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LOW NO_X COMBUSTION FOR LIQUID FUELS: ATMOSPHERIC PRESSURE EXPERIMENTS USING A STAGED PREVAPORIZER-PREMIXER

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ABSTRACT

Low emissions of NO_X are obtained for a wide range of liquid fuels by using a staged prevaporizing-premixing injector. The injector relies on two stages of air temperature and fires into a laboratory jet-stirred reactor operated at atmospheric pressure and nominal ϕ of 0.6. The liquid fuels burned are methanol, normal alkanes from pentane to hexadecane, benzene, toluene, two grades of light naphtha and four grades of No. 2 diesel fuel. Additionally, natural gas, ethane and industrial propane are burned. For experiments conducted for 1790 K combustion temperature and 2.3±0.1 ms combustion residence time, the NO_x (adjusted to 15% O₂ dry) varies from a low of 3.5 ppmv for methanol to a high of 11.5 ppmv for No. 2 diesel fuel. For the most part, the NO_X and CO are positively correlated with the fuel carbon to hydrogen ratio (C/H). Chemical kinetic modeling suggests the increase in NO_X with C/H ratio is caused in significant part by the increasing superequilibrium concentrations of O-atom created by the increasing levels of CO burning in the jet-stirred reactor. Fuel bound nitrogen also contributes NO_X for the burning of the diesel fuel.

This paper describes the staged prevaporizing-premixing injector, the examination of the injector and the NO_X and CO measurements and their interpretation. Optical measurements,

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using beams of He-Ne laser radiation passed across the outlet stream of the injector, indicate complete vaporization and a small variation in the cross-stream averaged fuel/air ratio. The later is determined by measuring the standard deviation and mean of the transmission of the laser beam passed through the stream. Additional measurements and inspections indicate no pressure oscillations within the injector and no gum and carbon deposition. Thus, the NO_X and CO measurements are obtained for fully vaporized, well premixed conditions devoid of preflame reactions within the injector.

INTRODUCTION

Lean-premixed combustion of natural gas is widely practiced in gas turbine engines applied to electrical generation and mechanical drive. Most of the engines emit NO_X less than 25 ppmv (at 15% O₂ dry), though for some engines in the field, the NO_X emission is less than 10 ppmv (at 15% O₂ dry). In general, lean premixed (LP) combustors are sensitive to fuel composition. For example, natural gas high in non-methane hydrocarbon content (NMHC), when premixed with the high temperature compressor discharge air, may experience autoignition and flashback. Further, for many dual fuel engines, the combustor is switched to diffusion flame mode for liquid fuel firing and uses water or steam injection for NO_X control. A

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preferred alternative is dry low NO_X (DLN) combustion for all fuels, since elimination of the water/steam injection generally improves the engine economics and efficiency. The prevaporizing-premixing injector used should be designed to minimize preflame fuel oxidation (e.g., coking and autoignition) and should not be prone to flashback. Further, it is important to understand the NO_X behavior of the combustor fitted with the prevaporizing-premixing injector.

The present study involves the application of the staged prevaporizing-premixing injector (Lee and Malte, 2000) for lean premixed combustion of liquid fuels. The staging is accomplished by using two stages of air temperature, including a relatively low temperature air to accomplish as much of the vaporization and mixing as possible and a high temperature air to bring the injector outlet stream to the desired combustor inlet temperature without causing preflame reaction and autoignition. The inside of the staged prevaporizer-premixer (SPP) is monitored and inspected to confirm the absence of reaction within the SPP. The outlet stream of the SPP is optically examined for completeness of vaporization and degree of mixedness between the fuel vapor and air. The objective of the study is to show DLN combustion for a wide range of fuels burned in a high-intensity combustor fed by the reactants from the SPP injector. Most significantly, the study provides a database of NO_X as a function of fuel type for lean, fully vaporized, well premixed combustion. The combustor is an atmospheric pressure jet-stirred reactor (JSR) operated at combustor inlet temperatures (up to 773 K) and flame temperature (normally 1790 K) typical of LP combustion turbines. The gaseous fuels burned are natural gas, ethane and industrial propane. The liquid fuels burned are methanol, normal alkanes of C_5 to C_{16} , benzene, toluene, two grades of light naphtha and four grades of No. 2 diesel fuel (DF2). The DF2s contain small amounts of fuel bound nitrogen (FBN), about 50 to 100 ppm by weight. One of the pure liquid fuels (ndodecane) was previously burned (Capehart et al., 1997) with and without a FBN dopant (n-ethylethylenediamine). The experiments, conducted under conditions very close to those of the present study, indicated complete conversion of small levels of FBN to NO_x.

The paper contains the following sections:

- Description of the SPP injector and JSR combustor.
- Description of the optical method used to evaluate the mixedness of the SPP outlet stream.
- Data and analysis on the mixedness of the SPP outlet stream.
- Experimental data of NO_X and CO as a function of fuel type.
- Analysis of the NO_X and CO data by chemical kinetic modeling.
- Conclusions and recommendations.

SPP INJECTOR AND DIAGNOSTICS

The experimental setup of the SPP injector with the JSR combustor is schematically depicted in Fig. 1.



Figure 1. Schematic Drawing of the Atmospheric Pressure JSR, of 15.8 cm³ Volume, with the Staged Prevaporizing-Premixing Injector

SPP Injector

The SPP injector is shown in the lower three-fourths of Fig. 1. First stage air, of relatively low temperature, enters at the bottom, i.e., upstream end of the SPP. The first stage air is accelerated through jets located at the upstream end of the film atomizer that is coaxial with the fuel nozzle. Two streams of the jetted first stage air are obtained, separated by the thin annular splitter plate constituting the film atomizer. Second stage air enters through a manifold near the top, i.e., downstream end of the SPP. This air is mixed into the internal flow of the SPP through several staggered jets. These jets enter the SPP at an angle of 45 degrees to the axial direction and do not have a tangential velocity component. The total air flow rate of the SPP as used for atmospheric pressure firing is 4.7 kg/hr. In the first stage of the SPP, the light ends and middle boiling compounds of a blended fuel are vaporized, while in the

second stage, the vaporization process is completed. As the temperature of the second stage air is increased, the residence time of the gases in the second stage can be decreased to small values to prevent reaction within the SPP.

Gaseous fuel is injected through a single port into the first stage air. As noted in Fig. 1, this port is located slightly upstream of the film atomizer. Liquid fuel is atomized by a Nukiyama-Tanasawa type, plain-jet, air-blast atomizer custom built for this application and located on the centerline of the first stage. The Nukiyama-Tanasawa type atomizer is described by Lefebvre (1989). The previous embodiment of this atomizer for research at the University of Washington is discussed by Lee et al. (1999). Within the Nukiyama-Tanasawa type nozzle, pressure atomization occurs first, followed by air-assist atomization and spray cone angle adjustment.

The Nukiyama-Tanasawa type nozzle provides good atomization and spray quality for the low fuel flow rates associated with the atmospheric pressure firing of this study. The nominal flow rate of the fuel is 0.2 kg/hr and that of the unheated atomizing air is 0.4 kg/hr. The atomizer nozzle flow is choked and the calculated SMD of the spray is about 10 μ m. However, for high pressure industrial applications, with significantly greater flow rates of fuel, a commercial air blast, pressure swirl or macrolaminated (Mansour et al., 2000) atomizer will be used for the SPP.

For the present study, the first stage temperature is varied from 293 to 623 K and that of the second stage, which is also the total temperature of the outlet stream, is varied from 293 to 773 K (though the data shown are limited to 723 K). The outlet nozzle of the SPP, which couples the SPP to the jet stirred reactor, is 4 mm in diameter. Nominal pressure within the SPP, downstream of the film atomizer, is 1.15 atm. The nominal nozzle exit velocity (from 293 to 773 K) is 85 to 230 m/s. The ratio of the 1st stage to 2nd stage air mass flow rates is set at 0.5, 1.0 and 2.0. Some variation in the performance of the SPP is obtained with respect to this air split, however, as shown in the results section, the variation is relatively small. For use in gas turbine engines, a low ratio of first stage to second stage air is preferable, since this would require the least amount of modification to the engine cycle for cooling the compressor discharge air to the desired first stage temperature of the SPP.

In the present work, the nominal residence time of the 1^{st} stage of the SPP is 12 ms and that of the 2^{nd} stage is either 5 or 12 ms, depending on whether the short or long version of the 2^{nd} stage is installed. These nominal values correspond to an airflow ratio of 1.0 and a temperature of 623 K in each stage.

Absence of preflame reactions in the liquid fueled SPP is confirmed by the absence of C_1 and C_2 hydrocarbons, by the absence of wall deposits of gum and carbon and by the absence of pressure oscillations. The absence of the C_1 and C_2 hydrocarbons is determined by probe sampling of the internal flow of the SPP, followed by GC analysis of the gas samples. The absence of pressure oscillations is determined by continuous monitoring of the SPP via a pressure probe and transducer. In earlier work (Lee et al., 1999) with a single stage prevaporizer-premixer of about 100 ms residence time and 2-3 atm pressure, several preflame reaction indicators (i.e., gum deposits and pressure oscillations) were observed when the temperature was approximately 100°C above the normal boiling point of the fuel.

The supporting components of the SPP system are the following:

- Electrical air preheaters.
- Cascade type temperature controller for setting and maintaining air preheating and SPP temperature levels.
- Air and fuel control: The mass flow rates of the air and gaseous fuels are controlled and measured by electronic mass flow controllers. The mass flow rates of the liquid fuels are control by placing the liquid fuels under nitrogen pressure and pushing the fuels through a control valve. The liquid flow rates are measured with a calibrated rotameter.

Laser Diagnostics

Two laser-based methods are used for examining the outlet stream of the SPP. 1) Completeness of vaporization is confirmed by observing the absence of droplet and aerosol scattering from a 5 mW, 0.63 μ m He-Ne laser beam passed through the outlet stream of the SPP. 2) A separate laser absorption system is used to investigate the mixedness of the fuel vapor-air stream as it departs the SPP injector. The laser absorption system is a relatively simple diagnostic tool based on the absorption of electromagnetic radiation of 3.39 μ m wavelength by hydrocarbons (Tsuboi et al., 1985). The major components of the system were provided by the University of California at Berkeley (Dibble, 1999). Mongia (1998), in his Ph.D. thesis, describes the technique and its application to premixer outlet streams.

Figure 2 is a schematic drawing of the laser absorption setup used. The major components are the 50 mW, $3.39 \mu m$ He-Ne laser with power supply and the infrared (IR) detector that is thermal electrically cooled and maintained at 5°C temperature. The neutral density filter shown is used to attenuate the laser beam, since the laser power is too great for the IR detector. The plano-convex focusing lenses are required in order to minimize the effects of beam steering caused by differences in index of refraction as the laser beam passes through the heated outlet stream of the SPP. The narrow bandwidth IR band pass filter is used to remove any thermal radiation emitted from the metal surfaces of the SPP. Signal display and processing are accomplished with the digitizing oscilloscope.

Temporal fluctuations spatially averaged over the line-ofsight path length are measured with the laser absorption system. The line-of-sight measurements are made along a 12.7 mm diametric path through the SPP outlet stream at a location 2 mm above the SPP outlet. The SPP outlet nozzle and JSR are removed.

By the Beer-Lambert law:

$$\frac{I}{I_o} = e^{-kPL}$$
(1)

where I is the beam intensity (or the transmission signal) leaving the absorbing medium, I_o is the beam intensity entering the absorbing medium (or the signal in the absorbed entering the absorbing species), k (cm⁻¹atm⁻¹) is the absorption coefficient at the given wavelength, P (atm) is partial pressure of the absorbing species (fuel) and L (cm) is the path length. Perrin and Hartmann (1989) determined the absorption coefficient for the 3.39 μ m laser wavelength for methane diluted in nitrogen at temperatures of 293 to 787 K and 1 atm total pressure. Their data may be expressed as follows:

$$k = 22.89e^{-0.003033T}$$
(2)



Figure 2. Schematic Diagram of the Laser Absorption System

Yoshiyama et al. (1996) examined absorption at the 3.39 μ m wavelength by methane and propane. Their results are expressed in terms of an extinction coefficient, ϵ (cm²/gmol). The definition of ϵ and its expression for CH₄ are given as follows:

$$\varepsilon = \frac{\log_{10} \frac{I_o}{I}}{C \cdot L} = \frac{110,000}{P_T^{0.302}}$$
(3)

where C (gmol/cm³) is the concentration of the absorbing species and P_T (atm) is the total pressure.

Equation (1) is rearranged for the case of fluctuations in the absorbing medium and laser/detector system. This is done as follows:

• I_o , I and kPL are assumed to have time-mean (m) and time-fluctuating (') components: $I_o = I_{om} + I_o$, $I = I_m + I'$ and kPL = (kPL)_m + (kPL).

- It is assumed that $(kPL)' \ll 1$. Thus, $e^{-kPL'} \cong 1 (kPL)'$
- The fluctuations in I_o (i.e., the signal without absorbing species present) and kPL (i.e., the absorbing medium) are assumed uncorrelated. Thus, the mean value of the product I_o['](kPL)['] is zero. Also, terms of order higher than two in the fluctuations are assumed negligible.

Substitution into Eq. (1) and rearrangement gives the following equation linking the standard deviation $(_{sd})$ over the mean $(_m)$ of the variables:

$$\frac{I_{sd}}{I_m} = \sqrt{\left[\frac{(kPL)_{sd}}{(kPL)_m} \cdot \ln\left(\frac{I_{om}}{I_m}\right)\right]^2 + \left(\frac{I_{osd}}{I_{om}}\right)^2}$$
(4)

The transmission data (I) are collected with the digitizing oscilloscope over a period of 50 ms at a rate of 10 samples per millisecond for a total of 500 samples. For each case of 500 samples, the mean (I_m) and standard deviation (I_{sd}) are determined. The noise base is determined in the absence of fuel flow with only the flow of air. The measurements indicate the base noise inherent in the laser/electronic system is independent of the inlet temperature (from 293 to 773 K) and is constant with a value of I_{osd}/I_{om} = 0.023. In the results section, I_{sd}/I_m is plotted as a function of I_m/I_{om} for different values of (kPL)_{sd}/(kPL)_m and the measurements with the fuel present are superimposed, thereby permitting (kPL)_{sd}/(kPL)_m to be determined.

Fluctuations in kPL can arise in at least three ways. 1) The absorption coefficient (k) can fluctuate through variations in temperature. 2) The partial pressure of the fuel (P) can fluctuate through variations in the fuel/air ratio (F/A). 3) And the path length (L) can fluctuate through fluctuations in the thickness of the mixing layer along the outer edge of the stream. Additionally, for the case of a blended fuel, differential diffusion of the fuel components could cause kPL to vary. Fluctuations in the transmission signal would also occur in the case of incomplete vaporization, though, as stated above, the evidence from the laser scattering tests indicates this effect is absent from the present experiments.

With increasing temperature, the absorption decreases, note Eq. (2). Thus, I_m approaches I_{om} and the effect of the kPL fluctuations on I_{sd}/I_m decreases as the temperature increases. This effect is illustrated in the results section.

JET-STIRRED REACTOR, JSR OPERATING CONDITIONS, DIAGNOSTICS, AND FUELS

Jet-Stirred Reactor

The jet-stirred reactor used in this study is described by Lee et al. (1999) and detailed in the Ph.D. thesis of Lee (2000).

The internal dimensions of the JSR are identical to the JSR used by Steele et al. (1995). The JSR is depicted in the upper part of Fig. 1. The internal volume is 15.8 cm³, the internal height is 45 mm and the internal diameter (at the widest point) is 25 mm. The JSR is fed by reactants and stirred by the outlet stream of the SPP accelerated through a 4 mm diameter nozzle. The nozzle is located in the Hastelloy[®] nozzle block. Exhaust gases leave the JSR through four drain holes located 90° apart near the bottom of the reactor. Temperature measurement, gas sampling and viewing of the JSR cavity are conducted at 2/3rd reactor height. There are four ports located at this height, 90° degrees apart. Two of these are blocked during operation. One of the remaining open ports accepts the thermocouple probe and the other accepts the gas sample probe.

JSR Operating Conditions

The JSR operating conditions are listed as follows:

- The combustion temperature (i.e., the measured, corrected temperature of the recirculation zone) is normally maintained at 1790 K.
- The air mass flow rate (given above) is maintained at 4.7 kg/hr.
- The mean residence time of the JSR is 2.3±0.1 ms, based on the air and fuel mass flow rates, the combustion temperature of 1790 K, the molecular weight of the combustion gases and the JSR volume.
- The inlet total temperature of the JSR is the 2nd stage temperature of the SPP. For the combustion experiments shown, it is varied from 423 to 723 K. An inlet total temperature of 623 K is used for the experiments of NO_X as a function of fuel type.
- The fuel-air equivalence ratio (ϕ) is adjusted to maintain the constant combustion temperature. For the experiments run at 1790 K combustion temperature and 623 K inlet total temperature, this results in $\phi = 0.61\pm0.02$ for most of the fuels. The exceptions are natural gas ($\phi = 0.65$), benzene ($\phi = 0.57$) and toluene ($\phi = 0.58$).

JSR Characterization

Calculations of the Damköhler number (Da) and the turbulence Reynolds number (Re_T) are performed for the JSR operated with the 623 K inlet temperature. With methane selected as the example fuel, the laminar flame speed (S_L) is estimated using the method of Göttgens et al. (1992). The laminar flame speed leads to the characteristic chemical time (τ_L), assuming $\tau_L \cong D_L/S_L^2$. The laminar diffusivity (D_L) is estimated based on the inlet temperature (Abraham et al., 1985), using the air value for thermal diffusivity. The result is $\tau_L \cong 0.15$ ms. The characteristic mixing time (τ_T) is evaluated assuming $\tau_T \cong d/u'$, where d is taken to be the inlet jet diameter (4 mm) and the RMS turbulence velocity (u') is assumed to be 10% of the inlet jet velocity. This gives the characteristic

mixing time as 0.2 ms. Hence, $Da = \tau_T / \tau_L \approx 1.3$. The turbulence Reynolds number (u'd/v) is 1350, where the kinematic viscosity (v) is based on air at the jet inlet temperature.

Under these conditions, the JSR operates as a two-zone reactor. Studies by Rutar et al. (2000) indicate the Damköhler number must be reduced to about 0.15 before the JSR can operate as a single-zone, well-stirred reactor. In the present experiments, the flame zone is wrapped around the inlet jet and represents about 5-10% of the reactor volume. The large recirculation zone serves as the post-flame zone. Because of the stirring within the recirculation zone, combined with the relatively short residence time (2.3 ms) and relatively low pressure (1 atm), free radical and intermediate species, in particular O, H, OH, H₂ and CO, remain at relatively large concentrations throughout the reactor. Both zones contribute NO_X as discussed in the "modeling and interpretation" section below.

Combustion Temperature and Species Concentration Measurements

For the work reported herein, all probe measurements of temperature and species concentrations are obtained in the recirculation zone of the JSR. This zone comprises the bulk of the JSR and exhibits nearly uniform temperature and composition.

Combustion temperature is measured with a 0.127 mm type-R thermocouple coated with a ceramic compound (to prevent oxidation of CO, H_2 and hydrocarbons at the thermocouple surface) and corrected for radiation losses (typically, a +40°C correction).

Gas composition is measured by drawing combustion gas through a small, water-cooled, quartz sampling probe and routing the gas through water removal impingers and into a bank of gas analyzers for CO, CO₂, O_2 , NO and NO_X determination. A metal bellows sample pump is located between the impingers and the bank of gas analyzers. In order to minimize the disturbance of the JSR flow field as well as to minimize internal probe reactions, the uncooled tip of the probe is made as small in diameter and as short as practical, i.e., 3 mm O.D. by 30 mm length. The I.D. of the probe is maintained constant, that is, the entry is not restricted. The remainder of the probe, which sits outside the JSR cavity, is jacketed with water flow. The water is made sufficiently warm to prevent condensation within the probe sample. The overall length of the sample probe is 300 mm. A 6 mm O.D. Teflon tube, also maintained warm, connects the sample probe outlet to the impingers. By the sampling technique used, most of the NO_X measured is NO, indicating conversion of NO to NO₂ in the sample probe is small. Hence, loss of NO_X by absorption of NO₂ in water is taken to be a minor-to-negligible effect in the present work. Gasdynamic calculations indicate the residence time of the sampled gas within the hot uncooled tip of the probe is approximately 0.1 ms. Although this time is small, some loss of CO by oxidation and a relatively small production of NO within the hot uncooled tip of the probe cannot be ruled out.

That is, the hot uncooled tip of the sample probe is an extension of the JSR. From time-to-time, gas chromatography is employed to check for light hydrocarbon gases in the JSR. Typically, total measured hydrocarbon for the JSR recirculation zone is small (i.e., less than 100 ppmv C_1 basis).

Fuels

The fuels used in this study are listed in Table 1. The empirical chemical formulas listed for the naphtha and diesel fuels are based on elemental analyses performed at commercial fuel analysis laboratories. Compound information obtained with the analyses indicates the light naphtha fuels are composed of n-alkanes (50%), iso-alkanes (30%), naphthenes (15%) and aromatics (5%), all in the C_5 - C_6 range.

Table 1. List of Fuels Used in Experiments (FBS: Fuel Bound Sulfur, FBN: Fuel Bound Nitrogen)

Fuel	Purity	Chemical	FBS	FBN
		Formula	(ppmw)	(ppmw)
natural	_	03% CH	negligible	negligible
gas	-	93 /0 CH4	riegligible	negligible
industrial	_	95% C.H.	nogligiblo	nogligiblo
propane	-	90% C3H8	negligible	riegligible
methanol	99%	CH₃OH	0	0
ethane	99%	C ₂ H ₆	0	0
propane	99%	C ₃ H ₈	0	0
n-pentane	99%	C_5H_{12}	0	0
n-hexane	99%	C ₆ H ₁₄	0	0
n-heptane	99%	C ₇ H ₁₆	0	0
n-dodecane	99%	C ₁₂ H ₂₆	0	0
n-hexadecane	99%	C ₁₆ H ₃₄	0	0
benzene	99%	C ₆ H ₆	0	0
toluene	99%	C ₇ H ₈	0	0
light naphtha				
(K-LN)	-	C _{5.9} H _{12.5}	negligible	<1
supplied by K				
light naphtha				
(U-LN)	-	$C_{5.9}H_{13.4}$	negligible	<3
supplied by U				
low sulfur				
DF2	_	CracHasa	~200	16
(C-LSD)	_	013.81 126.3	~200	40
supplied by C				
low sulfur				
DF2	-	C12 9H24 2	≈200	91
(T-LSD)		0 13.01 124.2	-200	<i>)</i> 1
supplied by T				
high sulfur				
DF2	-	C138H237	≈3000	84
(I-HSD)		- 1010 2011		
supplied by I				
low sultur				
DF2	-	C _{13.8} H _{24.2}	≈200	49
(U-LSD)		1010 2112		-
supplied by U				

EXPERIMENTAL RESULTS

Laser Absorption Measurements

Percent mean transmission $(I_m/I_{om} \times 100)$ as a function of the temperature for the outlet stream of the SPP is plotted in Fig. 3. Comparison to the literature, that is, to Eqs. (2) and (3) applied to the present experimental conditions, is also plotted. The fuels are natural gas and industrial propane, each at a mole fraction of 0.0277 in the stream. The corresponding fuel-air equivalence ratios are 0.27 for natural gas and 0.68 for industrial propane. The figure clearly shows the increase in transmission with increasing temperature. The figure also indicates a good agreement between the measurements for natural gas and Eq. (2). On the other hand, Eq. (3) predicts lower transmission than measured, though the trend with respect to temperature is consistent with the other results.



Figure 3. Effect of Temperature on the Transmission of the 3.39 μm He-Ne Laser for Methane/Air and Propane/Air Mixtures at 1 Atm

Percent standard deviation in transmission $[(I_{sd}/I_m) \times 100]$ is plotted versus the temperature of the outlet stream of the SPP in Figs. 4 and 5. The fuels are natural gas (Fig. 4) and No. 2 diesel fuel (Fig. 5). For all data, $\phi = 0.68$. The legend of each figure indicates the ratio of the 1st and 2nd stage airflow rates and the 1st stage temperature of the SPP. The measurements for methane exhibit a fall-off in the percent standard deviation as the temperature of the SPP outlet stream is increased. Also seen is a decrease in the percent standard deviation as the airflow rate of the 1st stage of the SPP is increased relative to the airflow rate of the 2nd stage. All of diesel fuel measurements (Fig. 5) lie close to the noise base of the experiment.

Analysis of the transmission signals of these measurements in the frequency domain indicates no predominant frequencies.



Figure 4. Effect of Temperature and Air Split on the Percent Standard Deviation in the Laser Transmission for the Outlet Stream of the SPP with Natural Gas-Air Mixture at $\phi = 0.68$. Legend: 1st Stage Airflow Rate Divided by the 2nd Stage Airflow Rate, and Nominal 1st Stage Temperature in Kelvin. Long 2nd Stage Used.



Figure 5. Effect of Temperature and Air Split on the Percent Standard Deviation in the Laser Transmission for the Outlet Stream of the SPP with No. 2 Low Sulfur Diesel Fuel-Air Mixture at $\phi = 0.68$. Legend: 1st Stage Airflow Rate Divided by the 2nd Stage Airflow Rate, and Nominal 1st Stage Temperature in Kelvin. Long 2nd Staged Used.

In Fig. 6, results from the laser absorption experiments are displayed on the basis of Eq. (4). The fuel-air equivalence ratio is $\phi = 0.68$, and the 1st to 2nd stage ratio of the SPP airflow rates is 1 and 2. Plotted as the dependent variable is I_{sd}/I_m . The independent variable is I_m/I_{om} . The parameter is the ratio of the standard deviation of kPL divided by the mean of the term. The curves are calculated from Eq. (4). The measurements are

superimposed on the curves. The asymptotic value of I_{sd}/I_m is 0.023, the noise of the laser/detector system.



Figure 6. Standard Deviation in Transmission versus Mean Transmission. Long 2nd Stage for the SPP.

From left to right in Fig. 6, the temperature of the outlet stream of the SPP increases and, thus, the transmission increases. The standard deviation over mean of the laser transmission changes by two effects: 1) temperature and 2) fluctuations in kPL.

With natural gas as fuel, Fig. 6 shows the percent mean transmission increases from 46% (corresponding to the stream temperature of 293 K) to 89% (corresponding to 723 K). The measurements at 293 K have the highest sensitivity of the experiment and indicate a percent standard deviation in kPL [i.e., $(kPL)_{sd}/(kPL)_m \times 100$] of 5 to 6%. Because of the 293 K temperature, there is temperature uniformity, and thus, negiglible variation in k. The stardard deviation in kPL represents the variation in the fuel partial pressure (or fuel/air ratio) integrated over the width of the stream. The 5-6% standard deviation indicates a small variation in the cross-stream averaged fuel/air leaving the SPP.

With increasing temperature, I_m/I_{om} increases and I_{sd}/I_m decreases. The I_{sd}/I_m measurement becomes less sensitive to the variation in kPL, and thus, there is more uncertainty in the values of $(kPL)_{sd}/(kPL)_m$ inferred from the experiment. The maximum percent standard deviation in kPL is about 10%, or double that of the 293 K data.

With the industrial propane, the mean transmission increases, since fewer fuel molecules are present with ϕ maintained constant. The temperature range is 293 to 623 K, corresponding to an increase in percent mean transmission from 73 to 87%. The maximum value of the percent standard deviation in kPL is again about 10%.

With diesel fuel, a further increase in mean transmission occurs. One measurement point is shown in Fig. 6. This indicates a percent mean transmission of about 85% and a value

of no more than about 5% in the percent standard deviation in kPL.

Measurements with a multiple-pass reflected laser beam or at greater total pressure would be useful for both improving the sensitivity of the experiment and permitting enhanced spatial resolution. Nonetheless, the measurements indicate the standard deviation of the cross-stream averaged fuel-air ratio of the outlet stream of the SPP is no more than about 10% of the mean fuel-air ratio.

NO_x as a Function of the Outlet Temperature of the SPP

The amount of NO_X formed in the jet-stirred reactor is first examined as a function of the outlet temperature of the SPP. In order to maintain a constant combustion temperature in the JSR, the fuel-air equivalence ratio is decreased as the outlet temperature of the SPP is increased.

Results for natural gas are shown in Fig. 7. [These experiments were run at a combustion temperature of about 1850 K, rather than the normal value of 1790 K for this study.] Two trends are noted in the figure. 1) A mild decrease in NO_X, from about 8.5 to 7.0 ppmv, occurs as the outlet temperature increases from 423 to 773 K and 2) a slight decrease in NO_X is noted when the SPP is adjusted to give equal airflow rates for the 1st and 2nd stages.



Figure 7. Effect of SPP Temperatures and Air Split on NO_X for Natural Gas-Firing of the JSR. Legend: 1st Stage Airflow Rate Divided by the 2nd Stage Airflow Rate and Nominal 1st Stage Temperature in Kelvin. Long 2nd Stage Used.

Results for ethane and industrial propane also indicate minimum NO_X with the SPP set for the equal 1st and 2nd stage airflow rates. Interestingly, however, these fuels do not exhibit a strong dependency of NO_X on the SPP outlet temperature.

The decrease in NO_X with increasing outlet temperature is probably caused mainly by a decrease in Fenimore prompt NO_X as the mixture is leaned. This behavior is suggested in the work of Rutar et al. (2001), in which a high-pressure jet-stirred reactor was operated for both preheated and unheated inlet streams. For running at short residence times, the NO_X dropped when the reactor was leaned upon preheating the inlet stream of premixed methane and air. Chemical kinetic calculations of the CH radical showed a significant decrease upon preheating, indicating a decrease in the formation of prompt NO_X. Improvement in fuel-air mixedness could in principle also explain the trend in NO_X. However, the measurements in Fig. 6 do not support this hypothesis, since the ratio (kPL)_{sd}/(kPL)_m does not decrease with increasing SPP outlet temperature.

NO_xand CO as a Function of Fuel Type

The measurement of NO_X for the full range of the fuels used in this study is plotted in Fig. 8. In this case, the SPP outlet temperature is 623 K and the ratio of the 1st to 2nd stage SPP airflow rates is 1.0. The combustion temperature of the JSR is 1790 K. The residence times are: SPP 1st stage: 12 ms, SPP 2nd stage: 5 or 12 ms and JSR: 2.3±0.1 ms. Lowest NO_X (3.5 ppmv) is measured for methanol, while highest NO_X (11.4 ppmv) is found for the diesel fuels containing 84-91 ppmw FBN. These measurements of NO_X, obtained in the recirculation zone of the JSR, closely represent exhaust emissions, since the recirculation zone is nearly uniform in NO_X and the exhaust leaves the JSR from the recirculation zone.



Figure 8. Effect of Fuel Type on NO_X JSR Combustion Temperature of 1790 K and Residence Time of 2.3 ± 0.1 ms. The SPP Conditions are Outlet Temperature of 623 K, and 1st to 2nd Stage Airflow Ratio of 1.

In Fig. 9, the NO_X data are adjusted by subtracting the contribution of the FBN for the diesel fuels. This is done assuming complete conversion of the FBN to NO_X . Noted now

is a relatively well-behaved increase in NO_X with increasing molar carbon-to-hydrogen ratio of the fuels from methane through the diesel fuels. Over this range of fuels, it appears possible to reasonably predict the NO_X emission (from fixation of the air-nitrogen) based on the fuel carbon-to-hydrogen ratio. The blended fuels, i.e., the naphthas and diesel fuels, are essentially indistinguishable from the pure alkanes tested on the basis of NO_X as a function of C/H ratio. However, methanol exhibits unique NO_X behavior. This is most likely the result of very little Fenimore prompt NO_X formed by the combustion of methanol.



Figure 9. Same Conditions as Fig. 8, Except the Fuel NO_X Formed Through 100% Conversion of FBN is Deducted for the Diesel Fuels.

The carbon monoxide (CO) measurements obtained for the recirculation zone of the JSR also exhibit a significant dependency on the fuel carbon-to-hydrogen ratio (see Fig. 10). A relatively well-behaved increase in CO with C/H ratio is noted for ethane through the diesel fuels. Methane (i.e., natural gas) and methanol, being relatively slow burning fuels, exhibit more CO than indicated by the extrapolation of data for ethaneto-diesel. The CO measurements for the recirculation zone of the JSR are 80 to 90% lower than the peak CO levels measured in the flame zone of the reactor that surrounds the inlet jet of the JSR. Nonetheless, the CO concentrations for the recirculation zone are significantly higher than exit plane emissions acceptable for a commercial combustor. This is caused because the JSR does not have a plug flow burnout zone for CO.

MODELING AND INTERPRETATION OF NO_X

Reactor modeling is conducted to help explain the increase in NO_X with increasing C/H ratio. Chemical kinetic modeling

is performed using simple, though realistic, chemical reactor arrangements to simulate the JSR. Thus, as a first step, the structure and behavior of the JSR is examined.



Figure 10. Effect of Fuel Type on CO for JSR Combustion Temperature of 1790 K and Residence Time of 2.3 ± 0.1 ms. The SPP Conditions are Outlet Temperature of 623 K, and 1^{st} to 2^{nd} Stage Airflow Ratio of 1.

The combustion field of the atmospheric pressure jetstirred reactor consists of a turbulent flame zone on and near the jet-centerline of the reactor, surrounded by the recirculating post-flame zone, which accounts for the bulk of the reactor. The flame zone volume is about 5-10% of the JSR volume, contains significant chemical energy release and exhibits peak concentrations of CO (of about 1-2% by mole). These points are known from sampling measurements for CO, CO₂ and O₂ on a path across the reactor and through the centerline (see Lee et al., 1999). Because the oxidation of CO is relatively slow at 1 atm pressure and because the backmixing delays CO burnoff, the CO levels of the recirculating post-flame zone only fall to about 0.15 to 0.4% by mole. These data are plotted in Fig. 10. On the other hand, equilibrium levels for CO for the temperature and stoichiometry conditions of the recirculating post-flame zone are much lower - about 0.005 to 0.007% by mole. Recombination of the active species O, H and OH is also relatively slow in the 1 atm reactor. The estimated chemical time for O-atom recombination under the present conditions is 10-20 ms (Nicol, 1995). This is significantly longer than the 2.3 ms residence time of the JSR. Thus, the O-atom remains at super-equilibrium levels throughout the reactor. This indicates significant formation of NO by O-atom attack on N2 for most points in the reactor. The mechanisms at work are the nitrous oxide and Zeldovich mechanisms.

The CH radical, on the other hand, is shorted-lived, resides mainly in the flame zone and does not survive into the postflame zone. Thus, prompt NO formation caused by the attack of the CH radical on N_2 mainly occurs in the flame zone.

Studies by Steel et al. (1998), Bengtsson et al. (2000) and Rutar et al. (2000) used a model of two perfectly stirred reactors (PSRs) in series to chemical kinetically study JSRs. This is the 2-PSR model. The first PSR simulates the flame zone, that is, the region of rapid oxidation and maximum free radical concentrations, while the second PSR simulates the recirculating post-flame zone. In Rutar et al. (2000), two independent methods are used to determine the fraction of the reactor that is the flame zone. In one method, the thickness of the turbulent flame zone is estimated from the literature results for premixed turbulent flame speed, while in the second method, the modeled values of both NO_X and CO are matched to the experimental values by adjusting the relative sizes of the two PSRs. The two methods show agreement. For the Damköhler number of 1.3 of the present research, the results of Rutar et al. (2000) indicate a flame zone size of about 10% of the reactor volume.

The chemical kinetic mechanism used for the present modeling of the methane, methanol, ethane and propane flames is GRI 3.0 (Smith et al., 1999). The computations are performed for the measured fuel and air flow rates of the experimental reactor. The first PSR is assumed adiabatic, since the rate of chemical energy release is large relative to the rate of heat loss for this zone. The second PSR is assigned the corrected measured temperature of 1790 K for the recirculation zone. Results from the 2-PSR modeling of NO_X are listed in Table 2. In this modeling, the first PSR has 5% of the reactor total residence time, and the second PSR has 95%.

Fuel	% Difference in NO _X of Model to Measurement	% NO _x by Zone PSR1:PSR2	% of NO _x as Prompt NO _x	
Methanol	-33%	20%:80%	5%	
Methane	+12 to +21%	60%:40%	34%	
Ethane	-6 to -19%	50%:50%	30%	

Table 2. Results for NO_x from the 2-PSR Modeling

The results in Table 2 indicate reasonable agreement of the modeled to the measured NO_X . The modeling shows the distinct difference between NO_X formation for methanol and methane-ethane. Little prompt NO_X is formed during the combustion of methanol. This is responsible for the relatively small percentage of NO_X formed in the methanol flame zone. On the hand, the modeling for methane and ethane shows about a 50:50 division in the NO_X formed in the flame and post-flame zones. Also, prompt NO_X (formed exclusively in PSR1) accounts for about $1/3^{rd}$ of the total NO_X modeled.

In subsequent modeling, the first PSR is split into two zones – an initial PSR operating at incipient blowout, followed by a second PSR. The initial PSR is meant to simulate the thin flame fronts, while the second PSR is meant to simulate reaction in the balance of the flame zone. The concluding PSR is the recirculating post-flame zone, as above. The initial PSR is assumed to be adiabatic, while the 2nd and 3rd PSRs are assigned the measured temperature of 1790 K. The initial PSR has a very short residence time. The 2nd PSR is assigned 10% of the reactor residence time, while the 3rd PSR is assigned the balance of the residence (i.e., almost 90%).

The three PSRs in series model shows good agreement to the measurements and simulates the increase in NO_X from methanol to methane and with increasing C/H ratio. The results are shown in Table 3 below.

Table 3. Comparison of NO _x by the
3-PSR Model to the Measured NO _x
[All NO _x expressed as ppmv (15% O_2 dry)]

Fuel	Modeled	Measured
Methanol	2.8	3.3
Methane	5.2	4.7-5.1
Ethane	5.2	5.3-6.2
Propane	5.9	5.8-6.5

The GRI 3.0 mechanism does not consider hydrocarbon fuels of order greater than C_3 . For the C_5 to C_{16} alkanes, toluene, benzene and the blended fuels studied, no satisfactory chemical kinetic mechanism for fuel oxidation with nitric oxide formation has been identified (though some have been tested) in the present work.

In order to chemically kinetically model the full range of fuels tested, fast oxidative pyrolysis is assumed. That is, CO and H_2 are the fuels fed into the models and the O_2 input is debited, per the following chemical equation:

$$C_{x}H_{y} + \frac{x}{2}O_{2} \rightarrow xCO + \frac{y}{2}H_{2}$$
(5)

The 1st PSR of the two and three PSR models is assigned the average temperature found in the methanol, methane, ethane and propane computations above and the 2nd and 3rd PSRs are again assigned the experimental temperature of 1790 K. The mechanism used is that due to Miller and Bowman (1989). This mechanism is used so that the NO_X resulting from the attack of O-atom on N₂ may be exclusively studied. Prompt NO_X is not a factor, since no hydrocarbon material is injected into the model reactor. Additionally, NO_X formed from NNH, which is a factor in the GRI 3.0 mechanism, is not present in the Miller-Bowman mechanism. The only mechanisms forming NO_X are the Zeldovich and nitrous oxide mechanisms.

The results are shown in Table 4 below. The modeling replicates the trend of the measurements, i.e., the increase in NO_X with increasing C/H ratio. The modeling shows an

approximate doubling in the NO_X from methane to benzene. The doubling is also seen in the experiment.

Fuel	C/H = 2CO/H ₂	2-PSR NO _X	3-PSR NO _X	Measured NO _X
Methane	0.25	3.0	3.7	4.7-5.1
n-Hexadecane	0.47	4.2	4.7	6.8-7.1
Benzene	1.00	6.4	6.5	10.2

Table 4. Modeling of NO _x as a Function of CO/H ₂ Ratio	כ
Also Listed are the NO _X Measurements of this Study	

The results provide evidence for the finding that NO_X increases with C/H ratio, because of increasing attack of Oatom on N₂ leading to increasing amounts of NO_X formed by the Zeldovich and nitrous oxide mechanisms.

The increasing amounts of O-atom result from the increasing amounts of CO oxidized. Key reactions are:

$$CO + OH \rightarrow CO_2 + H$$
 (6)

$$H + O_2 \rightarrow O + OH \tag{7}$$

The impact of O-atom on NO formation by the Zeldovich and nitrous oxide mechanism is contained in the following reactions.

$$O + N_2 \rightarrow NO + N$$
 (8)

$$N + O_2 \rightarrow NO + O \tag{9}$$

$$O + N_2 + M \rightarrow N_2 O + M \tag{10}$$

$$N_2 O + O \rightarrow NO + NO \tag{11}$$

In the case of the experiment, complex hydrocarbonnitrogen chemistry, leading to variable prompt NO formation is also occurring. How prompt NO_x changes with increasing C/H ratio under lean premixed combustion is unclear and must await chemical mechanism developments for large fuel molecules.

CONCLUSIONS AND RECOMMENDATIONS

The major findings of this study are as follows:

1. Low NO_X emissions are obtained for pure and practical blended liquid fuels burned under lean, fully vaporized, well premixed, high intensity combustion

conditions. The NO_X emission for No. 2 diesel fuel is about double that of natural gas, given the same combustion temperature and residence time.

2. The staged prevaporizing-premixing injector, that relies on two stages of air temperature, is described and used to obtain the fuel-air stream fed into the combustor. The operating conditions of the injector as used in the present research are discussed. Measurements and inspection of the injector indicate the NOx measurements were obtained for a fully prevaporized, well premixed inlet stream devoid of pre-flame reaction of the mixture.

Recommendations for future work on the staged prevaporizing-premixing injector are the following:

- 1. Operation for significantly reduced residence times within the injector. [Preliminary testing at double the flow rate of the present paper has already been conducted. This showed no significant increase in NO_X, indicating little if any degradation in the fuel vaporization and fuel-air mixing within the injector.]
- 2. Testing of the injector at elevated pressure, beginning at about 10 atm and ultimately approaching 30 atm.

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REFERENCES

Abraham, J., Williams, F.A. and Bracco, F.V. (1985), "A Discussion of Turbulent Flame Structure in Premixed Charges." SAE Paper 850345, in *Engine Combustion Analysis: New Approaches*, P-156, pp. 27 – 43.

Bengtsson, K. U. M., Benz P., Schaeren, R., and Frouzakis, C. E. (1998), "NyOx Formation in Lean Premixed Combustion of Methane in a High-Pressure Jet-Stirred Reactor," Proc. Combust. Inst., 27, pp. 1393-1401.

Capehart, S.A., Lee, J.C.Y., Williams, J.T. and Malte, P.C. (1997), "Effect of Fuel Composition on NO_X Formation in Lean Premixed Prevaporized Combustion," ASME Paper No. 97-GT-336 presented at the International Gas Turbine and Aeroengine Congress & Exhibition, Orlando, FL.

Dibble, R.W. (1999), Personal Communication, University of California, Berkeley, CA.

Göttgens, J., Mauss, F. and Peters, N. (1992), "Analytical Approximations of Burning Velocities and Flame Thicknesses of Lean Hydrogen, Methane, Ethylene, Ethane, Acetylene and Propane Flames," *Twenty-Fourth Symposium (International) on Combustion*, pp. 129 – 135, The Combustion Institute, Pittsburgh, PA.

Lee, J.C.Y., Malte, P.C. and Nicol, D.G. (1999), "NO_X as a Function of Fuel Type: C_1 – to – C_{16} Hydrocarbons and

Methanol," ASME Paper No. 99-GT-270 presented at the International Gas Turbine and Aeroengine Congress & Exhibition, Indianapolis, IN.

Lee, J.C.Y. (2000), "Reduction of NO_X Emission for Lean Prevaporized-Premixed Combustors," Ph.D. Dissertation, University of Washington, Seattle, WA.

Lee, J.C.Y. and Malte, P.C. (2000), "Staged Prevaporizer-Premixer," U.S. Patent No. 6,174,160B1, Jan. 16, 2001.

Lefebvre, A.H. (1989), *Atomization and Sprays*, Taylor & Francis, Bristol, PA.

Mansour, A., Benjamin, M.A., Straub, D.L. and Richards, G.A. (2000), "Application of Macrolamination Technology to Lean, Premix Combustion," ASME Paper No. 2000-GT-0115 presented at the International Gas Turbine and Aeroengine Congress and Exhibition, Munich, Germany.

Miller, J.A. and Bowman, C.T. (1989), "Mechanism and Modeling of Nitrogen Chemistry in Combustion," *Prog. in Energy and Combustion. Science*, Vol. 15, pp. 287 – 338.

Mongia, R.K. (1998), "Optical Probe for Measuring the Extent of Air and Fuel Mixing in Lean Premixed Combustors and the Effect of Air and Fuel Mixing on Combustor Performance," Ph.D. Dissertation, University of California-Berkeley, Berkeley, CA.

Nicol, D.G. (1995), "A Chemical Kinetic and Numerical Study of NO_X and Pollutant Formation in Low-Emission Combustion," Ph.D. Dissertation, University of Washington, Seattle, WA.

Perrin, M.Y. and Hartmann, J.M. (1989), "High Temperature Absorption of the 3.39 μ m He-Ne Laser Line by Methane," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 42, No. 6, pp. 459 – 464.

Rutar, T., Malte, P.C., and Kramlich, J.C. (2000), "Investigation of NO_X and CO Formation in Lean Premixed, Methane-Air, High-Intensity, Confined Flames at Elevated Pressures." *Twenty-Eighth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA (in print.)

Rutar, T. and Malte, P.C. (2001), "NO_X Formation in High-Pressure Jet-Stirred Reactors with Significance to Lean-Premixed Combustion Turbines," paper submitted to ASME Turbo Expo 2001.

Smith, G.P., Golden, D.M., Frenklach, M., Moriarty, N.W., Eiteneer, B., Goldenberg, M., Bowman, C.T., Hanson, R., Song, S., Gardiner, W.C. Jr., Lissianski, V. and Qin, Z. (1999), *GRI-Mechanism 3.0*, http://www.me.berkeley.edu/gri_mech.

Steele, R.C., Malte, P.C., Nicol, D.G. and Kramlich, J.C. (1995), "NO_X and N₂O in Lean-Premixed Jet-Stirred Flames," *Combustion and Flame*, Vol. 100, No. 3, pp.440 – 449.

Steele, R.C., Tonouchi, J.H., Nicol, D.G., Horning, D.C., Malte, P.C., and Pratt, D.T. (1998), "Characterization of NOx, N_2O , and CO for lean-premixed combustion in a high-pressure jet-stirred reactor," Transactions of the ASME, Journal of Engineering for Gas Turbines and Power, 120, pp. 303-310.

Tsuboi, T., Inomata, K., Tsunoda, Y., Isobe, A. and Nagaya, K. (1985), "Light Absorption by Hydrocarbon Molecules at 3.392 µm of He-Ne Laser," *Japanese Journal of Applied Physics*, Vol. 24, No. 1, pp. 8 – 13.

Yoshiyama, S., Hamamoto, Y., Tomita, E. and Minami, K. (1996), "Measurement of Hydrocarbon Fuel Concentration by Means of Infrared Absorption Technique with $3.39 \ \mu m$ He-Ne Laser," *JSAE Review*, Vol. 17, pp. 339 - 345.