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Secondary reactions and detonation hazards in the production of adipic acid

J.L. Gustin [a,*], P. Vidal [b]

[a] *Rhone-Poulenc Industrialisation, 24 av. Jean Jaurès, 69151 Decines, France*
[b] *Laboratoire d'Energétique et de Détonique, ENSMA-Rue Guillaume VII, 86034, Poitiers, France*

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Abstract

Solutions of organic diacids in nitric acid are processed in the manufacture of adipic acid, a Nylon intermediate. In these solutions, a secondary reaction can be initiated where the controlling reactants are the nitrogen oxides produced by the reaction itself. As the reaction takes place in a sealed vessel, the nitrogen oxides produced pressurize the vessel causing the reaction to speed up. Depending on the proportions of nitric acid, organic diacids and water, the reaction can be more or less violent, i.e. slow reaction, deflagration or detonation.

The slow reaction was investigated by considering two separate contributions: the exotherm, measured by DSC/DTA experiments, and the non-condensable gas production, measured in sealed Dewar flasks and autoclave experiments.

The deflagrating behaviour of the reaction was investigated using autoclave experiments in which the rate of pressure increase is allowed to reach around 10 000 bar s^{-1}. The sensitivity to detonation was investigated using a detonation test tube. The critical diameter, detonation velocity and curvature of the shock front were measured as a function of the solution composition.

Following the DIERS recommendations, a vent-sizing method is proposed for rupture discs to prevent explosion of pipes containing nitric acid solutions of organic diacids.

This experimental information helps in understanding the explosion hazard in adipic acid manufacture and provides a valuable basis for recommendations for safe handling of nitric acid solutions of organic diacids.

1. INTRODUCTION

Solutions of organic diacids (adipic, glutaric, succinic, oxalic) in nitric acid are processed in the manufacture of adipic acid, a Nylon intermediate. In all parts of the process where nitric acid solutions of diacids are present, nitrogen oxides NO, NO_2, N_2O and other decomposition gases, CO, CO_2, are evolved from the liquid solutions at the process temperature. Even at

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[*] Corresponding author.

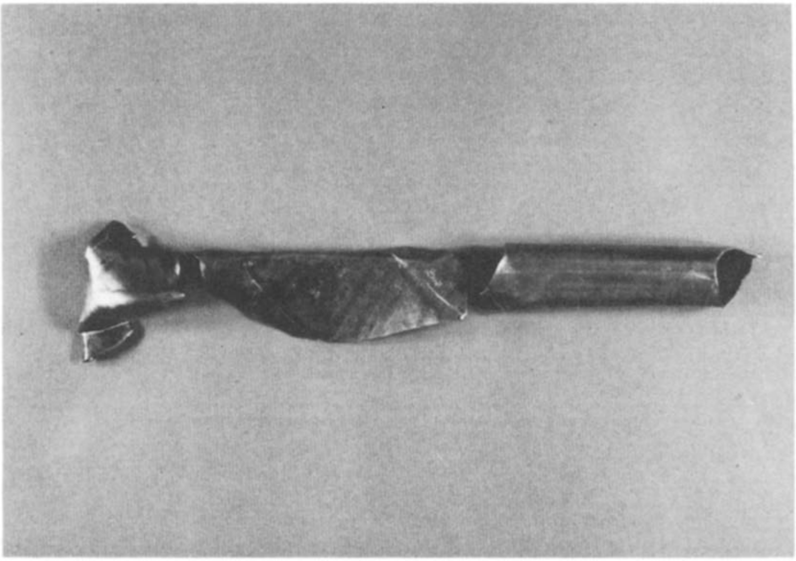

Fig. 1. Pieces of a stainless steel pipe in which nitric solutions of organic diacids had been inadvertently sealed.

ambient temperature, samples enclosed in a bottle will pressurize dangerously and possibly damage the cap or explode. In process plants, the presence of nitric solutions of diacids enclosed in a vessel with no vent is a hazard. This situation mostly occurs in pipes with valves closed at both ends, due to poor design, or in the inner volumes of valves, if any exist. Pressurization can also occur in a larger process vessel if all exits have been closed.

The pressurization produced by nitric oxidation of the diacids can exceed the pressure resistance of these pipes, in which case they explode. When such accidents have occurred there has been evidence of a fast propagating reaction. In several cases, it was observed that pipes were ruptured transversally into several pieces 10 cm in length, see Fig. 1. The same rupture pattern is also observed when cyclohexanol or cyclohexanone is inadvertently mixed with nitric solutions of diacids in a pipe. This rupture pattern was recognized as the consequence of a deflagrating decomposition.

The detonation of nitric solutions of diacids is also known [1]. This decomposition behaviour is possible for high-energy-content compositions of the nitric solutions. These compositions can be represented using a triangular diagram in which the corners represent nitric acid, organic diacid and water.

The energy content of the solution can be calculated using the CHETAH program. The high potential energy compositions are obtained for stoichiometric mixtures of nitric acid and organic diacids, for low concentrations in diluent (water).

The purpose of this paper is to describe the experimental information obtained for the slow decomposition reaction, the deflagrating decomposition, and the detonation of nitric solutions of diacids.

A method for determining the vent area required to prevent the decomposition from accelerating to a deflagration or detonation is also proposed, based on the DIERS methodology.

2. EXPERIMENTAL INVESTIGATION OF THE SLOW REACTION

The slow reaction is observed for compositions far from the oxidation reaction stoichiometry, for diluted solutions with a high cocentration in water, and for high energy compositions at ambient temperature if pressurization is not allowed.

The purpose of this paper is not to give extensive information on the variation of the slow reaction with composition, temperature and pressure, but to describe the investigation methods and to report typical results obtained.

The characteristics of the reaction can be investigated by considering two separate contributions: the heat release, and the production of non-condensable decomposition gases including NO_x.

The exotherm can be measured by DTA/DSC experiments using closed glass test cells. The heat release onset temperature is usually found at around 140–160°C with the usual onset detection sensitivity of such machines. The exotherm is Arrhenius-like near the onset temperature, i.e. the heat flux produced in a log scale is a linear function of the reciprocal of the temperature.

The heat released depends on the solution composition. Typical exotherms observed are 200 and 300 cal g^{-1}, and even 400 and 500 cal g^{-1} for high potential energy compositions, see Fig. 2. The shape of the exotherm is not that of a very fast reaction but due to the large heat release, there is a high potential for the reaction to runaway violently.

The non-condensable gas production can be investigated using isothermal themomanometry, autoclave experiments and Dewar flask experiments. The sensitivity of the detection methods depends on the duration of the experiment. A fast temperature scan, e.g. 5°C min^{-1} will give a high onset temperature for the gas production, whereas a very long exposition to a low temperature will readily show gas evolution.

A closed Dewar flask experiment is especially representative of what could happen when a nitric solution of organic diacids is enclosed in an insulated pipe. The experimental device used has been described elsewhere [2]. A 340 g sample of nitric solution of organic diacids was slowly heated in a 1-l stainless steel closed Dewar. The temperature of the furnace was set to 105°C. Owing to the weak heat transfer between the furnace and the sample, the temperature of the sample reached the set temperature after

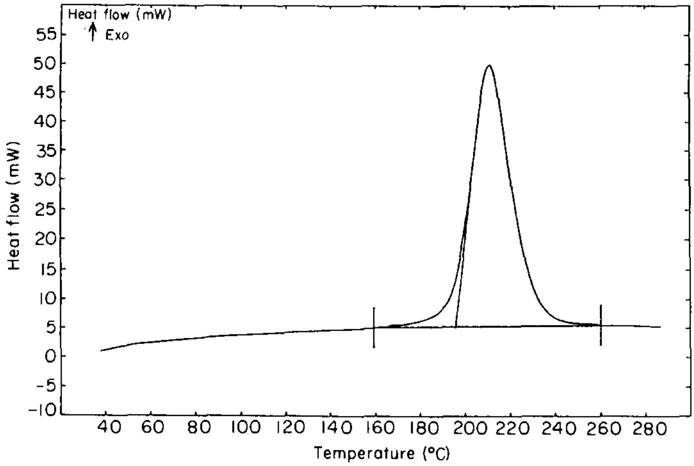

Fig. 2. DTA thermogram of a nitric solution of organic diacids measured in a closed glass cell. Heat of reaction, 820 J g^{-1}.

20 h. At that point, the heat production and the NO_x pressure allowed the reaction to runaway, see Fig. 3. A plot of the logarithm of the pressure corrected for the nitrogen pad enclosed in the Dewar flask as a function of the reciprocal temperatrure shows that above 50°C, the pressure exceeds the previously observed vapour pressure and then increases up to the pressure resistance of the Dewar flask rupture disc, above 20 bar.

Thus, the onset temperature for gas production is shown to be about 50°C, well below the exotherm onset temperature measured in DTA. The

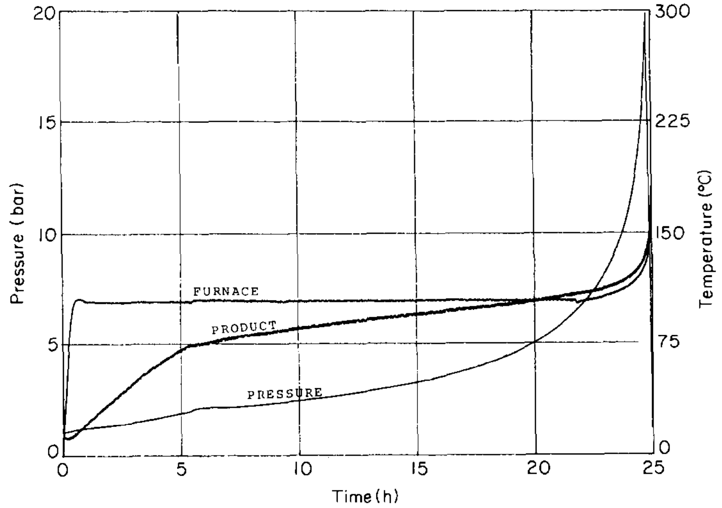

Fig. 3. Experiment on nitric solutions of organic diacids in a 1-l sealed Dewar: pressure and temperature vs. time curves.

reaction runs away mostly because of the NO_x pressurization. It is not a direct consequence of the exotherm as measured in DTA.

The nitric solutions of organic diacids can be processed safely at ambient pressure and temperatures below 100°C but there is a hazard when pressurization in allowed in a closed vessel.

3. EXPERIMENTAL INVESTIGATION OF THE DEFLAGRATION OF NITRIC SOLUTIONS OF ORGANIC DIACIDS

The evidence for a deflagrating decomposition of nitric solutions of organic diacids is obtained from the rupture pattern of pipes in which the solution has been enclosed. Multiple pipe fractures (Fig. 1) show that the reaction is propagating: rupture of the pipe in one place does not provide enough venting capacity to prevent the propagating reaction from causing similar ruptures nearby in the pipe.

The deflagrating behaviour of the nitric oxidation reaction was investigated using a method proposed by Grewer and Klaïs [3]. In this method, the decomposition reaction is initiated by a temperature scan of approx. $5°C\,min^{-1}$ on a sample enclosed in a 0.5 l Prolabo autoclave, as shown in Fig. 4. When the reaction becomes violent, a sharp pressure increase is obtained. A fast computerized data acquisition provides a follow-up of the pressure as a function of time.

A plot of the rate of pressure rise in a logarithmic scale as a function of pressure in a log scale, may show a linear variation. This is considered as proof of a deflagrating decomposition, according to Grewer and Klaïs [3]. The above result means that the rate of pressure rise is a power function of the pressure, as formerly observed by Belyaev [4] for solid propellants in combustion chambers

$$\frac{dP}{dt} \approx P^{\alpha} \qquad (1)$$

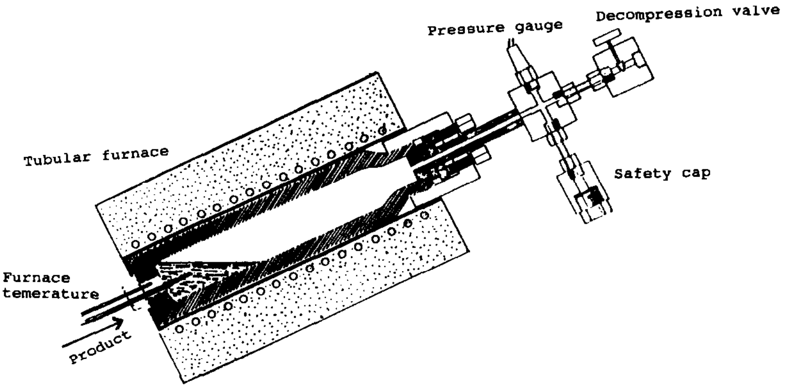

Fig. 4. Prolabo 0.5-liter autoclave used for deflagration tests.

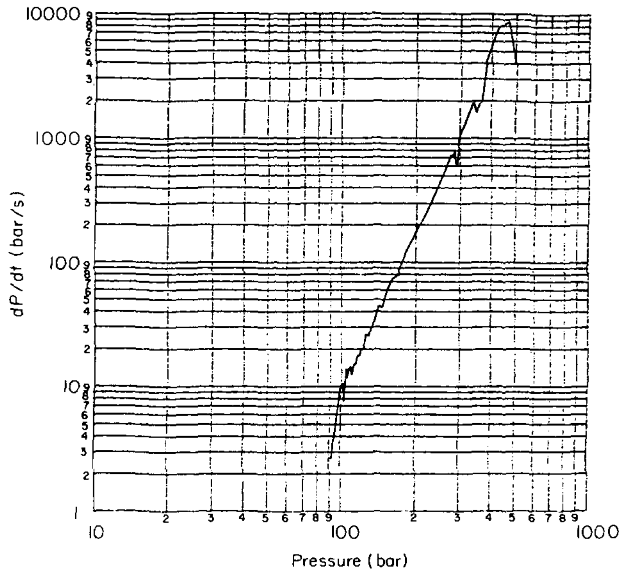

Fig. 5. Pressure rise rate as a function of pressure obtained in a 0.5-l autoclave for nitric solutions of organic diacids.

A typical result obtained for nitric solutions of organic diacids in an autocalve experiment with a filling ratio below 50% is shown in Fig. 5. Rates of pressure rise of the order of magnitude of 10 000 bar s^{-1} are obtained when the pressure is allowed to reach 400–500 bar.

Equation (1), which holds for nitric solutions of organic diacids, may also prove that the rate of reaction is influenced by the pressure of the decomposition gases including NO_x, as pointed out above. The reaction kinetics exhibits an order related to the concentration or pressure of the decomposition gases produced, when the reaction becomes fast. Thus, the reaction is autocatalytic when the pressure is allowed to build up in a vessel.

The reaction rate increases for chemical reasons (the pressure of the NO_x) rather than due to an increase in the temperature. It has been shown that the reaction is faster with stirring obtained by shaking the autocalve, and that solutions with a lower potential energy content will assume the same deflagrating behaviour if the autoclave filling ratio is increased. These results are interpreted as showing the influence of the pressure on the reaction rate through the dissolved NO_x concentration, rather than through the propagation of a reaction hot layer or flame in the unreacted medium.

Whatever the mechanism by which the deflagrating behaviour is produced, according to Grewer's method, the mechanical consequences are expected to be the same. The pipes are expected to rupture under pressures of around 250 bar, a pressure which is easily obtained if the filling ratio is close to 100%. At these pressures, the reaction is very fast and assumes a propagating behaviour causing multiple ruptures of the pipe as shown in Fig. 1.

4. EXPERIMENTAL INVESTIGATION OF THE DETONATION OF NITRIC SOLUTIONS OF ORGANIC DIACIDS

4.1. *Assessment of detonation hazard*

The possibility of a detonating decomposition of nitric solutions of organic diacids can be assessed by considering the energy content or potential energy release of solutions with a composition close to the stoichiometry, with a low concentration in water. Reference 1 demonstrated how high PEM compositions can be situated in a triangular diagram. It is considered on a thermodynamical basis, that solutions with a PEM above 700 kcal kg^{-1} contain sufficient potential decomposition energy to allow a detonation.

The experimental and theoretical data on condensed-phase detonation (solid or liquid) are not so widespread as data on gas-phase detonation.

The sensitivity of condensed materials to an ignition source for the detonation is obtained using empirical test methods more suitable for solids, namely shock sensitivity tests and friction sensitivity tests. These methods are difficult to apply to liquids. A better approach has been proposed by P. Vidal and Presles [5] whose findings are described in this section. Due to this difficult problem and in the absence of any other method to assess the detonation hazard of liquid substances, the determination of the conditions leading to the quenching of detonation is preferred to the determination of the sensitivity to an ignition source. The detonation quenching critical diameter measured in tubes filled with a liquid sample is a test characterizing the sensitivity to a shock wave.

The smaller the detonation quenching critical diameter, the higher the sensitivity of the substance to an ignition source. The sensitity of several liquid substances to an ignition source can be compared according to their detonation quenching critical diameters.

4.2. *Determination of the detonation quenching critical diameter*

The quenching critical diameter for the detonation of solutions of nitric acid, adipic acid and water, enclosed in steel tubes at ambient temperature was determined. The results were used to draw isocritical diameter tie-lines in a triangular diagram where the corners represent nitric acid, adipic acid and water. To ensure that difficulties encountered in the dissolution of adipic acid did not lead to wrong results, the same experimental technique was used to determine the detonation quenching critical diameter of nitric solutions of acetic acid which is already known in the literature [6].

In the experimental technique used, the critical conditions of propagation of the detonation are reached from strong detonation conditions initiated by a primary explosive.

4.2.1. *Experimental set-up*

The liquid samples were enclosed in steel tubes of 6, 11, 21 and 31 mm inner diameter. The tube wall thickness was 2 mm. The tube length was 300 mm for 6, 11 and 21 mm i.d. tubes and 400 mm for 31 mm i.d. tubes. The detonation is assumed to be self-sustained at a distance of three times the diameter from the ignition source. the tubes are placed in a vertical position. The detonation travels from the bottom to the top.

4.2.2. *Results obtained*

The results obtained for adipic acid and acetic acid are given in trinagular diagrams, see Figs. 6 and 7. The compositions for which the critical diameters were determined are shown together with isocritical diameter tie lines.

As expected, the undiluted stochiometric mixture are the most sensitive. Figures 8 and 9 show the influence of dilution with water and mixture

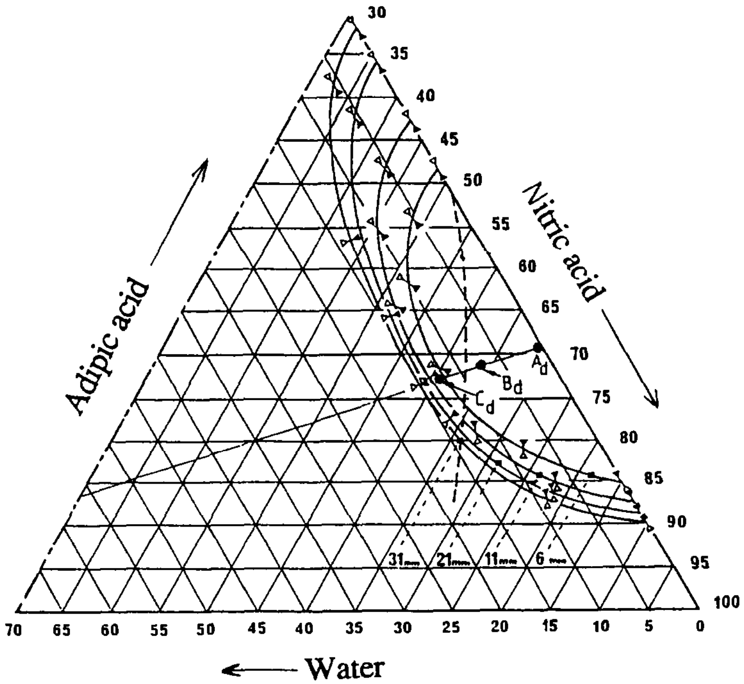

Fig. 6. Detonability limits of adipic acid, nitric acid, and water mixtures at 25°C in steel tubes (coordinates are mass percentages). Dashed line, limit of solubility. A_d, 0.5 wt.% water; B_d, 7.1 wt.% water; C_d, 12.8 wt.% water.

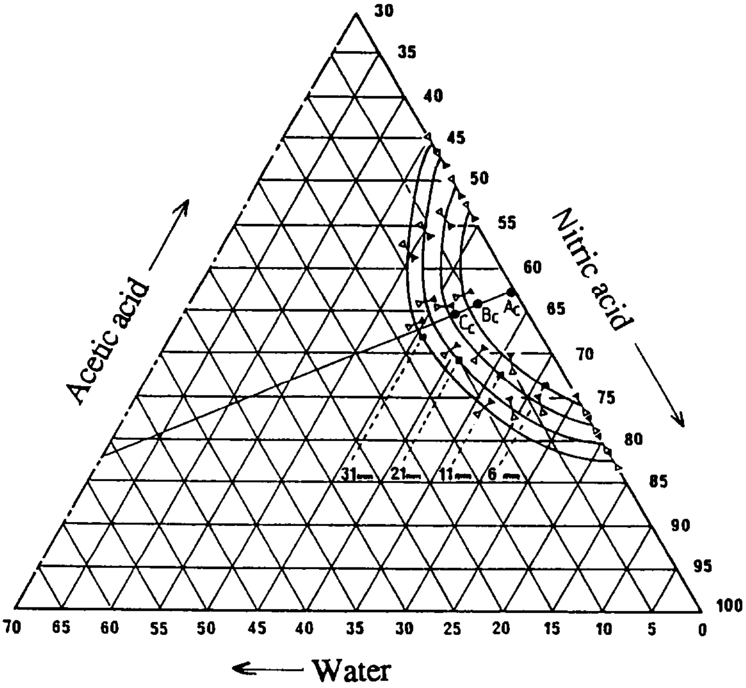

Fig. 7. Detonability limits of acetic acid, nitric acid, and water mixtures at 25°C in steel tubes (coordinates are mass percentages). A_c, 0.5 wt.% water; B_c, 4.8 wt.% water; A_c, 7.9 wt.% water.

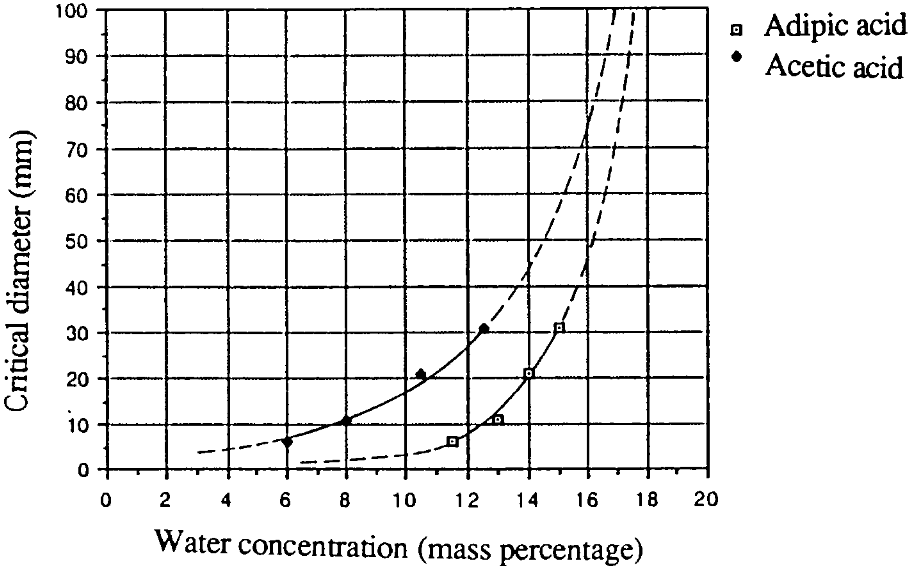

Fig. 8. Variation of critical diameter as a function of water concentration for stoichiometric mixtures: □, adipic acid; ◆, acetic acid.

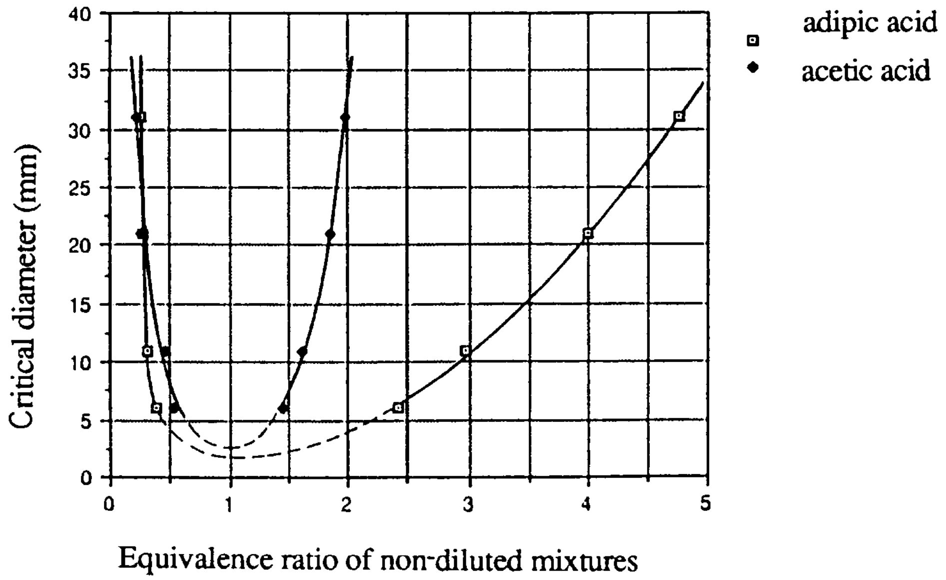

Fig. 9. Variation of critical diameter as a function of equivalence ratio for non-diluted mixtures: □, adipic acid; ◆, acetic acid.

richness on the critical diameter. For increased equivalence ratios, nitric solutions of adipic acid are more sensitive than nitric solutions of acetic acid. This can be explained by incomplete dissolution of adipic acid, as expected from the solubility limit drawn in Fig. 6.

4.3. *Detonation velocity*

The detonation velocity was measured for stoichiometric mixtures as a function of the tube diameter and for different dilutions with water. In addition, some tests were carried out in PVC tubes.

The detonation velocity was measured by the detection of the detonation shock wave at three different levels in the shock tube.

4.3.1. *Results obtained*

The detonation velocity decreases with increasing reciprocal diameter of the test tube. The influence of tube diameter on the velocity is stronger for acetic acid solution than for adipic acid solution, showing again the higher sensitivity of adipic acid solutions, see Fig. 10, (a) and (b).

The detonation velocity decreases with increasing dilution with water, faster for adipic acid solutions than for acetic acid solutions, see Fig. 11. The use of PVC tubes does not show any significant difference in velocity from tests in steel tubes.

The detonation velocities were extrapolated to infinite tube diameter and the extrapolated values were compared with the Chapman–Jouguet ideal

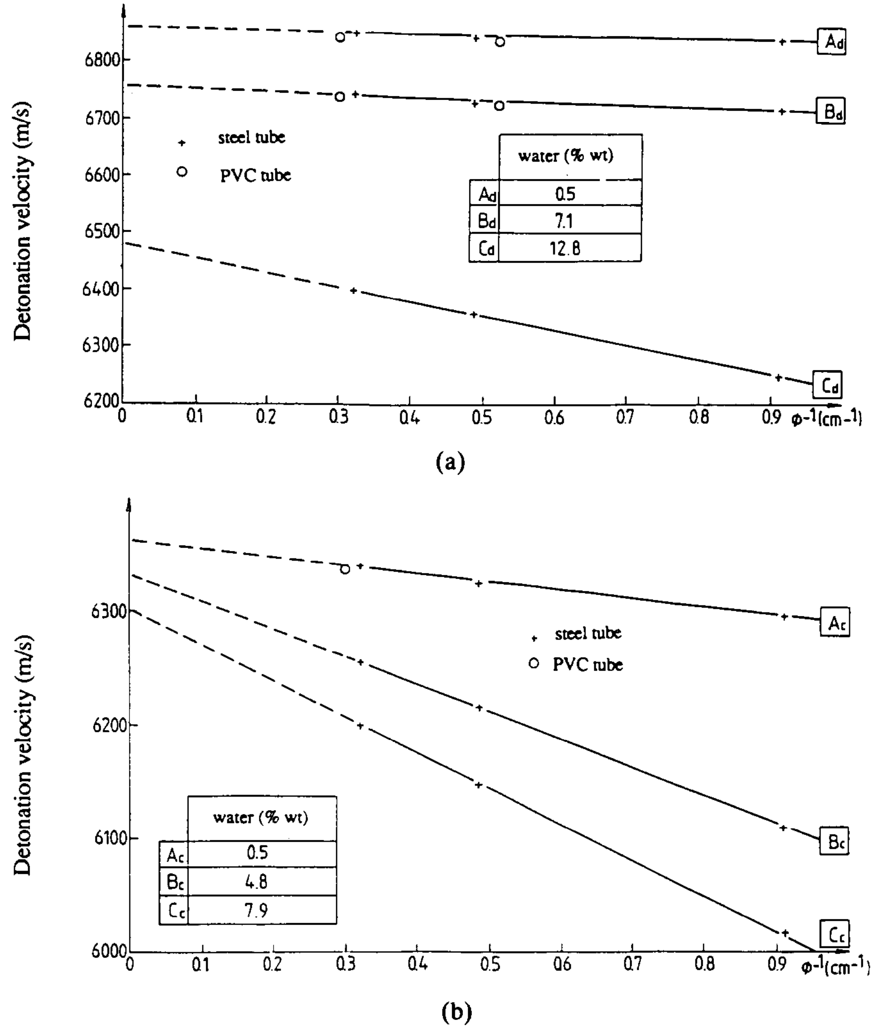

Fig. 10. (a) Detonation velocity as a function of the test-tube reciprocal diameter for stoichiometric mixtures of adipic acid, nitric acid and water: A_d, 0.5 wt.% water; B_d, 7.1 wt.% water; C_d, 12.8 wt.% water. (b) Detonation velocity as a function of the test-tube reciprocal diameter for stoichiometric mixtures of acetic acid, nitric acid and water: A_c, 0.5 wt.% water; B_c, 4.8 wt.% water; C_c, 7.9 wt.% water.

velocity, which were obtained with the QUATUOR computer code [7] in which the burnt gas properties are deduced from a real gas equation of state, a necessary precaution due to the very high pressures in the shock wave.

The comparison of the ideal Chapman–Jouguet velocity and of the experimental velocity extrapolated to infinite tube diameter showed reasonably good agreement for both adipic acid and acetic acid solutions at

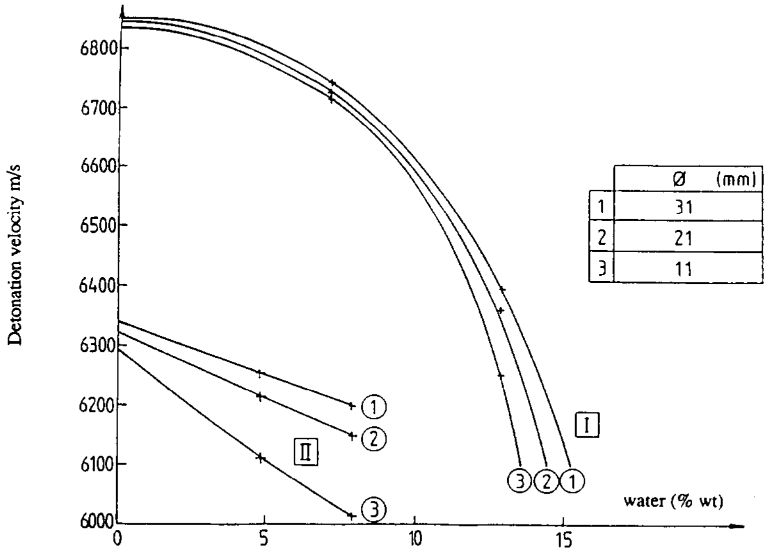

Fig. 11. Detonation velocity as a function of dilution. I, adipic acid, nitric acid, water mixtures; II, acetic acid, nitric acid, water mixtures. For different tube diameters ϕ: 1, 31 mm; 2, 21 mm; 3, 11 mm.

various dilutions with water, thus proving again that true detonation was obtained.

4.4. *Detonation wave curvature*

The detonation wave curvature was obtained from a fast camera record of the spreading of the detonation front in a plane perpendicular to the tube axis at the top of the test tube. The width of the luminous trace obtained as a function of time and the velocity of the shock wave give access to the detonation wave curvature. Results show that the detonation wave curvature decreases with increasing velocity.

4.5. *Conclusions drawn from detonation studies*

The occurrence of detonation in nitric solutions of adipic acid has been confirmed and studied experimentally in tubes.

The order of magnitude of the critical diameter is very small but quite similar to the values published earlier by Kurbangalina for other nitric solutions [8].

Detonation was obtained for mixtures with a maximum potential energy release (PEM) below 700 kcal kg^{-1}, see Fig. 12.

It is likely that the nitric solutions of diacids processed in industrial plants have a detonation critical diameter greater than that of the pipe. This point is difficult to prove experimentally because the critical diameter values are difficult to extrapolate to higher dilutions, and larger scale tests with more dilute solutions require more extensive measures.

These results support the processing of nitric solutions that are diluted sufficiently to exclude detonation. Any ignition source should be avoided. The most likely ignition source is a runaway reaction initiated in a closed pipe exhibiting a transition to deflagration and then to detonation. For this reason a method is proposed to size rupture discs to protect pipes where nitric solutions of diacids could be enclosed. The vent-sizing calculation method follows the recommended DIERS technology.

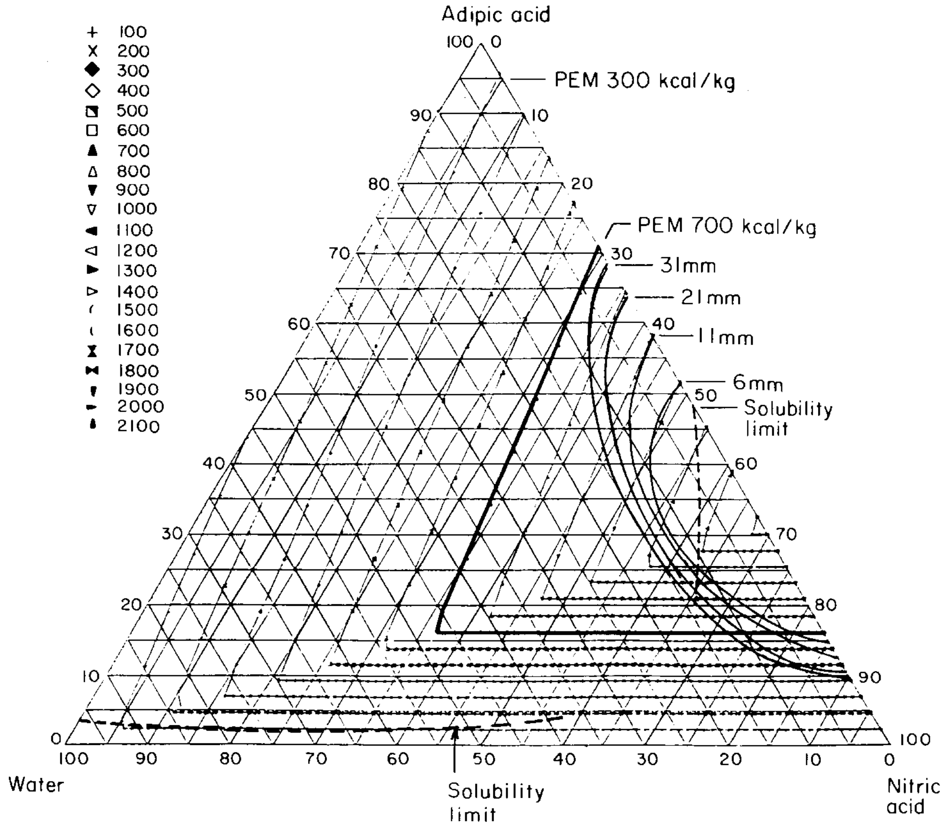

Fig. 12. Iso-PEM tie-lines, isocritical diameter tie-lines for mixtures of adipic acid, nitric acid and water.

5. VENT SIZING TO PROTECT PIPES CONTAINING NITRIC SOLUTIONS OF DIACIDS

5.1. *Choice of experimental method*

We now consider pipes insulated and traced with a heating fluid at temperatures below 160°C, in which nitric solution of organic diacids could be enclosed. These pipes are protected by a rupture disc. A rupture disc is preferred to a pressure relief valve which could be stuck closed after a first opening. A low rupture disc set-pressure of $P_s = 7$ ATA (at atmosphere absolute, bar) was chosen in order to obtain reasonable rates of gas production and to exclude a strong autocatalytic effect due to NO_x pressurization.

A 100% filling ratio is assumed for the pipe loading. It is also assumed that the pipe loading reacts homogeneously. This is a conservative assumption compared to the local reaction of limited amounts of solution.

It is assumed that this situation can be safely represented by an autoclave experiment with a temperature scan of $5°\mathrm{C\,min^{-1}}$. Nitric solutions of practical interest do not produce any exotherm above $5°\mathrm{C\,min^{-1}}$ at a temperature below 160°C, and the set pressure $P_s = 7$ ATA is obtained at temperatures below 160°C.

The influence of the filling ratio on the rate of gas production when the set pressure $P_s = 7$ ATA is obtained, was investigated. It was found that a higher rate of gas production is obtained with low filling ratios, i.e. 100 g sample in a 0.5-l autoclave.

This result can be easily understood if we consider experiments with ≈100% filling ratio where the set pressure of $P_s = 7$ ATA is readily obtained. For this reason, it was assumed that rates of gas production measured in autoclave experiments with a load of 100 g sample in a 0.5-l autoclave were conservative when applied to vent sizing for pipes with a 100% filling ratio.

5.2. *Vent-sizing equations*

The system is hybrid in nature. The only dimensioning consideration is the non-condensable gas production. The vent area is given by

$$A = \frac{\dot{Q}_{\mathrm{gas}}}{G V_{\mathrm{f}}} \tag{2}$$

where $V_{\mathrm{f}} = V/\mathrm{mo}$ is the released fluid specific volume.

The mass flux G for liquid flow is given by the old Fauske equation [9] for two-phase flow driven simultaneously by a vapour pressure and the pressure non-condensable gases

$$G = \sqrt{2P_G\rho_L + G_{ERM}^2} \tag{3}$$

where G_{ERM} is the ERM (equilibrium rate model) mass flux based on the slope of the vapour pressure curve

$$G_{ERM} = \frac{dP_v}{dT}\sqrt{\frac{T}{C_{PL}}} \tag{4}$$

The volumeric gas generation rate $\dot{Q}_{gas}$ is deduced from the rate of gas production for unit mass of sample measured in an autoclave experiment

$$\dot{Q}_{gas} = \frac{dn_G}{dt}\frac{RT}{P}m_0 \tag{5}$$

where m_0 is the pipe loading and P the total pressure. The non-condensable gas generation rate, measured when the set pressure $P_s = 7$ ATA is obtained, is used in eqn. (5).

The determination of P_v and P_G is obtained from an autoclave experiment. The non-condensable gas production rate is deduced from the increase of P_G due to the temperature scan.

Autoclave experiment:
Filling ratio, 100 g in 0.5 l
when $P = 7$ ATA
$P_v = 5$ ATA
$P_G = 2$ ATA
$T = 165°C$

$dn_G/dt = 7\ \text{mol h}^{-1}\ \text{kg}^{-1}$

Pipe and R.D. characteristics:
Pipe length = 5 m
Pipe diameter = 8 inches
Liquid density = 200 kg m^{-3}
P_s = 7 ATA
Filling ratio ≈ 100%
Loading = 216 kg
R.D. diameter = 0.012 m

Autoclave experiment:
Filling ratio, 100 g in 0.5-l
when $P = 7$ ATA
$P_v = 5.74$ ATA
$P_G = 1.26$ ATA
$T = 157°C$

$dn_G/dt = 4\ \text{mol h}^{-1}\ \text{kg}^{-1}$

Pipe and R.D. characteristics:
Pipe length = 5 m
Pipe diameter = 4 inches
Liquid density = 1200 kg m^{-3}
P_s = 7 ATA
Filling ratio = 100%
Loading = 50 kg
R.D. diameter = 0.005 m

Fig. 13. Typical results.

5.2.1. *Example of vent-size calculation*

Typical results of vent-size calculations are given in Fig. 13. Due to the choice of a limited R.D. (rupture disc) bursting pressure, small disc diameters are obtained. This would not be the case for higher R.D. set pressures for which the rate of gas production is notably increased.

6 CONCLUSION

The different modes of decomposition of nitric solutions of organic diacids processed in the manufacture of adipic acid were investigated on an experimental basis. It is likely that the most severe explosion involving deflagration and even detonation could be initiated if the slow oxidation reaction is allowed to pressurize vessels or pipes in which the solutions are enclosed.

Despite the fact that solutions with a high potential-energy release are not present in industrial processes, it is difficult to ensure that the critical quenching diameter for the detonation is everywhere greater than the diameter of the pipes or vessels, due to the difficult problem of carrying out large-scale detonation experiments.

Fortunately the runaway reaction involving the nitric oxidation of organic diacids can be easily controlled at an early step in its development using vents, provided that their actuation pressure does not exceed 7 ATA.

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