Experimental and kinetic modeling study of CO and NO formation under oxy-fuel conditions

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ABSTRACT

The present thesis focuses on the oxy-fuel combustion of methane doped with ammonia in a premixed, laminar and atmospheric burner. CO and NO formation/emission were examined as a function of the oxidizer composition and stoichiometry. The study includes both experiments and chemical kinetic modeling. The experimental results showed that, for all oxidizer compositions, an increase in the excess oxygen coefficient generally decreases both the CO and NO emissions. For O2/CO2 environments, increasing the oxygen concentration in the oxidizer leads to higher CO emissions, but lower NO emissions. In air firing, the CO emissions were found to be significantly lower than those by oxy-fuel firing, while the NO emissions were higher than those from the oxy-fuel cases. Simulations showed better agreement for CO than for NO, which was largely overpredicted. The main reactions that directly (with the aid of a rate-of-production analysis) and indirectly (through a sensitivity analysis) influence both CO and NO emissions were identified.

Keywords: Oxy-fuel combustion, experimental, kinetic modeling, CO, NO

1. INTRODUCTION

It seems to be consensual [1] that the current energy demand will be largely supplied by the combustion of fossil fuels in the near future, despite the limited reserves and the environmental issues. Renewable energy sources are being introduced to the energy scenario and, hopefully, will be the major contributor in the future, solving both issues, particularly, the increase in CO2 emissions. For the time being, the so-called oxy-fuel combustion technology is one of the most promising solutions to enable CO2 capture and sequestration. In this technology combustion takes place with pure oxygen instead of atmospheric air, which, combined with flue gas recirculation, generates combustion products rich in CO2 that greatly facilitates its sequestration.

This article concentrates on CO and NO formation during oxy-methane combustion under well-defined reacting conditions in a laboratory premixed, laminar, atmospheric burner. Related previous studies include those reported in references 2 to 12. Amato et al. [2] investigated the CO (and O2) emissions from a methane fired laboratory combustor operating under oxy-fuel conditions. The authors performed measurements and thermodynamic equilibrium and chemical kinetics calculations. They concluded that CO emissions are higher in combustion with O2 diluted with CO2 than in combustion with air. Moreover, for a given residence time, the CO emissions from oxy-fuel combustion are higher than the equilibrium values because of the slow oxidation of the intermediate CO formed in the flame. Also, they found that CO emissions increase exponentially with the flame temperature, and predicted that an increase in pressure would lower the emissions. Glarborg and Bentzen [3] evaluated the chemical effects of the presence of high CO2 concentrations in the oxy-fuel combustion of methane under well-defined conditions in a laboratorial flow reactor. Their experimental results were interpreted with the aid of a detailed chemical kinetic mechanism for hydrocarbon oxidation. They concluded that the presence of high CO2 concentrations lead to a significant increase in the CO concentrations, in the near burner region. The high levels of CO2 prevent complete oxidation of the fuel at higher temperatures despite the presence of excess oxygen. Heil et al. [4] investigated experimentally the effect of the N2 and CO2 (as bulk gases) on the burning rates during the oxy-fuel combustion of methane in a furnace operating under flameless oxidation conditions. In case of combustion in N2/CO2 atmospheres, the CO profiles for different O2 concentrations overlap indicating that changing the O2 concentration does not affect the combustion rates. However, in case of combustion in CO2/O2 atmospheres, the CO2 concentration had a significant impact on the CO formation and consumption rates, which was attributed to the CO2 participation in the chemical reactions. Abián et al. [5] used the detailed kinetic mechanism developed by Glarborg et al. [6], with minor changes and updates, to simulate and interpret the experimental results of the CO oxidation in a quartz flow reactor operating at atmospheric pressure. They concluded that, in general, the effect of the CO2 addition is to inhibit the CO oxidation, this suppression being more pronounced for fuel-rich conditions and lower CO2 concentrations. Their results also revealed that water vapor enhances the CO conversion, contrary to some literature results with higher O2 and H2O levels. Thus,
water vapor promotes or inhibits CO oxidation depending on the specific conditions.

In oxy-fuel combustion the only source of nitrogen (if any) is present in the fuel itself. Therefore it is critical to study and understand the fuel-NO formation mechanism under oxy-fuel combustion conditions, particularly, in coal applications. During coal combustion CH₄, HCN and NH₃ are released to the gas phase during devolatilization [7,8]. Wang et al. [9] studied the conversion of pyridine into NO and N₂ in O₂/CO₂ atmospheres in a flow reactor at temperatures between 1073 K and 1473 K for different stoichiometries. Their experimental results indicate that higher temperatures promoted the formation of NO from pyridine and that increasing the equivalence ratio led to a monotonic increase in NO formation. Their simulation results showed that high CO₂ concentrations reduced the availability of oxygen, thus altered the evolution of NO through the promotion of reaction HNO (+M) ↔ H + NO (+M) and limitation of reaction HNO + O₂ ↔ HO₂ + NO. The authors observed also that the major pathways for NO consumption occurred through reactions with NCO and NH as intermediates. Giménez-López et al. [10] examined experimentally and numerically the oxidation of HCN in O₂/CO₂ and air atmospheres in a quartz flow reactor at temperatures between 900 and 1450 K for different stoichiometries. The authors observed an inhibition of the HCN oxidation under high levels of CO₂, as compared to N₂. This effect resulted from the competition of CO₂ and O₂ for atomic hydrogen, reducing the formation of chain carriers and thus inhibiting HCN oxidation. The lower HCN burning rate observed was accompanied by a higher CO and HNCO formation and lower NO and N₂O concentrations, as compared to air combustion. Mendirada and Glaborg [8] investigated experimentally the oxidation of NH₃ during the oxy-fuel combustion of methane in a plug flow reactor and interpreted the results in terms of a detailed chemical kinetic model. The results showed that a high CO₂ level enhanced NO formation under reducing conditions, while it inhibited NO production under stoichiometric and lean conditions. According to the authors, the enhanced CO concentrations and alteration in the amount and partitioning of O/H radicals are responsible for the effect of a high CO₂ concentration on the NH₃ conversion. Watanabe et al. [11] studied experimentally and numerically the NO formation and reduction in staged O₂/CO₂ and air combustion using a flat CH₄ flame doped with NH₃. The authors observed that the NOₓ conversion ratios in O₂/CO₂ environments were lower than those in air combustion and that abundant OH radicals were formed in O₂/CO₂ environments through CO₂ + H ↔ CO + OH. Finally, very recently, Alves et al. [12] investigated the CO and NOₓ emissions from a laboratory combustor fired with methane doped with NH₃ under oxy-fuel combustion conditions. The results revealed that the CO emissions are significantly higher for the combustion in an oxidizer with 20.9%O₂/79.1%CO₂ than for the combustion in air. Under oxy-fuel conditions, the CO emissions decrease as the oxidizer O₂ concentration increases, with the oxidizer composed by 35% O₂/65% CO₂ presenting levels of CO emissions similar to those obtained for the combustion in air. The addition of high levels of H₂O to the oxidizer slightly decreases the CO emissions only for oxidizers with high CO₂ concentrations.

Despite several studies involving both experimental and chemical kinetics modeling under oxy-fuel combustion conditions, it should be pointed out that most of them are limited to plug flow reactors [3,5,8-10]. Studies on premixed flames under oxy-fuel conditions are relatively scarce and only very few include detailed chemical kinetics analysis [2,11]. In this context, the present study focuses on oxy-fuel combustion of methane in a premixed, laminar, atmospheric burner, including both experimental and chemical kinetics simulations.

2. EXPERIMENTAL

Figure 1 shows the experimental set-up used in this study. It consists of a vertically oriented stainless steel tube with an inner diameter of 4 cm and a length of 50 cm, and a premixed, laminar (the calculated Reynolds number was found to be below 162), atmospheric, water-cooled burner mounted at the bottom end of the stainless steel tube. Methane and small amounts of NH₃, from gas cylinders, are fed to the burner as fuel. As for the oxidizer, air, from a compressor, or mixtures of O₂, CO₂, from gas cylinders, are supplied to the burner. The flow rates of CH₄, NH₃, air, O₂ and CO₂ were measured with mass flow controllers.

![Figure 1. Experimental set-up](image)

Local mean gas temperature measurements along the centerline of the stainless steel tube were obtained using five wire (27 µm) thermocouples of platinum/platinum: 13% rhodium. The hot junction was installed and supported on 350 µm wires of the same material as that of the junction. The 350 µm diameter wires were located in a twin-bore alumina sheath with an external diameter of 4 mm and placed inside a stainless steel tube. The uncertainty due to radiation heat transfer was estimated to be less than 5% by considering the heat transfer by
involves 97 species and 779 elementary reactions. The chemical kinetic model employed in this work was developed by Mendiara and Glarborg [8], which involves 97 species and 779 elementary reactions. This reaction mechanism draws on results from oxidation of CO/H₂, C1-C2 hydrocarbons, NH₃ and HCN, as well as interactions of these components. The reaction path, for reactive N conversion in CH₄ oxidation, is divided in three main pathways. In the first pathway NH₃ is converted into NO through HNO. In the second pathway hydrogen cyanide is formed from NH₃ via CH₃NH₂ species. Finally, in the third pathway, HCN reacts to form NO. Once NO is formed it can stabilize to N₂.

4. RESULTS AND DISCUSSION

4.1 EXPERIMENTAL

Figure 2 shows the measured CO emissions as a function of the excess oxygen coefficient for all oxidizer compositions studied. Measurements reveal that as the mixture becomes leaner the CO emissions decrease mainly because there is more O₂ available for the oxidation of the CO. It is also seen that the CO emissions are lower for the oxidizer with the higher O₂ concentration. For the case wherein air is used as the oxidizer, CO emissions are essentially independent of the stoichiometry and always lower than those observed in the O₂/CO₂ atmospheres.

Figure 3 shows the measured NO emissions as a function of the excess oxygen coefficient for all oxidizer compositions studied. A condition where the fuel is leaner NO formation is higher for the oxidizer with the higher O₂ concentration. Figure 3 shows that NO formation is higher for the oxidizer with the higher O₂ concentration. For the case wherein air is used as the oxidizer, CO emissions are essentially independent of the stoichiometry and always lower than those observed in the O₂/CO₂ atmospheres.

A fixed fuel thermal input of 1.5 kW was used throughout the experiments. The NH₃ concentration used to simulate the fuel bound nitrogen was ~1.8%, which is a value close to that used by Mendiara and Glarborg [8] and that coincides with the typical nitrogen content found in many coals [14-16]. Five excess oxygen coefficients (1.05, 1.1, 1.15, 1.2 and 1.25), which for this particular study are defined as (m_oxegen/m_fuel)_actual/(m_oxegen/m_fuel)_stoichiometric were used throughout the experiments. For each excess oxygen coefficient, the oxidizer composition was varied by changing the CO₂ mass flow rate. The following oxidizers were studied: 21% O₂/79% CO₂, 23% O₂/77% CO₂; 25% O₂/75% CO₂, 27% O₂/73% CO₂; 29% O₂/71% CO₂, and air.

3. KINETIC MODELING

The chemical kinetic modeling study was performed with CHEMKIN PRO [17] using PREMIX. A number of approaches have been used in similar modeling studies. For example, Watanabe et al. [11] used a plug flow reactor to model their experimental premixed flame and Li et al. [18] used both a perfectly stirred reactor and a plug flow reactor to model experiments performed in a fully premixed flame. As in Amato et al. [2], PREMIX was used in the present study. Contrarily to Amato et al. [2], here the flame structure was modeled with downstream heat losses. To this end, temperature profiles obtained from the experiments were introduced in the PREMIX. The chemical kinetic mechanism employed in this work was developed by Mendiara and Glarborg [8], which involves 97 species and 779 elementary reactions. This reaction mechanism draws on results from oxidation of CO/H₂, C1-C2 hydrocarbons, NH₃ and HCN, as well as interactions of these components. The reaction path, for
transfer. The convective heat transfer is also different depending on the absorptivity and emissivity and, thus, the radiative heat transfer. CO dependence, but under oxy_29, CO is replaced by CO_2. Significant changes in the heat transfer characteristics occur when N\_2 is replaced by CO_2. Radiative heat transfer depends strongly on temperature due to its fourth order dependence, but under oxy-fuel conditions the presence of CO_2 and sometimes H\_2O greatly enhances the gas absorptivity and emissivity and, thus, the radiative heat transfer. The convective heat transfer is also different since it depends on the gas properties such as viscosity, thermal conductivity, heat capacity and density, as well as on velocity. Despite being a complex system, it is instructive to look at the residence time allowed for heat transfer between the combustion products and the surroundings.

Figure 3. Measured NO emissions as a function of the excess oxygen coefficient for all oxidizer compositions studied.

Figure 4 shows typical temperature profiles along the centerline of the stainless steel tube for four oxidizer compositions at a fixed excess oxygen coefficient of 1.15. These profiles, used in the simulations, were generated from the experimental data following the procedure proposed by Coppen et al. [19]. To account for the downstream heat losses, adiabatic flame profiles were calculated and modified ahead of the flame (beyond 2 cm from the burner) considering the temperature measurements. Figure 4 shows the measured temperatures as a function of the excess oxygen coefficient for four oxidizer compositions at the centerline of the stainless steel tube for axial distances from the burner of 10 cm and 40 cm. The figure reveals that the differences between the measured temperatures are higher in the flame region, decreasing towards the top end of the stainless steel tube.

The adiabatic flame temperatures for the cases represented in Figures 4 and 5 are 1648, 1856, 2030 and 2089 K for the oxy_21, oxy_25, oxy_29 and air cases, respectively. Combustion in air yields higher adiabatic flame temperatures since the molar heat capacity of N\_2 is 1.66 times lower than that of CO_2. Under oxy-fuel conditions, as the CO\_2 concentration in the oxidizer increases the adiabatic temperature decreases. It is interesting to note that the measured temperature closer to the flame (at 10 cm) are higher for air, decreasing as the excess air coefficient increases; and, under oxy-fuel conditions, increasing as the oxygen content in the oxidizer increases. However, at 40 cm, the measured gas temperatures are still higher for air; but increase as the excess oxygen coefficient increases; and, under oxy-fuel conditions, decrease as the oxygen content in the oxidizer increases.

Significant changes in the heat transfer characteristics occur when N\_2 is replaced by CO\_2. Radiative heat transfer depends strongly on temperature due to its fourth order dependence, but under oxy-fuel conditions the presence of CO\_2 and sometimes H\_2O greatly enhances the gas absorptivity and emissivity and, thus, the radiative heat transfer. The convective heat transfer is also different since it depends on the gas properties such as viscosity, thermal conductivity, heat capacity and density, as well as on velocity. Despite being a complex system, it is instructive to look at the residence time allowed for heat transfer between the combustion products and the surroundings.

Table 1 shows the unburned velocity as a function of the excess oxygen coefficient for four oxidizer compositions. Each inlet mixture has its own temperature profile, as discussed earlier. These two parameters have an important effect on residence time. Table 2 shows the residence time as a function of the excess oxygen coefficient for four oxidizer compositions. The residence time was calculated dividing the mean velocity of the burned mixture by the distance between the flame front (assumed to be at 2 cm, which coincides with the point where the temperature profiles were modified) and the sampling location (40 cm). Higher residence times allow for higher heat transfer between the combustion products and the surroundings, which is consistent with the temperature profiles behavior addressed earlier. This does not mean that it is the only factor that matters.

Amato et al. [2] used adiabatic flame calculations to predict emissions from non-adiabatic experiments, which
were measured at an axial position in their combustor corresponding to a residence time of 40 ms for all conditions. This is a very short residence time, which in this study would correspond to an axial position of 10 cm, where the measured temperatures behave exactly like the adiabatic flame temperatures when the stoichiometry and the oxygen concentration in the oxidizer are varied. Moreover, CO emission predictions under adiabatic conditions increase as the oxygen content in the oxidizer increases, unlike what happens in the present experiments (and predictions). This means that CO concentration depends strongly on temperature. Actually, Persis et al. [13] were confronted with completely disagreeing experimental and simulated CO trends as they modeled experiments with the freely propagating model, which solves the energy equation together with the transport equations to calculate both the temperature and the gas species. All these aspects corroborate the necessity of using actual temperature profiles.

It should be also emphasized that the unburned velocities used are not compatible with the theoretical flame propagating velocities from these conditions. Table 3 shows the burning velocity as a function of the excess oxygen coefficient for four oxidizer compositions. It is seen that oxy-fuel combustion with high amounts of CO₂ leads to a dramatic decrease in the burning velocity. However, as the flame was stabilized at the burner, the velocities in Table 1 were used as input data to the simulations.

### Table 1. Unburned velocity as a function of the excess oxygen coefficient for four oxidizer compositions.

<table>
<thead>
<tr>
<th>Unburned velocity (cm/s)</th>
<th>oxy_21</th>
<th>oxy_25</th>
<th>oxy_29</th>
<th>air</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>40.5</td>
<td>34.5</td>
<td>30.3</td>
<td>40.5</td>
</tr>
<tr>
<td>1.10</td>
<td>42.3</td>
<td>36.0</td>
<td>31.5</td>
<td>42.3</td>
</tr>
<tr>
<td>1.15</td>
<td>44.0</td>
<td>37.4</td>
<td>32.8</td>
<td>44.0</td>
</tr>
<tr>
<td>1.20</td>
<td>45.8</td>
<td>38.9</td>
<td>34.1</td>
<td>45.8</td>
</tr>
<tr>
<td>1.25</td>
<td>47.6</td>
<td>40.4</td>
<td>35.3</td>
<td>47.6</td>
</tr>
</tbody>
</table>

### Table 2. Residence time as a function of the excess oxygen coefficient for four oxidizer compositions.

<table>
<thead>
<tr>
<th>Residence time (ms)</th>
<th>oxy_21</th>
<th>oxy_25</th>
<th>oxy_29</th>
<th>air</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>189</td>
<td>220</td>
<td>250</td>
<td>170</td>
</tr>
<tr>
<td>1.10</td>
<td>184</td>
<td>213</td>
<td>241</td>
<td>164</td>
</tr>
<tr>
<td>1.15</td>
<td>178</td>
<td>207</td>
<td>233</td>
<td>159</td>
</tr>
<tr>
<td>1.20</td>
<td>172</td>
<td>200</td>
<td>225</td>
<td>153</td>
</tr>
<tr>
<td>1.25</td>
<td>167</td>
<td>194</td>
<td>218</td>
<td>148</td>
</tr>
</tbody>
</table>

### Table 3. Burning velocity as a function of the excess oxygen coefficient for four oxidizer compositions.

<table>
<thead>
<tr>
<th>Burning velocity (cm/s)</th>
<th>oxy_21</th>
<th>oxy_25</th>
<th>oxy_29</th>
<th>air</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>4.7</td>
<td>9.9</td>
<td>16.6</td>
<td>35.8</td>
</tr>
<tr>
<td>1.10</td>
<td>4.5</td>
<td>9.5</td>
<td>16.1</td>
<td>34.3</td>
</tr>
<tr>
<td>1.15</td>
<td>4.1</td>
<td>9.0</td>
<td>15.4</td>
<td>32.5</td>
</tr>
<tr>
<td>1.20</td>
<td>3.8</td>
<td>8.4</td>
<td>14.6</td>
<td>30.5</td>
</tr>
<tr>
<td>1.25</td>
<td>3.3</td>
<td>7.7</td>
<td>13.7</td>
<td>28.0</td>
</tr>
</tbody>
</table>

### 4.2 KINETIC MODELING

Figures 6 and 7 show the measured and calculated CO emissions as a function of the excess oxygen coefficient for air and three oxidizer compositions, respectively, and Figures 8 and 9 show the measured and calculated NO emissions as a function of the excess oxygen coefficient for air, with and without NH₃ in the fuel, and three oxidizer compositions, respectively. Note that the experimental and calculated data are plotted with different scales in order to gain qualitative insight to the results since CO is slightly underpredicted and NO is largely overpredicted (except for the condition where CH₄ is not doped with NH₃ when burned with air). The relationship between the experimental and calculated CO values is (simulated CO) = (experimental CO) – (K₁), where K₁ is 25 and 40 for the air and the oxy-fuel cases, respectively. In the case of the NO, the relationship is (simulated NO) = (experimental NO) × (K₂), where K₂ is 3.5 and 6.5 for the air and the oxy-fuel cases, respectively. The overall qualitative agreement between experiments and calculations is very satisfactory. However, quantitatively there are discrepancies, which are more pronounced on the NO results.

![Figure 6. Measured (scale on the left) and calculated (scale on the right) CO emissions as a function of the excess oxygen coefficient for air.](image)

![Figure 7. Measured (scale on the left) and calculated (scale on the right) CO emissions as a function of the excess oxygen coefficient for three oxidizer compositions.](image)
Figure 8. Measured (scale on the left) and calculated (scale on the right) NO emissions as a function of the excess oxygen coefficient for air with and without ammonia in the fuel.

Figure 9. Measured (scale on the left) and calculated (scale on the right) NO emissions as a function of the excess oxygen coefficient for three oxidizer compositions.

Figure 10. Typical calculated axial CO concentration profiles for four oxidizer compositions at a fixed excess oxygen coefficient of 1.15.

In order to gain further insight into the present results, a rate-of-production (ROP) together with a sensitivity analysis was performed for both CO and NO. Figures 10 and 11 show typical calculated axial CO and NO concentration profiles, respectively, for four oxidizer compositions at a fixed excess oxygen coefficient of 1.15. As expected, the CO formed in the flame region is subsequently oxidized to some extent. NO is initially formed and reaches a plateau level where it is very slightly reduced along the post flame zone. In air combustion NO is globally formed through the entire reaction zone.

CO formation is connected to the hydrocarbon oxidation. The set of reactions that have a major contribution to CO formation does not differ much between oxy-fuel and air fired combustion. However, in oxy-fuel combustion, due to the presence of large concentrations of CO2 and sufficiently reactive radicals such as methylene, the reaction where the CO2 molecule is broken forming CO has also a major contribution:

$$^{1}\text{CH}_2 + \text{CO}_2 \leftrightarrow \text{CH}_2\text{O} + \text{CO}$$  \hspace{1cm} (1)

Glarborg and Bentzen [3] found that steps where methylene reacts with CO2 are responsible for 10%-20% of the consumption of CO2.

The CO oxidation process is quite well established. CO oxidation takes place almost solely through reaction 2:

$$\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$$  \hspace{1cm} (2)

It is unambiguous that this is a key reaction in oxy-fuel combustion where a large amount of CO2 is present. Actually, its reverse step (reaction 2b) contributes to CO2 reduction at medium to high temperatures (flame region), due to equilibrium reasons [5,8]. In the presence of air this reaction is the only step to CO oxidation, according to the rate-of-production analysis.

CO concentration in the flame region is sensitive, (almost) regardless of the oxidizer composition or stoichiometry, to chain branching reactions (Reaction 3 is the main chain branching reaction):

$$\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$$  \hspace{1cm} (3)

$$\text{H} + \text{O}_2 (+\text{M}) \leftrightarrow \text{HO}_2(+\text{M})$$  \hspace{1cm} (4)

For high oxygen concentrations in the oxidizer (25-29%) in oxyfuel combustion, CO oxidation is also sensitive to reactions that contribute more to the CO formation according to the ROP analyses. For low oxygen concentrations in the oxidizer (21-25%) it was found that reaction 1 is also present. CO is equally sensitive to steps that consume CH4 (reaction 5) and that lead to chain propagation (reaction 6) or termination (reaction 7), (almost) regardless of the oxidizer composition or stoichiometry:

$$\text{CH}_4(+\text{M}) \leftrightarrow \text{CH}_3 + \text{H} (+\text{M})$$  \hspace{1cm} (5)

$$\text{CH}_3 + \text{HO}_2 \leftrightarrow \text{CH}_2\text{O} + \text{OH}$$  \hspace{1cm} (6)

$$2\text{CH}_3(+\text{M}) \leftrightarrow \text{C}_2\text{H}_6(+\text{M})$$  \hspace{1cm} (7)
In the oxidation region, CO concentration calculations are greatly and negatively sensitive to chain branching reactions 3 and 4. This means that an increase in these reaction rates would decrease CO formation. It is interesting to note that, in this zone, contrarily to the flame region, reaction 2 appears among the reactions to which CO is more sensitive (negatively). In fact, from a certain point it is, by far, the reaction to which CO is most sensitive. The importance of reactions 2 and 3 gives evidence of the competition between those two reactions, thus limiting the size of the O/H pool, under oxy-fuel conditions.

Figure 11. Typical calculated axial NO concentration profiles for four oxidizer compositions at a fixed excess oxygen coefficient of 1.15.

Formation of NO occurs under all conditions mostly with HNO as intermediate:

\[
\begin{align*}
HNO + H & \leftrightarrow NO + H_2 \quad (8) \\
HNO + OH & \leftrightarrow NO + H_2O \quad (9) \\
HNO + O & \leftrightarrow NO + OH \quad (10) \\
HNO + O_2 & \leftrightarrow NO + HO_2 \quad (11)
\end{align*}
\]

Reaction 8 has a major contribution, while reaction 9 contributes less. Reactions 10 and 11 have even less contribution to NO formation, only under oxy-fuel conditions. Another minor pathway proceeds via NH:

\[
NH + O \leftrightarrow NO + H \quad (12)
\]

And, under some conditions, through N:

\[
\begin{align*}
N + OH & \leftrightarrow NO + H \quad (13) \\
N + O_2 & \leftrightarrow NO + O \quad (14)
\end{align*}
\]

As pointed out by Mendiara and Glarborg [8], once NO is formed some NO to NO\(_2\) interconversion occurs. This interconversion takes place through the entire reaction zone.

The reaction responsible to NO reduction in the oxidation zone, for all oxidizer compositions, was found to be:

\[
H + NO (+M) \leftrightarrow HNO (+M) \quad (15)
\]

A closer examination of the rates of production of NO within all conditions studied lead to the conclusion that, contrarily to what is seen in the trends represented in terms of ppm, an increase to the oxygen concentration in the oxidizer results in lower NO formation. Actually, similarly to what Alves et al. [12] obtained experimentally in their parametric study, using a pollutant emission rate in ng/J, the oxidizer composition has little effect on NO formation from NH\(_3\). Figure 12 shows the measured and calculated NO emissions, in ng/J, as a function of the excess oxygen coefficient for three oxidizer compositions. These trends demonstrate that due to the fact that for a fixed thermal input, varying the oxygen flow rate for each stoichiometry and, then, for each stoichiometry, varying the CO\(_2\) flow rate to achieve the desired oxygen composition brings some dilution effects affecting the concentrations. However, although affected by dilution, the CO trends are kept, as well as the NO trends as a function of the excess oxygen coefficient.

Figure 12. Measured (scale on the left) and calculated (scale on the right) NO emissions as a function of the excess oxygen coefficient.
fuel showed that NO is formed mainly through the thermal-NO mechanism:

\[ \text{N + NO} \leftrightarrow \text{N}_2 + \text{O} \]  

(16)

NO formation in air combustion has been widely studied for many years and it is not important to discuss it in much detail here. Basically, the reverse step of reaction 16 controls the thermal-NO formation mechanism, which has high activation energy, requiring high temperatures to initiate. Since such temperatures are experienced in the present work (above 1800 K) the mechanism is activated. Reaction 21b is followed by reactions 13 and 14 completing the extended Zeldovic mechanism.

It was seen that reactions, which contribute more to the CO formation, are important in establishing NO concentration for the same conditions found for CO. However, the relative sensitivity is different. NO is positively sensitive to reaction 2, unlike CO. NO concentration, in the flame region, is particularly sensitive to steps that consume CH₄ and that lead to chain propagation and termination, such as reactions 5-7. In the post flame zone, steps involving amine species seem to affect NO concentration, while the chain branching reactions no longer play a significant role. In this region, NO sensitivity does not seem to vary much with stoichiometry or oxidizer composition.

5. CONCLUSIONS

The main conclusions of the present study are as follows:

- The experimental results showed that, for all oxidizer compositions, an increase in the excess oxygen coefficient generally decreases both the CO and NO emissions.
- For O₂/CO₂ environments, decreasing the oxygen concentration in the oxidizer leads to higher CO emissions, but lower NO emissions.
- In air firing the CO emissions are significantly lower than those found in oxy-fuel firing, while the NO emissions are higher than those from the oxy-fuel cases.
- Simulations showed better agreement for CO than for NO, which was largely overpredicted. The main reactions that directly (with the aid of a rate-of-production analysis) and indirectly (through a sensitivity analysis) influence both CO and NO emissions were identified.
- CO formation, under oxy-fuel conditions, has the contribution of CO₂ + H ↔ CO + OH and 1CH₂ + CO₂ ↔ CH₂O + CO additionally to those found in air fired combustion, while CO oxidation takes place through CO + OH ↔ CO₂ + H, for all studied conditions.
- Formation of NO occurs under all conditions mostly with HNO as intermediate, particularly through HNO + H ↔ H₂ + NO. Once NO is formed some NO to NO₂ interconversion occurs. The reaction responsible to NO reduction in the oxidation zone, for all oxidizer compositions, was found to be H + NO (+M) ↔ HNO (+M).

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