of catalysts and reducing particle emissions, these further reductions in sulfur levels will enable tighter emission standards to be met by the use of next generation "de-NOx" catalysts, which are very sensitive to sulfur.

Sulfur content is also known to have effects on engine wear and deposits, but appears to vary considerably in importance, depending largely on operating conditions. High sulfur content becomes a problem in diesel engines operating at low temperatures or intermittently. Under these conditions there is more moisture condensation, which combines with sulfur compounds to form acids and results in corrosion and excessive engine wear.

b) Lubricity

Diesel fuel has natural lubricity properties from compounds including the heavier hydrocarbons and organo-sulfur.

Diesel fuel pumps (especially rotary injection pumps in light duty vehicles), without an external lubrication system, rely on the lubricating properties of the fuel to ensure proper operation. Refining processes to remove sulfur and aromatics from diesel fuel tend to also reduce the components that provide natural lubricity.

In addition to excessive pump wear and, in some cases, engine failure, certain modes of deterioration in the injection system could also affect the combustion process, and hence emissions. Additives are available to improve lubricity with low sulfur fuels and should be used.

2. 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 napthenes in between the two.

Another proxy is the cetane index. This 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.

a) Impact

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 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.

Starting and white smoke emissions appear to be related primarily to ignition delay, and so cetane improved fuels generally perform as well as natural fuels of the same cetane number.

Experiments documented by the EPEFE study show a direct relationship between exhaust emissions and cetane number. An increase in cetane number resulted 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.

According to the EPEFE study, cetane number and density are the two most influential of the fuel parameters in relation to managing emissions from light duty diesel vehicle engines. It also found that after polyaromatic hydrocarbons, cetane number is the most influential parameter in relation to managing emissions from heavy duty diesel engines.

3. 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.

a) Impacts on Performance

Diesel fuel injection is calibrated and metered volumetrically, although the engine delivery is a function of the mass of fuel injected. Variations in fuel density (and viscosity) will therefore affect engine power and consequently fuel consumption. At high loads, too high a density affects the air: fuel ratio balance, and therefore the combustion emissions, for a given calibration. The EPEFE study found that fuel density influences the injection timing of mechanically controlled injection equipment, which has further effects on emissions and fuel consumption. (Fuel viscosity is also important in the injection system performance, notably in older mechanical/hydraulic systems).

Fuel consumption is expressed in volume per traveled distance, and is therefore influenced by the energy content of the fuel. For a given thermal efficiency of the engine, the fuel consumption is lower when the energy contained in a liter of fuel is higher. As the energy content is generally expressed on a mass basis (heating value), density and heating value are relevant fuel properties in relation to fuel consumption.

If the density is below that nominated by the engine manufacturer, the maximum power output of the engine will be reduced and the fuel pump delivery to the engine will need to be adjusted upward to maintain maximum power. Therefore, in order to optimize engine performance and tailpipe emissions, both minimum and maximum density limits should be defined in a fairly narrow range.

Black smoke output is sensitive to full load performance when excess combustion air availability is at its minimum. Too high a fuel density for the calibration has the effect of over-fuelling, increasing black smoke and other gaseous emissions output.

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.

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 NOx; but had no impact on the composition of the particle load.

- For heavy duty vehicles, reducing fuel density decreased emissions of NOx; 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 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.

4. 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 overall product slate.

a) Impacts on Performance

Volatility is an influence on 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 are high in 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, T95 and final boiling points. The heavy end has received the most attention with respect to its effect on tailpipe emissions.

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 NOx and higher hydrocarbon emissions with lower T95 was observed.

The interaction between distillation and other fuel properties such as viscosity, flash point, cetane and density, and the fact that it is recommended that a number of these other parameters also be managed on a national basis, suggests that the only and most effective distillation control required is T95. It has also been suggested that FBP is notoriously unreliable as measured by ASTM D86, and does not fully measure some of the potentially noxious materials that are left in the residue from distillation in any event. Gas chromatograph analysis can show exceptionally high end points whereas the volume involved in this ‘tail’ is extremely small.

5. 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) Impacts on Performance

A consequence of higher aromatic content in the fuel is poorer auto-ignition quality, increased thermal cracking and peak flame temperatures – and delayed combustion processes. From combustion perspective aromatics are, in general, a poor diesel fuel component. A higher density is frequently an indicator of a large aromatic compound content. The effects of density on engine performance are discussed above.

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 NOx, particles, carbon monoxide, benzene, formaldehyde and acetaldehyde emissions. In summary the EPEFE study showed that:

- For light duty vehicles reducing polyaromatics decreased NOx, particles, formaldehyde and acetaldehyde emissions, but increased hydrocarbon, benzene and carbon monoxide emissions.
- for heavy duty vehicles, reducing polyaromatics decreased NOx, particles and hydrocarbon emissions

6. 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.

a) Impacts on Performance

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.

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 raised the potential of increasing the ash content of the fuel. This elevated ash content could arise from the presence in the diesel extender/waste oil of residual oil soluble organo-metallic compounds added to the original oil products to bestow specific properties and of suspended solids due to the use of the oil.

Elevated ash content could lead to an increase in combustion chamber deposits and importantly the possibility of deposits on diesel fuel injectors, which could compromise their performance and affects emissions – specifically of fine particles.

7. 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.

a) Impact

Viscosity of diesel fuel is important for the operation of 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.

Too high a viscosity can cause poor combustion and loss of power and economy. The poor atomization of high viscosity fuels can lead to overspray in the injection process causing problems for the cylinder walls by washing away lubricating oil, resulting in excessive wear and also increasing the dilution of the lubricating oil in the engine. For rotary fuel injection pumps, seizure during start up can be experienced in excessively cold weather.

III. Gasoline

A. Introduction

Gasoline is a complex mixture of volatile hydrocarbons (compounds containing carbon and hydrogen atoms) used as a fuel in internal combustion engines. It is one of a large number of petroleum products made in a refinery from crude oil.

The pollutants of greatest concern from gasoline-fuelled vehicles are carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx), 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.

B. Key Environmental Gasoline Parameters

1. Sulfur

Sulfur occurs naturally in crude oil. Its level in refined gasoline depends upon the source of the crude oil used and the extent to which the sulfur is removed during the refining process.

a) Impact

Sulfur in gasoline reduces the efficiency of catalysts designed to limit vehicle emissions and adversely affects heated exhaust gas oxygen sensors. High sulfur gasoline is a barrier to the introduction of new lean burn technologies using DeNOx catalysts, while low sulfur gasoline will enable new and future conventional vehicle technologies to realize their full benefits.

Laboratory testing of catalysts has demonstrated reductions in efficiency resulting from higher sulfur levels across a full range of air/fuel ratios. The effect is greater in percentage for low-emission vehicles than for traditional vehicles. Studies have also shown that sulfur adversely affects heated exhaust gas oxygen sensors; slows the lean-to-rich transition, thereby introducing an unintended rich bias into the emission calibration; and may affect the durability of advanced on-board diagnostic (OBD) systems.

Sulfur has a significant impact on gasoline vehicle emissions by reducing the efficiency of catalysts designed to reduce noxious CO, HC and NOx emissions, and of new fuel efficient engine technologies that have the potential to reduce greenhouse gas emissions.

The lean-burn gasoline engine with direct fuel injection makes possible a 15% decrease in fuel consumption compared with conventional gasoline engines thereby reducing greenhouse emissions. In Europe, there is a clear recognition that to be able to comply with future 'severe emissions limit values', the use of NOx accumulator DeNOx catalytic converters will be necessary. Even low levels of sulfur in fuel lead to deterioration in the accumulation capacity of this catalytic converter and make more frequent regeneration intervals necessary, which causes an increase in fuel consumption. A reduction of the fuel sulfur content from 50 to 10 ppm lowers the frequency of the regeneration intervals, and decreases fuel consumption.

The EPEFE study demonstrated the relationship between reduced gasoline sulfur levels and reductions in noxious vehicle emissions. It found that reducing sulfur reduced exhaust emissions of hydrocarbons, carbon monoxide and NOx (the effects were generally linear at around 8-10%). The study results confirmed that fuel sulfur affects catalyst efficiency with the greatest effect being in the warmed up mode. In the case of air toxins, benzene and C3-12 alkanes were in line with overall hydrocarbon reductions, with larger reductions (around 18%) for methane and ethane.

The combustion of sulfur produces sulfur dioxide (SO2). Sulfur dioxide is an acidic irritant that also leads to acid rain and the formation of sulfate particulate matter.

In the European Union, the Euro 3 and 4 gasoline specifications set maximum sulfur content limits of 150 ppm and 50 ppm respectively (Euro 2 limits were 500 ppm). Subsequently, these limits were tightened to require 10 ppm sulfur fuel to be widely available in each member state in 2005 and for all gasoline to meet these limits by 2009. Several EU countries such as Sweden and Germany already provide fuels meeting these limits.

The recent USA Tier 2 Federal emission standards, finalized in December 1999, mandate further reductions in the sulfur content of gasoline. For new passenger cars and light vehicles, the standards will phase in from 2004 and be fully implemented by 2007. The program requires most refiners and importers to meet a 'corporate average gasoline sulfur standard' of 120 ppm and a cap of 300 ppm beginning in 2004. By 2006, the cap will be reduced to 80 ppm and most individual refineries must produce gasoline with sulfur content no more than 30 ppm on average.

Sulfur levels for all grades of gasoline in Japan are set at 100 ppm.

2. Lead

Lead additives have been blended with gasoline, primarily to boost octane levels, since the 1920s. Lead is not a natural constituent of gasoline, and is added during the refining process as either tetramethyl lead or tetraethyl lead. In addition to increasing the octane level of gasoline, lead also lubricates the engine valves/valve seat interface of vehicles that have soft valve seats, thereby minimizing wear.

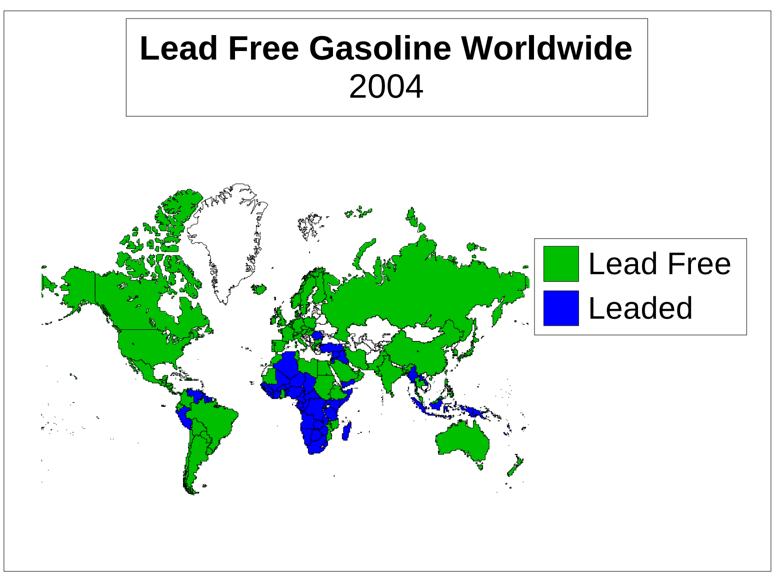
a) Impact

Lead in gasoline performs two functions: it raises the octane rating of gasoline and prevents exhaust valves from wearing out the valve seat.

Lead in gasoline contaminates or 'denatures' catalytic converters.

Vehicles using leaded gasoline cannot use a catalytic converter and therefore have much higher levels of CO, HC and NOx emissions. In addition, lead itself is toxic. Lead has long been recognized as posing a serious health risk. It is absorbed after being inhaled or ingested, and can result in a wide range of biological effects depending on the level and duration of exposure. Children, especially under the age of 4, are more susceptible to the adverse effects of lead exposure than adults.

About 90% of atmospheric lead emissions in urban areas come from the emissions of motor vehicles using leaded gasoline. It is estimated that about 75% of the lead in fuel is emitted from vehicle exhaust systems, with a further 2% from gasoline evaporation from the fuel tank, carburetor or spillage during transport and refueling.



A global consensus has emerged that the use of leaded gasoline should be phased out both to reduce public health risks and to facilitate the widespread use of catalytic converters to reduce carbon monoxide, hydrocarbon and NOx emissions from vehicles. A wide array of policy instruments, including tax incentives, have been used to encourage the use of unleaded gasoline, sales of which already amount to over 80% of all gasoline sold world-wide. The figure to the left shows that almost every country in the Asia-Pacific region has eliminated the use of leaded gasoline.

While unleaded gasoline specifications have previously allowed trace amounts of lead, the general move is now towards a zero lead content, with standards qualified by statements such as 'non-detectable' or 'at or below detection limit of test method used', or 'no intentional addition'.

3. 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.

a) Impact

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.

According to CONCAWE, there is concern that the Euro 2000 specification for RVP 60 kPa (max) will lead to increased drivability malfunctions during the early and late summer periods when ambient temperatures in some northern European Union countries can be as low as –15°C. These cold weather driveability malfunctions are caused by poor mixture formation in the engine leading to misfires or inefficient combustion which, as noted by the EPEFE study, leads to increased hydrocarbon exhaust emissions. There is, however, a special provision in the Euro fuel specifications in relation to RVP for arctic climate countries.

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. Any associated cold weather driveability-related problems can be addressed by either restricting limits to the summer period, or by shortening the summer period and/or setting regional volatility limits to take into account both climatic and seasonal temperature profiles.

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, with 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 have been 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.

4. 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 distils, while E100 is the percentage of gasoline distilled (‘E’ – evaporated) at 100°C.

a) Impact

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 NOx emissions.

The EPEFE study found that increasing E100 in gasoline reduces emissions of hydrocarbons but increases NOx 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. But 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 NOx 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.

5. 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 some hydrocarbons. As a result, there has been a move towards setting content limits on the different hydrocarbon fractions within gasoline. In general, attention has been focused on two classes of hydrocarbons – the aromatics and the olefins.

An olefin is 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.

a) Impact

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 NOx.

Emission of olefins into the atmosphere as chemically reactive species contributes to ozone formation and toxic dienes. A study by the US Auto/Oil program concluded that reducing total olefins from 20% to 5% would significantly decrease ozone-forming potential.

The study also showed that the same reduction in gasoline olefin levels would reduce the light-duty vehicle contribution to peak ozone by 13% to 25% in future years in the same cities. It is recognized, however, that the ozone reduction potential of managing olefin levels will vary between locations.

Reduction of low molecular weight olefins accounts for about 70% of the ozone reduction effect. Not only does the ozone formation potential of olefins predominantly derive from the lighter volatile olefin fractions, but also these fractions are typically removed where reductions in low levels of RVP at 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 except for ULP (RON 91), where content may be up to 21% 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.

6. 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.

a) Impact

Lower levels of aromatics enable a reduction in earlier 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 NOx.

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 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 NOx.

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 as follows:

Phase 1 (January 1995): 27%; and Phase 2 (January 2000): 25%.

The California specifications under the RFG program are also maximum limits by volume as follows:

Phase 1 (January 1992) 32%; and Phase 2 (January 1996) 22%.

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.

7. 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.

a) Impact

Benzene in gasoline leads to both evaporative and exhaust emissions of benzene. The EPEFE study found that benzene 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.

As noted in the preceding section on, the key health concern related to benzene exposure is leukemia.

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.

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.

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%.

8. 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 NOx exhaust emissions can occur with either oxygenate when the oxygen content is higher than 2 weight %. (There is some debate regarding the NOx 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).

9. Other Additives

Certain other **additives** which 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.

Deposit control additives can reduce the build up of deposits on various engine components including fuel injectors and carburetors thereby maintaining low emissions from vehicles.