

A SIMPLE TWO-STEP REACTION SCHEME FOR SOOT AND CO PREDICTION IN FDS

Kevin McGrattan^{1,3}, Randall McDermott¹, and Jason Floyd²

¹National Institute of Standards and Technology, Gaithersburg, Maryland, USA

²Jensen Hughes, Baltimore, Maryland, USA

³e-mail: kevin.mcgrattan@nist.gov

ABSTRACT

A relatively simple two-step combustion model is proposed for predicting soot and CO generation in under-ventilated fire simulations. The scheme consists of two mixing-controlled reaction steps performed in series. Validation calculations are described, ranging from a laminar diffusion flame to full-scale under-ventilated compartment fires.

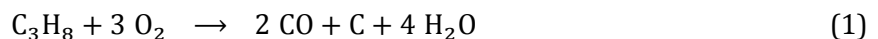
AUTHORS' NOTE

The material presented in this paper has all been extracted from the FDS Technical Reference and User's Guides, version 6.7.0. The results shown in the figures are stamped with the exact state of the FDS GitHub repository (<https://github.com/firemodels/fds>) at the time the calculations were performed.

BASIC THEORY

Since the release of FDS 1 in 2000, we have sought to extend the so-called "simple chemistry" combustion model in FDS to account for CO and soot production other than by specifying post-flame, constant yields. The simple chemistry assumption is fine for well-ventilated fire simulations where the objective is to predict the transport of smoke and hot gases throughout the space of interest, but it is not appropriate for under-ventilated compartment fires or near-field radiation emission, extinction, and other detailed fire phenomena. The most logical extension of the single-step simple chemistry model would be a two-step model in which soot and CO are produced in the first step, and then oxidized to CO₂ in the second.

Consider the combustion of propane. The simplest multi-step reaction scheme that includes the formation of soot, assumed to be pure carbon, and CO might look something like the following:

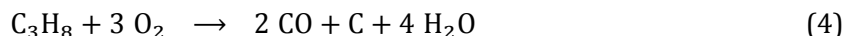


Add the three reactions together to recover the simple single-step ideal reaction. Of course, real propane combustion, under the best of conditions, involves many more reactions and intermediate species,

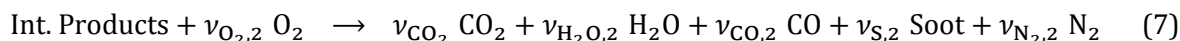
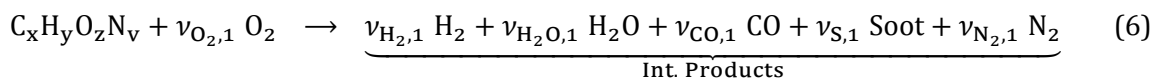
but it is well-known that the formation of soot and CO during the early stage of the reaction is faster than the subsequent oxidation of soot and CO. In practical fire simulations, it is not possible to include the detailed finite-rate kinetics because the calculated mean temperature within a grid cell is typically lower than the actual flame temperature. Instead, the three reactions are assumed to be mixing-controlled and temperature-independent, but the reaction of fuel and oxygen in the first step takes precedence over the oxidation of soot and CO in the second and third.

Consider a grid cell at the start of a time step that contains some fuel, oxygen and product species, as well as nitrogen. Depending on the local turbulence level and the size of the grid cell, a certain fraction of the reactants are mixed together and can potentially react. The oxygen within this mixed region first reacts with any fuel present, forming soot, CO and water vapor, and if any oxygen is left over, it is free to oxidize the soot and CO. Under well-ventilated conditions, these multiple reactions might occur within a single time step, which is essentially the “simple chemistry” model. However, in under-ventilated conditions, some soot and CO will remain when there is not enough oxygen present.

There are two problems with this simple approach. First, it is not clear, for a given fuel, how much of the carbon is converted into CO and how much into soot in the first reaction step. The stoichiometric coefficients of 2 and 1 in the first reaction are chosen arbitrarily here to simplify the algebra. Second, even though it is assumed that reaction 1 is faster than 2 and 3, it is not clear which of 2 or 3 is faster, in which case we might as well combine these two reactions:



In the latest version of FDS (6.7.0), the default “simple chemistry” single-step combustion model now has a two-step option. All of the other parameters that are appropriate for the default single-step model are still applicable. The two-step scheme basically takes all of the carbon in the fuel molecule and converts it to CO and soot in the first step, and then oxidizes most of the CO and soot to form CO₂ in the second step. The hydrogen in the fuel molecule can form either H₂ or H₂O in the first step as well.



By default, in the first step, two out of three carbon atoms in the fuel are converted to CO. There is not yet a solid basis for this assumption, and the distribution of carbon to CO and soot can be changed via a user-specified parameter. It is 2/3, by default. In addition, a fraction of the hydrogen in the fuel molecule can form H₂ in the first step. It is zero by default because this chemistry is not well understood and has been added to the two-step scheme as a placeholder for future research.

Note that the user-specified soot and CO yields retain their meanings from the single-step simple chemistry model; that is, they represent the post-flame yields of these species. Essentially, the two-step model acknowledges the fact that CO and soot are present at much higher concentrations within the flame envelop than their post-flame yields would suggest.

The two-step simple chemistry option should only be invoked when there is interest in near-flame phenomena or under-ventilated compartments where the increased concentration of CO and soot play

an important role in the flame chemistry and radiative emission. The resolution of the fire should be reasonably good, as well. What “reasonably good” means depends on the particular circumstances, but suffice it to say that one ought to experiment by running simple simulations with and without the two-step option to see if it leads to significantly different results. The cost of the two-step scheme is an additional transport equation for the scalar variable referred to as “Intermediate Products.”

A SAMPLING OF VALIDATION CASES

In the FDS Validation Guide, there are a variety of case studies that employ the two-step CO/soot production model, ranging from a laminar diffusion flame simulation performed as a direct numerical simulation (DNS) to full-scale simulations of flashed-over compartments.

Smyth Slot Burner Experiments

Kermit Smyth et al. [1, 2] conducted diffusion flame experiments at NIST using a methane/air Wolfhard-Parker slot burner, which consists of an 8 mm wide central slot flowing fuel surrounded by two 16 mm wide slots flowing dry air with 1 mm separations between the slots. The slots are 41 mm in length. Measurements were made of all major species and a number of minor species along with temperature and velocity.

Two-dimensional simulations of this experiment are performed using two different combustion models at two different grid resolutions, 0.250 mm and 0.125 mm. The first model is a modified version of the mechanism by Andersen et al. [3] where the hydrocarbon/oxygen reaction to CO is assumed to be infinitely fast followed by a reversible CO to CO₂ reaction modeled with Arrhenius kinetics. As discussed by Westbrook and Dryer [4], the kinetic constants for the reduced CO mechanism may be model dependent. Here, the Arrhenius constant for the forward CO to CO₂ reaction is tuned to match the Smyth experimental data.

A second set of simulations is run at the same two spatial resolutions, using the two-step reaction scheme described above, where only CO and no soot is generated in the first reaction step. Of interest here is that the time step size for the finer grid simulation is comparable to the chemical time scale which is on the order of δ/s_L , the flame thickness divided by the laminar flame speed. This means that the use of “fast chemistry” at these time and length scales becomes questionable. Nevertheless, the results of the simple two-step scheme are encouraging, as shown in Fig 1.

University of Maryland Line Burner Experiments

Experiments have been performed at the University of Maryland (UMD) by White et al. [5] using a burner consisting of a 50 cm by 5 cm fuel slot surrounded by a co-flowing air stream. Controlled suppression of the flame is achieved via the gradual introduction of nitrogen into the co-flowing air stream.

Simulations of these experiments are performed for a duration of 80 s. The first 10 s allow the flame to stabilize at ambient conditions. At 10 s, nitrogen is introduced in the co-flow air stream and linearly increased so that the oxygen concentration decreases to 10 % at 80 s. The calculations are performed at three grid resolutions: 12.5 mm, 6.25 mm, and 3.125 mm, using 24, 164, and 204 meshes respectively.

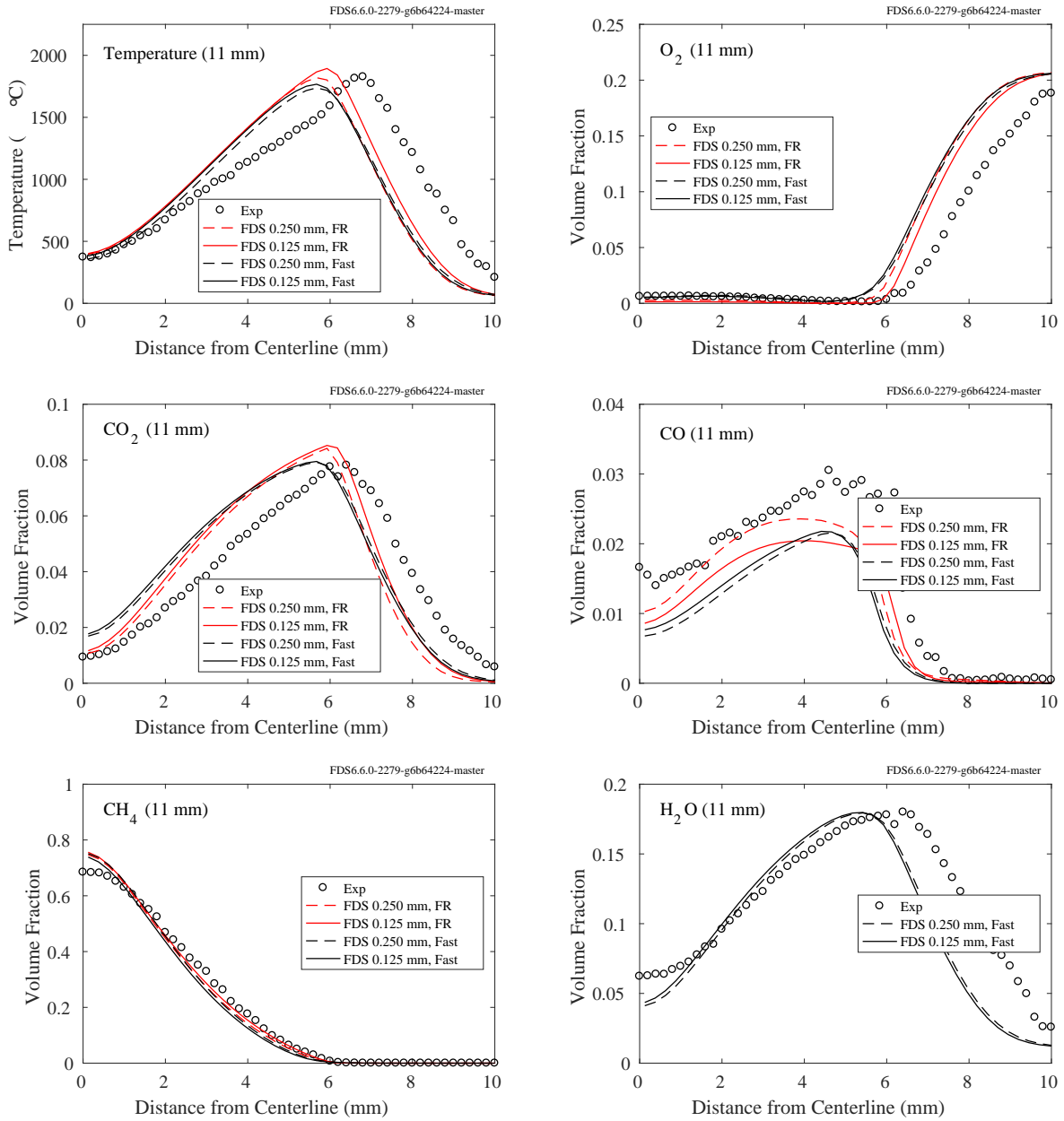


Figure 1: Predicted and measured quantities 11 mm above a Wolfhard-Parker methane-air slot burner.

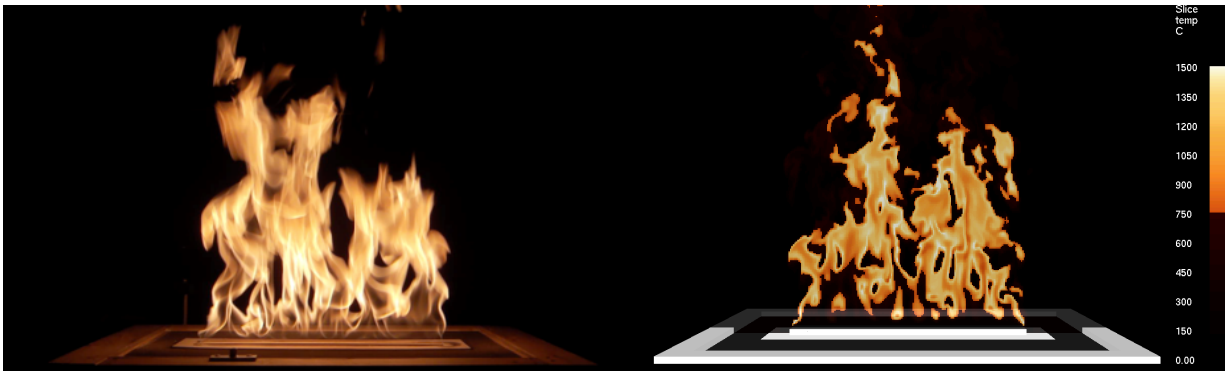


Figure 2: Photograph of the University of Maryland Line Burner Experiment (left) and the corresponding FDS simulation (right).

A snapshot of the fine resolution simulation is shown in Fig. 2.

The two-step combustion model described above is used in the simulations. For both the methane and propane fires, it is assumed that 2 moles of CO are produced for every mole of C (soot). The choice does have an affect on the predicted radiative fraction of the fire and the heat flux to the radiometer because the more soot generated in the first step, the greater the radiative fraction.

Extinction of the fire is achieved using the critical flame temperature concept, which is the default extinction model in FDS. The CFT is 1507 °C for methane and 1447 °C for propane [6]. In addition, combustion is suppressed below the auto-ignition temperatures of 540 °C and 450 °C for methane and propane, respectively, except in a small volume just above the burner where the fuel is allowed to burn on contact with oxygen. This is a simple way to simulate the effect of a spark igniter.

In the Maryland experiments discussed here, soot and CO were not measured. However, the heat flux to a distant radiometer was used to estimate the radiative fraction. In the FDS simulations, the radiative fraction is not specified but rather predicted based on the computed flame temperature and gray gas radiation model, RadCal. As seen in Fig. 3, the radiative fraction and heat flux decrease with decreasing oxygen concentration in the oxidizer stream. This is a remarkable result because the simple two-step reaction scheme is able to predict the decrease of soot and CO within the flame envelop as the oxygen stream is diluted. In the experiment, as the co-flow was diluted with more and more nitrogen, the flame color changed from yellow to blue as the in-flame soot volume fraction apparently decreased. A next step will be to try to reduce the grid-dependence of the simulations. Even though the two-step combustion scheme is temperature-independent, the predicted radiative emission is not.

NIST Reduced Scale Enclosure Experiments, 1994

The NIST Reduced Scale Enclosure (RSE) was a 40 % scale version of the ISO 9705 compartment [7]. It measured 0.98 m wide by 1.46 m deep by 0.98 m tall. A door, centered on the smaller wall, was 0.48 m wide by 0.81 m tall. A 15 cm diameter natural gas burner was positioned in the center of the compartment. The fires ranged from 50 kW to 600 kW. Species measurements, including CO concentration, were made near the ceiling in the front and back of the compartment.

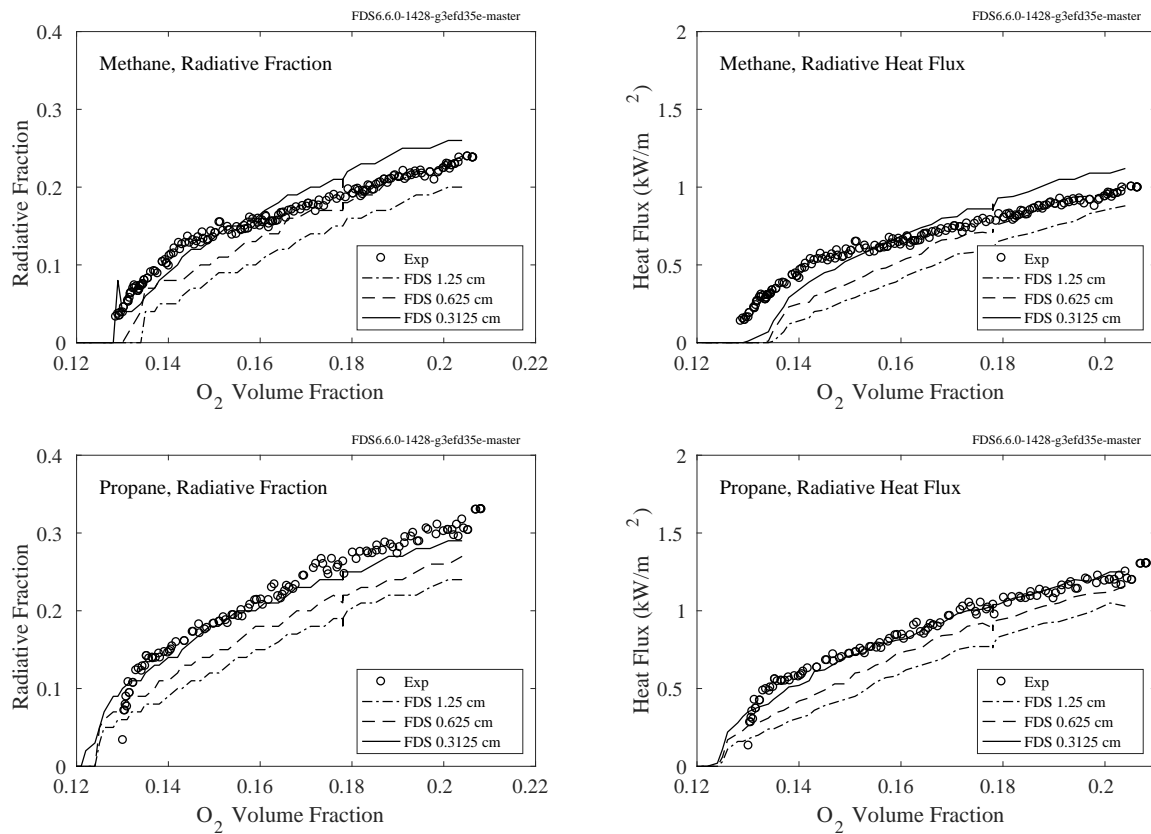


Figure 3: The plots on the left compare measured and predicted radiative fraction, and the plots on the right compare measured and predicted heat flux to a target 1 m away from the flame in the University of Maryland Line Burner Experiments.

Figure 4 shows the measured and predicted CO concentrations. The measurements were made 10 cm below the ceiling and 30 cm from the left side wall. The front position was 10 cm from the wall with the door; the back position was 30 cm from the rear wall. The simulations are run at three resolutions, for which the “resolution index” (RI), $D^*/\delta x$, is 5, 10, and 20. In all cases, it is assumed that 2 moles of CO are produced in the first reaction step for every 1 mole of C (soot).

NIST Full Scale Enclosure Experiments, 2008

The NIST Full Scale Enclosure Experiments were conducted in an ISO 9705 compartment [8]. The compartment was 2.4 m wide by 3.6 m long by 2.4 m high with a 2 m high door at one end. The door width varied between 0.1 m and 0.8 m. The experiments were designed to study the effects of fuel type, fuel distribution, and vent size on under-ventilated compartment fires. Twenty-seven experiments are simulated, which include 7 different fuels, 3 fuel sources, and 4 ventilation openings. Peak heat release rates range from approximately 100 kW to 2.5 MW. Species concentrations and temperature measurements were made at the front and rear of the compartment. Figure 5 shows the results from one experiment. Notice that the concentrations of CO and unburned hydrocarbons increase to substantial levels just as the oxygen concentration decreases towards zero. The simple two-step model mimics this behavior because these relatively high concentrations of CO and unburned fuel are the

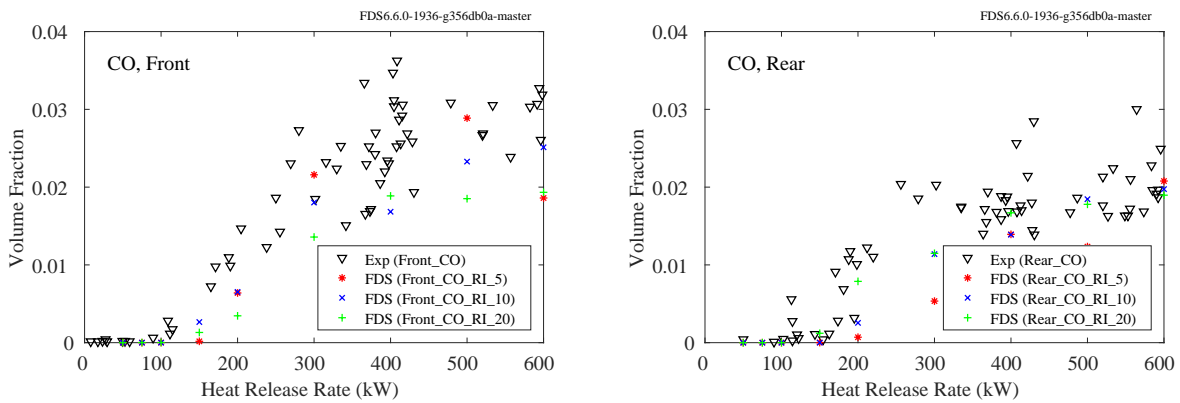


Figure 4: Comparison of measured and predicted CO concentration, NIST RSE experiments.

consequence of lack of oxygen rather than some detailed kinetic effect. Of course, the exact amount of CO and unburned fuel is not perfectly predicted. In all cases, it is assumed that 2 moles of CO are produced in the first reaction step for every 1 mole of C (soot). The simulations are all run with 10 cm resolution.

CONCLUSION

A summary of the results of CO predictions to date using the two-step scheme is shown in Fig. 6. On average, FDS over-predicts CO concentrations by about 10 %, and there is a considerable scatter in the results. There is certainly room for improvement, in particular:

1. Is there a way to decide how much soot and how much CO is generated in the first step of the two-step reaction scheme, based on the fuel stoichiometry or some bench-scale experiment?
2. Can we predict post-flame soot and CO yields, rather than specify them?

ACKNOWLEDGMENTS

The work presented in this paper is part of the Reduced Risk in Buildings Program at NIST.

REFERENCES

- [1] T.S. Norton, K.C. Smyth, J.H. Miller, and M.D. Smooke. Comparison of Experimental and Computed Species Concentration and Temperature Profiles in Laminar, Two-Dimensional Methane/Air Diffusion Flames. *Combustion Science and Technology*, 90:1–34, 1993. 3
- [2] K.C. Smyth. NO Production and Destruction in a Methane/Air Diffusion Flame. *Combustion Science and Technology*, 115:151–176, 1996. 3
- [3] J. Andersen, C.L. Rasmussen, T. Giselsson, and P. Glarborg. Global Combustion Mechanisms for Use in CFD Modeling Under Oxy-Fuel Conditions. *Energy & Fuels*, 23(3):1379–1389, 2009. 3

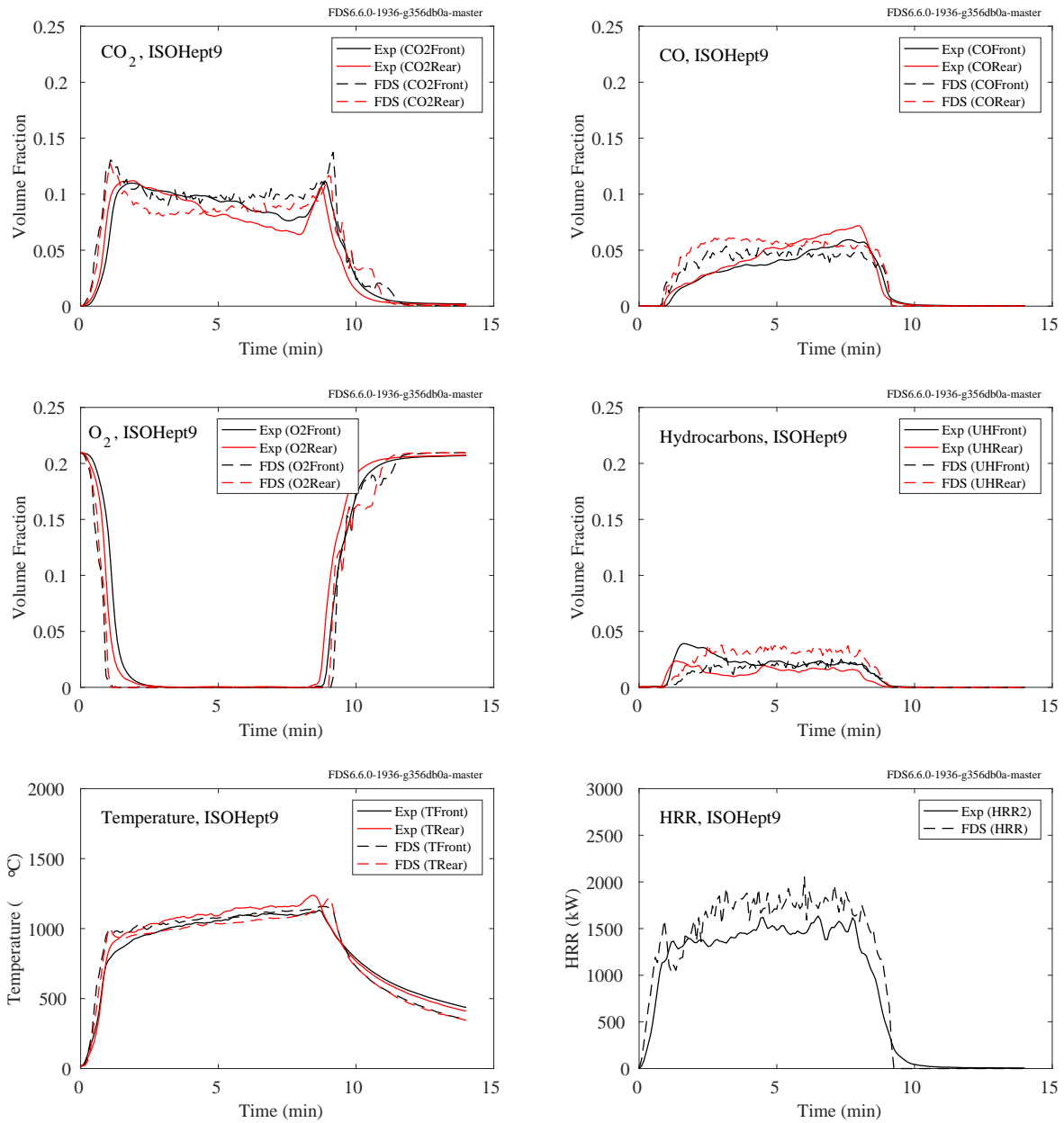


Figure 5: Summary NIST Full-Scale Enclosure Experiment, Test 9, heptane fuel.

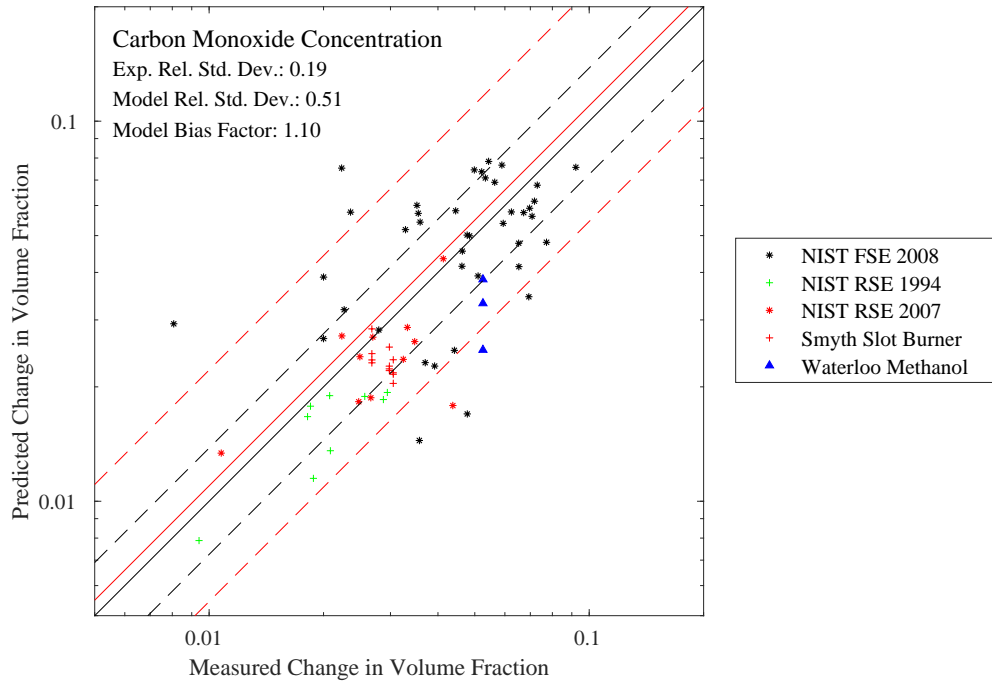


Figure 6: Summary of carbon monoxide predictions.

- [4] C.K. Westbrook and F.L. Dryer. Simplified Reaction Mechanisms for the Oxidation of Hydrocarbon Fuels in Flames. *Combustion Science and Technology*, 27:31–43, 1981. **3**
- [5] J. P. White, E. D. Link, A. C. Trouvé, P. B. Sunderland, A. W. Marshall, J. A. Sheffel, M. L. Corn, M. B. Colket, M. Chaos, and H.-Z. Yu. Radiative emissions measurements from a buoyant, turbulent line flame under oxidizer-dilution quenching conditions. *Fire Safety Journal*, 76:74–84, 2015. **3**
- [6] C. Beyler. *SFPE Handbook of Fire Protection Engineering*, chapter Flammability Limits of Premixed and Diffusion Flames. Springer, New York, 5th edition, 2016. **5**
- [7] N. Bryner, E. Johnsson, and W. Pitts. Carbon Monoxide Production in Compartment Fires - Reduced-Scale Test Facility. NISTIR 5568, National Institute of Standards and Technology, Gaithersburg, MD, 1994. **5**
- [8] A. Lock, M. Bundy, E.L. Johnsson, A. Hamins, G.H. Ko, C. Hwang, P. Fuss, and R. Harris. Experimental Study of the Effects of Fuel Type, Fuel Distribution, and Vent Size on Full-Scale Underventilated Compartment Fires in an ISO 9705 Room. NIST Technical Note 1603, National Institute of Standards and Technology, Gaithersburg, Maryland, 2008. **6**