Numerical analysis for double-base propellant combustion

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Abstract

A comprehensive hybrid Finite Volume (FV) Arbitrary Lagrangian–Eulerian (ALE) scheme has been implemented in order to study the combustion of a Double-Base (DB) solid homogeneous propellant (EC1 composition of 1100cal/g: 43% Nitrocellulose + 52% Nitroglycerine).

The formulation takes into account time dependent chemically reacting flows and is based on the complete set of conservation equations of mass, momentum, energy, and species concentration, considering finite rate chemistry, as well as thermodynamic and transport property variations with temperature and species concentration. The gas phase is treated as a compressible premixed chemically reacting flow, composed of 11 species. The condensed phase is treated as a homogeneous incompressible mixture of 12 reactive species. The chemical model is implemented with 7 unidirectional global reactions. A 1D model has been prepared in order to calculate the composition, flow pressure, temperature, velocity and heat release in the dark zone, the primary and secondary flame regions. The burning rate of the propellant results as a consequence of the zero concentration of solid in the last cell of the condensed phase in contact with the gas phase. The calculation employs an ALE technique in order to dynamically adapt the grid resolution to the gradients of concentration, temperature and heat release along the flame zone, and to incorporate new cells in the gas phase coming from the “burnt” cells of the condensed phase. The method developed provides an accurate description of flame structure and flame dynamics near the burning surface as compared with earlier publications and can be used to study a variety of time dependent processes including transient ignition and combustion instabilities.
1 Introduction

The Double Base Propellant (DBP) is a solid energetic material originally developed for tactical propulsion systems in which both oxidiser and reducer belong to the same molecular structure, usually composed of a homogeneous mixture of Nitroglycerine (NG) and Nitrocellulose (NC) with some plasticiser and other minor ingredients [1, 2]. \((NG = C_3H_5O_3(NO_2)_3, \text{ and } NC = C_6H_7O_2(NO_3)_3, \text{ respectively.})\) Because of this feature, the combustion of DBPs can be regarded as premixed from the beginning of the process. Although they don’t usually have high specific impulses \((I_s \lesssim 210s \text{ under normal conditions})\), they are still on high demand due to its smokeless combustion, and their relatively easy manufacturing, they can be made by solvent or semisolvent processes and extruded in various shapes. Numerical modelling of solid propellant combustion is of high interest not only for propulsion systems or aerospace manoeuvring devices, but also for small applications such as gas generators and air-bag systems [3].

Much effort has been done in research oriented to the CFD applied to solid propellant combustion, see for example [4, 5, 2]. The aim of this work is to develop a comprehensive numerical modelling for the unsteady laminar combustion of DBP’s.

Among the most familiar DB compositions, we can find the extruded Ballistite, the Russian Cordite, or the composite or the cast Double-Base. In this work the EC1 formulation \((52\% \text{ NG} + 43\% \text{ NC} + 5\% \text{ of minor additives})\) contemplated by A. Kubota [1], with 1100cal/g of heat of explosion has been adopted.

2 Theoretical formulation

The theoretical formulation [6] is based on the following average conservation of mass, species concentration, momentum and energy equations for a mixture of \(N_e\) species and \(N_r\) global chemical reactions:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (1)
\]

\[
\frac{\partial (\rho \mathbf{Y}_k)}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{Y}_k + \mathbf{q}^D_k) = \omega_k \quad (2)
\]

\[
\frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla (\mathbf{u}^T \rho \mathbf{u} + p + \sigma) = 0 \quad (3)
\]

\[
\frac{\partial (\rho \varepsilon)}{\partial t} + \nabla \cdot (\rho \mathbf{u} \varepsilon + \mathbf{q}^e) + p \nabla \cdot \mathbf{u} = -\sum_{k=1}^{N_e} \omega_k \Delta h^T_k, \quad (4)
\]

where subscript \(k\) denotes species, \(\omega_k\) is the reaction constant, \(\mathbf{Y}_k\) the mass fraction, \(p\) pressure, \(\mathbf{u}, \rho\) and \(\varepsilon\) are the average velocity, density and internal energy,
respectively, defined according to:

\[
\rho \mathbf{u} := \sum_{k=1}^{N_e} \rho_k \mathbf{u}_k \quad \text{and} \quad \varepsilon := \sum_{k=1}^{N_e} Y_k \left( \varepsilon_k - \varepsilon_k^T \right)
\]

where \( \varepsilon_k = \varepsilon_k^T + \int_{T_r}^{T} c_{v,k} (T')dT' \), being \( T \) and \( T_r \) the actual and reference temperatures, respectively.

### 2.1 Chemical model

The specific rate of \( j \)-th global reaction \( \kappa_{j,\beta} \) is calculated by mean of Arrhenius expressions of the form:

\[
\kappa_j = B_j \exp \left[ -\frac{E_0}{R_0 T} \right],
\]

where \( E_0 \) is the activation energy, \( R_0 \) is the universal gas constant, and \( B_j \approx \text{cte} T^\alpha \) is the frequency factor with \( 0 < \alpha < 0.5 \) and index \( j \). Thus, \( j \)-th rate reaction can be calculated by means of:

\[
\omega_j = \kappa_{j,f} N_e \prod_{k=1}^{N_e} C_{k,j}^*,
\]

where \( \nu_{jk}^* \) is the stoichiometric coefficient of the reactive species \( k \) in reaction \( j \), and \( C_k \) is the mole concentration of the species.

### 2.2 Thermodynamic and transport properties

In the gas phase, the following equation of state (EOS) is considered:

\[
p = \rho R_0 T \sum_{k=1}^{N_e} Y_k / M_k,
\]

where \( M_k \) the molecular mass, \( R_{\text{mix}} := R_0 \sum_{k=1}^{N_e} Y_k / M_k \) the mixture constant, \( c_{v,\text{mix}} = \sum_{k=1}^{N_e} Y_k c_{pk} - R_{\text{mix}} \) the mixture specific heat, and \( c_s \) the speed of sound. The condensed phase (CP) is considered incompressible, i.e. infinite sound speed. The specific heat at constant pressure of each component is evaluated using:

\[
c_{pk}(T) = A_k + B_k T + C_k T^2 + D_k T^3 + E_k / T^2,
\]

where \( A, B, C, D \) and \( E \) are constants obtained from [7, 8]. Then, the specific internal energy of the mixture becomes:

\[
c_{v,\text{mix}} = \sum_{k=1}^{N_e} Y_k c_{pk} - R_{\text{mix}}.
\]

Transport coefficients of species involved in energetic materials are not always available in published tables, therefore, they have to be approximated from the classical statistical theory of gases. The diffusive effects considered in eqs. (1) to (4) are viscosity, Fick’s diffusion and Fourier law for heat conduction. In this way \( q_{k}^{D} = -\rho D_{k,\text{mix}} \nabla Y_k \) in (2) is the Fick’s mass diffusive flux, \( \sigma \) is the viscous tensor in (3), and \( q^e = -\lambda_{\text{mix}} \nabla T - \rho \sum_{k=1}^{N_e} h_k Y_k u_k - \nabla (\sigma \mathbf{u}) \) is the diffusive flux of internal energy. The binary diffusion coefficient between species A and
B is calculated by mean of the Chapman–Enskog (C–E) theory and the transport Boltzmann equation [9], the final results is:

\[ D_{AB} = \frac{3}{16} \left( \frac{8\pi k_B T}{\mu_{AB}} \right)^{1/2} \frac{1}{n \pi \sigma_{AB}^2 \Omega_D} f_D \]  

(7)

where \( n \) is the number density of molecules in the mixture, \( \Omega_D \) the collision integral, \( \sigma_{AB} \) the Lennard-Jones (L–J) mixture length scale, \( f_D \) is the potential shape factor, \( k_B \) is the Boltzmann constant, and \( \mu_{AB} = m_A m_B / (m_A + m_B) \) is the reduced mass of the binary system. For the multi-component mixture, the effective diffusion coefficient \( D_{k, \text{mix}} \) of \( k \) with respect to the mixture is related to \( D_{AB} \) by mean of:

\[ D_{k, \text{mix}} = 1 - \frac{X_k}{\sum_{j \neq k} X_j D_{kj}} \]  

(8)

Viscosity for a single component is calculated using C-E theory and L–J potential according to:

\[ \eta = \frac{7}{16} \sqrt{\frac{\pi m k_B T}{(\pi \sigma^2 \Omega_D)}} \].

Then, in order to obtain an average value for the mixture \( \eta_{\text{mix}} \), Wilke’s mixing rule is applied [9] yielding:

\[ \eta = \sum_{i=1}^{N_e} \frac{X_i \eta_i}{\sum_{j=1}^{N_e} X_j \varphi_{ij}} \]  

and

\[ \varphi_{ij} = \left[ 1 + \sqrt{\frac{\eta_i}{\eta_j}} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2 \sqrt{8 \left( 1 + \frac{M_i}{M_j} \right)} \].

C–E theory can also be applied to obtain the thermal conductivity \( \lambda \) of pure monoatomic species with no internal degrees of freedom [9, 10], yielding:

\[ \lambda = \frac{25}{32} \sqrt{\frac{\pi m k_B T c_v}{(\pi \sigma^2 \Omega_D)}} \].

Then, Eucken’s correction factor given by:

\[ \lambda M \eta^{-1} = 1.32 c_v + 1.77 R_0 \],

is used to consider the internal degrees of freedom in polyatomic molecules, and finally, for the multi-component mixture, Wilke’s rule is used in the same way as for the viscosity coefficient (\( \eta \)) above. Reference values for the calculation of cross sections, dipole moments, and collision integrals can be obtained from refs. [9, 10, 11]

### 3 The DB propellant

Because of its relatively large stability under room conditions, an external source of heat (igniter) must be provided to initiate the DBP burning. During the ignition process, heat is transported by conduction inside the solid and the degradation reaction of NG and NC begins to accelerate generating reactive species like \( NO_2 \) and aldehydes - see reaction (9).

Then, further recombination takes place into the solid phase, as contemplated by reaction (10) yielding extra heat to reinforce the ignition. We call condensed phase (CP) to the region between gas and solid phase where solid propellant coexists with degradation and recombination products. (The CP consists of a pre-heated zone and a superficial degradation layer where molecular degradation of the propellant
and further recombination of the decomposed products takes place.) As degradation evolves, the solid concentration drops down from one to zero. The closer to the burning surface the higher degradation rates. When solid concentration reaches zero at the interface, convection process drags the unburnt condensed phase from the cold zone of the DBP thus replacing the decomposed material.

Then, a convective chemically reacting flow emerges from the burning surface toward the gas phase with a velocity ruled by eq.(1). The emerging molecules react with each other in the gas phase, developing an important amount of heat in the flame zone. The distribution of heat release along the flame zone is ruled by the coupling between the gas-phase reactions, hydrodynamics, and transport phenomena, thus yielding a particular flame structure as qualitatively shown in Fig. 1. Meanwhile, the heat released in the primary flame zone provides some energy feedback, which may maintain the degradation reaction in the CP, thus driving the combustion into a self-sustained steady, unsteady, oscillatory, or vanishing process depending on the intervening rates and amounts of available energy.

### 3.1 Reactions in condensed and gas phase

The following $N_r = 7$ global reactions were considered for the DBP modelling:

\[
DB \rightarrow 2.49NO_2 + 2.36CH_2O + 1.26(CHO)_2 + 0.17CO + \text{mr} \quad (9)
\]

\[
NO_2 + 0.56CH_2O + 0.16(CHO)_2 \rightarrow NO + 0.38CO
+ 0.5CO_2 + 0.5H_2O + 0.22H_2 \quad (10)
\]

\[
NO_2 + 0.56CH_2O + 0.16(CHO)_2 \rightarrow NO + 0.38CO + 0.5CO_2
+ 0.5H_2O + 0.22H_2 \quad (11)
\]

\[
CH_2O + CH_2O \rightarrow CO + 0.5C_2H_4 + H_2O \quad (12)
\]

\[
(CHO)_2 + (CHO)_2 \rightarrow 4CO + 2H_2 \quad (13)
\]
\[ NO + 0.16CO + 0.12C_2H_4 + 0.12H_2 \rightarrow 0.5N_2 + 0.4CO_2 + 0.36H_2O \] (14)
\[ C + NO \rightarrow CO + 0.5N_2, \] (15)

involving the following species: \( DB, NO_2, CH_2O, (CHO)_2, CO, NO, CO_2, H_2O, H_2, C_2H_4, N_2 \) and \( C \). Reactions given by (9) and (10) describe the DB decomposition and endothermic recombination, respectively, that take place in the CP, whereas reactions (11) to (15) take place in the gas phase and are mostly exothermic. The corresponding rate reactions, specific entalpies, and Arrhenius coefficients were obtained from refs. [12, 13, 11].

4 Interface boundary conditions

Coupling of processes in gas and CP at the burning surface (interface) is done by prescribing the conservation of mass and species equations:

\[ [\rho u]_{gas} = \rho p r_b, \quad \text{and} \quad [\rho u_k \cdot \hat{n} Y_k]_{gas} = \rho p r_b Y_k, \] (16)

respectively, and energy according to:

\[ -\lambda_{mix} \frac{\partial T}{\partial \hat{n}} + \rho \sum_{k=1}^{N_e} Y_k h_k u_k \cdot \hat{n} = -\lambda_s \frac{\partial T}{\partial \hat{n}} + \rho_r r_b \left[ c_p (T_s - T_r) + \sum_{k=1}^{N_e} Y_k \Delta h_k \right]_s. \] (17)

Where subscript \( s \) refers to the CP, \( r_b \) is the local propellant burning rate, \( T_s \) is the interface temperature, \( h \) is enthalpy and \( \Delta h \) the enthalpy at reference temperature. Because reactions in the CP have relatively high activation energy and occur in a very thin region (few microns in foamy zone), a matched asymptotic expansion technique as described in refs. [14, 12, 13] can be used to estimate a burning rate formula. The result for a steady self-sustained combustion is:

\[ r_b^2 \approx \beta' \frac{T_s^2}{T_s - T_0 - Q_s/(2c_s)} \exp \left[ \frac{-E_c}{R_0 T_s} \right], \] (18)

where \( \beta' := \lambda_s B c R_0 / (c_s \rho_s E_c) \) is a constant, \( T_0 \approx 293K \) is the initial temperature equal to the temperature at \( x \rightarrow \infty \) in the cold zone of the propellant. The following values were assumed: \( \rho_s = 1.6g/cm^3, c_s = 0.4cal/(gK), \lambda_s = 5.1 \times 10^{-2}cal/(smK), B_c = 10^{17} s^{-1}, \) and \( E_c = 40kcal/mol. \) Thus \( r_b \approx 10^{-2} m/s, \) and consequently: \( \delta x_c \approx 37 \mu m, \tau_c \approx 4 ms, \delta x_d \approx 2 \mu m, \tau_d \approx 0.2 ms, \) where \( \delta x \) indicates characteristic length, \( \tau \) residence time, and subscripts \( c \) and \( d \) preheated and foamy zone in the CP, respectively. Note that the typical Mach number in the flame zone is \( M \approx 10^{-3}, \) thus presenting a rather incompressible behaviour which will conditionate the numerical scheme.
5 Numerical scheme

A new variant of the Implicit Continuous Eulerian (ICE) method [15] with Arbitrary Lagrangian–Eulerian (ALE) technique was implemented in order to solve the 1D flame structure of the DBP. The scheme is based on the Finite Volume Method (FVM) in which each physical process is integrated in an independent way during the calculation time step. The scheme uses a Staggered Grid approach in which all diffusive fluxes \( q \) and flow velocities \( u \) are assigned to vertices (representing cell faces) whereas \( \varepsilon_{\text{mix}}, T, p, \text{cell volume} V \), and \( Y_k \) are assigned to cell centres as shown in Fig. 2(a).

A variation in time of any cell dynamic properties \( \psi \) is calculated as \( \delta \psi = \psi^{m+1} - \psi^m \), where \( m \) indicates time level, due to either Fick’s mass diffusion, Fourier thermal diffusion, or energy diffusion due to species migration is calculated in a Lagrangian way with a fully implicit time integration method. For example, in case of Ficks’ diffusion, we use:

\[
\delta Y_k = Y_k^{m+1} - Y_k^m \approx \delta t \frac{d}{dt} Y_k^{m+1}
\]  

(19)

where \( dY_k/dt \) at the advanced time level can be obtained by mean of:

\[
\frac{d(m_i^k Y_i^k)}{dt} \approx \gamma_{i-\frac{1}{2}}^k - \gamma_{i+\frac{1}{2}}^k, \text{ and } \gamma_{i-\frac{1}{2}}^k = (\rho_k D_{k,\text{mix}})_{i-\frac{1}{2}} \left( \frac{Y_{k,i-1}^k - Y_i^k}{V_i + V_{i-1}} \right) A,
\]

(20)

being \( A \) the cross section of the 1D problem, \( V \) the cell volume, and \( m \) the total mass of the cell.

Next, hydrodynamic update is integrated with a new variant of the ICE method (Implicit Continuous Eulerian) [15, 11]. Source terms in (2) and (4) from chemical reactions are explicitly integrated in time, according to:

\[
\delta Y_{k,i}^{m+1} = \frac{\omega_{k,i}^m}{\rho_i^m} \delta t, \quad \text{and} \quad \delta (m \varepsilon)^{m+1}_i = V_i^m \sum_{k=1}^{N_e} \omega_{k,i}^m \Delta h_k \delta t
\]

(21)

Each integration is performed in a Lagrangian way, thus temporally avoiding the convective terms. Then, after each calculation cycle, vertices are moved arbitrary
over the fluid in order to dynamically adapt the mesh to the solution. As a consequence, convective terms are restored. This reorganisation allows to automatically tune the grid resolution at each time level according to the gradients of $Y_k$, $T$ and heat release.

The numerical scheme consists of the following steps (detailed explanation of each stage can be found in [11]):

1. Read preprocessing parameters, initial and boundary information.
2. Adjust time step $\delta t$ and compute burning rate $r_b$.
3. **For all cells and vertices in gas and condensed phase; Do:**
   - Update $Y_k$ and $\varepsilon$ due to chemical reactions.
   - Update sequentially $Y_k$ and $\varepsilon$ due to all diffusion processes.
   - Update $p, \varepsilon, x$ and $u$ due to hydrodynamics (purely Lagrangian).
   - Redistribute vertices in order to adapt the mesh to the solution, such that the following distribution function:
     $$w = c \left( 1 + b_1 \frac{\partial T}{\partial x} + b_2 \frac{\partial \omega_k \Delta h_k}{\partial x} \right)$$
     where $b_1$ and $b_2$ are weighting constants and $c$ is determined such that $w(x)$ is normalised along the gas phase, i.e.: $\int_0^L w(x')dx' = 1$.
   - Update thermochemical, kinetic, and transport properties.
4. **Gasification of a CP cell:** If any cell $i \in$ CP achieved $Y_{i, DB} = 0$, then cell $i$ becomes now part of the gas phase, thus subjected to the gas EOS (5).
5. Update cell flow variables in gas phase $V, T, p, c_s$, etc. using EOS (5).
6. Update time: $t = t + \delta t$, and repeat step 2 until convergence is reached.

### 6 Results

The outlined method has been applied in order to solve the 1D combustion of the DBP shown in Fig.2(b). The burning surface is located at $x = 0$ where the FV version of matching conditions (16),(17) are prescribed. Boundary conditions are implemented by mean of phantom cells and vertices. The cold end of the DBP has $T = 293K$, $Y_{DB} = 1$, and $Y_k = 0$ for $k \neq DB$. Smooth outflow boundary conditions like $\partial (u_x, \varepsilon, Y_k)/\partial x = 0$ are prescribed at the gas exit and initial conditions given are summarised in table 1. An external source of heat has been added in

<table>
<thead>
<tr>
<th>$x$[m]</th>
<th>$Y_{DB}$</th>
<th>$Y_{N2}$</th>
<th>any other $Y_k$</th>
<th>$T$[K]</th>
<th>$p$[kg/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x &lt; 0$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>293</td>
<td>1</td>
</tr>
<tr>
<td>$x = 0$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>650</td>
<td>1</td>
</tr>
<tr>
<td>$x &gt; 0$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>650</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1: Initial conditions.
order to maintain a temperature of $650K$ during 1 ms so that reactions (9) and (10) can start. Once the combustion begins, this transient condition is removed, and later on a self-sustained laminar combustion is achieved. All transient effect due to ignition and flame build-up vanish after approximately $t = 0.2s$ when the process stable. Fig. 3 shows the concentration profile of all species in gas phase and CP at $t = 0.2s$. The results obtained are in good agreement with previous numerical simulations [13] and qualitative descriptions of the flame structure [14]. Fig. 4 shows the path of the grid vertices during the simulation. The local grid resolution is proportional to the gradients of concentration, temperature and heat release. It can be observed how the space resolution tries to capture the build-up processes of the primary and secondary flame zones at times $t = 0.02s$ and $t = 0.06s$ to $0.08s$, respectively.

7 Conclusions

A new hybrid Finite Volume (FV) Arbitrary Lagrangian–Eulerian (ALE) scheme has been successfully implemented in order to study the combustion of a Double-Base (DB) solid homogeneous propellant. The burning rate of the propellant is
obtained as a natural consequence of the gasification of the last cell in the condensed phase. The grid resolution was dynamically adjusted to the gradients of the main flow variables during each time step of the simulation by means of the Implicit Continuous Eulerian approach, thus allowing to capture in detail the steep gradients of concentration and temperature along the flame structure. The scheme has proven to be stable and provided accurate description of the flame structure and flame dynamics near the burning surface of the propellant. Hence, it can be used to study a variety of time dependent combustion processes including transient ignition and combustion instabilities.

References


