Hazardous materials: flammable liquids, UN class 3

By Colin Deiner, chief director, disaster management and fire brigade services, Western Cape Government

Zhangzhou chemical plant fire China 2015

This month we continue our series on hazardous materials where we will deal with flammable liquids. Flammable liquids and, in particular, petrochemicals in their various forms present more risks than just flammability, however, we will deal specifically with that risk here. Due to the large scope of flammable liquid incidents, I will focus only on fixed installation fire fighting operations in this article. Road and rail related incidents will be covered in future articles.

Responding to petrochemical incidents such as fires in refineries, terminals and bulk storage depots or tanker truck (or rail) incidents are significantly different for the municipal fire department than the usual structural fire or freeway accident. Despite the various types of hazardous products present in a storage facility, the quantity of product will most likely pose the biggest challenge. You could be dealing with anything from a few hundred litres to several hundred thousand litres.

Classification

Un Class 3: Flammable liquids cover those products which:

- Are liquids at 20 degrees Celsius and at a pressure of 101,3kPa with a melting point or initial melting point of 20 degrees Celsius or less at a pressure of 101,3kPa
- At 50 degrees Celsius have a vapour pressure of not more than 300kPa
- Have a flash point of not more than 60 degrees Celsius

The following products are also included:

- Liquid substances and molten solid substances that have a flash point of more than 60 degrees Celsius that are transported while heated at temperatures equal to or higher than, their flash point.

Venezuela Puerto La Cruz refinery fire 2013

- Liquid desensitised explosives. These are explosives that are dissolved and suspended in water or other forms of liquid to form a homogeneous mixture which suppresses its explosive properties.

The risk (where)

Due to the massive industry, flammable liquids can be found in a range of locations and processes; from fixed installations to roads and rail systems and on the oceans. Some of the most common locations include (not exhaustive):

- Oil refineries and processing facilities
- Storage tanks
- Tank farms
- Road tankers
- Rail cars
- Pipe lines

In their various configurations, flammable liquids can produce a number of different risks. These risks are generally dependent on the way in which they are stored, processed and transported. These include:

Explosive hazards

If the right conditions are present, flammable liquids can produce a number of devastating reactions that will happen suddenly and cause loss of life and damage on a large scale.

The first type of explosive risk we will look at is the unconfined vapour cloud explosions (UVCE). When a flammable vapour is released, its mixture with air will form a flammable vapour cloud. If ignited, the flame speed may accelerate to high velocities and produce significant blast overpressure.

A confined vapour cloud explosion (CVCE) occurs when a flammable vapour ignites within a confined space eg process vessel. This could happen inside an empty vessel, which has not been purged of any residual vapour. Should any form of flame be introduced into the space such as welding or exothermic cutting, it could lead to a sudden and rapidly progressing ignition, which could cause an over pressurisation in the vessel and resultant destruction of the container.

Although it is more commonly associated with liquid petroleum gas, a boiling liquid expanding vapour cloud explosions (BLEVE) can occur in any situation where a vessel containing a liquid is heated to a temperature substantially higher than that liquid's boiling point. The vapour that is propagated by the boiling liquid increases exponentially in pressure and, if not adequately vented, causes a catastrophic failure of the vessel with disastrous consequences. Should sufficient liquid still be present in the vessel at the time of the explosion, this could turn the vessel into a missile that can be propelled over a great distance destroying everything in its path. The resulting expanded gasses that are suddenly exposed to the atmosphere after the rupture, will in all probability ignite when it comes into contact with the flame source and cause a massive vapour cloud explosion, which could then, especially in a storage facility, cause a number of secondary fires.

Fire hazards

In the early days of the petroleum industry, storage tank fires were common. As the industry matured it demanded better design, construction, fire protection and improved legal compliance, which led to the development of better codes and standards. This all led to a decrease in the prevalence of tank fires. It is interesting, however, that although the fires decreased, the size of the storage tanks increased. The fewer fires now have a larger potential for a disastrous situation with a larger risk of financial impact, environmental damage, loss of business and property damage. The resources needed to deal with these fires are also more vast and specialised.

Flammable liquid bulk storage tanks are classified by their roof construction. The type of storage tank is dependent on the characteristics of the product and the location of the tank. Combustible liquids are stored in cone-roof tanks while flammable liquids are stored in floating-roof tanks in bulk quantities. In smaller quantities, such as service stations, flammable liquids are stored in smaller underground tanks or in low-pressure horizontal or vertical tanks.

Storage tanks will have the following fire risks:

- Overfill ground fires (bund fires): These fires generally occur due to operator error or an equipment malfunction that result in piping- or tank-leakage and are common in fixed-cone roof, internal and external floating roof and domed roof tanks.
- Vent fires are normally associated with fixed roof tanks ie cone roofs or internal floating roofs and is characterised by ignition at the vent area, sometimes caused by lightning
- Rim-seal fires comprise the majority of fires in external floating roof tanks although they have occurred in internal floating roof tanks. Lighting is a major fire risk here although, provided there has been no collateral damage, these fires are generally quite easily managed by well-designed fixed fire protection systems.
- Full surface fires will occur in fixed-cone roof, internal floating roof or external floating roof tanks. They pose the extra challenge of having to access the roof to reach the fire in the case of the fixed-cone roof. A

full surface fire in a floating roof occurs when flooding or pontoon failure causes the floating roof to sink thereby exposing the entire surface, which is then exposed to the fire.

Boilover, frothover and slopover

A boilover is a sudden violent ejection of crude oil (and other liquids) from a tank due to a reaction of the hot layer of the product with water that has accumulated at the bottom of the tank. This happens when a fire on the tank surface is gradually heated throughout its volume. When this heated layer makes contact with a volume of water that accumulates at the bottom of the tank over time, it will cause a rapid formation of steam (1 700:1) and, as a rule of thumb, expel the oil to ten times the tank diameter around the tank perimeter. A frothover occurs when water boils under the surface of a hot viscous oil that is not on fire such as hot asphalt introduced into a tank which has an accumulation of water of the bottom. A slopover occurs when water is applied to the surface of burning oil. This causes the burning oil to slop over the tank sides.

Other hazards

The general design and construction of petrochemical facilities makes any type of response more challenging. These facilities can be very congested with limited access routes. Responders will encounter a number of obstructions such as piping and other above ground structural elements. Most of these facilities are very congested. The security arrangements in such facilities could provide a further obstruction for fire fighting vehicles and equipment.

Although some facilities could be well staffed during daylight hours, they are not staffed at night, which could lead to more complications if an incident occurs at night. Depending on the type of facility, it may not be staffed around the clock and in some pipeline facilities they may not be staffed except during maintenance operations. In other facilities, operations are monitored and controlled by a remote master control centre.

Some of the more common other risks include, high noise levels, activated pressure relief systems, flaring operations, high temperature processes and high-voltage electrical systems. You could also be working on a fire or other emergency in close proximity to pressurised process, storage or cryogenic vessels. The presence of chemicals and fuel additives will always pose the additional risk of a potential for a secondary hazardous materials (hazmat) incident.

Management of incidents in petro-chemical facilities

The description of the hazards mentioned above makes it clear that dealing with a fire in a petrochemical complex is vastly different from your normal structural fire response. The type and significance of the fire/hazmat risk could vary from one facility to another. It is therefore important to ensure that your pre-incident planning should include an inventory of the types of products in any facility within your response area as well

Ohio oil refinery explosion 2015

as their hazards and positioning. It might be necessary to consider employing large water streams for exposure protection in some areas, which will have an impact on the water supplies available for fire fighting. You would want to know this in advance.

Larger facilities will generally have their own fire service on site. This is the case in most refineries and in many large storage facilities. In some cases the services are professional brigades that employ trained fire fighters on a 24/7 basis. In other cases you will find that people employed for other jobs eg process workers, security are utilised as fire fighting teams. These teams should not be underestimated. Some of the best fire fighting teams you

177 fire trucks and 929 fire fighters were deployed at the Zhangzhou chemical plant fire

can find are 'volunteer' units as they take a lot of pride in their group and in terms of the employer's health and safety policies undergo advanced fire training.

The fire protection systems at bulk petro-chemical facilities are generally highly advanced and may include fixed foam systems, deluge systems, and fixed turret monitors. Larger facilities will also have dedicated fire water systems with tanks and pumps, advance monitoring and on-site fire fighting apparatus. In such facilities the incident command function will most probably be performed by the facility's fire chief and the municipal brigade will act as a support service.

Incident command

The incident command arrangements for an 'on-site' petrochemical incident should be clearly detailed in advance. If the incident is of a significant magnitude, you could have a rapidly increasing number of responders within the first few hours of the incident. The incident command system (ICS) must be able to escalate accordingly. The expanded layout of a petrochemical facility will necessitate a division format of operations. Support functions such as foam supply, water supply, and crew decontamination must be established as sectors or groups. Also ensure that sufficient space is afforded for level I and II staging areas. A large response from outside services will include different types of vehicles and it will be necessary to prioritise the units, which might be needed for immediate deployment and make then most accessible.

A large petrochemical facility fire will include a wide range of stakeholders and the liaison officers within the system must be prepared to cater for the needs and interests of these groupings. This might include environmental and natural resources agencies, utilities departments such as water and electricity and various levels of governmental agencies. If the facility is bordering on a residential area or is situated in a commercial zone, it will also be necessary to provide timeous information to your neighbours. It might be necessary to consider evacuation of certain areas or shelter in place options. A consistent and accurate indication of events and interventions is very important when dealing with these various groups.

It is necessary that liaison with the plant process controllers is established early and maintained throughout. The site process operations such as shutting down certain areas, closing valves or transferring product could assist the fire fighting operation and it is therefore important that constant communication between the facility engineers and fire department is maintained.

Initial operations

The initial size-up of a petrochemical fire will have several aspects that would apply to a standard large structure fire but will include a number of process related issues.

As with any fire, the first few minutes spent doing the initial size-up is critical in plotting the course of action that will follow and ultimately determine the success (or failure) of the fire fighting effort. The size and complexity petro-chemical facilities make it difficult for a thorough size-up to be performed rapidly. It is therefore important that the assessment be done by someone who understands the specific area involved. What might be conceived as being a major incident initially could be dealt with by focussing all your resources on the origin of the fire and quickly controlling it therefore preventing a catastrophic fire. It might be as simple as isolating a certain storage tank or pipeline by turning off a valve.

Incident command should attempt to get as complete a view of the incident as possible. This can best be achieved by deploying a group of fire fighters accompanied by process specialists. This initial assessment should attempt to identify the source of the fire, identify the type and volume of products involved and gain knowledge on the immediate hazards in the affected area. The recon team should also identify ingress and egress routes from the incident location and identify any exposure concerns. The operation of any fire suppression systems currently active should also be appraised.

Zoning

Once a clear picture of the incident has become available, the next priority should be to establish zones of control; the entire affected area should be off limits until the initial assessment has been completed. In real life you will probably have a fair number of people already in the designated hot zone. These could be plant fire fighting teams, freelancing process workers or disoriented individuals. These non-essential personnel must be moved to a place of safety. If the plant fire crew is making progress in controlling the fire, it might be necessary to support their efforts by bringing in additional crews or replacing them with fresh resources.

In the petrochemical environment, the hot zone will initially be very large and as the incident progresses, will contract accordingly. The complex layout of the facility might make the control of entry and exit in and out of the hot zone difficult. Having a single point of entry and exit might address this concern. Factors such as changes in wind direction, pressure-relief valve activation, collapsing structures and other unforeseen problems would necessitate the rapid expansion of the hot zone and all sectors must be prepared for this. An on-going size-up will be necessary throughout the operation.

Virtually all modern facilities have a range of security cameras located at strategic points around the facility. These cameras can be a valuable tool for incident command to determine the course of the incident.

Remember at all times that every incident is a hazmat incident until proved otherwise. Make sure that all products involved in the fire must be clearly identified and the necessary precautions taken to protect personnel from harmful exposure.

Venezuela: Guaraguao Oil Refinery fire November 2016

Exposure protection

Protecting exposures must be a major tactical objective. Providing sufficient cooling for critical equipment is essential to help keep the incident from worsening or equipment may fail and rapidly increase the hazard level and fire potential. Instrumentation or electrical systems such as cable trays and major distribution systems could rapidly fail whereas pressurised vessels that are exposed to extreme heat could lead to BLEVE in a few minutes. Supporting structures will also fail if exposed for too long causing them to collapse. Significant volumes of water and extra resources might be required to protect these exposures.

Although there are certain indictors for cooling streams, the best indicator of success in cooling exposures is to observe the impact of the water on the exposed surface. If it is turning into steam, you are not cooling it down adequately. The moment the water is cascading off the exposure who have been successful. It is important to gain the advice of the process controllers regarding the types of vessels involved in the fire. If a water stream is applied to a component that is designed to operate at high temperatures, the resultant rapid cooling effect could cause a contraction of the materials and a possible violent release of product.

Incident types

Petro-chemical fires can be encountered in two broad types, the surface fire or a pressure fed fire. The surface fire will normally be encountered inside a vessel or bund, however you could also have a running flammable liquid fire that is not confined and will present an additional set of hazards. Fuel might flow under sensitive process areas or into low lying areas and cause fires to star in remote locations. In the flammable liquid environment, a pressure-fed fire is typically fed by liquid escaping under high pressure. You could also have the situation where a failure on a pipe rack might cause a leak expelling liquid at high pressure, which then come into contact with a heat source and ignites. The resultant fire could come into contact with a vessel and also ignite its contents. You then have a combination of fires, which require rather different methods of extinguishing.

The most common method of extinguishing a pressure-fed fire is to isolate the source, which can be done by a remote-control valve being shut off from a remote position. It might, however, happen that the fire is in very close proximity to the shut-off valve assembly and might be necessary to approach the fire and, by utilising fog streams, 'bend' the fire away from the shut-off valve whilst sending a fire fighter in to manually isolate it.

Fire fighting considerations

The first fire fighting consideration should be to determine the type of fire ie vent, rim-seal, piping, tank overfill, bund or full involvement of multiple tanks. This will in turn determine the resources required as well as the incident action plan to be implemented.

Weighing up the risk in relation to the benefit that can be gained from a particular strategy is important. It could be necessary to employ a strategy of non-intervention when the risks associated with taking any actions are unacceptable. Withdrawing to a safe area and monitoring the incident while addressing the environmental risk might be the best option.

A defensive strategy will entail protecting exposers and limiting or preventing any further fire extension. An offensive strategy would require positive and direct tactics to control the incident and ultimately extinguish the fire.

The importance of pre-planning for large scale flammable liquid fires is key

▸ The initial fire fighting strategy at a large petrochemical facility fire will be a defensive operation whereby teams will try to contain the fire and prevented from spreading. Once the initial size-up has been completed the decision can then be made to continue in a defensive mode or to implement an offensive/supported operation.

The main priority will always be the rescue of any trapped/injured victims and if this is the case your first-in units will have to be dedicated to locating and extricating any victims. This could include victims trapped in elevated positions, confined spaces ie inside vessels, victims trapped by heavy machinery or containers or by the fire itself. Be prepared for prolonged rescue operations that might be exasperated by the proximity of the entrapped victim to the fire. Additional hose teams might be needed to protect the rescue crews.

Persons in the immediate proximity to the incident might suffer burn injuries and inhalation difficulties. The establishment of a medical sector as well as a coordinated patient transport system must form part of the initial incident command structure.

Structures and processes that are exposed to the heat of the fire or are in direct flame contact, will react according to their specific properties and could have a catastrophic effect on the incident if not protected.

Tank overfill fires or fires resulting from pipe failure can be managed in the same way as spill fires. It is, however, difficult to calculate the foam requirements for an oddly shaped spill. The previous point regarding adequate resources being available before commencing the attack, is also important here. The need for protection of surrounding exposures could be especially important here. It goes without saying that entry into any bund or spill area that has been involved in the fire should be strictly forbidden.

Rim-seal fires can be largely extinguished with mobile or permanent water/foam systems. The fire department's role in such an incident will largely be a support operation. Tanks without fixed fire protection can be extinguished by deploying hose lines and monitors to fill the exposed rim-seal area. The 'over-the-top' application method will require the consideration of minimum application rates, application densities, minimum foam solution application durations as well as additional foam requirements for possible bund fires. These considerations will be dictated by the fuel involved, its flashpoint, the type of foam used and the application device. The calculation should also allow for the amount thereof that will be lost due to the thermal currents or foam that fails to reach the tank interior.

It is generally accepted that application rates will be determined by the surface area of the tank ie its diameter. Space precludes us from discussing application calculations in too much detail here; suffice to say that in the pre-planning phase the particular on-site fire service should ensure that they have provided for sufficient foam supplies to address their largest risk. Most municipal fire departments only carry enough foam to deal with relatively small incidents such as road or rail tank emergencies and will rely on the supplies of the industry to which they provide a back-up service. A regional agreement for assistance in providing more foam supplies in the event of a major incident becomes more important where multiple risks exist.

Large volume flammable liquid fires can also be extinguished by displacing the fuel source or removing the oxygen required for combustion by introducing an inert gas such as nitrogen into a closed vessel or by transferring the product out of the vessel at a point below the surface.

After the incident

Operational discipline must continue throughout the overhaul phase of the incident. Hazardous materials could still be present presenting an unreasonable health risk to personnel who are not adequately protected. Undetected fuel spills might ignite if exothermic processes are restarted without a thorough inspection of the affected area, which could have identified the spill pools. Incident command should not be in too much of a hurry to send units back to their bases unless they are certain that all risks have been neutralised and that plant overhaul and rehabilitation work can begin. Even at this stage it will be necessary to have some resources on standby.

In conclusion

The importance of pre-planning for large scale flammable liquid fires is key. Although, as mentioned earlier, municipal fire services will normally act in support of on-site fire services, it is vital that all responding agencies have a clear picture of the layout of the facility and the types of product kept there and their hazards.

Having adequate foam supplies, application devices and effective water supplies will determine your ultimate success. Petro-chemical fire fighting is more about logistics than heroics.