

LOW-SULFUR GASOLINE & DIESEL: THE KEY TO LOWER VEHICLE EMISSIONS

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Executive Summary

It is impossible to clean the air, or in particular to reduce air pollution from the transportation sector, without getting sulfur out of fuels. Sulfur is a pollutant directly, but more importantly, sulfur prevents the adoption of all major pollution control technologies. No significant air pollution reduction strategy can work without reducing sulfur to near-zero levels.

This paper addresses the need to reduce sulfur in transportation fuels and the benefits that can be realized in terms of total pollutant emissions. Sulfur fouls conventional and advanced technologies to control vehicle emissions, including carbon monoxide (CO), particulate matter (PM), nitrogen oxides (NO_x) and hydrocarbons (HC). Low-sulfur fuels are the key to reducing emissions from existing vehicles and enabling advanced control technologies and fuel-efficient designs for new vehicles.

Sulfur is a naturally occurring component of crude oil and is found in both gasoline and diesel. When those fuels are burned, sulfur is emitted as sulfur dioxide (SO₂) or sulfate particulate matter. Any reduction in fuel sulfur immediately reduces these sulfur compounds and, as sulfur levels decline past a certain point, the benefits increase to include total pollutant emissions.

Impact of Sulfur on Vehicle Emissions

Reduced sulfur fuels (~150 ppm) make existing vehicles cleaner. Reduced sulfur fuel decreases emissions of CO, HC, and NO_x from catalyst-equipped gasoline vehicles and PM emissions from diesels, with and without oxidation catalysts. These benefits increase as vehicles are designed to meet higher emissions standards and sulfur levels are reduced further.

Low sulfur fuels (~50 ppm) allow for the further benefit of advanced control technologies for diesel vehicles. Diesel particulate filters can be used with low sulfur fuel but only achieve approximately 50% control efficiency. Selective catalytic reduction can be used for over 80% control of NO_x emissions.

Ultralow sulfur fuels (~10 ppm) allow for the use of NO_x adsorbers, increasing NO_x control to over 90% in both diesel and gasoline vehicles. This enables more fuel-efficient engine designs, designs that are incompatible with current emissions control systems. Particulate filters achieve the maximum efficiency with ultralow sulfur fuels, approaching 100% control of PM.

Costs and Benefits of Reducing Fuel Sulfur

The technologies required to reduce sulfur to ultralow levels are in use in many areas of the world. Current costs are reasonable and the refining industry continues to make progress in developing more active catalysts and novel processes for removal of sulfur, reducing costs even further.

Studies show the benefits of sulfur reduction far outweigh the costs, even though required refinery investments continue to be significant. The U.S. EPA found human health and environmental benefits due to sulfur reduction were ten times higher than the costs. (This study assumed stricter emissions standards contingent on low-sulfur fuels.) Furthermore, a European study showed that ultralow sulfur fuels significantly reduce total fuel costs by increasing fuel economy. The considerable potential for greenhouse gas emission reductions adds further to the health, environmental, and social benefits of sulfur reduction.

Global Trends toward Low-Sulfur Fuels

In the developed world, auto makers and fuel refiners have had to apply their impressive technical and organizational capabilities to meet increasingly strict environmental regulations. The result has been reduced sulfur levels and ratcheted-down emissions standards for all types of vehicles. Meanwhile, long-term environmental challenges and the prospect of still stricter requirements in the future are spurring further research and technology development.

In developing countries, where vehicle numbers are increasing exponentially, high-sulfur fuels continue to be the norm and to inhibit the introduction of new vehicle technologies. By instituting policies to reduce sulfur and lower vehicle emissions, these countries can allay the mounting human health impacts associated with exponential increases in vehicle numbers. In doing so, countries relatively new to sulfur regulation may wish to build on the experience of countries that have achieved, and taken advantage of, low-sulfur fuels.

Further, countries should be increasingly willing to help each other overcome the fuel-quality barrier and move to low emission vehicles. Local health and environmental benefits, though themselves sufficient reason to require cleaner fuels, are no longer the only issue: vehicle emissions are of increasing global significance. Pollutants traditionally of local concern—such as PM and ground-level ozone—now appear to impact the global climate. Reducing sulfur in transportation fuels, and encouraging advanced emissions control and fuel-efficient vehicle technologies, are the necessary first steps to reduce the local and global impact of vehicle emissions.

Key Conclusions

In evaluating sulfur reduction options, several observations may be of use to policymakers.

1. While costs and benefits vary from region to region, depending on the state of existing refineries, current fuel quality and emissions standards, local air quality and other factors, studies have shown that the costs of sulfur reduction are affordable and are dwarfed by the benefits.
2. Both regulations and tax incentives have proven effective tools for moving the refining industry to low-sulfur products.
3. The schedule for upgrading refineries for higher quality fuel production has significant cost implications. (For example, timing upgrades to coincide with

needed refinery expansions can reduce costs.) Production and distribution of low-sulfur fuels must also be carefully coordinated with the introduction of new and retrofit vehicles that require low-sulfur fuels.

4. It is cost-effective and highly advantageous in most cases to make the jump to ultralow sulfur diesel in a single step. The total emissions benefits of further sulfur reductions from diesel fuel accrue most rapidly as levels decline from low to ultralow—both in terms of the retrofit potential for existing vehicles and emissions controls for new vehicles. Because of the large increase in incremental benefits, but relatively flat incremental costs, it makes sense to directly mandate ultralow sulfur diesel.
5. Measures should be taken to prevent sulfur extracted from one fuel stream from being diverted into another. For example, heavy fuel oil used in marine vessels can become a “dumping ground” for very high-sulfur feedstocks.

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LIST OF ACRONYMS

CARB	California Air Resources Board (also a reduced sulfur diesel designation)
CDPF	Catalyzed Diesel Particulate Filter
CH ₄	Methane
CNG	Compressed Natural Gas
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CR-DPF	Continuously Regenerating Diesel Particulate Filter
DECSE	Diesel Emissions Control Sulfur Effects
DOC	Diesel Oxidation Catalyst
DPNR	Diesel Particulate NO _x Reduction
DPF	Diesel Particulate Filter
DPM	Diesel Particulate Matter
ECD	Emissions Control Diesel (maximum of 15 ppm sulfur)
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency (U.S.)
FCC	Fluid Catalytic Cracking
FTD	Fischer-Tropsch Diesel
GHG	Greenhouse Gases
g/kWh	grams per kilowatt-hour
HC	Hydrocarbon
H ₂ SO ₄	Sulfuric Acid
IPCC	Intergovernmental Panel on Climate Change
MECA	Manufacturers of Emission Controls Association
Mt	megaton (10 ¹² grams)
N ₂	Nitrogen
N ₂ O	Nitrous Oxide
NO	Nitrogen Oxide
NO ₂	Nitrogen Dioxide
NO _x	Nitrogen Oxides
PM	Particulate Matter
ppm	parts per million
O ₂	Oxygen
O ₃	Ozone
SCR	Selective Catalytic Reduction
SO ₂	Sulfur Dioxide
SO _x	Sulfur Oxides
SOF	Soluble Organic Fraction
TWC	Three-way Catalyst

LOW-SULFUR GASOLINE & DIESEL: THE KEY TO LOWER VEHICLE EMISSIONS

I. INTRODUCTION

The first regulations regarding fuel specifications were passed in the U.S. and Japan in the 1970s. These regulations restricted use of lead in certain fuels. Lead poisoned the new catalytic technologies to control carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x). Unleaded gasoline was required by catalytic converters, first installed in model year 1975.

Sulfur is the lead of the new century. Like lead, emissions of sulfur compounds cause serious human health and environmental concerns*. More importantly, sulfur inhibits the use of advanced technology to control total pollutant emissions, including NO_x, HC, CO, and particulate matter (PM). Reducing sulfur levels in fuels will decrease the vehicle emissions of smog precursors and other pollutants that foul our air and choke our lungs.

Government policies to prevent use of lead in fuel have been implemented in most countries and are providing tremendous health benefits†. Similarly, low-sulfur fuels can become the rule—creating cleaner air, improving public health, and reducing environmental problems.

Fuel sulfur levels have begun to be reduced and regulated in much of the world. Often, fuel sulfur standards are coupled with stricter emissions standards for new vehicles or retrofit programs to reduce emissions in existing vehicles. The current and future benefits of low-sulfur fuels are substantial and more and more necessary in a world with increasing vehicle numbers and distances traveled.

Any reduction in sulfur reduces the SO₂ and sulfate emitted and, as sulfur levels decline past a certain point, the benefits increase to include total pollutant emissions. Reduced sulfur fuels (~150 ppm) make existing vehicles cleaner. Low sulfur fuels (~50 ppm) allow for advanced particulate filter and NO_x control technologies to further restrict pollutant emissions. And ultralow sulfur fuels (~10 ppm) enable tremendous advances in fuel-efficient vehicle design and advanced emissions control technology.

Reducing sulfur has its costs. Unlike lead, a fuel additive, sulfur is a naturally occurring component of crude oil and some types of sulfur compounds can be more easily (and cheaply) removed than others. Upgrading refineries to remove sulfur is expensive and

* Airborne lead is highly toxic and can impact human development and the nervous system. Sulfur is emitted as sulfur dioxide (SO₂) and sulfate particulate matter—pollutants which damage human health, impair visibility, and lead to the acidification of ecosystems.

† There is much progress to be made. Despite the obvious advantages, unleaded fuel is still not required or even available in some countries.

increases greenhouse gas emissions, despite the development of new catalysts and novel processes which reduce the energy requirements and costs. Yet, weighed against the emissions reduction potential of low-sulfur fuels, studies show the benefits far outweigh the costs.

This paper is intended to help policymakers weigh the costs and benefits of reducing sulfur in fuels, and decide what policies make the most sense in their own jurisdictions. In sum, this paper:

- Describes the direct and indirect impact of fuel sulfur on emissions and on pollution control technologies.
- Discusses the costs of desulfurization technologies and compares these costs with the benefits of sulfur reduction.
- Summarizes the pollution control policies around the world that require low-sulfur fuels.
- Provides observations of relevance to policymakers when designing new policies around low-sulfur fuels.

Also, the paper's appendices:

- Summarize the major pollutants from vehicles and their impacts on human health and the environment.
- Review refinery modifications to reduce sulfur levels and the economic, energy, and environmental costs of those technologies.

2. THE IMPACT OF SULFUR ON CONVENTIONAL POLLUTANT EMISSIONS

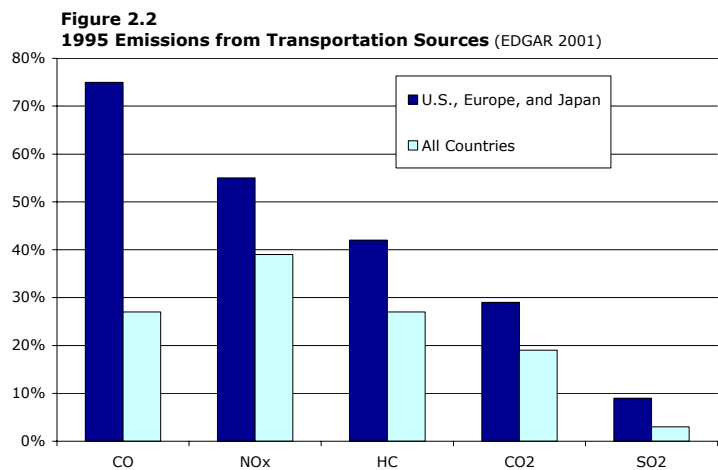
Motor vehicles continue to be the dominant source of air pollution, despite tremendous advances in engine technology and pollution control. In industrialized countries, even as cleaner vehicles are replacing older, dirtier ones and total transportation emissions are beginning to decline, vehicles are still the most important source of air pollution.



Meanwhile, in the developing world, vehicle numbers are growing exponentially and, without strict control standards in place, emissions from transportation sources are becoming an increasingly urgent concern. As shown in figure 2.1, vehicle numbers in developing countries, and thus pollutant emissions, could exceed vehicle numbers in the industrialized world within the next two or three decades.

Motor vehicles are a significant source of CO, HC, and PM, all of which are produced through inefficient or incomplete combustion. In addition, motor vehicles are one of the most important sources of NO_x, which along with HC, are the essential precursors to ground-level ozone (O₃), the main component of photochemical smog. All of these conventional pollutants have important local human health and environmental impacts, and there is increasing understanding of their global significance as well. Vehicles are also an important and growing source of carbon dioxide (CO₂), the principle greenhouse gas contributing to global warming. Appendix A gives an overview of each of the major pollutants associated with motor vehicles, including causes for concern and mechanisms of formation.

As seen in figure 2.2, transportation is a major source for CO, NO_x, HC, and CO₂, especially in areas of the world where motor vehicles are ubiquitous. While transportation is less significant as a direct source of SO₂, removal of sulfur from gasoline and diesel fuels will be critical for the control of other vehicle emissions.



This chapter outlines the regulatory pressures to reduce emissions, which have forced vehicle manufacturers to develop advanced emission control technology. It then goes on to discuss the impact of fuel sulfur on current and emerging technologies for the control of pollutant emissions from both gasoline and diesel vehicles.

2.1 Regulatory Pressures

The European Union, the U.S., and other industrialized countries have struggled to keep pace with increasing vehicle numbers through stricter controls on emissions. As demonstrated in figure 2.3, in a series of steps regulators have dramatically reduced allowable emissions of conventional pollutants from passenger vehicles. (For example, the next generation of vehicles is required to be over 90% cleaner than pre-control.)



Heavy-duty vehicles have also been

subject to increasingly strict emissions limits, sometimes with even more stringent standards set for urban buses. Recently regulators have begun to take aim at off-road vehicles, such as construction and farm equipment. Low-sulfur gasoline and diesel are the key to meeting emissions regulations for all these classes of vehicles.

All upcoming European, Japanese and U.S. emissions standards rely on availability of low-sulfur fuels. European and Japanese emissions standards distinguish between diesel and gasoline vehicles, allowing diesels to emit higher quantities of NO_x and PM and gasoline vehicles to emit higher quantities of CO and HC. (Passenger vehicle standards up to 2005 are included in table 2.1.) Euro 5 standards are expected to start closing the gap between vehicle types, requiring more substantial NO_x and PM reductions for model year 2010.

The new U.S. Tier 2 passenger vehicle standards are forcing development of advanced PM and NO_x control technologies for diesel vehicles. The standards are fuel neutral and do not distinguish between weight classes for passenger vehicles. Instead, Tier 2 offers a suite of standards from which automakers can select, provided their corporate average NO_x emissions are at or below 0.07 g/mi. (In table 2.1, bins 10 and 8 are the highest temporary and final standards.) Tier 2 will be phased in beginning in 2004, when sulfur levels in gasoline begin to drop. And the standards will be fully in effect in 2009, by which time low-sulfur fuels will be mandatory.

Table 2.1
Upcoming standards vs. pre-control emissions for passenger vehicles

grams/mile	PM		NO _x		HC		NO _x + HC		CO	
	Gas	Diesel	Gas	Diesel	Gas	Diesel	Gas	Diesel	Gas	Diesel
Pre-control (~1965)	.041	.655	3–4		7–11		10–15		80–120	
U.S. Tier 2 – bin 10	0.08		0.6		0.230		–		6.4	
U.S. Tier 2 – bin 8	0.02		0.2		0.125		–		4.2	
U.S. Tier 2 – bin 5	0.01		0.07		0.061		–		2.6	
Euro 3 – 2000	–	0.08	0.24	0.80	0.32	–	–	0.90	3.70	1.03
Euro 4 – 2005	–	0.04	0.13	0.40	0.16	–	–	0.48	1.61	0.81
Japan – 2005 (mean)	–	0.023	0.08	0.24	0.08	0.04	–	–	1.85	1.01

Upcoming heavy-duty diesel standards in Europe, Japan and the U.S. are dependent on availability of low-sulfur fuel. U.S. heavy-duty diesel standards will be phased in beginning in 2007, shortly after a 15 ppm sulfur cap for diesel fuel comes into effect, with full compliance of emissions standards required by 2010. Fifty ppm sulfur fuel will be required, and 10 ppm will be widely available, in Europe and Japan by the time 2005 standards come into effect.

The standards require an order-of-magnitude reduction in PM emissions from heavy-duty trucks. The U.S. is requiring an equivalent reduction in NO_x emissions, providing a substantial challenge for vehicle manufacturers.

Table 2.2
Heavy-duty diesel standards in the U.S., Europe, and Japan

	(g/kWh)	PM	NO _x	HC	CO
U.S.	2004	0.13	2.68	0.67	–
	2010	0.013	0.27	0.19	–
Europe	2000 (Euro III)	0.10	5.0	0.66	2.1
	2005 (Euro IV)	0.02	3.5	0.46	1.5
	2008 (Euro V)	0.02	2.0	0.46	1.5
Japan	2003	0.18	3.38	0.87	2.22
	2005	0.027	2.0	0.17	2.22

Initially manufacturers met emissions standards with simple catalytic converters in gasoline vehicles and engine improvements in diesel vehicles. Now, increasingly strict standards require more active catalysts, advanced technologies, and fully functioning emissions controls at all times. Further advances in control technology will also lead to substantial reductions in CO₂ emissions, by enabling use of more efficient engine designs which reduce fuel consumption by 15–45% (König et al. 2001). The export of these advanced technologies to developing countries is contingent upon the reduction of fuel sulfur levels.

Reducing sulfur levels in fuels can reduce vehicle emissions in three general ways: 1) by directly reducing SO₂ and sulfate PM, 2) by achieving better performance from emissions control systems in existing vehicles, and 3) by enabling new emissions control technologies and more efficient vehicle designs. The following sections discuss in detail the impacts of fuel sulfur on particular emissions control technologies for gasoline and diesel vehicles.

2.2 Gasoline Vehicles

Most gasoline vehicles currently in use are equipped with catalysts for the control of CO, HC, and NO_x, which are impacted by sulfur levels in the fuel. The sulfur impact increases in severity as vehicles are designed to meet stricter standards. Current sulfur levels in fuel are the primary obstacle in bringing advanced emission control technologies to market. These technologies will dramatically reduce conventional pollutants and also enable more fuel-efficient engine designs.

The following section describes the major issues relating to sulfur levels in gasoline:

- Sulfur increases emissions from three-way catalysts, the most common type of emission control technology in gasoline vehicles.
- The impact of sulfur increases with more efficient and advanced catalytic controls.

- Current sulfur levels present a significant barrier to the introduction of more efficient gasoline engine designs. These designs require advanced emission control technologies that are severely impacted by sulfur.

Current Three-way Catalysts

Worldwide, 85% of new gasoline vehicles are equipped with a three-way catalyst (TWC), which simultaneously controls emissions of CO, HC, and NO_x (MECA n.d.). Vehicles with TWCs must operate with a very exact air-to-fuel ratio, allowing just enough O₂ to fully oxidize the carbon and hydrogen in the fuel. The TWCs then use the NO_x in the exhaust to oxidize the CO and HC to CO₂ and H₂O, while the NO_x is reduced to N₂.

Sulfur levels in fuel impact 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 SO₂ during periods of fuel-rich, high-temperature operation, such as high acceleration (Maricq et al., *Gasoline*, 2002). 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 (WWFC 2000). Greater reductions have been demonstrated for low emission vehicles and high-speed driving conditions. Pollutant emissions appear to drop sharply as sulfur is reduced below 200 ppm, with emissions dropping even more steeply below 100 ppm (WWFC 2000).
- Sulfur inhibition in catalysts is not completely reversible. Although conversion efficiency will always improve with use of low-sulfur fuel, the efficiency of the catalyst does not always 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 (MECA 1998).
- 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 (MECA 1998). High regeneration temperatures also contribute to thermal aging of the catalyst. Sulfur raises the light-off temperature—the temperature at which catalytic conversion to take place—resulting in increased cold-start emissions (FEV 1999).
- 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 (Kittelsohn 1998). 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 less opportunities for desulfurization and catalyst regeneration.

Emerging Three-Way Catalysts

The benefits of reducing sulfur levels in fuels increase as vehicles are designed to meet stricter standards. These highly tuned engines come close to eliminating fuel-rich operation, which is required for desulfurization. The U.S. EPA tests new cars on a standardized 30 ppm sulfur fuel and estimates variable emissions increases with use of higher sulfur commercial fuels, depending on the vehicle's emissions standards. Emissions increases can be up to 13 times higher for certified "low emissions vehicles".

Table 2.3 Emissions change with sulfur increase from 30 to 330 ppm (Koupal 1999)

	NO _x	HC
Typical emissions increase	8–10%	14–24%
Increase for "low emissions vehicles"	42–134%	24–40%

One goal for the improvement of modern TWCs is to have the ability to store oxygen. This would allow for the efficient conversion of CO and HC during fuel-rich swings, including idle or acceleration periods. Effective storage materials—ones that can withstand the high temperatures of close-coupled catalysts (placed for rapid warm-up to improve cold-start conversion)—require the use of low sulfur fuels (Shelef and McCabe 2000).

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 100,000 miles in the U.S.). Many inefficiencies imposed by fuel sulfur jeopardize the ability of vehicles to meet these new stringent standards, including: reductions in conversion efficiency, additional fuel-rich operation requirements, increased catalyst light-off time, and reduced ability to store oxygen.

NO_x Storage Traps

Gasoline vehicles are under increasing pressure to raise fuel economy, and thus decrease CO₂ emissions. Lean-burn gasoline engine designs reduce fuel consumption by 15–20% (König et al. 2001). In order not to trade off higher fuel efficiency for increased pollutant emissions, lean-burn engines will require new aftertreatment technology for control of NO_x emissions. NO_x storage traps, the most efficient existing NO_x control technology for lean-burn engines, are much more dramatically impacted by fuel sulfur than TWCs. Because higher sulfur levels reduce the effectiveness of the traps and necessitate increased fuel consumption, ultralow sulfur gasoline is the key enabler for increasing the efficiency of gasoline vehicles.

The lean-burn engine increases the ratio of air to fuel, thus reducing fuel use. Lean-burn engines provide an automatic benefit for CO and HC control, which are formed in smaller amounts and can be more easily oxidized in the oxygen-rich exhaust. The challenge comes with control of NO_x in an oxygen-abundant environment. NO_x storage

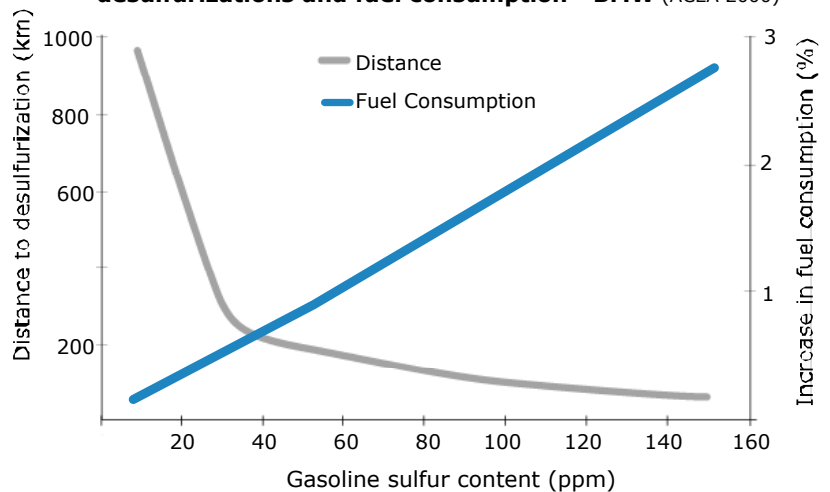
traps face fewer technical challenges in gasoline engines than in diesels, due to the fact that combustion temperatures can be more easily controlled. NO_x storage traps demonstrate over 90% efficiency in storage and conversion of NO_x to N₂, but require virtually sulfur-free fuels for efficient use (ACEA 2000).

Storage traps operate by incorporating basic oxides into the catalyst, which in turn reacts with the oxidized NO₂ in the presence of excess O₂ to form fairly stable nitrates. NO_x can be stored in this way during lean combustion (excess oxygen) conditions. As the storage medium approaches saturation, or whenever acceleration occurs, the engine will burn fuel-rich, generating CO and HC gases. This triggers the release of NO₂, which reacts, as in a TWC, to oxidize CO and HC to CO₂ and H₂O while simultaneously being reduced to N₂.

NO_x storage traps are highly efficient with sulfur-free fuels, but sulfur dramatically reduces their efficiency, lifetime, and durability (ACEA 2000). Sulfur dioxide competes with NO_x for storage space on the catalyst. The sulfates stored on the catalyst become more tightly bonded than the nitrates and can only be removed with prolonged fuel-rich, high temperature combustion. The original efficiency of the catalyst may never be fully recovered following sulfur poisoning, especially in highly tuned, low emission vehicles, which may not reach high enough temperatures for desulfurization (MECA 1998). Sulfur also precludes the use of more efficient catalyst materials that do not require such frequent regeneration for NO_x but are highly sensitive to sulfur (ACEA 2000).

The fuel-rich, high temperature combustion required to purge the catalyst of sulfur significantly reduces the fuel efficiency benefits of the lean-burn engine. When the efficiency of the catalyst drops from 95% to 90%, tailpipe NO_x emissions double and desulfurization occurs (ACEA 2000). With virtually sulfur-free fuel the NO_x storage trap will retain close to 95% storage efficiency without regeneration for over 5,000 miles. At 7 ppm sulfur, a drop to 90% efficiency occurs after 1,695 miles, necessitating desulfurization. As demonstrated in figure 2.4, at over 40 ppm the distance between desulfurization events drops to a little over 100 miles. This distance between desulfurization events relates directly to fuel consumption (ACEA 2000).

Figure 2.4
The effect of fuel sulfur on distance between desulfurizations and fuel consumption - BMW (ACEA 2000)



In Japan, commercially available NO_x absorber catalysts require the use of premium grade gasoline, which has

an average sulfur content of 6 ppm (EPA 1999; ACEA 2000). The full potential of this emissions control technology—one that dramatically increases fuel efficiency—will only be possible with ultralow sulfur gasoline.

2.3 Diesel Vehicles

Diesel engines offer some emissions benefits over gasoline. Conventional diesels typically use only 70% of the fuel of a comparable gasoline engine, significantly reducing per-mile CO₂ emissions. Like the lean-burn gasoline engines under development, diesels provide an automatic benefit for CO and HC control. When ample oxygen is available, fewer of these species are produced and they are easier to oxidize in the exhaust stream. Diesel fuel has the added benefit of low volatility, which virtually eliminates evaporative HC emissions. Average CO emissions from in-use diesel vehicles are an order of magnitude lower than for equivalent gasoline vehicles. Total HC emissions are almost one-third those of gasoline vehicles.

The primary concerns for diesel engines are NO_x and PM emissions. In the past, manufacturers have relied mostly on improved diesel engine technology to meet increasingly strict emissions standards. There is limited potential for further NO_x reductions through engine modifications (such as exhaust gas recirculation and injection timing retard) and emissions levels are not sufficient to meet upcoming U.S. standards. PM emissions, although dramatically lower than from early diesels, continue to be an order of magnitude or more higher than for properly functioning gasoline vehicles.

Recently, further improvements in diesel passenger vehicle engine calibration and design have cut NO_x and PM emissions by more than half, while maintaining a fuel economy advantage of 59% over average gasoline vehicles of equivalent weight (Stang, Koeberlein, and Ruth 2001). This puts the upcoming stringent emissions standards in the U.S. and other countries within reach, assuming use of advanced emissions controls. At an attainable diesel fuel economy of 70 mpg, light-duty trucks and sport utility vehicles will require approximately 60% post-combustion control efficiency for NO_x to hit bin 8, the least stringent of the U.S. Tier 2 standards, and approximately 85% efficiency to meet the bin 5, the average certification level. At 30 mpg, the required efficiencies will be 83 and 95% (Johnson 2002). Average efficiencies to meet Tier 2 standards for PM will be approximately 83% (Stang, Koeberlein, and Ruth 2001). Emerging engines are continuing to improve, reducing the levels of NO_x and PM control needed for diesel passenger cars to as low as 30 to 50% (Johnson 2003).

Because of their fuel efficiency and greater power, diesel engines have been strongly favored for heavy-duty applications. While past regulations have focused primarily on light-duty and passenger vehicles, recent regulations in the U.S., Europe, and Japan have targeted heavy-duty diesel vehicles as well. Emissions standards are also beginning to be extended to off-road engines, such as construction equipment and generators. Historically, these have faced little regulation and used the highest sulfur diesel fuels.

New emissions control technologies under development have the potential to allow all types of diesel engines to meet stricter emissions standards, while maintaining and even

increasing their fuel-efficiency advantage. A variety of particulate filter designs are being refined, and two types of advanced NO_x control systems are being developed. Ongoing research has been encouraging, thus the focus now is on cost reduction, system optimization, and long-term durability. While research to promote sulfur tolerance continues, it appears that all of these aftertreatment technologies require low or ultralow sulfur fuels to achieve their maximum benefit.

Without Emissions Controls

In diesel vehicles, reducing sulfur not only reduces SO₂ emissions, it also significantly reduces particle emissions. In the oxygen-rich exhaust of diesel vehicles several percent of the SO₂ formed during combustion is oxidized to SO₃, which dissolves in the water vapor present to form sulfuric acid (H₂SO₄) vapor. H₂SO₄ is one of the few substances that is capable of homogenous nucleation. This appears to be a major mechanism for initiation of ultrafine particle formation in diesel exhaust, producing newly formed particles of around 1 nm (Shi and Harrison 1999). Even though sulfate particles account for only a small fraction of particle volume or mass, they account for a large fraction of particle numbers. And sulfate nanoparticles provide a relatively large surface area onto which HC species condense, resulting in particle growth and increasing particle toxicity (Shi and Harrison 1999).

Even without the benefit of additional emissions controls, reducing sulfur levels in diesel fuel reduces both PM emissions and the carcinogenic and toxic effects of the particulate matter formed (Bünger et al. 2000). A variety of tests have supported this conclusion. In Denmark, a reduction in fuel sulfur levels from 440 to 0.7 ppm led to a 56% reduction in numbers of particles emitted from diesel vehicles (Wåhlin et al. 2001). Tests on Japanese diesel trucks have demonstrated that a reduction in fuel sulfur from 400 to 2 ppm cuts the mass of PM emissions in half (WWFC 2000). In heavy-duty diesel trucks in the U.S., a decrease in fuel sulfur from 368 to 54 ppm yielded a 14% reduction in PM emissions (MECA 1999).

Table 2.4 Sulfur impact on PM emissions

Study Location	Sulfur Range (ppm)		% PM Reduction
	high	low	
Denmark	440	0.7	54
Japan	400	2	50
U.S.	368	54	14

In addition, SO₂ emissions can lead to secondary particle formation—particles that form in the ambient air. EPA models predict that over 12% of the SO₂ emitted in urban areas is converted in the atmosphere to sulfate PM (Darlington and Kahlbaum 1999). This means that diesel and gasoline on-road vehicles in the U.S. may be responsible for up to eight times the PM emissions that are accounted for in inventories for direct diesel emissions (EPA 2001). Urban areas would benefit most from reductions in SO₂ emissions, as polluted urban air has higher concentrations of the constituents that catalyze the SO₂-to-sulfate reaction. Even with existing vehicle stocks, reductions of fuel sulfur levels would have a significant impact on primary and secondary PM concentrations in urban areas.

Diesel Oxidation Catalysts

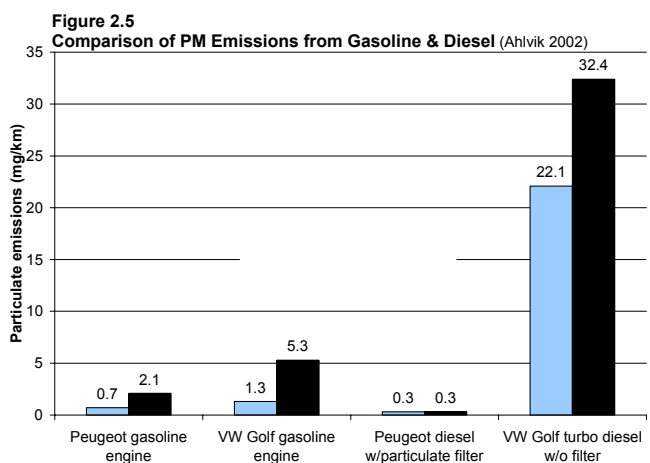
Diesel oxidation catalysts (DOCs) are the most common aftertreatment emissions control technology found in current diesel vehicles. Although not as widespread as the TWC in gasoline vehicles, DOCs are very similar to the earliest catalysts used for gasoline engines. Oxidation catalysts work by oxidizing CO, HC and the soluble organic fraction of the PM to CO₂ and H₂O in the oxygen rich exhaust stream of the diesel engine.

When sulfur is present in the fuel, DOCs also increase the oxidation rate of SO₂, 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 SO₂ in the exhaust to sulfate (VWFC 2000). With low sulfur fuel, a DOC can lead to a 15–31% reduction in PM emissions (with sulfur levels reduced from 368 to 54 ppm)—up to double the emissions benefit of low sulfur fuel alone (CARB 2000). At high temperature operation, generated under high speed or load operating conditions, the DOC accelerates oxidation of SO₂, increasing the formation of sulfate particles. Under these conditions, use of 350 ppm sulfur fuel almost triples the PM emissions over engine-out levels. With 150 ppm fuel this effect is much more muted, with only 15% increase in PM emissions (DECSE 2001). Most of the increase is due to sulfate particles, meaning that a DOC, when used with high-sulfur fuel, can dramatically increase emission of the smallest, potentially most damaging particles (Maricq et al., *Diesel*, 2002). Sulfur also delays the DOC light-off, increasing cold-start emissions (ACEA 2000; DECSE 2001).

Diesel oxidation catalysts will continue to play an important role in integrated aftertreatment and retrofit systems. However, once low and ultralow sulfur fuels are available, advanced technologies for control of NO_x and PM will provide much more effective emissions reductions. These advanced technologies will be required for diesel engines to meet upcoming standards in the U.S., Europe, and Japan.

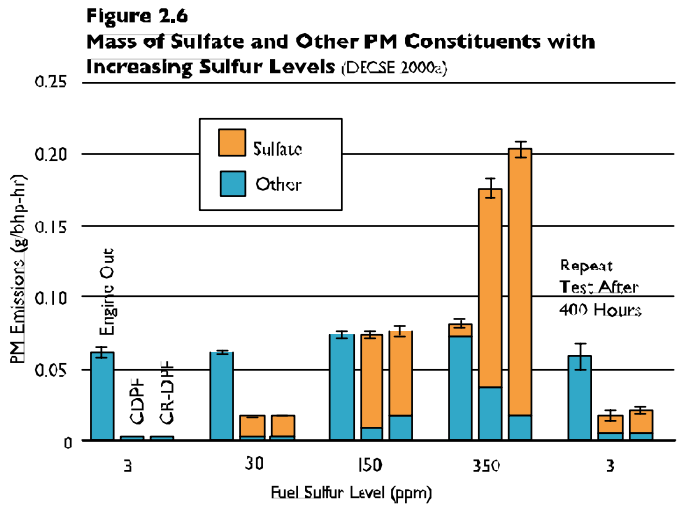
Diesel Particulate Filters

Diesel particulate filters (DPFs) already reliably demonstrate over 95% efficiency with ultralow sulfur fuel use, and further advances in performance and durability are expected. As figure 2.5 demonstrates, diesel filters are capable of reducing total number and mass of particle emissions below those of gasoline engines (Ahlvik 2002). Ceramic filters for use on diesel engines have been commercially available for nearly 20 years, but development actively continues for new fiber materials and filter designs. 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, without human intervention,

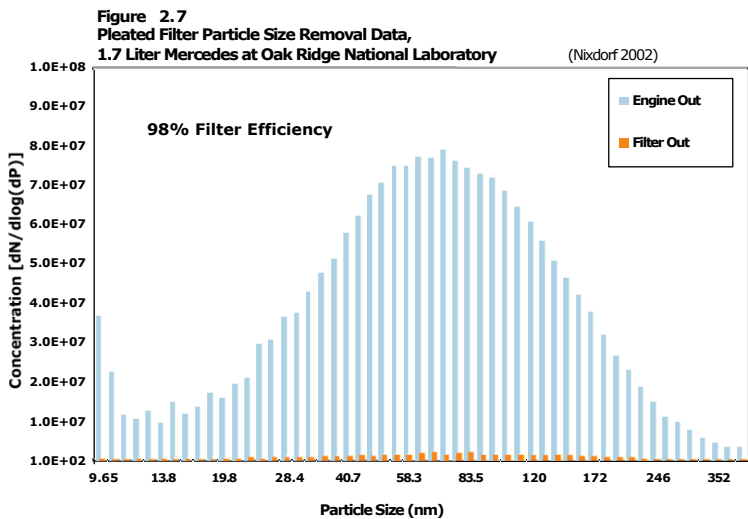


before reaching capacity in order to maintain vehicle performance and fuel and filter efficiency. Sulfur reduces the efficiency of DPFs and can lead to the formation of sulfate PM.

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, as demonstrated in figure 2.6, 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 ultralow sulfur fuels, but recovery takes time due to sulfate storage on the catalyst.

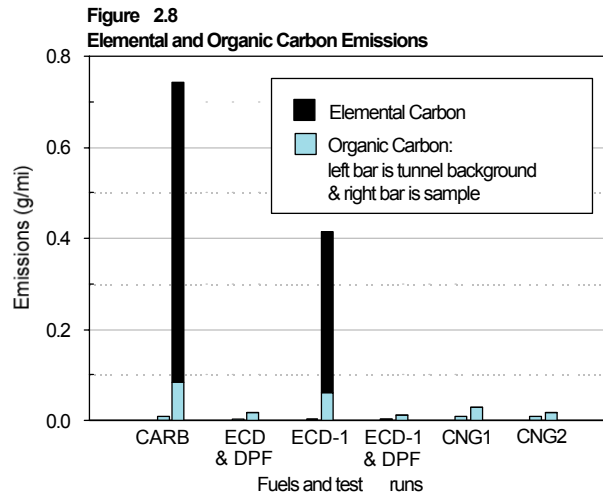


Sulfur also increases the required temperature for regeneration of the filter. In moving from 3 to 30 ppm sulfur fuel, the exhaust temperatures required for regeneration increase by roughly 25°C. The CDPF requires consistently higher temperatures but holds stable above 30 ppm, while the CR-DPF requires ever-increasing temperatures. (DECSE 2000a). In order to meet upcoming heavy-duty truck regulations in the U.S., at least 70% control of PM emissions will be required, necessitating fuel sulfur levels of 30 ppm or less (DECSE 2000a). But, as the Manufacturers of Emissions Control Association (MECA) points out, due to the 20–30°C increase in regeneration temperature from 3 to 30 ppm sulfur fuel, a sulfur limit of 15 ppm would be required in order to engineer and optimize the engine/filter system for ambient temperatures and all applications (MECA 2000).



With ultralow sulfur fuel use, DPFs provide effective control of all sizes of particles, including the smallest, which are considered most dangerous for human health (see figure 2.7). Diesels with particulate filters generate comparable PM emissions to Compressed Natural Gas (CNG) vehicles, which are often promoted as a low-emission alternative to diesel (Gautam et al. 2002; Smith 2002). Figure

2.8 demonstrates that a vehicle using ultralow sulfur fuel (ECD) and a DPF may, in fact, reduce total PM emissions below a CNG vehicle. In addition, this figure demonstrates that elemental carbon, also known as black carbon, is virtually eliminated by a DPF, as opposed to use of low-sulfur fuels (CARB and ECD-1) alone (Smith 2002; Gautam et al. 2002). Elemental carbon appears to be responsible for more than 90% of light absorption by atmospheric aerosols and has recently been implicated as a significant factor in global warming. All this highlights the potential for the DPFs, along with low-sulfur fuels, to reduce greatly the warming impact of diesel vehicles (Horvath 1993; Jacobson 2002).



In addition, particulate filters provide effective control of CO and HC emissions. DPFs greatly reduce emissions of benzene, polycyclic aromatic hydrocarbons, alkenes such as 1,3-butadiene, and other unregulated but harmful gaseous pollutants (Ahlvik 2002; Gautam et al. 2002; Smith 2002). Efficiency for control of CO is between 90 and 99%, and of HC is between 58 and 82%. This is one to two orders of magnitude lower than emissions of these pollutants from gasoline and CNG vehicles (Ahlvik 2002; DECSE 2000a).

NO_x Control Systems

Most diesel engines rely on injection timing retard to meet the most stringent 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 (about 2%), but this results in a 7% loss in fuel economy (EPA 2000b).

A variety of NO_x control technologies are being developed to allow diesel engines to meet more stringent upcoming standards. NO_x emissions reductions of up to 12% have been measured with DPFs but these reductions are neither reliable nor sufficient to meet tightening regulations (NYCTA 2001; Smith 2002). Exhaust gas recirculation (EGR), which is only indirectly impacted by fuel sulfur, is expected to play a prominent role in near-term NO_x control strategies. Two very different technologies—NO_x adsorbers and selective catalytic reduction (SCR) systems—are the most likely alternatives for further NO_x control.

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.

EGR is expected to be the leading technology used to meet the 2007 interim Tier 2 standards in the U.S., and upcoming passenger vehicle standards in Europe and Japan (Johnson 2003). The fuel economy impact of EGR is much less than injection timing retard, allowing NO_x emissions to be cut in half with little or no impact on fuel economy. EGR has also been effectively employed as part of a diesel retrofit system, in conjunction with a DPF. In this application, relatively simple engine modifications have achieved 40–60% reductions in NO_x emissions from existing vehicles (Chatterjee 2002).

NO_x Adsorbers: NO_x adsorbers are also known as NO_x storage catalysts or lean NO_x traps. They work by the same principle as the lean NO_x control system described in section 2.2 for fuel-efficient, lean-burn gasoline engines. NO emissions from the engine are oxidized to NO₂ and then stored as solid nitrate. Before the adsorbent becomes fully saturated a change in the air-fuel ratio produces fuel-rich exhaust. This triggers the release of NO₂, resulting in the reduction to N₂ over precious-metal catalyst sites. Dual-leg NO_x adsorber systems have demonstrated 95% efficiency in conversion of NO_x to N₂, with a nominal fuel penalty of 1.5% (Faulkner 2002).

Unfortunately, the NO_x traps also very efficiently store sulfur, following an almost identical reaction path as nitrogen. SO₂ emissions, stored as solid sulfates, are much more tightly bound to the substrate and require higher temperatures to remove. Over a period of time, fuel sulfur, even at low levels, fills the capacity of the trap, causing NO_x storage and conversion efficiency to decline significantly.

The regeneration of the trap and the release of stored sulfur present an additional technical hurdle for diesel engines, due to the fact that exhaust temperatures are lower and less controllable than in gasoline engines. The higher temperatures required for regeneration are also contrary to EGR systems, which would otherwise complement this aftertreatment technology. And turbocharged diesel engines, in particular, cannot achieve the temperatures required for desulfurization under urban driving conditions. Furthermore, diesel engines have a limited ability to operate fuel-rich, due to the unacceptable levels of smoke and HC emissions which result from the increased fuel-to-air ratio.

In order to overcome the desulfurization hurdle and to balance conversion efficiency with fuel penalty, various configurations of the NO_x adsorber system have been developed and tested. A dual-leg system, with duplicate adsorbers and particle filters, alternates the exhaust flow between legs, allowing the receiving leg to continue storing NO_x while fuel is injected into the other leg for regeneration. A simpler single-leg system offers significant savings, cutting in half the high capital costs associated with precious-metal catalysts, but presents greater challenges in terms of engine management and conversion efficiency. In a single-leg system with a bypass, fuel is injected while the exhaust stream is significantly

Table 2.5 Selected fuel economy & efficiency results for heavy-duty applications (Hakim, Hoelzer, and Liu 2002)

	Single leg		Single leg w/ bypass		Dual leg	
Conversion Efficiency (%)	78	88	80.4	80.4	94	90
Fuel Economy Penalty (%)	1.2	2.05	1.5	1.3	1.9	2.3

reduced, allowing a small amount of untreated exhaust to escape during regeneration. The single leg with bypass delivers some of the benefits and challenges associated with each of the other configurations. As demonstrated in table 2.5, in steady-state experiments, high conversion efficiencies and nominal penalties were found for all three configurations (Hakim, Hoelzer, and Liu 2002).

With availability of low-sulfur fuel, the single-leg system is well matched to passenger vehicles and other applications with low load levels. For heavy-duty applications at full load, the fuel economy penalty can increase substantially, from a maximum of around 4% at part load to almost 12%, with a corresponding decrease in NO_x conversion efficiency (Faulkner 2002). A single-leg system with bypass may provide a lower cost solution to reduce fuel penalties. The dual-leg system has demonstrated stability, durability, and consistent efficiency over 90%, with a fuel penalty of only approximately 2% (Parks 2002; EPA 2000b).

The major technical challenges facing NO_x adsorbers are regeneration and desulfurization control logics under transient conditions. Optimizing the system for maximum efficiency and minimum fuel penalty, already a challenge, is complicated by variability in operation and durability concerns (Parks 2002).

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. The engine is tuned for low PM and high fuel economy. Due to less stringent PM standards in Europe, this eliminates the need for a DPF, but further controls are required for NO_x. The regulations can be met with an SCR system with 65–80% NO_x conversion efficiency. The fuel economy benefits, even accounting for the reductant, can be as high as 7% (Johnson 2002).

SCR uses a reducing agent, injected into the exhaust gas before the catalyst, to achieve higher rates of NO_x conversion in the oxygen-rich exhaust. Typically ammonia has been used as the reducing agent in SCR systems for stationary sources and urea has been used for mobile source SCR. Stationary systems have over 90% conversion efficiency and are widely used for diesel generators and power production. While high levels of efficiency can also be achieved for mobile sources, SCR use in vehicles presents several obstacles. With the variable power required by vehicle systems, it can be difficult to achieve precise dosing of urea. This, in turn, necessitates the use of a downstream oxidation catalyst to prevent the unreacted urea from being emitted as ammonia (a pollutant with chronic and acute human health impacts). In addition, two issues—reliability of refilling the urea and infrastructure redesign for co-fueling—present obstacles for wide-spread passenger vehicle applications. Ensuring proper refueling of urea may be more practical in heavy-duty fleets.

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 (EPA 2000b; Khair 2002).

NO_x removal efficiencies of 80 to 90% have been demonstrated for urea-based SCR systems in light- and heavy-duty vehicles over a wide range of test conditions (Hammerle 2002). A great deal of progress has been made in efficiently achieving Tier 2 standards in the U.S. for trucks and sport utility vehicles using SCR systems. As can be seen from figure 2.9, the fuel economy advantages are tremendous compared to typical gasoline vehicles. And progress continues to be made



in meeting more stringent standards with increased fuel economy (Aneja et al. 2002).

Plasma-assisted SCR systems, which are not sulfur sensitive, are being tested with a variety of reducing agents, including diesel fuel and methanol. These systems have the potential to negate both refueling and sulfur-sensitivity concerns. However, despite more than ten years of research, they are still in early stages of development (Slone, Bhatt, and Puchkarev 2002; Aardahl 2002).

Integrated Systems

Upcoming regulations will require integrated systems for control of both NO_x and PM, thus necessitating low-sulfur levels required by the most sensitive technology. In areas where ultralow sulfur diesel is available, Toyota plans to introduce a new clean diesel system in 2003. Toyota's Diesel Particulate NO_x Reduction (DPNR) system incorporates the NO_x adsorber material into the particulate filter to reduce NO_x, PM, HC, and CO emissions by more than 80% (Johnson 2003). The system includes a fuel injection nozzle in the exhaust port to create a rich environment for the release and reduction of NO_x to N₂. Sulfur in the fuel, which is also captured and stored as SO₂ by the adsorber material, increases the fuel penalty associated with the system. This is due to the fact that more fuel must be injected to reach the high catalyst bed temperature of 600°C required for release of the stored SO₂.

Other integrated systems are being developed for use with low and ultralow sulfur fuels. An integrated DOC/SCR/DPF system on a direct-injection diesel passenger vehicle achieved 90% NO_x control efficiency and 98% control of PM (Hammerle 2002). An integrated EGR/DPF/SCR system demonstrated the ability to meet upcoming heavy-duty standards in the U.S., with a 96% reduction in NO_x and a 90% reduction in PM (Khair 2002). Integration of NO_x adsorbers with DPFs also shows promise, with around 87% efficiency for NO_x control and over 90% for PM control (Johnson 2002).

Retrofit Technologies

Heavy-duty vehicles last a long time. The expected median lifetime for heavy trucks from model year 1990, the most recent year estimated, is 29 years, and the median age for transit buses is 16 years (BTS 2001; Davis and Diegel 2002). In the U.S., early NO_x and PM standards for heavy-duty vehicles (circa 1984) were 50 times higher than upcoming standards (BTS 2001). Plus, emissions tend to increase as vehicles age. This means that the full emissions benefit of new standards will not be realized for many years. Programs to reduce emissions from older vehicles are therefore crucial to near-term efforts to improve air quality.

Where low-sulfur fuels are available, retrofit technologies can dramatically reduce emissions from existing vehicles. Oxidation catalysts and particulate filters for heavy-duty diesel vehicles are the most common retrofit technologies. Recent projects have also included EGR in combination with a DPF, for simultaneous control of NO_x and PM.

Diesel oxidation catalysts are the easiest, most flexible, and least expensive retrofit option. With use of reduced or low sulfur fuels, a DOC can achieve a 20 to 50% reduction in total PM, an over 90% reduction in CO and HC, and an over 70% reduction in toxic HC (Johnson 2000). While DOCs are less sensitive to sulfur than particulate filter technology, increasing fuel sulfur levels do result in reduced conversion efficiency of the catalyst and can lead to increased sulfate formation, resulting in even higher particle emissions than without a catalyst.

DPFs are also an easy, effective retrofit option but require at least low sulfur fuel use. (For maximum benefit, ultralow sulfur fuel is required, especially for retrofit programs with largely urban-use vehicles, tending to have lower exhaust temperatures.) Retrofit programs using CR-DPF and CDPF systems in the U.S. and Europe have demonstrated an 80–100% reduction of toxic contaminants found in diesel exhaust, an 85 to over 95% reduction in particle mass, and a 70 to over 90% reduction in HC emissions, with an insignificant impact on fuel economy (Friedrich 2000). Retrofit diesel buses are as clean as, or cleaner than, CNG buses, reliably delivering lower emissions of PM, CO, HC, and carbonyls, and comparable NO_x emissions (Johnson 2000).

Through Sweden's Clean Cities program, availability of 10 ppm sulfur fuel has enabled over 6,500 buses and trucks to be equipped with DPFs (MECA n.d.). The program was modified in the beginning of 2002 to add a NO_x control option to the standard retrofit (DieselNet 2002). There and in Hong Kong, over 1,200 trucks and transit buses have been retrofit with a combination of EGR and a patented type of CR-DPF, a continuously regenerating trap. These systems have proven to be durable and effective, with no impact on fuel economy. They have achieved reductions of over 40% for NO_x emissions and over 90% for PM, HC and CO (Chatterjee 2002). Enabled by ultralow sulfur fuel availability, more than 10,000 heavy-duty vehicles have been equipped with particulate filters in Europe alone, with a combined 5,000,000 miles traveled (Friedrich 2000). Tokyo, New York City, and California also all have DPF retrofit programs aimed at heavy-duty urban vehicles.

2.4 Summary

Table 2.6 provides a summary of available diesel and gasoline emissions control technologies that are impacted by fuel sulfur. Any level of reduction in fuel sulfur will lead to commensurate reductions in SO₂ emissions. Additional benefits for other pollutant emissions will begin to be realized as sulfur levels are reduced below 150 ppm, with more substantial benefits and use of advanced emission control technologies possible below 50 or 15 ppm.

Table 2.6 Sulfur Impacts on emissions Control Technologies

Technology	Pollutants Targeted	Sulfur Levels	Benefits	Applications
Gasoline Vehicle Technologies				
TWC	NO _x , HC, & CO	Below 50 ppm recommended	<ul style="list-style-type: none"> • Reductions from 18% for HC & CO and 9% NO_x with 50 ppm. • Up to 55% for HC & CO and 77% for NO_x with 15 ppm. 	Existing vehicles.
Advanced TWC	NO _x , HC, & CO	Below 30 ppm recommended	<ul style="list-style-type: none"> • Increasing emissions benefits, durability and fuel economy. 	New and upcoming vehicles.
NO _x Trap	NO _x	Below 15 ppm required	<ul style="list-style-type: none"> • 90-95% reduction in NO_x from uncontrolled emissions. • Allows for significant increases in fuel economy. 	Future vehicles, required to meet GHG reduction targets.
Diesel Vehicle Technologies				
No Controls	PM	Below 50 ppm recommended	<ul style="list-style-type: none"> • PM reduction of 14% for 50 ppm and 50% for 15 ppm. 	Existing vehicles.
DOC	PM, HC, & CO	At least below 150 ppm. Below 50 ppm, recommended.	<ul style="list-style-type: none"> • Reductions of 90-100% for HC and 88-99% for CO. • Reductions of 15-31% for PM with use of less than 50 ppm. 	Useful as a low-cost retrofit and in integrated control systems in new vehicles.
DPF	PM, HC, & CO	Below 50 ppm required. Below 15 ppm highly recommended.	<ul style="list-style-type: none"> • Reductions of 90-99% for PM with use of less than 15 ppm. • Efficiency drops to ~50% with 50 ppm. • Reductions of 58-82% for HC and 90-99% for CO. 	Critical retrofit and new vehicle technology.
NO _x Adsorber	NO _x	Below 15 ppm required.	<ul style="list-style-type: none"> • Reductions of 78-94% for NO_x 	New light- and heavy-duty vehicles.
SCR	NO _x	Below 50 ppm required.	<ul style="list-style-type: none"> • Reductions of 80-90% for NO_x 	Likely for heavy-duty but passenger vehicle use also being explored.

3. THE IMPACT OF SULFUR ON GREENHOUSE GAS EMISSIONS

Low-sulfur fuels will enable huge leaps in fuel efficiency, translating directly into reductions in CO₂ emissions. Currently available technology could dramatically reduce both greenhouse gas and conventional pollutant emissions. Plus, research continues on how to make zero-emission transportation technologies, such as the hydrogen fuel cell, economically viable. Sulfur is a major obstacle for technologies to both reduce and eliminate greenhouse gas emissions.

Sulfur levels in fuel have a range of direct and indirect impacts on greenhouse gas emissions. Sulfur prevents the efficient functioning of certain types of catalysts, which in turn translates into higher methane emissions from oxidation catalysts and higher CO₂ emissions from more advanced technologies. Sulfur also impedes the viability of emissions control technologies in several arenas: fuel-efficient gasoline engine designs, traditional diesels as a fuel-efficient alternative, and advanced or hybrid diesels. And fuel cells—the most promising long-term solution for eliminating greenhouse gas emissions—will require sulfur-free fuels in order to function.

3.1 Gasoline Vehicles

Methane and N₂O are two potent greenhouse gases emitted by gasoline vehicles. Methane is difficult to combust, resulting in emissions levels largely determined by the efficiency of the catalyst. As discussed above, sulfur impedes the full functioning of the TWC by taking up space on the catalyst and increasing the light-off and regeneration temperatures required for efficient functioning. Reduction of sulfur levels in the fuel from 330 ppm to less than 1 ppm would reduce methane emissions from gasoline engines by 20 to over 50%. The same reduction of sulfur levels would reduce N₂O emissions by 70 to almost 90% (AECC 2000).

There are many design features that could increase fuel economy, and thus reduce CO₂ emissions, of gasoline vehicles. The most dramatic advance in engine design, which could increase fuel efficiency by up to 25%, would be direct-injection gasoline engines using fuel-lean combustion. While this type of engine design has natural benefits for engine out NO_x, HC, and CO emissions, it requires a more advanced catalyst system for further reduction of NO_x in the oxygen-rich exhaust stream. It may also require control of PM emissions, which have thus far not been a concern for gasoline vehicles. Both types of aftertreatment technology require low-sulfur fuels.

Fuel-lean NO_x storage catalysts or traps, discussed in section 2.2, require ultralow sulfur fuel to achieve maximum efficiency. As sulfur levels rise, more frequent and longer fuel-rich operation is required to regenerate the traps and recover their efficiency. Even with 50 ppm sulfur fuel, the potential gains in fuel economy would be almost cut in half.

3.2 Diesel Vehicles

Because of their increased fuel economy, current diesel engines can reduce CO₂ emissions by 30%, over conventional gasoline vehicles (Stang 2001). With advanced engine designs, such as turbo direct-injection, diesels could achieve up to 45% reduction

in CO₂ emissions (König et al. 2001). In order to meet new emissions standards for conventional pollutants in the U.S. and Europe, both current and advanced diesel engines will require advanced exhaust aftertreatment. All of these technologies will be impacted by fuel sulfur levels to some degree, and in some cases fuel-sulfur levels are the primary obstacle to wide-scale commercialization. In addition, as described in section 2.3, due to the increased energy needs associated with desulfurization and regeneration, higher sulfur levels can increase fuel consumption of vehicles using DPF and NO_x adsorber technologies. With use of low-sulfur fuel, particulate filters can also greatly mitigate the warming impact of diesel vehicles. This is done by virtually eliminating elemental carbon emissions, identified as a significant factor in climate change.

3.3 Fuel Cell Vehicles

In the future, fuel cells could drastically reduce emissions of all transportation related pollutants of concern. Current fuel cell technology requires a clean fuel gas composed of pure hydrogen. In the near term this fuel is expected to be generated by reforming natural gas or petroleum fuels. Several scenarios are being considered: central reforming, with distribution of hydrogen; on-site reforming at distributed refueling stations; and on-board vehicle reforming, using diesel, gasoline or methanol fuels as the feedstock. Because sulfur significantly degrades the performance of fuel cells and most reforming catalysts, any of these scenarios will require a virtually sulfur-free gas or liquid fuel feedstock.

4. REDUCING SULFUR LEVELS IN GASOLINE AND DIESEL FUEL

Recently, the refining industry has made a great deal of progress towards developing more active catalysts and more economical processes to remove sulfur from gasoline and diesel fuel. At the same time, refineries throughout the world have demonstrated that low-sulfur fuels can be affordably produced with current technology. For example, California refineries are producing gasoline which contains 20 ppm sulfur on average (EPA 1999), despite the high sulfur content of the California and Alaska crude oils used as feedstock (up to 11,000 ppm). And due to incentives and regulations, 10 ppm sulfur diesel has been commercially available in Sweden for several years.

The capacity of refiners to reduce fuel-sulfur levels further depends on a number of factors: the sulfur level in the fuels currently produced; the refinery configuration and amount of excess desulfurization equipment on hand; the quality of crude oil being used; and the quality and types of products being produced. With a reasonable initial investment refiners can move from high-sulfur fuels to reduced sulfur fuels. An additional investment is required to achieve low or ultralow sulfur products.

This chapter briefly reviews technology options for low-sulfur fuel refining (explored further in Appendix B). It also discusses the capital and incremental costs associated with refining upgrades to reduce sulfur levels, and compares these costs to the many benefits that low-sulfur fuels can impart.

4.1 Technology Options

Crude oil has an average sulfur content of anywhere from 100 to 33,000 ppm, and the sulfur content and types of sulfur compounds vary greatly within a crude supply. As the density of the crude oil increases, sulfur levels and the difficulty of sulfur removal also tend to increase. Generally, refineries are built to process either premium priced “sweet” crude, with lower sulfur content, or “sour”, higher sulfur crude oil. While refiners gain some advantage in using higher quality crude, the price premium more than cancels the cost advantage for low-sulfur fuel refining.

Straight-run gasoline—the fraction of the crude that falls naturally within the appropriate density range—is one of the lightest portions of the crude and tends to have some of the lowest sulfur levels. More than 90% of the sulfur content, but generally less than 50% of the total gasoline supply, is contributed by heavier feeds, which are cracked in the fluid catalytic cracking (FCC) unit (EPA 1999). While the straight-run diesel feed tends to have relatively high sulfur content, much of the remaining sulfur comes from the FCC unit. A smaller portion of the diesel and gasoline comes from other thermal or catalytic refining units. These units convert heavy portions of crude oil to lighter liquid fuels.

Hydrotreating is the most common technology used by refineries to remove sulfur from gasoline and diesel feedstocks. Hydrotreating involves adding hydrogen to assist in removing sulfur. This process tends to improve diesel quality by raising the cetane number, and decrease gasoline quality by lowering the octane number (see Appendix B

for more detail). Refiners can treat all of the feed to the FCC unit, reducing sulfur contents of both diesel and gasoline feeds at the same time. But this is not sufficient to achieve low-sulfur products and is capital intensive, requiring large reactor volumes and expensive hydrogen and energy inputs.

Hydrotreating specific gasoline and diesel feedstocks is a more common, and is generally a lower cost solution. Many of the processes and catalysts recently developed for hydrotreating of gasoline feedstocks have greatly reduced the octane loss. These processes tend to operate at less severe conditions than conventional hydrotreaters. This helps to preserve gasoline yield and to lower capital expenditures, operating costs, and CO₂ emissions.

While hydrotreating improves diesel quality, diesel desulfurization is more challenging due to a higher initial sulfur content and more difficult to remove sulfur compounds in the feedstock. Hydrotreating diesel feedstocks for a low-sulfur product requires a larger reactor volume, longer processing times, and substantial hydrogen and energy inputs. While low-sulfur diesel can be produced with conventional hydrotreating technology, making the process cost-effective is difficult. However, more active catalysts and recent developments in fixed bed hydrotreater technology have reduced the time spent in the reactor, thus lowering the required reactor volume and operating costs.

Sulfur adsorption is a recently commercialized technology that reduces costs for removal of sulfur from gasoline. Laboratory tests have also shown that the technology may be appropriate for diesel desulfurization. Rather than adding hydrogen, sulfur is removed through the chemical process of adsorption. Adsorption does not require substantial hydrogen inputs and takes place at much lower temperature and pressure than hydrotreating technologies, thus requiring lower energy inputs. Sulfur adsorption significantly reduces operating costs, and potentially capital costs as well.

All of these desulfurization technologies are described in more detail in Appendix B. As the demand for low-sulfur fuels expands, new developments and cost reductions in desulfurization processes will continue.

4.2 Costs Associated with Desulfurization

As the global demand for low-sulfur fuels increases, new technologies are emerging that promise to lower substantially the cost of desulfurization. Most of the cost studies cited below do not include the emerging, potentially lower-cost technologies in their estimates. As a result, the costs described here likely overestimate the actual capital and ongoing costs of wide-scale refinery upgrades to reduce sulfur levels.

The costs of achieving low and ultralow sulfur levels depend on the sulfur standards being met. The following studies are arranged from highest to lowest cost, mirroring the sulfur standards in the regions studied. The incremental costs of achieving national low-sulfur diesel standards throughout Asia (where current standards may be as high as 10,000 ppm) appear quite high. But as demonstrated in the subsequent study, which provides a more detailed and nuanced look into refining in China, costs may be



substantially lower and more stringent standards for urban areas may be a cost-effective way to transition to low-sulfur fuels. As studies and tax incentives in Europe and the U.S. have demonstrated, once reduced sulfur levels have been achieved, a relatively easy transition can be made to ultralow sulfur fuels. Figure 4.1 indicates the range of costs associated with reducing sulfur levels in fuels. Costs are derived from the studies described in more detail below. The average, near-term, or official estimate is used as the cost-point, with error bars to indicate the outliers or the range indicated.

A report prepared for the Asia Development Bank estimated the costs associated with lowering sulfur levels in diesel fuel throughout Asia. The sulfur standards in the countries included ranges from 500 to 10,000 ppm for diesel, with an average standard of 2,000–3,000 ppm. The study found that costs are roughly constant, at around 4¢ per gallon, for product levels ranging from 1,000 to 250 ppm sulfur. There is a gap in sulfur levels considered, over which costs more than double. Costs remain roughly constant, at just over 10¢ per gallon, for 10 ppm and 50 ppm sulfur diesel fuel (Enstrat 2002). The estimates in the Asia Development Bank study are roughly double the near-term costs reported in the Trans-Energy study for China.

The Trans-Energy study modeled the costs of improving transportation fuel quality in China. Starting from a baseline of 800 to 1,000 ppm sulfur gasoline and 2,000 ppm sulfur diesel, the costs varied depending upon the final fuel quality achieved and the length of time over which the investment was stretched.

- Increases in diesel fuel costs for the 2005 scenario ranged from 1.9¢ per gallon, to achieve nationwide supply of 500 ppm sulfur diesel, to 2.1¢ per gallon for 350 ppm sulfur diesel. From a 500 ppm sulfur baseline, the cost rose to only 2.0¢ per gallon to provide higher quality 50 ppm sulfur fuel for up to 35% of total supply, intended for polluted urban areas. All the 2010 scenarios were priced at 3.2¢ per gallon to achieve a baseline of 350 ppm sulfur diesel, with up to 40% of the country receiving 50 ppm sulfur diesel.
- Costs associated with gasoline desulfurization were roughly half the costs for diesel in all scenarios. For 2005, increases in gasoline costs ranged from 0.8¢ per gallon, to achieve nationwide supply of 500 ppm sulfur gasoline, to 1.1¢ per gallon to reduce sulfur levels to 150 ppm. All of the 2010 scenarios for gasoline cost 1.5¢ per gallon for a 150 ppm sulfur gasoline baseline and up to 40% of the country receiving 50 ppm sulfur gasoline (Trans-Energy 2002).

The U.S. EPA found that desulfurization costs associated with meeting the new sulfur standard for diesel will be roughly twice the cost of meeting the standard for gasoline. In the U.S., current sulfur levels range from 300 to 350 ppm in gasoline (with the exception of California). The EPA found that average costs to meet the new, phased-in 30 ppm sulfur standard for gasoline will be over 1.9¢ per gallon in 2004 but will decline to less than 1.7¢ per gallon in 2010, as lower cost technology becomes more viable (EPA 1999). On the other hand, the costs of meeting the new 15 ppm standard for on-road diesel, from the baseline of a 500 ppm sulfur standard, are expected to start at a national average of 4.3¢ per gallon and increase to 5¢ per gallon in 2010 (EPA 2000b). Current non-road fuels in the U.S. can have sulfur levels as high as 3,000 ppm. The EPA recently announced plans to extend the 15 ppm sulfur cap to non-road diesel fuels, which could increase incremental costs for all diesel fuel. A MathPro study estimated that an extension of the 15 ppm sulfur cap to non-road diesel would raise the estimated range of incremental costs for all diesel fuel to 4.7–7.8¢ per gallon (MathPro 2000).

A study to assess the costs of lowering fuel sulfur levels from a maximum of 50 ppm to a maximum of 10 ppm in Europe, found that average costs to achieve ultralow sulfur levels were much lower once initial reductions had been made. Costs were expected to range from 0.4 to 1.1¢ per gallon for gasoline and from 1.1 to 2.3¢ per gallon for diesel, with a possible price premium for diesel that could reach as high as 3.4¢ per gallon (Birch and Ulivieri 2000). Giving a further indication of the possible costs associated with reducing sulfur levels, the German market has almost entirely switched to 10 ppm sulfur diesel due to a tax incentive of 3 pfennigs per liter (6¢ per gallon).

4.3 Comparing Costs and Benefits

Cost-benefit analyses in the U.S. and Europe have consistently found that the benefits of reducing sulfur in transportation fuels far outweigh the costs, regardless of the very different assumptions used. The U.S. EPA found the benefits of stricter emissions standards to be roughly ten times higher than the increased refining costs required. In Europe, the analysis investigated only the shift in sulfur levels, assuming new emissions standards were not contingent on sulfur standards. Air quality played a less important role in this analysis, which focused more on increased fuel economy resulting from design modifications made possible with ultralow sulfur fuels.

EPA performed a cost-benefit analyses for both the Tier 2 and the Heavy-duty Engine and Vehicle Standards. Reducing sulfur levels in gasoline and diesel are an integral parts of meeting the new emissions standards associated with each ruling and thus in achieving the expected benefits. Reduction in premature mortality due to reduced PM levels was the dominant benefit in each case. This was a greater benefit for the heavy-duty standard, which will result in significant reductions in direct PM emissions. But the benefit was also significant for Tier 2, due to a reduction in NO_x and SO_x emissions, both of which result in secondary PM formation. Additional benefits for each standard included reduction in health impacts (such as chronic bronchitis), visibility impairments, and crop damage.

U.S. EPA projected each analysis out to the year 2030 and net benefits for these two studies were \$86 billion (see table 4.1). Several aspects of the analysis, including the timeframe, introduced considerable uncertainty into the final numbers. Yet, because many benefits were not monetized, one can still assume that the final numbers are an underestimate. In fact, one plausible alternative to EPA's benefit analysis for the heavy-duty standards found over 150% increase in total benefits, which would make the net benefit of the rulings \$189 billion (EPA 2000b).

Table 4.1 Benefits & Costs in 2030

Regulation	Benefits (billions)	Costs (billions)	Net (billions)
Tier 2 (EPA 1999)	25.2	-5.3	19.9
Heavy-duty (EPA 2000b)	70.4	-4.3	66.1
Total	95.6	-9.6	86.0

In contrast, the analysis performed by the Directorate-General Environment of the European Union looked only at the shift from 50 to 10 ppm sulfur fuels, assuming all vehicle emissions standards remained constant. In this context the primary benefit was increased fuel economy of new models taking advantage of ultralow sulfur fuel to achieve modest 2-3% increases in fuel efficiency. (Much more substantial fuel efficiency increases are possible but the analysis took a conservative approach in predicting these benefits.) Air quality benefits due to the reduction in pollutant emissions from use of ultralow sulfur fuel in older vehicles were relatively minor. This analysis considered the net reduction in CO₂ emissions (see Appendix C) and the monetary benefits of seven different scenarios for the introduction or phase-in of ultralow sulfur fuel. The timing ranged from 2005 to 2011 for the introduction, and compulsory use of 10 ppm sulfur fuel and the benefit analysis stretched out to 2020. The net present value of the various scenarios ranged from 1.1 to 3.0 billion Euros (\$1.7 to \$3.2 billion U.S.) (Directorate-General Environment 2001).

These values are much lower than the U.S. analysis because they do not include the health and air quality benefits associated with more stringent vehicle emissions standards. In fact, the air quality benefits did not cancel out the increased refining costs in any of the European scenarios. The dominant benefits in this analysis derived from fuel savings.

While the analysis by the Directorate-General predicted only moderate air quality benefits from existing vehicles for the incremental decrease in sulfur levels, the actual air quality benefits associated with reducing sulfur levels have been dramatic. A study in Denmark, one year after the level of sulfur in diesel fuel was reduced from 500 ppm to 50 ppm, revealed a significant decrease in ultrafine particle concentrations in the ambient air. The study related the drop in ambient concentrations to a 56% reduction in average particle emissions from diesel vehicles (Våhlin et al. 2000).

These examples demonstrate that the benefits outweigh the costs of lowering the sulfur standards under a variety of assumptions. And benefits may be even greater when sulfur levels are reduced from a higher baseline. The U.S. EPA, in comparing current regulations to past measures, found that the cost-effectiveness was substantially higher for earlier regulatory efforts to strengthen emissions standards and reduce sulfur levels.

At the same time, the European analysis demonstrates that the benefits, purely in terms of fuel costs, continue to be positive down to the level of ultralow sulfur fuels.

5. ZERO-SULFUR ALTERNATIVE FUELS

At the same time as refinery techniques are becoming more efficient and cost-effective, non-petroleum fuels with zero sulfur content are becoming more economically viable alternatives. Biodiesel and Fischer-Tropsch Diesel are two zero-sulfur alternatives to petroleum-based diesel fuel. The costs for these zero-sulfur fuels are still less certain and marginally higher than for refined fuels, but there is much interest in the further development of each, especially as increasingly strict environmental standards in many parts of the world are allowing vehicle designers to take advantage of cleaner, higher-quality fuels.

5.1 Biodiesel

Use of biodiesel tends to result in low PM emissions, with reduced carcinogenic and toxic properties (Bünger et al. 2000). This is probably due to the high quality of the fuel. Produced from rapeseed, soybean, sunflower, palm, and other vegetable oils, renewable fuels known collectively as biodiesel have zero sulfur content and relatively high cetane numbers.

Biodiesel has much lower lifecycle CO₂ emissions than petroleum-based fuels. Production methods and sources of biodiesel vary greatly, however, resulting a large range of CO₂ emissions per amount of product produced. Production of biodiesel also results in substantially less pollutant emissions and hazardous and waste byproducts (such as heavy residual oil and coke produced in refineries).

Due to potential concerns about component degradation and other fuel properties (such as inferior low temperature behavior), biodiesel is generally recommended as a blendstock. Blendstocks can help improve the quality of low-sulfur refined fuels, especially lubricity (see Appendix B). Mixtures of up to 5% biodiesel are currently used in France (Arcoumanis 2000).

5.2 Fischer-Tropsch Diesel

Fischer-Tropsch Diesel (FTD) is a premium diesel product with a very high cetane number (75) and zero sulfur content. FTD is generally produced from natural gas in three steps: (1) production of syngas, (2) syngas conversion, and (3) hydroprocessing to achieve a diesel fuel product. In the first step, the natural gas is desulfurized and then converted into syngas, a mixture of H₂ and CO. The second step is Fischer-Tropsch synthesis, in which cobalt- or iron-based catalysts are used at low pressure. The final stage takes the waxy products and converts them to a variety of liquid products, including high-quality diesel and gasoline feeds (Wang and Huang 1999; Eilers, Posthuma, and Sie 1991).

The lifecycle CO₂ emissions associated with FTD production are roughly equivalent to the refinery process. However, production of FTD results in significant reductions in other greenhouse gases, pollutant emissions, and hazardous and waste byproducts (PwC 2001).

6. GLOBAL TRENDS TOWARD LOW-SULFUR FUELS

Progress is being made in many areas of the world to reduce sulfur levels in fuels. Areas which have switched to low-sulfur fuels have seen fairly immediate improvements in air quality, and some areas have also taken advantage of lower sulfur levels to encourage retrofit programs, achieving even greater improvement in air quality. Increasingly strict environmental regulations in the developed world have forced automakers and fuel refiners to apply their impressive technical and organizational capabilities to produce vehicles and fuels that meet the goals. At the same time, long-term environmental challenges are spurring research and technology development in anticipation of even stricter future requirements.

In many developing countries, over 2,000 ppm sulfur is still the norm for diesel and 1,000 ppm is a common standard for gasoline. These low-quality fuels inhibit the introduction of new vehicle technologies. By instituting policies to reduce sulfur and lower vehicle emissions, these countries can make major advances in allaying the mounting human health impacts of exponential increases in vehicle populations. In doing so, countries relatively new to sulfur regulation may wish to build on the experience of countries that have reached, and taken advantage of, lower sulfur levels.

Further, countries should be increasingly willing to help each other overcome the fuel-quality barrier and move to low emission vehicles. Local health and environmental benefits, though themselves sufficient reason to require cleaner fuels, are no longer the only issue: vehicle emissions carry an increasingly global significance. Local air quality could be significantly impacted by distant sources of NO_x , which can be transported over long distances as more stable reservoir species. In addition, pollutants previously thought to only have local impacts (such as PM and ground-level O_3) now appear to have a significant impact on the global climate. And the most efficient, lowest-greenhouse-gas vehicle designs require ultralow sulfur or zero-sulfur fuels. Sulfur removal from transportation fuels, and the advanced emissions control technologies and fuel-efficient designs that this enables, are the most accessible near-term methods to reduce vehicle emissions.

The remainder of this chapter highlights fuel-sulfur regulations in some of the countries at the forefront of vehicle emission reductions.

6.1 United States

Current sulfur levels average between 300 and 350 ppm for gasoline and are capped at 500 ppm for diesel fuel. Recent regulations in the U.S. require significant reductions in sulfur levels for both gasoline and diesel, in order to meet increasingly stringent emissions standards for passenger and heavy-duty vehicles.

The Tier 2 Rule, made final in 1999, set fuel-neutral emissions standards for passenger vehicles and required a reduction of sulfur in gasoline to a 30 ppm average. The emissions standards are for the full useful life of the vehicle and are based on a bin system rather than weight classes. Each vehicle must meet all the emissions standards in

one of the available bins, with all models meeting a corporate average for NO_x emissions of 0.07 g/mi. While some models may have higher emissions, up to a ceiling of 0.20 g/mi for NO_x, these will have to be balanced by vehicles in the lower emissions bins. The emissions standards are scheduled to be phased in, with full implementation by 2009. The sulfur guidelines for gasoline will also be phased in. By 2004, all gasoline will meet a corporate average of 120 ppm, with a firm cap of 300 ppm sulfur. By 2006, sulfur levels in gasoline will average 30 ppm, with an 80 ppm cap.

Heavy-duty diesel regulations, finalized in 2000, established a program to regulate heavy-duty vehicles and their fuel as a single system. This rule reduced NO_x and PM standards by an order of magnitude for all heavy-duty diesel vehicles. All new vehicles are expected to comply fully with the PM standard by 2007, with full compliance for NO_x by model year 2010. To support these new standards, most on-road diesel fuel is expected to meet a firm 15 ppm sulfur cap by June 2006.

The next stated priority of the Office of Transportation and Air Quality of U.S. EPA is a non-road diesel engine standard, which will regulate fuel and emissions in a single rule, similar to the recent heavy-duty vehicle standard. The administration has announced plans to extend the 15 ppm sulfur cap to off-road diesel fuel by 2007 or 2010, but new emissions standards for off-road diesel engines have yet to be proposed. A new rule setting non-road emissions standards for recreational marine diesel boats and industrial and recreational gasoline engines, including forklifts and snowmobiles, was finalized in September 2002.

In 2001, the California Air Resources Board approved a plan to require all diesel fuel sold in the state to meet the 15 ppm sulfur cap by 2006. California also has planned and begun to implement its In-Use Diesel Retrofit Plan, to reduce diesel PM emissions by 75% by 2010 and 85% by 2020 (CARB 2000). Transit agencies are required to retrofit their diesel buses, and funding is being allocated to help clean up school buses. Other retrofit programs will be based on regulatory requirements, incentives, or voluntary action. Retrofit programs for transit and government fleet vehicles have also been implemented in other states and urban areas. Furthermore, sulfur limits have been extended to include off-road fuels.

6.2 Europe

Sulfur levels have been declining in the European Union (EU) since at least 1980, as demonstrated in figure 6.1. They are currently set at 350 ppm for highway diesel and 150 ppm for gasoline and are scheduled to be reduced to a uniform standard of 50 ppm in 2005. In 2001, the European Commission also proposed a directive calling for the phase-in of “zero sulfur” fuels, which were defined as 10 ppm maximum. The final directive requires



these ultralow sulfur fuels to be introduced in 2005 and for 10 ppm to be the maximum allowable sulfur level in all transportation fuels by 2009.

Incentives are in place throughout Europe to promote early adoption of low and ultralow sulfur fuels. Sweden introduced a tax incentive for 10 ppm sulfur city-grade diesel in 1991, and by 1999 it constituted 95% of the entire diesel market. The widespread availability of ultralow sulfur diesel has allowed Sweden to come to the forefront of diesel retrofit implementation. Germany, the United Kingdom, Finland, Switzerland, Belgium, and the Netherlands have all structured tax incentives to encourage early introduction of low or ultralow sulfur gasoline and diesel. Germany's current incentive for has led to almost complete market penetration of ultralow sulfur fuels. Other countries in Europe have also planned incentives for 10 ppm sulfur fuels (ECMT 2000).

The sulfur content of off-road diesel fuel is also under consideration in Europe. It is expected that the 10 ppm standard will also be applied to non-road fuels but the issue is subject to review when the Commission proposes new non-road standards. Sweden currently supplies all non-road applications with 10 ppm sulfur road-quality diesel fuel. Denmark supplies all non-road applications with heating fuel limited to 500 ppm sulfur (DeSanti 2002).

In addition, the EU plans to phase in a 20% substitution of alternative fuels for diesel and gasoline by 2020. Biofuels and hydrogen are sulfur-free and natural gas has very low sulfur content, or zero sulfur when transformed into a liquid diesel. This goal is consistent with the EU target of 8% reduction in greenhouse gas emissions by 2010 under the Kyoto protocol.

European regulations for vehicle exhaust emissions are not unified for diesel and gasoline engines and allow for higher diesel NO_x and PM emissions in a trade-off for higher fuel efficiency. Several European countries, including Germany, are expected to request that the Commission close this gap in the Euro V passenger vehicle standards, which are scheduled for 2010 but could be implemented as early as 2008.

6.3 Japan

For many years, Japanese gasoline has had a very low sulfur content as a result of modifications designed to lower direct refinery emissions. In recent years diesel fuel sulfur reduction has picked up pace, driven by serious air quality concerns in Tokyo and other urban areas. The sulfur standard for highway diesel fuel was 12,000 ppm in 1976, but by the 1990s it had been reduced to 2,000 ppm. In 1997 a 500 ppm sulfur standard was implemented for diesel fuel, with an additional order-of-magnitude reduction scheduled for 2007. The Tokyo government, along with the court system, pushed for faster action and the reduction to 50 ppm was moved up to 2004. Low sulfur diesel is already being supplied to the Tokyo metropolitan area, and the Petroleum Association of Japan has announced that it will extend this supply to most of the rest of the country by April 2003 (Nemoto 2002).

Although current heavy-duty diesel truck standards in Japan are more relaxed for PM, new emissions standards scheduled for 2005 will bring PM emissions more in line with the U.S. and Europe. The 2005 standards also require sharp declines in NO_x emissions from diesel trucks, similar to Europe but not as stringent as the U.S.. Emissions reductions required for the 2005 passenger vehicles standards are also significant, although the reductions are less severe for diesels.

The fifth report from the Japan Central Environment Council on “Future Policy for Motor Vehicle Exhaust Emission Reduction” (2002) calls for a 2005 report on the need for more stringent exhaust emissions standards and further reductions in sulfur levels in fuel. Further emissions reduction must be balanced with another important Japanese goal, the reduction of greenhouse gas emissions. Technology-enabling low-sulfur fuel should help achieve both goals.

Nationwide reductions to 50 ppm sulfur diesel fuel will support the Tokyo Metropolitan Government’s mandate that all diesel trucks and buses in use in the Tokyo area be retrofitted with particulate filters or retired by April 2003. Diesel vehicles failing to meet PM emissions standards will be banned from use in the Tokyo metropolitan area seven years after their initial registration, unless retrofitted with a particulate filter (Odaka 2001).

6.4 Other Areas

Hong Kong

Initially low sulfur diesel was offered with a tax incentive as part of a government program to visibly reduce air pollution in the city. The incentive was so effective that since 2000, only 50 ppm sulfur diesel fuel has been available in Hong Kong. Sulfur standards for gasoline match Europe at 150 ppm.

Euro III vehicle emissions standards have been in place since 2001. Hong Kong has also started a progressive retrofit program, fitting 80% of the pre-Euro heavy-duty diesel fleet with particulate trap/catalytic converter devices and conducting trials to expand the program to the medium- and heavy-duty fleet with CR-DPFs. Approximately 2,000 older buses have also been retrofitted with DOCs (Environmental Protection Department 2002).

Australia

Australian standards for diesel are currently 500 ppm throughout the country and are scheduled to be further reduced to 50 ppm in 2006. Sulfur levels for gasoline are currently either 150 or 500 ppm, depending on the location, and are being reduced to 150 ppm throughout the country for all gasoline grades in 2005. New sulfur standards accompany several other fuel specifications, including the elimination of lead from gasoline. These changes in fuel quality will facilitate adoption of cleaner engines and emissions control technologies in Australia.

6.5 Summary

Table 6.1 offers a summary of existing regulations and incentives for low-sulfur fuels in selected countries. While regulations have been the primary tool for long-term reductions in sulfur levels, incentives have been effectively used in many areas to promote the early introduction, and typically the full market penetration of low-sulfur fuels.

Table 6.1 Sulfur standards for gasoline and diesel fuels

Country	Regulation	Date	Sulfur Limit (ppm)
U.S	Tier 2 – gasoline	2006	80 (30 ppm avg.)
	Heavy-duty – diesel	2006	15
	Off-road – diesel	Proposed – 2007 or 2010	15
EU	98/70/EC EURO4	2005	50
	Amendment to 98/70/EC	2009	10
	Incentives in Belgium, Denmark, Finland, Germany, Netherlands, Sweden, Switzerland, and the United Kingdom for early introduction of low & ultralow sulfur fuels		10 & 50
Japan	National regulations	2004	50
	Due to incentives low sulfur fuel is already available in Tokyo		50
Hong Kong	National incentive – diesel	2000	50
	Regulation – gasoline	2001	150
Australia	Regulation – gasoline	2005	150
	Regulation – diesel	2006	50

7. CONCLUSION

The benefits of removal of sulfur from transportation fuels are clear. While any level of reduction of fuel sulfur reduces emissions of SO₂ and sulfate PM, further emission benefits accrue with larger step-down reductions.

Reduced sulfur fuels (~150 ppm) make existing vehicles cleaner. Reduced sulfur fuel decreases emissions of CO, HC, and NO_x from catalyst-equipped gasoline vehicles and PM emissions from diesels, with and without oxidation catalysts. These benefits increase as vehicles are designed to meet higher emissions standards and sulfur levels are reduced further.

Low sulfur fuels (~50 ppm) allow for the further benefit of advanced control technologies for diesel vehicles. Diesel particulate filters can be used with low sulfur fuel but only achieve approximately 50% control efficiency. Selective catalytic reduction can be used for over 80% control of NO_x emissions.

Ultralow sulfur fuels (~10 ppm) allow for the use of NO_x adsorbers, increasing NO_x control to over 90% in both diesel and gasoline vehicles. This enables more fuel-efficient engine designs, designs that are incompatible with current emissions control systems. Particulate filters achieve the maximum efficiency with ultralow sulfur fuels, approaching 100% control of PM.

Low-sulfur fuels can lead to enormous reductions in all pollutant emissions from vehicles, with benefits ranging from improved human health to reduced global warming. PM emissions can be cut by close to 100% in existing vehicles and by over 90% in retrofitted diesel cars and trucks. NO_x emissions can be reduced by 90% from new diesel vehicles and up to almost 80% from existing gasoline vehicles. Control of CO and HC approaches 100% for new diesel vehicles and 55% for existing gasoline vehicles. Potential greenhouse gas reductions are also great—road transport accounts for 14% of global CO₂ emissions and advanced engine designs, enabled by low-sulfur fuels, make possible a 20–45% reduction in these emissions. Even direct sulfur reductions are substantial, with new U.S. standards predicted to reduce annual SO₂ emissions by approximately 6% (Darlington and Kahlbaum 1999).

Even as pollution-control technologies become increasingly efficient, reliable, and durable, high-sulfur fuels continue to provide a barrier to their widespread use. At the same time, low-sulfur fuel costs are dropping, as new desulfurization technologies are becoming commercialized and traditional refinery techniques are being improved. All these advances allow for dramatic reductions in vehicles emissions, at low cost and in the near term. Low-sulfur fuels are the key to reducing the local and global impacts of vehicle emissions, and are the necessary first step toward an end goal of zero-emission vehicle technologies.

Throughout the world, experience and studies have demonstrated that production of low-sulfur fuels is affordable and beneficial with current technology. Incentives and taxes

in Europe, Japan, and Hong Kong have led to full market penetration of low and ultralow sulfur fuels much more rapidly than expected. Studies for Asia have shown that the investments required for refinery upgrades are relatively flat over a range of sulfur levels. These studies suggest that making the jump to reduced or directly to ultralow sulfur levels in a single step provides the greatest ratio of benefits to costs. Investment in significant refinery upgrades is necessary, although an initial mixed-standard approach, with ultralow fuels supplied to urban areas, may also decrease costs.

U.S. and European studies have demonstrated that the benefits of sulfur reduction far outweigh the costs of refinery upgrades, regardless of the criteria used. By assuming that stricter emissions standards were contingent on low-sulfur fuels, the U.S. EPA found human health and environmental benefits due to sulfur reduction were ten times higher than the costs, with net benefits of \$86 billion. In Europe, ultralow sulfur fuels were considered on their own, without the added benefit of stricter emissions standards. Here, increased fuel economy provided the primary benefit. The European study was conservative in estimating the potential fuel-economy gains, but nonetheless found a net benefit of \$1.7 to 3.2 billion U.S.. The potential for greenhouse gas emissions reductions also adds substantially to the total benefits of low-sulfur fuels.

Instituting policies to reduce sulfur in transportation fuels and lower vehicle emissions can allay the mounting human health and environmental impacts associated with increasing vehicle numbers. In evaluating sulfur reduction options, several observations may be of use to policymakers.

1. While costs and benefits vary from region to region, depending on the state of existing refineries, current fuel quality and emissions standards, local air quality and other factors, studies have shown that the costs of sulfur reduction are affordable and are dwarfed by the benefits.
2. Both regulations and tax incentives have proven effective tools for moving the refining industry to low-sulfur products.
3. The schedule for upgrading refineries for higher quality fuel production has significant cost implications. (For example, timing upgrades to coincide with needed refinery expansions can reduce costs.) Production and distribution of low-sulfur fuels must also be carefully coordinated with the introduction of new and retrofit vehicles that require low-sulfur fuels.
4. It is cost-effective and highly advantageous in most cases to make the jump to ultralow sulfur diesel in a single step. The total emissions benefits of further sulfur reductions from diesel fuel accrue most rapidly as levels decline from low to ultralow—both in terms of the retrofit potential for existing vehicles and emissions controls for new vehicles. Because of the large increase in incremental benefits, but roughly equal incremental costs, it makes sense to directly mandate ultralow sulfur diesel.
5. Measures should be taken to prevent sulfur extracted from one fuel stream from being diverted into another. For example, heavy fuel oil used in marine vessels can become a “dumping ground” for very high-sulfur feedstocks.

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APPENDIX A – MOTOR VEHICLE EMISSIONS

Vehicle pollution is distinguished from other sources of pollution in that emissions are released in close proximity to those exposed. For example, vehicles are 300 times more effective in contributing to human exposure than emissions from a 200-meter smokestack (Colvile et al. 2001). Urban areas and surroundings are most seriously affected by vehicle pollution, with human health impacts, decreased visibility, and material and environmental damage. In addition to the local and regional impacts, transportation is a major and growing source of greenhouse gases responsible for global warming.

This appendix will briefly introduce each of the major pollutants associated with motor vehicles, including causes for concern and mechanisms of formation.

A.1 Carbon Monoxide (CO)

Carbon monoxide is a product of incomplete combustion that occurs when not enough oxygen is present to completely oxidize the carbon in the fuel to carbon dioxide (CO₂). Even if sufficient oxygen is available overall, CO will form in fuel-rich regions of the flame (regions where there is not enough oxygen to allow complete combustion). At combustion temperatures, CO will readily oxidize to CO₂ in the presence of oxygen. However, CO can be frozen at very high concentrations, regardless of oxygen availability, if the exhaust gases cool rapidly, as occurs in vehicles. At ambient temperatures, the primary loss mechanism is oxidation by the hydroxyl radical (OH) to CO₂. The lifetime of CO is several weeks, long enough for the gas to escape the urban air basin and become well mixed in the atmosphere.

Transportation is the major source of CO in the industrialized world, accounting for 70% of emissions in U.S. (EPA 2001). In urban areas vehicles are an even more important source, accounting for up to 95% of emissions (EPA 2002a). In developing countries, transportation sources are less important but growing rapidly, with emissions increasing in some regions by as much as 9% per year (EDGAR 2001).

Carbon monoxide is a colorless, odorless gas that bonds strongly with hemoglobin in red blood cells, impairing the blood's oxygen-carrying capacity. Exposure to elevated ambient concentrations of CO is most dangerous for those with cardiovascular disease. At higher levels, CO exposure can impair visual perception, work capacity, and manual dexterity in healthy individuals. In unventilated areas, CO poisoning can be fatal.

In addition to direct impacts, CO indirectly influences global warming through competition with methane for oxidation by OH in the atmosphere. With higher CO concentrations, less OH is available to oxidize methane, a potent greenhouse gas, leading to higher concentrations of that pollutant as well (Bruhl and Crutzen 1999).

A.2 Hydrocarbon (HC)

A class of pollutants that includes thousands of species, HC is also known as volatile organic compounds (VOC) or non-methane organic gases (NMOG). Vehicles are a source of both evaporative HC emissions and “tailpipe” HC resulting from incomplete combustion. Evaporative HC emissions occur when vapors escape from the gasoline tank during refueling or from unsealed vehicle components. HC species are also formed by incomplete combustion, which occurs in the fuel-rich regions of the flame, under fuel-rich operating conditions, or when the flame is quenched by low temperatures at the cylinder walls. Like CO, HC emissions are greatly reduced under fuel-lean operating conditions (when excess oxygen is available). Transportation sources are responsible for approximately 25% of human-caused HC emissions globally and over 35% in the industrialized world (EDGAR 2001; EPA 2001).

Hydrocarbons are problematic, both because they are essential precursors for ground-level ozone and also because many HC species are themselves toxic or carcinogenic. The primary loss mechanisms of hydrocarbons—photolysis in sunlight and reaction with OH—both lead to ozone production through reactions with nitrogen oxide. The harmful effects of ozone are discussed later in this appendix.

Transportation sources are responsible for 50 to 75% of the HC species (all known or probable carcinogens): benzene, acetaldehyde, 1,3-butadiene, and formaldehyde (EPA 2000). Effects of elevated exposure of HC emissions can include neurological, developmental and reproductive effects; respiratory impacts; and cancer.

A.3 Nitrogen Oxides (NO_x)

Nitrogen oxide (NO), the primary form of NO_x emissions from vehicles, is quickly oxidized to nitrogen dioxide (NO₂), the primary precursor for ozone formation, in the atmosphere. In vehicles, NO_x are formed primarily in a thermal process that increases with combustion temperature. At high temperatures and in the presence oxygen, nitrogen (N₂) in the air is split by oxygen radicals, forming NO. As opposed to CO and HC, NO_x formation is favored under slightly fuel-lean conditions. The combustion temperature, however, is reduced as the air-to-fuel ratio increases, resulting in reduced NO_x formation for fuel-lean engines designs, such as diesels.

Transportation is the dominant source of NO_x in the industrialized world, accounting over 50% of emissions (EPA 2001; Guegele and Ritter 2002; EDGAR 2001). In the U.S. and other industrialized countries, increasing vehicle numbers have kept pace with stricter emissions standards, resulting in NO_x emissions from vehicles remaining roughly constant over the past 20 years.

Nitrogen dioxide is a respiratory irritant and chronic exposure to elevated levels can lead to increased incidence of acute respiratory disease in children and lower resistance to respiratory infections in adults. NO₂ also absorbs blue light, resulting in a visible brown tint in polluted air.

NO_x is an essential precursor and the principle driver for ground-level ozone production. The NO is oxidized to NO_2 in the atmosphere through reaction with HC species. NO_2 then photolyzes in sunlight to lose an O , which reacts rapidly with oxygen (O_2) to form ozone (O_3). The atmospheric lifetime of NO_x is approximately one day. However, NO_x can become widely distributed through the formation of much more stable reservoir species, which can be transported over long distances and then decompose to release NO_x (Jacob 1999).

The primary loss mechanism for NO_x is oxidation to nitric acid (HNO_3). Because it is highly water soluble, HNO_3 is scavenged by precipitation on a timescale of a few days. HNO_3 is one of two critical acid species in rain, contributing to widespread ecosystem damage of lakes, rivers and forests. Nitrate (NO_3^-) provides a source of easily assimilable nitrogen and is a principle contributor to eutrophication, the excessive fertilization of lakes, estuaries and bays. Eutrophication results in excessive algae growth which damages other aquatic plants and fish. Nitrate can also react in the atmosphere to form nitrate aerosol particles, causing human health concerns and impacting visibility.

A.4 Ozone (O_3)

Ground-level ozone has no direct emissions sources; it is entirely a secondary pollutant that is formed through photochemical reactions in the atmosphere. As described in the previous sections, NO_x and HC species, in the presence of sunlight, are the essential precursors to O_3 formation at the ground level. O_3 production can be limited either by HC or NO_x concentrations. The relationship between O_3 production and precursor concentrations is complex and non-linear. In fact, the very high NO concentrations found near roadways and in urban areas can actually inhibit O_3 . Dilution and oxidation of NO_x , in combination with ongoing HC emissions, may lead to peak O_3 levels downwind of urban areas and sources.

The primary loss mechanisms for O_3 are reaction with NO and deposition onto surfaces. Ozone's lifetime at ground level is less than a day. It demonstrates a strong peak during daylight hours and then drops to near zero concentrations overnight.

In the stratosphere, ozone is naturally occurring and provides a protective layer against harmful ultraviolet radiation. At the ground level, however, ozone is a dangerous pollutant and the primary constituent of photochemical smog. Increased hospital admissions and emergency room visits for respiratory concerns have been linked to high ambient concentrations of O_3 . Short-term exposure can aggravate pre-existing respiratory diseases (such as asthma) and can cause chest pain, coughing, nausea, and lung inflammation. Chronic exposure can cause permanent damage to lungs. O_3 can also damage agricultural crops and forests.

A.5 Sulfur Oxides (SO_x)

Sulfur oxides, primarily emitted as sulfur dioxide (SO_2), are formed through oxidation of sulfur in fuel during combustion. Typically close to 100% of the sulfur in the fuel will be emitted as SO_2 . In the industrialized world, as emissions of SO_2 from coal burning are reduced, transportation sources gain a greater share of the total. In the U.S.,

transportation sources—primarily non-road diesel equipment and marine vessels—now account for 10% of SO₂ emissions (EPA 2001). Worldwide, however, transportation sources are responsible for less than 3% of emissions (EDGAR 2001). While crude oil can have relatively high overall sulfur content, the portion used for highway fuels tends to have lower sulfur content and the refining process removes some of that. Non-road and marine fuels often have a much higher sulfur content. Over the past ten years, regulations in industrialized countries have begun to reduce the allowable levels of sulfur in transportation fuels.

A small fraction of the SO₂ in diesel exhaust is oxidized to sulfur trioxide (SO₃). SO₃ reacts easily with water to form sulfuric acid (H₂SO₄) and sulfate particulate matter. In the diesel exhaust stream, sulfate aerosol is an important initiator of particle formation, providing a nucleus onto which other gases can condense (Shi and Harrison 1999; Tobias et al. 2001).

SO₂ can also be oxidized to SO₃ in the atmosphere, primarily by constituents of polluted urban air. Model estimates in the U.S. predict that over 12% of SO₂ emitted in urban areas is converted in the atmosphere to sulfate PM (Darlington and Kahlbaum 1999). This secondary PM formation means that diesel and gasoline on-road vehicles in the U.S. may be responsible for up to eight times the urban primary diesel sulfate PM emissions that are typically accounted for in inventories.

Sulfur dioxide is a respiratory irritant that can aggravate existing cardiopulmonary conditions and contribute to respiratory illness and trouble breathing. Sulfuric acid is the other critical acid species contributing to widespread ecosystem damage. Sulfate particulate matter is a significant health concern as well as one of the primary pollutants responsible for impaired visibility.

A.6 Particulate Matter (PM)

Particulate matter is a general term for solid particles or liquid droplets suspended in the air. Particulate matter includes anything from a complex mixture of acids and heavy hydrocarbons to a dust grain. The U.S. Environmental Protection Agency (EPA) has developed two categories to measure particles, PM_{2.5} and PM₁₀.

PM_{2.5} includes all particles of less than 2.5 μm in diameter (fine, ultrafine and nanoparticles). These particles can form in the atmosphere through condensation and can grow through further condensation onto, or collisions with, existing particles. Particles of this size range can also be emitted as primary pollutants—either as soot formed by incomplete combustion or acid particles that form in the exhaust. The atmospheric persistence of PM_{2.5} can range from a few days to several weeks. Nanoparticles, with a diameter of less than 0.05 μm, have a shorter lifetime of minutes to hours, primarily due to coagulation with other particles.

PM₁₀ includes all particles under 10 μm in diameter, both coarse and fine particles. Coarse particles are primarily formed by mechanical generation processes, including

such sources as tire wear and wind-blown dust. Due to settling, the atmospheric lifetime of the larger coarse particles is less than a day.

Transportation is an important source of $PM_{2.5}$. In the U.S., transportation accounted for 27% of $PM_{2.5}$ human-caused emissions (not including fugitive dust, agricultural sources, and smoke from forest fires). Almost one quarter of that was highway diesel vehicles, with non-road diesel engines accounting for another half. Emissions inventories suggest that engines and vehicles are the principal contributors of fine particles and, with the inclusion of road wear and construction, coarse particles in urban areas. In downtown L.A., 51–69% of $PM_{2.5}$ was estimated to be vehicle-related and, in London, 90% of PM_{10} was found to be road transport-related (Kittelson 1998).

Diesel particulate matter (DPM) is almost entirely emitted in the $PM_{2.5}$ size range and is primarily made up of soot, the solid carbon particles formed during fuel-rich combustion, in combination with volatile organic and sulfur compounds. Diesel vehicles run fuel-lean but rich regions form in the interior of the combustion zone, resulting in soot formation. A small amount of the fuel and evaporated lube oil escapes oxidation and ends up as organic compounds in the exhaust; this is known as the soluble organic fraction (SOF). The sulfur in the fuel is mostly oxidized to SO_2 , but a small amount is oxidized to SO_3 , which forms sulfuric acid and condenses to form sulfate nanoparticles. As the exhaust gas cools, soot and sulfates serve as important sites for condensation and absorption of other HC gases. Particle composition can be an important factor in the health impacts of PM, with the SOF imparting increased toxicity and mutagenicity.

While PM regulations are currently based on total mass of emissions, particle numbers may turn out to be more important. Nanoparticles may make up only 1–20% of the mass of vehicle PM emissions but generally contribute over 90% of the number of particles. The smallest particles are very respirable and can lodge deeply in the lungs, resulting in greater health impacts than larger particles, which are more likely to either be re-exhaled or caught by the body's filtering defenses in the head or throat. While the mass of uncontrolled PM emissions for a typical diesel vehicle is ten to 100 times higher than for gasoline engines, when considering the number or size of particles, gasoline vehicles may also be a concern. Under most driving conditions, properly-operating gasoline vehicles produce many fewer particles than diesel vehicles, but under high-speed highway cruise conditions the numbers of particles emitted can be similar (Rickeard et al. 1996). In addition, newer diesel engines, designed to reduce PM mass, may actually emit equivalent or higher numbers of smaller particles (Kittelson 1998).

Ambient levels of $PM_{2.5}$ have been associated with premature death, chronic bronchitis, cardiovascular and pulmonary diseases, and asthma (Lloyd and Cackette 2001). Particles impact visibility, especially small particles which effectively scatter light. Diesel particles can have strong absorption properties, due to a high black carbon content. The scattering abilities of particles and aerosols can contribute to a cooling effect, slightly mitigating climate change. But recent research suggests that this is more than canceled out by the absorption of black carbon particles, which demonstrates a much stronger warming impact than previously believed (Jacobson 2002). Fine particles, especially the

sulfate and nitrate aerosols described in sections above, also cause material damage and acid deposition.

A.7 Greenhouse Gases (GHG)

Some solar radiation is absorbed in the ozone layer at the top of the atmosphere, but much of it reaches the surface to warm the Earth. Incoming solar radiation is balanced by the earth radiating heat out to space. Due primarily to human activities, concentrations of greenhouse gases that absorb outgoing terrestrial radiation are increasing, reducing the efficiency with which the earth radiates heat. More outgoing terrestrial radiation is being absorbed by these atmospheric gases, resulting in the warming of the lower atmosphere and earth's surface. Carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄) are all naturally occurring atmospheric gases that have increased significantly over the last century due to human activity. Recent research has determined that shorter-lived atmospheric pollutants such as O₃ and PM, which have generally been considered primarily of local concern, may also powerfully impact the global climate. The earth's mean surface temperature has increased by about 0.6 ± 0.2°C (~1°F) over the last century (Albritton et al. 2001).

Carbon dioxide is the primary greenhouse gas responsible for global warming. CO₂ is formed by complete combustion in the presence of sufficient oxygen to oxidize fully the carbon in the fuel. Transportation is a significant and increasing source of CO₂ in the atmosphere, accounting for over 20% of anthropogenic emissions worldwide (EDGAR 2001). In the U.S., transportation is responsible for 30% of emissions, approximately 7% of global CO₂ emissions. CO₂ emissions from transportation sources in the U.S. and the European Union have increased by 16–18% from 1990 to 1999, with any increases in vehicle efficiency being outweighed by increases in vehicle weight and numbers (EPA 2002b; Gugele and Ritter 2002).

Methane, with only a half-percent the atmospheric concentration but 62 times the near-term warming potential of CO₂, is generally considered to be the second most important greenhouse gas contributing to global warming (Albritton et al. 2001). Methane has an atmospheric lifetime of 12 years and is emitted primarily by natural and agricultural sources. Transportation is a relatively minor source of emissions, accounting for less than 1% of methane emissions globally (EDGAR 2001). Methane is one of the least reactive HC species that can be emitted by vehicles and therefore does not play an important role in ozone formation. Methane is the primary component of natural gas, resulting in relatively higher methane emissions for Compressed Natural Gas (CNG) vehicles than for other technologies. Due to lower CO₂ emissions, however, the overall well-to-wheel global warming potential of CNG vehicles appears to be comparable to diesel vehicles and slightly lower than gasoline vehicles (General Motors 2001). Due to better control of HC emissions, methane emissions from transportation are declining in the industrialized world, falling 30% in the European Union and 11% in the U.S. from 1990 to 1999 (EPA 2002b; Gugele and Ritter 2002).

Nitrous oxide emissions and concentrations in the atmosphere are much lower than CO₂, but N₂O is considered to be 275 times more powerful at trapping heat in the

atmosphere over a 20-year timeframe (Albritton et al. 2001). N_2O has an atmospheric lifetime of 114 years and, like methane, is formed primarily by natural and agricultural sources (Albritton et al. 2001). Transportation is responsible for about 1% of N_2O emissions globally but is more important as a source in the industrialized world, accounting for 5% of U.S. emissions (EDGAR 2001). Catalytic converters intended to reduce NO to N_2 and to oxidize CO and HC can also form N_2O , although the mechanism of formation is poorly understood. Transportation sources of N_2O emissions are increasing in the industrialized world, by 105% in Europe and 17% in the U.S. from 1990 to 1999 (EPA 2002b; Guegle and Ritter 2002).

Ground-level (tropospheric) ozone has strong warming effect. (The loss of stratospheric ozone, on the other hand, has a cooling effect that may have offset some of the some of the warming that would have otherwise occurred in the past decades.) Local ground-level O_3 concentrations have a lifetime of less than one day and respond quickly to changes in precursor emissions. Even in pristine environments, however, background ozone concentrations have been rising, with an average increase of 35% over pre-industrial levels. Because of the short atmospheric lifetime of ground-level ozone, there is less certainty about the overall climate impact than for well-mixed greenhouse gases. But based on the estimated magnitude of its warming influence, the 2001 International Panel on Climate Change (IPCC) technical summary states that tropospheric ozone is the third most important greenhouse gas after CO_2 and methane (Albritton et al. 2001).

As stated above, particles can also have an impact on climate, demonstrating either a cooling or a warming effect depending on their composition. Black carbon particles warm the atmosphere by absorbing solar radiation and lighter colored sulfate aerosols have a cooling impact due to their ability to scatter solar radiation back out to space. Recent modeling efforts have found a much stronger effect from black carbon than was previously suspected. The new study suggests that warming from black carbon balances the cooling effect of other atmospheric aerosols and that, in the near term, the magnitude of direct warming from black carbon appears to exceed the warming impact of methane. This would make black carbon constituents in PM the second most important component of global warming (Jacobson 2002). Due to a short atmospheric lifetime of weeks, the warming impact of black carbon particles could be reversed on the same timescale as emissions can be decreased.

A.8 Summary

Transportation is a major source for conventional pollutants such as CO, NO_x , and HC. As the major source of its precursors, especially in urban areas, transportation is also the most critical source of ground-level ozone. And, for CO_2 , the most important of the greenhouse gases, transportation is an already-significant and fast-growing source. Transportation is less significant as a direct source of SO_x , yet removal of sulfur from transportation fuels will be critical in controlling emissions of all the other pollutants discussed.

Table A.1 provides a summary of the local and global impacts of all these pollutants, including the major human health, environmental, and climate change impacts.

Table A.1 Summary of major pollutants from transportation sources

Pollutants	Local Impacts	Global Impacts	Comments
CO	<ul style="list-style-type: none"> • Aggravates existing cardiovascular diseases, impairs visual perception and dexterity 	<ul style="list-style-type: none"> • Indirect influence on warming through competition with methane for oxidation 	<ul style="list-style-type: none"> • Transportation can be responsible for up to 95% of CO emissions in urban areas. • Globally distributed gas
HC	<ul style="list-style-type: none"> • Range of health impacts including respiratory, neurological & carcinogenic • Photochemical smog precursor 	<ul style="list-style-type: none"> • Class of compounds includes methane, a potent greenhouse gas • Indirect warming influence through ozone formation 	<ul style="list-style-type: none"> • A range of natural and anthropogenic sources ensures that HC species are generally available as ozone precursors
NO _x	<ul style="list-style-type: none"> • Respiratory irritant • Visibility impairment • Acid precursor • Photochemical smog precursor 	<ul style="list-style-type: none"> • Indirect warming influence through ozone formation 	<ul style="list-style-type: none"> • Acid and ozone production impacts of NO_x can be widely distributed through long-range transport of reservoir species
O ₃	<ul style="list-style-type: none"> • Primary constituent of photochemical smog • Severe respiratory impacts • Material & crop damage 	<ul style="list-style-type: none"> • Global warming impacts due to increasing background concentrations 	<ul style="list-style-type: none"> • O₃ has no direct emissions sources—NO_x, HC, and sunlight are required for production
SO _x	<ul style="list-style-type: none"> • Respiratory irritant • Visibility impairment • Acid precursor 	<ul style="list-style-type: none"> • Sulfate has some cooling impact due to light scattering 	<ul style="list-style-type: none"> • SO₂ has a relatively long atmospheric lifetime leading to widespread acid impacts
PM	<ul style="list-style-type: none"> • Cardiovascular & respiratory impacts • Visibility impairment • Includes acid species 	<ul style="list-style-type: none"> • Particles can influence warming or cooling, depending on carbon content & scattering abilities 	<ul style="list-style-type: none"> • Atmospheric lifetime varies with particle size
GHG		<ul style="list-style-type: none"> • Leading to global warming through long-term atmospheric accumulation 	<ul style="list-style-type: none"> • Transportation is a major source of CO₂ but less important for methane & N₂O

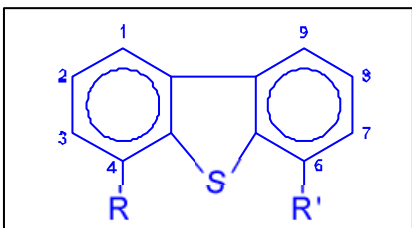
APPENDIX B – REFINING TECHNOLOGIES FOR REDUCING SULFUR

Crude oil has an average sulfur content of anywhere from 100 to 33,000 ppm, and sulfur levels within a supply of crude oil can vary greatly with density. Refineries are generally built to process either premium-priced “sweet” crude, with lower sulfur content, or “sour”, higher sulfur crude oil. Types of sulfur compounds within the crude oil also vary greatly, based upon ease of removal. Because physical contact can be made with the sulfur atom, sulfur bonded to straight-chain or single-ring aromatic hydrocarbons is relatively easy to remove. When sulfur is bonded between two aromatic (ring-shaped) hydrocarbons, especially with additional hydrocarbon groups attached to either side, the physical shape of the compound provides an obstacle to contact between the sulfur atom and the catalyst. The sulfur in these sterically hindered compounds (figure B.1) is much more difficult to remove.

Table B.1
Ranges in Typical Sulfur Content of Crude (IPCC 2000)

Region	Typical Values of Average Sulfur Content (% wt)	High (ppm)	Low (ppm)
Middle East	0.8–2.3	33,000	1,000
Africa	0.1–0.3	21,000	1,000
Asia	0.1–0.2	10,000	200
Former Soviet Union	0.2–1.2	12,000	100
Europe	0.28–0.5	13,000	1,400
North America	0.2–1.1	11,000	2,000
Latin America	0.8–2.5	33,000	5,000

Figure B.1
Sterically Hindered Sulfur Compound



When crude oil enters the refinery it is fractionated into different boiling ranges. Much of the gasoline and diesel fuel is produced from “straight run”, the fractions of crude oil that falls naturally within the appropriate boiling ranges for these fuels. The lightest liquid fraction, naphtha, is used to make gasoline. The next fraction, known as distillate, is in the proper range for diesel and jet fuel, and can also be used for heating oil and kerosene. Heavier

portions of the crude are cracked—broken into smaller, lighter compounds in order to produce more gasoline and diesel. As the density of the crude fraction increases, sulfur compounds tend to be increasingly common and increasingly difficult to remove.

The fluid catalytic cracking (FCC) unit is the processing stage responsible for moving most of the sulfur into gasoline and a large portion of the sterically hindered sulfur into diesel (EPA 2000b). This cracked feedstock contributes 30–50% of the gasoline feed in most refineries but is responsible for more than 90% of the sulfur content (EPA 1999). Around 60% of the diesel fuel in the U.S. comes from straight run, which has a higher sulfur content than straight-run gasoline. But much of the remaining diesel comes from the FCC unit. Depending on the desired product yield, some of the distillate fraction may also be cracked to produce more gasoline. A variable portion of the diesel and gasoline—depending on crude quality, refinery capacity, and desired product yield—

comes from other thermal or catalytic refining units. These units—the coker conversion and hydrocracker conversion units among them—convert heavy portions of the crude oil to lighter liquid fuels.

This appendix reviews the range of refinery technologies that can be used to reduce sulfur levels in fuels. The ability of refiners to reduce the sulfur levels of their products depends on a number of factors: the sulfur level in the fuels currently produced, the refinery configuration and amount of excess desulfurization equipment on hand, the quality of crude oil being used, and the quality and types of products being produced. New sulfur removal catalysts and refining processes are rapidly being developed that increase product value, while reducing capital and operating costs. At the same time, examples throughout the world demonstrate that low-sulfur fuels can be, and have been for several years, achieved with current technology.

B.1 Fuel Properties Affected by Desulfurization

There are several fuel properties, aside from sulfur content, that are important to consider when seeking desulfurization solutions. Surprisingly, the same process for sulfur removal has an opposite effect on product quality in gasoline and diesel fuels. Hydrogenation, the addition of hydrogen to assist in the removal of sulfur, reduces double carbon bonds to single bonds. In gasoline, hydrogenation results in reduced octane levels and lower fuel quality. In diesel, it leads to a higher cetane number and therefore higher quality fuel.

Octane

The octane number is a measure of gasoline's ability to resist auto-ignition. Octane is an innate property of the fuel, though it can also be enhanced through additives or refining processes. Engines are tuned for certain octane values and lower levels will cause the engine to knock, potentially causing severe engine damage. Octane is related to the level of olefins, which contain carbon double bonds, in the blendstock. Octane loss can be reversed through energy-intensive processes and refiners are developing effective new catalysts and processes to reduce octane loss associated with desulfurization.

Cetane

The cetane number is a measure of the compression ignition behavior of diesel fuel. A higher cetane number will increase the vehicle's ability to start in cold weather and has been shown to decrease HC and CO emissions, as well as fuel consumption. While hydrogenation is an effective way to reduce sulfur in diesel fuel and at the same time improve fuel quality, it is also highly energy intensive and expensive. Refiners are beginning to develop less energy-intensive processes for diesel desulfurization.

Lubricity

The final concern regarding the impact of desulfurization on fuel quality is the reduction of diesel lubricity. Diesel fuel pumps, injection systems, and other engine components often rely on the lubricating properties of the fuel for protection against excessive wear and failure. Refining processes that reduce sulfur can also reduce the lubricating properties of the fuel, although no single fuel property appears to be a reliable predictor

of lubricity. Lubricating additives have been effective in increasing lubricity to acceptable levels but must be chosen carefully to avoid serious maintenance problems. Biodiesel, which naturally has a zero sulfur content, also can increase lubricity. In tests done by a biodiesel manufacturer, a blend of 2% biodiesel was found to be sufficient to achieve acceptable lubricity levels in refined diesel (EPA 2000b). Refiners are expected to blend in lubricity additives on a batch-by-batch basis when poor lubricity is expected; this does not appear to have any impact on exhaust emissions.

B.2 Naphtha Hydrodesulfurization

Most of the sulfur in gasoline is derived from naphtha produced in the FCC unit. The lighter portion of the FCC naphtha tends to contain sulfur species that are more easily removed and a higher portion of olefins. The heavier portion of the stream contains sulfur compounds that are more difficult to remove and is typically treated in a conventional hydrotreater. In a fixed bed hydrotreater, the gasoline blendstock is heated, pressurized, and combined with hydrogen. The sulfur combines with hydrogen over the catalyst bed, forming hydrogen sulfide that can be stripped and converted to elemental sulfur in a separate unit. In addition, some of the hydrogen reacts with olefins in the hydrocarbon feed, resulting in octane loss and hydrogen consumption.

To reduce octane loss, refiners may choose to separate the streams through distillation into a lighter, high-octane fraction to be treated catalytically and the heavier, higher-sulfur portion for hydrotreating. Many of the processes and catalysts recently developed, however, have greatly reduced the octane loss associated with hydrotreating for sulfur reduction. New catalysts are either designed to avoid saturating olefins or to cause other reactions to improve octane if saturation occurs. Many of these processes also operate at less severe conditions than conventional hydrotreaters. The less severe conditions preserve gasoline yield and also lower capital and operating costs and CO₂ emissions. Typical costs for a new hydrotreater for low-sulfur gasoline production range between \$20 and \$40 million U.S. for a medium to large refinery (EPA 1999).

Several companies have developed improvements to the conventional hydrotreating process, allowing refiners to preserve octane levels, operate at lower pressure and temperature, and potentially achieve low sulfur levels by retrofitting an existing reactor rather than building a new unit.

- Mobil Oil's Octgain 125 allows hydrogen saturation but then recovers lost octane through processes known as isomerization and alkylation. Severe conditions are required for octane recovery, resulting in yield loss that can be significant. Mobil's more recent process, Octgain 220, discourages hydrogen saturation and recovers lost octane through isomerization. This process generally results in less yield loss, but for deep desulfurization both yield and octane loss can be worse than with the 125 process (EPA 1999).
- Exxon's Scanfining I process discourages hydrogen saturation. While this process results in very little yield loss, octane loss at high levels of desulfurization can be significant. For higher sulfur feeds, octane loss can become severe as ultralow

sulfur levels are reached. Scatfining II is a more recent development from Exxon that maintains octane levels, even with very deep desulfurization and high sulfur feeds. Exomer, an additional new development to maintain octane levels, prevents recombination reactions between hydrogen sulfide and olefins. To produce a 10 ppm sulfur product from a 1,000 ppm sulfur feed, Scatfining I with Exomer results in octane loss of less than one, as opposed to an octane loss of over four without Exomer (Stuntz and Plantenga 2002).

- A recent development from CDTECH utilizes catalytic distillation, with both catalytic sulfur removal and distillation taking place in a single reactor vessel. This process allows a refiner to treat all or a portion of the gasoline, without necessitating an additional distillation column. The process includes two distillation columns loaded with desulfurization catalyst, one which treats the lighter compounds and the other to treat the heavier fraction.

All of the FCC naphtha is fed into the first column and the lighter compounds rise with the hydrogen, also injected at the base of the column, through the catalyst. The sulfur compounds undergo unique reactions to form heavier sulfur compounds, which sink to the bottom and are fed to the next column with the rest of the heavier fraction of the stream. Because the pressure and temperature in this first column is much lower than conventional hydrotreating, there is very little saturation of olefins and little use of hydrogen. Octane can even be gained through use of an isomerization catalyst, which can counteract octane loss in the other column. In the second column, heavy compounds again sink and lighter ones flow upwards, with hydrogen injected at the bottom of the column to react with the most difficult-to-remove sulfur compounds. Throughout the process pressure and temperature are lower than conventional hydrotreating. Pressures and temperatures are especially low in the first column and the top of the second, where most of the olefins are found, resulting in minimal octane loss (EPA 1999).

These new catalysts and processes decrease capital and operating costs, reduce octane loss for a higher value product, and produce lower greenhouse gas emissions. The next section describes an additional new development in gasoline desulfurization technology that is a major departure from conventional hydrotreating.

B.3 Sulfur Adsorption

This is a recently commercialized technology that appears to offer a low-cost solution for highly effective removal of sulfur from gasoline. Laboratory testing has shown that the technology would also be appropriate for diesel desulfurization.

Rather than adding hydrogen this process uses the chemical process of adsorption to remove sulfur from fuel. Adsorption processes operate at much lower temperature and pressure than hydrogenation and thus require much lower energy inputs. This lowers operating costs and has the potential to lower capital costs significantly as well.

Phillips reports that its S Zorb technology can reduce sulfur content of gasoline to less than 10 ppm with minimal octane loss, minimal hydrogen consumption, and near zero volume loss. The sorbent selectively removes sulfur from the hydrocarbon molecules, cycling between the reactor and regenerator for continuous use. The sorbent operates in a fluidized bed reactor and, under certain conditions, existing hydrotreaters may be converted to adsorption units. Run lengths of the S Zorb unit are matched to the FCC unit in order to maintain continuous production cycles for the refinery.

The sorbent removes the sulfur and stores it, maintaining the hydrocarbon portion with virtually no detectable hydrogen sulfide in the product stream. The sorbent is cycled between the reactor and regenerator to provide a continuous supply of regenerated sorbent for high sulfur removal activity. The sorbent is regenerated in an oxidizing atmosphere, producing SO₂ and CO₂. The sulfur can be separated out from this gas stream in a variety of ways, depending on the reactor configuration.

Octane loss with S Zorb depends on the target sulfur level and the sulfur level of the feedstock. More severe operating conditions are required for lower sulfur endpoints and will cause octane loss to increase. Production of less than 10 ppm sulfur fuel from 220 ppm feed results in approximately 0.2 octane loss; with a feed of 1,435 ppm sulfur, the octane loss increases to approximately 1.2 (Greenwood et al. 2002)

Phillips estimates that the lower net hydrogen requirements of this process can decrease operating expenses by up to \$2 million U.S. per year in a 35,000 barrel per day unit. Capital costs are estimated to be \$800 to \$900 U.S. per barrel capacity (\$28 to \$32 million U.S. for a 35,000 barrel per day plant), with operating expenses of 0.9¢ to 1.2¢ per gallon (Greenwood et al. 2002).

A pilot plant is currently demonstrating use of this desulfurization process for diesel blendstocks. And Phillips reports that the adsorption catalyst more readily desulfurizes sterically hindered sulfur compounds than the sulfur compounds found in gasoline. The primary operating difference is a moderate increase in reactor pressure compared with the gasoline application, which is still relatively low compared to distillate hydrotreating. Near-zero hydrogen consumption results in little or no change in diesel properties (aside from sulfur removal) and can result in significant savings in operating costs.

B.4 Hydrotreating of Middle Distillates

While refiners are not faced with the concern of maintaining octane levels for diesel fuel, low-sulfur diesel production has its own challenges. Unlike gasoline, all of the crude fractions used to produce diesel, including straight-run distillate, tend to have high initial sulfur levels. This means that a much larger quantity of feedstock must be processed than is required for gasoline production. Conventional diesel desulfurization catalysts and processes can remove the majority of the sulfur compounds but the removal of the sterically hindered sulfur compounds, required to produce low-sulfur diesel, significantly slows the process. Using conventional desulfurization techniques, removal of sterically hindered compounds can be up to 30 times slower than removal of similar non-sterically hindered molecules (EPA 2000b).

While production of low-sulfur diesel can be accomplished with conventional refinery technology, the challenge is to make the process cost effective. To do so run times must be sped up without requiring significant increases in reactor volume or hydrogen consumption. In some areas refineries have already made capital investments to reach the 350 to 500 ppm sulfur levels. Without additional developments in process or catalyst technology, as much as a four-fold increase in reactor volume would be required to increase desulfurization from a 500 to 10 ppm endpoint (Stuntz and Plantenga 2002). Recent developments in fixed bed hydrotreater technology have demonstrated methods to reduce the time spent in the reactor, thus reducing the reactor volume needed for low-sulfur diesel production.

More active catalysts are currently being developed which may alleviate the need for larger reactor volumes for some refiners. Much of the improvement in catalyst technology in recent years has been a result of better dispersion of the active metal on the substrate and increased activity of the reaction sites. New catalysts from Akzo Nobel, Haldor-Topsoe, and Criterion Catalyst increase activity over previous generations of catalysts by 25 to over 80% (EPA 2000b). Developers of the new NEBULA catalyst, ExxonMobile and Akzo Nobel, claim a factor of two increase in catalyst activity at moderate pressure. This catalyst has not yet had widespread application and is currently significantly more expensive than conventional catalysts (Stuntz and Plantenga 2002).

Many additional changes can improve sulfur removal performance of current distillate hydrotreaters.

- A 3–6% reduction in hydrogen sulfide concentrations by chemical scrubbing of recycled hydrogen can reduce final sulfur levels by 60%.
- An improved vapor-liquid distributor to increase contact between the hydrogen and feedstock can reduce the final sulfur level by 50%.
- Increasing hydrogen purity, which is preferable to the more energy-intensive increase of hydrogen partial pressure, can increase the amount of sulfur removed by approximately 40%.
- Increasing reactor temperature can also lead to lower sulfur endpoints but can significantly reduce catalyst lifetimes (EPA 2000b).
- More extensive changes include increased reactor volume and additional reactors. An additional reactor could be used as a second, high-pressure stage with the addition of a hydrogen sulfide scrubber in between the first and second reactor. A new single stage hydrotreating technology under development in China claims to be able to use the second reactor in series to achieve ultralow sulfur diesel, with high yields and moderate pressure (Xiao-dong et al. 2002).

The benefits of these changes will not necessarily combine additively and may not be sufficient to achieve 50 or 10 ppm sulfur diesel in existing refineries, depending on unique aspects of feedstock, reactor design, and operating conditions.

Refiners can choose to either revamp an existing diesel hydrotreating unit or build a new “grassroots” unit. A revamp is less capital intensive, costing on the order of \$40 million U.S. per unit as opposed to \$80 million for a new diesel hydrotreater. The revamp may, however, be less flexible with respect to feedstock and end-product properties. The decision is generally based on the age of the existing reactor, the quality of the feedstock being used, and the end-product properties desired. In addition, many refiners choosing to install a grassroots system may do so because they wish to use the old hydrotreater elsewhere in the refinery or they want to expand diesel production capacity. Many cost estimates for meeting new low-sulfur regulations in Europe and the U.S. have predicted close to half of the refineries will install grassroots diesel hydrotreating systems. However, EPA’s more recent predictions, used in the heavy-duty standards, predict only 10–30% of refiners will choose to install grassroots systems rather than revamp an existing unit (EPA 2000b).

B.5 Hydrocracking

This is a flexible process to convert heavy fractions of the crude primarily into middle distillates for production of diesel. It is particularly important with use of heavy crude oil, in which the heavier and typically higher-sulfur fractions dominate. In the past mild hydrocracking was used to prepare feeds for FCC, but it can also be used to reduce sulfur content of products and to produce higher diesel yields, offering increasing flexibility in the gasoline/diesel ratio.

Table B.2 Comparison of Process Requirements for Diesel Desulfurization Technologies

Desulfurization Technology	Hydrotreating (Cooper 2000)		Adsorption (Greenwood 2000)	Hydrocracking (Belato 2002)
	Revamp	Grassroots		
Pressure	32 bar	54 bar	34 bar	~ 180 bar
Hydrogen Consumption	.91	1.8	.99	~ 3.5
Temperature	300–400°C	300–400°C	370–420°C	~ 410°C
Relative Reactor Volume	3.4	1.6	2	1

New developments in hydrocracking catalysts and process design have improved product yields, selectivity, and cycle lengths. As can be seen in table B.2, much higher pressure and hydrogen consumption are required, compared to adsorption or hydrotreating, but the required reactor volume is lower (Belato, Lima, and Oddone 2002). At lower severity operation all products have low sulfur content—less than 50 ppm. High quality diesel is produced with a high cetane number.

B.6 Hydrotreating Feeds for Cracking Units

Because a large portion of the sulfur in diesel and gasoline is supplied by blendstock coming from the FCC unit, one way to remove sulfur is to treat the feed to this unit, reducing sulfur levels in gasoline and diesel products at the same time. This process, designed to operate at high pressure and temperature to reduce sulfur, also removes nitrogen and certain metals in the feed which would adversely affect the catalyst in the FCC unit. While this unit alone will not allow the refiner to produce ultralow sulfur gasoline or diesel, it may allow refiners to switch to lower quality crudes, which would otherwise foul the FCC unit, while producing higher quality products at the same time. But capital and operating expenses are often prohibitive. For a medium-to-large refinery

the capital costs for installation may exceed \$100 million U.S. (EPA 1999). And because of the high temperatures and pressures, combined with the large volume of feed to be treated, the utility costs are expensive relative to other forms of sulfur removal.

B.7 Emerging Desulfurization Technologies

A couple of emerging technologies, which are not commercially proven at this point, use sulfur removal processes that are very different from conventional refinery technology.

Biodesulfurization

This process involves the use of bacteria to remove sulfur-containing hydrocarbon compounds from naphtha or distillate streams. The feed is combined with a water-based mixture of bacteria, caustic soda and nutrients for the bacteria. Enzymes in the bacteria oxidize the sulfur atoms and then cleave some of the sulfur-carbon bonds to produce a sulfur product that can be used as a commercial feedstock for the soap industry. Researchers envision biodesulfurization used in combination with conventional refinery desulfurization units (EPA 2000b). The process has been tested in the laboratory, but engineering designs and cost estimates have not been developed (EIA 2001).

Chemical Oxidation and Extraction

This refining process involves the formation of a water emulsion with the diesel fuel. The sulfur is oxidized using a catalyzed acid. The oxidized sulfur either can be separated from the hydrocarbon and removed or the compound will move into the aqueous phase, forming a commercial feedstock similar to biodesulfurization (EPA 2000b). This process preferentially treats the hardest-to-remove sulfur compounds but does not work well on straight-run distillate. Construction of a pilot plant is planned, with capital costs estimated at \$1,000 per barrel of daily installed capacity, less than half the cost of a new high-pressure hydrotreater (EIA 2001).

B.8 Summary

The following table provides a summary of desulfurization technologies available to produce low-sulfur diesel and gasoline. Capital costs vary primarily according to reactor volume and thus tend to be higher for diesel refining. Operating costs vary according to operation conditions, including pressure, temperature, and hydrogen consumption.

Table B.3 Summary of Desulfurization Processes for Gasoline and Diesel

Process	Comments	Operating Conditions	Product Properties (10 ppm)	Cost
Hydrotreating FCC feed	<ul style="list-style-type: none"> Hydrogenation of the feed to the FCC Reduces gasoline and diesel sulfur levels together 	<ul style="list-style-type: none"> High temperature and pressure required High reactor volume requirements due to large quantity of feed 	<ul style="list-style-type: none"> Products require further desulfurization to reach low-sulfur levels Reduces nitrogen & metals that foul the FCC 	\$100 million capital & high operating
Gasoline				
Hydrotreating Naphtha	<ul style="list-style-type: none"> Hydrogenation of the naphtha from the FCC New catalysts and processes are reducing 	<ul style="list-style-type: none"> Pressure: 50–56 bar Temp: 320–350°C Typical hydrogen consumption 	<ul style="list-style-type: none"> Octane loss: <ul style="list-style-type: none"> Ranges depending on process and feed 1 from 1,000 ppm 	\$20–40 million capital & moderate operating

	process severity and octane losses		(Exxon's Scavfining I with Exomer)	
Adsorption	<ul style="list-style-type: none"> • Uses a sorbent in fluidized bed reactor • Commercially available new technology 	<ul style="list-style-type: none"> • Pressure: 6–21 bar • Temp: 370–420°C • Lower hydrogen consumption 	Octane loss: <ul style="list-style-type: none"> • 1.2 from 1,435 ppm • 1.0 from 675 ppm • 0.1 from 220 ppm 	\$15–30 million capital & lower operating
Diesel				
Hydrotreating Middle Distillates	<ul style="list-style-type: none"> • Hydrogenation of middle distillates from FCC • New catalysts and processes are reducing the required volume and hydrogen consumption 	<ul style="list-style-type: none"> • Pressure: 32–54 bar • Temp: 300–400°C • Higher hydrogen consumption • Moderate to high reactor volumes 	<ul style="list-style-type: none"> • Raises cetane number by 4 to 7 	\$40–80 million capital & high to moderate operating
Adsorption	<ul style="list-style-type: none"> • Uses a sorbent in fluidized bed reactor, similar to gasoline desulfurization but at slightly higher temperature and pressure • Still in pilot stage 	<ul style="list-style-type: none"> • Pressure: 34 bar • Temp: 370–420°C • No net hydrogen consumption • Moderate reactor volume requirements 	<ul style="list-style-type: none"> • No change in product cetane number 	Unknown capital & low to moderate operating
Hydrocracking	<ul style="list-style-type: none"> • An alternative to the FCC, this process cracks heavy crude portions and removes sulfur 	<ul style="list-style-type: none"> • Pressure: 90–180 bar • Temp: 320–410°C • High hydrogen consumption 	<ul style="list-style-type: none"> • Raises cetane number 	Unknown capital & higher operating
Emerging Technologies	<ul style="list-style-type: none"> • Biodesulfurization uses bacterial enzymes for sulfur extraction • Chemical Oxidation oxidizes sulfur with a catalyzed acid 	<ul style="list-style-type: none"> • Processes are still in the lab or pilot stage so operating conditions are unknown 	<ul style="list-style-type: none"> • Additional refinery processes will be required for each technology to achieve desired sulfur levels 	Estimated \$35 million capital

APPENDIX C – IMPACT OF DESULFURIZATION ON GREENHOUSE GAS EMISSIONS

While increased desulfurization will cause some increase in refinery greenhouse gas emissions, these increases are dwarfed by the greenhouse gas reduction potential of new vehicle technologies enabled by low-sulfur fuels.

C.1 Direct Refinery Impacts

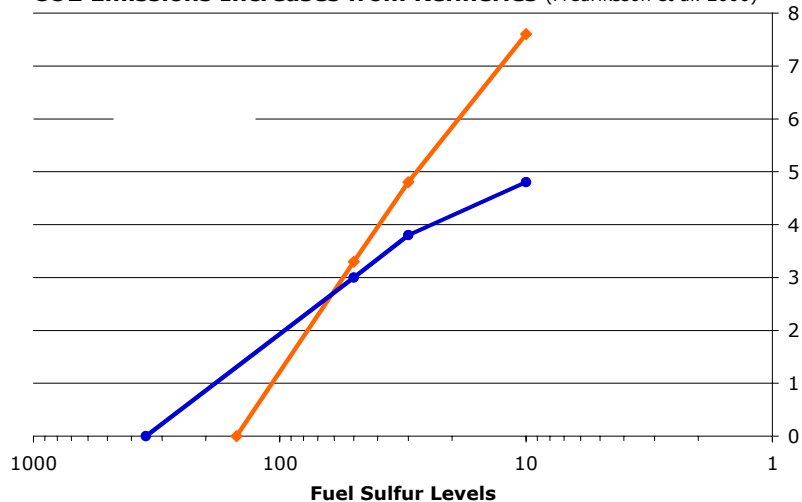
The production of low-sulfur fuel is generally more energy intensive, often requiring higher temperatures and pressures, as well as increased hydrogen consumption. And because hydrocarbons are used for hydrogen production, the process is very CO₂ intensive, creating 8 to 15 tons of CO₂ for every ton of hydrogen used (Martino and Van Wechem 2002). Yet, these increases are clearly outweighed by the GHG reduction potential of new vehicle technologies.

A report prepared by Concawe, the European oil industry association, in response to a European Commission directive to reduce sulfur levels in fuels to 10 ppm, offered an analysis of the CO₂ emissions impact of this reduction. Concawe found that the reduction of sulfur in gasoline from 150 ppm to 50 ppm would result in approximately a 3.3% increase in refinery CO₂ emissions. For diesel, a reduction from 350 to 50

ppm sulfur resulted in an approximately 3% increase in refinery emissions. To get to even lower sulfur levels, the report suggested that emissions would increase substantially for gasoline and less so for diesel. From 50 to 10 ppm CO₂ emissions increased by an additional 4.3% for gasoline refining and 1.8% for diesel (see figure C.1). The report suggested that the total impact on refinery emissions for production of both gasoline and diesel at 10 ppm sulfur would be worse than additive, with a 12.9% increase in CO₂ emissions to achieve both 10 ppm sulfur diesel and gasoline (Fredriksson et al. 2000).

While these increases in refinery emissions are significant—particularly to the industries which are trying to demonstrate their commitment to reducing emissions—oil production, including refining, transmission, and handling, amounts to less than 1% of the global CO₂ emissions. Use of these fuels in vehicles, on the other hand, is the source of 14% of global CO₂ emissions. The total potential CO₂ emissions increase estimated for the European refinery industry translates into less than half a percent of total on-road

Figure C.1
CO₂ Emissions Increases from Refineries (Fredriksson et al. 2000)



CO₂ emissions in Europe (Directorate-General Environment 2001; EDGAR 2001). In addition, the CO₂ emissions increases reported may be high, considering the additional efficiencies of new catalysts and the likelihood of adsorption refining techniques to reduce energy and hydrogen inputs for gasoline, and perhaps also diesel, desulfurization.

A 20–45% reduction in fuel use is possible with advanced engine designs, enabled by low-sulfur fuels. This translates into an emissions reduction potential of 700–1,700 Mt CO₂ per year or 3–7% of the global fossil fuel source of CO₂ (EDGAR 2001). The Directorate General of the European Commission used much more conservative estimates of fuel economy benefits. They assumed that, initially, approximately 20% of new cars would reap fuel efficiency benefits of 2–3%, with use of low-sulfur fuel, rising to 90% of new cars over a period of three years. Several scenarios for the phase-in of 10 ppm sulfur fuels were considered, from 100% market penetration in 2007 to an approach that balanced ultralow sulfur fuel introduction with the number of new cars on the road. The study found a net benefit, ranging from a reduction of 53.3 Mt CO₂ to 74.6 Mt CO₂ over a 12 year period (0.6–0.8% of road transport emissions annually), for each of the scenarios. The completely phased-in approach demonstrated the greatest benefit (Directorate-General Environment 2001).

C.2 Transport and Re-refining of Contaminated Batches

There is some concern that low-sulfur diesel for use in highway vehicles could be contaminated in transport by significantly higher sulfur content of non-road fuels and heating oil. As the differential between the fuel grades grows, the risk increases. Even a small amount of contamination with a several thousand ppm fuel would be likely to bump the low-sulfur diesel over a 10 or 15 ppm cap. This would not be a concern for gasoline, which only has a single use, unless several grades were available with dramatically different sulfur contents.

Diesel fuel is often transported via pipeline, shipped through the same line as non-road fuels, without a physical separation between the two grades. The mixing between the two products generally results in a lower value product. Sulfur contamination can also occur when low-sulfur diesel is stored or transported in a tank or line that was previously used for a high-sulfur product.

The need for strict separation of diesel and gasoline lends some perspective. Although both fuels are shipped in the same pipeline, mixing of any amount of gasoline into diesel can cause an explosion hazard. Extreme care is taken to prevent mixing, and none of the interface between the two products is allowed into the diesel batch. In addition, ratios of similar maximum concentrations were managed under lead phase-outs.

While there may be some need to return contaminated batches to the refinery for reprocessing, distributors will most likely quickly optimize transport practices to reduce contamination events. There may also be additional options for handling contaminated batches, such as blending into a diesel that is below the cap or blending into a non-road fuel. If the fuel does need to be reprocessed, it will be a very low-sulfur blendstock and will not require excessive reprocessing.