## Linkage Between Fuels, Vehicles and Emissions – The Role of Sulfur

Reducing sulfur levels in fuels can reduce vehicle emissions in three general ways: 1) by directly reducing sulfur dioxide (SO2) and sulfate PM from all existing vehicles, 2) by achieving better performance from those emissions control systems (especially catalysts) which are already on existing vehicles, and 3) by enabling the use of new emissions control technologies such as diesel PM filters. The following sections give an overview of the impacts of fuel sulfur on particular emissions control technologies for diesel and gasoline vehicles.

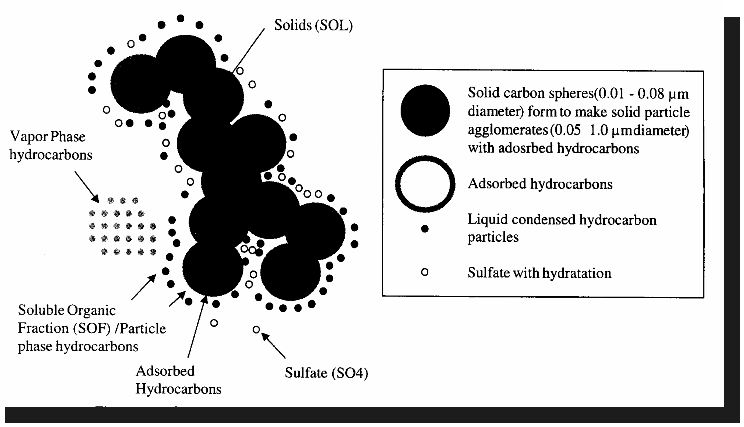
### A. Diesel Fueled Vehicles

Conventional diesels typically use only 70% of the fuel of a comparable gasoline engine, significantly reducing per-mile $CO_2$ emissions. Even without pollution controls, diesels provide an automatic benefit for CO and HC control. Diesel fuel has the added benefit of low volatility, which virtually eliminates evaporative HC emissions. The primary concerns for diesel engines are $NO_x$ and PM emissions. The impact of fuel sulfur on diesel vehicle emissions is dependent on the control technology contained on the vehicle which can range from no controls to very advanced aftertreatment controls. These impacts will be discussed below.

#### *i. No Controls/Pre-Aftertreatment Controls*

**For diesel vehicles with no controls, the amount of sulfur in the fuel is directly related to $SO_2$ and PM emissions; some SO2 emissions are converted in the atmosphere to sulfate PM.**

The amount of SO2 emissions is directly proportional to the amount of sulfur contained in the fuel. In addition, total PM emissions are proportional to the amount of sulfur in the diesel fuel although the carbon and the soluble organic fractions are not affected. In the oxygen-rich exhaust of diesel vehicles several percent of the $SO_2$ formed during combustion is oxidized to $SO_3$, which dissolves in the water vapor present to form sulfuric acid ($H_2SO_4$) vapor. $H_2SO_4$ forms very small (so called ultrafine) particles in diesel exhaust which are considered especially hazardous because of their ability to penetrate deeply into the lungs. Even though sulfate particles account for only a small fraction of particle volume or mass, they account for a large fraction of particle numbers.

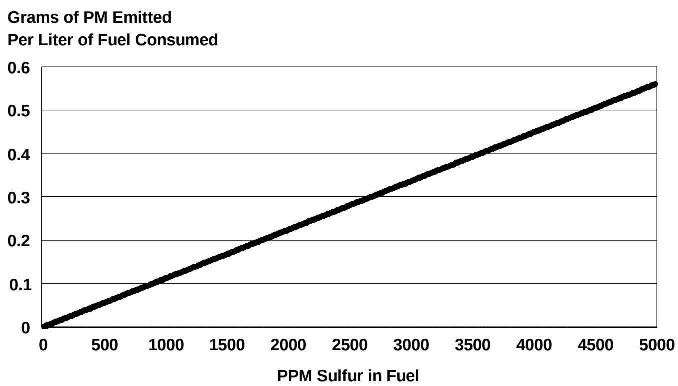


According to the US EPA, approximately 2% of the sulfur in the diesel fuel is converted to direct PM emissions which are the basis of the figure below.

In addition, $SO_2$ emissions can lead to secondary particle formation—particles that form in the ambient air. US EPA models predict that over 12% of the $SO_2$ emitted in urban areas is converted in the atmosphere to sulfate PM. Urban areas would benefit most from reductions in $SO_2$ emissions, as polluted urban air has higher concentrations of the constituents that catalyze the $SO_2$-to-sulfate reaction. Even with vehicle stocks without advanced pollution controls, reductions of fuel sulfur levels would likely have a significant impact on primary and secondary PM concentrations in urban areas.

### *ii. Post Combustion Controls*

**Direct PM Emissions As A Function Of Diesel Fuel Sulfur Level**




**With high sulfur levels, diesel catalysts produce high levels of hazardous sulfate. Some advanced catalyst technologies such as NOx adsorbers are precluded by high levels of sulfur. Finally, PM filter performance is impaired by higher levels of sulfur**

#### *a) Diesel Oxidation Catalysts*

Diesel oxidation catalysts (DOCs) are the most common aftertreatment emissions control technology found in current diesel vehicles. DOCs are very similar to the earliest catalysts used for gasoline engines. Oxidation catalysts work by oxidizing CO, HC and the soluble organic fraction of the PM to $CO_2$ and $H_2O$ in the oxygen rich exhaust stream of the diesel engine.

When sulfur is present in the fuel, DOCs also increase the oxidation rate of $SO_2$, leading to dramatic increases in sulfate nanoparticle emissions. Sulfate conversion depends on overall catalyst efficiency, with more efficient catalysts capable of converting nearly 100% of the $SO_2$ in the exhaust to sulfate. Generally, one should restrict the use of DOCs to areas which have fuel sulfur levels of 500 PPM or below. With low sulfur fuel, a DOC can reduce PM emissions by 25 to 30%.

#### *b) Diesel Particulate Filters*

Diesel particulate filters (DPFs) already reliably demonstrate over 95% efficiency with near-zero sulfur fuel use. They are also capable of reducing the total number of particle emissions below those of gasoline engines. One important area of research—the area most impacted by sulfur levels—is the passive regeneration or cleaning of the collected particles from the filter surface. Filters need to be cleaned, ideally without human intervention, before reaching capacity in order to maintain vehicle performance and fuel and filter efficiency.

The Continuously Regenerating Diesel Particulate Filter (CR-DPF) and the Catalyzed Diesel Particulate Filter (CDPF) are two examples of PM control with passive regeneration. The CR-DPF and CDPF devices can achieve 95% efficiency for control of PM emissions with 3 ppm sulfur fuel. But efficiency drops to zero with 150 ppm sulfur fuel and PM emissions more than double over the baseline with 350 ppm sulfur fuel. The increase in PM mass comes mostly from water bound to sulfuric acid. Soot emissions also increase with higher sulfur fuel but even with the 350 ppm sulfur fuel DPFs maintain around 50% efficiency for non-sulfate PM. The systems eventually recover to original PM control efficiency with return to use of near-zero sulfur fuels, but recovery takes time due to sulfate storage on the catalyst.

Sulfur also increases the required temperature for regeneration of the filter. In moving from 3 to 30 ppm sulfur fuel, the exhaust temperatures required for regeneration increase by roughly 25°C. The CDPF requires consistently higher temperatures but holds stable above 30 ppm, while the CR-DPF requires ever-increasing temperatures.

### *iii. NOx Control Systems*

Many diesel engines rely on injection timing retard to meet the $NO_x$ standards currently in place. Injection timing retard reduces the peak temperature and pressure of combustion, thus reducing $NO_x$ formation. Unfortunately, this solution both increases PM emissions and significantly decreases fuel economy. For example, $NO_x$ emissions can be decreased by 45% by retarding the injection timing 8 degrees, but this results in a 7% loss in fuel economy. Injection timing retard is not impacted by sulfur in fuel.

Exhaust gas recirculation (EGR), another NOx control strategy which is being used extensively today, is only indirectly impacted by fuel sulfur. Two very different technologies—$NO_x$ adsorbers and selective catalytic reduction (SCR) systems—are the most likely alternatives for further $NO_x$ control.

#### ***a) Exhaust Gas Recirculation:***

Major advances in diesel $NO_x$ control have been made with exhaust gas recirculation (EGR), which lowers combustion temperatures and thus reduces thermal $NO_x$ formation. Fuel sulfur does not impact emissions from EGR systems in diesel engines, but it does hinder system durability and reliability due to sulfuric acid formation. In order for EGR to be effective, the exhaust gases must be cooled, which causes sulfuric acid to condense in the recirculation system. Acid formation raises system costs, due to the need for premium components and increased maintenance costs.

#### ***b) NOx Adsorbers:***

$NO_x$ adsorbers are also known as $NO_x$ storage catalysts or lean $NO_x$ traps. $NO_x$ adsorber systems are still under development and are not expected to be widely used, even in highly industrialized countries such as the US, until later in this decade, if then. They have demonstrated 95% efficiency in conversion of $NO_x$ to $N_2$, with a nominal fuel penalty of 1.5%. However, without significant technological breakthroughs, it is generally recognized that this system can only operate with near zero sulfur fuels.

### *c) Selective Catalytic Reduction (SCR):*

SCR is emerging as the leading $NO_x$ reduction technology in Europe to meet Euro IV and Euro V heavy-duty diesel standards. SCR uses a reducing agent, injected into the exhaust gas before the catalyst, to achieve high rates of $NO_x$ conversion in the oxygen-rich exhaust. Stationary systems have over 90% conversion efficiency and are widely used for diesel generators and power production.

Sulfur does not reduce conversion efficiency in SCR systems as dramatically as in other advanced control technologies, but emissions are impacted in a couple of ways. Fuel sulfur will increase the PM emissions from the downstream oxidation catalyst. Sulfur reactions in urea-based SCR systems can also form ammonium bi-sulfate, a severe respiratory irritant.

### *iv. PM Retrofits*

A growing body of data continues to show that the combination of very low sulfur fuel (usually with 50 ppm sulfur or less) and particulate filters can bring about approximately 90% reductions in PM and further substantial reductions in CO and HC from existing diesel vehicles, even after 400,000 miles of operation.[1] To obtain these reductions however requires a careful matching of the technology to the vehicles with special attention given to operational patterns and exhaust temperature profiles.

Diesel oxidation catalysts can also be retrofitted to existing diesel vehicles as is occurring in Hong Kong, with overall PM reduction on the order of 25%.

## B. Gasoline Fueled Vehicles

The primary pollutants of concern from gasoline fueled vehicles, after elimination of lead, are carbon monoxide, hydrocarbons and the oxides of nitrogen. Certain of the hydrocarbons are known or suspected to be toxic. The vast majority of gasoline vehicles currently in use in **developed** countries and in **many developing** countries are equipped with catalysts for the control of CO, HC, and $NO_x$ and emissions from these vehicles can be impacted by sulfur levels in the fuel. In some developing countries, including most African countries, however, vehicles have no catalysts or the catalysts have been rendered ineffective through poisoning with lead or otherwise.

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[1] "The Success of Diesel Retrofits: A Fuel Supplier Perspective", Bob Schaefer, BP Global Fuels Technology, December 2003.

Many developing countries, especially in Africa, import used vehicles from countries such as Japan which should be equipped with catalysts. Anecdotal information indicates that many of these catalysts are removed and sold for their precious metal content. If not removed, they are quickly destroyed by lead which is currently still used in most gasoline on the continent. If lead is removed from gasoline, steps could be taken to assure that these used imported vehicles arrive with functioning catalysts, the performance of which could be improved with the use of low sulfur fuel.

The adverse sulfur impact increases in severity, at least in percentage terms, as vehicles are designed to meet stricter standards. Current sulfur levels in fuel are the primary obstacle against bringing advanced emission control technologies to market in many developing countries, such as China or India. These technologies could dramatically reduce conventional pollutants and also enable more fuel-efficient engine designs.

*i. No Controls/Pre Catalyst Controls*

**The amount of sulfur in the fuel is directly related to $SO_2$ emissions; some SO2 emissions are converted in the atmosphere to sulfate PM.**

For gasoline fueled vehicles with no catalytic converters, reducing sulfur will have no effect on the principal pollutants of concern, CO, HC or NOx. While the amount of $SO_2$ emitted is in direct proportion to the amount of sulfur in the fuel, gasoline vehicles are not usually a significant source of $SO_2$. Since $SO_2$ can be converted in the atmosphere to sulfates, however, these emissions will also contribute to ambient levels of particulate matter ($PM_{10}$ and $PM_{2.5}$) which is frequently a serious concern.[2]

*ii. Catalyst Based Controls*

**All catalyst technology is adversely impacted by sulfur with resulting increases in CO, HC and NOx.**

Worldwide, approximately 90% of new gasoline vehicles are equipped with a three-way catalyst (TWC), which simultaneously controls emissions of CO, HC, and $NO_x$. Sulfur in fuel impacts TWC functioning in several ways:

- Fuel sulfur reduces conversion efficiency for CO, HC and $NO_x$. Sulfur competes with these gaseous emissions for reaction space on the catalyst. It is stored by the TWC during normal driving conditions and released as $SO_2$ during periods of fuel-rich, high-temperature operation, such as high acceleration. Reductions in sulfur levels in gasoline—from highs of 200–600 ppm to lows of 18–50 ppm—have resulted in 9–55% reductions in HC and CO emissions and 8–77% reductions in $NO_x$ emissions, depending on vehicle technologies and driving conditions. Greater percentage reductions have been demonstrated for low emission vehicles and high-speed driving conditions.

[2]As noted earlier, US EPA models predict that over 12% of the $SO_2$ emitted in urban areas is converted in the atmosphere to sulfate PM.

- Sulfur inhibition in catalysts is not completely reversible. Although conversion efficiency will always improve with return to reduced sulfur levels, the efficiency of the catalyst does not usually fully return to its original state after desulfurization. In tests using 60 ppm sulfur fuel followed by a single use of 930 ppm sulfur fuel, HC emissions tripled from 0.04 g/mile to 0.12 g/mile. With a return to low sulfur fuel, emissions dropped again to 0.07 g/mile but fuel-rich operation (resulting in high exhaust temperatures) was required to regenerate the catalyst fully and return to original emissions levels.

- Sulfur content in fuel contributes to catalyst aging. Higher sulfur levels cause more serious degradation over time and, even with elevated exhaust temperatures, less complete recovery of catalyst functioning. The high temperatures necessary to remove sulfur from the catalyst also contribute to thermal aging of the catalyst. Sulfur raises the light-off temperature—the temperature at which catalytic conversion can take place—resulting in increased cold-start emissions.

- Regeneration requirements add to overall emissions and reduce fuel efficiency. Fuel-rich operation, required to reach regeneration temperatures, results in significant increases in CO and HC emissions. And PM emissions under these circumstances can actually rival diesel emissions. In addition, fuel-rich combustion requires increased fuel use. Vehicles that tend to operate at low speed and low load will have lower exhaust temperatures and fewer opportunities for desulfurization and catalyst regeneration.

*iii. More Advanced Catalyst Controls*

**All catalyst technology is adversely impacted by sulfur with resulting increases in CO, HC and NOx. Some advanced catalyst technologies such as NOx adsorbers which may enter the market later this decade are precluded by high levels of sulfur.**

The percentage benefits of reducing sulfur levels in fuels increase as vehicles are designed to meet stricter standards. Increasingly strict emissions standards require extremely efficient catalysts over a long lifetime. Recent regulations in Europe and the U.S. require warmed-up catalysts to have over 98% HC control, even towards the end of the vehicle's lifetime (100,000 km in Europe and over 100,000 miles in the U.S.). While these sophisticated technologies will not be in widespread use in many African countries for many years, they are likely to be introduced in countries such as China and India if near zero sulfur fuels become widely available, which is possible.