CHEMICAL ENGINEERING TRANSACTIONS

VOL. 36, 2014

Guest Editors: Valerio Cozzani, Eddy de Rademaeker

ISBN 978-88-95608-27-3; **ISSN** 2283-9216

A publication of

AIDIC

The Italian Association
of Chemical Engineering
www.aidic.it/cet

DOI: 10.3303/CET1436002

Investigation and Analysis of an Explosion in a Research Laboratory at a French University

André Laurent[*a,b], Laurent Perrin[a,b], Olivier Dufaud[a, b]

[a]Université de Lorraine, Laboratoire Réactions et Génie des Procédés, UMR 7274, ENSIC, 1 Rue Grandville, BP 20451, F – 54001 NANCY Cedex
[b]CNRS, Laboratoire Réactions et Génie des Procédés, UMR 7274, BP 20451, F – 54001 NANCY Cedex
andre.laurent@univ-lorraine.fr

The accident occurred on March 24th, 2006 at 0:24 pm in a research laboratory building of the National Institution of Higher Learning in Chemistry of Mulhouse (ENSCMu) at University of Haute Alsace (France). Due to a leak from a gas cylinder, a violent explosion of ethylene took place in the enclosed laboratory space and was followed by a fire. The accident killed one professor, seriously injured a young trainee and injured 20 persons. The initial blast of the Vapour Cloud Explosion and the fire that burned for about 5 hours caused several major damages within the laboratory and the surrounding. The corresponding facilities were destroyed. Fragments were hurled up to 100 m. The sound of the shock wave was heard 10 km away. The estimated cost of the accident was about 25 M€.
The paper intends to summarize a detailed investigation report of the event. It points out the absence of hazard identification or risk analysis as a potential root cause factor, among others.

1. Introduction

A major accident took place on March 24th, 2006 in the research laboratory “Safety and Chemical Engineering” located in the building No 5 of the university's chemistry department “ENSCMu” in Mulhouse (France). The paper describes and discusses the accident and the nature of the explosion. The resulting overpressure is analysed and estimated. Particular attention is paid to the probable causes of the accident.

2. The accident

The explosion occurred on the ground floor of the three storey research building No 5 on the university campus. The research laboratory was devoted to the study of the safety of chemical reaction. The accident occurred at 0:24 pm when most of the persons working in this laboratory were gone out for lunch. The used experimental set up consisted in a gas feed line, which interconnects the gas cylinder of ethylene via a pressure regulator and the reactor vessel. Experiments were performed to study a polymerization process in presence of gaseous ethylene. At the time of the explosion the experimental setup was stopped. The immediate plausible cause of the major event was the failure of the connection line generating a loss of ethylene. The gas cylinder was left opened and, within a few minutes, the concentration of ethylene reached the lower explosive limit in the laboratory. At this stage, even a small electrical spark can create a disaster.
The explosion killed one professor in his office at the first floor, seriously injured a young trainee in an adjacent room and injured 20 persons. The initial blast and the subsequent fire which lasted about 5 h caused several major damages within the laboratory, the building No 5, the other opposite building No 2 and the surrounding. The blast blew out windows, ceilings and blackened walls. Fragments were hurled up to 100 m. The sound of the shock wave was heard 10 km away.

Figure 1: Selection of relevant photographs indicative of the damage on the building No 5 (front of the building – inside laboratory room – collapse of the floor).

3. Analysis

The causes underlying the ENSCMu accident were not quoted in real detail in the open literature. The criminal proceedings of the event have only concluded in September 2012. It is yet possible to publish the information of the putative root causes concerning the technical aspects.

The investigation revealed a number of unsafe practices, those have become accepted practices. The expert report showed that the experimental assembly used inadequate substandard rubber tubes and that the gas cylinder was maintained open, although the experiment was stopped. The diameter of the rubber tube was not adapted to the nozzle hose of the valve of the pressure regulator. The whole absence of clamping rings for a safe interlocking of the connecting line was also established. The brittleness of the glass pieces (derivation, stopcock valve...) was underlined. From the expert's point of view, the assembly of the experimental apparatus was qualified as 'a doing odd jobs with decayed and used materials' (Louvel, 2012).

Moreover the valve hand wheel used to open and close the gas cylinder was full open (two turns), when the good practice recommended only a quarter of a turn, at the most half a turn. Before the event, the used gas cylinder of ethylene (initial conditions: 70 bars, 10 m^3) was filled two third. After the accident, the gas cylinder was found completely empty. The order of magnitude of the volumetric flow rate of the leak was estimated between 300 L/min and 500 L/min during 4 to 14 min.

A check has to be made after the event to determine which ignition sources were likely to ignite ethylene – air mixtures. The Minimum Ignition Energy (MIE) is 0.07 mJ; the auto-ignition temperature is 490 °C. The indexed sources present in the laboratory room are the electric spark from a switch of the drying oven, the phone and the computer. Static electricity of the gas was excluded owing to the absence of solid particles. Self heating of the gas mixture during the flow rate of the leak was also impossible.

To sum up, the immediate underlying cause of this major event was the failure of the connection line generating a loss of ethylene. The leak was caused by the spontaneous removal of the inadequate hosepipe from the nose of the pressure reducer. The ignition source, a spark, came probably from the switch of an oven.

4. Effect

4.1 The potential explosive atmosphere

When a flammable gas mixture burns, a large increase in volume occurs, principally due to the high temperature of the combustion products formed. If this process occurs within a confined (or semi-confined) space such as a laboratory, a building or enclosure, the presence of the confining walls prevents free expansion of the combustion products and results in a pressure increase. The presence of obstacles (called congestion) within the flow field of the gas cloud produces turbulence which enhances the burning velocity, accelerates the combustion rate and increases the flame speed. For very high flame speeds, a transition from deflagration to detonation can occur. Ethylene is a colourless gas highly flammable and explosive. Gaseous ethylene is well known for its susceptibility to detonate when mixed with air. The deflagration and confined detonation limits in air are respectively 2.7-36 %v/v and 3.3-14.7 %v/v, i.e. the detonation domain is narrower than the flammability zone. It should be noted that these limits should be treated with great caution (James, 2003).

By considering the tri-dimensional 10 m x 3.5 m x 2.9 m laboratory room, it is possible to determine the potential concentrations of ethylene in air. For example, by using the values of the flow rate and the duration of the leak previously indicated, the estimated volumetric concentrations are respectively 3.5 %v/v and 7 %v/v. Remember that the corresponding Lower Explosive Limit LEL of a gaseous mixture of ethylene in air is 2.7 %v/v.

Consider the global combustion reaction of ethylene in air:

$$C_2H_4 + 3[O_2 + 3.76\ N_2] \rightarrow 2CO_2 + 2H_2O + 11.28\ N_2$$

In the combustion reaction in air the stoichiometric concentration of any reactant is the concentration theoretically required for complete conversion by reacting completely with oxygen. In this case, at the stoichiometry, the reaction involves the direct combination of three moles of oxygen (or approximately 15 moles of air) with one mole of ethylene. The corresponding stoichiometric concentration is 6.6 %v/v. Hence, for a leak of 500 L/min during 14 min the concentration of the obtained mixture present in the laboratory room is of the same order, consequently stoichiometric.

4.2 Overpressure effects

An explosion typically generates overpressure, thermal and mechanical effects. Due to the difficulties to observe and to point out precisely the impacts of the damages, we will only concentrate on overpressure effects. Overpressure effects are visible up to 200 m from the explosion source. They appear as more or less severe damages to the buildings, broken windows glasses, damaged doors, ruptured window frames, bent metal structures and claddings, partial collapse of floor and dispersal of interior content. The damage caused by the explosion has also impacted the buildings surrounding the research laboratory. Shattered windows were found up to a distance of 100 m away from the source. The photograph in Figure 1, showing the wreckage of the laboratory room, clearly illustrates elements of obstructed confinement. The explosion was unusual because it generated much higher overpressure than would usually have been expected from a vapour cloud explosion.

4.3 Deflagration or detonation?

Detonation limits tend to widen as the size of the delimited space volume increases. But the detonation pressure depends on the detonation velocity and is not a function of the dimensions of the volume (but volume shape and size affect deflagration velocity). A useful indicator of the materials susceptibility to detonation is the Maximum Experimental Safe Gap (MESG). The lower the MESG, the more easily the gas will detonate. The reported value of MESG for ethylene is 0.65 mm.

A detonation wave has a complex three-dimensional cellular structure. The cell width λ and the cell length L_C are two fundamental characteristics of a detonation wave. The corresponding values for an ethylene-air mixture are respectively 20 to 31 mm and 39 mm. For a given mixture there is a critical dimension below which detonation will not occur. For rectangular channels (as the examined laboratory room) the requirement for successful propagation of detonation is $h > \lambda$, where h is here the height of the laboratory room. It should be noted that a safety factor is needed to allow for the dispersion of the reported values of λ (James, 2003).

Deflagration ignition energies are usually on the order of 10^{-4} J (here for ethylene 0.07 mJ), whereas direct initiation of detonation requires an energy of approximately 10^{6} J. (CCPS, 1994). Considering the high energy required for direct initiation a detonation, it is a very unlikely occurrence. But a classical deflagration flame in a detonable mixture can be accelerated to detonation by turbulence induced by friction with the walls and by the degree of confinement and/or obstruction.

4.4 Attempt to assess the values of the overpressure

First an estimation of the overpressure was deduced from the analysis of the damage on the structures. Observed damages were compared to the database of typical damages related to overpressure levels. An interval of overpressures was then determined. No consideration is given to the details of elements fixings and ruptures. For example, Figure 2 shows the overpressure damages observed on the façade of the building No 2 located at 50 m in front of the building No 5, source of the explosion. The correlated values of the overpressure are in the range of 20 to 50 mbar (window glass cracks – warped frames, some of them ruptured). This estimation may not be very accurate, but it gives a good order of magnitude.

Figure 2 – Example of overpressure damages in the building No 2 located at 50 m in the front of the building No 5, source of the explosion (Neunlist, 2007).

Then, the most frequently used prediction method, TNO multi-energy, was applied to the flammable vapour cloud present in the laboratory room. The volume of the room was considered as semi-confined with congestion obstacles. The method uses the classical graphical relationship between dimensionless overpressure and combustion energy scaled distance.

The real blast side-on overpressure P_S and the positive impulse i_+ can be calculated at some distance R from the source from the Sachs-scaled quantities:

$$\overline{\Delta P_S} = P_S / P_0 \qquad \overline{i_+} = 2\left[\frac{c_0}{P_0^{2/3}E^{1/3}}\right]i_+ \qquad \overline{R} = \frac{R}{\left[E/P_0\right]^{1/3}}$$

where $\overline{\Delta P_S}$ is the scaled side on-overpressure, $\overline{i_+}$ the scaled positive impulse, $\overline{R}$ the scaled distance, P_0 the atmospheric pressure, E the charge combustion energy and c_0 the ambient speed of sound (Alonso et al. 2006).

The most probable selected scenario considers that ethylene presents a high reactivity (group II B). The laboratory room contains, at stoichiometric conditions, an initial mass of 8 kg of ethylene mixed with air. The stoichiometric combustion energy is estimated to be 3.64 MJ/m^3. Because it is usually very difficult to evaluate subsequently the conditions which may induce the initial blast, a conservative approach is to apply an initial strength index of 10 to the charge blast model. The local partial confinement due to the presence of obstruction congestion of the laboratory room may easily act as an initiation for detonation, which may propagate well along the length of the laboratory room. The explosion type is a detonation for this scenario. Remember nevertheless that the TNO model applies, at best, to the far field. Near field blast effects are mostly directional as a consequence of a potential direction in the combustion process induced by confinement.

These assumptions are supported by different explosion tests on ethylene - air mixtures conducted by the MITI in Japan (Mannan, 2012). In one of these tests, an ethylene mixture containing 4.08 kg of C_2H_4 (i.e. 7 % v/v mixture) exploded with a detonation. The obtained blast pressures were respectively 4.9 bars at 5 m and 0.49 bar at 20 m distance. The TNT equivalent of the explosion was estimated at 49.2 kg.

French regulation defines the following blast overpressure thresholds concerning the damage to the structures: 20 mbar = windows breakage (safe distance probably of 0.95 of no serious damage beyond the value); 50 mbar = minor damage to house structures; 140 mbar = major serious destruction (partial collapse of walls and roofs of houses); 200 mbar = domino effects and 300 mbar = severe damage, partial demolition (cladding of light buildings ruptured). More detailed information concerning the damage produced by blast is given in the appendix B of CCPS (1994).

Table 1 summarizes the variations of the overpressure and of the positive impulse, calculated with the TNO model, as a function of the distance *R* from the source

Table 1: Variation of the overpressure and of the positive impulse with the distance

P_S (mbar)	$\overline{R}$(-)	R (m)	$\overline{i_+}$ (-)	i_+ (Pa.s)
20	11.6	178	0.009	20.5
50	5.1	78	0.021	47.9
140	2.2	34	0.050	114
200	1.7	26.2	0.065	148
300	1.3	20.3	0.087	198

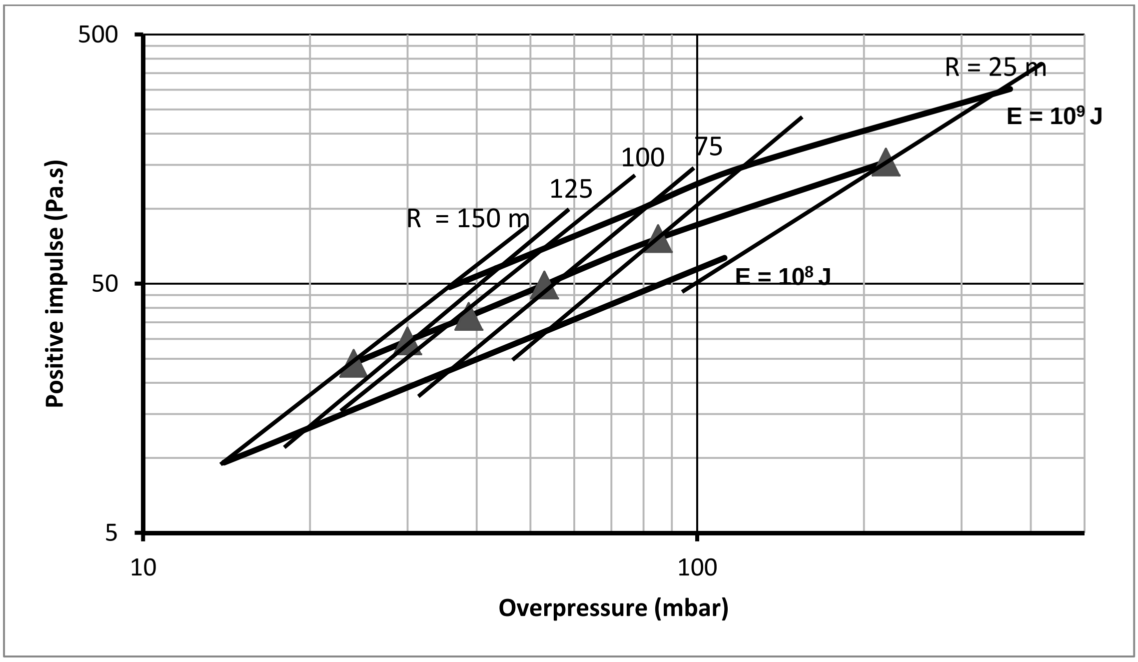

Figure 3: Characteristic curves (overpressure - impulse relationship) and iso-distance lines of the explosion with different energies and a charge strength of 10. Black triangles: the present case.

The observed damages are consistent with the respective values of the overpressure with the distance *R*. At shorter distances, i.e. in the near field, the effects are probably significantly higher. It explains the importance of the existing damages inside the building housing the laboratory room.

For an explosion it is possible to obtain the overpressure – impulse – distance relationship called the ‘characteristic curves’ following the simple and fast methodology proposed by Alonso et al.(2006). Figure 3 shows these curves for two values of the explosion energy with the corresponding iso-distance lines. The characteristic curve (black triangle caption) illustrates the potential effects of the explosion of the ethylene – air stoechiometric mixture which occurred in the laboratory room. It should be underlined that the greater the explosion energy for a fixed strengh index (here 10), the higher the impulse for the same overpressure.

5. Conclusion and lessons learned

The detailed investigation into this major accident provides an opportunity to improve the laboratory safety. It is therefore important that the lessons have been learnt. The US Chemical Safety and Hazard Investigation Board reported that the academic laboratory accident rate was 10 to 50 times higher than that in industrial laboratories (Leggett, 2012).

The direct recommendations resulting from the tragic explosion in the ENSCMu can help to avoid other damaging events in the future:

- A flammable gas cylinder should be stored in a detached and well ventilated or open sided building.
- The gas cylinder in use should only be present near the experimental apparatus during the duration of the practical work.
- The proper selection and assembly of adapted and unused components in an experimental system are critical factors.
- Do not mix different brands of tube fittings in the same assembly apparatus and install fittings correctly.
- The fixed permanent lines of connection of the equipment and piping should be examined and realized with a great care.
- Whenever possible, avoid the use of glass ware.
- In the academic laboratories it is not uncommon to build a temporary rig with connections made to certain services by a hose rather than fixed piping. If this is accepted in certain applications, care is still needed to ensure that the practice does not extend to unsuitable cases or to operation over extended periods.
- The ATEX regulations should be full applied to the explosive environment of the laboratory room.
- Equip the laboratory room with gas detectors.
- Check the presence of clear written operating procedures and checklists at all steps of the experimentation.

More generally improving laboratory safety is not an easy task and requires support at every level within an organization. Jensen and Jorgensen (2013) reported a system for safety assessment in university research and teaching laboratories. Schmidt (2003) proposed that process and plant safety competences should be developed at university and must be taught through mandatory lectures. More specifically Louvel (2012) identified deficiencies at several levels of the safety management structure at ENSCMu and University of Haute Alsace. Particularly the subsequent investigation findings pointed out the absence of a hazard identification or risk analysis as a root cause factor. Finally, safety is a collective responsibility that requires the full cooperation of everyone in the laboratory. However, the ultimate responsibility for safety is incumbent upon the person actually carrying out some type of experimental procedure. For example, in the case of the present accident, the Supreme Court of Appeal finally found the person in charge of these experiments guilty of involuntary homicide and causing injury by negligence. The Court gave him a suspended 18-months prison sentence and a fine of 8,000 € (Louvel, 2012).

References

Alonso F.D., Ferrada E.G., Sanchez Perez J.F., Aznar A. M., Gimeno J.R., Alonso J.M., 2006, Characteristic overpressure-impulse-distance curves for vapour cloud explosions using the TNO Multi-Energy model, Journal of Hazardous Materials, A 137, 734-741.

CCPS, 1994, Guidelines for Evaluating the Characteristics of Vapour Cloud Explosions, Flash Fires and BLEVES, AIChE, New York, USA.

James H., 2003, Detonations, Report TD5/039, Health and Safety Executive, Bootle, Merseyside, UK.

Jensen N., Jorgensen S.B., 2013, Learning safety assessment from accidents in a university environment, Chemical Engineering Transactions, 31, 427-432.

Leggett D., 2012, Identifying hazards in the chemical research laboratory, Process Safety Progress, 31(4), 393-397.

Louvel M., 2012, Supreme Court of Appeal, Criminal Court, Judgment of September 11th, 2012, Appeal No 11-87119 (in French).

Mannan S., 2012, Lees' Loss Prevention in the Process Industries, Fourth Edition, Elsevier Butterworth Heinemann, Oxford, UK.

Neunlist S., 2007, Explosion at ENSC Mulhouse, Assessment of the disaster occurred on March 24th, 2006, Day seminar, ADHYS Lille, March 23th, 2007 (in French).

Schmidt J., 2013, Process and plant safety – Research & education strategy to keep long term competences, Chemical Engineering Transactions, 31, 421-426.