A COMBUSTION MODEL FOR COMPOSITE SOLID PROPELLANTS BASED ON AN/HTPB-IPDI

P. Carvalheiro, J. Campos
Lab. of Energetics and Detonics, Mech. Eng. Dept., Faculty of Sciences and Technology
Universidade de Coimbra, Pólo II, Pinhal de Marrocos, P-3030 Coimbra, Portugal

and

G. M. H. J. L. Gadiot
TNO Prins Mauritius Laboratorium, Lange Kleiweg 137, Postbus 45, 2280 AA Rijswijk, The Netherlands

ABSTRACT

The development of a combustion model for composite solid propellants, based on ammonium nitrate (AN) and hydroxyl terminated polybutadiene (HTPB) cured with isophorone diisocyanate (IPDI) is presented and correlated with experimental results. The results of the model are correlated to the experimental measurements of burning rate of propellants PSAN/HTPB-IPDI (75.00/25.00 wt.%) and PSAN/HTPB-IPDI (80.00/20.00 wt.%) in the range 2-10 MPa, at initial temperature of 288 K and a good agreement is obtained.

1. INTRODUCTION

The development of a combustion model for composite solid propellants, based on AN and HTPB cured with IPDI is presented and correlated with experimental results. This model applies concepts of previous combustion models for composite solid propellants: the multiple flames (MF) concept introduced in the BDP model, (Beckstead et al., 1970); the separate surface temperature (SST) concept introduced by Andersen et al. (1959), and both applied by Beckstead (1989), in his SST combustion model. The proposed new concept of the present work takes in account the phenomena associated to radiative heat transfer from the propellant flames and combustion products to the surface of the two main propellant ingredients, as a function of the geometry and temperature of the flames and of propellant surface.

The results of the model are correlated to the experimental measurements of burning rate of propellants PSAN/HTPB-IPDI (75.00/25.00 wt.%) and PSAN/HTPB-IPDI (80.00/20.00 wt.%) in the range 2-10 MPa, at initial temperature of 288 K. The used phase stabilised ammonium nitrate (PSAN) includes 1.0 % NiO as phase stabilising agent and its particle size distribution is $d_{10} = 50 \mu m$, $d_{50} = 140 \mu m$ and $d_{90} = 275 \mu m$. The pre-exponential factor of Arrhenius approach, used for calculations of the ammonium nitrate monopropellant flame stand-off distance, was determined from measurements of the temperature profile of a propellant PSAN/HTPB-IPDI (75.00/25.00 wt.%). These measurements allowed to measure surface temperature of ammonium nitrate and AN flame stand-off distance. The pre-exponential factor was calculated from a value for the activation energy (Beckstead, 1989), AN flame stand-off distance and pressure at which measurements were made, assuming a second order reaction. The temperature wave was measured using microthermocouples type K. 12.7 \mu m in diameter, at 7.0 MPa. The heat of pyrolysis of the fuel binder system HTPB-IPDI was calculated based in a correlation found by the authors for the heat of vaporization of hydrocarbons, at the temperature of vaporization, for hydrocarbons with H/C ratio in the range 1.25-1.75 and molecular weight in the range 54-134 g/mol.

The geometry of the diffusion flames was calculated using the classical Burke-Schumann (1928) analysis. The diffusion coefficients for the gases were calculated using an expression derived from the kinetic theory of gases for the binary diffusion coefficient between two non polar gases, and assuming highly probable product compositions for the gases of decomposition of ammonium nitrate and of pyrolysis of the fuel binder HTPB-IPDI.
The temperature wave measurements of the burning propellant at 7.0 MPa, the work of Spadaccini and TeVelde (1982) and the results of the model indicate that even if the diffusion phenomena of the primary diffusion flame start in the surface of the propellant the primary diffusion flame is not attached to the surface of the propellant and ignition occurs away from the surface when the temperature of gases reach a value of about 800 K.

The contribution of radiative heat transfer to the burning rate is small and highly dependent on the concentration and size of the solid particles in the combustion products.

2. HEAT OF PYROLYSIS OF THE FUEL BINDER SURFACE

Heat of pyrolysis of inert fuel binders of the type of HTPB are in the range 0 to -200 cal/g (0 to -836.8 kJ/kg), (Beckstead et al., 1970). The value of -433 kJ/kg, (Beck, 1987) was from an experimental measurement specifically for HTPB. Enthalpy vaporisation at 298.15 K, $\Delta_{vap}H(298.15 \text{ K})$, of a very broad range of hydrocarbons with H/C in the range 1.25 < H/C < 1.75 is in a relatively narrow range of 382 kJ/kg < $\Delta_{vap}H(298.15 \text{ K})$ < 408 kJ/kg, vd. Table 1. The value of $\Delta_{vap}H$ at the temperature of surface of the fuel binder can be obtained from the correlation between the enthalpy of vaporisation, at the boiling temperature, $\Delta_{vap}H(T_b)$, and the boiling temperature of these hydrocarbons. The hydrocarbons presented in Table 1, were chosen from a large list, (Lide, 1991), having their H/C ratio as close to 1.5 as possible, because H/C = 1.5 is the ratio for polybutadiene. These hydrocarbons show an excellent correlation between $\Delta_{vap}H(T_b)$ and $T_b$, presented by Eq. (1).

$$\Delta H_{vap}(T_b)/(\text{kJ/kg}) = 601.4 \cdot 0.6709 \cdot (T_b/\text{K})$$  \hspace{1cm} (1)

| Molecular Formula | Name         | Molecular weight (g/mol) | $T_b/\text{K}$ | $\Delta_{vap}H(T_b)/(\text{kJ/kg})$ | $\Delta_{vap}H(298.15 \text{ K})/(\text{kJ/kg})$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>1,3-Butadiene</td>
<td>54.092</td>
<td>268.8</td>
<td>415.4</td>
<td>385.6</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_8$</td>
<td>Spiropentane</td>
<td>68.119</td>
<td>312.2</td>
<td>392.8</td>
<td>403.6</td>
</tr>
<tr>
<td>$\text{C}<em>4\text{H}</em>{10}$</td>
<td>Cyclohexene</td>
<td>82.145</td>
<td>356.3</td>
<td>370.8</td>
<td>407.4</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{12}$</td>
<td>Ethylene</td>
<td>106.17</td>
<td>409.3</td>
<td>335.04</td>
<td>397.9</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{14}$</td>
<td>Decane</td>
<td>110.20</td>
<td>399.5</td>
<td>325.14</td>
<td>383.9</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{22}$</td>
<td>Butylbenzene</td>
<td>134.22</td>
<td>456.5</td>
<td>289.6</td>
<td>382.7</td>
</tr>
</tbody>
</table>

Consequently the value of the heat of pyrolysis of HTPB/IPDI fuel binder at the temperature of surface of the fuel binder during combustion of the propellant, $Q_{f,j}$, is given by Eq. (2).

$$Q_{f,j} = -\Delta H_{f}(T_s)/(\text{kJ/kg}) = -601.4 + 0.6709 \cdot (T_s/\text{K})$$  \hspace{1cm} (2)

3. AMMONIUM NITRATE MONOPROPELLANT FLAME DISTANCE

The total distance of the monopropellant flame to the surface of ammonium nitrate, $x_{FAN}$, is assumed only as the kinetic reacting distance and it is given by Eq. (3). It is assumed $\delta = 2.0$ corresponding to a second order reaction.

$$x_{FAN} = \frac{m_{AN}}{p^\delta A_{FAN} \exp \left( - \frac{E_{FAN}}{RT_{FAN}} \right)}$$  \hspace{1cm} (3)

For the monopropellant AN flame the activation energy was considered to be $E_{FAN} = 104.6$ kJ/mol (25 kcal/mol), (Beckstead, 1989). The pre-exponential factor, $A_{FAN}$, was calculated based in the flame stand-off distance measured experimentally for the monopropellant flame at known combustion pressure, burning rate, initial temperature of propellant, oxidizer particle size, oxidizer solid loading and with no burning rate modifier included in the composition, vd. Fig. 1.
4. MOLECULAR INTERDIFFUSION COEFFICIENTS

The molecular interdiffusion coefficients for binary mixtures of non-polar molecular species $A$ and $B$ are calculated according to the ordinary diffusion theory for gases at low density using Eq. 4 (Kuo, 1986) expecting a maximum error of 5%.

$$D_{AB} = \frac{2}{3} \left( \frac{K^3}{\pi^3} \right)^{1/2} \left( \frac{1}{2m_A} + \frac{1}{2m_B} \right)^{1/2} \frac{T^{3/2}}{p} \left( \frac{d_A + d_B}{2} \right)^2$$  \hspace{1cm} (4)

$$m_i = \frac{M_i}{N_A} \hspace{1cm} (5)$$

$$d_i = \frac{b}{\sqrt{N_A}} \hspace{1cm} (6)$$

$m_{O_2} = 5.3135 \times 10^{-26}$ kg, using Eq. (5), $d_{O_2} = 3.50 \times 10^{-10}$ m, (Mahan, 1965). $m_{N_2O} = 7.3085 \times 10^{-26}$ kg, using Eq. (5). $d_{N_2O} = 4.188 \times 10^{-10}$ m, calculated from the value of the van der Waals co-volume of NO$_2$, $b = 4.424 \times 10^{-5}$ m$^3$/mol, (Lide, 1991), using Eq. (6). $m_{C_4H_6} = 8.9823 \times 10^{-26}$ kg, using Eq. (7). $d_{C_4H_6} = 5.883 \times 10^{-10}$ m, calculated from the value of the van der Waals co-volume of n-butane, C$_4$H$_{10}$, $b = 1.226 \times 10^{-4}$ m$^3$/mol, (Lide, 1991), assumed to be equal to that of butadiene, C$_4$H$_6$, using Eq. (6). Equations (4) to (6) allow the calculation of the following molecular interdiffusion coefficients taking into account the composition of the reactants of each flame.

$$D_{N_2O C_4H_6} = 8.5328 \times 10^{-5} \frac{T^{3/2}}{p} \hspace{1cm} (7)$$

14.6.3
\[ D_{O_2C_4H_6} = 1.08000E-04 \frac{T^{3/2}}{P} \]  

Fig. 2. Results of the combustion model for AN/HTPB-IPDI formulations with unimodal 140 µm AN particle size distribution at 288 K, and of experimental measurements for PSAN/HTPB-IPDI formulations at 288 K.

5. CONCLUSIONS

The development of a combustion model for composite solid propellants AN/HTPB-IPDI is presented and correlated to experimental results. This model takes into account the multiple flames and separate surface temperature concepts. Used constants are determined both from bibliographic review and from experimental results. Obtained theoretical results show a good correlation with experimental values and prove the small contribution of radiative heat transfer to the obtained burning rate.

REFERENCES


14.6.4.
Funchal, Madeira
April 1-4, 1996

INSTITUTE
COMBUSTION

SECCTIONS OF THE
BRITISH, SPANISH
AND SWEDISH
PORTUGUESE

JOINT MEETING