DETONATIONS

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CONTENTS

Deflagration and Detonation
Materials Subject to Detonation
Detonation Limits
  General
  Effect of Initial Temperature, Pressure and Humidity
  Effect of Scale
  Effect of Oxygen and Diluents
Structure of a Detonation Wave
Detonation Theory
  Introduction
  CJ Theory
  ZND Theory
Enhanced Pressure Effects and Types of Unstable Detonation
  Overdriven Detonation
  Pressure Piling
  Retonation
  Spinning Detonation
  Galloping Detonation
  Quasi-Detonation
Deflagration to Detonation Transition (DDT)
  General
  Run Up Distance
  Effect of Initial Temperature and Pressure
  Effect of Scale
  Effect of Obstacles
  Effect of Vents
Direct Initiation of Detonation
Detonations in Unconfined Vapour clouds
Damage Caused by Detonations
  General
  Pipelines
  Deducing the Trajectory That a Detonation Has Taken Through a Plant
Detonation Mitigation
DEFLAGRATION AND DETONATION [1,2,3]

1. **Deflagrations** propagate at subsonic velocities. The rate of deflagration is controlled by diffusion of heat and reactive species from the reaction zone (flame front) to the unburnt material. In practice the velocity depends on the degree of confinement and the size and shape of the flammable mixture.

   Assuming that the unburnt gas is stationary, the flame propagates into the unburnt gas at a characteristic **laminar burning velocity**. This is a fundamental parameter whose value reflects the reactivity of the mixture.

   If the unburnt gas is turbulent, the burning velocity can increase and is then called the **turbulent burning velocity**.

   If the unburnt gas is moving, a stationary observer measures a flame velocity that is the sum of the unburnt gas velocity and the burning velocity. This observed flame speed is called the **deflagration velocity**.

   Typical deflagration speeds range from a few m/s in an unconfined cloud to several hundreds of m/s in a pipe or other volume containing repeated obstacles.

   In an enclosed vessel containing a fuel/air mixture, the deflagration pressure rise is typically 7 times the initial pressure. For a low velocity deflagration, the pressure increase at the flame front is very approximately given by $1.2M^2$, where $M$ is the Mach number (i.e., the deflagration speed divided by the sound speed of the unburnt mixture). Once the deflagration speed approaches sound speed, a shock wave will form.

2. A summary checklist of the key features of detonations is given in **Appendix 1**.

   A **detonation** travels at supersonic speeds. Typical velocities are of the order of 1,850 m/s for fuel/air mixtures and 3,000 m/s for fuel/oxygen mixtures. These velocities may be higher where hydrogen is the fuel.
The structures of deflagration and detonation waves are contrasted in Fig 1. In a detonation, a high pressure shock front travels approximately 1 to 10 mm ahead of the reaction zone, the reaction zone being the “flame” (in a fast deflagration, the reaction zone lags much further behind the shock front). Because chemical reaction rates depend exponentially on temperature, extremely rapid combustion occurs. High pressures arise from the strength (speed) of the shock.

Steady detonations have a characteristic pressure/time history. A typical example is shown in Fig 2. There is a sudden increase in pressure, followed by a smooth expansion to a roughly constant value. In some cases, the pressure of the shocked gas mixture can be detected before it ignites. This so-called “leading shock” region is termed the von Neumann spike and has a higher pressure than the detonation pressure\(^1\).

The initial pressure rise of a steady detonation is at a maximum close to the stoichiometric concentration, and decreases as the mixture approaches the detonation limits. Typical maximum detonation pressures are 15 to 19 times the initial pressure for stoichiometric fuel/air mixtures, and 25 to 30 times the initial pressure for stoichiometric fuel/oxygen. Turbulence can increase these pressures dramatically (see para 31).

The temperature of the detonation products is typically 3,000 K for stoichiometric fuel/air mixtures, again decreasing as the mixture approaches the detonation limits. For mixtures in oxygen, the maximum temperature increases to more than 4,000 K.

3. In practical explosions, there is an almost continuous spectrum of combustion front velocities, from laminar burning velocity, through deflagration and shock formation to detonation. In deflagrations, the flame speed is strongly affected by turbulence and a deflagration can be accelerated to detonation, for example by turbulence induced by obstacles. This phenomenon of deflagration to detonation transition, or DDT, is discussed further in paras 37-47.

4. The basis of operation of most commercial explosives is the direct initiation of detonation in the solid state. This subject is outside the scope of this report.

MATERIALS SUBJECT TO DETONATION

5. A recent limited study suggests that a useful indicator of a material’s susceptibility to detonation is its Maximum Experimental Safe Gap (MESG) value [4, 50]. The lower the MESG, the more easily a material will detonate, i.e., gases in Group IIC are most susceptible. MESG’s of some common materials are listed in Table 1, and those of many more materials are given in [5].

Bull [49] has collated data on the critical energies required (using a solid explosive initiator) to establish steady detonation in unconfined clouds of common fuel/air mixtures. This also gives an indication of a mixture’s susceptibility to detonation.

Unfortunately, no guidelines exist as to where the boundaries lie between those mixtures that will give low velocity deflagrations and those which will accelerate to far more destructive fast deflagrations and detonations. The situation is complicated by the dependence of flame acceleration on effects such as vessel geometry and the presence of repeated obstacles.

6. Hydrogen, acetylene, ethylene, ethylene oxide\(^2\), ethane and propane are some of the widely known materials that can detonate when mixed with air.
Detonations have also been induced under test conditions in many common solvent vapours such as acetone, benzene, methanol and xylene [2]. However, the power of the ignition source and other test conditions needed to detonate these solvent vapours were probably extremely severe. Similarly, methane can only accelerate to detonation under extreme conditions, usually involving very long pipe runs and high levels of turbulence.

7. Most experimental work on confined detonations in air has been done on hydrogen, acetylene, ethylene and propane. Other studies include ammonia, cyanogen, carbon disulphide and tetramethyl silane in air or oxygen. There is some limited information on detonations in other oxidants, including halogens (chlorine/hydrogen mixtures being the most studied), ozone, hydrogen peroxide vapour, nitrogen oxides and chlorine dioxide [3].

DETONATION LIMITS [3]

General

8. Detonation limits reported in the literature should be treated, and applied to industrial situations, with great caution. Literature values of detonation limits can be lower or higher than those in industrial plant. For example, some tests have been done in pipes which were too narrow and/or short to sustain a detonation. On the other hand, some tests have been done with excessively large ignition sources, which have overdriven the mixture (ie caused it to travel faster than the steady-state detonation velocity). This overdriven condition would not be sustained over long lengths of piping.

9. Detonation limits are typically measured in small vessels or tubes. Data is available for relatively few materials. The measured limits depend on the size, shape and geometry of the apparatus. The detonation limits of an unconfined mixture are narrower than for confined detonations. Deflagration and detonation limits for some common materials are given below:

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MESG (mm)</th>
<th>DEFLAGRATION LIMITS IN AIR (% v/v)</th>
<th>CONFINED DETONATION LIMITS IN AIR (% v/v)</th>
<th>UNCONFINED DETONATION LIMITS IN AIR (% v/v)</th>
<th>CONFINED DETONATION LIMITS IN OXYGEN (% v/v)</th>
<th>UNCONFINED DETONATION LIMITS IN OXYGEN (% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>0.92</td>
<td>4.0-60</td>
<td>Not reported</td>
<td>Not reported</td>
<td>Not reported</td>
<td>13.0-48.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.04</td>
<td>2.6-13</td>
<td>Not reported</td>
<td>Not reported</td>
<td>3.3-40.0</td>
<td>Not reported</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.37</td>
<td>2.5-100</td>
<td>4.20</td>
<td>Not reported</td>
<td>2.90</td>
<td>6.70</td>
</tr>
<tr>
<td>Benzene</td>
<td>Not reported</td>
<td>1.3-7.9</td>
<td>1.60-5.55</td>
<td>Not reported</td>
<td>1.55-36.0</td>
<td>Not reported</td>
</tr>
<tr>
<td>Butane</td>
<td>0.98</td>
<td>1.8-8.4</td>
<td>1.98-6.18</td>
<td>2.5-5.2</td>
<td>2.05-38</td>
<td>Not reported</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Not reported</td>
<td>1.3-7.8</td>
<td>Not reported</td>
<td>Not reported</td>
<td>1.4-29.0</td>
<td>6.7-39.0</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>0.87</td>
<td>1.9-36</td>
<td>2.8-4.5</td>
<td>Not reported</td>
<td>2.6-&gt;40</td>
<td>4.7-29.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.91</td>
<td>3.0-12.4</td>
<td>2.87-12.20</td>
<td>4.0-9.2</td>
<td>3.60-46.6</td>
<td>11.0-39.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.89</td>
<td>3.3-19</td>
<td>5.1-9.8</td>
<td>Not reported</td>
<td>Not reported</td>
<td>Not reported</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.65</td>
<td>2.7-36</td>
<td>3.32-14.70</td>
<td>Not reported</td>
<td>4.1-60.0</td>
<td>9.2-51.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.29</td>
<td>4.0-75</td>
<td>18.3-58.9</td>
<td>15.0-90.0</td>
<td>Not reported</td>
<td>Not reported</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.92</td>
<td>6.7-36</td>
<td>Not reported</td>
<td>Not reported</td>
<td>9.5-64.5</td>
<td>Not reported</td>
</tr>
<tr>
<td>Octane</td>
<td>0.94</td>
<td>LFL 0.95, UFL</td>
<td>1.45-2.85</td>
<td>Not reported</td>
<td>1.55-17.3</td>
<td>Not reported</td>
</tr>
</tbody>
</table>
Table 1: Maximum Experimental Safe Gaps [5], Deflagration Limits [6] and Detonation Limits [3] For Some Common Materials

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>not reported</td>
<td>2.1-9.5</td>
<td>2.57-7.37</td>
<td>3.0-7.0</td>
<td>2.50-42.5</td>
</tr>
<tr>
<td>Propane</td>
<td>0.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>0.74</td>
<td>2.4-11</td>
<td>3.55-10.40</td>
<td>3.5-8.5</td>
<td>2.5-50.0</td>
</tr>
<tr>
<td>Xylene</td>
<td>Not reported</td>
<td>1.1-6.4</td>
<td>Not reported</td>
<td>Not reported</td>
<td>1.05-26.5</td>
</tr>
</tbody>
</table>

Whilst a given mixture and pipe/vessel geometry may be capable of sustaining a detonation, it is not always the case that a detonation will develop.

10. There are methods available to estimate detonation limits using deflagration limits [3.1]. These usually tend to overestimate the detonable range.

11. Le Chatelier’s Rule can be used to calculate the composite lower detonation limit:

\[
L_c = \frac{100}{n_1 \cdot \frac{L_1}{100} + n_2 \cdot \frac{L_2}{100} + \ldots + n_n \cdot \frac{L_n}{100}}
\]

where: \(c\) = proportion of each detonable gas (% v/v)

\(L\) = lower detonable limit of each gas (% v/v)

As with the calculation of composite flammable limits, this rule works well for mixtures containing hydrogen, methane, carbon monoxide and simple alkanes, but is not accurate for more complex molecules, or for sulphur-containing materials such as hydrogen sulphide and carbon disulphide.

Effect of Initial Temperature, Pressure and Humidity

12. There is very little data on the effect of temperature on detonation limits. Generally, increasing the initial temperature and pressure tends to widen the detonation limits, with the upper limit being more strongly affected. There are inconsistencies in the experimental results. For example, the detonable range of hydrogen/oxygen was found to narrow with a temperature rise of 50 deg C, however the limits of methane/oxygen widened.

13. Laminar burning velocity tends to increase with temperature. The increase is more dramatic in mixtures with relatively high burning velocities, such as hydrogen/oxygen.

It is recognised in the testing community, but seldom reported, that changes in air humidity can affect flame acceleration properties [4.1], although interpretation of the results in this reference is not straightforward because these tests were carried out at varying ambient temperatures.

Effect of Scale

14. Detonation limits tend to widen as the size of the vessel increases [7]. The detonation pressure depends on the detonation velocity and is not a function of the vessel’s diameter or volume [2.8] (but vessel shape and size do affect deflagration velocity [2]).

Effect of Oxygen and Diluents

15. All mixtures are more susceptible to detonation when mixed with oxygen alone. The resulting detonation will have a higher detonation velocity, pressure and detonation product temperature than an equivalent detonation in air (see para 2). Diluents tend to narrow the detonation limits, particularly the upper limit. Relatively large amounts of diluent can be needed to suppress detonability and experimental data is needed
for individual situations. Significantly more diluent is required at higher temperatures, as found in one study \[10\] in which the initial temperature was increased from 293 to 373 K. A recent study \[50\] showed that the nitrogen content of a fuel/oxygen/nitrogen mixture can critically control the explosion behaviour. This work suggests that the main reason for differences in the detonability of fuel/air mixtures is the differing nitrogen contents of the stoichiometric mixtures, not the fuel type per se.

**STRUCTURE OF A DETONATION WAVE** \[1\]

16. A planar detonation wave has a complex 3-dimensional cellular structure. A number of transverse waves run across the leading wave, reflecting from one another and from the walls and obstructions, creating a continually changing cellular structure with a characteristic “fish-scale” pattern (see Fig 3). The surface of the leading front consists of a series of bulges (the so-called “Mach stems”) and depressions (which are the decaying incident blast waves), separated by triple points at the points where the shocks interact. The reaction zones trail behind. Ref \[3.5\] gives further information on the structure of a detonation wave.

17. The cell width \(\lambda\) is a fundamental characteristic of a detonation wave, and varies from approximately 8 mm for hydrogen to 20 mm for ethylene. It can be used to calculate various parameters such as the critical pipe diameter (the narrowest pipe diameter in which a self-sustaining detonation can propagate - see para \[20\]). The cell length is usually termed \(L_c\). The cell width is typically 0.5 to 0.6 times \(L_c\), although Nettleton \[3\] quotes 0.7 to 0.8 times \(L_c\) at atmospheric pressure.

18. \(\lambda\) is affected by the initial pressure, mixture composition and sensitivity to detonation. \(\lambda\) is measured by experiment and variations of a factor of two in reported values are not uncommon \[11\]. More easily detonated (ie more reactive) mixtures have smaller cell widths:

<table>
<thead>
<tr>
<th>FUEL IN AIR</th>
<th>CELL LENGTH (L_c) (mm)</th>
<th>CALCULATED CELL WIDTH (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>13.6</td>
<td>6.8 to 10.9</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>15.9</td>
<td>8.0 to 12.7</td>
</tr>
<tr>
<td>Ethylene</td>
<td>39</td>
<td>20 to 31</td>
</tr>
<tr>
<td>Propane</td>
<td>72</td>
<td>36 to 58</td>
</tr>
<tr>
<td>Ethane</td>
<td>88</td>
<td>44 to 70</td>
</tr>
</tbody>
</table>

**Table 2: Average Measured Cell Lengths for Various Fuel/Air Mixtures** \[3\]

The variation of cell width with mixture composition for various alkanes is given in \[1.1\].

19. Cell width tends to fall as the initial temperature and pressure are increased, and is more sensitive to temperature than pressure. Further information is given in \[10\].

20. For a given mixture, there is a critical pipe diameter, below which detonation will not occur. This is because, in a sufficiently narrow pipe, there is not enough room for the detonation's cellular structure to exist \[9\]. For propagation of a detonation in a circular pipe, the critical pipe diameter is of the order \(\frac{\lambda}{4}\) \[1, 4\]. This corresponds to a single detonation cell, wrapped around the circumference of the pipe. For square and rectangular pipes, see Fig 4.

21. Refs \[11.1\] and \[1\] are useful for evaluating the likelihood of transmission of a detonation from a confined area (building, ventilation duct, culvert etc) into an unconfined situation. For successful propagation of a detonation from the end of a pipe into an unconfined area, the critical diameter is 13 \(\lambda\) for a circular pipe and 10 \(\lambda\) for a square pipe. Experimental work on propagation of a detonation wave through orifices and slots is summarised in Ref \[1\].

22. When using any of these relationships, a safety factor is needed to allow for variations in the reported values of \(\lambda\) \[11\], although a suitable safety factor is not suggested in this reference). Using a critical diameter of \(\frac{\lambda}{40}\) (i.e. 50% lower than the theoretical value of \(\frac{\lambda}{4}\)) has been suggested by one leading expert \[56\].

**DETONATION THEORY**
Introduction [3]

23. The two well-known detonation theories are those of Chapman and Jouguet (CJ) and Zel'dovitch, von Neumann and Doring (ZND). The first is based on pure gasdynamic and thermodynamic arguments, assuming infinitely fast chemistry. The latter introduces finite rate chemistry.

Despite the omission of detailed chemistry, CJ predictions can be very accurate. The accuracy of ZND calculations is limited by the accuracy of the chemical reaction schemes used.

CJ Theory [3]

24. This was proposed in the early 1900's. It combines an analysis based on the conservation of mass, energy and momentum with basic thermodynamics. It is a one-dimensional model, and assumes that the reaction rate is infinitely fast. The model’s representation of a detonation, with an infinitely thin reaction zone, is known as an “ideal” detonation. The model neglects the high momentary pressure in the von Neumann spike at the leading edge of the detonation wave.

A CJ analysis can be used to calculate detonation properties such as velocity and pressure. Predicted values compare reasonably well with experimental data, and the model is still widely used.

<table>
<thead>
<tr>
<th></th>
<th>Hydrogen</th>
<th>Ethylene</th>
<th>Propane</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>CJ pressure</td>
<td>15.8</td>
<td>18.6</td>
<td>18.6</td>
<td>17.4</td>
</tr>
<tr>
<td>CJ velocity</td>
<td>1968</td>
<td>1822</td>
<td>1804</td>
<td>1802</td>
</tr>
</tbody>
</table>

Table 3: Examples of Calculated CJ Pressures and Velocities [11]

25. The CJ model cannot be used to calculate parameters which require a knowledge of the structure of the detonation wave, such as detonation limits, initiation energy, critical pipe diameter and the thickness of the reaction zone. These so-called “dynamic detonation parameters” can be calculated (with varying degrees of accuracy) using the ZND theory, discussed in paras 29 to 30.

26. The CJ (ie average) detonation pressure \( P_{CJ} \) in bar is calculated by:

\[
P_{CJ} = \frac{\gamma P_i}{M^2} [2,3]
\]

where: \( \gamma \) = ratio of specific heat at constant pressure to specific heat at constant volume

\( P_i \) = initial pressure (bar absolute)

\( M \) = detonation Mach number (ratio of detonation velocity to velocity of sound in the unreacted gas).

27. The peak pressure \( P_{vn} \) behind the lead shock wave in the von Neumann spike is approximately twice the CJ pressure:

\[
P_{vn} \approx \left( \frac{2\gamma P_i}{\gamma+1} - \frac{\gamma-1}{\gamma+1} P_i \right) [2]
\]

28. Munday [2] suggests that the maximum pressures achieved in practice could be twice the calculated CJ values, due to the combined effects of high sustained pressure and shock loading.

Much higher pressures are often achieved in the overdriven detonation, which exists momentarily before the steady state detonation. Further information is given in paras 31 and 54 to 57.

ZND Theory [3]

29. In the early 1940’s Zel'dovitch, von Neumann and Doring independently proposed a more detailed model. Instead of an infinitely fast chemical reaction assumed in the CJ theory, the
ZND model assumes that the shock wave is separated from the reaction zone (this is a so-called “non-ideal” detonation). This separation corresponds to the so-called “induction delay period”, which arises from the finite rates of the combustion reactions [1].

30. The ZND theory predicts similar detonation velocities and pressures to the CJ theory [11]. These compare fairly well with experimental data, however the theory relies on the integration of detailed chemical kinetics schemes and is too complex for calculations to be done by hand. Detonation limits, initiation energy, critical pipe diameter and the thickness of the reaction zone can be calculated, but their accuracies depends on the accuracies of the coefficients and reactions included in the kinetic schemes. These calculated values do not agree particularly well with experimental results.

ENHANCED PRESSURE EFFECTS AND UNSTABLE TYPES OF DETONATION

Overdriven Detonation [3]

31. This is a detonation wave that is artificially supported above its CJ velocity and hence also has a much higher peak pressure than the CJ value. There is a rapid increase in pressure with the degree of overdriving (ie the increase in velocity above the CJ value). Overdriving can occur during the transition from deflagration to detonation, or during initiation by a solid explosive. This overdriven detonation can generate much higher pressures than the steady state detonation - up to 100 times the initial pressure (5 times the CJ pressure). Usually this pressure is short lived, but it can be sufficient to cause local mechanical damage.

Pressure Piling

32. This occurs when a detonation propagates through a medium that has been pre­pressurised by an earlier flame, for example in interconnected vessels. The CJ pressure is enhanced by the pre-compression ratio. The pressure is further enhanced if the detonation wave reflects off a wall or propagates into a corner. Pressure waves ahead of the flame front may also be reflected, for example by bends, obstructions or the far end of the line), and merge to form a pressure wave which travels back towards the flame. This reflected shock can accelerate a deflagration to detonation, and the initial pressure is increased by a factor of 2 to 5, due to the shock pre-compression. Both can result in devastating detonation pressures.

Retonation

33. When a detonation is formed, a strong pressure wave can propagate back through the burnt gas. This is called the retonation. It can be enhanced if it propagates back through gas that has not all been burned during the flame acceleration phase. It can reflect (for example off a closed end or bend), and travel back towards the main detonation wave. Because of the increased speed of sound in the hot burnt gases, the reflected retonation overtakes the detonation. Under appropriate conditions, a combined detonation/retonation wave front can exist for a very short time. During this time, the overdriven pressure can be between approximately 2 and 5 times the usual detonation pressure [3].

Spinning Detonation [2, 3]

34. Close to the detonation limits, or as the pressure drops to a critical level, the detonation front spins in a stable manner, producing a helical track on the inner surface of a dusted tube. It is more easily observed in pipes of circular cross-section.

Galloping Detonation [3, 9]

35. This can occur near to the detonation limits in a pipe. The velocity of the detonation wave front fluctuates dramatically between approximately 0.5 and 1.5 times the CJ velocity (see Fig 5).

A galloping detonation occurs because of repeated transitions to detonation in a mixture that is very near to the limits of propagation. Detonation is established initially but eventually decays to a shock-flame. The shock-flame is accelerated by wall boundary layer effects and undergoes a further transition to detonation, and the process becomes cyclical. The oscillations can be remarkably consistent over a large number of cycles. Galloping detonation can cause severe damage at the locations where the transition to the overdriven
state occurs. [46] contains further references on galloping detonation, and details of experiments using propane/air mixtures.

**Quasi-Detonation** [8]

36. In a quasi-detonation, the shock front and the burning zone are more decoupled (ie more separated). A quasi-detonation is effectively a fast deflagration following a lead shock wave. This configuration is not naturally stable and requires the presence of repeated obstacles. These provide energy and momentum loss that slow the wave but the obstacles also promote rapid energy release during turbulent combustion and transverse shock formation. When both these influences balance, a stable low velocity (compared to the CJ velocity) reaction wave can exist.

**DEFLAGRATION TO DETONATION TRANSITION (DDT)**

**General**

37. Detonation incidents in the chemical industry frequently involve DDT. A deflagration flame in a detonable mixture (typical velocity 1 m/s) can be accelerated to detonation by turbulence induced by friction with pipe walls, obstructions etc. Turbulence accelerates the flame because it wrinkles the flame front, which increases its surface area and therefore increases the rate of reaction. This results in a shock forming ahead of the flame as the flame approaches sonic velocity. The shock front acts like a piston [2], heating and compressing the unburnt gas ahead of the flame. Eventually the unburnt gas autoignites, and a detonation wave is formed ahead of the flame. This occurs at a flame speed of approximately 1,000 m/s [4].

A shock forms and there is a volume of compressed gas, with undisturbed gas ahead of it. DDT leads to overdriven detonation in the compressed gas. If the shocked gas volume is large enough, a steady detonation propagates through it. Once the shocked gas has been burned, the detonation continues into the unshocked gas, initially as an overdriven wave which then decays to a steady detonation [56]. Following DDT, a blast wave is also transmitted back into the burnt gas.

38. Very reactive fuels such as hydrogen, acetylene and ethylene in air [8], and other fuels in oxygen-enriched atmospheres, are particularly susceptible to DDT. Nevertheless, DDT has been observed in mixtures of less reactive fuels in air. In one experiment using propane/air and a weak ignition source in a test vessel with confinement and obstructions, DDT occurred in less than 10 m [11]. In British Gas experiments using propane/air in a pipe rack layout, DDT occurred after 15 m. **DDT is therefore foreseeable in a gas cloud within the detonable range, if there is a high degree of confinement and/or obstruction [11].**

39. The composition of the mixture and the size, shape and geometry of the vessel have a strong effect on the transition to detonation. **Great care is needed when extrapolating the results of research to a particular application.** Often, in very critical circumstances, recourse has had to be made to direct testing, using apparatus as close to the application geometry as possible.

**Run Up Distance**

40. This is the distance between the steady deflagration and the formation of a steady detonation wave. **Ref 12** presents experimental data on DDT and an equation to calculate the run-up distance. A length to diameter ratio \( \frac{L}{D} \) of 10-60 is usually required for DDT, with an \( \frac{L}{D} \) of 10 for more sensitive turbulent mixtures. Exceptions are highly reactive, unstable fuels such as acetylene and ethylene, which require an \( \frac{L}{D} \) of only 3. It is important to bear in mind that \( \frac{L}{D} \) ratios are highly system-specific and it is extremely difficult to apply them to other situations or experiments [13]. Nettleton [3] suggests that run up distances in industrial pipes could be 50% of the measured values.

Recent measurements of transition distances in pipes of diameter 150 mm and 300 mm with hydrogen/air and ethylene/air mixtures were of the order of 9 m and 15 m respectively [4]. A strong dependence on ambient atmospheric conditions (temperature and humidity) was also noted [4 Fig 5.1.6].
41. The pipe must be at least as wide as the critical diameter (see paras 20 to 22) for DDT to occur.

**Effect of Initial Temperature and Pressure** [14,15]

42. There is little data on the effect of temperature, although it appears that an increase in temperature tends to increase the run-up distance, possibly due to the reduction in density. The run up distance tends to decrease as pressure increases and as the mixture tends towards stoichiometric.

**Effect of Scale**

43. From the limited data available, it appears that run up distance increases with pipe diameter (ie DDT occurs at a constant length to diameter ratio). Most tests have been done in relatively narrow pipes (maximum diameter 50 mm). It is difficult to extrapolate the results to pipes typical of chemical plants due to the unknown effects of bends, junctions etc. Also, drag effects (which tend to reduce flame acceleration) are less significant in larger bore pipes.

44. Sudden changes in pipe direction and decreases in pipe diameter tend to favour DDT because of the additional turbulence they introduce. Increases in pipe diameter reduce the likelihood of DDT and can even cause a detonation to decay into a fast deflagration.

**Effect of Obstacles**

45. The effects of obstacles on DDT can be classified into four regimes [16,17]:

- Quenching regime - the flame extinguishes as it passes over the obstacles, due to rapid entrainment and mixing;
- Choking regime - quasi-steady propagation at 600-1,000 m/s;
- Quasi-detonation regime - DDT occurs, velocity > 1,000 m/s but less than CJ velocity;
- Steady state detonation regime - with sensitive mixtures, obstacles have no effect and a steady CJ detonation develops.

**Refs** 18 and 19 describe experiments on these effects, and tentative relationships between critical tube diameter and cell width.

**Effect of Vents** [21,22,23]

46. Carefully designed venting can prevent transition to detonation by relieving the pressure. However, once a detonation is established in a confined volume, venting will not reduce the explosion pressure [44, 55].

47. **Where only limited venting is provided, vents can act like obstacles and induce turbulence.** For example, in large scale tests using hydrogen/air mixtures, the flame speeds and overpressures were higher than for the unvented case when a small amount (13%) of top venting was used with a rich mixture (>18% hydrogen). However, flame speeds and overpressures were lower for leaner mixtures. It was also found that obstacles can negate the effects of even very large vents in sufficiently sensitive mixtures [22]. Where obstacles were absent, a large amount of top venting (50%) **did suppress** DDT and reduce the overpressure.

**DIRECT INITIATION OF DETONATION**

48. This is where a mixture is ignited, for example by a solid explosive or an extremely energetic spark and, due to the strong blast source, forms a detonation without any intervening deflagration phase. In practice, detonation tends to occur in gases/vapours by DDT, and direct initiation is unlikely in typical industrial situations. Further information on direct initiation is given in Refs 1, 3, 9 and 24.

**DETONATIONS IN UNCONFINED VAPOUR CLOUDS** [3]

49. If a deflagration propagates from an obstacle filled region into an unconfined and unobstructed area, the flame front will usually decelerate and the explosion pressure will decrease. However, in a similar situation a **detonation** emerging from the confined region may propagate unabated into the unobstructed area, resulting in even the unconfined parts of the
gas cloud generating very high explosion pressures \([11,44]\). An exception may be if a detonation emerges from a pipe, where the critical conditions for propagation in \textit{para 21} apply. 

50. The Port Hudson incident was the only example of an incident in which a detonation \textit{may} have occurred in an unconfined vapour cloud in air (see Appendix 2), although the valley may have provided a degree of confinement.

51. The detonation limits of unconfined mixtures are narrower than those measured in the smallest tubes. There is little information available on specific detonation limits of unconfined mixtures, due to the source energies and test volumes of mixtures required to carry out the tests. Some data is given in Table 1.

52. Bull \([49]\) has collated data on the critical energies required (using a solid explosive initiator) to establish steady detonation in unconfined clouds of common fuel/air mixtures.

53. There is a technique \([3.3]\) for estimating the minimum cloud diameter needed for detonation. Evidence from incidents suggests that this is at least 50 m for a relatively low energy ignition source such as a spark.

There are theories which attempt to model the acceleration of an unconfined flame front.

\textbf{DAMAGE CAUSED BY DETONATIONS [3]}

\textbf{General}

54. The theoretical CJ and peak pressures can be calculated using the equations in paras 26 and 27 respectively, or more accurately using an appropriate numerical calculation procedure using real gas thermodynamics. Munday \([2]\) suggests that \textit{the maximum values achieved in practice could be twice these values}, due to the combined effects of high sustained pressure and shock loading.

Pressures increase significantly when a detonation reflects off a solid wall. For example, for ethylene/air the peak pressure increases instantaneously from approximately 18 bar to 45 bar.

55. There is no general theoretical treatment of the interaction of a detonation wave with confinement. Even a simplified theory can only deal with the diffraction of a shock by an isolated wall. In more complex systems, the interactions of the various reflected wave systems make analysis extremely difficult, and there are many discrepancies between predicted and observed phenomena. Further information on the theory is given in Ref 3.4.

56. The dynamic load of a detonation inside a vessel is a combination of a constant, high intensity "running load" and a transient impact load \([2]\). The running load can be withstood by comparatively weak structures. The transient impact can be up to 100 times the initial pressure, but has a very short duration. \textit{Both peak pressure and overall impulse must be included when considering the failure potential of vessels and other structures.}

A detailed discussion of equipment failure under detonation loads is given in \([2]\) and some recent results for pipelines are given in \([52]\).

Detonation can produce large numbers of small fragments \([25]\) due to brittle failure, however large distorted and twisted fragments can be produced if the vessel is sufficiently strong \([26]\). Another typical sign is balls missing from valves \([20]\). Estimates of effective detonation pressures, based on measurements of deformation, can often vary by up to an order of magnitude. \textit{It can be difficult to distinguish a detonation from a fast deflagration.}

57. \([44]\) As with blast waves, a detonation which occurs outside a vessel generates a so-called "diffraction load" and a "drag load". The diffraction load arises from the differential pressure across an object as the blast wave travels over it, the difference in pressure generating the loading. The drag load arises from the blast wind (ie the air movement caused by the explosion) exerting a load on the object. Further information is given in \([45]\).

\textbf{Pipelines}

58. Experiments have shown that pipelines designed for a nominal pressure of 10 bar tend to rupture at the points where DDT occurs, but can withstand the steady-state detonation pressure without rupturing \([8,11]\). This is due to the short duration of the transient overpressure.

59. Failure of a pipeline can occur at fairly regularly spaced intervals due to galloping detonation (see \textit{para 35}). This is due to acceleration of the flame up to detonation, followed by
the quenching of the unstable overdriven wave as the pipe fails. This process is repeated as the flame re-accelerates [2].

60. Frequently, failure occurs in regions such as bends and junctions, due to the high pressures generated by the partial reflection of the incident wave. Sometimes elbows can be missing [20]. Damage is less severe for more gradually sweeping bends and junctions (ratio of radius of curvature to bore radius of at least five), because this helps to preserve the planar nature of the front as it propagates around the bend. The bend configuration has a critical effect on the point at which the maximum pressure is generated [53].

61. A detonation exerts tremendous stresses on the pipe mountings as well as on the pipe itself, and pipes typically bounce off their supports [20]. Failure usually occurs because the supports are designed to carry the static pipe load, not severe internal transient pressures [52].

Deducing the Trajectory That a Detonation Has Taken Through a Plant

62. Information on the trajectory that a detonation has taken through a plant can be obtained by metallurgical analysis of so-called Luders lines, which appear in steel that is stressed beyond its elastic limit, and the herringbone patterns associated with brittle failure. It is also possible to calculate the detonation trajectory from the positions of plant fragments, although this can involve a fair degree of uncertainty.

DETONATION MITIGATION

63. There is a German standard on containment of detonations, which specifies a design pressure of 50 bar [27]. Enhanced pressure effects could create transient pressures greatly in excess of this (see paras 31 to 33). However, if the characteristic response time of the vessel or key components is less than the duration of the potentially damaging overpressure, catastrophic failure may not occur. In some circumstances, finite element calculations may be appropriate although these are not that well validated.

64. Passive detonation arresters are used in the UK and many other countries. There are many different designs. The arresting element can be similar to those used in deflagration arresters, but the element has to be stronger or more rigidly held to withstand the higher pressures generated by detonations. Drawbacks are the back-pressure created, and the potential for blockage.

65. German detonation arresters are tested against stable detonations, whereas UK ones are tested against overdriven detonations. The current UK standard is BS 7244 [29]. All European standards will be superseded in 2003 by a new harmonised CEN standard [30].

66. There is a US Coast Guard procedure [43] which requires many tests and subjects a detonation arrester to a wide range of conditions. Some observers contend that USCG tests are more challenging than those in the new CEN standard. The Explosion Control Group at HSL Buxton has carried out many US Coast Guard tests on detonation arresters, and all the arresters tested to this procedure failed. However, the HSL tests were done some years ago, and since then new detonation arresters have been developed that can apparently pass the US Coast Guard Tests.

An important element in both the US Coast Guard and new CEN standards is the inclusion of deflagration tests, even for devices intended for detonation use. These tests have been included because arrester designs have been identified that can protect against detonations but not against slower deflagrations. The reason for this behaviour is not well understood.

67. Active detonation arresters are systems that detect the propagating flame front and activate suitably located rapid isolation valves and pressurised suppressor canisters (see Fig 6). The rapid acting valves close in 20-40 ms [28], and suppressors activate within 10-20 ms. They rely on sophisticated ancillary electronic systems. Often, suppressors are located ahead of the valves to reduce the potential for deformation of the valve plate when the detonation shock wave hits it. Venting may also be needed. It is not possible to rely on venting alone to successfully mitigate a detonation [55].

68. For partially confined explosions, conventional water spray deluge systems have been shown to be capable of providing beneficial effects against fast deflagrations [54].
1 The detonation pressure is the CJ pressure $P_{\text{CJ}}$ referred to in para 26.

2 For general information on the hazards of ethylene oxide, see [47]. For further information on detonation of ethylene oxide vapour in pipelines, see [48].

3 Only the lower detonation limit is reported because acetylene can decompose explosively, even in the absence of air.

4 Calculated using $\frac{\Delta}{\Delta E}$.

5 The von Neumann pressure can be calculated using a technique called non-reactive shock theory once the detonation velocity is known.

6 CJ pressures and velocities can also be calculated using computer programs such as STANJAN.

7 Calculated CJ pressures for some other mixtures are given in Ref 3.2.

8 Whilst peak pressure is a key parameter, the impulse (integral of pressure with time) of the von Neumann pressure is often sufficiently low that it is of limited interest in damage calculations, unless the duration is close to the characteristic response time of a vessel or pipe [53]. See also para 56.

9 The detonation front is composed of a single transverse wave during spinning detonation.

**APPENDIX 1: SUMMARY CHECKLIST OF INFORMATION ON DETONATIONS**

**Factors That Are Essential for Detonation**

- Mixture within detonable range (paras 8-11)
- Pipe diameter critical diameter. For a pipe with circular cross-section the theoretical critical diameter is $\frac{D}{2}$ (para 20), however in practice a suitable safety factor is needed and a critical diameter of $\frac{D}{2}$ (i.e. 50% lower than the theoretical value of $\frac{D}{2}$) has been suggested by one leading expert (para 22). For other shapes see Fig 4. For a detonation which emerges from the end of a pipe into an unconfined area see para 21
- Pipe length to diameter ratio critical ratio for DDT (para 40). The critical ratio is approximately 3 for very sensitive fuels such as acetylene or ethylene in air, and varies from approximately 10 to 60 for other fuels in air
- For an unconfined detonation, cloud diameter greater than the critical cloud diameter (para 53). The critical cloud diameter can be calculated using Ref 3.3, but is likely to be at least 50 m

**Factors That Favour Detonation**

- Low MESG value (para 5, Table 1)
- Proximity to stoichiometric (para 2). This increases detonation pressure and decreases DDT run-up distance
- Pipe diameter not much greater than the critical diameter (para 20). This promotes turbulence, so decreases DDT run-up distance
- Obstacles and bends (paras 37-8, 44-5). These increase turbulence, so decrease DDT run-up distance and encourage overdriven detonations
- Confinement (para 14). Detonation limits are wider in confined than in unconfined areas, but there is some evidence that detonation limits are wider in larger vessels
- Elevated temperature (paras 12-13, 42). This widens detonation limits, particularly the upper limit, but may increase the DDT run-up distance
- Elevated pressure (paras 12, 42). This widens detonation limits, particularly the upper limit, and decreases the DDT run-up distance
- Oxygen enrichment or presence of other reactive oxidants (para 7)
- Absence of diluents
Other Information

Detonation Limits

- Detonation limits can be estimated using deflagration limits, but the methods tend to over-estimate the detonable range (para 11, Ref 3.1)
- Le Chatelier’s Rule can be used to estimate the lower detonable limit of a composite mixture of relatively simple molecules (para 11)

Detonation Pressures

- The peak pressure $P_{\text{vn}}$ and average pressure $P_{\text{ CJ}}$ can be estimated using the equations in paras 26 and 27, but the pressures generated in practice could be up to double these values
- Much higher pressures (up to 100 times the initial pressure, or 5 times the CJ pressure) are often achieved in the overdriven detonation (para 31). This pressure, although shortlived, can be sufficient to cause local mechanical damage
- Pressure piling (para 32) or retonation (para 33) can result in pressures of 2 to 5 times the usual detonation pressure

Damage Caused By a Detonation

- Both peak pressure and overall impulse must be included when considering the failure potential of vessels and other structures (para 56)
- It can be very difficult to distinguish a detonation from a fast deflagration by the damage caused (para 56)
- The size of fragments arising from a detonation depends on the vessel strength. Typically, large numbers of small fragments are produced, but large distorted and twisted fragments can be generated if the vessel is sufficiently strong (para 56)
- Typical pipelines (nominal pressure 10 bar) tend to withstand the steady-state detonation, but rupture where DDT occurs (para 58)
- A detonation can knock pipes off their supports and cause severe damage at pipe bends and obstructions (paras 60-1)
- Damage that has occurred at regular intervals may have been caused by a galloping detonation (paras 35, 59)

APPENDIX 2: REPORTED DETONATION INCIDENTS

Incidents Investigated by HSE

Courtaulds, Derby, 1991 [31]
69. An explosion occurred in an acetone recovery unit. At the time, two out of the four vessels were under repair and the other two were still in use. Acetone vapour escaped from a flange and was ignited by welding. Localised areas of the ductwork were severely damaged, although the majority of the ductwork remained intact.

British Gas, Westfield, Fyfe, February 1985 [32]
70. In an experimental gasification plant, oxygen was being blasted through a red-hot bed of coal in a 10 m$^3$ combustion chamber. The bed was too cool, and when the vapour/oxygen mixture passed to the flare stack the plant suffered what appeared to be a detonation. The plant was subsequently closed.

Incidents Reported in the Literature

71. The incidents below were reported to involve detonations, however in practice it can be difficult to distinguish a detonation from a fast deflagration.

Location Not Reported, US, 1955 [26]
72. A large US refinery unit was destroyed, resulting in a loss of over $20 million. Extensive destruction was caused by fires started when vessel fragments landed. The fragments weighed up to 65 tons and were hurled as far as 1200 ft.
ICI, UK, 1962 [33]

73. A detonation occurred in a pipeline containing ammonia and nitrous oxide. Damage occurred at dead ends and at points where the pipe changed direction, particularly at T-junctions. Estimates, based on examination of the damage, indicated that local pressures of several thousand psi had occurred.
Union Carbide, Texas City, US, 1969 [34]

74. An explosion occurred in a separation column containing vinyl acetylene. A deflagration spread upwards from the base of the column, and detonated when a sufficiently high concentration of vinyl acetylene vapour was reached. Much of the refining unit was destroyed and the adjacent plant was severely damaged.

75. Liquid propane was released from a pipeline and flowed into a valley. About 20 mins after the leak started, the gas cloud exploded violently in what was probably a detonation. The investigation concluded that the detonation was initiated by an explosion in a pump house which triggered a detonation in the unconfined cloud.
Coode Island, Australia 21st August 1991 [20]

76. Twenty-eight solvent storage tanks were interlinked and connected to a vent collection system, which fed a carbon absorber unit. An explosion lifted a 2,000 te tank over the other tanks and into an adjacent car park. Only fourteen tanks remained intact. Out of a total site inventory of 7,000 te, 4,000 te was lost.

APPENDIX 3: OTHER ASPECTS OF DETONATIONS

Gases and Vapours that are Detonable in the Absence of an Oxidant [3]
77. These include gaseous acetylene, ethylene at pressures above approximately 69 bar, ozone and hydrogen peroxide, various azides, chlorine dioxide and nitric oxide. Other materials which are detonable under certain conditions include diazomethane, ethylene oxide (but not propylene oxide), possibly butadiene, cyanogen, proparyl bromide, vinyl acetylene and possibly hydrides of boron. Each material has a minimum pressure needed for sustainable detonation. For further information, see Bretherick [35].

78. There are no recorded well-authenticated examples of detonations in these types of self-decomposing materials in the absence of confinement.

Detonations in Dusts [3]
79. There are few, if any, examples of a powder detonation in an industrial situation. Typical conditions in which a dust detonation could occur are long (several hundred metres), wide lines such as in pulverised fuel power plants [32]. It is much more difficult to detonate a powder than a gas, and run up distances for powders are much larger [1]. Li et al [36,37] states that, in some cases, transition to detonation has occurred in the secondary explosion of accumulated dust, and that the K\textsubscript{st} value is not a reliable indicator of detonability.

80. Confined clouds of aluminium powder in oxygen (possibly also unconfined), coal dust in oxygen and probably corn dust in air or oxygen can run up to detonation. DDT is more likely with finer powders approaching 10 m diameter. Bartknecht [8] states that, in pipes between 20 m and 40 m long, and dusts with K\textsubscript{st} values greater than 200 bar m/s (eg polyethylene, wood, aluminium), a deflagration can run up to a detonation. Similar pressures are generated to those from gas explosions, and the detonation velocity can vary widely but averages 2,000 m/s. It has not been established whether these events are true stable detonations or quasi-detonations. Detonations occur more readily in narrow pipes, but a greater run-up distance is required than for gases with comparable K\textsubscript{st} values.

81. There is some evidence that the addition of flammable gas, in amounts well below the lower flammable limit, can convert a non-detonable mixture to a detonable one.
82. Fangrat et al [38] carried out experiments on dust/oxygen mixtures with a "weak" ignition source. Detonation velocities of 1,550-2,160 m/s were recorded. Tests using corn starch in oxygen and air are reported in [39].
83. A useful reference for further information is Ref 40.

**Detonations in Mists** [3]

84. Mists (typical droplet diameter <10m) can be detonable under confined conditions, although it is much more difficult to detonate a mist than a gas, and run-up distances for mists are much larger [13]. In oxygen, hydrocarbon droplet with diameters upwards of 1 mm can be detonable. Mist detonation velocities can be up to 50% lower than the CJ value, hence the detonation pressure tends to be lower than for gases.

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**APPENDIX 4: REFERENCES**

*Refs 2 and 9 are good "straightforward" introductions to detonation and DDT. Ref 3 appears to be the only textbook available on detonations. It has a lot of useful information, but is very theoretical.*

   1.1 Fig 5.


   3.1 pp 77-8.
   3.2 Table 7.1.
   3.3 pp 108-9.
   3.4 Chapter 6.
   3.5 pp 53-5.

   4.1 Section 5.1 and Fig 5.1.6


9. "Flame acceleration and transition to detonation", unreferenced paper.
   9.1 p 5.


11.1 Fig 87.


13. Informal discussion with Prof SB Dorofeev, Kurchatov Institute of Applied Chemical Physics, Moscow, at 23rd UKELG Meeting, Aberystwyth, 17-19/4/00.


21. "FLAME facility: the effects of obstacles and transverse venting on flame acceleration and transition to detonation for hydrogen/air mixtures at large scale", Sherman and Tieszen, publication not referenced.


32. Informal discussion with A Tyldesley, TD 5, HSE, 18/2/00.


42. "PIPEX Project - flame acceleration in pipelines", unpublished talk by F Nicholls, ICI, at 23rd UKELG Discussion Meeting on Deflagration to Detonation Transition, ICI Runcorn, 21/4/98.
44. Informal communication, Dr D Pritchard, HSL, 15/1/01.
51. "Establishment limits of fuel-oxygen detonations in pipes at ambient and elevated temperatures and pressures for a low energy ignition source", GO Thomas, N Lamoureux and GL Oakley, Report UWA/070600, 2000, University of Wales Aberystwyth Department of Physics (paper to be submitted to Trans I Chem E).
56. Informal communication from Professor GO Thomas, University of Wales Aberystwyth Department of Physics, 27/7/01.
Fig 1: Comparison of Deflagration and Detonation Waves [42]

Fig 2: Example of a Pressure Time Transient for a Stoichiometric Acetylene-Air Mixture [41]
Fig 3: Cellular Structure of a Detonation Wave [1]

Figure 4: Requirements for Successful Propagation of a Planar Detonation in Pipes and Channels [11]
Fig 5: Typical Velocity-Time Transient for Galloping Detonation [3]

Fig 6: Active Detonation Arrester System [28]