EFFECT OF FUEL COMPOSITION ON NOX FORMATION IN LEAN PREMIXED PREVAPORIZED COMBUSTION


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ABSTRACT

The effect of fuel composition on NOx formation in lean premixed prevaporized (LPP) combustion is examined using an atmospheric pressure jet-stirred reactor fitted with a prevaporizing-premixing chamber and liquid fuel atomizing nozzle. Four liquid fuels are studied, including the pure hydrocarbons n-heptane (C7H16) and n-dodecane (C12H26), No. 2 low sulfur diesel fuel oil (LSDF042) with 0.0195% sulfur and 0.0124% nitrogen by weight, and n-dodecane doped with n-ethyl-ethylenediamine (C12H27NH2CH2NH2) to give 0.0096% nitrogen by weight in the doped fuel. For comparison, propane (C3H8) is burned. The combustion temperature range of the experiments is 1625 to 1925K, and the nominal residence time of the reactor is 3.5ms. The first objective of the work is to determine the effect which increasing fuel carbon number has on the NOx yield of high-intensity LPP combustion. For combustion at 1800K, an increase of 15 to 20% is measured in the NOx yield when the fuel is changed from C7H16 to C12H26. Comparison to earlier work on CH4 and C3H8 combustion in the jet-stirred reactor operating at 1800K shows essentially an identical increase in NOx yield between CH4 and C3H8 as between C7H16 and C12H26. The second objective of the work is to determine the conversion of fuel-nitrogen to NOx for the combustion of low nitrogen content fuels in high-intensity LPP combustion. The measurements indicate a fuel-nitrogen to NOx conversion of 70 to 100%. These conversion values should be regarded as preliminary since only two nitrogen-containing fuels have been examined and only one prevaporizer-premixer system has been used.

INTRODUCTION

For many gas turbine engines used for electrical power generation, low sulfur fuel oil is required as a replacement fuel for natural gas during the coldest months of the year. Additionally, some stationary gas turbine engines burn oil as the primary fuel. The burning of oil in these engines is accomplished by diffusion-flame combustion, and NOx control is accomplished by water injection. Environmental impact statements for proposed combined cycle turbine electric power generating stations indicate that a significant part of the annual NOx emission arises from the periods of the year when the engine is switched from lean premixed (LP) gas combustion to diffusion-flame oil combustion. Thus, the development of lean premixed prevaporized (LPP) combustion technology for liquid firing is important. Compared to diffusion-flame combustion, LPP combustion has the advantage of significantly reducing thermal NOx formation. However, in LPP combustion the fixation of atmospheric nitrogen to NOx can occur by non-thermal mechanisms, such as the prompt, nitrous oxide, and Zeldovich (with super-equilibrium O-atom) mechanisms. Since these mechanisms are strongly affected by super-equilibrium free-radical levels in the flame zone, the formation of NOx from N2 can be complex (e.g., see Nicol et al., 1995) and should be studied for LPP combustion. Further, and perhaps most important, the organic nitrogen contained in the oil may react quantitatively to NOx under LPP combustion conditions. Even though the amount of organic nitrogen in low sulfur fuel oil is small (typically about 0.01 to 0.02% by weight), complete oxidation of this nitrogen gives an NOx yield of about 5.5ppmv.

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(15% O₂) for every 0.01% nitrogen. Thus, the fuel-NOx yield from LPP combustion of an oil of 0.02% nitrogen content could be as great as 11ppmvd (15% O₂), a level which is significant compared to the NOx range of 9-to-25ppmvd (15% O₂) of gas-fired LP combustors.

The present research has been undertaken to answer two questions:

- Is the fixation of atmospheric nitrogen increased as fuels of increasing carbon number are burned in LPP combustion?
- Do small amounts of fuel nitrogen react completely to NOx in LPP combustion?

With respect to the second question, it is well established in the coal combustion literature that the percentage conversion of fuel nitrogen to NOx increases with decreasing nitrogen content of the fuel. Further, work by Stoffel and Reh (1995) involving the application of a ceramic fiber / surface combustion type burner to this problem suggests that fuel nitrogen conversion is high for LPP combustion.

The present work addresses this problem with a much different type of burner, a jet-stirred reactor (JSR), than used by Stoffel and Reh (1995). Within the JSR, the NOx forms in the turbulent shear layer and turbulent recirculation zone, a situation similar to that thought to occur in LP and LPP combustors, though the intensity of turbulence in the JSR is greater than in the engine combustors, and the scale of turbulence is smaller. As discussed by Steele et al. (1996), JSRs have been used since the 1950s to study chemically dominated events in gas turbine combustion.

In the following sections of this paper, the JSR system used is described and the results are presented and discussed.

**EXPERIMENTAL**

The experimental system used in this study is shown schematically in Figure 1. The major components are the jet-stirred reactor (JSR), the prevaporizing-premixing chamber, and the liquid fuel atomizing nozzle. For the experiments reported herein, the fuel-air equivalence ratio range is 0.48 to 0.80, the combustion temperature is 1625 to 1925K, the temperature of the fuel-air mixture entering the reactor is 405 to 725K, and the nominal mean residence time of the gas in the reactor is 3.5ms. The fuels burned are n-heptane (C₇H₁₈), n-dodecane (C₁₀H₂₁), No. 2 low sulfur diesel fuel oil (LSDFOIt2) with 0.0195% sulfur and 0.0124% nitrogen by weight, n-dodecane doped with n-ethylethylenediamine (C₁₀H₁₇N₂H₂ or C₁₀H₂₁N₂) to give 0.0096% fuel-nitrogen content by weight, and propane (C₃H₈). Normally, the reactor is operated at constant air flow rate, and the fuel flow rate is adjusted to give the desired combustion temperature.

**Jet-Stirred Reactor**

The JSR cavity has a volume of 16cc and is stirred by a single jet. The design and geometry of the JSR are essentially identical to the 1am, single jet reactor used by Steele et al. (1995, 1996). Figure 2 shows the JSR cavity, including the inlet jet, the recirculating flow, the drain holes (4) for the exhaust, and the probing-path (at 65% reactor height) along which the temperature and gas sampling measurements are taken. The reactor has two zones, including the jet zone in the center of the reactor, which comprises 10 to 20% of the total JSR volume, and the recirculation zone, surrounding the jet zone, which comprises 80 to 90% of the total JSR volume. For the present work, an inlet jet diameter of 2mm is used. The height of the reactor is 45mm and the diameter (at the widest point) is 25mm. Thus, the recirculation zone has characteristic dimensions of about 4cm length by 1cm width. For operation of the reactor at conditions of 3.5ms residence time, 1800K combustion temperature, and 420K inlet jet temperature, which are the nominal conditions for the present work, the characteristic time scales of the flow are 1ms for one cycle of the recirculation zone by a fluid particle, and 0.05ms for one turn-over of an inlet-jet eddy (i.e., τ = d₅₀/U₅₀). The average number of cycles made by a fluid particle in the present JSR is estimated to be about 4 (based on the reactor flow analysis of Thornton et al., 1987). Examination of the length and time scales of gas turbine engine LP
combustors indicates that compared to the JSR, 1) the recirculation zone size is somewhat greater in LP combustors (several centimeters characteristic length), 2) the number of cycles of a fluid particle in the recirculation zone of LP combustors is less, and 3) the integral scale of the eddies entering the LP combustor from the premixer outlet stream (jet) is larger and the inlet jet velocity is lower, leading to a larger inlet-jet eddy turn-over time (as large as 1ms).

Selection of Inlet Jet Diameter

The 2mm jet diameter of the present JSR is used in order to improve the uniformity of the reactor, that is, to minimize the depression of NOx on the centerline of the reactor. Selection of the 2mm jet diameter is based on the study of different inlet jet diameters. Processes which affect the NOx as gas from the recirculation zone is entrained into the jet are the following:

1. Non-uniform jet (in which the fast oxidation reactions are concentrated), and the surrounding recirculation zone. The recirculation zone is the region of CO oxidation, high free radical concentrations (O, H, and OH), and non-thermal NOx formation by free radical attack on N₂. It has been argued by Steele et al. (1996) that JSRs operated lean premixed at atmospheric pressure are essentially well-stirred with respect to NOx formation from N₂.

Figures 3a and 3b show profiles of temperature and NOx measured along the probing-path from the centerline to the wall \( (r/R_j)^2 = 1 \) of the JSR, and into the sampling port \( (r/R_j)^2 > 1 \). The radius at the measurement point is \( r \), the radius of the JSR wall is \( R_j \). As shown, at the 65% reactor height used for the probing, 80 to 90% of the cross-sectional area of the JSR is nearly uniform in temperature and NOx concentration. This is the recirculation zone of the reactor. The other species measured in this work (CO, CO₂, O₂, and N₂O) show uniformity in the recirculation zone similar to that noted in Figure 3b for the NOx.

It is desired for the jet-stirred reactor to exhibit spatial uniformity in the measured (time-mean) temperature and gas composition. When this condition is attained, the reactor is assumed to be well-stirred, and the time-mean rates of reaction are assumed the same everywhere within the reactor. However, at combustion temperatures the oxidation reactions are very rapid, with a characteristic chemical time of order 0.01ms. Thus, the hydrocarbon fuel converts very rapidly to CO, CO₂, and H₂O, and for a reactor operating with a residence time of a few milliseconds (the case here), it is essentially impossible to fully disperse the fuel throughout the reactor prior to the onset of oxidation. Consequently, the JSR exhibits the two zones stated above, the
Dilution of the NOx as fresh reactants (in the jet) mix with the burnt and burning gas (of the recirculation zone).

Reduction of the NOx due to chemical attack by hydrocarbon fragments created during the oxidation process in the jet.

Formation of NOx in the jet.

In Figure 4, the percentage depression in NOx on the jet centerline relative to the recirculation zone is plotted versus the jet entrainment ratio, which is calculated using the following equation based on Beer and Chigier (1983):

\[
\frac{\text{mass flow rate entrained}}{\text{jet inlet mass flow rate}} = 0.25 \left( \frac{T_{\text{ave}}}{T_{\text{in}}} \right)^{0.25} L d_i
\]

where \(T_{\text{ave}}\) = average temperature of gas in recirculation zone, \(T_{\text{in}}\) = temperature of inlet jet, \(L\) = distance from jet inlet to sampling location (see Figure 2), and \(d_i\) = inlet jet diameter.

The curve labeled complete mixing assumes that the gas entrained by the jet has fully mixed with the jet gas and no chemical reaction has occurred.

The data plotted in Figure 4 are taken from several studies of single-jet JSRs, and cover inlet jet diameters of 2mm (Capenhart, 1995), 2.73mm diameter (Steele, 1995), and 3.97 and 5.56mm diameters (Williams, 1995). The experiments with the two smallest jet diameters were conducted in the 16cc JSR, and the experiments with the two largest jet diameters used a JSR of 63cc volume (Williams, 1995). The 63cc reactor is geometrically similar to the 16cc reactor. The fuel is CH\(_4\) except for the experiments for the 2mm jet, in which case C\(_2\)H\(_6\), C\(_3\)H\(_8\), and C\(_4\)H\(_{10}\) are burned, and the residence time is 3.5ms (nominal).

Poorest uniformity (i.e., greatest depression of NOx) is seen for the large jets (3.97 and 5.56mm) operated cold (300K). With increasing inlet jet temperature (600K) and decreasing jet size the uniformity in NOx improves and reaches (and possibly surpasses) the complete mixing prediction for the smallest single jet tested (2mm). The 2mm jet becomes choked for the highest inlet temperatures used in this study. On this basis, and given the relatively low depression in centerline NOx, the 2mm jet was selected for use in the present study.

The trend shown by the data plotted in Figure 4 suggests incomplete mixing of the recirculation zone gas into the center of the jet when large, cold inlet jets are used. With decreasing jet size and increasing inlet temperature, the mixing becomes more complete. However, chemical reaction of the NOx in the jet cannot be ruled out based on the data shown in Figure 4.

Prevaporizing-Premixing Chamber and Liquid Fuel Nozzle

The prevaporizing-premixing chamber consists of two sections. In the lower section, the fuel is injected, atomized, mixed with heated air, and vaporized. In the upper section, the vaporization and mixing processes are permitted to reach completion. Also, the upper section contains holes for injection of gaseous fuel, such as the startup fuel (hydrogen), methane, and propane. The air is heated with an electrical resistance heater. For work with gaseous fuels, manual or single loop feedback control of the air heater is adequate. However, for work with the liquid fuels, particularly the fuel oil, feedback control of the air heater, using a cascade-type controller, is required. Typically, the pressure of the prevaporizing-premixing chamber is 2atm. Acceleration of the prevaporized-premixed gas occurs across the nozzle block (containing the 2mm diameter hole for the jet). The nozzle block is constructed of inconel and serves as the interface between the prevaporizing-premixing chamber and the jet-stirred reactor.

Two liquid fuel atomizing nozzles are used in this work. Because of the low fuel flow rates used (0.04 to 0.07cc/s), most commercial nozzles are oversized by an order of magnitude for the present work. Nonetheless, for the pure liquid fuels tested it has been possible to use a commercial nozzle operated at below its minimum recommended operating regime. Specifically, a Delavan
Experimental preheat conditions with the jet-stirred reactor outlet jet of the prevaporizing-premixing chamber operated under light scattering from a 5mW He-Ne laser beam passed through the prevaporizer has not been experienced after extensive use of the ethylethlenediamine, a new nozzle has been designed and experiments with n-dodecane and with dodecane doped with ethylene glycol. The use of the Delavan nozzle included instability in the liquid fuel flow at low flow rates and extended vaporization time due agglomeration of fuel droplets caused by the impact of the fuel spray on the prevaporizer wall.

For experiments with the fuel oil, and for comparative experiments with n-dodecane and with dodecane doped with ethylene glycol, a new nozzle has been designed and incorporated into the system. The nozzle is essentially a two stage atomizer that entails a pressure atomizer housed in an air atomizer as shown in Figure 5. Liquid fuel is initially atomized by the pressure atomizer. Second stage atomization and final cone angle adjustment is then provided by the air atomizer. The double atomization process provides a wide range of operating conditions for complete atomization of liquid fuel. Although a detailed analysis (i.e., a Doppler particle analysis) has not been performed on the nozzle, initial inspection of the spray indicates a cone angle of approximately 17° at 15cm for distilled water operated at a nominal flow rate of 0.05cc/s with a back pressure of about 3atm and air of 95cc/s flow rate (at 3atm). Pressure oscillation of the prevaporizer has not been experienced after extensive use of the two stage atomizing nozzle.

![Figure 5. Schematic Drawing of the Two Stage Liquid Fuel Atomizer used in the Current Study.](image)

Completeness of vaporization is confirmed by examining light scattering from a 5mW He-Ne laser beam passed through the outlet jet of the prevaporizing-premixing chamber operated under experimental preheat conditions with the jet-stirred reactor removed. No side scattering is observed by the naked eye when the prevaporizing system is properly set, indicating the lack of droplets (and aerosol) in the flow and complete vaporization of the liquid fuel.

The residence time of the prevaporizing-premixing chamber is 150 to 250ms. Since the air flow rate of the present experiments is nominally constant, the variation in the residence time is due to variation in the temperature. For the present experiments, the JSR inlet jet temperature is 405 to 725K. The lower (vaporizing) section of the chamber accounts for about 1/3 of the total residence time, and the upper (mixing) section accounts for the 2/3 balance of the residence time in the prevaporizing-premixing chamber. As shown in Figure 1, mixing is enhanced by baffle plates located in the upper section. [Gaseous fuel (i.e., C₆H₆ in the present work) is injected through tiny jets in the tube located below the lower baffle plate (see Figure 1)]. The baffle plates create turbulent eddies which have a turn-over time of about 5ms (t = Lₐ/Uₐ, where gap denotes the space between the baffle plate and chamber wall). Residence time in the space between the upper baffle plate and the JSR nozzle is 30 to 50ms. Comparison of this residence time to the turn-over time of the eddies created by the baffle plate indicates that the degree of premixing in the chamber is good. Further, because of the intense mixing in the JSR, any fuel and air not completely mixed prior to entry into the JSR are rapidly mixed within the JSR (Rutar et al., 1997). Thus, the experiments are treated as fully premixed.

For the experiments with the pure hydrocarbon fuels, the inlet jet temperature is 420K. For this case, conditions within the prevaporizing-premixing chamber are just adequate to fully vaporize the pure liquid hydrocarbons (Capchart, 1995). For the experiments with the fuel oil, the inlet jet temperature is increased to 700-725K, in order to ensure vaporization of all fuel components. For comparison, dodecane and doped dodecane are also run at this temperature. Given the combination of relatively high temperature (at least 700K) and relatively long residence time (about 150ms), fuel pyrolysis reactions are possible in the prevaporizing-premixing chamber at this condition.

**Temperature, Gas Species, Fuel/Air Ratio, and Fuel Composition Measurements**

Temperature is measured with a 0.13mm type-R thermocouple, coated with a ceramic compound (to prevent catalytic oxidation of CO, H₂, and hydrocarbons at the thermocouple surface), and corrected for radiation loss (typically, about a 30°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 the bank of gas analyzers, including process analyzers for CO, CO₂, O₂, NO, and NOx. Additionally, nitrous oxide (N₂O) and hydrocarbon gases (for a few cases) are measured by gas chromatography. The thermocouple and gas sampling probe are traversed across the jet-stirred reactor in order to measure the temperature and gas composition profiles; however, for the results presented below all
RESULTS AND DISCUSSION: NOx FROM LPP COMBUSTION IN THE JSR

Pure Hydrocarbon Fuels

Results for NOx yields for the three pure hydrocarbons burned in this study (n-dodecane, n-heptane, and propane) are plotted versus the measured combustion temperature in Figures 6 and 7. The complete data set, including all data taken at the nominal sampling location, as well as profiles of all species concentrations and temperature taken across the reactor are given in the thesis of Capehart (1995). The NOx data in Figure 6 are presented on the basis of ppmv, wet, actual O2, and in Figure 7 the data are re-plotted on the basis of ppmvd, 15% O2. For these experiments, the inlet temperature variation is 405 to 420K and the residence time variation is 3.1 to 3.6ms. The average residence time is 3.3ms. Generally, the residence time decreases with increasing combustion temperature (and increasing fuel air ratio). The data plotted in Figures 6 and 7 cover combustion temperatures from 1675 to 1890K, the corresponding equivalence range is 0.53 to 0.71 (based on gas analysis).

The elemental composition of the fuel oil used in this study is determined by analysis at outside laboratories. The carbon, hydrogen, and sulfur contents are 86.7, 12.45, and 0.0195% by weight, respectively. The nitrogen content is 124ppmw, and the uncertainty in the nitrogen content is estimated to ±10ppmw. The carbon, hydrogen, and nitrogen contents of the dodecane-doped-with-ethyleneaminediamine fuel are determined from the respective weights of the pure compounds used. The carbon and hydrogen contents are 84.7 and 15.3% by weight, respectively. The nitrogen content is 96ppmw, and the uncertainty of this is estimated to be ±20ppmw.
The data show that the main variable affecting the NOx yield is combustion temperature (or fuel-air equivalence ratio, since the inlet temperature is nominally constant). With respect to fuel composition, the data are closely grouped, though there is a slight increase in NOx with increasing fuel carbon number, i.e.:

\[ [\text{NOx}]_{C_{12}H_{26}} > [\text{NOx}]_{C_{7}H_{16}} > [\text{NOx}]_{C_3H_8} \]

The dependency of NOx on fuel carbon number is plotted in Figure 8. The data plotted have been adjusted to the conditions of 1800K and 3.5ms. This has been done by fitting the data of Figures 6 and 7 with curves of the form \( \text{NOx} = A \exp(E/RT) \), where \( E/R \) is the empirical activation temperature, and using the curve fits to determine the NOx yields for 1800K. Adjustment for residence time is based on the finding of Steele et al. (1996) that NOx yield varies as \( \tau \) (where \( \tau \) is the residence time) for the formation of NOx from \( \text{N}_2 \) in the atmospheric pressure JSR operated at residence times in the range of 1.5 to 7.5ms. The results plotted in Figure 8 show that the NOx yield for the fuels covered in this study, i.e., normal alkanes from \( C_1 \) to \( C_{12} \), when burned under identical conditions, exhibit a small but noticeable increase in NOx with increasing fuel carbon number.

For reference, also plotted in Figure 8 are NOx data from Steele et al. (1995) for methane, ethylene, and propane. For these data, the nominal inlet temperature was 600K, the pressure was 1atm, and the nominal residence time was 3.5ms. The JSR was the same reactor as used to obtain the pure hydrocarbon NOx data of the present study; however, the JSR nozzle block contained 8 small diverging jets corresponding in total area to a single jet of 2.73 mm diameter. These data have also been adjusted to the conditions of 1800K and 3.5ms. The NOx yields of the \( \text{CH}_4 \)-\( \text{C}_2 \text{H}_6 \) data are greater than the NOx yields of the \( \text{C}_3 \text{H}_8 \)-\( \text{C}_7 \text{H}_{16} \) data because of the higher inlet temperature of the \( \text{CH}_4 \)-\( \text{C}_2 \text{H}_6 \) data, and the fact that the small multiple jets yield a more uniformly high temperature in the JSR (i.e., the zone of temperature depression in the jet, due to incomplete combustion, is reduced in size) than the single jet. The main point to be noted from the \( \text{CH}_4 \)-\( \text{C}_2 \text{H}_6 \) data is that the relative change in NOx from \( C_1 \) to \( C_7 \) is about as great as the relative change in NOx from \( C_7 \) to \( C_{12} \). With NOx expressed on a wet basis (actual \( O_2 \)), both \( C_1 \)-to-\( C_7 \) and \( C_7 \)-to-\( C_{12} \) have a 20% increase in NOx. On a dry (15% \( O_2 \)) basis, the increase is 17% for the \( C_1 \)-\( C_7 \) case and 15% for the \( C_7 \)-to-\( C_{11} \) case.

In Figure 9, the concentrations of nitrous oxide (\( \text{N}_2 \text{O} \)) are plotted for the combustion of the propane, n-heptane, and n-dodecane fuels. The \( \text{N}_2 \text{O} \) is measured because it is thought to be an important intermediate in the formation of NOx in lean premixed combustion (e.g., see Nicol et al., 1995).
In the paper by Steele et al. (1995), based on NOx data for methane, ethylene, propane, and CO/H2 mixtures (cited above), it is argued that the NOx forms essentially by the same chemical kinetic mechanisms for the different fuels, and that the mechanisms are predominantly the Zeldovich and the nitrous oxide mechanisms (Nicol et al., 1995). The second conclusion is supported by chemical kinetic modeling by Steele (1995), which shows good agreement between the measured and predicted NOx and N2O for lean premixed combustion of methane and CO/H2 mixtures in the 1 atm JSR. The present NOx and N2O data, which show small sensitivity to fuel type, and show similarity in NOx and N2O concentrations to the earlier data obtained in the University of Washington JSR, appear to extend the conclusions of Steele et al. (1995) to the C5-C11 normal alkane fuels.

The small increase in NOx measured for increasing fuel carbon number is consistent with an increase in O-atom concentration with increasing fuel C/H ratio. This trend has been observed in chemical kinetic modeling of the combustion of methane, ethylene, and CO/H2 under assumed perfectly stirred conditions (Jarrett, 1995; Horning, 1996). That is, as the fuel C/H ratio increases, yields of intermediate CO tend to increase, which in turn tend to promote higher O-atom concentrations as the fuel oxidizes to CO2 and H2O. Yields of NOx increase because of the greater availability of O-atom to attack N2. Another possible explanation for the measured small increase in NOx with increasing fuel carbon number is an increase in the yield of prompt NOx, that is, NOx formed by the attack of CH radicals on N2. The same chemical kinetic modeling which indicates that the increase in NOx is due to an increase in O-atom as the fuel C/H ratio increases also shows that about 10 to 20% of the total NOx can arise from the prompt NOx mechanism at 1 atm perfectly stirred combustion. [Prompt NOx yields are also discussed by Nicol et al. (1994).]

It is possible that fuels of increasing carbon number cause an increase in the CH radical concentration, and thus an increase in the prompt NOx yield. Further, less than perfect mixing in the JSR may enhance the prompt NOx contribution, by permitting CH radicals to reach relatively high concentrations in the jet zone. (Since CH radicals have a short lifetime, of order 0.1ms, it is not thought that they survive at significant concentrations into the recirculation zone of the JSR.)

**Nitrogen-Containing Fuels**

Results for the NOx yields of the fuels containing small amounts of organic nitrogen are plotted in Figures 10, 11, and 12. The plots cover three fuels, including the No. 2 low sulfur diesel fuel oil (LSDFO#2) with 124 ppmw nitrogen, n-dodecane doped with n-ethylethylenediamine (EEDA) to give a nitrogen content of 96 ppmw, and pure n-dodecane. The measurements were taken in a new JSR of the same geometry and general design as the JSR used for the pure hydrocarbon NOx measurements presented above. The nominal temperature of the JSR inlet jet is 700K, and nominal residence time is 4.0ms. Because of the new JSR, and the new conditions for inlet temperature and residence time, the dodecane data are based on new measurements, rather than on adjustment of the data contained in Figures 6 and 7. The relatively high inlet
The temperature of 700K is used to ensure complete vaporization of the LSDFO#2. However, as mentioned above, because of the elevated temperature and long residence time in the prevaporizing-premixing chamber, pre-flame pyrolysis reactions likely occurred in the prevaporizing-premixing chamber, though no explosion or significant pressure oscillations occurred in the chamber.

Figure 10 shows the NOx data for the dodecane doped with EEDA and for the pure dodecane. The residence time varies from 4.0 to 4.4 ms with a mean value of 4.2 ms. Also shown are results obtained assuming 100% conversion of the EEDA nitrogen to NOx and adding this NOx to the measured NOx for the pure dodecane. The results calculated by this method lie just under the measured data for the doped fuel, and suggest that the doped fuel experienced 100% conversion of the organic nitrogen to NOx.

Figure 11 shows the NOx data for the LSDFO#2 and for the dodecane. In these experiments there was a small difference between the residence times of the LSDFO#2 and dodecane runs. Thus, the dodecane NOx data are adjusted to the residence time of the LSDFO#2 data for each temperature, assuming the linear dependency of NOx (from N₂) on residence time used above for adjusting the pure hydrocarbon NOx data. The residence time range of the measurement is 3.7 to 4.2 ms, and the mean residence time is 3.9 ms. The LSDFO#2 data are the sum of separate experiments, one run for 700K inlet temperature, the other run for 725K.

The LSDFO#2 data relative to the dodecane data show an approximate doubling of the NOx at 1800K, and a greater slope of NOx versus temperature (i.e., a greater activation temperature). Comparison of the calculated NOx assuming 100% conversion of the organic nitrogen (added to the dodecane data) to the NOx measured for LSDFO#2 suggests that the organic nitrogen underwent 100% conversion, especially for temperatures above 1800K. For the lowest temperatures studied, the comparison suggests that the organic nitrogen conversion may have fallen to about 70%.

In Figure 12, the NOx data are re-plotted on the basis of ppmv, 15% O₂. Comparison of the data shows that the two nitrogen-containing fuels produced nearly identical levels of NOx for temperatures below 1800K. For the highest temperatures attained (>1900K), the NOx from the LSDFO#2 approached 25ppmv (15% O₂).

\[
NOx (ppmv, wet, actual O_2) = 893\phi / (3.1134\phi + 49.336) \quad \text{Eq.}(2)
\]

where \(\phi\) = fuel-air equivalence ratio.
CONCLUSIONS

The major results of this study are the following:

- A liquid fuel fired jet-stirred reactor system has been developed and applied.

- Under high-intensity LPP combustion in the JSR, NOx from the fixation of \( N_2 \) appears to increase slightly (15 to 20\%) as the fuel carbon number increases from \( C_\alpha \) to \( C_{17} \).

- The yield of NOx versus combustion temperature is provided for a No. 2 low sulfur diesel fuel oil of 124ppmw fuel-nitrogen content burned under LPP conditions in a high-intensity reactor (i.e., a JSR).

- Under LPP combustion in the JSR, the yield of NOx from small amounts of fuel nitrogen appears to be 100\%, except possibly at the lowest temperature tested (1630K) for the LSDFO\#2, where conversion of about 70\% is indicated. The results on fuel nitrogen conversion should be regarded as preliminary, since only two nitrogen containing fuels and only one prevaporizer-premixer system have been studied. Further, because of the relatively low amounts of NOx measured, and the small amounts of nitrogen in the fuel, the measurements are subject to an uncertainty of about ±20\% (absolute) in the determination of fuel nitrogen conversion.

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