Non Catalytic NO_x Removal from Gas Turbine Exhaust with Cyanuric Acid in a Recirculating Reactor

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Abstract

A novel technique to remove oxides of nitrogen (NO_x) from stationary gas turbine exhaust has been investigated. The technique employs the use of cyanuric acid (CYA), a non-toxic, dry powder, combined with the injection of auxiliary turbine fuel and recirculation. Recirculation minimizes the auxiliary fuel consumption, reduces residence time and reactor size and enhances NO removal chemistry. This selective non-catalytic method is decoupled from the combustion source and could also be applied to other exhaust gas producers.

Exhaust gases, generated by a 150 kW gas turbine, are treated in an insulated recirculation reactor, with a mean residence time of 0.65 to 0.71 seconds and a pressure drop of 660 Pa. In the reactor, autoignition of injected auxiliary gas turbine fuel raises the flue gas temperature to an operating temperature of 700 to 800ºC. The auxiliary fuel increases the overall system fuel consumption by 14 to 30%.

Temperature rise and NO_x reduction occur simultaneously, which reduces residence time. At all temperatures, significant NO_x reduction from initial concentrations of 106 to 124 ppm to as low as 18 ppm at 15% O_2 have been observed. The process efficiency increases with decreasing reactor temperature and increasing CYA/NO_x ratio. Load following has been achieved. The process generates N_2O emissions, which vary from 45 to 163 ppm, increasing with increasing CYA/NO_x ratio. These high emissions are a process concern since N_2O is a stable strong greenhouse gas.

The performance of CYA ($(HNCO)_3$) is compared to that of ammonia (NH_3) and urea ($(NH_2)_2CO$). When injected under the same conditions as CYA, NH_3 is entirely consumed and forms NO_x. Urea exhibits hybrid behavior, combining the characteristics of NH_3 and CYA. At a reactor temperature of 800°C, NO_x concentration increases while 20% NO_x reduction is achieved at 715°C. No significant N_2O emissions are detected with NH_3, while urea yields 17 to 83 ppm N_2O, increasing with urea/NO_x ratio.

A numerical model, which combines a detailed chemical kinetic mechanism with recirculation, has been developed. It describes hydrocarbon autoignition and concurrent NO_x removal in an ideal, adiabatic environment. The model captures all observed trends well and is an invaluable guide to improved understanding of the interactive NO_x removal process.

While excellent qualitative agreement is achieved, disparities in absolute values of NO_x reduction, N_2O formation and autoignition times exist. Autoignition delay discrepancies might be reconciled with the advent of more complete chemical kinetic hydrocarbon mechanisms. N_2O formation and NO_x reduction disparities are assumed to stem from the incomplete model for decomposition of CYA.

Future results from this work are expected to improve process efficiency, reduce observed N_2O emissions and to be of practical significance for the application to stationary gas turbines of as much as 20 MW capacity.

Introduction

In recent years public concern about air pollution and its side effects have resulted in a variety of regulations and standards (e.g. 1990 Clean Air Act) limiting pollutant concentrations in exhaust produced by combustion processes. Particular attention has been given to NO_x, the oxides of nitrogen. NO_x play an important role in photochemical smog, acid rain and in the stratospheric ozone chemistry [1]. Consequently various methods have been introduced in order to reduce the amount of NO_x emitted.

In general one can distinguish between pre-combustion fuel treatment, combustion modification and post-combustion exhaust gas treatment. Fuel treatment has led to cleaner, reformulated fuels eliminating the problem of fuel bound nitrogen. Combustion modification attacks the production of thermal NO_x generally by lowering the peak temperature inside the engine or burner. Among the post combustion techniques a distinction is made between catalytic and non catalytic processes.

An example of a catalytic exhaust gas treatment is the catalyst used in the exhaust of a spark ignited modern automotive engine. In it NO_x is reduced and CO oxidized as long as stoichiometric conditions ($\Phi \approx 1$) exist. Selective catalytic processes do not have this requirement and employ a catalytic converter in combination with a process reagent, generally ammonia, to reduce nitrogen oxides [2]. Under overall lean conditions such as in the flue gas stream of a gas turbine or a Diesel engine selective non catalytic reduction (SNCR) techniques are often preferred. These methods rely on gas phase reactions to selectively reduce NO_x with a process reagent. Currently three main process reagents are used: Ammonia [3], Urea [4] and Cyanuric acid (CYA) [5]. They are similar in requiring a minimum temperature (800 to 1400 K), necessary to obtain a sufficient concentration of specific radicals which initiate the desired chain of reactions but differ in the corresponding reaction path. Beyond a certain maximum temperature NO_x is produced by oxidation of the process reagent. Their efficiency varies with exhaust gas composition and the addition of hydrocarbons. CYA for example has been found to become more efficient in reducing NO with high O_2 and CO concentrations in the exhaust gases while for NH_3 the opposite is true [6]. Urea is essentially a mixture of both.

The drawbacks of these processes find their origin in the temperature requirement. Exhaust gases generally have to be heated up, which leads to potential energy losses and can limit the ability to follow load. In addition concerns about reagent slip and N_2O formation [7] exist. N_2O is considered a strong greenhouse gas and is believed to play a role in stratospheric ozone chemistry.

The object of this research is to explore the applicability of a SNCR post combustion treatment process using CYA as process reagent to the exhaust gases produced by a stationary gas turbine.

Process description

The process reagent CYA ($HNCO_3$) is a non toxic solid and can be used where the presence of a hazardous substance such as ammonia cannot be tolerated (i.e. on an oil platform or in certain residential areas). In this process CYA is administered directly into the gas turbine exhaust as a water based slurry. CYA sublimes at approximately 330ºC and cracks upon further heating to HNCO. The NO removal chemistry is described by :

$$HNCO + OH \Rightarrow NCO + H_2O$$

$$NCO + NO \Rightarrow N_2 + CO_2$$

$$NCO + NO \Rightarrow N_2O + CO$$

Peak stationary gas turbine exhaust temperatures range between approximately 550ºC and 650ºC. Previous work with CYA on Diesel engines [8] showed high NO_x reduction at an operating temperature of 700-800ºC. The necessary temperature boost to this range is achieved here by autoignition of fuel injected into the exhaust gases. The point of injection is next to that of the process reagent. Recirculation provides mixing of hot combustion products with the incoming cooler, less reactive, stream. The subsequent temperature rise combined with the increased concentration of radicals triggers the combustion of the mixture to so establish a stable reaction zone and enhance the concurrent NO_x reduction chemistry. Achieving temperature rise and NO_x reduction simultaneously has the advantage of minimizing residence time and reactor size.

Typically a variety of bluff bodies or vanes are used to induce recirculation. The immersion of such objects in the flow introduces a pressure drop. Since any applied back pressure constitutes an additional load on a gas turbine and therefore reduces its efficiency recirculation was here achieved by manipulating the flow geometry while minimizing the corresponding restriction.

Numerical Modeling

The model used in this study assumes all mixing processes to be ideal such that they can be represented by a combination of perfectly stirred and plug flow reactors (PSR and PFR). This simplification allows for the use of detailed chemical kinetic mechanisms. Since the oxidation chemistry of higher order hydrocarbons (> C3) is not as well understood a mechanism based on Westbrook and Pitz [9] for propane and propene oxidation was used to model the reheating process (i.e. the addition of turbine fuel). A mechanism by Miller and Perry [10] modeled the CYA/NO_x as HNCO/NO_x chemistry. In combination a total of 69 species and 311 elementary reactions were considered.

To explore the effect of recirculation on the autoignition process a combination of PSR and PFR with a back mixing option was developed. The so called PSRPFRX algorithm is schematized in Figure 1.

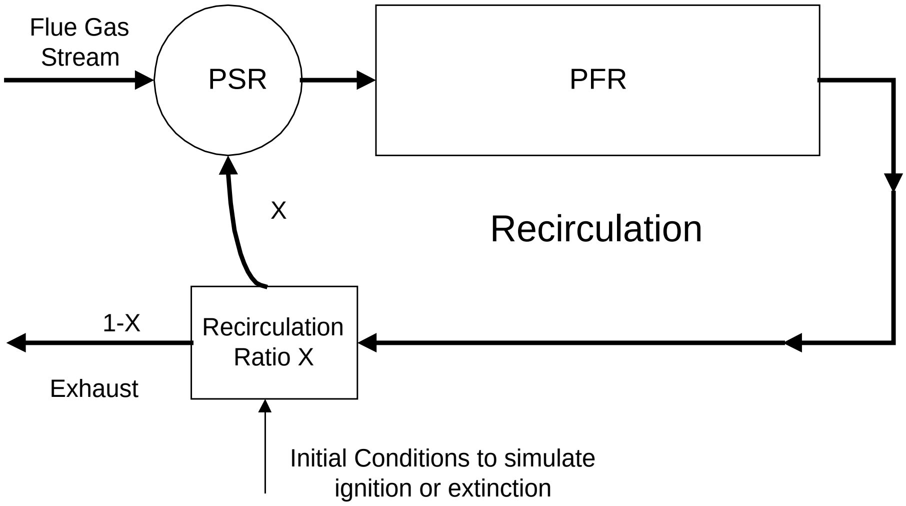

Figure 1: *Schematic of the PSRPFRX Algorithm. A part of the output from the combination of PSR and PFR is injected into the PSR alongside of the incoming stream.*

In the PSR incoming flue gases are mixed with gases coming out of the plug flow reactor according to a variable ratio X. Residence times in the PSR are short (1-3 ms). Most of the chemistry therefore occurs in the PFR. Initial conditions for the back mixed component can be input. This allows simulation of cold ignition as well as extinction of a hot, burning process. The program iterates until a steady state is obtained. Results from these calculations can be used to determine the theoretical minimum residence time inside of a reactor to induce autoignition or once ignited, to operate at steady state. This is demonstrated in Figure 2.

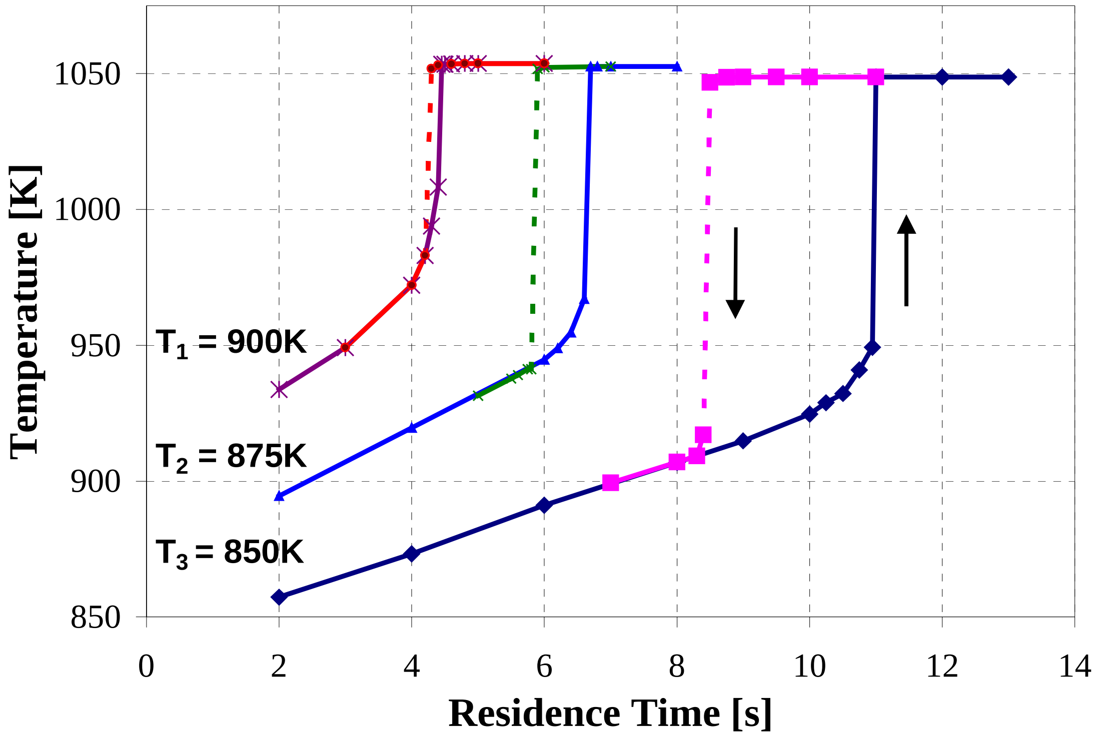

Figure2: *Ignition and Extinction Behavior of a Recirculating Reactor at 30% Recirculation and a Final Temperature of 1050 K.*

In Figure 2 the recirculation ratio is held constant at 30% while intake temperature is varied. The initial exhaust gas contains 15% O_2, 3.6% H_2O, 4% CO_2 and 200 ppm CO with the remainder being nitrogen. The amount of propane added varied from case to case to reach the same final temperature of approximately 1050 K. The corresponding equivalence ratios were 0.047 for 850 K, 0.055 and 0.061 for 875 K and 900 K respectively. Ignition residence times are larger for lower temperatures and are shorter at higher temperatures ranging from 11 seconds at 850 K to 4.4 seconds at 900 K. The size of the obtained ignition extinction hysteresis plots are found to increase with decreasing intake temperature. At 900 K the time difference between ignition and extinction is about 0.2 seconds while at 850 K almost 2.5 seconds are recorded. This sensitivity of propane oxidation to temperature in this range under the given conditions emphasizes the need for recirculation in any practical system.

Experimental Setup

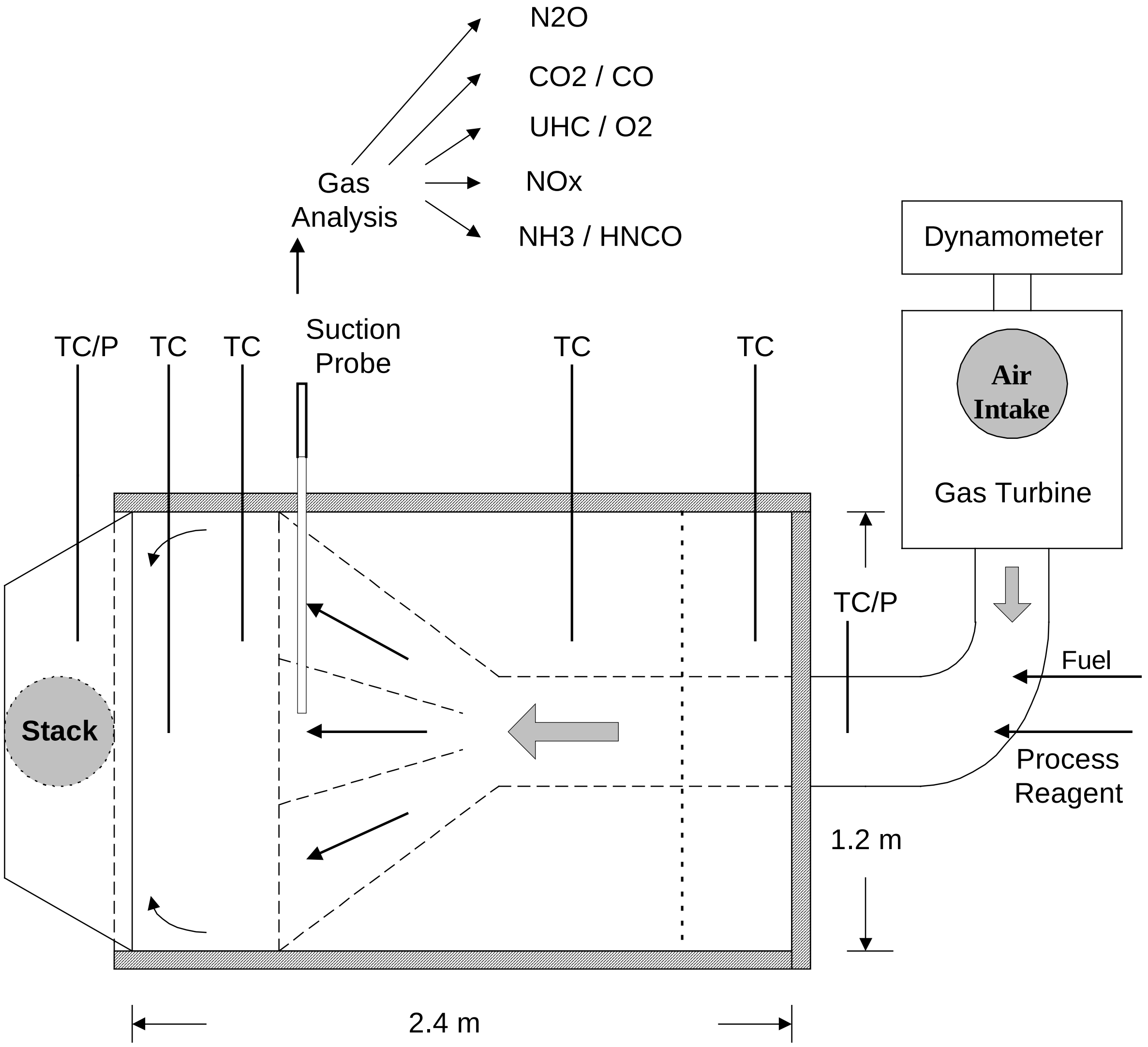

Figure 3: ***Schematic of the Experimental Setup*** **(top view)**

An experimental apparatus has been built, using a 150 kW rated gas turbine (~800 kW thermal) as an exhaust gas producer. This turbine operates on a variety of liquid fuels at constant speed. A controllable load is applied by a dynamometer. Flue gas temperature and composition are varied up to a maximum of 640ºC at approximately 15% O_2. The exhaust gases are treated in an internally insulated recirculating reactor with a mean residence time of 0.75 seconds variable up to 2 seconds at an operating temperature of 750ºC. Autoignition of additionally injected gas turbine

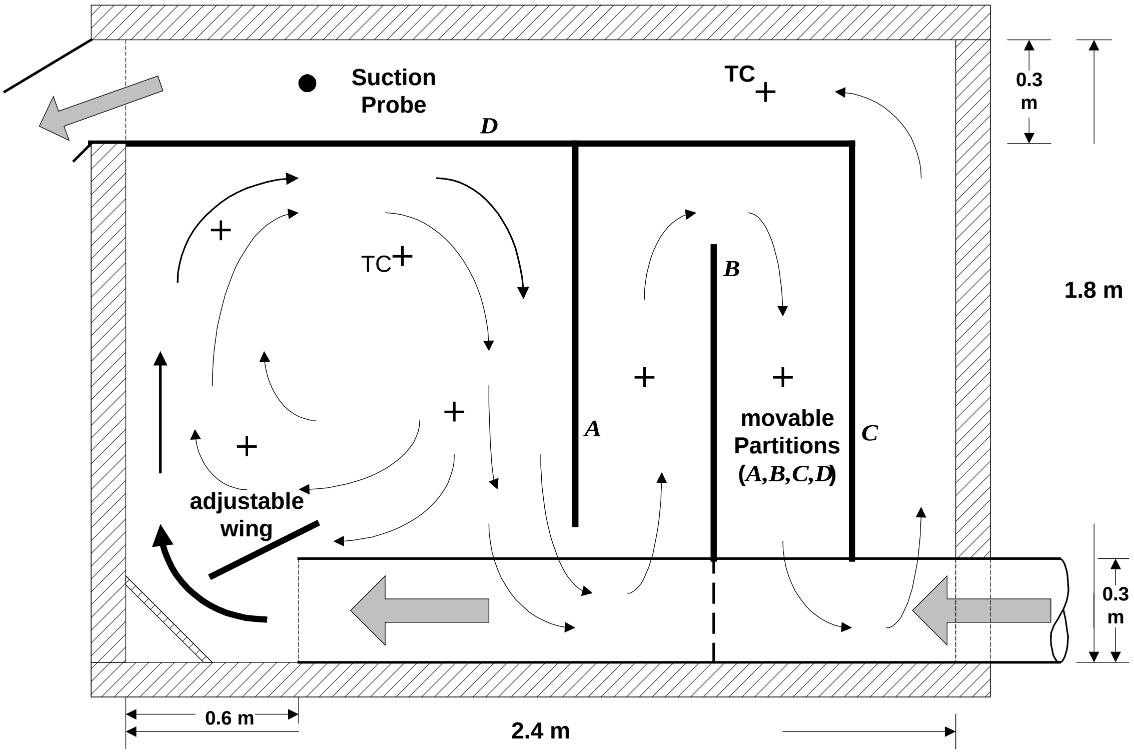

Figure 4: *Schematic of the Reaction Chamber (side view)*

fuel boosts the flue gas temperature to the desired range. CYA is injected as a slurry with a rotating or an air assisted injector both designed particularly to accommodate a wide range of feed rates reliably. Control mechanisms are being employed to allow load following and NO_x content based variation of these injection rates. Both CYA and the additional fuel are injected directly into the exhaust gas stream as it leaves the turbine and mixed in the highly turbulent flow through a 30 cm pipe connecting the engine to the reactor. Operating temperatures in this recirculating reactor are controlled between 700 and 800ºC. NO_x content is varied to match emissions from commonly used gas turbines.

In addition to numerical simulation a scale water model has been used to optimize recirculation, mixing and reduce the associated maximum pressure drop across the reactor to 660 Pa. The reaction chamber contains movable ceramic partitions which allow changing of flow geometry and residence time. Thermocouples, pressure tabs as well as a water cooled suction probe are inserted though the insulated walls. See Figures 3 and 4.

Gas analysis is performed with UHC (flame ionization), an O_2 (magneto pneumatic), a set of infrared CO and CO_2 as well as chemiluminescent NO_x analyzer. The sample stream is filtered and dried in the gas phase. All lines, filters and the sample pump are heated to avoid condensation of water. The determination of N_2O is carried out using samples drawn through a NaOH solution to scrub out any SO_x and a gas chromatograph with an electron capture detector [11], [12].

There are various techniques available to perform an NH_3 or HNCO analysis. Here a wet chemical approach is chosen using an NH_3 electrode [13]. With it a minimum concentration of approximately 5 - 10 ppm of HNCO in the flue gas stream can be detected depending on the amount of gas sampled.

With the exception of HNCO and N_2O all temperature and gas composition data are collected at a 1 Hz frequency. Steady state operating conditions at ‘full’ load can be summarized as follows :

Turbine Engine:	
Load	90 kW +/- 1 kW
Intake temperature	18 – 32°C
Exhaust temperature	600 – 630°C
Fuel consumption	1.11 – 1.25 kg/min
Air flow rate	0.97 – 1.08 kg/sec (constant)

Reaction chamber at steady state full load conditions:	
Pressure loss	660 Pa
Mean final reactor temperature	700 – 780°C
Auxiliary fuel consumption	150 – 320 g/min
Residence time in recirculating zone	0.65 – 0.71 sec

Gas composition		
	before reactor	*after reactor*
O_2	15%	13.4 – 14.7%
CO_2	3.74 – 4.0%	4.2 – 5.2%
CO	380 ppm	30 – 150 ppm (T > 700°C)
NO_x	18 – 23 ppm (@15% O_2, dry)	20 – 34 ppm (@15% O_2, dry)
HC	60 -70 ppm	< 15 ppm

Table 1: *Average Turbine and Reactor Operating Conditions (without NO Doping)*

Discussion of Experimental and Numerical Results

Reactor Operation

The reactor temperature was found to be controllable at a mean residence time of 750 ms at full load. The amount of recirculation was determined in a scale water model to be approximately 30%. The desired temperature boost (to 700 to 800ºC) was obtained at loads of 50% to 100% resulting in turbine exhaust temperatures of 440ºC and 640ºC respectively. These observations are in contrast to the predictions of the model for 30% recirculation (Figure 2). Even in the best case the model over predicts minimum residence times by a factor of 5. Besides that, trends seen in the numerical study were verified experimentally. At a load of 30% and a temperature of less than 410ºC reactor extinction was observed. The discrepancy between the residence times predicted and observed might find its origin in the simplifications used in the model and the fact that the set of elementary reactions is a comprehensive oxidation mechanism and not necessarily expected to properly predict autoignition at extremely low equivalence ratios of close to 0.05 as in this study. Considering that modeling autoignition itself is difficult the numerical results are reasonable.

Under full load steady state conditions were reached in a matter of minutes. With the decay of thermal transients fuel flow was kept constant thereby controlling the reactor temperature. At steady state operation CO and unburned HC emissions were found to be reduced from 380 ppm and 70 ppm in the turbine exhaust to between 30 and 120 ppm and less than 4 ppm respectively.

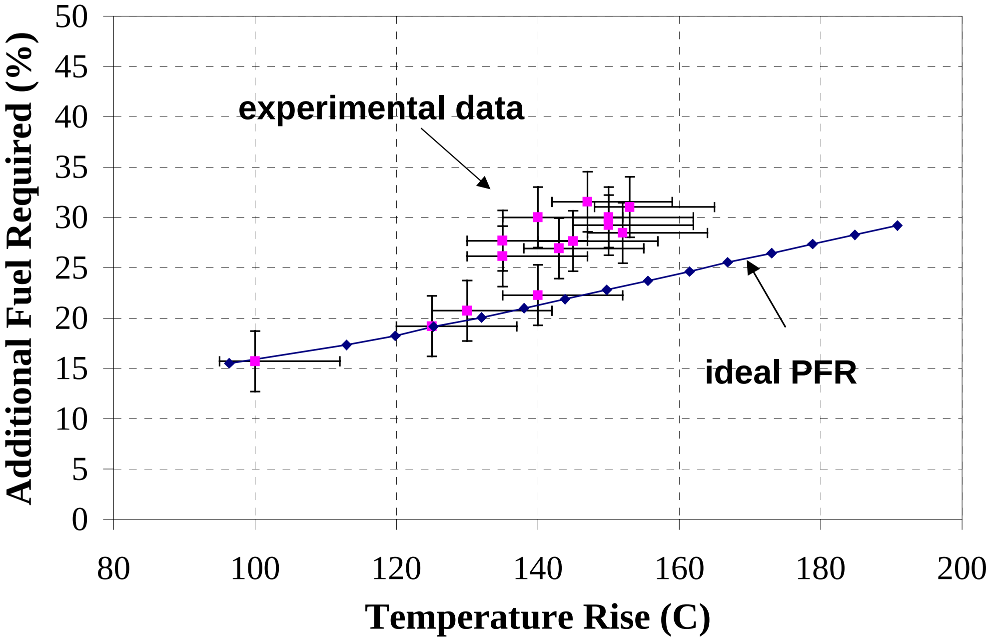

Figure 5: *Comparison of Experimental and Theoretical Additional Fuel Consumption. The theoretical values were obtained with exhaust gas composition similar to the experiment and an entry temperature of 600°C at adiabatic conditions.*

One of the process concerns is the necessity of fuel addition. The numerical model assumes adiabatic conditions and any auxiliary fuel input therefore produces ideal final reactor temperatures. In the experiment, fuel was added such, that the desired process temperature was reached. Figure 5 compares the theoretical, ideal values with those obtained when operating the reactor. Reactor inlet temperature in the model is 600°C, which corresponds to the average inlet temperature observed in the experiments. Under ideal circumstances, i.e. no heat loss, the model predicts between 15.5 and 29% additional fuel injection to heat an exhaust gas stream with an initial temperature of 600°C, to a process temperature of 700 to 791°C, respectively.

In the experiment the auxiliary fuel needed to increase the reactor temperature to 700 to 800°C was 16 to 30% of the turbine fuel consumption. At final temperatures of 740 to 750°C, 5 to 7% more auxiliary fuel is consumed than in the model. With the large surface area of the reactor and an outside surface temperature of 40 to 80°C heat losses of this order are expected. With an overall limited heat loss of 5 to 7%, approximately adiabatic conditions can be claimed.

NO_x Removal with CYA

When comparing experimental and numerical NO_x reduction with cyanuric acid, the assumption that the thermal decomposition of CYA yields three molecules of isocyanic acid, HNCO, is used. An experimental CYA/NO_x ratio of unity, for example, is compared to a numerical HNCO/NO ratio of 3. In Figure 6, NO_x concentration versus temperature and reagent/NO_x ratio are shown. Experimental and numerical curves for constant reagent addition, are similar in shape but shifted.

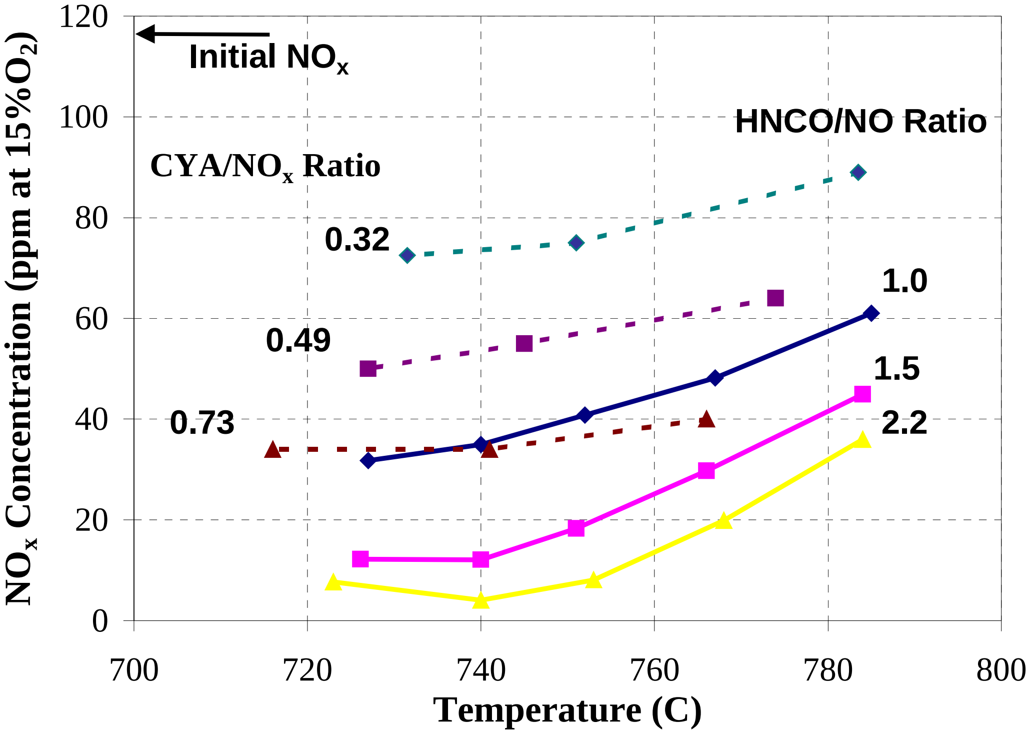

Figure 6: *Comparison of Experimental and Numerical NO_x Reduction with CYA. The solid lines are numerical values while the broken lines represent experimental results. Experimental and numerical reagent/NO_x ratios are indicated on the left and right respectively.*

The NO_x removal process improves with decreasing temperature and increasing CYA/NO_x ratio. In the experiment a minimum of 34 ppm NO_x was observed. This minimum NO_x concentration corresponds to 71% reduction. Lowest efficiency was observed at a ratio of CYA/NO_x = 0.95 resulting in a NO_x concentration of 80 ppm, which equals 32% reduction. In all cases the initial NO_x concentration was 117 ppm +/- 2 ppm, and all concentrations are adjusted to 15% O_2.

The experimental NO_x concentrations are in every case higher than the numerical values, corresponding to an over prediction of NO_x reduction by 21 to 27%. Besides this obvious disparity in absolute NO_x values, the general agreement between the modeled and observed trends is good. Increasing NO_x removal with increasing reagent injection and the temperature dependence is properly modeled. The model captures the apparent maximum in NO_x reduction at 740°C for a CYA/NO_x ratio of 0.73 (which corresponds to a numerical HNCO/NO ratio of 2.2). The relative differences between the resulting NO_x concentration at changed temperature and reagent/NO_x ratio are similarly replicated.

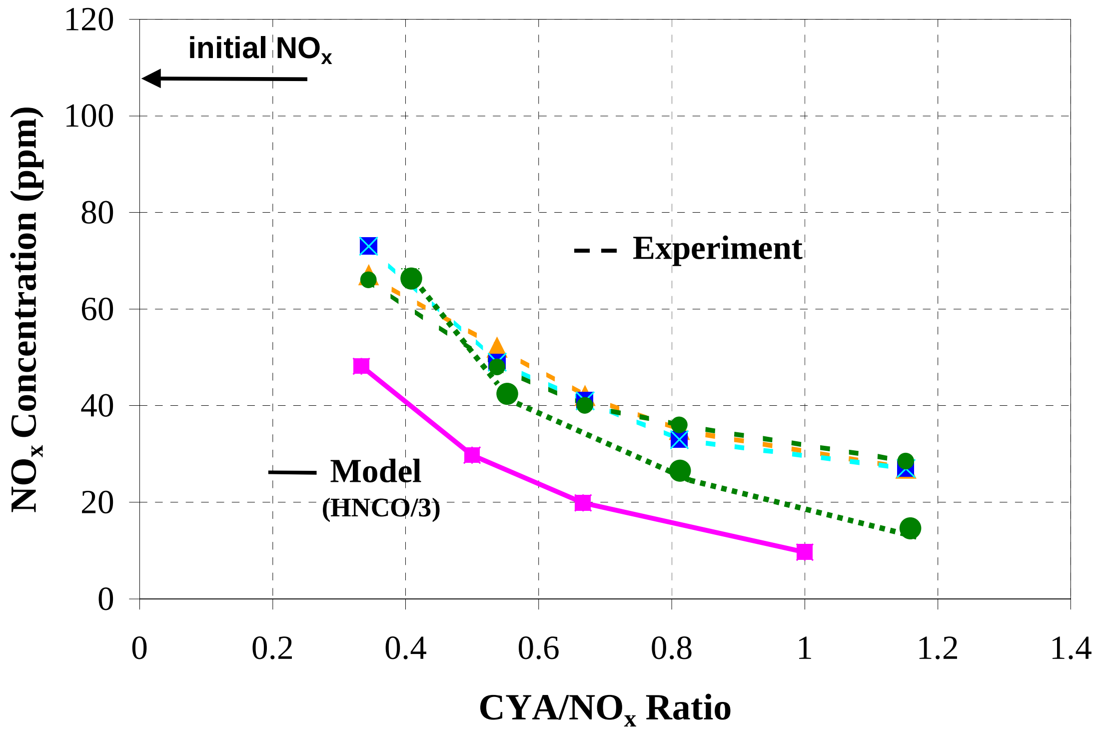

Figure 7: *NO_x Removal at Fixed Temperature versus CYA/NO_x Ratio. Experiments were performed at an average temperature of 750℃ at 100% turbine load.*

Figure 7 shows final NO_x concentration versus CYA/NO_x ratio at a fixed average temperature of 736 to 750°C. In the experiment NO_x concentrations decreased with increasing CYA/NO_x ratio to a minimum of 18 ppm at a CYA/NO_x ratio of 1.14 and a temperature of 736°C. The other plotted values were observed at a slightly higher temperature of 750°C. Although numerically obtained NO_x concentrations are approximately 10 to 20 ppm lower, corresponding to an over prediction in NO_x removal of 8 to 21%, experimentally observed trends are replicated well by the model. The rate of numerical NO_x concentration decrease, with respect to CYA/NO_x, ratio properly matches the experimental observations.

Investigation of the effect of reactor inlet (= turbine exit) temperature on the NO_x reduction chemistry is central to the issue of turbine load following. The final NO_x concentrations, obtained by experimental and numerical variation of reactor inlet temperatures, are contrasted in Figure 8. The lowest experimental NO_x emission of 26 ppm was found at maximum load and the highest CYA/NO_x ratio of 1.06. The process efficiency decreases with decreasing intake temperatures. Such a behavior can be explained with less efficient CYA sublimation and cracking to HNCO at lower temperatures.

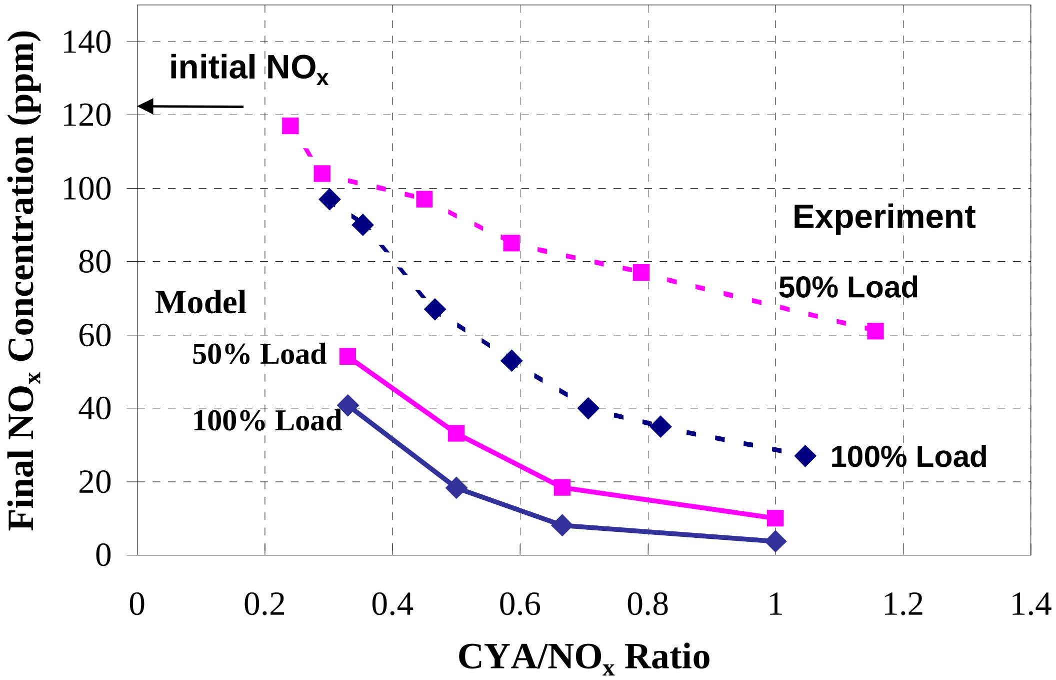

Figure 8: *NO_x Concentration versus Turbine Load; Numerical and Experimental Values. Final reactor temperature remained fixed at 760℃ (+/- 10℃), while the intake temperature varied with turbine load. A load of 50 and 100% corresponds to 440℃ and 610℃ respectively.*

The numerical values are based on initial experimental conditions, such as exhaust gas composition and temperature measured at 50 and 100% turbine load. The numerical differences in NO_x reduction between initial conditions generated by 50 and 100% load are of the order of 5 to 15%. Experimentally, a much larger discrepancy is observed. The model predicts better than 50 to 90% NO_x reduction with a CYA/NO_x ratio of 0.33 to 1.0, respectively. Similarly to the previous results, the model agrees well with the overall behavior but does not reproduce the exact

NO_x concentration values. A difference of as much as 47% at the lowest CYA/NO_x ratio and 20% at the highest CYA/NO_x ratio, at 100% load, is seen.

N_2O Formation and Reagent Slip

Within the limits of detection uncertainty, CYA (i.e. HNCO) slip was determined to be less than 10 ppm. Thus HNCO and NH_3 slip is negligible in these experiments. In Figure 9, measured N_2O concentrations with respect to CYA/NO_x ratio are shown. All plotted values are adjusted to 15% O_2.

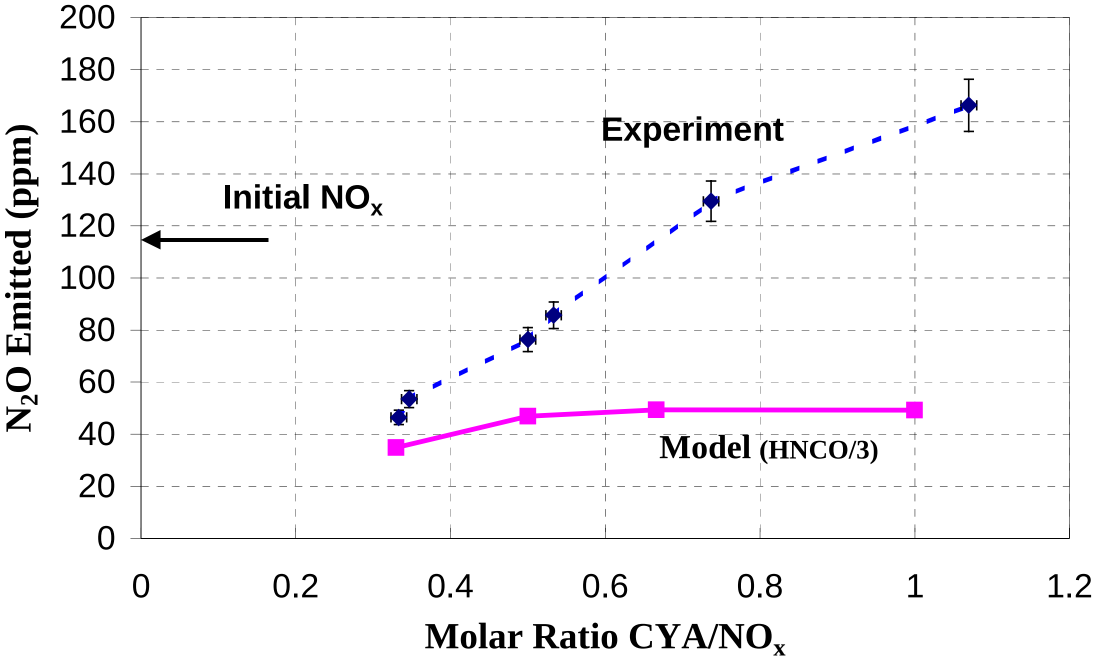

Figure 9: *Experimental and Numerical N_2O Emissions versus CYA to NO_x Ratio. The reagent to NO ratio of the model is adjusted corresponding to CYA = 3 HNCO. Initial conditions such as temperature and exhaust gas composition, are similar.*

A clear increase with increasing CYA/NO_x ratio can be seen. At a molar ratio of CYA/NO_x = 0.33, 46.5 ppm of N_2O are found while at a CYA/NO_x ratio of 1.08 as much as 166 ppm are observed. When the experimentally obtained N_2O concentrations are compared to the modeled N_2O concentrations, agreement between model and experiment is not as good. As shown in Figure 9, N_2O concentrations deviate by as much as a factor of 3. As before, observed reactor temperatures are input into the model, so that initial experimental conditions are simulated. The model only in part captures the trend of increasing N_2O emissions with increasing CYA/NO_x ratio. Numerical N_2O emissions appear to plateau at approximately 50 ppm independent of CYA/NO_x ratio, while the experimental values increase with reagent ratio. The maximum N_2O concentration measured exceeds the initial NO_x concentration in the turbine exhaust. Since N_2O formation is primarily a byproduct of the NO reduction along the NCO + NO pathway, detected N_2O cannot be a result of conversion of the initial NO concentration alone. Another pathway, to explain these emissions has to be active. Further evidence for the existence of a mechanism not considered by the model is provided by Figure 10. Measured concentrations of "N_2O formed" versus "NO_x reduced" are compared to the values determined by the numerical model.

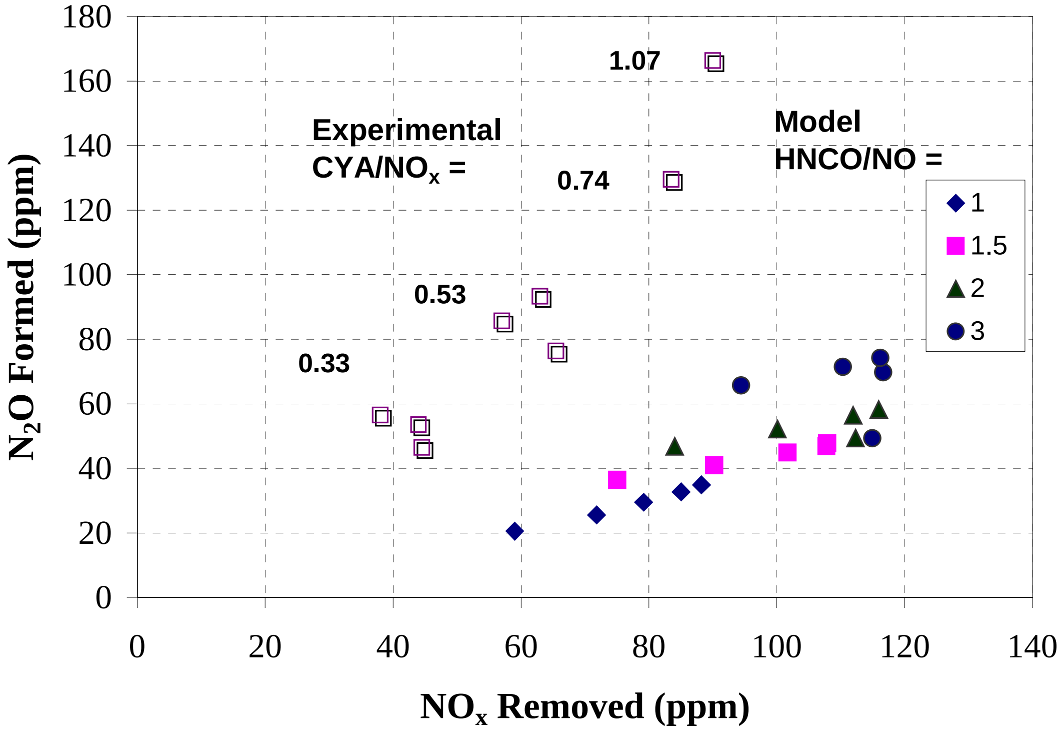

Figure 10: *Experimental and Numerical N_2O Formed versus NO_x Removed.*

Experimental N_2O emissions follow an approximate 1.5 to 1.0 ratio of "N_2O formed" to "NO removed". In contrast, modeling results are clustered about a slope of 0.3 to 0.5. The needed CYA/NO_x ratios, i.e. 3HNCO/NO_x ratios, (of ~1), to achieve maximum reduction are significantly higher than the observed CYA/NO_x ratios for gaseous isocyanic acid injection [14].

The assumption used by the model is ‘perfect‘ thermal decomposition of cyanuric acid to three molecules of HNCO. The phenomena seen here might be explained by a possible mechanism, that reduces the effective conversion of cyanuric acid to isocyanic acid in a lean-burn environment [15].

$$(HNCO)_3 + OH \Rightarrow (HNCO)_2NCO + H_2O \qquad (1)$$

$$(HNCO)_2NCO + O_2 \Rightarrow (HNCO)_2NCO(O_2)\ \text{(Adduct)} \qquad (2)$$

$$(HNCO)_2NCO(O_2)\ \text{(Adduct)} \Rightarrow 2HNCO + NO + CO_2 \qquad (3)$$

The proposed mechanism describes CYA decomposition starting with an H abstraction, to a product of NO and HNCO at a ratio of 1-to-2. This mechanism would predict the experimentally needed CYA/NO_x ratio (of ~1) to reduce NO and the high production of N_2O when using slurry based CYA injection. To incorporate this alternative decomposition path into the model, additional chemical kinetic data and an associated branching ratio is required.

In Comparison: Ammonia as a Process Reagent

The experimental use of NH_3 in the recirculating reactor led to a significant increase in NO_x concentrations in the flue gases, while NH_3 slip was not detected. The observed NO_x concentration increases are plotted in Figure 11. NH_3 addition to a turbine exhaust gas stream containing 118 ppm NO_x (at 15% O_2) at a NH_3/NO_x ratio of 1.5 resulted in a 50 ppm increase in NO_x concentration. To further investigate the apparent thermal oxidation in the recirculation zone, NH_3 was added to the exhaust stream at a temperature range of 620 to 800°C. The formation of NO by NH_3 in the recirculating reactor appears to be weakly related to chamber temperature and to the amount of NH_3 added. Approximately 30% of the added NH_3 decomposed to form NO in a temperature range of 620 to 800°C. Under conditions of no auxiliary fuel consumption, a similar increase of NO_x was found. This suggests that the oxidation process appears to continue even when no hydrocarbon radicals from the auxiliary fuel combustion are present. It can be concluded that NH_3 thermally decomposes, and, in part, oxidizes, with and without the presence of hydrocarbon radicals in the recirculating reactor.

The numerical model, also shown in Figure 11, replicates these experimental findings. In the PSRPFRX model, NH_3 is entirely consumed and partially oxidized to NO, leading to an increased NO_x concentration.

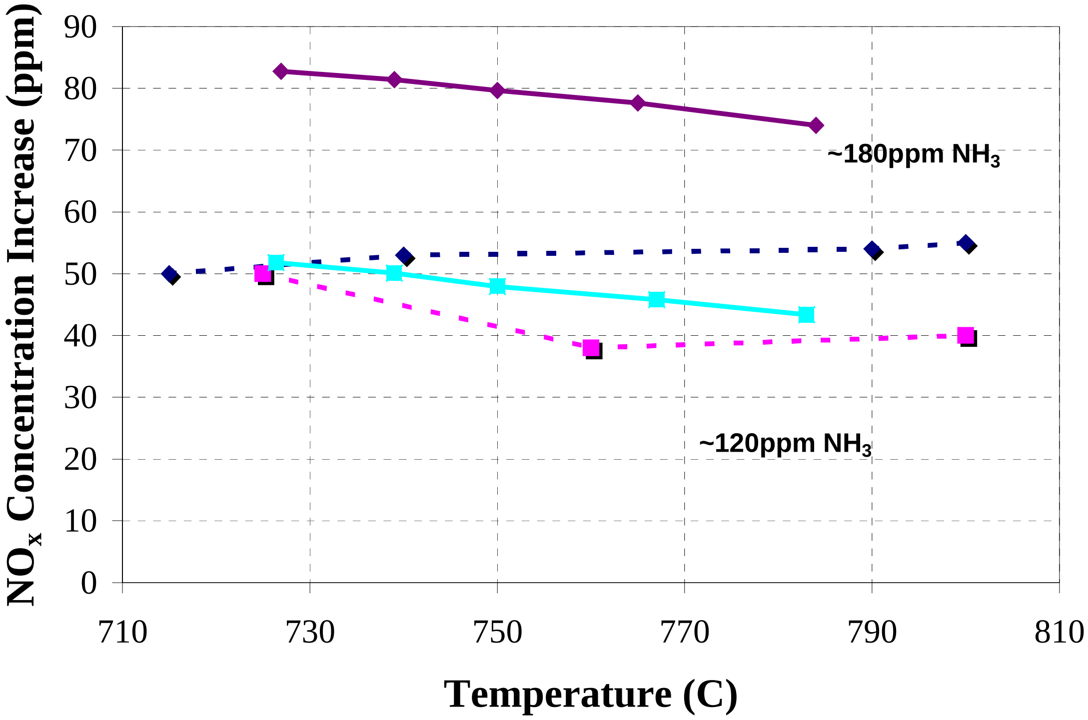

Figure 11: *Experimental and Numerical* NO_x *Increase due to Injection of* NH_3*. Solid lines represent numerical results while broken lines connect experimental values. The experimental conditions varied in initial* NO_x *concentration between 40 and 120 ppm* NO_x*; the absolute increase was found to be solely a function of* NH_3 *injection rate.*

At an addition of 120 ppm of NH_3, corresponding to a NH_3/NO_x ratio of 1, modeled and observed NO_x concentrations are in very good agreement, with a maximum discrepancy of 15%. At 180 ppm NH_3 addition, or an NH_3/NO_x ratio of 1.5, NO_x increase in the experiment reached a maximum of 55 ppm while the model predicts an 80 ppm increase. Predicted N_2O emissions are in the single digit ppm range, which agrees with the experimental findings.

The model captures the salient features and properly describes the behavior of NH_3 in a recirculating reactor. the results shows how the interaction with hydrocarbon decomposition can significantly change the performance characteristics of NH_3 as an NO_x reduction agent.

It can be concluded that the developed model is a valuable tool to predict the behavior of NH_3 when added under the given conditions into a recirculation zone and when used without the addition of fuel or recirculation.

In Comparison: Urea as Process Reagent

The performance of urea was tested at three reactor temperatures of 715, 755 and 800°C at 100% turbine load. While the reactor was kept at constant temperature, the amount of urea injection was varied. Injection rates are provided as a molar urea/NO_x ratio.

Since it is assumed, that $(NH_2)_2CO$ decomposes into two molecules, once heated, the effective ratio of reagent to NO_x, here $[NH_3 + HNCO]/[NO_x]$, is simply double the given urea/NO_x amount. The initial NO_x concentration was held at 120 ppm (at 15% O_2). Final NO_x emissions are plotted in Figure 12. Urea addition was found to increase the NO_x concentration at the highest test temperature of 800°C and decrease the total amount of NO_x at both lower test temperatures. Both tendencies, increase and decrease, are increased with increasing urea/NO_x ratio.

At a reactor temperature of 800°C, a NO_x concentration of 133 ppm, was observed at a urea/NO_x ratio of 1.34. The smallest NO_x increase was recorded with a final NO_x concentration of 124 ppm at urea/NO_x = 0.415. At the intermediate temperature of 755°C a moderate, 8 to 19%, NO_x reduction was observed. The reduction increased with urea/NO_x ratio to reach a final NO_x concentration of 97 ppm at a urea/NO_x ratio of 1.59, corresponding to a 19.2% NO_x reduction.

The numerical results of the model assuming ‘perfect’ decomposition of $(NH_2)_2CO$ into NH_3 and HNCO reproduced the experimental behavior of urea very well. In addition, the assumed decomposition of urea to HNCO and NH_3 also explains the experimental observations. Urea appears to combine the characteristics of both decomposition products when used in the described environment. Moderate NO_x removal can be attributed to (1) the added NO formed by NH_3 and (2) the simultaneous removal of NO_x by HNCO. The agreement between model and experiment with respect to the absolute values of NO_x concentration is good (Figure 12). NO_x values are under predicted by approximately 5%. The temperature dependence of the NO reduction with urea is in excellent agreement with the model.

The observed increase in NO_x concentration above 800°C as well as the decrease in NO_x concentration at 715°C, is replicated by the numerical model. Similarly well captured is the NO_x removal dependence on urea/NO_x ratio.

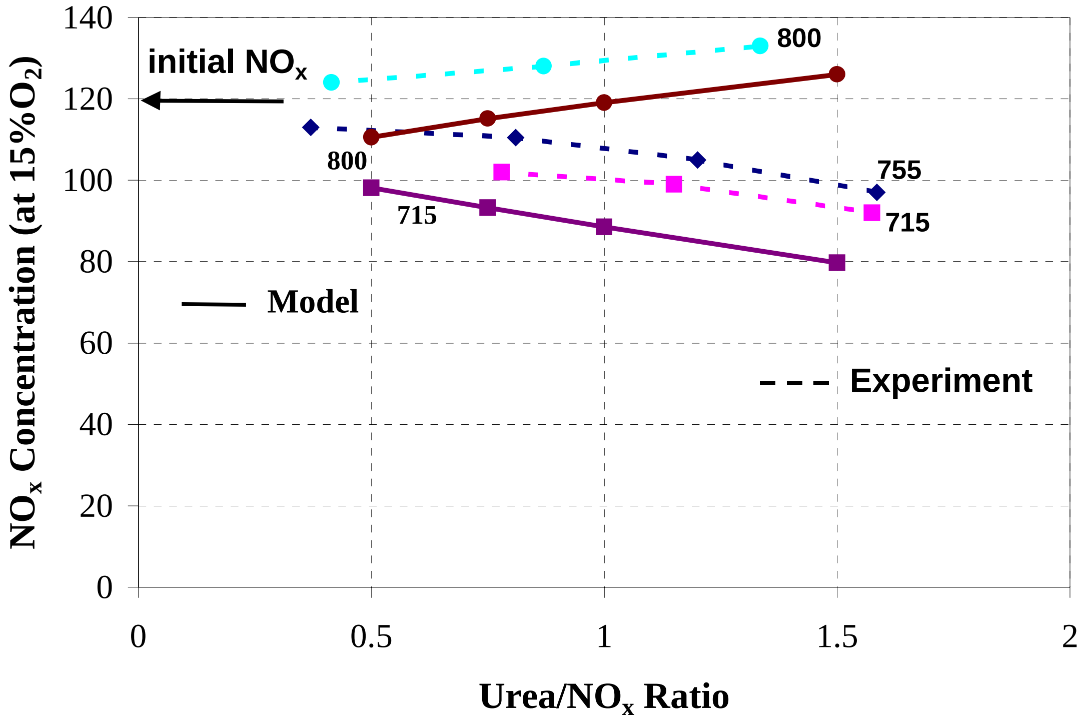

Figure 12: *NO_x Concentration with Urea Injection versus Reagent Injection Ratio and Temperature. The lines connecting individual data are isotherms at the indicated temperature (in °C).*

In Figure 12, experimental and numerical N_2O concentrations are compared. In the experiment N_2O emissions varied from 17 to 82 ppm, depending on reactor temperature and urea/NO_x ratio. N_2O concentration are observed to increase with decreasing temperature and increasing urea/NO_x ratio in the investigated temperature range. The N_2O formation is not as well predicted as the changes in NO_x concentration, i.e. the model under predicts the experimental values by as much as 57%. The qualitative agreement is better at the higher temperature of 800°C. The numerical values differ from the experimental observations by 34 and 49%, only. At 715°C, the quantitative difference between model and experiment varies from 57 to 27%. At both temperatures, the model correctly captures the trend of increasing N_2O emissions with increasing urea/NO_x ratio.

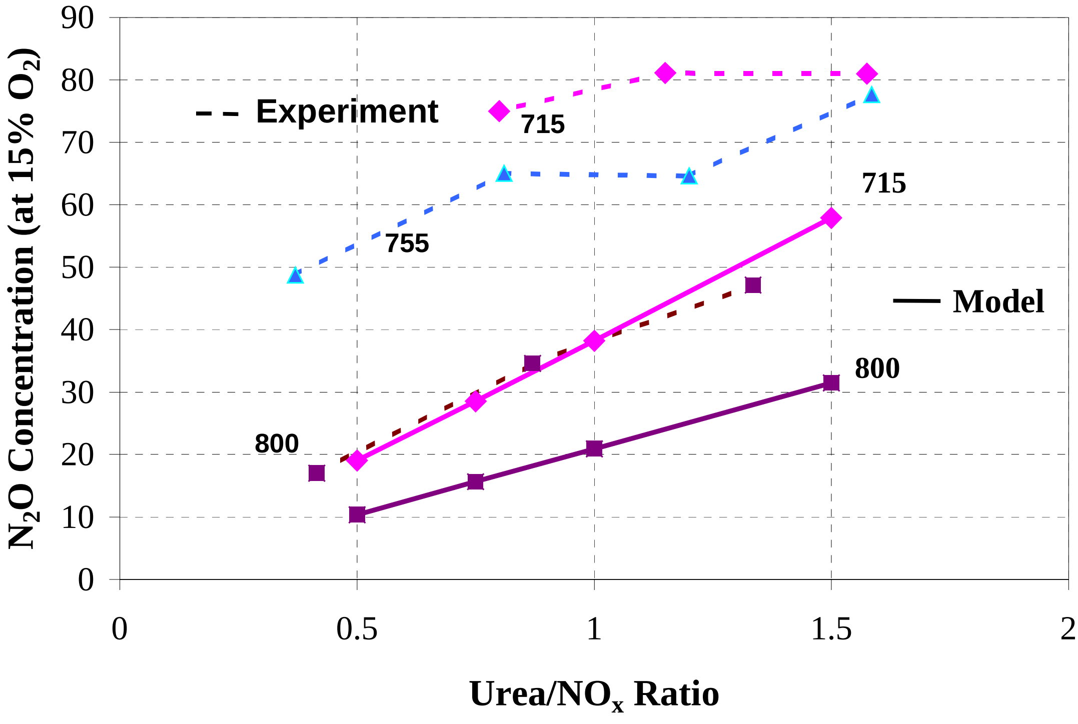

Figure 13: *N_2O Formation versus Urea Injection and Temperature. Lines connecting data are isotherms at the indicated temperature (in °C). Numerical initial conditions match the experiment.*

Summary and Conclusions

Experiment

A pilot scale operational test stand with an 800 kW thermal input gas turbine and an exhaust reaction chamber was built. At a steady state 100 % load of 90 kW, the turbine generated an average of 1.0 kg exhaust per second at a temperature of 600 to 640°C. The geometry inside the reaction chamber was optimized. The resulting reactor chamber produced approximately 30% recirculation at a pressure drop of 660 Pa. The recirculation provided a stable reaction zone where fuel injected into the exhaust stream, prior to entering the chamber, auto ignited. Autoignition and the associated heat release, allowed temperature control and load following, at intake temperatures as low as 440°C, corresponding to 50% steady state load. The reactor operating temperature was varied between 700 and 800°C.

The required auxiliary fuel injection, at 100% steady state turbine load, increased the overall fuel consumption by 16 to 30% depending on intake temperature and target operating temperature.

Once operating temperature was reached, unburned hydrocarbon and CO emissions, produced by the gas turbine, were significantly reduced from 70 to 4 ppm and 380 to 120 ppm, respectively.

The process reagent, primarily a water slurry of cyanuric acid, was added at the same location as the injected auxiliary fuel. Selective non catalytic reduction of NO_x from the exhaust gases, at operating temperatures as low as 700°C, was achieved in the recirculation zone of the reactor at 0.65 to 0.71 seconds residence time. Both processes, fuel oxidation with corresponding temperature rise and NO_x reduction, occurred simultaneously. A positive synergism between hydrocarbon oxidation and NO_x removal reactions with CYA was found lowering the typical operating temperature by as much as 200°C.

NO_x concentrations of 106 to 124 ppm in the turbine exhaust were reduced to as low as 18 ppm at 15% O_2. The NO_x reduction increased with decreasing reactor temperature and increasing CYA/NO_x ratio.

The level of nitrous oxide (N_2O) produced in the reduction process was found to increase with increasing CYA/NO_x ratio resulting in values ranging from 46 ppm at a CYA/NO_x ratio of 0.33 to 166 ppm at a CYA/NO_x ratio of 1.06. N_2O emissions higher than the initial NO_x concentrations were detected and found to increase with increasing CYA addition. The exacerbated formation of N_2O is attributed to incomplete decomposition of cyanuric acid when added in solid form.

Similar experiments with NH_3 as process reagent and combined fuel injection showed NO_x formation rather than destruction. Under the given exhaust gas composition and recirculating conditions, NH_3 was found to completely decompose. Neither NH_3 nor increased amounts of N_2O were detected in the effluents. NO_x concentration increase suggested, that approximately 1/3 of the injected NH_3 is converted to NO.

Urea exhibited hybrid behavior, combining the characteristics of NH_3 and CYA. At the highest operating temperature of 800°C, NO_x concentration increased with urea addition by as much as 10%. At temperatures of 755°C and 715°C, up to 23% NO_x reduction occurred with a trend, of increasing NO_x reduction with increasing urea/NO_x ratio. N_2O concentrations of 17 to 80 ppm were measured. The largest amount of N_2O was formed at the lowest experimental temperature.

Numerical Model

A numerical model has been constructed that simulates recirculation. The model combines a PSR and a PFR reactor in series. Part of the exiting PFR gases are recycled into the PSR. A steady state solution is reached by iteration.

A detailed chemical kinetic mechanism combines propane oxidation with nitrogen chemistry. The model assumes rapid sublimation of the CYA solid, followed by ideal decomposition of the cyclic CYA trimer to three molecules of HNCO. Mixing is ideal and instantaneous.

The agreement between model and experiment is good and the observed trends are captured. Disparities have been found predicting ignition delay and matching absolute values of NO and N_2O concentrations.

Final (outlet) NO_x concentrations were under predicted, observed NO_x removal differed from the numerical predictions by a maximum of 27%. At less than 100% turbine load, the experimental trend of decreasing NO_x removal with decreasing reactor inlet temperature was numerically reproduced. A 50% difference between the numerical and the observed value was found at 50% steady state turbine load.

The model failed to reproduce the experimental N_2O emissions. Absolute N_2O values were not matched. The predicted ratio of N_2O emitted to NO reduced, found in the experiment to be larger than one, varies between 0.3 and 0.5. N_2O formation in the model increases with HNCO/NO_x ratio to asymptotically reach a plateau of 50 ppm. The experimental values, in contrast, increased approximately linearly with CYA/NO_x ratio.

The discrepancies between the observed and the numerical N_2O concentrations are primarily attributed to the model assumption of “perfect” CYA decomposition to HNCO. A possible mechanism, that could reconcile the apparent disparity, is proposed. The proposal describes the pyrolysis of one CYA molecule into two molecules of HNCO and one molecule NO.

The model was successful in predicting the behavior of ammonia (NH_3) and urea ($(NH_2)_2CO$) and observed trends were captured. Absolute values of NO_x removal in the case of urea injection were well matched while N_2O emitted was under predicted by up to 60%.

The overall agreement between experimental findings and numerical simulation is good. All trends are properly featured in the model. Given that the model does not consider sublimation and decomposition of the injected reagents and ignores mixing as well as three-dimensional turbulent fluid dynamics, the agreement is remarkable.

The model therefore allows meaningful predictions of NO_x reduction potential with respect to temperature and reagent injection rate of cyanuric acid as well as that of the most common alternative reagents, urea and ammonia.

Acknowledgment

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