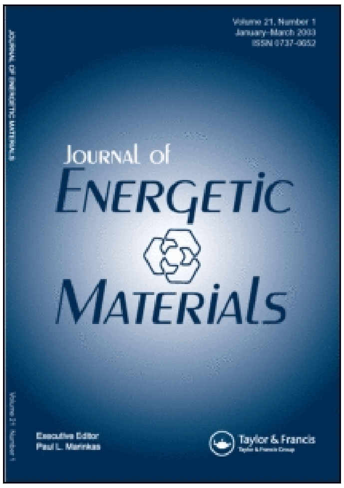

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DETONATION FAILURE DIAMETERS AND DETONATION VELOCITIES OF NITRIC ACID, ACETIC ACID AND WATER MIXTURES

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ABSTRACT

Detonation failure experiments and detonation velocity measurements were carried out with homogeneous liquid compositions of nitric acid , acetic acid and water contained in steel tubes with different diameters. The criterion for failure or propagation of detonation was based upon the type of damage exhibited by the tubes after the experiments. Mixtures with the same critical diameter were determined by varying the composition in experiments performed in a set of tubes with the same diameter. These results were used to construct iso-critical diameter curves in the ternary diagram of the system of mixtures. The critical diameters were found to be strongly dependent on the mass fraction of water and the equivalence ratio. The detonation velocity measurements were performed on some oxygen - balanced mixtures contained in tubes with different diameters. The Detonation Velocities versus the Inverse of Tube Diameter curves were found to be linear, their slopes increasing with the mass fraction of water. The detonation velocities were found to be in the range 6000-6400 m/s.

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1. INTRODUCTION

Sensitivity tests are performed to establish sensitivity scales for explosives in order to assess their behaviour in hazardous situations that may occur in practice. Each type of test defines a particular sensitivity scale for a particular type of excitation. This approch however does not in general give a unique sensitivity scale because explosives can respond differently to different types of excitation.

Accordingly, the assessment of an explosive's potential hazard is a difficult task that requires either the performance of a large number of tests or the knowledge of the most probable hazardous environment. The detonation risk, for example, is often determined by means of shock wave sensitivity tests. (Card-Gap Test, ...).

Price(1) however suggested that a complete assessment of the shock sensitivity of an explosive substance should be based not only on the thresholds for shock initiation of detonation under transient conditions but also on the threshold for propagation of self-sustaining high-velocity detonation (H.V.D.). The latter threshold is the H.V.D. critical diameter and is defined as the value of the diameter of an explosive charge below which no self-sustaining H.V.D. detonation can propagate. Campbell et al.(2) and Kurbangalina(3) also report that this critical diameter may, to a certain extent, be associated with the sensitivity of an explosive substance.

As a matter of fact, a number of liquid explosives are known to undergo a high- velocity detonation regime and a low-velocity detonation (L.V.D.) regime. In laboratory experiments, H.V.D. are commonly generated by using a strong-shock initiation device. L.V.D. are more difficult to obtain. It is usually admitted that the latter regime may be observed if the initiation device generates a mild-to-low-strength excitation(4,5), if the confinement of the explosive is sufficiently thick(5) and if the sound speed in this confinement is greater than that of the explosive in its initial (unshocked) state(6).

At least for homogeneous liquid explosives, the validity of the shock sensitivity-H.V.D. critical diameter association is strenghtened by the works of Walker(7) and Engelke(8). These works deal with chemical sensitization of liquid nitromethane by the addition of the liquid organic base di-ethylene tri-amine (DETA). Walker studied the shock initiation of these mixtures and Engelke studied their self-sustaining detonation properties. Comparison of their results shows a parallel decrease of chemical reaction induction delays and of H.V.D. critical diameters with the increase of DETA concentration in nitromethane, that is with the increase of the shock-sensitivity of the mixtures.

Consequently, the approach in the present work was to base a scale for assessing potential hazards of mixtures of nitric acid, acetic acid and water (Table 1) on experimentally determined values of their H.V.D. critical diameters. This approach, which strictly speaking is more a detonability test than a sensitivity test, is therefore tantamount to assuming that, under the same strong-shock initiation conditions, an explosive mixture with a given critical diameter is more sensitive than an explosive mixture with a bigger critical diameter. Contrary to usual sensitivity tests, this approach is also directly applicable to safety in chemical industrial processes because a fortuitously initiated H.V.D. cannot propagate in a pipe whose diameter is lower than the associated critical diameter of the mixture enclosed in it. However, in an industrial environment, low-velocity detonations are more likely to occur than high-velocity detonations. In this paper, the method used to determine H.V.D. critical diameters and the results obtained with it are presented.

It is important to emphasize that the H.V.D. critical diameter of a given homogeneous liquid explosive depends upon the nature and the thickness of the confinement of this explosive(3,9). Under sufficiently strong conditions of confinement, an explosive mixture which is undetonable in a given diameter tube can be detonated in a smaller or same diameter one, the walls of which are thicker. Conversely, and under similar conditions of confinement, an explosive mixture which can be detonated in a given diameter tube can be undetonable in a bigger or same diameter one, the walls of which are thinner.

As part of an additional work(10) aiming to characterize other detonation properties of those mixtures, experiments were performed to measure detonation velocity as a function of tube diameter for some oxygen-balanced compositions. The results of these measurements are also presented.

TABLE 1. Properties of the Components

Coumpound	Nitric Acid	Acetic Acid	Water
Chemical Formula	HNO_3	$C_2H_4O_2$	H_2O
Molecular Weight (g/mole)	63.01	60.05	18.01
Specific Mass (25°c, g/cm3)	1504	1043	997
Heat of Formation (25°c, kcal/mole)	-41.5	-116.4	-68

2. THE EXPLOSIVE MIXTURES

Nitric acid is used for its highly efficient oxidising action in many industrial chemical processes such as the manufacture of textiles, fertilizers and explosives. It was also used as an oxidising agent in rocket fuels. Nitric acid is a good solvent for many organic compounds. Accordingly, when combined with organic fuels, it often yields potentially explosive mixtures because the latter contain molecular combinations of both a fuel and an oxydizer. Such mixtures were even once considered as intentional explosives.

Mixtures of nitric acid and 2-nitropropane(11), of nitric acid, nitrobenzene and water(12) and of nitric acid, acetic anhydride and water(13) are known to detonate and Kurbangalina(3) has measured detonation velocities and critical diameters of mixtures of nitric acid with various fuels. It is thus important to assess the sensitivity of mixtures of nitric acid, acetic acid and water because these mixtures are used in the chemical industry. One way to prevent detonation hazards is to dilute these mixtures with water, but this dilution significantly reduces the efficiency of the industrial processes. Prior to any attempt to improve this efficiency, by reducing the dilution, a study to assess the potential hazards of the less diluted mixtures has to be conducted. For the reasons given in the Introduction (§ 1), H.V.D. critical diameters were measured to assess the sensitivity of these mixtures.

In preparing the explosive mixtures, their components were weighed out with an accuracy of 0.01g. The smallest mass of a component in any mixture was always greater than 5 g. In order to avoid thermal runaways and partial decompositions of the mixtures, the components were mixed in an open vessel immersed into a 10 C fixed temperature water bath. A suction fan ensured removal of nitrous vapors. The temperature of the mixtures when the shot was fired was

25 C± 1 C. The time interval between the end of preparation of a mixture and the firing of the shot was always lower than 5 mn so as to prevent possible aging effects on the result of the test.

3. PROCEDURE TO DEFINE THE DETONABLITY LIMITS

The procedure to define the detonability limits consisted of sets of detonability experiments performed in sets of tubes with the same diameter. The criterion for failure of detonation was based upon the type of damage exhibited by the recovered confining tubes. The tubes were set up vertically and partially filled : the mixture level was located about 1 cm below the top of the tube. A shock initiation device was attached to the bottom of the tube (Fig. 1).

When the detonation propagated, the part of the tube adjacent to the explosive was completely destroyed and the other part was left intact. The final separation between the two parts occured when the detonation wave reached the upper end of the explosive column and showed a clean cut (Fig. 2-a). On the other hand, when the detonation failed to propagate, a part of the explosive column was left unreacted. The piece of tube adjacent to the latter was recovered after the shot and was observed not to be as cleanly cut as when the detonation propagated : The separation exhibited shreds akin to that caused by high static pressure damages (Fig. 2-b).

In order that this procedure may be considered valid, it was necessary to ensure that the induced shock was strong enough to induce a strong detonation regime and to choose tubes long enough to allow this regime to slow down to the self-sustaining H.V.D. detonation regime. This was suggested after considering work by Campbell et al.(14), who studied the shock initiation of detonation in homogeneous liquid explosives, and work by Desbordes et al.(15), who studied the critical diameter for strong detonation. Campbell's work shows that the self-sustaining detonation regime is reached after a strong time-decreasing detonation regime running over a distance usually estimated to be 3 to 5 times the tube diameter. Desbordes's work shows that the stronger the detonation regime, the lower the critical diameter.

The strength of the induced shock was estimated in a control experiment using the inert liquid chloroform, that has a density of the same order as the density of our mixtures : the length of the destroyed part of the tube was then observed to be much shorter than the length of the destroyed part of all tubes filled up with explosive mixtures that did not detonate. It was concluded from these observations that the shock initiation device always generated shocks strong enough to induce a strong detonation regime in all the tested mixtures.

In order to minimize the number of test shots, it was decided to find compositions with the same critical diameter instead of finding the critical diameter of a given composition. The detonation test tubes had internal diameters of 6 mm, 11 mm, 21 mm and 31 mm. The 31 mm i.d. tubes were 400 mm long, and the others were 300 mm long. Therefore, all the tubes were assumed to be long enough to allow the strong detonation regime to slow down to the self-sustaining regime.

Because of the highly corrosive nature of nitric acid, stainless steel tubes were chosen. The wall thickness was 2 mm for all tubes. The experimental set up (Fig. 1) consisted of the steel detonation test tube and a P.V.C. tube containing the high explosive donor charge (FORMEX = 87% pentrite, 13% binding agents). The steel tube and P.V.C. tube were coaxial and were separated by a 1 mm thick plexiglas gap. The internal diameter of the P.V.C. tube was always chosen to be much greater than the external diameter of the steel tube to ensure as plane a shock-induced initiation as possible .

4. PRINCIPLE OF DETONATION VELOCITY MEASUREMENTS

Mean detonation velocities of some oxygen-balanced compositions were obtained as a function of the tube diameters by measuring the time taken for the detonation to travel a given distance along a generatrix of the tubes. The sizes of the tubes and the initiation devices were the same as in detonability experiments.

Short-circuit contact gauges were set up in 0.4 mm depth circular grooves that were machine-tooled on the outer surface of the 2 mm-thick-test-tube walls. As the detonation wave passed, each gauge generated a signal used to trigger or to stop a THOMSON TSN 630-10 electronic chronometer (accuracy ± 5 ns). Three gauges were set up on each tube, thus defining two 10 cm ± 0.02 mm long measurement bases. The order of magnitude of the measured time intervals then yields a 0.2% accuracy on the velocities. The velocity difference between two measurement bases was always found to be lower than the experimental accuracy.

5. RESULTS AND DISCUSSION

The boundaries of the detonability domains were determined by varying the proportions of the components and by marking the closest compositions that did or did not detonate in a fixed diameter tube.

These results are summarized in Figure 3 as a set of iso-critical diameter curves in the ternary diagram of the system. Each curve separates the diagram into two parts. One is associated with detonating mixtures and lies on the concave side of the curve, and the other is associated with non-detonating mixtures.

On the basis of the critical diameter, the most sensitive mixture appears to be the non-diluted oxygen-balanced mixture. Starting from the point in the diagram representing the latter mixture, the sensitivity decreases in all directions. Similar comments were made by Mason et al.(12) for mixtures of nitric acid, nitrobenzene and water, that were tested by using the classical card gap test, and also by Dubar et al.(13) for mixtures of nitric acid, acetic anhydride and water, that were tested by using different masses of a same donor explosive.

Variations of critical diameter with water concentration in oxygen-balanced mixtures and with equivalence ratio in non diluted mixtures were then inferred from the diagram and are presented in Figure 4 and Figure 5.

Figure 4 shows a marked increase of critical diameter with water concentration. These results cannot be extrapolated to find the dilution of mixtures that would have critical diameters of the same order as the diameters of the industrial process reactors (1 meter). They tend to show however, that high water concentrations are not necessary to obtain large values of critical diameter. Additional shots aiming to determine mixture dilutions for critical diameters ranging from 50 to 100 mm should confirm this hypothesis.

The curve in Figure 5 is similar to flammability limit curves for hydrocarbon gaseous mixtures and has a minimum located at the oxygen-balanced mixture point (equivalence ratio = 1). At this point, the extrapolated value of the critical diameter is very small (1 mm). This result seems to indicate that the non-diluted oxygen-balanced mixture composition is quite unstable.

Detonation velocities of some oxygen-balanced mixtures are plotted as a function of the inverse of the charge diameter in Figure 6.

These plots show a linear decrease of the velocity with an increase of the inverse diameter. This behavior is characteristic of liquid homogeneous explosives(16) and therefore suggests that homogeneous bulk kinetics can be used to model the chemical decomposition process in the reaction zone.

Also, the absolute value of the slope of these plots increases with water concentration. This result tends to support the idea that the critical diameter may be a good criterion for assessing the shock sensitivity of homogeneous liquid explosives. Indeed, the most sensitive liquid explosive mixtures are thought to have the smallest detonation velocity variations.

The grooves that were machine-tooled on the outer surface of the detonation test-tube create local variations in the thickness of the confinement. In this work, the detonation velocity measurements were assumed not to be influenced by the latter variations because the approximate time taken for an acoustic perturbation to travel from the inner surface of the tube to the bottom of the groove was estimated to be much greater than total reaction times of typical homogeneous liquid explosives.

6. CONCLUSIONS

The experimental results presented in this paper demonstrate that homogeneous liquid mixtures of nitric acid, acetic acid and water can support self-sustaining H.V.D. detonations. These mixtures belong to the wide class of nitric solutions used in many important industrial nitration processes.

H.V.D. critical diameters were determined, to define the detonability limits of these mixtures, and they were found to be very dependent on water dilution and equivalence ratio. The results presented here emphasize that the possible explosive hazards of these mixtures should always be borne in mind and also that H.V.D. detonation propagation risks in these media may be avoided by choosing pipes or reactors with diameters lower than the H.V.D. critical diameters of the mixtures.

Finally, it is important to stress again that the H.V.D. critical diameter of a given homogeneous liquid explosive depends upon the nature and the thickness of the confinement(3,9) and also upon the initial temperature of this explosive(2). Here, these parameters were kept the sames (see § 3, Procedure) and the results of the detonability experiments presented in § 5, Results, cannot be used for evaluating the H.V.D. critical diameters of the mixtures under different conditions of confinement or initial temperature. The influence of these parameters on this critical diameter can, at the present time, be determined only by detonability experiments similar to the ones used in the work presented in this paper.

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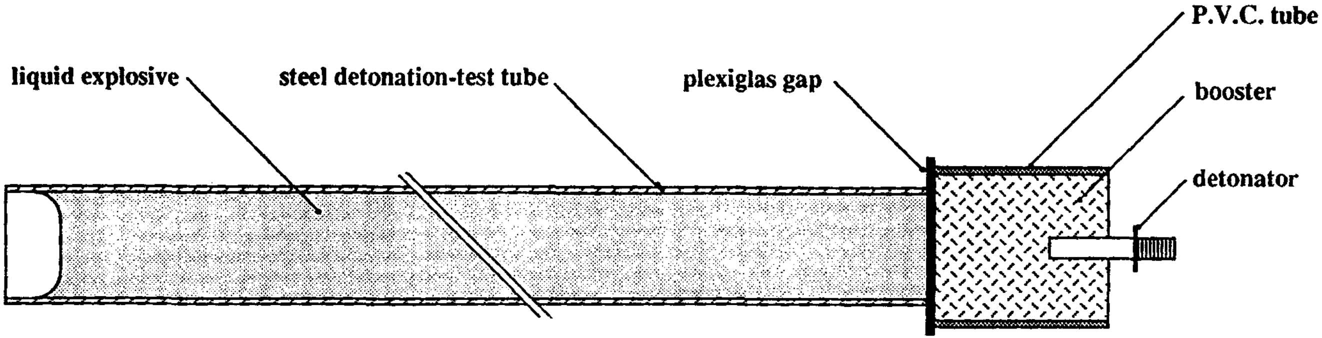
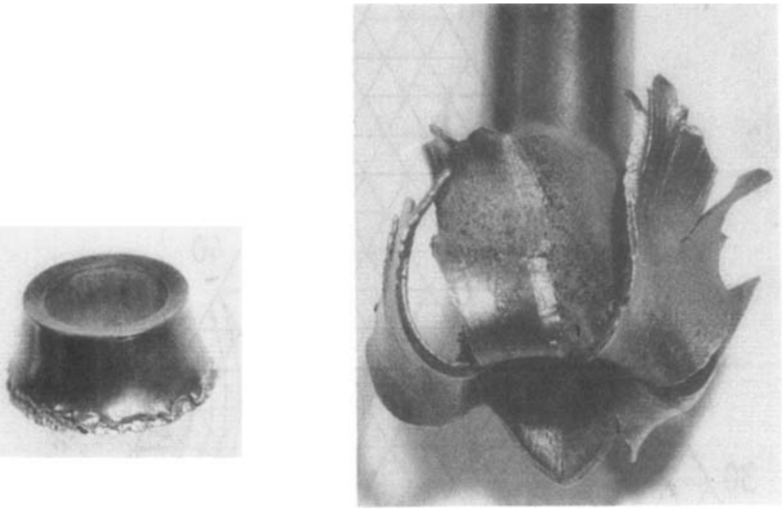


FIGURE 1. Scheme of The Detonation-Test Tube.



-a- -b-

FIGURE 2. The Detonation Test-Tube After The Shot.
-a- Propagation of Detonation
-b- Failure of Detonation

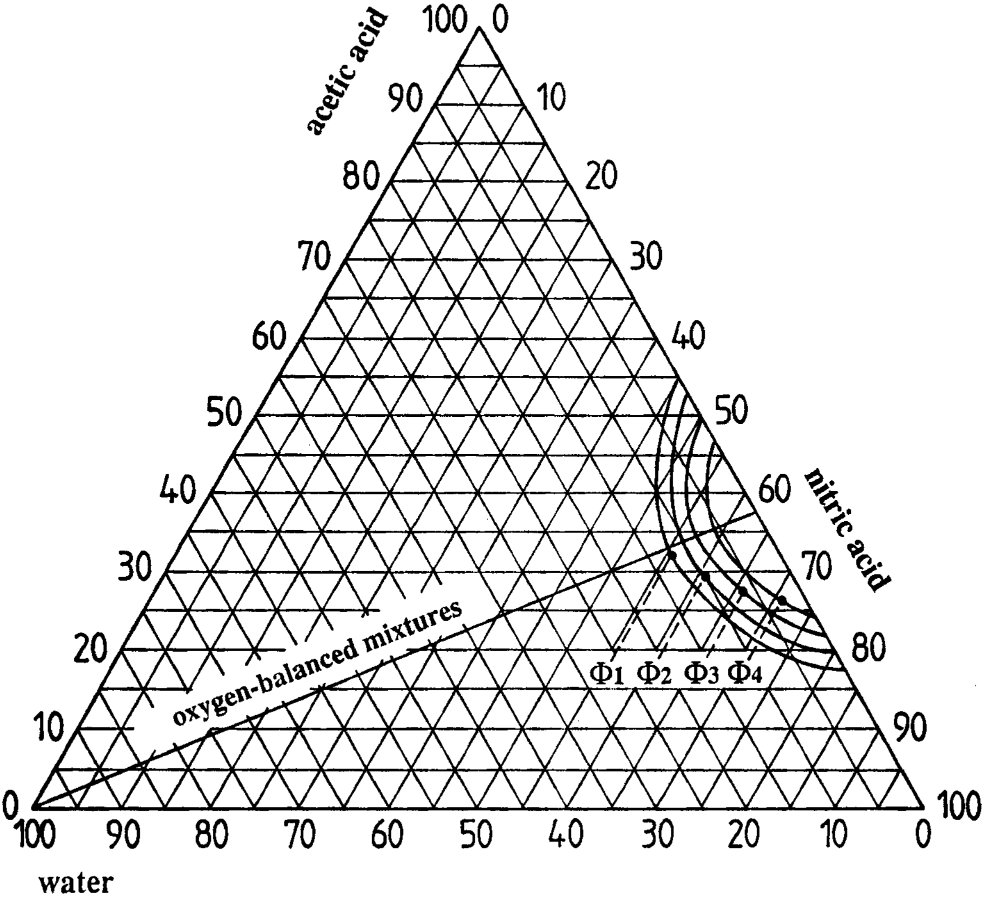


FIGURE 3. Iso-Critical Diameter Curves at 25°c
In Steel Tubes With a 2 mm Wall Thickness.
Coordinates are Mass Fractions.
Φ_1 = 6 mm, Φ_2 = 11 mm
Φ_3 = 21 mm, Φ_4 = 31 mm

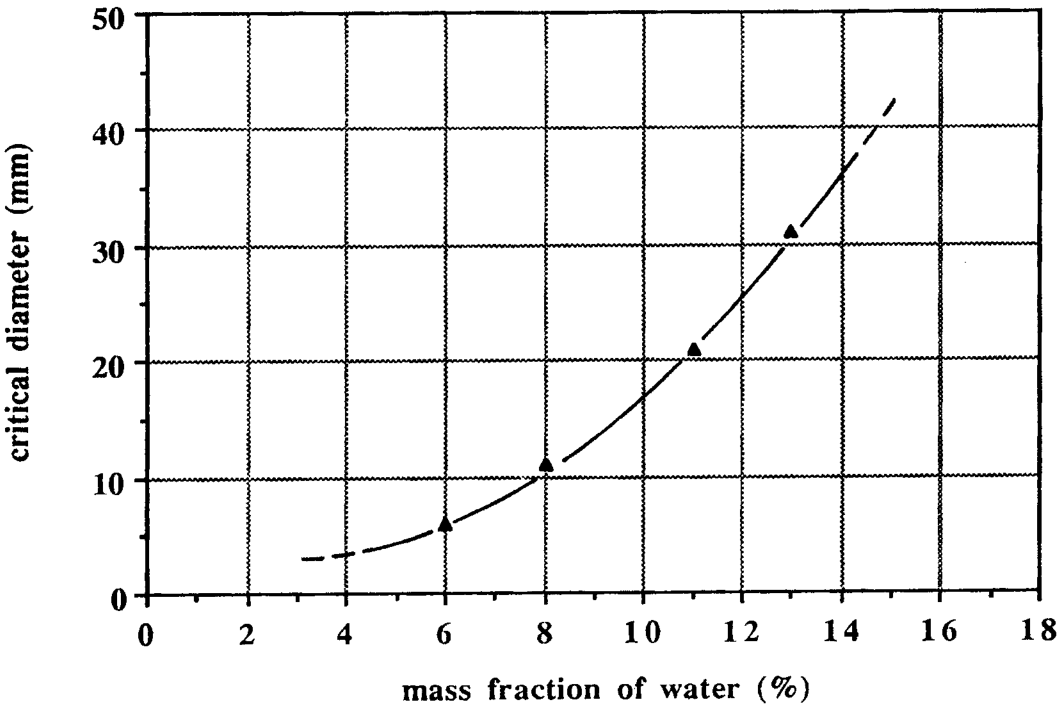


FIGURE 4. Critical Diameter of Oxygen-balanced Mixtures as Function of Their Mass Fraction of Water.

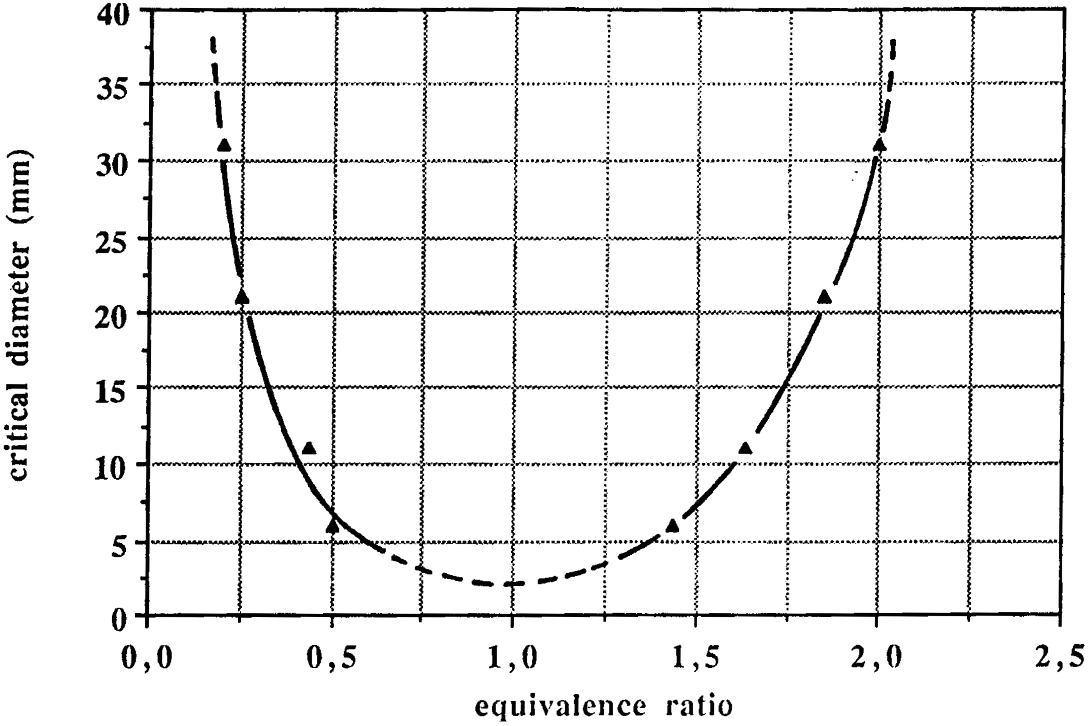


FIGURE 5. Critical Diameter of Non-Diluted Mixtures as Function of Their Equivalence Ratio.

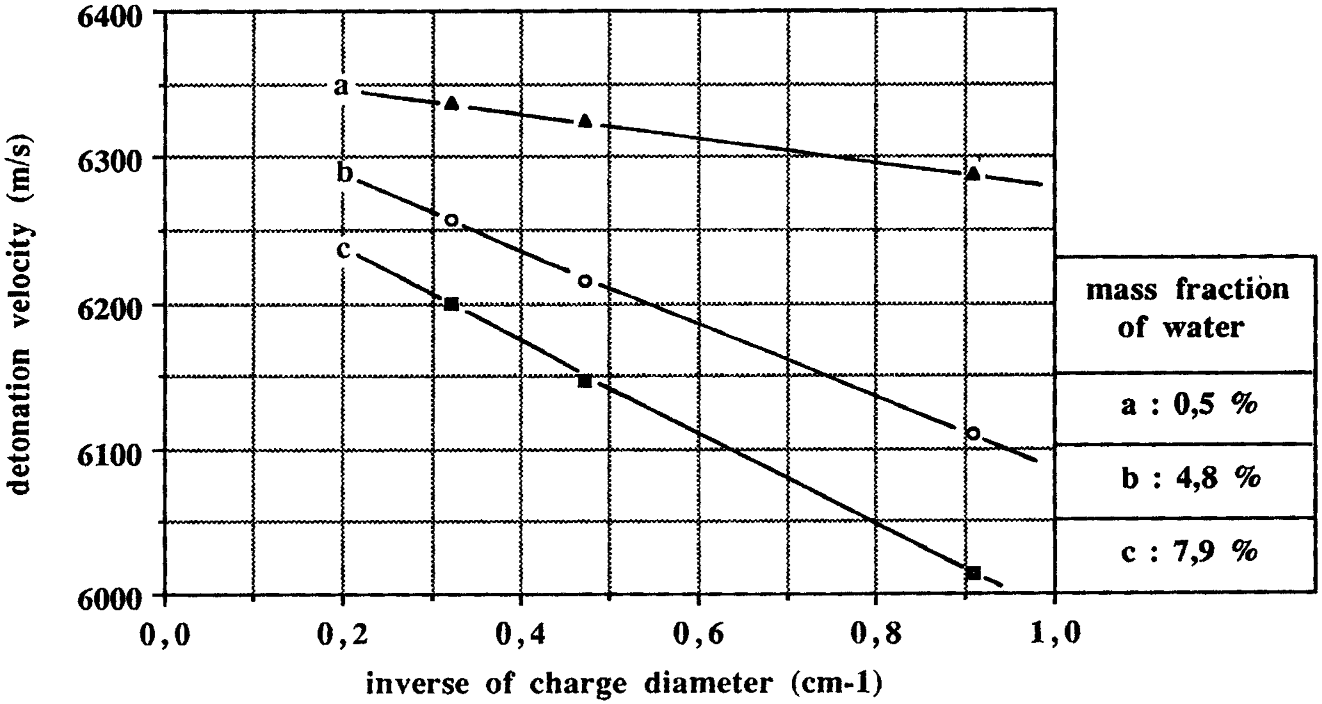


FIGURE 6. Detonation Velocity of Oxygen-Balanced Mixtures as Function ofTheir Mass Fraction of Water.