

# FLOW REACTOR EXPERIMENTS ON THE SELECTIVE NON-CATALYTIC REMOVAL (SNCR) OF NITRIC OXIDE USING A UREA-WATER SOLUTION

by

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## ABSTRACT

An experimental investigation on the removal of nitric oxides using an electrically heated, quartz lined, laminar flow reactor was completed at ambient pressure for temperatures between 800 and 1300 K. Exhaust gas was simulated by using mixtures from bottled gases. A solution of urea and water was injected into the simulated exhaust gas. Removal of nitric oxide was observed along with by-products for various inlet oxygen and carbon monoxide concentrations. A Fourier transform infrared (FTIR) spectrometer was used to determine concentrations of all species. Species measured were nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), ammonia (NH<sub>3</sub>), isocyanuric acid (HNCO), carbon monoxide (CO), and carbon dioxide (CO<sub>2</sub>).

Nitric oxide removal was a strong function of temperature and concentrations of oxygen and carbon monoxide. The greatest nitric oxide removal (up to 95%) was achieved for temperatures near 1150 K for 5% oxygen. With oxygen present in the gas composition, NO removal is strongly enhanced for higher CO concentrations below a certain temperature. Above that temperature, carbon monoxide inhibited the removal of nitric oxides. This temperature which caused a significant change of the reaction behavior was dependent on the O<sub>2</sub> concentration. This temperature was identified as 1200 K for 1% O<sub>2</sub> concentration, 1150 K for 5% O<sub>2</sub> concentration, and 1100 K for 15% O<sub>2</sub> concentration.

## INTRODUCTION

Air pollution continues to be a concern throughout the world, and consequently, regulations on the emission of pollutants continue to become more restrictive. Nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are two species that are regulated. Together these two species are known as nitric oxides, NO<sub>x</sub>. To satisfy the NO<sub>x</sub> regulations, combustion systems have been modified or exhaust treatment has been applied. For exhaust treatment, catalytic and non-catalytic approaches are possible [1, 2]. These approaches may be applied to a number of combustion systems including boilers, furnaces, gas turbines, and reciprocating engines (e.g., diesel engines).

Selective non-catalytic removal (SNCR) of nitric oxides is an exhaust gas treatment process [2, 3]. SNCR is applied by using a reducing agent such as ammonia (NH<sub>3</sub>) or urea (NH<sub>2</sub>CONH<sub>2</sub>) which is injected into the exhaust stream. When properly done, all the gases in the exhaust stream are exposed to the reducing agent. For the appropriate conditions, a series of chemical reactions will occur and the NO<sub>x</sub> is converted to N<sub>2</sub> [2].

For the SNCR processes, ammonia, urea and cyanuric acid have been proposed as the reducing agent. Ammonia has been widely used in SNCR processes, but in some forms it is both corrosive and toxic. Cyanuric acid has found limited applications to date [3]. Urea continues to be considered as a promising alternative to ammonia [7]. Urea decomposition products include ammonia and isocyanic acid (HNCO) [5]. Both NH<sub>3</sub> and HNCO have been shown to be effective in removing NO [1,3,11]. The use of urea, therefore, is of interest. The two most common methods for introducing urea into the exhaust gases is by injection of dry urea, or injection of a urea-water solution. For the efficient use of either of these methods, knowledge is necessary about the decomposition and oxidation products for a wide range of conditions [5].

The lack of fundamental data from well-controlled experiments on the SNCR process using urea motivated the work outlined in this paper. Specifically, the SNCR process using a urea-water solution was examined, and detail results of product species have been obtained.

## DESCRIPTION OF THE EXPERIMENTS

Figure 1 is a schematic of the experimental equipment. The gases were stored in standard gas cylinders under pressures up to about 100 bar. Prior to the entrance to the mass flow controllers, the pressure was regulated to about 4 bar. After the flow controllers, the desired composition was mixed at about atmospheric pressure. Teflon tubes were used to transport the gas to the reactor entrance. This region was subject to tape heating to ensure preheating of the gas mixture above the vaporization point of water. The gas mixture passed through a section with increasing diameter and small baffles, then the gases entered the reactor which was heated by a three-stage furnace.

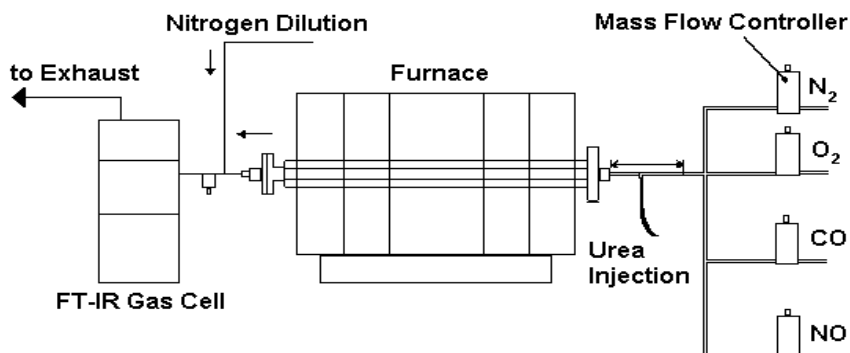


Figure 1 Schematic setup of the experimental apparatus.

The reactor was a straight steel pipe which was lined with a quartz tube (ID of 1.8 cm) to minimize any catalytic surface reactions. The flow in the reactor was laminar with Reynolds numbers below about 100. The total flow through the reactor was 1100 sccm (Standard conditions were 0°C and 1 atm.), and was the same for all experiments. The residence time in the reactor was estimated to be between 1.3 sec (at 1300 K) and 2.1 sec (at 800 K). The reactor quartz tube was sealed from the outer steel tube by using Gra-foil™ sealing tape. This prevented gas from flowing between quartz and steel tube, and hence, prevented any reactions due to the steel surfaces.

After passing through the furnace, the gases were diluted by 5000 sccm of nitrogen to prevent further reactions and to decrease the temperature to a level consistent with use in the gas cell of the FTIR spectrometer. The excess nitrogen also prevented the water vapor in the mixture from condensing which could have affected the chemical composition of the gases.

The gases passed through a 0.5 micron filter, and then entered the gas cell before being exhausted out of the laboratory.

Table 1. Experimental Conditions for the Experiments

Parameter	Value	Inlet Species	
Temperature Range	800 – 1300K	Nitric Oxide (NO)	330 ppm
Residence Time	1.3 – 2.1 sec	Nitrogen Dioxide (NO <sub>2</sub> )	1.5 ppm
Residence Time Expression (secs)	= 1705/T (K)	Urea (NH <sub>2</sub> CONH <sub>2</sub> )	0, 900 ppm
Total Reactor Flow	1100 sccm	Oxygen (O <sub>2</sub> )	0, 1, 5, 12, 15%
		Carbon Monoxide (CO)	0, 100, 600, 900 ppm
		Nitrogen (N <sub>2</sub> )	Balance

The product gases from the reactor were analyzed with a Fourier transform infrared (FTIR) spectrometer, which possesses dynamic alignment with up to 0.1 cm<sup>-1</sup> resolution. The FTIR is ideally suited to this application due to its ability to provide on-line analysis of a wide variety of species.

The FTIR was calibrated with known concentrations of the relevant species. The calibrations were indirectly verified by comparison with species balances of certain atoms (e.g., nitrogen and carbon atoms). Some discrepancy (less than about 20%) was noted for the higher concentrations of carbon dioxide. Since the absolute values of carbon dioxide were not needed, this discrepancy does not affect the results of this investigation.

Table 1 is a summary of the major experimental conditions for this study. A small amount of

nitrogen dioxide ( $\text{NO}_2$ ) was present with the nitric oxide, and resulted in a reactor concentration of about 1.5 ppm.

Due to lack of space, the complete experimental description can not be present here [4,5,9].

## RESULTS AND DISCUSSION

As outlined above, the major independent variables were the reactor temperature, and the inlet oxygen and carbon monoxide concentrations. For the five (5) oxygen concentrations, this resulted in over 30 figures to show each of the significant outlet species as a functions of reactor temperature. The complete set of results is available from Gentemann [9]. To simplify the current presentation, representative results will be examined.

The removal of nitric oxide will be examined for 5%  $\text{O}_2$  concentration as a function of temperature. This  $\text{O}_2$  concentration, 5%, provided the most nitric oxide removal at the lowest temperatures.

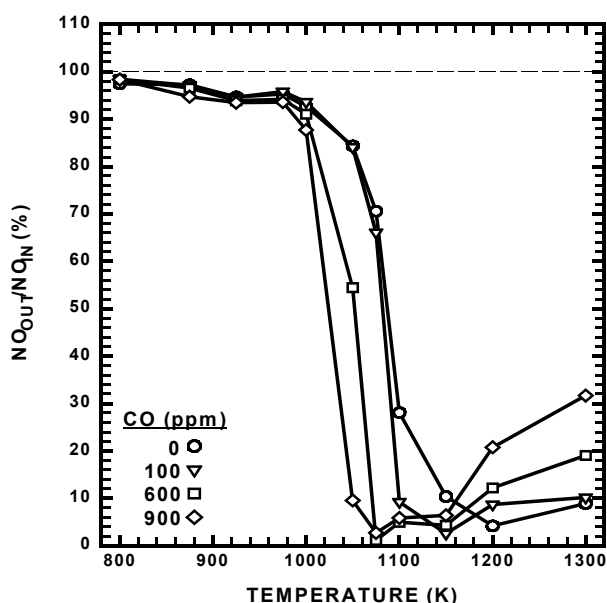


Figure 2 Nitric oxide reduction as a function of reactor temperature for four (4) values of carbon monoxide concentration for 5% oxygen.

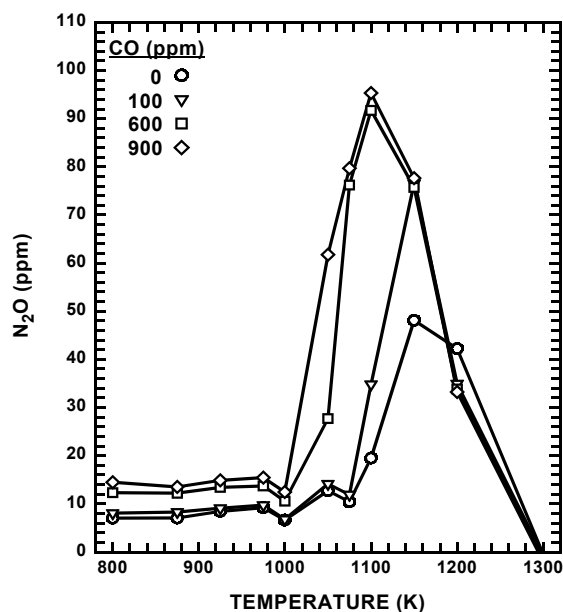


Figure 3 Nitrous oxide concentrations as a function of reactor temperature for four (4) values of carbon monoxide concentration for 5% oxygen.

Figure 2 shows the ratio (in percentage) of the outlet and inlet nitric oxide as a function of reactor temperature for four (4) inlet concentrations of CO for 5%  $\text{O}_2$ . On this scale, 100% represents no removal and 0% represents complete removal of nitric oxide. Significant NO removal occurs for temperatures greater than about 1000 K, and is greatest for the highest inlet CO concentrations for the same temperature. The greatest NO removal, about 97% removal, is obtained for a reactor temperature of 1075 K for 900 ppm inlet CO. For temperatures greater than about 1150 K, the outlet NO increases slightly. This temperature "window" is typical of these types of SNCR processes. The other outlet species for this case will now be discussed.

Figure 3 shows the concentration of nitrous oxide ( $\text{N}_2\text{O}$ ) as a function of temperature for the case of 5%  $\text{O}_2$ . For temperatures below about 1000 K, the  $\text{N}_2\text{O}$  concentration ranged between 6 and 16 ppm with the higher values corresponding to the higher inlet CO cases. The maximum values of  $\text{N}_2\text{O}$  were about 95 ppm for a temperature of 1100 K and an inlet CO concentration of 900 ppm.  $\text{N}_2\text{O}$  concentrations decreased for temperatures above about 1150, and were near zero for temperatures of about 1300 K.

Figure 4 shows the ammonia ( $\text{NH}_3$ ) concentration as a function of reactor temperature for the four (4) inlet CO concentrations. For temperatures less than about 950 K, the  $\text{NH}_3$  concentration ranged between 670 and 740 ppm. For temperatures greater than about 1000 K, the  $\text{NH}_3$  concentration decreased rapidly, and decreased the most for the highest values of the inlet CO. For

the two highest inlet CO concentrations (600 and 900 ppm), the NH<sub>3</sub> outlet concentration was near zero, and for all cases the NH<sub>3</sub> outlet concentration was near zero for a temperature of 1300 K. These concentrations of NH<sub>3</sub> are consistent with the results for NO removal (figure 2): the NH<sub>3</sub> is consumed in proportion to the NO removal.

Also, for this case of 5% O<sub>2</sub>, HNCO was observed. With respect to HNCO, no calibration was possible due to the lack of a calibration gas for HNCO. Gaseous HNCO is not stable, and cannot be obtained as a commercial calibration gas. Although a quantitative measure of HNCO was not available, a relative measurement was possible by using the absorbance characteristics. Absorbance detected by the FTIR at a wave number of 2282.178 cm<sup>-1</sup> was identified as HNCO.

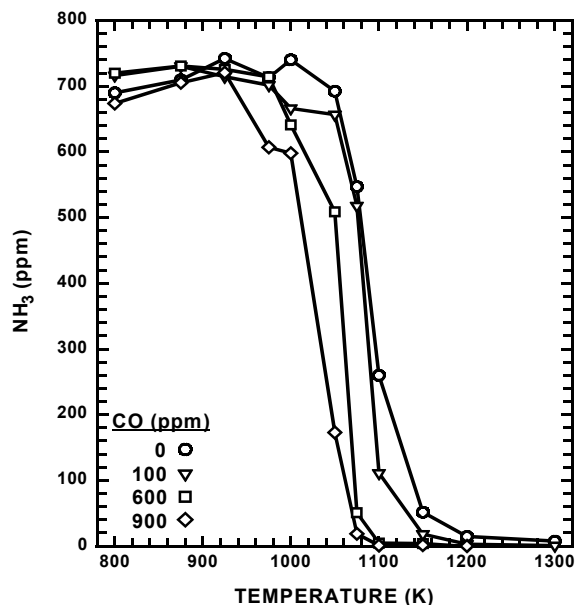


Figure 4 Ammonia concentrations as a function of reactor temperature for four (4) values of carbon monoxide concentration for 5% oxygen.

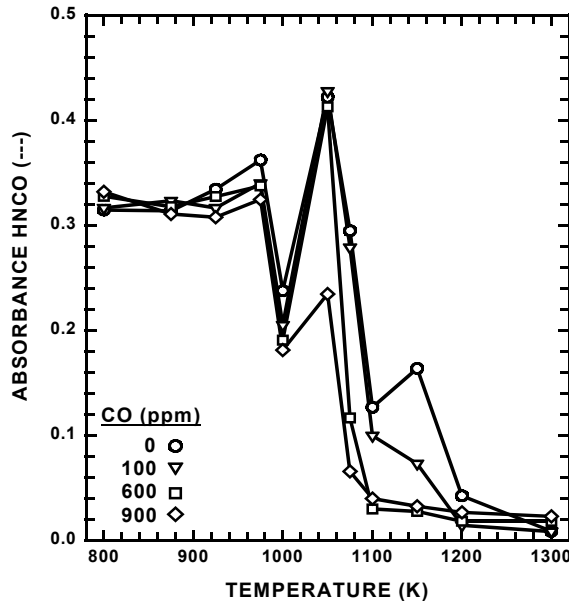


Figure 5 Absorbance of HNCO as a function of reactor temperature for four (4) values of carbon monoxide concentration for 5% oxygen.

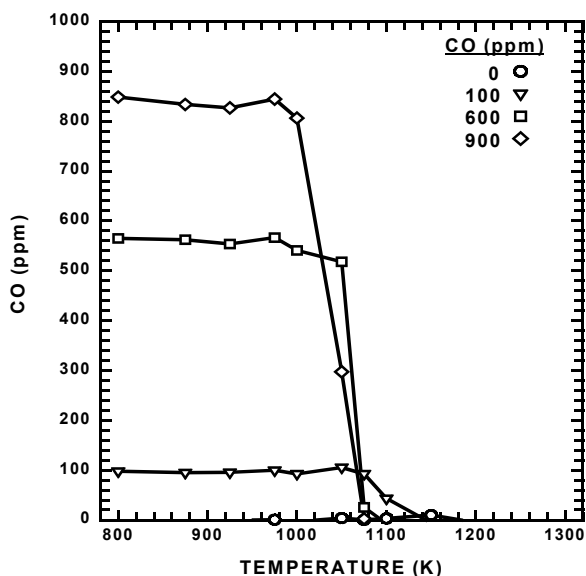


Figure 6 Carbon monoxide concentrations as a function of reactor temperature for four (4) values of carbon monoxide concentration for 5% oxygen.

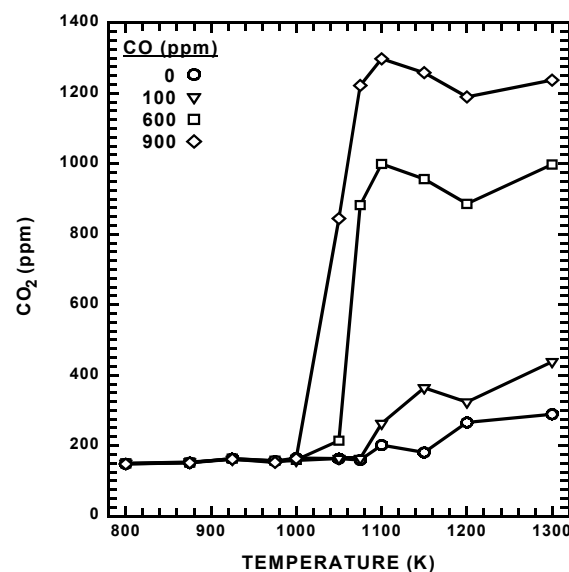


Figure 7 Carbon dioxide concentrations as a function of reactor temperature for four (4) values of carbon monoxide concentration for 5% oxygen.

Figure 5 shows the HNCO absorbance as a function of reactor temperature for the 5% O<sub>2</sub> case. For this case, the absorbance due to HNCO was significant for temperatures less than about 1050 K for all inlet CO concentrations. This suggests for these conditions that the HNCO was a product of the urea decomposition, but was not participating in any significant reaction. For temperatures above about 1000 K, the HNCO absorbance decreased rapidly until at about 1300 K the absorbance was near zero. For the higher temperatures, therefore, the decreasing absorbance suggests that HNCO was participating in the nitric oxide removal process. In addition, the presence of HNCO in the nitric oxide removal process is indirectly confirmed by the identification of N<sub>2</sub>O. N<sub>2</sub>O has been identified as an intermediate species in the nitric oxide removal process using HNCO.

The last two figures for the case of 5% O<sub>2</sub> show the outlet concentrations of CO and CO<sub>2</sub>. For the most part, when CO decreases, CO<sub>2</sub> increases. Figure 6 shows the outlet CO concentration. The concentration is near the inlet value for each case for temperatures below about 1000 K. These values decrease rapidly for higher temperatures, and for temperatures greater than about 1100 K, the outlet CO concentration is near zero.

Figure 7, on the other hand, shows the outlet CO<sub>2</sub> concentrations, and for the most part, is the inverse of figure 6.

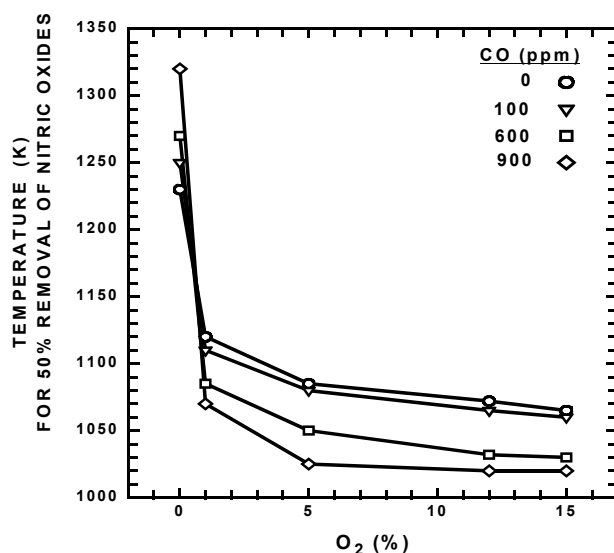


Figure 8 The temperature for 50% removal of nitric oxides as functions of the inlet oxygen concentration for four (4) inlet carbon monoxide concentrations.

Figure 8 shows the temperature for 50% removal of nitric oxide as a function of the O<sub>2</sub> concentration for each of the four (4) inlet CO concentrations. This figure clearly shows the effect of O<sub>2</sub> and helps consolidate the results. As shown, the temperature for 50% removal of nitric oxide is highest for zero oxygen, and then rapidly decreases for the finite values of oxygen. The decrease in the temperature for 50% removal is much more modest as the O<sub>2</sub> concentration increases above about 5%.

These results suggest the following. The SNCR process requires some oxygen, and is probably most effective for about 5% O<sub>2</sub>. For higher levels of oxygen, the removal temperature decreases ever so slightly.

#### SUMMARY AND CONCLUSIONS:

This investigation considered the removal of nitric oxide in an SNCR process using a urea-water solution. The main independent parameters were the reactor temperature and the inlet concentrations of O<sub>2</sub> and CO. The removal of nitric oxide, and the outlet concentrations of a number of species were obtained. The following are the major observations:

- A general temperature boundary could be observed for the reaction behavior at about 1050 K where the many aspects of the different reactions change their behavior. For the conditions examined, the temperature range between 1050 and 1200 K would be most favorable to apply

the urea process in practice.

- A minimum temperature range to avoid extensive ammonia and HNCO slip would need to be maintained. The temperature of 1050 K could also be stated as the minimum boundary, but the tendency was always: the higher the temperature, the less the ammonia slip. A minimum concentration of O<sub>2</sub> and CO was necessary for the ammonia removal reactions.
- The optimum temperature for NO removal depended strongly on the actual gas composition. If the temperature could be chosen freely, a tendency towards higher temperature should be favored to avoid massive N<sub>2</sub>O production, to achieve CO removal along with still acceptable results in terms of NO removal above 80%. Under such conditions, HNCO and ammonia slip could also be kept very low.
- N<sub>2</sub>O production was enhanced by HNCO rather than NH<sub>3</sub>. Therefore, it is desirable to find a way to reduce HNCO as a decomposition product of urea.
- In spite of the production of N<sub>2</sub>O, the favored result of the process was the removal of NO to form molecular nitrogen.
- Addition of O<sub>2</sub> (by adding excess air) to enhance the performance of the process could be considered, but is not advised since increased O<sub>2</sub> level enhanced the NO removal much less than it increased N<sub>2</sub>O production.
- CO could be identified to enhance reactions (i.e., lower minimum reaction temperature for NO removal and CO removal, etc.) for most species and conditions.
- Fluctuations and uncertainty of experimental data was noted mainly for HNCO and NH<sub>3</sub> (HNCO varied much more than NH<sub>3</sub>).

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