Eurasian Chemico-Technological Journal 16 (2014) 159-168

Non-Catalytic NO_x Removal from Gas Turbine Exhaust with Cyanuric Acid in a Recirculating Reactor; Small Scale Evaluation and Industrial Application

M. Streichsbier[1], R.W. Dibble[2*], and R.A. Perry[3]

[1]ESW Group, Montgomeryville, Pennsylvania 18936
[2]Department of Mechanical Engineering, University of California at Berkeley,
Berkeley, California 94720, USA
[3]Technor, Inc., Livermore, California 94550, USA

Abstract

A novel SNC technique to remove oxides of nitrogen (NO_x) from stationary gas turbine exhaust has been investigated and applied. The technique employs the use of cyanuric acid (CYA), a non-toxic, dry powder, combined with the injection of auxiliary turbine fuel and recirculation.

During the initial investigation, exhaust, generated by a 150 kW gas turbine, was 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 between 700 and 800 ºC. CYA slurry is injected. Temperature rise and NO_x reduction occur simultaneously. Load following has been achieved. 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. However, The process generates N_2O emissions, which vary from 45 to 163 ppm, increasing with increasing CYA/NO_x ratio. The ratio of N_2O formed to NO removed was found to be between 1 to 1.5 to 1.

The performance of CYA ($(HNCO)_3$) is compared to that of ammonia (NH_3) and urea ($(NH_2)_2CO$).

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

The process was then successfully scaled up and applied to a variety of industrial 3.7 MW gas turbines and similarly significant NO_x reduction has been achieved.

Introduction

In recent years concern about air pollution and its side effects have resulted in a variety of regulations and standards, 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.

This paper examines a selective non catalytic reduction (SNCR) technique. These SNCR methods rely on gas phase reactions to selectively reduce NO_x with a process reagent. They are typically applied in overall lean scenarios, i.e. in the presence of oxygen in the exhaust stream. 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

---

[*] Corresponding author. E-mail: dokdibble@gmail.com

varies with exhaust gas composition and the addition of hydrocarbons.

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 paper is to comparatively explore the applicability of a SNCR post combustion treatment process using CYA as process reagent and a recirculating reactor to the exhaust gases produced by a stationary gas turbine engine.

Process description

In this process exhaust gases are ducted into a recirculating reactor. The process reagent CYA ($HNCO_3$), a non toxic solid, is administered directly into the gas turbine exhaust as water based slurry. CYA sublimes at approximately 330 ºC 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 550 ºC and 650 ºC. To elevate the exhaust gas temperature to a range of 700-800 ºC, suggested as optimal by previous work with CYA on Diesel engines, additional fuel is injected. The point of injection is next to that of the process reagent. Sufficient residence time in the reactor allows the fuel to autoignite. 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 trigger the combustion of the mixture to so establish a stable reaction zone and enhance the concurrent NO$_x$ reduction chemistry. Simultaneous temperature rise and NO$_x$ reduction thereby minimize residence time and reactor size.

Since any applied backpressure constitutes an additional load on a gas turbine and therefore reduces its efficiency, recirculation was here achieved by manipulating the flow geometry while minimizing any corresponding restrictions.

Numerical Modeling

The model used in this study assumes all mixing processes to be ideal, 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 and simultaneous NO$_x$ reduction process a combination of the PSR and PFR with a back mixing option was developed. The so called PSRPFRX algorithm is schematized in Fig. 1.

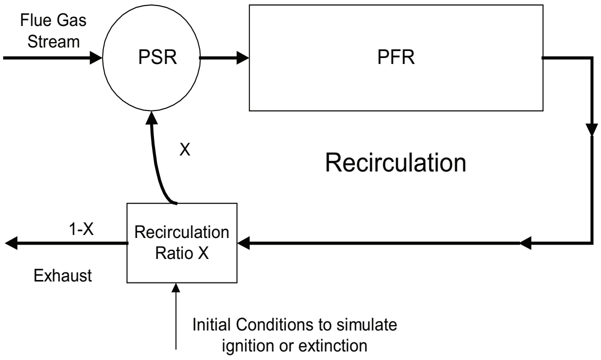

Fig. 1. Schematic of the PSRPFRX Algorithm. A part of the output from the combination of PSR and PFR is injected into the PSR alongside of the incoming stream.

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.

Small Scale Experimental Setup

A small scale 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 640 ºC 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 750 ºC. CYA slurry is injected with a rotating or an air assisted injector both designed particularly to accommodate a wide range of feed rates reliably.

Fuel is pressurized and injected through a nozzle. Additional NO can be added to the intake air stream. Control mechanisms are being employed to allow load following, reactor temperature 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. 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 Figs. 2 and 3.

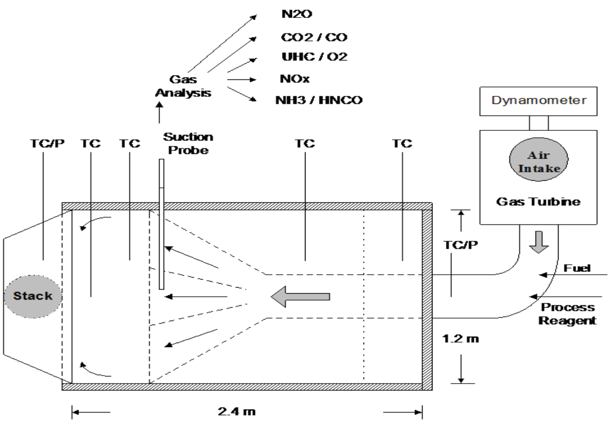

Fig. 2. Schematic of the Experimental Setup (top view).

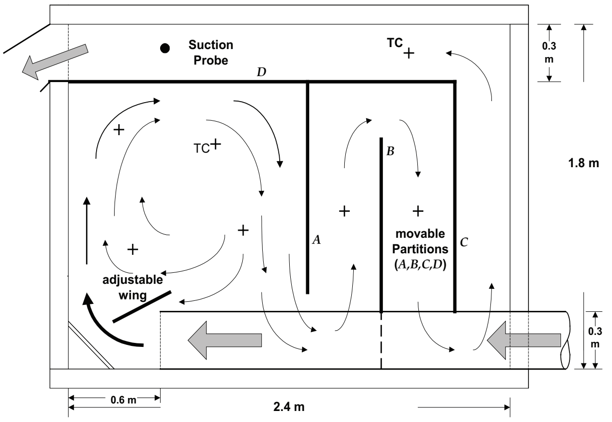

Fig. 3. Schematic of the Reaction Chamber (side view).

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 :

Engine load	90 kW
Intake temperature	18 – 32C
Exhaust temperature	600 – 630 °C
Fuel consumption	1.11 – 1.25 kg/min
Air flow rate	0.97 – 1.08 kg/sec
Pressure loss in reactor	660 Pa
Auxiliary fuel consumption	150 – 320 g/min
Residence time in recirculating zone	0.65 – 0.71 sec

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 800 ºC) was obtained at loads of 50% to 100% resulting in turbine exhaust temperatures of 440 ºC and 640 ºC respectively. These observations are in contrast to the predictions of the model for 30% recirculation. 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 410 ºC 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. One of the process concerns is the necessity of fuel addition. 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 predicted by the model. 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 Fig. 4, NO$_x$ concentrations versus temperature and reagent/NO$_x$ ratio are shown. Experimental and numerical curves for constant reagent addition, are similar in shape but shifted.

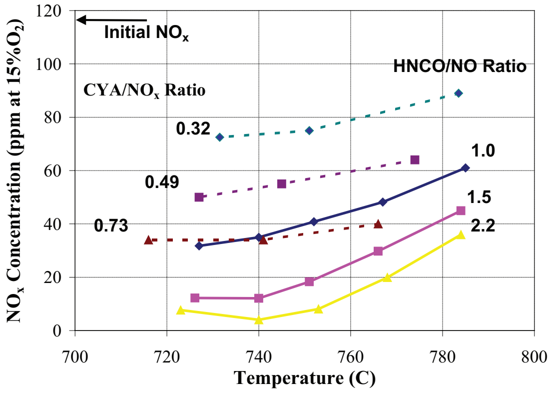

Fig. 4. Comparison of Experimental and Numerical NO$_x$ Reduction with CYA. The solid lines are numerical values while the broken lines represent experimental results. Experimental and numerical reagent/NO$_x$ ratios are indicated on the left and right respectively.

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 5 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.

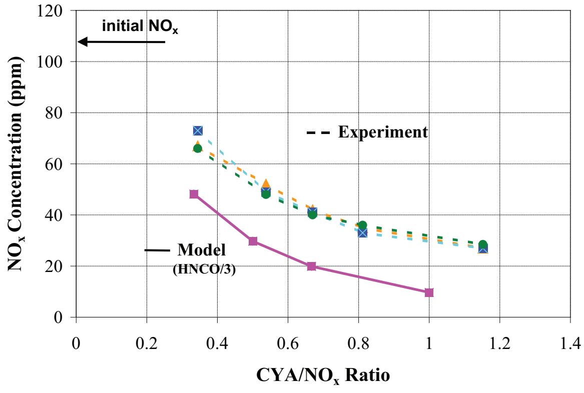

Fig. 5. NO$_x$ Removal at Fixed Temperature versus CYA/NO$_x$ Ratio. Experiments were performed at an average temperature of 750 °C at 100% turbine load.

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 Fig. 6. 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.

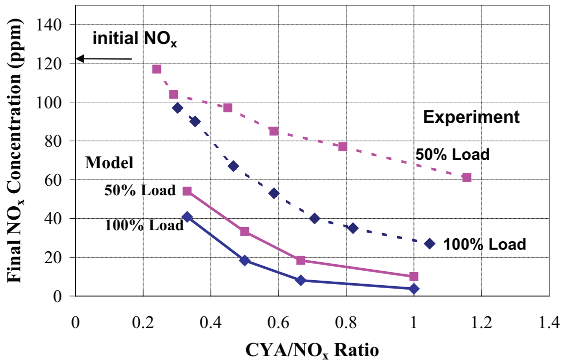

Fig. 6. NO_x Concentration versus Turbine Load; Numerical and Experimental Values. Final reactor temperature remained fixed at 760 °C (+/- 10 °C), while the intake temperature varied with turbine load. A load of 50 and 100% corresponds to 440 °C and 610 °C respectively.

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 Fig. 7, measured N_2O concentrations with respect to CYA/NO_x ratio are shown. All plotted values are adjusted to 15% O_2.

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 Fig. 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.

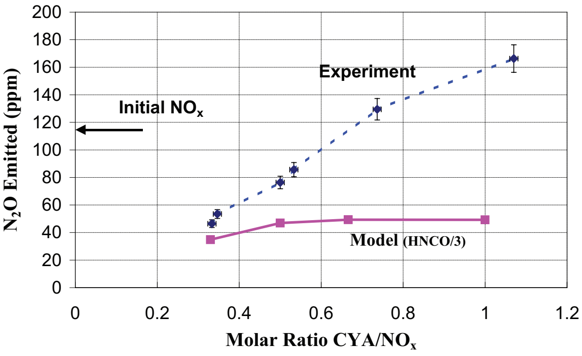

Fig. 7. Experimental and Numerical N_2O Emissions versus CYA to NO_x Ratio. The reagent to NO ratio of the model is adjusted corresponding to CYA = 3 HNCO. Initial conditions such as temperature and exhaust gas composition, are similar.

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. Figure 8 provides further evidence for the existence of a mechanism not considered by the model. Measured concentrations of "N_2O formed" versus "NO_x reduced" are compared to the values determined by the numerical model.

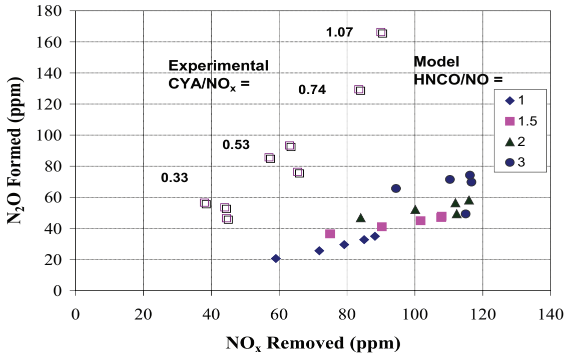

Fig. 8. Experimental and Numerical N_2O Formed versus NO_x Removed.

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].

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

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

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

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~ 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. NH_3 slip was not detected. The observed NO_x concentration increases are plotted in Fig. 9. 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 increased the NO_x concentration by 50 ppm. 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. 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 numerically obtained results, also shown in Fig. 9, replicate this behavior. In the PSRPFRX model, NH_3 is entirely consumed and partially oxidized to NO, increasing the NO_x concentration.

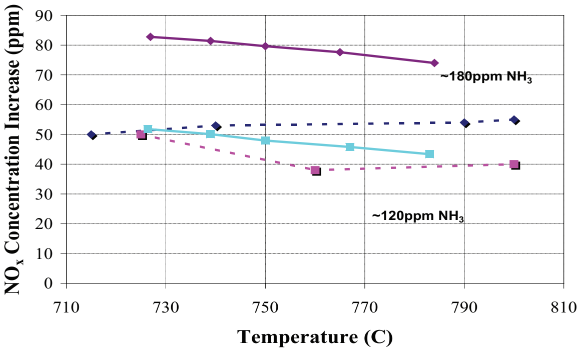

Fig. 9. Experimental and Numerical NO_x Increase due to Injection of NH_3. Solid lines represent numerical results while broken lines connect experimental values. The experimental conditions varied in initial NO_x concentration between 40 and 120 ppm NO_x; the absolute increase was found to be solely a function of NH_3 injection rate.

At an addition of 120 ppm of NH_3, i.e. an NH_3/NO_x ratio of 1, modeled and observed NO_x concentrations are, with a maximum discrepancy of 15%, in very good agreement. At 180 ppm NH_3 addition, or an NH_3/NO_x ratio of 1.5, NO_x reached a maximum of 55 ppm in the experiment 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. It also shows how the interaction with hydrocarbon decomposition can significantly change the performance characteristics of NH_3 as an NO_x reduction agent.

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 urea, $(NH_2)_2CO$, once heated, decomposes into two molecules 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 Fig. 10. 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 the lower test temperatures. Both tendencies become more pronounced with increasing urea/NO_x ratio.

At a reactor temperature of 800 °C and a urea/NO_x ratio of 1.34, 133 ppm NO_x were measured. The smallest NO_x increase with a final NO_x concentration of 124 ppm was recorded 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 percentage increased with urea/NO_x ratio. A final NO_x concentration of 97 ppm at a urea/NO_x ratio of 1.59 was reached, resulting in a 19.2% NO_x reduction.

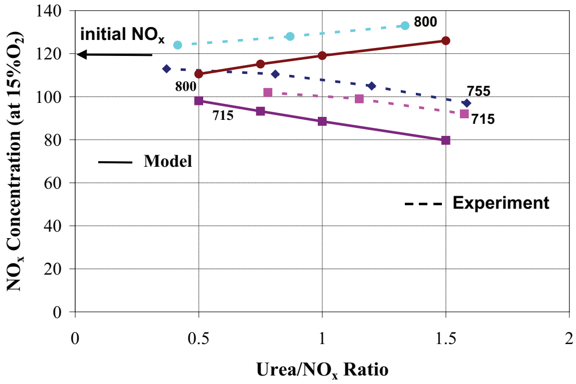

Fig. 10. NO_x Concentration with Urea Injection versus Reagent Injection Ratio and Temperature. The lines connecting individual data are isotherms at the indicated temperature (in °C).

The numerical model assumes ‘perfect’ decomposition of $(NH_2)_2CO$ into NH_3 and HNCO and reproduced the experimental behavior of urea very well. In addition, treating urea as a mix of HNCO and NH_3 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) NO formed by NH_3 and (2) 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. 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, the decrease in NO_x concentration at 715 °C and the dependence on urea/NO_x ratio are well captured.

In Figure 11, 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 concentrations are observed to increase with decreasing temperature and increasing urea/NO_x ratio in the investigated temperature range. Here the agreement between model and experiment is not quite as good. The N_2O formation is under predicted by as much as 57%. The qualitative agreement is better at the higher temperature of 800 °C. 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.

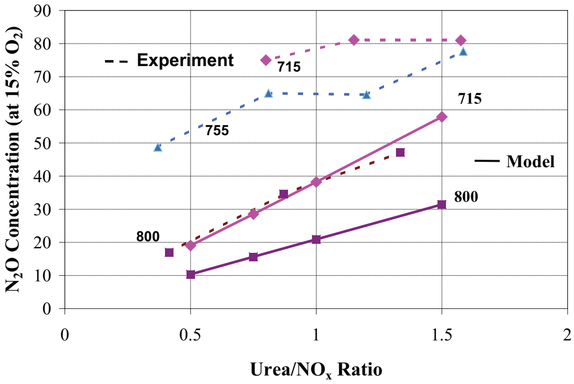

Fig. 11. N_2O Formation versus Urea Injection and Temperature. Lines connecting data are isotherms at the indicated temperature (in °C). Numerical initial conditions match the experiment.

Application of the Process to Industrial Size Gas Turbines

The process was applied at the National Airmotive / Rolls Royce Gas Turbine Testing Facility in Oakland, CA. The Testing Facility tests a variety of Allison 501 K and T56A style engines. A scaled up reactor similar in design to the described experimental reactor was installed. The inside reactor dimension were: length 4.5 m, height 4 m and width 3 m, to allow for residence times of 1.1 to 1.38 sec of a typical exhaust flow of 14 to 15 kg per second. The reactor replaced the standard turbine exhaust system and was connected to the turbine with a duct 1 m in diameter and a length of 10 m. During a typical test cycle turbines were loaded in incremental steps to reach maximum output of approximately 2.9 MW (~ 3900 hp).

Table 1 shows some of the experimental turbine operating conditions and exhaust gas composition at high applied loads. The listed turbine exit temperature is the temperature of the exhaust gases leaving the turbine.

Table 1

Experimental Turbine Operating Conditions. Note that a value of $\lambda > 1$ corresponds to fuel lean conditions. (* liquid fuel equivalent, since engine was run with propane)

m_{fuel}		λ	m_{air}	Temperature	Load	Efficiency	Exhaust Gas Composition (dry)			
kg/min	kW		(kg/s)	turbine exit (C)	kW	%	CO_2 (%)	O_2 (%)	NO (ppm)	CO (ppm)
15.32	11670	2.86	13.900	490.0	2596	22.2	3.78	15.05	83.0	63
15.59	11874	3.02	14.900	526.0	2700	22.7	4.02	15.45	95.2	80
16.40*	12490	3.74	15.040	522.0	2898	23.2	3.56	14.9	93.4	195

Exhaust gas temperatures were found to reach a peak maximum of 560 °C. The average recirculation reactor temperature was controlled at a range of 700 to 800 °C, with a mean residence time inside the recirculation zone of 1.1 to 1.38 sec.

Since turbine exhaust has a maximum temperature of 560 °C at full turbine load, the exhaust gas temperature had to be increased by at least 140 °C. In this experimental setup this was done with a duct burner and by injection of turbine fuel. The duct burner fulfilled two purposes: 1) it raised the exhaust temperature to an average of approximately 620 °C and 2) it facilitated load following, since it provided a constant average exhaust temperature. The backpressure of exhaust duct, duct burner and reactor combined reached a maximum of 1800 Pa (~7 inches of H_2O) at maximum reactor temperature.

At full load and maximum auxiliary fuel injection, steady state conditions were reached within minutes. With the decay of thermal transients, duct burner set point was decreased while the auxiliary fuel flow was held constant, thereby controlling the reactor temperature. The fuel consumed by the duct burner was not monitored. The duct burner fuel input at a turbine exhaust temperature of 525 °C was calculated to be initially 14% of the turbine fuel consumption. At steady state operation and a final reactor temperature of 740 °C a combined 32% fuel consumption increase was assumed.

The reactor geometry allowed for 30 to 40% recirculation, a value determined with a water model.

Results

At steady state operation, CO emissions were reduced in the reactor from initial concentrations in the turbine exhaust. The level of CO reduction increased with increasing reactor temperature. At temperatures below 700 °C an increase in CO due to incomplete auxiliary fuel combustion was observed.

NO$_x$ reduction in magnitude similar to the small scale experiments were observed. The process was therefore successfully scaled up.

In contrast to the earlier described experiments, NO$_x$ reduction efficiency was found to be strongly dependent on the location of fuel and CYA injection in the duct. CYA injection close to the reactor, can result in incomplete decomposition to HNCO and injection at a location further upstream can increase residence time of CYA in the hot exhaust gases, improve mixing and result in a more efficient process. If the injection occurs to close to the burner, with burner flame lengths of approximately 1 m, CYA is partially oxidized and results in a NO increase.

These results indicate the importance of the performance of the duct burner. Careful control of the average duct temperature in combination with a homogeneous temperature profile allows further optimization of the positive synergism between fuel and CYA injection.

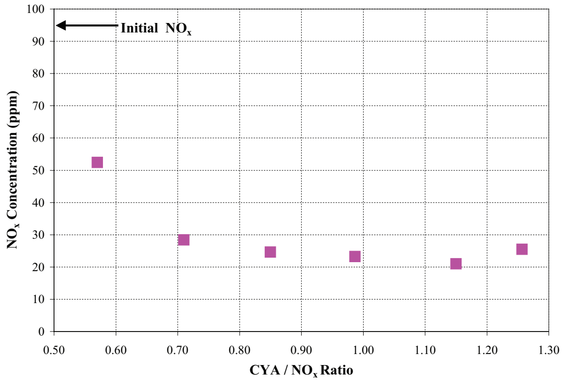

Fig. 12. Ratio of Initial and Final NO$_x$ Concentrations versus CYA/NO$_x$ ratio. All NO$_x$ measurements are adjusted to 15% O_2 content. CYA and auxiliary fuel injection location differed from previous tests.

Given the used duct burner, the optimal injection location for CYA was determined to be 5 m downstream of the flame front. At this location the exhaust flow was sufficiently mixed to eliminate high temperature zones. Fuel was injected at the entrance of the reactor.

Figure 12 shows the measured NO_x reduction results. In the figure dry NO_x concentrations are adjusted to 15% O_2. These NO_x concentrations were obtained for four molar CYA/NO_x ratios and an average temperature of 750 °C in the recirculating section of the reactor.

A maximum reduction from the initial NO_x concentration of 96 ppm to a final NO_x concentration of 20.8 ppm was observed. The reduction process improved with increased CYA/NO_x ratio to find the maximum at a value of 1.15. NO_x removal increases with increasing CYA injection.

Summary and Conclusions

Small Scale Experiment

A pilot scale operational test stand with a 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 reactor chamber geometry produced approximately 30% recirculation at a pressure drop of 660 Pa. The recirculation provided a stable reaction zone. Autoignition of auxiliary injected engine fuel and the associated heat release, allowed temperature control and load following. 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, cyanuric acid, was added simultaneously with 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. 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. A detailed chemical kinetic mechanism combines propane oxidation with nitrogen chemistry. 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.

These discrepancies 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 describing the behavior of ammonia (NH_3) and urea ($(NH_2)_2CO$) and observed trends were captured.

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.

*Industrial Application of the CYA Proces*s

The evaluated process was successfully scaled up to industrial size gas turbine engines of up to 3.7 MW. In addition to auxiliary fuel injection a duct burner was used to elevate the exhaust gas temperature. NO_x reductions from an initial concentration of 96 ppm to a minimum of 20.8 ppm were observed. NO_x reduction efficiency was found to depend strongly on the CYA injection location and the homogeneity of the temperature profile produced by the utilized duct burner.

Acknowledgment

This research has been supported by the Minerals Management Service, Department of Interior contract number 14-35-0001-30765.

References

[1]. J.H. Seinfeld and S.N. Pandis, "Atmospheric Chemistry and Physics; From Air Pollution to Climate Change" Wiley - Interscience, ISBN 0-471-17815-2, 1998.

[2]. H.S. Rosenberg et al. "Post Combustion Methods for Control of NO_x Emissions" Prog. Energy Combustion Sci. 6 (1980) 287–302.

[3]. R.K. Lyon, "Method of the Reduction of the Concetration of NO in Combustion Effluents Using Ammonia", U.S. Patent 3,900,554, 1975.

[4]. J.K. Arand, L.J. Muzio, and J.G Sotter, "Urea Reduction of NO_x in Combustion Effluents", U.S. Patent No. 4,208,386, 1982.

[5]. R.A. Perry and D.L. Siebers, Nature, 324 (1984) 657–658.

[6]. D.L. Siebers and J.A. Caton, Combust. Flame 79 (1990) 31-46.

[7]. L.J. Muzio and J.C. Kramlich, "Potential Errors in Grab Sample Measurements of N_2O from Combustion Sources" Western States Section, The Combustion Institute, Fall 1988.

[8]. R.A. Perry, "Application of $RAPRENO_x$ to Diesel Emission Control" Technology Assessment and Research program for Offshore Minerals Operations, U.S. Department of the Interior Minerals Management Service, DOI No. 85K-SC293V, pp 185-190, 1991.

[9]. C.K. Westbrook and W.J. Pitz "A Comprehensive Chemical Kinetic Reaction Mechanism for Oxidation and Pyrolysis of Propane and Propene" Combustion, Science and Technology, Vol. 37, 1984.

[10]. J.A. Miller and R.A. Perry, Int. J. Chem. Kinet. 28 (1996) 217–234.

[11]. L.J. Muzio, T.A. Montgomery, G.S. Samuelsen, J.C. Kramlich, R.K. Lyon, and A. Kokkinos, " Formation and Measurement of N_2O in Combustion Systems" 23rd Symp. (Int.) Combust., The Combustion Institute, pp. 245-250, 1990.

[12]. A.R. Mosier, and L. Mack, Soil Sci. Soc. Am. J., 44 (1980) 1121–1123

[13]. M. Elsener, and M. Koebel, "Analyse von Isocyansaeure, Blausaeure, Ammoniak und Lachgas in den Abgasen von Entstickungsprozessen", [Analysis of HNCO, HCN, NH_3 and N_2O in Effluents from NO_x Reduction Processes], Paul Scherrer Institut (Verbrennungstechnik), Reg. No. TM-51-89-21, Jul. 1989.

[14]. R.A. Perry, "Application of $RAPRENO_x$ to NO_x Control in Diesel Generators", First Int. on Combustion Technologies for a Clean Environment, Lisbon, Portugal, 1991.

[15]. M. Streichsbier, R.W. Dibble, and R.A. Perry, "Non-Catalytic NO_x Removal from Gas Turbine Exhaust with CYA in a Recirculating Reactor", AIChE, Proceedings of the 1997 Annual Meeting, Paper No. 256a, 1997.

Received 12 March 2014