Perfectly Stirred Reactor Network Modeling of NOx and CO Emissions from a Gas Turbine Combustor with Water Addition

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Andrew North
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Abstract

A Perfectly Stirred Reactor (PSR) network model, with the capability to treat liquid droplet addition, was developed for predicting NOx and CO emissions from a gas turbine combustor. Computational Fluid Dynamics (CFD) results were utilized to establish targets in CO$_2$, temperature, residence time, and Fuel Air Ratio (FAR) for each reactor in the network. Known boundary conditions were utilized as inputs for the fuel, air, and water distribution at the boundaries of the network. NOx and CO predictions from the model correspond well with experimental results with FAR as a parameter. NOx emissions trend well with Water Fuel Ratio (WFR), though CO emissions trends with WFR are unsatisfactory. More work is needed to improve wet CO emissions predictions with the model used.

Introduction

A network PSR model was constructed with the purpose of replicating experimental NOx and CO emissions trends and extrapolation of these results outside of rig capabilities so that alternative designs can be investigated in a simplistic manner in terms of how emissions might be affected and for scaling results to pressures that have not been investigated experimentally. The model consists of 124 perfectly stirred reactors, and utilizes an existing network Perfectly Stirred Reactor (PSR) tool to for solving the chemistry. The Chemkin subroutine StanJan is called by the code for each reactor in the network, and the outlet concentrations of each species and the temperature for each reactor is passed on to downstream reactors as defined in the model construction. The code iterates through the network until changes in species concentrations fall below the user specified (or default, if desired) threshold relative and absolute tolerance values.

The model has been set up such that a FLUENT CFD result is as closely matched as possible with regard to local CO$_2$ concentration, Fuel Air Ratio (FAR), temperature, and residence time. PSR cell sizes were selected such that gradients in temperature, FAR, velocity, and CO$_2$ concentration are minimized in each volume. Only parameters that were not already known (boundary conditions from the experiment for example) were modified to ensure that the CFD parameters were met. The parametric knob needing to be tuned to match the CFD solution to the PSR result is the amount of mass that is exchanged among the volumes. Only mass between adjacent volumes was allowed.

Methodology

Figure 1 shows a representative schematic of a gas turbine combustor similar to the one analyzed.
Fuel is injected at the beginning of the combustor as well as part of the total air budget. More air is injected downstream of the fuel injector, resulting in an overall lean condition at the exit of the combustor. The air distribution around the network was determined from experimental cold flow measurements. None of the air “splits” were adjusted to match the CFD solution.

Figure 2 shows the layout of the PSR network. PSR sets 3-18 are arranged 3-dimensionally to capture circumferential gradients. The rest of the network was designed 1-dimensionally.
Figure 2: Diagram showing the PSR volume locations and orientation
Figure 3 through Figure 6 show schematically how fluid moves into, around, and out of the network. The arrows are color-coded, with red representing fuel, air and water entering the combustor in the front end, yellow representing air entering the combustor at in the combustor walls, blue representing convective and diffusive exchange between volumes, green representing convected flow downstream, and magenta representing flow exiting the combustor.
Figure 3: Rich section with fuel air and water splits (red and yellow), mass transfer assignments in the forward direction (green) and mass transfer assignments between parallel volumes (blue).

The core section in the first set of reactors is separated into 3 separate sections. The “jet” volumes represent a high velocity region. This volume is intended to represent the low residence times experienced by the gas. The “recirculation region” is intended to represent a low velocity recirculation region. The rest of the core volume is “medium velocity”.

The second set of reactors has the largest volume in the network owing to an apparent homogeneity in this region. The other volumes attempt to resolve steep gradients at the boundary.
The quench zone is split into 15 individual volumes to time resolve the transition through stoichiometric. The quench air is distributed throughout all of the volumes.
Figure 5: First part of lean section with air splits (yellow), mass transfer assignments in the forward direction (green) and mass transfer assignments between parallel volumes (blue).

The set of reactors following the quench zone (first part of lean section) maintains circumferential variation to capture circumferential gradients.
Figure 6: Last part of lean section with air splits (yellow), mass transfer assignments in the forward direction (green), mass transfer assignments between parallel volumes (blue) and all combustor exit flow (magenta).

The size of each volume in the last part of the lean section was chosen to match those of the upstream reactor set as closely as possible. The products from the core volumes in the last set of reactors pass onto the “Core Collector”. The core collector is in place to serves as a tool to help compare PSR network results to experimentally measured results. Results reported in this document, however, are from the final collector volume, and consequently represent a true mean value of the emissions exiting the combustor.

**PSR Model Performance**

The model has been developed solely based on information gleaned from the CFD solution and experimental measurements of the CO\(_2\) concentration and temperature profile at the exit of the combustor. Once all of the boundary conditions were determined, the NOx and CO emissions predictions as a function of FAR agreed with experimental data superbly, as shown in Figure 7.
Figure 7: Experimental and calculated NOx and CO emissions versus fuel-air ratio.

Figure 8 shows the real CO$_2$ exit concentration profile alongside the PSR results.
Agreement was deemed acceptable, especially given the NOx and CO emissions agreement. Figure 9 shows the average CO concentration profile at the combustor exit as well as the PSR results.
The CO exit profile seems to trend well with experimental results. Note that regions of high CO concentrations coincide with regions of high CO$_2$ concentrations, indicating that lean quenching does not dominate CO emissions for this case. Instead, richer regions have had less time for CO to CO$_2$ oxidation, since richness is an indication of how long these regions have been lean enough for CO oxidation (richer regions transition through stoichiometric last).

**Wet NOx Emission Predictions**
NOx predictions as a function of WFR also agree with experimental data quite well, as shown in Figure 10.
At high watering, NOx emissions fall below the experimental trend when the assumption is made that the water takes the same path as the fuel. This assumption can be viewed as the ideal case, because the water will reduce the flame temperature uniformly with this assumption. When water is distributed radially in the front end of the combustor according to the bulk flow, however, the trend agrees much better with experimental results. Consequently, this analysis suggests that the water distribution is dominated by the flow characteristics of the bulk flow, and the fuel follows a slightly different distribution pattern. Figure 11 elucidates where the water impacts NOx emissions by plotting the local NOx emissions index (change in NOx mass flow in each reactor in g/s normalized by total fuel mass flow rate entering the combustor in kg/s). The running total of the emission index is also plotted, which is annotated as the “NOx Progression Metric”.

Figure 10: Experimental and calculated NOx emissions versus water fuel ratio.
As WFR is increased, NOx production in the quench zone (3A1 through 17C2) is reduced significantly, and is completely quenched in the lean section. Figure 12 shows the same information, but zoomed in on the front end.
In further analyzing the impact of a “non-ideal” water distribution pattern, the NOx progress variables are plotted in Figure 13 for both ideal and non-ideal cases.
For both cases, the NOx is produced primarily in the quench zone, and rich section NOx is nearly identical between both cases. This analysis supports the hypothesis that non-ideal water distribution results in a non-uniform reduction in the flame temperature with water addition.

Since NOx emissions predictions agree well with experimental data for various FAR and WFR conditions, it was deemed a valuable tool for determining how NOx emissions might change as combustor pressure is varied. Commonly, NOx pressure dependence is characterized by a “pressure exponent”, where the ratio of the pressure of interest to the experimentally measured pressure is raised to a known exponent that NOx emissions are dependent upon. Figure 14 summarizes the results of this work:

As pressure is increased, NOx emissions predictions generally increased due to kinetic effects, leading to a positive NOx pressure exponent. The computed dry pressure exponent agrees well with values observed with different combustors. As WFR increases the value of the computed pressure exponent decreases.

Wet CO Emissions Predictions and Discussion
The CO predictions as a function of WFR do not follow the experimental trend, as shown in Figure 15. CO predictions reduce as WFR increases, whereas experiments demonstrate that eventually, CO emissions increase with WFR.
Theory and model predictions agree that CO formation under rich conditions should reduce quite markedly when WFR increases. This effect is due to reduced reaction rates with finite residence times as well as an equilibrium shift from CO to CO$_2$ as watering increases due to increased levels of OH which hastens CO oxidation. Table 1 shows tabulated CO concentrations using various mechanisms in a single perfectly stirred reactor for equilibrium and finite residence time conditions.

Table 1: CO mole fraction results for various mechanisms and equilibrium results for various equivalence ratios.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>NASA Equilibrium Code</th>
<th>GRI Mech Large tau</th>
<th>Heptane Mech Finite tau</th>
<th>LEEDS Mech Finite tau</th>
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<tbody>
<tr>
<td>0.5</td>
<td>1.6E-5</td>
<td>2.37E-4</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1.26</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
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<td>.0187</td>
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<tr>
<td>2</td>
<td>.0408</td>
<td>.0340</td>
<td>.0417</td>
<td>.0400</td>
</tr>
<tr>
<td>2.5</td>
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<td>.0379</td>
<td>.0419</td>
<td>.0264</td>
</tr>
<tr>
<td>3</td>
<td>.0496</td>
<td>.0370</td>
<td>.0367</td>
<td>.0322</td>
</tr>
</tbody>
</table>
“X”’s denote cases that were not run, and “DNC” denotes cases that did not converge. Note that CO levels increase only for lean conditions. When residence time is made a parameter, however, it is possible to achieve an increase in CO under slightly rich conditions, as shown in Table 2.

Table 2: CO mole fractions for various residence times for various equivalence ratios and real network results.

<table>
<thead>
<tr>
<th>Φ</th>
<th>GRI tau ~ 0.055 ms</th>
<th>GRI tau ~ 1 ms</th>
<th>GRI tau ~ 1 ms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WFR = 0</td>
<td>WFR = 1</td>
<td>WFR = 0</td>
</tr>
<tr>
<td>0.5</td>
<td>X</td>
<td>X</td>
<td>9E-4</td>
</tr>
<tr>
<td>1.265</td>
<td>.023</td>
<td>.024</td>
<td>X</td>
</tr>
<tr>
<td>1.265 (PSRnet)</td>
<td>.023</td>
<td>.018</td>
<td>X</td>
</tr>
<tr>
<td>1.265 (PSRnet2)</td>
<td>.023</td>
<td>.015</td>
<td>X</td>
</tr>
<tr>
<td>1.265 (PSRnet simulated)</td>
<td>.0135</td>
<td>.0147</td>
<td>X</td>
</tr>
<tr>
<td>1.32</td>
<td>X</td>
<td>X</td>
<td>.007</td>
</tr>
<tr>
<td>2</td>
<td>X</td>
<td>X</td>
<td>DNC</td>
</tr>
</tbody>
</table>

Cases labeled “PSRnet” are actual results from the network, where the opposite trend is seen in comparison to the cases with a single perfectly stirred volume. The only presumable difference between “PSRnet” cases and single volume cases is the change in minor species concentrations emanating from neighboring reactors. The “PSRnet simulated” cases is set up such that the water vapor, CO, fuel, and CO₂ concentrations entering the network where the equivalence ratio is 1.265 is comparable, but still an increase is seen in CO with water addition here because water makes the CO oxidation reaction more kinetically limited. Presumably, an increase in OH volume fraction resulting from water addition, which facilitates CO oxidation, is responsible for the reduced CO concentration with water addition in the network cases at this equivalence ratio.

CO formation generally ceases when the equivalence ratio falls below about 1.27 and CO oxidation begins shortly thereafter. This is also the equivalence ratio where NOx formation increases dramatically. In the PSR model, when water is added at the point where the equivalence ratio is 1.27 (near the beginning of the quench zone), the CO oxidation rate increases dramatically with water addition. In the lean section, however, water addition quenches the CO oxidation reaction. The combined effect, however, is that when water is added anywhere in the combustor in a manner that maintains consistency with experimental NOx measurements, the net CO emissions predictions are significantly under predicted. Possible causes of this error are:

1. Poor assumption of a perfectly stirred condition in the lean section
2. Poor resolution in the rich section, where the “sweet spot” in terms of equivalence ratio which maximizes CO formation is not resolved well enough
3. Turbulence chemistry interactions. Near the stoichiometric region, as water is added, OH volume fraction should increase which will increase CO oxidation (seen in the PSR network). In reality, however, OH, H, O, and H$_2$O have higher diffusivities than the bulk gas. As such, these constituents should diffuse away from the thin reaction zone faster than the other constituents. When this preferential diffusion is significant, CO oxidation could be substantially reduced, which cannot be captured by a PSR network or most Large Eddy Simulation (LES) methods.

Figure 16 shows progression metrics for CO similar to those previously shown for NOx.

![Figure 16: Wet and dry CO emissions indices and running total along combustor.](image)

CO is formed in significant quantities in the beginning of the combustor, and slowly oxidizes thereafter. With water addition, CO formation is slowed significantly in the front end, and the reduced reaction rates for lean conditions are not significant enough to cause a net increase in CO with water addition. This effect is shown more clearly in Figure 17 which zooms in on the lean section.
Wet NOx emissions predictions suggest that water may not follow the fuel in an ideal manner. In investigating how this “non-ideal water distribution” effect might impact the wet CO prediction problem, an analysis was conducted where water was injected downstream of the front end to investigate whether this strategy can ameliorate the problem. The goal of this analysis is to determine how far downstream of the front end would the water need to be well mixed, and consequently delay CO formation reduction, for model results to agree with experimental results. Figure 18 summarizes these results.
The following summarizes the various “water placement redistribution schemes” codified in the legend of Figure 18:

- **Redist1**: 30% reactor set 1, 50% reactor set 2, 20% reactor set 3; distributed radially by volume
- **Redist2**: 30% reactor set 1, 50% reactor set 2, 20% reactor set 3; distributed radially by fuel flow rate
- **Redist3**: Water placed at beginning of quench zone; distributed radially by fuel flow rate
- **Redist4**: Water placed at second set of quench zone volumes; distributed radially by fuel flow rate
- **Redist6**: Water placed as late as possible to maintain NOx predictions at reasonably low levels, consistent with experimental data, and only in volumes which require NOx formation quenching; distributed radially by fuel flow rate

Figure 19 shows the same results, but zoomed in on the lean section.
Regardless of where the water is placed, the reduced CO formation under rich conditions with water addition dominates the net CO emissions, and water placement any further downstream of what was investigated in this analysis will compromise NOx emissions predictions (already the case for some of the conditions plotted in Figure 18 and Figure 19).

**Summary and Conclusions**

A PSR network model was developed, which has been shown capable of reproducing emissions trends and values as functions of FAR without artificial tuning to improve NOx and CO emissions predictions. The network is capable of reproducing NOx emissions trends and values as a function of WFR, but currently does not trend with experimental results for CO emissions as a function of WFR. Water distribution according to the bulk flow rather than the fuel mass flow results in more accurate wet NOx emissions predictions. The non-ideal mixed front end assumption, however, does not ameliorate the wet CO predictions problem. Further work is required if wet CO emissions predictions are deemed necessary. Due to acceptable agreement between predicted and experimental NOx emissions results, the PSR network was utilized to estimate pressure exponents for NOx at various WFR values. The computed dry NOx pressure exponent agrees reasonably with values measured for similar combustors, giving confidence in the use of the computed values for the wet cases.
References