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Author(s): J. LOUWERS, G. M. H. J. L. GADIO, M. Q. BREWSTER, AND S. F. SON

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A Model for Steady-State HNF Combustion

J. Louwers* and G.M.H.J.L. Gadiot†, TNO Prins Maurits Laboratory, Rijswijk, The Netherlands,
M.Q. Brewster‡, University of Illinois, Urbana, Illinois 61801, U.S.A.,
S.F. Son§, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 U.S.A.

Abstract

A simple model for the combustion of solid monopropellants is presented. The condensed phase is treated by high activation energy asymptotics. The gas phase is treated by two limit cases: high activation energy, and low activation energy. This results in simplification of the gas phase energy equation, making an (approximate) analytical solution possible. The results of the model are compared with experimental results of Hydrazinium Nitroformate (HNF) combustion.

1 Introduction

The modeling of solid propellants may be a cost effective way to determine properties such as regression rates, and temperature sensitivity before even carrying out any experiment. Composite propellants are contemporary workhorses for many applications, but modeling of these *heterogeneous* propellants is very complex. Some models for composite propellant combustion have been developed, such as the PEM model [1]. However, these models require extensive experimental calibration.

It is therefore currently recognized that more complex models are needed, to be able to compute regression rates, and other properties *a-priori*. As starting point for composite propellant models, many models of solid monopropellant combustion were recently developed [2]. These models are often based on simplified chemical kinetics, coupled with a multi-phase one-dimensional space domain. Due to the complexity of these models, basic principles are often not revealed.

In this article a very simple model for the combustion of a solid monopropellant is presented. Goal of the model is maximal predictive capability and accuracy, coupled with minimal complexity. This is achieved by using essential physics and chemistry only, yielding an understandable model. The condensed phase is treated by a high activation energy approximation method. The gas phase is treated in two ways: high activation energy limit, and low activation energy limit. Both limits allow for an analytical solution of the gas phase energy equation. The exposition here is based on the work of Ward et al. on the combustion modeling of HMX [3]. However, due to the research interests of TNO, Hydrazinium Nitroformate (HNF) is used as study case.

2 Model

The combustion of HNF is modeled as a one dimensional, steady state process. The condensed phase is described by a unimolecular, irreversible, zero-order decomposition reaction

$$\mathrm{A} \rightarrow \mathrm{B}\,, \tag{1}$$

where A represents the solid HNF, and B some kind of unstable intermediate species. B reacts further according to the following bimolecular, irreversible, gas phase reaction

$$\mathrm{B+M} \rightarrow \mathrm{C+M}\,, \tag{2}$$

where M is a third body (B or C), and C the final product species. This reaction is second order overall, and first order with respect to B. B represents the decomposition products (NO_2, HONO), C represents intermediate gas phase products, such as NO, and M represents unstable species such as N, H, OH, etc. For purposes of modeling species conservation, no distinction is made between the M species that appear on the left and right hand sides of Eq.(2) although they would in general be different (i.e., unimolecular

*Graduate Student
†Research Scientist
‡Professor of Mechanical Engineering, Department of Mechanical and Industrial Engineering
§Technical Staff Member, High Explosives Science and Technology Group

dissociation is not being implied). The process is assumed to be a bimolecular exchange reaction, which for species bookkeeping purposes, assumes only two gas species, B (reactant) and C (product).

The molecular weights of the various species are assumed to be equal, and mass diffusion in the gas phase is assumed to be described by Fick's law. The heat capacity and thermal conductivities are assumed to be constant. The gas phase and condensed phase heat capacity are assumed to be equal. To simplify solution of the gas phase equations, the Lewis number is assumed to be unity, $Le = k_g/\rho_g d c_p = 1$ (for symbols see nomenclature at end of article). The gas phase is assumed to obey the ideal gas law. Mass diffusion in the condensed phase is neglected.

2.1 Condensed phase

With the above assumptions, the condensed phase is described by the following energy equation

$$mc_p \frac{dT}{dx} = k_c \frac{d^2T}{dx^2} + Q_c \epsilon_c \,, \tag{3}$$

with boundary conditions

$$T(0) = T_s \,, \quad \text{and} \quad \lim_{x \to -\infty} T(x) = T_0 \,. \tag{4}$$

As a zero-order condensed phase reaction was assumed, the reaction rate is given by

$$\epsilon_c = \rho_c A_c \exp\left(-\frac{E_c}{RT}\right) \,. \tag{5}$$

It was shown by Von Elbe et al. [4], and Louwers et al. [5] that the condensed phase of HNF has a thin reactive zone, i.e. a high activation energy for the decomposition process as given by Eq.(1). This means that activation energy asymptotics (AEA) may be used to find the solution of Eq.(3). The well known solution is [7]

$$m^2 = \frac{A_c R T_s^2 k_c \rho_c \exp(-E_c/RT_s)}{E_c(c_p(T_s - T_0) - Q_c/2))} \,. \tag{6}$$

2.2 Gas phase

Solution of the gas phase equations is less straightforward. Most early models are based on the flame sheet approach, i.e. a very thin reactive zone, where all the gas phase heat release occurs. This process is typical for gas phase kinetics with high activation energy ($E_g \to \infty$). Mathematically the heat release can be described by a Dirac delta function. It was recently argued by Ward et al. that a very low gas phase activation energy ($E_g \to 0$) is more physical [3]. Their perspective is based on the fact that the temperature profile of HMX could be much better replicated by $E_g = 0$, than $E_g = \infty$. Analogs in gas phase combustion provide further evidence that such an approach is not unrealistic. Most of the energy of a hydrogen/oxygen system is released during the initiation/branching process, which has a low activation energy barrier. It is true that the final recombination/termination step has a high energy barrier, but this step is almost energetically neutral. The regression rate of the solid propellant will therefore not be determined by this step, but by the more exothermic initiation/branching step. Both limit cases ($E_g = 0$, and $E_g = \infty$) will be discussed here, to see the overall effect on the model.

The energy equation in the gas phase is

$$mc_p \frac{dT}{dx} = k_g \frac{d^2T}{dx^2} + Q_g \epsilon_g \,, \tag{7}$$

with the reaction rate given by

$$\epsilon_g = \rho_g^2 B_g Y T^2 \exp\left(-\frac{E_g}{RT}\right) \,, \tag{8}$$

where Y is the mass fraction of B. The density of the gas phase, ρ_g is found from the ideal gas law. The interface conditions are found from energy conservation at the surface

$$T_s = T_0 + \frac{Qc}{c_p} + \frac{k_g}{mc_p}\left(\frac{dT}{dx}\right)_{x=0} \,, \tag{9}$$

and

$$T_f = T_0 + \frac{Q_c + Q_g}{c_p} \,. \tag{10}$$

The species equation of the gas phase is

$$m\frac{dY}{dx} = \rho_g d \frac{d^2Y}{dx^2} - \epsilon_g \,. \tag{11}$$

For the species equation, the boundary conditions are

$$Y_s = 1 + \frac{\rho_g d}{m}\left(\frac{dY}{dx}\right)_{x=0} \,, \tag{12}$$

and

$$\lim_{x \to \infty} Y = 0 \,. \tag{13}$$

Because of the assumption $Le = 1$, the gas phase energy equation, and species equation have identical forms, and can be written as two similar nondimensional equations (nondimensional quantities denoted by *) [3]

$$m^* \frac{dT^*}{dx^*} = \frac{d^2T^*}{dx^{*2}} - D_g(T_f^* - T^*) \exp\left(-\frac{E_g^*}{T^*}\right) \,, \tag{14}$$

and

$$m^* \frac{dY}{dx^*} = \frac{d^2Y}{dx^{*2}} - D_g Y \exp\left(-\frac{E_g^*}{T_f^* - YQ_g^*}\right) . \quad (15)$$

The boundary equations transform accordingly. For arbitrary values of E_g^*, Eq.(14) has to be solved iteratively with Eq.(6) to yield T_s^* and m^*. Note that solution of this set requires solution of a 2nd order differential equation. For the two limiting cases, $E_g = 0$, and $E_g \to \infty$, it is possible to obtain an analytical solution.

The first limit is that of a very low activation energy in the gas phase, $E_g \to 0$. For this case an analytical solution of Eq.(14) can be obtained

$$\frac{T^* - T_f^*}{T_s^* - T_f^*} = \exp\left(-\frac{x^*}{x_g^*}\right) . \quad (16)$$

In this equation x_g^* is a dimensionless characteristic gas reaction zone thickness, given by

$$x_g^* = \frac{2}{\sqrt{m^{*2} + 4D_g} - m^*} . \quad (17)$$

In summary: In the limit of a high condensed phase activation energy, coupled with a low activation energy gas phase, the analytical solution of the problem is given by the (nondimensional) form of Eq.(6)

$$m^{*2} = \frac{A_c^* T_s^{2*} \exp(-E_c^*/T_s^*)}{E_c^*(T_s^* - T_0^* - Q_c^*/2)} . \quad (18)$$

This equation is solved simultaneously with Eq.(17) The energy balance is given by the nondimensional result of Eq.(9)

$$T_s^* = T_0^* + Q_c^* + \frac{Q_g^*}{x_g^* m^* + 1} . \quad (19)$$

For the high activation energy gas phase ($E_g \to \infty$), the regression rate is given by Williams's gas phase controlled analytical solution (for $E_g/RT_f \gg 1$) [8]

$$m^2 = \frac{2k_g B_g M^2 p^2 c_p T_f^4}{E_g^2 Q_g^2} \exp\left(-\frac{E_g}{RT_f}\right) . \quad (20)$$

For this case the characteristic gas zone thickness x_g is given by

$$T_s^* = T_0^* + Q_c^* + Q_g^* \exp\left(-x_g^* m^*\right) . \quad (21)$$

For the high activation energy limit case, the AEA result, Eq.(18), is still used for the determination of the surface temperature T_s^*. Results of this traditional analytical limit case will be compared with the new concept of $E_g = 0$ to show the overall improvements of the model's predictive capability.

3 Results

The properties of HNF as used for the calculations are summarized in Table 1. During all calculations these values were held constant. The condensed phase activation energy $E_c = 75\,\mathrm{kJ/mole}$ was found to give good results in the whole pressure range of interest. This value is close to the $84\,\mathrm{kJ/mole}$ required to break-up HNF into liquid hydrazine and nitroform. The values of the Arrhenius prefactors, A_c and B_g, were determined from the experimental observation that $T_s = 553\,\mathrm{K}$ and $r_b = 0.85$ mm/s at $0.1\,\mathrm{MPa}$ [4, 5]. After this *gauging* of the model, the regression rate is calculated at different pressures, without modification of any of the other parameters.

Q_g		3512	kJ/kg
Q_c		−50.0	kJ/kg
A_c		$9.37 \cdot 10^8$	1/s
B_g	$E_g = 0$	$7.99 \cdot 10^{-2}$	m^3/kgK^2s
	$E_g = \infty$	$1.63 \cdot 10^4$	m^3/kgK^2s
c_p		1.4	kJ/kgK
k_g		0.07	W/mK
k_s		0.20	W/mK
E_c		75	kJ/mole
E_g		167	kJ/mole
ρ_c		1860	kg/m^3
M		25.6	kg/kmole

Table 1: Input values used for HNF calculations.

Fig. 1 shows the results of the calculated regression rate for both models, compared with experimental data. The high activation energy limit yields the familiar $n = \frac{\delta}{2} = 1$, whereas $n = 0.83$ was found experimentally for HNF combustion. Because the regression rate was gauged at $0.1\,\mathrm{MPa}$, the flame sheet overpredicts the regression rates above $0.1\,\mathrm{MPa}$. The low activation limits shows remarkable agreement with the experimental results. This model predicts $n = 0.85$ (at $1\,\mathrm{MPa}$).

Fig. 2 shows the results of the calculation of the temperature sensitivity σ_p for both limiting cases. This sensitivity is defined as

$$\sigma_p = \frac{1}{r_b}\left(\frac{\partial r_b}{\partial T_0}\right)_p . \quad (22)$$

It is seen that the low activation energy limit accurately predicts the temperature sensitivity, whereas the flame sheet approximation overestimates σ_p at elevated pressures. The $E_g \to \infty$ model is not capable of capturing the experimental observed pressure variation of σ_p. The $E_g = 0$ model follows the experimental determined pressure dependence closely.

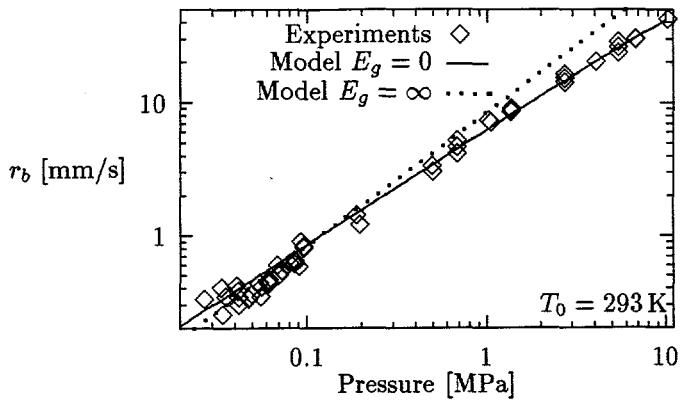

Figure 1: Comparison of calculated and measured regression rate of neat HNF samples.

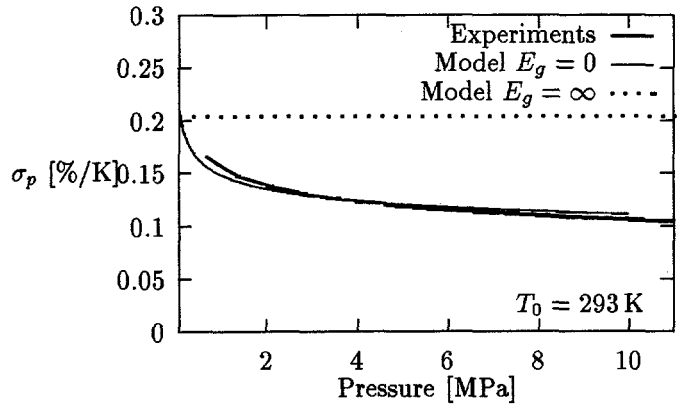

Figure 2: Experimental vs. theoretical temperature sensitivity of HNF.

As already mentioned, the $E_g = 0$ model shows good agreement with experimental determined temperature profiles in the gas phase of HMX. No accurate experimental results have been obtained in the past for the gas phase temperature profile of HNF. Recently it was found by absorption experiments that temperatures very close to the adiabatic flame temperature are reached within 1 mm above the surface [5]. Similar results were also obtained from a detailed kinetical model [6]. Fig. 3 compares the temperature profile as found from both limit cases, and this detailed modeling.

Fig. 4 shows the calculated value of the characteristic gas reaction zone thickness x_g in comparison with several experimental results. The flame standoff distance in of Fig. 4 is obtained from visual observation of the flame. The CN profile peak location was determined by planar laser induced fluorescence (PLIF). The flame standoff distance and CN profile

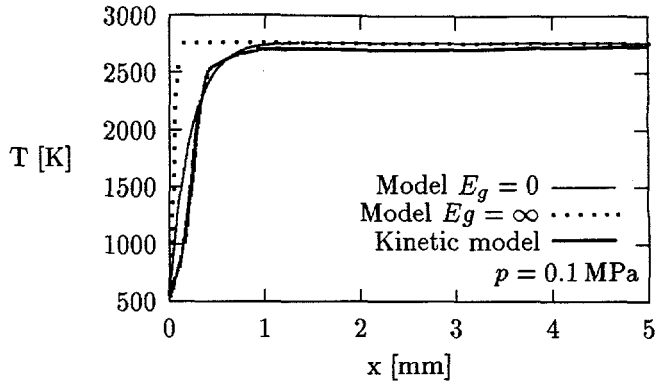

Figure 3: Gas phase temperature profile of HNF for both limit models, and a comprehensive detailed kinetical model.

peak do not necessarily coincide with x_g, but should at least follow the same trend.

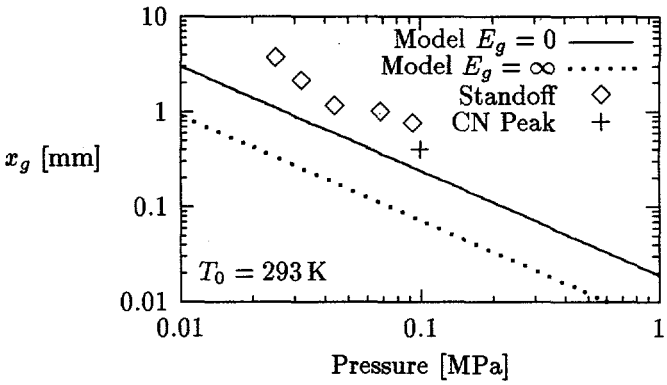

Figure 4: Reaction zone thickness as calculated from both models, compared with experimental determined flame standoff and CN profile peak position.

4 Conclusions

A very simple model for the combustion of HNF is presented. The model follows a new approach by using a zero gas phase activation energy. This approach shows great predictive capability, in both regression rates, and temperature sensitivity. The aggreement of these propellant properties is much better than with the usual assumption of infinite gas phase activation energy.

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Nomenclature

Symbols

A	Arrhenius prefactor
B	Arrhenius prefactor
c_p	Heat capacity
D_g	Damkohler number
d	Diffusion coefficient
E	Activation energy
k	Thermal conductivity
Le	Lewis number
M	Molecular weight
m	Mass flow rate
n	Pressure exponent
Q	Heat release
R	Universal gas constant
r_b	HNF regression rate
T	Temperature
x	Space coordinate
Y	Mass fraction
δ	Reaction order
ϵ	Chemical reactivity
ρ	Density

Sub- and superscripts

c	Condensed phase
f	Final
g	Gas phase
ref	Reference value
s	Surface
0	Initial
$*$	Nondimensional parameter

Nondimensional quantities

$$D_g = k_g B_g p^2 M^2 / ((m_{ref} R)^2 c_p)$$
$$E^* = E/(R(T_f - T_0))$$
$$m^* = m/m_{ref}$$
$$Q^* = Q/(c_p(T_f - T_0))$$
$$T^* = T/(T_f - T_0)$$
$$x^* = x/(k_g/(m_{ref} c_p))$$