

Charge Diameter Effect in 2-Nitropropane/ Nitric Acid Mixtures

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1 Introduction

2-Nitropropane ($C_3H_7NO_2$, 2-NP) is widely used in industry and, in particular, as a component of liquid propellants. Its detonability in mixtures with Nitric Acid (HNO_3 , NA) was studied by Claude [1]. Bouyer et al. [2] investigated static compression of this mixture and estimated linear burning rates for 57% to 85% NA mole fraction. Since one cannot measure the burning rate under detonation conditions, we are developing a model to estimate it in detonation wave and to compare with the above results. However, such a model must be based on shock sensitivity tests or measurements of charge diameter effect on detonation velocity. Here we study the latter effect and present the critical diameters (below which the detonation cannot propagate in the given charge) for equivalence ratio ranging from 0.5 to 2. Preliminary results of numerical modeling are also shown.

2 Experimental studies

We use steel 2-mm thick tubes to obtain detonation velocity dependence on charge diameter of 2 – NP/NA mixtures at equivalence ratio $\phi = 0.5, 0.8, 1, 1.5$ and 2. Figure 1 presents our results for tube diameters 4, 6, 8, 12, 14, 16 and 21 mm.

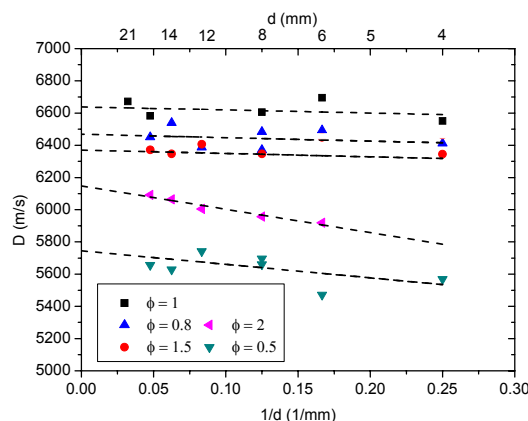


Figure 1- Detonation velocity against inverse of charge diameter for different equivalence ratio at 298K.

Increase of inverse charge diameter, from $1/21 \text{ mm}^{-1}$ to $1/4 \text{ mm}^{-1}$ results in about 2% decrease in detonation velocity. We made a linear regression to find the coefficients of $D = D_\infty - D_1 \frac{1}{d}$. The results

are summarized in Table 1 with the values of critical diameter (no detonation velocity measurements were done in this series of experiments).

ϕ	Our results				TDS	Our results
	$D_\infty(m/s)$	D_1	R	SD	$D_{CJ}(m/s)$	$d_{cr}(mm)$
0.5	5749	0.843	0.54	85	5756	3.5 ± 0.5
0.8	6469	0.215	0.24	65	6476	2.5 ± 0.5
1	6638	0.189	0.27	60	6765	1.1 ± 0.35
1.5	6370	0.211	0.43	28	6515	
2	6177	1.448	0.97	18	6194	2.5 ± 0.5

Table 1 - Coefficient of the equation $D = D_\infty - D_1 \frac{1}{d}$ and critical diameter d_{cr}

Here D_∞ is the extrapolation of our experimental results to an infinite diameter d , R the correlation coefficient, SD the standard deviation error of the fit. D_{CJ} is given by the thermodynamics code TDS [3]. One can see that there is a good agreement between ideal detonation velocity, especially for poor mixtures.

3 Numerical studies

3.1 The model

In homogenous explosives, the decrease of the normal detonation velocity against the inverse of charge diameter is typically one percent between infinite charge diameter and critical charge diameter. In order to model this evolution, we need to solve Euler equations with a kinetic equation and an equation of state (EOS) describing the behavior of unreacted explosives, their products and their mixtures. The EOS described here is based on the HOM equation of state developed and used extensively in Los Alamos National Laboratory during the last few decades [4]. It uses polynomial representation function of logarithm of volume for shock temperature for condensed explosive, and isentropic pressure and temperature for detonation products. However in numerical simulation, for example during initiation, one can easily arrive to a situation where volume is beyond the range for which the aforementioned polynomial fits were obtained. This is why we replaced HOM fits by some analytical functions which reflect physical behaviour of reaction products under compression and thus provide correct asymptotical behaviour. Like in HOM EOS, we use a development of Mie-Grüneisen for inert reactants and products.

3.1.1 Modified HOM EOS for the reactants

For the inert reactants the reference state is the shock curve H . The shock pressure P_H is found from the standard linear experimental Hugoniot $D_H = a_H + b_H u$ (we use the method given in [5]) and first two balance equations. Shock temperature T_H is found via Walsh and Christian technique [6]. We found an approximation of T_H :

$$T_H(v) = T_1(v) + \Delta T \left\{ \exp \left[-\frac{v}{v_0} - \frac{\varepsilon}{\eta} \right] - \exp \left[-\frac{1 - \varepsilon}{\eta} \right] \right\} \quad (1)$$

where ΔT , ε and η are the best fitting coefficients. T_1 is the first order approximation, valid at small compression ($v/v_0 \ll 1$):

$$T_1(z) = e^{b_w(v_0 - v)} \left\{ T_0 - \frac{a_H^2}{b_H^2 c_s k^3} (2 - e^{-z} [2 + z(2 + z)]) \right\} \quad (2)$$

with $z = b_w(v_0 - v)$, $b_w = \frac{\gamma_0}{v_0} = \frac{3\alpha c_0^2}{v_0 c_v}$, where c_0 is the initial sound speed, $k = \frac{b_w v_0}{b_H}$. Eq. (1) fairly describes T_H up to a few thousand Kelvin. Table 2 sums the values of those parameters.

	$a_H(m/s)$	b_H	$b_w(kg/m^3)$	$c_s(J/kg.K)$	k	$\Delta T(K)$	ε	η
NM [4]	1647	1.637	1053	1730	0.571	3629	0.5095	0.0404
2-NP/NA ($\phi = 1$)	2016	1.464	960	1700	0.508	1671	0.5221	0.0509

Table 2 - Coefficients of $D_H = a_H + b_H u$ (D_H shock velocity, u particle velocity) and Eq. (1), (2)

3.1.2 Modified HOM EOS for the products

The reference state for the detonation products is the isentrope S . The pressure at the isentrope, P_S , has the following form:

$$P_S(v) = \frac{P_1}{v^{\gamma_g+1}} + \frac{P_2}{v^n} \quad (3)$$

Apparently, pressure along the isentrope has two branches the first of which (the first term) is dominant at small pressures while the second one governs the behaviour of products at larger pressures ($\gamma_g < n$). Finally, the isentropic temperature T_S is fitted as follows:

$$T_S(v) = T_0 + T_1 \left[1 - \exp\left(-\frac{T_2}{v}\right) \right] + T_3 \left[1 - \exp\left(-\frac{T_4}{v}\right) \right] \quad (4)$$

where $P_1, P_2, T_0, T_1, T_2, T_3, T_4, n$ and γ_g are found by fitting isentropic pressure, energy and temperature calculated via the thermodynamic code TDS [3] in the large domain of specific volumes with a particular attention paid to the Chapman-Jouguet point. Table 3 indicates a set of parameters used in the simulation.

	γ_g	n	$P_1(Pa)$	$P_2(Pa)$	T_0	$T_1(K)$	T_2	$T_3(K)$	T_4
NM	0.25	2.68	1.59×10^5	31.87	298	651	0.053	12505	1×10^{-4}
2-NP/NA ($\phi = 1$)	0.32	2.70	0.87×10^5	23.69	298	793.04	0.033	6519	2.3×10^{-4}

Table 3 - Coefficients of Eq. (3) and (4), v in m^3/kg and P in Pa .

3.1.3 Kinetic modeling

Reaction rate was described by a one step Arrhenius law: $\frac{dy}{dt} = A(1-y)^n \exp\left(\frac{-E}{RT}\right)$ with : A pre-exponential factor, E activation energy and n reaction order. For NM the values are : $A = 15.10^9$ 1/s, $E = 30$ kcal/mol, $n = 1.1$ and for 2-NP/NA ($\phi = 1$): $A = 2.63.10^9$ 1/s, $E = 20$ kcal/mol, $n = 1.1$.

3.2 Numerical results

Figure 2 shows results of calculations for Nitromethane (NM) and our stoichiometric mixture using the proposed equation of state. Calculations were done using quasi one-dimensional approximation for tube expansion with EFAE code [7]. Euler equations are solved using the Flux Corrected Transport (FCT) technique developed by Oran and Boris [8]. Figure 2 displays the calculated effect of inverse charge diameter on detonation velocity in 2-mm thick steel tubes. One can see that in the case of NM the model gives reasonable agreement with available experimental data [9]. Particularly, the detonation velocity deficit is about 1.5% and critical diameter is close to 1 mm. In the case of our stoichiometric mixture, the coupling between the preliminary set of coefficients of equation of state and of kinetic Arrhenius equation also gives reasonable agreement with experiments.

4 Conclusions

We present experimental charge diameter effect for 2-Nitropropane/Nitric Acid mixtures with equivalence ratio ranging from 0.5 to 2. We propose a new equation of state MHOM (Modified HOM) and use it to describe the detonation of tested mixture. Comparing the results of calculations with experimental

charge diameter effect, at present, we find a reasonable agreement. To improve the agreement between the model and experiment, we need to provide better description of our mixture, especially for shock temperature which is a key parameter of our model since Arrhenius law is very sensitive to temperature effect. With this improvement it should be possible to estimate burning rates under high pressure and make large scale simulations.

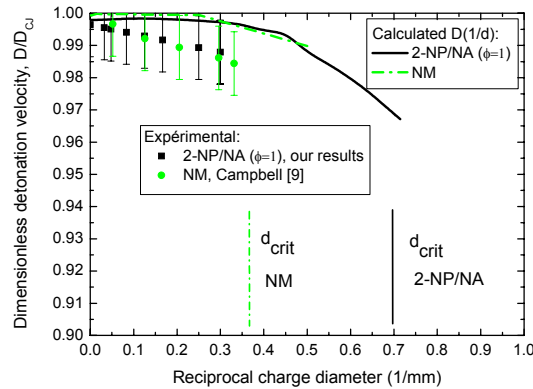


Figure 2- Detonation velocity against reciprocal of charge diameter for stoichiometric mixture 2-NP/NA and NM.

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References

- [1] Claude P. (1965) *Contribution à l'étude de la détonation des mélanges acide nitrique nitropropane*, PhD at University of Poitiers, 97 p.
- [2] Bouyer V., Hébert P., Doucet M., Bouton E. (2006) *Laser-Induced decomposition of energetic materials at static high pressures study of the HNO₃/2-Nitropropane mixture*, 13th Symposium on Detonation, Norfolk, VA, July 23-28
- [3] Victorov S. B. et al. (2001), *An equation of state and detonation properties of hydrazine-nitromethane liquid mixtures*, Shock waves, vol. 11, p.105
- [4] Mader C. L. (1998) *Numerical Modeling of explosives and propellants*, CRC Presse. Boca Raton, New York
- [5] Afanasenkov A. N., Bogomolov V. M., Voskoboynikov I. M. (1969) *Generalized shock hugoniot of condensed substances*, Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, vol. 10, n°4, pp. 137-141
- [6] Walsh J. M., Christian R.H. (1955), *Equation of state of metals shock wave measurements*, Physical Review, vol. 97, n°6, pp 1544-1556
- [7] Khasainov B. A., Veyssiere B. (1996) *Initiation of detonation regimes in hybrid two-phases mixtures*, Shock Waves, vol 6, p.9
- [8] Oran E.S., Boris J.P. (1987) *Numerical Simulation of Reactive Flow*, Elsevier Science Publishing Co, pp.1-601
- [9] Campbell A. W., Engelke R. (1976) *The diameter effect in high-density heterogeneous explosives*, 6th Symposium on Detonation (ACR-221), p. 642-652