SULFUR POISOING

APPLICATION NOTE CI-00050

Diesel, locomotive, and gas turbine exhaust contains a complex mixture of solid particles and semi-volatile material that is found in both the particle and the vapor phase. Physical and chemical characterization of these exhaust aerosols in the environment enables a better understanding of potential health effects, effectiveness of alternative combustion technologies and emission control devices, and also the impact of new fuel and lubricant formulations on emissions. To reflect the growing consensus that solid, elemental carbon is a relevant metric and to force the use of diesel particulate filters, Euro 5b regulations introduced a protocol for measuring the solid particle number concentration for particles larger than 23 nm. Similarly, the aerospace SAE E-31 program aims to develop a methodology to measure solid particle mass and number concentration in gas turbine exhaust. These measurements are enabled through the use of catalytic stripper (CS) technology whereby semi-volatile material is removed so that the solid fraction can be measured[1-4].

While efforts in optimizing CS geometry and composition for oxidation and solid particle penetration have been successful, some issues remain. Sulfur dioxide (SO_2) incident on a catalyst reduces its lifetime due to “poisoning” whereby the sulfur stores on the catalyst washcoat[5]. Incident sulfur can be adsorbed and stored as SO_2 or can be oxidized and combine chemically with the washcoat material. Additionally, sulfur can pass through the catalyst unchanged (remain SO_2) or be oxidized and emitted as SO_3. The latter leads to the formation of sulfuric acid particles. The goal of this proposed research is to better understand these effects for a specific catalyst formulation and prevailing conditions (e.g. temperature, flowrate, etc).

Objectives

- To determine the sulfur storage capacity of a 8 L/min catalytic core when operated at 350°C and challenged with 30 ppm sulfur dioxide.
- To determine whether sulfur poisoning can be reversed by heating sulfated catalysts to 550°C in air for one hr.
- To determine whether sulfur poisoning can be reversed by heating sulfated catalysts to 550°C in a reducing environment one hr.

Experiment 1: Sulfur storage capacity

Sulfur dioxide (31 ppm) is mixed with air and used to challenge a 8 L/min catalytic core. The determination of storage capacity is not impacted by the upstream concentration of SO_2, so 31 ppm is a nominal value[5].

Before and after loading with SO_2, the propane oxidation efficiency is measured.

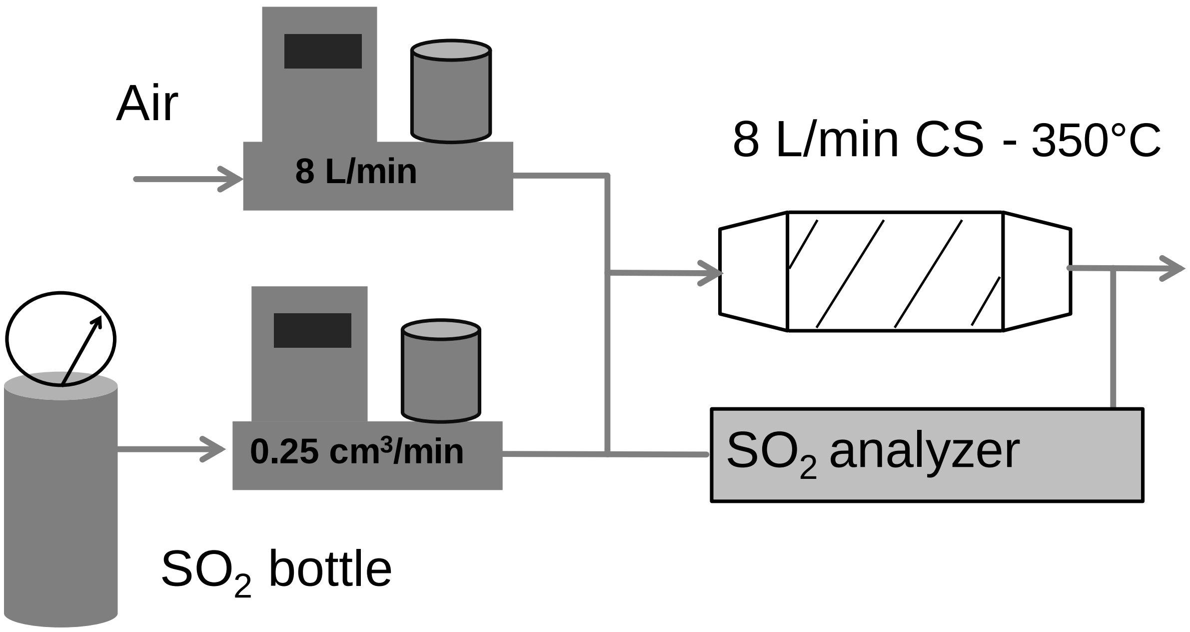

Figure 1 shows the apparatus consisting of a SO_2 bottle and mass flow controller, clean air supply, 8 L/min CS heated to 350°C and a SO_2 analyzer. The outlet concentration is monitored continuously.

Experiment 2: Regeneration of the catalyst by heating

The experimental was as follows:

- After exposure to a prescribed amount of sulfur, heat the CS to 550°C or 600°C
- Set the reducing gas flowrate to 1 L/min and run for 150 min
- Monitor outlet SO_2 concentration

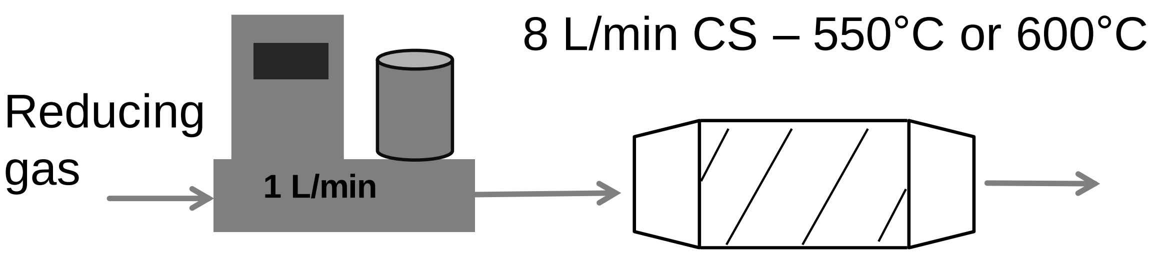

Figure 2 Apparatus to desorb SO_2 from poisoned catalyst

RESULTS

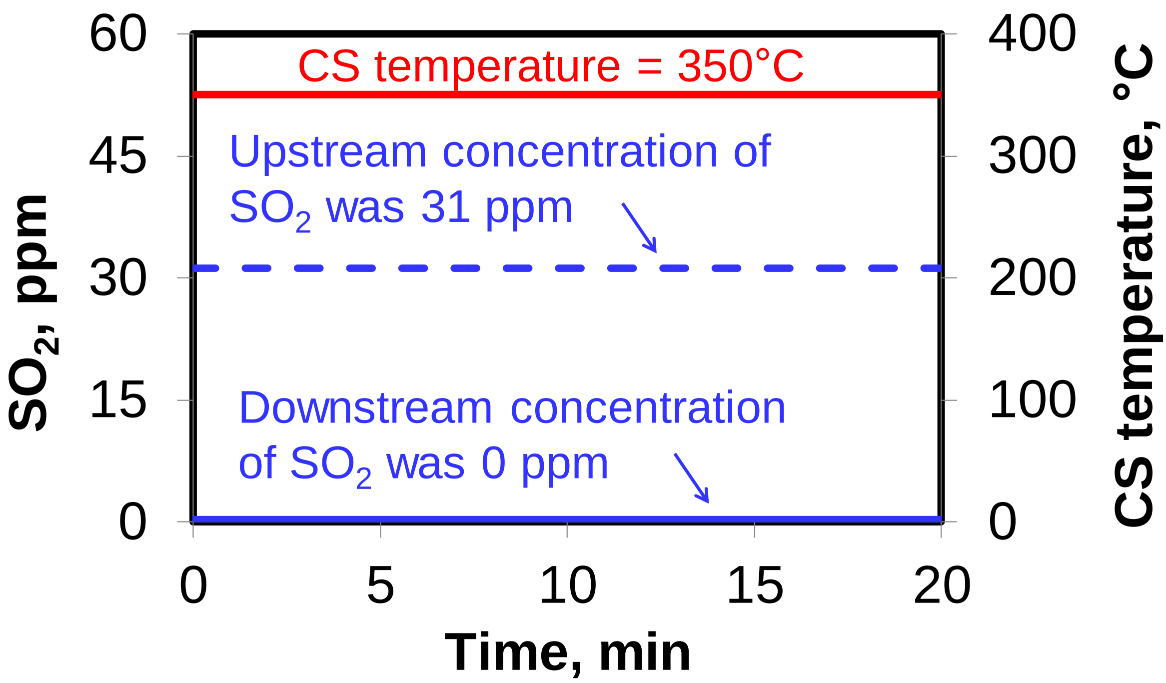

Figure 3 shows a loading event when a clean catalyst was loaded with 31 ppm SO_2. No SO_2 was observed downstream during the duration of the accelerated test, indicating all SO_2 is initially retained in the CS.

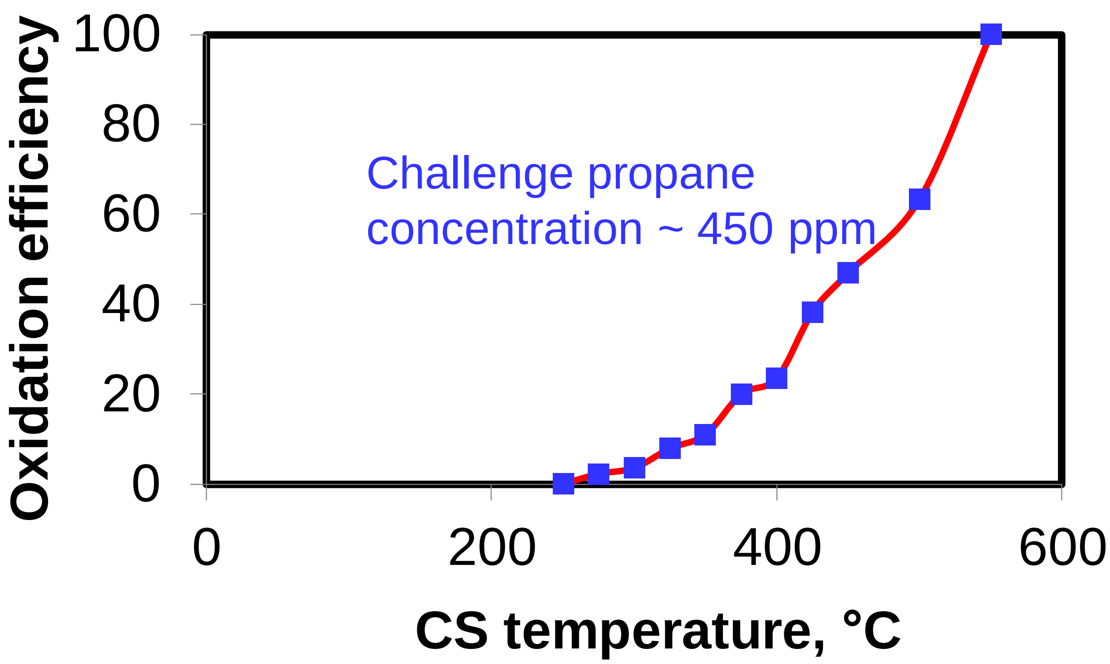

Figure 4 shows the oxidation efficiency of a highly sulfur-poisoned CS. The poisoning effect demonstrates the need for a regeneration procedure, as described next.

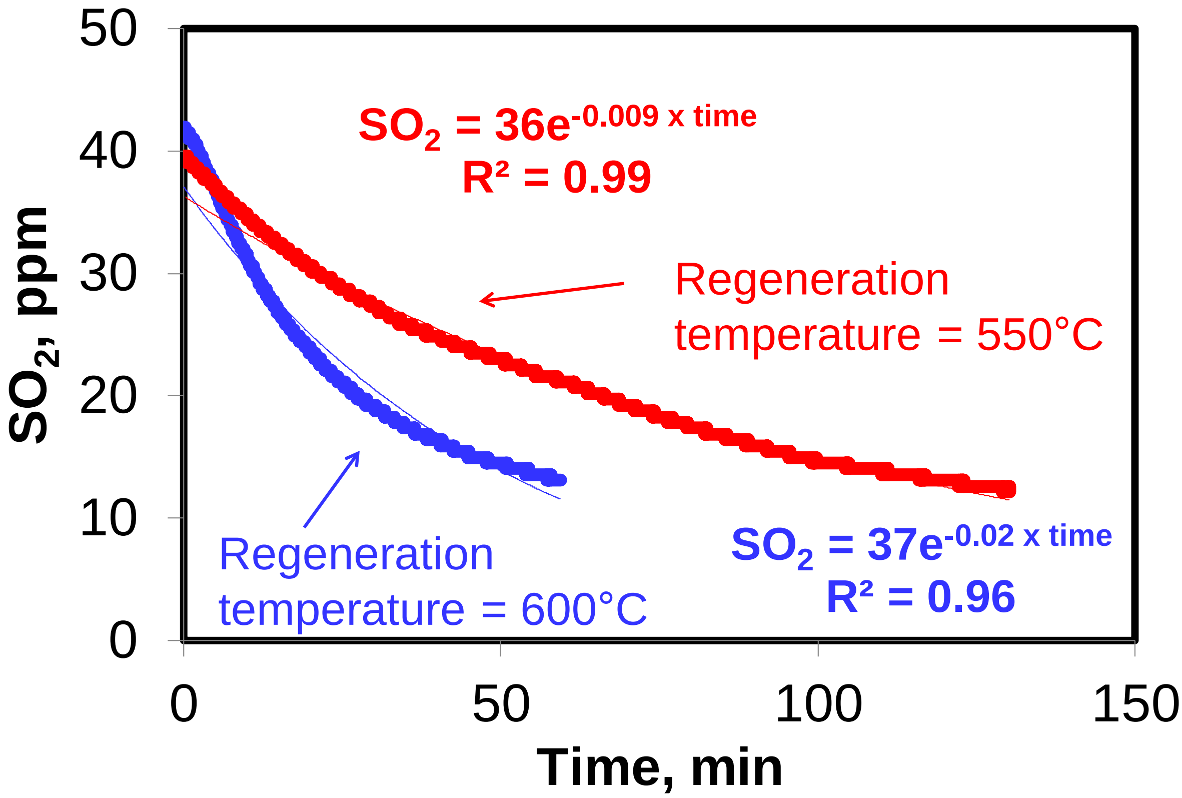

Figure 5 demonstrates the regeneration of highly poisoned CS units. The outlet SO_2 concentration decreases with time, approaching zero and indicating the end of regeneration and a fresh catalyst.

- Typical sulfur exposure levels in dilute diesel exhaust are very low (~1 ppb)
- The catalyst formulation proved to be susceptible to some level of sulfur poisoning as evidenced by zero levels of SO_2 downstream of a fresh catalyst during the equivalent of 1 yr of sulfur exposure.
- Poisoned catalysts exhibit reduced oxidation efficiency
- Regeneration in a reducing gas environment demonstrated the reversible nature of the poisoning. Regeneration depends on time, temperature, and the use of a reducing gas – high temperature alone is insufficient to fully regenerate these devices

REFERENCES

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