NOx DEPENDENCY ON RESIDENCE TIME AND INLET TEMPERATURE FOR LEAN-PREMIXED COMBUSTION IN JET-STIRRED REACTORS

Teodora Rutar[‡], **David C. Horning, John C. Y. Lee, and Philip C. Malte**
Department of Mechanical Engineering
Box 352600
University of Washington
Seattle, WA 98195-2600
(‡ Corresponding author)

ABSTRACT

The effect of the residence time variation on NOx formation in high-intensity, lean-premixed (LP) methane combustion is explored through experiments conducted in a high-pressure jet-stirred reactor (HP-JSR) operated at 6.5 atm pressure. The residence time is varied between 0.5 ms and 4 ms, holding the measured reactor recirculation zone temperature constant at 1803 K. Air preheat is not used. The results indicate a minimum NOx level of 3.5 ppmvd (15% O_2) for reactor mean residence times between 2 and 2.5 ms. As the residence time is reduced from 2.0 ms to 0.5 ms, the NOx increases, consistent with a spreading of super-equilibrium concentrations of free-radicals throughout the reactor. For the shortest residence times examined, PSR modeling agrees with the NOx measurements. At long residence times, (i.e., above 2.5 ms), the measured CO behavior indicates the super-equilibrium free radicals, and thus the rapid NOx production, are confined mainly to the jet zone of the reactor. For the long residence time range, the measured NOx increases with increasing residence time, and is significantly less than the PSR predictions. A simple two-zone model of the HP-JSR is used to interpret and evaluate the NOx formation.

Experiments exploring the effect of inlet temperature on NOx are conducted in an atmospheric pressure, methane-fired, jet-stirred reactor (A-JSR). The reactor temperature is held constant at 1788 K, and the inlet mixture temperature is varied between the no-preheat case and 623 K. These experiments show that increasing the inlet air temperature over the full range tested decreases the NOx by about 30%. Several explanations are offered for the behavior. For both reactors, i.e., the HP-JSR and A-JSR, single inlet jet nozzles are used. The results lead to a practical conclusion that very low NOx levels can be achieved for combustion in strongly back-mixed reaction cavities adjusted to optimal residence time and inlet temperature.

INTRODUCTION

This study has been undertaken to determine if a jet-stirred reactor operated in lean-premixed (LP) mode at high pressure could attain well-stirred behavior for NOx formation. Initial work by Steele (1995) and Steele et al. (1996) on NOx formation in a high-pressure jet-stirred reactor (HP-JSR) showed this not to be the case. That is, the NOx was indicated to form non-uniformly in the reactor, mainly in the inlet jet, rather than uniformly, as in a well-stirred reactor (WSR). However, Steele (1995) only examined residence times of 2.0 and 4.0 ms. In the present work, a reactor, geometrically similar to Steele's, has been operated at 6.5 atm for residence time as low as 0.5 ms, and examined for WSR formation of NOx. As a consequence, the NOx dependency on residence time has been examined over an eight-fold range, from 0.5 to 4.0 ms, while holding measured combustion temperature constant. Interestingly, minimum NOx is formed in the 2.0 to 2.5 ms range. In an attempt to further decrease the NOx, inlet temperature was increased, while holding combustion temperature constant. (That is, the fuel-air ratio was decreased.) These measurements have been performed in the atmospheric pressure jet-stirred reactor (A-JSR), and clearly show a decrease in NOx with increasing inlet temperature.

Laboratory jet-stirred reactors provide important process data on the effect examined, in this case the NOx, even if not well stirred, i.e., even if the chemical effect examined is not uniformly dispersed throughout the reactor. If the ratio of the chemical time to the mixing time can be increased to the point where well-stirred behavior is approached, the data can be interpreted by chemical kinetics. That is, global rates of reaction can be obtained, and the measurements can be compared to full chemical kinetic mechanisms, thereby gaining insight and providing a test of the full mechanism. Thus, it is important to strive for WSR behavior in the jet-stirred reactor (JSR).

When examining the fixation of air-nitrogen to NOx, two chemical times are of importance: the lifetime of the CH-radical and the lifetime of the O-atom. The lifetime of the CH-radical in flames is very short, less than about 0.1 ms. Thus, WSR behavior for prompt NOx, initiated by reaction between CH and N_2, is essentially impossible to obtain. But, in lean-premixed (LP) combustion, this may be of secondary importance, especially since O-atom should be the free radical that mainly impacts NOx formation. The impact occurs through the nitrous oxide and Zeldovich mechanisms (Nicol et al., 1995). O-atom has a lifetime of order 10 ms in atmospheric pressure flames, and consequently it appears possible to operate atmospheric pressure, lean, methane-fired JSR's essentially well-stirred for NOx formation, (Steele et al., 1996). At high pressure, however, the O-atom lifetime falls to order 1 ms, (Nicol, 1995). Thus, WSR behavior becomes difficult, unless the reactor is operating at very short residence time.

This is indicated in the measurements of Steele et al. (1996). Those results indicate NOx formation mainly in the center of the reactor, i.e., in the jet zone. The NOx formation was not dispersed throughout the HP-JSR. That is, in Steele's (1995) measurements, the zone of high free-radical concentrations, and thus high NOx formation, was confined mainly to the jet zone.

Optical access to the HP-JSR is very limited. Thus, the free radicals are not measured. However, Nicol (1995) showed a fairly strong correlation between O-atom and CO for lean-premixed combustion. Therefore, in the present work, measurements of CO across the reactor are used as an indicator of free radical (O, H, OH) concentrations and the degree to which NOx formation moves from the jet zone to the bulk of the reactor.

The HP-JSR is operated at constant measured temperature, i.e., the recorded thermocouple temperature is held at 1803 ± 5 K. Because heat loss from the thermocouple varies with flow conditions in the reactor, heat transfer analysis of the reactor and the thermocouple has been undertaken to estimate rather closely the gas temperature. The analysis indicates the gas temperature increases from about 1825 K at 0.5 ms to about 1880 K at 4.0 ms. Reactor pressure is held constant at 6.5 atm, and the flow rate is increased by eight-fold, providing residence times from 0.5 to 4.0 ms. For the A-JSR tests, where the inlet temperature effect is studied, the measured, radiation-corrected combustion temperature is held constant at 1788 K. The A-JSR residence time is 3.5 ms, nominal, and the mixture inlet temperature is varied from the non-preheat case to 623 K.

As shown below, the NOx concentration is observed to increase as the residence time is reduced from 2.0 to 0.5 ms, and it appears there is an NOx minimum in the 2.0 to 2.5 ms range. The increase in NOx with decreasing residence time (above 2.5 ms) was anticipated, since the perfectly-stirred reactor (PSR) solution for the HP-JSR experimental conditions gives an NOx concentration substantially above the level measured by Steele (1995) at 2.0 and 4.0 ms. The minimum of NOx in the 2.0 to 2.5 ms range was not anticipated, however, but can be explained if a tradeoff in the effect of residence time is considered. At long residence times, (i.e., longer than 2.5 ms), the predominant effect is increased time for NOx formation, while at short residence times, (i.e., shorter than 2.0 ms), the predominant effect is mixing intensity. That is, at short residence time, the strong continual mixing of fresh reactants into the gases recirculating in the reactor acts to maintain free radical levels high throughout the reactor. This overcomes the effect of reduced residence time available for NOx production. At the long residence times, since the mixing intensity is low, the free radicals responsible for the NOx formation have time to decay towards equilibrium levels. NOx forms at a high rate in a jet-zone of the reactor, and then at a low rate in the bulk of the reactor.

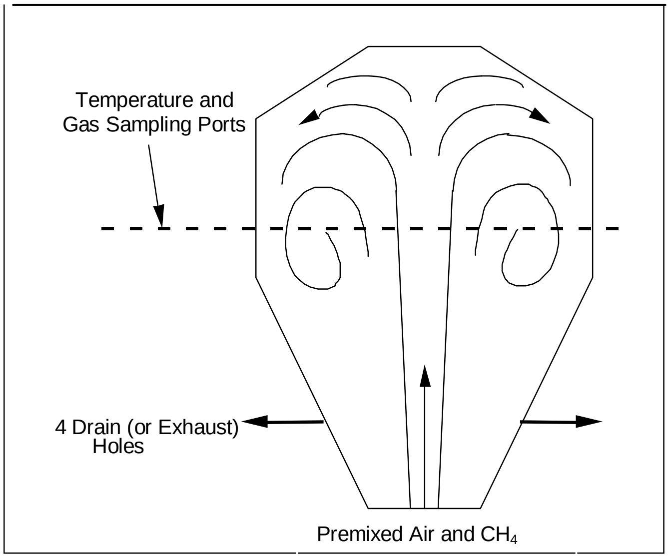

Fig. 1. Schematic of the jet-stirred reactor cavity

A simple model is introduced to explain the NOx behavior. The model is based on two-zone NOx formation: 1) high-rate formation in the jet zone, which is governed primarily by the reactions with super-equilibrium free radicals; and, 2) low-rate formation in the recirculation zone, which is governed by reactions with the approximately equilibrium O-atom. The fraction of the overall JSR residence time the gases spend in those two zones varies as a function of the overall JSR residence time.

In the following sections of the paper, the experimental approach is summarized, the reactor temperature analysis is explained, the measurements and their interpretation for the HP-JSR and A-JSR are presented, and practical application to a design for a low-emission combustor is shown.

EXPERIMENTAL APPROACH

The residence time effect on the NOx formation is studied at 6.5 atm in the high-pressure jet-stirred reactor (HP-JSR), whereas the inlet temperature effect is studied in the atmospheric jet-stirred reactor (A-JSR). The two reactors are geometrically similar. The volume of the HP-JSR is 1.5 cm^3 and that of the A-JSR is 15.8 cm^3. The schematic of the axisymmetrical reactor cavity cross-section is shown in Fig. 1. The HP-JSR may be thought of as a micro reactor. The diameter at the widest point is 0.012 m, height is 0.020 m, and the inlet nozzle diameter is 0.0014 m, giving the height/diameter ratio of 14.4. Though geometrically similar to the HP-JSR used by Steele (1995), the present reactor is 25% smaller then Steele's reactor, and the jet diameter is 40% larger. The smaller volume promotes short residence time, and the larger jet diameter permits high mass flow rate, and thus short residence time operation. The reactor material is cast alumina, whereas Steele (1995) used cast zirconia. With the changes made in the HP-JSR, it is possible to obtain 0.5 ms operation with an inlet jet that is close to sonic. The A-JSR is ten times larger in volume than the HP-JSR. Diameter at the widest point is 0.025 m, height is 0.044 m, and the inlet nozzle diameter is 0.002 and 0.004 m, giving the height/diameter ratio of 22 and 11, respectively. Differences compared to the atmospheric pressure, 15.8 cm^3 JSR used by Steele (1995) are the refractory material (cast alumina in this case), thicker wall, and different inlet jet diameter.

With the single inlet jet diameter of 1.4 mm, the HP-JSR could be run over the 0.5 to 4.0 ms residence time range. Because of the eight-fold range in the corresponding flow rates, the jet velocity and system pressure loss vary significantly. For operation at 0.5 ms mean residence time, the pressure loss is 45% and the jet velocity is close to sonic. Whereas, for operation at 4.0 ms mean residence time, the pressure loss is about 3% and the velocity is about 60 m/s. For the A-JSR, the residence time is held constant at 3.5 ms (nominal).

Both reactors use single inlet jets, and the fuel is exclusively methane.

The methane and air entering the JSRs are premixed in a pre-chamber positioned below the jet nozzle and the JSR. The residence time in the pre-chamber exceeds 100 ms for all of the flow rates used in this study. Calculations indicate the premixer residence time is two orders of magnitude greater than the eddy turnover times associated with the baffles in the premixer. This argues for the assumption that the gases enter the JSR well premixed. Further, because of the mixing intensity within the JSRs, any unmixedness entering the reactor tends to be washed-out. Calculations with a partially stirred reactor model indicate that the effect of unmixedness on NOx formation in JSRs is weak to negligible (Rutar et al., 1997).

The sample-probing and temperature measurements are done at the two-thirds height of the JSR, which is the widest part of the reactor, as shown in Fig. 1. Gas sampling is done with small probes. A ceramic probe is used for the HP-JSR experiments, and a quartz probe is used for the A-JSR experiments. The quartz suffers intense devitrification in the HP-JSR, and its use is not practical. Temperature measurements are described in the next section. The HP-JSR facilities are fully described in Steele et al. (1996), and the A-JSR facilities are fully described by Capehart et al. (1997).

GAS TEMPERATURE

Knowledge of gas temperature is important for the interpretation of NOx measurements. Two temperature zones are observed in JSRs – the jet zone and the recirculation zone. Steele (1995) and Steele et al. (1996) have shown typical temperature profiles in the JSRs. Temperature sharply increases from the jet centerline to the edge of the jet zone. Farther out in the reactor and throughout the recirculation zone, the temperature is uniform. The temperatures reported herein are measured with the thermocouple positioned in the middle of the recirculation zone. This region has the lowest level of CO, which might react at the thermocouple surface and, consequently, increase the measured temperature over the true gas temperature. All of the temperature measurements are done with R-type thermocouples coated with alumina based coating. Thermocouples are inspected daily for cracks in the alumina to assure minimal catalytic reaction at the surface of the thermocouple wires and bead. The measured reactor temperature is held constant at 1803 ± 5 K throughout the HP-JSR experiments, as shown by the dark circles in Fig. 2. During the experiments, sufficient time was allowed for the reactor to reach steady state temperature conditions. Optical pyrometry is used to measure the HP-JSR inside wall temperature. These measurements, shown in Fig. 2 as dark triangles, have been adjusted for finite transmissivity through the viewing ports of the high pressure housing.

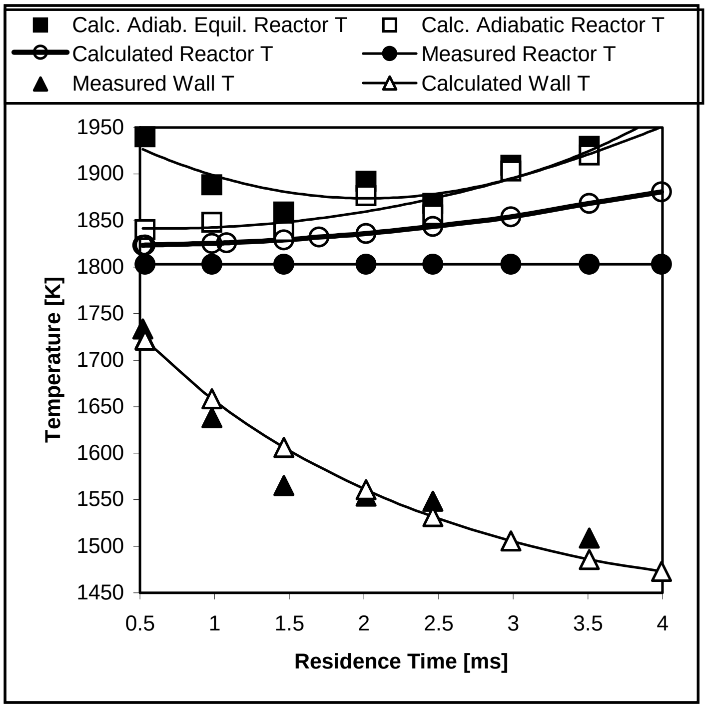

Fig. 2. HP-JSR temperature measurements and calculations.

As noted in Fig. 2, the reactor inside wall temperature falls with increasing residence time. The increasing temperature difference between the reactor gas and the inside wall is indicative of increasing thermal resistance in the boundary layer as the reactor mass flow rate and velocity decrease with increasing residence time.

Although the HP-JSR measurements are conducted for constant thermocouple temperature, the gas temperature in the reactor increases with increasing residence time. The gas temperature in the recirculation zone is calculated by two methods. The first method is based on a heat balance for the thermocouple. Convective thermocouple heating is balanced by radiative loss to the walls and ports of the reactor. As the reactor residence time increases and velocity decreases, the convective heat transfer coefficient for the thermocouple surface decreases. Further, as shown in Fig. 2, the wall temperature drops with increasing residence time. This increases the radiative loss of the thermocouple, since the thermocouple views a surface of decreasing temperature. Both effects, i.e., the greater radiative loss and the smaller convection coefficient, drive up the temperature difference between the gas and thermocouple, and thus indicate an increasing gas temperature with increasing residence time in the experiment.

The second method is based on a procedure that considers the chemical energy release in the reactor, and the reactor heat loss. In the first step of the procedure, the adiabatic equilibrium temperature for the measured fuel-air equivalence ratio and measured mixture inlet temperature is computed. This is plotted in Fig. 2 with dark squares. The fuel-air equivalence ratio is determined in two ways. It is based on the measurement of the sum of CO_2 and CO in the recirculation zone of the reactor, i.e., on the total carbon, and on the measurements of the O_2 concentration in this zone. The fuel-air equivalence ratio calculated with these two methods is only up to 1.5% different. For the present experiments, unburned hydrocarbon has a weak influence on the carbon balance. Reactor profiles of unburned hydrocarbons were measured at different reactor temperatures at 0.5 and 1.0 ms residence times using a packed-column, FID chromatography. Based on these measurements, the hydrocarbon levels estimated for the recirculation zone in the present experiments cannot exceed a few hundreds of parts per million. This would change the calculated fuel-air equivalence ratio based on measured CO and CO_2 concentrations by less then 1%. The mixture inlet temperature is measured with a thermocouple located in the downstream end of the premixer. Because of heat transfer from the reactor, some preheating of the reactants occurs. Measurements of inlet mixture temperature for residence times of 2.5 to 4.0 ms have been extrapolated to the full regime of residence times, and used in this analysis. At 4.0 ms the inlet temperature is measured as 384 K, whereas at 0.5 ms it is estimated as 330 K. Inlet temperature decreases with decreasing residence time, because the higher gas flow rates inhibit the heating of the inlet gases.

A minimum fuel-air equivalence ratio of 0.68 occurs in the 1.5 ms to 2.5 ms residence time range. At longer residence times, the mixture is enriched to overcome heat loss, and reaches 0.73 at 4.0 ms. At shorter residence times, incomplete combustion occurs, i.e., CO is not oxidized to CO_2, and the fuel-air equivalence ratio is enriched to overcome this. At 0.5 ms, the fuel-air equivalence ratio is 0.74.

As the second step in the gas temperature calculation, the gas temperature is adjusted for the unburned CO. If this CO were burned, significant energy would be released. Our estimates, (using chemical equilibrium and chemical reactor modeling), show that 1% ppmv CO, if oxidized forming CO_2, increases the gas temperature about 80 K. The adiabatic equilibrium temperature is debited using this result, giving the adiabatic temperature plotted in Fig. 2 as open squares. Detailed CO measurements are shown in the next section (see Fig. 5). For the recirculation zone, i.e., for the $(R/Rmax)^2$ between 0.36 and 1.00, the volume-averaged, as-measured CO increases from about 0.05% (dry) at 4.0 ms residence time to about 0.65% (dry) at 0.5 ms. The CO measurements are adjusted for CO loss in the sampling probe based on the chemical kinetic modeling of the probe reactions by Steele (1995) and Horning (1996). The probe loss is dependent on the initial CO concentration and increases at higher CO levels, because the reaction rate for CO destruction is dependent on the initial CO concentration as well as the OH concentration. In lean-premixed combustion there is tendency for OH levels (and O-atom levels) to correlate with CO levels (Nicol, 1995). The CO concentration in the reactor [%, wet] is calculated from the measured CO (CO meas.) by the following equation, which is a curve fit from the modeling results given by Steele (1995) and Horning (1996).

$$[\text{CO in reactor, \% wet}] = [\text{CO meas., \% wet}]/\{1.6327-0.1366 \ln[\text{CO meas., ppm wet}]\} \quad (1)$$

The third step in the calculation of the reactor temperature is the treatment of the reactor heat loss. This is conducted using engineering analysis to estimate the resistances for the convective, conductive, and radiative heat transfer processes. Because of the small view factor from the inside of the reactor to the outside environment, the radiative resistance is high, and because of the high gas velocities inside the reactor, the internal convective resistance is low. Comparison of the measured and calculated inside wall temperature serves as a check on the calculation. As shown in Fig. 2, this agreement is good, and provides confidence in the heat loss calculation for the reactor. The loss in gas temperature predicted by the reactor heat loss is about 10 K at 0.5 ms and 68 K at 4.0 ms. Consequently, the difference between the predicted gas temperature and the measured thermocouple temperature is 28 K at 0.5 ms, and 80 K at 4.0 ms. These values are in close agreement with the independent calculation of thermocouple heat loss, which gives the following difference between the gas temperature and measured temperature: 13 K at 0.5 ms, and 75 K at 4.0 ms. The two methods, because of this close agreement, are averaged to give the final result for the reactor gas temperature. This average is plotted in Fig. 2 as the open circles. In the region from 0.5 to 2.0 ms, the reactor gas temperature (in the recirculation zone) is nearly constant at 1825 K, whereas in the region from 2.0 to 4.0 ms, the reactor gas temperature increases to 1880 K.

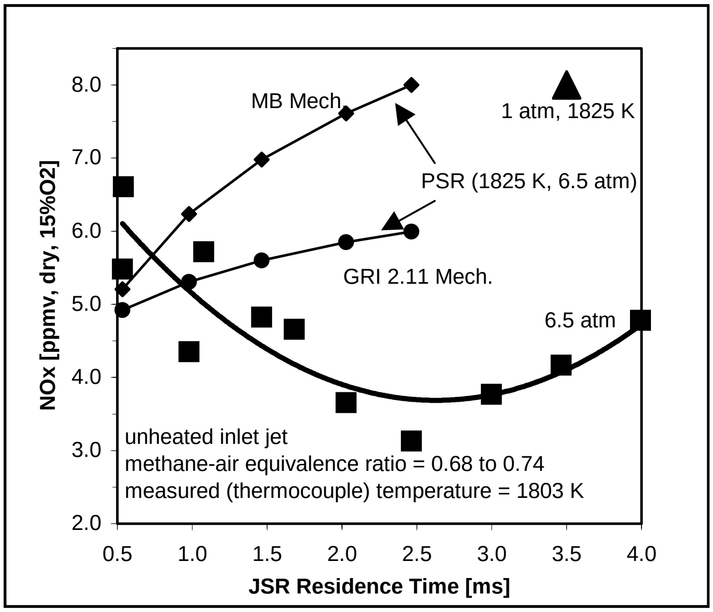

Fig. 3. NOx versus residence time at 6.5 atm for methane combustion. Measured temperature is 1803K.

NOx AS A FUNCTION OF MEAN RESIDENCE TIME IN THE HP-JSR: RESULTS AND DISCUSSION

The effect of the residence time on measured NOx is shown in Fig. 3, for the pressure of 6.5 atm. Over the mean residence time range, starting with 0.5 ms, the NOx concentration drops substantially with increasing residence time, attains a minimum in the vicinity of 2.5 ms, and then increases as the time is increased to 4.0 ms. The measurements of NOx are for the recirculation zone of the HP-JSR. Generally, the recirculation zone is nearly uniform in temperature and NOx concentration, and the measurements of NOx may be treated as reactor emissions.

In order to more exactly assess the influence of the residence time on the NOx concentration, the data of Fig. 3 are corrected to the NOx concentration which would occur if the reactor gas temperature, (i.e., recirculation zone temperature), were constant at the 1825 K, (the gas temperature of the 0.5 ms case). The NOx correction is made using the NOx temperature dependence for lean-premixed methane combustion developed by Steele (1995):

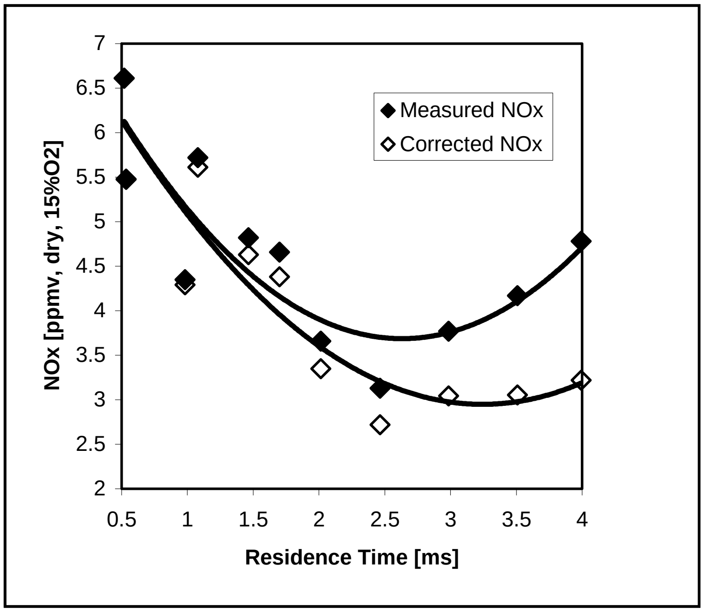

Fig. 4. Measured and corrected NOx data. Corrected values correspond to a reactor temperature of 1825 K.

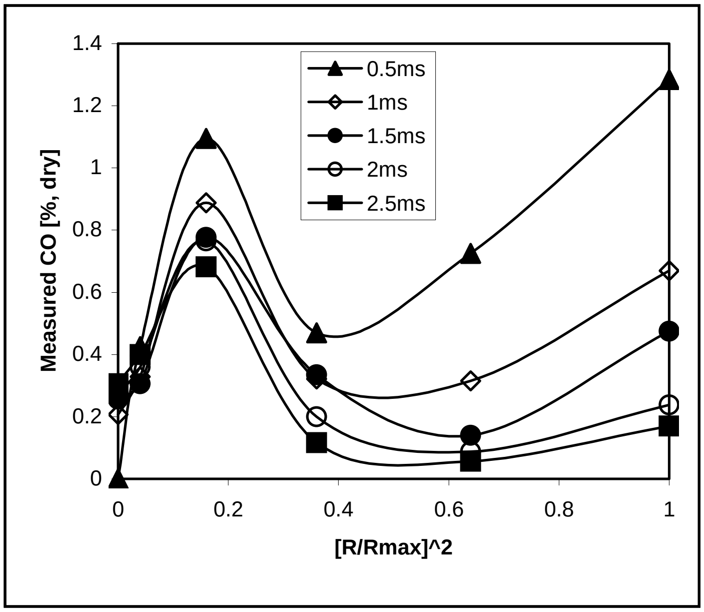

Fig. 5. CO profiles in the HP-JSR for residence times between 0.5 and 4.0 ms.

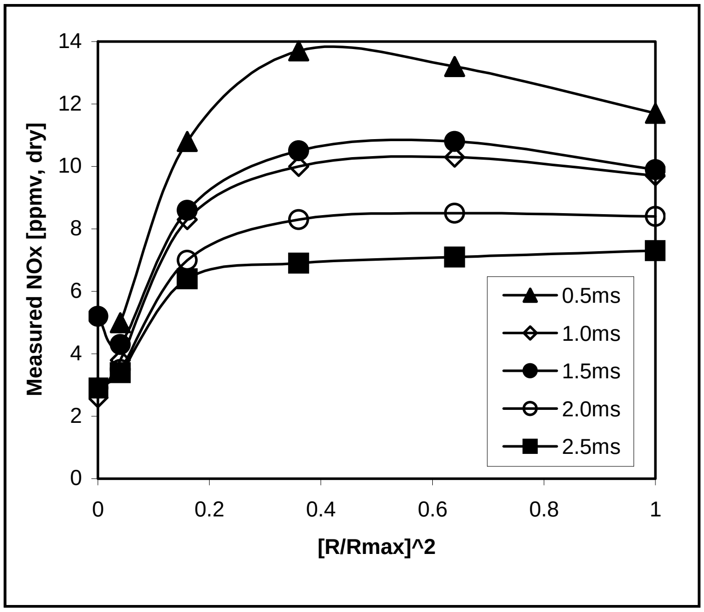

Fig. 6. NOx profiles in the HP-JSR for residence times between 0.5 and 4.0 ms.

$$\mathrm{NOx}\ [\mathrm{ppmvd},\ 15\%\ O_2] = 1.724 \cdot 10^6 \exp(-23650/T). \qquad (2)$$

Figure 4 shows the measured data and data corrected to a constant temperature of 1825 K. The correction suggests about 30% of the NOx formed at 4.0 ms comes from the reactor temperature rise, and the increase in NOx above the 2.5 ms case is mainly caused by the increase in the gas temperature.

Profiles of CO and NOx concentration measured between the centerline and the wall of the HP-JSR at the two-thirds reactor height are shown in Figures 5 and 6, respectively. The CO profiles clearly show that as the mean residence time of the reactor is decreased, the recirculation zone becomes increasingly filled with high concentrations of CO. This implies a spreading of the free-radical rich gas from the jet zone (i.e., the centerline region) into the recirculation zone (i.e., the bulk of the reactor). For lean-premixed combustion, NOx should form mainly in the free-radical rich (high CO) regions due to attack of super-equilibrium concentrations of O-atom (and the CH radical) on N_2 through the Zeldovich and nitrous oxide mechanisms (and the prompt mechanism). In Fig. 6, one can note the decrease in the peak NOx as the residence time increases. For the data taken at 2.5 ms residence time, an increase of the NOx in the jet zone is noted followed by a near flattening out of the profile in the recirculation zone. This behavior, considered together with the sharp fall-off in the CO concentration at $(R/Rmax)^2 \cong 0.2$, suggests that the NOx forms predominantly in the jet zone (or jet shear layer). On the other hand, for 0.5 ms residence time, the NOx profile, together with the CO profile, suggests NOx formation in the recirculation zone. Evidence for this is the inverse correlation between the NOx and CO concentrations in the recirculation zone. In the region of $(R/Rmax)^2 \cong 0.4$, the NOx reaches its maximum and the CO reaches its minimum concentration. This region appears to be the *eye* of the recirculation zone. Here the NOx has greater time to form, and the CO has greater time to oxidize.

These results suggest a conceptual model for NOx formation in the HP-JSR. At the shortest mean residence times tested, there is insufficient time for the O-atom to relax to equilibrium concentration. [The characteristic O-atom relaxation time is about 1 to 2 ms for the pressures tested in the HP-JSR, per Nicol (1995) and Steele et al.

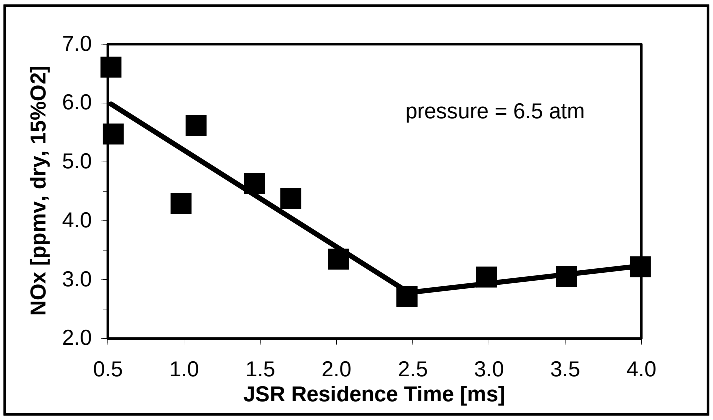

Fig. 7a. NOx data corrected to a constant temperature of 1825 K. Two linear curve-fits are used. One for data in the 0.5 to 2.5 ms range, and the other for the data in the 2.5 ms to 4.0 ms range.

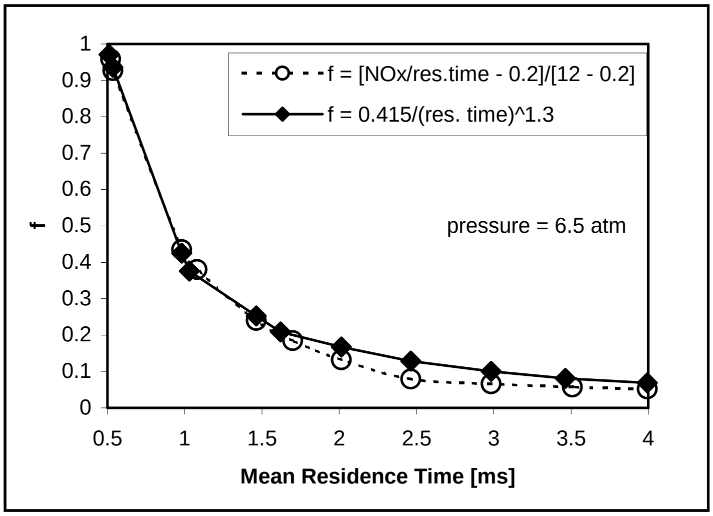

Fig. 7b. Function f, calculated using Eq. (3) and the power law, versus residence time.

(1996)]. Thus, there is an opportunity for the recirculation zone to maintain high O-atom concentration and to form NOx at a significant rate. On the other hand, as the mean residence time is increased, it appears that the free-radical rich, high NOx production region exists mainly in the jet zone (or jet shear layer), and the overall rate of NOx production decreases. For the longest residence times tested, the increase in NOx with residence time noted in the data is probably caused by two factors, i.e., an increase in reactor gas temperature and an increase in the time available for the NOx to form.

As the pressure is decreased, the O-atom relaxation time increases until it reaches a value of 10 to 20 ms for lean-premixed combustion at 1 atm (Nicol, 1995). In this case, the bulk of the reactor again becomes free-radical rich, and NOx forms at a high rate throughout most of the reactor. This is indicated in Fig. 3: note the datum point at 3.5 ms for the atmospheric pressure JSR operated at 1825 K, (thermocouple temperature corrected for radiation heat loss). The NOx concentration at 1 atm is about double that of the 6.5 atm reactor operating at the same residence time (3.5 ms).

Figure 3 also shows calculations of the NOx, assuming the HP-JSR to be a PSR operating at the measured conditions. The NOx production rate calculated at 0.5 ms is 10.1±0.3 ppmvd (15% O_2) per ms. The spread in the calculated value is caused by the two chemical kinetic mechanisms used. The GRI 2.11 (1995) mechanism gives less NOx production at the conditions tested than the Miller-Bowman (1989) mechanism. If the NOx measured at 0.5 ms (left most data points) is assumed to have formed uniformly in the reactor, then the measured NOx production rate is found to be 13.5±0.3 ppmvd (15% O_2) per ms. The agreement between the measured and calculated rates at the minimum residence time tested is relatively good. However, for the longer residence time tested, the PSR model significantly overpredicts the measured NOx.

Much slower rates of NOx formation are calculated when the O-atom concentration is assumed the equilibrium value. For conditions of 6.5 atm and 1825 K, the thermal NOx formation is only 0.05 ppmvd (15% O_2) per ms. The nitrous oxide mechanism, assuming the nominal concentration of 2 ppmvd N_2O measured for the reactor recirculation zone, and again using the equilibrium O-atom concentration (as well as the equilibrium H-atom concentration), forms NOx at about 0.15 ppmvd (15% O_2) per ms. Thus, the total NOx production rate for the recirculation zone under the assumption of equilibrium free-radical concentrations is about 0.2 ppmvd (15% O_2) per ms.

In order to explain the NOx production by a two-zone model, the following expression is introduced:

$$\mathrm{NOx} = \tau * [r_H * f + r_L * (1 - f)] \tag{3}$$

The terms r_H and r_L are the NOx production rates in the high- and low-NOx forming regions, respectively; τ is the residence time of the reactor; and f is the fraction of the residence time associated with the high-NOx production rate.

The function f is determined in a two step process. First, the NOx data for 6.5 atm, adjusted to 1825 K, are curve-fitted. The data are best fitted with two linear equations, one for 0.5 to 2.5 ms and the other for residence times greater than 2.5 ms, as shown in Fig. 7a. Then, the function f is determined from the fitted data, assuming r_H = 12 ppm/ms and r_L = 0.2 ppm/ms. (The term *ppm* denotes ppmv, dry @ 15% O_2.) The function f is plotted in Fig. 7b. For mean residence times below 2 ms, the function f is well approximated as $f = 0.415/\tau^{1.3}$. Thus, as the overall residence time of the reactor decreases, and the mixing intensity increases, NOx formation occurs predominately at the high production rate.

The high-NOx production rate used in the model, i.e., r_H = 12 ppm/ms, is a rounded off intermediate value between the measured NOx production rate of 13.5±0.3 ppm/ms and the calculated rate of 10.1±0.3 ppm/ms for the reactor operated at 0.5 ms residence time. The value of the low-NOx production rate, i.e., r_L = 0.2 ppm/ms, is the value estimated above assuming equilibrium free-radical levels. By this interpretation of the data, the fraction of the reactor time used in high-NOx production varies from f = 0.96 to 0.05. Under the minimum f condition, 75% of the NOx forms in the high-NOx production region. If, instead, r_L = 0 is assumed, then the minimum value of f is 0.07, and the NOx forms exclusively in the high-NOx production region for all conditions. If r_L = 0.80 is assumed, which is the maximum value possible based on the NOx data, (i.e., 3.2 ppm NOx formed at 4.0 ms), then the minimum value of f is 0, and all of the NOx forms in the low-NOx production region under minimum f conditions.

Although the results and discussion given in this section are centered on the residence time effect, and draw the reader away from the original objective of well-stirred behavior, it is interesting to examine the evidence for well-stirred NOx formation. Two pieces of evidence exist for the approach to well stirred behavior at 0.5 ms residence time. The relatively good agreement between the measured and PSR predicted NOx for 0.5 ms supports an approach to WSR NOx formation. Additionally, the spreading of the high concentrations of CO into the bulk of the reactor at 0.5 ms is consistent with a spreading of high O-atom levels throughout the reactor, and thus WSR NOx formation.

NOx AS A FUNCTION OF INLET TEMPERATURE IN THE A-JSR: RESULTS AND DISCUSSION

The atmospheric pressure JSR (A-JSR) is used to determine the effect of inlet temperature on NOx. Measurements are done with two inlet jet nozzle sizes (i.e., 2 and 4 mm diameter). The results are described below. The inlet temperature recorded is that measured for the fuel-air mixture just before the mixture leaves the premixer and accelerates through the nozzle to form the JSR inlet jet. With no preheating of the inlet air, the inlet temperature is 390 K. Because of back heating from the JSR to the premixer, the measured inlet temperature is greater than the ambient temperature. The maximum inlet temperature tested is 623 K. This is obtained by applying electrical resistance heating to the air entering the premixer (Capehart et al., 1997).

Results are plotted in Fig. 8. The measured NOx, corrected to 15% O_2, is plotted versus the inlet temperature. The measured reactor temperature is corrected for radiation losses. The corrected temperature in the recirculation zone is 1788 K for all inlet temperatures, and the nominal residence time of the reactor is 3.5 ms. All NOx data are adjusted to 3.5 ms assuming a linear dependency of NOx on residence time for atmospheric pressure, lean-premixed JSRs, (Steele et al., 1996). This adjustment does not affect the trends shown in the data.

The effect of the inlet temperature on the NOx is seen to be significant. An increase in the inlet temperature from 390 K (i.e., without preheating) to 623 K decreases the NOx from about 6 to about 4 ppmvd, 15% O_2. The results do not appear to be significantly affected by the change in the jet diameter from the 2 to 4 mm, though more data are needed for the 4-mm diameter jet to confirm this.

Because O-atom relaxation times are relatively long at atmospheric pressure, super-equilibrium concentrations of O-atom uniformly fill the recirculation zone of the A-JSR, and thus, the A-JSR should be effectively well stirred with respect to NOx formation. Steele et al. (1996) discuss this. Given this situation, PSR modeling of the NOx is useful. In previous work, PSR modeling has correctly predicted NOx as a function of combustion temperature (Steele et al., 1995). Application of the PSR code with the GRI 2.11 (1995) mechanism to the present condition predicts a small decrease in NOx with increasing inlet temperature. Although this trend matches that of the data, the levels of NOx reduction obtained by the modeling are significantly less than those measured. Application of the Miller Bowman (1989) mechanism gives a slight increase in the NOx with increasing inlet temperature.

Modeling of the A-JSR as a PSR should provide a fairly good prediction of O, H, and OH free-radical concentrations within the recirculation zone of the reactor, and thus, a good prediction of the NOx formed by the reaction of these free radicals with N_2 and N_2O in the recirculation zone. However, since it is not possible to explain the inlet temperature effect through such chemical kinetic modeling, it may be that the turbulence-chemistry interactions within the jet zone, which cannot be treated by the PSR model, are affecting the total NOx yield. [This effect was not resolved in the earlier work (Steele et al., 1995).] High inlet temperature causes the jet gas to mix more rapidly with the reactor gas than in the unheated inlet jet case, and effects quicker ignition. Reaction in the jet zone could influence the NOx through changes in the free-radical levels leaving the jet zone and flowing into the recirculation zone. In addition, reactions leading to reduction of NOx might be promoted by higher jet temperature. That is, NOx mixed into the jet zone from the recirculation zone could be converted into cyano species by reaction with hydrocarbon radicals. Although some of the cyano nitrogen would be re-converted to NOx under the lean conditions, some would be converted to N_2, leading to a net reduction in NOx and to a decrease in reactor NOx with increasing inlet temperature.

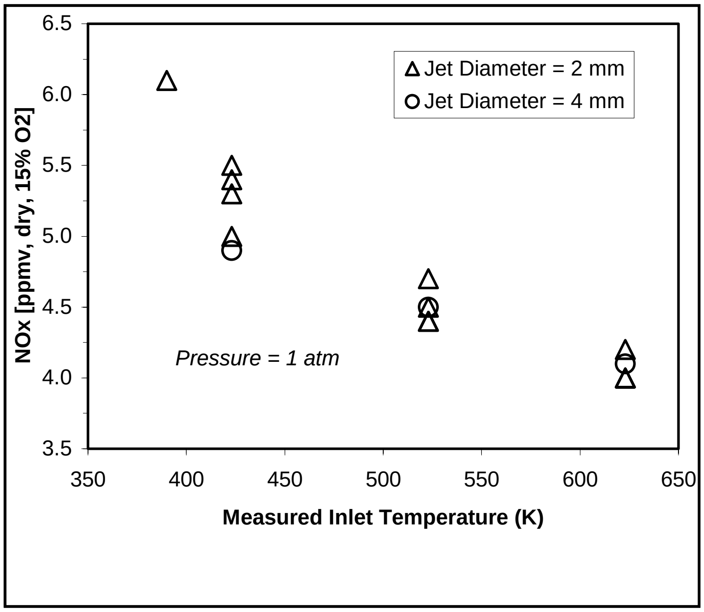

Fig. 8. NOx versus inlet temperature for 1788 K gas temperature in the A-JSR. Inlet nozzle diameters are 2 and 4 mm.

Prompt NOx is another possible explanation. With increasing inlet temperature, the fuel-air ratio decreases (for constant combustion temperature of 1788 K), and thus prompt NOx, which is related to fuel concentration, should decrease. This explanation would require the prompt NOx to be a significant fraction of the reactor NOx, because of the significant dependency of the measured NOx on inlet temperature. The prompt NOx explanation is not strongly supported by PSR modeling of the reactor, which shows a prompt NOx contribution of only 10 to 30% (Nicol et al., 1995). If there were a significant prompt NOx effect, it would have to occur in the jet zone. Although possible, such behavior is not consistent with interpretation of the available database on NOx formation in the atmospheric pressure jet-stirred reactors. As shown by Steele et al. (1996), the NOx depends linearly

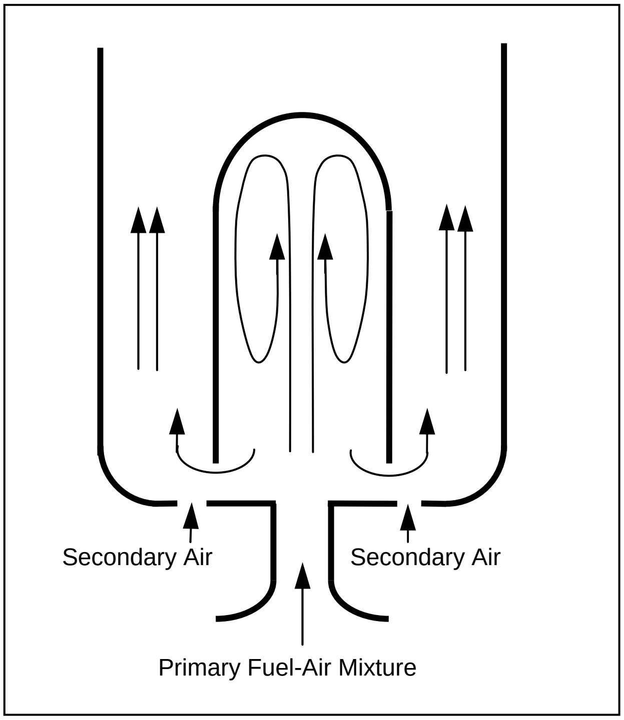

Fig. 9. Conceptual design of the circular cavity positioned above single premixed fuel-air nozzle in a lean-premixed combustor primary zone.

on reactor residence time for the atmospheric pressure JSR, which implies NOx formation throughout the reactor and argues against a large fraction of jet zone NOx formation. In addition, the PSR modeling predicts absolute NOx concentrations rather well, though not the trend of NOx with inlet temperature, by mainly considering O-atom attack on N_2 leading to NOx through the Zeldovich and nitrous oxide mechanisms. Although prompt NOx cannot be ruled out as the explanation for the trend of decreasing NOx with increasing inlet temperature, it is suspected the effect may be more complex than prompt NOx alone.

APPLICATION TO COMBUSTOR DESIGN

The findings for laboratory jet-stirred reactors with a single-jet nozzle indicate the following:

1. There appears to be an optimum residence time range for which NOx levels are at their minimum.
2. Preheating the inlet combustion air appears to favor the reduction in NOx formation.

The present work proposes a conceptual design for the primary zone of a lean-premixed combustor that takes advantage of the above findings. The findings may have practical applicability because the measured pressure loss of the reactor, between the premixer and the outside environment into which the reactor exhaust gases flow, is about 5% at minimum NOx conditions, and because combustion temperatures correspond to the new generation of gas turbine engines. The restrictions on the design are the following: combustion in a relatively small cavity strongly back-mixed by a single jet reflecting at the end-wall of the cavity; operating conditions resulting in optimal residence time; and, materials which withstand combustion temperatures.

A sketch of the conceptual design is given in Fig. 9. It is proposed that each such structure enclose one premixed fuel/air nozzle.

The advantages of this design are as follows:

1. NOx formation is reduced, i.e., NOx is formed primarily in the jet zone. Based on the results shown in this paper, the NOx should be in the 2 to 4 ppmvd (15% O_2) range for engine operating temperatures and pressures. In order to terminate all post-flame NOx formation, a relatively small amount of secondary air could be injected at the exit of the back-mixed cavity.
2. Low CO levels. The HP-JSR shows CO levels of a few hundreds of parts per million. By providing additional residence time in the coaxial space between the back-mixed cavity and the outer wall of the combustor, CO should oxidize to low levels of order 10 ppmvd (15% O_2).

Still to be tested with this design are variations in the length and geometry of the premixer. As discussed earlier in the paper, the laboratory experiments have been conducted with a premixer of long residence time, thought to give nearly complete fuel-air premixing. As also indicated earlier, modeling by Rutar et al. (1997) supports the theory that mixing in JSR's washes out the tendency of fuel-air unmixedness to increase NOx levels. Thus, if future work shows it possible to inject the fuel into the air stream in the nozzle close to the reactor entrance without increasing NOx, the design will have two additional advantages:

1. Reduction of preignition in the premixer, and
2. Ability to burn a relatively wide range of fuel compositions.

Drawbacks to this design are as follows:

1. Limited turn-down ratio (approximately 2 for the minimum NOx condition).
2. Material for the construction of the cavity should be ceramic in order to withstand combustion temperatures. Cost and mechanical properties of ceramics, although rapidly improving, still pose a challenge for combustor design.

CONCLUSIONS

Experiments in the HP-JSR at 6.5 atm show that NOx decreases between 0.5 and 2.5 ms, attains a minimum at approximately 2.5 ms, and then increases from 2.5 to 4.0 ms. The minimum NOx is approximately 3.5 ppmvd (15% O_2). The measured thermocouple temperature is 1803 K and the fuel is methane. The CO and NOx profiles across the reactor indicate that there are two zones: the jet zone rich in free radicals in which most of the NOx may be formed, and the recirculation zone where NOx formation rates appear to be much slower. The reactor approaches well stirred reactor behavior with respect to NOx formation at the lowest residence time tested (0.5 ms). At this condition, the reactor is filled with free radicals that contribute to the increased NOx formation. At residence times of 2.5 to 4.0 ms, the reactor losses progressively more heat as residence time increases, so the gases are enriched and true reactor temperature increases. This increasing temperature coupled with the prolonged time in the reactor, results in increased NOx formation. The HP-JSR results are obtained without air-preheat. Results obtained in the A-JSR indicate the NOx emissions decrease when preheated air is used. About a 30% decrease in NOx is observed as the mixture inlet temperature is increased from the no-preheat case to 623 K (with combustion temperature held constant at about 1788 K). These results were obtained using methane fuel and a single inlet jet, and may be restricted to these conditions.

The data from the HP-JSR and A-JSR suggest that primary combustion zones based on the back-mixed cavity design could be useful for obtaining very low NOx emissions from LP combustors. A conceptual design is proposed.

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