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UNIVERSITY OF CENTRAL FLORIDA**

CONTROL FOR NO_x EMISSIONS FROM COMBUSTION SOURCES

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ABSTRACT

The Environmental Program Office at the Kennedy Space Center is interested in finding solutions and to promote R&D that could contribute to solve the problems of air, soil and groundwater contamination. This study is undertaken as part of NASA's environmental stewardship program. The objective of this study involves the removal of nitrogen oxides from the flue gases of the boilers at KSC using hydrogen peroxide. Phases 1 and 2 of this study have shown the potential of this process to be used as an alternative to the current methods of treatment used in the power industry.

This report summarizes the research done during the 10-week summer program. During this period, support has been given to implement the modifications suggested for Phase 3 of the project, which focus on oxidation reactions carried at lower to medium temperatures using UV lights as a source for the hydrogen peroxide dissociation and the effect on the NO conversion.

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1. Introduction

NASA launches the Space Shuttle from a 149,000-acre Wildlife refuge. NASA is committed to Environmental Stewardship and has explicitly stated this commitment in the NASA Strategic Plan. Nitrogen Oxide (NO_x) emissions are a primary criteria pollutant regulated by the USEPA. The Kennedy Space Center is permitted to emit approximately 60 tons of NO_x annually under their Title V air permit. NASA is pursuing R&D to minimize the detrimental environmental effects of KSC operations on the environment. This study is undertaken as part of NASA's environmental stewardship program.

This study involves the removal of nitrogen oxides from the flue gases of the boilers at KSC. The primary focus of the research is the conversion of NO_x to nitrogen acids for the purpose of scrubbing them from the gas stream. NO is virtually non-soluble and NO₂ is only slightly soluble; however, nitrogen acids (HNO₂ and HNO₃) are highly soluble and can be removed via scrubbing.

Phase 1 of this study was completed in December 1998 and consisted of oxidation of the NO_x at high temperatures (~930 °F). Phase 2 focused on oxidation at lower temperatures utilizing an ultraviolet (UV) light source. Key to the success of this study was the redesign, operation and optimization of the scrubber operation. The redesign included the following: 1. Conversion from batch to continuous reservoir flow. 2. Lower temperatures in the scrubber recirculation system. 3. Continuous and Batch caustic feed. 4. Providing for sampling and analysis in-line. 5. Increase recirculation flow rate.

Phase 3A started in January 2000 and concluded in March 2001. This phase focused on the oxidation at low temperatures utilizing a microwave source. Laboratory experiments have shown that microwaves promote the conversion of H₂O₂ into hydroxyl radicals, thus helping the desired NO to NO₂ conversion. Also, a new configuration to connect the flue gas pipe from the convection section at the boiler to the inlet gas port at the reactor was designed and built.

Phase 3B started in March 2001. For this phase a UV light unit with 2 lights replaced the microwave unit. The difference of this experimental setting than the one used in phase 2 is that the hydrogen peroxide was exposed to the UV lights prior entering the reaction chamber. This report summarizes the research done during the 10-week program at NASA-KSC.

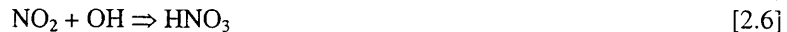
2. Background

Laboratory studies have demonstrated that hydrogen peroxide (H_2O_2) when injected under proper conditions into hot gases of the exhaust stream it oxidizes nitric oxide (NO) into NO_2 , HNO_2 and HNO_3 . The formation of nitrogen acids allows for more inexpensive methods of post treatment for nitrogen removal, such as, scrubbing. Sulfur dioxide can also be added to the combustion source to simulate the exhaust of an industrial power plant.

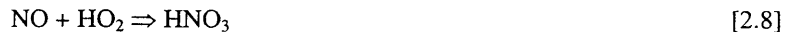
The primary reactions that are expected to occur during this process are as follows:



Hydroxyl-Radical Reactions:



Hydroperoxyl-Radical Reactions:



To demonstrate the viability of such process in an industrial setting, researchers at NASA-KSC and the University of Central Florida (UCF) joint efforts to implement this process from a laboratory scale to a pilot plant scale. The experimental setting is located at the KSC Central Heat Plant (CHP). This study is part of Phase III of the BES Project. Highlights of Phase I and Phase II results are given below.

BES Phase 1: Phase 1 of this project was performed on a 35 mmBTUH natural gas boiler. The fuel used in the boiler consists mainly of methane and varying amounts of ethane, propane, butane, a sulfur-containing mercaptan added to natural gas, and inerts, such as, nitrogen, carbon dioxide and helium. When burning natural gas the major pollutant in the exhaust gases is mainly NO_x . The percentage of NO_x presence depends on the temperature of the combustion chamber as well on the fuel/oxygen ratio.

Part of the flue gas was diverted to the experimental apparatus consisting of different sections: Injection Zone, Reaction Zone, Quenching and Scrubbing. At the Injection Zone hydrogen peroxide (H_2O_2) was injected to the system. NO and SO_2 was added to the exhaust gases to simulate the composition of a flue gas from an industrial power plant. Once passed the Injection Zone the mixture of flue gas, NO, SO_2 and (H_2O_2) went through an auxiliary gas burner to bring the slipstream gases to the desired reaction temperature. From this point, the gases went through the Reaction Zone, where the conversion of NO to NO_x and nitric acids took place. The Reaction Zone consisted of a 12-inch diameter, 8-ft long stainless steel pipe, having sampling ports and thermocouples

distributed along its length. Reactions were carried out up to 500 °C. The reaction products and by-products passed then through the Quenching system, where water was added to cool off the gas mixture before entering the Scrubbing System. The scrubber was a packed column consisted of an 8-ft tall acrylic column with a 6-ft bed depth. 1-inch Hyflow 25-7 polypropylene rings were used as packing material. The scrubber had a 30x60x30 inch³ reservoir, a 1¼ - inch PVC recirculation line with a Hayward diaphragm valve, a by-pass valve, a ½ HP submersible pump and reservoir drain and sampling port. Sodium bicarbonate was used to control the pH of the fluid at the reservoir.

Figure 2.1 shows the process schematics for Phase 1. A Data Acquisition System (DAQ) using LabView software from National Instruments was used to obtain instant readings of the key parameters in the process. Figure 2.2 shows the schematics of the experimental system as the computer monitor displays it.

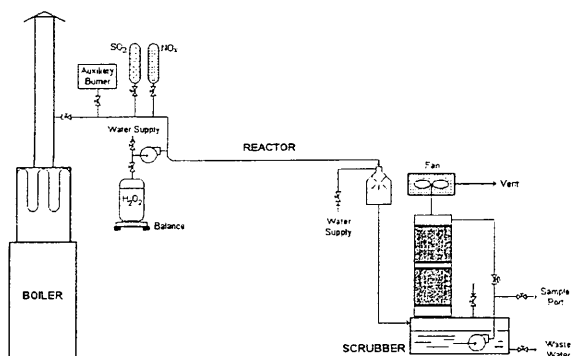


Figure 2.1. Process Schematics (Phase I)

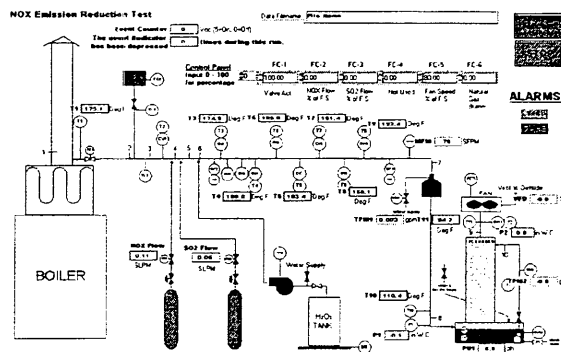


Figure 2.2. LabView Diagram (Phase I)

Several runs were made with this experimental configuration changing the following variables: Reaction temperature, NO, SO₂ and H₂O₂ concentration, NO/H₂O₂ ratio, SO₂/H₂O₂ ratio and residence time. The results obtained during Phase 1 were encouraging but some modifications were required in order for the system to perform to the optimum expected values. The conversion from NO to NO_x worked very well, getting conversions greater than 96% for NO/ H₂O₂ ratios of 1:1. Conversion from NO₂ to nitric acids was not as high as expected. Operating the reactor at high temperatures and having the surface of the stainless steel reactor without any type of coating could have been part of the problem. The removal of the nitric acids by the scrubber was not as efficient as expected. The scrubbing system was never optimized for the kind of removal required by the process. The submersible pump provided was under-specified, since the rates of liquid flow recommended for optimal scrubbing operation were never achieved. The implementation of these modifications led to Phase 2 of the project.

BES Phase 2: Based on the results obtained during Phase I, several modifications were proposed for Phase 2 of the project. The sections to be re-designed were the Reaction Zone and the Scrubbing System. The reaction zone pipe (12" diameter, 8' long SS pipe) was coated with a boron-nitride paint to prevent the release of iron during the reaction. The paint selected was high temperature ceramic boron nitride paint from Carborundum. UV lights were used as a heat source to carry the reaction at lower temperatures.

Scrubbing System: The scrubber used during Phase 1 of the project was designed and manufactured by Rauschert Industries, Inc. Based on the parameters supplied, they estimated the size, material, packing material, optimum gas and liquid rate within the column and the operation temperature. The packing material selected by the vendor was 1-inch Hyflow 25-7 polypropylene rings. This packing material is proprietary, meaning that its characteristics and hydraulic behavior can not be found in the open literature. Once the vendor specified the unit, he recommended 500 scfm for the gas rate and 35 gpm for the liquid rate. Since the recirculation pump provided with the unit was under-specified the maximum liquid flow achieved was approximately 15 gpm, which proved to be too low for the scrubber operation.

The scrubber was re-designed for continuous operation having inlet, outlet and recirculation lines. Fresh water was introduced in the system through the inlet line. Two Hayward diaphragm valves control the flow through the outlet line and the recirculation line in the system. Mass flowmeters hooked up to the DAQ provided accurate flow measurement at the inlet, outlet and recirculation lines. Liquid recirculation was provided through a new 1-HP pump, able to deliver 35 gpm if desired. A continuous and batch caustic feed was also added to the system. The submersible pump at the reservoir provided continuous mixing of the tank fluid and the caustic solution added to the tank. Figure 2.3 shows the process schematics of Phase 2 and Figure 2.4. shows the scrubber with the modifications.

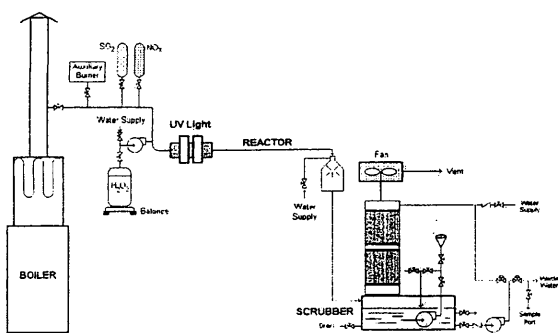


Figure 2.3. Process Schematics (Phase 2)

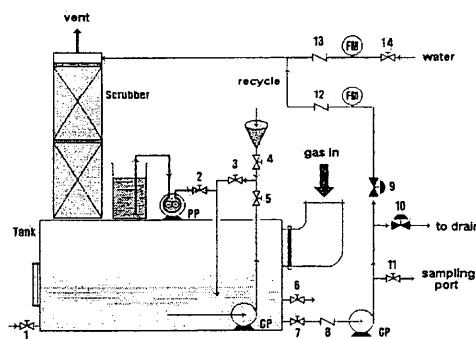


Figure 2.4. Scrubber Modifications

Many tests were performed during Phase 2 of the project. The parameters varied included: the reaction temperature (350, 400 and 450 °F), the injection point location, the

$\text{NO}_2/\text{H}_2\text{O}_2$ ratio, and $\text{SO}_2/\text{H}_2\text{O}_2$ ratio, the pH of the scrubber reservoir solution and the recycle flow at the scrubber.

The Phase 2 data showed that the use of UV lights was slightly to moderately effective in oxidizing NO to NO_2 at low to moderate temperatures. The improvements in the scrubber re-design provided a better temperature control and the capability to perform steady state operations.

BES Phase 3A: Laboratory experiments have shown that microwaves promote the conversion of H_2O_2 into hydroxyl radicals, thus helping the desired NO to NO_2 conversion. In Phase 3A of the project, a microwave source replaced the UV lights unit. The microwave commercial unit was built by one of the industrial partners of this project.

A new configuration to connect the flue gas pipe from the convection section at the boiler to the inlet gas port at the reactor was designed and built. The streams coming from the convection section and the radiation section at the boiler were mixed to obtain the desired working temperature at the reactor. Tests were conducted having the microwave unit in two configurations: parallel (Figure 2.5a) and perpendicular (Figure 2.5b) to the inlet flue gas. The schematic diagram of the process for Phase 3A is presented below.

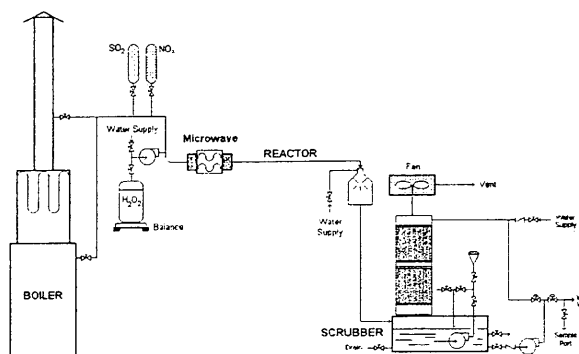


Figure 2.5a. Schematic Diagram (Phase 3A)

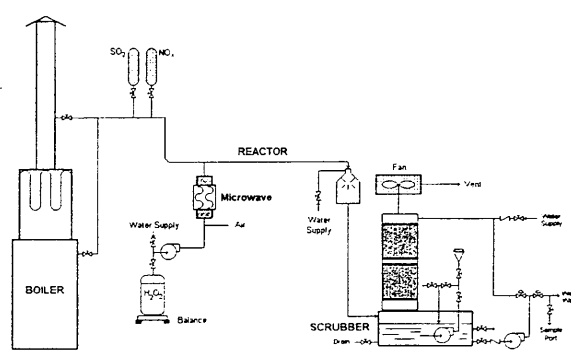


Figure 2.5b. Schematic Diagram (Phase 3A)

3. Experimental

For Phase 3B, UV lights were placed where the microwave unit was. In this case, the stream of hydrogen peroxide and the gas inlet stream were perpendicular to each other. The purpose of studying this configuration was to find out the capabilities of the UV lights to initiate the H_2O_2 dissociation without being affected by the flue gas stream as it happened in Phase 2 (see figure 2.3)

First the injection nozzle for the hydrogen peroxide was heated using heating tape; placed inside a PVC pipe and later inside the UV light chamber. Only a small part of the whole

injection nozzle was exposed to the UV lights. In this configuration the results were not as good as expected. In a second attempt, the injection nozzle was placed directly inside the UV light chamber without being covered, exposing the hydrogen peroxide directly to the UV lights.

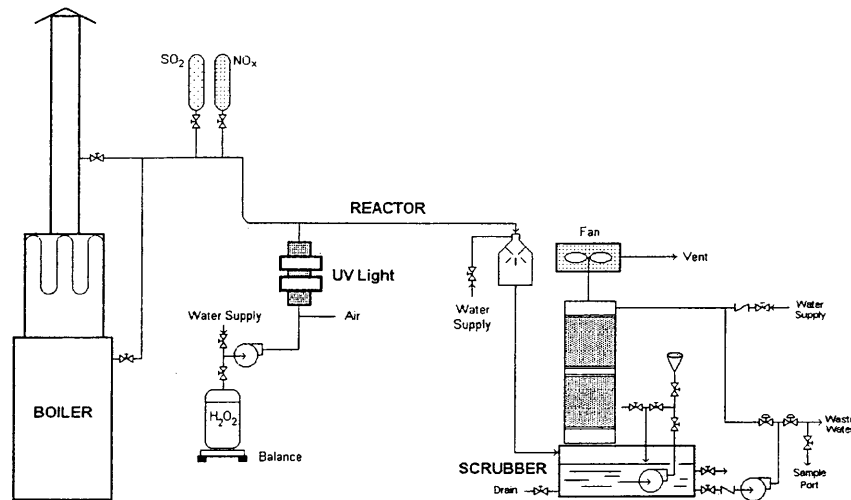


Figure 3.1. Schematic Diagram (Phase 3B)

Based on the results obtained during Phase I, it was determined that the conversion of NO to NO_x was favorable at high temperatures. To check whether or not the UV lights had an effect in the NO conversion reaction, the experiments were performed using no lights, using only 1 light and using 2 lights. The experiments were carried out at three reaction temperatures: 186, 340 and 580 °F. A total of 43 experimental runs were performed and the average of the experimental results obtained at each temperature are presented in the following table.

Table 3.1. Experimental Results (Average Values) for Phase 3B.

Run	T (°F)	T (°C)	# UV Lamps	NO Conversion %	NO _x conversion %
1	186	85.5	0	1.1	0.0
2	186	85.5	1	1.9	0.0
3	186	85.5	2	2.5	2.2
4	340	171.1	0	0.2	0.0
5	340	171.1	1	6.5	1.9
6	340	171.1	2	8.2	2.4
7	580	304.4	0	33.9	15.4
8	580	304.4	1	42.6	20.4
9	580	304.4	2	55.4	26.5

A graph of percentage conversion versus temperature for NO and NO_x were obtained and it is shown in figure 3.2. It can be observed that the trendline of the data at different temperatures for both NO and NO_x conversion follow an exponential behavior. It is observed also, that the % conversion for NO and NO_x increases with temperature and with the number of UV lights used.

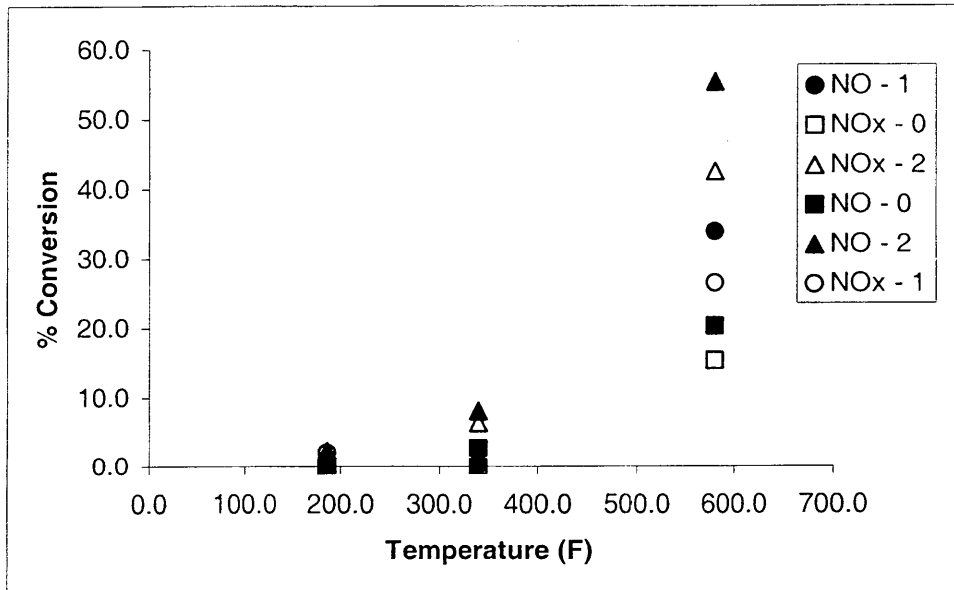


Figure 3.2. Percentage Conversion versus Temperature

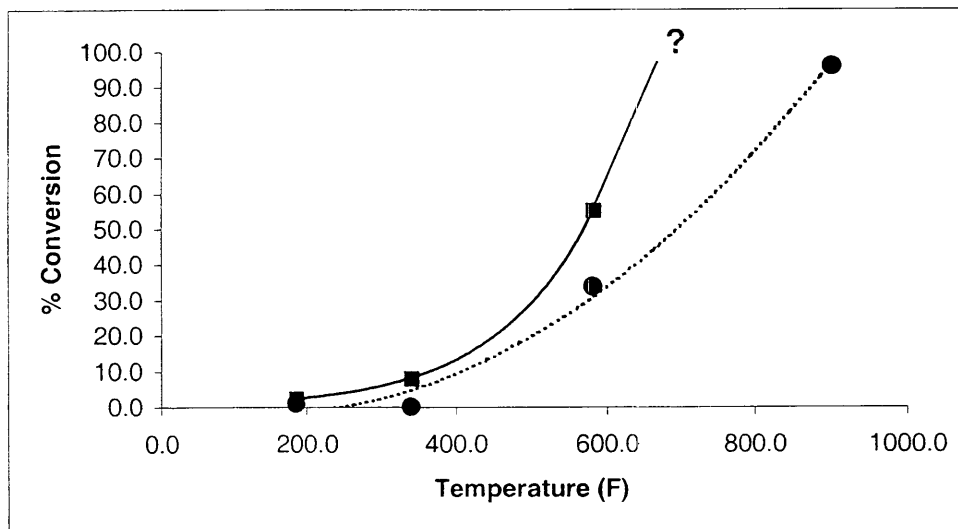


Figure 3.3. Percentage Conversion NO versus Temperature
 Legend: --■-- 2 UV lights --●-- No lights

To compare the effect of the UV lights in the reaction, a second graph was obtained using the data for NO. The % conversion data for NO was plotted versus the temperature using the experimental data for “no lights” and for “2 UV lights” as it is shown in figure 3.3. The “no lights” data (---●---) shows the temperature dependence of the reaction. At higher temperatures the % conversion increases. The value for the % conversion for the data point at 900 °F was obtained from previous results at Phase I.

The experimental results for “2 UV Lights” (---■---) for the % conversion for NO versus temperature were plotted in the same graph. The data shows that at the same temperature the % conversion increases when the UV lights are used. From the results it is observed that the presence of the UV lights increases the % conversion. Since there were no experiments done with this configuration at temperatures higher than 580 °F, it will be recommended to check whether or not the exponential trendline continues at higher temperatures values than the ones used in this investigation.

4. Summary

This experimental work has shown the impact of using UV lights as precursors for the dissociation of hydrogen peroxide (H_2O_2). The dissociation of the peroxide and the production of OH radicals is the key in the process to oxidize nitric oxide (NO) into NO_2 , HNO_2 and HNO_3 .

The experiments were carried out at three different temperatures and from the results it can be concluded that the dissociation of H_2O_2 in the presence of UV lights favors the formation of the OH radicals, and subsequently the conversion of NO. The best results were obtained at higher temperatures.

5. References

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