Fire Protection Manual

For Hydrocarbon Processing Plants

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1 Case Histories of Fires, Explosions, and Detonations

Introduction

Back in October, 1969, an $8-million fire and explosion at Union Carbide's Texas City olefins plant helped to close out a year of fire/safety bad news for the HPI. Crossing over into 1970, the industry embarked on a year that saw four fires in HPI plants listed among the 10 most costly industrial fires that year. The costliest of all, according to the National Fire Protection Association, was a $50-million disaster at Humble Oil & Refining Company's Linden, New Jersey, refinery. Also listed were a $6-million fire at the Mobil Oil refinery in Beaumont, Texas, and a $3-million fire at Witco Chemicals Amalie refinery, near Franklin, Pennsylvania.

Moving on through 1971 and 1972, the chain of these frustrating experiences continued. And even though according to NFPA, the number of costly incidents in the HPI is decreasing, the cost per incident is skyrocketing. This is due to the growing size of plants, and their increasing capacities. So it seems that no matter how hard the HPI tries, it will never eliminate fires, detonations and explosions. Too much volatile material is handled for a fail-safe operation.

But looking back at the Carbide incident, something good did come out of it. The company openly bared its soul at a scheduled press conference in March, 1970. Management "told it like it was." No excuses—no alibis. They candidly presented the technical aspects of what went wrong and remedial action taken.

Then Carbide notified all producers of butadiene in the free world of the explosion's cause. Eventually, they released a technical paper, and it has been republished, from the pages of *Hydrocarbon Processing* magazine, in this chapter.

This openness is a good sign. In my many years as HP's fire and safety editor, I recall few times when a company explained the causes of its misfortune with such candor. Carbide can take a prideful place beside the other companies which have shared detailed information on safety problems. Many of these companies have material in this chapter.

Willingness to share these case histories with others means that an example has been set which hopefully all other HPI companies will follow. Too many companies still do not share such information. Fear of lawsuits and "complications" haunt management. These negative aspects sadly overshadow concern for human life. They thwart needed safety communication. They polarize companies.

"If you don't tell us, we won't tell you."

"The other companies don't open up. Why should we?"

"It doesn't pay to air your dirty linen."

"We didn't really understand why it exploded and don't want to release partial information that may be worse than none at all."

But, in this chapter are examples of incidents that have been released. This trust, plus mutual respect, plus a quest for objectivity, plus concern for human life hopefully equals a safer HPI.

Reformer Detonation Triggers the Great Whiting Fire

R.B. Jacobs, W.L. Bulkley, J.C. Rhodes, T.L. Speer
American Oil Co.

The time was 6:12 a.m., August, 1965. Location: American Oil Co.'s Whiting, Indiana, refinery. At this moment a series of internal detonations took place in a large fluid reformer. Principal explosions occurred within the reactor vessel and a high-pressure separator, completely destroying them. Other explosions occurred in piping, exchangers, a separator drum and an absorber tower, but the damage to these was less severe. No other ruptures occurred except in two pipe elbows.

Explosions in the reactor and separator drum caused extensive fracturing. The fragments, particularly those from the reactor, were scattered over a 1,200-foot wide area. Some pieces fell into tank fields just north of the reformer, causing a number of fires. These fires eventually involved 40 acres, resulting in total destruction of 63 tanks and approximately 1,270,000 barrels of crude oil and various products.

At the time of the explosion, the unit was being started up after a shutdown. Two major vessels, a reactor and regenerator, were being heated simultaneously. The regenerator was heated with compressed air via a combustion air line. The reactor was heated by circulation of inert gas through the combination furnace. The air system was normally held at about 10 psi lower pressure than the inert gas system.

Naphtha circulation through the unit (except the reactor, which was by-passed for this operation) was in progress. Through a series of unfortunate circumstances, the recirculating inert gas became contaminated with air and naphtha vapors. This formed a flammable mixture containing about 19 percent O^2 and 3 percent naphtha vapor at about 105 psig. No catalyst was present.

The fluid reformer was 260 feet high. The reactor vessel was 127 feet long and 23.5 feet in diameter. It was made of alloy steel plates varying in thickness from 2-3/8 to 2¾ inches. Two regenerator exhaust stacks and six relief valve outlets were on top of the unit. The explosion hurled about 44 percent of the reactor vessel beyond the unit area.

At the time of the explosion, a number of people in the immediate vicinity saw luminous flames issue from near the top of the reformer. After several seconds they heard a loud report from that direction. They saw the "large" vessel (reactor) disintegrate and the pieces fly through the air. Then they heard a second, more violent report, and soon the area was enveloped in smoke and flames.

Most unit operators were near the control room. They recalled a rumbling noise—then a first explosion which knocked some of them down. This was followed by a cloud of smoke and dust which greatly reduced visibility. After they had recovered their footing and started to run, a second violent explosion occurred, again knocking some of them off their feet. After this there were several smaller explosions.

The vessel fragments were scattered for several hundred feet away from the unit site. One 60-ton piece landed on a tank of gasoline, smashing it severely and igniting and scattering its contents.

The key source of "evidence" for investigation was a large pile of wreckage in the unit area. Some instrument records were intact. Others were recovered from the grime and oil where they had fallen.

Investigation of Damage

There were two aspects of the investigation. The first was determination of the exact sequence of events which produced the flammable mixture and caused ignition. Through accident, a flammable mixture was produced in certain parts of the unit, including the reactor vessel. Ignition probably occurred on the heated surfaces of the furnace tubes in the recycle gas circuit.

The second aspect (reconstruction of the disaster from the scattered and fragmentary evidence) was difficult, especially because the investigation was confronted with a number of apparent contradictions. The first was how could a mixture of hydrocarbons and air generate enough destructive violence to shatter the reactor and hurl it apart? Calculations of the explosive pressure made by the usual method would predict, under conditions which existed, that the reactor should not have failed. Furthermore, the calculated available energy was short of that needed to hurl the fragments by the most efficient probable mechanism.

A second question was how could two, almost equally violent explosions occur several seconds apart? It was difficult to visualize a mechanism whereby the two vessels (reactor and high-pressure separator), separated by ¼ mile of piping, could blow up, one several seconds after the other. One could reason that if ignition occurred in one vessel and it exploded, thus opening the system to the atmosphere, it would be very difficult for the flame to travel into another vessel, because the latter would be rapidly discharging its contents against the direction of flame travel.

Another question was did the several eyewitnesses near the site of the disaster really see a large flame issue from the unit several seconds before it exploded? And, if they did, how did this happen? Also, how could those eyewitnesses about 1 mile away first hear a loud report and then see the reactor blow apart? Only when it was realized that a series of internal detonations had taken place was it possible to fit the pieces of the story together.

Characteristics of Detonation

The following characteristics of detonation played significant roles in this disaster:

1. Predetonation flame travel, especially the effect of vessel size and geometry upon the length of the predetonation period.
2. The effect of turbulence in accelerating detonation.
3. The high pressure developed in the detonation front.
4. The concentration of energy in the detonation front.

Reactor fragments had a herringbone pattern along the torn edges. This pattern yielded information concerning (a) the direction in which the cracks propagated and (b) the type of failure (cleavage), and hence the approximate speed of crack propagation (about 5,000 feet per second).

The long, uninterrupted cleavage marks suggested that the detonation velocity was less than 5,000 feet per second. Once cracking of the vessel was initiated, the original cracks propagated extensively. Had the detonation velocity been greater than 5,000 feet per second, the detonation pressure wave probably would have produced a large number of new cracks ahead of the old, frequently interrupting the latter and producing greater fragmentation of the vessel.

While a detonation does not produce a greater total energy release than does an ordinary explosion, it has the effect of a more efficient propellent because the energy is concentrated in the detonation wave.

A number of observations of internal reactor damage and the calculated pressures required to produce this damage were made. Investigations revealed proof of instantaneous local pressures far exceeding 800 to 900 psi, the highest pressure that would have been possible without detonation.

The upper half of the catalyst stripper was crushed inward in a number of places, whereas the lower half was bulged outward at several places. The upper half was damaged by an upward moving detonation wave in the reactor (external to the stripper) which attained enough violence midway up the vessel to produce the damage.

The bulged portions were caused by a later downward traveling detonation inside the stripped well, presumably ignited by the first detonation as it passed the open port in the stripper (about one-third the way up the structure).

Five locations of crack origin were found three quarters of the way up the vessel. This means that the detonation wave first reached enough intensity at this point to shatter the vessel, and it did so in five separate places. After this, cracks propagated upward and downward. At a lower elevation, secondary cracks apparently originated because of bending stresses. Most of the pieces above the center line were hurled far beyond the battery limits, while the bottom of the vessel shifted slightly through recoil, unfolded and toppled over.

Careful examination of the wreckage gave many clues as to the direction of flame travel in the different pipe runs. The most useful clue were the luders lines. These crisscross, hatched lines are produced when metal is stressed beyond its elastic limit. They are particularly noticeable after rusting has taken place on the freshly exposed metal surfaces.

Another form of evidence came from internals such as baffles, butterfly valves and orifice plates. Some of these were dislodged and even blown through nearby elbows. The direction in which they move established local directions of flame travel. From such information, flame directions were determined.

In some lines, flame travel was in one direction only, while in others it was in both directions, meeting at an intermediate point. In the overhead reactor line leading to one exchanger, flame travel was toward the reactor. It reached the atmosphere through the pressure relief valve.

Lines were circuited through the recycle furnace in four parallel passes. There was a marked decrease in damage to these different lines, all four of which showed evidence of internal explosion. One line blew first, partially relieving pressure on the others. Then another line blew, further reducing pressure on the next line, etc. In two of these lines, butterflies were blown in one direction and orifices in the other. This proves that these lines contained two simultaneous explosions traveling in opposite directions.

A detonation front travels at about 3,000 to 4,000 feet per second, which is probable for a 19 percent O_2, 3 percent C_5 hydrocarbon mixture. Predetonation time in the highly turbulent (50 to 100 feet per second) recycle lines is very short (a few thousandths of a second), and predetonation time is much longer in the relatively quiescent vessels, depending upon the size of these vessels.

Ignition is assumed to have occurred in a hot recycle furnace tube. At 0.3 seconds after ignition, two detonation waves were traveling in opposite directions in the unit. One traveling downstream toward the reactor ignited the other three furnace lines, and flames progressed upstream in these toward an exchanger.

At 0.6 seconds after ignition, flames had ignited the reactor. At 0.9 seconds after ignition, the detonation traversed the entire unit, blowing the butterfly disc to the right and the orifice plate in the vertical run in the upward direction. A detonation wave followed, similar to the first one, except for a lessened intensity because of a reduced local pressure. This pressure reduction resulted from an opening to the atmosphere in this section.

Two sections of the unit, by this time, were ignited at both ends and had oppositely directed flame fronts advancing toward their centers. These secondary flame fronts were ignited by the front as it reached the common header. By this time, the flame fronts also had reached the shell side of one exchanger and ignited the unit dry drum.

At one point two seconds after ignition, two major sections had exploded, the valve discs being driven to the right and the orifice plates downward by the two oppositely directed flame fronts. A detonation developed in one exchanger, rupturing a number of tubes and allowing the flame to jump from the shell side to the tube side. This was the only possible means of ignition which would develop a flame front traveling toward the reactor in the overhead vapor line. This is because a flame could not come from the direction of the high-pressure quench drum, because the contents of this drum were too rich to burn.

Although the external examination clearly predicted this mode of flame travel, validity of this hypothesis was questionable. A detonation of enough violence to rupture the tubes would easily have disintegrated the condenser shell. Yet, the shell was only bulged. This suggested that the tubes had not been ruptured but had been heated sufficiently to serve as a source of ignition. This also was difficult to explain because of the short residence time of the detonation in the exchanger. When the exchanger shell was finally cut open for inspection, a number of tubes had been sheared by action of a baffle plate which was dislodged by the explosion.

Five seconds after ignition, flames were issuing from relief valves on top of the unit. This explains the observation of several people near the unit who saw these flames before they heard the explosion. The flame front which entered the shell side of an exchanger passed through the centrifugal recycle compressor, blowing the blading in its direction of travel.

It advanced to a separator, where a well-developed flame front was established. This detonation exerted great force upon impact with the vessel head, shattering the vessel and hurling the pieces generally to the right and upward. The explosion of this vessel is, for several reasons, believed to have preceded that of the reactor. First, the location of the pieces of wreckage, although not conclusive, point in this direction. Second, the vessels are believed to have exploded about 4 seconds apart, and had the reactor exploded first, the separator would have lost too much pressure in the intervening 4 seconds to have exploded in the indicated manner. The pressure loss in the reactor as a result of the rupture of the separator would be considerably less due to its much greater volume.

About 11 seconds after ignition, the flame front in the reactor had developed enough intensity to rupture that vessel, hurling the pieces of the upper half through the air in the way previously described. This sequence of events is in agreement with the account of witnesses 1 mile away who first heard "the explosion" and who, upon looking up, saw the reactor unfold and fly apart. Undoubtedly, their attention was attracted by the explosion of the separator, since they would not have heard the reactor explosion until 4 or 5 seconds after it disintegrated.

Conclusions

Calculated explosion energy and pressure based on observed damage indicated the existence of shock waves in the principal vessels and lines. Metallurgical evidence obtained from careful examination of the wreckage enabled the location of the shock wave front at the time of rupture to be determined in the principal vessel. Through both the location of luders lines and the position of unit parts, the direction of flame travel was established. These facts, coupled with the known properties of detonations, enabled the sequence of events after ignition to be reconstructed, thus reconciling apparently conflicting physical evidence and eyewitness accounts.

Chlorine-Naphtha Detonation

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American Oil Co.

On April 11, 1961, a violent explosion fragmented the inlet section of a small mixing chamber in naphtha processing equipment at the Wood River refinery of American Oil Co. The explosion was heard for miles, and steel fragments were projected throughout the area. No one was injured, and damage, including that from the subsequent fire, was limited to small, inexpensive equipment.

A solvent naphtha was being treated with an aqueous caustic-hypochlorite solution. The accident occurred just after a routine injection of liquid chlorine had been made to refortify the hypochlorite solution.

Explosive chlorine-hydrocarbon reactions were suspected as being the probable source of the violent energy release. However, an analysis of the operation was necessary to determine how these materials could have come together in sufficient quantities and under conditions favorable to an explosion.

Description of Operation

A desulfurized naphtha stream was fractionated in a two-tower system, removing both lower and higher boiling factions. This naphtha, having a boiling range of 325° to 380°F (ASTM D86), flowed from the condenser and entered the reflux drum at 100°F.

To avoid a vacuum with the possibility of air being drawn in, nitrogen was bled into the reflux drum to maintain a positive pressure of a few pounds per square inch gauge. The pump on the outlet of this drum returned a portion of the naphtha to the tower as reflux and provided pressure to move the net naphtha stream through the treating equipment and then to product storage tanks. This naphtha typically consists of 50 percent by volume of paraffin hydrocarbons, 10 to 15 percent aromatics, less than 1 percent olefins and the remainder naphthenes.

In the treating section, the naphtha and caustic-hypochlorite solution flowing through separate lines (3-inch and 2-inch pipe, respectively) joined in a short, swaged spoolpiece flanged to the inlet of an orifice mixer. Intimate contacting of the streams was achieved in passing through the mixer, which consisted of four drilled plates spaced in a 5½-foot length of 6-inch pipe.

Several return bend loops in the piping downstream of the mixer provided some additional contacting enroute to the settler drum where the aqueous treating solution separated from the naphtha. Naphtha product, 2,500 barrels per day, flowed from the top outlet of the settler drum to tankage; the treat solution was pumped back to the inlet of the mixer at a rate of two volumes for each volume of naphtha. At these flow rates, pressure at the inlet of the mixer was 45 psig with 25 psig in the settler drum. Stream temperatures were 90° to 100°F.

At 1-week intervals, a major portion of the spent hypochlorite solution was drained from the settler drum and replaced with 600 gallons of fresh 15 percent aqueous sodium hydroxide solution. Circulation and naphtha flow continued during this operation. Chlorine was then added to react with the caustic to prepare the hypochlorite solution in place according to the following equation:

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

Thereafter, two more additions of chlorine were made at regular intervals during each week to fortify the solution.

Each addition of chlorine consisted of a given weight of liquid released from inverted chlorine cylinders resting on platform scales. The chlorine entered the 2-inch treat-solution line, a few feet downstream of the pump and about 120 feet ahead of the mixer.

For the first three months of operation, beginning in June, 1960, each addition consisted of 10 pounds of chlorine; thereafter, this was increased to 15 pounds per addition. Sometimes these additions were made while the treat solution was flowing.

Explosion and Fire

The explosion occurred just after one of the mid-week additions of chlorine had been made to fortify the solutions. The treat-solution pump had been shut down and blocked in, 15 pounds of liquid chlorine added and the manual suction and discharged valves at the pump reopened. After starting the pump, the operator started to walk away. He had taken only a few steps when the explosion occurred.

The mixer, 18 feet above grade, was torn loose from its piping and landed on a walkway about 6 feet below. The swaged spoolpiece at the inlet to the mixer was fragmented. A 12- to 14-gauge orifice plate clamped in the flanged joint between the spoolpiece and the mixer was ruptured and pushed into the mixer, and the front end of the mixer was torn open 1½ to 2 feet.

Roughly 50 pounds of steel fragments ranging from a few ounces to 7¼ pounds were propelled and scattered over an area extending to more than 300 feet from the source. A 6-ounce piece of bolt produced a 1-inch deep dent in a 3-inch pipe that was over 40 feet away. A 3¼-pound piece of pipe flange punched a 6-inch square shaped hole in the web of an 8-inch I-beam at about the same distance.

Naphtha released from the lines as a result of the explosion ignited and resulted in a substantial but localized 25-minute fire. The fire was extinguished by shutting off the flow of naphtha from the distillation section and from tankage. Four hoses were used during the fire to cool the structure.

Flammable mixtures of combustible gases or vapors dispersed in air or oxygen are by far the most common cause of explosions in refinery operations. The presence of these flammable mixtures in systems where only traces or safely low concentrations of oxygen would have been expected has resulted in a number of major disasters. In view of the experience, a check was made to see if sufficient amounts of air or oxygen could have entered the treating sections to have caused this explosion. Such was not the case.

No air or oxygen was being used in the processing. Even if air had been dissolved or entrained in the naphtha feed, all except traces would have been expelled with the overhead stream from the first distillation tower. Any remaining air would have preferentially collected in the nitrogen-blanketed vapor space of the reflux drum on the second tower. An analysis of this vapor space following the incident showed some oxygen present—1.2 percent by volume oxygen, 0.9 percent carbon dioxide and the remainder nitrogen—but in much lower concentration than necessary to result in flammable mixtures.

The treating section remained under a pressure of about 25 psig during the chlorine addition so no air could have leaked in. An analysis of the content of the cylinders confirmed that the material added was chlorine.

Having eliminated air or oxygen as the source of the trouble, explosive reactions of chlorine and naphtha hydrocarbons were considered. A search of the literature revealed more than 20 references, several of which attest to the very violent, explosive and detonative reactions between chlorine and saturated hydrocarbons.

An internal pressure in excess of 5,000 psig is necessary to rupture 6-inch, schedule-40 steel pipe used in the mixer body and the large end of the swaged inlet piece. Strength added by the flanges and the swage contour tends to be offset by the effects of corrosion and impact loading. This suggests that a force equivalent to a pressure of at least 5,000 psi must have developed to fragment the inlet section of the mixer.

Thus, based on the initial pressure of 45 psig at the inlet to the mixer, the ratio of the final to the initial absolute pressures was at least 84. The ratio of these pressures is referred to as pressure multiplication.

No data were found on pressure multiplications obtained with chlorine-hydrocarbon explosions. However, for normal gas-phase explosions of air-hydrocarbon and oxygen-hydrocarbon mixtures, peak pressure multiplications are only about 10 and 20, respectively. For gas-phase detonations of oxygen-hydrocarbon mixtures, in the absence of impact and pressure piling effects, which would not be expected in the small mixer section involved, pressure multiplications of about 40 are typical.

Further, corresponding gas-phase reactions involving chlorine-hydrocarbon mixture would result in lower pressure multiplications because the heat release per mole of chlorine reacted is only about one-fourth that for oxygen. The substantially greater pressure multiplication experienced suggests that the reaction must have occurred in liquid phase.

Consideration of the energy evolved provides additional evidence that a liquid-phase reaction must have occurred. The small mixer inlet section could not have contained enough chlorine-hydrocarbon reactants in vapor phase to provide energy to fragment and tear the mixer, project the missiles and punch the 6-inch hole in the web of the I-beam. The extensive fragmentation and the violence with which the missiles were projected suggests that this was a detonation rather than an explosion.

When the treat-solution pump was shut off and blocked in (in preparation for chlorine injection), the line remained full of caustic-hypochlorite solution at 90°F. With only naphtha flowing through the mixer orifices, the pressure at the mixer inlet and at the chlorine injection point dropped to 27 psig. Chlorine boils at 18°F at this pressure.

When the 15-pound charge of liquid chlorine at 50°F was released into the line, about 1 pound would have immediately flashed to vapor. Heat available from the 7- to 10-foot section of 2-inch line contacted by the remaining liquid would have vaporized another 2 to 3 pounds. Further, some of the chlorine would have combined with the caustic in the line, thus liberating some heat for additional vaporization.

Combining the foregoing heat effects, it is conceivable that over half of the 15-pound charge remained as liquid when the circulating pump was started just after the chlorine injection. With the pump running, more heat would have been picked up by the slug of liquid chlorine in passing along the 120-foot length of line to the mixer, but the rise in pressure to 45 psig would have tended to suppress further vaporization.

Thus, introduction of at least 1 pound of chlorine in the liquid state, and probably more, into the mixer is consistent with the operating conditions. Also, only small changes in conditions would be necessary to obtain sufficient vaporization of the chlorine to prevent a dangerous quantity reaching the mixer as a liquid. This small margin of difference in conditions