

This White Paper was issued by legacy Praxair as of the date indicated therein. It reflects engineering calculations made at the time. Linde's view is that these calculations remain valid. The White Paper may be updated periodically.



A White Paper

Authors

*Dante Bonaquist,
Corporate Fellow and Chief Scientist
Riva Krut,
Sustainable Development Director*

The Role of Hydrogen in Minimizing Black Carbon Emissions from Diesel Engines

May 2010

Visit www.praxair.com

The Role of Hydrogen in Minimizing Black Carbon Emissions from Diesel Engines

A White Paper

Authors

Dante Bonaquist, Corporate Fellow and Chief Scientist
Riva Krut, Sustainable Development Director

Abstract

Hydrogen has proven effective in the desulfurization of diesel fuel. Reductions in sulfur and aromatic levels achieved by the use of hydrogen in hydrotreaters at refineries has led to lower black carbon (BC) emissions and reductions in equivalent carbon dioxide emissions (CO₂e) in diesel engines that use particulate filters. The CO₂e from the production of hydrogen used for hydrotreating is 15 times lower than CO₂e enabled by ultra-low sulfur diesel (ULSD) fuel.

Introduction

The Policy Context

Recent studies have shown that BC has a significant effect on climate on a global and regional scale. On a short-term basis (measured in days or weeks), BC remains in the atmosphere and absorbs sunlight, thus contributing to global warming. Over a period of years, BC decreases the reflectivity of surfaces on which it is deposited and causes an increase in absorbed solar energy. This increase in absorbed energy has been equated through modeling to the effect of atmospheric carbon dioxide (CO₂) (1).

If sources of BC can be controlled in the near term, reductions in BC can produce faster results than reductions in greenhouse gas (GHG) emissions. In particular, reducing BC from diesel tailpipe emissions by the use of ultra-low sulfur diesel (ULSD) and a tailpipe

diesel particulate filter (DPF) could help to avoid a forecasted increase in global temperature. This does not solve the challenge over the long term — reducing CO₂ and other GHG emissions will remain the primary means for reaching long-term goals of limiting potential temperature increases — but scientists agree that BC reductions are a crucial tool in developing a comprehensive response to climate change (2).

In the European Union (EU) and the United States, road diesel engine emissions are the largest sources of BC. In both areas, ULSD is mandated. ULSD is made by adding hydrogen at a selected point within the refining process.

ULSD, when used with a DPF in the truck tailpipe, significantly reduces BC emissions. Figure 1 shows how current regulations have resulted in, and will continue to produce, continued BC reductions through 2025. The reductions are almost entirely from geographies with ULSD regulations (the OECD North America and OECD Europe). Within the OECD North America, U.S. transportation-related BC emissions are projected to decline by almost 70 percent from 2001 to 2020, and will account for only 2 percent of global on-road BC in 2020 (3).

However, in the business-as-usual case shown in Figure 1, projections show that in the years 2020 to 2050, the trend will be reversed and will climb to 20 percent above 2000 levels because of the increase in vehicles in use in emerging economies. Public policy analysts have argued that if ULSD was more widely mandated in

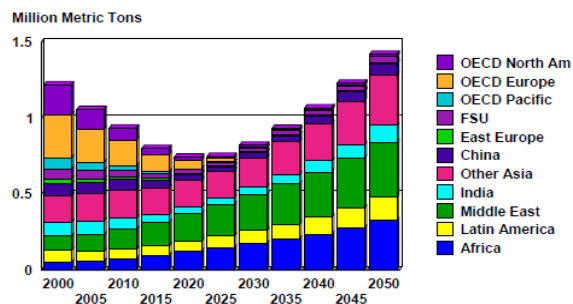


Figure 1: Road Vehicle BC Emissions by Country/Region (2000 to 2050) (4)

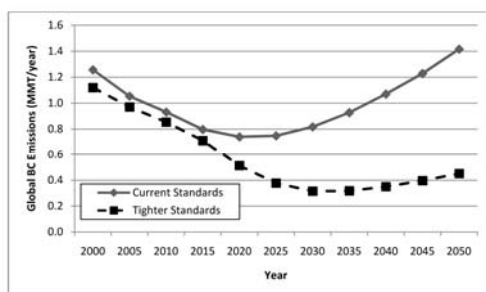


Figure 2: Global Trends in On-Road BC Emissions (normalized to 2000) (5)

developing economies, the level of global BC emissions could continue to be held down. (See the “Tighter Standards” projection in Figure 2.)

Regulations that promote ULSD, produced by the injection of hydrogen, are crucial to keep down the level of BC in the global atmosphere. In addition, U.S. Environmental Protection Agency (EPA) research shows that high levels of sulfur dioxide (SO₂) elevate incidences of respiratory illness, such as asthma, and cause acid rain. In helping to reduce sulfur dioxide emissions, ULSD also has other significant positive consequences for human health and the environment (6).

Hydrogen Production

Oil refineries use several catalytic processes that are both hydrogen producers (catalytic reforming) and consumers (hydrotreating and hydrocracking). Hydrotreating removes contaminants (sulfur, nitrogen) and saturates olefins and aromatics to yield a clean product for further processing or sales. Hydrocracking also removes contaminants while converting low-value gas oils to higher value products (naphtha,

middle distillates, and ultra-clean lube base stocks) (7).

Hydrotreating and hydrocracking are critical levers available to refiners to deal with the challenges created by the interaction of reduced crude quality, environmental requirements, and market demand (8).

As shown in Figure 3, refineries have become net consumers of hydrogen over the past 50 years, requiring reliable sources of “on purpose” production to achieve high conversion and meet clean fuel specifications (9).

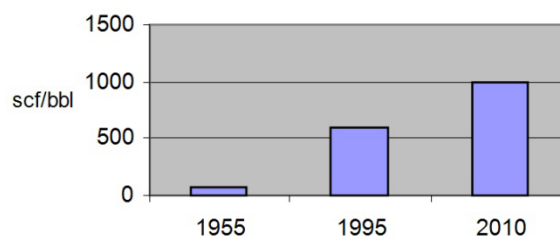


Figure 3: Refinery Hydrogen Demand

Figure 4 is a schematic of a hydrotreating process used to desulfurize diesel fuel. Hydrogen performs three critical roles in this process:

- Reaction with sulfur compounds to form hydrogen sulfide that can be removed for sulfur recovery.
- Hydrogenation of unsaturated compounds.
- Hydrogenolysis of certain undesirable compounds, such as thiophenes.

Diesel as a Transportation Fuel

The diesel engine is more efficient than its gasoline-fueled counterpart due primarily to a higher compression ratio and operating temperature. Additionally, the volumetric energy content (btu/gallon) of diesel is higher than other liquid fuels, such as gasoline, liquefied natural gas, methanol, ethanol, and butanol.

Diesel engine exhaust contains several constituents that are harmful to human health and to the environment, including SO₂ and diesel particulate matter (DPM). SO₂ is generated from the sulfur present in diesel fuel. The concentration of SO₂ in the exhaust gas depends on the sulfur content of the fuel.

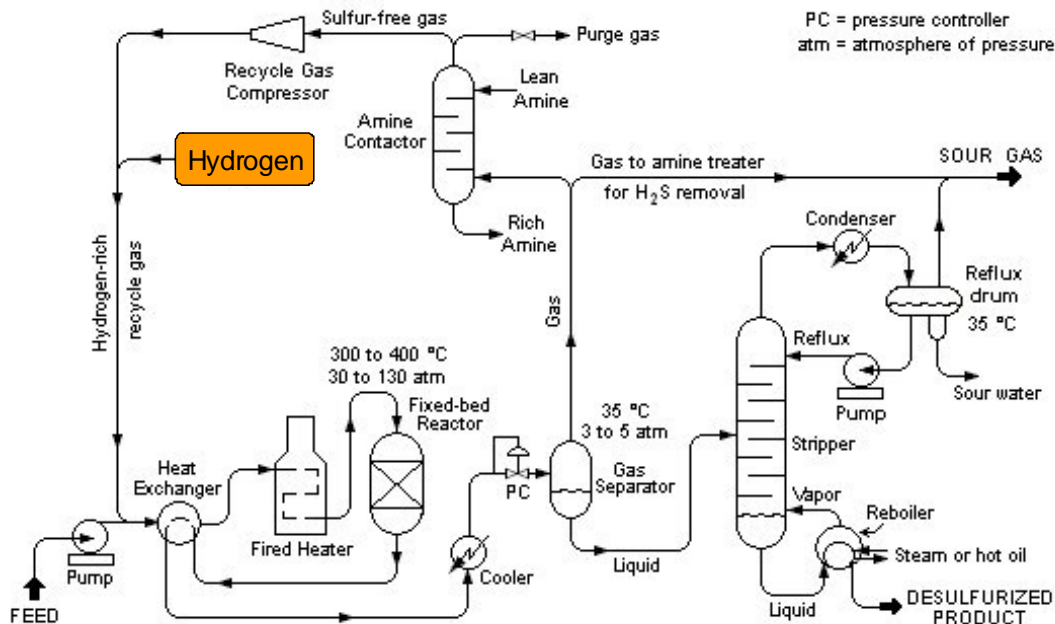


Figure 4: Hydrotreater Process (10)

As of 2006, almost all of the petroleum-based diesel fuel available in the EU and in North America is ULSD, which contains less than 15 ppmw sulfur (11).

BC Control with Filters

Among the constituents of DPM is BC, an elemental form of carbon emitted as an aerosol and distributed globally by wind currents. As shown in Figure 5, transportation accounts for 19 percent of global BC emissions.

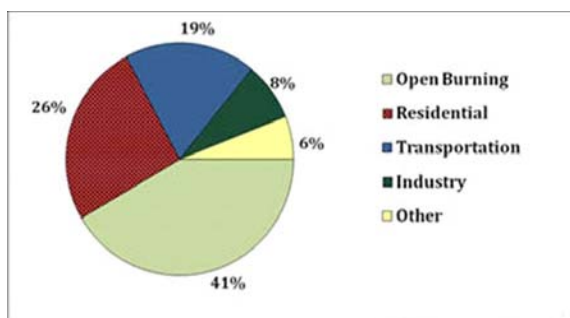


Figure 5: Global Black Carbon Emissions by Source (12)

It is estimated that BC constitutes 75 percent of DPM by mass. BC decreases the reflectivity of surfaces on which it is deposited, thereby causing an increase in absorbed solar energy. This increase in absorbed energy has been equated through modeling to the effect of atmospheric CO₂.

Global warming potential (GWP) is a weighting factor that compares the integrated radiative forcing of other greenhouse gas emissions to emissions of carbon dioxide. Integrated radiative forcing is the sum of the radiative forcing that a greenhouse gas emission produces over a chosen time horizon (13). With CO₂ assigned a value of 1, BC GWP₁₀₀ values range from 460 to 1500 and GWP₂₀ values range from 1600 to 4480. A GWP₂₀ of 1600 means that 1 mass unit of BC released into the atmosphere has the same time-integrated radiative forcing as 1600 mass units of CO₂ over a 20-year period following the release.

BC emissions can be reduced by the use of DPFs. L. Bruce Hill of the Clean Air Task Force has developed an estimate of the equivalent CO₂ reduction benefit for using DPFs on U.S.

Table 1
Diesel Particulate Filter Carbon Dioxide Equivalent Reduction ULSD

	Mass (grams/gal)	CO ₂ e (grams/gal)	GWP	Notes
Diesel fuel	3220.5			
Diesel fuel carbon content	2737.4			
Diesel fuel CO ₂ emissions	10,037.2	10,037.2	1	
Black carbon emissions	1.2	2640	2200	
Organic carbon emissions	0.4	(100)	(250)	
Diesel fuel total CO ₂ e without DPF		12,577.2		
DPF fuel efficiency penalty		205.8		
DPM removed by DPF		2286		
Diesel fuel total CO ₂ e with DPF		10,497		90% removal
Net percent reduction in CO ₂ e		16.5		

Class 8 trucks with ULSD fuel (14). The estimate assumes a 90 percent particle trapping efficiency. The net equivalent CO₂ reduction (taking into account the impact of the filter on fuel efficiency) is 16.5 percent using GWP₂₀ = 2200. The results of Hill's calculations are shown in Table 1. The near-term focus reflected in the use of GWP₂₀ is consistent with the goal of identifying ways to mitigate the impact of greenhouse gas emissions today while longer-term solutions are developed.

Diesel Hydrotreating Enables Black Carbon Control

The effectiveness of DPFs is highly dependent upon the sulfur content of the diesel. As reported in the Department of Energy's (DOE's) Diesel Emissions Control – Sulfur Effects Project: (DECSE) Summary of Reports, sulfur levels of 30 ppmw or less are necessary to achieve a particle trapping efficiency of 73 percent or higher (15). The same report states the following about filter effectiveness: “When tested with the 150 ppm sulfur fuel, particulate matter (PM) reductions were near zero, and when tested with 350 ppm sulfur fuel, PM actually increases.”

Albemarle, a supplier of catalysts, technologies, and related services to the petroleum refining industry, states that low sulfur levels are necessary, but not sufficient, to achieve emissions reductions in BC, carbon monoxide (CO), and nitrogen oxides (NOx) (16). A total aromatic content of 5 percent or less in the diesel fuel is also needed, Albemarle concluded.

Both sulfur reduction and aromatic saturation take place in hydrotreating units. Hydrogen is necessary to carry out the corresponding chemical reactions; therefore, hydrogen may be considered an enabling agent in the production of ULSD and the BC emissions reductions that are realized by particle filters

CO₂ Equivalent Reduction for Diesel Hydrotreating

Estimating the equivalent CO₂ reduction attributable to diesel hydrotreating can be done as an extension of Hill's work. First, we must recognize that sulfates emitted from the tailpipe of diesel vehicles have a global cooling effect. Thus, the equivalent CO₂e for a diesel engine using ULSD is higher than with fuel containing 350 ppmw sulfur. As reported in DECSE (17), 40 to 60 percent of the sulfur in diesel fuel is.

Table 2
Diesel Particulate Filter Carbon Dioxide Equivalent Reduction ULSD

	Mass (grams/gal)	CO ₂ e (grams/gal)	GWP	Notes
Diesel fuel	3220.5			
Diesel fuel carbon content	2737.4			
Diesel fuel CO ₂ emissions	10,037.2	10,037.2	1	
Black carbon emissions	1.2	2640	2200	
Organic carbon emissions	0.4	(100)	(250)	
Sulfate emissions	1.6	(534.6)	(330)	
Diesel fuel total CO ₂ e without DPF		12,042.6		
DPF fuel efficiency penalty		205.8		
CO ₂ emissions from hydrogen		129		
DPM removed by DPF		2286		90% removal
Diesel fuel total CO ₂ e with DPF		10,091.4		
Net percent reduction in CO ₂ e		16.2		
CO ₂ e reduction enabled by hydrogen*		1951.2		
*Calculated as diesel fuel total CO ₂ e without DPF minus CO ₂ e with DPF.				

converted to sulfates (SO₄). Using this factor, the change in sulfate emissions by hydrotreating from 350 ppmw to 15 ppmw sulfur is calculated as:

$$3,220.5 \text{ g/gal} * (350-15) * 10^{-6} * (96/32) * 50\% \text{ conversion} = 1.62 \text{ g of SO}_4/\text{gallon}$$

(96/32) is the molecular weight ratio of SO₄ to sulfur (S)

The GWP₂₀ of atmospheric SO₄ proposed by SCS (18) is -330, resulting in a CO₂e increase of 534.6 g/gal for the sulfate emission change given above.

Second, we must account for the CO₂e from the process supplying hydrogen to the diesel hydrotreater. Each barrel of diesel treated requires 600 scf of hydrogen, of which 240 scf come from hydrogen plants. The balance is available from internal refinery sources. CO₂e from reforming natural gas, the primary means of hydrogen production employed in the United

States, is 22.7 g of CO₂/scf of hydrogen (based on the widely accepted figure of 2500 tons of CO₂ emitted per 100 million scf of hydrogen from a large-scale hydrogen plant). CO₂e due to the hydrogen used for hydrotreating are:

$$22.6 \text{ g/scf} * 240 \text{ scf/bbl} * (1/42) \text{ gal/bbl} = 129 \text{ g/gal of diesel fuel}$$

With the above information, Table 1 can be modified to include the effects of diesel hydrotreating. See Table 2.

Note that reduction in CO₂e enabled by hydrogen (1951.2 g/gal) is 15 times greater than the CO₂ emitted in producing the hydrogen (129 g/gal), assuming that ULSD is used in vehicles equipped with particle filters.

U.S. refining capacity data from Purvin and Gertz (19) show that 32 percent of the hydrogen used in refineries is for distillate hydrotreating (based on installed capacity). Praxair's survey of existing refinery customers indicates that 20

to 40 percent of hydrogen supplied by Praxair goes to distillate hydrotreating. Assuming 20 percent and the 15:1 ratio calculated above, it is apparent that the total CO₂e from Praxair's hydrogen plants are more than offset by the potential CO₂e reductions enabled by the hydrogen. (In fact, the reduction in CO₂e enabled by hydrogen used for diesel hydrotreating is potentially three times greater than the total CO₂e from the hydrogen plant.) In addition to CO₂e reduction at the tailpipe of the diesel vehicle, hydrogen also enables up to 28 percent lower CO and 4 to 10 percent lower NO_x emissions by saturating aromatic compounds (20).

Conclusions

Published methods for determining CO₂ equivalency have been extended to evaluate the benefits of hydrogen used for desulfurization of diesel fuel. DOE reports shows that ULSD is necessary to obtain the demonstrated reduction in BC emissions from diesel engines that use DPFs. Without the corresponding reductions in sulfur and aromatic levels achieved by the use of hydrogen in hydrotreaters, the lowering of BC emissions leading to reductions in equivalent CO₂e would not be achieved by DPFs.

The reduction in equivalent CO₂e per unit of diesel fuel consumed (taking into account CO₂e from the production of hydrogen) is 16.2 percent of equivalent CO₂ tailpipe emissions based on the accounting methodology of Hill. The contribution of CO₂e from the production of hydrogen used for hydrotreating is 15x lower than the CO₂e enabled by ULSD and particulate filters. Additionally, other benefits of hydrotreating include reductions in CO and NO_x, as well as reduction in sulfur emissions.

Acknowledgments

The conclusions in this paper were independently confirmed by Professor Adel Sarofim of the University of Utah. We also thank him for several helpful suggestions to sharpen the argument.

References

1. Bachmann, John. Black Carbon: A Science/Policy Primer; Vision Air Consulting, LLC, Pew Center on Global Climate Change, December 2009, p.2-10; Terry Keating, Ph.D., EPA Office of Air and Radiation, and Marcus Sarofim, Ph.D., AAAS Environmental Science Fellow, "Black Carbon 101". March 6, 2009, <http://www.pewclimate.org/science/black-carbon-primer>.
2. *ibid.*, p. 36-38.
3. Walsh, Michael P. On and Off Road Policy Strategies. ICCT International Workshop on Black Carbon, London, January 2009.
4. *ibid.*, p.2.
5. Bachmann, p.27.
6. http://cfpub.epa.gov/eroe/index.cfm?fus_eaction=detail.viewInd&lv=list.listByAlpha&r=219694&subtop=341.
7. Colwell, R. Oil Refinery Processes: A Brief Overview; Process Engineering Associates, LLC, <http://www.processengr.com/>.
8. Ackelson, D. Chapter 7.2, UOP Unicracking Process for Hydrocracking: Handbook of Petroleum Refining Processes, 3rd Edition. Robert Meyers, ed. McGraw Hill, 2003.
9. Patel, N., et al. Creating Value Through Refinery Hydrogen Management, <http://www.h2alliance.com/>.
10. <http://www.hydrocarbons-technology.com/projects/shellultralow/shellultralow1.html>.
11. <http://www.nett.ca/faq/index.html>.
12. Bond, T.C., D.G. Streets, K.F. Yarber, S.M. Nelson, J.H. Woo, and Z. Klimont. A Technology-Based Global Inventory of Black and Organic Carbon Emissions from Combustion. J. Geophys. Res. 109, D14203, 2004, p.31.
13. Hill, L. Bruce. The Carbon Dioxide-Equivalent Benefits of Reducing Black Carbon Emissions from U.S. Class 8 Trucks Using Diesel Particulate Filters: A Preliminary Analysis; Clean Air Task Force, September 10, 2009.

-
14. Diesel Emissions Control – Sulfur Effects Project (DECSE): Summary of Reports; NREL/TP-540-31600, February 2002.
 15. Next Step to Cleaner Diesel Fuels. Catalyst Courier. Albemarle Catalysts, Spring 2005, Vol. 59.
 16. Hill, L. Bruce. (see footnote 13).
 17. Albemarle Catalysts (see footnote 15).
 18. Life Cycle Stressor-Effects Assessment, Greenhouse Gas Accounting Framework, proposed climate annex to SCS-002. Scientific Certification Systems, Inc., www.SCScertified.com, 2009.
 19. Purvin & Gertz. Global Petroleum Market Outlook. Petroleum Balances, Houston, April 2009.
 20. Albemarle Catalysts (see footnote 15).