conf-780813--10

LA-UR -78-836

TITLE: CHEMISTRY OF BUILD-UP OF A DETONATION WAVE

AUTHOR(S): Charles L. Mader

MASTER

SUBMITTED TO: Symposium (International) on High Dynamic Pressures
Paris, France
August 28 - Sept. 1, 1978

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

Form No. 836
St. No. 2629
1/75

UNITED STATES
ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

CHEMISTRY OF BUILD-UP OF A DETONATION WAVE

Charles L. Mader
Los Alamos Scientific Laboratory
of the University of California
Los Alamos, New Mexico, U.S.A.

A carbon coagulation or condensation mechanism is compatible with the experimental observations of large changes of the effective C-J pressure of heterogeneous explosives and associated small changes in detonation velocity as a function of the distance the detonation wave has proceeded.

As the distance of run increases, the Taylor wave becomes less steep and the process of carbon coagulation ($C_{gas} \rightarrow C_2 \rightarrow C_5 \rightarrow C_n \rightarrow C_{graphite}$) has more time to proceed before the expansion of the products decreases the amount of interaction of carbon species that can occur. A model is described that is suitable for numerical modeling of the two-dimensional detonation wave build-up as a function of gradient of the Taylor wave near the detonation front.

I. INTRODUCTION

In 1965, Craig[1] first discovered the nature of the nonsteady behavior of explosives. He studied the interaction of the explosive 9404 in one-dimensional plane geometry at four charge lengths with Dural, magnesium, and Plexiglas plates. If the 9404 has steady-state behavior, the experimental data should have scaled as a function of plate vs explosive thickness. The data did not scale and the data clearly indicate that the effective Chapman-Jouguet (C-J) pressure (P_{ECJ}) for underinitiated detonating 9404 increases, or builds up as the detonation wave runs.

The result was not unexpected, because at about the same time, Davis et al.[2] had shown from other experimental studies that the steady-state C-J theory did not accurately describe the behavior of real explosives. The exact nature of the nonsteady-state behavior shown by Craig's data[1] (a change of 25% in P_{ECJ} with less than 1% in detonation velocity) was a surprise to most detonation scientists; however, it permitted one to understand why thin layers of explosives behaved so differently than expected from the simple calculations calibrated with data from thicker explosive charges.

Craig's experimental data show that the effective C-J pressure of underinitiated, detonating 9404 increases or builds up as the detonation wave runs. Craig found that the effective C-J pressure increases with distance as shown in Fig. 1 for 9404 initiated with a Baratol plane wave lens. Effective C-J pressures were obtained using Dural, magnesium, and Plexiglas plates that were identical within experimental error for the same distance of run. The experimental data used in Fig. 1 are shown in Fig. 2. Craig also observed that the detonation wave velocity remains within 100 m/s of 8800 m/s for all the systems studied. Assuming that a real nonsteady-state detonation can be approximated by a series of steady-state detonations whose effective C-J pressures vary with the distance of run, we can use

$$\gamma = \rho_o D^2/P_{ECJ} - 1 \quad ,$$

(where ρ_O, the initial density, is 1.844 g/cm^3, D, the detonation velocity, is 0.88 cm/μs, and P_{ECJ} is the effective C-J pressure in Mbar) to calculate gamma as a function of distance of run. This may be described by the equation called the "build-up equation"

$$\gamma = 2.68 + 1.39/(\text{distance of run in cm}) \quad .$$

Since the initial discovery of build-up in 9404, additional studies were made by Craig for TNT and by Davis for Composition B. Figure 3 shows that these explosives also exhibit a change in the effective detonation pressure as a function of distance of run. They also exhibit a detonation velocity that remains essentially constant within the experimental measurement error. A curve is shown for self-overdriven nitromethane for comparison with the other explosives that are underdriven by the Baratol plane wave initiation. The infinite-medium C-J pressures are shown on the right-hand side of the figure. The build-up behavior is apparently different for the various explosives, with a lesser difference between 9404 and Composition B as distances of run decrease. It seems possible that explosive build-up curves could cross and that the ordering of the performance characteristics of explosives could change, depending upon the distance of run and perhaps also on the initiating system. It is possible that some explosives may not exhibit appreciable amounts of build-up. PETN has been observed to have minimal build-up behavior.

II. CHEMISTRY OF BUILD-UP

We shall attempt to speculate as to the possible chemistry of the build-up process.

One of the most unexpected and puzzling results of the experimental studies of recent years has been the observed constancy of the detonation velocity of an explosive and associated large variations of the effective C-J pressures and Taylor waves. The observed lack of appreciable curvature at the front of unconfined and confined explosive charges[3] is further evidence that the detonation velocity cannot be related to the other state parameters in any simple manner. The lack of appreciable front curvature in charges with length-to-diameter ratios of one-half or greater is difficult to understand considering the observed steeper Taylor waves for such charges compared with charges where two-dimensional effects are not present.

¶ The physical and chemical processes that cause the nonsteady-state behavior of explosives are still unknown. The solution of the Navier-Stokes equations of fluid dynamics, using Arrhenius chemical reaction and accurate equations of state for condensed explosives, results in detonations that exhibit unstable periodic behavior.[4] The steady-state Chapman-Jouguet theory of the detonation process cannot properly describe the behavior of real explosives that exhibit unstable periodic behavior. The calculations give no hint of the nature of the actual behavior that is to be expected and may have no physical reality because the real chemical reactions are more complicated than is assumed by the calculations.

Real explosives, that have solid carbon as a detonation product, exhibit behavior that is not adequately described without the inclusion of some time-dependent phenomenon, such as diffusion-controlled carbon deposition or some other kinetic behavior of the detonation products. A time-dependent carbon deposition is the only process that is known that could account for the large energy deficits required by the build-up model. We have found that the observed constancy of velocity and large variations of the C-J pressure can be reproduced by the time-dependent carbon deposition mechanism.

We postulate that as the distance of run increases and the Taylor wave becomes less steep, the process of carbon coagulation ($C_{gas} \rightarrow C_2 \rightarrow C_5 \rightarrow C_n \rightarrow C_{graphite}$) has more time to proceed before the expansion of the products decrease the interactions of carbon species. The increasing energy from near the C-J plane results in increasing C-J pressures and densities. It is not obvious what the detonation velocity would do, but the first guess might be to expect it to increase along with the other state parameters. To determine the effect on C-J state values, calculations were performed using BKW[5] and LJD[6] equations of state and holding the amount of carbon and other detonation products fixed at the usual equilibrium value but permitting part of the carbon to remain as C, C_2, or C_5.

In Table I the calculated C-J state parameters are shown using BKW and changing the $C_{gas}/C_{graphite}$ ratio of carbon in the reaction for 9404 at 1.844 g/cc of

$$C_{4.4236}H_{8.6597}N_{8.075}O_{8.467}Cl_{0.0993}P_{0.0331}$$

$$\rightarrow 4.3298\ H_2O + 2.07\ CO_2 + 4.0375\ N_2 + 0.033\ POCl_3 + 2.35\ C.$$

The velocity is found to be nearly constant while the pressure is decreasing by 20% if C, C_2, or C_5 gas is formed instead of graphite.

In Table II the calculated C-J state parameters are shown using LJD and changing the $C_{gas}/C_{graphite}$ ratio. The velocity change is again small compared with the pressure change.

Since BKW is calibrated for explosive charges about 10 cm long, to obtain the infinite medium C-J pressure for 9404 of 390 kbars, the constants were recalibrated. The new set of constants is called the "Infinite Geometry BKW Parameter Set" and are alpha = 0.71, beta = 0.05, kappa = 92, and theta = 400. The calculated C-J state parameters for 9404 with various carbon gas/graphite ratios are shown in Table III. The calculated pressures vary from 390 to 320 kbars while the velocity changes by less than 3%. The calculated temperatures are too low and suggest that this set of BKW parameters should be used with caution.

The conclusion is that the carbon coagulation mechanism is compatible with the experimental observation of large changes in effective C-J pressures associated with small changes in detonation velocity. The conclusion is valid for BKW with different equation-of-state parameters and for the LJD equation of state.

Since little build-up has been observed for PETN, similar calculations were performed for PETN at 1.77 g/cc in the reaction

$$C_5H_8N_4O_{12} \rightarrow 4.0\ H_2O + 3.95\ CO_2 + 0.096\ CO + 2.0\ N_2 + 0.95\ C$$

and are shown in Table IV. The calculated pressures and velocities are only slightly changed by the changing carbon gas/graphite reaction.

The constant detonation product composition used for TNT at 1.64 g/cc was

$$C_7H_5N_3O_6 \rightarrow 2.5\ H_2O + 1.75\ CO_2 + 1.5\ N_2 + 5.25\ C.$$

With all the carbon present in the TNT detonation products, one might expect a larger build-up for TNT than 9404. However, if only 1.70 moles of the 5.25 moles of carbon are gaseous, the heat of detonation becomes positive. As shown in Table V, the pressure and temperature drop rapidly and the velocity changes slowly with increasing carbon gas. The RDX parameters were used.

The observed change of slope of the TNT detonation velocity-density curve[7] from 3163 to 1700 m/s at 1.55 g/cc can be reproduced if the heat of formation of the 5.25 moles of carbon is changed by 6 kcal/mole between 1.55 and 1.64 g/cc. Perhaps with large amounts of carbon present the carbon coagulation process is inhibited at higher densities. The exact mechanism that could cause this is obscure.

Another method of reproducing the observed change in slope of 1500 m/s would be to have a mole more of carbon gas present in the detonation products at 1.64 g/cc than 1.55 g/cc. This is an attractive possibility because it also brings the C-J pressure and detonation velocity into agreement with the experimental observations at 1.64 g/cc without changing from the BKW parameter set. We need a mechanism for inhibiting the coagulation process for large amounts (∿ half of the number of moles of detonation products) of carbon at higher densities that is insignificant for explosives with less (∿20 mole percent) carbon in the products.

The calculations shown varying the carbon composition appear to be consistent with the experimentally observed build-up model. Other reactions are not excluded and the time-dependent behavior may be a result of several important reactions interacting with the unstable periodic nature of the detonation wave.

III. A TWO-DIMENSIONAL MODEL FOR BUILD-UP

Assuming that build-up for 9404 proceeds along the Rayleigh line from "A" with an initial gamma-law detonation product equation of state with a P_{ECJ} of 300 kbars ($\gamma = 3.76$), to "B" with a P_{ECJ} of 388 kbars ($\gamma = 2.68$), one can use the build-up equation $\gamma = 2.68 + 1.39/x$ (x is distance of run) to calculate the pressure as a function of distance of run from $P_{ECJ} = \rho_o D^2/(\gamma + 1)$ where ρ_o is 1.844 and D is 0.88 cm/μs.

$$P_{ECJ} = \frac{1}{2.577 + \dfrac{0.9733}{x}} \quad .$$

With additive volumes and energies for the mixture equation of state one finds

$$P_{ECJ} = W[P_{ECJ}(A)] + (1 - W)[P_{ECJ}(B)] \quad ,$$

where W is mass fraction of (A). For any given x we can find W, P, V, and I.

The gradient of the slope of the Taylor wave near the front is

$$\frac{dP}{dx} = \frac{2P_{ECJ}}{x} \quad .$$

If we assume that the gradient behind the detonation wave determines the detonation wave build-up, then as a function of the gradient we can calculate the appropriate P_{ECJ} from

$$P_{ECJ} = 0.388 - 0.1888 \frac{\Delta P}{\Delta x} \quad ,$$

where $\Delta P/\Delta x$ is less than 0.46 and greater than 0. We have used this method of describing build-up in two-dimensional problems where side rarefactions keep the Taylor wave steep and prevent the increase of P_{ECJ} to occur. In two dimensions dP/dx becomes the pressure gradient in the direction of the velocity vector. We propose that steep pressure gradients behind the detonation front prevent the carbon coagulation from occurring and thus prevent the increase in effective C-J pressure.

The calculated mass fraction and distance of run as a function of pressure are shown in Fig. 4. Also shown is the amount of carbon present as graphite as a function of pressure from Table III.

IV. CONCLUSIONS

Real explosives, which have solid carbon as a detonation product, exhibit behavior that is not adequately described without the inclusion of some time-dependent phenomenon, such as diffusion controlled carbon deposition or some other kinetic behavior of the detonation products. A time-dependent carbon deposition is the only process that is known that could account for the large energy deficits required by the build-up behavior of heterogeneous explosives. We have found that the observed constancy of velocity and large variations of the C-J pressure can be reproduced by the time-dependent carbon deposition mechanism. We postulate that as the distance of run increases and the Taylor wave becomes less steep, the process of carbon coagulation ($C_{gas} \rightarrow C_2 \rightarrow C_5 \rightarrow C_n \rightarrow C_{graphite}$) has more time to proceed before the expansion of the products decreases the interaction of the carbon species. The increasing energy from near the C-J plane results in increasing C-J pressures and densities. To determine the effect on C-J state values, calculations were performed using BKW and LJD equations of state and holding the amount of carbon and other detonation products fixed at the usual equilibrium value but permitting part of the carbon to remain as C, C_2, or C_5.

The conclusion is that the carbon coagulation mechanism is compatible with the experimental observation of large changes in the effective C-J pressures associated with small changes in detonation velocity. The conclusion is valid for BKW and the LJD equation of state and for the explosives 9404, PETN, TNT, and Composition B.

A build-up model dependent upon the pressure gradient in the direction of the velocity vector near the detonation front has been found useful for describing two-dimensional detonation flow with build-up.

REFERENCES

1. Charles L. Mader and B. G. Craig, "Nonsteady-State Detonations in One-Dimensional Plane, Diverging and Converging Geometries," Los Alamos Scientific Laboratory report LA-5865 (1975).
2. W. C. Davis, B. G. Craig, and J. B. Ramsay, "Failure of the Chapman-Jouguet Theory for Liquid and Solid Explosives," Phys. Fluids 8, 2169 (1965).
3. Charles L. Mader, "Detonation Induced Two-Dimensional Flows," Acta Astronaut. 1, 363 (1974).
4. Charles L. Mader, "One- and Two-Dimensional Flow Calculations of the Reaction Zones of Ideal Gas, Nitromethane, and Liquid TNT Detonations," in Twelfth Int. Symp. on Combustion, (The Williams and Wilkins Company, Baltimore, MD, 1968), p. 701.
5. Charles L. Mader, "Detonation Properties of Condensed Explosives Computed Using the Becker-Kistiakowsky-Wilson Equation of State," Los Alamos Scientific Laboratory report LA-2900 (February 1963).
6. Wildon Fickett, "Detonation Properties of Condensed Explosives Calculated With an Equation of State Based on Intermolecular Potentials," Los Alamos Scientific Laboratory report LA-2712 (1962).
7. M. J. Urizar, E. James, Jr., and L. C. Smith, "Detonation Velocity of Pressed TNT," Phys. Fluids 4, 262 (1961).

TABLE I

9404 BKW FIXED COMPOSITION

Moles	D(m/s)	P(kbars)	T(°K)	γ	Q(kcal/g)
$C_{graphite}/C_{gas}$					
2.35/0.0	8897	363	2468	3.02	1.03
2.0/0.35	8921	357	2017	3.10	0.83
1.7/0.65	8940	351	1660	3.19	0.65
1.4/0.95	8953	342	1328	3.32	0.48
1.15/1.2	8951	332	1075	3.45	0.34
0.95/1.4	8891	322	889	3.57	0.23
0.85/1.5	8917	315	804	3.64	0.17
0.60/1.75	8841	297	613	3.85	0.025
$C_{graphite}/C_{2\ gas}$					
2.35/0	8897	363	2468	3.02	1.03
1.85/0.25	8902	356	2032	3.10	0.84
1.35/0.50	8909	347	1626	3.22	0.51
0.85/0.75	8911	334	1249	3.38	0.47
0.35/1.0	8891	318	912	3.58	0.29
0.15/1.1	8869	3.09	793	3.68	0.21
$C_{graphite}/C_{5\ gas}$					
2.35/0	8897	363	2468	3.02	1.03
1.5/0.170	8855	354	2165	3.08	0.85
1.0/0.27	8831	349	1935	3.12	0.82
0.5/0.37	8808	342	1828	3.18	0.75
0.0/0.47	8785	336	1667	3.23	0.68

TABLE II

9404 LJD FIXED COMPOSITION

Moles	D(m/s)	P(kbars)	T(°K)	γ
$C_{graphite}/C_{gas}$				
2.35/0.0	8975	341	4148	2.93
2.0/0.35	8915	330	3685	3.03
1.7/0.65	8848	319	3279	3.52
1.4/0.95	8767	307	2864	3.61
0.95/1.4	8611	287	2222	3.76

TABLE III

9404 INFINITE GEOMETRY BKW PARAMETERS

Moles	D(m/s)	P(kbars)	T(°K)	γ
$C_{graphite}/C_{2\ gas}$				
2.35/0.0	8878	389	1415	2.73
2.0/0.35	8977	385	1065	2.86
1.4/0.95	9113	370	631	3.14
1.15/1.20	9131	359	509	3.28
0.85/1.5	9099	341	392	3.48
0.60/1.75	9013	320	315	3.68
$C_{graphite}/C_{2\ gas}$				
1.85/0.25	8953	382	1077	2.86
0.85/0.75	9077	361	592	3.21
0.35/1.0	9070	343	439	3.41
0.0/1.176	9013	326	355	3.59
$C_{graphite}/C_{5\ gas}$				
1.5/0.171	8887	380	1176	2.83
1.0/0.271	8895	374	1049	2.89
0.5/0.371	8902	369	933	2.96
0.0/0.471	8908	363	827	3.03

TABLE IV

PETN BKW FIXED COMPOSITION

Moles $C_{graphite}/C_{gas}$	D(m/s)	P(kbars)	T(°K)	γ
0.95/0.0	8417	318	2832	2.94
0.50/0.45	8436	310	2217	3.06
0.0/0.95	8452	300	1607	3.21

PETN INFINITE GEOMETRY BKW PARAMETERS

Moles $C_{graphite}/C_{gas}$	D(m/s)	P(kbars)	T(°K)	γ
0.95/0.0	8383	339	1726	2.67
0.50/0.45	8492	335	1231	2.81
0.0/0.95	8605	326	798	3.02

TABLE V

TNT BKW FIXED COMPOSITION

Moles $C_{graphite}/C_{gas}$	D(m/s)	P(kbars)	T(°K)	γ
5.25/0.0	7166	209	2869	3.02
4.25/1.0	7019	183	1165	3.41
4.0/1.25	6868	165	777	3.67
(ρ = 1.55) 5.25/0.0	6830	181	3000	3.22

TNT INFINITE GEOMETRY BKW PARAMETERS

Moles $C_{graphite}/C_{gas}$	D(m/s)	P(kbars)	T(°K)	γ
5.25/0.0	7311	237	2103	2.70
4.25/1.0	7302	210	637	3.16
4.0/1.25	7142	186	408	3.50

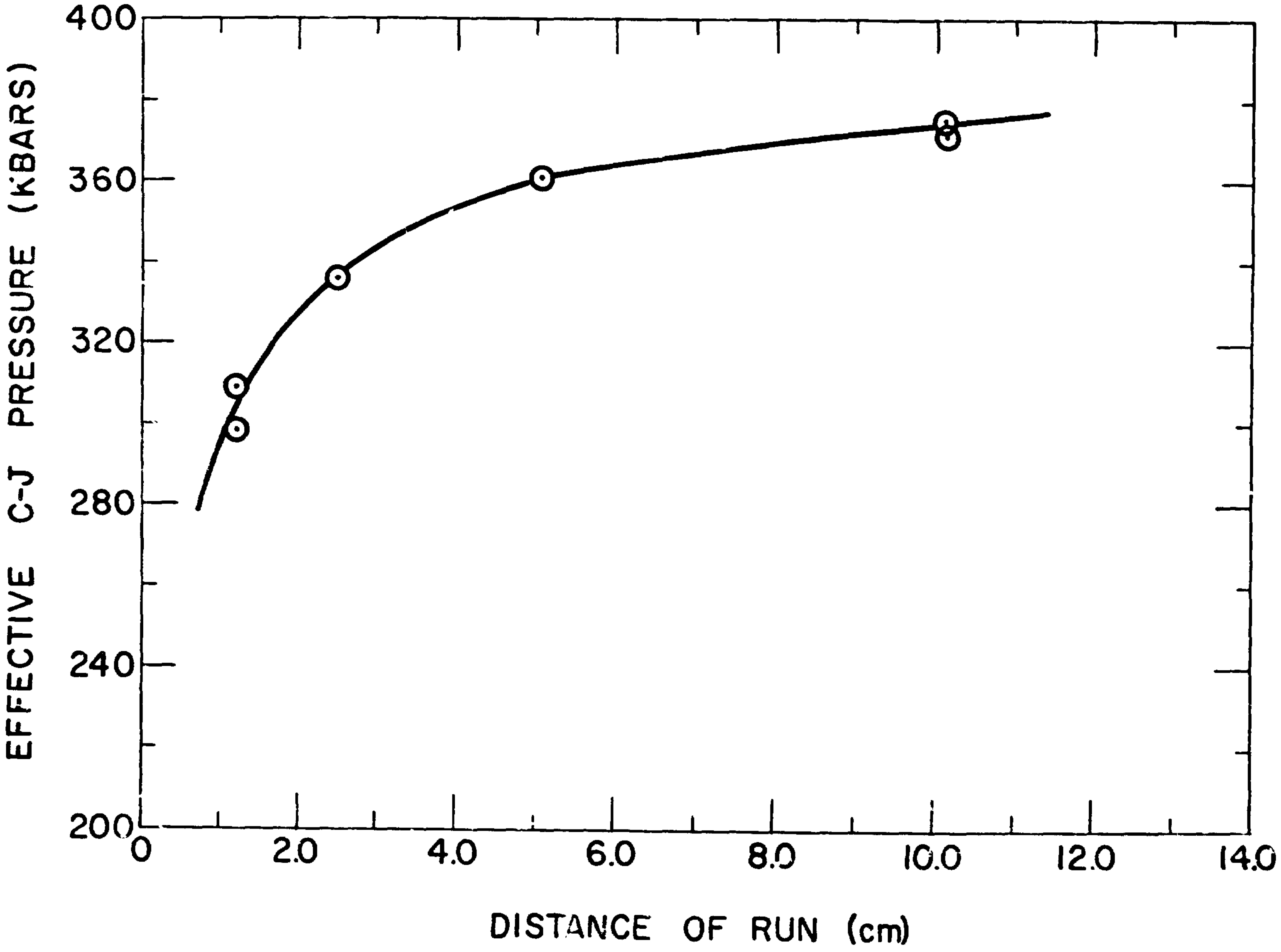

Fig. 1. Craig's experimental effective C-J pressures of 9404 vs distance of run for Baratol plane wave initiation of 9404 slabs.

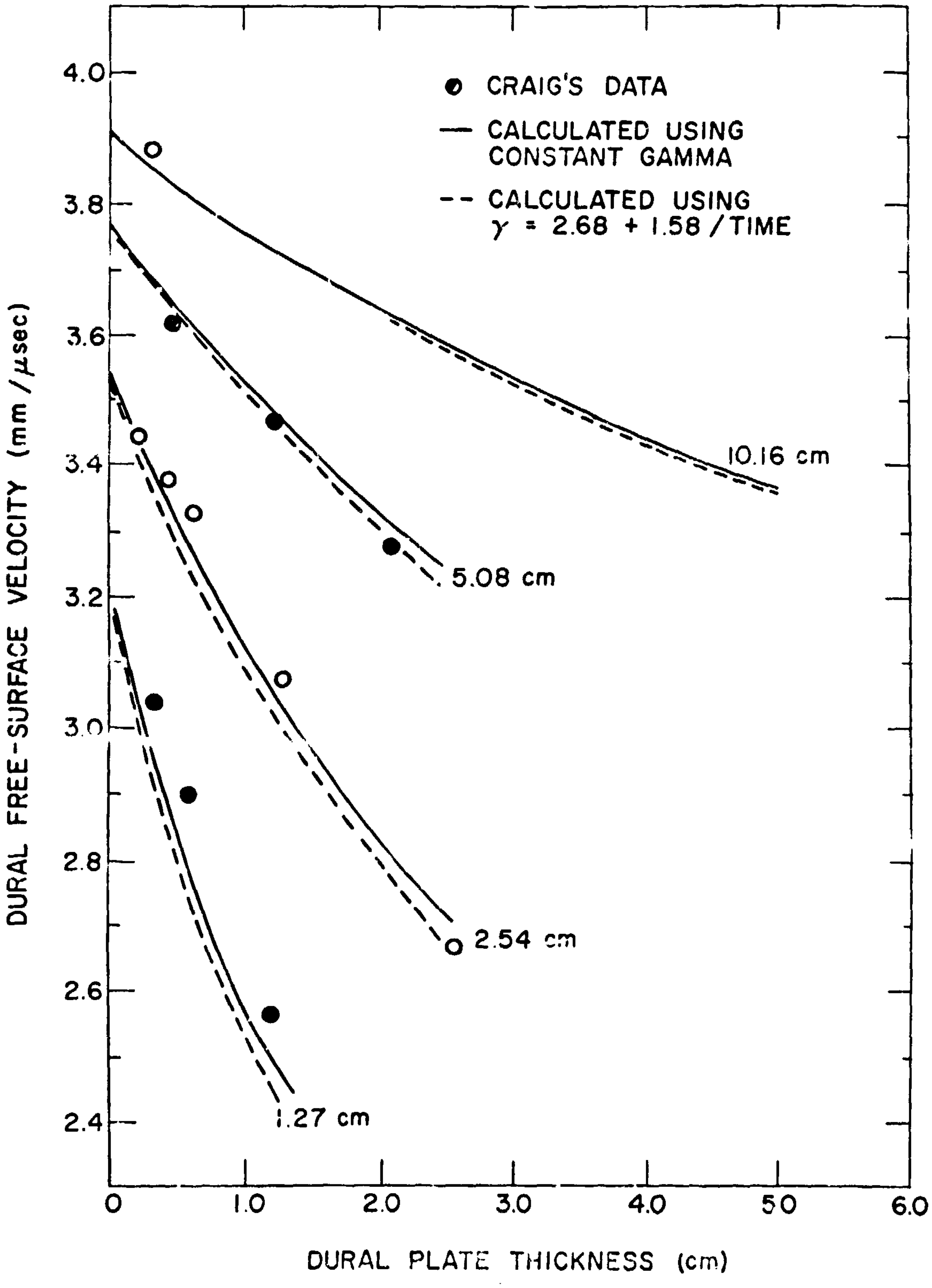

Fig. 2. Dural free-surface velocities vs Dural plate thickness for 1.27 2.54, 5.08, and 10.16 cm of 9404. Curves show Craig's data and the calculated results obtained for constant gamma Taylor waves (3.77, 3.227, 2.9536, and 2.817, respectively) and $\gamma = 2.68 + 1.38/x$ Taylor wave.

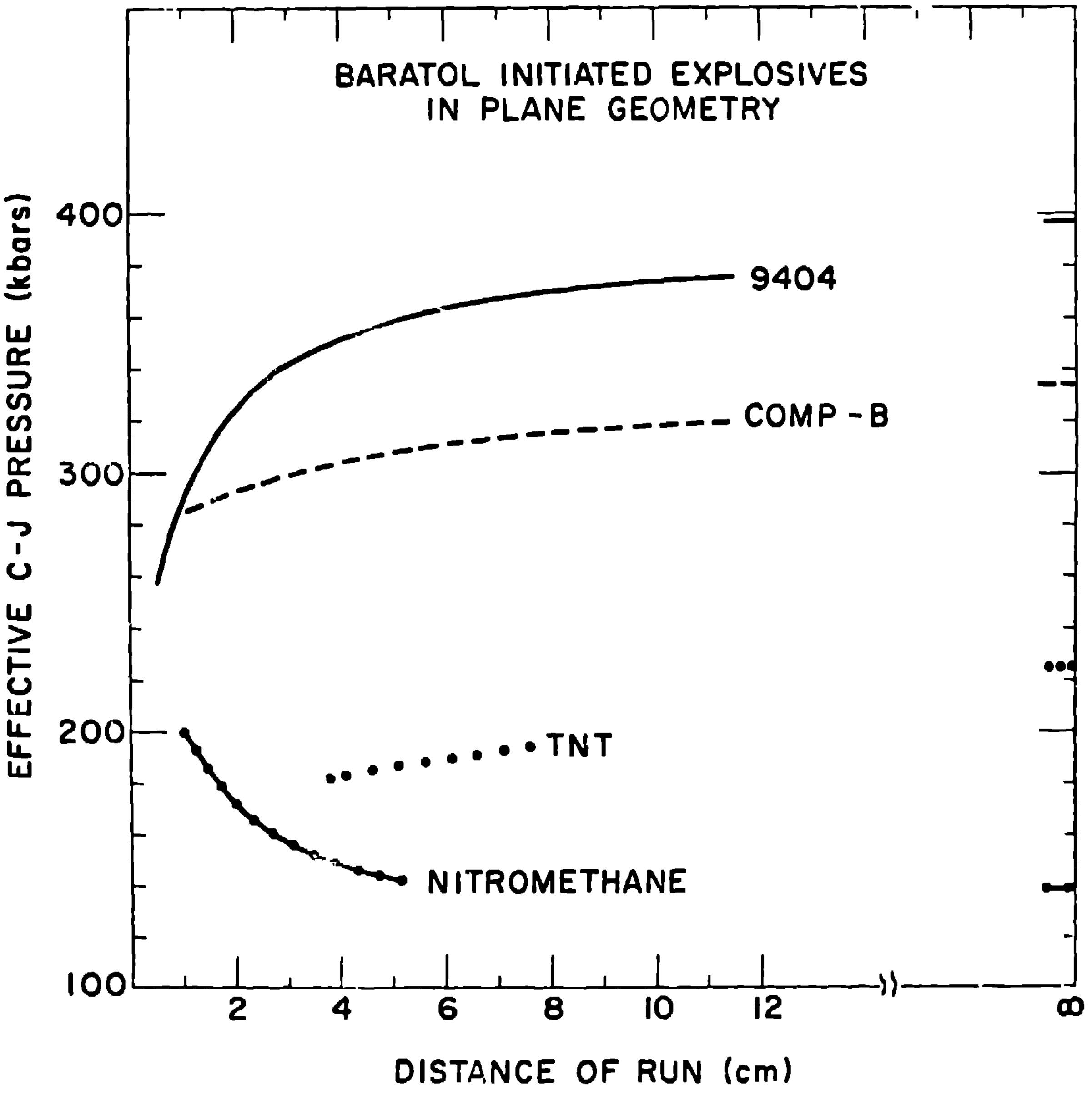

Fig. 3. Experimental effective C-J pressures of 9404, Composition B, TNT, and nitromethane initiated by a plane wave Baratol lens vs distance of run. The infinite-medium C-J pressures are shown on the right-hand side of the figure for each explosive. The nitromethane is self-overdriven and the other explosives are underdriven.

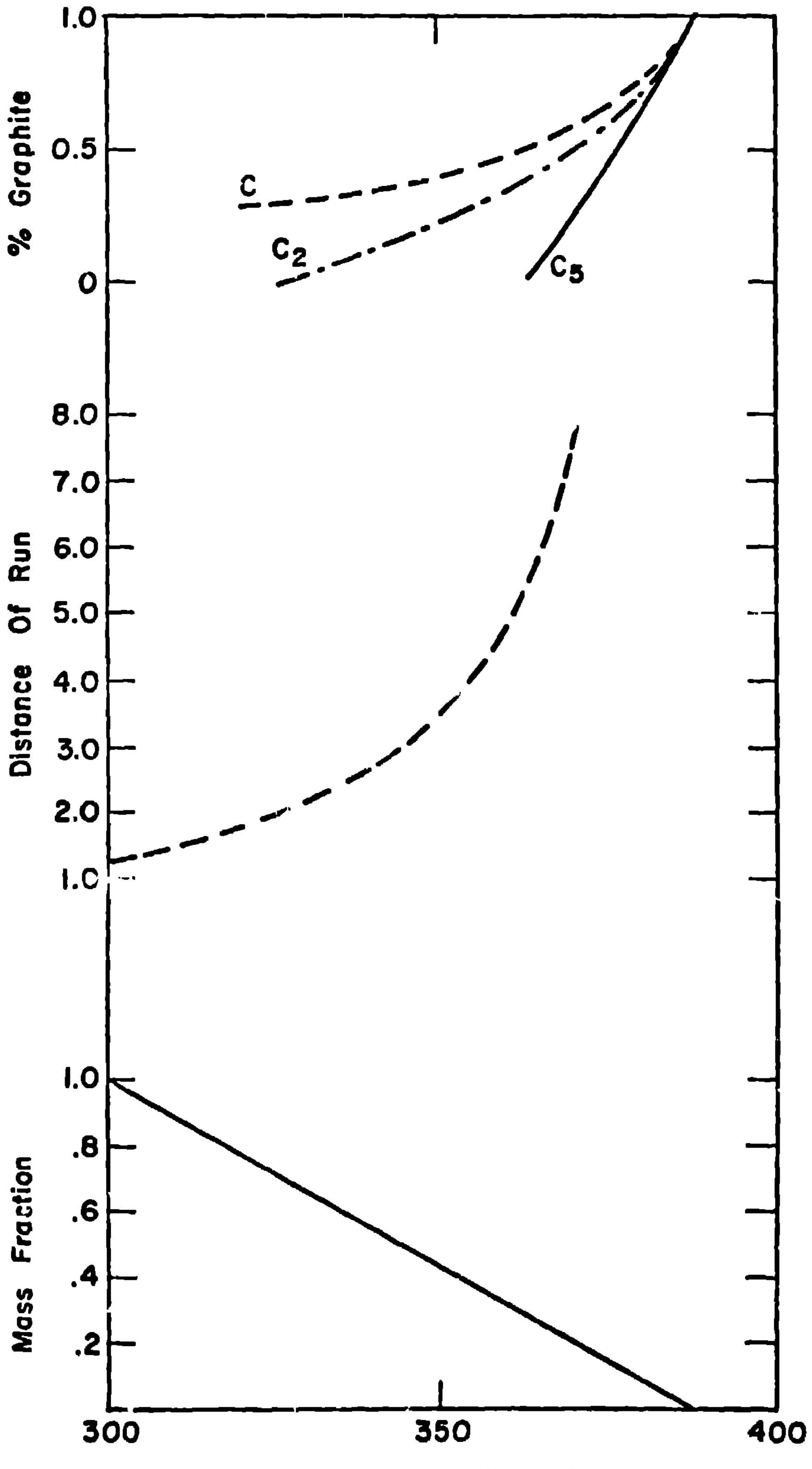

Fig. 4. The build-up of 9404 as a function of pressure. The percent of carbon present as graphite for various carbon gas/graphite compositions is shown as a function of pressure.