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Benefits of Molybdenum Use: Hydrodesulfurization Catalysts

Key highlights

- **Concerns about the environmental and human health impacts of sulfur dioxide have led to very large reductions in the sulfur content of diesel for road vehicles from 2000 ppm by weight to 10 ppm over the past 20 years**
- **Innovations in the molybdenum–based catalysts used in the hydrodesulfurization process have made these reductions possible**
- **Annual emissions of sulfur dioxide from diesel vehicles in the EU are now 100 times lower than in 1993, despite a doubling in demand for diesel fuel**
- **This has resulted in significant improvements in key environmental impact categories including acidification, smog creation and impacts related to human health**
- **Additional impacts from increased catalyst production are negligible (less than 0.01%) compared to impacts from fuel production and combustion**

Diesel and Sulfur Emissions

Organically bound sulfur is a natural component of crude oil, the feedstock from which mineral diesel is derived. Crude oil can have a sulfur content as high as 5%, but after processing into diesel this is reduced to between 0.1-2.5% by weight, with a typical value of around 1% prior to desulfurization.

Sulfur in diesel results in a number of negative effects if left unchecked. When combusted, fuel containing sulfur creates sulfur dioxide (SO_2) which leads to acidification (which is responsible for acid rain) and can cause or aggravate respiratory problems, particularly in vulnerable groups such as children, the elderly and people with asthma. In addition, sulfur damages emissions-control technology in vehicles, notably the catalytic convertors used to remove carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbons.

As far back as the 1960s, some level of desulfurization took place at refineries and by the late 1980s the sulfur content in diesel as sold at filling stations was typically in the range of 0.2% - 0.3% by weight, equivalent to 2000 – 3000 ppm (parts per million).

Pine trees damaged by acid rain. Acid rain damage to forests has reduced in Western Europe in the past 20 years, but remains an issue in other regions.

During the 1980s, growing concern over the effects of acidification on sensitive ecosystems such as pine forests, coupled with increasing demands to improve air quality in urban areas, led the European Union to enact legislation to reduce key air emissions. This included the European Emissions Standards for vehicles, regulations for power plants such as the Large Combustion Plant

Directive and, in 1993, a directive limiting sulfur content in diesel fuel for passenger vehicles to 2000 ppm (known as Euro I) with an aim to reduce the sulfur limit to 500 ppm by 1996. Subsequent, more ambitious targets further reduced the sulfur limit in diesel consumed in vehicles in the EU to 50 ppm (known as the Euro IV standard) by 2005 and 10 ppm (0.001%) by 2009 (Euro V), also known as ultra-low sulfur diesel (ULSD).

Outside the EU, sulfur limits in diesel for road vehicles reduced to 15 ppm in most US states. China adopted a 50 ppm limit for automotive diesel at the end of 2014, with a 10 ppm limit planned by 2017 and already in place in Beijing.

These rapid improvements in sulfur removal were made possible by innovations in the hydrodesulfurization process, which removes sulfur through the use of a molybdenum-based catalyst, usually cobalt-molybdenum (CoMo) or nickel-molybdenum (NiMo).

This case study captures some of the key benefits associated with the reduction of sulfur emissions from modern diesel fuel by comparing the impact of 2000 ppm Euro I diesel against the 10 ppm Euro V diesel used today. It also quantifies additional impacts associated with the increased intensity of hydrodesulfurization and the increased use of molybdenum based catalyst.

Hydrodesulfurization

Hydrodesulfurization takes place in fixed-bed reactors containing a molybdenum-based catalyst, most commonly a cobalt-molybdenum (CoMo) catalyst or a nickel-molybdenum catalyst (NiMo) on an alumina carrier. The catalyst increases the rate at which hydrogen reacts with organically bound sulfur in the hydrocarbon feedstock, reducing the amount of energy required for the process and enabling more complete removal of sulfur.

The products from the process are hydrogen sulfide gas, which may subsequently be converted to sulfuric acid to be sold, and low-sulfur hydrocarbons, which form the final diesel product.

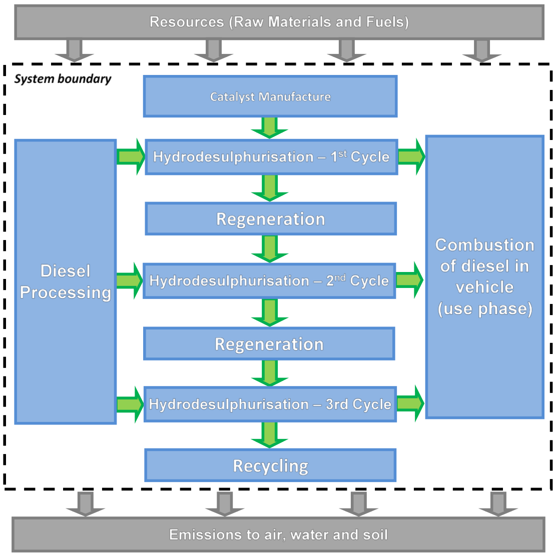
The catalyst is not consumed during the desulfurization reaction. However, it does slowly deactivate during the cycle limiting the production cycle of the plant to around two years. At the end of the two-year operation of the hydrodesulfurization plant, the catalyst is regenerated to remove coke formation that has built up on its surface, and so reduce or reverse activity loss in the catalyst. Regenerating the catalyst means it can be used for two further cycles before it is considered spent, at which point the molybdenum, cobalt and nickel are recycled primarily for use in the steel industry.

Assessing the Benefit

When determining the relative environmental impacts associated with 2000 ppm and 10 ppm diesel it is important to account for the complete lifecycle of the fuel from extraction of the crude oil, through refining, production of materials used to process the oil such as the catalyst and ending with its combustion in a vehicle.

Lifecycle assessment (LCA), a widely used method for assessing the total lifetime environmental impacts of products, has been used to analyze the two fuels.

As defined in ISO 14040, “*LCA is the compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle.*”



Full lifecycle of catalysts used in the hydrodesulfurization of diesel.

In assessing the environmental performance of the two fuels and the catalytic hydrodesulfurization process, six lifecycle stages were modeled in greater detail:

- Diesel production from crude oil extraction to the desulfurization plant
- Catalyst production
- Hydrodesulfurization
- Catalyst regeneration
- Catalyst recycling at end-of-life
- Combustion of the diesel fuel in a passenger vehicle, referred to as the “use phase”

For fuels, the vehicle use phase where the fuel is combusted is generally the dominant lifecycle stage. However, as the two fuels require different quantities of catalyst and different levels of processing, it is also important to take into account the manufacture of catalyst, its regeneration and recycling to identify any potential ‘trade-offs’ between using lower sulfur diesel and a potential increase in impacts associated with hydrodesulfurization. The functional unit used as the basis for comparison is the production and combustion of 1000 liters of diesel in a mid-sized Euro V passenger vehicle.

A number of environmental metrics relevant to the performance of vehicles have been assessed as part of this study. These cover air pollution, climate change and energy resource use, among others. Addressing a range of potential impacts leads to a more complete understanding of the overall environmental performance of the product. The metrics assessed are:

Acidification Potential: Used to quantify atmospheric acidification, which leads to acid rain and damages ecosystems and buildings. Acidification was the major driving force behind the imposition of sulfur limits in fuel. The other key contribution to acidification comes from nitrogen oxides (NO_x), which are also regulated as part of the European Emissions Standards.

Global Warming Potential: Used to quantify climate change, which governments and legislators consider to be the primary environmental concern related to vehicles. CO_2 emissions are increasingly subject to strict limits and, in some countries, are used as a basis for vehicle taxation. Sulfur dioxide emissions do not contribute to global warming.

Smog Creation Potential: Used to quantify ‘summer smog’ (such as that experienced in Los Angeles and Beijing) and strongly associated with vehicle emissions by members of the public. Although generally driven by hydrocarbon emissions, sulfur dioxide also contributes to smog creation.

Exhaust fumes from a passenger car. Cars are a significant source of emissions that cause smog and reduce air quality in urban areas.

Particulate Matter/Respiratory Inorganics: Used to capture the health and environmental risks associated with the emission of particulates and inorganic air emissions including sulfur dioxide.

Eutrophication Potential: Used to quantify the effects of over-nutrification that can result in algal blooms and other effects detrimental to ecosystems. Nitrogen oxides emitted from the combustion of diesel contribute to eutrophication.

Primary Energy Demand: Quantifies the total energy consumption associated with the lifecycle of the fuel (from both renewable and non-renewable energy sources).

Data and Assumptions

Catalyst Production

Key data on the production of the cobalt-molybdenum catalyst were provided by Haldor Topsoe, a market leader in the manufacture of industrial catalysts. This included information on the quantities of materials, energy and fuels required. No data on potential reductions in impacts related to catalyst production between 1993 and 2013 were available, so the primary data for 2013 were used for modeling both scenarios. Production impacts for Ni-Mo catalysts are not covered by this study, but are expected to be broadly similar.

Upstream datasets related to alloys, materials and fuels have been sourced from the GaBi database developed and maintained by PE INTERNATIONAL.

Hydrodesulfurization

Haldor Topsoe also provided data on the quantity of catalyst required to desulfurize the diesel to the 1993 level of 2000 ppm and to the modern day limit of 10 ppm. Although the level of desulfurization has increased by a factor of 200, the quantity of catalyst required has only doubled thanks to significant innovations and improvements, which have optimized the performance of the catalyst over the past 20 years.

Desulfurization requires an input of energy in the form of electricity for compressors and fuels for firing the heater. Differences in plant design and the characteristics of the diesel feedstock result in significant variations in fuel and electricity consumption.

When comparing the hydrodesulfurization process in 2013 with that in 1993, it is reasonable to expect that more energy would be required now, as a much greater level of sulfur removal is required. However, during this period both the catalysts and the plant efficiency in the industry have been greatly improved, counteracting potential increases in energy consumption.

For the purposes of this study median values within the typical range for hydrodesulfurization plants in the industry have been used, with an assumption made that the energy consumption in 2013 is the same as the energy consumption in 1993. The sensitivity of the results to this assumption is addressed in the results section.

Other refinery processes related to the production of diesel are modeled as being unaltered between 1993 and 2013. This is partly due to a lack of data for 1993 but also to ensure that any changes in impacts between the two scenarios can be directly attributed to changes in the desulfurization process.

TK-578 BRIM® cobalt-molybdenum catalyst for hydrodesulfurization produced by Haldor Topsoe

Regeneration and Recycling

Regeneration of the catalyst at the end of each two-year operation cycle is modeled based on information from Haldor Topsoe. During removal from the desulfurization unit and the regeneration process itself, a maximum 10% of the catalyst mass is lost. Furthermore, there is an activity loss over each production and regeneration cycle of the catalyst of a maximum 20% before the 2nd cycle and a further 10% before the 3rd cycle.

Losses in mass or activity in the 2nd and 3rd cycle are compensated by the addition of virgin catalyst to the unit. In effect, the original catalyst can be said to complete around two and half cycles, meaning that over its lifetime, 1 kg of catalyst produces around 70,000 liters of ultra-low sulfur diesel.

Nowadays, activity loss in the catalyst is commonly reversed by conducting a "ReFRESH™" of the catalyst following regeneration, a reconditioning process that reactivates the catalytically active sites. This results in around a 5% mass loss, but yields a catalyst with original levels of activity during the 2nd and possibly 3rd production cycle.

For the purposes of this study, it is assumed that in 2013 a ReFRESH™ of the catalyst was conducted after each production cycle, but that in 1993, ReFRESH™ technology was not available resulting in the activity loss outlined above for each cycle.

Catalyst used for hydrodesulfurization is sent for recycling at end-of-life with the molybdenum, cobalt and nickel constituents recovered for use in other sectors such as the steel industry. Credits for the avoided production of primary molybdenum trioxide and cobalt and nickel metal have been applied.

Use phase

The emissions profile of diesel vehicles has changed significantly in the past two decades as emissions control and engine technologies have improved. The aim of this study is to present the changes attributable to the changes in the sulfur content of diesel fuels, so an average mid-sized Euro V diesel passenger car (engine size in the range of 1.4-2.0 liter) has been used as the basis for comparison in both the 1993 and 2013 scenarios. Comparing with a Euro I vehicle of the type used in 1993 would yield results showing significant reductions in a number of impact categories that would be due to improvements in the vehicle performance rather than to improvements in the fuel.

	10ppm Ultra-low sulfur diesel (2013)	2000ppm Diesel (1993)	% Reduction (2013 vs. 1993)
Acidification Potential [Mol. H^+ eq.]	*14.1*	*18.4*	*23.7*
Global Warming Potential [kg CO_2 eq.]	*2970*	*2970*	*0.0%*
Eutrophication Potential [kg P eq.]	*0.0200*	*0.0200*	*0.0%*
Smog Creation Potential [kg NMVOC]	*5.60*	*5.87*	*4.6%*
Particulate matter/Respiratory inorganics [kg PM 2.5 eq.]	*0.262*	*0.465*	*43.8%*
Primary Energy Demand (Total) [MJ]	*43126*	*43125*	*0.0%*

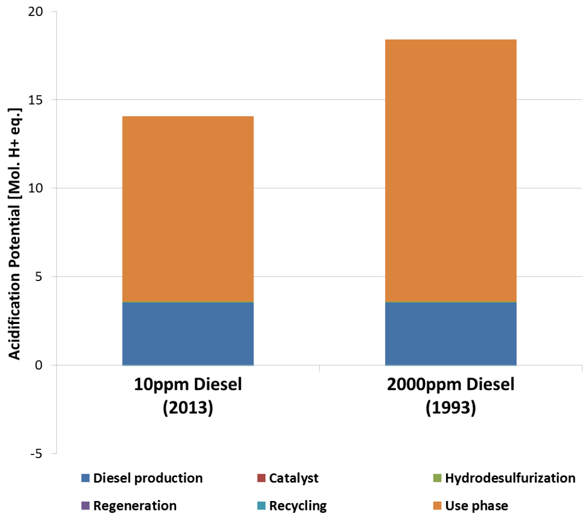
Environmental Assessment Results

Results for the full lifecycle of the two fuels from 'well-to-wheels' show that ultra-low sulfur diesel with a 10 ppm sulfur content has a lower impact than the 2000 ppm sulfur diesel in three of the impact categories assessed – acidification, smog creation potential and particulate matter/respiratory inorganics. For the remaining three impact categories, there is effectively no change in the results. Emissions of sulfur dioxide do not contribute to these impact categories, while the additional impacts associated with increased catalyst use and hydrodesulfurization result in increases in the overall impact for these categories of less than 0.01%. Overall results for the production and combustion of 1000 liters of the two fuels in a mid-sized Euro V passenger vehicle are summarized in the table above.

Overall, hydrodesulfurization has been extremely effective in reducing sulfur dioxide emissions from road vehicles across the EU. According to the International Energy Agency (IEA), annual total diesel consumption for road vehicles in the EU was just over 226 billion liters in 2011. This means that across the region the use of 10 ppm instead of 2000 ppm diesel in 2011 represents an annual reduction of 754,000 tons or 287 million m^3 of sulfur dioxide emissions.

The use of 10 ppm diesel means that despite a doubling in demand for diesel fuel for road vehicles in the past 20 years, sulfur dioxide emissions from this sector are at least 100 times lower across countries in the EU-28 than they were in 1993.

Acidification Potential



Lifecycle acidification impact for both 10 ppm ultra-low sulfur diesel and 2000 ppm diesel

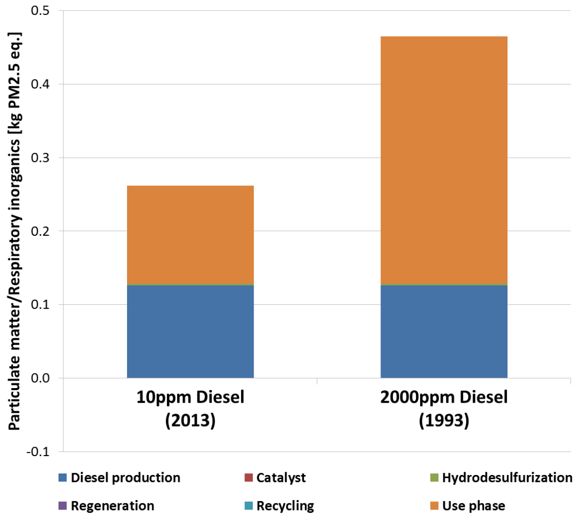
Compared to 2000 ppm diesel, the 10 ppm diesel shows a reduction in acidification of 24%. A breakdown of the acidification results by process stage is shown in the graph above. This illustrates the dominance of the use phase, which accounts for 74% of the total acidification potential for 10 ppm diesel and 80% of the impacts for 2000 ppm diesel. Diesel production processes other than hydrodesulfurization contribute almost all of the remaining impact. Processes and materials related to hydrodesulfurization contribute only 0.3% of the overall impact, with the production of the catalyst itself (including regeneration and recycling) accounting for only 0.06% of the overall acidification impact for 10 ppm diesel.

Given the significant reduction in the sulfur content in the fuel (a factor of 200) it might be expected that an even greater reduction in the acidification impact would be seen.

While use-phase sulfur dioxide emissions are indeed 200 times lower for 10 ppm diesel than for 2000 ppm diesel, the majority of the acidification impacts in the use phase are actually generated by emissions of nitrogen oxides, rather than sulfur dioxide, which are less affected by the fuel improvement covered in this case study. However, rapid reductions in NO_x emissions from vehicles are being driven by improvements in noble-metal catalytic convertors (NO_x limits for Euro VI diesel vehicles are less than half those for Euro V vehicles) so overall acidification potential from vehicles is likely to continue to reduce rapidly in the next few years.

Particulate Matter/Respiratory Inorganics

Another key area of improvement is in the particulate matter/respiratory inorganic impact category shown below. In the past, sulfur dioxide has been a major contributor to poor air quality that contributes to respiratory problems. In this study it was found that the potential impact from 10 ppm diesel was 44% lower than the impact of 2000 ppm diesel. Again, this category is dominated by the use phase and diesel production processes, with impacts from the hydrodesulfurization process representing only 0.1% of the total.



Lifecycle PM/respiratory inorganic impact for both 10 ppm ultra-low sulfur diesel and 2000 ppm diesel

Global Warming Potential

In terms of global warming potential, a key metric for all stakeholders in the automotive industry, almost no difference is observed in the impacts of the two fuel types. The hydrodesulfurization process contributes 0.7% to the total of which a mere 0.005% is attributable to the catalyst.

Discussion and Sensitivity

As highlighted in 'Data and Assumptions' the energy required for desulfurization can vary greatly depending on the characteristics of the incoming diesel fuel and plant design. To test the sensitivity of the results to this variability the fuel and electricity consumption required for the hydrodesulfurization process were doubled to model a plant with energy demand at the highest end of the range.

This resulted in an increase in overall impact of 0.7% for the global warming potential of 10 ppm diesel. Primary energy demand and eutrophication increased by 0.8% and 0.03% respectively, while for acidification, smog creation and particulate matter/respiratory inorganics, increases of between 0.3% and 0.8% are seen – significantly lower than the reductions in impacts from increased desulfurization.

As the impacts from catalyst manufacture are extremely low (0.06% of total acidification potential, 0.005% of total GWP) the results are highly unlikely to be sensitive to the assumption that catalyst production impacts in 1993 were the same as in 2013.

Another important assumption was the comparison of the two fuels in the same Euro V vehicle. In reality, significant improvements have been made in vehicle technology over the past two decades. These improvements have resulted in better fuel consumption, so 1000 liters of diesel carries a mid-sized vehicle further than it did 20 years ago. A comparison of a Euro I and Euro V vehicle over a set 200,000 km vehicle life shows improvements in global warming, eutrophication and primary energy demand of at least 17%, improvements in acidification of 75% and a ten-fold reduction in impacts from PM/respiratory inorganics.

Despite its benefits in reducing impacts related to a number of key environmental metrics, ultra-low sulfur diesel has been criticized for having an energy content around 1-2% lower than diesel with higher sulfur levels. This effect has not been modeled in this study.

Conversely, removing sulfur from fuel improves the operation and longevity of noble metal catalytic convertors used to control emissions of carbon monoxide, hydrocarbons and nitrogen oxides as sulfur damages or 'fouls' these catalysts. An analysis from the EU's DG-Environment also found 2-3% increases in fuel economy of new models in moving from 50 to 10ppm sulfur. These secondary benefits have also not been covered in this study.

Summary and Conclusions

For impacts related to acidification and air pollution (affecting health and smog creation), ultra-low sulfur diesel represents a significant improvement on the 2000 ppm diesel used when fuel specifications were first introduced in the EU in 1993. Importantly, the additional catalyst and regeneration required to produce 10 ppm diesel does not result in any meaningful increase (less than 0.01%) in other important metrics such as those related to climate change, eutrophication or primary energy demand. In other words, removing sulfur from diesel does not result in 'trade-offs' whereby some categories improve while others are negatively impacted.

Across the EU, the use of 10 ppm diesel has meant that despite a doubling in demand for diesel fuel for road vehicles in the past 20 years, sulfur dioxide emissions from this sector are at least 100 times lower across countries in the EU-28 than they were in 1993.

The lifecycle impacts are dominated by the use phase and diesel production processes other than hydrodesulfurization. Overall, impacts from hydrodesulfurization represent less than 1% of the total impact for all impact categories, with the majority of these impacts arising from the consumption of natural gas and electricity required to run the hydrodesulfurization unit. Given that the catalyst can be regenerated for use in two additional two-year production cycles, each kg of catalyst is, on average, responsible for removing around 600 kg of sulfur from 70,000 l of diesel.

The energy requirement for hydrodesulfurization units is highly dependent on plant design and the composition of the incoming fuel, but even a doubling of the fuel/electricity consumption of the hydrodesulfurization plant results in increases of less than 1% in the overall impacts of the fuel.

From a social perspective, the benefits of reducing levels of sulfur dioxide in the atmosphere are seen in air quality improvements in cities and reduced damage to sensitive natural environments such as forests. A study by the US EPA[1] found that reducing sulfur in fuel led to a significant reduction in respiratory problems resulting in premature death. The financial benefits of improving public health by reducing sulfur in fuel were 10 times higher than the increased refining costs. Another benefit is the reduced damage to historic buildings in cities, many of which were badly affected by acid rain in the last decades of the 20th century.

Overall, the results demonstrate that small increases in the consumption of molybdenum-containing catalysts and processing at the refinery can have a very large positive impact in the vehicle use phase, which is encouraging many countries and regions to adopt similar policies and reduce sulfur limits for their fuels.

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[1] EPA, 1999. *Regulatory Impact Analysis – Control of air pollution from new motor vehicles: Tier 2 motor vehicle emissions standards and gasoline sulfur control requirements.*

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