

Diesel Exhaust Aftertreatment with Scrubber Process: NO_x Destruction

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ABSTRACT

Oxides of nitrogen (NO_x) emissions, produced by engines that burn fuels with atmospheric air, are known to cause negative health and environmental effects. Increasingly stringent emissions regulations for marine engines have caused newer engines to be developed with inherent NO_x reduction technologies. Older marine engines typically have a useful life of over 20 years and produce a disproportionate amount of NO_x emissions when compared with their newer counterparts. Wet scrubbing as an aftertreatment method for emissions reduction was applied to ocean-going marine vessels for the reduction of sulfur oxides (SO_x) and particulate matter (PM) emissions. The gaseous absorption process was explored in the laboratory as an option for reducing NO_x emissions from older diesel engines of harbor craft operating in ports of Houston and Galveston. A scrubber system was designed, constructed, and evaluated to provide the basis for a real-world design. The details of this research have been presented in previously reported work. The main byproduct of the scrubber process was a weak nitric acid solution (<10 wt%). This paper presents an exploration of a method developed to destroy the NO_x emissions captured and stored during the scrubbing process. This method utilized a stainless steel acid boiler vessel and catalyst for the NO_x destruction process. The acid boiler vessel allowed for the injection of weak nitric acid (<10 wt%) and diesel fuel into a chamber for evaporation. The thermal decomposition of the nitric acid produced a nitrogen dioxide rich stream that then reacted with metered diesel fuel over two automotive-style, platinum based, three way catalysts (TWCs). In the laboratory, heat energy for acid evaporation and reduction was provided by electric resistance heaters. Real world applications would use waste heat from the engine and scrubber process for acid evaporation and reduction. The system was evaluated with a fixed acid injection rate and various fuel flow rates to validate the thermal decomposition of nitric acid and overall NO_x reductions. Exit stack emissions were measured on a 'semi-raw' and dilute basis. Acid to fuel ratios of 49.8:1 and 58.9:1 yielded NO_x reductions of 99.7% and 98%, respectively. The fuel utilized for the destruction process added a 1% fuel penalty to the complete scrubber system. The scrubber component of the whole system was capable of reducing NO_x emissions by 42% and 62% over a high flow and low flow cycle, respectively. The scrubber section of the overall system was therefore the primary limitation to the level of NO_x reduction.

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INTRODUCTION

NO_x emissions are harmful to the environment and contribute to human health problems, including respiratory issues. NO and NO₂ are immediately dangerous to humans above concentrations of 100 ppm and 20 ppm, respectively. NO_x gas reacts with hydrocarbons in the presence of sunlight to form photochemical smog [1, 2].

The combustion process in diesel engines generates NO_x emissions. These emissions exist in a number of different molecular forms: NO, NO₂, NO₃, N₂O, N₂O₃, N₂O₄, and N₂O₅. The primary form of NO_x emissions from combustion is NO [3]. NO_x formation occurs from diatomic nitrogen in the intake air disassociating at high temperatures and reacting with oxygen or hydroxide radicals [1]. Temperature has a profound effect on the rate of NO_x production; significant

levels of NO_x are generated above combustion temperatures of 2,500 K. Other factors that influence NO_x generation are combustion time, pressure, and the air-to-fuel ratio.

The United States Environmental Protection Agency (EPA) found that total US NO_x emissions from all sources was 16.6 million metric tons for 2005 [4]. NO_x emissions for the ports of Houston and Galveston were found to be 18.1 and 3.4 metric tons per day [5]. Older marine engines such as those in tugs typically have a useful life of over 20 years [6] and produced a disproportionate amount of NO_x emissions when compared with their newer counterparts. The EPA first regulated non-road heavy-duty diesel emissions in 1996 [7]. The most recent and stringent regulations for diesel marine engines are the Tier 3 and 4 emissions standards. For Category 2 engines, these standards will be phased in over the years 2013 through 2017. New regulations only apply to new engines or remanufactured engines above 600 kW (800 hp).

As NO_x emissions continue to rise, the need for control technologies becomes more apparent [2]. Many engines used today were produced at a time when there were no marine engine emissions regulations. Retrofitting them with aftertreatment technologies has the potential to reduce NO_x emissions significantly. Exhaust aftertreatment options for NO_x reduction include lean NO_x traps (LNT) [8], selective NO_x recirculation [9], selective catalytic reduction (SCR) [10], hydrocarbon SCR [11], and wet NO_x scrubbers [12]. Researchers of these technologies often find that reducing NO_x emissions by 20% is easily achieved but difficulty was experienced when attempting NO_x reduction above 50%. It is expected that in the future marine emissions control will closely follow that of the on-road diesel engines. At present, SCR is the most popular control technology for on-road NO_x emissions [2].

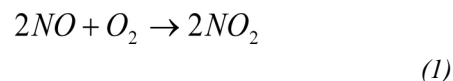
WET SCRUBBER FOR NOX ABSORPTION

Wet scrubber systems hold promise for use in diesel marine applications for the following reasons: seawater may be used as a cooling agent, they operate independently of the engine, and they require a limited quantity of on-board chemicals. Flue gas scrubbers have been used since 1935. They are primarily used to remove oxides of sulfur (SO_x) emissions from the flue gas and can have SO_x removal efficiencies of up to 98% [13]. Wet scrubber systems were used to reduce NO_x emissions from stationary applications like chemical plants and power stations for decades. NO_x scrubber units consisted of a packed tower, where a liquid stream entered through the top and contacted a gas stream that flowed counter currently. The liquid stream was referred to as the liquor. The packing in the tower was designed to maximize the interfacial surface area between the liquor and gas for NO_x absorption. When only water was used as the

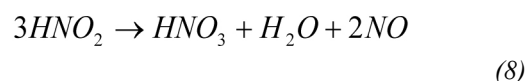
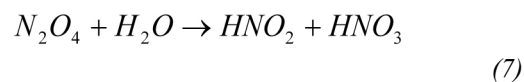
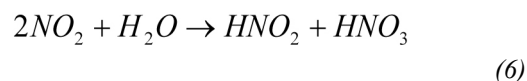
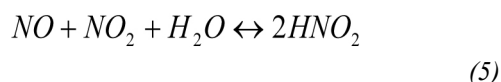
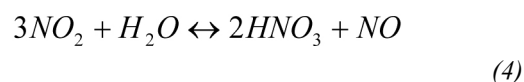
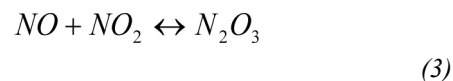
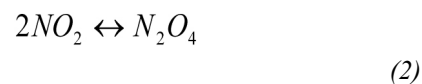
liquor for NO_x absorption, two byproducts were produced, nitric and nitrous acid [14].

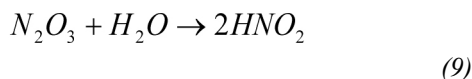
Previous work focused on developing an aftertreatment technology to reduce the amount of NO_x emissions from diesel marine engines, specifically harbor craft. A scrubber system was designed, fabricated, and evaluated in the laboratory. The system used a hydrogen peroxide solution liquor (1 wt%) and produced a byproduct of weak nitric acid (<10 wt%). The details of this research were presented in [12].

The design of the wet scrubber was based on the theory of absorption of various NO_x species. NO was virtually insoluble in water. However, NO_x species of higher valences were soluble in water. The species of interest included NO₂, N₂O₃, and N₂O₄. Both N₂O₃ and N₂O₄ occurred in equilibrium with NO and NO₂. Their respective concentrations were a function of the temperature and the partial pressures of NO and NO₂ [14]. A catalyzed particulate filter and diesel oxidation catalyst oxidized engine out NO to NO₂ and created the more soluble NO_x species. This is shown as the reaction in Equation 1.



The exhaust gas was cooled to increase the equilibrium concentrations of N₂O₃ and N₂O₄. These species were absorbed via the following reactions into water or hydrogen peroxide within the wet scrubber.

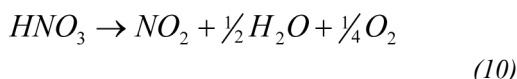




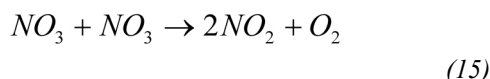
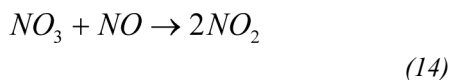
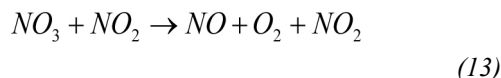
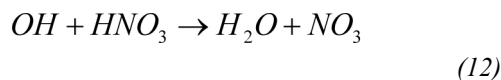
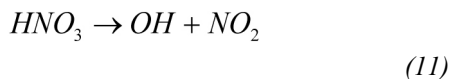
The scrubber byproduct represented captured NO_x from the engine exhaust. To create a complete system, if direct discharge is unacceptable, byproduct disposal must be considered. It was not desirable to discharge the nitric acid from the marine vessel into the surrounding waters as the acid negatively affects ocean water ecosystems [15]. The nitric acid could be used as a process input for the manufacture of fertilizer or other chemical, or else the acid must be decomposed on-board. This paper describes the method developed to destroy the NO_x emissions captured and stored during the scrubber process. Destruction refers to nitric acid being converted into H_2O , O_2 , CO_2 , and N_2 . The method demonstrated utilized a stainless steel acid boiler vessel and catalyst for the NO_x destruction process. The details are presented below.

THEORY

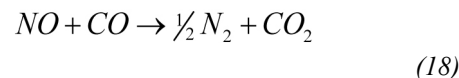
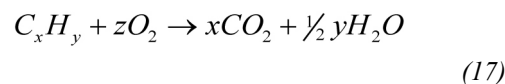
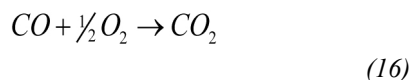
As nitric acid was heated, water evaporated first resulting in a concentrated acid solution. At 68 wt%, the heat of vaporization of water and acid were equal and the azeotropic mixture evaporated. When 47 kcal/mol of heat was added to the acid vapor the following reaction proceeds to the right [16].



Above 256°C, nitric acid fully decomposes according to the reaction of Equation 10 [17]. Other intermediate steps may occur according to the following equations [16].



TWCs use precious metals such as platinum, palladium, and rhodium as catalyst material to reduce NO_x laden streams. The main reactions to describe emissions reductions of typical TWCs follow [1]:



TWCs are typically able to reduce CO, HC, and NO_x emissions by over 95% when their temperature is above 400 °C and when the equivalence ratio is between 0.99 and 1.01 [1]. The fuel utilized for this project was standard diesel fuel that was available for on-board use. The fuel acted as the HC needed for the reaction in equation 17 that consumed the oxygen produced from the decomposed acid. It was also thought that diesel fuel reacted with the NO_2 stream and produced the CO needed for NO_x reduction.

EXPIRIMENTAL APPARATUS

ACID DESTRUCTION APPARATUS

The main components of the experimental apparatus were the acid boiler vessel, two TWCs, peristaltic pumps for acid and diesel fuel injection, storage vessels, heaters, and gaseous emissions measurement equipment. The acid boiler vessel sidewall was constructed from 0.20 m schedule 40 stainless steel pipe. The height of the acid boiler vessel was 0.25 m. Top and bottom plates were made from 6.35 mm stainless steel and were TIG welded to the ends of the pipe. A port was welded to the side of the vessel for the introduction of ultra high purity nitrogen (UHPN) for primary dilution. The base of the acid boiler vessel rested on a 2,500 W electric resistance-heating coil. The vessel was insulated with exhaust wrap. On the top plate of the acid boiler vessel were two ports, one each for acid and diesel fuel introduction. A 0.31 m long K-Type was connected at the top of the vessel, ran to the bottom of the vessel, and measured the internal base temperature. A 0.05 m exhaust exit was welded to the top of the vessel. This allowed for the series placement of two TWCs and a stainless steel pipe for gas eduction to the dilution tunnel. The dilution tunnel was customarily used to characterize exhaust gas concentrations in conjunction with dilute analyzers. The TWCs were universal fit automotive style converters from Catco® Catalytic Converters, Part Number 6004. The combined volume of both catalysts was approximately 1.5 liters with a cell density of 62 cells per square centimeter. A 1.59 mm K-Type thermocouple was used for catalyst temperature measurement.

The TWCs were heated to an initial temperature of 450 °C with two 620 W heat wraps. Both catalysts were utilized to ensure complete acid destruction through the added heat and surface area. The base heater was temperature controlled to an initial set point of 450 °C. A sample port and heated line were connected to the system before and after the catalyst section. K-Type thermocouples 3.1 mm in diameter were