

MODELING NON-EQUILIBRIUM CO OXIDATION IN COMBUSTION SYSTEMS

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ABSTRACT

Performance of industrial and utility combustion systems is becoming increasingly affected by limits on pollutant emissions such as NO_x and CO. CO emissions impact design and operation of combustion systems, particularly when coupled with NO_x reduction technologies that involve lower temperature operation or staged firing. Lower combustion temperatures or delayed mixing of fuel and air helps minimize NO_x formation, but can increase CO concentrations and minimize CO oxidation rates. Reacting computational fluid dynamics (CFD) models have been shown to be useful in evaluating and optimizing performance of these new technologies and operating conditions. These CFD models have traditionally used equilibrium chemistry models to predict specie concentrations throughout the combustor, however equilibrium assumptions for CO oxidation at lower temperatures is inaccurate. A non-equilibrium CO model is required to accurately predict the oxidation of CO at temperatures lower than ~1150 K. This paper reviews the development of a non-equilibrium CO model and integration with a reacting CFD model. The use of the resulting model is illustrated on two combustion systems - a waste gas incinerator and a cyclone-fired utility boiler. Results show that low temperature CO oxidation can be accurately predicted with the use of the non-equilibrium CO model.

INTRODUCTION

Performance of industrial and utility combustion systems is often constrained by limits on pollutant emissions such as NO_x. NO_x emissions are often controlled by reducing furnace temperatures or by

delaying mixing of fuel-rich and fuel-lean combustion reactants. While lower temperatures and delayed mixing are beneficial for NO_x control, they can be detrimental to CO emissions. CO oxidizes rapidly at high temperatures in the presence of oxygen, but does not oxidize as well at the cooler temperatures or less mixed conditions common with some in-furnace NO_x control technologies.

Reacting Computational Fluid Dynamics (CFD) tools can be used to evaluate NO_x reduction technologies and their impact on CO emissions, provided the chemistry in the combustion model is sufficiently accurate to represent the actual system behavior. CFD models for chemically reacting flows commonly use an equilibrium chemistry approach to compute the chemical reactions in the combustion or reaction process. This is based on the fact that in diffusion flames, the fuel and oxidizer are initially separated in different streams which must be intimately contacted on a molecular level before reaction can occur. The assumption is made that this micromixing process (and therefore not the kinetic reaction process) is what controls the rate at which chemical reactions proceed. This allows the chemistry to be computed from equilibrium considerations.

Only one differential equation is required to describe the degree of "mixedness" between fuel and oxidant at a point, a great simplification compared to the immense system of equations required for a detailed chemical kinetic scheme. This improves computational times without compromising accuracy and allows chemistry calculations to be coupled with fluid flow, heat transfer and particle phase calculations. Alternative techniques that focus on detailed chemistry require tracking of multiple species and significantly

greater computational effort, making it difficult to couple with full fluid flow and heat transfer calculations for complex geometries typical of actual combustion systems.

The assumption of chemical equilibrium is generally adequate for most species at the high temperatures produced during combustion. A notable exception to this is the chemical reactions of NO_x species, which occur at finite rates even at combustion temperatures and require special treatment. As temperatures drop in post combustion zones or in low temperature combustion systems, other species such as CO also require special treatment as the equilibrium chemistry assumption becomes less accurate.

At temperatures greater than ~1150 K, CO oxidation is rapid and can be modeled with chemical equilibrium approaches. In the range from 975-1150 K, CO oxidation is slower and should be modeled with finite-rate kinetics. Below 975 K, CO oxidation does not occur even with oxygen present. Figure 1 illustrates the differences between equilibrium CO calculations and non-equilibrium or finite-rate CO calculations at various temperatures. The calculations are for an initial CO concentration of 100 ppm in a fuel-lean environment.

The plot has two lines at each temperature. The right line of each pair shows the equilibrium calculation, constant for all times. The left line shows non-equilibrium CO values that start at 100 ppm and decrease with residence time. Above 1150 K, equilibrium and finite-rate calculations give similar results. In the temperature range of 975-1150 K, the equilibrium calculations become increasingly inaccurate and below 975 K the equilibrium calculations are in error as the reactions are too slow to allow any noticeable reduction for the residence times common in combustion systems.

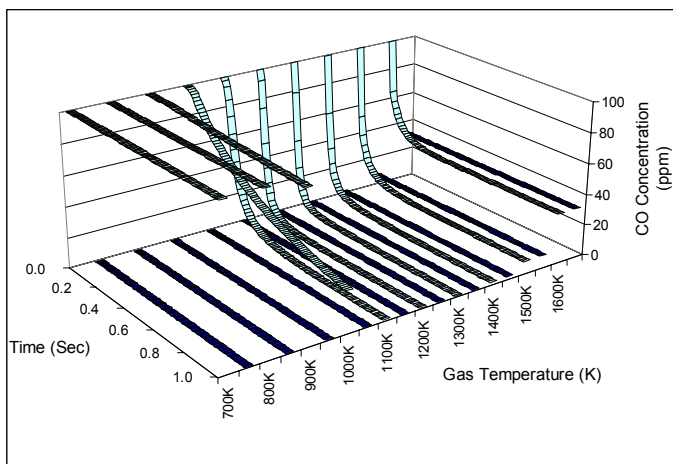


Figure 1. Equilibrium calculation for 100 ppm of CO in a fuel-lean environment. Equilibrium calculations are on the right and finite-rate calculation on the left of each temperature pair.

MODEL DESCRIPTION

The computer model used for this study is a CFD-based reacting flow code, *GLACIER*, developed by Reaction Engineering International (REI). The code couples together the effects of turbulent fluid mechanics, gas-phase combustion chemistry, turbulent particle dispersion, heterogeneous particle reactions, and convective and radiative heat transfer. The REI combustion code assumes that the flow field is a continuum field that can be described locally by general conservation equations. The flow is assumed to be steady state and gas properties are determined through local mixing calculations. The fluid is assumed to be Newtonian and dilatation is neglected. The comprehensive model uses an Eulerian framework and handles either Reynolds- or Favre-averaging. The code couples the turbulent fluid mechanics and the chemical reaction process, using progress variables to track the turbulent mixing process and equilibrium chemistry to describe the chemical reaction process.

One progress variable is used to track each fuel and oxidant stream. Specie concentrations are calculated as properties based on the local stream mixture and enthalpy. This is much more computationally efficient than tracking individual species. The exceptions to this are NO_x species, which are calculated using finite-rate chemistry.

Particle mechanics are solved by following the mean path or trajectory for a discretized group or ensemble of particles in a Lagrangian reference frame. Particle mass and momentum sources are converted from a Lagrangian to an Eulerian reference frame where they are coupled with gas phase fluid mechanics. The radiative intensity field is solved based on properties of the surfaces and participating medium and the resulting local flux divergence appears as a source term in the gas-phase energy equation. More detailed information regarding the computational model have been previously published (Adams and Smith, 1995, Adams, 1993a, Adams and Smith, 1993b, Smoot and Smith, 1985).

In order to more accurately simulate CO oxidation rates at lower temperatures, global CO oxidation kinetics were incorporated into *GLACIER* to replace the equilibrium CO calculations. The rate of CO oxidation was based on the global mechanism proposed by Dryer and Glassman (1973):

$$\frac{d[CO]}{dt} = A[CO]^a[H_2O]^b[O_2]^c \exp\left\{-\frac{E_a}{RT}\right\} \quad (\text{Eq. 1})$$

where [CO], [H₂O], and [O₂] are the CO, H₂O and O₂ mole fractions, respectively, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, T is the gas temperature, and a, b and c are constants (see Table 1).

The rate parameters used in this study were optimized over the temperature range 800-1600 K by comparison with a detailed chemical mechanism based on the work of Miller and Bowman (1989) consisting of 277 reversible steps and 66 chemical species. These comparisons were performed with the chemical kinetics software Chemkin. The original rate parameters of Dryer and Glassman along with the optimized parameters used in this study are listed in Table 1.

Table 1. CO Oxidation Kinetics Parameters (in reference to Eq. 1).

Parameter	Dryer and Glassman	Optimized (Used in this study)	
		T<1150 K	T>1150K
A	2.24E+12	2.61E+12	6.52E+6
E _a	40,000	45,566	15,968
a	1.0	1.0	1.0
b	0.5	0.5	0.5
c	0.25	0.25	0.25

Units: m³, kg-mol, sec, K, Kcal

The use of the global CO kinetics necessitated the incorporation and solution of an additional transport equation in the CFD model for the local CO concentration. The assumed rate of CO oxidation depends on the local gas temperature and concentrations of CO, H₂O, and O₂ as represented in Eq. 1. The effect of turbulence on this rate is also taken into account by convolution over the assumed probability density function of the local mixture fractions. The model allows for coupling between the effects of the local oxidation of CO on the other local species concentrations and gas temperature.

Comparisons between the detailed and the global mechanism for a simple plug flow reactor geometry at stoichiometries of 1.05 and 1.18 with initial CO levels of 100 ppm are shown in Figures 2 and 3, respectively. Good agreement between the optimized global mechanism and the detailed mechanism over a range of temperatures (and stoichiometries) demonstrates the ability of the optimized global mechanism to represent the CO oxidation kinetics for the conditions of interest here, i.e., fuel-lean regions of the combustors.

The following sections illustrate the use of the non-equilibrium CO model for two combustion examples – a waste gas incinerator and the back pass of a coal-fired utility boiler.

WASTE GAS INCINERATOR

A waste gas incinerator is used to oxidize waste gas from a chemical process. The incinerator modeled here is approximately 20 meters long and 3 meters in diameter. Air and natural gas are fed through a burner at the front of the incinerator and waste gas is fed tangentially around the circumference of the incinerator at several downstream stages. Some natural gas is added in some of the downstream stages to aid combustion. The waste gas stream accounts for over 95% of the flow through the incinerator. Total heat release in the system is around 250 MMBtu/hr, with approximately half of the thermal input coming from the waste gas.

The waste gas is comprised mostly of oxygen, nitrogen, and water vapor, but also contains a significant amount of carbon monoxide and a small fraction of higher order hydrocarbons. In this sense the waste gas stream is similar to a visciated air stream. It does not contain sufficient CO to be self-igniting, but does have significant thermal heat release due to the large volume of gas flow through the system.

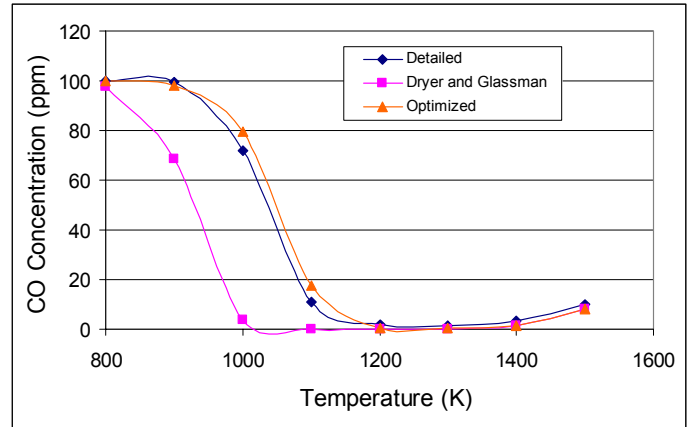


Figure 2. Comparison of predicted CO oxidation between detailed chemistry, global mechanism of Dryer and Glassman (1973), and the optimized global rate parameters used in this study for a residence time of 200 milliseconds in a simple plug flow reactor at stoichiometric ratio 1.05.

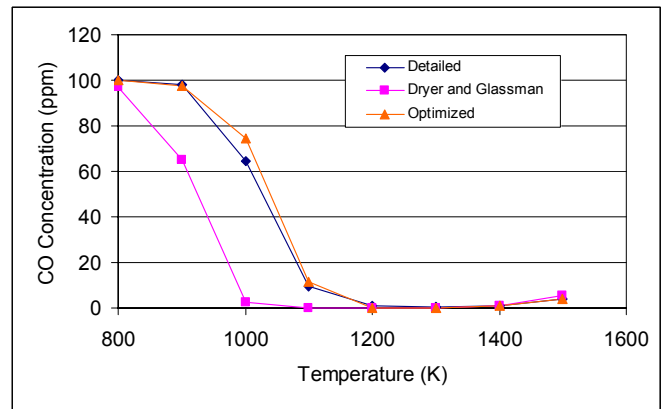


Figure 3. Comparison of predicted CO oxidation between detailed chemistry, global mechanism of Dryer and Glassman (1973), and the optimized global rate parameters used in this study for a residence time of 200 milliseconds in a simple plug flow reactor at stoichiometric ratio 1.18.

The objective of the incinerator is to oxidize the CO and other hydrocarbons in the waste gas at sufficiently low temperatures to avoid significant NO_x formation. NO_x and CO emissions are designed to be less than 10 ppm.

The three-dimensional computational grid for the incinerator was comprised of 918,000 computational cells. Reacting CFD calculations were performed to compute the mixing and flow patterns, temperature and specie concentration profiles (e.g., CO, CO₂, NO, N₂, H₂O), and surface heat transfer. Wall temperatures were computed based on net heat flux to the inner surface, thermal resistance through the incinerator wall, and convective heat transfer to ambient air.

Figure 4 shows the gas temperature contours at a vertical plane along the centerline of the incinerator. Flow is from left to right. The highest temperatures (~1800 K) are in the burner region at the left of Figure 4. Coolest temperatures (700-800 K) are along the outer circumference where the waste gas is introduced. The back end of the incinerator has well-mixed combustion products at approximately 1150 K.

The gas temperatures along the vertical line in Figure 4 are plotted in Figure 5. The waste gas inlet temperature (600 K) is too cool to allow immediate reaction between the CO and oxygen in the waste stream. As a result temperatures remain cool and the CO concentrations remain high until the waste stream becomes heated by mixing with the core flow further downstream.

Figures 6 and 7 show CO profiles for the incinerator at the same plane. There are two regions of high CO, one along the incinerator centerline, one along the outer annulus of the incinerator after the conical expansion. The high CO along the centerline is caused by the lack of oxygen in this region. Temperatures are sufficiently high to react any CO and O₂ that mix here, but the core burner is operated slightly fuel-rich, so the natural gas rapidly consumes the available O₂. Farther downstream as the oxygen in the waste gas streams mix into the core, this CO is reduced.

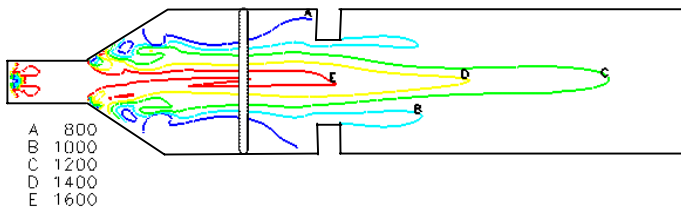


Figure 4. Predicted temperature profiles in a waste gas incinerator showing hot core temperatures and lower annular temperatures where the waste gas stream has not reacted. Temperatures are in K.

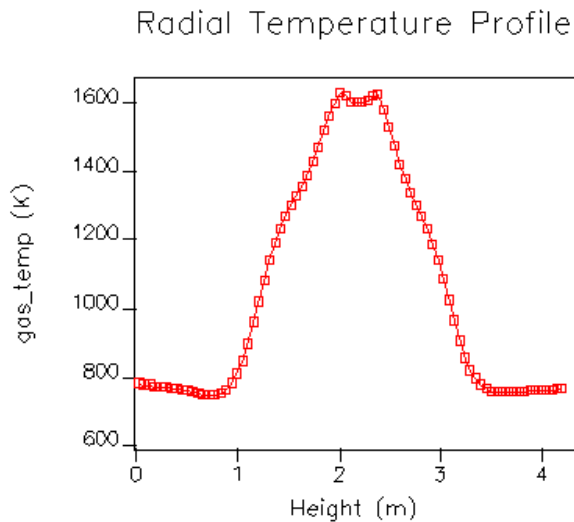


Figure 5. Predicted radial temperature profile for a waste gas incinerator illustrating cooler gas temperatures at outer radii that inhibit CO reactions.

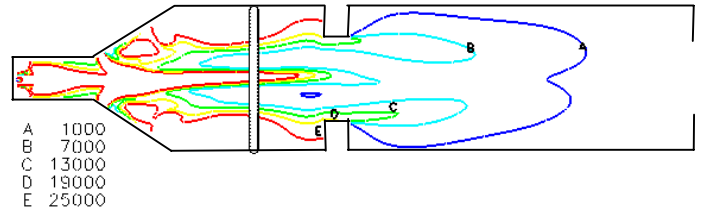


Figure 6. Predicted CO profiles in a waste gas incinerator showing high CO concentrations in the core and around the outer circumference where the waste gas stream has not reacted. CO concentrations are in ppm.

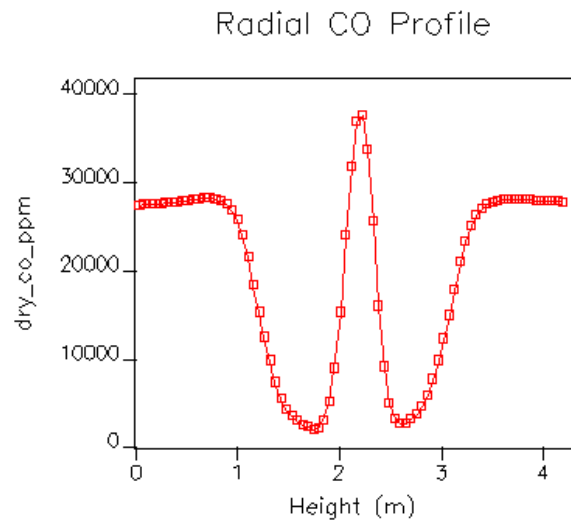


Figure 7. Predicted radial CO profile for a waste gas incinerator illustrating high CO concentrations in the oxygen deficient core and in the outer circumference where the waste gas is too cool to oxidize CO.

The high CO in the outer annulus is caused by temperatures that are too low to react the CO and O₂. Local oxygen concentration in these regions is over ten percent. Once the waste gas stream begins to mix with the hotter core gases, the temperature rises and the CO begins to oxidize. The rate of oxidation is slow consistent with the gas temperature. Exit CO concentrations are predominantly due to the unreacted CO from the outer circumference where the waste gas was too cool to fully react. The CO in the hotter core is oxidized as soon as it mixes with oxygen. The asymmetries in Figure 6 concentration profiles are due to the tangential rotation of the gas flow.

Calculating CO concentrations with an equilibrium model under these conditions would predict zero CO anywhere there was sufficient oxygen to react with the CO, independent of the local temperature. Thus the oxidation of CO is dependent on both mixing (O₂ availability) and temperature. An equilibrium chemistry model coupled with CFD or a detailed finite-rate chemistry model not coupled with CFD are both insufficient to accurately model this system. A non-equilibrium CO model coupled with CFD was required to accurately determine ppm levels of CO in this system. Predicted average exit CO and NO_x values less than 10 ppm were verified by field measurements.

UTILITY BOILER

Coal-fired utility boilers utilize combustion reactions to produce heat, which boils water in tubes that enclose the combustion process. The resulting steam is used to drive turbine generators that produce electricity. Figure 8 shows a schematic of a coal-fired utility boiler. Combustion in the main heat release zone occurs at temperatures sufficiently high that chemical reactions, other than NO_x, can be modeled with equilibrium. Furnace gas temperatures drop as heat is extracted from the combustion products by radiative and convective heat transfer. In the furnace back pass (the region downstream of the furnace "nose") the flue gases quickly lose heat, resulting in a rapid temperature decline. Temperatures in the back pass are cool enough that CO oxidation cannot be modeled with chemical equilibrium assumptions.

Tracking CO is important as several current NO_x reduction strategies rely on delayed mixing of combustion fuel and oxidants, resulting in increased CO concentrations in the upper furnace. If CO is not mixed out (oxidized) before the flue gases exit the back pass, subsequent temperatures are too low to allow oxidation irrespective of O₂ availability and the CO exits into the atmosphere.

In this study the main furnace heat release zone and the back pass are modeled separately to provide accurate resolution for both sections of the furnace. The main furnace is a 590 MW cyclone-fired boiler. As part of a NO_x reduction technology evaluation, the furnace was modeled under staged conditions with overfire air (OFA) added in the upper furnace. Operating the cyclone barrels and lower furnace under fuel-rich conditions has been shown to provide significant NO_x reduction (O'Connor, et al., 1999), but also increases the amount of CO in the upper furnace. Different OFA designs were evaluated to determine the optimal design for maximizing NO_x reduction while maintaining acceptable CO levels. As significant CO reduction can occur in the back pass of the furnace, it is important to model the back pass to obtain an accurate estimate of CO emissions.

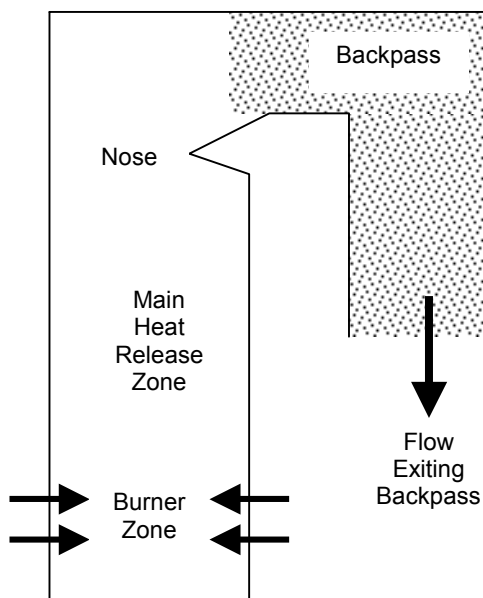


Figure 8. Schematic of a cyclone-fired utility boiler.

The extent of the back pass geometry modeled in this study is shown in Figure 9 and consists of over 600,000 computational cells (97x84x74). The back pass model inlet corresponds identically to the exit of the previously completed lower furnace model and is located immediately upstream of the secondary superheat panels. At this inlet plane, all gas phase properties (temperature, velocities, species concentrations) are interpolated from the results at the exit of the lower furnace model. The convective surfaces corresponding to the secondary superheat, reheat, primary superheat, and economizer (Figure 9) are represented in sufficient detail to accurately model the heat transfer to these surfaces. Figure 9 also includes a description of various planar locations at which average properties were computed and reported in subsequent figures. The exit plane of the back pass model is located immediately downstream of the economizer tubes.

The predicted gas temperature decay through the back pass is shown explicitly in Figure 10. The simulation results show that the gas temperatures are sufficiently high and the rate of mixing is sufficiently fast so that prior to the economizer exit, very little CO remains in the flue gas. The BWOFA case shows that mixing additional air into the inlet stream only has the effect of hastening the oxidation of CO in the back pass, as can be seen in Figure 10. Figure 11 compares the predicted decay of CO through the back pass for the baseline case and two staged cases with higher CO entering the back pass. The predicted CO at the exit of the lower furnace model for the OFA-2 design was significantly higher than that for the OFA-1 design (248 ppm vs. 140 ppm), but the remaining CO is predicted to oxidize quickly through the back pass in both cases. At the model exit, nearly the same low levels of CO (1 ppm or less) are attained for all cases. The installed overfire air system produced stack CO emissions less than 10 ppm.

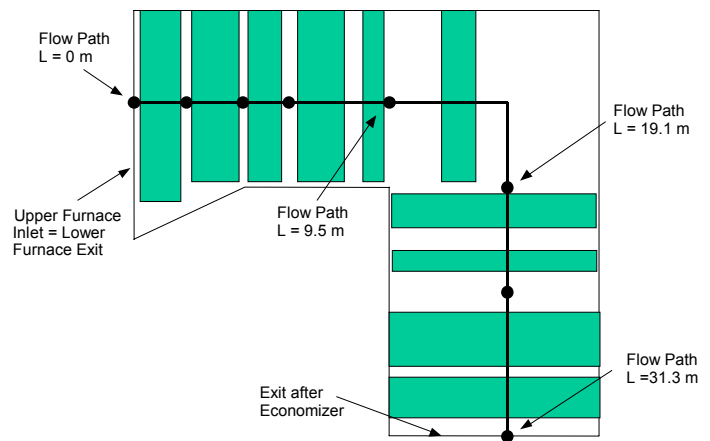


Figure 9. Schematic of the backpass model for the cyclone-fired utility boiler. The flow path shown corresponds to the temperature and CO profiles plotted in Figures 10 and 11.

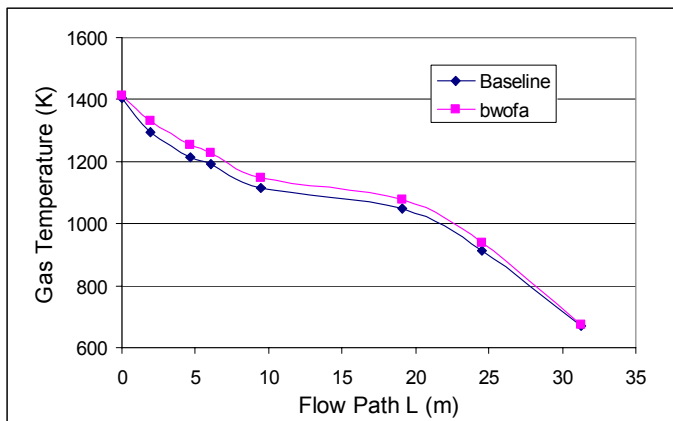


Figure 10. Predicted average flue gas temperature through the boiler back pass for two OFA designs.

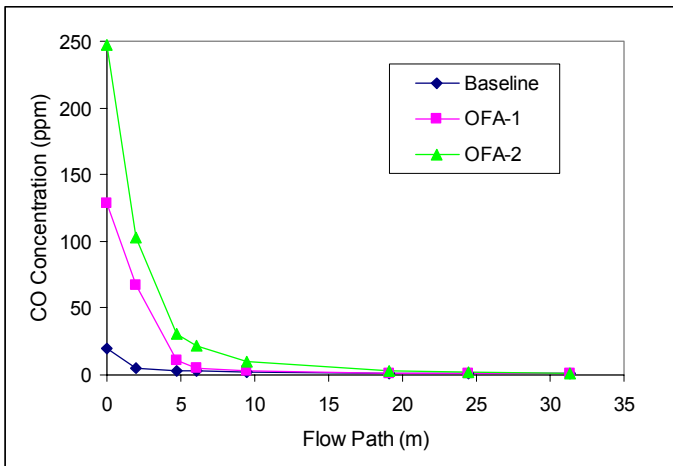


Figure 11. Comparison of predicted CO decay in a cyclone-fired boiler back pass for different OFA designs with different initial CO concentrations entering the back pass.

SUMMARY

This paper described the development of a non-equilibrium CO model and its implementation into a reacting CFD code. Accurate modeling of CO was shown to be important in combustion systems, particularly as NO_x and CO regulations tighten and fuel-rich operation and lower temperature combustion become more common NO_x reduction technologies. The usefulness and accuracy of the reacting CFD model with the non-equilibrium CO chemistry was illustrated using two examples, a waste gas incinerator and a cyclone-fired boiler back pass. Conclusions for this study may be summarized as follows:

- CO predictions from equilibrium chemistry models are in significant error at temperatures below ~1150 K. Non-equilibrium CO models are necessary to accurately predict CO oxidation rates at cooler temperatures (even with O₂ present).
- CO oxidation is dependent both on temperature and O₂ availability, therefore the non-equilibrium CO model needs to be coupled with reacting CFD model to accurately predict both mixing and reactions.
- Incinerator combustion temperatures are kept low to minimize NO_x formation, but this results in reduced CO oxidation. Equilibrium CO calculations for this system predict zero CO concentration, whereas the non-equilibrium CO model predicts slow oxidation extending through the incinerator exit where average CO values are less than 10 ppm. Accurate prediction of both CO oxidation rate and gas mixing are necessary to evaluate incinerator performance.
- A cyclone-fired boiler produces increased furnace exit CO concentrations due to staged furnace firing conditions (a common NO_x reduction technique). CO oxidation occurs in the boiler back pass at temperatures too cool for equilibrium chemistry assumptions. Predictions show there is sufficient mixing, temperature and residence time in the boiler back pass to reduce CO concentrations to ppm levels before the flue gases exit the stack.

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