

Model Based Assessment of the Novel Use of Sour Water Stripper Vapor for NO_x Control in CO Boilers

Marc Cremer and Dave Wang
Reaction Engineering International
cremer@reaction-eng.com

Jerry Zhang and Deke Lincoln
Norton Engineering
Jerry.Zhang@nortonengr.com

Abstract

CO boilers are commonly utilized in oil refineries to produce process steam by burning the low BTU, CO-containing gasses that are produced during regeneration of the fluid catalytic cracking (FCC) catalysts. Supplemental heating through fuel gas burners is necessary to carry out complete oxidation of the CO containing regeneration gases. The regeneration gases may contain varying concentrations of fuel nitrogen species including HCN, NH₃, and NO, which can be sources of NO generation along with thermally produced NO in the CO boiler.

This paper discusses the results of a Computational Fluid Dynamics (CFD) based evaluation to guide the design of selective non-catalytic reduction (SNCR) for NO_x control in two typical CO boiler configurations. In addition to the regeneration gases that are combusted in both boilers, a significant quantity of sour water stripper (SWS) vapor is injected into the combustion zone, subsequently generating fuel NO_x emissions. The CFD simulations show the potential for reducing NO_x emission by relocating a portion of the SWS vapor from the combustion zone to the post-combustion zone, where the SWS vapor acts as an SNCR reagent. Potential impacts on H₂S emissions by relocation of the SWS vapor are also examined.

1 Introduction

In the hydrocarbon processing industry, the operation of a fluid catalytic cracking unit (FCCU) produces low BTU, CO-containing gases. To reclaim the energy in these gases and reduce CO emission, a CO boiler is commonly included in the FCCU design to combust CO and to generate steam. Supplemental heating through fuel gas burners is necessary to carry out complete oxidation of the CO containing regeneration gases and to generate additional steam required by the refinery. Depending on the operating mode of the FCCU, the regeneration gases may contain varying concentrations of fuel nitrogen species including HCN, NH₃, and NO, which can be sources of NO generation along with thermally produced NO in the CO boiler.

Sour water stripping is used to remove ammonia (NH₃) and hydrogen sulfide (H₂S) from sour water streams, which can come from distillation, fluid catalytic cracking, catalytic reforming, coker and acid gas removal units etc. in a refinery. Sour water stripper (SWS) vapor can be mixed with the regeneration gases, then combusted in a CO boiler. The presence of NH₃ in the SWS vapor has potential to generate a significant quantity of fuel NO_x emissions in the CO boiler.

This paper discusses the results of a CFD-based evaluation to guide the design of selective non-catalytic reduction (SNCR) using SWS vapor as a SNCR reagent for NO_x control in two typical CO boiler configurations. In both boilers, sour water stripper (SWS) vapor is mixed with the regeneration gas before the mixture is injected into the combustion zone to be combusted, subsequently generating a significant quantity of fuel NO_x emissions. The CFD simulations evaluate the significant potential for NO_x reduction by relocating a portion of the SWS vapor from the combustion zone to the post-combustion zone, where the SWS vapor acts as an SNCR reagent. Potential impacts on H₂S emissions by relocation of the SWS vapor are also examined since the SWS vapor also contains H₂S.

2 Methods

2.1 CO Boiler Descriptions

Two typical refinery CO boiler configurations are shown in Figures 1 and 2. The first typical style, a “wall fired” CO boiler (shown in Figure 1), includes fuel gas burners that are fired horizontally from the end of the boiler, while regeneration gas mixed with SWS vapor is injected into the combustion zone from the top of the boiler. The CFD evaluation included the relocation of a portion of the SWS vapor from the regeneration gas to new SNCR ports located in the post combustion zone. Different SWS vapor rates to the combustion and SNCR zones were evaluated through the CFD simulations in order to determine optimum operation for NO_x reduction.

A typical tangentially fired CO boiler configuration is shown in Figure 2. In this style of CO boiler, the regeneration gas ports and the fuel gas burners are located at the corners of the CO boiler, with the burner region of the boiler lined with refractory and the upper region of the boiler enclosed with bare waterwall tubes. The CFD evaluation for this style of CO boiler reviewed the relocation of a portion of the SWS vapor from the regeneration gas to new SNCR ports installed above the burner region where conditions are more favorable for SNCR chemistry. Different SWS vapor rates to the regeneration gas and SNCR ports were evaluated in order to optimize operation for NO_x reduction.

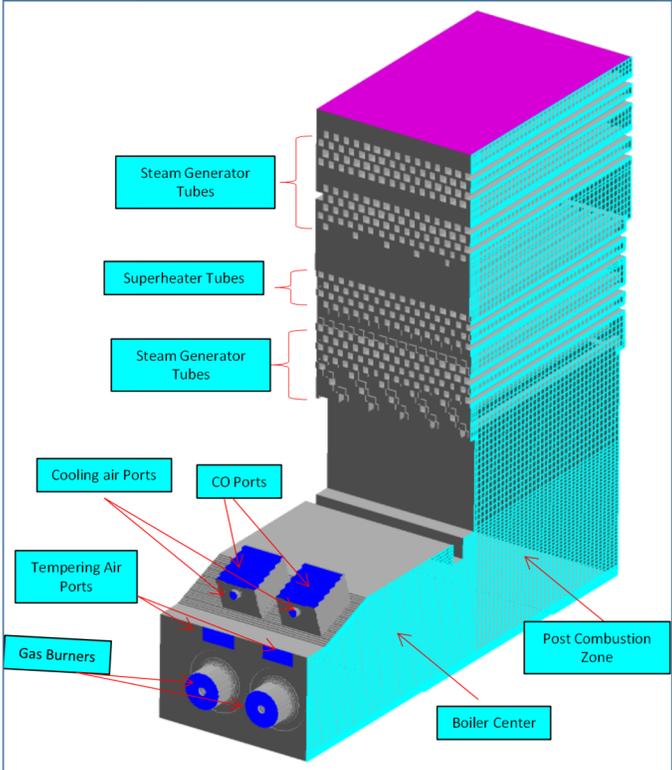


Figure 1: A wall fired CO boiler

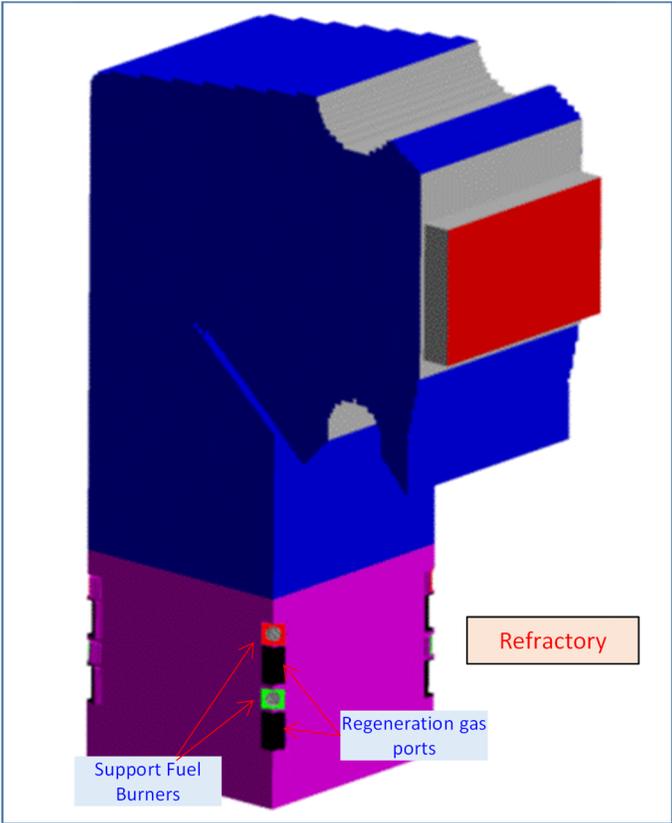


Figure 2: A tangentially fired CO boiler

2.2 CFD Model Description

Reaction Engineering International (REI)'s proprietary CFD code, *ADAPT*, was used for the evaluation reported in this paper. *ADAPT* is a three dimensional, reacting CFD code that has been extensively utilized to simulate gas-fired combustion applications requiring an accurate treatment of chemistry and turbulence-chemistry interactions [1, 2].

The gas-phase fluid mechanics, heat transfer, thermal radiation and species transport are solved through conservation governing equations in an Eulerian framework. This software is a Reynolds Averaged Navier Stokes based CFD tool using a standard k- ϵ two equation turbulence model. The code utilizes the discrete-ordinates model for radiation heat transfer [3, 4]. This method retains the directional dependency of the radiation intensity in a way that other flux models are unable to achieve, yet provides for a finite-difference or finite-volume solution that is more computationally efficient than zone methods and more deterministic than Monte Carlo methods.

The computational mesh is unstructured Cartesian with localized mesh refinement. Finite rate chemical kinetics are implemented through use of reduced mechanisms developed from the Computer Assisted Reduced Method (CARM) [5], based on steady state assumptions. The detailed mechanism used to develop the reduced mechanism is the GRI3.0 mechanism with addition of SNCR NO_x chemistry. The reduced Mechanism used in this study contains 22 non-steady state species (H₂ H O₂ OH H₂O HO₂ H₂O₂ CH₃ CH₄ CO CO₂ CH₂O CH₃OH C₂H₂ C₂H₄ C₂H₆ NH₃ NO N₂O HCN HNCO N₂). In-situ Adaptive Tabulation (ISAT) is used to reduce the computational time associated with integration of the finite rate chemical kinetics. Turbulence-chemistry interactions are represented using the eddy dissipation concept (EDC).

3 Results and Discussion

3.1 Wall Fired CO Boiler

The gas temperature profile under baseline operation is shown in Figure 3. Even though some temperature variations are observed, the overall gas temperatures between plane 1 and plane 3 are favorable for SNCR, with residence time between plane 2 and plane 3 adequate for SNCR chemistry. Figure 4 shows the CO concentration profile under baseline operation. Although the CO concentration is relatively high in the horizontal combustion region, the CFD predicted average CO concentration is very low after the gases make the 90° turn (i.e., plane 2). The predicted NO_x concentration profile under baseline operation is shown in Figure 5. Most of the NO_x is formed in the horizontal combustion section, with some formed between plane 1 and plane 2. The NO_x chemistry is essentially quenched after plane 2.

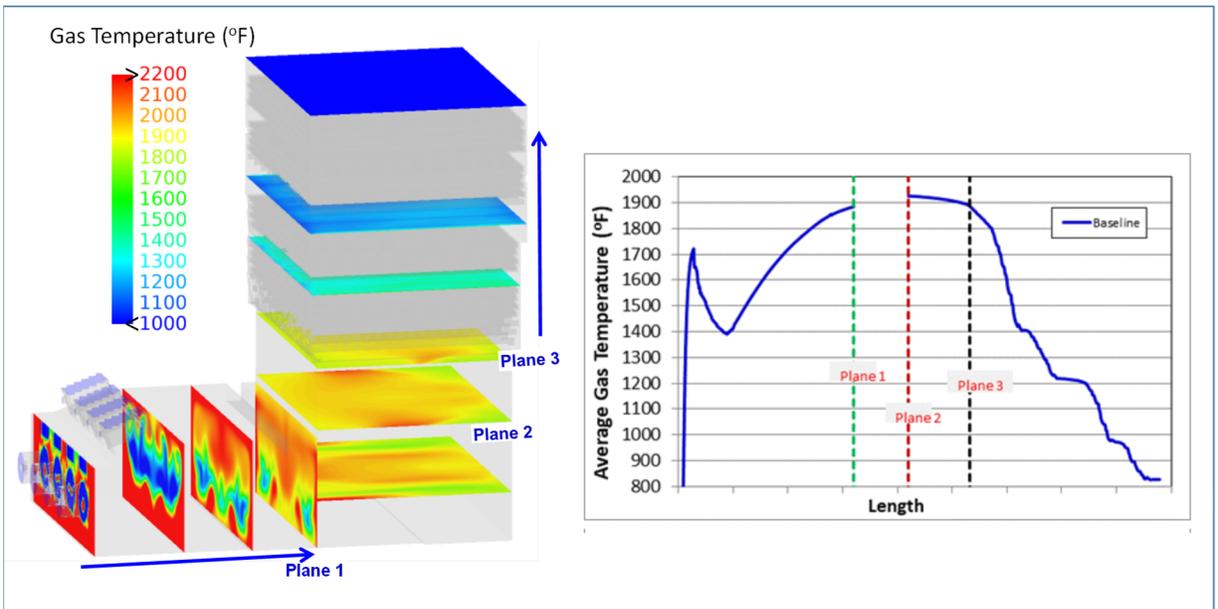


Figure 3: Flue gas temperatures for baseline operation

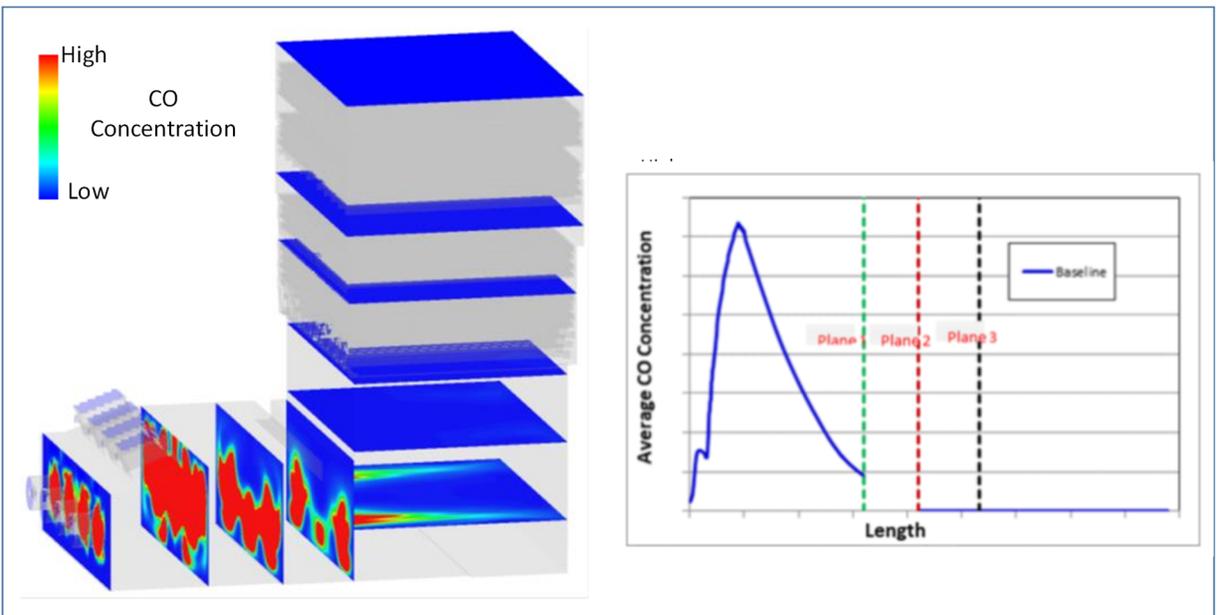


Figure 4: Flue gas CO concentrations for baseline operation

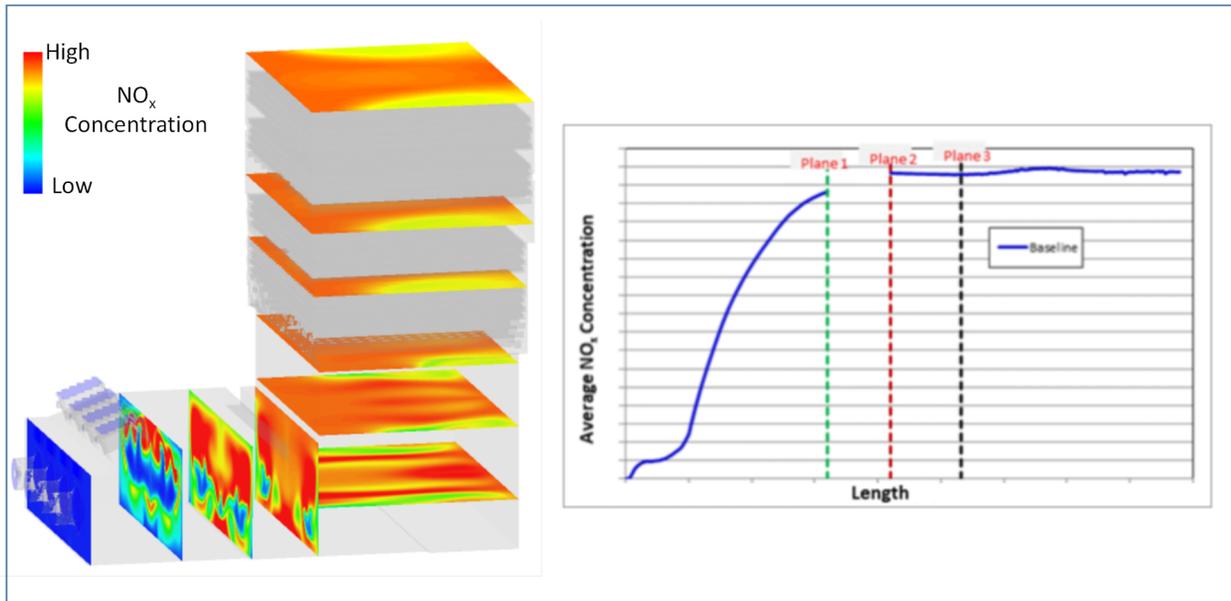


Figure 5: Flue gas NO_x concentrations for baseline operation

Figure 6 and Figure 7 show average flue gas temperatures and CO concentrations for simulations involving potential modifications to relocate a portion of SWS vapor to downstream SNCR ports. The influence of modifications on the gas temperature in the horizontal combustion section can be seen from Figure 6. However, downstream of plane 2, the average gas temperatures are similar for the modification cases and the baseline. Figure 7 also shows that the CO concentration is low for all the cases after plane 2. This suggests that the simulated modifications have negligible effects on the combustion efficiency. Figure 8 and Figure 9 show the NO_x concentrations and NH₃ concentrations for the baseline in comparison with the modification cases. As can be seen from Figure 8, significant reduction in NO_x emission is predicted for both cases involving relocation of SWS vapor to the SNCR ports. The NO_x reductions come from both reduced NO_x formation in the horizontal combustion zone due to less fuel-N species, and conversion of NO_x to N₂ in the post combustion zone with SNCR chemistry using SWS vapor as an SNCR reagent. These results indicate that the relocation of SWS vapor to the post combustion SNCR zone is a very attractive approach to abate the NO_x emission in this type of CO boiler. Since the SWS vapor also contains H₂S, a potential concern is increased H₂S emissions with this approach. This issue is discussed later in this paper

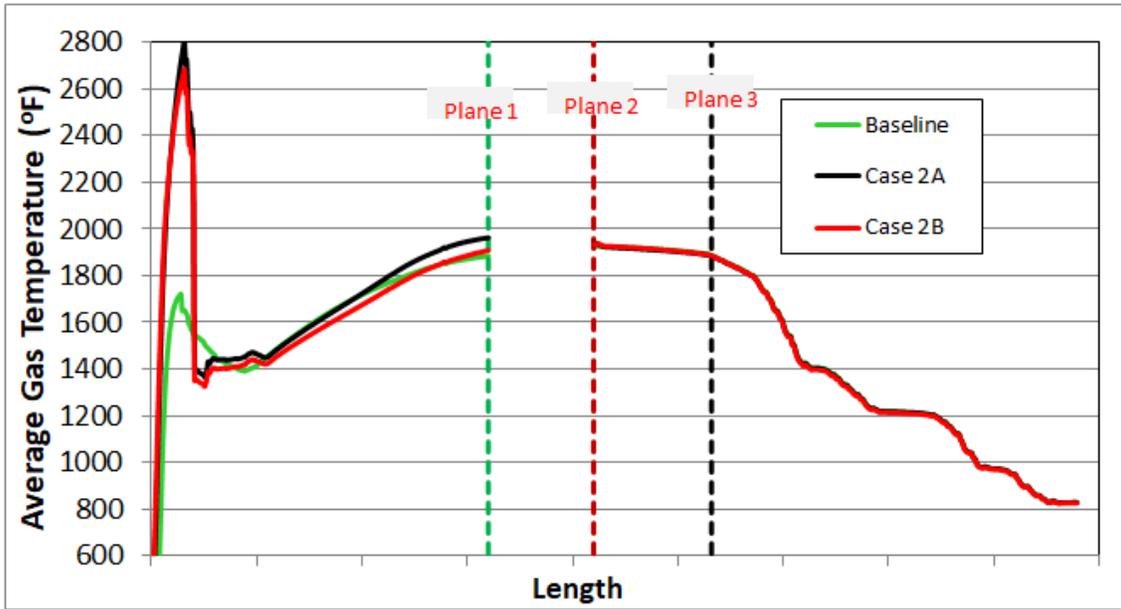


Figure 6: Average gas temperatures vs boiler length

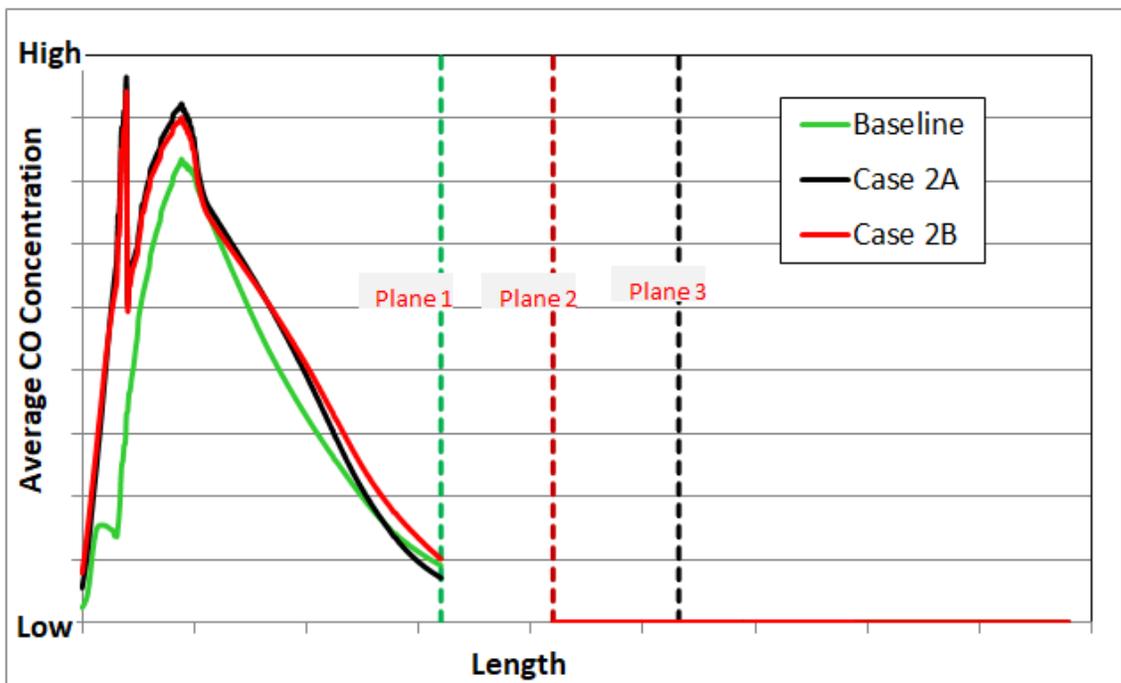


Figure 7: Average CO concentrations vs boiler length

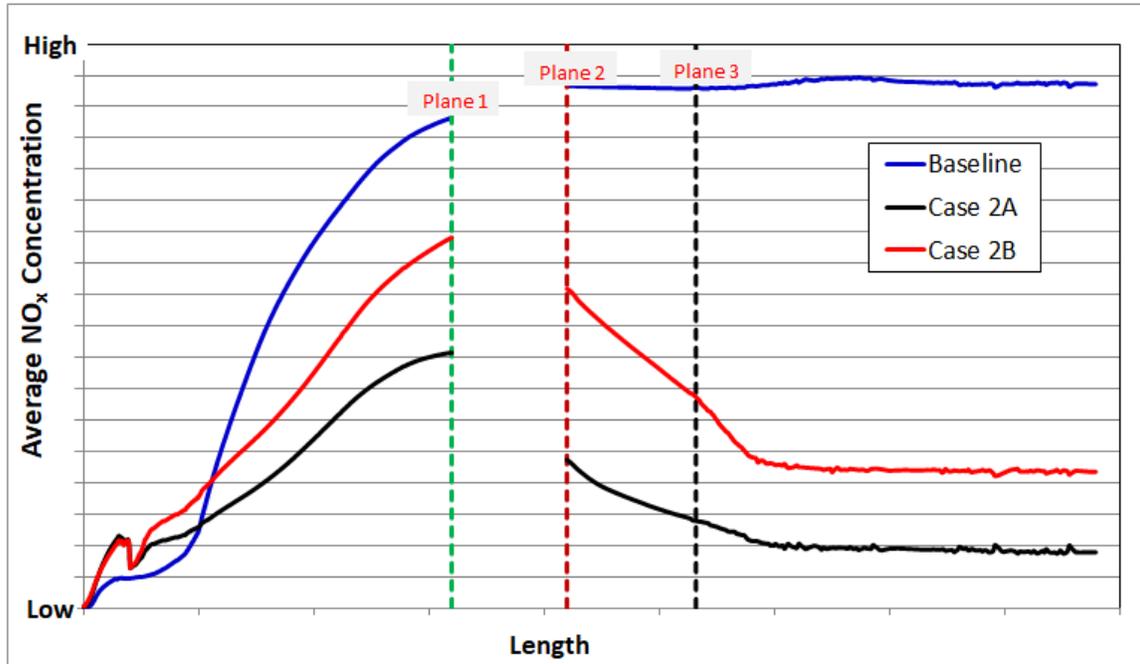


Figure 8: Average NO_x concentrations vs boiler length

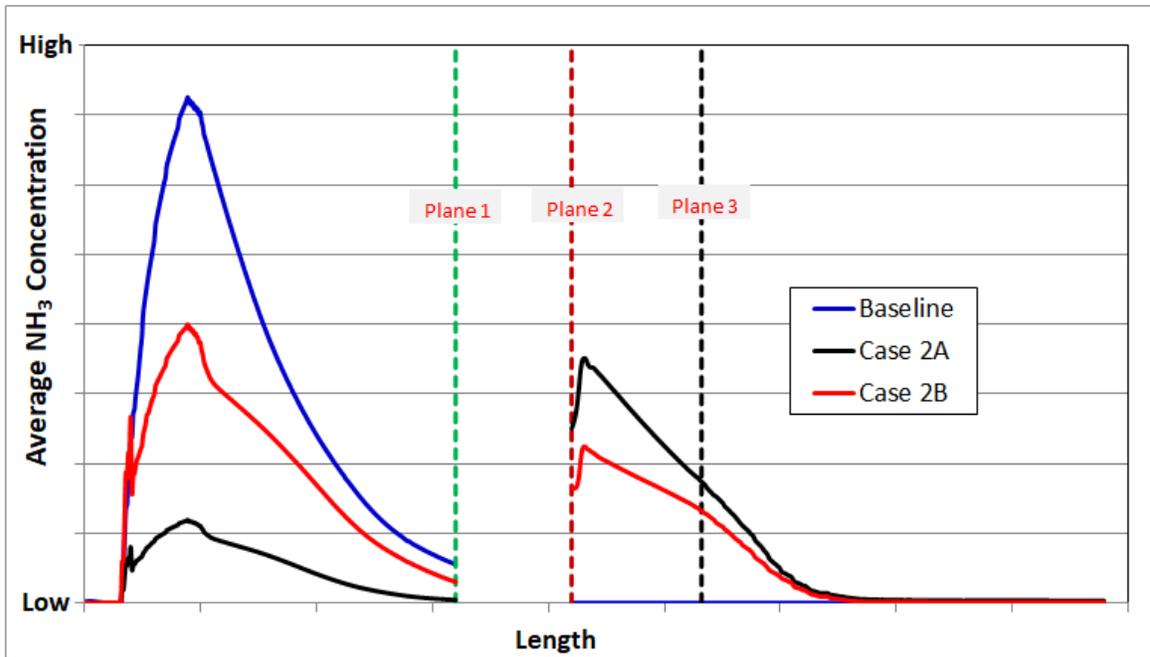


Figure 9: Average NH₃ concentrations vs boiler length

3.2 Tangentially Fired CO Boiler

For the tangentially fired CO boiler, Figure 10 shows the baseline predicted gas temperatures, CO concentrations, and NO_x concentrations before any proposed modifications. Based on predicted temperatures and CO concentrations, SNCR ports were simulated at a suitable location above the upper burner elevation. In this evaluation, a fixed portion of the total SWS vapor was mixed with the regeneration gas in the combustion zone, and incrementally increasing SWS vapor flow rates through the SNCR ports were simulated, from low (SNCR1) to median (SNCR2) and to high (SNCR 3). The predicted NO_x and NH₃ concentrations as a function of boiler height are shown in Figure 12 and Figure 13. Significant NO_x reduction is predicted at the different SWS rates to the SNCR ports. NO_x reduction increases as the amount of SWS gas to the SNCR ports increases. However, NH₃ slip is also increased, primarily due to reduced flue gas temperature in this boiler. These results indicate that optimization of the quantity of SWS relocated to the SNCR ports will be dependent on what levels of ammonia slip are acceptable.

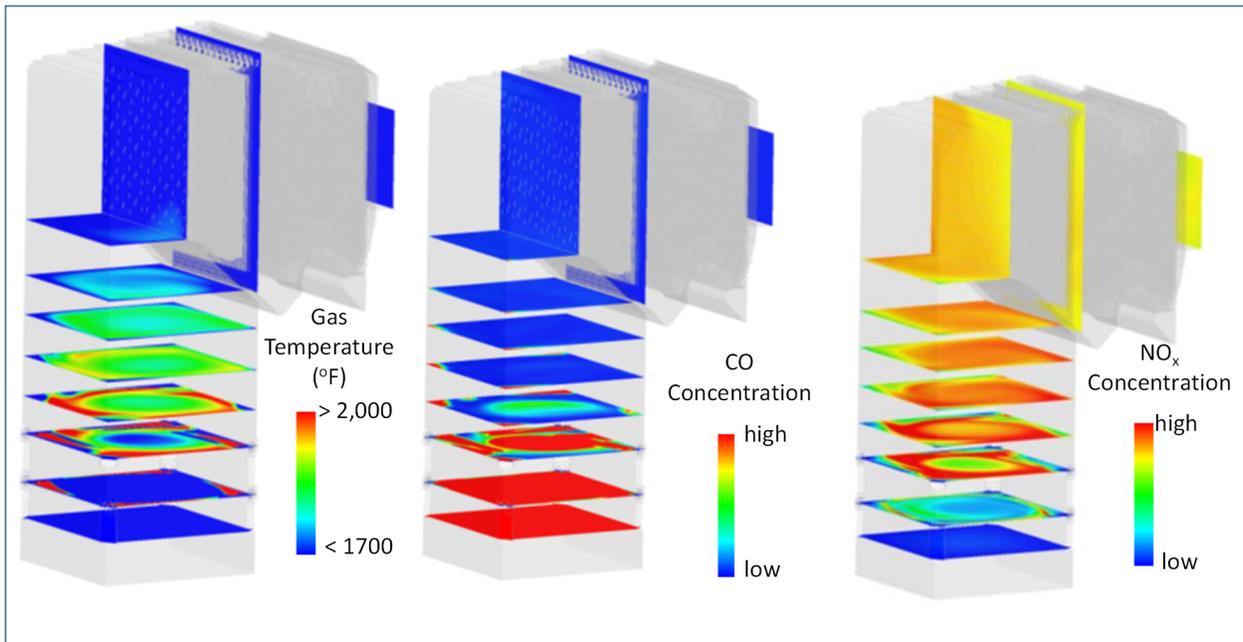


Figure 10: Gas temperatures, CO concentrations, and NO_x concentration in a tangentially fired CO boiler under baseline operation

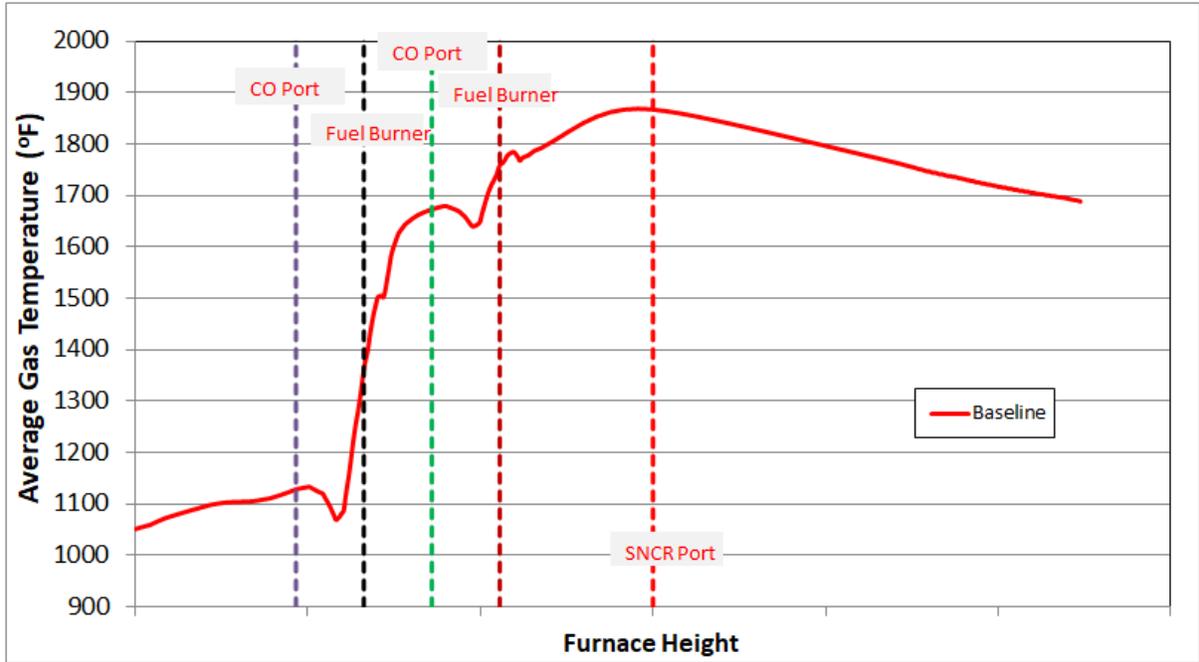


Figure 11: Average gas temperatures as a function of boiler height under baseline operation

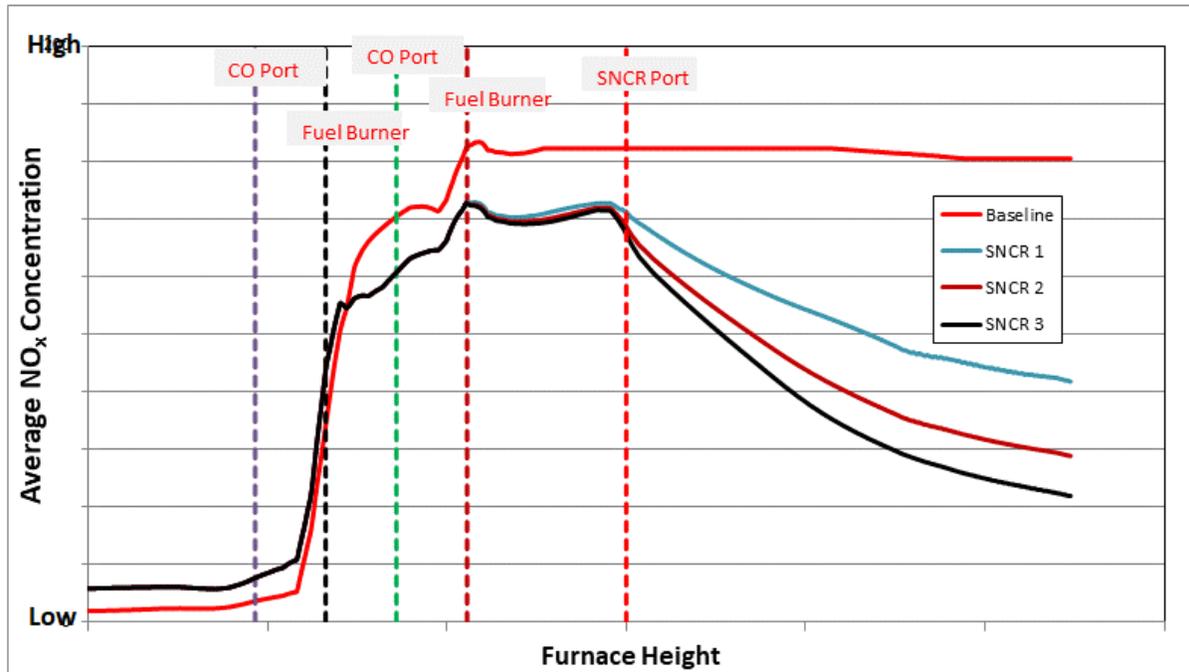


Figure 12: Predicted NO_x concentration as a function of boiler height

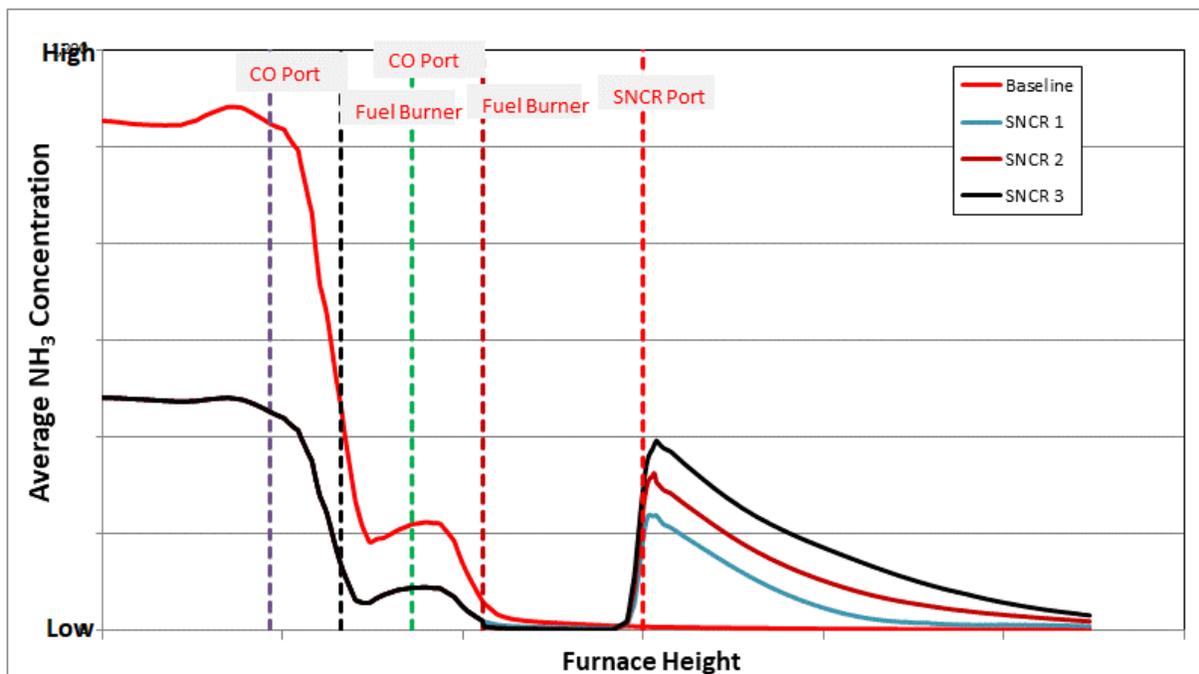


Figure 13: Predicted NH₃ concentration as a function of boiler height

3.3 H₂S Oxidation Chemistry

The SWS vapor may also contain H₂S and the relocation of this vapor from the combustion zone to the SNCR ports in a CO boiler raises the potential concern of increased H₂S emissions. A cursory evaluation was carried out to evaluate the potential for increased H₂S emissions. Using a detailed mechanism based on GRI3.0, combined with the sulfur mechanism developed by Haynes [6], a series of isothermal plug flow calculations were carried out to evaluate the rate of oxidation of H₂S over a relevant temperature range. The results, as shown in Figure 14, indicates a time lag associated with generation of the radical pool before the H₂S oxidation takes off. The residence time needed at higher operating temperature for complete oxidation of the H₂S is relatively short. The results show potential for significant H₂S oxidation at typical SNCR zone temperatures for the residence times that exist in both CO boilers simulated here. However, quantitative predictions of H₂S emissions should include the impacts of mixing, which can be achieved by integration of the chemical mechanism for H₂S oxidation into the CFD model.

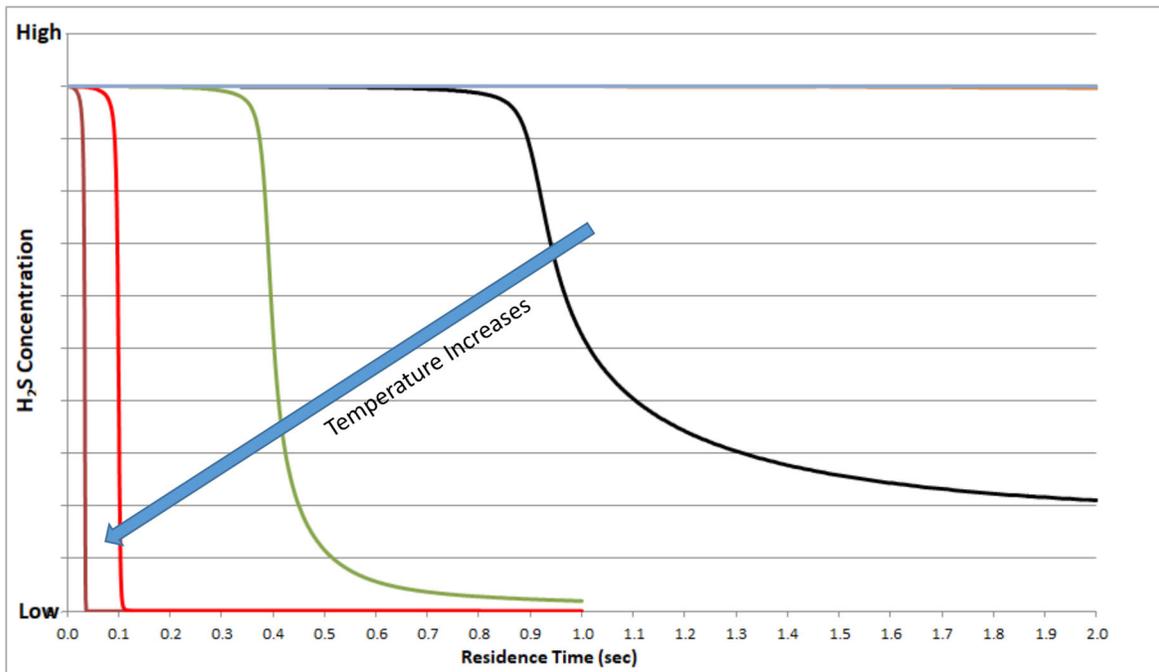


Figure 14: Isothermal plug flow calculation of H₂S oxidation

4 Conclusions

Results of a CFD-based evaluation performed on two typical styles of CO boilers show that significant NO_x reduction can be obtained by relocating SWS vapor from the combustion zone to downstream SNCR ports in the boiler. Potential NO_x reduction is dependent on the flue gas temperature, available residence time, and the mixing of reagent and flue gas. NO_x reduction was also impacted by the amount of SWS vapor that was directed to the SCNR ports, with higher NO_x reduction seen with higher SWS rates to the SNCR ports. The overall NO_x reduction may be limited, however, by NH₃ slip, as the modeling also showed increased NH₃ slip at higher SWS vapor rates to the SCNR ports, especially for boilers that have colder operating temperatures. Detailed chemical kinetics calculations to evaluate the impact of temperature on H₂S oxidation indicate that there is significant H₂S oxidation at typical SNCR zone temperatures. However, impacts of mixing also needs to be considered, ideally within a CFD simulation, to obtain accurate predictions of the impact of SWS relocation on H₂S emissions.

References

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