Explosion of a VOC recovery pipeline at a petrochemical plant

October 21st, 2011

Loon-Plage (Nord-Pas-de-Calais) France

Explosion
Hydrocarbons
VOC
Management of change
Design
Risk analysis

THE FACILITIES INVOLVED

The site:

This site is located in the Dunkirk Port industrial zone, straddling the municipalities of Mardyck and Loon-Plage. The facility was created in 1978 and employs a workforce of 436. The plant produces major stocks of intermediate chemicals resulting from the steam cracking of petroleum-based products as well as polyethylene.

The site's main activities consist of:

- steam cracking of liquid or gaseous hydrocarbons;
- fabrication of radical low-density polyethylene, low and very low-density linear EVA copolymers;
- storage of raw materials, end products and chemicals in transit on behalf of third parties;
- polyethylene packaging;
- acceptance and shipping of hydrocarbons by sea, rail and road.

The closest residential zones are located in the village of Mardyck, at a distance of 500 m from the village centre to the site's fenced boundary. The first individual houses lie 50 m from the fence heading south. The other two municipalities near the site are separated by a stretch of 3 to 4 km: Loon-Plage to the south-west, Fort-Mardyck to the east.

The facility is laid out with distinct installations, positioned some 100 metres apart. The first, encompassing a 75-ha land area, is dedicated to production activities and comprises (see Fig. 1):

- an ethylene steam-cracker with a capacity of 350,000 tonnes/year;
- a 180,000-tonne/year unit producing radical polyethylene and EVA copolymers;
- a 135,000-tonne/year linear polyethylene production unit;
- generation of utilities, overhead services: safety, maintenance, warehousing.

The second installation, covering 32 ha, is dedicated to storage and logistics:

- raw materials for the steam-cracker (naphtha, LPG);
- steam-cracker end products (cryogenic tanks for ethylene and propylene, spherical tanks for the C3 and C4 fractions, etc.);
- loading / unloading of these products: wharf, lorry dock and rail station.

The site has developed its internal emergency plan and moreover has been assigned an external emergency plan. It features an in-house team of fire-fighters equipped with 4 fire-fighting vehicles.

This facility has been classified as Seveso.

Figure 1: Aerial view of the site (source: SPPPI Pollution Prevention Agency, Opal Coast, Flanders)

The specific unit involved:

During 2009-2010, the site operator remodelled the low-density polyethylene (LDPE) unit by adopting a tubular process that allows producing an LDPE with improved optical properties, along with the EVA copolymers. This production line's capacity amounts to roughly 180,000 tonnes/year.

The main modifications provided by this remodelling process include: the installation of a tubular reactor and its bay, expanded primary and secondary compression capacity, and the introduction of a decompression system. The EVA properties are derived by using vinyl acetate as a co-monomer.

The melted polymer stemming from the reaction zone is conveyed into extrusion hoppers that feed the extruders for degassing and solidification (granulation process). At the output of this extrusion system, the solid polymer is then channelled towards the silo section. The evacuation unit allows operating the extruders' degassing sections. In this part, the polymer is partially degassed prior to the final degassing stage inside the silos. Depending on the type of polymer being fabricated, the extracted gases may contain ethylene, nitrogen, vinyl acetate and solvent. At the level of the evacuation unit, gases are cooled and the heaviest products condensed.

Gaseous effluent at the evacuation unit output is composed of various VOC (volatile organic compounds, such as ethylene, butene, vinyl acetate and solvents) and nitrogen. The VOC flow rate ranges from 25 to 50 kg/h, depending on the polymer under production.

Figure 2: Exterior view of the site (source: Google)

VOC are also emitted during polyethylene degassing inside the storage silos. This flux, composed of air and a small proportion of VOC (< 10% of the Lower Explosive Limit), crosses a cyclofilter and is then conveyed to the boilers via a

fan with discharge through a duct (L = 300 m / D = 1.5 m). This flux is mixed with combustion air from the site's two steam production boilers, a process that ensures the destruction of these compounds by combustion.

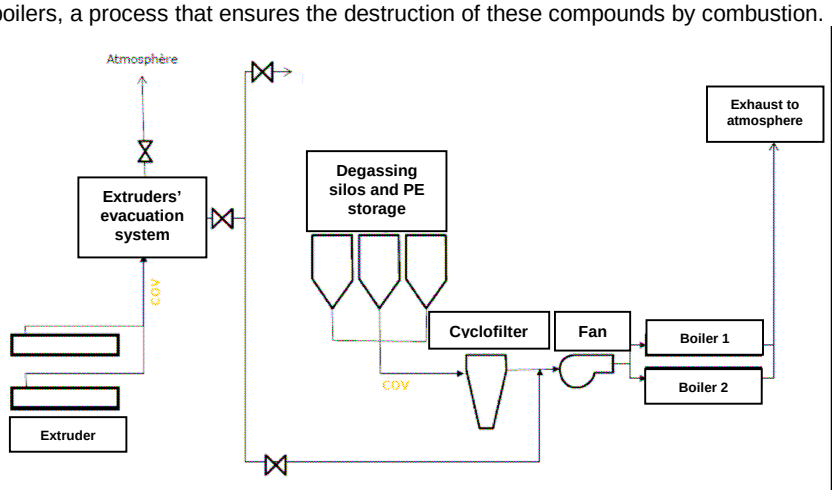

Figure 3: Diagram of the VOC recovery system on the polyethylene production line (source: Site operator)

As part of the LDPE unit remodelling project, the operator decided to improve the VOC emissions collection process in order to keep up with applicable regulatory changes. More specifically, a collection device was installed at the level of the extruders. This flux is thus channelled to the fan suction station via a collection pipe, where it then mixes inside the duct with the flux originating from the degassing silos (see Fig. 3).

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

The condition of the site's production units before the incident was as follows:

- The steam-cracker was in a stable operating mode;
- The remodelled EVA polyethylene production unit and the neighbouring LDPE polyethylene production unit were both operating under stable conditions as well;
- Boilers 1 and 2 were also operating in stable mode.

At 3:40 pm, an initial explosion occurred at the outer part of the air supply pipe feeding steam production to Boiler no. 2. Twenty to thirty seconds later, a second explosion destroyed the VOC recovery pipeline, spewing debris in all directions.

The two boilers stopped upon automatic triggering of the integrated safety features, while the polyethylene production and steam-cracker installations were secured by the operator working from explosion-proof control rooms.

The internal emergency plan was activated, causing the general alarm siren to sound, thus leading to evacuation of the site's 250 employees and subcontracted personnel. The local fire rescue services, administrative agencies and neighbouring town halls were all informed.

The VOC duct explosion was followed by an outbreak of fire on a 1,000-litre bag-in-box of vinyl acetate (an easily flammable product) at the base of a column intended for product distillation, along with the break of a pipe connected to a 1-m³ oxygen (O_2) tank whose contents then emptied into the atmosphere. Another fire broke out on the dome of the cyclofilter upstream of the VOC duct (Fig. 4).

Figure 4: Location of the explosions and their domino effects (source: Site Operator)

Both the in-house fire-fighting crew and Second Responders were at the scene by 3:44 pm to contain and control the blaze using onsite resources, which proved to be sufficient, i.e.: sprinkler ring placed on the equipment, 4 refinery vehicles (using water, foam, powder), and high-pressure mobile rotary nozzles. Emergency workers installed a water curtain in order to dilute the oxygen leak. Fire-fighters with local Rescue Services arrived to offer backup protection with a 40-man crew and several vehicles; their intervention however would not be required (Fig. 5).

The situation was under control by 4:15 pm, and the internal emergency plan was lifted at 6:42 that evening.

Consequences of this accident:

At the time of the explosion, 250 plant employees and subcontractors were onsite. The accident occurred on a Friday afternoon, i.e. during a less busy period, in the presence of a limited number of staff inside the facility.

Two employees had to be taken to the emergency room for a hearing check-up; three others sustained shock due to the explosion and also had to be transported to the emergency room. A worker employed by a subcontractor was examined at the site's infirmary. Two of the three employees under shock were subsequently placed on medical leave; their medical state did not have any long-term consequences.

No redundancies had to be announced given that facility restoration works were initiated and scheduled to last several weeks.

No environmental impacts were caused according to the rating on the European industrial accident scale. The quantity of vinyl acetate released was estimated at between 0.05 and 0.5 tonnes. Nonetheless, the safety flare exposed a flame and a tremendous black smoke plume was visible over a great distance. Given the lack of steam supplied by the boilers once they were shut down, the remaining production ingredients (mix of naphtha and polyethylene) in the cracking and gas furnaces present in the installations had to be burned using the flare. The black smoke emanating from this combustion could not have been "removed" with steam for this very reason, despite an attempt to restart the intact boiler around 4:15 pm.

The two pipelines that exploded were exposed to atmospheric air. The damaged boilers could not be restarted while maintaining the required safety measures. The VOC recovery duct was destroyed over a length of 200 m.

The cost of repairs to damaged equipment was appraised at €4 million, with many machines, structures and miscellaneous instruments being broken or completely destroyed, including:

- the VOC duct,
- the boilers,
- cracking furnaces damaged by shutdown of the steam-cracker without producing any steam, thereby necessitating verification and repairs of the radiation tubes.

The damaged machinery was inspected and the repair work would be completed around 15th December, 2011. The VOC recovery duct on the polyethylene storage silos would be rebuilt within a 6-month time frame.

Production margin losses and variable costs were valued at €2 million.

Figure 5: Intervention of the public agency's rescue services (Source: C. FREMIN & DELTA FM / J.C. BAYON)

The European scale of industrial accidents

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the '*SEVESO*' directive on handling hazardous substances, and in light of information available, this accident can be characterised by the four following indices:

Dangerous materials released	■	□	□	□	□	□
Human and social consequences	■	□	□	□	□	□
Environmental consequences	□	□	□	□	□	□
Economic consequences	■	■	■	□	□	□

The parameters composing these indices and their corresponding rating protocol are available from the following Website: http://www.aria.developpement-durable.gouv.fr.

The "dangerous materials released" index was rated a "1" due to the 0.5-tonne leak of vinyl acetate.

The "human and social consequences" index was scored a "1" as well, as a result of the slight injuries sustained by 5 employees, two of whom were placed on medical leave.

The "environmental consequences" index was not rated owing to the non-observation of any consequences of this type.

The "economic consequences" index was assigned a "3" score due to the property damage sustained by the unit as well as significant operating losses, whose total amounted to between €2 million and €10 million.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

Several investigations and expert appraisals were carried out, i.e.:

- police investigation;
- administrative investigation commissioned by the DREAL Departmental Environment Agency;
- workplace health and safety investigation;
- investigation conducted by the CARSAT (health insurance) organization;
- investigation performed by the CHSCT Committee for Hygiene, Safety and Working Conditions;
- internal Group investigation relying on the assistance of a third-party expert.

Analysis of the events leading to this incident:

- Presence of liquid containing hydrocarbons in the extruders' VOC recovery pipes (a mix of water / vinyl acetate / solvent);
- Forced flow of the liquid towards the silos' VOC recovery duct;
- Creation of a flammable atmosphere by evaporation of the liquid inside the connection duct, thereby leading to an explosion at the level of Boiler no. 2 and then in the vicinity of the fan.

Analysis of incident causes:

- **Partial condensation of hydrocarbons:** The expert appraisals performed after the incident confirmed the possibility of VOC condensation in the form of liquid hydrocarbon, with accumulation in the extruders' VOC recovery pipes;
- **Forced flow of liquid into the recovery pipes via both the extruders' VOC recovery evacuation system and accumulation:** The hypothesis of driving hydrocarbon liquid via the evacuation system cannot be excluded. The initial safety studies for this process, conducted between 2008 and 2010 by a group of experts, had not addressed the possibility of a change in VOC state (condensation of the VOC gaseous phase into liquid hydrocarbon) nor for that matter the risk of such a liquid entering into this particular line.

ACTIONS TAKEN

The operator's medical service set up a psychological treatment unit to care for employees working at posts close to the accident scene.

At the behest of the Classified Facilities Inspectorate, the Prefect's office served the operator an emergency Prefecture order dated 2nd November, 2011; this order stipulated the conditions the operator would need to satisfy in order to restart site installations.

LESSONS LEARNT

This accident has highlighted a design problem within the VOC recovery system on the polymerisation unit. The initial safety studies carried out on this process (between 2008 and 2010) by a group of third-party experts and the Group's in-house experts had not addressed the possibility of a change in the state of captured VOC followed by forced flow of the liquid phase into this recovery line, despite the considerable VOC enrichment in the line's atmosphere compared to the initial situation before extrusion unit remodelling (limited to the capture of VOC degassed by silos).

The operator commissioned a third-party expert to verify the content of these initial 2008-2010 safety studies conducted on the extrusion unit remodelling project, with an emphasis on incorporating feedback stemming from the first few months of operations for this new extrusion unit.

The set of actions decided subsequent to this study were implemented prior to restarting the polymerisation unit set up with an EVA configuration.

The operator also decided to build a new system for reprocessing the VOC emitted by operating the EVA configuration polymerisation unit, making it independent of the recovery system for VOC emitted by polyethylene bead storage and degassing silos. The independence of this system relative to other production units (boilers, steam-crackers) thereby increases the level of installation safety and eliminates the possibility of accident recurrence.