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Mechanisms and occurrence of detonations in vapor cloud explosions

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ABSTRACT

Not all accidental releases of flammable gases and vapors create explosions. Most releases do not find an ignition source, and of those that do ignite, most of them result in deflagrations that generate low or moderate overpressures. Under some circumstances, however, it is possible for deflagration-to-detonation transition (DDT) to occur, and this can be followed by a propagating detonation that quickly consumes the remaining detonable cloud. In a detonable cloud, a detonation creates the worst accident that can happen. Because detonation overpressures are much higher than those in a deflagration and continue through the entire detonable cloud, the damage from a DDT event is more severe.

This paper first provides a brief summary of our knowledge to date of the fundamental mechanisms of flame acceleration and DDT. This information is then contrasted to and combined with evidence of detonations (detonation markers) obtained from large-scale tests and actual large vapor cloud explosions (VCEs), including events at Buncefield (UK), Jaipur (India), CAPECO (Puerto Rico), and Port Hudson (US). The major conclusion from this review is that detonations did occur in prior VCEs in at least part of the VCE accidents. Finally, actions are suggested that could be taken to minimize detonation hazards.

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1. Introduction

Accidental explosions of hydrocarbon-air mixtures in oil and gas industries are known hazards that are a danger to life and property. When such explosions occur, industry carries out detailed investigations to determine the root cause of the accident. This information is then used to design facilities or create procedures that will minimize the chance of recurrence.

There are now significant advances in knowledge and understanding of the fundamental properties of deflagrations, detonations, and their similarities and differences. There are also a significant number of accidental vapor cloud explosions (VCEs) for which there is significant quantitative and qualitative information preceding and following the explosion event that generated overpressures. Finally, this information has now been supplemented by field tests demonstrating damage created in large-scale systems after detonations. Given all of this information, it is now an appropriate time to review and to re-evaluate circumstances of prior accidents with intense VCEs.

For many years, the combustion and process safety communities have understood that intense explosions can arise from ignition of flammable gases or vapors, such as mixtures of air and hydrogen or hydrocarbons. Recent events have shown that an extremely destructive explosion can arise from ignition of large clouds containing hydrocarbon-air mixtures. Now as a result of in-depth investigations of the recent VCEs at Buncefield [1–4], Puerto Rico [5], and Jaipur [6,7], our concepts of the intensity of combustion that can occur in a VCE have changed dramatically. We now understand that, under circumstances defined by congestion, confinement, atmospheric conditions, and the specific fuel-air mixture, the most intense and dangerous combustion phenomena, fast deflagrations and detonations, can occur in VCEs.

Preceding and parallel to these investigations of accidental large-scale VCEs, fundamental knowledge of deflagrations, detonations, and the transition of a deflagration to a detonation (DDT) in fuel-air mixtures has improved to the point where we now have some understanding of the mechanisms underpinning the events that create and allow this transition (see, e.g., [8–11]). For example, we now have knowledge of the temporal and spatial scales on which DDT can occur. We know that shock waves and the background congestion and confinement are extremely important for flame acceleration, and these can set the stage for DDT. Finally, from very recent work, we now know that if the mixture is sufficiently reactive and the mixtures become turbulent, DDT can occur with minimal [12,13] or even no congestion [14]. As shown in Section 2, we are even beginning to understand how and when these mechanisms can come into play.

Fig. 1 presents a qualitative picture of how flame acceleration and DDT occurs. The figure separates the process into five phases:

- *Slow deflagration phase*, in which the speed of the deflagration increases due to increases in the surface area of the flame which, in turn, is caused by flame and flow interactions with congestion, confinement or background turbulence. In this stage, there is also a contribution to the flame surface area from flame instabilities. The very early stages of this slow deflagration, when the velocity is in the range 10–30 m/s, is often called a *cloud fire* when referring to large-scale deflagrations. The deflagration speed in this phase can eventually reach the speed of

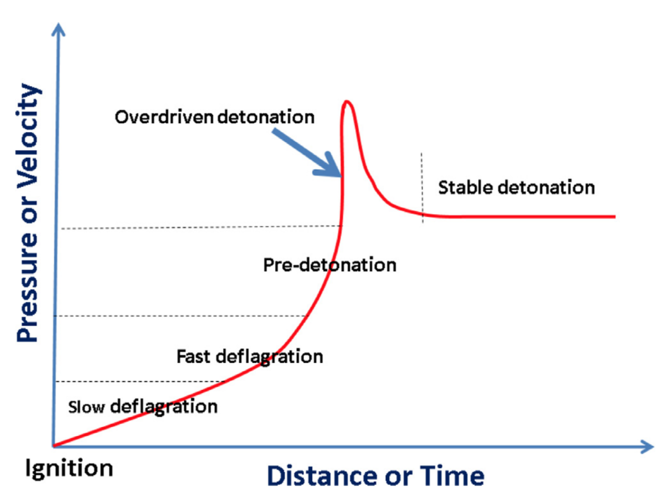

Fig. 1. Schematic showing the phases in the evolution of a combustion system from a deflagration to a detonation.

sound in the mixture. For hydrocarbon-air mixtures, this is the region up to ∼350 m/s. (As described in the next section of this paper, the increase of flame surface area is due to congestion, confinement or turbulence.)

- *Fast deflagration phase*, also called the *fast flame stage*. Here the accelerating turbulent flame generates pressure waves that eventually form into a strong leading shock downstream of the flame. The shock waves compress the flow ahead of the deflagration, and so decrease the reaction time.

The area between the deflagration and leading shock waves becomes extremely turbulent and may contain many interacting shock waves. These shock waves also interact with the turbulent flame, and so further increase the flame surface area. The result is that the turbulent deflagration speed increases further, to the point where it may approach $\sim 0.5D_{cj}$, that is, about half of the Chapman-Jouguet detonation velocity, D_{cj}, of the detonable mixture.[1]

- *Pre-detonation phase*. The is a relatively short time in which shocks and shock interactions create conditions in which DDT will occur. One of the salient features of this phase is the coupling between the leading shock and deflagration. There is often no clear transition between the most intense part of the fast deflagration and pre-detonation phases.
- *Overdriven detonation*, which occurs when conditions behind a leading shock front reach a critical value, the system transitions to a detonation. Immediately after this transition, the detonation is originally overdriven and the local pressure at the DDT site can become very large. However, the overdriven detonation phase is of very short duration, hence it generates proportionally smaller impulse and, therefore, for a real plant environment, it is of less concern compared to other combustion phases presented.
- *Stable detonation propagation*, in which the steady detonation propagates at a speed of ∼1800 m/s, until it runs out of detonable material or is disrupted in some way.[2]

A more detailed explanation of the physical processes occurring in each phase and transition is given in Section 2, where numerical simulations and laboratory experiments are used to describe details of these stages and the transition among them.

There are critical differences in the properties of deflagrations and detonations that indicate that if a detonation does occur in a flammable cloud, it is much more devastating than a deflagration alone. First, the overpressure generated by a detonation is much larger than could be generated in a deflagration. A deflagration initially travels through the flammable regions of the cloud, starting at speeds of a few m/s. Within congested areas, deflagration speeds can rise to the sound speed, ∼350 m/s, and generate overpressures from $\sim 10^{-3}$ atm to a few atm in fast deflagrations. A propagating detonation, however, travels through the vapor cloud at ∼1800 m/s with overpressures of ∼18 atm or more behind a leading shock front. The detonation thus consumes the detonable mixture very rapidly. As it exits the detonable mixture, the detonation wave travels as a lower-speed shock wave that is, however, still strong enough to break glass many kilometers away.

The value of the peak overpressure is not the only parameter to consider in assessing response of a structure to overpressure. The impulse, which is the integral of overpressure over time, is an important parameter. The most damaging case is that of a high overpressure that lasts for a long time. In the initial phase of detonation development, or in the case of a reflected detonation wave, the overpressures are very high. The impulse, however, might not be that damaging as the duration of these overpressures is relatively short.

Various types of obstructions, such as process equipment, piping, trees, buildings, or vehicles, have a significant effect on flame acceleration. This complexity will be discussed continually throughout this report. Nonetheless, once a detonation is created, even in a very small region of a detonable mixture, the detonation will propagate through the entire detonable material. That is, *no congestion is necessary to sustain detonation propagation through the detonable mixture*. In contrast to the case of a detonation, congestion is required to sustain the overpressure in deflagrations. Outside of the congested regions, the flame speed decays quickly and, therefore, the deflagration overpressure decreases quickly.

This paper first describes some of the fundamental concepts developed and published over the past twenty years on the nature of deflagrations, detonations, and the complex transition processes. The emphasis here is on those fundamentals that the authors feel will be most relevant to DDT in VCEs. From there on, the report is focused on a description and analysis of the detailed situations surrounding past intensive VCEs, including the Buncefield, Jaipur, and the Puerto Rico explosions mentioned above. This analysis begins by accumulating and describing "detonation markers," which are objects that are deformed in a characteristic way by the detonation. A number of such markers have been determined recently in the post-Buncefield investigation. After that, the VCEs are discussed using these markers and other available knowledge of the behavior of deflagrations, detonations, and DDT in order to get better insight into which combustion phenomena, deflagration or detonation, are most likely to have occurred in the accident. When it is concluded that a detonation occurred, an attempt is made to identify the most likely mechanisms for causing it.

In its essence, this paper is a revised and modified version of an internal report written for Shell Global Solutions [15]. The original report contained Appendices that described each of the VCE's discussed in considerably more detail. This Appendix is now available online for interested readers on the website www.arXiv.org.

It is hoped that this review will produce insights that can be used to understand the hazards of VCEs, improve risk management, and review control measures (in design, operation, and maintenance) and mitigation systems. Perhaps even more, it is believed that this review will show beyond reasonable doubt that detonations occurred in several accidents and thus improve awareness of the detonation hazard as a first requirement for changes and new approaches to lower the risk and consequences of a VCE. Implementation of such changes could save human lives, maintain confidence in industry, and reduce operational and capital cost in handling hydrocarbons.

2. Mechanisms of flame acceleration and DDT

There are a several important concepts that should be defined before this description of DDT mechanisms begins. First, there is the technical definition of an explosion, which is generally an ambiguous term, but has been defined as: "... any type of scenario in which energy is injected into a system faster than it can be smoothly equilibrated through the system. The result of this rapid injection of energy is a local pressure increase. If the system is unconfined, or if the confinement is weak and can be broken, strong pressure waves (shock waves or blast waves) develop and spread outward, traveling considerable distances before they are dissipated" [10].

[1] The Chapman-Jouguet velocity, D_{cj}, is a property of the energetic gas that does not vary greatly with equivalence ratio. It does vary somewhat with temperature, pressure, etc. This is a topic discussed in many textbooks on combustion.

[2] There are are relatively stable detonation states (galloping detonations, marginal detonations) that form and propagate at lower or highly oscillating velocities, but this property of detonations is left for a more thorough review of possible detonation states.

The words *flame* and *deflagration* are often used interchangeably in both common language and the combustion literature. Here, we refer to a flame as an idealized laminar, essentially one-dimensional reaction front propagating normal to itself, in which fuel is converted to product and heat is released. A deflagration, or a turbulent flame, however, is a more complex structure consisting of a collection of convoluted and distorted flame fronts. Because of the large flame surface area and consequent enhanced energy release, a deflagration (or turbulent flame) can accelerate and reach even faster flame velocities. As shown below, a small, laminar flame can evolve into a turbulent flame, and this deflagration may evolve into a detonation, all due to the presence of congestion, confinement, turbulence, and shock waves.

The importance of shock waves in the descriptions that follow cannot be overstated. We will see that on the small scale, shock waves create scenarios in which flames accelerate and DDT may occur. They also comprise the leading fronts of fast flames and detonations, and so they cause large, impulsive overpressures that can be the source of considerable damage. Shock waves are also the features that allow a fast flame or detonation to reignite and thus to survive, even after it has passed through regions of inert materials.

The material presented in this section describes a number of different ways a detonation can be created once a turbulent flame exists. We begin by analyzing an example of spark ignition in a closed, congested channel filled with a detonable gas mixture. This example is used to describe this sequence of events: the evolution of a small flame or spark to a deflagration, the development of shock waves, a transition from a deflagration to a shock-flame complex (the fast flame), hot-spot formation, and finally DDT. The formation of hot spots, which are gradients in ignition time that may subsequently develop into a detonation, is explained here as one way in which a detonation can be triggered. The mechanism by which a hot spot can make this transition is discussed in more detail below in Section 2.2.

The example is then expanded to discuss several other mechanisms that can trigger a detonation, such as energy focusing, direct initiation, and turbulence. Depending on the properties of the system, such as the geometry, amount of congestion, and type and concentration of fuel, any or all of these transition mechanisms might occur separately or simultaneously in different parts of the system. They are, in fact, similar in one way: all rely on shock formation and shock interactions. This section concludes with a brief discussion of properties of detonations and considerations of the likelihood of occurrence of DDT in a hydrocarbon vapor cloud.

Much of the material in this section is based on extensive theory, experiments, and numerical simulations carried out in the last fifty years. In particular, we have used results from large-scale numerical simulations to help us understand existing mechanisms for DDT as well as to discover additional effects and pathways. The ability to do these types of simulations rests on the development of high-order, low-dissipation algorithms for computing fluid dynamics, reasonable models of chemical reactions and energy release, and the availability of high-performance computing. Some of this has been summarized in prior papers [16,17] and a number of the papers contained in the volume edited by Oran and Williams [10]. Specific references to each of the simulations used to illustrate the different points are given in the text that follows. As explained in the text, the simulations that form the basis for the description that follows have been repeatedly tested and compared to experimental data, where possible. In some cases, which will be noted, they themselves are the basis for new experiments and tests.

In the material presented below, most, but not all, of the discussion is based on studies of confined DDT. VCEs, however, are usually thought of as unconfined, even if there is ground below. Detonation ignition in confined regions, however, is very relevant to VCEs, because the most likely location for DDT in a fuel facility is in a region that has some confinement or obstructions. After it is ignited in this region, it can spread into more open areas. This is, in fact, the situation we have seen from analysis of actual VCEs such as the CAPECO event discussed in Section 5.

2.1. Overview of DDT in an obstacle-laden channel

An overview of the evolution of a system undergoing DDT was shown qualitatively in Fig. 1. The purpose of this section is to familiarize the reader with the shock, deflagration, and turbulence interactions that cause the evolution of the deflagration phase to a detonation phase. These interactions are fundamentally the same in small or large explosions. What does vary are the specific fuels and types of congestion, all of which lead to different specific events in which DDT can occur.

A curious point is that the basic DDT mechanisms described here occur on scales that are microscopic in comparison to the scale of the explosions that may occur in VCEs. This, unfortunately, does not make them irrelevant, but actually gives us a clue into how a small spark might evolve into a turbulent flame which, in turn, could become a detonation. This, in turn, gives us some insight into how we might be able to prevent the occurrence of DDT.

One approach to understanding the underpinning mechanisms of deflagration acceleration has been to examine the evolution of a small flame after spark ignition in a channel containing a flammable gaseous mixture. The overview follows the progression shown in Fig. 1: Once the gas is ignited, a flame is produced, accelerates, and becomes a turbulent flame. Then, depending on the mixture and system geometry, the turbulent flame system may transition to one in which there is a detonation wave. This configuration has been studied extensively experimentally (see, e.g., [18–22]) and by large-scale numerical simulations (see, e.g., [12,13,23–25]) in many laboratories and for many types of flammable gas, system sizes, and channels with and without obstacles.

An example of the deflagration-to-detonation transition in a hydrogen-air mixture is shown in Figs. 2 and 3 (extracted from [23]). These figures are taken from an unsteady, multidimensional simulation with a model for chemical reactions and energy release [23]. DDT is a problem for which the growth in the capability of numerical simulation has allowed significant insight into physical mechanisms. The type of physical domain shown schematically in Fig. 2, a channel containing obstacles and filled with flammable mixture, is the canonical problem setup used to study DDT. In both the experiments and simulations, the channel length and height, obstacle spacing and height relative to the channel size (the blockage ratio), type of fuel, and type of ignition all might vary.

More specifically, Fig. 3 is a sequence of frames taken from a computer-generated movie of a numerical simulation of the flame-acceleration process in a channel with obstacles and filled with a homogenous hydrogen-air mixture. This example illustrates many of the features of the flame-acceleration and DDT process that are related to obstacles, confinement, and the presence of shock waves. *The important points here are not the specific fuel system, or even the specific geometry, but the acoustic waves, shock waves, and different stages of the flame and flame-shock interactions that can de-*

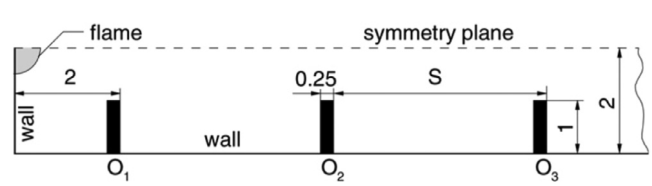

Fig. 2. Schematic of computational domain.

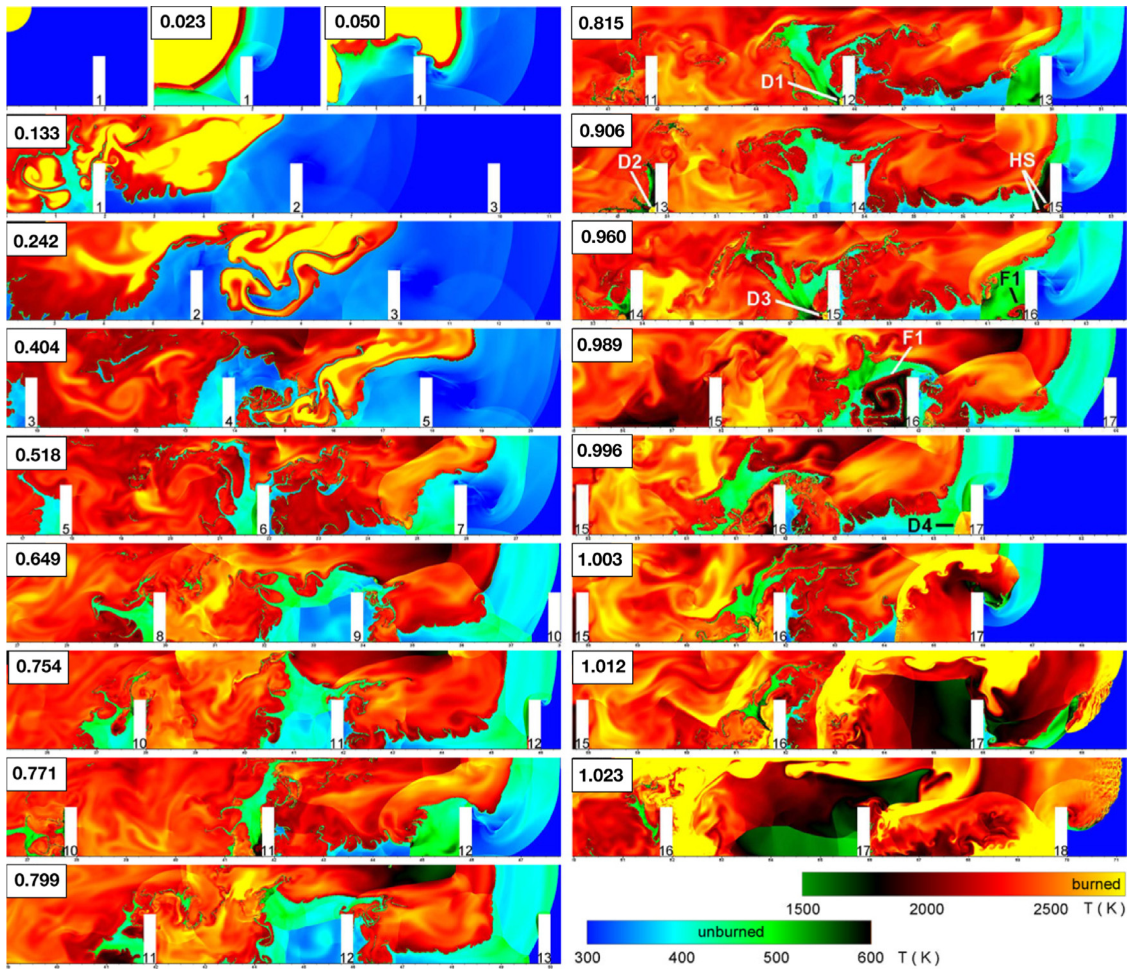

Fig. 3. Results from a numerical simulation showing the transition from a small spark, to a turbulent flame, to a fast deflagration, and finally transition to a detonation, which propagates through the system [23]. This particular simulation was done for a hydrogen-air mixtures in a channel 4 cm high with obstacles 1/2 the height of the channel (blockage ratio = 0.5). Times are given in milliseconds in the upper left corner of each frame. The two temperature scales, shown on the bottom right, are for burned and unburned material as noted. Obstacles are numbered. Symbols D1, D2, D3, D4, F1, and HS indicate hot spots (discussed in Section 2.2), failed detonations, and successful detonations (described in more detail in Sections 2.1 and 2.2). D4 indicates the hot spot that evolves into the detonation that finally dominates the combustion process in the entire channel. The simulations were obtained by solving the unsteady, two-dimensional Navier-Stokes equations with a model for chemical reactions and energy release that was calibrated to conditions produced by a stoichiometric hydrogen-air gas initially at atmospheric temperature and pressure.

velop. Many similar simulations and laboratory experiments have been done with other gaseous fuels, including, methane, acetylene, propane, and ethylene in air, and the results are qualitatively if not quantitatively similar.

In numerical simulations and in laboratory experiments, obstacles in the flow have two important functions. The practical reason is to allow and even force the flame to become turbulent more quickly, so that DDT may occur more quickly and studied more “economically.” The second function of the obstacles is to simulate the effects of flame acceleration and DDT in obstructed flows in a controlled environment that has features of obstacles in an actual, accidental explosion.

The sequence of the frames in Fig. 3 proceeds from the top left to the bottom left frames, and then resumes in the second column from the top right to the bottom right. The physical time for each frame, given in milliseconds (ms), which marked in the small white boxes on the upper left of each frame. The legend at the very bottom shows that the frames use a dual temperature scale, one for the burned and another for unburned material. Obstacles are numbered from the left wall. The absolute location of each frame moves along with the front of the combustion wave. More information about this particular simulation is given in [23], which describes the numerical methods, physical assumption, and gives a more detailed analysis. An important point is that these simulations have been repeated with many different numerical algorithms on many different computers, and results have been compared to many experiments, so the confidence level in the description of the overall process is very high.

The addition of a small amount of energy into the upper right corner of the system ignites a flame that results in flame propagation and expansion of the post-combustion products. This flame quickly spreads after passing the first obstacle. The initial expansion is followed by gradual flow acceleration produced by expansion of burning products, which push unreacted material downstream. The average velocity of the leading edge of the flame starts at the laminar flame speed, about 3 m/s, and then accelerates to about 400 m/s (slightly above the speed of sound in unburned mixture) by ∼0.15 ms, and then to about 820 m/s at 0.65 ms in the laboratory frame of reference. Weak shocks initially produced by the spark ignition decay quickly, but then strengthen again because of the flame acceleration that generates acoustic waves. The flow and flame acceleration are related to the increase in the total burning rate in the system.

Several mechanisms cause the burning rate increase, most of which are related to the growth of the flame surface area and how this surface area interacts with waves in the system. Initially, the flame surface increases as the leading edge of the flame propagates with the fast flow along the centerline. This leaves unburned material in the lower part of the channel (as seen at 0.649 ms). The result is an extended "reaction zone" that spreads over several obstacles, but eventually stabilizes as the gas behind the leading flame front eventually burns out.

The surface area of the flame increases when the flame interacts with shear layers and recirculation flow in wake of obstacles. As the flame passes obstacles, it wrinkles due to the fluid instabilities caused by the flow acceleration and by shock-flame interactions that trigger flow instabilities.

High temperatures behind shocks also contribute to the increased energy-release rate. As the shock and the flame accelerate, the leading edge of the flame remains at a relatively constant distance behind the leading shock, and this can be seen, for example, in the sequence 0.771 ms to 0.989 ms. This is the regime of the *fast deflagration* or *fast flame*. In the laboratory frame of reference, the flame appears to be moving at supersonic speeds, the speed of the leading shock. We have often called this regime a "shock-flame complex" to emphasize the coupling between the deflagration and the shock front. The transition to detonation occurs in some region of highly turbulent, heated, compressed, but unreacted gas between the leading shock and the detonation.

The particular sequence of event in Fig. 3 proceeds in this way: The leading shock diffracts over each obstacle and reflects from the bottom wall, creating a series of Mach stems (stronger, curved shocks). When the leading shock collides with an obstacle, it reflects and produces a hot region behind the reflected shock. Some of these hot regions have the properties that of a "hot spot," a region that is able to undergo a transition to a detonation. There are a number of these hot spots marked in the figure:

- D1 (0.815 ms, Obstacle 12), evolves into a detonation, but cannot survive the transmission through reacted material
- D2 (0.906 ms, Obstacle 13), evolves into a detonation, but cannot survive through reacted material
- HS (0.906 ms, Obstacle 15) evolves into D3 (0.960) but as seen at 0.989 ms, cannot survive as a detonation
- F1 (0.960 ms and 0.989 ms, Obstacle 16) has decoupled into a flame and a shock wave which is seen interaction with main deflagration behind Obstacle 16
- D4 (0.996 ms, Obstacle 17) evolves into a detonation before it can interact with the deflagration, and so is transmitted into the unburned material as a detonation.

The mechanism of hot-spot ignition is reviewed briefly below in Section 2.2. Here we just need to note that the properties of these spots, that is, the temperature, pressure, stoichiometry, and gradients of these quantities, all contribute to whether a hot spot will evolve into a detonation or decouple into shock and flame. The corrugated structure at the reaction front in the last frame (1.023 ms) indicates the complex shocks structure, the detonation cells, at the front of a steadily propagating gas-phase detonation.

The stages in the evolution from deflagration to detonation for this reactive gas (hydrogen-air) and geometrical configuration, as shown in Fig. 3, can be related to the stages shown schematically in Fig. 1. The slow deflagration stage is from the beginning to about 0.4 ms. The fast deflagration stage is roughly from about 0.60 to 0.90 ms. The pre-detonation region here starts at about 0.9 ms, and lasts until detonation ignition of the whole system, which is at about 1 ms. Beyond that, a propagating detonation forms. All of these interactions among shocks, flame surfaces, and obstacles are typical of what happens when a turbulent flame interacts with obstacles in congested regions during flame acceleration and development to detonation. Thus for this particular scenario, we can redraw Fig. 1 to show the flow and flame structure in the various regimes marked on that figure. This is shown in Fig. 4.

As the reactivity of the gas and the geometrical properties of the system change, the time to detonation also changes. For example, for changes of the stoichiometric methane-air in a channel 17 cm high, with a blockage of 0.3, the distance to detonation is more like 10 m instead of the 10 cm for shown for hydrogen-air,

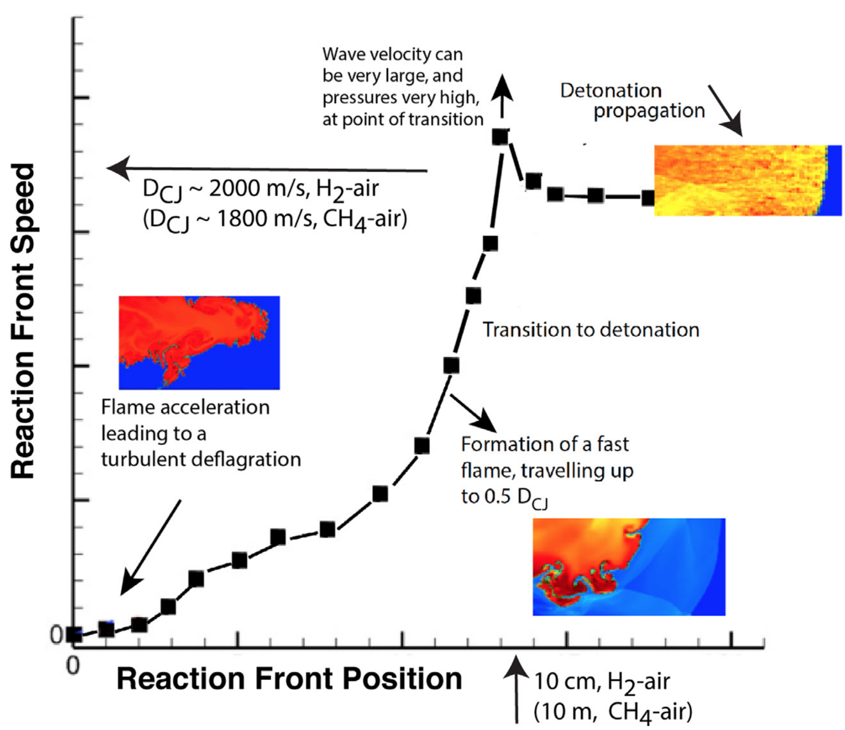

Fig. 4. The details of Fig. 3 related to the stages of flame acceleration and DDT shown in Fig. 1. Figure is marked for both hydrogen-air in a small, 4-cm channel [23] and, in parentheses on the axes, for methane-air in 17-cm channel [25].

the time to detonation increases, and the final detonation velocity changes appropriately for the different fuel. Qualitatively, however, the flow looks and evolves in a similar way, as can be seen by comparing the results in [25] and [23].

There are additional details shown in Fig. 3 that are not shown on Figs. 1 or 4. These include information about the flame front interacting with obstacles, shocks, and shock interactions leading to hot-spot formation. In fact, there are multiple hot spots formed, but there is one main event that can become a propagating detonation that will run through the entire system.

The final detonation waves have a complex shock and reaction zone structure: In addition to the leading shock wave at the front of the detonation, there are transverse shock waves that start at the detonation front, expand upstream, and move vertically through the reacted gas. These transverse shock waves are characteristic of gaseous detonation and are an integral part of the process of detonation propagation. There are many other features that could be discussed here, but these are left to future text books and the many existing journal articles.

The most extensive studies of the type shown in Fig. 3 have been carried out for DDT in hydrogen-air and methane-air gases. For example, the study of methane-air combustion and DDT, reported in [20,25,26] combines experiments in relatively large (1 m diameter) channels, intensive numerical simulations, and scaling analyses. Throughout the remainder of this section, results for studies of methane-air, hydrogen-air, and other hydrocarbon-air mixtures will be used to illustrate mechanisms of DDT. The relation to the types of hydrocarbons that explode in VCEs is discussed in Section 2.7.

2.2. Flame acceleration, shock waves, and hot-spot ignition

As shown in Figs. 1 and 3, when the flame accelerates to a certain velocity, pressure waves are generated. When these waves interact with each other or with obstacles, reactive fluid can be compressed, resulting in both temperature and pressure increases that lower the ignition delay time. When this process becomes intense enough, it creates “hot spots” in the flow, which are relatively small, local regions of very high temperatures and pressures. As discussed in detail below, at high enough temperatures, pressures, and gradients in reactivity, a hot spot may lead to a sequence of autoignition events that can, in turn, evolve into a detonation.

The relations among shocks, which can be detected relatively easily in experiments, to autoignition in gradients in reactivity, which were primarily studied by theoretical analyses, to hot spots, which were seen in numerical simulations, were discussed in depth in a previous review [16]. This review summarized existing evidence showing that explosion centers, which were the site of DDT, have the chemical and physical structure of gradients in reactivity. It also showed how turbulent, shocked flow can create hot spots that are prone to autoignition. Thus the review linked several apparently different concepts to explain where and when a detonation might be initiated.

Here the “gradient mechanism” of detonation ignition refers to a spatial gradient in reactivity, which can be caused by gradients in properties such as temperature, pressure, composition, or stoichiometry. An illustration of the mechanism is shown in Fig. 5. Consider an unreacted gaseous fuel at fixed stoichiometry, dilution, temperature, and pressure, and let the autoignition time be denoted as τ_c. Then if a hot spot has a critical length L_c, and the appropriate gradient of reactivity, $d\tau_c/dx$, ignition delay time in the hot spot generates “reaction waves” or “spontaneous waves.” These spontaneous waves are not initially true waves, but phase waves of reaction, which, after they appear, seemed to be moving through the gradient at enormously high speeds. Each location in the gradient field, however, initially represents an independent reaction site. Because the entire process is moving so quickly, there was not enough time for acoustic communication along the region of the gradient. When the process slows enough to allow acoustic communication, a shock wave forms and becomes a propagating detonation as it leaves the hot spot and propagates into unreacted background gas. The development of a spontaneous wave in a gradient of reactivity, and the subsequent transition to a detonation, is shown in Fig. 5.

As a result of explaining the role of hot spots (or gradients of reactivity) in DDT, the review explained a second important observation: *It is not the flame front itself that undergoes a transition to a detonation, but the turbulent flame creates the conditions that can lead to shock generation, hot-spot formation, and the transition to a detonation in the unreacted flammable mixture.*

As in Fig. 3, the turbulent flame generates acoustic and shock waves as it propagates through a channel. Hot spots are created in unreacted gas that had been shocked repeatedly, so that it was substantially preheated and compressed before ignition. As a result, hot spots are formed at temperatures and pressures significantly higher than those in the background unperturbed gas, that is, in conditions for which auto-ignition times are much shorter. A typical example of a hot spot formed behind a reflected shock and its transition to a detonation is shown in Fig. 6, taken from [10], which is extracted and enlarged from frames in the simulation shown in Fig. 3. If the reflected shock is too weak, the conditions in the hot spot might not be favorable for a transition to detonation, and so result in a flame and a shock that separate quickly.

A third observation relates to the shock-flame complex that is formed in the evolution shown in Fig. 3. This complex is composed of a leading shock, which has reached about half of the theoretical steady-state Chapman-Jouguet detonation velocity, D_{CJ}, of the unburned material, followed at some fairly constant distance by a turbulent flame. This state is not a detonation, which is a very tight complex of a shock followed by a reaction zone, but a much more loosely coupled state. Here the flame and the shock are separated by a highly turbulent, repeatedly shocked gas. This complex is sometimes called a *fast flame* or *supersonic flame*. Fast flames create high-pressure, high-temperature regions in which detonations might occur.

The unreacted gas surrounding the turbulent flame is extremely turbulent. Generally, it has been shocked repeatedly before a hot spot arises. These shocks have a range of strengths and come from any direction in the flow. An example of this flow is shown in Fig. 7, taken from a study of DDT in stoichiometric methane-air mixtures. The nature of this kind of turbulence itself is a challenge and has yet to be addressed adequately [26]. One of the critical roles of turbulence in this process is to create the conditions that allow this transition in the fundamental nature of the propagating front, the transition from a deflagration to a detonation to occur. Feedback between the flame, turbulence, and shocks created in the flow are the key to creating these conditions. Research into how the different stages of the DDT process affects and is affected by various levels and types of turbulence is an important area of current research.

Obstacles (or obstructions) in the flow and their properties (such as material strength, flexibility, or surface roughness) play important roles in the development shocks and turbulence in the flow. First, they provide surfaces from which shock reflect, thus changing the properties of the medium. In addition, they provide the added complication of boundary layers, which themselves may have a range of effects on the flow, including, for example, acting like a nozzle that increases the central flow velocity, or even providing stratified heat layers that can themselves act as reactivity gradients. In a study discussed in some detail in Section 2.4, the wall boundary happened to be one of the natural places for shock

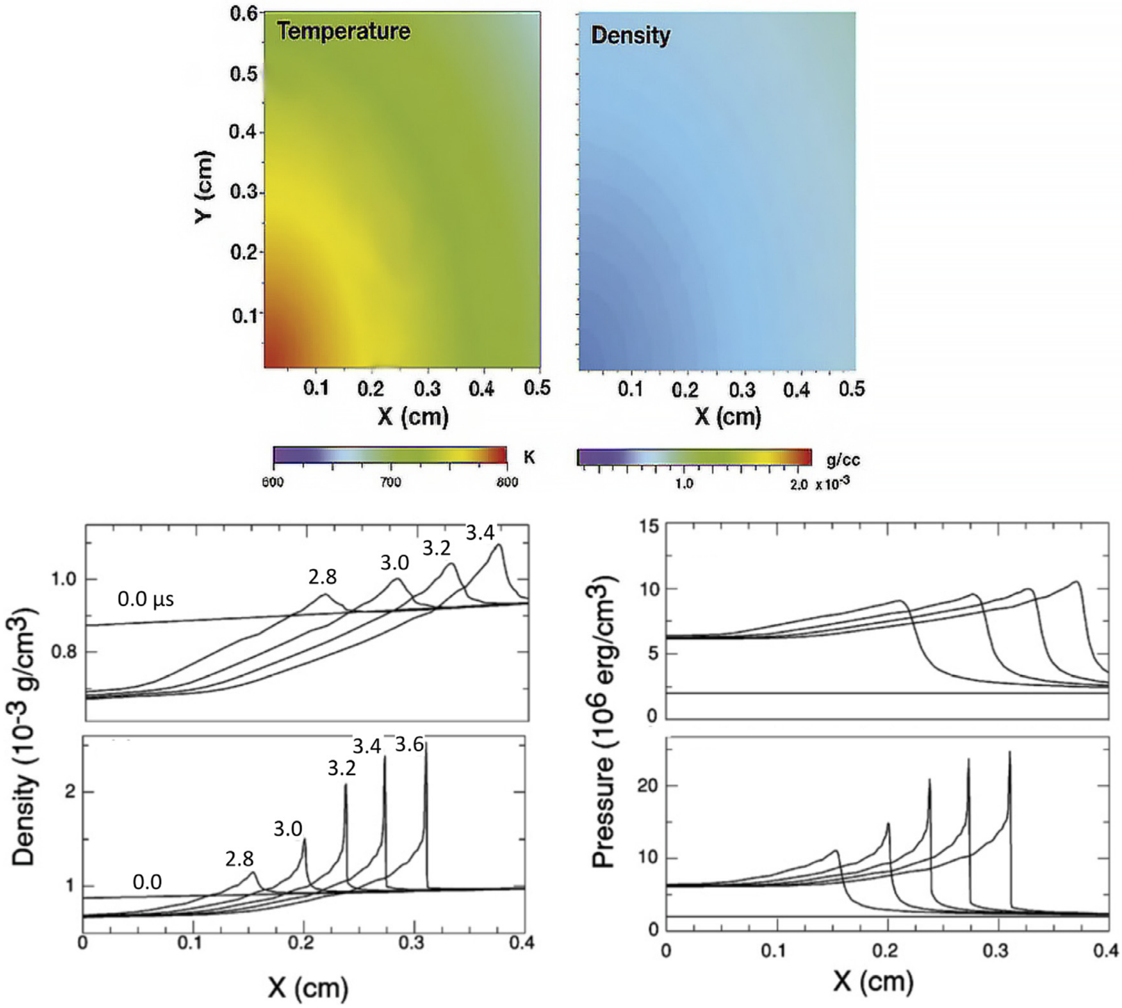

Fig. 5. Evolution of a gradient in reactivity [16]. Top figure: Maps of the initial temperature and density, with pressure held constant. Bottom figure: Profiles showing the evolution of density and pressure for the vertical and horizontal directions. Top row: The shallower gradient never becomes a detonation before leaving the hot spot. Instead, it decays into a shock with a flame left behind it. Bottom row: A spontaneous wave shows transition to a shock and detonation inside the hot spot. Times in μs.

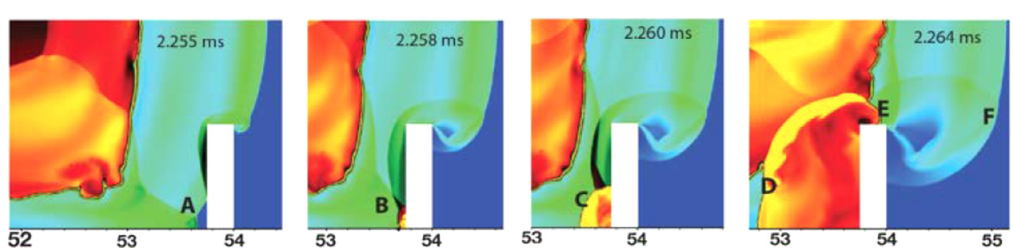

Fig. 6. Sequence taken from a computation of a propagating turbulent flame in an obstacle-laden channel initially filled with a fuel-air mixture at atmospheric conditions at the moment of the transition: after a shock (A) reflects from an obstacle, a hot spot (or gradient in reactivity) forms and ignites near the obstacle (B). This produces a spontaneous combustion wave (C) that propagates into shocked, heated, unreacted gas. This wave eventually transitions into a detonation that moves into the flame (where it becomes a shock) (D) and also passes over the top of the obstacle (E). Eventually this transmitted detonation will catch up with the leading shock, (F). Details are given in [24].

reflections in a heated, reactive medium, a process that caused intense hot spots.

There have been both numerical simulations and laboratory experiments to determine under what conditions the mechanism of DDT might change as the blockage in the channel changes (see e.g., [12,18,19,23,24]). Fig. 3 shows a case for which the obstacle blockage in the channel was relatively large. Then a well-defined hot spot eventually either transitioned into a detonation that moved into unreacted material, or decoupled into a flame with a shock moving out ahead of it, as presented in the detailed description of points D and F in Fig. 3. As the blockage was reduced greatly, however, the detonation arose through complex interactions of multiple shocks and boundary layers in unreacted material. This detonation initiation scenario is discussed further below in Section 2.4.

2.3. Transition to detonation by "Direct Initiation"

One way a detonation can be created is called "direct initiation" of detonation in the combustion and detonation literature. Here it is referred to either as direct initiation or "energy focusing." As shown in the discussion below, direct initiation seems to

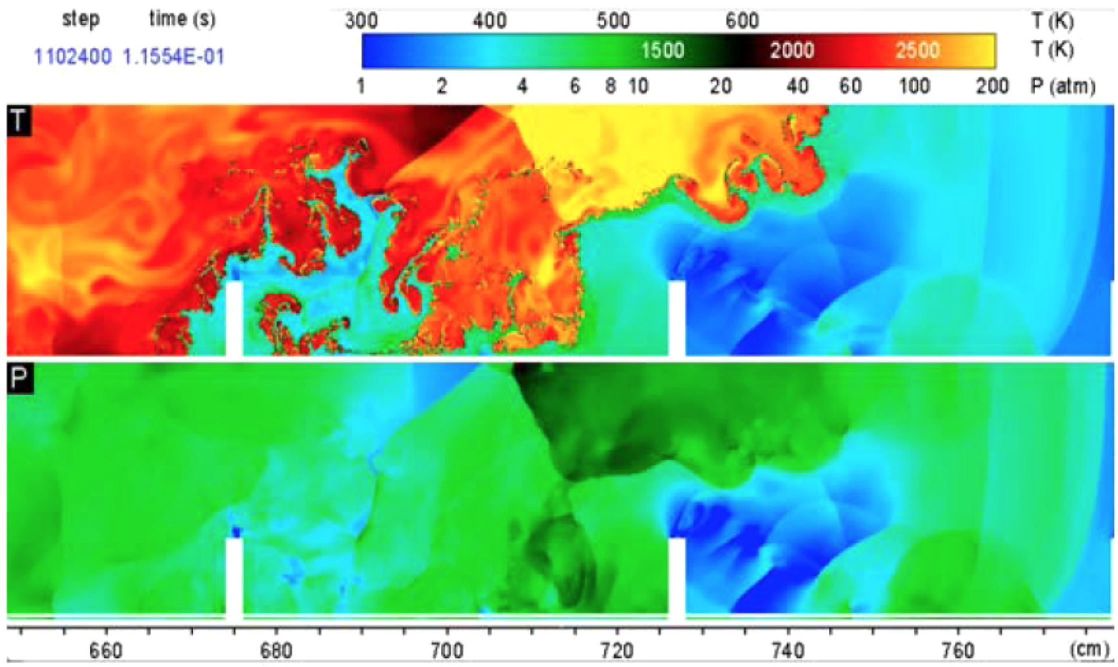

Fig. 7. One time in a simulation of a turbulent deflagration propagating in an obstacle-laden channel containing a *stoichiometric mixture of methane and air* initially at atmospheric conditions. Top frame is temperature and bottom frame is pressure. Color bars across the top show two temperature scales, the upper for unburned fuel and the lower for burned fuel. The turbulent, unreacted flow contains many shocks in both the fuel and product. Many of these, especially those generated at the flame surface, propagate forward and strengthen the leading shock (on the far right). Other shocks interacting with the flame front wrinkle the front more through shock-flame interactions. This is discussed further in [25].

be an extreme form of energy focusing, and the term “energy focusing” may give a clearer picture of what is actually happening.

In direct initiation of a detonation, a large amount of energy is deposited very quickly into a relatively small region in a flammable mixture. The energy can be delivered in many ways, including igniting a condensed phase explosive, igniting a different, more energetic gas-phase explosive, or firing a high-intensity laser into the fuel-air mixture. The result is an intense explosion that initially creates an extremely complex state of matter far from equilibrium, and the system is overdriven. This highly disturbed, high-energy, reactive flow evolves to a steady flow, after which it may be examined to determine if it has become a steady, propagating detonation. If it has, the mixture is considered to be “detonable.”

In experiments to determine the detonability of a gaseous fuel, there are two main indicators, or markers, that are used to determine whether or not the system is able to support a stable detonation. One marker is the final velocity of the leading reaction wave. If this wave reaches and stabilizes approximately at the detonation velocity, D_{CJ}, there has been a transition to a stable detonation.

After detonation initiation, the reaction wave velocity may be higher than D_{CJ}, and this state is called an overdriven detonation. The overdriven detonation velocity decays to $\sim D_{CJ}$ and propagates at that speed until the detonable mixture is consumed.

A second marker that is definitive of a gaseous detonation is the presence of detonation cells. These diamond-shaped patterns are inscribed on surfaces by the leading and transverse shocks at the front of a gaseous detonation. These cells may be visible on the walls of the channel when there are soot coatings on the channels. In the case of GETF, the cells were visualized by covering steel plates with soot and inserting them near the channel exit. In general, however, detonation cells are not easily visible on other than specially prepared surfaces. Cells have also been visualized by open-shutter photography, which is sensitive to the increased light from ionization at shock triple points.

In most cases, detonation cell patterns are highly irregular, but characteristic structures can be identified. At the rich and lean detonability limits, these structures can be extremely large, as shown in [22]. When the numerical simulation shown in Fig. 3 finally produced a detonation, there were horizontal lines across the front of the propagating shock front. Those lines are the transverse shock waves that are a part of the process creating detonation cells. Detonation cells and their relation to fuel reactivity will be discussed further at the end of this section.

Results from an extensive study of the detonation properties of methane-air mixtures in relatively large channels are shown in Fig. 8. The Gas Explosion Test Facility (GETF), built at Lake Lynn Experimental Laboratory (since demolished) was a shock tube, ∼70 m long and ∼1 m in diameter, equipped with diagnostics to define the position of the shock wave and the flame front as a function of time [20]. The experiments proceeded by filling the tube with a methane-air gas in a series of tests in which the mixture composition was varied in the range from fuel lean to rich. Fig. 8b and c show measured pressures behind the leading shock and the shock velocity as a function of the percentage of methane in air. Theoretical values of these quantities are superimposed on experimental data. From data, such as those in Fig. 6, it is possible to find the detonability limits for methane-air for this system, which were determined to be 5.3% and 15.6% for the fuel-lean and fuel-rich mixtures, respectively.

One important point is that the amount of energy required for direct ignition and all of the physical and chemical processes that occur in the process, are essentially incalculable from first principles. It is generally estimated for a series of experiments such as those just described, which show detonation or no detonation for a given amount of energy input. This experiment becomes more difficult at the detonation limits where very large amounts of energy are required. Reference [22] discuss possible ways to extrapolating the minimum energy required for direct initiation based on known or more easily measured detonation parameters. From these exper-

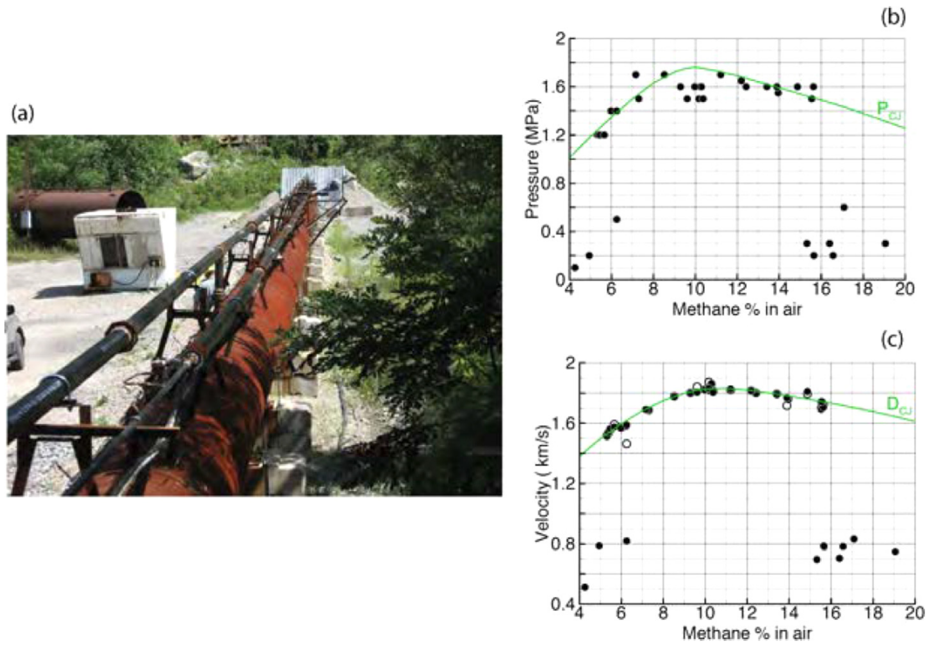

Fig. 8. (a) The Gas Explosion Text Facility (GETF) at Lake Lynn Experimental Mines, showing the 72 m long, 1-m-diameter shock tube used for methane-air detonability studies. (b) and (c) Data obtained for front velocity and pressure behind the shock wave as a function of the stoichiometry in the channel. Black points are data, green lines marked P_{CJ} and D_{CJ} are theoretical values of pressure and detonation velocity. Details of experiment and interpretation of the data are given in [20]. Note that the fall-offs in the values of velocity and pressure at high and low values of % of methane indicate the detonability limit, which is not predicted by theory. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

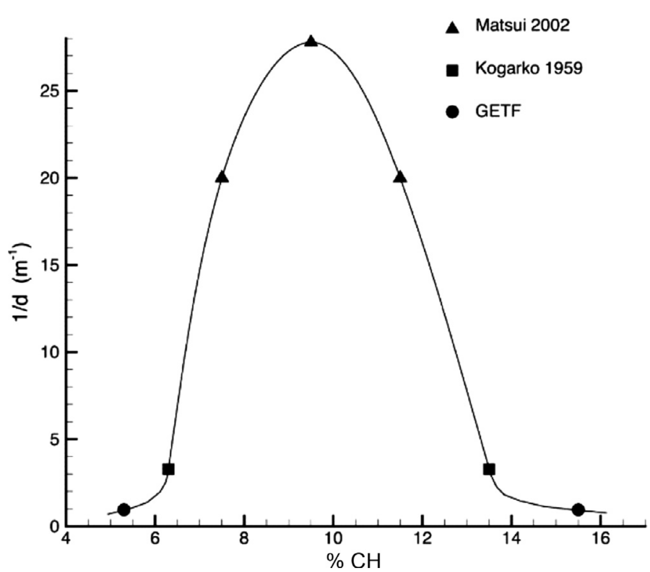

Fig. 9. Comparison of GETF detonability limits to measurements in smaller diameter channels as a function of 1/d, the inverse of the diameter of the channel. The limits expand with the size of the channel [20].

iments, however, we at least know whether a mixture is detonable. If the material is detonable, then a detonation can be created with much less initial energy input by a flame acceleration process, as shown in Fig. 3, if there is congestion, confinement, or other mechanism of flame acceleration.

There is another important point that can be seen from experiments. In general, a set of experimental tests done to determine detonability limits are performed in channels of fixed diameter. It is known, however, that the measured *lean and rich limits of detonability expand as the experimental system size increases*. The effect of changing the system size is shown for methane in Fig. 9, which shows measured detonation limits as a function of channel diameter. Knowing how detonation limits of a fuel-air mixture vary with increasing system size gives us further insight into whether a detonation can be ignited or sustained for large systems.

It is curious that the detonability limits are approaching the lean and rich flammability limits for methane air, which are 5% and 16% respectively. The ability of gaseous detonations to sustain themselves at lower equivalence ratios, or in fact, at any equivalence ratio, is that detonations have the additional multidimensional physical mechanism of interacting shock waves that continually form reignition centers at shock triple-point intersections. For this reason, we might be able to assume that for very large systems, the flammability limits might give a reasonable estimate of detonability limits. This is another topic for further thought, analysis, and measurements.

2.4. Transition to detonation by energy focusing

There is another way to deposit enough energy to create DDT, and that is by energy-focusing, which is part way between something that can be calculated, as hot-spot ignition, and the types of direct initiation occurring in the experiments described by Figs. 8 and 9. Consider Fig. 10, which is taken from a simulation similar to that shown in Fig. 6, but with very small, widely spaced obstacles [13]. The new feature shown here is the region in which a number of shocks "accidentally" collided. The analysis of these event showed that the local energy deposition in a very small region was large, hot spots were formed, and then a detonation emerged. Recent theoretical analyses in [27] and experiments [28] also describe and show this type of detonation initiation.

Energy focusing due to converging shock-waves brings up several intriguing possibilities of DDT occurring in lower-pressure, less intensely shocked fuel-air mixtures. In such cases, the leading shock might not have reached the usual speed before DDT and the deflagration might not coupled loosely as a fast flame or

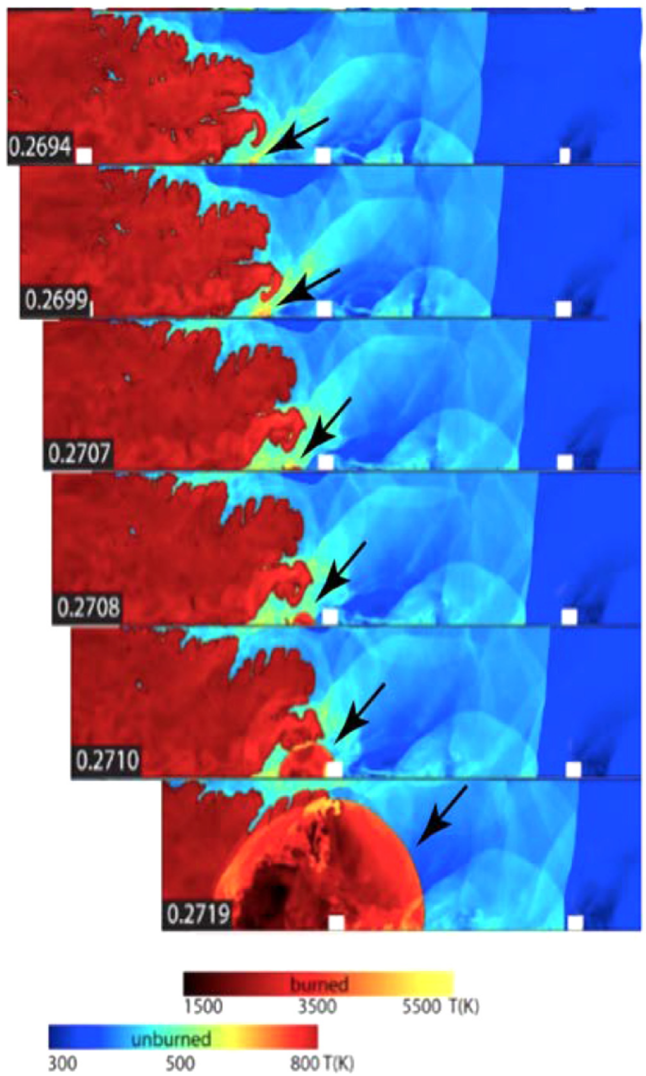

Fig. 10. Simulation showing the transition to detonation in an obstacle-laden channel filled with a fuel-air mixture and for low blockage in the system. The obstacles are indicated by the small white squares on the bottom wall. The mechanism for transition in this case is multiple shock collisions leading to energy focusing at a location near the lower boundary. The arrows point to the location of detonation ignition. Details are given in [12,13].

shock-flame complex and reached the typical high speeds before a hot spot is formed. What is simply needed is enough shocks in the system. The process, in fact, seems essentially stochastic, and might be related to the fuel, the particular confinement or congestion. This is something that could be investigated on the laboratory scale with other means of depositing energy locally, such as by lasers. On a large scale, it must be considered on a case-by-case basis.

2.5. DDT In a turbulent flame (unconfined, no congestion)

Very intense turbulence can have a strong effect on flame development, and this could even lead to a detonation [14]. When the turbulence is intense and the mixture reactive enough, the flame surface quickly becomes very large, convoluted, and densely packed in a small volume. As the packing becomes more intense, energy can be released in a relatively short time in a small volume. Then the pressure rises so quickly that it cannot be equilibrated by acoustic waves. There is then an explosion that generates shock waves. These shocks interact in the unreacted gas between convoluted flame surfaces. The result is then a scenario that looks similar to the focusing effect described above. This process is shown in Fig. 11.

The point here is that the transition location occurred on a very small spatial and temporal scale, one on which energy was released so quickly in the turbulent environment that a shock was formed locally. This shock interacted with surrounding flame surfaces and created complex shock and shock-flame interactions that led to more intense turbulence and more shocks. This resulted in a detonation. This is the type of energy focusing shown above in Fig. 10 for flow in a channel with small obstacles, only now has occurred on an even more compressed time and space scale.

The importance of this result is that it tells us that if the turbulence is strong enough, and shocks are somehow generated, a detonation could form. Another result of the simulations is that at some point in the development of a very turbulent deflagration, the turbulence can self-intensify. At that point, conditions leading to a detonation could occur.

Now to tie this back to situations in which there are obstructions, consider the following scenario. Shortly after a flammable vapor cloud ignites in a region of minimal or no confinement, the turbulent intensity is usually much lower than what is required to generate a detonation. Nevertheless, if there were obstacles present, such as grates, hardwood trees, or other types of congestion. the turbulence could intensify as a deflagration passes through these obstacles.

Experiments to test the predictions for purely turbulence-induced DDT described above have been started at several laboratories (See, for example, [29]). Currently there is an indication that it is, in fact, a valid and actual mechanism. At the time of this writing, it is more certain for hydrogen and is not yet tested for hydrocarbons.

2.6. Fundamental observations from scale studies

The discussion above provided general information and understanding of flame acceleration and DDT. Results that are particularly relevant to understanding VCEs are:

1. It is not the turbulent flame itself that transitions to a detonation, but the turbulent flame creates the conditions in a flammable mixture in which a detonation arises.
2. The actual transition to a detonation occurs in a small tiny region of space and in a very short time compared to times and scales characteristic of surrounding processes in the flow.
3. Fast flames, defined here as turbulent flames loosely coupled to a leading shock, may be precursors to DDT. They do, in fact, create the environment in which DDT can occur.
4. Shocks and turbulence are important and even critical for flame acceleration and DDT.
5. DDT can occur at some distance from the turbulent flame, but in a flammable gas that has been shocked and preheated, provided the gas is sufficiently reactive.
6. If the turbulence level is high enough at some location, and mixture is reactive enough, confinement is not necessary for a transition to detonation. (This has been shown for hydrogen and methane gases in simulations, and for hydrogen so far in experiments.)
7. Once a detonation arises, it can propagate through confined or unconfined regions containing detonable material.
8. For large enough regions, such as, perhaps, in large enough vapor clouds, a detonation can propagate in fuel-air mixtures generally considered outside of the detonation limits measured in smaller systems.

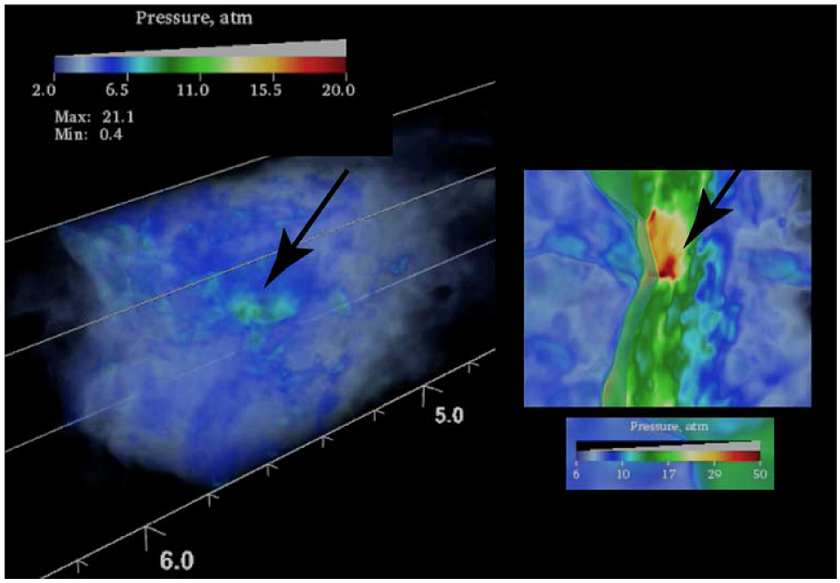

Fig. 11. Simulation of a hydrogen-air flame embedded in a high-intensity turbulent background. Inflow-outflow boundary conditions on end walls. Periodic boundary conditions on sides. Left: Pressure build-up late in the calculation before detonation appears. The highest-pressure areas, indicated by an arrow, are deeply embedded in the flame. Right: Expanded view of small region inside the deflagration shows the development of a shock, again indicated by an arrow. Note the pressure scales for each figure. Details are given in [14].

2.7. How likely is a fuel-air mixture to detonate?

This is an important question. Unfortunately, each type of system geometry, size, specific fuel and reactivity, spatial fuel distribution, turbulence intensity, and background turbulent intensity in the vapor cloud at the time of ignition bring up different issues and possibilities. Fortunately, however, some statements can be made, given the initial conditions.

First, consider the mechanisms of DDT initiation described above:

1. *Flame acceleration in congestion or (semi)confined space* occurs when a sufficiently large and reactive flammable vapor cloud encompasses a sufficient level of congestion. A weak ignition source initiates flame propagation, which accelerates to high velocity (either due to congestion of semi-confinement) creating regions of higher temperature and pressure. Once this happens, DDT may occur [11] due to hot spots (reactivity gradients), shock reflections (Fig. 3), or shock focussing (Fig. 10). This is the most likely cause of DDT in a vapor clouds in industrial settings.
2. *Direct initiation* occurs due to very intensive local, purposeful, input of energy. This is not a likely event during VCEs, unless there is a strong initiator within the cloud.
3. *Energy focusing,* which may occur for minimal confinement or specific arrangements of obstacles, results when shocks, which are naturally generated in unreacted, shock-compressed gases, collide and locally deposit considerable energy.
4. Strong-turbulence initiation might occur without or far from obstacles. In this case, it is necessary to have or create extremely intense turbulence. Once a strong turbulent deflagration is created in sufficiently reactive mixture, it is able to self-intensify as it propagates, and this can lead to a detonation. These are results that have been shown in simulations and are now being tested in experiments.

Thus, there are four mechanisms that may be differentiated, but these are not completely independent. For example, strong explosions due to venting are likely combinations of interactions of turbulence, shocks, shock focusing, and the creation of hot spots in hot turbulent mixtures. This is an area of current research.

The next question is: How likely it would be for a specific mixture to detonate? One way to address this is to examine the detonability of a mixture, that is, to determine the range of equivalence ratios (ϕ) over which detonation has been achieved in well-controlled experimental conditions. An example of this type of study was given above for methane. *The important point for VCEs is that if there is enough volume of flammable mixture and enough congestion or confinement, and if the mixture is within the detonability range, the mixture can be ignited by a weak spark and flame may accelerate to such velocities that the mixture there can be a transition to a detonation.*

Then we need to ask: What do we know about the detonability limits of fuels? Based on the discussion of methane given above, we have seen that in the specific confined system, the detonability limits for methane *approximately* correspond to equivalence ratios:

- Methane: $0.55 < \phi < 1.5$ (or $\sim$5% –16% volume of fuel in air).

For hydrogen, these limits are broader (see, e.g., [30],

- Hydrogen: $0.5 < \phi < 2.0$ (or $\sim$10% – 75% hydrogen in air).

For most hydrocarbons, these limits have not been definitively determined for large systems, although there are some initial estimates [31] for lighter hydrocarbons, such as ethane, propane and butane,

- Light hydrocarbons: $0.75 < \phi < 2$,

and for heavy hydrocarbons, such as hexane, heptane and decane,

- Heavy hydrocarbons: $0.75 < \phi < 1.8$.

We know, however, that detonability depends on scale and boundary conditions. For example, detonability limits measured in different configurations produce different limits (as shown by the limits discussed by [8]). Because these limits are estimated, and the information is incomplete, it is a topic needing further analysis and study. Part of the confusion is due to the wide variety of experimental conditions, such as confined, unconfined, shape of the confinement. Flammability limits are much better defined.

A Possible Route to Estimating Absolute Detonability

Another possible way to assess detonability was suggested in [22]. They combined the data obtained in the Lake Lynn experiments, described above for direct ignition of methane in air, with a scaling law based on properties of detonation cells in measurable regimes. From their analysis, they were able to “predict” the cell size for detonations in large channels. The interesting result is that the predicted cell size agreed well with experimentally determined values.

Then using the notion that a certain number of cells are needed to propagate a detonation, they could estimate a limit for a particular size system. The important point is that really only one correct measurement of cell size was needed to then predict the entire range of cell sizes as a function of equivalence ratio. Whereas this method worked surprisingly well for methane, it has not yet been tested for any other reactive gas.

2.8. Detonation transmission and survival

The material presented above in Sections 2.1–2.7 was not meant to be a review of all properties of detonation ignition, propagation and quenching, which is a very broad topic now that deserves a full article in itself and perhaps several books. It has focused on mechanisms of DDT, and, as 16 most relevant to VCE, on mechanisms of detonation arising from flame acceleration. We have examined how flame acceleration can cause background changes in which DDT may occur.

Now we need to attempt to address at least briefly the question of how, once a detonation is initiated in a confined, partially confined, congested, or highly turbulent fuel-air mixture, it can survive the transition to a region of less confinement or obstruction, and thus it can propagate into the more open spaces of a vapor cloud. From a fundamental reactive-flow point of view, this seems to be a topic that is less well understood than some of the basic mechanisms of DDT.

The question then is: *How do you quench a detonation?* But first, it is important to consider what is meant by “quenching.” When a flame is quenched, we mean that the burning is stopped or reduced to a state where it will stop burning. When we say that a detonation is quenched, we mean that coupling of the reaction front and leading shock is disconnected to the point where it reverts back to the stage of a leading shock wave followed at some distance by a turbulent flame. This is a transition to a shock-flame complex, of some system-dependent degree of coupling, in which the shock and deflagration are more loosely coupled than in a detonation.

The important point here is that quenching a detonation does not mean that the combustion is quenched. The burning or the deflagration may still persist. The shock-flame complex could then be reestablished to transition to a detonation if there continues to be enough fuel present, for example, just as just as was shown in Section 2.2. Alternately, if there is not enough fuel or the mixture is not detonable, the shock-flame complex decays: the shock will decay and the burning will eventually stop.

On a more fundamental level, detonations are known to be quenched by a background change or flow variation that disrupts the continual formation of detonation cells, thus disrupting the basic propagation mechanism. The deflagration will persist as long as there is a flammable fuel-air mixture present. There are, however, a number of ways that detonation cell structure can be disrupted. Here we will mention a few.

- *The fuel runs out.* The most obvious case is when the detonation front enters into a region where there is no flammable mixture present. At the point, the deflagration and leading shock decouple and the leading shock and combustion behind it eventually die. Nonetheless, If the shocks propagate first through a region of no fuel, and then are strong enough when they reenter a region with detonable fuel, they can ignite the fuel and this can restart a detonation. How this occurs is geometry and fuel dependent, and so it is a topic that could use further study.
- *Detonation diffraction.* This refers to the situation in which the detonation propagates over obstacles or into regions of different dimensions. This case has been studied intensively because of its consequences for safety. The important result is that the detonation will survive the diffraction process if it propagates into a channel in which some critical number of detonation cells can exist. More detailed studies have shown that survival depends on the presence and interactions of the transverse waves that comprise the detonation front. Using water or sand are other ways to disrupt the detonation, but these alone will not stop a detonation from reforming unless the flame is also quenched.
- *Change in the reactivity gradient.* A related situation that disrupts a detonation is propagating into a gradient of reactivity which goes in the direction from a stronger to a weaker detonation. Again, the important physics that allows detonations to survive are the transverse waves, the transverse waves structure, and often the formation of transverse detonations in what seems to be a region of the separated shock and deflagration front. This is a case in which the detonation is very robust and usually reignites after it is disrupted (Praveen Honhar, private communication).
- *Turbulence.* Another physical processes that can disrupt detonation cell formation is propagating into background turbulence of a scale on the detonation reaction zone size and with a high enough intensity to effect the leading shock wave. To have a sustained effect so that reignition does not occur, the high-intensity, small scale turbulence must be sustained. This also is a topic for further analysis and study.
- *Thickness of the detonable mixture.* If the size of the detonable mixture is below a critical thickness (typically on the order of three times the detonation cell size), the detonation structure is disrupted and the leading shock front becomes decoupled from the reaction zone.

In summary, we find that propagating multidimensional detonations are very robust. Once started, they are likely to propagate through all of the detonable mixture present. If disrupted, they are likely to reignite at some point if detonable fuel is in the path of the leading shock wave. Much of this, however, needs further study and quantification.

3. Explosion scenarios for VCEs

From the information provided in Section 2, we see that the scales on which a fast flame or a detonation develops are orders magnitude smaller than the scales of a refinery, a chemical plant, or a pipeline. We also learned that congestion helps a detonation to develop, but once it is formed, it will propagate through the entire detonable fuel mixture irrespective of congestion in the background. Most surprising, we learned that when the turbulence and shocks are intense and strong enough, transition to detonation can occur at some distance from any wall or obstacle in the flow. This disparity in scales, the robustness of a detonation once started, and turbulence-induced initiation of detonations present issues we must struggle with here. We now ask:

How can we use the knowledge obtained from carefully controlled laboratory experiments, theory of combustion, and numerical simulations to interpret the events that lead to industrial-scale VCEs?

Fig. 12. Pancake cloud of gasoline vapor formed before the Buncefield explosion [2].

To answer this, we must consider what has been learned about mechanisms of flame acceleration and DDT in confined or partially confined accelerating flames.

An intense VCE can occur when a flame accelerates in a flammable fuel cloud engulfing an industrial plant or natural vegetation (e.g., [1,5,6,8,9,11,32–34]). These regions can be described as "partially confined" or congested on a large scale. Fast deflagrations, that is, turbulent flames generally preceded by a shock wave, may reach sonic speeds and overpressures of several atms. Then before the flame accelerates to 0.5 *Dcj*, a detonation may develop, and this can cause extensive damage to an industrial plant or surroundings. In most cases, however, the leading shock of a fast deflagration, which was created by flame acceleration through repeated obstacles, will die rapidly once the deflagration has emerged from the congested region [9,35]. The deflagration decelerates, and then it proceeds more slowly as a weakly turbulent deflagration, or *cloud fire* through any remaining uncongested or unconfined flammable cloud.

Cloud fires have characteristic velocities in the range of ∼10-30 m/s in the frame of reference relative to the ground. This is slow enough that there are no noticeable overpressures developing. As discussed briefly in Section 1, in the very early stages of the flame ignition problem, when the turbulent intensity is low and before there is no noticeable pressure buildup, falls under the category of a cloud fire. (This was also discussed in Section 2.2 and shown in Fig. 3.)

If, however, a critical supersonic deflagration flame speed[3] is reached before the fast flame leaves the congested area, DDT may occur [9,14]. Then whether DDT occurs or fails depends on the reactivity of the fuel-air mixture and geometrical characteristics of the system. In some cases, DDT can occur once the turbulent flame has left the congested area. In other cases, DDT can occur inside a congested area. Once detonation develops in the vapor cloud, it is a worst case scenario, as it is likely to propagate as a detonation through the remaining detonable cloud. Then, in milliseconds, very high overpressures of 16–20 atm can be generated with a detonation front traveling at around 2 km/s. Devastation of any common objects in the path of such an explosion would be extensive. Following the Buncefield incident, for example, large-scale experiments [1,11] proved that DDT occurred in dense vegetation, and then a stable detonation propagated throughout the remaining vapor cloud in unconfined and uncongested areas. Outside of the flammable cloud, however, the overpressure decay was rapid and it depended on the shape and height of the vapor cloud.

Confined or partially confined regions within a vapor cloud are also hazardous [8,35,36]. A deflagration exiting from a confined region, often called a "vented explosion," can dramatically increase the likelihood of an explosion in an external cloud leading to a detonation. If the external cloud is inside a congested space, DDT is more likely. Even when there is no external congestion, if the scale is large enough, jet ignition by an explosion venting from a confined region into the external unburned cloud can also lead to detonation [37]. (Vented explosions were mentioned briefly at the end of Section 2.7 in terms how they might be initiated through a combination of several of the fundamental mechanisms described in Section 2.)

When fuel is released continuously after an initial momentum-driven dispersion, and there is a significant time between an initial vapor release and its ignition, a gravity-driven vapor cloud is created. If the fuel vapor is heavier than air, it does not rise. The result is a spreading, pancake-shaped, flammable cloud that is more-or-less oval shaped and considerably wider than its height.

Evaporation from a liquid pool might also result in large flammable clouds mainly shaped by the terrain and wind. The height of such clouds depends on their vapor density compared to air, but usually is not higher than 2–3 m.

When fuel releases are large and occur in relatively short times (that is, ten to a hundred seconds), and result from a high-pressure release at certain orientations, so that they remain largely momentum dominated, the result is a hemispherical cloud. The right amount and types of congestion can also contribute to this, although congestion is not necessary. The most important factors are the high momentum and direction of the release, which can create a turbulent cloud that is roughly hemispherical.

An example of a pancake-shaped cloud that resulted from the gasoline spill at Buncefield is shown in Fig. 12. These images were taken a few minutes before ignition. The air temperature at Buncefield was about 0 °C. As fuel droplets evaporated, the fuel temperature decreased (-9 °C), and this cooled surrounding air somewhat. The atmosphere was near the dew point, so this reduction in local temperature was sufficient to create a fog. This fog then contained both water and fuel mist and vapor. Considerable measurements and modeling were done by Chamberlain et al. [5], Moen [8], Bun [32], Johnson et al. [38], Atkinson et al. [39].

Starting with this pancake shape, we look at four practical ignition scenarios of a pancake-shaped flammable cloud and congestion, such that the flammable cloud extends outside the congested region. These are a prelude that will help us understand and categorize the specific VCEs discussed in Section 5. These scenarios, which are illustrated schematically in Fig. 13, are:

1. Deflagration of a large flammable pancake-shaped cloud containing a congested plant with ignition inside the congestion.
2. Deflagration of a large flammable pancake-shaped cloud containing a congested plant with ignition outside the congestion.

[3] Technically, this speed is the Chapman-Jouguet *Deflagration* Speed, S_{CJ}, which is $\sim 0.5 D_{CJ}$. It is discussed in Section 2.5 and in most standard combustion textbooks.

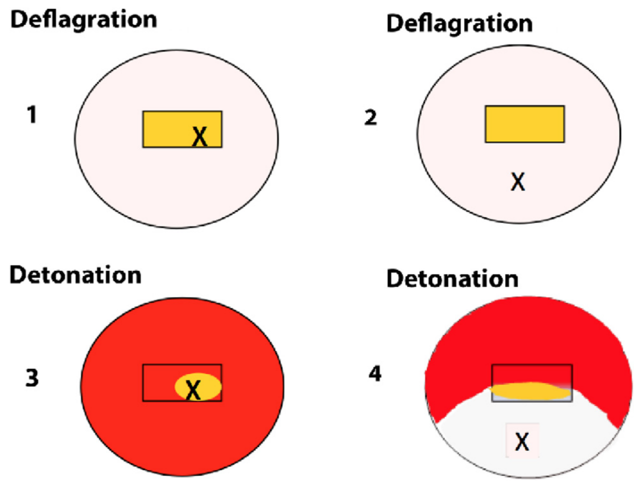

Fig. 13. Four VCE scenarios. The ovals represent a top view of a pancake-shaped flammable cloud, the rectangles are congested regions of industrial plants and X marks the ignition point. Red indicates detonation regions, pink indicates the cloud fire, and yellow indicates a deflagration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Detonation of a large flammable pancake-shaped cloud containing a congested plant with ignition inside the congestion.
4. Detonation of a large flammable pancake-shaped cloud containing a congested plant with ignition outside the congestion.

In *Scenario 1*, ignition inside the congested region starts as a slow deflagration that accelerates rapidly as the flame interacts with the turbulence created by flow around objects. The deflagration does not undergo DDT and stops accelerating when it emerges from the congestion. The remaining cloud burns as a cloud fire. The maximum overpressure reached in the portion of the cloud that engulfs the congested region depends on the size of the cloud, the level and type of congestion and the type and stoichiometry of the vapor. (As explained in detail in Section 2.)

In *Scenario 2*, ignition is outside of the congested region. A cloud fire propagates through the flammable cloud until it reaches the congested region of the plant. At that point, the deflagration can accelerate, but not transition to a detonation. The maximum overpressure that can arise is related to the size of the flammable cloud. The maximum overpressure that can arise is related to the same parameters as defined in Scenario 1.

Scenarios 1 and 2 are the most likely scenarios for VCEs.

In *Scenario 3*, ignition inside the congested region starts a cloud fire that rapidly accelerates through interactions of the deflagration with the turbulence created by flow around obstacles. The deflagration velocity then exceeds the critical value, and DDT occurs inside the congested region. The entire flammable cloud could then detonate and contribute to the overpressure, which is assumed to occur. The VCE at Skikda [5,40] is an example of this type of explosion.

In *Scenario 4*, ignition is outside the congested area. The flame propagates as a cloud fire at around 10–30 m/s, consuming part of the cloud, until it reaches the congested region where flame acceleration occurs leading to a DDT. The detonation propagates into and consumes the remaining unburned detonable cloud. An example of this type of VCE are the explosions at Buncefield and Puerto Rico (CAPECO).

The overpressures reached in each scenario are good measures of the hazard such explosions can cause. Estimates of the overpressures were made using the software package FRED (*Fire, Release, Explosion, Dispersion*), which includes models such as CAM2, (*Congestion Assessment Method*). FRED has been extensively tested and benchmarked, as described in [41,42]. The computations in CAM are based on an effective source radius, R_o, where R_o is defined in terms of volume of the congested and flammable space, V, engulfed by the flammable cloud.

Table 1 shows the effective source size in the final column that is used in the CAM computation. Overpressures are based on values derived from experiments such as Harris and Wickens [9], Mercx [43], For a stoichiometric propane vapor cloud, the maximum overpressure for a fast deflagration is about 5–6 atm for propane before DDT. This value becomes lower as the fuel reactivity increases [16,44] (not shown here). For example, ethylene reaches a critical overpressure of only 2–3 atm before a DDT becomes possible.

Of the VCEs discussed in detail in following sections, the one at Skikda will be shown to follow Scenario 3, whereas Buncefield, Jaipur, and Amuay follow the Scenario 4. The Texas City and Norco explosions are examples of Scenario 1, and Kuwait is an example of Scenario 2. These are discussed in [45].

4. Detonation markers and large-scale tests

In laboratory and in controlled gaseous detonation tests, there are three markers that prove definitively that there was a detonation in a gas-phase fuel. First, there is the speed of the leading shock front, which, for a detonation, reaches and levels off at roughly the ideal Chapman-Jouguet velocity for that mixture, $D_{CJ} \sim 1800$ or more m/s. The second is a high overpressure that follows the leading shock. For typical hydrocarbon fuels, this pressure can be as high as 20 atm. A third definitive marker, when it is present, is the detonation cell structure traced out by the very high pressures occurring in the vicinity of triple shock intersections that comprise the leading detonation front. These diamond-like patterns are observed, for example, when they are traced on a sooty wall or appear in open-shutter photographs, and usually specially prepared surfaces are needed to observe them. (They have not been observed on other harder surfaces.)

For detonations in actual, large-scale explosions, sometimes it might be possible to determine that the wave front moved at speeds approaching D_{CJ} or that walls or objects experienced damage that could only have been caused by overpressures much higher than a deflagration can generate. It is, however, very unlikely (despite a number of interesting, apocryphal stories) that detonation cells would be observed as a result of large-scale accidental explosions.[4]

Because of the extensive large-scale tests performed after the Buncefield explosion, there are now a number of detonation markers that can be used to help determine if a detonation occurred in a VCE [6,37,46]. The result is that we can now use specific forms of property damage (here cars, tanks, oil drums, instrument boxes, oil filters, and directional indicators) to indicate whether the objects were in the path of a detonation. There are direction indicators, such as the way in which poles and trees have been tumbled, that indicate the directions from which detonations were coming when they encountered an object. There is also the persistence of the strong shock wave, as indicated by the level on a Richter scale and distant glass breakage. These large-scale detonation markers and the tests used to define them are summarized below from the more extensive descriptions given in [33,34].

[4] One of the authors, ESO, went to significant lengths (in 2010 and again in 2016) to check a story she had been told (by Gary Schott, then of Los Alamos National Laboratory, in 1984) of detonation cells appearing on the walls of a coal mine after a large-scale coal mine explosion. No living or documented source of information was found until the Lake Lynn Experiments using a methane-air gas, as described in Section 2.

Table 1
Extent of the VCE hazard as measured in overpressures achieved in the four scenarios in Fig. 13. *V* is the volume of the congested area engulfed by the cloud region, and R_o is the radius of the effective source [42].

VCE Scenario	Ignition Location	Overpressure	Source Size, R_o
1. Deflagration	Inside congestion	$<$ 6 atm for propane	$= (3V/2\pi)^{1/3}$
2. Deflagration	Outside congestion	$<$ 6 atm for propane	$= (3V/2\pi)^{1/3}$
3. Detonation	Inside congestion	$\sim$18 atm	Entire cloud remaining after flame acceleration
4. Detonation	Outside congestion	$\sim$18 atm	Cloud remaining after cloud fire

Fig. 14. Damage to cars placed inside a detonating propane-air cloud [33,34].

4.1. Damage to property

The high pressures characteristic of fast flames and detonations can cause substantial damage to property. Here observations and tests are reported that evaluate the effects of high pressures on objects such as cars, oil drums, instrument cases, isocontainers, and storage tanks. This is mainly material summarized and extracted from the Buncefield studies [33,34] and put into the context of this paper.

The value of the peak overpressure is not the only parameter to consider in assessing response of a structure to overpressure. Another often more important quantity is the impulse, which is the integral of overpressure over time. In fact, the most damaging case is that of a high overpressure that lasts for a long time. Generally, the time period over which a detonation remains overdriven is very short, hence the effect of this type of detonation in industrial plants can be ignored. For a stable, propagating detonation, the duration is much longer than the duration of an overdriven detonation, but is generally much smaller than the duration of a deflagration. In general, it would be best to use impulse rather than overpressure to describe the mechanical response of a structure to a blast. Nonetheless, it is simpler and there is more information available if we use overpressure to categorize damage, as is presented in this paper.

Damage to Cars

One of the most striking effects of large explosions on property is the way in which automobiles are destroyed with increasing pressure. Experiments in which cars were placed inside and outside a propane-air cloud that was then detonated by igniting a small high-explosive charge [33,34]. Figs. 14 and 15 are typical of those discussed in [33,34] that recorded damage to the test vehicles.

The tests show that the level of damage depends on whether the cars were inside the detonation region, where pressures and impulses are the highest, or outside the detonation, where the car is subjected to a lower-pressure shock wave. Inside the detonation, measurements showed peak overpressures from 20–27 atm. The side of the car facing the direction of detonation propagation was driven inwards, and generally, the car was completely mangled. Overpressures greater than 1 atm caused some damage to cars placed at a range of distances outside the detonation, but such damage is small compared to damage caused by overpressure inside the detonation region.

Automobile wheels have small grooves into which the edge of the tire, the tire bead, sits. When the tire is inflated, the pressure in the tire keeps the bead in the groove. Debeading tires due to explosions was studied by Haider et al. [47], who concluded that an overpressure on the sidewall of the tire of at least 8 atm is needed to debead it.

Damage to Steel Oil Drums

Fig. 16 shows damage to steel oil drums that were inside the region of the detonation. These drums showed various types of crimping which depended on how much liquid they contained. For steel drums placed outside the detonation, incident overpressures in excess of 3 atm caused similar damage, whereas incident overpressures of 2 atm did not. In particular, the damage at 2 atm was only minor creasing at the top and sides when the level of liquid it contained was above 50% [33,34].

Damage to Instrument Boxes

Fig. 17 shows the effects of overpressure on a small and a large instrument box. At incident overpressures of 1 atm or less, there was no effective damage. The doors may have been opened by the pressure waves, most likely in the rarefaction phase. At incident pressures over 3 atm but less than $\sim$5 atm, distortion occurred to the front doors and, in most cases, to the sides of the box. At incident pressures of over 5.2 atm, the damage to the large box is comparable to the damage of the same box located inside the detonating vapor cloud [33,34].

Damage to Oil Filters

Fig. 18 shows damage to an oil filter that was inside a detonation [33,34]. The filter shows crimping similar to that observed on filters in the Buncefield and Jaipur explosions. Experiments revealed that overpressure of more than 10 atm is needed to cause the damage level seen in on Fig. 18. A detonation is capable of generating such high overpressures. The only way in which a deflagration could produce such pressures is if the waves were somehow amplified exactly on the filter. This would require very high-pressure waves, as could have been caused by fast deflagrations. (See Section 2.) So the crushed oil filter, when combined with debeaded tires (where overpressure should be above 8 atm) and uniformly crushed tanks (overpressure above 8 atm), are strong indications that other combustion phenomena than detonations were not able to inflict such damage.

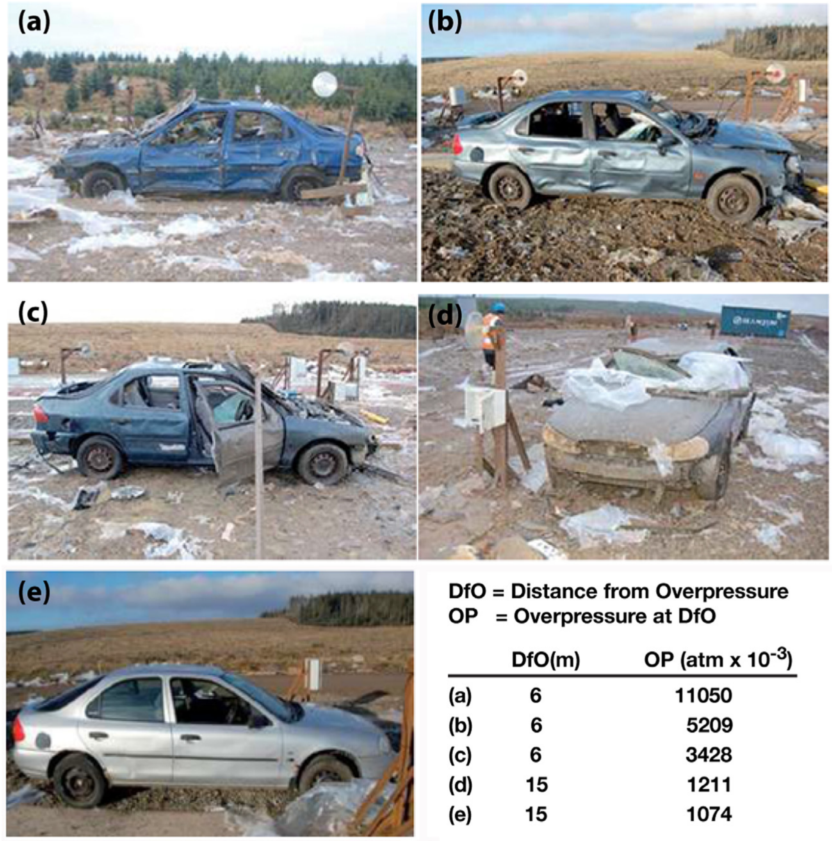

Fig. 15. Damage to cars placed outside the detonation. Peak pressure of the entire overpressure duration is presented. Only minor damage occurred when the overpressure was around 1 atm [33,34].

Fig. 16. Damage to standard steel oil drums placed inside the detonation, (photographs reproduced from [33,34]).

Damage to Iso-Containers

An isocontainer, typical of that used for shipping, was placed at various distances from the detonation. No damage was sustained when the incident overpressure was less than 0.320 atm. There was some minor creasing on the front face when the incident overpressure was 0.426 atm. When the incident overpressure was 2 atm and pulse duration about 5 ms, however, the degree of creasing on the front face was greater and the roof was damaged. This is shown in Fig. 19. At the high pressures, the container was displaced and rotated through an angle of 27^o.

Damage to Storage Tanks

Fluid Gravity Engineering Ltd (FGE) carried out simulations of the incident overpressure and impulse on a 5 m radius, 8 m high storage tank inside a detonation [48]. This was done using their fluid dynamics code, EDEN, and was reported in [33,34]. A typical result is that the pressure loading on a large tank, typical of a detonation, was high on both the front and the rear surface of the tank. It was, however, 30% less on the rear surface. When the tank was placed just outside of the cloud, the drop in loading was about a factor of 5.

A similar study by Venart and Rogers [49] concluded that a detonation was responsible for the damage at Buncefield storage transfer tank 601, as seen in Fig. 20. Uniform crushing of the tank was simulated using the Abaqus Explicit version 6.12-1 finite-element model. The damage computed is typical of that expected for a partially empty storage tank subjected to a detonation propagating around the tank. The minimum overpressure

Fig. 17. Damage to small and large instrument boxes placed inside the detonation, (photographs reproduced from [33,34]). Left figure: A small box, 30 cm × 30 cm. Middle figure and right figures: Two views of a larger 60 cm × 60 cm box.

Fig. 18. Air-filled oil filters placed inside the detonation (photograph reproduced from [33,34]) compared to an oil filter recovered from the Buncefield explosion (shown on the extreme right).

Fig. 19. Damage to an isocontainer when the incident overpressure was 2 atm (photograph reproduced from [33,34]).

Fig. 20. Crushing damage to partially empty tank 601 at Buncefield [49].

required to create this amount of damage was given as 8.5 atm with a detonation wave transit time of 3 ms, estimated from the tank diameter of 6 m and a detonation speed of 2000 m/s [49]. Fig. 21 shows a similar, but less extensive, uniformly crushed empty tank in the VCE at Jaipur [6]. The figure also shows crushed empty tanks at CAPECO in Puerto Rico (tanks 406 and 407 were uniformly crashed and do not have any burn marks; tanks 404 and 405 had thermal damage) [5] and Amuay (Venezuela), where the crushed tanks do not have signs of thermal damage [50].

Fig. 21 also shows a close-up of the empty crushed tank at Jaipur and the absence of crushing on a full tank in the background. There was also an internal explosion in the crushed tank, and this can explain the lesser damage compared to the other tanks in Fig. 21. In addition, the tanks at Jaipur were at the slight elevation, so that the flammable cloud at that location was thinner and therefore inflicted less crushing and bending damage. The

Table 2
Summary of the relationships between directional indicators and their locations relative to the vapor cloud. "Y" = yes, it will create indicators in that location. "N" = no, it will not create indicators in that location.

VCE Type	Inward Deflection towards initiation		Outward Deflection away from initiation	
	In congestion	In open area	In congestion	In open area
Detonation –				
Pancake-shaped cloud				
	Y	Y	N	N
Hemispherical cloud detonated				
at center	N	N	Y	Y
off center	Y	Y	Y	Y
Fast deflagration	Y	Not possible - cloud fire only	N	Not possible - cloud file only
Slow deflagration	N	Cloud fire	Y	Cloud fire
Blast wave outside cloud				
positive pulse	N	N	Y	Y
negative pulse	Y	Y	N	N

Fig. 21. Views of a crushed, empty firewater tank at Jaipur (a) from a distance and (b) close by Johnson [6]. Empty tanks at (c) Puerto Rico [5] (reproduced by permission of the Fire and Blast Information Group, (FABIG), www.fabig.com) and (d) Amuay [50].

vegetation in the foreground of Fig. 21b is broken and leaning towards the east. This type of directional information is an important observation in explosion incidents and is discussed now in Section 4.2 that follows.

4.2. Directional indicators

Experiments were performed [33,34] in which standing poles[5] were subjected to detonations. Typical results, some of which are reproduced in Fig. 22, show that poles were scoured in the direction *opposite* to the direction of detonation propagation. The conclusion then is that inside the vapor cloud, there is a net reverse impulse on objects with respect to the direction of the detonation propagation.

There are, in fact, several scenarios that could generate flow velocities with such negative impulses on poles. The first is a detonation and the second is a fast flame, both of which involve a strong shock wave that could be followed by a strong rarefaction leading to flow reversal. Other scenarios could, for example, include the formation of rarefactions generated by localized explosions of unburned material surrounded by the deflagration region. The important point is the generation of strong rarefactions.

[5] Here we refer to all posts, tree trunks and other poles simply as "poles."

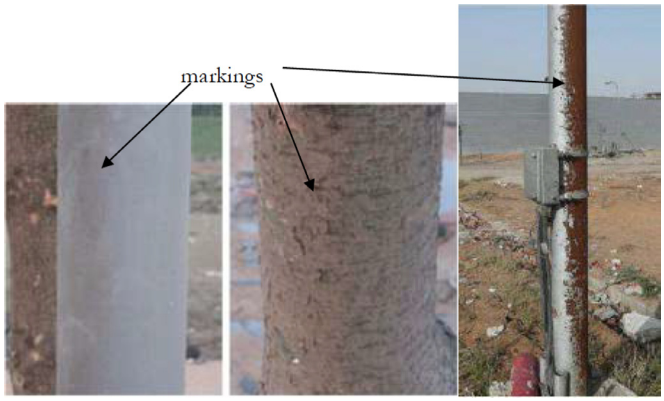

Fig. 22. Marks generated on post (left) and tree trunk (middle) caused by the flow induced behind the propagating detonation [33,34]. The picture on the right shows scouring on a post after the incident at Jaipur [6]. The markings are on the side opposite to the direction of propagation of the wave.

Thus when all poles are considered together over a site that has been subjected to an intense VCE, the directions in which the objects bend or collapse could be indicators of whether a detonation has occurred. Indicators that are in open areas and that bend towards a common region are consistently found when there has been a detonation in pancake-shaped clouds [6,32]. It is important to recognize, however, that inward-pointing poles do not exclusively mean that a detonation has passed. Forensic evidence from directional indicators should be used in conjunction with other evidence.

Nevertheless, in incidents where there is already considerable evidence or certainty that a detonation has occurred, the directional indicators inside a pancake-shaped cloud all bend towards a common point, whereas indicators just outside the cloud and beyond all point away from the cloud. Fig. 23, taken from the Buncefield [1] and Jaipur [6] investigations, well illustrates the point.

Table 2 summarizes information on directional indicators. Detonations in hemispherical clouds are less likely to deflect objects inwards. If the detonation starts in the center of the hemispherical cloud, the spherically symmetric reverse flows of combustion products compress the combustion products uniformly. Then there is little or no reverse flow. A detonation starting off-center or at the edge of a hemispherical cloud results to greater flow complexity behind the detonation, and it creates reverse flows of combustion products over part of the cloud. The important point is that a detonation in a vapor cloud in open space is the only explanation for inward deflection of items.

4.3. The importance of broken glass

Broken glass windows commonly result from shock waves and acoustic stress or thermal stress. It is one type of damage generally associated with accidental VCEs. Accident reports often quote the distances from the explosion at which windows were broken, but with no details about the type of glass, its thickness, or the types of shards created. In addition, there are usually large uncertainties associated with ground reflections and effects of atmospheric inversion layers on the strength of the blast wave at its source. For the present study, therefore, the overpressure threshold for window breakage is assumed to be $\sim$0.01 atm, as suggested by the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers [51].

4.4. The effects of congestion

Evidence from the Buncefield investigation suggested that the deflagration accelerated as it was propagating in a row of trees and hedges [33,34]. A subsequent field test, using 2-m-wide, very dense vegetation (6.5 trees per m^2, area blockage $1.602\,m^2/m^3$) produced a flame speed of about ~ 150 m/s and no transition to detonation. Two other tests, in which a 4.5-m-wide row of vegetation was used, resulted in detonations [33,34]. The tree density in these two tests was 5 and 1.5 trees/m^2, corresponding to area blockages of 0.888 and $0.384\,m^2/m^3$, respectively. Thus, there appears to be no simple correlation between regimes separating deflagration and detonation due to flame acceleration through vegetation.

The continued flame acceleration leading eventually to DDT seems to be a function of the effectiveness of burnt gas venting through the sides and top of the tree line. A 4.5-m-wide row offers considerably more resistance to venting, and faster flames would be the expected outcome. Taylor and Bimson [52] have shown theoretically and experimentally that, for flames in a vented duct, the turbulent flame continues to accelerate if the blockage ratio is greater than about 30%.

Using vegetation as congestion, the area of blockage resulting in high flame speeds was considerably lower than it would be with piping or other types of industrial equipment. One reason for this may be the contribution to small-scale turbulence made by the many repeated small obstacles in the form of leaves, pine needles and small twigs and branches. This should be consistent, however,

Fig. 23. Examples of directional indicators found in the detonation incidents at Buncefield (left) [1] and at Jaipur (right) [6]. The yellow boundary on Jaipur marks the edge of the vapor cloud. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with more fundamental simulations of DDT that can now be carried out.

As shown in Section 2, detonations can develop in fuel-air mixtures in confined, congested areas. On a larger scale, experiments [9,53] have shown that propane-air mixtures can develop into a detonation in sufficiently large spaces. A flame speed of about 600 m/s using round obstacles, corresponding to about 6 atm overpressure, was reached before DDT. In ethylene-air mixtures, the equivalent transition requires an overpressure of about 3 atm [43,54]. Ethane-air has been shown to detonate in pipework congestion [11,44]. These observations are consistent with the theory and experiments discussed earlier in Section 2.

4.5. Pressures from explosions leaving the flammable cloud

Extensive modeling and simulation efforts following the Buncefield explosion provided information about the overpressure produced outside of a pancake-shaped vapor cloud (See, for example, [33,34]). From our knowledge of shock waves, we understand that overpressures *outside* of the cloud decrease rapidly with distance from the edge of the cloud. Simulations performed using the FGE code, EDEN [48], showed a correlation between the maximum overpressure outside the cloud and the ratio of cloud height to distance from the edge of the cloud. From this work, an expression was derived to estimate the maximum overpressure applicable to clouds with a radius greater than 50 m,

$$P = 6.571\left(\frac{H}{D}\right)^{0.975} \tag{4.1}$$

where P is the overpressure (atm) at distance D (m) from the edge of a pancake shaped cloud of height H (m). A simplified form of Eq. (4.1) is

$$P = 7.8\left(\frac{H}{D}\right). \tag{4.2}$$

For smaller clouds (less than 50 m radius), either the Multi-Energy Method or TNT Equivalence was accurate enough within the limitations of tests and simulations performed [33,34]. For example, simulations of large pancake-shaped vapor cloud detonations show that the external overpressure from a detonation would require objects to be within 20 m of the vapor cloud to experience a 1 atm overpressure, assuming a fully detonating pancake-shaped cloud of 3 m high [33,34].

An earlier analysis [55] of the decay of overpressure from a detonating pancake-shaped cloud also showed the rapid fall-off of overpressure with distance. They derived an expression for the overpressure P(atm) as a function of the distance r(m) from the center of the detonating pancake cloud as

$$P(r) = P_s\left(\frac{r-R}{\delta H}+1\right)^{1/2}\frac{2R}{r+R}. \tag{4.3}$$

where P_s (atm) is the initial overpressure of the detonation (assumed to be 0.7 of the CJ pressure), R(m) is the radius of the cloud, H(m) is the cloud height, and δ is the fraction of the cloud height that represents the blast source volume (estimated to be equal to 0.1 based on hemispherical detonations).

Rearranging this equation to obtain P in terms of distance from the cloud edge, D, gives,

$$P(D) = P_s\left(\frac{\delta H}{D+\delta H}\right)^{1/2}\frac{2R}{D+R}. \tag{4.4}$$

Note the dependence of P on H/D and that P is only weakly dependent on R.

A comparison of the Geiger equation with the simplified H/D expression based on the EDEN code is shown in Fig. 24. The Geiger equation gives higher pressure by a factor of 2.8 at 400 m, in the worst instance. For a 100 m radius cloud, the discrepancy reduces to a factor of 2 at 200 m. Close agreement can be obtained by changing δ and P_s, but further research is needed to justify such changes.

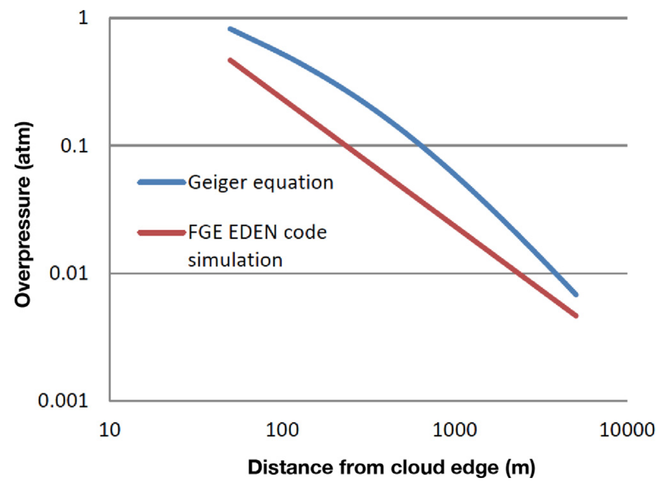

Fig. 24. Comparison of the Geiger result (Eq. (4.4), [55]) with the simplified form of a correlation based on the FGE EDEN code (Eq. (4.2), [48]) for a pancake shaped cloud of radius 200 m and 3 m height.

4.6. Miscellaneous other properties of detonations in vapor clouds

There are a number of important properties of detonations that are complementary to or in addition to those described in prior sections of this paper. They are especially important to our discussions of the possibility of detonations in vapor clouds, and derive from both the material presented in Section 2 and the experimental work that came from the large-scale detonation studies as a result of Buncefield explosion studies [33,34].

First, small variations in fuel concentration from stoichiometric have little effect on the detonation overpressures within the cloud and the blast pressure outside the cloud.

Detonations are robust. Once started, they can find a pathway through a detonable cloud and propagate until the detonable cloud is consumed. A detonation can even survive propagation through regions with no fuel provided shocks are strong enough to reinitiate a detonation in adjacent detonable cloud. This is because of the complex shock structure at the detonation front and how these shocks can reignite once they encounter the detonable cloud. Additionally, we know from experimental tests [33,34] that a detonation can propagate through relatively thin,[6] detonable clouds and find a propagation paths towards adjacent flammable cloud. Hence, once a detonation is initiated, the remainder of such a cloud is likely to detonate and thus contribute to the overpressure. Detonations will stop propagating if the height of a flammable cloud is below a critical thickness. This critical thickness of a flammable layer is not constant for all fuels, but it depends on fuel type, its concentration, temperature and pressure.

The net impulse on objects that are well within a pancake-shaped detonable vapor cloud acts in the opposite direction to the direction of propagation of a detonation. Close to the cloud boundary, where the reverse flow will be shorter in duration, net impulse may act in the direction of propagation of the detonation [56].

[6] Generally considered to be about 3 times the detonation cell thickness for the fuel mixture.

Table 3
Major accidental VCEs summarized in this study.

Event, Date (d/m/yr) Fuel	Release amount[a]	Type of release	Wind (m/s)	Cloud size	Cloud type[b]	Ignition delay (min)
Buncefield, UK, 11/12/2005						
Gasoline	300 MT	Tank overfill	calm	120,000 m^2 200 m radius	A	40
Jaipur, India, 29/10/2009						
Gasoline	1000 MT	Tank-valve failure	calm	350 m radius	A	75
CAPECO, Puerto Rico, 23/10/2009						
Gasoline	600 MT	Tank overfill	calm	370 m radius	A	26
Amuay Refinery, Venezuela, 5/8/2012						
Olefins	4 MT/min before ignition	Pump failure	calm SE drift	300 m radius	A	>3000
Skikda, Algeria, 9/1/2004						
Paraffins C_2-C_4, C_2H_4	10 kg/s	Pipe failure	calm	50 m radius	B, then A	2
Brenham, TX, US, 7/4/1992						
Paraffins, mainly C_2-C_4	500–1600 m^2	Outflow from cavern storage	calm	500 m radius 700,000 m^2 1500 m maximum range	A	30
Ufa, Russia, 4/6/1989						
LPG	2000 - 10,000 MT	Pipeline rupture	calm	2.5 km^2 ($\sim$ 900 m radius)	A	70
Port Hudson, LA, US, 9/12/1970						
Propane	800 l/s, 70MT 120,000 l	Pipeline rupture	Light wind	100,000 m^2 Max 500 m	A	24
Newark, NJ, US, 7/1/1983						
Gasoline	100 l/s 114 - 379 m^3	Tank overfill	1.5 m/s	450–600 m by 60–90 m	A	20
Flixborough, UK, 1/6/1974						
Cyclohexane	2500-5000 kg/s 30 MT	Pipeline rupture	2.5 m/s	60,000 m^2	B	0.3-0.6
Pasadena, CA, US, 23/10/1989						
Ethylene/isobutane	37.8 MT, in seconds	Reactor failure	??	100,000 m^2	B	1-1.5
Decatur, IL, US, 19/7/1974						
Isobutane	176 kg/s reported	Railcar puncture	Light breeze	1200x800 m^2	A	8-10
Beek, Netherlands, 7/11/1975						
C_2-C_4 olefins	40 kg/s 5.5 MT	40 mm pipe break	2 m/s	30–90 m from source	B	2

[a] Conversion is 1 MT (metric tonne) = 10^3 kg.
[b] The cloud type is described in the text.

5. A review Of intense VCEs

This section reviews fourteen actual VCEs and assesses the likelihood of DDT based on prior discussions of the structure and properties of detonations and the physical mechanisms of DDT (Section 2), typical scenarios (Section 3), and detonation markers (Section 4), and results of large-scale field tests to evaluate the cause of the Buncefield explosion (Section 4). The results are presented in terms of tables of properties for each event, including pictures to support observations and conclusions. When available and for most of the VCEs included, there is more detail and occasionally additional analysis in [57].

Throughout this section and in [57], the software package FRED (Fire, Release, Explosion, Dispersion) has been used to compute estimates of overpressures and other explosion characteristics. FRED consists of many submodels, such as CAM2 (Congestion Assessment Method) and these have been extensively tested and benchmarked. All of the models in FRED are described in the *FRED Operational Guide to FRED 7.0* [41]. Publicly available reports using FRED or CAM software are also available, see Puttock [54] and references therein.

Previous reviews of VCEs by Slater [58] and Lenoir and Davenport [59] identified several intense VCEs involving hydrocarbons. Table 3 contains a list of these as well as a number of more recent events, such as Buncefield and Jaipur. The order of the VCE in the table and in subsequent discussions was based on the authors' evaluations of the best to the least studied. The description of the Donnellson event, given in Section 5.14, includes new information and puts forward a hypothesis for why the event did not cause an explosion.

The VCE descriptions are based on photographs and reports that show the results of high overpressures, such as high levels of vehicle damage, debeaded car tires, crushed oil drums and oil filters, directional indicators, and crushed storage tanks. Supplementary evidence came from damaged buildings, broken reinforced concrete, broken windows, and Richter-scale measurements. In particular, these criteria were important to the selection of events discussed:

- Reliable data available.
- Windows broken at a distance of over 3 km from the explosion.
- Richter-scale measurements greater than 2.
- TNT equivalence greater than tonnes.
- Type of hydrocarbon fuel.

In Table 4, damage indicators characteristic of high overpressures and gas detonations are shown for each VCE. Switch boxes and oil drums with damage estimated to have occurred at over 3 atm have been observed in open spaces and therefore indicate that a detonation wave could have passed. Such strong indicators are: the crushed oil filter (above 15 atm), combined with

Table 4
Damage effects revealed by accident reports and published data for the events listed in Table 2.

Event	Vehicle Damage	Car Tires	Switch Boxes	Oil Drum	Oil Filters	Directional indicators		Storage Tanks
	> 5 atm	Debeaded > 8 atm	> 3 atm		> 10 atm	Radially Inwards	Scouring (One Side)	Crimped
Buncefield	Y	Y	Y	Y	Y	Y	Y	Y
Jaipur	Y	Y	Y	Y	Y large filter	Y	Y	Y
Puerto Rico	N/A	N/A	Y	Y	Y	Y?	Y	Y
Amuay	Y	Y	?	Y	?	Y	?	Y
Skikda	Y	Y	?	Y	?	Y	?	N/A
Brenham	Y	Y	N/A	N/A	N/A	unclear	?	N/A
Ufa	Y	N/A	N/A	N/A	N/A	Y	?	N/A
Port Hudson	N/A	N/A	N/A	N/A	N/A	Y	?	N/A
Newark	Y	N/A	N/A	?	?	?	?	Y flattened
Flixborough	Y	Y	?	?	?	unclear	?	?
Pasadena	N/A	N/A	N/A	N/A	N/A	N/A	?	Y
Decatur	Y	?	N/A	N/A	N/A	unclear	?	N/A
Beek	N/A	N/A	?	?	?	unclear	?	Y?

N/A = data not available/applicable, “?” indicates result is unknown or undecided, ‘Y’ indicates “Yes” result to type of damage or marker indicated.

Table 5
Additional information on damage effects. (The question mark in the last column indicates some there is some uncertainty, but that the proposed mechanism is the most likely origin of DDT in each case.

Event	Buildings Severe damage	Reinforced concrete Severed, or very damaged	Windows Broken at < 3km	Richter scale < 2	Detonation? Yes, No ?	Condition for DDT?
Buncefield	Y	Y	Y	2.4	Y	Tree congestion
Jaipur	Y	Y	?	?	Y	Jet ignition?
Puerto Rico	N/A	N/A	Y	2.9	Y?	Jet ignition?
Amuay	Y	Y	Y	?	?	DDT? (insufficient evidence)
Skikda	Y	Y	Y	?	Y	Plant congestion
Brenham	Y	N/A	Y	3.5 - 4	Y?	Tree congestion or drain in road
Ufa	N/A	N/A	Y	?	Y	Tree congestion
Port Hudson	Y	?	Y	~3	Y	Jet ignition
Newark	?	N/A	Y	?	Y?	Jet ignition?
Flixborough	Y	Y	Y	2.7	Y	Plant congestion
Pasadena	Y	Y	Y	3.5 - 4	Y	DDT?**
Decatur	Y	N/A	Y	?	?	DDT?**
Beek	Y	Y	Y	?	Y?	DDT?**

** Most likely plant congestion played a major role.

debeaded tires (where overpressure is needed to be above 8 bar), cars massively damaged (section 4.1), and uniformly crusted tanks (overpressure above 8 atm). The conclusions that a detonation could have occurred in the various events listed in the table is based on considerations of the types of possible combustion phenomena, the overpressures these can generate in open space, and the high level of damage as indicated by markers that require overpressures greater than 8 atm.

A striking factor common to most of these events was the relative calm or low wind conditions at the time of the fuel vapor release. Combined with the fact that many of the released vapors are heavier than air, and there is enough time lapsed before ignition, the initial condition for the VCE was a pancaked-shaped, gravity-driven vapor cloud. Following the discussion in Section 3, we define two types of vapor clouds:

Type A. Flat pancake-shaped, gravity driven, and stratified clouds.

Type B. Approximately hemispherical, momentum-dominated, and more turbulent clouds.

Table 5 gives supplementary information based on other detonation markers observed for each incident. One of the major conclusions of the work performed here is the evaluation of whether DDT occurred and how it was set up (last column of Table 5) based on the evidence gathered and explained in this report, including the detailed evaluations of each incident given in Chamberlain et al. [57]. The Decatur and Beek incidents, included here at the bottom of the table, are the only VCEs, where there is some doubt as to whether a detonation occurred. In these cases, there is not enough information to make an evaluation, although these were powerful events.

5.1. Buncefield, UK, 11 December 2005

The Buncefield explosion on 11th Dec 2005 is the most-studied accidental, intensive, VCE in history [1,60]. As shown in Table 3, ~300 MT of winter-grade gasoline[7] overflowed from a storage tank on a large storage site over a period of 40 minutes before ignition. The ignition most likely occurred when the electric firewater pump was being switched on Buncefield Major Incident Investigation Board [3]. The area covered by the large pancake-shaped vapor cloud was estimated to be around 120,000 m^2. The ensuing explosion was much more severe than any considered previously in major hazard assessments of this type of facility.

The investigation of the incident was overseen by the Buncefield Major Incident Investigation Board [3]. A separate Explosion Mechanism Advisory Group [1] examined the evidence and reported on the severity of the explosion. It concluded that addi-

[7] Summer-grade gasoline has a lower volatility than winter-grade gasoline. The switch is made to reduce the unhealthful evaporation that increases with warm weather.

Table 6
Summary of the Buncefield accident.

Location/Date	Buncefield, UK, December 11, 2005
References	[1–3,32,60–62]
Flammable Substance	Winter-grade gasoline
Release details (rate/time/total)	300 MT spilled over 40 min before ignition. Calm winds, atmosphere near the new point at 1°C
Source of vapor	Overfill of fuel storage tank
Terrain	Tank farm and nearly empty car park
Location of ignition, explosion sequence	Ignition in pump house next to bund ~6.01 am
Directional evidence	Posts, trees, cars, skip drawn inwards towards a common point
Overpressure evidence	Cars, drums, oil filters, buildings, tanks all suffered extensive damage typical of detonation
Fatalities and injuries	No fatalities, 43 minor injuries
Financial cost	~1.5 billion GBP (in 2012) [63]

Fig. 25. The destroyed south side of the Fuji Building at Buncefield. The building was on the west side of an open car park [3].

tional work was necessary and recommended initiation of a two-stage project, which was completed in 2014 [33,34]. The evidence considered is summarized in Table 6.

There were many damaged items at Buncefield characteristic of a blast resulting from a detonation [33,34]. The trees and undergrowth at the site of detonation transition were torn apart, whereas trees near the point of ignition were largely intact, indicating that the initial flame had a relatively low speed, but then accelerated in the congestion created by trees and undergrowth. It has now been shown by many tests that the flame continued to accelerate, and then DDT occurred in the vicinity of tree-lined crossroads at ~100 m from the ignition point.

Parked vehicles located in open, uncongested spaces showed signs of the high overpressures observed in the detonation tests described in Section 4. Partially empty storage tanks not distorted by fire, oil filters, and oil drums were uniformly crushed. As shown in Fig. 25, the Fuji building, on the west side of an open car park, was completely destroyed on one side. Fig. 26 shows evidence for a rapid drop in overpressure from the edge of the cloud. Directional indicators provided by trees, lampposts, fence posts, and a displaced skip and cars all pointed inwards towards the most likely DDT location. A deflagration would have decayed into a cloud fire a few meters into the car park and could not have created the extreme overpressures required to explain the destruction. Figs. 26 and 27 shows some of the many damaged items. Many of these items were located in the open car park and inside the vapor cloud.

5.2. Jaipur, India, 29 October 2009

In the Jaipur explosion [6,7] an estimated 1000 MT of gasoline were released from a defective "hammer blind valve" at the base of a storage tank over a period of 75 min before ignition. The cloud dispersed over the entire 700-m by 600-m site, giving an equivalent radius of 350 m. Although the ignition source remains unknown, the explosion is thought to have ignited in the northeast of the site as a deflagration.

The Jaipur incident showed many similarities to the damage effects at Buncefield. Trees, vehicles, oil drums and buildings were damaged in the same manner. Information about this incident is summarized in Table 7. Directional indicators within the vapor cloud pointed inwards towards a common location, as shown in Fig. 23.

The conclusion, then, is that the VCE incident at Jaipur experienced a detonation. The vapor cloud explosion could not have been caused by a deflagration alone, given the widespread occurrence of high overpressures and directional indicators in open uncongested areas containing the cloud. The overpressure damage and the directional indicators show that the flammable vapor cloud covered almost the entire site, as shown in Fig. 23, and dispersion of the flammable cloud was limited only by a surrounding wall. The evidence from overpressure damage and directional indicators is consistent with a detonation propagating through most of the pancake-shaped cloud. The directional indicators point to the source of the detonation being in the pipeline division area in the north east corner of the site. The most likely cause of the detonation is a flame entering either the pipeline area control room or the pipeline pump house, causing a confined or partially confined explosion that then initiated a detonation as it vented from the building into the remaining cloud.

5.3. CAPECO, Puerto Rico, 23 October 2009

This VCE in Puerto Rico [5,64] occurred within days of the Jaipur explosion. A gasoline storage tank overflowed for 26 min, resulting in a vapor cloud of 370-m radius that subsequently ignited. A site visit was made by one of the authors (GAC) at ~5 months after the event. At that time, most of the damaged items

Table 7
Summary of the Jaipur accident.

Location/Date	Jaipur, India 29 October 2009
References	[6,7]
Flammable Substance	Gasoline
Release details (rate/time/total)	1000 MT released over 40 min before ignition.
Source of vapor	Failure of a hammer bind valve connected to the base of a storage tank. Atmospheric temperature 35°C.
Extent of Flammable cloud	Cloud dispersed over the entire site (700 m by 600 m) bounded by a wall. 350 m equivalent radius.
Terrain	Tank farm
Location of ignition, explosion sequence	Ignition source unknown. Explosion thought to have ignited in the NE of the sites as a deflagration, and then vented explosion from control room or pipeline pump house. Then jet ignition initiated a detonation in the rest of the cloud.
Directional evidence	Posts, trees, cars, were drawn inwards towards a common point. Scouring on one side of the posts opposite to the direction of propagation of the flame.
Overpressure evidence	Cars, drums, oil filters, steel boxes, buildings, tanks all suffered extensive damage typical of detonation.
Fatalities and injuries	11 fatalities
Financial cost	N/A

Fig. 26. A few of the many damaged items at Buncefield [3].

were intact, but vegetation had grown back at the east end of the site (called the bamboo area).

The entire explosion was recorded on CCTV and thousands of photographs were taken just after the incident. Nonetheless, an interpretation of the course of events is not straightforward. Apart from lines of LPG vessels, known as "bullets," there were no congested areas in the site. Evidence from both the CCTV and internal explosions in huts containing electrical switchgear show that ignition occurred at the west end of the site, probably by the switchgear. Then a cloud fire propagated to the east and sped up as it burned around the LPG bullets. The flame then slowed as it emerged from the bullet region, but sped up again a few seconds later as it propagated towards the east end of the site. Then there was a major explosion.

The origin of the main blast, however, remains uncertain. A triangulation of a sudden build up and flash of light, which occurred ~7 s after ignition, suggests a major explosion between two tanks. As explained in the Chamberlain et al. [57], there is evidence that a detonation developed in the long pipes of the drain system before exiting into and detonating the existing vapor cloud. Then the high-pressure detonation or fast flame emerging from the pipe collided with outside articles and this led to DDT in the vapor cloud. The evidence used is given in Table 8. This explosion is described in considerably more detail in the Chamberlain et al. [57].

5.4. Amuay, Venezuela, 25 August 2012

For several days, olefins were leaking from a pump on the plant. The operators assumed that the gases would naturally disperse in the prevailing winds. On the day of the event, however, the wind direction changed, so that a large vapor cloud formed across the site and surrounding area. Ignition was probably caused by a vehicle driving into the cloud. The greatest devastation was to the south of the plant and to the east in residential areas. Both of these areas had relatively little congestion.

Buildings within the cloud were totally annihilated, and their reinforced concrete supports were ripped apart. Some broken fence poles pointed inwards towards the refinery. Part of a damaged footbridge also pointed inwards. The level of damage to vehicles in the explosion region is consistent with a detonation. Some storage tanks were uniformly crushed, and crushed oil drums indicate at least 3 atm overpressure in an open area. All of these observations are consistent indicators of a detonating cloud rather than a deflagration, but it is not clear where or by what mechanism DDT occurred. Ignition from a fast flame or detonation (here called "jet ignition") from confinement or buildings leading to subsequent DDT in the external cloud is one possibility. Table 9 summarizes the event, which is discussed in considerably more detail in the Chamberlain et al. [57].

Table 8
Summary of the CAPECO, Puerto Rico accident.

Location/Date	CAPECO, Bayamon, Puerto Rico, 23 October 2009
References	[5,64]
Flammable substance	Gasoline
Release details (rate/time/total)	600 MT (757 4m^3) over 26 min before ignition.
Source of vapor	Tank overfill, Wind very light, 1.5 m/ s from the SE.
Extent of flammable cloud	433,000 m^2, 370 m radius
Terrain	Tank farm, scrub land, bamboo, trees.
Location of ignition, explosion sequence	Electrical switchgear to the west of the site, followed by flame propagation through a long culvert, empty LPG bullets, Piperack, drain system, finally into highly congested, dense vegetation, and congested pipework between tanks 404 and 405.
Directional evidence	Damaged items inside the bamboo area pointed inwards. Damaged items outside pointed away from this area. Overall, the vast majority of directional indicators point towards the area between tanks 404 and 405.
Overpressure evidence	2.9 on the Richter scale
Discussion	Possible DDT
Fatalities and injuries	No fatalities, no injuries.
Financial cost	???

Table 9
Summary of the Amuay Refinery accident.

Location/Date	Amuay Refinery, Venezuela, 25 August 2012
References	[40,65,66]
Flammable substance	Olefins
Release details (rate/time/total)	At ~1.10 am, a leak from an olefin pump ignited. The flow rate seems to have been about ~8 m^3/min, according to the PDVSA[a] report.
Source of vapor	The leak started several days earlier. Operators were told to continue working and allow the wind to disperse the vapors. Wind reduced to near calm ~12 am. The vapor drifted from the NW to SE over the plant.
Extent of flammable cloud	4 MT/min. See https://doi.org/10.31224/osf.io/cmazh for discussion.
Terrain	Refinery plant with lower areas around bunds.
Location of ignition, explosion sequence	Allegedly, ignition caused by a car traveling down Avenida Bolivar Road into cloud.
Directional evidence	Some broken fence poles point inwards towards the refinery. Part of damaged footbridge points towards the plant. Both are indicators of detonating cloud.
Overpressure evidence	Vehicle damage consistent with detonation. Also, buildings within the cloud were totally annihilated. Tank damage consistent with high overpressure and detonation.
Discussion	Damage evidence is confusing. Some of it is consistent with overpressures from a detonation, but it is difficult to understand how the DDT occurred.
Fatalities and injuries	55 people died, over 100 injured.
Financial cost	????

[a] PDVSA, Petróleos de Venezuela, S.A. (Petroleum of Venezuela) is the state-owned oil and natural gas company. It has activities in exploration, production, etc.

5.5. Skikda, Algeria, 19 January 2004

Of the collection of case histories of large-scale VCEs discussed in this paper, this is the only one that took place in an LNG plant. Table 10 summarizes the event. Sonatrach (Société Nationale pour la Recherche, la Production, le Transport, and la Commercialisation des Hydrocarbures) is a company owned by the Algerian government for the purpose of exploring the hydrocarbon resources of Algeria. Of its many operations, it ran Skikda, an industrial zone ~300 km east of Algeriers. Skikda had one of the largest oil refineries in Africa until the large explosion in 2004 [40,67].

A photograph of the damaged area is shown in Fig. 27. The composition of the fuel released in the Skikda explosion is unknown, but it has been narrowed down to either LNG (methane) or mixed refrigerant as used in the proprietary PRICO process. As such, it could contain a substantial amount of highly explosive and detonable ethylene. The equivalent fuel for this composition is propylene, as calculated by CAM2 model contained in the Shell FRED suite of hazard software [41].

The release rate is unknown, but eye witnesses reported that a visible cloud, which would be at least the extent of the flammable cloud, traveled about 80 m towards the Maintenance Building. This would be consistent with a leak of liquid refrigerant from a 1″ pipe break. Simulations using FRED "Pressurized Release" [41] predict that the release rate is about 15.75 kg/s, and that the dispersion distance to the lower flammable limit of the mixture is 85 m.

An operator noticed that the steam pressure in the boiler drum was rising to the point where the pressure safety valve was activated, which is consistent with the eye witness accounts that a vapor cloud was developing. The operator then cut the fuel gas supply, but the pressure continued to rise. An outside operator reported to the control room that he could see a large vapor cloud developing in Unit 40. Several witnesses saw the cloud developing towards a Maintenance Building to the west and towards Unit 30 to the east. At this time, there was a small explosion in Unit 40, followed quickly by a second explosion, then a third larger explosion and fireball.

Photographs of the damage show that the Control Room and Maintenance Building were totally destroyed. Some reinforced concrete supports from the remains of the Maintenance Building were displaced towards Unit 40. Several poles in the open space between Maintenance Building and Unit 40 and a tower support were bent inwards towards Unit 40. This space also contained a few crushed oil drums, which indicates overpressures greater than 3 atm. A large truck was damaged in a manner indicative of overpressure >5 atm. A collapsed flash drum and railings were drawn to the SW on Unit 40. These indicators, such as lamp posts in open space and part of the unit, were bent towards the origin of the explosion. Deflagration cannot cause such damage. The areas pro-

Table 10
Summary of the Skikda accident.

Location/Date	Skikda, Algeria, 19 January 2004
References	[40,67]
Flammable substance	Cold LPG, or methane, or mixed refrigerant. Most likely mixed refrigerant.
Release details (rate/time/total)	The release time is approximately 2 min, as per presentation by Achour and Hached [40]. The hole size is not known, but it is estimated as 2.5 cm to match the cloud cover. Estimated release rate is 15.75 kg/s. Thus the total fuel released is ~2000 kg.
Source of vapor	Gas leaking from pipework above a boiler created a high-pressure steam. The boiler ignited the dispersing gas cloud. It is suggested that the gas came from one of the cold boxes in Unit 40. Five minutes earlier, there was no vapor. There was no wind that day.
Extent of flammable cloud	Not known, but eye witnesses report that a vapor cloud reached the Maintenance building ~80 m from the release point.
Terrain	Process trains, typical LNG process plant layout.
Location of ignition, explosion sequence	Ignition to the north of Unit 40 in the boiler furnace. Furnace explosion followed quickly by vapor cloud explosion.
Directional evidence	Many items moved inwards towards Unit 40. refinery. Part of damaged footbridge points towards plant. Both are indicators of detonating cloud.
Overpressure evidence	Administration and Maintenance Buildings completely destroyed. Windows shattered at least 2 km away.* Some metal projectiles were found 100–200 m from train 40. Crush injuries from collapsed buildings, similar to earthquake incidents. Three trains (40/30/20) were totally destroyed. Minor damage on Train 10. On Train 5, at 100 m from Train 40, there was no damage, except for few broken windows on side facing the explosion. Adjacent town suffered minor damage.
Discussion	See text with overpressures from a detonation, but it is difficult to understand how the DDT occurred.
Fatalities and injuries	27 killed, 74 injured.
Financial cost	~$800 million.

* Evidence from report by S. Davis. There were no buildings beyond this distance.

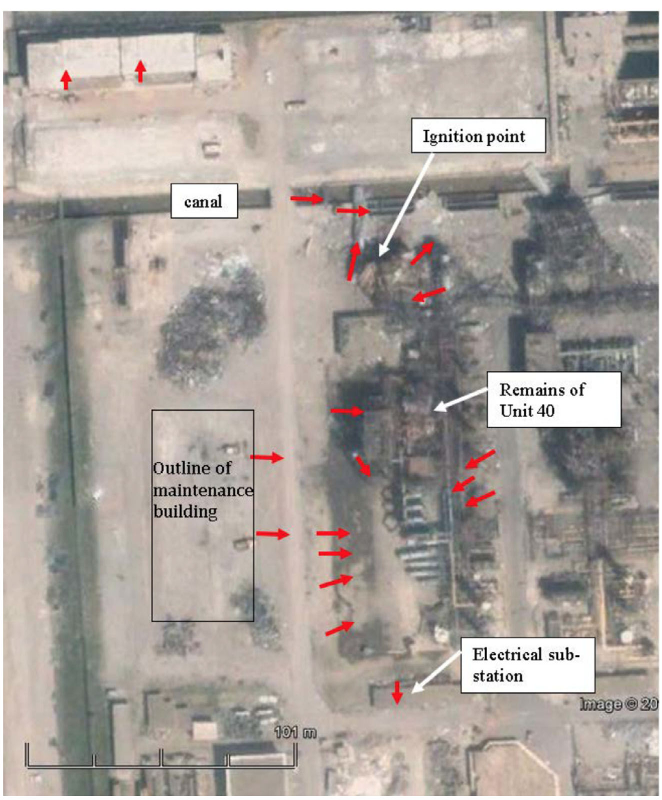

Fig. 27. Directional indicators derived from photographic evidence of the Skikda explosion (Google Earth image with overlays).

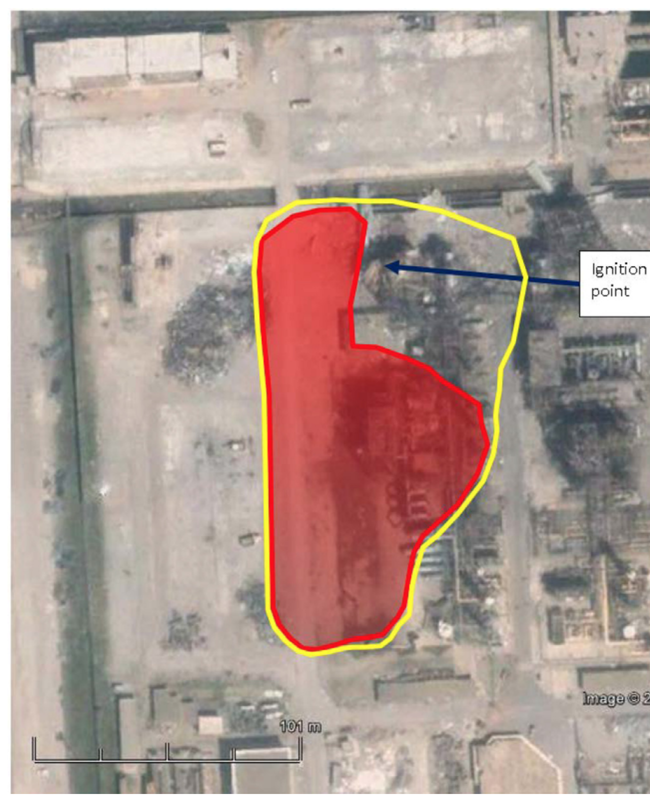

Fig. 28. Proposed area of detonation (red) and cloud size (yellow boundary) (Google Earth map with overlays). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

posed for the extent of the flammable cloud and detonation are shown in Fig. 28.

In summary, the following course of events is proposed. A leak of mixed refrigerant liquid occurred from a pipe-break in Unit 40 at a rate of about 15.75 kg/s for about 2 min forming a large vapor cloud. An explosion first occurred in the furnace of Unit 40 after inflow of vapors into the furnace. The vapors consisted of mixed refrigerant, equivalent to propylene vapor, which vented into the cloud that had formed in approximately 2 min release time. The external cloud ignited, thus creating a deflagration in Unit 40. The flame speed increased rapidly in the congested unit and generated around 3 atm over-pressure, thereby causing gross damage to the northern end of Unit 40 and adjacent Unit 30. The combustion then underwent a transition to detonation in the mid-western side of Unit 40 and continued to detonate in the remaining cloud in

Table 11
Summary of the Brenham explosion accident.

Location/Date	Brenham, TX, 7 April 1992
References	[68]
Flammable Substance	Highly volatile liquids. 33% propane, 33%, ethane, 14% n-butane, plus other liquids. Pressure ~56 atm.
Release details (rate/time/total)	500–1600 m^3. ~30 min from release to ignition. Estimates from cloud size and explosive power: 159 - 1590m^3, i.e., 1000 - 10,000 barrels.
Source of vapor	Overflow from a storage cavern. Early morning (7.08 am) Weather was calm. Wind speed <0.5 m/s).
Extent of flammable cloud	~743,000 m^2. Maximum cloud dimension ~1500 m. Pipeline employees on scene before the explosion testified that the vapor cloud was above tree-top level, 6 to 9 m high, mushroom-shaped, and covered the entire station area.
Terrain	Open rural, with trees and with some significant gradients, cloud collected in a small valley.
Location of ignition, explosion sequence	Cloud ignited by a car driving into the cloud. A large blast followed immediately by 2 smaller ones. Descriptions from witnesses: "There were a series of explosions that sounded like thunder." "It was somewhat like a lightning storm." One witness reported feeling three distinct concussions.
Directional evidence	Not available
Overpressure evidence	Houses destroyed over1.6 km from the edge of the cloud, indicating high overpressures and a significant cloud depth. 26 buildings in a 2.5km radius destroyed totally, 33 residences within 2.5- 3.2 km radius moderately damaged. Fences and power lines were leveled. An overground storage tank was shifted on its concrete base. Tops of trees ripped off and branches lay splintered and scorched. Homes had been moved from their foundations and toppled, their contents strewn for hundreds of feet. Measured 3.5-4.0 on the Richter scale.
Discussion	See text with overpressures from a detonation, but it is difficult to understand how the DDT occurred.
Fatalities and injuries	4 killed, 17 injured.
Financial cost	$9 million (value at the time of accident).
Discussion	The area around the gas storage station appears uncongested. A TNT equivalence of 3000 kg has been reported [59].

the 50–70 m open space between Unit 40, the Maintenance Building, electrical substation and canal releasing high overpressure, as shown in Fig. 28. This is discussed further in the Chamberlain et al. [57].

5.6. Brenham, Texas, US, 7 April 1992

The explosion was caused when a large cloud of LPG escaped from an overfilled 1325 m^3 (350,000 gallon) salt-dome storage facility in the Seminole Pipeline system [68]. Table 11 summarizes the event. A car passed into a cloud of gas accumulated in a gully. It was assumed that the car ignited the cloud. The car itself suffered damage typical of that caused by over 5 atm of overpressure. The explosion blew the car off the road and flattened it. Three separate blasts in quick succession were reported. The first, most intense blast was followed by two lesser blasts.

Despite the apparent lack of congestion and directional indicators, there are other strong indications that there was a detonation. For example, one side of the car was dented inwards, suggesting that it was on the edge of the detonating cloud. The car damage, torn tree trunks, building destruction, and Richter scale record all indicate an intense explosion and possible DDT or fast deflagration. The first analysis of this incident in 1992 was when it was first suspected that turbulence created by trees and vegetation could accelerate a flame in a manner similar to that caused by pipe obstacles in experiments.

5.7. Ufa, Russia, 4 June 1989

Failure of a 700 mm pipeline, pressurized to 38 atm and leaking for ~70 min created a very large vapor cloud in an ~2.5 km^2 woodland on steeply rolling terrain. The pipeline contained mainly propane and butanes with small amounts of methane, ethane, pentanes and hexane. Estimates of the spill range from 2 to 10 MT. The cloud was ignited when two passing trains entered it. Table 12 summarizes the event.

Several accounts have been published on this event, but there are inconsistencies. Our conclusion is that there is definite evidence of a detonation occurring. There also is some evidence that there could have been a fire storm, although this is still a point of contention. Given the large volume of spill, there would have been a significant amount of the cloud that was too rich to burn. Other parts of the cloud, particularly at the cloud edges, would have supported premixed combustion and flame acceleration through the woodland.

One interesting observation is the pattern formed by large trees that were toppled, some at their base and others about 3 m off the ground. The fallen trees indicate a high-velocity swirling wind from a firestorm burning the rich part of the cloud, but this can also be interpreted as the damage caused by high overpressure. The original explanation [69] for the tree fall was that it was caused by high winds generated in a rising fireball.

Flattened railway coaches and the intensity of the blast that broke windows 15 km away both suggest that DDT occurred. There is also a sharp cut-off between the region of overpressure damage and both the thermally affected trees and the original forest, indicating rapid decay of blast at the cloud edges. This is consistent with the detonation of a flat pancake-shaped cloud, as discussed earlier.

5.8. Port Hudson, Missouri, US, 9 December 1970

Full bore rupture of a propane pipeline created a large vapor cloud covering about 40,000 m^2 of a shallow valley. It was established some time ago [59,71] that the cloud detonated after ignition by electric switching of a refrigerator in an outbuilding. Table 13 summarizes the event.

The evidence for detonation came from eye-witness reports of the entire valley lighting up instantaneously with no observed significant period of deflagration. Also, all broken trees and utility poles pointed towards the blast origin at the outbuilding on the western edge of the cloud. There were no failures of trees or poles in the opposite sense away from the blast origin. This directional damage was very similar to that observed at Buncefield. The damage to trees and buildings was extreme, indicating overpressures of well over 1 atm. The detonation of the external cloud was initiated by jet ignition from the vented explosion in the building.

Table 12
Summary of the Ufa explosion.

Location/Date	Ufa, Ural Mountains, Russia, 4 June 1989
References	[69,70]
Flammable Substance	LPG: 41% propane, 26% n-butane, 15% i-butane 16% heavier hydrocarbons by mass [69], but differs in [70], see text.
Release details	∼1000 l/s (see text) in ∼70 min (prior to ignition) or a total of 2–10 MT. Calculations in this review suggest 10 MT.
Source of vapor	Pipeline failure (700 mm diameter at 38 atm)
Extent of flammable cloud	2.5 km^2
Terrain	Steeply rolling woodland. Person 4–7 km away smelled hydrocarbons (presumably diluted below lower flammability limit) Open rural, with trees and with some significant gradients, cloud collected in a small valley.
Location of ignition	Passing trains.
Directional evidence	Many trees pointing towards a possible blast origin near point A described in https://doi.org/10.31224/osf.io/cmazh. Possibility of high-velocity winds in the subsequent firestorm contributed to the tree fall. Evidence is also consistent with DDT.
Overpressure evidence	Trees fallen over a large area, overpressures at least 1 atm. Similarities to tree damage at Buncefield and Port Hudson. Trees at Brenham and Amuay are similarly damaged. Ductile damage (permanent metal bending) to trains similar to that of vehicles at Buncefield: “ ... all of the 38 carriages were flattened not against each other like a pleat [as might occur in a collision] but as if they likewere clamped in a vice.” Window broken at distance of 15 km. Estimates range from 0.250 to 10 MT (metric tons, MT) of TNT equivalent.
Fatalities and injuries	One reference reports that 1224 died or were severely injured. Another reports 575 dead.
Discussion	Eye witnesses report several explosions, The intensity of the main explosion suggests DDT in the vegetation.

Table 13
Summary of the Port Hudson explosion accident.

Location/Date	Port Hudson, Missouri, USA/ 9 December 1970
References	[59,71]
Flammable Substance	Propane
Release details	Rate 80 l/s for 24 prior to ignition. Total 120,000 l
Source of vapor	Pipeline failure (200 mm diameter at 66 atm)
Extent of flammable cloud	Maximum length ∼500 m. The gas plume visible by water condensation
Terrain	Gently rolling farmland and woods.
Location of ignition, explosion sequence	Ignition in concrete block warehouse (10 m × 18 m). Immediate illumination of the entire valley. No significant period of flame propagation or acceleration observed by witness.
Directional evidence	All broken trees, poles, etc. pointed towards the blast origin on the western edge of the cloud. No failures in the opposite direction, indicating the drag forces were not caused by entrainment into the fire plume, which would have approximate radial symmetry. Directional damage closely matched the type found at Buncefield.
Overpressure	Damage to buildings, trees, etc, inside the cloud was severe. Likely overpressures least 1 atm in cloud-covered area.
Discussion	Long assumed to have been a detonation, based on witness reports of the rapid burning rate in open country. Directional damage is *now* known to be consistent with what is known about detonations in pancake-shaped clouds."

5.9. Newark, New Jersey, USA, 7 January 1983

Overfill of a gasoline storage tank produced a large vapor cloud ∼90 m × 600 m across. This cloud can be analyzed with dispersion simulations in FRED version 6.1 [41]. Ignition could have occurred [72] in the incinerator of a neighboring drum-finishing plant 300 m NW from the overfilled tank. Two smaller explosions immediately preceded the main one. Table 14 summarizes the event.

While there is not enough evidence to confirm that a detonation occurred, the severity of the explosion in a large open area and damage to storage tanks and flattened rail cars is consistent with a detonation. It is likely that either ignition from a fast flame or detonation leaving buildings to the NW, or from an open road trailer near the point of ignition, triggered the detonation, in a manner similar to that which occurred at Jaipur.

5.10. Flixborough, UK, 1 June 1974

The general view of the Flixborough incident is that a detonation occurred [73]. Buildings and vehicles in open areas within the exploding cloud were either annihilated or destroyed, as shown in Fig. 29. Directional indicators within the exploding cloud, however, were random, but this can be expected of a turbulent hemispherical-type cloud, Type B, described above. Table 15 summarizes the event.

5.11. Pasadena, Texas USA, 23 October 1989

This incident at Phillips Petroleum Chemical Plant is the largest insurance loss for an accident in the chemical-process industry. The presence of ethylene in the released fluid suggests a high likelihood of detonation in the highly congested area of the plant. Photographic evidence showed silos crushed in a manner consistent with detonation and a high Richter scale measurement. Table 16 summarizes the event.

5.12. Decatur, Illinois, US, 19 July 1974

A tank car carrying isobutane rolled down a track too rapidly during switching operations and slammed into an empty boxcar. Then the boxcar coupler rode up over the coupler on the tank car and punctured the tanker. The puncture hole released liquid at about 176 kg/s and created a vapor cloud 800 m × 1200 m in the yard. Then after 8–10 min, the cloud was ignited by an unknown source. Table 17 summarizes the event.

Table 14
Summary of the Newark accident.

Location/Date	Newark, New Jersey, USA, 7 January 1983
References	[72]
Flammable Substance	Gasoline
Release details (rate/time/total)	~100 l/s. 114 to 379 m^3.
Source of vapor	Tank overfill. Wind very light, 1.5 m/s from the SE.
Terrain	Tank farm and nearly empty car park.
Location of ignition, explosion sequence	Ignited 300 m from the overfilled tank, in an incinerator of a neighboring drum finishing plant. Two smaller explosions immediately before main blast.
Directional evidence	Not recorded.
Overpressure evidence	Flattened rail cars. Empty storage tanks 400–500 m away destroyed or badly damaged. Tank trucks rolled over. One open road trailer near the point of ignition had internal explosion. Rail cars and locomotives damaged 180 m away. Glass breakage 5.6 km away. Explosion heard 209 km away over water in Connecticut.
Discussion	Appears to have generated substantial overpressures in a lightly congested area. This matches what occurred at Buncefield, Jaipur, and CAPECO. The absence of directional indicators and clear information on the extent of the cloud makes a definite conclusion about detonation impossible.
Fatalities, Injuries, Cost	1 dead. 24 injured. $42M property damage (in 3rd Q 1991 values).

Table 15
Summary of the Flixborough event explosion accident.

Location/Date	Flixborough, UK, 1 June 1974
References	E.g., [73]
Flammable Substance	Cyclohexane, ~9 atm. Half cyclohexane, half nitrogen at 155 C.
Release details (rate/time/total)	2500 - 5000 kg/ s. 30 MT. 50.8 cm (20") hole.
Source of vapor	Pipeline rupture. 2.5 m/s wind.
Terrain	Chemical plant.
Location of ignition, explosion sequence	Ignition point unknown. Occurred 20–40 s after pipeline rupture.
Directional evidence	Unclear due to hemispherical nature of cloud. There was no time for the cloud to develop into a pancake shape.
Overpressure evidence	Considerable damage to plant and cars in car park is a characteristic of detonation. (See https://doi.org/10.31224/osf.io/cmazh) Buildings damaged up to 4500 m. Heavy damage ~100 m from cloud edge. Moderate damage approx. ~1000 m. Light damage up to around 4500 m.
Fatalities	28 fatalities, 89 major injuries.

Table 16
Summary of the Pasadena explosion accident.

Location/Date	Pasadena, Texas, USA, 23 October 1989
References	[72,74]
Flammable Substance	Ethylene or Isobutane
Release details (rate/time/total)	37,800 kg through an 8″ ball valve released instantaneously at 48 atm.
Terrain	Chemical processing unit
Location of ignition, explosion sequence	Ignition 60–90 s after release.
Directional evidence	Little can be observed from the photographs.
Overpressure evidence	Metal and concrete debris found 9.6 km away. Loss calculations indicate equivalent of 6 MT of TNT with 2%%
Fatalities/injuries	23 died. 314 injured.
Cost	A business interruption loss of more than $700 M (1989). It was the largest single-owner property damage loss in the petrochemical industry.

The VCE was intense, crushing vehicles on rail trailers and breaking windows over 5 km away. The calculations of the extent of the cloud, using FRED software [41], matched eyewitness reports. The main explosion occurred about 300 m from the release point where the congestion created by rail cars was greatest. Although directional indicators are not very clear, there are some indications that rail cars and debris were drawn inwards towards the location of the main explosion. In addition, vehicles on the rail cars were crushed in a manner typical of high overpressures.

5.13. Beek, Netherlands, 7 November 1975

An escape of mixed paraffins and olefins (mainly olefins) occurred from a depropanizer (that is, a distillation column used in the natural gas industry to isolate propane from a mixture containing butane and other heavy components). Table 18 summarizes the

Table 17
Summary of the Decatur accident.

Location/Date	Decatur, Illinois, USA, 19 July 1974
References	[75,76]
Flammable Substance	Isobutane
Release details	The puncture hole was 560 mm x 660 mm in the 115 m^3 railcar.
(rate/time/total)	Liquid escaped at about 19 m^3/min (176 kg/s).
Extent of flammable cloud	800 m × 1200 m
Terrain	Rail yard and freight.
Location of ignition, explosion sequence	Ignition source unknown.
Directional evidence	Unclear, but indications are that rail cars near the damage center were pulled inwards.
Overpressure	Damage to cars suggest > 5 atm.
evidence	Windows broken over 5 km away
	20–125 MT of TNT equivalence reported.
Fatalities/injuries	7 people died, 349 were injured.
Financial Cost	Property damage $18M (at time of the accident).

Table 18
Summary of the Beek accident.

Location/Date	Beek, Netherlands, 7 November 1975
References	[77–79]
Flammable Substance	C3 - C4 hydrocarbons, ethylene, propylene, butylene and butadiene.
Release details	Release rate ∼40 kg/ s for ∼2 min (prior to ignition).
(rate/time/total)	Totaling 5.5 MT
	(of which 800 kg was thought to have exploded)
Source of vapor	Process leak. Wind NW at 2 m/s. 98% humidity.
Extent of flammable cloud	Cloud extended 30 and 90 m from source in different directions and was reported to have been 3 m - 3.5 m high.
Terrain	Chemical plant. Some highly congested plant areas.
Location of ignition, explosion sequence	Ignition thought to have occurred at a cracker furnace
Directional evidence	Not reported. Investigators showed that the focus of the blast was approximately at the center of the cloud. Not clear whether this was based on directional information or variations in overpressure damage.
Overpressure evidence	A range of overpressure indicators were analyzed, with the largest indicating overpressure of at least 1 atm in the cloud. Some vessels dented and pushed from their original locations. Engineer's room was totally destroyed. Window damage up to 4.5 km away (0.005 atm assumed). Severe damage to the concrete walls of the control room. The most severe damage was in areas of highest concentrations of equipment, e.g., pipe tracks.
Fatalities and injuries	14 people died, 106 were injured.

event. The result was a massive VCE. The explosion caused significant damage and started fires in the plant. Fourteen people were killed and 107 people were injured, three of whom were outside of the site. Evidence suggested that the release was due to low-temperature embrittlement at the depropanizer feed drum. It was thought that the initial fracture had occurred on a 40 mm pipe connecting the feed drum to its relief valve.

Fig. 29. Aftermath of the detonation at Flixborough.

For the Beek accident, it was very difficult to find any photographic evidence for this 1975 event. This is similar to the situation discussed above for in Pasadena: There are reports, but the reports contain pictures that are not specific to our interests and not good quality.

No directional indicators were recorded, but damage estimates suggest overpressures well over several atmospheres. This estimate is supported by FLACS simulations [77], which assumed that the cloud consisted of stoichiometric ethylene mixtures and was about 3.5 m high, produced 9.7 atm of pressure. DDT may have occurred as the flame accelerated from the ignition point at the south of the plant through nearby units (number 2, 3 and 5). The occurrence of a detonation is supported by tank damage and broken widows up to 4.5 km away.

5.14. Donnellson, Iowa, US, 4 August 1978

An 8″ LPG pipeline under approximately 83 atm pressure ruptured in a cornfield near Donnellson, Iowa. Propane leaked from a 33″ long split and then vaporized. The heavier-than-air gas rapidly moved through the field and across a highway following the contour of the land. It was reported that the propane gas eventually covered ∼303,514 m^2 of woods and fields and surrounded a farmhouse and its facilities. The night was clear with high visibility. There was a light N-NW wind of 2–4 m/s and temperature was over 10 C. After ∼5 min, the propane was ignited by an unknown source. Three people died in the ensuing fire, but no blast was reported [80]. Approximately 600 m^3 of propane spilled from the pipe.

Table 19
Summary of the Donnellson Fire.

Location, Date	Donnellson, Iowa, USA, 4 August 1978
References	[80]
Flammable Substance	Propane
Release details (rate/time/total)	Full bore release from 8″ pipeline, ∼10 min before ignition. Calculation suggest steady release rate of ~150kg/s and dispersion distance ~310m to lower flammability limit over flat land Wind N-NW at 2–4 m/ s. 600 m^3 fuel, or 31,7145 kg. In 10min, average release rate = 529 kg/s. (Considerably larger than FRED calculation [41] which does not account for the initial large release rate from the ruptured burst (estimated to be 1770 kg/s)
Source of vapor	Full bore rupture of propane pipeline at initial operating pressure of 84 atm.
Extent of flammable cloud	Quoted as 0.3 km^2, but this seems to refer to the burned area, not the extent of the propane cloud.
Terrain	Tank farm and nearly empty car park
Location of ignition, explosion sequence	Ignition source unknown. Only fire reported. No explosion damage.
Directional evidence	None
Overpressure	None
Fatalities and injuries	3 people died because of fire.

The main question about this incident is why did the vapor cloud, which is reported to have been heavy in propane, *did not explode*. Similar incidents (for example, Brenham) also produced large LPG clouds covering similar terrain and a significant blast. The type of terrain could account for the lack of blast, but another explanation could be related to the type of grain growing in the fields. If, for example, the grain were wheat rather than maize, a fire could propagate through it, but not accelerate greatly. Wheat stems are flexible, and they would bend in the deflagration instead of acting like a grate and causing the deflagration to accelerate.

Apart from the apparent lack of congestion, there are significant differences between the conditions of this spill compared to those that eventually detonated. The source of vapor originated from a turbulent release, initially at 84 atm. The wind was a light breeze rather than calm, and ignition took place early in the release when the cloud was still turbulent and not stratified.

Table 19 summarizes the effect and a detailed review of the Donnellson incident is given in the Chamberlain et al. [57].

5.15. Other Intense VCEs

The surveys of intense VCE events in the publications by Slater [58], Lenoir et al. [59] and Marsh [45] contain a number of intense VCEs for which the evidence suggests that a detonation occurred. The lists in Tables 20 and 21 contain the result of their review and show that an additional nine events may have involved transition to detonation. The incidents have been chosen on the basis of type of fuel (paraffin or olefin), amount of fuel exploded, severe building damage, and broken windows at distances greater than 3 km. The incident at Ludwigshafen involved dimethyl ether, which is close to ethylene in terms of the severity of explosion. This is included because photographs show distinct signs of a severe VCE.

This survey of accidents in lists cited above [58,59] identified no detonations involving methane or natural gas and very few VCEs involving hydrogen. The hydrogen explosions at Hull (1921), Nevada (1964), and Watson (1975) were air blasts in turbulent clouds ignited very soon after release from containment. Lack of detail does not allow decisions to be about whether there was a detonation, but there is no doubt that these were intense VCEs. It seems that the natural buoyancy of these gases does not favor the development of sufficiently large flammable clouds in open space. Nevertheless, release of these gases in confined surroundings can create the right conditions for powerful explosions, including detonation.

Although these are not discussed in the paper, there have been a number of explosions of hydrogen gas mixed with air in confined or congested scenarios. For example, these occurred in Holland (1972), India (1977), and Sarnia (1984). These were chemical explosions, not nuclear explosions. Another example of hydrogen explosions were those at Fukushima (2011), where hydrogen detonations started in confined areas (see, e.g., [81,82]). Discussions of these and other hydrogen explosions can be found in [83–85].

6. Summary, Recommendations, and Conclusions

It has been well known that large vapor cloud explosions (VCEs) could involve deflagrations, but it was also generally believed that VCEs could not support the more powerful form of combustion, detonations. The Buncefield investigations and subsequent research represent a significant change in the approach to understanding the evolution of events in VCEs. The conclusion that a deflagration-to-detonation transition, DDT, occurred at Buncefield, and that the detonation propagated over a region of ∼100,000 m^2 was confirmed by subsequent large-scale experimental studies.

It is also known that fuel-air vapors in congested environments may lead to detonations. This was confirmed by extensive laboratory and large scale experiments and numerical simulations over the past twenty years. Finally, we know that once a detonation is initiated, it is capable of spreading as a powerful explosion with high overpressures and consuming the surrounding all of the detonable fuel in a very short time.

These observations naturally led to the major question addressed here: *Which of the recent and historical large-scale VCEs were likely to also have involved detonations?*

6.1. Summary

This paper first provided a review of some of the fundamental knowledge of the transition processes from a deflagration to a detonation (DDT). From this review, we learned that DDT can be initiated in strong, shocked flow conditions, the actual detonation ignition sites are very small regions of space, and DDT occurs and establishes a detonation in a very short time. Although it might be extremely unusual and likely not possible for DDT to occur in completely open space. Nonetheless, the presence of any flame acceleration mechanism, such as caused by congestion and confinement, create conditions for shock formation and the development of a detonation. Once a detonation has formed, however, it is robust. It can find a pathway through detonable gases and maintain itself until the detonable cloud is consumed. Furthermore, a detonation can even survive propagation through regions with no fuel provided shocks are strong enough to re-initiate detonation in adjacent detonable region.

Post-accident investigations of recent VCEs, such as those that occurred at Buncefield, Jaipur, and Puerto Rico (CAPECO), have allowed us to accumulate enough information to define a number of

Table 20
Additional major VCEs that may have involved detonation, but evidence is lacking.

Event and Date / Fuel	Release amount[1]	Type of release	Estimated cloud size	Ignition delay (min)
Ludwigshafen, Germany, 28 July 1948				
Dimethyl ether	30,000 kg	Rail car rupture overheating in sun	–	–
Linden, New Jersey, US, 5 December 1970				
Hydrocarbons $>C_{10}$ & H_2	114,000 kg	Reactor failure	–	–
Baton Rouge, Louisiana, US, 19 January 1971				
Ethylene	3,600 kg	Truck tanker failure	–	–
Longview Texas, US, 25 February 1971				
Ethylene	450 kg	Pipe failure	–	–
East St. Louis, Illinois, US, 22 January 1972				
Propylene	53,500 kg	Railcar puncture	20,000 m^2	–
Climax, Texas, US, 29 June 1974				
Vinyl chloride	110,000 kg	Rail car derailed 1.2 × 1.2 m^2 hole	490 m	–
Petal, Mississippi, US, 25 August 1974				
Butane	–	Salt dome release	2 km diameter	–
Englewood Yard, Houston, US, 2 September 1974				
Butadiene	< 80,000 kg	Rail car puncture	–	2–3
Dallas, Texas, US, 20 February 1977				
Isobutane	68,200 kg	Rail car derailed	–	2–5
Commerce City, Colorado, US, 3 October 1978				
Propane	–	Pipe failure	2.4-3 m × 150 m Richter scale 3.5	–
Pitesti, Romania, 30 October 1978				
Propane/ propylene	–	–		–
Texas City, Texas, US, 21 July 1979				
Liquid and gaseous hydrocarbons	15,000-19,000 liters	12″ line failure	~200 m long	2
Romeoville, Illinois, US, 23 July 1984				
Propane/butane	40,000 kg	Weld failure on column	–	–
Baton Rouge, Louisiana, US, 24 December 1989				
Ethane/ propane/butane		Pipeline failure 200 mm, 52 atm	At least 300 m	2–3
Wilmington, California, US, 8 October 1992				
Hydrogen/ mixed hydrocarbons		6″ pipe failure		seconds
La Mede, France, 9 November 1992				
Propane/butane/propylene	5,000 kg-	5 cm^2 pipe rupture on catalytic cracker	14,000 m^2	10

Table 21
Further information on the data in Table 20.

Event	TNT equivalent	Buildings Severe damage?	Windows Broken (> 3km)	Detonation? Yes or No
Ludwigshafen	20	Y	Y	Y?
Linden	45	?	?	Y?
Baton Rouge (71)	0.45	Y	Y	Y?
Longview	0.5	?	?	N?
East St. Louis	2.5	Y	Y	Y?
Climax	?	Y	Y	Y?
Petal	?	Y	Y	Y?
Englewood Yard	57	Y	Y	Y?
Dallas	1.6	?	Y	?
Commerce City	?	?	?	?, 3.5-4 on Richter scale
Pitesti	?	Y	Y	?
Texas City	?	Y	Y	?
Romeoville	?	Y	Y	?
Baton Rouge (89)	14	?	Y	Y?
Wilmington	?	Y	Y	?
La Mede	?	Y	Y	Y?

“detonation markers.” For example, large-scale experiments evaluated the possibility of flame acceleration and DDT in regions with tree congestion and pipe racks. Other tests were performed in which typical items exposed to an explosion, such as cars, oil drums, oil filters, and switch boxes, were exposed to a range of measured overpressures and impulses. These items, which are typical of the contents of industrial plant, provide useful markers that relate overpressure and impulse to the type of damage commonly found after explosion events. Detonation markers generally reflect the ways in which objects respond to a passing detonation. Generally these are specific types of damage done to surroundings of property, but they also include evidence such as high Richter-scale measurements, which indicate that strong shocks occurred. The presence of such markers is evidence that a detonation occurred.

Then by combining the basic information on flame acceleration, detonations and DDT (Section 2), a general analysis of explosion scenarios (Section 3), and descriptions of large-scale detonation markers (Section 4), a series of 14 specific explosions were examined to determine if a detonation could have occurred. Specifically, we considered:

1. Buncefield, UK, 2005. Detonation occurred.
2. Jaipur, india, 2009 Detonation occurred.
3. CAPECO, Puerto Rico, 2009. Detonation probable.
4. Amuay, Venezuela, 2012. Detonation occurred.
5. Skikda, Algeria, 2004. Detonation occurred.
6. Brenham, TX, US, 1992. Might have occurred.
7. Ufa, Russia, 1989. Detonation occurred.
8. Port Hudson, LA, US, 1970. Detonation occurred.
9. Newark, NJ, US, 1983. Detonation might have occurred.
10. Flixborough, UK, 1974. Detonation occurred.
11. Pasadena, CA, US, 1989. Detonation occurred.
12. Decatur, IL, US, 1975. Detonation most likely occurred, evidence lacking.
13. Beek, Netherlands, 1975. Detonation might have occurred.
14. Donnellson, IO, US, 1979. Detonation did not occur. No mechanism for flame acceleration.

These explosions occurred at locations around the world from 1970 to 2012, and for a variety of vapor fuels including gasoline, propane, LPG, ethylene, isobutane and cyclohexane. When it was concluded that a detonation occurred, an attempt was made to identify the most likely mechanisms that caused it. Summaries of each event and overviews of all 14 are given in Table 4. Extensive additional details, explanations, and justifications are included in the Chamberlain et al. [57]. The conclusion of this review is that detonations in VCEs did occur, contrary to what was previously believed.

6.2. Suggestions for fuel-storage safety

There are a number of ideas for plant design, layout, and personnel training that are suggested by this review. There are in fact official standards now and these should be and are followed. They do not, however, consider the possibility of a detonation. Existing standards assume that deflagrations could occur in congested areas of plants, but that these should decay rapidly as the flame emerges from the congestion to an external cloud. The overpressure decay associated with deflagrations is defined by the size of the congested area engulfed by a potential flammable cloud, and not solely by the size of the flammable cloud. If DDT or a detonation should occur, there is a strong possibility that the detonation will propagate through the remaining cloud present in open areas. As we have seen, the area into which the cloud spreads depends on the size and duration of the release, the local topography, and weather conditions. Thus the extent of the cloud before ignition cannot be predicted with any certainty. When a detonation occurs, the volume that generates the very high overpressure is much larger than that generated by a deflagration. Hence, the damage is much more extensive.

One possibility for limiting the extent of a flammable cloud could be to have a vapor fence that contains the cloud. This may have the advantage of limiting the spread of heavier-than-air pancake-shaped clouds. At Buncefield, for example, gasoline vapors remained inside the bund for a considerable time before spilling over into the surroundings. At Jaipur, the vapor cloud was contained by a solid wall that kept it from leaving the depot area. One suggestion, then would be to install fuel gas sensors that would give the size of hazardous flammable clouds in congested areas. This could, for example, be used to trigger remedial action.

Other possibilities include various methods of active suppression of shocks by, for example, water spray or sand, and deflagrations by, for example, water spray or selected chemicals. Considerable work has been done on this, although a comprehensive review is yet to be written. Direct suppression of detonations, as discussed previously in this paper, is really a multistep process of first disrupting the detonation and then mitigating the separated shock and deflagration. The timescales for this would be extremely short. Again, this is a topic requiring further creative research.

Where environmental screening is required around sites, the exact use of trees and vegetation should be carefully considered. Current information, based on the studies performed after the Buncefield explosion, shows that vegetation no more than 2 m wide led to flame acceleration, but not to DDT for a propane-air mixture. Any further increase in width cannot be guaranteed to prevent DDT of an engulfing cloud. One common feature of vapor clouds of heavier hydrocarbons when the cloud has has been passively dispersed in calm wind conditions is that the flammable cloud height is typically below about 3–4 m. Thus, elevated vegetation, such as large tree branches, would play little or no part in flame acceleration whereas ground level vegetation should be cleared away or limited in width to less than 2 m.

CCTV coverage of the entire site is important both to help prevent problems as well as being a diagnostic if something should occur. This coverage allows rapid and effective response to unusual behavior, such as the sudden development of a misty cloud. As CCTV records also help accident investigators, it is extremely helpful when clocks on the cameras are synchronized with each other.

Drainage systems should be equipped with water traps to prevent flammable vapors from penetrating into the drain system. Drains can provide confined tunnels in which deflagrations can develop and naturally accelerate, leading to fast flames and DDT.

If possible, the use and quantity of more reactive combustible materials, such as olefins and acetylene, should be minimized or more emphasis should be put into active leak prevention. Research would be necessary to correlate the amount of olefins mixed in refrigerants in, for example, LNG plants, with other plant parameters, such as the size and density of congestion.

When new plants are designed, some consideration should be given to separating congested spaces to limit flame acceleration. Unoccupied buildings near or within process units could have a collapsible wall to prevent the build-up of high over-pressures inside the building. This would prevent high-velocity jet ignition of an external flammable cloud and the possible transition to detonation. Occupied buildings, such as control rooms, should be designed to avoid ingress of flammable vapors where there is a risk of exposure to flammable gas. Even simpler is to have a vapor-tight building of one with a positive inside pressure so that the flammable cloud cannot penetrate the building.

Process safety training courses should acquaint operators and maintenance engineers with the hazards created by detonations. Maintenance procedures should increase the surveillance of parts of the plant containing the more reactive flammable liquids and vapors. A suggested priority list of combustibles, in order of decreasing propensity to detonate is: acetylenes, olefins, paraffins (propane and higher homologues), ethane, hydrogen, natural gas, the least reactive is methane.

Finally, if there is an accidental VCE, investigators should be called in before the site has started to be cleared. As shown by the detonation marker analysis, important information in terms of initial cause and event markers comes from looking at individual pieces of debris as well as the site as an entirety.

6.3. Suggestions for future basic research in DDT

Throughout this paper, we have noted topics in detonation-related research that merit further studies. Here we list a few of these as related to basic research on the full cycle of initiation, DDT, propagation, and quenching.

- *Fundamental Mechanisms of Detonation Initiation.* There are some very basic issues in deflagration, DDT, and detonations that need further clarification, whether it is done by experiments or simulations or theoretical analyses. These include, but are not limited to addressing questions such as exactly how shock focusing works and whether it is predictable, the role of turbulence and hot, shocked materials, and the direct transition to detonations either through shock-turbulence interactions or shock interactions. These are all related in a fundamental way that needs clarification.
- *Detonability Limits for Hydrocarbons and Mixtures.* What are the detonation limits as a function of system size? What exactly is happening at the limits? Can detonability for large system be approximated as the flammability limit?
- *Quenching a Detonation*. How do we do this effectively? Are there active and passive ways that it can be quenched for long enough time for the burning to be quenched? When, besides when it runs out of fuel, can it be quenched?
- *DDT Prediction*. Can we predict DDT for large Systems? Now, we can use simulations to model and give scaling rules for predicting DDT in moderate-sized (10's of meters) systems. More studies are needed that look at the effects of gradients in reactivity with and without obstructions, so that some rules and scaling can be found.

6.4. Concluding remarks

There has often been a statement that DDT cannot occur in VCEs because of the lack of confinement or obstructions. In this paper, we have shown the importance of confinement and obstructions, although detonations in unobstructed space are not ruled out due to intense turbulence that may lead to detonation. The analysis of prior VCEs, however, indicate that DDT occurred in obstructed regions, and then propagated to less obstructed regions containing reactive gas. There is no mystery or contraction here, just a complex and evolving reactive-flow in a complex geometrical system containing shocks and deflagrations.

When the fuels are complex and not distributed uniformly in the background environment, when there are many irregular obstacles, varying confinement throughout the area, and other small- and large-scale perturbations to the flow, many possible “anomalies” can arise in the evolution of the deflagration, transition state, and the propagating detonation itself. Usually, however, it is possible to decipher what happened in terms of what we know about explosions and DDT. Buncefield is an example: We learned through extensive testing that the extra rigidity of hardwood trees was a fundamental key to understanding how the deflagration could be accelerated to create an environment in which DDT could occur. Another factor which we see could cause anomalies in DDT, that is, cause it to occur at lower or different overall deflagration velocities, is shock focusing. If shock waves focus in detonable regions, they can create a local hot spot which might lead to DDT. These local phenomena may not appear as a global deflagration. Again these are special cases involving fuels, inhomogeneities, obstacles and confinement that require further investigation.

It is hoped that this review will produce insights that can be used to understand the hazards of VCEs, improve risk management, and review control measures (in design, operation, and maintenance) and mitigation systems already in place. By showing beyond reasonable doubt that detonations occurred in several accidents, this review is meant to improve awareness of the detonation hazard and suggest changes and new approaches to lower the risk and consequences of a VCE. Implementation of such changes could save human lives, maintain confidence in industry, and reduce operational and capital cost in handling hydrocarbons.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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