Sulphur Dioxide Reduction from Exhaust Gas via Ammonia Injection and Ammonium Sulphate Production

Author: Dr Steven Iglesias and Dr William Ramsay
Date: December 16, 2022

DAPHNE® TECHNOLOGY
Chemin de la Venoge 7, 1025 Saint Sulpice, Switzerland
www.daphnetechnology.com
+41 (0) 21 357 54 56 | info@daphnetechnology.com

Table of Contents

1. Introduction

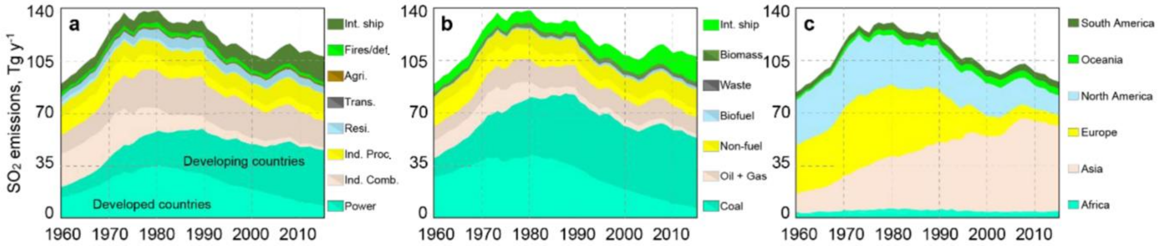


Figure 1. Annual trends of sulphur dioxide (SO_2) emissions by sector (a), fuel type (b), and region (c).[1]

SulPure®, developed by Daphne Technology, is a turnkey solution for the petrochemical, power, and transportation industries to remove sulphur oxides (SO_x) emissions in exhaust or flue streams to the levels required by international and national regulations. As shown in **Figure 1**, international shipping has contributed strongly to sulphur dioxide (SO_2) air emissions from the combustion of Heavy Fuel Oil (HFO) with high sulphur content.

This document summarizes the test results that were obtained by the operation of a full-scale (1.5MW) SulPure® pilot at the Maritime Centre of Flensburg University of Applied Sciences (Hochschule Flensburg) (**Figure 2**). The 1.5MW SulPure® prototype was installed on the exhaust outlet of a 700 kW marine diesel engine (based on MaK M 452 and M 282 engine components) combusting 2.4%m S content marine residual HFO. Marine engines can typically use fuel with a sulphur content ranging from 3.5%m to 0.5%m S, which translates into SO_2 emissions above marine regulations[2] and above land-based combustion plants in Europe[3] .

The exhaust gas cleaning technology behind SulPure® is the conversion of SO_2 in exhaust gas into ammonium sulphate ($(NH_4)_2SO_4$), a technique mentioned in the Best Available Techniques Reference Document (BRef) for Large Combustion Plants written by the European Commission[4]. However, the technique cited in BRef uses an architecture that consumes 1 – 3% of the power generated, which results in a considerable carbon footprint even for petrochemical applications, where the carbon footprint can be translated in terms of the carbon factor of the power used for removal. In contrast, the 1.5MW SulPure® prototype resulted in 0.7% of power consumption following the same rational.

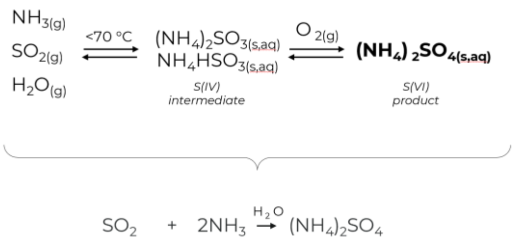
Figure 2. SulPure® prototype installed at the Maritime Centre of Flensburg University of Applied Sciences (Hochschule Flensburg).

---

[1] Zhong, Qirui; Shen, Huizhong; Yun, Xiao; Chen, Yilin; Ren, Yu'ang; Xu, Haoran; Shen, Guofeng; Du, Wei; Meng, Jing; Li, Wei; Ma, Jianmin; Tao, Shu (2020). *Global sulfur dioxide emissions and the driving forces. Environmental Science & Technology, acs.est.9b07696–.* doi:10.1021/acs.est.9b07696
[2] *IMO 2020 – cutting sulphur oxide emissions* (no date). Available at: https://www.imo.org/en/MediaCentre/HotTopics/Pages/Sulphur-2020.aspx.
[3] European Commission DG Environment (no date) *Directive (EU) 2015/2193 of the European Parliament and of the Council of 25 November 2015 on the limitation of emissions of certain pollutants into the air from medium combustion plants (MCP Directive)*. Available at: https://unece.org/DAM/env/documents/2015/AIR/WGSR/European_Union_2015.pdf.
[4] *Large Combustion Plants | Eippcb* (no date). Available at: https://eippcb.jrc.ec.europa.eu/reference/large-combustion-plants-0.

2. SulPure® Technology

The purification process in SulPure® uses ammonia (NH_3) and water (H_2O) injections into exhaust gas to react with SO_2, which produces ammonium sulphate ($(NH_4)_2SO_4$) as the product (**Figure 3**). The removal of SO_2 by NH_3 gas injection at various temperatures and moisture contents has been studied experimentally, and the product compositions of the NH_3-SO_2-H_2O vapor reactions have also been reported. It is generally agreed that the main reaction product from NH_3-SO_2-H_2O vapor reactions is $(NH_4)_2SO_4$ (**Equation 1**). Both the experimental results and thermodynamic analysis indicated that SO_2 removal and the product compositions are sensitive to the reaction temperature. Moisture content, once in large excess of the stoichiometric requirement, does not have a strong effect on the product compositions but plays an important role in the SO_2 removal. The $(NH_4)_2SO_4$ that is formed in the exhaust gas is collected as a liquid solution (5 – 41wt%) via partial condensation of the water content in the exhaust gas.
The technique gives a competitive advantage in terms of efficiency over other available technologies reducing SOx, which consist mainly of scrubbers. The scrubbing process requires an important amount of energy, which is translated into a carbon footprint. SulPure uses condensation as a mechanism to trap pollutants instead of scrubbing. As a consequence, SulPure requires to pump water through a heat exchanger at a rate of 0.7 kg/h of water per 1 kg/h of exhaust gas flow (with minimal pressure drop), whereas scrubbers require to pump pressurised washing fluid at a rate of 6.5 kg/h per 1 kg/h of exhaust gas flow. The exhaust gas pressure drop in SulPure® is minimal and does not require forced convection, compared to scrubbers where the gas/droplet mixture needs to be filtered in a mist eliminator, which can require the use of forced convection. Therefore, the implementation of the novel SulPure® technology can reduce up to 76.6% the carbon footprint.



Eq.1

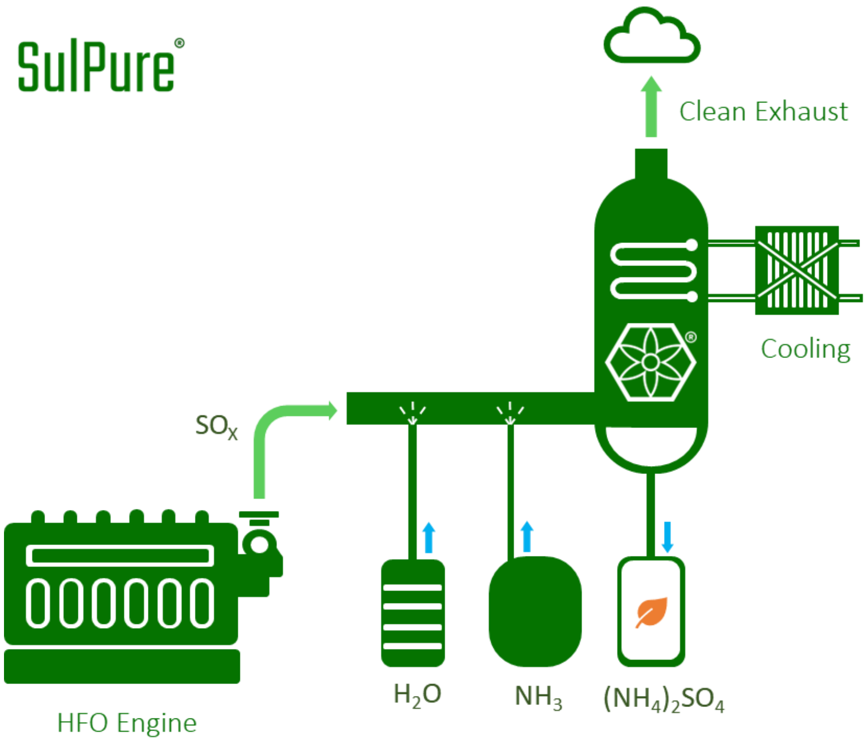


Figure 3. Schematic of SulPure® process

3. SulPure® Pilot

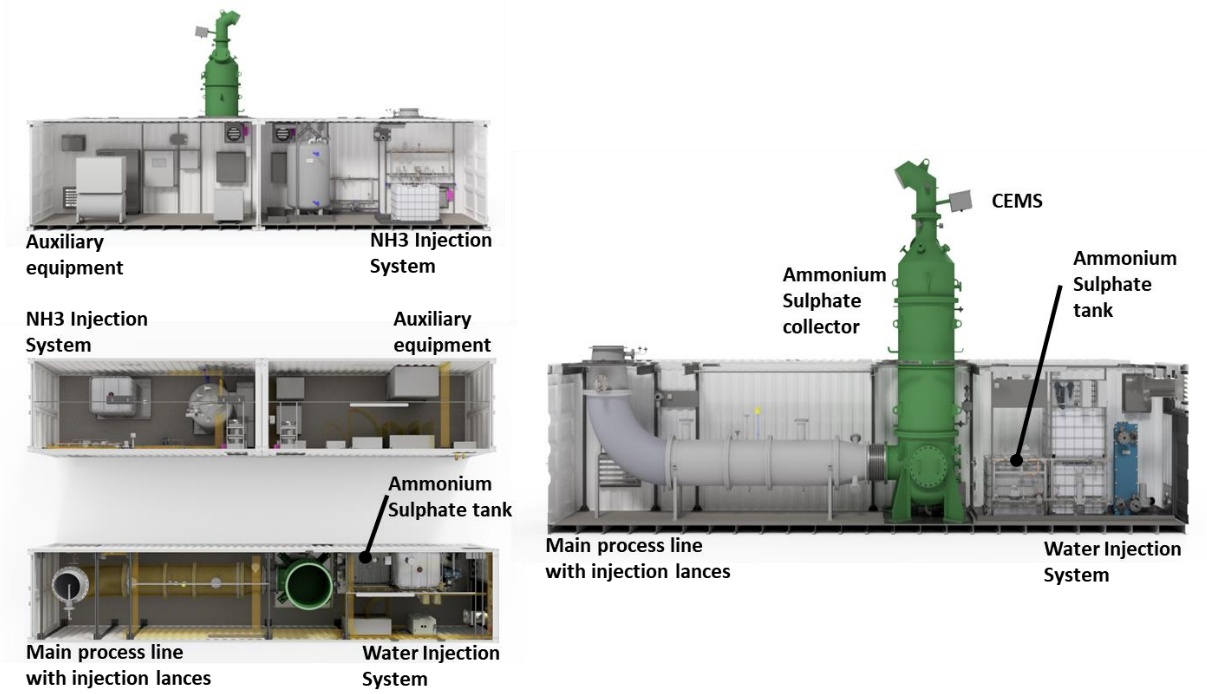


Figure 4. Views of the 1.5MW SulPure® prototype.

Figure 5. SulPure® CSP at the Maritime Centre of Flensburg University of Applied Sciences

The 1.5MW SulPure® prototype is a standalone system delivered as three ISO high-cube containers (1x40’ and 2x20’) and is designed to remove >97% SO_x emissions in exhaust or flue gas (**Figure 4**). SulPure® uses a chemical reagent aqueous ammonia, or ammonium hydroxide (NH_4OH), to remove SO_x pollutants from exhaust gas. The SO_x pollutant is converted into a water solution of ammonium sulphate that is collected and stored.

The 1.5MW SulPure® prototype was installed on the exhaust outlet of a 700 kW marine diesel engine (based on MaK M 452 and M 282 engine components) combusting 2.4%m S content marine residual HFO at the Maritime Centre at Flensburg University of Applied Sciences (Hochschule Flensburg) in Flensburg, Germany (**Figure 5**).

The aim of the pilot was to demonstrate the capability of a low carbon footprint technology to reduce SO_2 concentration in exhaust gas in accordance with maritime regulations (MARPOL Annex VI Regulation 14[5,6]). Specifically, this is to record a SO_2 concentration via the marine certified Continuous Emission Monitoring system (CEMs) equivalent to ≤0.1%m S (SO_2(ppm)/CO_2(%v/v) = ≤4.3). The main novelty compared to the techniques shown in BRef[7] is the use of partial condensation as a method to trap and collect the by-product of SO_2 removal, whereby the need to pump large quantities of a water solution is mitigated by a simple cooler, which condenses the exhaust stream and traps the by-product.

[5] *RESOLUTION MEPC.340(77) (adopted on 26 November 2021) 2021 GUIDELINES FOR EXHAUST GAS CLEANING SYSTEMS* (no date). Available at: https://wwwcdn.imo.org/localresources/en/OurWork/Environment/Documents/Air%20pollution/MEPC.340%2877%29.pdf (Accessed: November 25, 2022)

[6] *Guidelines for exhaust gas-SO x cleaning systems – MARPOL Annex VI, regulation 14(4)(b)* (no date). Available at: http://www.marpoltraining.com/MMSKOREAN/MARPOL/AddInfo/9_annex.pdf (Accessed: November 25, 2022).

[7] *Large Combustion Plants | Eippcb* (no date). Available at: https://eippcb.jrc.ec.europa.eu/reference/large-combustion-plants-0.

4. Equipment and implementation

Figure 6. SulPure® Main Process Line container

The functional systems identified in **Figure 4** are provided in detail here. In the Main Process Line container (40' high-cube container), an exhaust gas inlet connected the SulPure® system to the exhaust gas outlet piping of the 700 kW marine diesel engine. Water and aqueous ammonia injection lances injected required quantities of these reagents into exhaust gas to achieve optimal SO_x removal efficiency. Then, the exhaust gas was cooled via a shell tube heat exchanger to an optimal point to allow for efficient reaction conditions and ammonium sulphate collection (via condensation). Both the water injection and ammonium sulphate collection systems are located in the Main Process Line container (**Figure 6**). A Continuous Emission Monitoring System (CEMS) monitors the exhaust gas chemical composition at both the inlet and outlet of the system to verify the SO_x removal efficiency.

The aqueous ammonia storage tank and injection system is provided in a separate 20' high-cube container (**Figure 7**). Additional auxiliary equipment, including electrical control cabinets and air compressor, are provided in the last 20' high-cube container.

The SO_2 concentration in exhaust gas was proportional to the sulphur content of the HFO combusted in the engine, which was 2.4%m S content during the tests, and the amount of exhaust gas flow ranged from 0.3 kg/s to 1.1 kg/s. Exhaust gas inlet temperatures ranged from 266 - 283 °C.

Figure 7. SulPure® injection systems

5. Results and Findings

In a typical procedure, with exhaust gas containing SO_2 (produced from combusting 2.4%m S in HFO) flowing through the SulPure® prototype, the cooling system was set to achieve an exhaust gas outlet temperature of 45 – 55 °C and water was injected into the exhaust gas to achieve a 7 – 14%vol water content. Then, the ammonium hydroxide injection system was set to achieve the maximum SO_2 removal efficiency with concomitant lowest ammonia slip. Under these process parameters, across a load range of 35 – 85% (13 – 63 kg/min exhaust gas flow), the marine certified CEMs recorded a SO_2 concentration equivalent to ≤0.1%m S (SO_2(ppm)/CO_2(%v/v) = ≤4.3).

As a representative example of the results achieved, at 35% load, setting the cooling system to achieve an exhaust gas outlet temperature of 47 °C, injecting water into the exhaust gas to achieve a water content of 9.9%vol, and injecting ammonium hydroxide into the exhaust gas to achieve 1:1.6 – 1:1.7 ratio of SO_2:NH_3, achieved a SO_2/CO_2 ratio within compliance[8,9] (<4.3) and ammonia slip <20 ppm (**Figure 8**). It was observed that when the SO_2:NH_3 ratio was <1.6, this resulted in an increasing CEMs SO_2/CO_2 ratio (i.e., decreasing SO_2 removal efficiency). In addition, if the SO_2:NH_3 ratio was >1.6, this resulted in an increasing ammonia slip. Thus, the stoichiometric ratio of SO_2:NH_3 could be optimized to achieve the maximum SO_2 removal efficiency with the lowest ammonia slip (below the requirement of solvents used for carbon capture[10]).

It was also observed at 75% load that the SO_2:CO_2 ratio decreased only marginally when the water content increased from 7.7 to 9.0%vol, and with little difference in SO_2 removal efficiency observed between 8.2 and 9.0 %vol (**Figure 9**). Although additional verification is required, a water content of 8%vol in the exhaust is estimated to be the minimal value for compliance (provided sufficient residence time for the reaction is provided). Thus, the amount of water injected into the system can be optimized.

---

[8] *Guidelines for exhaust gas-SO x cleaning systems – MARPOL Annex VI, regulation 14(4)(b)* (no date). Available at: http://www.marpoltraining.com/MMSKOREAN/MARPOL/AddInfo/9_annex.pdf (Accessed: November 25, 2022).

[9] *RESOLUTION MEPC.340(77) (adopted on 26 November 2021) 2021 GUIDELINES FOR EXHAUST GAS CLEANING SYSTEMS* (no date). Available at: https://wwwcdn.imo.org/localresources/en/OurWork/Environment/Documents/Air%20pollution/MEPC.340%2877%29.pdf (Accessed: November 25, 2022)

[10] Puxty, Graeme; Wei, Steven Chiao-Chien; Feron, Paul; Meuleman, Erik; Beyad, Yaser; Burns, Robert; Maeder, Marcel (2014). *A Novel Process Concept for the Capture of CO2 and SO2 Using a Single Solvent and Column. Energy Procedia, 63, 703–714.* doi:10.1016/j.egypro.2014.11.078

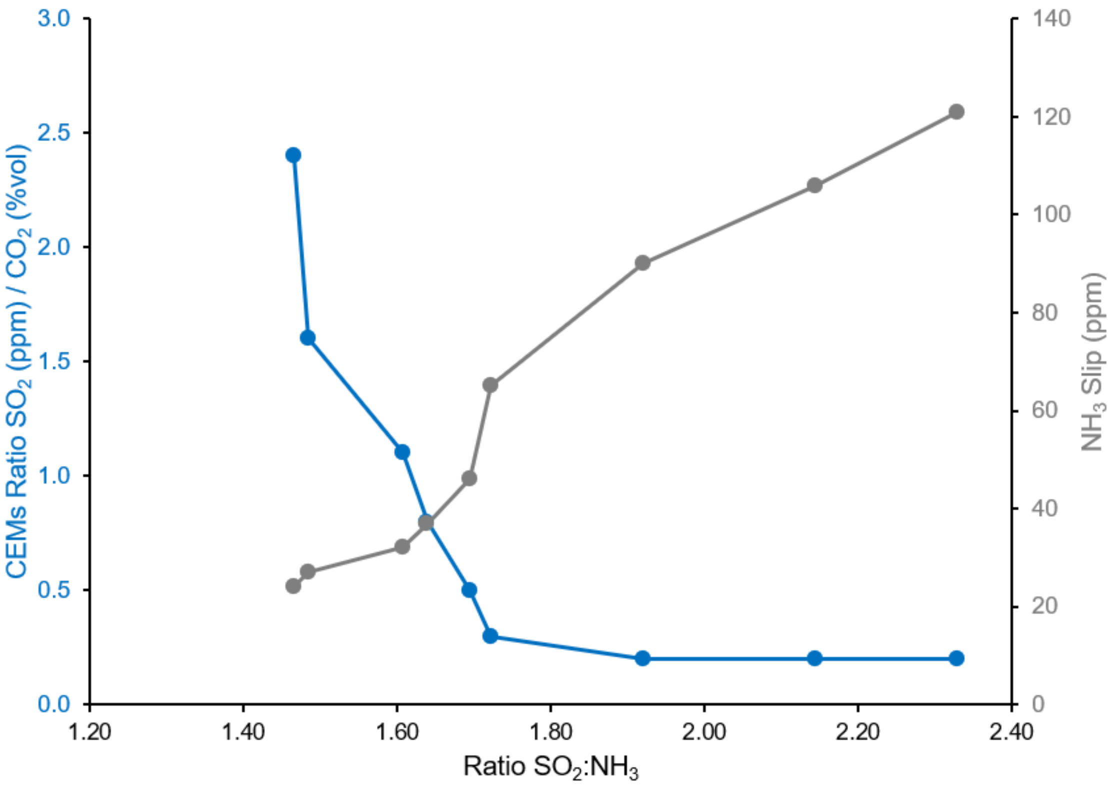


Figure 8. Graph of CEMs SO_2/CO_2 ratio and ammonia slip as a function of $SO_2:NH_3$ ratio in the exhaust gas

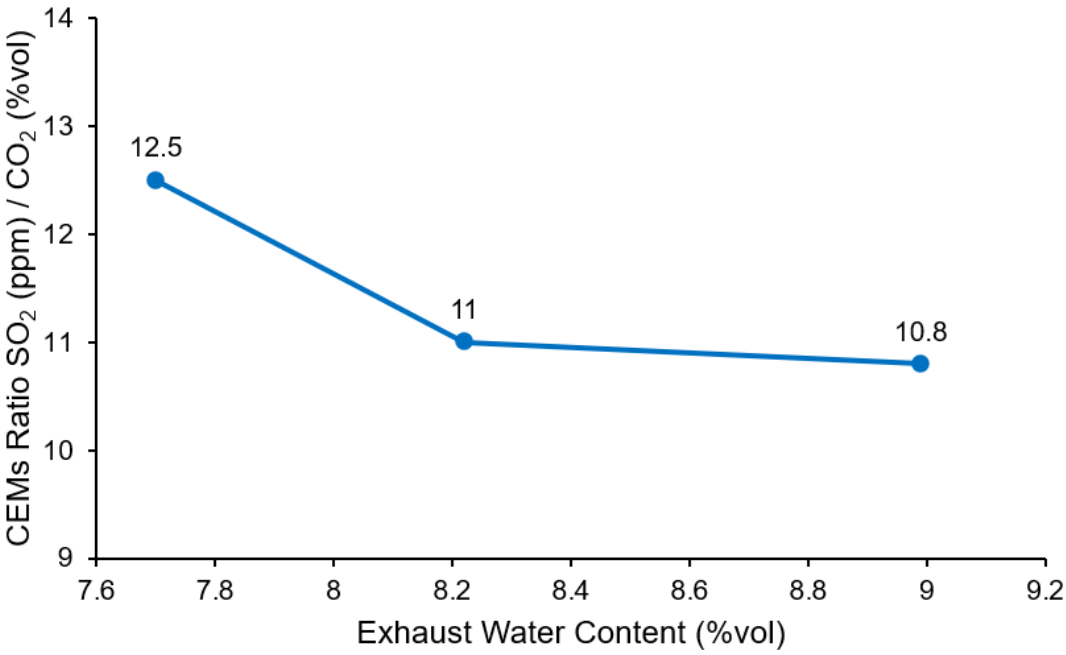


Figure 9. Graph of CEMs SO_2/CO_2 ratio as a function of exhaust gas water content (%vol) at 75% load.

6. Conclusions

Daphne Technology's 1.5MW SulPure® prototype was installed on a 700kW marine diesel engine combusting 2.4%m S content (equivalent to SO_2(ppm)/CO_2(%v/v) = 103.9) marine residual heavy fuel oil (HFO) at the Maritime Centre at Flensburg University of Applied Sciences (Hochschule Flensburg) in Flensburg, Germany. Testing procedures were performed with exhaust gas flow (35 – 85% load or 13 - 63 kg/min) at a temperature range of 283 - 266 °C. Across the range of exhaust gas flows (and temperatures) investigated, the marine certified Continuous Emission Monitoring system (CEMs) recorded a SO_2 concentration equivalent to ≤0.1%m S (SO_2(ppm)/CO_2(%v/v) = ≤4.3). Optimization of the SO_2:NH_3 ratio and water injection quantity allowed for optimized results. These trials demonstrated that a new technique based on the optimization of Equation 1 can reduce SO_2 emissions using new principles. In addition, the SO_2 reduction achieved allows the use of Carbon Capture Systems, which require a very low inlet SO_2 content (often < 15ppm). From an economic perspective, SulPure® allows the use of cheaper fuels, and produces ammonium sulphate as a by-product, which can be used in the agricultural industry as a fertiliser.