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Analysis of RDX-TAGzT pseudo-propellant combustion with detailed chemical kinetics

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A detailed model of steady-state combustion of a pseudo-propellant containing cyclotrimethylene trinitramine (RDX) and triaminoguanidinium azotetrazolate (TAGzT) is presented. The physicochemical processes occurring within the foam layer, comprised of a liquid and gas bubbles, and a gas-phase region above the burning surface are considered. The chemical kinetics is represented by a global thermal decomposition mechanism within the liquid by considering 18 species and eight chemical reactions. The reactions governing decomposition of TAGzT were deduced from separate confined rapid thermolysis experiments using Fourier transform infrared spectroscopy and time-of-flight mass spectrometry. Within the gas bubbles and gas-phase region, a detailed chemical kinetics mechanism was used by considering up to 93 species and 504 reactions. The pseudo-propellant burn rate was found to be highly sensitive to the global decomposition reactions of TAGzT. The predicted results of burn rate agree well with experimental burn-rate data. The increase in burn rate by inclusion of TAGzT is due in part from exothermic decomposition of the azotetrazolate within the foam layer, and from fast gas-phase reactions between triaminoguanidine decomposition products, such as hydrazine, and oxidiser products from the nitramine decomposition.

Keywords: premixed combustion; detailed chemical kinetics; RDX; TAGzT; burn rate; temperature sensitivity

Nomenclature

- \( A_i \) Pre-exponential constant for reaction \( i \)
- \( c_{pi} \) Specific heat at constant pressure for species \( i \)
- \( C_i \) Molar concentration of species \( i \)
- \( h_i \) Enthalpy of species \( i \)
- \( h_f \) Heat of formation of species \( i \) at standard conditions
- \( L_f \) Foam layer thickness
- \( m_i'' \) Mass flux
- \( R_u \) Universal gas constant
- \( N \) Number of chemical species
- \( P \) Pressure
- \( r_b \) Burn rate of solid propellant
- \( s \) Sticking coefficient

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1. Introduction

Ignition and combustion of solid propellants have been the subject of numerous experimental and theoretical investigations. The significant aims remain reduction in cost, improvement in safety, increase in performance and minimisation of emission of harmful pollutants. Cyclotrimethylene trinitramine (RDX) is an energetic compound used widely in composite propellants. It can produce a high specific impulse along with less smoke, toxicity and corrosion. Many complex models for RDX combustion have been developed in the past decade [1–4]. A detailed gas-phase reaction mechanism of RDX was formulated by Melius [2] and used to solve for the steady-state combustion, where the condensed-phase region was treated as a dense gas. The chemical kinetic scheme developed by Melius was later improved by Yetter et al. [5] and used in steady-state combustion modelling by Prasad et al. [1]. The condensed phase was recognised as an important aspect of RDX combustion by Liau and Yang [3] by accounting for a foam layer, in which a global decomposition mechanism of RDX was considered. Such a foam layer consists of liquefied RDX and bubbles of gaseous RDX and its decomposition products. Davidson and Beckstead [4] made further modifications in Liau and Yang’s model. These modifications highlighted the need for a better treatment of the foam layer. Recently, Anderson et al. [6] compared the chemical kinetic scheme due to Yetter et al. [5] with another detailed gas-phase mechanism for RDX.
attributed to Chakraborty et al. [7], who added species and reactions to the mechanism of Yetter et al. [5]. The major difference between the models was that NO₂ scission dominated the initial step in Yetter’s mechanism, whereas HONO elimination was found to be the dominant step in the latter scheme. Though both mechanisms accurately predicted the burn rates of RDX over a wide range of pressures, neither mechanism was able to generate all the experimentally measured species profiles satisfactorily.

In practical applications, an RDX-based propellant may contain various ingredients, such as a binder, plasticiser, and stabiliser as well as a burn-rate modifier. The choice of ingredients depends on many different aspects, including, among others, desired flame temperature, burn rate, and temperature sensitivity. Commonly employed binders and energetic ingredients include fuel ones, such as hydroxyl-terminated polybutadiene, or energetic ones, such as glycidyl azide polymer (GAP), bis-azidomethyl oxetane, 3-azidomethyl-3-methyl oxetane, nitrocellulose, and nitroglycerine. Liau et al. [8] performed detailed modelling of the physico-chemical processes involved in RDX/GAP pseudo-propellant combustion. They concluded that addition of GAP to RDX led to a decrease in burn rates compared to pure RDX, despite higher burn rates of pure GAP, due to the production of inert gases leading to a decrease in the gas-phase heat feedback. However, addition of butanetriol trinitrate (BTTN) to the pseudo-propellant increased the burn rates considerably, as shown by steady-state combustion modelling by Yoon et al. [9].

It may be of interest to add ingredients that cause less barrel erosion. In this context, recent interest has been focused on high-nitrogen compounds due to their large positive heats of formation and potential for reduced barrel erosion. These novel energetic materials produce molecular nitrogen as one of the primary decomposition products, achieving a high specific impulse without undesirable smoke or soot. Triaminoguanidinium azotetrazolate (TAGzT) is one such material. Figure 1 shows the molecular structures of RDX and TAGzT. A few studies related to the decomposition and burning behaviour of TAGzT are available in the literature.

Vibrational and nuclear magnetic resonance (NMR) spectroscopy, elemental analysis and safety testing were performed by Hammerl et al. [10] on TAGzT. Burning rate experiments, T-Jump/ Fourier transform infrared (FTIR) spectroscopy measurements, and laser-ignition studies of TAGzT were performed by Tappan et al. [11]. It was found that TAGzT had extremely high low-pressure burn rates compared to conventional explosives, such as cyclotetramethylene tetranitramine (HMX). The authors concluded that ignition and decomposition behaviour of TAGzT was controlled by condensed-phase reactions. The kinetics of decomposition pathways of TAGzT were investigated by Min-Hsien et al. [12] by molecular modelling using ab initio methods. The condensed-phase thermal decomposition chemistry of TAGzT was studied by Chowdhury and Thynell [13] by FTIR spectroscopy and time-of-flight mass spectroscopy (ToFMS). It was found that deprotonation from the triaminoguanidinium cations initiated the decomposition. Thermogravimetry, differential thermal analysis, FTIR spectrometry and mass spectrometry experiments were performed.

Figure 1. Structures of RDX and TAGzT.
Table 1. Liquid-phase reactions and associated rate parameters.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$A^{a,c}$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>RDX$_0$ $\rightarrow$ 3 CH$_2$O + 3 N$_2$O</td>
<td>$6.02 \times 10^{13}$</td>
<td>36,000</td>
</tr>
<tr>
<td>2.</td>
<td>RDX$_0$ $\rightarrow$ 3 HCN + 1.5 (NO$_2$ + NO + H$_2$O)</td>
<td>$2.51 \times 10^{16}$</td>
<td>44,100</td>
</tr>
<tr>
<td>3.</td>
<td>TAGzT$_0$ $\rightarrow$ 2 TAG + AzT</td>
<td>$1.00 \times 10^{16}$</td>
<td>39,200</td>
</tr>
<tr>
<td>4.</td>
<td>TAG$_0$ $\rightarrow$ N$_2$H$_4$ + N$_2$H$_2$ + NH$_2$NC</td>
<td>$5.00 \times 10^{15}$</td>
<td>42,000</td>
</tr>
<tr>
<td>5.</td>
<td>AzT$_0$ $\rightarrow$ 2 HCN + 4 N$_2$</td>
<td>$1.00 \times 10^{16}$</td>
<td>35,000</td>
</tr>
<tr>
<td>6.</td>
<td>NH$_2$NC + NO$_2$ $\rightarrow$ HONO + HNHC</td>
<td>$1.00 \times 10^{6}$</td>
<td>5,000</td>
</tr>
<tr>
<td>7.</td>
<td>NH$_2$NC $\rightarrow$ NH$_2$CN</td>
<td>$1.00 \times 10^{14}$</td>
<td>40,000</td>
</tr>
<tr>
<td>8.</td>
<td>2 HNHC $\rightarrow$ 2 HCN + N$_2$</td>
<td>$1.00 \times 10^{10}$</td>
<td>20,000</td>
</tr>
</tbody>
</table>

$a$: preexponential factor. $b$: activation energy. $c$: All units are in mol, cm, s, K, and cal.

on TAGzT by Damse et al. [14]. They stated that rapid initial exothermic decomposition of the nitrogen-rich TAGzT is responsible for its high burn rate. More recently, decomposition of TAGzT was studied by Hayden [15]. She investigated the underlying chemical and physical processes that control the thermal decomposition behaviour of TAGzT alone and in the presence of RDX. The methods used were simultaneous thermogravimetric modulated beam mass spectrometry and Fourier transform ion cyclotron resonance mass spectrometry involving very slow heating rates ($\sim 10^2$ C/min).

In the present work, the objective is to develop a comprehensive model of steady-state combustion of RDX with TAGzT as an energetic additive. In this regard, special attention is given to the foam layer, since TAGzT decomposes at slightly lower temperatures compared to pure RDX. Thus, it is relevant to discuss first the decomposition of RDX and TAGzT.

2. Chemical kinetics mechanism

The decomposition pathways for RDX and TAGzT, as well as subsequent reactions between the decomposition products in the liquid phase of the foam layer are listed in Table 1. The reaction scheme consists of 18 species and eight reactions. Two global decomposition pathways were considered for RDX, an exothermic pathway producing CH$_2$O and N$_2$O, and a second endothermic pathway favoured at high temperatures, leading to the formation of HCN, NO$_2$, NO, and H$_2$O. The rate parameters for reactions 1 and 2 were assumed to be the same as that of Liau and Yang [3].

The approximate TAGzT decomposition model was obtained from the limited data available in literature and the decomposition studies undertaken by Chowdhury and Thynell [13]. These studies were conducted under high heating rates on the nitrogen-rich compounds TAGzT and guanidinium azotetrazolate (GzT) to elucidate the initiation and subsequent secondary reactions occurring in the condensed-phase. The decomposition studies on TAGzT revealed the presence of many reactive species, including hydrazine and ammonia. The source of these species can be traced back to either the triaminoguanidinium cation, or the neutral triaminoguanidine (TAG). However, the lack of clear evidence of TAG in the gas phase, both in the FTIR spectra and the ToFMS spectra, led to further tests with the more stable GzT. As established by previous differential scanning calorimetry (DSC) studies [10], the decomposition temperatures of GzT were approximately 100$^\circ$C higher compared to TAGzT, due to the absence of the three amino groups on the terminal nitrogens of the cation.

The activation energy for the initiation step involving the proton transfer to form two molecules of TAG and one molecule of azobistetrazole (AzT) was assumed to be.
39.2 kcal/mol, as proposed by Hammerl et al. [10]. Azo decomposes through ring-opening pathways to liberate molecular nitrogen and traces of HCN through various intermediates. The activation energy and the pre-exponential factor for this step, detailed by reaction 5, were chosen in accordance with values observed for unimolecular decomposition of nitrogen-rich tetrazoles. Decomposition in guanidine is initiated by a C=N bond scission to form the amino radical, which then proceeds to extract a hydrogen atom from the neighboring amino group to form ammonia. In the case of triaminoguanidine, the onset may be through an N=N bond scission to form the amino radical or a C=N bond scission to form the hydrazinyl radical.

The activation energy for the decomposition of TAG, described by reaction 4, to form N2H4, N2H2, and NH2NC was assumed to be close to the difference between the enthalpies of the reactant and the products. Reaction 6, involving a hydrogen-extraction reaction between NO2 and NH2NC, was assigned a small value for the activation energy, typical of hypergolic reactions. The isomerisation of NH2NC to form NH2CN has an activation energy of approximately 40 kcal/mol [16]. In addition to these thermal decomposition reactions in the liquid phase, to complete the description of the mass conversion process, a liquid to gas phase transition of RDX was considered.

\[
RDX_l \leftrightarrow RDX_g \tag{1}
\]

This process was modelled using gas kinetic theory. The rate of evaporation \( \dot{m}_{evap}'' \) is given as

\[
\dot{m}_{evap}'' = A_s s \bar{v}_n C_{RDX} \left( \frac{P_{v,eq}}{P} - X_{g,RDX} \right) \tag{2}
\]

where \( A_s \) is the specific surface area, \( s \) is the sticking coefficient which depends on the local conditions at the interface, \( \bar{v}_n \) is the average molecular velocity component normal to the interface obtained from the kinetic theory of gases and \( P_{v,eq} \) is the equilibrium vapour pressure. It is approximated by the Clausius-Clapeyron equation. Further details on Equation (2) are given by Liau and Yang [3].

Reactions in gas bubbles in the foam layer and the gas-phase region above the burning surface are considered. Two reaction mechanisms as shown in Table 2 are used. Mechanism 1 is from the work of Yetter et al. [5] on RDX, which is in a large part based on the work of Melius [2]. Chakraborty et al. [7] subsequently augmented the mechanism of Yetter et al. by introducing more details in the RDX decomposition pathways. In both mechanisms,

<table>
<thead>
<tr>
<th>Table 2. Gas-phase reaction mechanisms used.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanism 1</td>
</tr>
<tr>
<td>i. 76 species, 468 reactions</td>
</tr>
<tr>
<td>ii. RDX combustion reactions given by Yetter et al. [5]</td>
</tr>
<tr>
<td>iii. TAGzT decomposition reactions same as in liquid phase (Table 1)</td>
</tr>
<tr>
<td>v. Ammonia oxidation mechanism given by Thaxton et al. [18]</td>
</tr>
</tbody>
</table>
reactions covering hydrazine oxidation by nitrogen dioxide are included as hydrazine is an early decomposition product of TAGzT and nitrogen dioxide is an important decomposition product of RDX. Hydrazine oxidation and ammonia oxidation are the major subgroups of reactions playing an important role in the gas-phase region and also to some extent in gas bubbles in the foam layer. The chemical kinetics parameters for these newly added reactions were obtained from the compilation made by Dean and Bozzelli [17], and by using results of molecular modelling \textit{ab initio} calculations as described in section 3. The ammonia oxidation mechanism included in both mechanisms is that proposed by Thaxton \textit{et al.} [18].

3. Molecular modelling

\textit{Ab initio} quantum chemical calculations provide an avenue for corroborating existing data and providing information otherwise unavailable experimentally. The Gaussian 03 [19] suite of programs was utilised to this end. The species considered in the gas phase during decomposition of the nitrogen-rich compounds were optimised using the density functional theory (DFT) method with the widely popular Becke, three-parameter, Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional. A split valence basis set with additional polarised functions, 6-31G(d,p), was used to account for the significant charge delocalisation in the cations and the anion. The geometries were optimised to ensure that local energy minima were achieved. Frequency calculations on the optimised geometries provided information on rovibrational bands in the mid-infrared region of possible generated species, enabling some comparison with experimental FTIR data, and elimination of certain products from an extensive list of possibilities. Furthermore, various gas-phase thermodynamic properties of species [20], which are essential to complete the propellant combustion model, were computed, including heat of formation, enthalpy, entropy, specific heat and free energy. Transport properties of all the species such as thermal conductivities, binary viscosity diffusion coefficients and thermal diffusion coefficients required for the model were calculated using the ChemKin transport properties package [21] in conjunction with Gaussian 03 [19]. Transition-state optimisations were carried out to calculate activation energies and pre-exponential factors for selected reaction pathways (reactions 6 and 8 in Table 1), and intrinsic reaction coordinate calculations were performed to ascertain that the transition state indeed connects the reactants and the products.

4. Theoretical formulation

Physically, the system is a one-dimensional RDX-TAGzT composite pseudo-propellant burning in a stagnant environment. The processes involved are shown in Figure 2. In the solid-phase region, RDX and TAGzT are physically pressed together and heated by conduction. As the temperature is low, chemical reactions are assumed to be absent in this region. Only conduction occurs, and it raises the temperature to the melting point of RDX. The location where melting occurs is the interface between the solid phase and the foam layer. The temperature at this location is 478.5 K. The foam layer is a multiphase region, treated as a liquid along with gas bubbles. Thermal decomposition of RDX and TAGzT as well as subsequent reactions occur in this region. Evaporation of RDX takes place at the interface between the liquid and gas bubbles. In addition, decomposition products also collect in the bubbles from the liquid phase [3, 8]. TAGzT is assumed to remain in the liquid phase in the foam layer. Oxidation reactions and heat conduction cause an increase in the foam-layer temperature.
Figure 2. General description of reaction zones in foam layer and gas-phase region, with an approximate temperature profile of pure RDX at a low pressure where the dark zone is present.

The primary reaction zone is located close to the surface and largely responsible for the conductive heat feedback to the foam layer. Depending on the magnitude of the applied system pressure, a dark zone may be present. In the dark zone, relatively slow reactions occur, usually involving NO, N₂O and HCN. At some distance from the surface, chemical and thermal equilibrium are established, producing equilibrium products and the adiabatic flame temperature.

4.1. Governing equations

In order to solve for the combustion wave structure, it is usually necessary to solve the conservation equations in the solid, foam layer and gas-phase regions. It is assumed that no chemical reactions take place in the solid-phase region. Hence for the steady-state case, the solid-phase energy equation has a closed form solution as it is bounded by fixed temperatures: from \( T = T_{\text{ini}} \) at \( x = -\infty \) to \( T = T_{\text{melt}} \) at \( x = -L_f \). Thus, it is not considered here.

The gas-phase region utilises the complete assumptions and computational framework of the ChemKin package [22, 23]. Thus these expressions are not repeated here. Instead, we focus our attention on the expressions for the conservation equations in the foam layer. A multitude of processes occur in the foam layer such as thermal decomposition, bubble formation, chemical reactions in liquid and gas, as well as transfer of mass and energy at the liquid–bubble interfaces. As there are numerous gas bubbles distributed randomly in this region, the concept of fractional area void fraction is used to formulate the foam layer equations. We introduce some new features compared to previous works. First, we assume that the small bubbles are entrained by the liquid and have the same velocity, that
is, \( u_l \approx u_g \equiv u_f \). This is in contrast to earlier works \([3, 8]\) which involved the assumption that \( \rho_l u_l = \rho_g u_g \) and thus bubble velocities were very large due to the density difference. Second, we consider the same species and reactions in the gas bubbles as considered in the gas-phase region. Thus a broader range of radicals is included. The one-dimensional mass, liquid and gas-bubble species as well as the energy conservation equations are given by

\[
\frac{d}{dx}[(1 - \phi) \rho_l u_f + \phi \rho_g u_f] = 0
\]

(3)

\[
\frac{du_f}{dx} = \sum_{j=1}^{N_l} \frac{\dot{\omega}_{l,j}}{\rho_{l,j}} + \frac{\dot{\omega}_{g,j}}{\rho_g} \frac{N_l}{N_g} \frac{\dot{\omega}_{g,j}}{W_j} + \frac{\phi(1 - \phi)}{T_f} u_f \frac{dT_f}{dx}
\]

(4)

\[
u_f \frac{d\phi}{dx} = -\phi \sum_{j=1}^{N_l} \frac{\dot{\omega}_{l,j}}{\rho_{l,j}} + (1 - \phi) \frac{\dot{\omega}_{g,j}}{W_j} + \frac{\phi(1 - \phi)}{T_f} u_f \frac{dT_f}{dx}
\]

(5)

\[
\frac{dY_{g,i}}{dx} = \dot{\omega}_{g,i} - Y_{g,i} \sum_{j=1}^{N_g} \frac{\dot{\omega}_{g,j}}{W_j}, \quad i = 1, \ldots, N_g
\]

(6)

\[
(1 - \phi) \rho_l u_f \frac{dY_{l,i}}{dx} = \dot{\omega}_{l,i} - Y_{l,i} \sum_{j=1}^{N_l} \frac{\dot{\omega}_{l,j}}{W_j}, \quad i = 1, \ldots, N_l
\]

(7)

\[
[(1 - \phi) \rho_l u_f c_{pl} + \phi \rho_g u_f c_{pg}] \frac{dT}{dx} = \frac{d}{dx} \left[ ((1 - \phi) \lambda_l + \phi \lambda_g) \frac{dT}{dx} \right] - \sum_{k=1}^{N_l} h_{l,k} \dot{\omega}_{l,k} - \sum_{k=1}^{N_g} h_{g,k} \dot{\omega}_{g,k}
\]

(8)

where

\[
\dot{\omega}_{l,i} = \omega_{l,i} - \dot{\omega}_{l \rightarrow g,i}, \quad \dot{\omega}_{g,i} = \dot{\omega}_{g,i} + \dot{\omega}_{l \rightarrow g,i}, \quad i = RDX
\]

\[
\dot{\omega}_{l,i} = \dot{\omega}_{l,i}, \quad \dot{\omega}_{g,i} = 0, \quad i = TAGzT
\]

(9)

\[
\dot{\omega}_{l,i} = 0, \quad \dot{\omega}_{g,i} = \dot{\omega}_{l,i} + \dot{\omega}_{g,i}, \quad i = \text{other species}
\]

The chemical production terms, \( \dot{\omega}_{l,i} \) and \( \dot{\omega}_{g,i} \), for the liquid and gaseous species, respectively, are calculated from the chemical rate equations in accordance with the respective reaction schemes. The evaporation of RDX within the foam layer is described by \( \dot{\omega}_{l \rightarrow g,i} \) with \( i = RDX \) \([3, 8]\). Since hydrazine is an important decomposition product of TAGzT, it potentially will react with liquid-phase species. Hence it is necessary to allow secondary reactions both within the liquid and gas bubbles. Like in previous models \([3, 8]\) products from liquid-phase reactions are assumed to vaporise and collect inside the bubbles instantaneously. The mixture enthalpies \( h_l \) and \( h_g \) for liquid and gases, respectively, were calculated as weighted averages of the mass fractions. Specific heats \( c_{pl} \) and \( c_{pg} \) were also calculated in the same manner. Additionally, the liquid density, gas density and average
molecular weight were computed from

\[ \frac{1}{\rho_l} = \sum_{i=1}^{N_l} \frac{Y_{l,i}}{\rho_{l,i}} \quad (10) \]

\[ p \bar{W}_g = \rho_g R_u T_f \quad (11) \]

\[ \frac{1}{\bar{W}_g} = \sum_{i=1}^{N_g} \frac{Y_{g,i}}{W_i} \quad (12) \]

### 4.2. Boundary conditions

Transport of species, mass and energy must be balanced at the two interfaces. These matching boundary conditions are instrumental in determining the propellant surface conditions and burn rate. At the solid-foam interface, the temperature is equal to the melting point of the solid propellant. This and other boundary conditions are given by

\[ T|_{x=-L_f} = T_{melt} \quad (13) \]

\[ \lambda_f \left( \frac{dT}{dx} \right)|_{L_f} = \dot{m}''[h_f(T_{melt}) - h(T_{ini})] \quad (14) \]

\[ ((1 - \phi)\rho_l u_f Y_{RDX})|_{x=0} = \dot{m}''_{evap} \quad (18) \]

In addition to the governing equations and boundary conditions, the following equation is used in conjunction with Equation (18) to relate the surface temperature to the burn rate

\[ \left( \dot{m}''_{RDX,evap} \right)|_{x=0} = A_{evap} \exp \left( -\frac{E_{As}}{R_u T_s} \right) \quad (19) \]

This formulation is in line with that used by Miller and Anderson [24], but is also quite similar to the non-equilibrium expression used by Liau et al. [3, 8].

### 5. Numerical method

The above mathematical description is unique in that the mass burning rate represents an eigenvalue. In such a problem, there is an insufficient number of equations to solve for the number of unknowns. Here we introduced Equation (19) as the additional expression
needed. There are other potential conditions that can be used, such as a boiling temperature or a prescribed temperature at a specified node. Since it has proven quite effective to utilise a non-equilibrium evaporation expression [3, 8] we choose to employ a similar approach here. Conservation equations for the foam layer, other than the energy equation, were solved using the Livermore Solver for Ordinary Differential Equations (LSODE) routine within ODEPACK, which employs Gear’s method for integrating stiff ordinary differential equations [25]. The obtained species mass fractions, velocity and void fraction were used to solve the energy equation and the equation for foam layer thickness by the globally convergent multidimensional Newton-Raphson method along with the heat feedback from the gas-phase region. The equation for foam-layer thickness was obtained by integrating the energy equation from \( x = -L_f \) to \( x = 0 \). The surface temperature and species mass fractions at the foam-gas interface thus obtained were used to calculate a new value of velocity at \( x = -L_f \). The whole process was repeated until the change in the surface temperature, velocity and species mass fractions were within the tolerance values. These values were then given as input to the ChemKin one-dimensional premix flame code [23], which solved the gas-phase conservation equations. On solving for temperature and species distribution in the gas phase, a conductive heat feedback was obtained which was then used to solve for new values \( u_f, \phi, T, Y_l, Y_g \) and \( L_f \) again in the foam layer in the manner described above. This back and forth iteration between the foam layer and gas phase was continued until convergence was obtained. In addition, the results for burn rate have been checked for grid independence as shown in Table 3. Values of the adaptive grid control parameters GRAD and CURV in the ChemKin premix code were chosen such that results are in agreement to four significant digits irrespective of the number of nodes. The LSODE routine used RTOL = 10^{-10} and ATOL = 10^{-15}.

6. Results and discussion

Results of simulation of RDX-TAGzT pseudo-propellant combustion within the framework of the model formulated above corroborated experimental observations. As already mentioned, for these simulations, it was assumed that products of liquid-phase reactions were collected immediately in the bubbles, producing a high void fraction at the surface. The RDX may only enter the gas bubbles through evaporation; no evaporation is considered for the TAGzT, however. The initial void fraction is assumed to be \( \phi|_{x=-L_f} = 0.0001 \), since RDX and TAGzT crystals do contain small imperfections and removal of all voids is very

<table>
<thead>
<tr>
<th>P (atm)</th>
<th>GRAD = 0.3</th>
<th>GRAD = 0.15</th>
<th>GRAD = 0.075</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CURV = 0.5</td>
<td>CURV = 0.25</td>
<td>CURV = 0.125</td>
</tr>
<tr>
<td></td>
<td>No. of grid points</td>
<td>Burn rate (cm/s)</td>
<td>No. of grid points</td>
</tr>
<tr>
<td>Pure RDX</td>
<td>1</td>
<td>37</td>
<td>0.0356</td>
</tr>
<tr>
<td></td>
<td>10</td>
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</tr>
<tr>
<td></td>
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<tr>
<td>RDX+TAGzT</td>
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<td>0.0443</td>
</tr>
<tr>
<td>(8:2)</td>
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<td></td>
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difficult during manufacturing of a propellant containing crystals. Due to these assumptions only the first three reactions given in Table 1 are active in the liquid phase and only RDX and TAGzT are present in the liquid as shown in Figure 4.

Figure 3 shows the variation of burn rate for pure RDX with pressure. Burn rate increases with increasing pressure because of the increased concentration of reactants near
Figure 5. Variation of major gaseous species mole fraction and temperature in the foam layer for pure RDX at a pressure of 10 atm considering mechanism 2.

the surface, which produce an increased heat feedback to the foam layer. As can be seen, calculated burn rates are in good agreement with measurements from several experimental works and other models [24, 26–28]. The present model predicts relatively higher burn rates with mechanism 2 as compared to mechanism 1 (see Table 2) at low pressures. This can be attributed to the fact that the RDX decomposition in mechanism 2 has more pathways than in mechanism 1.

Figure 4 shows the variation of mole fractions of RDX and TAGzT for a propellant composition of 9:1 mass ratio at 10 atm. As a result of the immediate transfer of liquid-phase products into the bubbles, it can be seen that the liquid-phase mole fractions of RDX and TAGzT remain close to 94% and 6%, respectively. However, TAGzT decomposes slightly faster than RDX, producing mole fractions of RDX and TAGzT at the propellant surface of 0.937 and 0.063, respectively. The void fraction reaches a value close to 90% near the surface, which means that the thermal conductivity is dominated by gas-phase products near the surface, whereas the thermal conductivity is dominated by the liquid RDX near the melt front.

Figure 5 shows mole fraction profiles of species in gas bubbles in the foam layer for pure RDX at 10 atm. As a result of the liquid-phase reactions, the mole fraction of RDX decreases quickly, but increases again as non-equilibrium evaporation of RDX becomes important. Other than RDX, the prominent species in the bubbles are seen to be CH₂O and N₂O. Foam-layer composition at 10 atm for RDX-TAGzT pseudo-propellant is shown in Figure 6 on the same axis scale as that of Figure 5 for comparison. At the solid-foam interface, it was assumed that the bubbles initially contained pure RDX. In this case TAG, AzT, and N₂ are the major species in addition to CH₂O and N₂O. The melt layer is thinner and the propellant surface temperature is higher than in the case of pure RDX. The gradient of the temperature profile is also larger, which is expected as the burn rate is higher. As we proceed from the melt front to the propellant surface TAG and AzT mole fractions first
increase and then decrease as these species decompose to give other products. Exothermic decomposition of AzT produces a higher temperature which causes a faster evaporation of the liquid. As the liquid is converted to gas more rapidly, the foam layer for the pseudo-propellant is thinner than that for RDX monopropellant. It can be noted that in both Figure 5 and Figure 6, the CH$_2$O and N$_2$O profiles overlap. Also the ratio of the mole fraction of TAG to that of AzT remains close to two throughout the foam layer. The concentration of NO$_2$ is nearly zero as it reacts with hydrazine.

In Figure 7, the velocity and temperature in the foam layer are shown for propellant containing 10% TAGzT by mass at 10 atm. The temperature rises from the melting point of RDX to 667K at the propellant surface. The velocity increases significantly from about 0.36 cm/s to about 2 cm/s. This increase in velocity occurs in a very small region near the propellant surface, where the void fraction increases rapidly from evaporation and chemical reactions. The temperature rise is caused primarily by the conductive heat feedback from the gas-phase region, partly by the exothermic decomposition of AzT and partly by reactions among RDX and TAGzT decomposition products in gas bubbles. The initial proton transfer in the decomposition of TAGzT and the initial stages of the TAG decomposition reaction are endothermic, however.

Figures 8 and 9 display the variation in mole fraction of important species with pressure at the foam-layer surface for various pseudo-propellant compositions. It can be seen that RDX and TAGzT are the only major components of the substrate before it enters the gas phase. This is because even though a large void fraction exits on the surface most of the mass is contained in the liquid. The mole fraction of the product species emerging from the decomposition of RDX and TAGzT on the surface increases with increasing pressure. The profiles of CH$_2$O, N$_2$O and HCN for the RDX-TAGzT mixture deviate considerably from those of the same species for pure RDX.

Figure 10 gives the species mole fraction variations in the gas phase for the RDX-TAGzT mixture (10% TAGzT). It can be seen that HCN, NO and H$_2$O are the major
Figure 7. Variation of fluid velocity and temperature in the foam layer for RDX-TAGzT pseudo-propellant (mass ratio 9:1) at a pressure of 10 atm considering mechanism 2.

Figure 8. Variation of species mole fraction on the foam-layer surface with pressure.
intermediate species in the primary reaction zone near the propellant surface. Figure 11 shows a magnified view of the gas-phase species mole fractions very close to the surface. RDX and TAGzT decompose very quickly. TAGzT decomposition products, in particular the hydrazine, reacts with NO₂ to produce a sharp temperature rise in the gas-phase region.

Figure 9. Variation of species mole fraction on the foam-layer surface with pressure.

Figure 10. Species mole fraction profiles in the gas phase for RDX-TAGzT pseudo-propellant (mass ratio 9:1) at a pressure of 10 atm considering mechanism 2.
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Figure 11. Species mole fraction profiles in the gas phase near the surface for RDX-TAGzT pseudo-propellant (mass ratio 9:1) at a pressure of 10 atm considering mechanism 2.

Since the temperature rise is very fast, there is no evidence of a dark zone. In the luminous flame zone, oxidation of HCN and NO to the final products like CO and N₂ is responsible for raising the temperature to its final value. In all these results, only 10% of TAGzT is present in the propellant, and hence its products are not very prominent. However, the combustion process is affected by its presence as can be seen from the surface temperature rise and increase in burn rate.

Comparison of the gas-phase temperature profiles for pure RDX and RDX-TAGzT mixture is useful to understand the effect of the addition of TAGzT to RDX. As seen from Figure 12 at 10 atm, the surface temperature in the case of mixture is higher than that in the case of pure RDX. As already mentioned, this occurs due to the reactions taking place in the foam layer and near the propellant surface, which are highly exothermic. However, final flame temperature for the mixture is lower than compared to pure RDX as can be seen in Figure 13. This is because the nitrogen content of TAGzT is high which results in formation of gaseous combustion products in including molecular nitrogen having a lower temperature in the final stage.

Burn rate of a solid propellant is a very important performance parameter. In Figure 14, the effect of the initial mass fraction of TAGzT on the burn rate of the propellant with mechanism 1 is predicted. At low pressure (p < 30 atm), the burn rate increases considerably by adding only 10% TAGzT to the RDX. As mentioned previously, the burn-rate augmentation is caused in part by exothermic decomposition of the AzT in the liquid phase, and by fast reactions in the gas-phase region near the surface between hydrazine and NO₂. However, at high pressures, we observe that the burn rate curves for RDX-TAGzT pseudo-propellant flatten, and the burn rates are less than that of pure RDX at the corresponding pressures. In order to investigate this phenomenon, an extensive sensitivity analysis was performed. All the reactions that are considered due to the presence of TAGzT were analysed. A sensitivity coefficient $S_i$ was defined as given in Equation (20). The $A$ factors of the reactions were increased by 0.1% one at a time, as shown in Equation (21) and the corresponding burn rates
and sensitivity coefficients were calculated. The reactions whose sensitivity coefficients satisfied Equation (22) were considered as sensitive reactions.

\[ S_i = \frac{A_i}{r_b} \frac{\partial r_b}{\partial A_i} \approx \frac{A_i}{r_b} \frac{\Delta r_b}{\Delta A_i} \]  

(20)

Figure 12. Temperature profiles for pure RDX and RDX-TAGzT pseudo-propellant for the gas phase in the near-surface zone at a pressure of 10 atm considering mechanism 2.

Figure 13. Temperature profiles for pure RDX and RDX-TAGzT pseudo-propellant for the gas phase at a pressure of 10 atm considering mechanism 2.
Figure 14. Variation of burn rate with pressure for RDX-TAGzT pseudo-propellant of various compositions and pure RDX considering mechanism 1.

\[
\frac{\Delta A_i}{A_i} = 0.001 \ (0.1\%)
\]

\[
|S_i| \geq 0.9 |S_{i,max}|
\]

Sensitivity coefficients calculated in this way are displayed in Figure 15. Some important gas-phase reactions are shown. Although any decisive statement about the burn-rate variation shown in Figure 14 cannot be made from these results, it can be inferred that reactions involving oxidation of hydrazine by nitrogen dioxide and nitrous oxide play an important role in the combustion process. To explain the decrease in burn-rate enhancement as observed in Figure 14, sensitivity data shown in Figure 16 are useful. Figure 16 illustrates the variation of sensitivity coefficients of the three global decomposition reactions of TAGzT with pressure. It is observed that these three reactions are responsible for enhancing the burn rate at low pressure and reducing the burn rate at high pressure.

It is important to note that the three global reactions involving TAGzT are written as unimolecular in mechanism 1. In mechanism 2, they were changed to bimolecular reactions via a third body M as displayed in Table 4. This resulted in a density effect which accelerated the species generation and decomposition rates. Mechanism 2 also contains the RDX decomposition mechanism given by Chakraborty et al. [7] which contains the most recent and the most detailed reaction scheme. The resulting burn rates are plotted in Figure 17. The burn rate curves for the RDX-TAGzT mixture do not cross over the curve for pure RDX before 100 atm and also a good agreement is obtained with the measurements of Mason et al. [29]. The three reactions shown in Table 4 have to be at their low pressure limits for the inclusion of the third body term M to be justified. Whether this is true is not known for sure and more work on TAGzT decomposition chemistry is needed for its confirmation. The approach adopted here is phenomenological and it works probably because the fast decomposition of TAGzT which actually occurs is captured by it.
Figure 15. Sensitivity coefficients for important gas-phase reactions considering mechanism 1.

An important performance parameter for a solid propellant is the sensitivity of its burn rate to initial temperature. This sensitivity is given by

\[
\sigma_{T_1} = \frac{1}{r_b} \frac{\partial r_b}{\partial T_{ini}} \approx \frac{1}{r_b} \frac{\Delta r_b}{\Delta T_{ini}}
\]  

(23)

Figure 16. Sensitivity coefficients for global decomposition reactions of TAGzT considering mechanism 1.
Figure 17. Variation of burn rate with pressure for RDX-TAGzT pseudo-propellant of various compositions and pure RDX considering mechanism 2.

Figure 18 shows the variation of burn rate temperature sensitivities for pure RDX calculated from the present model as well as from previous models and measurements [4, 8, 26, 27]. There are differences in the experimental data from the various sources, and models are unable to reproduce the measurements accurately although they show the same general trend. It can be seen that the burn rate is more sensitive to the initial propellant temperature at low pressure than at high pressure. Beckstead et al. [30] have stated that typically the

Table 4. Global decomposition reactions of TAGzT in mechanisms 1 and 2.

<table>
<thead>
<tr>
<th>Reactions in Mechanism 1</th>
<th>Reactions in Mechanism 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAGzT → 2TAG + AzT</td>
<td>TAGzT + M → 2TAG + AzT + M</td>
</tr>
<tr>
<td>TAG → N₂H₄ + N₂H₂ + NH₂NC</td>
<td>TAG + M → N₂H₄ + N₂H₂ + NH₂NC + M</td>
</tr>
<tr>
<td>AzT → 2HCN + 4N₂</td>
<td>AzT + M → 2HCN + 4N₂ + M</td>
</tr>
</tbody>
</table>

Table 5. Burn rate results indicating significance of foam-layer reactions.

<table>
<thead>
<tr>
<th>P (atm)</th>
<th>Pure RDX</th>
<th>TAGzT reactions in foam layer</th>
<th>TAGzT reactions in foam layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>absent</td>
<td>present</td>
</tr>
<tr>
<td>RDX+TAGzT (9:1)</td>
<td>1</td>
<td>0.0321</td>
<td>0.0427</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.2353</td>
<td>0.3153</td>
</tr>
<tr>
<td></td>
<td>100</td>
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</tr>
<tr>
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<td>0.0455</td>
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<td>0.3480</td>
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<td>100</td>
<td>1.8507</td>
<td>1.9899</td>
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</table>
condensed-phase heat released affects burn rate sensitivity significantly. At an elevated pressure, the enhanced heat transfer from the gas phase to the propellant surface due to increased heat release and reduced flame standoff distance overrides the influence of the condensed-phase heat release and consequently the temperature sensitivity decreases. To ascertain this, simulations were carried out by preventing TAGzT decomposition in the foam layer. This enabled us to understand the relative significance of those reactions that
take place in the foam layer and involve TAGzT. Thus, TAGzT decomposition in the gas-phase region above the surface of the propellant remains the same. Comparison of the burn rates so obtained with the ones when the full mechanism is active is given in Table 5. It can be seen that the burn rate is slightly underpredicted when TAGzT is not allowed to undergo decomposition in the foam layer. The relative magnitude of this underprediction decreases with increase in pressure. This shows that the foam-layer reactions and thus the condensed-phase heat release play a greater role in enhancing the burn rate at low pressures. To further ensure the validity of this inference, calculation of burn rate temperature sensitivities was carried out for RDX-TAGzT mixtures. Both the cases (i) decomposition and (ii) no decomposition of TAGzT in the foam layer were again considered. The results thus obtained are shown in Figures 19 and 20. They corroborate that the condensed-phase heat release plays a greater role in the combustion of RDX-TAGzT solid propellant at low pressures. The difference between the burn rate sensitivities in cases (i) and (ii) diminishes as pressure increases because the decomposition of TAGzT and subsequent reactions in the foam layer becomes less important in determining the burn rate. Also from Figures 19 and 20, with the current set of assumptions, burn rate temperature sensitivity of the RDX-TAGzT mixture is observed to be slightly higher than that of pure RDX.

7. Conclusions

A comprehensive numerical model was formulated and solved that describes steady-state combustion of a solid propellant containing RDX and TAGzT. The model considers a foam layer containing a liquid with 18 species and eight reactions. Gas bubbles and the gas region above the foam layer were analysed using two recent RDX mechanisms. The species mass fractions, void fraction, velocity, temperature and foam-layer thickness were computed in the foam layer, whereas species mass fractions and temperature were computed for the gas-phase region. The input on the thermal decomposition behaviour of TAGzT was derived from separate experiments involving confined rapid thermolysis coupled with FTIR
spectroscopy and time-of-flight mass spectrometry. Within the current modelling framework and assumptions, the following major conclusions were obtained.

1. TAGzT enhances the burn rate over the pressure range considered.
2. The model predicts burn rates that are in quite close agreement with measurements.
3. The burn-rate enhancement is caused by exothermic decomposition of the azotetrazolate in the liquid phase, and by fast reactions between triaminoguanidine decomposition products and oxidiser products from RDX decomposition in the gas bubbles and in the gas-phase region close to the surface.
4. Burn rate is quite sensitive to the global decomposition reactions involving TAGzT.
5. At low pressures, the burn rate of the RDX-TAGzT pseudo-propellant is slightly more sensitive to initial temperature than that of pure RDX.
6. By using the assumptions that liquid decomposition products except RDX and TAGzT immediately collect into the bubbles and \( u_l = u_g = u_f \) in the foam layer, the void fraction at the surface is generally quite large, reaching values around 0.9 at 1 atm.

Acknowledgements
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References


