THE ROLE OF CARBON MONOXIDE IN NO₂ PLUME FORMATION

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ABSTRACT

Through a series of computational studies, carbon monoxide has been identified as an important promoter of NO oxidation to NO₂ in combustion turbine exhaust gas at intermediate temperatures (450 to 750°C). NO₂ formation is accompanied by enhanced CO burnout at these temperatures. Perfectly stirred reactor and plug flow reactor calculations indicate that concentrations of CO as low as 50 ppmv in exhaust gas containing 25 ppmv NO can result in the conversion of 50% of the NO to NO₂ in less than 1 second. NO₂ concentrations as low as 15 ppmv can result in visible, yellow-brown plumes from large diameter exhaust stacks. If NO₂ plumes are to be prevented, then designers of gas turbines and heat recovery steam generators need to be aware of the relationships between time, temperature, and composition which cause NO₂ to form in exhaust gas.

Reaction path analysis indicates that the mutually promoted oxidation of CO and NO occurs through a self-propagating, three-step chain reaction mechanism. CO is oxidized by OH,

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \tag{R2} \]

while NO is oxidized by HO₂:

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \tag{R23} \]

In a narrow temperature range, the H-atom produced by R2 can react with O₂ in a three body reaction to yield the hydroperoxy radical needed in R23:

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \tag{R9} \]

where M is any third body. The observed net reaction is:

\[ \text{CO} + \text{O}_2 + \text{NO} \rightarrow \text{CO}_2 + \text{NO}_2 \]

which occurs stoichiometrically at temperatures below about 550°C. As the temperature increases, additional reaction pathways become available for H, NO₂, and OH which remove these radicals from the chain and eventually completely decouple the oxidation of CO from NO.

An abbreviated set of elementary chemical reactions, including 15 species and 33 reactions, has been developed to model CO-enhanced oxidation of NO to NO₂. This reaction set was derived from a larger reaction set with more than 50 species and 230 elementary chemical reactions, and was validated by comparison of PFR and PER calculations using the two sets.

INTRODUCTION

The fractional distribution of NO₂ between NO and NO₂ in the exhaust from combustion systems is of considerable importance. The toxicity of NO₂ is greater than the toxicity of NO, and some localities have regulated the color and/or opacity of exhaust gas plumes (NO is colorless, while NO₂ is red-brown in color). NO₂ can be found in the exhaust from boilers, reciprocating engines, and combustion turbine engines. However, NO₂ is generally not produced in significant quantities within combustors themselves. The principal in-combustor formation mechanism is the mixing of hot gases containing NO with cooling or dilution air in the latter portion of the combustor, leading to the production of HO₂ and then NO₂ via NO + HO₂ = NO₂ + OH (Sanò, 1985). The resulting NO₂ formed is usually a small fraction (less than 5%) of the total NO present. Furthermore, this pathway is physically removed in lean premixed gas turbine combustion systems because there is no wall (or “liner”) film cooling and there is no dilution jet air. Measurements made in the bottoming cycle equipment downstream of these gas turbines tend to confirm the hypothesis that there is initially little or no NO₂ present in the gas turbine exhaust, but a large fraction (more than 50%) of the NO may be oxidized to NO₂ as the gas is cooled from the gas turbine exhaust temperature (about 600°C) to the stack exit temperature, resulting in visible NO₂ plumes (Corr, 1995). At typical stack diameters, NO₂ should become visible at a concentration of about 10 - 15 ppmv.

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One potential pathway identified in the literature is the reaction of unburned fuel with flame-generated NO downstream of the combustor. Previous experimental and theoretical studies (Jaasma and Borman, 1980; Bromly et al., 1988; Bromly et al., 1992; Hori et al., 1992) have shown that low concentrations (1 to 1000 ppm) of fuels can be strong promoters of NO oxidation to NO₂ at intermediate temperatures (300 to 700°C). Hydrocarbons vary in their effectiveness in promoting NO oxidation to NO₂, with C₃ and C₄ species generally being more effective than C₂ and C₃ species and H₂. CO has been reported to be relatively ineffective at promoting NO oxidation (Hori et al., 1992).

However, observations from gas turbine power plants equipped with lean premixed combustion systems suggest that installations operating at part load with high CO emissions (~50 ppmv) can have visible yellow-brown exhaust plumes, even when total NO is relatively low (~25 ppmv) and significant quantities of unburned hydrocarbons are not found. Since the unburned fuel pathway to NO₂ can be ruled out in these cases, the question of the importance of CO in converting NO to NO₂ is reopened.

Glarborg et al. (1995) recently completed an experimental and theoretical study of interactions between CO, NO, NO₂, and H₂O in a flow reactor. They concluded that the presence of NO may enhance or inhibit CO oxidation, depending on the exact temperature and composition of the exhaust gas mixture. However, their experimental test conditions were somewhat different from the conditions expected in turbine exhaust. For example, their CO concentrations (450 to 1600 ppm) were much higher than typically found in turbine exhaust, and their O₂ concentrations (2.0 to 4.3%) were lower than usually found.

The purpose of the present computational study was to extend the analysis of Glarborg et al. to more closely match the conditions found in gas turbine exhaust, with the overall objective of gaining a better understanding of the role of CO in the oxidation of NO to NO₂ at intermediate temperatures (400 to 850°C). Perfectly stirred reactor (PSR) and plug flow reactor (PFR) calculations, as well as a reaction path analysis, were completed with both Miller and Bowman’s (1989) detailed chemical reaction set (more than 50 species and 230 elementary reactions) and a reduced reaction set (15 species and 33 elementary reactions) derived from their work. Predictions from both reaction sets were also compared to calculations using the reaction set proposed by Glarborg et al. (54 elementary reactions) and the reaction set developed by Bowman et al. for the Gas Research Institute (277 elementary reactions). Comparisons of the predictions of the four different reaction sets served to validate the reduced reaction set presented here. PFR calculations were performed because the cooling of turbine exhaust gas in a heat recovery steam generator (HRSG) is, to a first approximation, a plug flow process. The PSR calculations are shown in Figures 1 and 2, and indicate results using the Miller and Bowman (MB) reaction set. Symbols represent calculations with either the reduced reaction set in Table 1 ( ), the GRI-Mech 2.11 reaction set ( ), or the GRI-Mech 2.11 reaction set ( ). Figures 1 and 2 show that calculations with the reduced reaction set in Table 1 are indistinguishable from calculations with the complete MB reaction set. In addition, the four different reaction sets are in excellent qualitative agreement for all species and very good quantitative agreement for most species. Differences between reaction sets are largest for HO₂, with a maximum difference of about a factor of 3 at high temperatures. Notice, however, that the differences between reaction sets are much smaller for the important species of interest: CO, NO, and NO₂.

PSR AND PFR CALCULATIONS

The initial gas composition used for all PSR and PFR calculations was determined by assuming complete combustion of methane in air (21% O₂, 79% N₂) at a particular equivalence ratio (φ). CO and NO were then added to the mixture at the desired concentrations. Unless otherwise indicated, the only species present in the initial mixture were O₂, N₂, CO₂, and H₂O, as well as any added CO and NO.

PSR and PFR calculations were completed on a VAX 760 computer using the Chemkin II package of subroutines and associated programs (Kee et al., 1989; Glarborg et al., 1986; Luiz 1987). The Chemkin software allowed adjustment of absolute and relative tolerances to insure computed mole fractions contained roughly four significant digits, even for species with concentrations as low as 10⁻⁶ ppm. For calculations at P = 1 atm, four different reaction sets were used: (1) the well-known reaction set of Miller and Bowman (1989); (2) a reduced, 33-step reaction set derived from Miller and Bowman’s work (see Table 1); (3) the reaction set developed by Glarborg et al. (1995); and (4) the most recent version of the Gas Research Institute reaction set, GRI-Mech 2.11 (Bowman et al.). For calculations at elevated pressures, the modifications recommended by Michaud et al. (1992) were added to the Miller and Bowman reaction set. The reaction path analysis aided in the selection of the key reactions to be retained in the reduced reaction set in Table 1. This reduced set consists of reactions 51-64, 130-139, 143, 145-150, 166, 188-191, 204-207, and 232-234 in Appendix A of Miller and Bowman (1989).

RESULTS

The results from typical constant temperature and pressure PSR calculations are shown in Figures 1 and 2. The inlet composition for the PSR calculations shown in Figures 1 and 2 is burned gas resulting from complete combustion of methane in air at φ = 0.5 (5% CO₂, 10% H₂O, 10% O₂, 75% N₂) with 50 ppmv of CO and either 25 ppmv (solid lines and symbols) or 0 ppmv (dashed lines) of NO added. PSR pressure was set to P = 1 atm and the residence time was 0.5 seconds. For these conditions the fractional conversion of NO to NO₂ peaks at about 650°C, with about 30% of the NO converting into NO₂ and total NO₂ remaining constant. CO decreases monotonically as temperature increases.

The solid and dashed lines in Figs. 1 and 2 indicate results using the Miller and Bowman (MB) reaction set. Symbols represent calculations with either the reduced reaction set in Table 1 ( ), the 1995 Glarborg et al. (G et al.) reaction set ( ), or the GRI-Mech 2.11 reaction set ( ). Figures 1 and 2 show that calculations with the reduced reaction set in Table 1 are indistinguishable from calculations with the complete MB reaction set. In addition, the four different reaction sets are in excellent qualitative agreement for all species and very good quantitative agreement for most species. Differences between reaction sets are largest for HO₂, with a maximum difference of about a factor of 3 at high temperatures. Notice, however, that the differences between reaction sets are much smaller for the important species of interest: CO, NO, and NO₂.

With the inlet NO concentration set to 0 ppmv (the dashed lines in Figures 1 and 2), CO oxidation is greatly suppressed at low tem-
<table>
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<tr>
<th>REACTION</th>
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<tbody>
<tr>
<td>$\text{CO} + O + M = \text{CO}_2 + M$</td>
<td>$6.17 \times 10^{14}$</td>
<td>0.00</td>
<td>3000.</td>
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<tr>
<td>$\text{CO} + \text{OH} = \text{CO}_2 + H$</td>
<td>$1.51 \times 10^{07}$</td>
<td>1.30</td>
<td>-758.</td>
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<tr>
<td>$\text{CO} + O_2 = \text{CO}_2 + O$</td>
<td>$1.60 \times 10^{13}$</td>
<td>0.00</td>
<td>41000.</td>
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<tr>
<td>$\text{HO}_2 + \text{CO} = \text{CO}_2 + \text{OH}$</td>
<td>$5.80 \times 10^{13}$</td>
<td>0.00</td>
<td>22394.</td>
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<tr>
<td>$\text{H}_2 + \text{O}_2 = 2 \text{OH}$</td>
<td>$1.70 \times 10^{13}$</td>
<td>0.00</td>
<td>47780.</td>
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<tr>
<td>$\text{H} + \text{H}_2 = \text{H}_2\text{O} + H$</td>
<td>$1.17 \times 10^{08}$</td>
<td>1.30</td>
<td>3626.</td>
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<tr>
<td>$\text{O} + \text{OH} = \text{O}_2 + H$</td>
<td>$4.00 \times 10^{14}$</td>
<td>-0.50</td>
<td>0.0</td>
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<tr>
<td>$\text{O} + \text{H}_2 = \text{OH} + H$</td>
<td>$5.06 \times 10^{04}$</td>
<td>2.67</td>
<td>6290.</td>
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<tr>
<td>$\text{H} + \text{O}_2 + M = \text{HO}_2 + M$</td>
<td>$3.61 \times 10^{17}$</td>
<td>-0.72</td>
<td>0.0</td>
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Enhanced third-body efficiencies: $\text{H}_2\text{O} = 18.6$, $\text{CO}_2 = 4.2$, $\text{H}_2 = 2.9$, $\text{CO} = 2.1$, $\text{N}_2 = 1.3$

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<tr>
<td>$\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$</td>
<td>$7.50 \times 10^{12}$</td>
<td>0.00</td>
<td>0.0</td>
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<td>$\text{H} + \text{HO}_2 = 2 \text{OH}$</td>
<td>$1.40 \times 10^{14}$</td>
<td>0.00</td>
<td>1073.</td>
</tr>
<tr>
<td>$\text{O} + \text{HO}_2 = \text{O}_2 + \text{OH}$</td>
<td>$1.40 \times 10^{13}$</td>
<td>0.00</td>
<td>1073.</td>
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<tr>
<td>$2 \text{OH} = \text{O} + \text{H}_2\text{O}$</td>
<td>$6.00 \times 10^{08}$</td>
<td>1.30</td>
<td>0.0</td>
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<td>$\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$</td>
<td>$1.00 \times 10^{18}$</td>
<td>-1.00</td>
<td>0.0</td>
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Enhanced third-body efficiencies: $\text{H}_2 = 0.0$, $\text{H}_2\text{O} = 0.0$, $\text{CO}_2 = 0.0$

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<tr>
<td>$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$</td>
<td>$1.60 \times 10^{22}$</td>
<td>-2.00</td>
<td>0.0</td>
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Enhanced third-body efficiencies: $\text{H}_2\text{O} = 5.0$

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<td>$\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$</td>
<td>$1.89 \times 10^{13}$</td>
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<td>-1788.</td>
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<td>$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$</td>
<td>$1.25 \times 10^{13}$</td>
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<td>0.0</td>
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<tr>
<td>$2 \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$</td>
<td>$2.00 \times 10^{12}$</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 + \text{M} = 2 \text{OH} + \text{M}$</td>
<td>$1.30 \times 10^{17}$</td>
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<td>45500.</td>
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<td>$\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$</td>
<td>$1.60 \times 10^{12}$</td>
<td>0.00</td>
<td>3800.</td>
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<td>$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$</td>
<td>$1.00 \times 10^{13}$</td>
<td>0.00</td>
<td>1800.</td>
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<td>$\text{CO}_2 + \text{N} = \text{NO} + \text{CO}$</td>
<td>$1.90 \times 10^{11}$</td>
<td>0.00</td>
<td>3400.</td>
</tr>
<tr>
<td>$\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$</td>
<td>$2.11 \times 10^{12}$</td>
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<td>-479.</td>
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<tr>
<td>$\text{NO}_2 + \text{H} = \text{NO} + \text{OH}$</td>
<td>$3.50 \times 10^{14}$</td>
<td>0.00</td>
<td>1500.</td>
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<tr>
<td>$\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$</td>
<td>$1.00 \times 10^{13}$</td>
<td>0.00</td>
<td>600.</td>
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<tr>
<td>$\text{NO}_2 + \text{M} = \text{NO} + \text{O} + \text{M}$</td>
<td>$1.10 \times 10^{16}$</td>
<td>0.00</td>
<td>66000.</td>
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<tr>
<td>$\text{N}_2\text{O} + \text{H} = \text{N}_2 + \text{OH}$</td>
<td>$7.60 \times 10^{13}$</td>
<td>0.00</td>
<td>15200.</td>
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<td>$\text{N}_2\text{O} + \text{M} = \text{N}_2 + \text{O} + \text{M}$</td>
<td>$1.60 \times 10^{14}$</td>
<td>0.00</td>
<td>51600.</td>
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<td>$\text{N}_2\text{O} + \text{O} = \text{N}_2 + \text{O}$</td>
<td>$1.00 \times 10^{14}$</td>
<td>0.00</td>
<td>28200.</td>
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<tr>
<td>$\text{N}_2\text{O} + \text{O} = 2 \text{NO}$</td>
<td>$1.00 \times 10^{14}$</td>
<td>0.00</td>
<td>28200.</td>
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<tr>
<td>$\text{N} + \text{NO} = \text{N}_2 + \text{O}$</td>
<td>$3.27 \times 10^{12}$</td>
<td>0.30</td>
<td>0.0</td>
</tr>
<tr>
<td>$\text{N} + \text{O}_2 = \text{NO} + \text{O}$</td>
<td>$6.40 \times 10^{09}$</td>
<td>1.00</td>
<td>6280.</td>
</tr>
<tr>
<td>$\text{N} + \text{OH} = \text{NO} + \text{H}$</td>
<td>$3.80 \times 10^{13}$</td>
<td>0.00</td>
<td>0.0</td>
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Note: forward rate coefficients ($k_i$) are of the form $k_i = A T^b \exp(-E/R \gamma)$, where the dimensions of $A$ are mole-cm·sec·K, the units of $E$ are cal/mole, $T$ is absolute temperature, and $R$ is the ideal gas constant.
Fig. 1  Calculated concentrations of CO (top), NO (middle) and NO\(_2\) (bottom) in constant pressure (P = 1 atm) perfectly stirred reactors (PSRs) at various temperatures. Inlet gas composition = 75\% N\(_2\), 10\% O\(_2\), 10\% H\(_2\)O, 5\% CO\(_2\), 50 ppmv CO, and either 25 ppmv NO (solid lines and symbols) or 0 ppmv NO (dashed line). Solid and dashed lines indicate calculations using the Miller and Bowman reaction set. Symbols are points calculated using the reaction set in Table 1 (■), Glarborg et al. (●), or GRI-Mech 2.11 (△).

Fig. 2  Calculated concentrations of OH (top), HO\(_2\) (middle), and H (bottom) at the same conditions as shown in Figure 1.
increases the OH concentration by almost a factor of 1000. NO has a similar effect on H atom concentrations, while HO₂ concentrations are only slightly affected by the presence of NO in the inlet gas. At high temperatures, the presence of NO in the inlet gas has no effect on these radical species concentrations.

A reaction path analysis provides useful insight into the chemical mechanisms causing the effects observed in Figures 1 and 2. Under all conditions, the primary pathway for CO oxidation is reaction R2 in Table 1:

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \]  
(R2)

and the primary pathway for NO oxidation is

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \]  
(R23)

However, key differences are observed in the reaction pathways for radical species. At low temperatures (450 - 650°C), when NO is present in the inlet, almost all of the H atom is destroyed through

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  
(R9)

Under these conditions R2, R23, and R9 form a self-sustaining set of chain reactions. The sum of the three reactions is the overall reaction

\[ \text{CO} + \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{CO}_2 \]

with no net consumption of radical species. The key chain initiation step is not thermal dissociation of stable species, but rather the slow reaction

\[ \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} \]  
(R3)

\[ \text{O} \text{ atom produced through R3 then participates in an important chain branching reaction.} \]

\[ \text{H}_2\text{O} + \text{O} \rightarrow 2 \text{OH} \]  
(R13)

which produces the OH needed for R2, thus initiating the 3-step chain reaction. Reactions R2, R23, and R9 then propagate the chain reaction, and proceed to oxidize NO and CO, with no net consumption of radicals. At temperatures below 550°C, almost every mole of CO oxidized to CO₂ also results in one mole of NO oxidized to NO₂.

At very low temperatures (below 450°C), R3 is too slow to provide sufficient quantities of O atom for the chain reactions to proceed at a significant rate. At high temperatures (above 650°C), R3 and the reverse direction of R13 are still the key chain initiation and chain branching reactions. However, additional reaction pathways become available for H, HO₂, and OH. These reactions remove radicals from the chain and decouple the oxidation of CO from NO. For example, as temperature increases, R9 becomes a less important pathway for H atom destruction as the alternate H + O₂ pathway

\[ \text{H} + \text{O}_2 + \text{OH} \rightarrow \text{OH} + \text{O} \]  
(R7)

becomes more important. At 850°C, about 50% of the H atom destruction occurs through R9, the remainder being destroyed through the reverse direction of R7. In addition, only 20% of the HO₂ that is consumed results in oxidation of NO to NO₂ through R23 (versus almost 100% at 500°C). The remainder of the HO₂ is being destroyed through

\[ \text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_3 \]  
(R10)

NO₃ production reaches a maximum and then slows down as temperature increases, and CO oxidation increases monotonically with temperature, because as temperature increases (i) R10 consumes HO₂ that would have produced NO₂ at lower temperatures through R23, and (ii) the reverse direction of R7 produces the OH needed for CO oxidation that R23 produced at lower temperatures.

If NO is not present at low temperatures, CO oxidation slows considerably, as shown in Figure 1. R3 and the reverse direction of R13 are still the important chain initiating and chain branching reactions. OH produced through the reverse direction of R13 still oxidizes CO, and the H from R2 reacts through R9 to form HO₂. However, without NO to convert HO₂ back to OH through R23, OH concentrations remain depressed (see Figure 2) and CO oxidation slows down. At higher temperatures, new sources of OH become available (primarily through the reverse direction of R7), allowing CO oxidation to proceed without NO.

The results from typical constant temperature and pressure PFR calculations using the Miller and Bowman (1989) reaction set are shown in Figures 3 and 4. The initial condition for the calculations shown in Figures 3 and 4 is again burned gas resulting from complete combustion of methane in air at q = 0.5 (5% CO₂, 10% H₂O, 10% O₂, 75% N₂) at P = 1 atm, T = 600°C, with 50 ppmv CO added, and either 25 or 0 ppmv NO. For all of the species shown, the curves produced using the reduced reaction set in Table 1 are indistinguishable from the curves produced using the full MB reaction set, and so have not been shown. Calculations performed using the Glarborg et al. (1995) reaction set and GRI-Mech 2.11 were again in good agreement with the MB and Table 1 reaction sets, but have not been shown for clarity.

When NO is present (the solid lines in Figs. 3 and 4), there is a short induction period (about 0.2 s) during which time radical species build up to relatively high concentrations. The end of the induction period is marked by the onset of a period of relatively rapid CO and NO oxidation and a gradual decrease in radical species concentrations. In this particular case, approximately 0.6 moles of NO are oxidized to NO₂ for every mole of CO oxidized to CO₂. After about 1 s, 50% of the NO has been oxidized to NO₂. When NO is not present (the dashed lines in Figs. 3 and 4), the chemistry of the PFR is quite different. Concentrations of H, OH, and O are initially suppressed, while HO₂ concentrations increase by nearly a factor of 10. Without NO, overall CO burnout is reduced by a factor of 2. Additional calculations (not shown in Figures 3 and 4) indicate that if CO is not present, NO oxidation does not occur under these conditions.

A careful examination of Figs. 1 - 4 reveals that both with and without NO, the composition of the PFR at 0.5 s is very similar to a 0.5 s residence time PSR operating at the same temperature. This similarity arises because (1) the reactions in the PSR and the PFR are the same and relatively slow, and (2) total conversion of CO and NO is low at 0.5 s.

**DISCUSSION**

At typical gas turbine exhaust temperatures, NO is rapidly oxidized to NO₂ if CO is present. This observation has substantial consequences for the design of downstream process equipment, including HRSGs in bottoming cycles. The gas residence time in a typical HRSG is approximately 2 seconds, which is more than sufficient time to produce 10 - 15 ppmv of NO₂ if gas cooling is slow (see Figure 5). Under part load conditions, when CO is relatively high, rapid quenching of turbine exhaust gas may be needed to prevent the formation of visible NO₂ plumes.
Because the net rate of NO oxidation to NO\textsubscript{2} in exhaust gas is of considerable importance to the designers of boilers (and other downstream process equipment) trying to minimize NO\textsubscript{2} formation, Figure 5 has been prepared. Figure 5 is intended as an engineering tool that provides quick estimates of maximum NO\textsubscript{2} formation rates (due to only CO-enhanced oxidation) in exhaust gas as a function of temperature, pressure, and initial CO:NO mole ratio. Figure 5 is not intended to be a substitute for more detailed model calculations. The net rates of NO\textsubscript{2} production shown in Fig. 5 are taken from the maximum slope of NO\textsubscript{2} profiles computed in constant temperature and pressure PFR calculations at the indicated conditions. The maximum slope typically occurs immediately after the induction period, typically between 0.2 and 0.4 seconds (see Figure 3). NO\textsubscript{2} production rates greater than 10 ppmv per second are possible at temperatures between 575 and 725°C.

The net rate of NO\textsubscript{2} formation shown in Figure 5 exhibits extremely non-Arrhenius behavior and unusual pressure dependence. At P = 1 atm, the rate of NO\textsubscript{2} formation reaches a maximum at temperatures between 600 and 750°C, depending upon the initial CO:NO ratio, and then decreases rapidly as temperature increases. This non-Arrhenius temperature dependence is not surprising, once the competition between R7 and R9 is recognized as a major factor in joint CO/NO oxidation. Elementary reaction R9 is a well-known addition/stabilization reaction which has been widely reported to exhibit non-Arrhenius behavior (Mallard et al., 1992). The non-Arrhenius behavior of R9 explains the unusual temperature dependence of NO\textsubscript{2} formation from NO. The slow rate of NO\textsubscript{2} formation at high temperatures also explains why NO\textsubscript{2} is typically not found in exhaust gas immediately exiting a gas turbine. The residence time in the combustor and the turbine is too short (on the order of 25 ms), and the temperature is too high, for significant NO\textsubscript{2} formation to take place.

At temperatures below 550°C, the net rate of NO\textsubscript{2} formation is roughly proportional to P\textsuperscript{2}. At higher temperatures the pressure dependence becomes more complex as additional reaction pathways become available. At temperatures above 675°C, the net rate of NO\textsubscript{2} production can actually decrease as pressure increases. Again, the unusual pressure dependence of the overall reaction is a direct result of the non-Arrhenius behavior and pressure dependence of R9.

The coupling of CO and NO oxidation at low temperatures also has important implications for modeling chemistry in turbulent flow. A typical approach used to include chemistry in turbulent flow models is to determine the flow, temperature, and species concentration fields using only the fuel and air chemistry, and initially neglecting NO\textsubscript{2} formation. Once the flow field has been solved, NO\textsubscript{2} chemistry is overlaid on top of the existing solution, the assumption being that small concentrations of NO\textsubscript{2} will not perturb the composition or temperature fields significantly. While NO\textsubscript{2} and CO chemistry can be decoupled at high temperatures, this work shows that this assumption is poor at low temperatures. If NO is present, models that decouple CO and NO\textsubscript{2} chemistry will under-predict CO burnout at low temperatures (450 - 750°C).

Fig. 3  Calculated composition profiles in a constant temperature (600°C) and pressure (1 atm) PFR. Initial gas composition = 75% N\textsubscript{2}, 10% O\textsubscript{2}, 10% H\textsubscript{2}O, 5% CO\textsubscript{2}, 50 ppmv CO, and either 25 ppmv NO (solid lines, —) or 0 ppmv NO (dashed line, - - -).

Fig. 4  Calculated PFR composition profiles of important radical species at the conditions of Figure 3.
CONCLUSIONS

The yellow-brown plumes sometimes observed in the exhaust from gas turbine power plants are caused by 10 - 15 ppmv of NO$_2$. Measurements and prior experience indicate that the NO$_2$ is not formed in the gas turbine combustor itself. This work has shown that CO plays a critical role in forming NO$_2$ downstream of the gas turbine. PSR and PFR calculations with four different reaction sets have shown that at temperatures below 800°C, the oxidation reactions of CO and NO are linked together through a chain reaction mechanism. The presence of each enhances the oxidation of the other. Below 550°C, the net reaction stoichiometry of CO + NO + O$_2$ → CO$_2$ + NO$_2$ is expected. CO and NO$_2$ chemistry cannot be decoupled in this temperature regime, and this observation has important implications for designers of boilers and exhaust gas systems trying to minimize NO$_2$ plume formation.

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REFERENCES


