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GASFLOW COMPARISONS WITH BUREAU OF MINES EXPERIMENTS

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ABSTRACT

At the request of the Department of Energy and Westinghouse Hanford Company, the Bureau of Mines has investigated the flammability of mixtures of hydrogen, ammonia, nitrous oxide, and air. The tests were performed in a spherical chamber under quiescent and turbulent conditions.

This paper describes combustion calculations using the GASFLOW code and compares the calculated pressure ratios with experiments mentioned above. GASFLOW is a finite-volume computer code that solves the transient, three-dimensional, compressible fluid, Navier-Stokes equations with multiple species coupled with finite-rate chemical kinetics. The computational results show good agreement with the experimental data and confirm GASFLOW to be a valuable tool for evaluating the above combustion process.

INTRODUCTION

Radioactive wastes produced during the recovery of plutonium and uranium from the nuclear reactors at Hanford, Washington, are stored in underground storage tanks. In Tank 101-SY, a slurry growth and gas evolution cycle has been observed. During the periodic gas releases, mostly hydrogen, nitrous oxide, nitrogen, and small amounts of ammonia have been emitted from the slurry. Air and water are also present in the dome vapor space. These gaseous mixtures are within lower flammability limits (LFLs).

The deflagration study carried out by the Bureau of Mines (BOM) provided a flammability database essential for a quantitative risk assessment of the explosion hazard associated with the gas releases in Tank 101-SY. Flammability data include LFLs, peak explosion pressures, and maximum rates of pressure rise. The tests were performed in a 120-L, 61-cm- (2-ft-) diam spherical chamber.¹ Most of the tests were conducted at ambient temperature and pressure under both quiescent and turbulent conditions using both electric spark and pyrotechnic ignition.

GASFLOW² is a three-dimensional (3D) code developed at Los Alamos National Laboratory (LANL) to be a best-estimate tool for predicting the transport, mixing, and combustion of hydrogen gas in nuclear reactor containments. Using this code, the combustion of several mixture compositions in the test geometry was calculated, and peak pressures were compared with the experimental data.

METHODOLOGY

GASFLOW is a finite-volume computer code that solves the transient, 3D, compressible fluid, Navier-Stokes equations with multiple species coupled with chemical kinetics. The code uses thermodynamic data from the JANAF³ tables and species and mixture transport properties from CHEMKIN.⁴

Detailed descriptions of the mathematical and computational models in GASFLOW are given in Refs. 1 and 5. The models are based on the proven Los Alamos ICE'd-ALE methodology presented in Refs. 6–10. See Refs. 11 and 12 for details about computing thermodynamic and transport properties.

The governing equations represent the conservation of mass, momentum, and energy. An equation of state is included to relate pressure to density and internal energy.

Because the computational method used to model the flow is facilitated by dividing the three-dimensional computational domain into parallelepiped Eulerian volumes (cells) in either cartesian or cylindrical geometry, it is natural to present the continuous equations in integral form.

The integral form of the generalized conservation law is

$$\frac{d}{dt} \int_{V^*} \Phi dV = \int_{S^*} \Phi (\mathbf{b} - \mathbf{u}) \cdot \mathbf{n} dA + \int_{V^*} S_{\Phi} dV \quad (1)$$

It states that the time-rate-of-change of Φ in an arbitrary control volume, V^* , (left side) is equal to the inflow of Φ through the boundary plus the source term (right side). The term $\mathbf{b} - \mathbf{u}$ is the relative velocity between the control surface and the fluid.

The mixture mass conservation equation follows directly from Eq. (1) by letting $\Phi = \rho$:

$$\frac{d}{dt} \int_{V^*} \rho dV = \int_{S^*} \rho (\mathbf{b} - \mathbf{u}) \cdot \mathbf{n} dA + \int_{V^*} S_{\rho} dV, \quad (2)$$

where ρ is the mixture density or the sum of the macroscopic densities for each individual species, $\mathbf{u}$ is the mass-average velocity vector, and S_p is the mass loss (condensation) per unit volume and time. Similarly, setting $\Phi = 1$ in Eq. (1) gives an expression for the change in volume

$$\frac{dV}{dt} = \int_{s^*} \mathbf{b} \cdot \mathbf{n} dA . \quad (3)$$

The transport equation for individual species is given by

$$\frac{d}{dt} \int_{v^*} \rho_\alpha dV = \int_{s^*} \rho_\alpha (\mathbf{b} - \mathbf{u}) \cdot \mathbf{n} dA + \int_{v^*} \nabla \cdot \left[\rho \mathcal{D} \nabla \left(\frac{\rho_\alpha}{\rho} \right) \right] dV + \int_{v^*} S_\alpha dV , \quad (4)$$

where α denotes the gas species, ρ_α is the mass per unit volume (macroscopic density), $\mathcal{D}$ is the mass diffusivity coefficient, and the source or sink term, S_α , represents the species mass created or destroyed by chemical reactions and the loss of steam as a result of condensation. The diffusion of species, α , is represented by the second integral on the right side of Eq. (4).

The mixture-momentum conservation equations are given by

$$\begin{aligned} \frac{d}{dt} \int_{v^*} \rho \mathbf{u} dV = & \int_{s^*} \rho \mathbf{u} (\mathbf{b} - \mathbf{u}) \cdot \mathbf{n} dA \\ & + \int_{v^*} [-\nabla p + \rho \mathbf{g}] dV - \int_{s^*} (\boldsymbol{\tau} \cdot \mathbf{n}) dA + \int_{s_i} \mathbf{D} dA_s , \end{aligned} \quad (5)$$

where p is the pressure, $\boldsymbol{\tau}$ is the viscous stress tensor, $\mathbf{g}$ is the gravitational vector, and $\mathbf{D}$ is the internal structure drag vector. The right-side integrals represent, respectively, the flux of momentum through the control surface, the sum of pressure gradient, gravity, and viscous forces on the control volume, and fluid drag forces acting on structural surfaces.

The equation of change for total internal energy is

$$\frac{d}{dt} \int_{v^*} \rho I dV = \int_{s^*} \rho I (\mathbf{b} - \mathbf{u}) \cdot \mathbf{n} dA - \int_{v^*} \left[p \nabla \cdot \mathbf{u} + \frac{p}{V} \frac{\partial V_s}{\partial t} \right] dV$$

$$- \int_{S^*} \mathbf{q} \cdot \mathbf{n} dA + \int_{V^*} Q dV, \quad (6)$$

where I is the mixture specific internal energy and Q is the energy source or sink per unit volume and time as a result of combustion, condensation, and energy exchange with internal structures, floors, ceilings, and walls. Because condensation effects can dominate the $p \nabla \cdot \mathbf{u}$ work term, we must account for the remaining gas in a computational cell expanding into the volume change associated with the condensate. We account for this effect by using the ideal gas equation of state to arrive at

$$\frac{1}{V} \frac{\partial V_s}{\partial t} = \frac{R_{H_2O} T}{V_c p} \sum_i \dot{m}_i = - \frac{R_{H_2O} T}{p} S, \quad (7)$$

where R_{H_2O} is the gas constant for steam, T is the gas mixture temperature, V_s is the steam volume, and $\sum_i \dot{m}_i$ is the sum of all mass per unit time of steam condensing on all surfaces internal to or bounding the computational cell V_c . Note that S is the same mass loss per unit volume and time as Eq. (7). The energy flux vector $\mathbf{q}$, is given by

$$\mathbf{q} = -\phi \nabla T - \rho D \sum_{\alpha} h_{\alpha} \nabla \left(\frac{\rho_{\alpha}}{\rho} \right), \quad (8)$$

where ϕ is the apparent or turbulent conductivity, D is the apparent or turbulent mass diffusivity, and h_{α} is the enthalpy for species α .

We use a one-step chemical kinetics model that oversimplifies the actual chemical processes. In this model, the only reactions modeled are

(which we call reaction a),

(which we call reaction b),

(which we call reaction c), and

(which we call reaction d).

The reaction rate in these equations is modeled by a modified Arrhenius law. The general expression for the reaction rates are

$$\dot{\omega}_a = C_a [H_2]^{f_a} [N_2O]^{O_a} e^{(-E_a/RT)} , \quad (9)$$

$$\dot{\omega}_b = C_b [H_2]^{f_b} [O_2]^{O_b} e^{(-E_b/RT)} , \quad (10)$$

$$\dot{\omega}_c = C_c [NH_3]^{f_c} [N_2O]^{O_c} e^{(-E_c/RT)} , \quad (11)$$

and

$$\dot{\omega}_d = C_d [NH_3]^{f_d} [O_2]^{O_d} e^{(-E_d/RT)} , \quad (12)$$

where E_a through E_d are activation energies for reactions a through d, respectively. The fuel exponents, f_a through f_d , and the oxidizer or reactant exponents, O_a through O_d , are set equal to 1 for this application. The terms in [] represent concentrations in moles/m³, R is the universal gas constant, and T is the local gas temperature.

The finite-rate chemical kinetics can then be written for the hydrogen/nitrous oxide reaction as

$$-\frac{d[H_2]}{dt} = -\frac{d[N_2O]}{dt} = \dot{\omega}_a , \quad (13)$$

for the hydrogen/oxygen reaction as

$$-\frac{d[H_2]}{dt} = -2 \frac{d[O_2]}{dt} = \dot{\omega}_b , \quad (14)$$

for the ammonia/nitrous oxide reaction as

$$-\frac{d[NH_3]}{dt} = -\frac{2}{3} \frac{d[N_2O]}{dt} = \dot{\omega}_c , \quad (15)$$

and for the ammonia/oxygen reaction as

$$-\frac{d[NH_3]}{dt} = -\frac{4}{3} \frac{d[O_2]}{dt} = \dot{\omega}_d . \quad (16)$$

These equations are weighted by the reactant volume fractions so that there is a partitioning function of hydrogen and ammonia reacting with the available oxygen and nitrous oxide. The chemical energy of combustion, Q_c , is computed as a source term for the energy equation by

$$Q_c = 4.184 \cdot 10^{10} \left(77.4 \dot{\omega}_a + 57.8 \dot{\omega}_b + 105.1 \dot{\omega}_c + 75.7 \dot{\omega}_d \right) \quad (17)$$

We have not attempted to quantify the effects of chemical decomposition at elevated temperatures of any gas specie not consumed in the combustion process.

In practice, when solving the finite-rate chemical equations, we implicitly solve for the fuel concentration when the fuel-oxidizer mixture is fuel lean and for the oxidizer or reactant concentration when the fuel-oxidizer mixture is fuel rich. This ensures that combustion components will never be driven negative, regardless of the timestep size.

COMPARISON OF COMPUTED RESULTS

GASFLOW was used to calculate predicted results for the BOM experiments. Mixture compositions considered were hydrogen concentrations from 5 to 40 vol % diluted in air, 1:1 ratios of hydrogen and nitrous oxide in air, and very low hydrogen and nitrous oxide concentrations in air with 1 and 2% NH_3 added. The initial conditions were set to ambient temperature and pressure. The spherical chamber shown in Fig. 1 was considered to be adiabatic on the time scales of complete combustion. The computational volume consists of three-dimensional cells in cartesian coordinates and is enclosed within rigid, free-slip walls, which means that the gradient of the tangential velocity components on the boundaries is zero. In these calculations, the internal energy was approximated with fourth-order fits, and the specific constant volume heat capacity was computed with coefficients from Gordon and McBride.¹³ The transport properties were approximated with fourth-order fits.

In Fig. 2, the pressure ratio (the ratio of the final to the initial pressure) is shown as a function of the hydrogen concentration ranging from 5 to 40 vol % diluted in air. The line represents the GASFLOW results, while the solid diamonds show the experimental data from Ref. 2.

The calculated results agree well with experimental data and show the correct behavior for both fuel-lean and fuel-rich mixtures, where the maximum pressure ratio is reached for the stoichiometric mixture (29.6% H_2). For very low hydrogen concentrations (5 to 7%), the results indicate almost no pressure rise. This reflects the LFLs for quiescent mixtures observed in the experiments. There is a rapid increase in the pressure ratio at about 8% H_2 where the mixture is rich enough to allow downward flame propagation and nearly complete combustion of the available hydrogen.

Fig. 1. 120-L flammability test sphere.

Hydrogen - Air (quiescent, spark)

Fig. 2. Pressure ratio vs hydrogen concentration.

A second series of experiments, which is presented in Fig. 3, was carried out using equal volume percentages of hydrogen and nitrous oxide mixtures diluted with air. The GASFLOW calculated results are shown to be in good agreement with the experimental data. Near the LFL, the calculated results are shown to be higher than those observed. Theoretically determining the exact LFL is an extremely difficult, if not impossible, task. We chose to be conservative in our modeling approach near the LFL. With the one-step chemical kinetics equation model discussed above, we allow combustion reactions to occur, when in fact the observed data indicates combustion does not occur.

In a third series of experiments, which is presented in Fig. 4, we show the same equal volume percentages of hydrogen and nitrous oxide mixed with air, as seen in Fig. 3, as well as the additional experiments and calculations of adding 1 and 2% ammonia. Again, GASFLOW's calculated results are shown to be in good agreement with the experimental data above the LFL. Near the LFL, the calculated results are once again shown to be higher than that observed. However, the calculations are conservative near the LFL combustion. When small amounts of ammonia are added to the hydrogen/nitrous oxide/air mixtures, the experiments indicated that the LFL of downward propagation is lowered. The calculation results follow this tendency.

In Figs. 5 and 6, we present a comparison between GASFLOW and an experiment involving 10% H_2 and 10% N_2O in air. The actual pressure trace or time history for the

Fig. 3. Pressure ratio vs hydrogen concentration for quiescent mixtures of 1:1 ratios of hydrogen/nitrous oxide in air.

Fig. 4. Pressure ratio vs hydrogen concentration for quiescent mixtures of 1:1 ratios of hydrogen/nitrous oxide in air, compared to data with 1 and 2% added ammonia.

Fig. 5. Absolute pressure vs time for 10% quiescent hydrogen/nitrous oxide mixtures in air.

Fig. 6. Time rate of pressure change vs time for 10% quiescent hydrogen/nitrous oxide mixtures in air.

experiment and calculated pressure history is shown in the first of these figures, while in the second figure, the time derivative of the pressure behavior is given. From the pressure traces, we note that the rise time from ignition to maximum pressure is longer in the calculation than what was observed in the experiment. The time rate of rise shown in Fig. 6 indicates that in the early phase of combustion and immediately following ignition, the calculation is delayed in comparison to the experiment, while during the terminal phase of combustion, the calculation shows ~20% higher than the observed rise rate. Even though there are tradeoffs between actual pressure rise time and the time rate of pressure rise, it is generally felt that the time rate of pressure rise is the most critical parameter for driving the structural dynamics response to combustion. In this instance, the calculated pressure is conservative because the maximum rate of pressure rise is about 20% higher than that observed.

In a parametric study we changed the activation energies and preexponential coefficients in the Arrhenius equations. We found that the lag in the pressure jump could be reduced, but that the comparison of the calculated time rate of pressure change compared with the observed data was in poor agreement.

CONCLUSIONS

The combustion results computed with GASFLOW are shown overall to agree well with the BOM experimental data. The maximum combustion pressures above the LFL are within 5% of the data. Near the LFL, the approach is conservative, but the correct behavior can be seen. At concentrations lower than the LFL, no combustion occurs. The time rate of pressure rise is found to be in reasonable agreement with the experimental observations.

We conclude that the one-step finite-rate chemical kinetics model we used yields good results but is limited. For more complex problems we suggest using reduced chemical kinetics mechanisms or a two-step method based on an induction parameter model. Both of these improved models are derived from detailed chemical kinetics mechanisms.

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