DETONATION AND EXPLOSION PROPERTIES OF COMMERCIAL EXPLOSIVES

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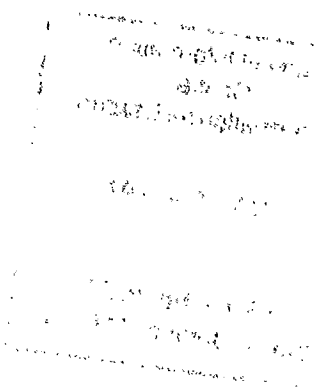

DETONATION AND EXPLOSION PROPERTIES OF COMMERCIAL EXPLOSIVES

by

D.E.G. Jones* and K.K. Feng*

SUMMARY

Most slurry and emulsion commercial explosives are ammonium nitrate (AN) based compositions. Determination of their detonation properties is important to the end use of these compositions.

The theoretical basis for estimation of these properties is outlined and a description of the TIGER computer code embodying this theory is given. TIGER code calculations are presented for a number of slurry and emulsion explosives.

Detonation and explosion parameters are calculated for a number of different equations of state (EOS). The detonation parameters are discussed in light of the composition of the explosives.

The singular value decomposition method is discussed as a mechanism for dealing with singularities in the solution of the iteration equations in the code.

The effect of different ingredients in the composition, oxygen balance, density and wrapping material on the detonation calculations is determined and discussed.

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INTRODUCTION

Commercial explosives are generally ammonium nitrate (AN) based compositions in contrast with military explosives, such as TNT, which may be termed "molecular".

The former explosives require a "fuel" and fuel oil (FO) is commonly used since it is readily available and inexpensive. The ANFO thus produced has replaced dynamite in many applications since 1960.

The disadvantages of ANFO, such as its low water resistance and density, led to the development of slurry explosives. The latter are obtained by predissolving the oxidizer, eg AN, in a small amount of water, thickening the solution, using guar gum or starch and, optionally, crosslinking the thickener. Fuel components or other additives are added as soluble or finely divided materials. These compositions may be sensitized chemically or physically by small gas bubbles. Ingredients may be selected to vary the energy output, sensitivity, oxygen balance, density, etc. This allows adjustment of the fume and detonation characteristics as well as the physical properties of the slurry.

Slurry explosives are generally less sensitive than "molecular" explosives to impact, friction, fire or accidental detonation.

Formulations with zero oxygen balance have sufficient oxygen to stoichiometrically react with all the "fuel", resulting in complete combustion and formation of the highest energy products. In contrast with formulations having "negative" oxygen balance i.e. insufficient oxygen, the above formulations generally yield less toxic gaseous products.

Recently, water-in-oil emulsions have been developed as commercial explosives. In these systems, an oil is the continuous phase and the aqueous oxidizer solution is dispersed as small droplets throughout this phase. Emulsions have the advantages of improved water resistance and the absence of thickeners. Increased contact area between fuel and oxidizer results in improved sensitization, although glass microballoons may be added for increased sensitization.

From a practical point of view, some of the common ingredients of commercial explosives are not well characterized chemically; e.g., fuel oil, guar gum. Additionally, these compositions are often used in their wrapped state. The wrapper may be paper or polymer, such as a woven ethylene propylene copolymer. Whatever the wrapping material is, it generally acts as an additional source of "fuel" for the explosive composition, resulting in a more negatively oxygen - balanced system.

It is possible to achieve a wide range of fume and detonation properties using slurry and emulsion explosives. Measurement of these properties and analysis of the detonation products is often time consuming, costly and impractical but this information is important since it determines the end use of an explosive. Fortunately, it is possible to estimate these properties from theory with some degree of success.

METHOD FOR ESTIMATION OF EXPLOSION AND DETONATION PROPERTIES

THEORY

The Rankine - Hugoniot equations for a shock propagating at velocity D in a stationary material, (u_o=o) express the conservation of mass, momentum and energy as follows.

$$\rho_o D = \rho_1 (D - u_1) \qquad [1]$$

$$p_1 - p_o = \rho_o D u_1 \qquad [2]$$

$$p_1 u_1 = \rho_o D (e_1 - e_o + \tfrac{1}{2} u_1^2) \qquad [3]$$

where o and 1 refer, respectively to the unshocked and shocked material and ρ is the density (1/v, v the specific volume), u is the velocity of the material, p is the pressure and e is the specific internal energy.

Combination of [1] and [2] and of [1], [2] and [3] yields, respectively,

$$p_1 - p_o = (D/v_o)\ (v_o - v_1) \text{ (Rayleigh line)} \qquad [4]$$

and

$$e_1 - e_o = \tfrac{1}{2}\ (p_1 + p_o)\ (v_o - v_1)$$
(Hugoniot equation) [5]

An initial condition defined by e_o, p_o and v_o together with a complete EOS of the detonation products in chemical equilibrium ($e = e\ (p, v, n_i)$ where n_i is the amount of each detonation product) and equation [5] define the Hugoniot curve in the p, v plane (Figure 1). A reactive shock does not pass through the point p_o, v_o in this plane.

To determine a unique value of D an additional condition is required. This condition is supplied by the Chapman - Jouguet (C-J) hypothesis, which states that

$$D = u_1 + c_1 \qquad [6]$$

where c_1 is the speed of sound in the detonation products.

In order to determine the complete EOS mentioned above, the chemical equilibrum problem must be solved. The equilibrum composition of detonation products must satisfy the stoichiometric condition and an explicit EOS must be assumed for the gas phase and the condensed phase. The equilibrium condition for each constituent is determined from the chemical potential of all the elements in the gaseous and condensed phases. In order to do this the chemical potential of each constituent is expressed in terms of the variables of the EOS and of the stoichiometric condition.

From the composition of the explosive a linearly independent set of product species is selected from a library of species. This library also includes basic thermodynamic data and EOS parameters for each of these species which in turn permit the calculation of the equilibrium composition of gaseous and condensed products and derived thermodynamic information.

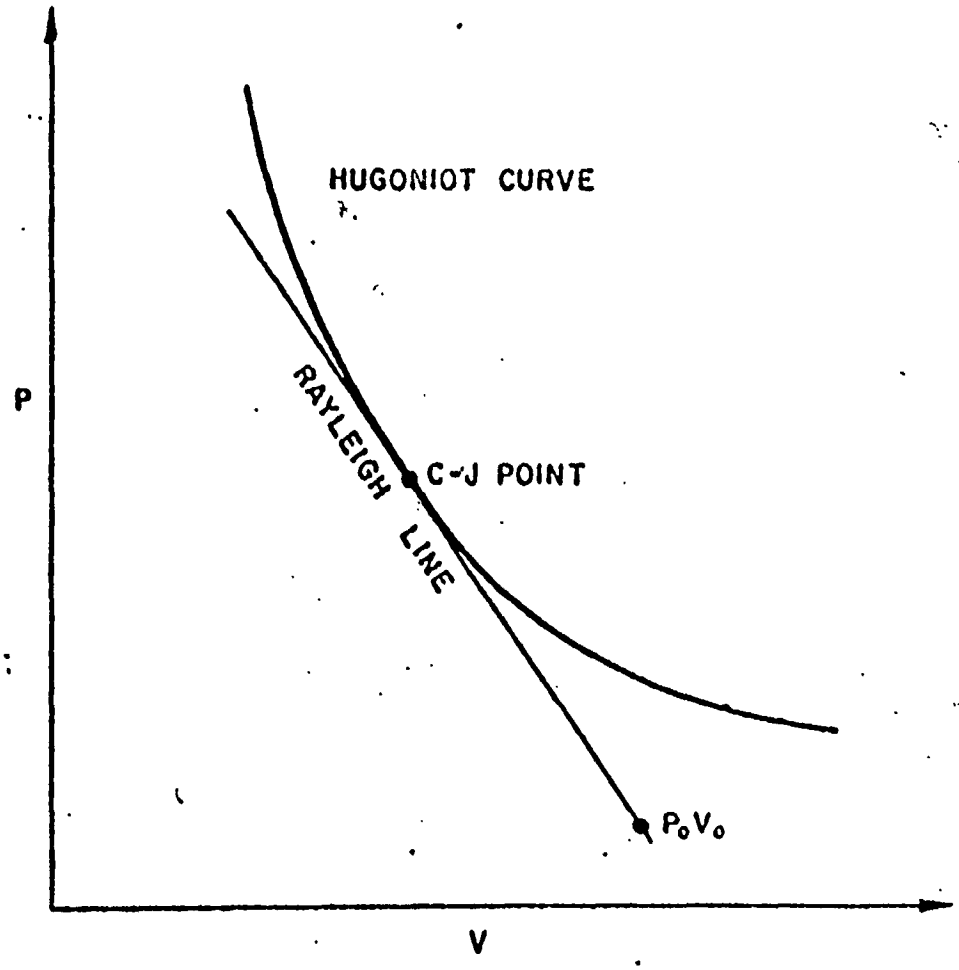

Fig. 1 - The tangency of the Rayleigh line to the Hugoniot curve at the Chapman-Jouguet point

THE TIGER CODE

All of these calculations are embodied in TIGER, which is a FORTRAN code originally written at Stanford Research Institute in 1968 (2). This code has been modified both in our laboratory and elsewhere and improvements have been specifically made to the library and input data in our work.

As input data, the following are required:

(a) a selected EOS
(b) the chemical formula and enthalpy of formation at 298 K of each component in the composition
(c) the weight percent of each component in the composition
(d) the density of the composition.

Apart from the density this code does not treat any other physical property of the system. It therefore does not distinguish between a mixture, slurry or emulsion having the same composition. Further, the particle size of the ingredients is not a factor in these calculations. Finally, it should be emphasized that the theoretical basis for TIGER is hydrodynamic - thermodynamic. It therefore does not deal with the dynamics of the reacting system under shock but merely treats the initial state, the condensed explosive and the final state, the detonation products in equilibrium at the detonation conditions, in the absence of any condensed explosive.

RESULTS AND DISCUSSION

The TIGER code was originally developed to deal with C, H, O, N condensed explosives but may be extended to treat compositions containing other elements, notably Al, Cl, Na, Ca and Si. Additional information has been added to the library data in order to use TIGER with compositions containing these elements.

Numerically, these compositions often present difficulties in the solution of equations in the code as a result of very small amounts of certain species in the gas phase. It is necessary to solve linear equations, for example, in the calculation of the equilibrium composition of the detonation products. The method used in the code is Gaussian elimination with partial pivoting. When a singular matrix is encountered no solution is possible from this method. A singular value decomposition (SVD) technique (3) (4) has been used to solve for x in the system.

$$A \cdot x = b \qquad [7]$$

where the matrix A is singular.

A slurry composition which was known to yield singular matrices in the code was used to test the SVD method. The singular matrix A for this composition is listed in Table I. The corresponding right hand vector b is given in Table II, together with the solution x and the product A • x identified by the array, test (N). It can be seen that matrix x determined from SVD reproduces accurately the input values of the right hand vector b. The SVD technique is in the process of being added to the TIGER code and will be tested on other systems.

The effect of using a wrapped explosive including varying the weight percent of wrapper is illustrated by the calculated results for a slurry explosive, as given in Table III. The wrapper in this case is an ethylene - propylene copolymer. Both the detonation temperature, T and pressure, p decrease as the relative amount of wrapper increases. The amounts of CO_2, CO, H_2, CH_4 and NH_3 increase and the amounts of H_2O (g) and N_2 decrease, in the detonation products, as the relative amount of wrapper increases.

Table I - Sample Singular Matrix

A(1,1) = 1.0	A(1,2) = -.669521414035
A(1,3) = -.2473202912008	A(1,4) = -.1187084807148
A(1,5) = -.07208155018632	A(1,6) = 0
A(1,7) = -1.107917773058	A(1,8) = -31.87679805868
A(2,1) = 0	A(2,2) = .4459368378351
A(2,3) = -.1090722348147	A(2,4) = -.073415056214
A(2,5) = -.06020389722261	A(2,6) = 0
A(2,7) = -.4011916235376	A(2,8) = .5057515737236
A(3,1) = 0	A(3,2) = -.109071235541
A(3,3) = .1613225737236	A(3,4) = -.03216434323246
A(3,5) = -.008402534363976	A(3,6) = 0
A(3,7) = -.2116012056873	A(3,8) = .2264623019599
A(4,1) = 0	A(4,2) = -.0734143584223
A(4,3) = -.03216424270827	A(4,4) = .09063891234362
A(4,5) = .0149948031729	A(4,6) = 0
A(4,7) = -.1071190864691	A(4,8) = .0959217270423
A(5,1) = 0	A(5,2) = -.06020377713005
A(5,3) = -.008402592308167	A(5,4) = .01499474502166
A(5,5) = .1030990872592	A(5,6) = 0
A(5,7) = -.01558794878377	A(5,8) = -.1740887457258
A(6,1) = 0	A(6,2) = 0
A(6,3) = 0	A(6,4) = 0
A(6,5) = 0	A(6,6) = 0
A(6,7) = 0	A(6,8) = .00001670170079025
A(7,1) = 0	A(7,2) = -.0002254047392646
A(7,3) = -.00008326420124042	A(7,4) = -.00003996504605097
A(7,5) = -.00002426736872779	A(7,6) = 0
A(7,7) = -2.040306258986	A(7,8) = 2.041811100374
A(8,1) = -.006952508546018	A(8,2) = .1084552106547
A(8,3) = .0163073287034	A(8,4) = -.01046739329299
A(8,5) = -.1890454760301	A(8,6) = 0
A(8,7) = -2.129482966545	A(8,8) = 7.98490012814

Table II - Vector b, solution vector x by SVD and product A.x in [7]

```
b(1) = -.0008721345384402
b(2) = .0001566343634903
b(3) = .0000357169945833
b(4) = -.00002253897676349
b(5) = -.0001962553412307
b(6) = 0
b(7) = .0002851694445241
b(8) = .0007752490819257
```

```
x(1) = -.0006658093946349
x(2) = -.0001410537963932
x(3) = -.0002163526199648
x(4) = -.0002803262744979
x(5) = -.0019458395881113
x(6) = .0000000000000000
x(7) = -.0001190057010434
x(8) = .0000206939493777
```

```
test(1) = -.0008721345384402
test(2) = .0001566343634904
test(3) = .0000357169945584
test(4) = -.0000225389767632
test(5) = -.0001962553412327
test(6) = .0000000003456242
test(7) = .0002851694445253
test(8) = .0007752490819246
```

Table III

Effect of wrapping material on detonation properties

Detonation Properties	Weight % wrapper			
	0.92	1.00	1.56	2.70
T/kK	1.53	1.52	1.52	1.51
p/kbar	23.9	23.8	23.8	23.7
Detonation Product	Amount of detonation product/mol kg -1			
H_2O	26.43	26.19	25.58	24.39
N_2	9.07	8.94	8.80	8.53
CO_2	4.75	4.84	5.01	5.36
NH_3	1.69	1.81	2.02	2.38
H_2	0.58	0.60	0.65	0.71
CO	0.38	0.40	0.45	0.55
CH_4	0.68	0.36	0.24	0.18

$\rho_o = 1.35\ g/cm^3$

Table IV presents the results of some calculations on ANFO. This Table shows the effect of oxygen balance and density on the detonation parameters.

The 93:7 mixture has a negative oxygen balance and produces relatively large amounts of NH_3 and CO compared to the 95:5 mixture which has a positive oxygen balance. The latter mixture additionally produces both NO and O_2 on detonation.

As the initial density increases both the detonation pressure and velocity increase (Table IV). This result is expected on theoretical grounds and has been observed for a number of explosives (5). Similarly, the C-J density is directly proportional to the initial density.

In Table V the detonation velocity and pressure obtained using three different EOS and those parameters obtained from the Kamlett equations (5) are compared with the experimental results for a few AN based explosives. In general, it appears that the results obtained using the CS (7) EOS correspond more closely to the experimental results than the JC3 (8) and BKW (5) EOS. It is known (5) that detonation velocity is sensitive to the charge diameter, d. Further, in the case where the predicted results are greater than those obtained from experiment, Mader (6) has explained the difference by asuming that AN based explosives are "nonideal", in the sense that a portion of the AN is unreacted on explosion or detonation.

CONCLUSION

The TIGER code has been used to assess the impact of some factors on the explosion and detonation properties of a number of commercial explosives. It has been shown that this code can treat systems which are numerically troublesome by a specific numerical technique. In summary, the TIGER code is a useful tool for predicting explosion and detonation parameters and products for commercial explosives.

Table IV

Effect of O_2 balance and initial density on detonation parameters

Weight ratio AN:FO	ρ_o/cm^3g^{-1}	p/kbar	V/cm^3g^{-1}	T/kK	D/km s^{-1}	Amount of detonation product/mol kg^{-1}							
						H_2O	N_2	CO_2	NH_3	CO	H_2	NO	O_2
93:7		78.2	0.737	2.75	5.45	25.46	10.86	4.39	1.51	0.62	0.40	--	--
94:6	1.111	97.3	0.675	2.77	5.92	26.78	11.47	4.15	0.53	0.14	0.09	0.00	--
	1.000	78.9	0.739	2.81	5.50	26.89	11.54	4.05	0.41	0.25	0.18	0.00	--
	0.9091	64.0	0.806	2.83	5.17	26.98	11.60	3.95	0.28	0.34	0.26	0.00	--
95:5		76.1	0.742	2.73	5.43	27.23	11.78	3.58	--	0.00	0.00	0.18	0.52

Table V - Comparison of Calculated and Experimental Values of D and p

Explosives	D/km s $^{-1}$					p/kbar				
	Calculated				Experimental[1]	Calculated				Experimental[2]
	JC3	BKW	CS	K[3]		JC3	BKW	CS	K[3]	
A1	5.61	5.10	4.24	5.92	4.1(d=60 mm)	91.1	85.9	52.3	97.7	50.9
A2	5.77	5.36	4.62	6.13	3.9(d=60 mm)	106	101	65.4	133	49.8
A3	6.34	5.55	4.99	6.44	3.8(d=60 mm)	119	108	71.4	148	45.7
B	5.15	4.70	3.73	5.03	4.2(d=32 mm)	72.4	68.3	39.1	81.8	50.3
C1	5.26	4.80	3.90	5.25	4.3(d=40 mm)	77.3	72.1	45.5	87.9	51.7
C2	5.23	4.80	3.88	5.32	4.6(d=40 mm)	77.7	72.4	47.4	91.2	59.1

1. our unpublished results

2. obtained from experimental D and gamma law $p = \rho D/(1 + \Gamma)$ assuming $\Gamma = 3.0$

3. Kamlett's equations (5)

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