Non-Catalytic NO\textsubscript{x} Removal from Gas Turbine Exhaust with Cyanuric Acid in a Recirculating Reactor; Small Scale Evaluation and Industrial Application

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Abstract

A novel SNC technique to remove oxides of nitrogen (NO\textsubscript{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 °C. CYA slurry is injected. Temperature rise and NO\textsubscript{x} reduction occur simultaneously. Load following has been achieved. At all temperatures, significant NO\textsubscript{x} reduction from initial concentrations of 106 to 124 ppm to as low as 18 ppm at 15% O\textsubscript{2} have been observed. However, the process generates N\textsubscript{2}O emissions, which vary from 45 to 163 ppm, increasing with increasing CYA/NO\textsubscript{x} ratio. The ratio of N\textsubscript{2}O formed to NO removed was found to be between 1 to 1.5 to 1.

The performance of CYA ((HNCO)\textsubscript{3}) is compared to that of ammonia (NH\textsubscript{3}) and urea ((NH\textsubscript{2})\textsubscript{2}CO). 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\textsubscript{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\textsubscript{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\textsubscript{x}, the oxides of nitrogen. NO\textsubscript{y} 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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{x} is produced by oxidation of the process reagent. Their efficiency
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 N₂O formation [7] exist. N₂O 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 (HNCO₃), 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:

\[
\text{HNCO + OH} \rightarrow \text{NCO + H₂O} \\
\text{NCO + NO} \rightarrow \text{N₂ + CO₂} \\
\text{NCO + NO} \rightarrow \text{N₂O + CO}
\]

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 NOₓ reduction chemistry. Simultaneous temperature rise and NOₓ 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/NOₓ as HNCO/NO 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 NOₓ 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.](image)

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% O₂. 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 °C. 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 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 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).](image)

![Fig. 3. Schematic of the Reaction Chamber (side view).](image)

Gas analysis is performed with UHC (flame ionization), an O₂ (magneto pneumatic), a set of infrared CO and CO₂ as well as chemiluminescent NOx 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 N₂O is carried out using samples drawn through a NaOH solution to scrub out any SO₂ and a gas chromatograph with an electron capture detector [11, 12].

There are various techniques available to perform an NH₃ or HNCO analysis. Here a wet chemical approach is chosen using an NH₃ 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 N₂O 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 – 32°C
- 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 °C) was obtained at loads of 50% to 100% resulting in turbine exhaust temperatures of 440 °C and 640 °C 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 °C 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.

**NOx Removal with CYA**

When comparing experimental and numerical NOx reduction with cyanuric acid, the assumption that the thermal decomposition of CYA yields three molecules of isocyanic acid, HNCO, is used. An experimental CYA/NOx ratio of unity, for example, is compared to a numerical HNCO/NO ratio of 3. In Fig. 4, NOx concentrations versus temperature and reagent/NOx ratio are shown. Experimental and numerical curves for constant reagent addition, are similar in shape but shifted.

![Fig. 4. Comparison of Experimental and Numerical NOx Reduction with CYA. The solid lines are numerical values while the broken lines represent experimental results. Experimental and numerical reagent/NOx ratios are indicated on the left and right respectively.](image)

The NOx removal process improves with decreasing temperature and increasing CYA/NOx ratio. In the experiment a minimum of 34 ppm NOx was observed. This minimum NOx concentration corresponds to 71% reduction. Lowest efficiency was observed at a ratio of CYA/NOx = 0.95 resulting in a NOx concentration of 80 ppm, which equals 32% reduction. In all cases the initial NOx concentration was 117 ppm +/- 2 ppm, and all concentrations are adjusted to 15% O2.

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

Figure 5 shows final NOx concentration versus CYA/NOx ratio at a fixed average temperature of 736 to 750 °C. In the experiment NOx concentrations decreased with increasing CYA/NOx ratio to a minimum of 18 ppm at a CYA/NOx 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 NOx concentrations are approximately 10 to 20 ppm lower, corresponding to an over prediction in NOx removal of 8 to 21%, experimentally observed trends are replicated well by the model. The rate of numerical NOx concentration decrease, with respect to CYA/NOx, ratio properly matches the experimental observations.

![Fig. 5. NOx Reduction at Fixed Temperature versus CYA/NOx Ratio. Experiments were performed at an average temperature of 750 °C at 100% turbine load.](image)

Investigation of the effect of reactor inlet (= turbine exit) temperature on the NOx reduction chemistry is central to the issue of turbine load following. The final NOx concentrations, obtained by experimental and numerical variation of reactor inlet tem-
temperatures, are contrasted in Fig. 6. The lowest experimental NO\textsubscript{x} emission of 26 ppm was found at maximum load and the highest CYA/NO\textsubscript{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.

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\textsubscript{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\textsubscript{x} reduction with a CYA/NO\textsubscript{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\textsubscript{x} concentration values. A difference of as much as 47% at the lowest CYA/NO\textsubscript{x} ratio and 20% at the highest CYA/NO\textsubscript{x} ratio, at 100% load, is seen.

**N\textsubscript{2}O 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\textsubscript{3} slip is negligible in these experiments. In Fig. 7, measured N\textsubscript{2}O concentrations with respect to CYA/NO\textsubscript{x} ratio are shown. All plotted values are adjusted to 15% O\textsubscript{2}.

A clear increase with increasing CYA/NO\textsubscript{x} ratio can be seen. At a molar ratio of CYA/NO\textsubscript{x} = 0.33, 46.5 ppm of N\textsubscript{2}O are found while at a CYA/NO\textsubscript{x} ratio of 1.08 as much as 166 ppm are observed. When the experimentally obtained N\textsubscript{2}O concentrations are compared to the modeled N\textsubscript{2}O concentrations, agreement between model and experiment is not as good. As shown in Fig. 9, N\textsubscript{2}O 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\textsubscript{2}O emissions with increasing CYA/NO\textsubscript{x} ratio. Numerical N\textsubscript{2}O emissions appear to plateau at approximately 50 ppm independent of CYA/NO\textsubscript{x} ratio, while the experimental values increase with reagent ratio. The maximum N\textsubscript{2}O concentration measured exceeds the initial NO\textsubscript{x} concentration in the turbine exhaust. Since N\textsubscript{2}O formation is primarily a byproduct of the NO reduction along the NCO + NO pathway, detected N\textsubscript{2}O 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\textsubscript{2}O formed” versus “NO\textsubscript{x} reduced” are compared to the values determined by the numerical model.
Experimental \( \text{N}_2\text{O} \) emissions follow an approximate 1.5 to 1.0 ratio of “\( \text{N}_2\text{O} \) formed” to “\( \text{NO} \) removed”. In contrast, modeling results are clustered about a slope of 0.3 to 0.5. The needed CYA/\( \text{NO}_x \) ratios, i.e. 3\( \text{HNCO} / \text{NO}_x \) ratios, (of ~1), to achieve maximum reduction are significantly higher than the observed CYA/\( \text{NO}_x \) 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].

\[
\begin{align*}
(\text{HNCO})_3 + \text{OH} &\rightarrow (\text{HNCO})_2 \text{NCO} + \text{H}_2\text{O} \quad (1) \\
(\text{HNCO})_2 \text{NCO} + \text{O}_2 &\rightarrow (\text{HNCO})_2 \text{NCO} (\text{O}_2) \quad \text{(Adduct)} \quad (2) \\
(\text{HNCO})_2 \text{NCO} (\text{O}_2) \quad \text{(Adduct)} &\rightarrow 2 \text{HNCO} + \text{NO} + \text{CO}_2 \\
(3)
\end{align*}
\]

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/\( \text{NO}_x \)~ ratio (of ~1) to reduce NO and the high production of \( \text{N}_2\text{O} \) 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 \( \text{NH}_3 \) in the recirculating reactor led to a significant increase in \( \text{NO}_x \) concentrations. \( \text{NH}_3 \) slip was not detected. The observed \( \text{NO}_x \) concentration increases are plotted in Fig. 9. \( \text{NH}_3 \) addition to a turbine exhaust gas stream containing 118 ppm \( \text{NO}_x \) at 15% \( \text{O}_2 \) at \( \text{NH}_3/\text{NO}_x \) ratio of 1.5 increased the \( \text{NO}_x \) concentration by 50 ppm. To further investigate the apparent thermal oxidation in the recirculation zone, \( \text{NH}_3 \) was added to the exhaust stream at a temperature range of 620 to 800 °C. The formation of NO by \( \text{NH}_3 \) in the recirculating reactor appears to be weakly related to chamber temperature and to the amount of \( \text{NH}_3 \) added. Approximately 30% of the added \( \text{NH}_3 \) decomposed to form NO. Under conditions of no auxiliary fuel consumption, a similar increase of NO 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 \( \text{NH}_3 \) 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 PSRPFPRX model, \( \text{NH}_3 \) is entirely consumed and partially oxidized to NO, increasing the NO\(_x\) concentration.

![Fig. 9. Experimental and Numerical \( \text{NO}_x \) Increase due to Injection of \( \text{NH}_3 \).](image)

At an addition of 120 ppm of \( \text{NH}_3 \), i.e. an \( \text{NH}_3/\text{NO}_x \) ratio of 1, modeled and observed \( \text{NO}_x \) concentrations are, with a maximum discrepancy of 15%, in very good agreement. At 180 ppm \( \text{NH}_3 \) addition, or an \( \text{NH}_3/\text{NO}_x \) ratio of 1.5, \( \text{NO}_x \) reached a maximum of 55 ppm in the experiment while the model predicts an 80 ppm increase. Predicted \( \text{N}_2\text{O} \) 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 \( \text{NH}_3 \) in a recirculating reactor. It also shows how the interaction with hydrocarbon decomposition can significantly change the performance characteristics of \( \text{NH}_3 \) as an \( \text{NO}_x \) 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/\( \text{NO}_x \) ratio.

Since it is assumed, that urea, \( (\text{NH}_3)_2\text{CO} \), once heated, decomposes into two molecules the effective ratio of reagent to \( \text{NO}_x \), here \( [\text{NH}_3 + \text{HNCO}] / [\text{NO}_x] \), is simply double the given urea/\( \text{NO}_x \) amount. The initial \( \text{NO}_x \) concentration was held at 120 ppm (at 15% \( \text{O}_2 \)). Final \( \text{NO}_x \) emissions are plotted in Fig. 10. Urea addition was found to increase the
NO\textsubscript{x} concentration at the highest test temperature of 800 °C and decrease the total amount of NO\textsubscript{x} at the lower test temperatures. Both tendencies become more pronounced with increasing urea/NO\textsubscript{x} ratio.

At a reactor temperature of 800 °C and a urea/NO\textsubscript{x} ratio of 1.34, 133 ppm NO\textsubscript{x} were measured. The smallest NO\textsubscript{x} increase with a final NO\textsubscript{x} concentration of 124 ppm was recorded at urea/NO\textsubscript{x} = 0.415. At the intermediate temperature of 755 °C a moderate, 8 to 19%, NO\textsubscript{x} reduction was observed. The reduction percentage increased with urea/NO\textsubscript{x} ratio. A final NO\textsubscript{x} concentration of 97 ppm at a urea/NO\textsubscript{x} ratio of 1.59 was reached, resulting in a 19.2% NO\textsubscript{x} reduction.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig10}
\caption{NO\textsubscript{x} Concentration with Urea Injection versus Reagent Injection Ratio and Temperature. The lines connecting individual data are isotherms at the indicated temperature (in °C).}
\end{figure}

The numerical model assumes ‘perfect’ decomposition of (NH\textsubscript{2})\textsubscript{2}CO into NH\textsubscript{3} and HNCO and reproduced the experimental behavior of urea very well. In addition, treating urea as a mix of HNCO and NH\textsubscript{3} explains the experimental observations. Urea appears to combine the characteristics of both decomposition products when used in the described environment. Moderate NO\textsubscript{x} removal can be attributed to (1) NO formed by NH\textsubscript{3} and (2) simultaneous removal of NO\textsubscript{x} by HNCO. The agreement between model and experiment with respect to the absolute values of NO\textsubscript{x} concentration is good. NO\textsubscript{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\textsubscript{x} concentration above 800 °C, the decrease in NO\textsubscript{x} concentration at 715 °C and the dependence on urea/NO\textsubscript{x} ratio are well captured.

In Figure 11, experimental and numerical N\textsubscript{2}O concentrations are compared. In the experiment N\textsubscript{2}O emissions varied from 17 to 82 ppm, depending on reactor temperature and urea/NO\textsubscript{x} ratio. N\textsubscript{2}O concentrations are observed to increase with decreasing temperature and increasing urea/NO\textsubscript{x} ratio in the investigated temperature range. Here the agreement between model and experiment is not quite as good. The N\textsubscript{2}O 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\textsubscript{2}O emissions with increasing urea/NO\textsubscript{x} ratio.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig11}
\caption{N\textsubscript{2}O Formation versus Urea Injection and Temperature. Lines connecting data are isotherms at the indicated temperature (in °C). Numerical initial conditions match the experiment.}
\end{figure}

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.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Condition & Temperature (°C) & NO\textsubscript{x} Concentration (ppm) \\
\hline
High Load & 800 & 133 \\
Medium Load & 755 & 124 \\
Low Load & 715 & 97 \\
\hline
\end{tabular}
\caption{Experimental Turbine Operating Conditions and Exhaust Gas Composition.}
\end{table}
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)

| $m_{\text{fuel}}$ (kg/min) | $\lambda$ | $m_{\text{air}}$ (kg/s) | Temperature (turbine exit) (°C) | Load (kW) | Efficiency (%) | Exhaust Gas Composition (dry) |
|----------------------------|-----------|-------------------------|--------------------------------|-----------|----------------|-------------------------------|
| 15.32                      | 2.86      | 13.900                  | 490.0                          | 2596      | 22.2           | CO$_2$ (%) 3.78  O$_2$ (%) 15.05  NO (ppm) 83.0  CO (ppm) 63 |
| 15.59                      | 3.02      | 14.900                  | 526.0                          | 2700      | 22.7           | CO$_2$ (%) 4.02  O$_2$ (%) 15.45  NO (ppm) 95.2  CO (ppm) 80 |
| 16.40*                     | 3.74      | 15.040                  | 522.0                          | 2898      | 23.2           | CO$_2$ (%) 3.56  O$_2$ (%) 14.9  NO (ppm) 93.4  CO (ppm) 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$_2$O) 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.

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.

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.
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$_2$O) 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$_2$O emissions higher than the initial NO$_x$ concentrations were detected and found to increase with increasing CYA addition. The exacerbated formation of N$_2$O 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$_2$O 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$_2$O concentrations of 17 to 80 ppm were measured. The largest amount of N$_2$O 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$_2$O 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$_2$)$_2$CO) 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 Process**

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\textsubscript{x} reductions from an initial concentration of 96 ppm to a minimum of 20.8 ppm were observed. NO\textsubscript{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.

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