Mechanisms and Occurrence of Detonations in Vapor Cloud Explosions – Supplementary Material

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Abstract

The material in this paper comprise a compendium of more detailed information and analyses of the 14 large-scale explosions described the paper *Mechanisms and Occurrence of Detonations in Vapor Cloud Explosions* by Oran, Chamberlain, and Pekalski [1]. Each section begins with a general description of the incident and then, where possible, more analysis (based on the work of GC) and useful information about the incident. The events all have certain physical similarities, but vary greatly in terms of the level of information available for analysis. Taken together, however, they present a powerful picture of what a detonation can do as well as indications of what might be done in the future to avoid such an incident.

S1. Introduction

These additional materials are a compendium of more detailed information and analyses of the 14 large-scale Vapor Cloud Explosions (VCEs) described in [1]. The specific explosions and the conclusions concerning them are:

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.

Each section begins with a general description of the incident and then, where possible, more analysis (based on the work of GC) and useful information about the incident. The events all have certain physical similarities, but vary greatly in terms of the level of information available for analysis. Taken together, however, they present a powerful picture of what a detonation can do as well as indications of what might be done in the future to avoid such an incident. More detailed conclusions from assessing all of the information are given in the discussion in [1].

The levels of description in the materials presented here vary considerably. There is minimal description for incidents such as Buncefield, UK and Jaipur, India, where there has been extensive recent analysis that can be summarized and referenced, and for which relatively little detail exists, such as Ufa, Russia. On the other hand, the CAPECO incident is discussed in considerable detail because of a lack of a prior report and evidence gathered and analysis carried out by one of the authors of this paper (GAC).

1. Buncefield Accident

A full description of this incident and follow up tests are available in [2] of the main text. It is generally accepted that ignition occurred in the pump house when the electric powered pumps were turned on. A vented explosion then occurred which ignited the external cloud. Flame acceleration along the tree line to the north of the site then led to a DDT in the region of the crossroads at Buncefield Lane and Three Cherry Trees Road. There is considerable evidence from subsequent tests that a DDT occurred and that the detonation propagated through the remaining cloud.

The layout of the site and location of some damaged objects are shown in Figure-S 1.1 and Figure-S 1.2. Figure-S 1.3 shows the direction of net drag on objects inside and just outside the detonation. The deformation exhibited by such objects provided information on the net drag impulse sustained by these objects. Other directional evidence was provided by the directional abrasion found on one side or one part of painted surfaces and tree bark. There was also evidence of large objects such as cars and skips being displaced in a particular direction.

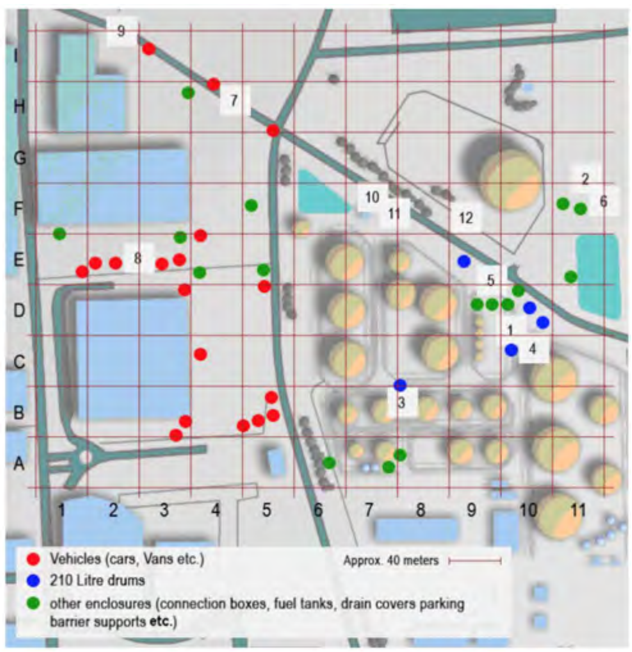

Figure-S 1.1 Location of vehicles, drums and other enclosures which exhibited damage consistent with overpressures in excess of 200 kPa [2, 3]. For images of selected objects identified by numerical tags, see Figure-S 1.2.

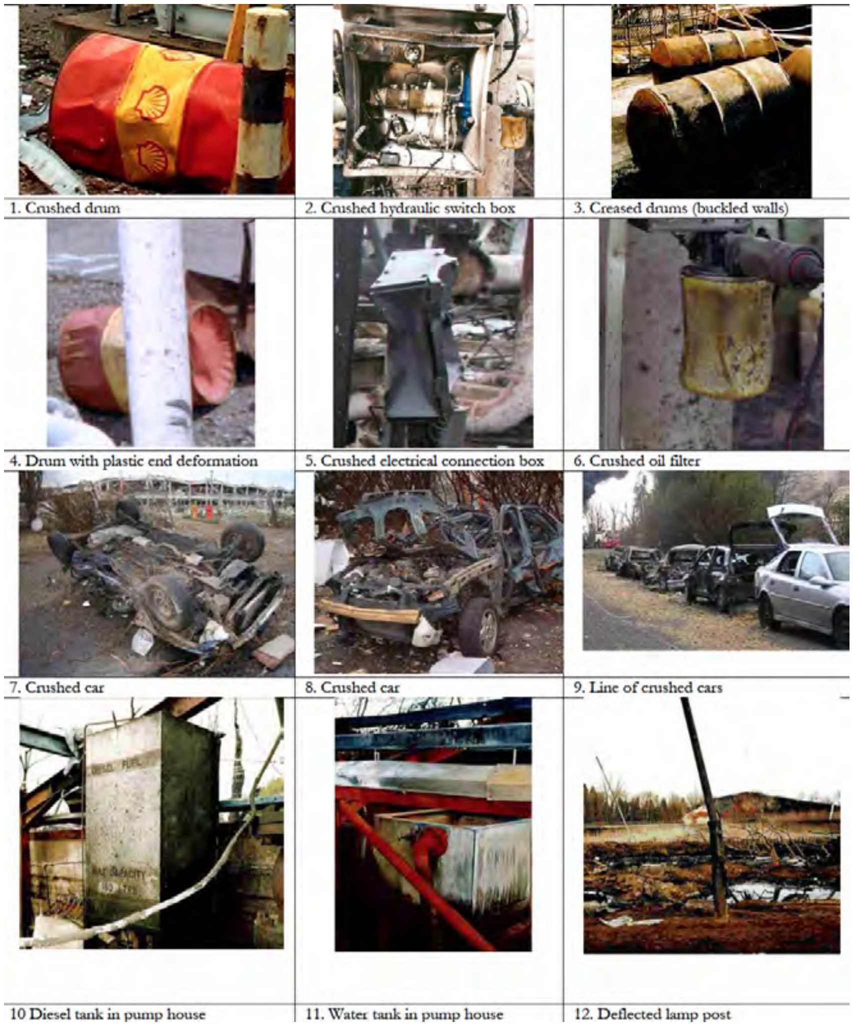

Figure-S 1.2 Objects identified by numerical tags Figure-S 1.1[2, 3].

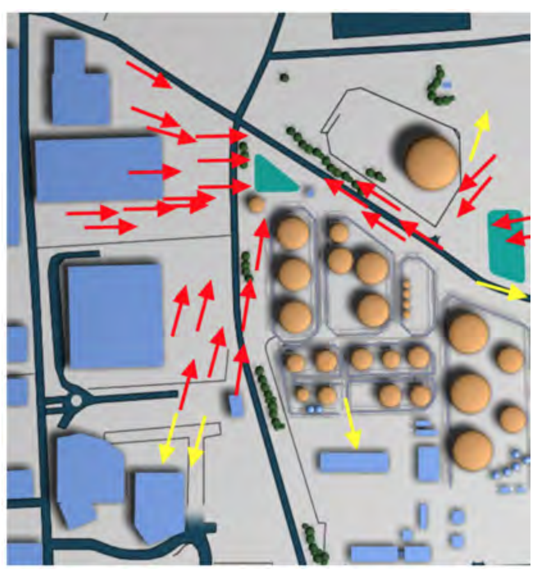

Figure-S 1.3 Direction of net drag impulse across the Buncefield site [2, 3].

2. Jaipur Accident

Description of the Event

During the evening of the 29th October 2009, preparations were being made at the Indian Oil Corporation (IOC) depot for the transfer of kerosene and motor spirit (MS)[1] to a neighboring terminal operated by Bharat Petroleum Corporation Limited. At approximately 6:10 pm, during the process of preparing the MS tank for pumping, a large leak occurred from a hammer blind valve on the tank outlet.[2] The leak resulted in a jet of MS directed upwards from the valve. The leak continued for ∼75 minutes in the background calm, low-speed wind. The nature of the release, with an upwards jet of MS, is likely to have assisted in the production of vapor. Post-incident analysis indicates that a flammable vapor cloud covered much of the IOC site. The Independent Investigation Committee (IIC) estimated that of the order of 1000 MT of MS were released from the tank. The vapor cloud was not visible, unlike the vapor cloud at Buncefield, where the vapor appeared as a by mist in the low-temperature weather conditions. Personnel on site were aware of the presence of the vapor by its odor. A full and concise description of this incident are available in [4, 5] and in Section 5.2.

Discussion

The directional indicators and damaged items in this incident are all consistent with a detonation of the vapor cloud over a large portion of the site. The northeast corner of the site, however, shows no evidence of high overpressure and only a random set of directional indicators, as indicated by the red arrows in Figure-S 2.1. The area that shows evidence of the flammable cloud, but no significant pressure generation, has been marked in light yellow. Approximate directional indicators interpreted from pictures and video are shown as dark yellow arrows. Similarly, approximate directional indicators corresponding to two boxes that appear to have been exposed to a directional pressure loading are shown as blue arrows. Also shown are the positions of the tree to the north of the control room that does not appear to have suffered severe pressure or flow damage.

Figure 4.8a,b in the main report show damaged tanks, and Figure-S 2.2 shows various kinds of damage caused by overpressure. Figure 4.10 (right) in the main report shows directional indicators, and others are shown in Figure-S 2.3. These figures are taken from the detailed paper by [4] and in the additional technical report [5].

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[1] Motor spirit volatile liquid used as a fuel in internal-combustion engines. It is usually gasoline or petrol.

[2] The valve at Jaipur had two positions, one providing full flow through the tank outlet pipe and the other completely blocking the flow. It was an 'on/off' valve that was manually moved and had no other control over the liquid rate.

Figure-S 2.1 Jaipur directional indicators in the Pipeline Division area and area without apparent pressure generation. Figure taken from [4]. The partial transparency through the yellow area shows the green tank, and the wall that is not damaged is the northern edge of the blue area. The main firewater pump house is just south of the firewater ponds.

The main evidence for the lack of pressure generation in this yellow shaded area is:

- The lack of damage to the wall. It remained standing in this area, but collapsed further to the west on the north wall and to the south on the east wall.
- The limited damage to the trees to the east of the main firewater pump house.
- The lack of scouring on the lamppost by a green firewater tank on the western side of the shaded area (not visible due to the shading).
- The lack of significant pressure damage in the area of the green firewater tank.
- The blue arrow marked in the shaded area is consistent with a pressure wave traveling into the area from an explosion event to the south of the shaded area.

It is postulated here that a flammable cloud was present in the shaded area at the time of the explosion, as the trees along the section of the north wall to the east of the green firewater tank were all fire damaged. In addition, there was no particular change in the ground level in the vicinity of the green firewater tank that would have prevented the vapor cloud from spreading into this area. Nonetheless, it is possible that the fire damage occurred as a result of fire propagating along the tree line after the explosion. In this scenario, it is possible that the vapor cloud in this area was below the lower flammable limit, which thus explains the absence of pressure damage.

Another mechanism that would prevent pressure generation in this area is if it had been burned prior to the main vapor cloud explosion.

Alternatively, it is possible that the vapor cloud was so thin in this area that it could not sustain a detonation. This hypothesis, however, is inconsistent with the ground level in this area and the persistence of the detonation throughout the rest of the site. The most likely explanation is that the vapor cloud burned out before the main explosion. This also suggests that the ignition point was located in this area.

Figure-S 2.2 Examples of pressure damage on the IOC site [4].

Figure-S 2.3 Examples of directional indicators: bent trees and scoured poles [4].

3. CAPECO Accident

Description of the Event

On the night of 23 October, 2009, a large explosion occurred at the Caribbean Petroleum Corporation (CAPECO) facility in Bayamón, Puerto Rico, as gasoline was being offloaded from the tanker ship, Cape Bruny, to the onshore CAPECO tank farm. A 5-million gallon ($\sim$19,000 m^3) aboveground storage tank overflowed into a secondary containment dike. The gasoline spray evaporated, forming a large vapor cloud, which ignited after reaching an ignition source in the wastewater treatment (WWT) area of the facility. The blast and fire from multiple secondary explosions resulted in significant damage to 17 of the 48 petroleum storage tanks and other equipment onsite, as well as to neighborhoods and businesses offsite. The fires burned for almost 60 hours. What follows now is a summary of the forensic study carried out by one of the authors (GAC) to determine the sequence of events that led to the VCE.

Discussion

One of the authors (GAC) visited the site in March of 2010 at the invitation of the Chemical Safety Board (CSB). Most of the items damaged in the explosion were still in place, but the barren area of vegetation at the east end of the site had begun to grow back. Many photographs of the site were taken after the explosion, and the videos of the actual incident taken from fixed CCTV cameras were supplied to GAC by the CSB. The locations of the cameras are shown in Figure-S 3.1. Selected frames from the videos are used in the analysis given below. A selection of frames pertinent to the discussion is shown here in Figure-S 3.11 to Figure-S 3.15.

The video frames showed that the flame traveled through the site as a flash fire with occasional small explosions in confined and congested regions. Severe explosions occurred towards the far eastern end of the site in dense vegetation (the "bamboo area") and between tanks 404 and 405 at the western end of the site at the time when most of the fuel had been consumed (see Figure-S 3.2). This overall sequence of events is in some ways opposite to the sequence at Buncefield, where the main DDT explosion occurred early in the sequence of events, and a detonation was able to propagate through the rest of the cloud.

The three main videos were taken from the top of the tower of the fluidized catalytic cracker (FCC), the waste water treatment plant (WWT), and the gatehouse (see Figure-S 3.2). The timers on each video were all synchronized to the same time base, thereby allowing events to be cross correlated.

The time between ignition and the main explosion was about $\sim$7 s, during which there were several explosions and flash fires. Nearly all of the blast effects can be explained by conventional understanding of flame acceleration. There are examples of flame acceleration through repeated LPG tank obstacles (see Figure-S 3.3), flame acceleration down a 240-m-long buried water duct, an external explosion at the far end (see Figure-S 3.4), and flame acceleration in highly congested regions of dense vegetation (see Figure-S 3.5).

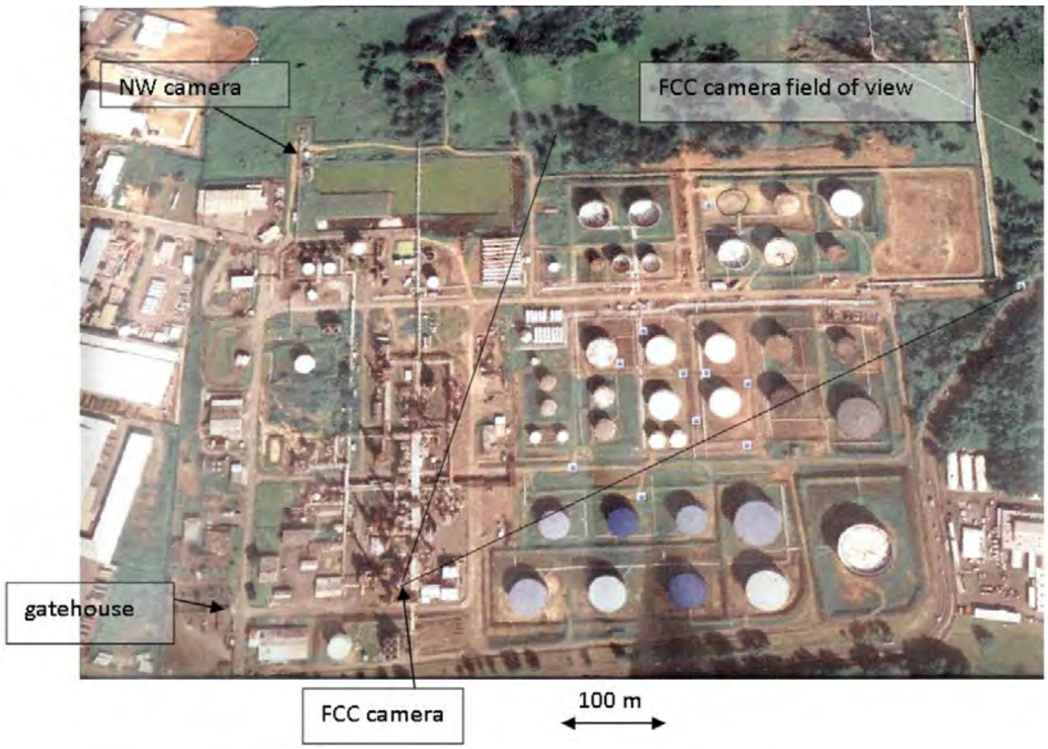

Figure-S 3.1 Location of CCTV cameras [6].

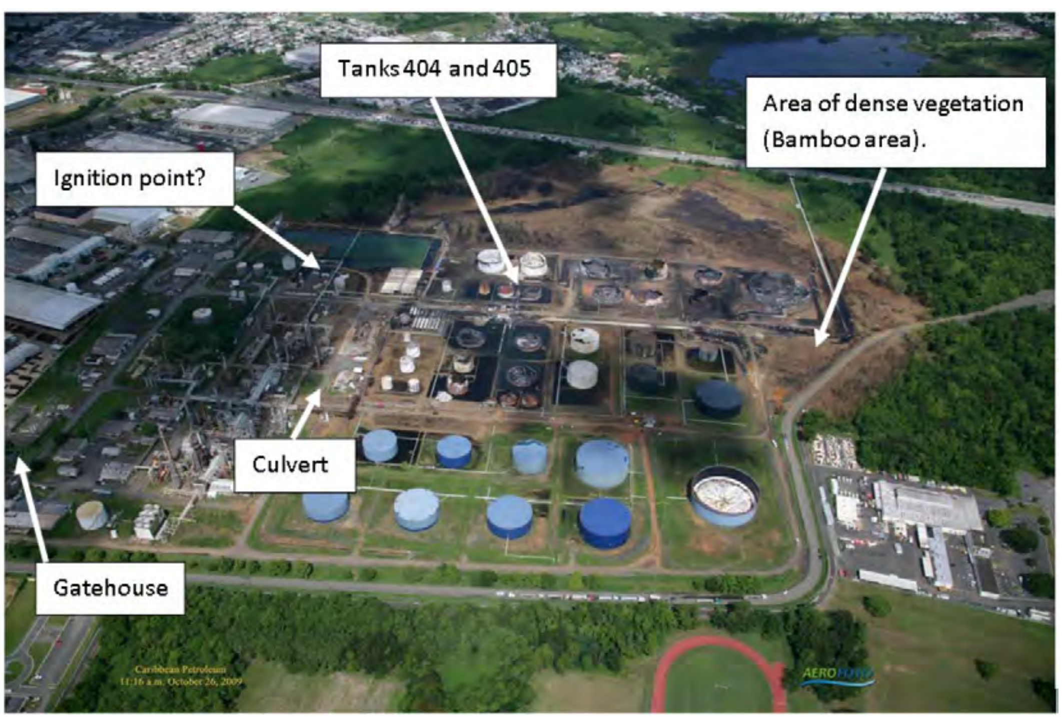

Figure-S 3.2 Overview of site showing burn area [6].

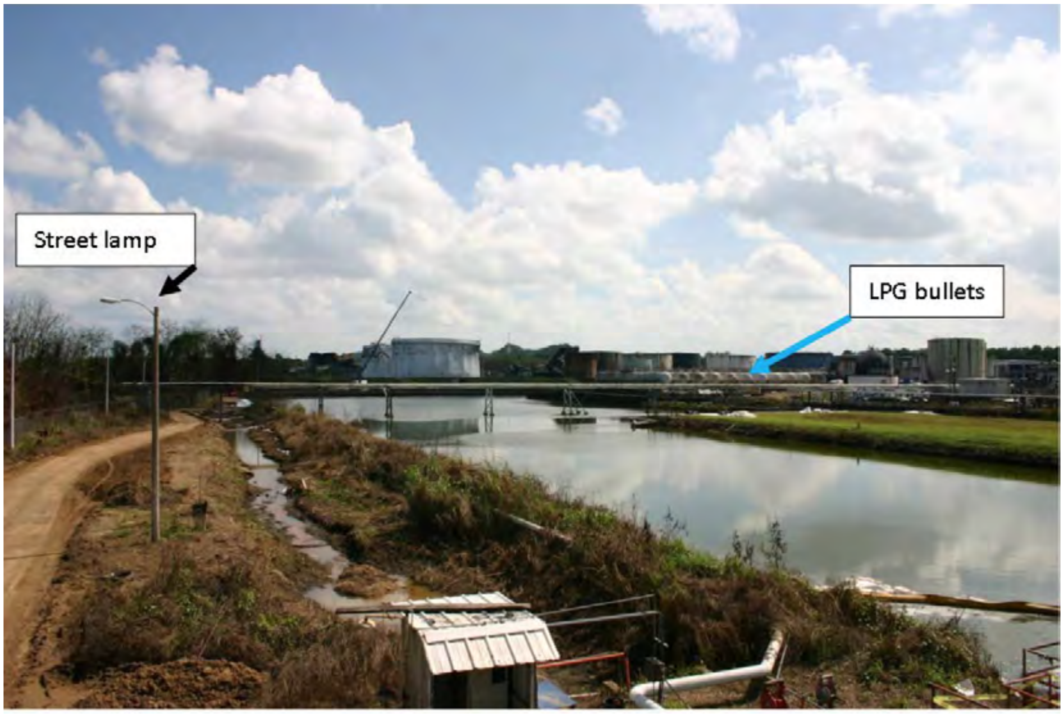

Figure-S 3.3 View from the waste water treatment CCTV camera (also called the NW camera). Note crushed white tank [6].

Figure-S 3.4 Damage to road above water culvert [6].

Figure-S 3.5 The damage to the area that once contained dense vegetation is shown inside the superimposed black oval ring in the middle of the left side of the photograph [6].

There are several anomalies. One is the increase in brightness of an area on the left viewed from the WWT (see Figure-S 3.3). This was at the same time as the first main flash from the right. This brightness could be a reflection of light from trees in the field of view. A more likely explanation is a street lamp (Figure-S 3.3) that was recorded when the camera was triggered by the light of the ignition.

The second anomaly concerns the damage to tanks 406 and 407 (Figure-S 3.6). These tanks did not catch fire, and their damage is typical of a blast impact. Yet they are, respectively, 300 m and 350 m from the location of the explosion in the bamboo area at the east end of the site. Equation (4–2) (from Section 4 of main report) gives 0.08 atm overpressure at tank 407 and 0.07 atm at tank 406. CAM [7] gives approximately the same values, using a highly congested region of 100 m x 40 m. These overpressures are not sufficient to cause the level of damage sustained. The situation is further complicated by the fact that another tank containing fuel oil, number 603, was only about 60 m from the edge of the bamboo explosion, and yet it sustained only superficial damage (Figure-S 3.7).

One possibility here is that tanks 406 and 407 were hit to their southwest position by a blast from fast flames propagating through the line of 11 empty LPG bullets located to their southwest. If the flame speed through this region were $\sim$180 m/s, as observed from the northwest video, then an overpressure of around 0.6 atm would be generated. CAM then predicts overpressures of 0.15

Figure-S 3.6 Blast damage to empty tanks 406 and 407. Figure Figure-S 3.3 was taken from left side of this figure [6].

Figure-S 3.7 Tank 607 is the smaller tank near the center of the picture [6].

and 0.09 atm at tanks 406 and 407, respectively. which is insufficient to account for the damage. Additionally, the blast at the gatehouse, ∼450 m away, is then ∼0.026 atm, but nothing appears on the gatehouse video at the elapsed time of 23.06 frame 7. The questions, then are: *Why is there no evidence in the video? How do we explain the level of damage?*

The third anomaly concerns a slightly damaged switch box (Figure-S 3.8) located ∼100 m from the bamboo area. Tests following the Buncefield explosion have shown that the incident overpressure must be greater than 1 atm to cause distortion of the box. Yet, assuming a detonation in the bamboo area, the overpressure estimated from Equation (4–2) is only ∼0.16 atm.

Nonetheless, it is still possible that a DDT occurred in the bamboo area. The region is devastated and some items have been drawn inwards, e.g., tree trunks, railings, wire netting, and roadside barriers (see, e.g., Figure-S 3.8). The overpressure at the gatehouse, some 720 m distant, is estimated to be ∼0.03 atm, which is sufficient to shatter large windows as observed.

Figure-S 3.8 Damaged switch box, front face (left figure) and side view (right figure) [6].

Another feature that supports the hypothesis of DDT is an analysis of bent railings ∼60 m from the bamboo area (Figure-S 3.10). The minimum overpressure required to produce the measured distortion of 483 mm is about 0.6 atm (static). For a 1-ms pulse, the required overpressure is about 10 atm. The overpressure estimated from Equation (4–2) (Section 4 of main report) is ∼0.4 atm. The lack of agreement between the two values indicates that the railing was much closer to, or even on the edge of, a detonating cloud.

Following a meeting at the UK Health and Safety Laboratory (HSL) between author GAC and G. Atkinson, on 3 February 2016, it was decided that further analyses were necessary to try to resolve at least some of the anomalies. It was agreed that the first blast to reach the gatehouse at 23.03 frame 21 originated from the south end of the culvert (at 23.02 frame 17) shown in Figure-S 3.2. Figure-S 3.11 shows the explosion. It was also agreed that a major explosion also took place in the bamboo area, probably around the same time as the other explosion identified in frames 23.07.21 to 23.08.08 (Figure-S 3.15).

Figure-S 3.9 Trees, railings and posts drawn inwards towards bamboo area [6].

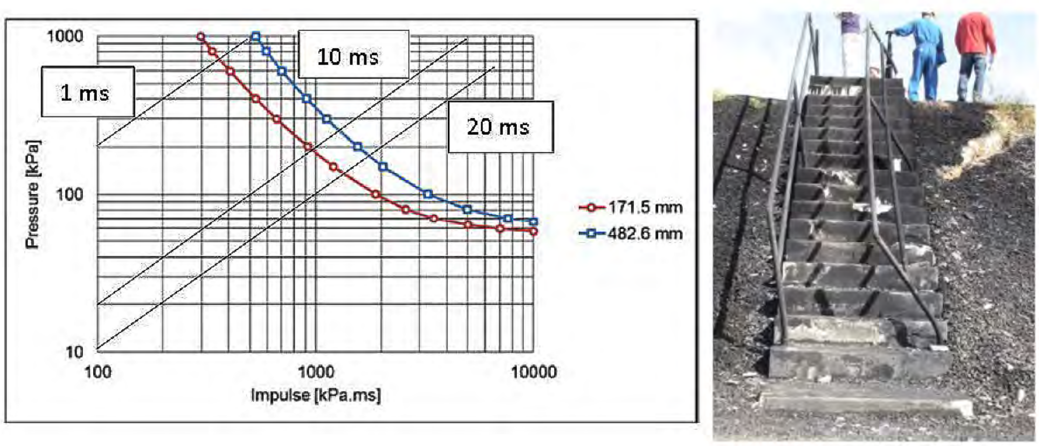

Figure-S 3.10 Pressure-impulse diagram for bent railings. Left: Pulse durations are shown assuming a triangular shaped pulse. (The pressure-impulse calculation was performed by B. Burgan of the Steel Construction Institute, private communication, 2016). Right: From [6] showing bent railing.

Figure-S 3.11 Explosion from the south end of the culvert along 4th Street [6, 8].

Figure-S 3.12 Flash fire has begun to propagate from the culvert, and also into both LPG bullet areas at 23.04 frame 25 [6, 8].

Figure-S 3.13 First light at east end of site, 23.06 frame 24 [8, 6].

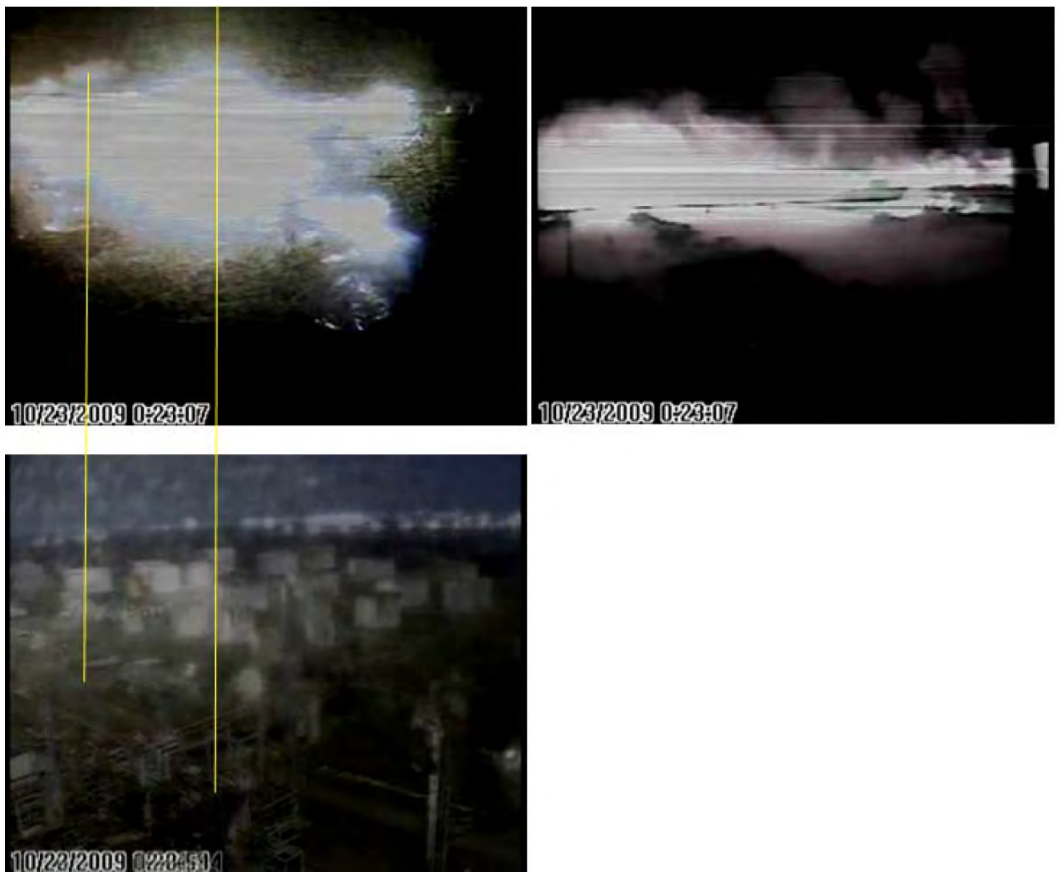

Figure-S 3.14 First frame of a major explosion at 23.07 frame 21 referenced to site photo (lower). The frames on the left are from FCC camera, and the frames on the right are from the WTT camera [8, 6].

Frame 10

Frame 13

Figure-S 3.15 Progression of the main explosion event [8, 6].

Attention turned to the severe explosion in the region of tanks 404, 405, 406 and 407. Triangulation from frames taken from FCC and northwest videos (Figure-S 3.16) indicate that the explosion originated in a region of congested pipework between tanks 404 and 405 (Figure-S 3.17). A blast in this area could account for damage to tanks 406 and 407 and to the fence line and trees to the north of the site (see [6]). Further evidence supporting a major explosion in this area came from the arrival of blast at the FCC camera and at the gatehouse. The FCC camera lost its imaging 1.24 s after the video image of the explosion, indicating a distance of 430 m from the blast origin, assuming a sound speed of 350 m/s. This is the exact distance between FCC camera and congested pipework. The correspondence of distance between the gatehouse and pipework, 560 m, compared with 630 m derived from glass breakage and sound speed, is not as close, but perhaps still within reasonable error.

The question, then, is: *Was there enough congestion in this pipework area to create such a major explosion?* At first, it appears that there was not. The author (GAC) then asked the CSB to send diagrams of the drainage systems around the site. It appears that there are two 4-inch drains and a clean-out pipe to the sides and underneath the pipework in question (Figure-S 3.18 and Figure-S 3.19). We know that flammable vapors entered the drain system, and it likely that vapors entered others, also, as manhole 13 showed signs of blast. *This suggests that high-velocity jet flames from the two drains or the clean out pipe induced a detonation in the vapor cloud surrounding the pipework. Then this detonation propagated through the remaining cloud.*

There could also have been a detonation in the drain system itself, and then this detonation could have exited into the existing vapor cloud. The distance from manhole 13 to the 4-inch open drains is approximately 44 m, consisting of a 6-inch pipe for about 40 m then branching into the three 4-inch pipes of about 3 m, 8 m and 2 m. There is most likely enough distance and pipe interconnections, leading to more shocks, for DDT to occur in this configuration.

Another possibility is that a detonation propagated all the way to the bamboo area from the tank area, as opposed to a DDT that starts in the bamboo area after the remaining fuel had burnt out. The second case, in which DDT occurred in the bamboo area after the remaining fuel burned out, would have created the positive pulse to cause the directional indicators in Figure-S 3.20.

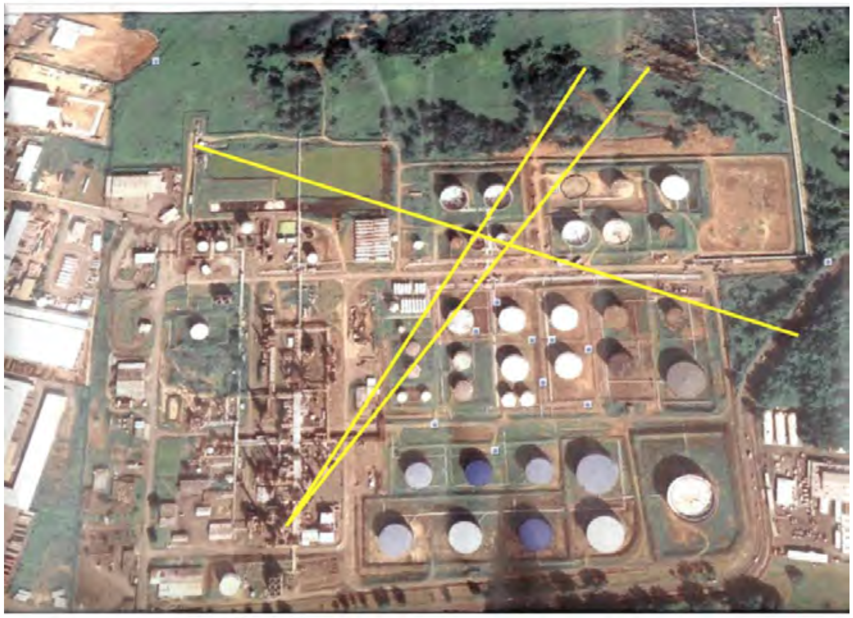

Figure-S 3.16 Triangulation of the explosion shown in frames 23.07.21 to 23.08.8 [6]. .

Figure-S 3.17 Congested pipework in the region between tanks 404 and 405 (triangulated area) (left) and crushed steel box (right) 70 m to the east of the triangulated region [6]. . Note uniformly crashed tank.

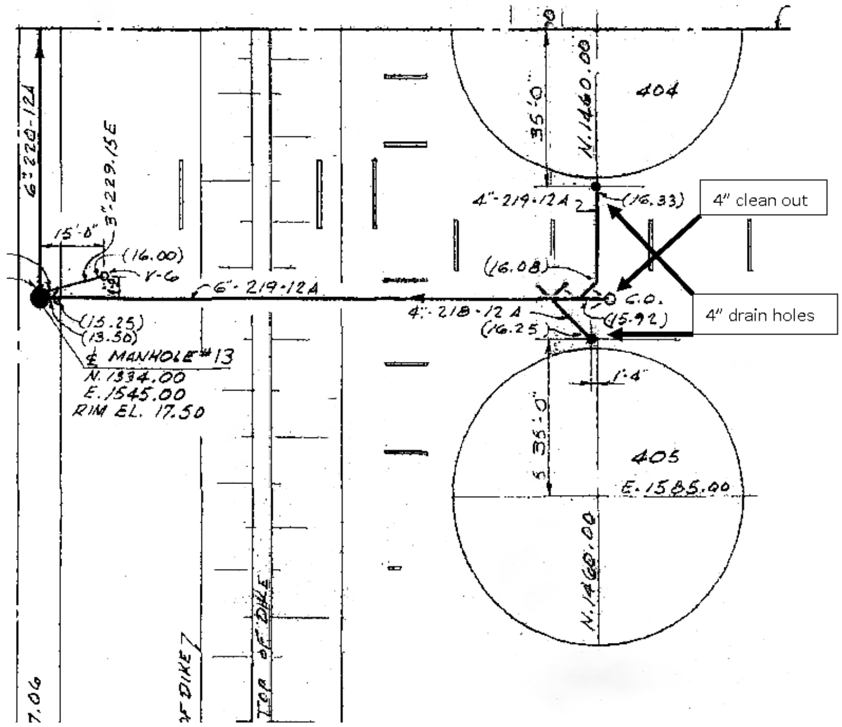

Figure-S 3.18 Drain system in the region of tanks 405 and 406. Note the two 4-inch drains between the tanks, and the clean out. It would seem that the clean out pipe exits underneath the gasoline pipework [8].

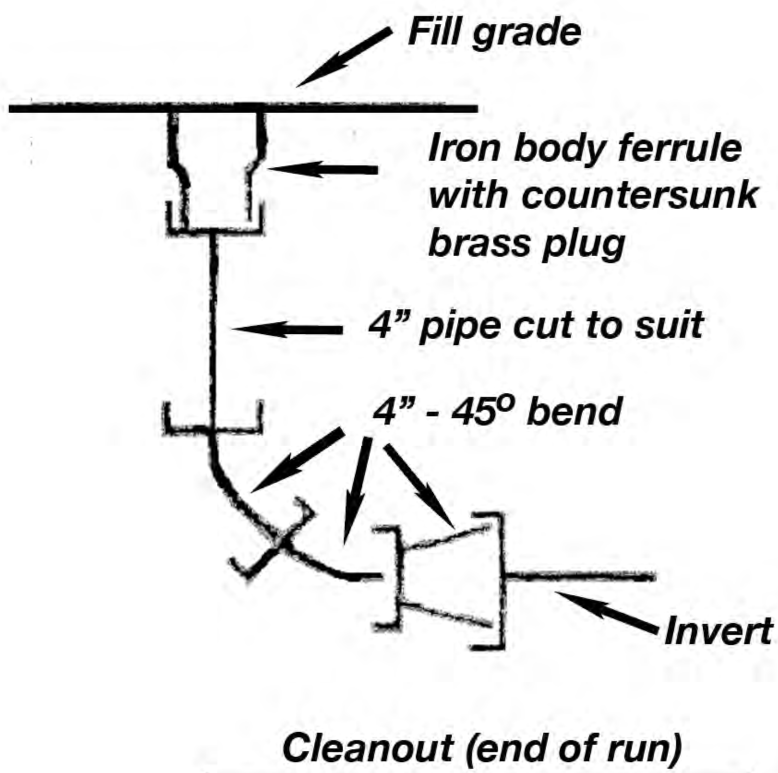

Figure-S 3.19 Close up of clean-out section of drain system [8].

Figure-S 3.20 Directional indicators on the eastern side of the site [8, 6].

Thus the current hypothesis is that a detonation of the vapor cloud occurred by ignition from a high-velocity jet flame emerging from the drain system between tanks 404 and 405. The vapor cloud in this region was close to the original leaking tank and occupied a large volume, possibly 10-m high. The detonation propagated through the vapors that remained after a partial burnout in the northern part of the site, and it then continued into the bamboo area at the east end.

4.Amuay Accident

Description of the Event

An operational decision was made to continue using a leaking olefin pump and to rely on the wind to disperse the vapors. The leak started days before the explosion, and the wind conditions reinforced the decision. At about midnight on the night of the incident, however, the wind slowed, became NW to SE, and vapors started to accumulate in the refinery. The flow rate of the leak also increased. The leak rate has been reported in the PDVSA report [9] as $\sim 8\ m^3/min$. The cloud drifted around the low points surrounding the tank and traveled at least 600 m towards the SE, engulfing the lube oil plant and houses in the town to the east. It is thought that a car traveling down the Avenida Bolivar Road, to the east of the refinery, ignited the cloud (Figure-S 4.1).

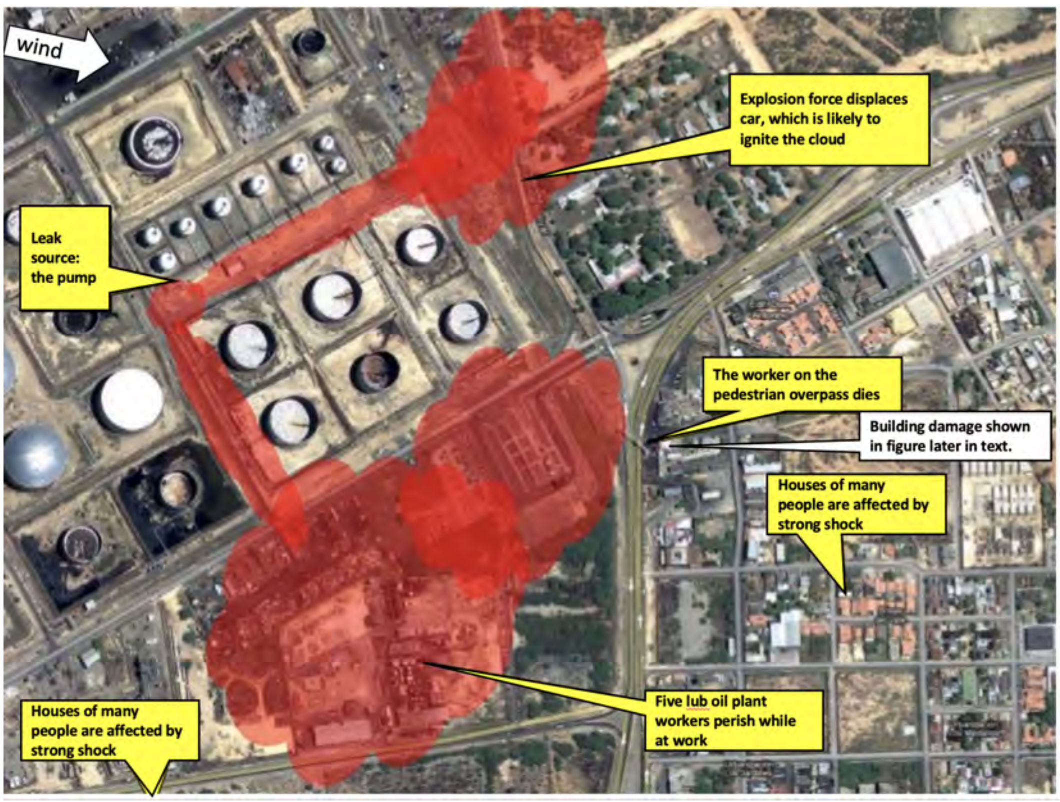

Figure-S 4.1 Rough extent of the flammable cloud. Note location of car reported to have ignited the cloud and location of pedestrian overpass (footbridge) [9].

Discussion

The damage pattern is confusing. The car that is supposed to have ignited the cloud shows damage signs equivalent to at least 5 atm of overpressure (Figure-S 4.2). The fence posts near this car point towards the refinery and away from the car, yet posts further along point in the opposite direction, and the car itself is pushed away from the refinery.

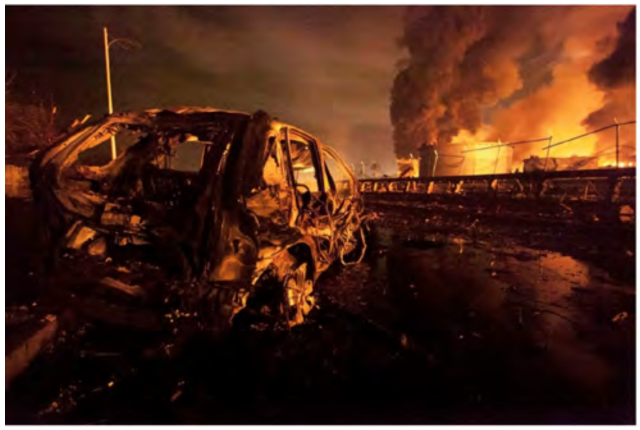

Figure-S 4.2 Fence poles bent inwards towards refinery. Car close to, or responsible for, point of ignition. (Figure taken from [10].)

The olefin storage spheres to the north, close to the leaking pump and storage tanks further to the north, were largely undamaged. Yet oil storage tanks to the south were severely damaged. The lube oil area was totally destroyed, and there was significant damage to buildings just over the road from the lube oil plant (Figure-S 4.3). Figure-S 4.4, Figure-S 4.5, and Figure-S 4.6 show various crushed storage tanks.

Figure-S 4.3 Houses adjacent to road running east of the lube oil area. Notice displacements of reinforced concrete poles. (Figure taken from [10].)

Figure-S 4.4 Crushed storage tank. (Appeared on website of *Christian Science Monitor*, 16 September 2013.)

Figure-S 4.5 Crushed storage tanks. (Appeared on website of *Christian Science Monitor*, 16 September 2013.)

Figure-S 4.6 Crushed storage tanks. (Appeared on website of *Christian Science Monitor*, 16 September 2013.)

The footbridge (Figure-S 4.7 and Figure-S 4.8) was damaged, and it appears that the supports and railings were drawn towards the lube oil area.

Figure-S 4.7 Note footbridge drawn inwards towards refinery, suggesting footbridge inside detonation. (Figure taken from [10].)

Figure-S 4.8 Close up of footbridge showing damaged railings and supports drawn towards the refinery. (Figure taken from [10].)

Figure-S 4.9 and Figure-S 4.10 show damage to trucks inside the lube oil area, representative of overpressures greater than 5 atm. Car and tree damage indicate detonation (Figure-S 4.11). The oil drums in Figure-S 4.12 indicate overpressures of at least 3 atm.

Figure-S 4.9 Damage to truck inside the lube oil plant. Damage suggests detonation.

Figure-S 4.10 Lube oil plant damage to truck and oil drums. Note building destroyed, but poles not bent.

Figure-S 4.11 Car and tree damage suggest detonation.

Figure-S 4.12 Top: Drums and car damage. Bottom: Enlargement of Figure-S 4.10showing creased drums. (Figure from CTV News, August -September, 2012.)

If a detonation did occur in the lube oil area, the overpressure at the buildings in Figure-S 4.3 can be estimated using the correlation in Equation (4–2) from the main text. Assuming $H = 3$ m and $\Delta R = 40$ m, we have $P \sim 0.6$ atm. This is sufficient to create the devastation seen in Figure-S 4.3.

Note also that there is significant distortion and failure of reinforced concrete supports.

It seems unlikely that a fast deflagration in the lube oil area would lead to a strong enough blast at these buildings. The distance from the lube oil area is around 350 m. Assuming a source pressure of 5 atm and a radius of 27 m, and using CAM [7], the overpressure at the buildings is less than 0.1 atm.

Figure-S 4.13 shows tank damage due to blast impact (suggesting detonation) with a subsequent phenomenon called top tank fire that destroys the impact evidence because it melts walls. The overpressure at the nearest fuel tank (∼10 m from the edge of the cloud) would have been around 0.23 atm, sufficient to deform and open up the tank. Additionally, a large storage tank ∼470 m to the west remained largely undamaged. The overpressure there would have been around ∼0.05 atm. Other storage tanks inside the cloud show definite uniform crushing (Figure-S 4.14 to Figure-S 4.15), suggesting detonation impact.

Figure-S 4.13 Crushed storage tank with tank top fire that melts and deforms the tank walls.

Figure-S 4.14 Crushed storage tank. Notice damaged cars.

Figure-S 4.15 Crushed storage tank suggesting detonation impact. (From website Runrun.es, by permission [11].)

A likely hypothesis on the course of events is as follows: The car on Avenida Bolivar road ignited the olefin cloud. A cloud fire ensued which propagated through the cloud covering lower ground between olefin spheres and fuel storage tanks and eventually reached the lube oil plant (Figure-S 4.1). The flame speeds at this stage were not great, and little blast damage was caused to the nearby olefin spheres. Plant congestion and vented explosions caused a DDT in the lube oil area which propagated through the remaining cloud over a largely uncongested region towards the footbridge and buildings to the east.

The hypothesis does not explain the bent posts near the ignition point towards the refinery, nor does it explain the lack of bent posts in the lube oil plant itself (Figure-S 4.10). The displacement of the car to the other side of the road and its significant damage also remain an anomaly.

Unless, and here is another hypothesis, there was another fast flame or detonation near this location. Building and tree damage suggest a considerable blast in the vicinity (Figure-S 4.16), which was strong enough to be a detonation.

Figure-S 4.16 Building damage in the vicinity of the car allegedly responsible for ignition of the cloud [10].

5. Skikda Accident

Description of the Event

Skikda LNG facility was operated by Sonatrach, a government-owned Algerian corporation formed explicitly to explore the hydrocarbon resources of the country. Sonatrach operated the LNG plant at Skikda, Algeria, a modern city on Mediterranean Sea coast. A layout of the plant is given in Figure-S 5.1 [12].

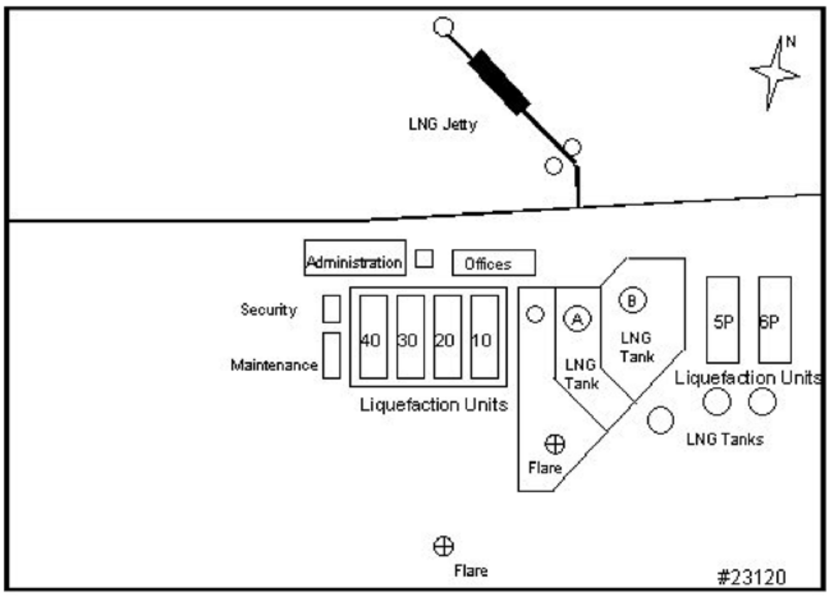

Figure-S 5.1 Layout of the Skikda LNG plant (private communication to GAC, 2004. Source: Sonatrach, Poten and Partners).

At 18:34 pm on 19 January 2004, an operator noticed the steam pressure in the boiler drum was rising to the point where the pressure safety valve was activated. The operator cut the fuel gas supply, but the pressure continued to rise. At 18:40 pm, the outside operator reported to the control room that he could see a large vapor cloud developing in Train 40, pole 1. At this time in Train 40, there was a small explosion that was quickly followed by a larger explosion and fireball. Contributing factors include semi-confined conditions (confinement on three sides) and no wind.

Sonatrach's best interpretation of these events is as follows:

1. A cold hydrocarbon leak occurred near the boiler of Train 40.
2. A mixture of hydrocarbons and air was introduced by the fan to the boiler.
3. The pressure in the boiler drum rose quickly.
4. The gas in an entrance to the boiler developed into explosive mixture.
5. An explosion inside boiler destroyed the boiler water wall and ignited the vapor cloud outside.
6. There was a massive VCE.

Sonatrach's investigation reported that the following inventory and equipment were in the vicinity of the explosion in Train 40:

- Cold Fluids
  - LPG at a temperature of -40 C.
  - High pressure flash gas* (47% inert gas and 53% fuel, temperature = -148 C) [12].
  - LNG at temperature = -161 C
- Equipment
  - Fuel gas exchanger
  - Fuel gas compressor
  - Fuel gas flash drum
  - LNG pumps
  - Piping that transfers these gases and fluids.

Discussion

An outside report (private communication, S. Davis) confirmed that Sonatrach confirmed that Train 40, where the leak occurred, used the proprietary PRICO Liquefaction Process. Extensive efforts were required to confirm the composition of the mixed refrigerant used to liquefy the methane, and which was the likely source of leaked volatile liquid. The presence of a considerable amount of ethylene makes the vapor cloud more susceptible to detonation.

The timing of the leak, as reported on the radio by an eye witness who was later killed by the explosion, suggests that the leak duration was $\sim$2 min. This is consistent with a leak of liquid refrigerant from a 1" pipe break. Simulations using CAM2 [7] 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 eye witnesses reported that the visible cloud, i.e., at least the extent of the flammable cloud, traveled around 80 m towards the Maintenance Building. At least five eye witnesses reported a vapor cloud extending to the Maintenance Building and to Unit 30 (Figure-S 5.1). One witness said that there was a first small explosion in unit 40 and immediately thought that the boiler had leaked, because a similar incident had occurred six months earlier. He looked towards the boiler and saw a cloud of white vapor. He then saw a second small explosion, followed by the third, much louder explosion that destroyed the plant.

Some pictures show damaged cars, although it is not known where these cars were located at the time of the explosion. The damage sustained indicates overpressures of around 5 atm, but not necessarily detonation. The damage could be explained by a fast deflagration in the highly congested region of the release.

It might be possible that methane vaporized from LNG could have created such high overpressures. A more likely candidate would be LPG or mixed refrigerant. The equivalent fuel based on the

* Flash gas is a spontaneous vapor produced from the heating or depressurizing the oil mixture extracted during various phases of oil production

PRICO mixed refrigerant composition is propylene. The results of CAM2 simulation suggests that overpressure greater than 3 atm were generated at source. This could be sufficient to create the conditions for transition to detonation.

Photographs of the damage reveal several interesting features. The Control Room (Figure-S 5.2) and Maintenance Building (Figure-S 5.3 and Figure-S 5.4) 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 the Maintenance Building and Unit 40 (Figure-S 5.5, Figure-S 5.6, and Figure-S 5.7) and a tower support (Figure-S 5.8) are bent inwards towards Unit 40. Figure-S 5.9 shows a considerably crushed heavy duty truck located away from congested space. The damage indicated overpressure significantly higher than 5 atm. This space also contains a few crushed oil drums, indicative of overpressures over 3 atm. The collapsed flash drum and railings in Figure-S 5.10 and Figure-S 5.11, and especially the bent poles in Figure-S 5.5, Figure-S 5.6, and Figure-S 5.7, have been drawn to the SW on Unit 40. When these directional indicators are plotted on a Google Earth snapshot of the site (Figure 5.3 in Main Text) they suggest that a detonation may have occurred. Consistent with this hypothesis is the fact that the vapor cloud was observed to have reached the Maintenance Building.

Three separate explosions were heard. The first was probably the furnace explosion, the second could be the deflagration in the congested area of Unit 40, and the third, the largest, the transition to detonation.

Figure-S 5.2 Control Room at Skikda (private communication to GAC, 2004).

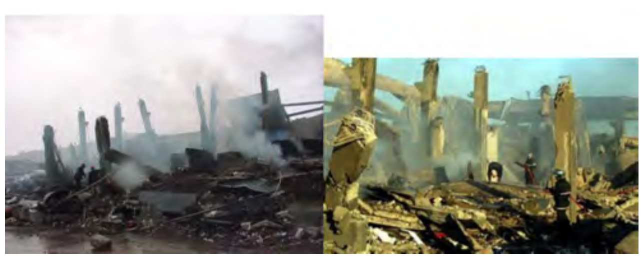

Figure-S 5.3 The remains of the Maintenance Building. Note that some of the reinforced concrete supports have been drawn inwards (towards the center of the flammable cloud) (Figure taken from Reuters.).

Figure-S 5.4 Another view of the wrecked Maintenance building. Note also the crushed drums in the foreground left [12].

Figure-S 5.5 Panorama of the west side of Unit 40 south end looking SE. The remains of the maintenance building are behind this photograph. Note the bent poles. (Private communication to GAC, 2004).

Figure-S 5.6 Panorama of the south side of Unit 40, electrical building, looking SE. Note the bent lamppost 38 E 25 and fence drawn inwards. (Private communication to GAC, 2004).

Figure-S 5.7 Panorama of the west side of Unit 40 south end, electrical building. Note the bent lampposts all drawn inwards, i.e. towards the centre of the flammable cloud. (Private communication to GAC, 2004).

Figure-S 5.8 West side of Unit 40. Note that the tower by the yellow truck has been drawn towards Unit 40, similarly the lamppost (in front of the truck). (Private communication to GAC, 2004).

Figure-S 5.9 Unit 40 and the heavy duty car crushed; overpressure above 5 atm away from congestion. (Private communication to GAC, 2004).

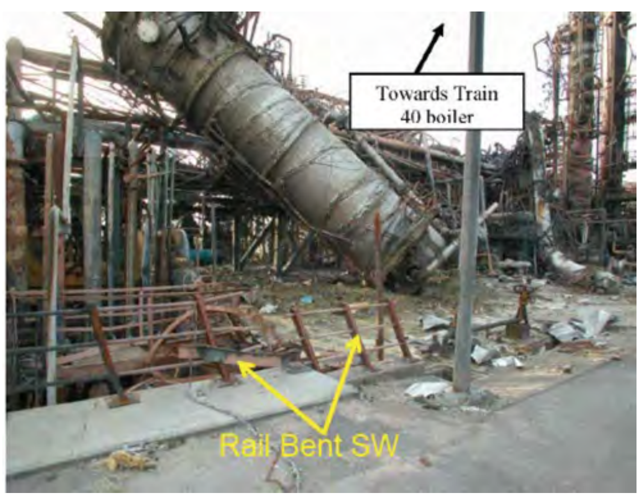

Figure-S 5.10 View of collapsed flash drum and bent railing Unit 40. (Private communication to GAC, 2004, also [12]).

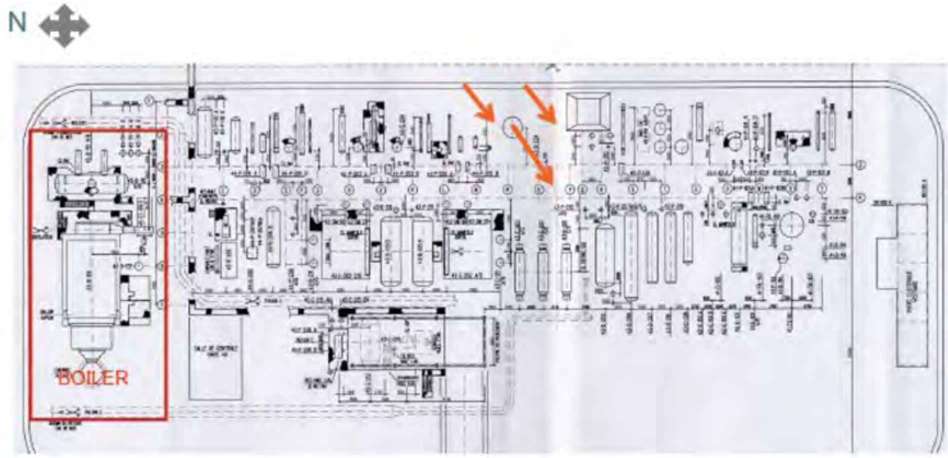

Figure-S 5.11 Location of a flash drum and railings Unit 40 indicating direction of bend. (Private communication to GAC, 2004, and [12].).

It is unlikely that the detonation reached the electrical substation to the south of Unit 40 or to the offices to the north-west of the site. Both were badly damaged, indicating high overpressures, but unlike the Maintenance Building or Security Hut to the west of Unit 40, they were not completely annihilated.

Then, in summary, the following course of events can be proposed: An explosion first occurred in the Unit 40 furnace after ingress of leak vapors from within the unit. The vapors consisted of mixed refrigerant, equivalent to propylene vapor. This vented into the vapor cloud which had become established over the 2 min of release. The external cloud ignited, thus creating a deflagration in Unit 40. The flame speed increased rapidly in the congested unit, generating an ~3 atm overpressure and thereby causing gross damage to northern end of Unit 40 and adjacent Unit 30. There was then a transition to detonation in the mid-western side of Unit 40, and then detonation consumed the remaining cloud in the open space between Unit 40, the Maintenance Building, the electrical sub-station, and the canal. Figure 5-4 in the main text. shows the proposed area over which the detonation took place.

6. Brenham Accident

Description of the Event

The explosion occurred when a large cloud of LPG escaped from a 1335 m^3 salt-dome storage facility that had been over-filled. A car passed into the cloud of gas accumulated in a gully. The explosion flattened the car and blew it off the road. A 5-year-old child was thrown 46 m from his home. His mother was also thrown from the house. The trailer home was completely destroyed. The complete annihilation of houses and trailers within the cloud and the damage to trees and cars suggest overpressures greater than 5 atm. The blast registered 3.5 - 4 on the Richter scale. The explosion was most likely detonation of the hydrocarbon vapors.

Discussion

The location of ignition remains unknown, but evidence points towards the car entering the cloud, as shown in Figure-S 6.1. The level of damage resembles that of overpressures > 5 atm, which could only have been generated by a fast deflagration or detonation. Ignition of the cloud would not in itself create large overpressures and the flame would have to have accelerated. The car may have traveled some distance before being damaged to the extent shown in Figure-S 6.1.

Figure-S 6.1 The video shows a damaged car, shown in the captured image above. The crushing resembles damage caused overpressures > 5 atm [13].

There is evidence that 3 separate blasts occurred. The first blast was the strongest, and it was immediately followed by 2 other blasts. This suggests that there was a detonation followed by 2 deflagrations. The spread of the cloud, the undulating terrain, and the distribution of trees, suggest that the detonation terminated, but was quickly followed by a flash fire that propagated to 2 isolated, tree-covered areas as fast deflagrations. Alternatively, the 2 weaker blasts may have arisen from explosions in houses, but this seems less likely given eye witness testimony.

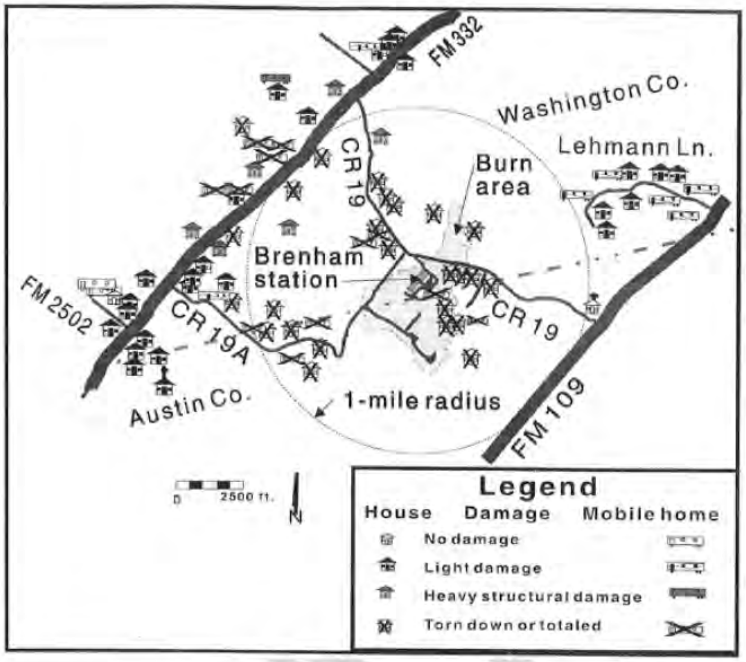

Figure 19: Damage to homes and structures near the accident site from Pipeline Accident Report: Highly Volatile Liquids Release from Underground Storage Cavern and Explosion, MAPCO Natural Gas Liquids, Inc. Brenham, Texas April 7 1992, NTSB-PAR-93-01.

Figure-S 6.2 Sketch reproduced from [14].

Figure-S 6.3 Brenham burn area. Sketch reproduced from [14].

Houses within 1.6 km radius of the explosion station were totally destroyed, but many of these were within only 800 m from the cloud edge where the overpressure may have been of the order

0.05 atm. This would have been sufficient to destroy the mainly wooden houses, as observed in Figure-S 6.2 and Figure-S 6.4.

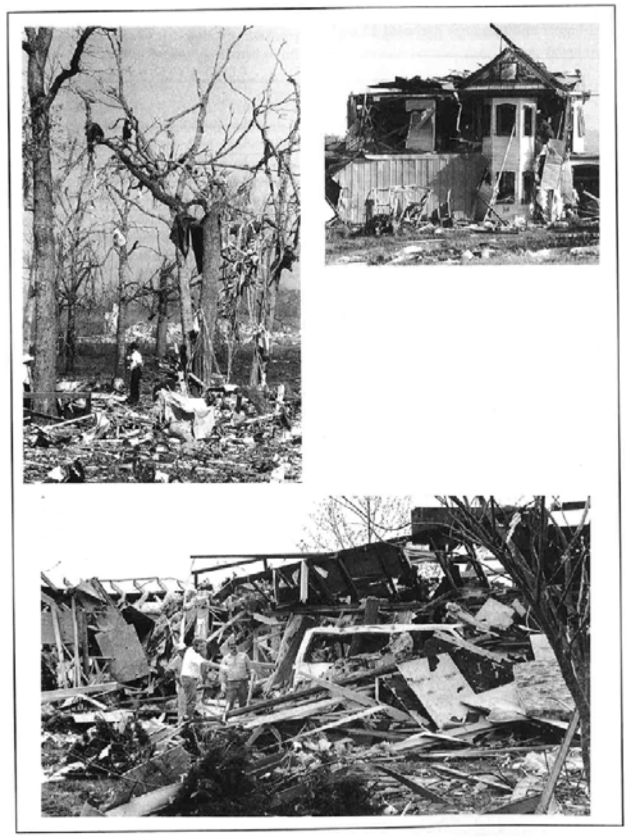

Figure-S 6.4 Area residences damaged by blasts. Sketch reproduced from [14]. Top right: a building about ~800 m from the release point.

7. Ufa Accident

Description of the Event

The description in the next few paragraphs is essentially taken from [15]. (Additional information has been obtained from G.M. Makhviladze in private communication with one of the authors, AP). The incident occurred in the Ural Mountains area of Russia near the city of Ufa, 1710 km from Moscow. The damaged forest area, shown in Figure-S 7.1 and enclosed by the solid line, covered about 2.5 km^2. The cause of the accident was the rupture of a large pipeline (total length 1852 km) that transported liquefied oil products from Siberia to large chemical plants in European Russia. The pipeline, of inner diameter 70 cm, lies at a depth of about 1.2–1.5 m below the surface and passes under the railway. It conveys about 10 MT/day (116120 kg/s) at a working pressure of 38 bar.

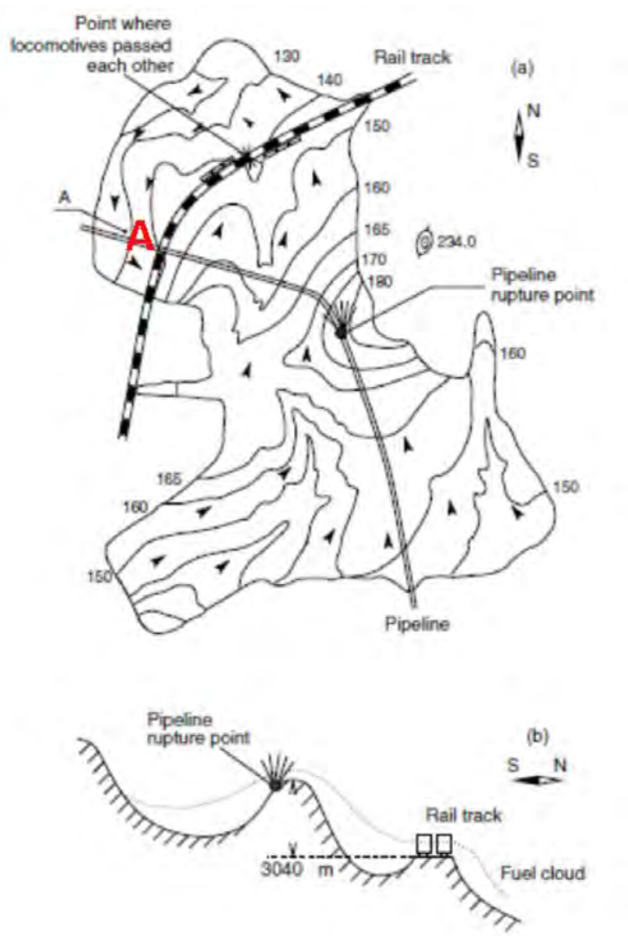

Figure-S 7.1 Ufa explosion event: (a) Sketch of demolished area (direction of tree fell is shown by arrows); (b) terrain profile (not to scale). View of accident site from region of point A is shown in Figure-S 7.2. (Figure reproduced with permission from [15]).

The pipeline was ruptured near the head of the valley (Figure-S 7.1, [15]) about 900 m from the railway track. The total area of this breach was 0.77 m^2, twice the cross-section area of the pipe.

The original dent at the point of rupture may have occurred during the laying of the pipeline. The pipeline operates in severe winter conditions, under mechanical vibrations caused by possible hydraulics shocks, unavoidable in such a long pipeline over a hilly area. These factors could have contributed to the sudden fracture of the pipeline. The rupture of the pipeline at the head of the valley led to the release of hydrocarbons and the formation of a huge flammable vapor cloud that covered the dense forest area and part of the nearby rail line. Before the accident, at about midnight, the pressure in the pipeline dropped. The staff, unaware of the reason for this, powered the pumps to increase the pressure. At that time, inhabitants of the nearby villages, 4-7 km away, smelled the gas condensate. At 12:50 a.m., a goods train passed this site. The driver noticed the strong smell of gas and saw a "white cloud" along the railway tracks. Twenty minutes later, two passenger trains traveling in opposite directions approached the site and came into the cloud.

At 1:14 a.m., a violent explosion occurred, followed by a very large fire. There were 1284 people total in both trains, of whom 1224 died or were severely injured. The majority of the victims suffered from the strong heat radiation. In one train, 6 cars of out of 20 were thrown off the track. In the other, 5 cars out of 17 were thrown off. Seven cars of the 11 thrown off were completely destroyed; all other coaches of both trains were partly burned on the outside and burned up inside. Shock waves demolished the mound and consoles and dislodged 1800 m of overhead and contact wires.

Figure-S 7.2 Accident site viewed from region of point A in Figure-S 7.1. On the right of the railway is the remainder of one of the trains. (Reproduced from [15] by permission).

Windows were broken in a local hospital, 15 km from the site. A photograph of the site (Figure-S 7.3) from Figure 10 in [15] was taken several days later. The tree fall in the valley below the railway track reflects the vortex character of the flow in this region (Figure-S 7.1).

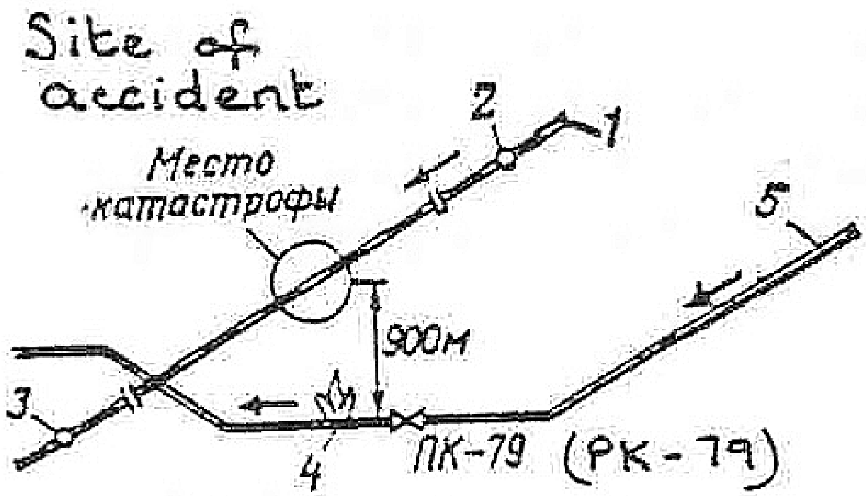

Figure-S 7.3 Site of accident (G.M. Makhviladze, private communication).

According to the Center for Chemical Process Safety, two explosions took place in quick succession, and a flash fire ran down the railroad track in both directions. A considerable part of each train was derailed.

Discussion

The first step is to establish the facts surrounding this incident. There are several discrepancies between the accounts in [15] and [16], and the information provided in private communications (with G.M. Makhviladze to author AP), and these are listed and discussed below.

- The total amount of fuel released between initial burst and ignition was estimated by various methods as 2 MT and 10 Mt [15] and [16].
- The composition of the liquefied product, quoted in [16] in mass percentages as: 0.02% methane, 2%,ethane , 36% propane, 15$ iso-butane, 27% n-butane, 7% iso-pentane, 6% n-pentane, and 7%hexane. This differs from that quoted in [15] which has no methane or ethane, 41% propane, 26% n-butane, 15% iso-butane, and 16% heavier hydrocarbons. Since [16] is a later publication, we assume that the composition quoted there is correct.
- The initial release rate calculated by FRED's [7] "pressurized release scenario" is 2700 kg/s. Using FRED's "2-phase blowdown scenario," and assuming propane fuel, the initial release rate is 2300 kg/s. FRED's "unified scenario" gives 2662 kg/s. These rates refer to release from one side, which is consistent with the break being near one end of the pipeline.
- The volume of the pipeline is 713,000 m^3 and liquid density 569 kg/m3, giving a total mass of 4.05×10^8 kg in the pipeline before rupture. Using FRED's "unified scenario," this reduces to 3.9×10^8 kg after 1 hour, and a release rate of 420 kg/s. The mass lost after 1 hour (assuming no top-up of the pipeline by further pumping, which *actually did* take place) is therefore about

10^7 kg or 10 MT tonnes. This is reasonably close to the upper estimate in [15].

– The spill occurred at an elevation of 40 m above and 900 m away from the railway track where the two passenger trains met. Figure-S 7.1, however, incorrectly indicates an elevation of 3,040 m above the railway track.

Figure-S 7.4 Sharp borderline between demolished and original forest, indicating sharp change of overpressure [15].

– References [15] and [16] refer to 22 m/s winds causing tree trunks to break, according to the Beaufort wind force scale of wind-speed effects. The speed of 22 m/s (Force 9) is, however, a lower limit on the breakage of small branches. A wind speed of >25 m/s (Force 10 and greater) is more likely to cause uprooting and breakage of tree trunks according to standard Beaufort scaling.

– References [15] and [16] report that the majority of trees were snapped at about 3 m above the ground, which is typical of hurricane-force winds. Photographs (Figure-S 7.2, Figure-S 7.4, Figure-S 7.5, and Figure-S 7.6). however, show many trees uprooted and many upright trees burned.

Figure-S 7.5 View after the accident. Note crushed train on left side (G.M. Makhviladze, private communication).

Figure-S 7.6 Taken from a short video of the incident. Tree breakages near point of release. Note damage to the trees includes breakage of branches and trunks, burnt trunks and uprooting (private communication, G.M. Makhlivadze to author AP).

Given all of this evidence, the original theories of damage caused by the explosion seem inadequate. Information from the Buncefield studies now suggests that the Ufa incident involved the detonation of the vapor cloud. The explosion took place in a dense forest and the collapsed trees fell inwards towards the cloud. Rail cars were crushed. There was a distinct line of lesser damage at the edge of the cloud, which is consistent with the overpressure decaying rapidly outside the cloud, yet the blast damaged windows 15 km away. Using Equation (4-2) from the main text, the height of the detonating cloud would have to be of the order 20 m to cause window breakage at this distance. Although this seems extreme, it may have been possible, given the profile of the dispersing cloud (see Figures) and the assertion from [15] that the cloud was of this height.

The "pressurised release scenario" in [7] indicates an initial release of 2.7 tons/s and a dispersion distance to the lower flammability limit (LFL) of ~2000 m (using propane horizontally released and flat earth assumed, and pipeline height 1.2 m above ground). Interestingly, even using the unrealistic conditions assumed by FRED, the cloud height reaches about 20 m. FRED cannot handle the actual composition of the release for the dispersion calculation, so propane was used instead. The actual composition contains lighter fractions, and hence is more buoyant, than propane. These fractions are also more volatile and distill off the released liquid preferentially. The cloud height may be considerably higher than the 20 m predicted by FRED. Reference [16] estimates a cloud height of 140 m to reach the LFL.

It is outside the validation for FRED to predict the release rate for this long pipeline. Nevertheless, from FRED's "unified scenario," after 30 minutes the release rate is still high at 1400 kg/s, even though there is no continuous pumping in the calculation. After 1 hour (maximum permitted in the model) the release rate is still 420 kg/s. At the rate of decay of the release, it is estimated that at the time of ignition, the release rate would be around 300 kg/s. This would burn as a jet fire within a surrounding pool fire and a transient fireball. The jet fire would reach a height of 110 m.

The directional evidence at Ufa has been interpreted by [15] to be the result of of air entrained into a strong convection plume. This is possible, but it is probably not the only interpretation. The damage to trees covers only areas where gas flow would have occurred, as shown by the burnt area rather than all of those that would have been affected by entrainment into the updraft. Reference [15] shows that fairly high velocities (22 m/s) can be generated by an updraft, but this requires all gas to be concentrated in a deep (30 m) layer near the point of release. Given the duration of the release and the steep slopes leading away from the release point, this is unrealistic. As occurred at Port Hudson and Buncefield, the gas should be widely spread in a relatively thin layer over the slopes, but may also have accumulated in valleys and depressions in the landscape. The sharp cut-off in both pressure and thermal damage at the edge of the cloud (also observed at Port Hudson and Buncefield) indicates that the damage was caused by blast, rather than convection driven winds. Windows breaking at 15 km from the site also indicates a severe blast.

Now let us examine the idea that high velocity winds were created by the buoyant updraft in a firestorm that followed the ignition. The main assumptions in this analysis are that the fireball is cylindrical, burning is stoichiometric, and entrainment is uniform up the cylinder, and the height of the cloud is guessed based on the topography. Then, taking the values from [15] and [16] we have:

- Radius of cloud $R = 1000$ m,
- Height of cloud controlling air entrainment $H = 30$ m,
- Fuel mass $M = 3000$ T,
- Duration of fireball $t = 30$ s,
- Cloud has a curved surface area $= 2\pi RH = 1.88 \times 10^5$ m^2,
- Burning rate $= M/t = 1 \times 10^5$ kg/s
- Air/fuel mass requirement for stoichiometric burning = 15.

Thus,

- the rate of air entrainment $= 1.5 \times 10^6$ kg/s $= 1.8 \times 10^6$ m^3/s. which entrained over the surface area of the cloud cylinder, thus the
- speed of air flow at the cloud flame edge $= 1.8 \times 10^6 / 1.88 \times 10^5 = 9.6$ m/s.

Thus, we have an air speed of only about 10 m/s at the edge of the cloud, assuming stoichiometric burning. A rich flame will entrain less air. The value is in stark contrast to 22 m/s (or greater as discussed above) required for trees breaking in [15] and [16]. This analysis shows that the rate of air entrainment is inversely proportional to the cloud height controlling the entrainment. A cloud height of 10 m would increase the air speed to 30 m/s. So the conclusion that high wind speeds were responsible for some of the tree fall cannot be ruled out.

Another theory was put forth by B. Gelfand (private communication to M. Johnson), who was part of the original investigation, has another theory about the causes of the characteristic inward breakage of trees: "Unusual forest fall was due to the character of the explosion. Along the edges of the disaster area the gas concentration decreased and detonated: there was an explosion. Inside the gas cloud with practically 100% concentration there began intensive but not explosive burning." This explanation seems closer to what happened, but does not completely explain all the facts.

Now consider a hypothesis to explain the detonation. The passing trains are strongly suspected of causing ignition, creating turbulence in the cloud and enhancing the mixing of rich pockets of fuel with air. Internal explosions, as shown in Figure-S 7.7 [15] occurred in some of the coaches. Vented jet flames would emerge into the external turbulent cloud caused by movement of the trains. A fast deflagration would then propagate into the nearby forest area, and transition there to detonation. Therefore, we suggest a transition somewhere near point A in Figure-S 7.1. This would explain the trees falling in the opposite direction to the propagation, an occurrence remarkably similar to that at Port Hudson, where a detonation was accepted as the only explanation of the tree-fall and explosion severity.

Figure-S 7.7 Internal explosion(s) evidenced by the barrel like shape of coaches and locomotives [15].

Figure-S 7.5 shows another view of the devastated area next to the railway line. Here the uprooted and totally flattened area of trees is only to the top of the picture and is largely separated from the railway line by broken but not flattened trees. The broken trees bear a striking resemblance to the trees broken by detonation at Buncefield and at Brenham.

The detonation might then propagate some way towards the spill point but cease where the cloud became too rich. Then a fireball, pool fire and jet fire would take over as the main combustion events. As a consequence of these nonpremixed combustion events, the tree fall and breakage and burnt trunks would occur nearer the spill point. Any high speed winds generated by this firestorm would account for the tree fall to the south of the site.

8. Port Hudson Accident

Description of the Event

At 10:20 pm on 9 December 1970, a pipeline carrying pressurized propane, operating at approximately 65 bar, ruptured in Port Hudson, Missouri, USA. The location was a rural area with scattered farmhouses [17, 18, 19, 20]. At the time of the incident, the ground-level weather conditions at the meteorological center at Lambert Field, Missouri (90 km east-north-east of the incident) were: Wind speed, 2.5 m/s; wind direction, NE; temperature 1.0 C; relative humidity, 100%

A 2 m long split on the underside of the pipe produced a crater in the ground (3 m in diameter and 1.2 m deep) and a white plume 15-20 m above the release. The rupture was noticed by the occupants of the Menner property (140 m from the rupture location), who evacuated the property and alerted their neighbors (see Figure-S 8.1).

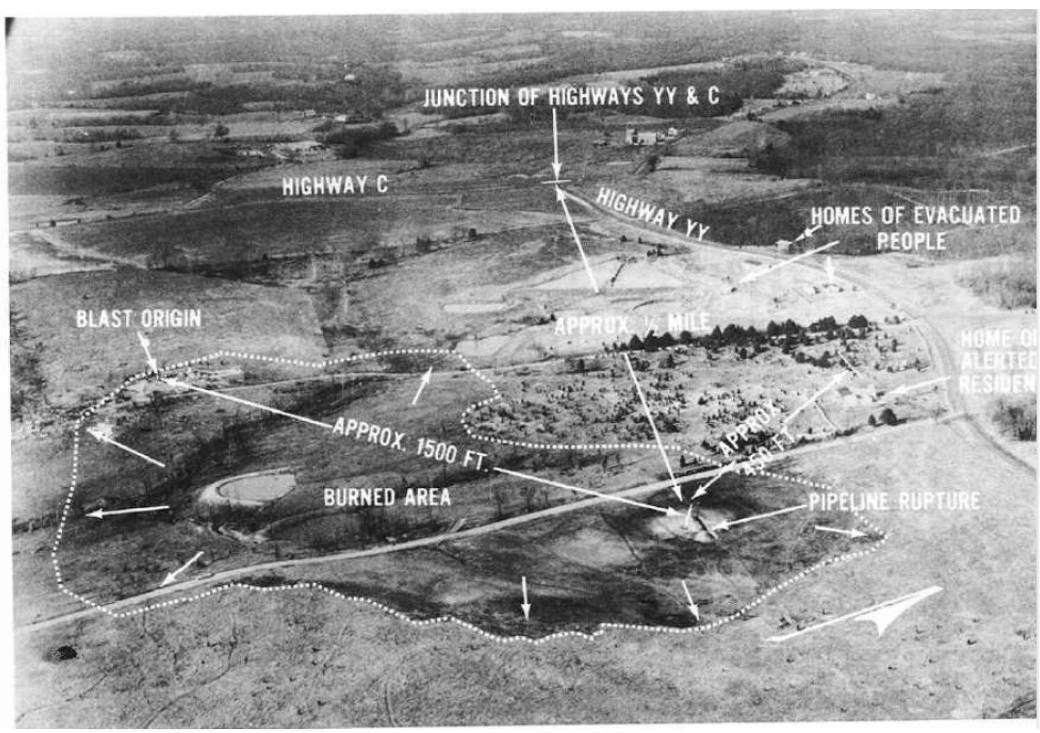

Figure-S 8.1 Accident site at Port Hudson [18].

Discussion

From the eye witness testimony, at the time of the ignition at 10:44 pm, ~0.12-0.14 km^2 of the valley was covered in a mist (assumed to correspond to the propane cloud). The explosion itself was essentially described as the entire valley lighting up. Notably, it was not described as a flame burning across the valley as would be expected for a deflagration. Following the main explosion, there was a flash fire, presumably burning up any residual unburnt propane-air, before a jet fire was produced burning the propane escaping from the pipeline.

At the time of the explosion, ~70 MT of propane had been released. There was extensive damage at the bottom of the valley. Trees were uprooted, snapped, burned, and strewn over the ground. Buildings were completely destroyed at the Menner property, and other properties were extensively damaged. Within 3 km of the accident site, there was major damage to 14 houses, minor damage to 14 houses, and window damage to 37 houses. Between 3 km and 11 km, there was minor damage to another 17 houses and window damage to 124 buildings.

The incident was investigated by the US Bureau of Mines [17], which concluded that the most likely ignition source was a freezer unit located inside a concrete warehouse approximately 30 m from the Menner property (Figure-S 8.2). This warehouse was completely destroyed. The terrain around the rupture was gently sloping, which would have allowed the heavier-than air propane to disperse into the valley. The area of the valley described as being filled with the mist, approximately corresponded to the area of burning and scorching observed following the incident.

Figure-S 8.2 Area identified as origin of the detonation [18].

It was estimated that about 25% of the valley covered by the propane mist comprised woodland. Overall, the initial investigation concluded that the propane-air mixture had detonated.

Additional Discussion

Estimates of the release rate and total released amount of propane over the 24 min before ignition seems low. Full bore rupture of an 8" propane pipeline operating at 66 atm give an initial rate of about 140 kg/s and 86 kg/s at ignition, using FRED's "Unified Scenario" [7]. Reference [17] gives a steady flow of $\sim$25.5 m^3/s at STP, equating to 51 kg/s (which gives 73.7 MT in 24 min), which is about a factor of 2 less than estimated from FRED. The mass of propane originally contained in the pipeline, assuming no continuous pumping, is about 773 MT, from estimates of the pipeline length (46 km) between Villa Ridge and Rosebud, Missouri. Estimates [18] of the total released mass are 750 barrels, equating to 119.25 m^3 or 64 MT of propane in 24 min. This is close to the 70 MT noted elsewhere in reports, but is an order of magnitude less than that in the pipeline. The total loss of propane after burn out of the pipeline was given as 722 $m^3$3, or 4538 barrels, or 386,000 kg, still considerably less than the inventory of the closed line.

Using the correlation derived from detonation experiments in the Buncefield Explosion Mechanism, Equation (4-2) and assuming the cloud height is about 3 meters, overpressures at a given distance D from the detonating cloud edge can be computed. The result is that buildings within 3 km of the accident site are about 2 km from the edge of the detonating cloud, where the overpressures are at least 0.01 atm, sufficient for window breakage and greater damage.

9. Newark Accident

Description of the Event

The explosion occurred on 7 January 1983 in Newark, New Jersey, at a Texaco tank farm [21]. Because of concerns over potential litigation, Texaco did not co-operate with the National Fire Protection Association (NFPA) investigation. It is not known if such litigation took place, and, if so, what further information was made public during this process.

A schematic diagram of the facility is shown in Figure-S 9.1. Tank 67 was a floating roof type storage tank, 24 m in diameter and 15 m high, and located in a large bunded area that also housed tanks 64 and 65. On the evening of 6 January 1983, tank 67 was being filled with super unleaded gasoline. This was supposed to have been completed at approximately 12:10 am on 7 January 1983. The incoming shipment was $\sim 6.05 \times 10^6$ liters ($\sim$1.6 million US gallons).

While this was happening, 4.1×10^6 liters was to be transferred to tank 5. At about 12:00 am on 7 January, two workers visited the tank and found gasoline flowing out of the vent pipes at the top of tank 67. At 12:02 am, workers at the adjacent railroad yard reported a strong smell of fuel, and shut down their diesel engines.

At approximately 12:10 am, workers at a metal drum refinishing plant 300 m northwest of tank 67 reported a strong smell of fuel outside the building. At this time, several small explosions were heard before a "tremendous blast."

The winds were very light and nearly still during the overfill. Just before the ignition, the wind speed was 1.5 m/s from the southeast.

The explosion flattened the empty storage tank Number 9, which was 370 m away and damaged tank 4, which was 460 m away.

This incident was the first case for which an explosion following such a release produced extensive damage. It was consequently reported in both the USA and the UK. Additionally, NFPA standard NFPA 30, "Flammable and Combustible Liquids Code," was revised to incorporate requirements to prevent overfilling.

In [22], it said that "It is now apparent that the explosion of vapors from spills of flammable liquids at ambient temperatures and pressures is possible under some circumstances."

Discussion

Could this incident be similar to the one in Jaipur 2009? The gasoline cloud covered a large area and penetrated the drum finishing plant where ignition is thought to have occurred at an incinerator. An explosion inside a building could have initiated a bang-box type event, which then caused a DDT in the remaining cloud. It is interesting that "several (two) small explosions were heard before" the main blast.

A FRED calculation [7] using a 50 kg/s vapor rate release and 1.5 m/s wind from a 200 m × 100 m bund gives a dispersion distance downwind to a lower flammability limit of 200 m, but about 500 m in the crosswind direction. The downwind distance roughly matches that from the bund edge to the incinerator. (See Figure-S 9.1 and Figure-S 9.2.)

There is insufficient evidence to confirm that a detonation took place, but the severity of the explosion in the large open area is difficult to explain otherwise. It is interesting that an open road trailer suffered an internal explosion, and this may have been an alternative source of a jet ignition of the cloud.

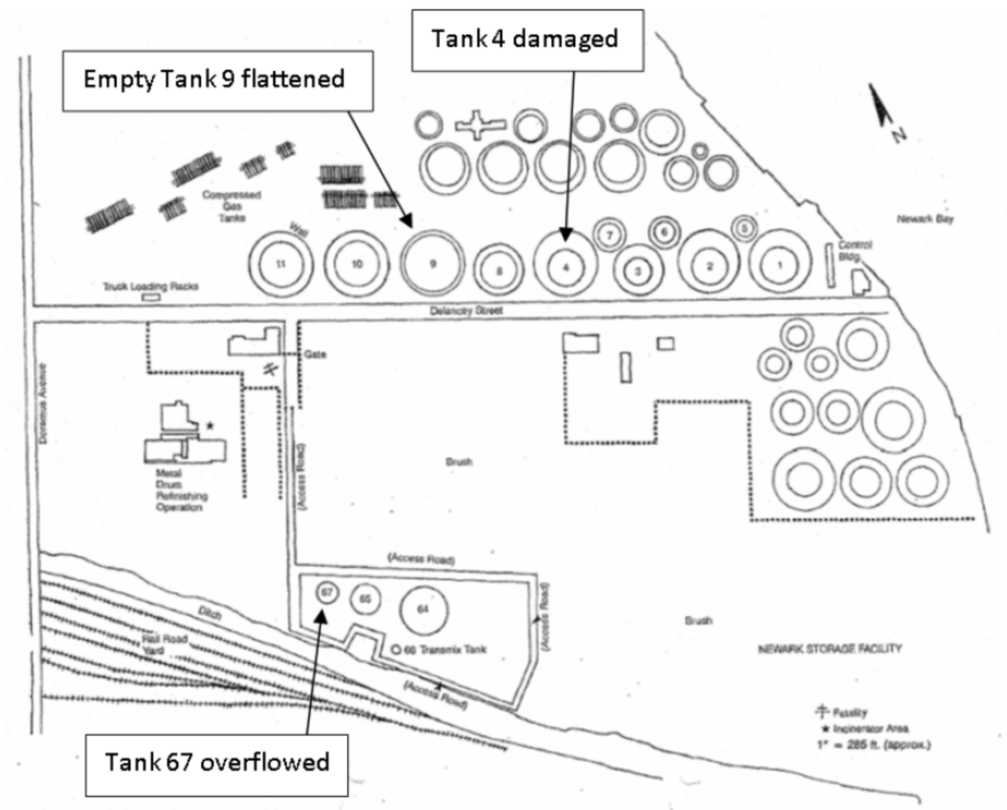

Figure-S 9.1 Plan of the Newark Facility [21].

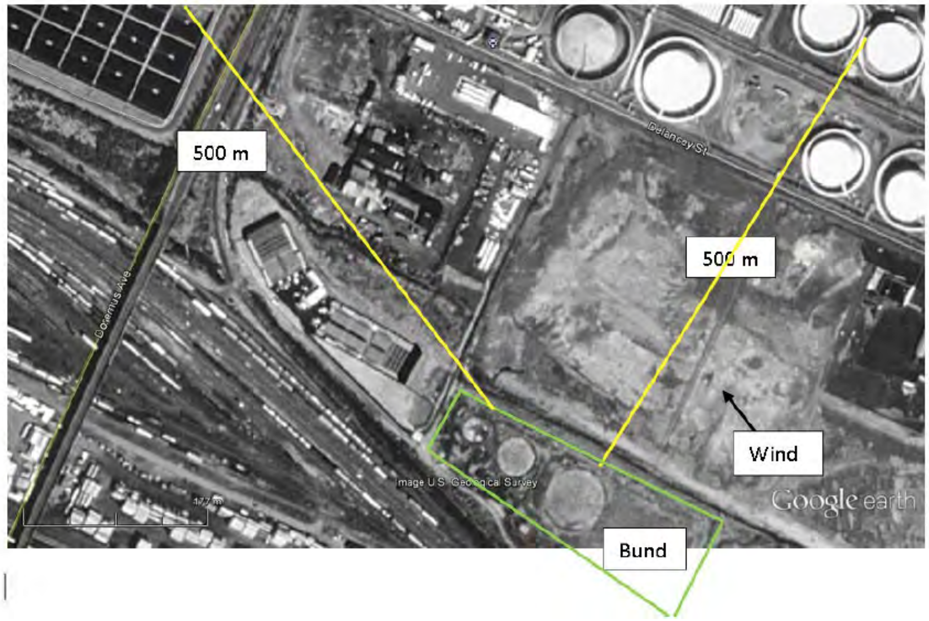

Figure-S 9.2 Distance markers superimposed on a Google Earth photograph 29 March 1995.

10. Flixborough Accident

Description of the Event

This incident, which occurred in Flixborough, UK, on 1 June 1974, was at a chemical plant owned by Nypro, which was a joint Dutch-UK venture [23, 24]. The plant produced caprolactam, a chemical needed to make nylon and which is made from cyclohexanone.

The area where cyclohexane was released produced cyclohexanone and cyclohexanol by the oxidation of cyclohexane with air in the presence of a catalyst. The reaction normally took place in a connected series of 6 adjacent reactors. At the time of the incident, the fifth reactor had been removed for repair and replaced with a bypass pipe, as shown in Figure-S 10.1. This bypass was connected to the reactors on either end using a flexible bellows dog-leg type fitting. It appears that the temporary connection was not subject to appropriate structural analysis or pressure test.

Figure-S 10.1 Photograph of part of the reactor train after the incident [23, 24]. The dog-leg bypass connecting the gap to the last vessel was lost completely. The scaffolding was been erected after the incident

On Saturday 1 June 1974 at 4:53 pm, the bypass pipe failed completely and there was a massive double ended release of cyclohexane at a pressure of at least 9 atm and a temperature of 155 C. Before the rupture, the 5 remaining reactors would have contained approximately 120 MT of cyclohexane, of which 80 MT were recovered after the incident. Of the 40 MT that was lost, it has been estimated that 30 MT contributed to the cloud before ignition.

Discussion

There have been many studies of this incident and the main conclusion is that a detonation of cyclohexane vapor occurred. The most likely mechanism is believed to be a DDT in the region of congested plant. Figure-S 10.1 – Figure-S 10.3 show general views of the damage.

Figure-S 10.4 shows the direction of fallen of lamp posts around the site. Two of these lamp posts are shown in Figure-S 10.5 andFigure-S 10.6. The blue arrows are lamp posts that are outside the vapor cloud, and these generally point away from the cloud. There is no clear pattern of direction indicated by the red arrows, which are lamp posts inside the detonation. The random nature of direction indicators is to be expected of a large turbulent cloud ignited within seconds of the release. There was no opportunity for the cloud to become pancake shaped and to develop the inward net drag during detonation.

Figure-S 10.2 View of damaged items [23, 24].

Figure-S 10.3 View of damaged items [23, 24].

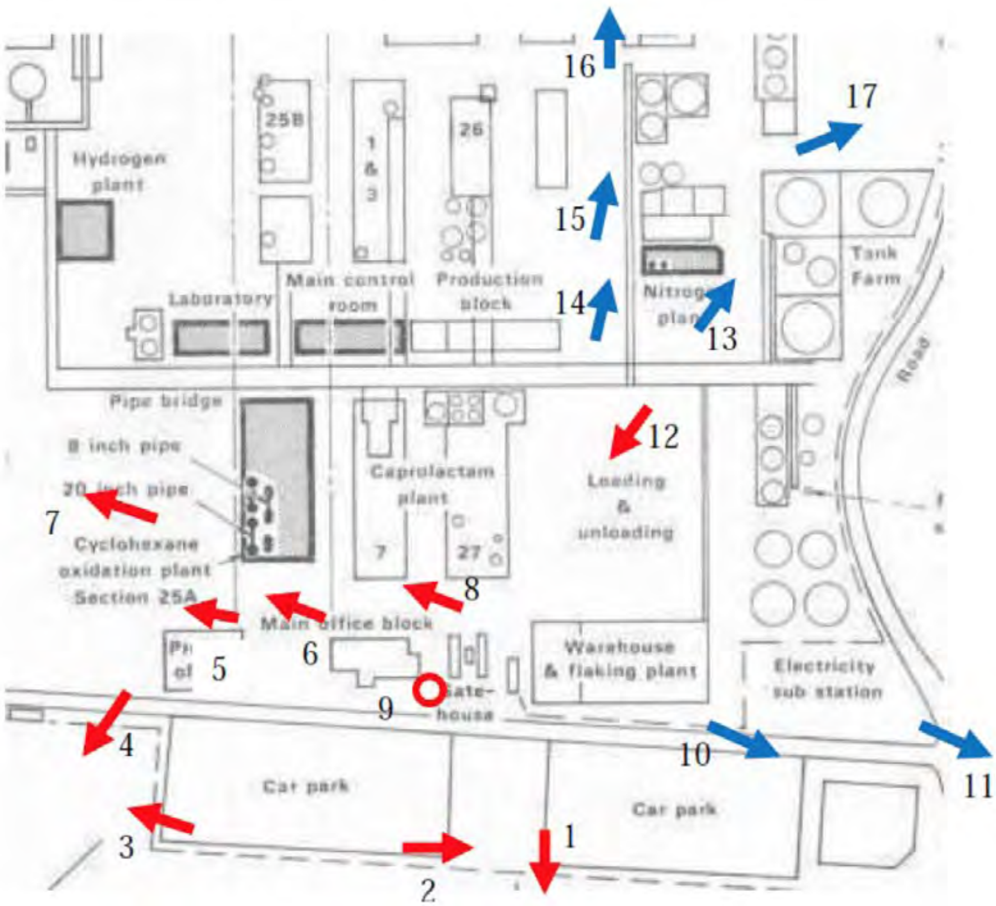

Figure-S 10.4 Direction of fallen of lamp posts [23, 24].

Figure-S 10.5 Lamp post 3 [23, 24].

Figure-S 10.6 Lamp post 12 [23, 24].

11. Pasadena Accident

Description of the Event

A photograph of the Phillips plant prior to the explosion is shown in Figure-S 11.1. During routine removal of a fluff settling leg on a high density polyethylene reactor, the entire 68 m^3 reactor contents of ethylene and isobutane at 4.8 MPa (44 atm) was discharged to the atmosphere.

Figure-S 11.1 Aerial view of the Phillips plant taken prior to the explosion (taken from [25]).

At approximately 1:00 pm. on October 23, 1989, an explosion occurred as a result of a massive gas release: more than 38,000 kg, or 99% of the reactor contents, were released almost instantaneously. Figure-S 11.2 shows the location of the plant relative to the area affected by the explosion, and Figure-S 11.3 shows the layout of the plant.

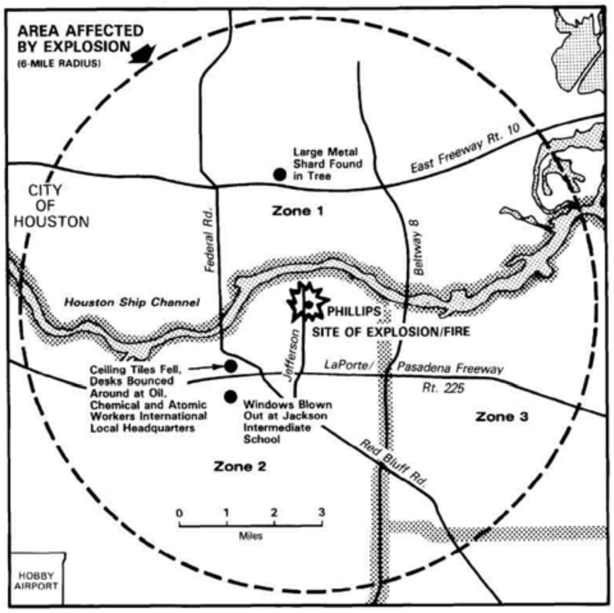

Figure-S 11.2 Location of the plant (taken from [25]).

The vapor cloud drifted northward toward the center of the high-density-polyethylene process area before ignition. Within 90-120 s, this gas mixture ignited (by a still-unidentified ignition source) and exploded with the force of 2.4 MT of TNT. Potential ignition sources were a forklift, a gas-fired catalyst release from reactor activator with an open flame, nearby welding and cutting-torch operations, vehicles near the polyethylene plant office building, and electrical gear in the finishing building and control rooms.

This initial explosion threw debris for ~9.6 km and, according to seismographic data from Rice University, registered between 3 and 4 on the Richter scale. A pair of secondary explosions (BLEVES) occurred about 10-15 min after the first one, when two 76 m^3 isobutane storage tanks exploded. About 25-45 min after the first explosion, another polyethylene reactor failed catastrophically. There may have been as many as six more explosions in all. Other process units at this chemical complex sustained only minor damage and resumed normal production within a few weeks of the incident.

Discussion

The presence of ethylene ignited in a congested area and the force of the resulting explosion suggest DDT. There is, however, no direct evidence of this except that Figure-S 11.4 from the FEMA report [25] shows uniformly crushed silos, consistent with detonation damage. Figure-S 11.5 shows the damage and metal fatigue.

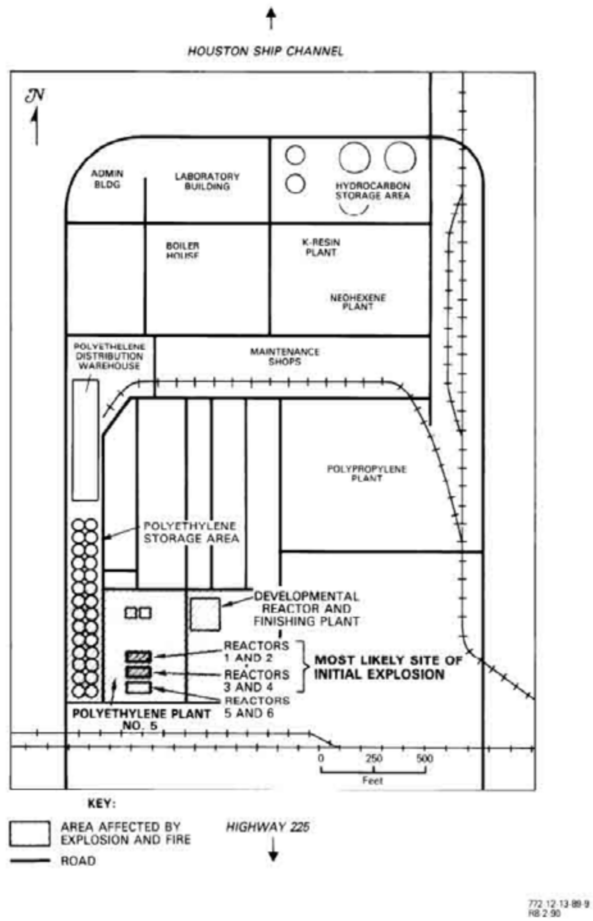

Figure-S 11.3 Layout of the plant (taken from [25]).

Figure-S 11.4 Silo holding areas to the northwest of the main blast area. The blast wave partially flatten the silo sides (taken from [25]).

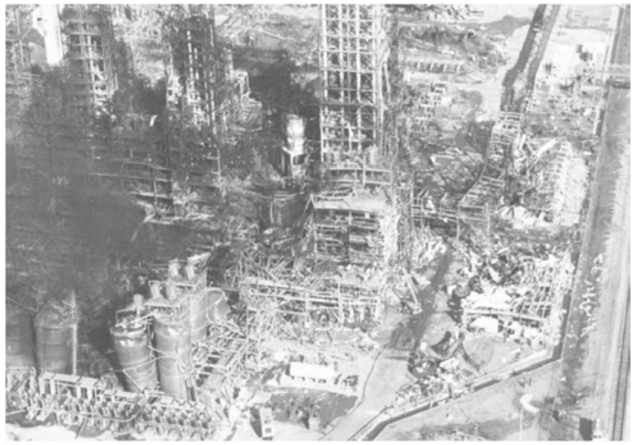

Figure-S 11.5 View from southwest corner towards north/northeast. Metal fatigue clearly visible in remaining superstructure. Note crushed tanks on bottom left (taken from [25]).

Using the correlation derived from detonation experiments in the Buncefield Explosion Mechanism Phase II, given in Equation (4–2), and assuming the cloud height was about 5 m, it is possible to obtain overpressures as a function of distance from the detonating cloud edge. These can be related to photographic damage. Windows were blown out at Jackson Intermediate School approximately 5000 m away. This may be consistent with the 0.008 atm overpressure estimated above.

12. Decatur Accident

Description of the Event

The explosion occurred when a tank car GATX 41623 (see point A in Figure-S 12.1) carrying isobutane rolled down a track too rapidly during switching operations and slammed into an empty boxcar. The coupler rode up over the tank cars coupler and punctured the tanker. The puncture hole was 560 mm × 660 mm in the 115 m^3 rail car. Escaping liquid at about 19 m^3/min (176 kg/s) created a vapor cloud 800 m × 1200 m in the yard, and after 8-10 min, at 5:03 am, it ignited. The wind was described as a breeze from the NW. The sky was clear. The ignition source is unknown.

Figure-S 12.1 The aerial view of the explosion area in Decatur Yard (taken from [26]).

Discussion

First consider the release and dispersion. Using FRED [7] with input parameters of 0.5 m hole diameter, liquid density of 557 kg/m^3, inventory of 100 m^3, the initial release rate at the vapor pressure (bubble point) of 3 atm is 1760 kg/s (liquid). The cloud disperses to the lean flammability limit a distance of 1500 m in 10 min with a width of 700 m, derived from a temperature of 20 C, wind speed 2 m/s, F stability[1], and surface roughness 0.1[2]. These values are close to the reported dispersion distances of 1200 m $\times$ 800 m. Dispersion reached a steady state after about 9 min, coincident with the reported time of ignition, which suggests that the cloud just then reached an ignition point.

Several of the photographs (see Figure-S 12.2, Figure-S 12.3, Figure-S 12.4, Figure-S 12.5) show evidence of high overpressure, for example, the dented rail cars and crushed vehicles on the rail trailers. The crushed vehicles, shown in Figure-S 12.6 on the rail trailers, are typical of overpressures >5 bar. By comparing an aerial photograph of the site in Figure-S 12.1 with a Google Earth picture, we see that the edge of the main explosion damage on the rail yard is around 300 m from the release point, marked A in Figure-S 12.1. This suggests that either the ignition was in the congested region of boxcars and trailers, or that ignition occurred when the cloud reached an ignition point at the cloud edge, as suspected above. In the second case, a flash fire would have propagated through the cloud and then flame acceleration and deflagration could have occurred in the congested area. DDT may have occurred in the remaining cloud.

Similar rail car accidents, involving possible detonations of propylene and butadiene, respectively, occurred at East St. Louis, Illinois, in 1972 and at Englewood Yard, Houston Texas, in 1974.

Figure-S 12.2 Damage area (taken from [26]).

[1] F is the Pasquil-Gifford atmospheric stability class [27], which is applicable when atmospheric inversion occurs and the air is fairly calm. It is typical of cool clear mornings.

[2] The surface roughness is a parameter describing the state of the terrain over which dispersion occurs. A value of 0.1 is typical of lightly congested process sites.

Figure-S 12.3 View of damaged items (taken from [26]).

Figure-S 12.4 View of damaged items (taken from [26]).

Figure-S 12.5 The explosion leveled the new school addition to the Lakeview High School building (taken from [26]).

Figure-S 12.6 View of damaged items. Note the crushed vehicles (taken from [26]).

13. Beek Accident

Description of the Event

Start-up of the naphtha cracker commenced on the ethylene plant at the Dutch State Mines (DSM) works at Beek. At 6:00 am, compressed gas was sent to the low temperature system. At 9:48 am, vapor escaped from the depropanizer. It then ignited, resulting in a massive vapor cloud explosion. The explosion caused significant damage and started numerous fires around the plant. There were 14 people were killed and 107 people injured, three of whom were outside of the site. There are some photographs in the investigation report (in Dutch) by the Ministry of Social Affairs [28].

The investigation was hampered by the destruction of instrument records during the explosion, but 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. The normal operating temperature of the drum was 65 C, however, due to a process upset in the de-ethanizer column, the stream feeding into the depropanizer drum was a liquid at about 0 C (or lower) with a high C2 content. This would flash within the drum, resulting in a temperature that could be as low as -10 C. The feed drum material could normally be used at temperatures as low as -20 C, however the fracture occurred at a weld, which with aging may fail at up to 0 C.

Discussion

No directional indicators were recorded, but damage estimates suggest overpressures well over 1 atm (see Figure-S 13.4). This is supported by FLACS simulations [29]. For stoichiometric ethylene mixtures in clouds greater than about 3.5 m height, however, they predicted very high overpressures. Some investigators suspect detonation in the SE corner of the site, considering the fuel and extent of congestion, although evidence is scant. (See Figure-S 13.1, Figure-S 13.2, and Figure-S 13.3).

DDT may well have occurred as the flame accelerated from the ignition point at the south of the plant through units 2, 3 and 5. There is continuous congestion connecting these units. Figure-S 13.5 shows circumferential bends on the tank, suggesting detonation. Such damage is intriguing because flammable cloud should have not been in the tank area. The picture quality, however, is not the best. The detonation hypothesis is also supported by broken windows up to 4.5 km away [30].

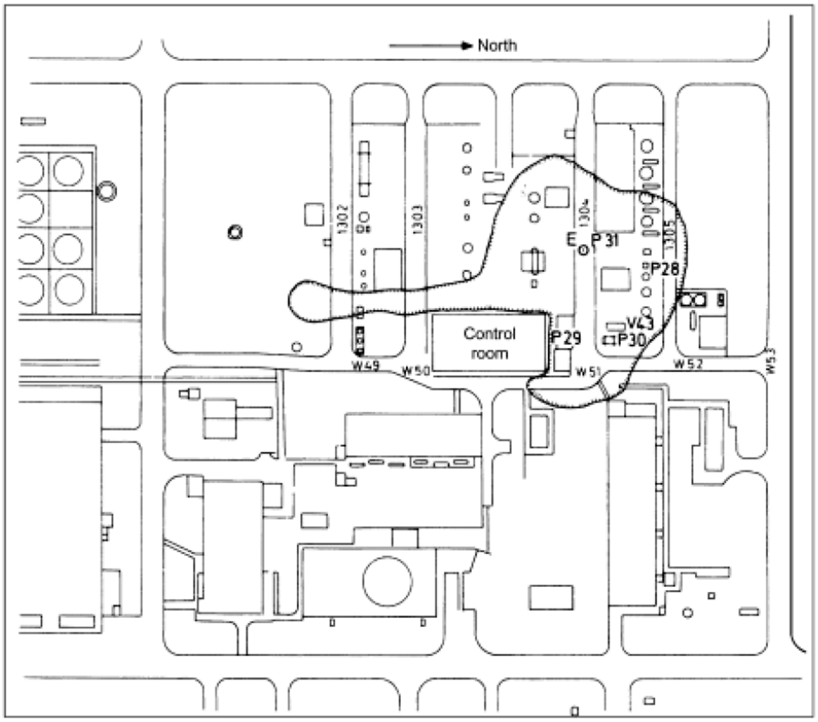

Figure-S 13.1 Simplified site plan of Beek showing estimated dimensions of the vapor cloud. (Reproduced by permission from [30]).

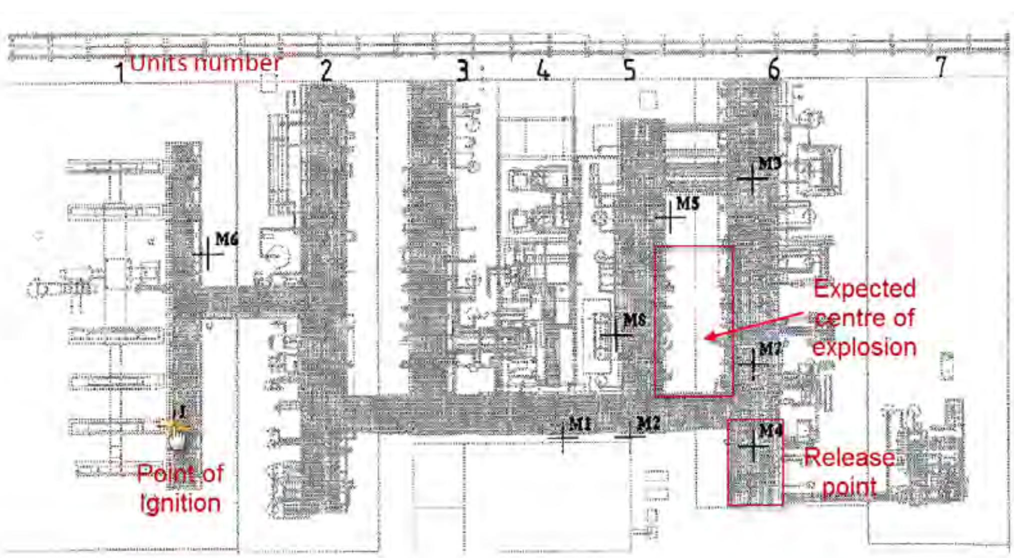

Figure-S 13.2 Account of the accident. (Reproduced with permission of [29].)

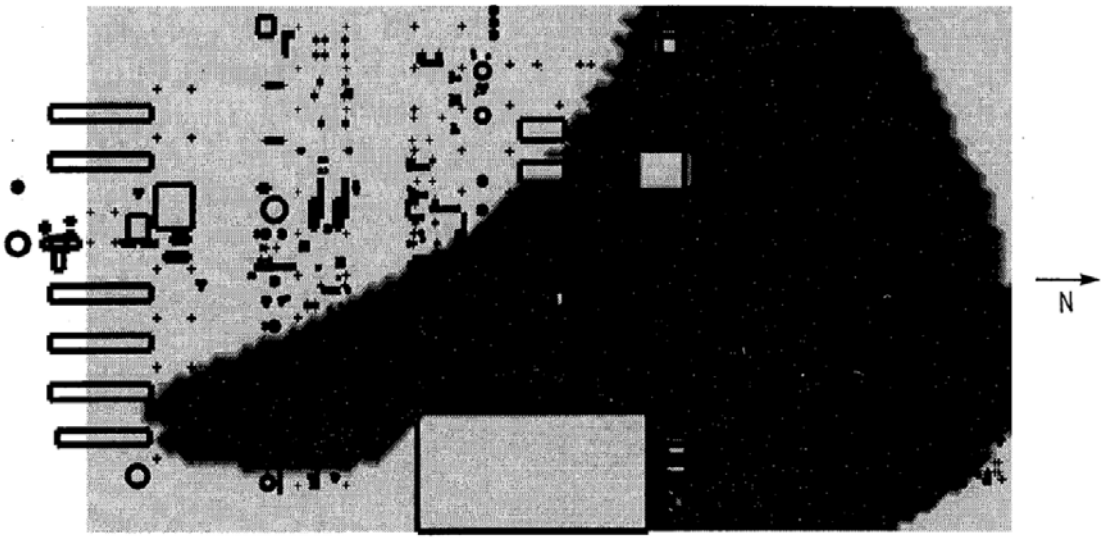

Figure-S 13.3 Naphtha cracker unit with cloud contour. (Reproduced with permission of [29].)

Monitoring point	Ministry of Social Affairs (1976)	Trense and Groothuizen (1976)	Company report (confidential)
M1 (west side of control room)	0.2–0.3 bar	1 bar (75 ms positive phase duration)	>0.3–0.5 bar
M2 (north-west edge of control room)	0.2–0.3 bar	1 bar (75 ms positive phase duration)	>0.3–0.7 bar
M3 (concrete platform, section 6)	0.6–0.7 bar	3500 Pa·s (pressure impulse)	—
M4 (section 6, center)	>0.3 bar	1 bar	—
M5 (gas analysis building; section 5)	—	—	0.7 bar
M6 (gas analysis building; section 1)	—	—	0.14–0.21 bar
M7 (section 6, east)	—	—	0.7 bar
M8 (engineers' room)	—	—	>0.7 bar

Figure-S 13.4 Damage estimates. (Table reproduced with permission of [29].)

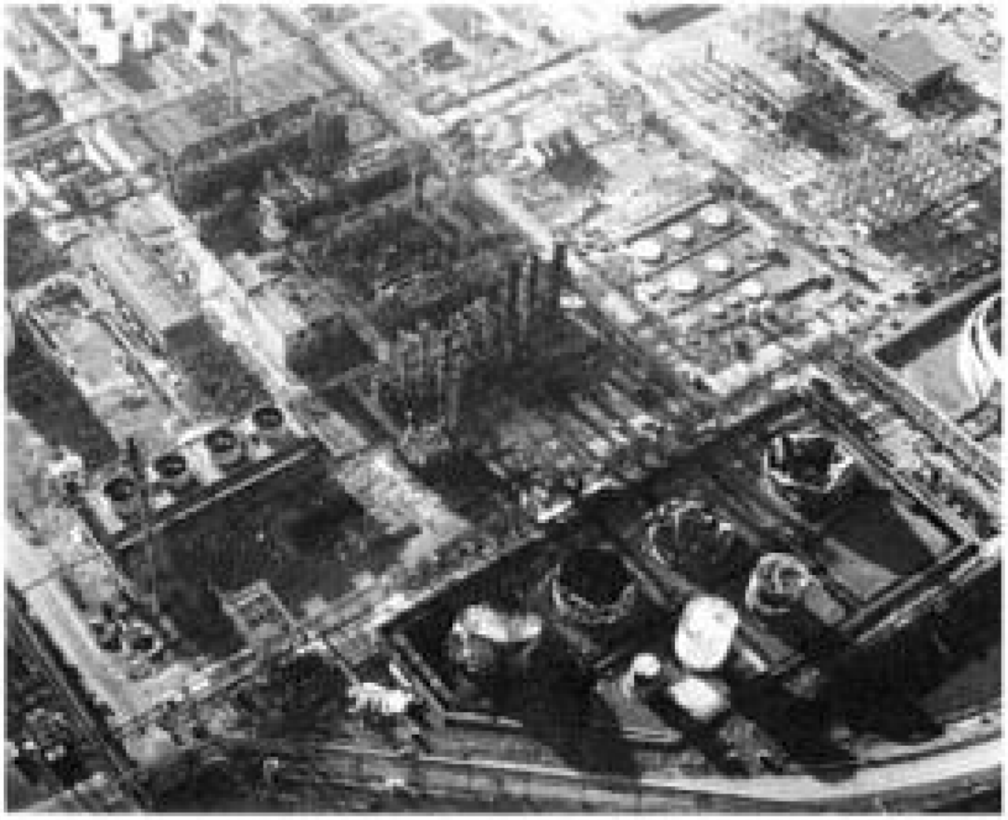

Figure-S 13.5 Damaged plant. Note the tank damage Reproduced with permission from [30]).

14. Donnellson Accident

Description of the Event

The main description of this event is from [31].

Several minutes before midnight on Aug 3 1978, an 8” LPG pipeline under ∼1200 atm pressure ruptured in a cornfield near Donnellson, Iowa. Propane leaked from a 33” long split and vaporized. The heavier-than-air gas rapidly moved through the field and across a highway following the contour of the land. The propane gas eventually covered ∼300,000 m^2 of woods and fields and surrounded a farmhouse and its facilities. At 12.02 am, the propane was ignited by an unknown source.

The night was clear with visibility of 19 to 24 km. There was a light N-NW wind of 2-4 m/s and temperatures were above 10 C. The wind was nearly constant from the surface to about 1220 m above mean sea level, meaning there was no stratification up to that height.

Three people died in the ensuing fire, but no blast was reported. Approximately 600 m^3 of propane were reported to have been released.

Discussion

The main concern with this incident is: *Why did the propane* NOT *explode?* Other similar incidents, e.g., Brenham, also produced large LPG clouds covering similar terrain and significant blast. The type of terrain might account for the lack of blast, but there is another explanation, involving the type of vegetation that covered the fields, that should be considered. Here we give one hypothesis to explain why the propane did not detonate.

It was reported that the fields contained “corn,” but there is some confusion over what was meant by corn. Reference [15] quotes dispersion over a “flat corn field” of height 1-1.5 m, which suggests that the “corn” could have been wheat. After considerable investigation of many accounts of the event, this appears to be the only reference to the content of the field.

Spring wheat is harvested from mid-July to mid-August, as you move to the north. At the time of this fire, spring wheat would be fairly dry and about ready for harvesting.* Therefore, a fire could easily propagate through it. The stems are flexible, and so a fast flame may not be generated through the types of stems that can accommodate the explosion winds.

In a field of corn, the stems are more rigid, and the leaves are closely packed. The normal spacing between corn stems is around 100 mm (as observed in local fields in Cheshire, UK). This close packing and resistance of the stems to flow might present enough congestion for flame acceleration and associated blast.

The report [31] quotes a vapor cloud of ∼300,000 m^2. Later in the report, however, it says that ∼300,000 m^2 of fields and woodland were burned. The burnt area and the spread of propane

* Corn would not be ready for harvesting until October or November in Iowa.

vapor may not be the same. A plausible scenario is that the cloud burned and then the fire spread through the dry wheat.

The "Pressurised release" scenario in FRED [7] gives a steady release rate of 153 kg/s, given the 85 atm operating pressure, a dispersion distance of 310 m to the lower flammability limit at 15 C, and 1.5 m/s wind. The plume is then about 130 m across at its widest point. The area covered is therefore $\sim$20,000 m^2, roughly an order of magnitude less than the burned area. (FRED assumes "flat earth" and does not properly account for the varying release rate as the pipeline blows down).

The plume would be about 5 m high for a considerable distance along its length. Also the bulk of the plume is between the flammable limits, with only a small volume above the upper flammability limit near the source. FRED also predicts that there is 5174 kg of propane inside the plume of volume 81,000 m^3.

Apart from the lack or type of congestion, there are significant differences between the conditions of this spill compared to those that could have eventually detonated. The source of vapor originated from a turbulent release, initially at 84 atm, the wind was a light breeze, and ignition took place early in the release when the cloud was still turbulent.

This brings up the interest issue of the type of congestion, which was an important point in the Buncefield investigation.

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