Experimental and Numerical Evaluation of Nitrous Oxide in Lean Combustion of Alternative Fuels

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NOx which mainly refers to nitrogen dioxide (NO2) and nitric oxide (NO) is considered as a major pollutant due to adverse effects on respiratory systems. Many studies on formation of NOx in both mobile sources and stationary applications have been carried out. Nitrous oxide (N2O), which is considered as a relatively new pathway of NOx formation, is a strong absorber of infrared radiation in troposphere, thus is itself a greenhouse gas. There are few studies where the emission level of N2O is studied for coal fueled burners, and gas fueled burner in high temperatures. The present work is focused on very low temperature lean combustion conditions. N2O in the exhaust might be a concern in these cases because N2O formation reaction rates are at their maximum at temperatures around 1250K. In this work, N2O in the exhaust of a model gas turbine combustor is measured experimentally for (1) firing temperatures as low as 1200K, (2) different natural gas and hydrogen blends, (3) different levels of air preheat, and (4) different residence times. The experimental work is supported by chemical kinetics simulations using a chemical reaction network (CRN) to provide details regarding the emission formation rates. Reacting computational fluid dynamics are also applied to develop the CRN accurately. The results confirm that a simple CRN can provide reasonable predictions of CO, NOx, and N2O. Also, it was shown that the N2O levels are always negligible for natural gas and hydrogen blends even in very low temperatures near the extinction limits.

1 Introduction

NOx or nitrogen oxides mainly refer to nitrogen dioxide (NO2), nitric oxide (NO), nitrous acid, and nitric acid. Though, from air pollutions point of view, NOx mostly refers to sum of NO2 and NO which contribute to formation of ground level ozone, and small particles which both have adverse effects on respiratory systems [1]. US EPA has regulations for NOx emissions from both vehicles and stationary power plants. In addition to the federal regulations, many states have more restrictive regulations for NOx emissions in electricity production in gas turbines. Currently, the most common NOx control technology in gas turbines is lean premixed combustion [2,3]. NOx formation in lean premixed systems has been studied extensively in recent years. For instance, four NOx formation pathways have been identified as: 1) Zeldovich 2) nitrous oxide 3) Fenimore prompt, and NNH [4, 5]. It is known that each pathway has specific contribution to total NOx in different combustion conditions, such as temperature, pressure, residence time, and fuel composition. It is fairly convenient to determine each pathway contribution to total NOx through chemical kinetic simulations.

It is noted that nitrous oxide, which is corresponded to one of the NOx formation pathways, is actually a very strong greenhouse gas by itself. N2O is a strong absorber of infrared radiation in troposphere, and thus, is noted as a contributor to the greenhouse effect [6]. Although the concentration of N2O is about 1000 time less than CO2, it is estimated that doubling its concentration will result in a 0.3 °C increase in climate temperature [7]. Although N2O is clearly an important contributor to global warming, relatively little work has been done to study its emissions. It could be because of the fact that it was shown that N2O levels in traditional combustion systems with high firing temperatures is negligible [6]. However, for low temperature systems, where evidence indicates a stronger potential for N2O emissions, little work has been done. Of interest are high hydrogen content fuels which would allow sustained reactions at very low temperatures.

It is known that two major pathways to formation of N2O consist of HCN and NHx pathways. For HCN, N2O could form through following reactions [8, 9]:

\[ \text{HCN} + \text{OH} \rightarrow \text{HNCO} + \text{H} \]
HNCO + H → NH₂ + CO
HNCO + OH → NCO + H₂O
HCN + O → NCO + H
NCO + NO → NO + CO + H

HCN, or hydrogen cyanide, is the primary nitrogen containing intermediate formed during the combustion of fuel nitrogen [10]. Kinetic modeling suggests that if HCN appears in the gas phase between 1150K and 1500K, it will be partially converted to N₂O. The peak conversion of HCN to N₂O mechanisms occurs at temperature of about 1250K [8]. Below 1250K, N₂O concentrations are controlled by the formation of NCO and the conversion of NCO to N₂O, and above 1250K, removal of N₂O through reactions with H and OH control the level of N₂O. It is also noted that if HCN appears in a fuel lean post flame zone, it can result in a large N₂O emission level. In hydrogen flames, the absence of carbon excludes the HCN mechanism, allowing the NH₄ pathway to dominate [11].

On the NH₄ side, the reactions are:

\[
\begin{align*}
\text{NH}_3 + \text{OH} & \rightarrow \text{NH}_2 + \text{H}_2\text{O} \\
\text{NH}_2 + \text{OH} & \rightarrow \text{NH} + \text{H}_2\text{O} \\
\text{NH} + \text{NO} & \rightarrow \text{N}_2\text{O} + \text{H} \\
\text{NH} + \text{NO} & \rightarrow \text{N}_2\text{O} + \text{H} \\
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2\text{O} + \text{H}_2
\end{align*}
\]

and also

\[
\begin{align*}
\text{NH} + \text{NO} & \rightarrow \text{N}_2\text{O} + \text{H} \\
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2\text{O} + \text{H}_2
\end{align*}
\]

Usually, N₂O formed through above reactions will be rapidly destructed. Concentrations of N₂O in hydrogen flame and methane flame are high (for H₂ is higher) near the burner zone, though as you move towards downstream, the concentration decreases fast [11]. The most important N₂O destructive mechanism is:

\[
\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH}
\]

In general, a threshold in temperature for coal fired combustion applications below which N₂O formation becomes the major nitrogen oxide product. It depends on the fuel type and flow rates. The question addressed in the present work is whether the same threshold exists in alternative fuel combustion with firing temperature as low as 1200K.

N₂O levels are both measured and modeled in a lean premixed combustion application. The measurement of N₂O is done with Siemens N₂O analyzer in conjunction with a Horiba PG-250 gas analyzer. The details are be discussed in the experimental section. The modeling is carried out using chemical reaction network approach. It consists of combining flow field information from computational fluid dynamics (CFD) simulations with detailed chemical kinetic modeling of the reacting flow. CFD is done with Fluent v. 14 and chemical kinetic modeling is conducted using Chemkin Pro. The measured values for NOₓ and CO were used to compare with the same values from the chemical reaction network modeling results to validate the modeling approach.

2 Methods

In this section experimental setup is explained. Also, the steps of developing a CRN to study the details of emission formation will be discussed.

2.1 Experimental Setup

Experimental measurement was done in a model lean premixed high swirl combustor shown in Figure 1. Fuel and air are mixed well before entering the plenum to ensure complete mixing before the reaction zone. A helical swirler is used to generate swirl to stabilize the reaction.

For vane swirlers, the following correlation can be used to estimate the swirl number [12].

\[
S' = \frac{1}{1-\psi} \times \left(\frac{1}{2}\right) \times \frac{1-(R_h/R)^4}{1-(R_h/R)^2} \times \tan a_0 = 1
\]

where

- \( R_h \) is the radius of the hub and
- \( R \) is the outside radius of the swirler module
- \( a_0 \) is the angle of the vanes
\( \psi \) is the block factor of the modules

In the combustor used, \( \psi = 0.41, a_0 = 45^\circ, \) and \( R_p/R = 0.4 \) which gives a swirl number of 0.98.

The mixing zone allows any wakes and flow structures from the swirler to decay prior to the combustion zone. The quarl accelerates the flow and increases the resistance to upstream propagation of the flame into the mixing zone. The centerbody contributes to formation of center recirculation zone and enhances the stabilizing the flame. A quartz cylinder with 80mm diameter and 175mm length is used as the transparent liner of the combustion zone to allow optical access to the reaction zone. A contracting piece at the exit prevents any backflow of gases under either reacting or non-reacting conditions thus providing a clear boundary condition for application of CFD.

Air is fed to the combustor through a sonic orifice and a pressure regulator to control the flow rate. The sonic orifice provides up to 170 kg/hr air. A Delta T® in line heater with a PID controller can provide constant preheat up to 700K for the entering the combustor.

**Figure 1-Schematic of the model combustor**

Fuel flows are introduced to the test rig through Brooks Instruments® mass flow controllers (MFC), and master control units. A fuel mixing unit establishes the desired fuel composition using individual fuels each metered by a separate MFC. Each specific fuel circuit is calibrated using NIST traceable laminar flow elements. Natural gas is provided by a gas compressor and hydrogen is provided by high pressure cylinders. Hydrogen and natural gas flow rates up to 1 kg/hr and 7 kg/hr, respectively were required for this study.

A Labview® based data acquisition system was developed to record and monitor air and fuel flow rates as well as temperatures of interest. Four thermocouples monitor the temperatures in mixing zone, heater, and plenum. The two thermocouples in the mixing zone are used to detect flashback, the heater thermocouple is used in the PID control of the air heater to maintain a constant air temperature at the entrance of the rig, and the plenum temperature is used as the reference. The input and output signals from the MFC master control units are used to measure and control the mass flow rates.

For emission measurement, a sampling chimney is placed on top of the burner to make sampling possible. A water cooled port exists in the sampling chimney where a portion of exhaust gases is probed to emission measurement instruments. Two instruments are used at the same time. The one for measurement of NO, NO\(_2\), and CO is Horiba® PG-250 which collects gas samples through a water cooled probe in conjunction with a vacuum pump. The water drop out unit collects all the moisture from the gas sample, so what is measured by Horiba® PG-250 is based on dry mixture. The analyzer measures NO\(_2\), NO, CO, CO\(_2\), and O\(_2\) using EPA approved methods. This device utilizes the same principal as
CEMS to measure NO\textsubscript{x}. It utilizes the heated catalyst to convert all NO\textsubscript{x} to NO first. NO is a fairly unstable molecule which will react with O\textsubscript{3} to form NO\textsubscript{2}. This reaction produces a quantity of light for each reacted NO molecule. This light can be measured with a photomultiplier (PMT) tube or other devices. If the volume of sample gas and O\textsubscript{3} are carefully controlled, measured light level, which is proportional to the concentration of NO, can be interpreted as NO\textsubscript{x} level in the sample. In conjunction with Horiba\textsuperscript{®} PG-250, a Siemens N2O analyzer is used to measure N\textsubscript{2}O. The outlet of Horiba\textsuperscript{®} PG-250 enters the Siemens N\textsubscript{2}O analyzer. The gas sample leaving the Horiba\textsuperscript{®} PG-250 has already lost all of its moisture through the water drop unit before. This configuration allows simultaneous measurement of NO\textsubscript{x}, CO and N\textsubscript{2}O. The schematic of emission measurement process through the explained sampling method is shown in Figure 2.

![Schematic of emission measurement](image)

**Figure 2-Schematic of emission measurement**

To take accurate measurement and monitor all air and fuel flow rates, a DAQ device in conjunction with Labview\textsuperscript{®} software is used. Four thermocouples monitor the temperatures in mixing zone, heater, and plenum. The two thermocouples in the mixing zone are used to detect and prevent flashback. The heater thermocouple is used in the PID control of the air heater to maintain a constant air temperature at the entrance of the rig, and the plenum temperature is used as the reference. There are two Brooks Instrument\textsuperscript{®} master control units that control eight mass flow controllers. Each control unit controls four MFCs and is connected through a 25 pin cord to the DAQ device. Currently, four MFCs are being used for hydrogen and a big MFC is used for methane. The input and output signals to measure and control the mass flow rates are received and generated in Labview software. PG-250 and Siemens N\textsubscript{2}O analyzer are connected to DAQ to facilitate time average emission measurements. For each specific test, appropriate programming in Labview is conducted to provide a user friendly interface to maintain the test conditions and take needed measurements. It is especially hard to provide a high hydrogen fuel composition flame, so the stable combustion from natural gas will be gradually switched to the desired combustion using control and monitoring system provided by Labview.

To get insight into the flame shape a position, OH\textsuperscript{*} chemiluminescence imaging is also applied in this study. The OH\textsuperscript{*} chemiluminescence setup consists of an ICCD camera, a programmable gate pulse generator, a camera controller, a bandpass filter, and a computer with WinView32 software that controls the image acquisition process. ICCD camera is ITE/CCD-565, the programmable gate pulse generator is PG-200 and the camera controller is ST-133, all from Princeton Instrument\textsuperscript{®}. The bandpass filter is from Melles Griot\textsuperscript{®} with the peak at 308 nm where the chemically exited OH\textsuperscript{*} emission spectra is at its maximum. The location with highest concentration of OH\textsuperscript{*} can be corresponded to the flame front where the chemical reaction rates are maximum. Thus, the image can be used to verify the CFD results which will be discussed later.

In this study, a mixture of natural gas and hydrogen was used to study N\textsubscript{2}O in intermediate and low temperatures for both natural gas as conventional fuel, and high hydrogen content fuel as a common form of alternative fuels. The fuel composition varies between pure natural gas and 80/20 hydrogen/natural gas blend. Preheating temperature, flow rate, and firing temperature are the other variables studied here to determine whether they have any impact on N\textsubscript{2}O formation in different conditions. Two different preheating temperatures were 300K and 500K. Two different flow rates were 53 and 85 kg/hr. The firing temperature starts at 1800K for each set and decreases down to 1200K for 80/20 H\textsubscript{2}/NG mixture. For all other mixtures, it decreased down to the blowoff level where reaction couldn’t sustain itself in the combustor zone.
2.2 Simulation approach

To model the chemical kinetics associated with formation of NO\textsubscript{x}, CO, and N\textsubscript{2}O, a chemical reaction network (CRN), which is a combination of known reactor models, was developed for the combustor. Depending on the flame regimes and different flow field regions in the combustor, different reactor models can be used to analyze the combustion properly to achieve information about pollution formation. Different reactor models include PSR, PFR, and MIX. Perfect stirred reactor (PSR) assumes an ideal reactor in which perfect mixing is achieved inside the control volume. Plug flow reactor (PFR) assumes perfect mixing in the radial direction while ignoring mixing and diffusion in the flow direction. Moreover, MIX stands for an element in which the entering streams are uniformly mixed without chemical reaction [4, 13, 14]. For instance, in swirl stabilized lean premixed combustion, the flame zone where the rapid adiabatic reactions occur can be considered as a PSR with proper volume. The post flame zones can be considered as other PSR with different modeling conditions or PFR. Recirculation zones can be modeled with PSR with larger residence time [4, 15, Error! Bookmark not defined.,]. Dividing the combustor chamber to different zones with specific flow field, and reaction characteristics is the key to the CRN approach.

Although it is possible to develop a very complicated CRN with several elements associated with any zones in the combustor, results have been obtained using simple CRN with two or three key elements in the flow. In this study, a PSB which is a PSR element with volume slightly above the blowoff limit is used to model the beginning of the flame zone. To define the PSB, the volume of a PSR was decreased until blowoff limit, and then a PSR with volume 5% larger than the blowoff volume was defined as PSB. This element represents the initiation of fast reaction. Then a PSR was used to model the flame. The volume of the PSR was obtained from CFD results. Then the recirculation zone was modeled by a PFR element. The outlet of PFR was split to two streams, one that goes to the outlet, and one that comes back to the PSR element which models the recirculated gas coming back to the fresh reactant in the flow. The percent of recirculated gas was defined by calculating the mass of recirculating gas inside the recirculation bubble in CFD results. For this study, this amount was calculated to be 16% of the main flow. A schematic of the CRN in this work is shown in Figure 3.

![Figure 3-Diagram view of CRN used in this study](image)

CFD simulations were carried out to model different aspects of flow field properly. Ansys 14 including Fluent 14 was used to develop the CFD simulation. The Ansys Geometry was used to draw the 2D axisymmetric schematic of the burner. Due to the axisymmetric physics of swirling flow for round cylinder burners, this approach is reasonable. The swirler was modeled by adjusting the tangential to axial velocity ratio to match the swirl number calculated for the swirling vanes. Around 23,000 cells were generated with Ansys Mesher software to provide structured mesh for the domain. Calculation was carried out using Reynolds-Averaged-Navier-Stokes (RANS) equations and the 5 equation Reynolds Stress Model (RSM) turbulence model. The RSM model was chosen over k-epsilon because of (1) the recirculation flow in the combustor, (2) high pressure gradient fields, and (3) it is a less dissipative turbulence model. Higher order discretization schemes are used. For Pressure, the PRESTO spatial discretization mode was used. For momentum, the QUICK discretization was used. For species and energy, a Third-Order MUSCL Scheme was used. The turbulent combustion within the reactor is computed using the Eddy-Dissipation-Concept (EDC). The Discrete Ordinates (D-O) model accounts for the radiation from gases inside the combustor. A skeletal mechanism was incorporated to Fluent as the chemistry set for modeling chemistry in CFD simulations [16]. An example of temperature contour for the case of 1800 adiabatic flame temperature for the mixture of 50/50 H\textsubscript{2}/NG with 500K preheat temperature is shown in Figure 3.
To verify the accuracy of the CFD results, the predicted flame front from CFD is compared to the measured OH* chemiluminescence image. In the CFD results, the flame front was considered to be the maximum reaction rates for the species. An example of this comparison is shown in Figure 5.

In Figure 5 the top half represents the flame front region, the bottom half represents the flame front based on the measured OH* chemiluminescence concentrations. The flame length predicted by CFD is in a good agreement with the extent of the flame based on the measured values.

3 Results and discussion

In this section measured NOx and N2O levels are compared with the ones from CRN chemical kinetic simulations. For some cases, the measured CO values are also compared to CRN values. Therefore, emission levels of different pollutants, especially N2O, are both experimentally and numerically studied under different testing conditions, and for different fuel compositions. To prevent any confusion between testing conditions, each set of testing condition will be studied separately for different firing temperatures. In most cases the firing temperature starts at 1800 AFT and decreases down to the blowoff limit temperature.

The first set of results is presented for 85 kg/hr air flow rate with 500 K Tp, and natural gas as the fuel is shown in Figure 6. In Figure 6, CRN and measured results for CO, NOx, and N2O are shown. It is clear that the agreement between the modeled CRN results and measured values is good. As expected the NOx goes up with increasing temperature. For the CO though, it decreases first, then it goes up. From emission versus temperature in lean region, it is expected that both NOx and CO go up with increasing the temperature. Though, in very lean zone, near the blowoff, CO goes up abruptly. It could be due to the fact that the temperature is too low for formation of CO2 through CO, so formed
CO will remain in the exhaust. Also, near extinction, the combustion is unstable which could lead to high CO levels. The general emission and temperature distribution versus equivalence ratio is shown in Figure 7.

![Figure 6- CRN vs measured results for natural gas, 85 kg/hr, and 500K preheat temperature.](image)

The increase in CO observed at temperatures below 1700 are an indication that combustion is approaching the blowoff limit which is around 1600 K in this case. For N₂O, it is clear that the measured values are around zero for all the cases. It is verified from CRN simulations that the amount of N₂O for this set of cases is negligible, so N₂O is not a concern for this case.

The second set of conditions is for lower air flow rate, 53 kg/hr, same preheated temperature 500 K and natural gas as the fuel. The purpose was to investigate the impact of increasing residence time on formation of N₂O. The summary of comparison between CRN and measured values is shown in Figure 8.

CO was not measured for this set of test. It is again clear that NOₓ levels go up with increasing temperature, but N₂O levels are almost zero. Therefore, decreasing the air flow rates didn’t have an impact of formation of N₂O for natural gas combustion.

Next, the impact of preheat temperature on N₂O formation was investigated. This time the air flow rate is 85 kg/hr with no preheat temperature and natural gas as the fuel.
In Figure 9 it is clear that NO\(_x\) goes up with increasing the adiabatic flame temperature. For N\(_2\)O, the measured levels below 1650K are high, with maximum of 30 ppm in 1600K. However, the CRN shows that the amount of N\(_2\)O is negligible in those temperatures. Looking into the conditions more closely, it is obvious that the reaction is not complete inside the combustion chamber, and the reaction continues in the sampling chimney which was shown in Figure 2. Apparently, incomplete reaction downstream of the combustion chamber and sampling from post flame zone in the sampling chimney leads to high level of measured N\(_2\)O here. Thus, the level of N\(_2\)O for complete reaction was not measured here, and CRN simulations show that the level of N\(_2\)O is negligible. Another interesting point is that even if the level of N\(_2\)O is negligible for a complete reaction, very high amount of N\(_2\)O exists a little bit upstream of the exhaust. It means that a huge amount of N\(_2\)O is trapped in the post flame zone, even for natural gas fuel, and if any condition disturbs the final N\(_2\)O decomposition reactions, the emitted level of N\(_2\)O can be high.

Figure 9-CRN vs measured results for natural gas, 53 kg/hr, and no preheat temperature

Now, N\(_2\)O levels in alternative fuel combustion will be discussed. Fuel composition consists of hydrogen and natural gas. For the first case, the fuel composition is 50/50 NO/H\(_2\) volume based. The air flow is 85 kg/hr and the preheated temperature of 500K.
In Figure 10, measured and CRN results are shown. Because of the wider flammability limit of hydrogen combustion, the temperature of blowoff limit is lower than natural gas combustion. It is obvious that below 1500K, the combustion becomes unstable, and CO level goes up. Below 1500K, CO goes up which is consistent with Figure 7. NO, levels go up with increasing the adiabatic flame temperature. N₂O levels, even for temperatures as low as 1400K, are insignificant both experimentally and numerically. This can answer the question that whether the N₂O levels are high in very lean regions where the temperatures are low or not. This point is further investigated in the next set of testing where the adiabatic flame temperatures are as low as 1200K at some point.

Another set of cases with the fuel composition set at 20%/80% NG/H₂ (by volume). Higher concentration of hydrogen in fuel is also possible, but HCN which is an important intermediate species in N₂O formation cannot be generated without hydrocarbons. The air flow rates is 85 kg/hr and the preheat temperature is 500K. The measured and CRN results for this set is presented in Figure 11.

As shown in Figure 11, the NO₅ levels in low temperatures are almost zero. However, as temperature increases, the NO₅ levels increases. However, even at adiabatic flame temperatures as low as 1200K, no N₂O is observed. This is
an important finding for this lean premixed combustor where, even with reaction temperatures at the maximum formation of N$_2$O in the reaction, no N$_2$O is observed in the combustion products. For natural gas cases, the blowoff occurs in temperatures around 1600 K, so investigation of natural gas combustion below this temperature was not possible. In addition, CRN simulations support this finding. Therefore, it can be said that in lean premixed application of gaseous fuels including natural gas and hydrogen, N$_2$O was not a point of concern based on the finding from a model combustor with lean premixed swirl stabilized flame. The one exception could be a case where the reaction is quenched prior to completion, a situation which was mimicked in the case where the sampling probe was actually probing the reacting flow.

As side note it should be noted that simple CRN simulations can provide good insight into emission formation for different combustion applications. As it was presented over this paper, the CRN results were in a very good agreement with experimental results, for all CO, NO$_x$, and N$_2$O.

4 Conclusions

Emission levels from a model combustor with lean premixed swirl stabilized flame are experimentally measured for different air flow rates, fuel compositions, preheated temperatures, and adiabatic flame temperatures. The studied emissions include CO, NO$_x$, and N$_2$O. Emission level of N$_2$O in lean premixed combustion application with very low temperatures has not been extensively studied in the literature. Besides experimental measurements, chemical kinetics simulations are applied with assistance of CFD results for the reaction flow to develop a chemical reactor network (CRN).

It was shown that if a CRN is carefully developed, it can provide appropriate information about emission formation even in complex flow fields. A good agreement between CRN simulations and experimental results is reported here. For CO emission levels, in low temperatures near the blowoff limits where the reaction is not stable, the emission levels are higher than stable conditions even with higher temperatures. This was reported in other work also, but the point is that even CRN simulations can capture this phenomenon.

N$_2$O levels are negligible in this study even for cases with adiabatic temperature as low as 1200K. The interesting point is that sampling the gas from slightly upstream of the exhaust where the reaction is not complete indicates presence of very high amount of N$_2$O which will be destroyed later in the complete reaction. All the reported data is for conditions tested and simulated in UC Irvine Combustion Lab high swirl burner that is a good example of lean premixed application. More robust conclusion about all lean premixed applications might need more extensive investigation.

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