Development of Reduced Analytical Models for Explosion Dynamics

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G. A. Melhem, Ph.D., FAIChE
melhem@iomosaic.com

ioMosaic Corporation

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Process Safety and Risk Management Practices

authored by

Georges A. Melhem, Ph.D., FAIChE

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1 Introduction

The modeling of explosion dynamics for vessels, enclosures, energy storage systems, and other interconnected and complex geometries requires detailed chemical equilibrium calculations to properly resolve the transient PVT behavior during the explosion.

Performing detailed chemical equilibrium calculations by computational fluid dynamics computer codes is not practical and cost prohibitive, even though it can be done using well established methods by direct minimization of the Gibbs free energy [1, 2]. However, we can create a reduced analytical model, often referred to as a constant γ model, that can be easily matched to detailed chemical equilibrium calculations. The reduced analytical model is constructed to optimize the fidelity of the representation of the overpressure properties, which is of most interest and importance for practical explosion dynamics modeling. The constant γ model is optimized to provide the best match of the Chapman-Jouguet solutions as produced by detailed chemical equilibrium calculations.

We demonstrate how constant γ models can easily be developed with SuperChems Expert™ , a component of Process Safety Office® , for use in explosion dynamics codes and the explosion dynamics models of SuperChems Expert .

2 Steady One Dimensional Flow

We consider once again the case of one-dimensional steady flow of a fluid in a constant flow area duct. Ignoring friction, heat and work exchange with the surroundings, the mass, momentum, and energy conservation equations can be written as follows:

Mass:

$$\rho_1 u_1 \;=\; \rho_2 u_2 \tag{1}$$

Momentum:

$$P_1 + \rho_1 u_1^2 \;=\; P_2 + \rho_2 u_2^2 \tag{2}$$

Energy:

$$h_1 + \frac{1}{2} u_1^2 \;=\; h_2 + \frac{1}{2} u_2^2 \tag{3}$$

Where ρ is the fluid mass density, h is the specific enthalpy, P is the pressure, and u is the flow velocity. In addition to the above equations, an equation of state is required to relate pressure, density, and temperature. For gases with ideal behavior, we can relate pressure, density, and temperature using the ideal gas equation of state:

Ideal Gas Equation of State:

$$P = \frac{\rho R_g T}{M_w} \tag{4}$$

Where M_w is the molecular weight, T is the temperature, and R_g is the universal gas constant which is equal to 8314 J/kmol/K.

It can be shown thermodynamically that for an ideal, non-reactive gas, the enthalpy is a function of temperature only and is independent of the pressure. However, when the products are a reactive ideal gas, one must express the enthalpy as a function of temperature and extent of reaction. If the gas is in chemical equilibrium, then the enthalpy becomes a function of temperature and pressure:

$$h_2 = h_2(T, P) \tag{5}$$

3 The Rayleigh Line Equation

If we solve the mass and momentum conservation equations above to eliminate either u_1 or u_2 we obtain the equation:

$$[\rho_1 u_1]^2 = [\rho_2 u_2]^2 = \frac{P_2 - P_1}{v_1 - v_2} \text{ which is always} > 0 \tag{6}$$

Here v is the specific volume in m^3/kg. The right hand side of this equation is the negative slope of a line connecting states 1 and 2 in the (P, v) plane. Both the left hand side and the middle part of this equation represent the square of mass flow. Thus, to be physically meaningful, the left hand side must always be positive. This restricts all end states for a steady one dimensional flow to the regions illustrated in Figure 1. Note that, for such a flow to be meaningful, either the pressure must increase when the volume decreases, or the pressure must decrease when the volume increases. Furthermore, all thermodynamic states of the system in such a flow must lie on a single straight line through the point (P_1, v_1). This line is called the Rayleigh line.

The Rayleigh line does not represent a complete solution to the problem since the energy equation has not yet been included. The Rayleigh line requirement is derived independent of any equation of state considerations. It represents a fundamental constraint on one dimensional steady flow regardless of the substance being considered.

4 The Rankine-Hugoniot Equation

If we eliminate both u_1 and u_2 from the equations above, we arrive at the Rankine-Hugoniot relationship. The Rankine-Hugoniot relationship can be written in terms of the specific internal energy, e:

$$e_2 - e_1 = \frac{1}{2}(P_2 + P_1)(v_1 - v_2) \tag{7}$$

Figure 1: (P, v) plane showing regions where solutions are excluded or allowed according to the Rayleigh line
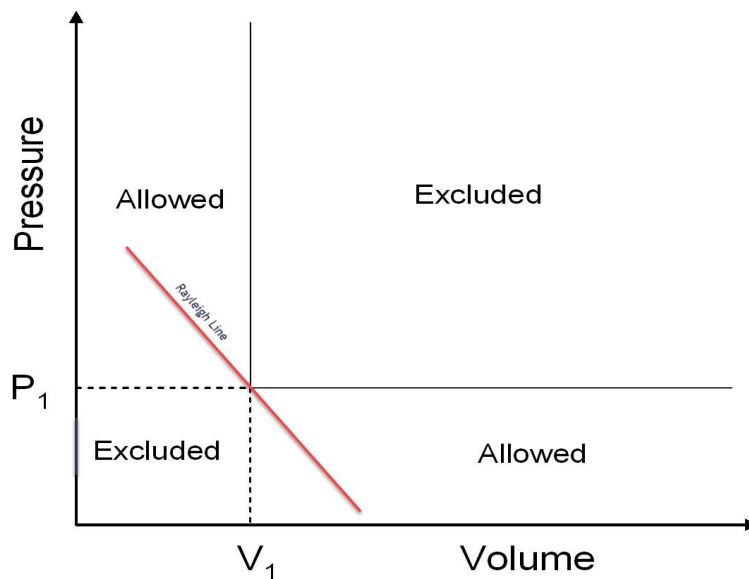
or specific enthalpy:

$$h_2 - h_1 \quad = \quad \frac{1}{2} \left(P_2 - P_1 \right) \left(v_1 + v_2 \right) \tag{8}$$

Like the Rayleigh line, the Rankine-Hugoniot equations were also derived without any consideration of an equation of state. They are applicable to a chemically reactive system as well as a non-reactive system. For a reactive system, the specific enthalpies or internal energies used in the equations for states 1 and 2 must be compatible. The specific enthalpy and internal energy must both use the same standard reference state. Thus, heats of reaction will implicitly be accounted for in the equation for the Rankine-Hugoniot when chemical transformations are occurring.

5   Working Fluid - Heat Addition Model

Chemical reactions involve the breaking of weak chemical bonds to form stronger ones. The energy that is released is absorbed by the system as thermal and Pv energy and as a result the system temperature increases.

The calculation of this temperature (adiabatic flame temperature) for a constant pressure combustion process for a gaseous fuel-oxidizer mixture is performed by requiring that h_2 equal h_1. The enthalpy-temperature relationship for the products cannot simply intersect the enthalpy-temperature relationship for reactants because the temperature increases significantly during a combustion process. If air is the oxidizer, dilution with nitrogen causes the enthalpy-temperature relationship to be almost a straight line. In such a dilute combustion system, even though there is a slight change in the average molecular weight during the combustion process, this change is usually small.

Figure 2: Typical working fluid heat addition model enthalpy - temperature relations
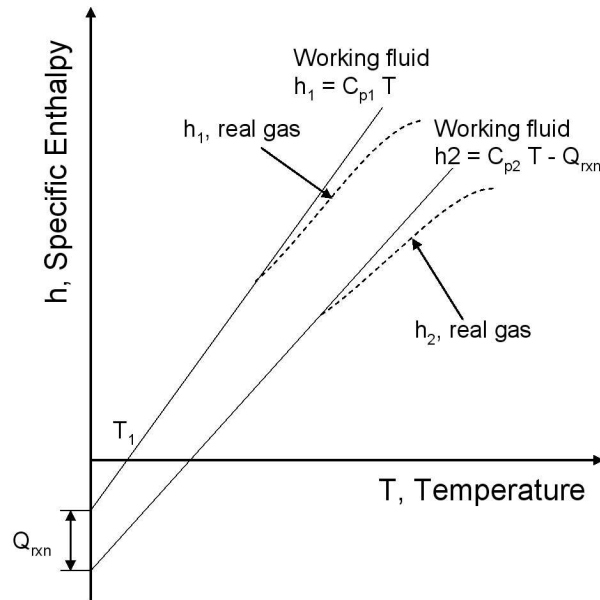
As a result, one can replace the actual gas that is undergoing the combustion reactions with an inert working fluid of constant heat capacity. However, the enthalpy-temperature relationship for the product fluid must be displaced from that of the reactants because of the highly exothermic reactions that are occurring during the combustion process.

$$h_1 \quad = \quad c_{p1}T \tag{9}$$
$$h_2 \quad = \quad c_{p2}T - Q_{rxn} \tag{10}$$

c_p is the specific ideal gas heat capacity and Q_{rxn} is the heat of combustion. Figure 2 illustrates how the real enthalpy relationships are approximated in this simple working fluid heat addition model. We can have constant heat capacities that are different, i.e. c_{p1} is different from c_{p2}. It is very common to set c_{p1} equal to c_{p2}, especially when using the simple working fluid heat addition model to represent explosion phenomena as discussed in Section 7.

Substituting the average molecular weight working fluid heat addition model with equal product and reactant heat capacities into the Rankine-Hugoniot relationship (see Equation 8) yields the following equation:

$$\frac{\gamma}{\gamma - 1}\left(P_2 v_2 - P_1 v_1\right) - Q_{rxn} \quad = \quad \frac{1}{2}\left(P_2 - P_1\right)\left(v_2 + v_1\right) \tag{11}$$

Where γ is the ideal gas heat capacity ratio and is constant. This equation exhibits both a pressure and volume asymptotes as P_2 tends to infinity or v_2 tends to infinity:

$$\frac{v_2}{v_1} \rightarrow \frac{\gamma - 1}{\gamma + 1} \tag{12}$$

$$\frac{P_2}{P_1} \rightarrow -\frac{\gamma - 1}{\gamma + 1} \tag{13}$$

If we rewrite the Rankine-Hugoniot equation in terms of a new coordinate system (η, ξ) in which the variables are defined as follows:

$$\eta = \frac{v_2}{v_1} - \frac{\gamma - 1}{\gamma + 1} \tag{14}$$

$$\xi = \frac{P_2}{P_1} + \frac{\gamma - 1}{\gamma + 1} \tag{15}$$

$$q_{rxn} = \frac{Q_{rxn}}{P_1 v_1} \tag{16}$$

$$\eta\xi = \frac{4\gamma}{(\gamma + 1)^2} + 2q_{rxn}\left(\frac{\gamma - 1}{\gamma + 1}\right) \tag{17}$$

The new equation is a rectangular hyperbola in the (η, ξ) plane, i.e., a displaced rectangular hyperbola in the (P, v) plane. See Figure 3.

A vertical Rayleigh line on Figure 3 from the point (P_1, v_1) represents constant volume combustion and a horizontal Rayleigh line from the point (P_1, v_1) represents constant pressure combustion. There are no waves in the system in either of these cases.

The asymptotes are independent of the value of Q_{rxn}. A positive value of Q_{rxn} displaces the Rankine-Hugoniot towards the right and upwards. When Q_{rxn} equals zero, the Rankine-Hugoniot passes through the point (P_1, v_1). At the point (P_1, v_1) the tangent to the $Q_{rxn} = 0$ Rankine-Hugoniot is the equation for a sonic line.

A Rayleigh line represents an approach flow velocity just equal to the velocity of sound. In addition, it can be shown that the Rankine-Hugoniot for $Q_{rxn} = 0$ is the normal shock Rankine-Hugoniot when the pressure rises and the volume decreases and is physically impossible in the branch where the pressure is lower than the initial pressure. All Rankine-Hugoniot curves that are displaced to the right and upward represent Rankine-Hugoniot curves for combustion processes. The lower branch, which lies between $P_1 > P_2 > 0$ is called the deflagration branch. A Rayleigh line of very small slope connecting the point (P_1, v_1) with a point on this branch represents subsonic flames. This is because the flow velocity associated with ordinary flames is so low that the pressure drop is very small.

The upper branch solutions which are represented by the condition that the solutions lie between the $P = \infty$ asymptote and the $v_2 = v_1$ line are called the detonation branch solutions (all Rayleigh slopes above the slope $u = c$ represent supersonic approach flows). In this region, there is a minimum supersonic velocity for steady, one-dimensional flows. This is called the upper Chapman-Jouguet point (CJ) and is physically observed as a self-sustaining detonation. Intersections of the Rayleigh line with the Rankine-Hugoniot line above this CJ point are called strong or over driven

Figure 3: Pressure-volume diagram of end states for a 1D steady process with heat addition
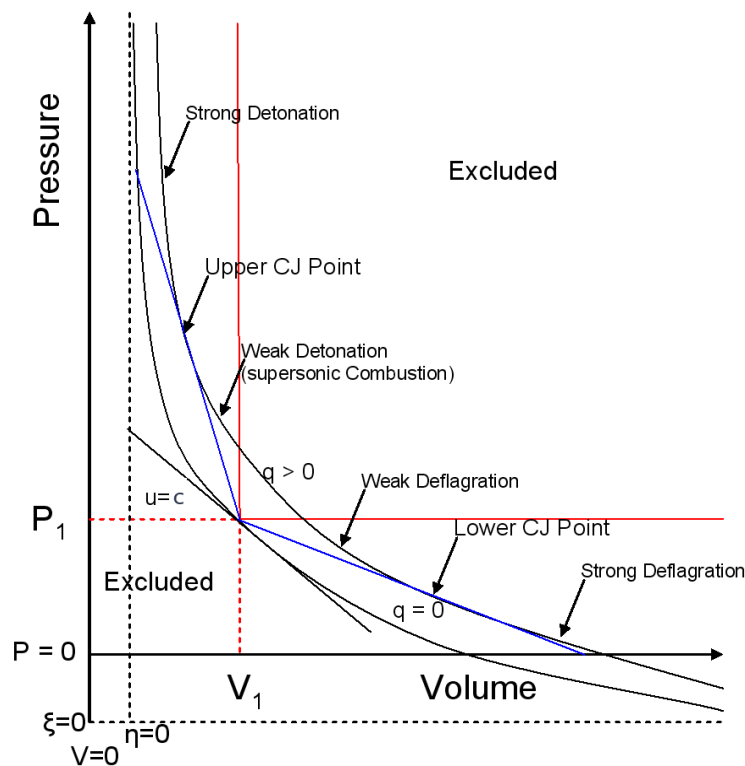
detonations. Strong detonations are observed physically when a shock wave in an exothermic reactive system is supported by a high velocity piston. The weak detonation branch, or supersonic combustion branch, is observed physically when one can somehow trigger the chemistry at a high supersonic velocity without having a shock wave in the system. This can be done, for example, by having a supersonic stream of air heated above the auto-ignition temperature of the fuel and injecting fuel into this very hot supersonic flow. The transition then takes place directly from the point (P_1, v_1) to the intersection of the Rayleigh line with the Rankine-Hugoniot and there is no shock in the flow.

Neither weak nor strong CJ detonations occur as a steady phenomenon (see 2). It has been observed that steady premixed gas detonations tend to propagate at the CJ condition [3]. Deflagration waves usually behave as weak deflagrations and are influenced by finite reaction and transport rates. Therefore, the CJ deflagration velocity is typically not as reliable as the CJ detonation velocity.

As shown in Figure 2, we note that a CJ detonation corresponds to an increase in pressure and a decrease in specific volume and is a compression wave. A CJ deflagration corresponds to a decrease in pressure and increase in specific volume and is an expansion wave.

6   Chemical Equilibrium Considerations

In a real chemical system, the composition of the equilibrium gases changes continuously as one travels along the Rankine-Hugoniot. As one travels along the Rankine-Hugoniot in a direction of decreasing final volume, both the temperature and pressure increase monotonically.

If we differentiate the Rankine-Hugoniot relationship given in terms of specific internal energy along the Rankine-Hugoniot we develop the following relation:

$$de_2 \;\; = \;\; -\frac{1}{2}\left(P_1 + P_2\right) d\left(\frac{1}{\rho_2}\right) + \frac{1}{2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right) dP_2 \tag{18}$$

In differential form, we can write the first law of thermodynamics as follows:

$$de_2 \;\; = \;\; -P_2 d\left(\frac{1}{\rho_2}\right) + T_2 ds_2 \tag{19}$$

Where s is specific entropy. As a result,

$$T_2 \frac{ds_2}{d\left(\frac{1}{\rho_2}\right)} \;\; = \;\; \frac{1}{2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\left[-\frac{\left(P_1 - P_2\right)}{\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)} + \frac{dP_2}{d\left(\frac{1}{\rho_2}\right)}\right] \tag{20}$$

When the left hand side of the above equation equals 0 at any point along the Rankine-Hugoniot, the Rankine-Hugoniot curve must coincide with an isentrope at that point. This leads to the following expression:

$$\left[\frac{dP_2}{d\left(\frac{1}{\rho_2}\right)}\right]_s \;\; = \;\; \frac{P_1 - P_2}{\frac{1}{\rho_1} - \frac{1}{\rho_2}} \tag{21}$$

The right hand side of this equation is the negative slope of a Rayleigh line to that point on the Rankine-Hugoniot. If we substitute the equation for the Rayleigh line in the above equation we obtain:

$$\left[\frac{dP_2}{d\left(\frac{1}{\rho_2}\right)}\right]_s \;\; = \;\; -u_2^2 \rho_2^2 \tag{22}$$

Since the square of the speed of sound (choking condition) is equal to the change of pressure with respect to density at constant entropy, we can write:

$$c_{s_2}^2 \;\; = \;\; \left[\frac{dP_2}{d\rho_2}\right]_s = -\frac{1}{\rho_2^2}\left[\frac{dP}{d\left(\frac{1}{\rho_2}\right)}\right]_s = -\frac{-u_2^2 \rho_2^2}{\rho_2^2} = u_2^2 \tag{23}$$

The equilibrium Rankine-Hugoniot coincides with an equilibrium isentrope at a point that is tangent to a Rayleigh line. The flow velocity in state 2 is exactly equal to the equilibrium velocity of sound at that point. This is the condition for thermal choking in a one-dimensional flow and applies equally well to both the upper and lower CJ points. Only the upper CJ point is observed physically.

To construct a complete Rankine-Hugoniot one must have access to a chemical equilibrium computer code that is capable of determining the equilibrium compositions and thermodynamic properties at specific temperature and pressure points of interest. For example, Rankine-Hugoniot curves are constructed in SuperChems Expert using direct minimization of the Gibbs free energy with real fluid effects [1, 2, 4, 5]. Solids, liquid, and gas phases are allowed in the Gibbs free energy methods used in SuperChems Expert .

The CJ points can be approximated for an ideal gas from maximum constant volume adiabatic temperature and pressure estimates [3]:

$$P_{CJ} \simeq 2P_{max} \tag{24}$$
$$T_{CJ} \simeq \left(\frac{2\gamma}{\gamma+1}\right) T_{max} \tag{25}$$

where T_{max} and P_{max} are the calculated constant volume maximum temperature and pressure and γ is the ideal gas heat capacity ratio. The CJ detonation pressure is approximately twice the constant volume pressure. The CJ temperature is higher than the constant volume temperature due to the shock compression process in a detonation. For a burnt gas heat capacity ratio of 1.2, $T_{CJ} \simeq 1.09T_{max}$, or is 9 % hotter than T_{max}.

The constant volume maximum pressure can be approximated for an ideal gas from the starting initial pressure and the calculated adiabatic flame temperature at the starting initial pressure [3]:

$$P_{max} = P_0 \left[1 + \gamma \left(\frac{T_f}{T_0} - 1\right)\right] \simeq \gamma P_0 \left(\frac{T_f}{T_0}\right) \tag{26}$$

where T_f is the calculated or measured adiabatic flame temperature and T_0 is the initial starting temperature. The constant volume temperature can also be approximated for an ideal gas from the calculated adiabatic flame temperature at the starting initial pressure:

$$T_{max} = T_0 + \gamma (T_f - T_0) \simeq \gamma T_f \tag{27}$$

where T_0 is the starting initial temperature in K.

7   Working Fluid - Heat Addition Model Parameters Estimation

The new Rankine-Hugoniot equation derived earlier is often regressed from real-gas Rankine-Hugoniot estimates in order to establish best values of heat capacity and heat of reaction for the

working fluid heat addition model. Two parameters are regressed from the real fluid Rankine-Hugoniot that is established using detailed chemical equilibrium calculations:

$$\left(\frac{v_2}{v_1} - \beta_1\right)\left(\frac{P_2}{P_1} + \beta_1\right) \quad = \quad \beta_2 \tag{28}$$

The constants β_1 and β_2 are determined from the regression to yield the best values of γ and Q_{rxn}:

$$\beta_1 \quad = \quad \frac{\gamma - 1}{\gamma + 1} \tag{29}$$

$$\beta_2 \quad = \quad \frac{4\gamma}{(\gamma + 1)^2} + \frac{2Q_{rxn}}{P_1 v_1}\left(\frac{\gamma - 1}{\gamma + 1}\right) \tag{30}$$

Or

$$\gamma \quad = \quad \frac{1 + \beta_1}{1 - \beta_1} \tag{31}$$

$$q_{rxn} \quad = \quad \frac{Q_{rxn}}{P_1 v_1} = \frac{1}{2}\left[\beta_2 - \frac{4\gamma}{(\gamma + 1)^2}\right]\left(\frac{\gamma + 1}{\gamma - 1}\right) \tag{32}$$

For a number of common fuel-air mixtures it can be shown that this curve fit is very good (to within 0.25% on pressure at any specified final value over the range 1-20 bars). Therefore, the overall behavior of a gas phase detonation can be modeled accurately using the working fluid heat addition model. Curve fit constants for six common fuels are given in Table 1.

Table 1: Rankine-Hugoniot Curves Regression Data (stoichiometric combustion)

Fuel	Heat of Combustion MJ/kg fuel	Heat of Combustion h. MJ/kg mixture	Best Fit for h/ $P_1 V_1$	Best Fit for q_{rxn}=Q_{rxn}/$P_1 V_1$	γ
H_2	120.00	3.40	28.86	33.89	1.173
CH_4	50.01	2.74	30.90	39.27	1.202
C_2H_2	48.22	3.38	39.12	44.79	1.195
C_2H_4	47.16	2.99	34.91	43.29	1.199
C_2H_4O	28.69	3.24	40.78	47.27	1.203
C_3H_8	46.35	2.78	35.68	47.42	1.208

Notice that the values of $h/(P_1 v_1)$ are determined from the actual heat of combustion and are always lower than $q_{rxn} = Q_{rxn}/(P_1 v_1)$, the dimensionless heat addition which is needed to model the behavior of the real Rankine-Hugoniot. This is simply an artifact of the model. Note that this working fluid-heat addition model does not recognize molecular weight changes (which are small); nor does it correctly model the temperature or velocity of sound of the product gases.

Using the values in the last two columns of Table 1, the CJ Mach number of the detonation may be calculated from the equation below using the positive sign solution (a negative sign on the inner

square root sign yields the CJ deflagration Mach number):

$$M_{CJ} = \sqrt{[\mathcal{H} + 1] \pm \sqrt{[\mathcal{H} + 1]^2 - 1}} \tag{33}$$

$$\mathcal{H} = \frac{\gamma^2 - 1}{\gamma}q \tag{34}$$

The CJ detonation velocity, pressure, temperature, and density ratios may then be calculated as follows:

$$\frac{P_{CJ}}{P_0} = \frac{1 + \gamma M_{CJ}^2}{\gamma + 1} \tag{35}$$

$$\frac{T_{CJ}}{T_0} = \left[\frac{P_{CJ}}{P_0}\frac{1}{M_{CJ}}\right]^2 \tag{36}$$

$$\frac{\rho_{CJ}}{\rho_0} = \frac{P_0}{P_{CJ}}M_{CJ}^2 \tag{37}$$

$$\frac{u_{CJ}}{c_0} = M_{CJ} \text{ or } u_{CJ} = \left(\sqrt{\frac{\gamma P_0}{\rho_0}}\right) M_{CJ} \tag{38}$$

where c_0 is the speed of sound at the starting initial conditions, T_0 is the starting initial temperature, P_0 is the starting initial pressure, and ρ_0 is the starting initial mass density.

8 The Zeldovich, von Neumann, Döring (ZND) Theory

During the period, 1940 to 1945, these three investigators independently constructed a model for a one-dimensional detonation wave. The model consisted of a non-reactive shock transition followed by one-dimensional reaction flow in which the chemistry, triggered by shock heating goes to full chemical equilibrium, while the flow follows a Rayleigh line to the CJ point.

To construct a ZND flow, first calculate for the mixture and initial state conditions of interest the CJ Mach number M of the detonation. Use this Mach number to determine the non-reaction state (P, T) just behind the shock and use these conditions and the prescribed mass flow to numerically integrate the reaction flow equations for steady flow until chemical equilibrium is reached. Since, mathematically, the CJ point is a strong singularity, forward numerical integration to that point is impossible. However, it is usually possible to integrate to within 95% of complete reaction before the singularity starts to cause trouble. Since the CJ properties are known analytically, extrapolation is possible. The trajectory of the calculation is indicated schematically on Figure 3. In this figure the Rayleigh line tangent to the upper CJ point when extended to intersect the q = 0 Rankine-Hugoniot yields the conditions just downstream of the shock wave. Then the calculation follows the Rayleigh line to the CJ point.

One can also use the working fluid heat addition model to represent the chemistry. In this case one

must define an extent of heat addition:

$$\Phi \;\; = \;\; \frac{Q_{rxn}}{Q_{rxn_{CJ}}} \tag{39}$$

where $Q_{rxn_{CJ}}$ is the value of Q_{rxn} tabulated in Table 1. Then, for any value of Φ one can calculate all the state and flow variables using the equations for volume ratio:

$$\frac{v_2}{v_1} \;\; = \;\; \frac{(\gamma M^2 + 1) - (M^2 - 1)\sqrt{1 - \Phi}}{(\gamma + 1) M^2} \tag{40}$$

$$\frac{P_2}{P_1} \;\; = \;\; \frac{(\gamma M^2 + 1) + \gamma (M^2 - 1)\sqrt{1 - \Phi}}{(\gamma + 1)} \tag{41}$$

And flow velocity:

$$u_2 \;\; = \;\; \frac{v_2}{v_1} M c_{S_1} \tag{42}$$

In order to determine the flow structure from these relations one must know the effective reaction rate:

$$\frac{d\Phi}{dx} \;\; = \;\; \frac{1}{u_2 Q_{rxn_{CJ}}} \frac{dQ_{rxn}}{dt} \tag{43}$$

Where dQ_{rxn}/dt is the effective rate of heat release due to the chemical reactions and u_2 is the local flow velocity.

9   Example: Methane-Air Rankine-Hugoniot

Compute the constant volume temperature, constant pressure temperature, upper and lower CJ conditions for a methane-air mixture starting at 1 bar and 25 C. The mixture consists of 0.5 kmol of methane, 1 kmol of oxygen, and 3.76 kmol of nitrogen. Also compute from the complete Rankine-Hugoniot, the parameters β_1 and β_1 by least squares regression.

10   SuperChems Expert Solution

SuperChems Expert provides an automated method for calculating an entire Rankine-Hugoniot using direct Gibbs free energy minimization. The solution is obtained by first defining a mixture that contains methane, air and the potential combustion products. Then the initial temperature and pressure conditions are specified as shown in Figure 4. The mixture selected includes major combustion products. It can be defined to include more minor potential combustion products if needed.

SuperChems Expert computes the complete Rankine-Hugoniot, identifies the CJ points graphically, and fits the simple working fluid parameters. The simple working fluid parameters are used by the SuperChems Expert 1D explosion dynamics model to estimate overpressure from deflagrations, deflagrations to detonations transition, and prompt detonations in 1D geometries. The Rankine-Hugoniot estimates are shown in Figures 5, 6, and 7.

SuperChems Expert also provides utilities for quantifying the influence of composition on Rankine-Hugoniot curves and variables of interest.

Figure 4: SuperChems Expert Rankine-Hugoniot Inputs for Methane-Air combustion

	A	B	C
	Define Inputs		
1		Last Specified On Mon Sep 11 14:54:40 2006	
2			
3	Initial temperature. C	25	
4	Initial pressure. bara	1	
5			
6	✓ **Constant pressure temperature**		
7	✓ **Constant volume temperature**		
8			
9	✓ **Upper CJ curve**		
10	Upper Limit on CJ pressure ratio	25	
11	Maximum number of iterations for upper limit searches	50	
12			
13	✓ **Lower CJ curve**		
14	Lower Limit on CJ pressure ratio	0.5	
15	Maximum number of iterations for lower limit searches	100	
16			
17	Vapor Phase Compounds	Initial number of moles. kmol	
18	METHANE	0.5	
19	OXYGEN	1	
20	NITROGEN	3.76	
21	WATER	0	
22	CARBON MONOXIDE	0	
23	CARBON DIOXIDE	0	
24	AMMONIA	0	
25	HYDROGEN	0	
26	NITRIC OXIDE	0	
27	NITROGEN DIOXIDE	0	
28			
29	Solid Phase Compounds	Initial number of moles. kmol	
30	CARBON-REF	0	
31			

Using the best fit parameters of γ and q for the working fluid model, we can check how the model reproduces the SuperChems Expert calculated CJ detonation velocity, pressure, temperature, and density ratios:

$$\mathcal{H} = \frac{\gamma^2 - 1}{\gamma} q = \frac{1.2^2 - 1}{1.2} 39.348 = 14.4276$$

$$M_{CJ} = \sqrt{15.4276 + \sqrt{15.4276^2 - 1}} = 5.552$$

The CJ detonation velocity, pressure, temperature, and density ratios may then be calculated as

Figure 5: SuperChems Expert Rankine-Hugoniot Estimates for Methane-Air Combustion

3		INITIAL CONDITIONS	CONSTANT PRESSURE	CONSTANT VOLUME	UPPER CJ	LOWER CJ
4	METHANE. kmol	0.5000	0.0000	0.0000	0.0000	0.0000
5	OXYGEN. kmol	1.0000	0.0280	0.0492	0.0672	0.0142
6	NITROGEN. kmol	3.7600	3.7542	3.7445	3.7355	3.7575
7	WATER. kmol		0.9804	0.9647	0.9495	0.9896
8	CARBON MONOXIDE. kmol		0.0479	0.0941	0.1330	0.0230
9	CARBON DIOXIDE. kmol		0.4521	0.4059	0.3670	0.4770
10	AMMONIA. kmol		0.0000	0.0000	0.0000	0.0000
11	HYDROGEN. kmol		0.0196	0.0353	0.0505	0.0104
12	NITRIC OXIDE. kmol		0.0116	0.0309	0.0489	0.0050
13	NITROGEN DIOXIDE. kmol		0.0000	0.0000	0.0000	0.0000
14						
15	CARBON-REF. kmol		0.0000	0.0000	0.0000	0.0000
16						
17	Temperature. C	25.0000	1965.8997	2348.1790	2559.0049	1759.8662
18	Pressure. bara	1.0000	1.0000	8.9145	17.4217	0.4645
19						
20	Total mass. kg	145.3510	145.3510	145.3510	145.3510	145.3510
21	Total volume. m3	130.3025	985.6174	130.3025	72.4580	1920.1407
22	Total enthalpy. MJ	-37.4710	-37.4938	65.6781	129.0075	-92.3553
23	Total entropy. MJ/C	-0.0398	0.3387	0.2817	0.2730	0.3485
24						
25	Speed of sound in gas. m/s	352.8194	920.7535	998.1861	1039.5220	876.8480
26	Particle velocity. m/s				1012.6413	871.1251
27	Shock velocity. m/s				1821.0505	59.1153
28						
29	** SINGLE GAMA MODEL FIT					
30	Beta 1	0.0909				
31	Beta 2	8.1421				
32	Gama	1.1999				
33	Q - Total Heat Released. MJ/kg of mixture	3.5274				
34	q = Q/P1V1	39.3479				
35						
36	Predicted upper CJ Mach Number	5.5504				
37	Predicted upper CJ pressure ratio	17.2578				
38						
39	Predicted lower CJ Mach Number	0.1802				
40	Predicted lower CJ pressure ratio	0.4723				

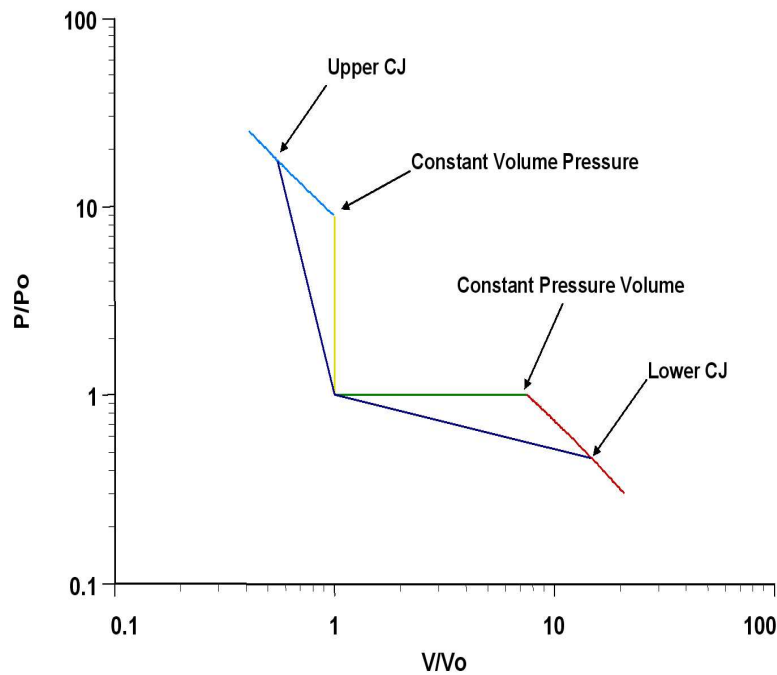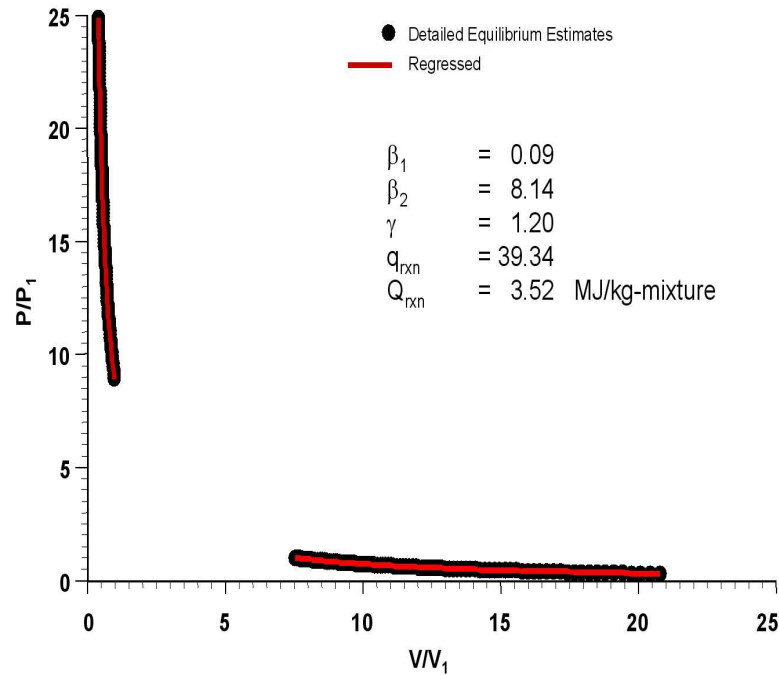Figure 6: SuperChems Expert Graphical Representation of Methane-Air Combustion Rankine-Hugoniot Example

Figure 7: SuperChems Expert Regression of Simple Working Fluid Parameters

follows:

$$u_{CJ} = \left(\sqrt{\frac{\gamma P_0}{\rho_0}}\right) M_{CJ} = \left(\sqrt{\frac{1.2 \times 10^5}{1.115}}\right) 5.552 = 1821.38 \text{ m/s}$$

$$\frac{P_{CJ}}{P_0} = \frac{1 + \gamma M_{CJ}^2}{\gamma + 1} = \frac{1 + 1.2 \times 5.552^2}{2.2} = 17.268$$

$$\frac{T_{CJ}}{T_0} = \left[\frac{P_{CJ}}{P_0}\frac{1}{M_{CJ}}\right]^2 = \left[\frac{17.268}{5.552}\right]^2 = 9.673 \text{ or } T_{CJ} = 9.673 \times 298.15 = 2884.16 \text{ K}$$

$$\frac{\rho_{CJ}}{\rho_0} = \frac{P_0}{P_{CJ}}M_{CJ}^2 = \frac{5.552^2}{17.268} = 1.785 \text{ or } \rho_{CJ} = 1.785 \times 1.115 = 1.99 \text{ kg/m}^3$$

The detailed values calculated by SuperChems Expert (as shown in Figure 5) are 1821.05 m/s, 17.4217, 2559 K, and 2.00 kg/m^3 respectively. The constant γ model as regressed shows excellent predictions and fidelity for critical parameters used in 1D gas dynamics.

11   Conclusions

Constant γ models can be easily developed using SuperChems Expert for complex gas and hybrid gas/dust mixtures. These parameters are then used as inputs to the SuperChems Expert 1D gas dynamics model to evaluate deflagrations, deflagrations to detonation transitions, and prompt detonations in complex and interconnected geometries. In addition, using the constant γ model

parameters and SuperChems Expert 1D gas dynamics modeling we can quickly and properly establish explosion relief requirements for complex and interconnected geometries.

How can we help?

In addition to our deep experience in process safety management (PSM) and the conduct of large-scale site wide relief systems evaluations by both static and dynamic methods, we understand the many non-technical and subtle aspects of regulatory compliance and legal requirements. When you work with ioMosaic you have a trusted ISO certified partner that you can rely on for assistance and support with the lifecycle costs of relief systems to achieve optimal risk reduction and PSM compliance that you can evergreen. We invite you to connect the dots with ioMosaic.

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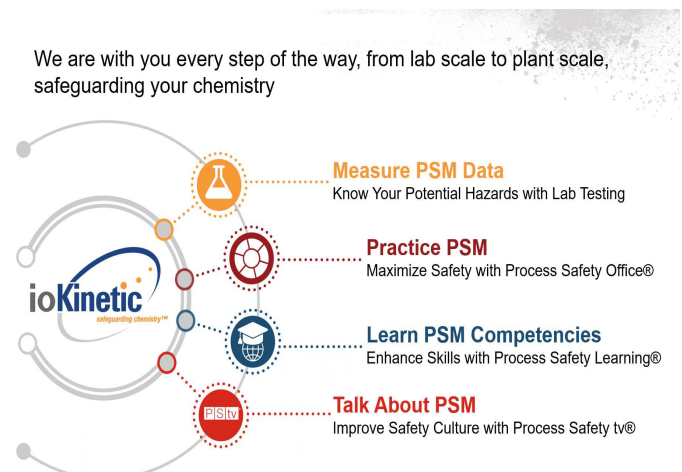
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About the Author

Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

Contact Information

Georges. A. Melhem, Ph.D., FAIChE
E-mail. melhem@iomosaic.com

ioMosaic Corporation
93 Stiles Road
Salem, New Hampshire 03079
Tel. 603.893.7009, x 1001
Fax. 603.251.8384
web. www.iomosaic.com

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As a certified ISO 9001:2015 Quality Management System (QMS) company, ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

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