NOX FORMATION IN HIGH-PRESSURE JET-STIRRED REACTORS WITH SIGNIFICANCE TO LEAN-PREMIXED COMBUSTION TURBINES

Teodora Rutar Department of Mechanical and Manufacturing Engineering Seattle University, 900 Broadway Seattle, Washington 98122-4340

ABSTRACT

Measurements of NOx and CO in methane-fired, leanpremixed, high-pressure jet-stirred reactors (HP-JSRs) independently obtained by Rutar [1] and Rutar et al. [2] and by Bengtsson [3] and Bengtsson et al. [4] are well predicted assuming simple chemical reactor models and the GRI 3.0 chemical kinetic mechanism. The single-jet HP-JSR of Rutar [1] and Rutar et al. [2] is well modeled for NOx and CO assuming a single PSR for Damköhler number below 0.15. Under these conditions, the estimates of flame thickness indicate the flame zone, that is, the region of rapid oxidation and large concentrations of free radicals, fully fills the HP-JSR. For Damköhler number above 0.15, that is, for longer residence times, the NOx and CO are well modeled assuming two PSRs in series, representing a small flame zone followed by a large post-flame zone. The multi-jet reactor of Bengtsson [3] and Bengtsson et al. [4] is well modeled assuming a large PSR (over 88% of the reactor volume) followed by a short PFR, which accounts for the exit region of the HP-JSR and the short section of exhaust prior to the sampling point. The Damköhler number is estimated between 0.01 and 0.03.

Our modeling shows the NOx formation pathway contributions. Although all pathways, including Zeldovich (under the influence of super-equilibrium O-atom), nitrous oxide, Fenimore prompt, and NNH, contribute to the total NOx predicted, of special note are the following findings: 1) NOx formed by the nitrous oxide pathway is significant throughout the conditions studied; and 2) NOx formed by the Fenimore prompt pathway is significant when the fuel-air equivalence ratio is greater than about 0.7 (as might occur in a piloted lean-premixed combustor) or when the residence time of the flame zone is very short. The latter effect is a consequence of the short lifetime of the CH radical in flames.

Philip C. Malte Department of Mechanical Engineering University of Washington Box 352600 Seattle, Washington 98195-2600

INTRODUCTION

Fundamental research on NOx formation from methanefired, lean-premixed combustion in high-pressure jet-stirred reactors (HP-JSRs) has developed through stages. First, the work of Nicol et al. [5] showed the significance of the nitrous oxide pathway to NOx formation in high-pressure combustion reactors operating at temperatures up to about 1800 K. Then Steele [6] built and operated a HP-JSR for residence times of 2.0 and 4.0 ms, pressures up to 7.1 atm, and combustion temperatures up to about 1900 K. Steele et al. [7] reported a weak decrease in NOx for the pressure increase from 1.0 to 7.1 atm, and an activation temperature of about 24,000 K for the NOx increase with combustion temperature. In fact, the NOx data obtained in Steele's HP-JSR resemble in magnitude and in trends for pressure and temperature, the data obtained in the porous-plate combustor of Leonard and Stegmaier [8] and the gas turbine type combustor of Joshi et al. [9].

The investigation of the effect of pressure (1 to 20 bar) on NOx in a HP-JSR operated at a fuel-air equivalence ratio of 0.55, at short residence times (1.0 to 2.0 ms), and at combustion temperatures around 1800 K, is contained in the PhD dissertation of Bengtsson [3]. This work is summarized in the subsequent Combustion Symposium Proceedings paper of Bengtsson et al. [4]. The work shows NOx decreases with pressure, and that the decrease is more pronounced at pressures up to 5 bar than for pressures above 5 bar. Furthermore, the effect of pressure is most pronounced for the 2.0 ms data, for which the NOx varies between about 8.5 ppmv, wet, at 1.0 bar, to about 5 ppmv, wet, at 5 bar. However, for the same pressure range, and for 1.0 ms residence time, the NOx decreases only from about 5.4 ppmv, wet, to about 4.5 ppmv, wet. The multijet reactor of Bengtsson [3] was sampled for species and temperature in the exhaust section attached to the reactor, close to the reactor outlet. The volume of the exit tubes up to the sampling point is approximately equal to 16% of the reactor volume. Bengtsson [3] and Bengtsson et al. [4] modeled the data as two PSRs followed by a PFR, with the PFR representing the exit tubes.

Studies of NOx formation in a single-jet HP-JSR are contained in the PhD dissertation of Rutar [1] and in a subsequent Combustion Symposium Paper by Rutar et al. [2]. In Rutar et al. [2], the focus is on interpreting the NOx measurements in terms of the flame structure. It is determined how well the turbulent flame zone, that is, the zone of rapid oxidation and large concentrations of free radicals, fills the HP-JSR.

The HP-JSR of Rutar [1] was operated for residence times between 0.5 and 4.0 ms, for unheated and preheated reactants, and for pressures of 3.0, 4.7, and 6.5 atm. The temperature of the reactor gas, as measured by a thermocouple (type R, coated) placed in the recirculation zone of the reactor, was held constant at 1800 K by making adjustments to the fuel-air ratio. Calculation of the corrected temperature is conducted by two methods (Rutar et al. [10]). The primary method is based on the heat balance for the thermocouple, and the confirming method is based on the wall heat loss of the HP-JSR. These methods indicate a corrected temperature of 1825±10 K for runs at short residence times (< 2 ms). For the largest residence times (of up to 4 ms), the corrected temperature increases to about 1880 K for pressures of 4.7 and 6.5 atm, and to about 1940 K for 3 atm. Probe measurements of species were obtained in the recirculation zone, which represents the bulk of the reactor and exhibits nearly uniform composition and temperature under most running conditions.

The measurements show a small decrease in NOx with increasing pressure (pronounced only above 1.5 ms), and lower NOx when the inlet is preheated (pronounced only below 1.5 ms). With respect to residence time, the behavior of the NOx is complex. Under several running conditions, minimum NOx is obtained when the residence time is about 2.0 ms.

In Rutar [1] and Rutar et al. [2], size estimates are made of the turbulent flame zone. When the residence time is short, and thus, the velocities in the reactor are high, estimates of the turbulent flame thickness indicate the turbulent flame zone fully fills the HP-JSR. Under this condition, the NOx and CO are well modeled assuming the full reactor to be a single perfectly stirred reactor (PSR). Typically, a critical residence time of $\tau \approx 1.5$ ms satisfies this condition, though as pressure decreases and inlet temperature increases, the critical residence time decreases. For long residence times, and thus, for relatively low velocities in the reactor, the turbulent flame zone is reduced in size. The flame zone now is situated around the centered jet of the reactor, and is surrounded by the recirculation zone of the reactor acting as a post-flame zone. Over the eight-fold increase in the residence time of the reactor, estimates indicate about a ten-fold decrease in the volume of the turbulent flame zone. Thus, for the largest residence times, the flame zone is a relatively small part of the reactor volume. Outside of the single-PSR regime, that is, typically for $\tau > 1.5$ ms, the HP-JSR is modeled as two PSRs in series (PSR-PSR). Generally good agreement of the modeled NOx and CO to the experimental values is obtained by using a small initial PSR, representing the flame zone, followed by a large concluding PSR, representing the recirculating post-flame zone. The residence time split between the two PSRs is set by optimizing the agreement between the measured and modeled NOx and CO. The volumes of the two PSRs obtained by this procedure are similar to the volumes of the flame zone and post-flame zone independently determined by the turbulent flame thickness estimates.

The present paper goes beyond the papers of Rutar et al. [2] and Bengtsson et al. [4]. It models the data of Rutar [1] and Bengtsson [3] for the pathways responsible for the NOx formation. It shows the NOx and CO data of the HP-JSRs are well modeled with the simple PSR, PSR-PSR, and PSR-PFR chemical reactor configurations and the GRI 3.0 chemical kinetic mechanism (Smith et al. [11]).

The authors believe the measurements of Rutar et al. [1] and Bengtsson et al. [3] represent important databases for the fundamental study of methane-air combustion at conditions of lean-premixed combustion turbines. The particular value is in testing of chemical kinetic mechanisms, in development of global mechanisms (underway), in determining contributions of each of the NOx formation pathways, and, consequently, in finding optimal operating conditions for lean-premixed combustors. The short residence times of less than 2 ms are used to drive the reactors to the well-stirred condition, which permits full chemical kinetic mechanisms to be applied to the datasets via PSR modeling. The longer residence times of 2 to 4 ms are useful, since they simulate the flame zone residence times of lean-premixed gas turbine combustors.

MODELING AND DISCUSSION OF EXPERIMENTAL DATA

The Damköhler number, Da = turbulent mixing time/chemical time, and the turbulence Reynolds number, Re = $u'd_o/v$, are estimated for the flames of the work of Rutar [1] and Bengtsson [3]. The estimates of Da and Re are made based on the paper by Abraham et al. [12]. The mixing time is calculated as d_o/u' , where d_o is the jet nozzle diameter, which is assumed to be the turbulent integral scale, and u' is the turbulent intensity, which is assumed to be 10% of the inlet jet velocity (u_o). The kinematic viscosity (v) is determined for the inlet temperature and reactor pressure.

Figure 1, redrawn from Abraham et al. [12], is used to identify regimes of turbulent combustion. The limiting experimental conditions are shown for the two data sets. Operation of the HP-JSR of Rutar [1] is shown for the

minimum and maximum residence times and for the minimum and maximum pressures, both for unheated and preheated inlets. Operation of the HP-JSR of Bengtsson [3] is shown for the pressure range between 5 and 20 bar. As shown in Fig. 1, both reactors operated at very low Damköhler numbers and very high turbulent intensities, hence in the flamelets-in-eddies regime (Turns [13]). Kobayashi et al. [14] have visualized flamelets in eddies by instantaneous Schlieren photography and laser-tomography. They explain that the flames wrinkle significantly, and, consequently, parcels of unburned gas are engulfed into the flame. In their experimental work, the Damköhler number was above 1.0 and the turbulent Reynolds number was below 3000. Because of the low Da and high Re, the flames in the present work are assumed to contain a significant number of parcels of unburned gas. These parcels, embedded into the thick flame, are strained by the flow while the reaction front moves into their periphery. It should be mentioned that the division between regimes of turbulent combustion is rather arbitrary, and that flames in the present work could be considered to be in the distributed reaction regime. This is based on Bray [15] and Chomiak [16], who call the regime of Da < 1 the distributed reaction regime. Regardless of the name for the regime, and keeping the physical picture in mind, the present flames can certainly be labeled as highly stirred with comparably slow chemistry.



Fig. 1. Parameters characterizing turbulent premixed combustion (Abraham et al. [12]). Operation of the HP-JSR of Rutar [1] at the minimum and maximum residence times are identified for the conditions: 6.5 atm (open circles), 3.0 atm (diamonds), 6.5 atm at 573 K inlet temperature (squares), and 3.0 atm at 573 K inlet temperature (triangles). Operation of the HP-JSR of Bengtsson [3] is for pressures between 5 and 20 bar (black circles).

For the cases for which the HP-JSR of Rutar [1] is operated in the regime of the single-PSR modeling ($\tau \le 1.5$ ms), the Damköhler number is 0.06 to 0.15. For the HP-JSR of Bengtsson [3], our estimate indicates the Damköhler number is between 0.01 and 0.03. Under these conditions, the turbulent flame zone fills the reactors. Utilizing a PSR to model the flame is reasonable for thick turbulent flames with low Damköhler numbers. Mixing of reactants and products in the turbulent flame is improved compared to molecular diffusion, which is the only mechanism for mixing within thin laminar or wrinkled laminar flames. Flames are thicker than the smallest turbulent eddies, that is, the Kolmogorov scale eddies roll within the flames, thus enhancing the mixing. The high mixing intensity at low Da establishes that the flame zone is reasonably



Fig. 2. NOx, CO and N₂O data of Bengtsson [3] compared to the results obtained using chemical reactor model PSR-PFR, where $V_{PSR}/V_{reactor} = 88\%$. Fuel-air equivalence ratio is 0.55. Reactor temperature is 1828 K.



Fig. 3. NOx and CO data of Rutar [1] compared to the results obtained using chemical reactor models PSR (at short residence times) and PSR-PSR (at long residence times). Inlet air and methane are not preheated.

well represented by the perfectly stirred reactor model. Such results provide support for modeling the HP-JSR as a single PSR.

Figure 2 shows the comparison between the modeled and measured NOx, CO, and N₂O of Bengtsson [3]. The premixed and preheated methane and air enter the 19-cm³ HP-JSR through twenty nozzles, each with a diameter of $d_0 = 0.6$ mm. The jets penetrate at 12° radial angle designed to create a highly swirling flow in the reactor. The chemical reactor configuration in the model is determined by matching both NOx and CO – a process described in Rutar [1] and Rutar et al. [2]. The model consists of a PSR (with a volume of 88% of the HP-JSR volume) followed by a PFR (with a volume of the remaining 12% of the HP-JSR plus an additional 16% for the exit tubes). The existence of a PFR is an indicator that the HP-JSR may not be completely filled by the flame zone and that regions closest to the exit may not be as well-stirred as the bulk of the reactor.



Fig. 4. NOx and CO data of Rutar [1] compared to the results obtained using chemical reactor models PSR (at short residence times) and PSR-PSR (at long residence times). Inlet air and methane are preheated to 573 K.

The PSR-PFR reactor configuration is different from the 30% first-PSR / 60% second-PSR / 10% PFR configuration used in Bengtsson [3] and Bengtsson et al. [4]. The 30%/60%/10% configuration was chosen to match the measured blowout conditions with a chemical kinetic mechanism available prior to the release of GRI 3.0. [It should be noted the GRI 3.0 mechanism is still unable to predict the reactor blowout conditions.]

Figures 3 and 4 show the comparison between the model and the NOx and CO measurements of Rutar [1]. The premixed methane and air enter the 1.5-cm³ HP-JSR through a nozzle with a diameter of $d_o = 1.4$ mm, which is positioned on the axis of symmetry for the reactor. The jet penetrates the recirculating flow in the reactor, hits the top of the reactor, and back-mixes to create that recirculation. The short residence time data were modeled as a single PSR, whereas the long residence time data were modeled as two PSR's in series. The transition occurs always for Da = 0.15, irrespective of the reactor pressure or inlet temperature. At Da = 0.15, the height to which the inlet reactants reach, estimated as $h = 5d_0u'/S_T$ in Rutar [1] and Rutar et al. [2], where S_T is the turbulent burning velocity, is equal to the height of the reactor. Any increase in the flow rate results in reactant back-mixing, and, coupled with the increasing flame thickness, leads to filling of the reactor with flame. The relation between Da and the turbulent flame thickness and flame volume is given in Rutar [1] and Rutar et al. [2]. As mentioned earlier, the first PSR (PSR1) represents the flame zone. The recirculating post-flame zone is also modeled with a PSR (PSR2). For the recirculating post-flame zone, the characteristic turbulent mixing time is longer than in the flame zone, because the characteristic length scale is the overall reactor dimension and not the inlet jet diameter. The chemical time is also longer than in the flame zone, since the rate of chemistry slows in the post-flame zone. Therefore, the Damköhler number remains relatively low and the recirculating post-flame zone is reasonably well represented by the perfectly stirred reactor model. Since conversion in PSR2 is highly dependent on the gas temperature, PSR2 is run at the corrected measured temperature. Adiabatic conditions are assumed for PSR1 because the chemical energy release rate in the flame zone is sufficiently high that any heat transfer is negligible. The volume (or residence time) of PSR1 is an adjustable parameter - as indicated above, this is determined by optimizing the agreement between the modeled and measured NOx and CO values.

The main trends in the experimental data of Rutar [1] are summarized in the following paragraphs.

Residence time: As stated above and also noted in Figs. 3 and 4, the variation of NOx with residence time is complex. There are several reasons for this. Over the eight-fold increase in the residence time of the experiment, more time is available for NOx to form. However, more time is also available for the super-equilibrium concentrations of the O-atom and CH-radical to decay, thereby decreasing the rate of NOx formation. Further, as the residence time increases, the fraction of the reactor filled with the highly reactive flame zone decreases. Additionally, because of the manner in which the experiment was conducted, the combustion temperature, as expressed by the corrected measured temperature of the recirculation zone, increases from a nearly constant value of 1825 K for $\tau < 2$ ms to 1880 K for the longest residence times (1940 K in the case of the 3 atm experiments). For runs at constant pressure and inlet temperature, the fuel-air ratio was adjusted upward at both the short and long residence time limits. Minimum fuel-air ratio was set at the intermediate residence times. Enrichment at the short residence times overcame the trapping of chemical energy by the unburned CO, and enrichment at the long residence times overcame reactor heat transfer losses.

The NOx data in Fig. 3, for the unheated inlet, show minimum NOx at a residence time of about 2 ms. With decreasing residence time the NOx increases, an effect most likely associated with an increase in the free radical concentrations at the short residence times. The CH-radical appears to be important to this regard. Modeling indicates [CH] grows significantly as the residence time decreases. (This is shown later in the paper.) Thus, an increase in prompt NOx could be responsible for a significant part of the increase in NOx with decreasing residence time for the NOx data of Fig. 3. Interestingly, the NOx data of Fig. 4 show little increase in NOx with decreasing residence time. However, these runs are made with a preheated inlet, and thus, are leaner than the data of Fig. 3 and consequently contain a lesser fraction of prompt NOx in the total NOx.

For residence times greater than about 2 ms, the NOx data in Fig. 3 show an increase in NOx with increasing residence time. This increase is also noted in the NOx data of Fig. 4. The increase is mainly associated with the increase in the temperature of the experiment with increasing residence time. A weaker contributing factor is the greater residence time available for NOx to form. This is noted in Rutar [1] through adjustment of all of the NOx data to 1820 K constant temperature (which is the approximate temperature of the short residence time runs), using the NOx activation temperature of Steele et al. [7]. The adjustment leads to a reduction of NOx for the intermediate and long residence times compared to the results in Figs. 3 and 4. Nevertheless, a mild increase in NOx with residence time remains in the adjusted data for $\tau > 2.5$ ms.

Pressure: NOx shows a mild decrease with increasing pressure for the intermediate and long residence times. This can be noted in Figs. 3 and 4 by comparing the 4.7 and 6.5 atm data. For given residence time, the combustion temperature is essentially identical for the two pressures – thus, the decrease in the NOx is indeed caused by the increasing pressure.

Inlet temperature: The effect of inlet temperature (and thus, equivalence ratio for given combustion temperature) is weak at the long residence times (above 2 ms). However, as noted above in the discussion of the effect of residence time on NOx, comparison of Figs. 3 and 4 indicates a decrease in NOx with increasing inlet temperature for the short residence times runs (of less than 2 ms).

Carbon monoxide: CO markedly decreases with residence time, falling from values as large as 6700 ppmv at short residence times to as low as 100 ppmv at the long residence times. This behavior is consistent with the significant change in the combustion structure within the reactor over the eightfold change in residence time.

Exit emissions: Although the present sampling measurements were conducted within the recirculation zone of the reactor, they represent exit emissions, since the recirculation zone is nearly uniform (especially in NOx) and the gases exit the reactor from the recirculation zone.

Also plotted in Figs. 3 and 4 are the curves obtained from the modeling. The modeling is conducted with either the PSR or PSR-PSR configuration, depending on the residence time, and is based on the experimental fuel-air ratio and the corrected measured temperature (except for the assumption of adiabaticity for PSR1 in the PSR-PSR model). The modeling shows good agreement to the measurements, except for a few situations. One such situation is the peak CO concentrations, seen in both Figs. 3 and 4 for the 4.7 atm runs at the short residence times. These CO concentrations are underpredicted by the PSR model. Another situation is noted in Fig. 4 for the 3.0 atm runs at intermediate and long residence times, where the CO is overpredicted by the model. Although not done in the present modeling, the addition of a small PFR zone to the PSR-PSR model reduces the CO to the experimental levels. A final situation is noted in the NOx predictions for 4.7 atm, which show more curvature with respect to residence time than seen in the measurements.

DISCUSSION ON NOx FORMATION PATHWAYS

The simple reactor configurations, particularly the single-PSR and PSR-PFR configurations, are useful for assessing the importance of the several chemical pathways that can form NOx. The four NOx formation pathways under lean premixed combustion of methane in air are the Zeldovich, nitrous oxide, Fenimore prompt, and NNH pathways. The exact algorithm for assessing the contribution of each pathway is described below.

Each NOx formation pathway exchanges species that form NOx with two or more other pathways. For example, N-atom, which oxidizes into NO primarily through the second and third Zeldovich reactions, i.e., $N + O_2 \rightarrow NO + O$ and $N + OH \rightarrow$ NO + H, is formed via the first Zeldovich reaction ($N_2 + O \rightarrow$ N + NO), the prompt reaction ($N_2 + CH \rightarrow HCN + N$), as well as through a series of reactions involving short-lived species such as NH and CN. However, the maximum contribution of each pathway is easily estimated. The present work uses estimates based on the discussion by Nicol et al. [17]. This is summarized in the following paragraphs.

The Zeldovich contribution to the total NOx can be easily determined by considering the first (or initiating) Zeldovich reaction, $N_2 + O \rightarrow N + NO$. Two NO molecules are formed from this reaction, one directly and the other from the oxidation of the N-atom. Thus, the rate of Zeldovich NO formation is $(dNO/dt)_{ZELD} = 2 k_{N2+O}$ [O] [N₂], where k_{N2+O} is the rate constant of the first Zeldovich reaction and [O] and [N₂] are the concentrations predicted by the integration of the GRI 3.0 mechanism in either the PSR, PSR-PSR, or PSR-PFR configuration.

Some of the collisions between N₂ and O result in the third-body-stabilized reaction to N₂O, nitrous oxide. The overall reaction is N₂ + O + M \rightarrow N₂O + M. Some of the nitrous oxide formed by this reaction is attacked by O-atom, and thus, converted to two NO molecules by the reaction, N₂O + O \rightarrow 2NO. Other N₂O molecules are attacked by H-atom, leading to a molecule of NO and a molecule of NH. The reaction is N₂O + H \rightarrow NO + NH. Under lean-premixed combustion, the NH oxides to NO. Thus, two NO molecules are formed by the reaction from N₂O + H \rightarrow NO + NH. The total rate of NO formation from N₂O may thus be expressed as (dNO/dt)_{N2O} = 2 k_{N2O+O} [O] [N₂O] + 2 k_{N2O+H} [H] [N₂O], where k_{N2O+O} and k_{N2O+H} are the respective rate constants, and [O], [H], and [N₂O] are predicted by the integration of the GRI 3.0 mechanism.

Within flame zones, N₂ is also attacked by CH. The reaction given in GRI 3.0 for this "prompt" NO is N₂ + CH \rightarrow HCN + N. Under lean-premixed combustion the HCN and N-atom are oxidized to NO. Thus, the reaction yields two NO molecules, and the rate of NO formation is (dNO/dt)_{PROMPT} = 2 k_{N2+CH} [CH] [N₂]. The term k_{N2+CH} is the rate constant for the prompt NO reaction and the concentrations [CH] and [N₂] are predicted by the integration of the GRI 3.0 mechanism.

The final NOx pathway in GRI 3.0 arises from the NNH radical. This radical forms by the reaction of N₂ with H-atom. Once formed, the NNH can be oxidized by the reaction NNH + $O \rightarrow NO + NH$. Since under lean-premixed combustion, NH is oxidized to NO, the NNH reaction yields two NO molecules. The resultant rate of formation is (dNO/dt)_{NNH} = 2 k_{NNH+O} [O] [NNH], where k_{NNH+O} is the rate constant and [NNH] and [O] are predicted by the integration of the GRI 3.0 mechanism.

Summation of the NO separately calculated by the four rate equations just derived equals the NO predicted by the full GRI 3.0 mechanism within \pm 5%. Because of the small concentrations of NO in lean-premixed combustion, reverse reaction of the NO-forming reactions is not a significant factor in accounting for the difference. However, reduction of NO by hydrocarbon attack, leading to cyano species such as HCN and HCNO, can occur in lean-premixed combustion. These molecules quickly form and then are reconverted to NO. This can lead to a slight distortion in the sum of the NO predicted by the separated pathways, yielding slightly less NO at short residence times, and slightly greater NO at long residence times.



Fig. 5. Amount of NO formed by each of the four pathways in a single-PSR at 6.5 atm with and without preheat. Also shown is the NO from the PSR output (model) and the measured NOx (data of Rutar [1]).



Fig. 6. Amount of NO formed by each of the four pathways in two-PSR model at 6.5 atm with preheat. Also shown are the NO from the PSR2 output (model) and the measured NOx (data of Rutar [1]).



Fig. 7. Amount of NO formed by each of the four pathways in a PSR-PFR at 1 and 2 ms with preheat. Also shown is the NO from the PFR output (model) and the measured NOx (data of Bengtsson [3]).

Nitrogen dioxide (NO_2) is not a factor in the modeling, since only negligible amounts of NO are oxidized to NO_2 by the application of the GRI 3.0 mechanism. The experimental sampling is conducted for the sum of NO and NO_2 , that is, for NOx, since some NO can be oxidized to NO_2 in the sample probe and line. Thus, in this work, NO predicted can be directly compared to NOx measured.

The NO computed using the separated rate equations for each pathway and multiplied by the residence time in the PSR is plotted in Figs. 5-7. The figures also contain the experimental data and the full mechanism predictions. Figure 5 compares the contribution of each pathway for the Rutar [1] data for unheated and preheated inlets at 6.5 atm for short residence times, i.e., for cases modeled with a single PSR. Fuel-air equivalence ratios for each data point are shown in parentheses. When the inlet is not preheated (upper graph), both the nitrous oxide and the prompt pathways dominate the NO formation. Prompt contributes as much as 5.3 ppmv, wet, at 0.5 ms reactor residence time (i.e., 48% of the total NO), but then decreases to approximately 2.7 ppmv, wet, at 1.5 ms. The trend is opposite for the contribution of the nitrous oxide pathway to NO. At 0.5 ms, it contributes 3.8 ppmv, wet, but at 1.5 ms, it contributes 4.8 ppmv, wet. The decrease in the prompt NO is explained by the decrease in the CH-radical concentration, [CH], with residence time. The CH-radical has a short lifetime in flame zones, so the only way to capture its existence in a PSR is if the PSR residence time is short. Figure 8 depicts [CH] versus PSR residence time for the single-PSR cases. It shows the [CH] decreases an order of magnitude over 0.5 to 1.5 ms. Also noted is the decrease in [CH] as the inlet temperature is increased, and thus, the reactor is operated leaner.

The NO formed by the nitrous oxide and Zeldovich pathways increases with residence time. The nitrous oxide NO and Zeldovich NO increase with residence time because the time available to form NO increases and overcomes decreases in [O] and [H]. Temperature is nearly constant (at about 1825 K) at these short residence times. The decrease of O-atom with residence time is plotted in Fig. 9 for the single-PSR cases. It is apparent the decrease in [CH], shown in Fig. 8. The O-atom also decreases with pressure, but the inlet temperature does not influence it.

For the preheated inlet cases at short residence times, shown in the bottom graph of Fig. 5, the nitrous oxide pathway is the predominant NO pathway, yielding 56-58% of the total NO. The prompt NO contribution is similar to the contributions of the Zeldovich and the NNH pathways. The decrease in NO obtained by preheating the inlet air is consistent with a diminished influence of the prompt pathway. The concentration of the CH-radical is significantly lower, because of the lower fuel-air equivalence ratio (shown in parentheses). The [O] is nearly insensitive to preheat, while [H] and [NNH] decrease slightly.

For the longer residence times, the influence of each pathway differs for the first PSR (PSR1), i.e., the flame zone, and the second PSR (PSR2), i.e., the post-flame zone. Figure 6 shows the experimental data of Rutar [1], the total GRI 3.0 prediction, and the contribution (summing each zone) of each of the four pathways, along with the fuel-air equivalence ratio (shown in parentheses) for 6.5 atm with preheated inlet. Table 1 contains the information used in the analysis of the PSR-PSR modeling. In the table, the experimental conditions, i.e., the residence time, corrected measured temperature, and fuel-air equivalence ratio, are presented first. The measured NOx [ppmv, wet] is also included for comparison with the modeling results. The next section of Table 1 contains the values of the NO in [ppmv, wet] that are formed via the Zeldovich, nitrous oxide, prompt, and NNH pathways, as well as the sum of the NO formed by the four pathways in each zone (termed Zone NO), and the sum of NO for the two zones (termed Modeled NO).



Fig. 8. Concentration of CH radical versus reactor residence time for single-PSR cases.



Fig. 9. Concentration of O-atom versus reactor residence time for single-PSR cases.

Results from the chemical kinetic modeling for the reactor operating in the PSR-PSR regime (i.e., for $2 \le \tau \le 4$ ms) are summarized as follows:

- The amount and the fraction of NO formed in PSR2 increase as the overall reactor residence time increases. This is caused by two effects: the increasing residence time and the increasing temperature of PSR2.
- The amount of Zeldovich NO formed in PSR2 increases as the overall reactor residence time increases, and becomes an important part of the total NO formed in the reactor.
- The formation of the nitrous oxide NO shifts from PSR1 to PSR2 as the overall reactor residence time increases.

	6.5 atm unheated				6.5 atm preheated			
Overall residence time [ms]	2 ms		4 ms		2 ms		4 ms	
PSR number	PSR1	PSR2	PSR1	PSR2	PSR1	PSR2	PSR1	PSR2
PSR residence time[ms]	0.126	1.897	0.0695	3.833	0.231	1.847	0.045	3.892
Temperature [K]	1757	1836	1748	1880	1820	1840	1764	1884
Fuel-air equivalence ratio	0.7		0.73		0.6		0.66	
Measured NO [ppmv,wet]	7.5		10.3		6.2		8.8	
Zeldovich NO [ppmv,wet]	0.20	0.74	0.11	2.36	0.74	0.63	0.11	2.85
Nitrous NO [ppmv,wet]	1.19	0.71	0.65	1.30	2.82	0.44	0.55	1.57
Prompt NO [ppmv,wet]	3.07	0.06	3.93	0.05	2.19	0.01	2.91	0.05
NNH NO [ppmv,wet]	1.24	0	1.00	0.07	1.45	0.01	1.06	0.08
Zone NO [ppmv,wet]	5.69	1.51	5.69	3.79	7.2	1.09	4.63	4.56
Modeled NO [ppmv,wet]	7.2		9.5		8.3		9.2	

Table 1. Numerical results for two-PSR model (for 6.5 atm)

- The volume and residence time of PSR1 decreases as the overall reactor residence time increases. This is linked to decreasing inlet jet velocity and reactor pressure drop, which lead to decreasing mixing intensity and flame zone thickness. The reduction in the residence time of PSR1 leads to greater [CH] and thus more prompt NO formation in PSR1. This leads to a significant impact of prompt NO to the total NO predicted for the reactor.
- The increase in NO with decreasing pressure is caused by the increase in free-radical concentrations in both zones. In PSR1, between 6.5 and 3.0 atm, [O] increases by threefold, [CH] by seven to eight-fold, [H] by four to five-fold, and [NNH] by two-fold. The NO formation rates in PSR1 increase between the two pressure levels from 2.2-fold at 2.0 ms to 3-fold at 4.0 ms. The contribution of each pathway changes, however. For example, at 2.0 ms, between 6.5 and 3.0 atm, the prompt NO contribution increases from 54 to 65%, the NNH contribution to NO increases from 22 to 28%, the nitrous oxide contribution to NO decreases from 21 to 6%, and Zeldovich contribution to NO decreases from 3 to 1%. In PSR2, the O-atom concentration increases with decreasing pressure. This causes Zeldovich and nitrous oxide pathways to increase, which in turn, increase NO formation rates in the PSR2 as the pressure drops from 6.5 atm to 3.0 atm. The increase is 1.8-fold at 2.0 ms to 2.8-fold at 4.0 ms. The prompt and NNH pathways have little contribution to the overall NO production in PSR2.

The contribution of each NO pathway for the reactor of Bengtsson [3] is shown in Fig. 7, for both the 1 ms and 2 ms data. For both residence times, the nitrous oxide pathway is predominant, followed by the Zeldovich pathway. The small influence of the prompt pathway is caused by the lean fuel-air equivalence ratio (0.55). It is beneficial to compare the single-PSR results for the HP-JSR of Rutar [1] for 6.5 atm, preheated inlet, and 1.5 ms (Fig. 5, lower section), to the results for the HP-JSR of Bengtsson [3] for the same pressure. In both cases the nitrous oxide pathway is predominant. The Zeldovich pathway follows it, then the prompt pathway and lastly the NNH pathway.

CONCLUSIONS

The paper uses the experimental data obtained in the HP-JSRs of Rutar [1] and Bengtsson [3], and the modeling approach of Rutar [1] and Rutar et al. [2], for a study of methane-air combustion at conditions of lean-premixed combustion turbines. Both reactors operate at low Damköhler numbers, i.e., between 0.01 and 1, which make them suitable for the study of chemical kinetic effects. The results are of significance to predicting and understanding NOx formation in lean-premixed combustion turbines. Points in this regard are the following:

1. The results indicate the GRI 3.0 mechanism is appropriate for modeling combustion pollutant formation/emission at the pressure, temperature, and equivalence ratio conditions of lean-premixed combustion turbines. [The conditions of high-pressure ratio aeroderivative engines have not been explored – however, if the trend of weak dependency of the NOx on pressure extends to 30-40 atm, the results of Bengtsson [3] and Bengtsson et al. [4] should apply.]

- 2. The results substantiate databases for developing reduced and global mechanisms for lean-premixed combustion.
- 3. The results provide additional understanding on the importance of the several pathways to NOx formation in lean-premixed combustion. The nitrous oxide pathway is important at all conditions, whereas the Zeldovich mechanism is important only at long-residence times and high temperatures. Additionally, the Fenimore prompt NOx must be carefully considered for lean-premixed combustion.

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