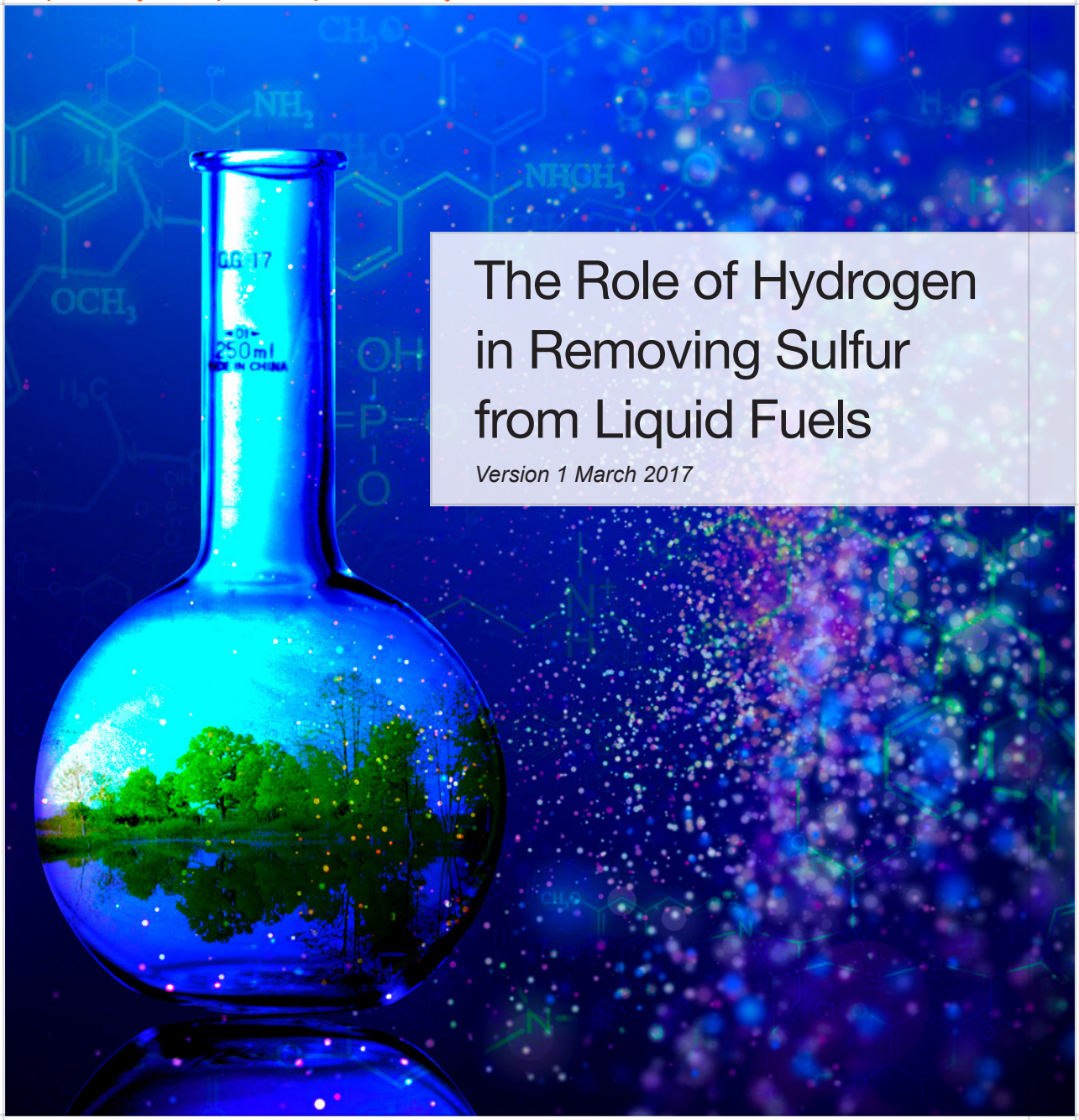
This White Paper was issued by legacy Praxair as of the date indicated therein. It reflects engineering calculations made at the time. Linde's view is that these calculations remain valid. The White Paper may be updated periodically.

PRAXAIR

Making our planet more productive



The Role of Hydrogen in Removing Sulfur from Liquid Fuels

Version 1 March 2017

Summary



This paper discusses the contribution of hydrogen, supplied by Praxair to refineries, in eliminating sulfur emissions from petroleum based fuels. Regulations in the USA and EU that have mandated the removal of sulfur from fuel have significantly reduced the overall volume of sulfur dioxide (SO_2) emissions to the environment. This result can be achieved in other markets – in particular, in emerging economies with acute problems of air pollution and SO_2 emissions from diesel exhausts in urban centers.

Hydrogen is a proven solution that can contribute to reducing the burgeoning problem of air pollution and SO_2 emissions from diesel exhausts in middle-income countries. We estimate Praxair supplies 194 million scf per day of hydrogen specifically to remove sulfur. This is equivalent to 1.6 million tons per year of SO_2. Moreover, the large market for elemental sulfur in the US is met by recovered sulfur.

The potential adverse health effects due to emissions of SO_2 into the atmosphere by fossil fuel combustion processes are well documented. Short-term exposures to SO_2 can harm the human respiratory system and make breathing difficult. Children, the elderly, and those who suffer from asthma are particularly sensitive to effects of SO_2 [1]. Adding hydrogen to crude oil significantly reduces sulfur content and effectively eliminates SO_2 emissions from diesel fuel.

SO_2 is principally emitted by fuel combustion in coal fired power plants, refineries, smelters, paper and pulp mills and food processing plants [2]. Crude oil, the raw material used to produce liquid fuels (gasoline, diesel, jet fuel and heating oil) contains significant amounts of sulfur. The average sulfur content of crude oil refined in the US today is approaching 1.4% by weight[3]. US regulations require that practically all of this sulfur be removed in the refining process to prevent SO_2 from being emitted when the fuel is burned. Furthermore, the operation of critical pollution control equipment such as diesel particulate filters on trucks and catalytic converters on light passenger vehicles requires low sulfur fuels[4].

Additionally, hydrogen enables the recovery of the elemental sulfur removed from petroleum products. In the US, the availability of sulfur as a byproduct has eliminated the need to mine for on-purpose sulfur. The vast array of products for which sulfur is an ingredient can now make use of recycled material from oil refineries and natural gas processing, rather than virgin sulfur from other sources[5].

[1] https://www.epa.gov/so2-pollution/sulfur-dioxide-basics#effects

[2] Koenig, Jane; and Therese F Mar: "Sulfur Dioxide: Evaluation of Current California Air Quality Standards with Respect to Protection of Children". Department of Environmental Health, Univ. of Washington, Seattle, WA 98195. Paper Prepared for California Air Resource Board, Ca. Office of Environmental Health Hazard Assessment, Sept. 1, 2000

[3] EIA data for October 2016: average sulfur content of crude input to US refineries = 1.38%; average API gravity = 31.36; http://www.eia.gov/dnav/pet/pet_pnp_crq_dcu_nus_m.htm

[4] Blumberg, K.O, et al., "Low-Sulfur Gasoline and Diesel: The Key to Lower Vehicle Emissions", http://walshcarlines.com/conventfuels.html (2003)
"Praxair White Paper: The Role of Hydrogen in Minimizing Black Carbon Emissions from Diesel Engines", http://www.praxair.com/-/media/documents/reports-papers-case-studies-and presentations/our-company/sustainability/praxair-h2-minimizing-black-carbon-emissions-white-paper.pdf

[5] Ober, Joyce A., "Material Flow of Sulfur", US Department of the Interior, US Geological Survey, Open-File Report 02–298.; http://pubs.usgs.gov/of/2002/of02-298/

Hydrotreating

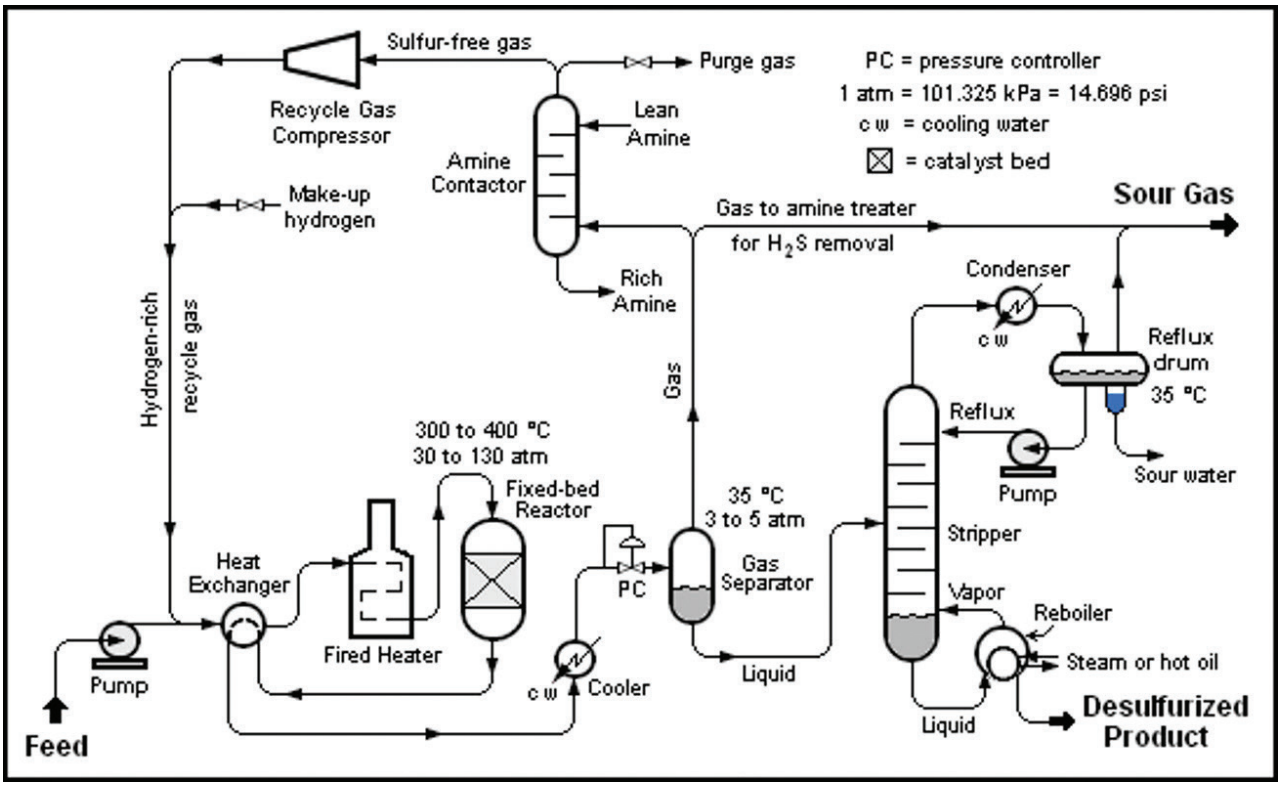
Hydrotreating is a refinery process used to catalytically stabilize petroleum products (saturate olefins) and remove impurities or unnecessary constituents from both products and feedstocks by reactions involving hydrogen. Sulfur, nitrogen, oxygen, halides and metals can be removed by hydrotreating. When the process is specifically used for sulfur removal, it is called hydrodesulfurization (HDS)[7].

Sulfur compounds are removed from diesel product and feed streams used to produce gasoline by reacting them with hydrogen in the presence of cobalt-molybdenum or nickel-molybdenum catalysts at elevated temperature and pressure. The bonds between the sulfur and carbon atoms of the organic sulfur molecule are cleaved. Hydrogen replaces sulfur on the organic molecule, while hydrogen sulfide (H2S) is formed as shown in the reaction below for an organic sulfide molecule. Note that 2 moles of hydrogen are required to remove one mole of sulfur in this instance. Other forms of organic sulfur require more or less hydrogen to treat. The typical hydrogen consumption for hydrodesulfurization is about 70 scf per barrel per percent sulfur[8], which suggests that the distribution of sulfur compounds is such that 1.85 moles of hydrogen are needed to remove 1 mole of sulfur. We will make use of this ratio in subsequent calculations.

$$\text{R-S-R'} + 2\ \text{H2} \Rightarrow \text{R-H} + \text{R'-H} + \text{H2S}$$

Figure 1 is a flow diagram for a hydrodesulfurization process. Note that the H_2S is separated from the desulfurized product steam after cooling by stripping. The disposition of the H_2S will be discussed later.

Figure 1.



[6] Manning, Francis S., "Oilfield Processing of Petroleum: Crude Oil", PennWell Books, (1995), p.12.
[7] Gary, James H. and Glenn E. Handwerk, "Petroleum Refining Technology and Economics", 3rd Edition, Marcel Dekker, Inc. (1994), p187.
[8] Ibid, p193.

Quantifying the Impact of Liquid Fuel Desulfurization

Table 2. *US Refinery Crude Oil Data*

Refinery input of crude oil	15,454,000 bbl/day[a]
Weighted average S content	1.38% by weight[b]
Weighted average API gravity	31.35 Degrees[c]
API gravity converted to density	**7.238 lbs/gallon**

a October 2016 EIA data; http://www.eia.gov/dnav/pet/pet_sum_snd_d_nus_mbblpd_m_cur.htm
b October 2016 EIA data; http://www.eia.gov/dnav/pet/PET_PNP_CRQ_DCU_NUS_M.htm
c Ibid

Data on crude oil processed in US refineries is given in Table 2.

Accounting for current sulfur specification for various liquid fuels, the disposition of sulfur in non-liquid fuel products such as petroleum coke, asphalt, road oil and refinery sulfur air emissions, it is estimated that 90% of the sulfur entering US refineries in the crude oil is converted to H_2S which is ultimately recovered as elemental sulfur[10]. Using this factor, together with the data in Table 2, the amount of sulfur removed by US refineries from liquid fuels is estimated to be 30,000 short tons per day based on October 2016 data.

Independent of this calculation, the US Energy Information Administration (EIA) reports the sulfur production capacity of US refineries in 2016 as 41,343 tons per day[11] with an overall refinery capacity utilization of 85.4%[12].

The EIA figures suggest that sulfur removed from liquid fuels by refineries could be as high as 35,300 tons per day.

The lower figure of 30,000 tons per day of sulfur recovered by US refineries equates to 60,000 tons per day of SO_2 or 21,900,000 tons annually. As previously stated, one mole of sulfur recovered requires an average of 1.85 moles of hydrogen as H_2. The volume of hydrogen needed for desulfurization can be calculated as: 30,000 tons of S per day x (1.85 x 2/32) x 384,000 standard cubic feet (scf) H_2 per ton = 1.33 billion scf of H_2 per day.

The EIA reports captive hydrogen production capacity at US refineries at 3.0 billion scf per day[13] in 2016. Data from the DOE estimates merchant hydrogen capacity (operated by industrial gas firms) at 3.9 billion scf per day in 2013[14], of which 90%[15] is sold to refineries.

We conclude then that 20.4% of all hydrogen produced for oil refineries is used for desulfurization of refined products.

Figure 2 shows the quantity and distribution of US SO_2 emissions as recorded in EPA National Emissions Inventory database for 2013[16]. The total from all sources is 5,170,000 tons per year. Fuel (coal) combustion at power plants is the largest contributor to SO_2 emissions. Less than 2% of all SO_2 emissions come from mobile sources that burn gasoline and diesel fuel. Desulfurization of liquid fuels produced by refineries has been an overwhelming success in our efforts to minimize SO_2 emissions. It can be argued that 99.5% of the potential SO_2 emissions from fuels produced from petroleum have been eliminated by technology that uses hydrogen for desulfurization.

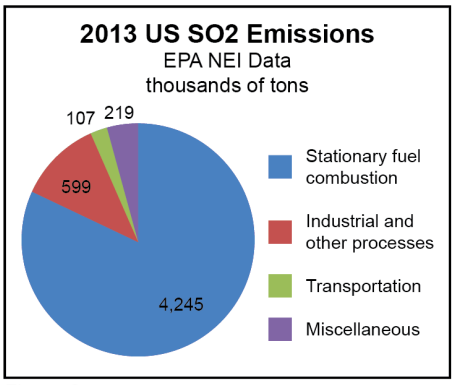


Figure 2.

[9] Hydrodesulfurization, http://en.wikipedia.org/w/index.php?title=Hydrodesulfurization&oldid=590911351 (last visited Jan. 24, 2014).
[10] Praxair estimate
[11] http://www.eia.gov/dnav/pet/PET_PNP_CAPPROD_DCU_NUS_A.htm
[12] http://www.eia.gov/dnav/pet/pet_pnp_unc_dcu_nus_m.htm
[13] http://www.eia.gov/dnav/pet/pet_pnp_capprod_dcu_nus_a.htmprojection and 2011 value).
[14] Joseck, F. "Current U.S. Hydrogen Production", DOE Hydrogen and Fuel Cells Program Record, Record #12014, June 18, 2012, (calculated by linear interpolation between 2016 projection and 2011 value).
[15] The Fredonia Group, "World Hydrogen", Study #2605 February 2010.
[16] http://www.epa.gov/ttnchie1/trends/

Sulfur Compounds in Petroleum

Sulfur is naturally present to varying degrees in all crude oils. Generally, crudes with sulfur contents above 0.5% by weight are considered sour. Most oils contain from 0.1% to 3% sulfur. Volatile sulfur compounds including hydrogen sulfide (H_2S) and some mercaptans are removed prior to the oil reaching the refinery[6]. The refinery is left to deal with a wide range of sulfur compounds including mercaptans, sulfides, disulfides and thiophenes. The structures for these compounds are given in Table 1.

Depending upon the compound's boiling point, the sulfur containing species will be distributed between various streams drawn from the refinery's atmospheric and vacuum distillation units and will have to be addressed by subsequent refinery operations.

Table 1. *Sulfur Compounds Present in Crude Oils*

Class	Structure
mercaptans	R-S-H
sulfides	R-S-R'
disulfides	R-S-S-R
thiophenes	

Recovering the Sulfur

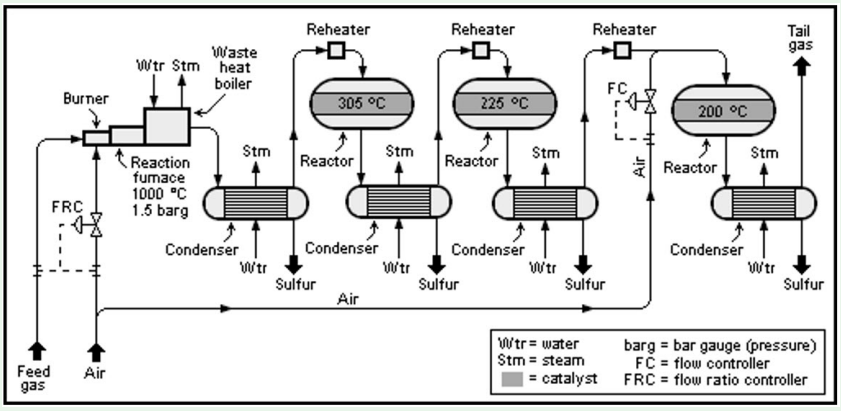


Figure 3.

Hydrogen replaces sulfur in the organic sulfur species found in crude oil converting that sulfur to H_2S. To recover elemental sulfur (S), a Claus plant, also known in the refining industry as a sulfur recovery unit (SRU), is employed. In this unit one-third of the incoming H_2S is burned to form SO_2. The heat released from combustion of H_2S and subsequent reactions is recovered as steam.

$$\mathbf{2\ H_2S + 3\ O_2 => 2\ SO_2 + 2\ H_2O + heat}$$

The balance of the H_2S is reacted catalytically with SO_2 produced by the first reaction to form elemental sulfur. Multiple catalytic stages are utilized to convert more than 98% of the H_2S to S.

$$\mathbf{2\ H_2S + SO_2 => 2\ S + 2\ H_2O + heat}$$

Figure 3 is a schematic of a Claus[17] plant. The underlying process was patented by C. F Claus in 1883. It remains as the industry standard for sulfur recovery in petroleum refining and natural gas processing.

[17] Claus process, http://en.wikipedia.org/wiki/Claus_process (last visited Jan. 27, 2014)
[18] Meyers, R. L., "The 100 Most Important Chemical Compounds: A Reference Guide", Greenwood Press, Westport, CT, (2007) p272.
[19] Ober, pp12-16.

Recovered Sulfur has Replaced On-purpose Production in the US

Sulfur and sulfur compounds are key ingredients in a number of industrial and consumer products. Among these is sulfuric acid, the use of which is so prevalent across a range of manufacturing and industrial processes, that the annual volume of sulfuric acid produced is often used as an indicator of economic activity. Sulfuric acid is the highest volume chemical made in the US and is the largest single consumer of sulfur. Both of the primary processes for making sulfuric acid begin by combusting S to form SO_2. SO_2 is subsequently further oxidized to sulfur trioxide (SO_3) which is ultimately reacted with water forming sulfuric acid (H_2SO_4). About 40,000,000 tons of sulfuric acid per year is produced in the US[18] accounting for 36,000 tons per day of sulfur.

$$S + O_2 \Rightarrow SO_2$$

$$2\ SO_2 + O_2 \Rightarrow 2\ SO_3$$

$$SO_3 + H_2O \Rightarrow H_2SO_4$$

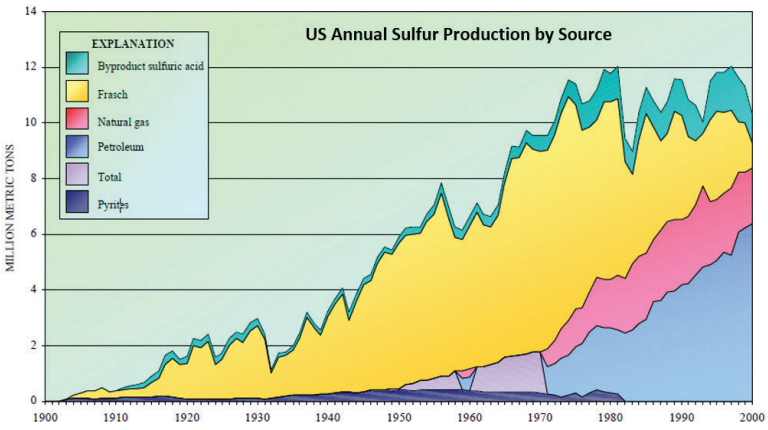


Figure 4.

Elemental sulfur occurs naturally together with salt in large underground deposits along the Gulf of Mexico in Louisiana and Texas. Historically, the US demand for sulfur has been met by solution mining these deposits using hot water to melt the sulfur. This method is known as the Fracsh Process after its inventor Herman Frasch. The Frasch Process was commercialized in the early 1900s, becoming the dominate means of producing sulfur until the early 1970s when the recovery of sulfur from petroleum and natural gas became significant. By 2000, Frasch mining of sulfur had been completely displaced by recovered sulfur as shown in Figure 4.

Conclusions

US refineries use 1.33 billion scf of hydrogen each day to remove sulfur compounds from gasoline, diesel fuel and other products. The amount of sulfur removed is equivalent to 21.9 million tons per year of SO2.

Using the ratio of total hydrogen produced for petroleum refining to that used by refineries for sulfur removal, we estimate Praxair supplies 194 million scf per day of hydrogen specifically to remove sulfur. This is equivalent to enabling the avoidance of 1.6 million tons per year of SO2 or about 31% of the total US SO2 emissions in 2013.

The sulfur recovered by refineries and natural gas processing plants has completely eliminated the need for sulfur mining and extraction from other minerals. The large market for elemental sulfur in the US is met by recovered sulfur.

Hydrogen is a proven solution that can contribute to reducing the burgeoning problem of air pollution and SO2 emissions from diesel exhausts in middle-income countries. The US experience for reducing tailpipe sulfur emissions culminating with the implementation of US EPA's Tier 3 standards, which lower gasoline sulfur content to less than 10 ppm starting in 2017, has demonstrated the ability to achieve air quality targets. [20]

[20] EPA Sets Tier 3 Motor Vehicle Emission and Fuel Standards, EPA-420-F-14-009, March 2014.

A Global Leader

Praxair is one of the largest industrial gases companies in the world, and the largest in North and South America. We operate in more than 50 countries and serve one million customers in a wide variety of industries including: energy, manufacturing, chemicals, metal production, and healthcare. To learn more about Praxair's gas supply expertise, call us at 1-800-PRAXAIR or visit our website at www.praxair.com.

USA
Praxair, Inc.
10 Riverview Drive
Danbury, CT 06810
Phone: 1-800-PRAXAIR
1-800-772-9247
www.praxair.com

Canada
Praxair Canada, Inc.
1 City Centre Drive, Suite 1200
Mississauga, ON L5B 1M2
Canada
Phone: 905.803.1600
www.praxair.com

Mexico
Praxair Mexico S.A. de C.V.
Biologo Maximino Martinez
No. 3804
Col. San Salvador Xochimanca
02870, Mexico D.F.
Phone: +52(55)5354.9500
www.praxair.com.mx

South America
White Martins Gases
Industriais Ltda.
Avenida das Américas, 3434,
Bloco 7, 6th fl.
22640-102 Rio de Janeiro
Brazil
Phone: + 55 (21) 3431.2000
www.whitemartins.com.br

Europe
Praxair España S.L.
c/ Orense, 11
E-28020 Madrid
Spain
Phone: +34(91)453.3000
www.praxair.es

Scandinavia
Praxair Scandinavia AS
PB 23 Haugenstua
0915 Oslo
Norway
Phone: 04277 (+47 21 49 34 34)
www.praxair.no

India
Praxair India Private Limited
"Praxair House"
No. 8, Ulsoor Road
Bangalore –560 042
India
Phone: +91.1800.425.8077
www.praxair.com/india

China
Praxair Asia Inc.
21 fl., Eton Place
69 Dongfang Road
Pudong, Shanghai 200120
PRC
Phone: +86(21)2894.7000
www.praxair.cn

Praxair Korea Co. Ltd
943-19, Shinan Building 16th fl.
Kangnam-gu, Daechi-dong
Seoul, 135-280
Korea
Phone: +82.2.569.4100
www.praxair.com/korea

PRAXAIR
Making our planet more productive™

© Copyright 2017 Praxair Technology, Inc.
All rights reserved.

Praxair, the *Flowing Airstream design*, *Making our planet more productive*, and (any other trademark name) are trademarks or registered trademarks of Praxair Technology, Inc. in the United States and/or other countries. Other trademarks used herein are the registered trademarks of their respective owners.

The information contained herein is offered for use by technically qualified personnel at their discretion and risk without warranty of any kind.

Printed in the United States of America
3-17

Printed on recycled paper
P-15-763

Praxair, Inc.
10 Riverview Dr.
Danbury, CT 06810
USA

www.praxair.com
info@praxair.com

Telephone:
1-800-PRAXAIR (1-800-772-9247)
(716) 879-4077

Fax:
1-800-772-9985
(716) 879-2040