

**DECOMPOSITION AND OXIDATION OF A UREA-WATER SOLUTION AS USED IN
SELECTIVE NON-CATALYTIC REMOVAL (SNCR) PROCESSES**

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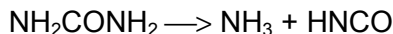
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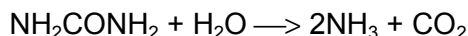
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The injection of urea (NH_2CONH_2) into combustion gases for use in SNCR processes is often accomplished as a urea-water solution. The decomposition and oxidation processes of urea-water solutions is, therefore, of interest. This investigation has examined these processes using a laminar flow reactor. A Fourier transform infrared (FTIR) spectrometer was used to determine concentrations of all species. A vaporized urea-water solution was injected into nitrogen and into nitrogen/oxygen gas streams at temperatures from 800 to 1300 K. The major products of the decomposition and oxidation processes were ammonia (NH_3), isocyanic acid (HNCO), carbon dioxide (CO_2), nitric oxide (NO) and nitrous oxide (N_2O). For temperatures below about 1000 K, the process appears to be largely thermal decomposition whereas for higher temperatures, the oxidation processes become dominant.

Depending on the form of the urea, two paths for the decomposition of urea have been identified. For dry solid forms of urea:



and for urea-water solutions:



INTRODUCTION

Air pollution continues to be a concern throughout the world, and consequently, regulations on the emission of pollutants continue to become more restrictive [1]. Nitric oxide (NO) and nitrogen dioxide (NO_2) are two species that are regulated. Together these two species are known as nitric oxides, NO_x . To satisfy the NO_x regulations, combustion systems have been modified or exhaust treatment has been applied. For exhaust treatment, catalytic and non-catalytic approaches are possible [1, 2].

Selective non-catalytic removal (SNCR) of nitric oxides is one possible exhaust gas treatment process [2, 3]. SNCR is applied by using a reducing agent such as ammonia (NH_3) or urea (NH_2CONH_2) 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 and as a result of a series of chemical reactions, the NO_x is converted to N_2 [2].

Other approaches for exhaust gas treatment exist including the use of urea in combination with a catalyst in selective catalytic removal (SCR) processes. A variety of combinations may be considered, and these have advantages and disadvantages. The actual implementation is site specific [3]. In these approaches, as with conventional SNCR processes, either ammonia or urea 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. Urea continues to be considered as an alternative to ammonia.

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,

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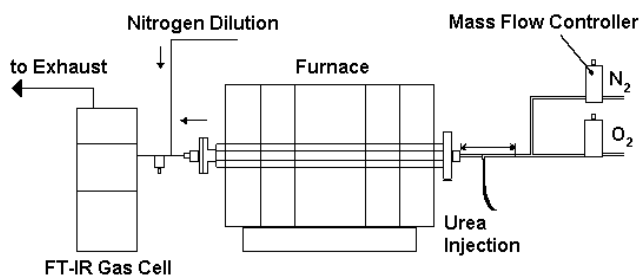
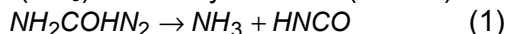


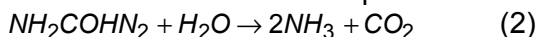
Figure 1. Schematic of the experimental apparatus.

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.

Previous Work: Caton and Siebers [4] studied the decomposition of dry urea in nitrogen, and reported that, at temperatures of about 720 K, the urea decomposed into roughly equal amounts of ammonia (NH_3) and isocyanic acid (HNCO):



The delivery of dry urea is often problematic in actual applications. An alternative way to deliver urea is in the form of a urea-water solution. Such a solution has the potential to be more easily stored and delivered. Previous work has indicated that urea-water solutions have a different decomposition path than dry urea. An example of this previous work was reported by Lentz and Wright [5]. They proposed that urea-water solutions produce ammonia as the main product:



Aoki *et al.* [6] completed an investigation on the decomposition of urea-water solutions using a small laminar flow reactor. They examined four temperatures (from 1083 to 1383 K) and residence times between about 0.03 and 0.17 seconds. The urea-water solution was sprayed into a nitrogen gas stream. They [6] were able to describe their results in terms of rate expressions.

Alzueta *et al.* [7] have examined the impact of the paths and rates of urea decomposition on the modelling of SNCR processes. They stated that detail knowledge of the decomposition of urea is important for accurate modelling of the SNCR processes.

Due to the recognized importance of understanding the urea breakdown processes, the purpose of the current investigation is to expand the experimental data on the urea-water solution decomposition. The goals of the current investigation included obtaining information on the urea decomposition and oxidation processes for oxy-

gen concentrations up to 15%, and for temperatures between about 800 and 1300 K.

DESCRIPTION OF THE EXPERIMENTS

In the present study, the decomposition of urea-water solutions was studied using a flow reactor. The urea-water solution was injected into a gas stream of nitrogen (N_2) with different concentrations of oxygen (O_2). For this purpose, the nitrogen and oxygen were mixed prior to the reaction zone.

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 of 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 a 3-stage furnace.

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 reactor quartz tube was sealed from the outer steel tube by using Grafoil sealing tape. This prevented gas from flowing between the quartz and steel tube, and hence, prevented any reactions due to the steel surfaces.

The total flow in the reactor was 1100 sccm^* , and this resulted in a laminar flow with Reynolds numbers below 100. The experiments were conducted for a constant mass flow. The residence time in the reactor, therefore, varied with temperature and was estimated to be between 1.3 secs (at 1300 K) and 2.1 secs (at 800 K).

A urea-water solution with 42.3 grams of urea per liter of water was used to ensure a urea injection that translated into 900 ppm of urea in the reactor. The feed rate of the solution was 0.023 ml/min. The region prior to the reactor was subject to tape heating to ensure that the urea-water solution vaporized. The urea-water solution was metered into the gas stream by using a 10 ml syringe. The plunger of the syringe was displaced with a calibrated DC stepper-motor.

* "sccm" is standard cubic centimeters, and the standard conditions are defined as 0°C and 1 atm.

Table 1 Experimental Conditions for Urea Decomposition Experiments.

Parameter	Value
Temperature Range	800 – 1300 K
Residence Time	1.3 – 2.1 sec
Residence time Expression (secs)	$= 1705/T$ (K)
Total Flow Rate	1100 sccm
Urea in water solution (mass percentage)	4.2%
Inlet Species (concentrations in the reactor):	
Urea (NH_2CONH_2)	900 ppm
Oxygen (O_2)	0, 1.0, 10, and 15%
Nitrogen (N_2)	Balance

The nominal movement was about 2 $\mu\text{m}/\text{sec}$. The solution was transported to the gas stream through a small teflon tube with an internal diameter of 1.6 mm.

After flowing through the furnace, the gases were diluted by 5000 sccm of nitrogen to minimize any further reactions and to decrease the temperature to a level consistent with use in the gas analyzer. The excess nitrogen also prevented the water vapor in the mixture from condensing, which could have had an effect on the chemical composition of the gases, as well. Then the gases passed through a 0.5 micron filter and into the gas cell before being exhausted out of the laboratory.

The product gases from the reactor were analyzed with a Fourier transform infrared (FTIR) spectrometer. The FTIR spectrometer is manufactured by Bio-Rad, model FTS 60A, and possesses dynamic alignment with up to 0.1 cm^{-1} 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 specific wave numbers used for each species are listed in appendix A. 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 CO_2 at high concentrations (these high concentrations were higher than the levels reported in the current study). Table 1 is a summary of the major experimental conditions for this study. Further details of the experiment are available from Gentemann [8].

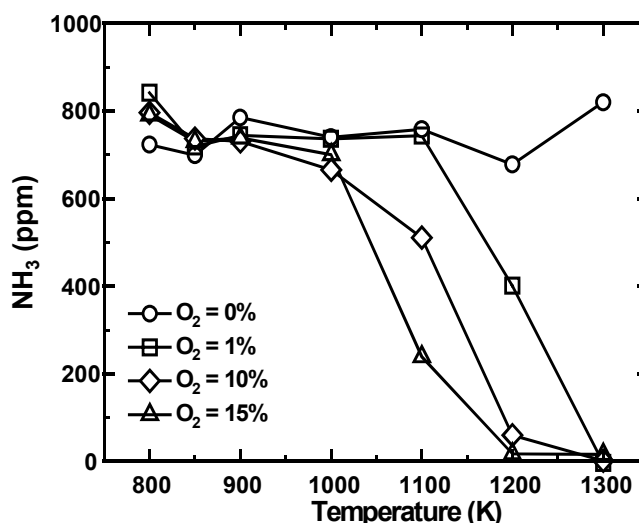


Figure 2. Ammonia (NH_3) concentration as a function of temperature for four oxygen levels for the base case conditions.

RESULTS AND DISCUSSION

Figure 2 shows the ammonia (NH_3) concentration as a function of temperature for four (4) oxygen concentrations. For lower temperatures (<1000 K), the NH_3 concentration was about 750 ppm. Since 900 ppm of urea was the input, 1800 ppm of "N" species must be produced. As shown in the following, HNCO, NO, NH_3 , and N_2O were detected. Another species that would account for "N" atoms would be N_2 (which could not be detected by the FTIR).

For higher temperatures (>1000 K), the NH_3 concentrations ranged between 0 and 800 ppm depending on the oxygen concentration and temperature. At these higher temperatures, the ammonia concentration decreased with increasing O_2 concentrations. For oxygen concentrations of 10 and 15% at 1200 K, the ammonia concentration decreased to less than about 60 ppm. For cases with oxygen present in the gas at the highest temperature (1300 K), the detected ammonia concentration was on the order of a few parts per million.

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.

Figure 3 shows the absorbance detected by the FTIR at a wave number of 2282.178 cm^{-1} (which was identified as HNCO) as a function of temperature. The detected absorbance of HNCO was similar for all four cases of oxygen concen-

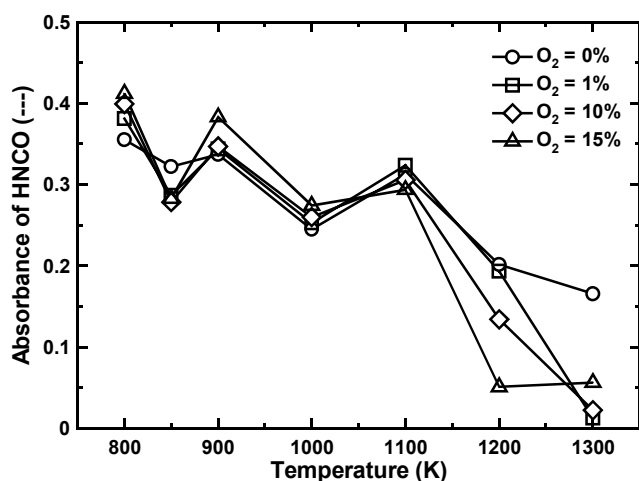


Figure 3. Absorbance of HNCO (at a wave number of 2282 cm^{-1}) as a function of temperature for four oxygen levels for the base case conditions.

trations up to a temperature of 1100 K. It was estimated that an absorbance of 0.325 represented about 400 ppm. This estimate was obtained by a comparison to dry urea decomposition, where equal amounts of NH_3 and HNCO were obtained [4].

Several important characteristics are exhibited by the results in this figure. As shown in figure 3, above a temperature of about 1100 K, higher concentrations of oxygen reduced the detected amount of HNCO down to a level of 0.05 absorbance for 1200 K and 15% O_2 concentration. For these conditions, the cases with the higher concentrations of oxygen for temperatures above about 1100 K lead to lower absorbances, and hence, lower concentrations. Only the case of no oxygen showed absorbances for HNCO that remained above about 0.15 at 1300 K.

One other feature exhibited by this data was the fluctuations in HNCO absorbance as temperature was varied. These fluctuations may be evidence that the HNCO was a result of decomposition from a form of solid urea that formed in the reactor. The implications of this "resolidification" of the urea are discussed further in a later subsection of this paper.

Figure 4 shows the CO_2 concentration as a function of temperature. Between about 800 and 1100 K, the CO_2 concentration was nearly constant at about 160 ppm for all cases. For higher temperatures and higher oxygen concentrations, the results showed higher CO_2 concentrations. For example, about 250 ppm CO_2 was detected for 10 and 15% O_2 concentration at 1300 K. The increasing concentrations of CO_2 for the higher temperatures ($>1100\text{ K}$) and higher oxygen con-

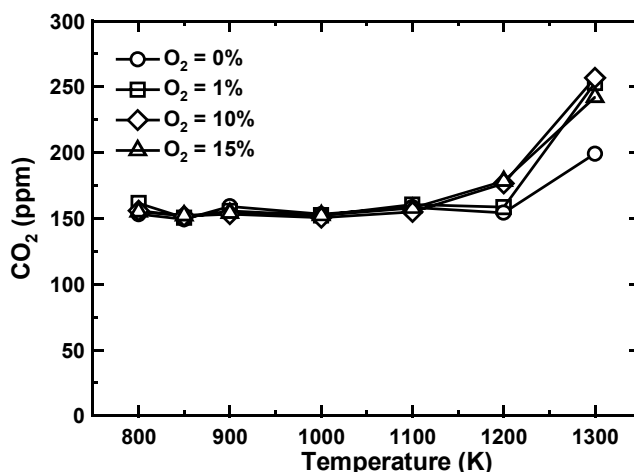


Figure 4. Carbon dioxide (CO_2) concentration as a function of temperature for four oxygen levels for the base case conditions.

centrations would be the result of oxidation of "C" containing species such as HNCO.

The low temperature ($<1000\text{ K}$) CO_2 results may be used to estimate the approximate contributions of the two major urea decomposition reaction paths. To complete this estimate the reaction of equation 2 is assumed to be the dominant source of CO_2 . For this assumption, therefore, the 160 ppm of CO_2 detected would mean that 320 ppm of the observed NH_3 would be from reaction 2. The remaining NH_3 could be a result of reaction 1. This is discussed in more detail below.

Two other species were detected, but at much lower concentrations. Figure 5 shows the NO concentration as a function of temperature. For no oxygen present in the reactor, NO was not detected. For 1% oxygen concentration about 2 ppm of NO could be reported at 1100 K, which increased to about 12 ppm NO for 1300 K. The same tendency could be observed for 10 and 15% oxygen with starting points of concentration increase at lower temperatures. Non-zero levels of NO were observed at 1000 K (about 2 ppm for 10% O_2 , and about 4 ppm for 15% O_2). At 1300 K, the NO concentration increased to values of about 27 ppm for 10% O_2 and to about 33 ppm for 15% O_2 . An overall tendency for higher NO production with increasing oxygen concentration was observed.

Figure 6 shows the N_2O concentration as a function of temperature. Below a temperature of 1000 K the concentration of nitrous oxide varied between 3 and 8 ppm for all cases with the tendency to decrease for higher temperatures. This tendency is followed only by the cases of 0 and 1% oxygen until lack of nitrous oxide was ob-

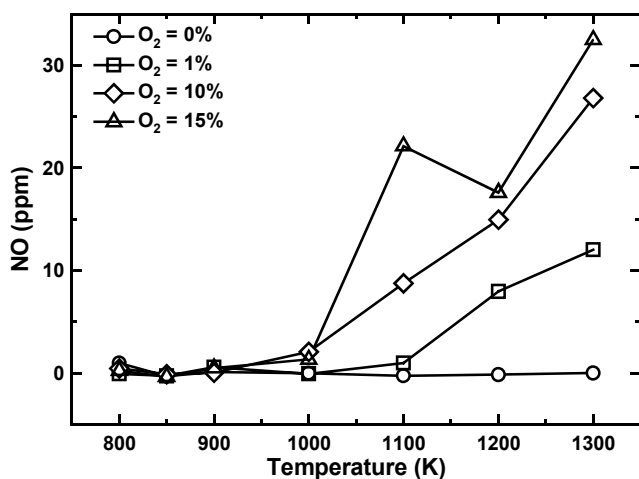


Figure 5. Nitric oxide (NO) concentration as a function of temperature for four oxygen levels for the base case conditions.

served at 1300 K for all cases. For 10 and 15% of oxygen, a peak of N₂O concentration could be reported between 1000 and 1300 K, which resulted in about 23 ppm (for 15% O₂ at 1100 K) and about 16 ppm (for 10% O₂ at 1200 K). The maximum value was observed for lower temperature with increasing oxygen concentration.

Species other than the ones reported in the figures above were not identified. The only exception to this was trace amounts of carbon monoxide. In general, carbon monoxide was detected at concentrations less than about 5 ppm. These values were not much greater than the “noise” or other uncertainties in the detection process. Never the less, it can be assumed that the level of CO was either zero or below the detection limit of the experimental setup. As a result, CO has not been reported here.

Discussion: Several observations are possible from the results of this investigation. From atom balances of the reported species, species other than the ones reported in figures 2 to 6 must have been present in the reactor. This could either be molecular nitrogen, solid urea, or an unknown by-product.

One observation that relates to the atom balances was that resolidified urea was found in the reactor and especially in the quartz pipe that was used for the injection of urea into the flow reactor. Because of the solidified urea that was found in the reactor, a combination of dry urea and urea-water decomposition probably occurred.

These two processes are presumed to be different in nature. As described above, Caton and Siebers [4] reported that dry urea decomposed into roughly equal amounts of ammonia

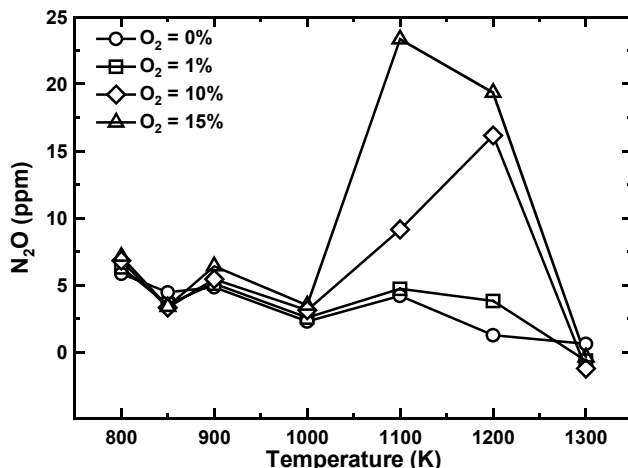


Figure 6. Nitrous oxide (N₂O) concentration as a function of temperature for four oxygen levels for the base case conditions.

and HNCO. A urea-water solution, on the other hand, is expected to decompose primarily into CO₂ and NH₃.

Another observation was the unsteady behavior of the experiment. This may be explained as a result of any resolidification and the following decomposition of dry urea which will probably be less steady in terms of variation of concentration over time or on different days of the experiments. Furthermore, the species that resulted from the decomposition of the urea-water solution would be expected to be more consistently repeatable.

A comparison of the data for NH₃, HNCO and CO₂ indicates that these species experienced different levels of variation. CO₂ and NH₃ exhibited much less variation than HNCO for the same cases. This observation is consistent with the idea that the HNCO is from the decomposition of the solid form of urea and would tend to be less repeatable. (Note that a data point for a certain O₂ concentration and temperature relates to the same experiments for all detected species since the FTIR takes a scan of the complete species composition). These facts lead to the following observations:

- ◆ CO₂ production at the lower temperatures (less than 1000 K) most probably resulted from urea-water solution decomposition,
- ◆ as mentioned above, evidence suggests that part of the injected urea deposited as solid urea (or as some other solid form) in the reactor. Solid products found in the reactor could support the latter conclusions. Parts of these products were not resolvable in water (in contrast to urea), which lead to an uniden-

tified decomposition product other than solid urea,

- ◆ at the lower temperatures, a portion of the detected ammonia was a result of decomposition of the urea-water solution, and an additional portion was due to decomposition of resolidified urea,
- ◆ little or none of the reported HNCO resulted from the decomposition of the urea-water solution,
- ◆ due to the fact that the summation of concentrations of the decomposition products of urea does not match the injected amount of 900 ppm, it was possible that some portion of the "N" from the injected urea reacted to molecular nitrogen.

These observations were also supported by a set of separate experiments which were conducted prior to the actual decomposition study. First, a urea-water solution was injected into the hot reactor at about 1100 K in a way that lead to injection of liquid into the reactor. This was done by using very high flow rates so the water did not have a chance to vaporize in the supply line. In this experiment, only ammonia and CO₂ could be found but no HNCO. In another experiment, pure water was fed into a reactor which contained a form of dry urea. The decomposition products were ammonia and HNCO. Once water was injected, CO₂ started to become visible, while the amount of HNCO decreased.

These separate experiments provided additional evidence that the injection of dry urea and the injection of a liquid urea-water solution result in different decomposition products. Specifically, dry urea results in NH₃ and CO₂, whereas urea-water solutions result in NH₃ and HNCO.

Alternative Urea Injection Device: Due to the delivery problems of the urea-water solution, where resolidification of urea prior to the reactor occurred, an alternative way to deliver the urea-water solution is recommended. Extensive testing of the setup used in the present study revealed that the delivery of a urea-water solution was dependent on the temperature surrounding the supply line.

Resolidification occurred for the case that the supply line reached the hot zone of the reactor. For this case the resolidification occurred inside the supply line. This observation lead to the conclusion that a cooled injector may be appropriate to deliver the urea-water solution in a liquid form into the reactor. In such a setup, the transition

from a liquid solution to urea decomposition products should be able to take place in a short time, and without resolidification. In other words, a successful injector design would attempt to rapidly mix the vaporized species from the urea-water solution immediately with the hot gases, and not allow the vaporized species to heat up prior to the mixing process.

SUMMARY AND CONCLUSIONS

This investigation has examined the decomposition and oxidation processes of urea-water solutions using a laminar flow reactor. A Fourier transform infrared (FTIR) spectrometer was used to determine concentrations of all species. A vaporized urea-water solution was injected into nitrogen and into nitrogen/oxygen gas streams at temperatures from 800 to 1300 K. From the results of this work, the following general conclusions may be stated:

- For temperatures below about 1000 K, thermal decomposition dominates. For these conditions, dry urea decomposes into NH₃ and HNCO, whereas urea-water solutions decompose into NH₃ and CO₂.
- For the conditions of this work, oxidation appears to be important for temperatures above about 1000 K. Oxidation products include low concentrations of NO (less than 30 ppm) and N₂O (less than 25 ppm). No significant amounts of CO or other species were detected.
- The concentrations of NO and N₂O were enhanced for the higher oxygen concentrations (for the higher temperature cases).
- The injection of urea-water solution was not effective in providing vaporization products of the urea without resolidification. To insure no resolidification, special injection techniques are necessary.

ACKNOWLEDGEMENTS

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REFERENCES

1. Heinsohn, R. J., and Kabel, R. L., 1999, *Sources and Control of Air Pollution*, Prentice Hall, New Jersey.

2. Bowman, C. T., 1992, "Control of Combustion-Generated Nitrogen Oxide Emissions: Technology Driven by Regulation," *The Twenty-Fourth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 859-878.
3. Ciarlante, V., 2000, "Achieving Moderate but Cost-Effective NO_x Control by Combining Proven Catalytic and Non-Catalytic Technologies," proceedings of the POWER-GEN International 2000 Conference, Orlando, FL, 14–16 November 2000.
4. Caton, J. A., and Siebers, D. L., 1989, "Comparison of Nitric Oxide Removal by Cyanuric Acid and by Ammonia," *Combustion Science and Technology*, Vol. 65, pp. 277–293.
5. Lentz, Michael J., 1999, "Alternative Ammonia Feedstock," 1999, Proceedings of the 1999 Annual Meeting of the American Power Conference, Vol. 61–I, pp. 495–500.
6. Aoki, H., Fujiwara, T., Morozumi, Y., and Miura, T., 1999, "Measurement of Urea Thermal Decomposition Reaction Rate for NO Selective Non-Catalytic Reduction," Fifth International Conference on Technologies and Combustion for a Clean Environment, pp. 115–118, Lisbon, Portugal, 12–15 July 1999.
7. Alzuetza, M. U., Bilbao, R., Millera, A., Oliva, M., and Ibanez, J. C., 2000, "Impact of New Findings Concerning Urea Thermal Decomposition on the Modeling of the Urea-SNCR Process," *Energy & Fuels*, Vol 14, No. 2, pp. 509–510.
8. Gentemann, A. M. G., 2001, "Flow Reactor Experiments on the Selective Non-Catalytic Removal of Nitrogen Oxides," Master of Science Thesis, Department of Mechanical Engineering, Texas A&M University, May 2001.

Appendix A

The following table is a list of the specific wave numbers used to quantify each species, and the estimated lower detection limit. Lower values could be obtained, but the accuracy would not be as high.

For some of the species, more than one wave number was used. This helped avoid using a wave number which was obscured by other species (particularly H₂O and CO₂). Complete details of the calibration procedures and results are provided by Gentemann [7].

Species	Wave Number (cm ⁻¹)	Lower Limit (ppm)
NO	1900.6	5
CO	2166.0	5
	2112.0	
	2162.4	
CO ₂	2359.2	5
	2336.4	
N ₂ O	2213.8	2
NO ₂	1602.7	2
NH ₃	966.3	5
	931.4	
	1084.8	
	868.0	