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Explosion of 14th January 2020 at IQOXE

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The explosion of 14th January 2020 at IQOXE (Industrias Quimicas del Óxido de Etileno) in Tarrogona, Spain, lead to the deaths of 3 people. In this paper we present:

- The ethoxylation reactor which exploded,
- The process used to make MPEG 500 (polyethylene glycol methyl ether of average molar mass 500),
- The damage resulting from the explosion,
- The technical causes of the explosion,
- Essential safety requirements for ethoxylation reactors, especially for pressure relief.

In the light of this accident and the large number of ethoxylation reactors which are operating worldwide, there are several lessons which can be learnt and we hope that they will help to avoid any repetition.

1. Introduction

1.1 IQOXE

IQOXE stands for Industrias Quimicas del Óxido de Etileno. This company was established in 1964 and is part of the CL industrial group. The main activity of the company is the manufacture of ethylene oxide (EO) and derivatives. It is located in an industrial complex in Tarragona, Spain, roughly 2 km from the sea (

1.2 Description of the reactor R3131

The reactor R3131 was of quite conventional design, being a vertical cylinder with rounded ends, a total volume of 37.2 m^3 and a design pressure of 45 bar gauge. It was equipped with

- a large circulation loop equipped with the pump P-3131, heat exchanger E-3131 and a Venturi injection nozzle to inject the reaction mixture back into the top of the reactor,
- a small circulation loop equipped with the pump P-3132, heat exchanger E-3132 and a Venturi injection nozzle to inject the reaction mixture back into the top of the reactor,
- an inlet system for EO including two pumps P-3135A and P3135B,
- a similar inlet system for propylene oxide (PO)
- a pressure relief valve (PSV),

The system used to inject EO is intended to avoid overcharging this material. There are two pumps, P3135-A and P3135-B. At a given moment, one or other pump is in service and running. The EO is recirculated back to the stock tank via a control valve. The position of this valve is piloted by a pressure control loop, intended to keep a constant pressure in the feed pipe to the reactor. There is another control valve, on the line to the reactor itself, which is piloted by a flow control loop, so that the EO feed rate is kept constant at the intended value during the reaction. A simplified diagram of the reactor is shown below in Figure 1.

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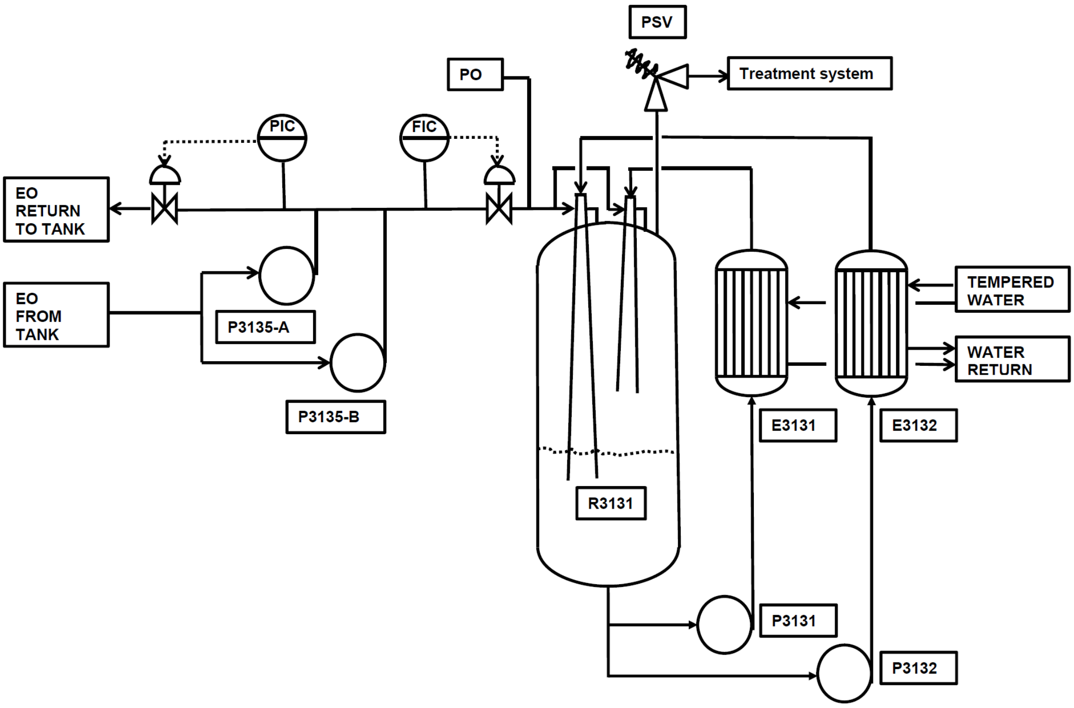

Figure 1: Simplified diagram of the reactor R3131

1.3 Description of the process operated

The reactor R3131 was being used to produce MPEG 500, i.e. poly(ethylene glycol) methyl ether of average molar mass 500, by the following reaction.

$CH_3OH + 10\ C_2H_4O \rightarrow CH_3O(C_2H_4)_{10}H$

The reaction is exothermic: $\Delta H = -115$ kJ/mole EO. At the start of a batch the reactor is empty under nitrogen at atmospheric pressure and room temperature. It is charged with:

- Methanol 1341 kg (41.9 kmol),
- 30 % solution of sodium methylate in methanol 47 kg (0.3 kmol).

The reactor is pressurized with nitrogen to 3 bar gauge (4 bar absolute). The mixture is circulated via the pump P-3132 and exchanger E-3132 of the small loop. It is heated to 100 °C using tempered water in the exchanger. Feeding is then started of

- Ethylene oxide 19104 kg (434 kmol)

Feeding of ethylene oxide continues over a period of several hours at 100-110 °C, whilst the mixture is cooled via E-3131 and the pressure rises to 11 bar gauge (12 bar absolute). During the addition of ethylene oxide, once the volume of mixture present is sufficient, the circulation via the pump P3131 and the exchanger E-3131 of the large loop is started up. Once the addition of ethylene oxide is complete, the mixture is heated to 140 °C and held for 30 minutes. The mixture is transferred under pressure to the post-treatment vessel V-3141 (not shown in figure 2) and neutralized by addition of:

- Acetic acid 16 kg (0.3 kmol).

Ethoxylation looks simple enough on paper but has some quite unique features. One of these is that the ethylene oxide is present in both the gas and liquid phases of the reactor. Ethylene oxide is injected into the gas phase but it reacts with the substrate in the liquid phase. The reaction rate depends on two steps:

- the rate of dissolution of the transfer of ethylene oxide from the gas to the liquid phase,
- the rate of reaction of the ethylene oxide with the substrate in the liquid phase.

Another is that there is no mechanical agitator. The agitation required is provided by the two injection loops.

2. Explosion of 14th January 2020

2.1 Outline description of the accident

The accident of 14th January 2020 involved the explosion of the ethoxylation reactor R3131 and led to the death of three people. The explosion of the reactor R3131 gave rise to over one hundred fragments, which were spread over a wide area. In particular the bottom plate of the reactor, weighing between 750 and 1000 kg, was projected 2.5 km and hit an apartment building, killing one person. The 3100 production unit, housing the reactor, was wrecked and the control room, situated 25 m away was destroyed, along with the process control unit. Two people working on the plant were killed in the explosion. The explosion led to the formation of two fireballs, the second one larger than the first. The blast wave led to widespread damage on the site of IQOXE and the surrounding area. For example, on the nearby site of BASF, situated about 600 m from the reactor, windows were shattered and there was some slight damage to buildings. The timeline is shown below in Table 1 (Hopwood et al, 2020).

Table 1: Timeline

Time	Observation	Reference
12.40	Batch 7 of MPEG 500 is started	
15.00	EO feeding starts	
17.58	EO feeding stops (17200 kg taken from EO tank)	Tank farm records
18.10	Heating applied for cook down phase	Factory records of steam usage
18.15	Power consumption stops	Factory records of power usage
18.30	Power consumption restored	Factory records of power usage
18.40	Loud depressurisation noise lasting 10-15 s	Witness
	Fire outside reactor captured on video	
	Reactor explodes	
	First fireball erupts	
	Second fireball erupts (larger than the first)	
	Fire on propylene oxide tank	

2.2 Hypothesis 1: thermal decomposition of MPEG 500

The intended product, MPEG, undergoes exothermic decomposition, giving some 700-1000 J/g above 350 °C in Differential Scanning Calorimetry (Sempere J. and Serra E., 2020). The threshold of detection is clearly above temperatures expected to be reached in the process. The normal temperature is 100-110 °C during the addition of ethylene oxide and 140 °C during the cook down phase.

There might have been a runaway reaction of ethylene oxide with the substrate (see hypothesis 2). But for this to happen and to approach 350 °C, the ethylene oxide content of the reactor would have to be substantial. If so, given that the thermodynamic critical temperature of ethylene oxide is 196 °C and its critical pressure 72 bar absolute, the reactor would have exploded before approaching temperatures where decomposition of MPEG might be expected.

Another possibility is that some material catalysing the decomposition of MPEG was present, so that it occurred at normal process temperatures, but we are not aware of any evidence of such contamination.

2.3 Hypothesis 2: runaway reaction

A runaway reaction is suggested by the fact that pumped circulation was lost for fifteen minutes during the incident and that the explosion occurred ten minutes after circulation was restored. The loud depressurization noise lasting 10 to 15 seconds could correspond to the opening of the pressure relief valve.

On the other hand, the inventory of ethylene oxide in this kind of reactor is normally quite small, in our experience around 1.5 % of total reaction mass at any given time. The limit is related to the system used to inject ethylene oxide. If too much is added the pressure goes up and this limits the flow rate of ethylene oxide into the reactor. In our experience, so long as the inventory is limited in this way, if agitation is lost there is a transient increase in temperature (by 15 to 20 °C) and pressure (by 2 to 3 bar) but well within the design limits of the system.

It may be that insufficient catalyst was added at the start of the reaction. This would have allowed unreacted ethylene oxide to build up in the reactor. The operators would have seen abnormally high pressures at the normal reaction temperature, but they may not have understood the significance of this and they may have carried on adding ethylene oxide. The runaway reaction seems to have occurred during the cook down phase where the normal temperature is 140 °C, higher than the range of 100 °C to 110 °C used during the ethylene oxide addition.

For a typical ethoxylation process operated by Solvay the reaction kinetics we have measured lead to the following estimation of Time to Maximum Rate:

- About 10 minutes from 110 °C,
- About 1 minute from 140 °C.

These figures refer to a typical mixture containing normal amounts of catalyst but an excess of ethylene oxide. The timeline indicates that 30 minutes elapsed between the start of the cook down phase and the explosion of the reactor. This supports the hypothesis that the reaction mixture did not have a normal amount of catalyst, leading to a delayed reaction.

2.4 Hypothesis 3: gas phase explosion

Pure ethylene oxide vapor is known the support gas phase explosions in the absence of any oxidant gas, such as oxygen. The reactions involved generate methane, hydrogen and carbon, for example:

$C_2H_4O \rightarrow \frac{1}{2} CH_4 + CO + H_2 + \frac{1}{2} C$

During the normal process, the vessel is pressurized with nitrogen to 4 bar absolute. During the addition of ethylene oxide, the pressure rises related to two factors:

- the volume of the liquid phase increases and that of the gas phase decreases,
- ethylene oxide is now present in the gas phase

The partial pressure of nitrogen is a function of the temperature and the volume of the headspace. The partial pressure of ethylene oxide is a function of the temperature and the inventory of this material in the system. During the addition of ethylene oxide the proportion of nitrogen is calculated, and the total pressure at any one time is limited to keep the proportion of nitrogen at 60 % volume or more, corresponding to the “Limiting Concentration of Nitrogen”. With 60 % volume or more of nitrogen, no explosion is expected.

It may be that there was a leak of some kind, in which case the process control system would have added more ethylene oxide to replace the nitrogen and the gas phase mixture might have been within explosive limits. Also, the fire outside the reactor, seen just before the explosion may have heated the gas phase, leading to ignition of the mixture. The absolute pressure would then have risen by a factor of 8, from 12 bar absolute to 96 bar absolute (95 bar gauge). This might have been enough to cause explosion of the vessel, whose design pressure was 45 bar gauge.

On the other hand, a gas phase explosion would have been very rapid, leading to an explosion of the vessel in under one second. This does not agree with the loud depressurisation noise, estimated to have lasted 10 to 15 seconds and thought to correspond to the opening of the PSV.

2.5 Hypothesis 4: runaway reaction followed by gas phase explosion

If a runaway reaction occurred as described in hypothesis 2, it may have been followed by an internal gas phase explosion. If excess ethylene oxide was present, then the reactor pressure would have reached 46 bar absolute at 165 °C, enough to open the pressure relief valve, whose set pressure was 45 bar gauge. At this point, the gas phase would have been rich in ethylene oxide, because the partial pressure of nitrogen would only have been around 7 bar absolute. We can estimate that the mixture contained only 15 % volume nitrogen and 85 % volume ethylene oxide. This is clearly in the explosive range.

Just before the explosion occurred, a fire was seen on the outside of the reactor. It may be that when the pressure relief valve opened it subjected the lines downstream high pressure causing a leak or a leak may have occurred from a flange on the reactor or from another point. This fire would have heated the metal of the vessel and the gas mixture inside leading to a gas phase explosion. This would have raised the internal pressure by a factor of 8 (Siwek R. and Rosenburg E., 1989), to some 367 bar g and caused the explosion of the reactor.

2.6 Analysis of blast damage

We have estimated the explosion energy and the distance to overpressure effects for the four hypotheses formulated above, using the method given in the TNO yellow book (Van den Bosch C.J.H., and Weterings R.A.P.M., 1996). For hypothesis 1 we have considered the explosion of a mass of 20500 kg MPEG with an energy content of 1000 J g^{-1}. For hypotheses, 2 to 4 we have considered a pressure vessel burst and our estimation of energy is based on a free space volume of 15 m^3. In all cases, we have doubled the effective explosion energy, E_{ex}, to take account of the reflection of the pressure wave at ground level. The results are shown below in Tables 2 and 3.

Table 2: Effective explosion energy

Hypothesis	Description	E_{ex}
1	Decomposition of 20500 kg MPEG	4.10×10^{10} J
2	Runaway reaction leading to vessel burst at 135 bar g	1.01×10^{9} J
3	Gas phase explosion leading to vessel burst at 95 bar g	1.14×10^{9} J
4	Runaway reaction leading to vessel burst at 367 bar g	4.40×10^{9} J

Table 3: Distance to pressure effects

Pressure	Effects expected	Hypothesis 1	Hypothesis 2	Hypothesis 3	Hypothesis 4
20 mbar	50 % of glass windows broken	900 m	260 m	270 m	430 m
50 mbar	75 % of glass windows broken	450 m	130 m	135 m	215 m
140 mbar	Partial collapse of walls and roofs of houses	205 m	60 m	65 m	100 m
300 mbar	Damage to buildings	125 m	35 m	40 m	60 m

The damage caused by the explosion was widespread. According to Hopwood et al., 2020, the distance to broken windows was 200 m, but we understand that windows were damaged on the site of BASF, some 600 m away. The distances for 20 mbar predicted seem too small in the case of hypotheses 2 and 3. Hypotheses 1 and 4 are not far from predicting the observed effects, with respective distances of 900 m and 430 m to 20 mbar. All four hypotheses predict the destruction of the control room, situated 25 m away.

2.7 Sizing of pressure relief valve

It might be asked whether the explosion of the reactor could have been prevented with by correctly sized pressure relief valve. The technique of pressure relief is widely used in the chemical industry. Many reactors are fitted with pressure relief valves and rupture discs, designed to open in the case of excessive pressure. Some reactors are indeed fitted with pressure relief valves to cope with a runaway reaction. In such cases, the sizing of the valve or rupture disc has to be adapted to the rate of the reaction concerned. We know that the pressure relief valve of the reactor R3131 had a 3 inch inlet flange. We have assumed the following characteristics, based on a typical 3 inch valve whose characteristics are known to us.

- Orifice area = 1840 mm^2
- Discharge coefficient (gas) = 0.6
- Discharge coefficient (liquid) = 0.3

We have tried to see whether the relief valve is correctly sized in this case, by using kinetic and pressure-temperature data for a typical Solvay process operating under comparable conditions. We have used the international standard on two phase pressure relief valves ISO 4126-10 (2010). We have considered four different set pressures from 6 to 9 bar gauge, as shown below in Table 4.

Table 4: Size of pressure relief valve required as a function of set pressure

Set pressure	Peak temperature reached	Self heat rate	Orifice area required	Diameter
6 bar g	101 °C	0.01 °C/s	1058 mm^2	37 mm
7 bar g	118 °C	0.04 °C/s	5835 mm^2	86 mm
8 bar g	136 °C	0.16 °C/s	21193 mm^2	164 mm
9 bar g	153 °C	0.49 °C/s	194889 mm^2	498 mm

In order for a 3 inch valve, with an orifice area of 1840 mm^2, to be useful in controlling a runaway reaction, the set pressure would have to be 6 bar gauge or less. Indeed, to our knowledge, pressure relief is only considered for the runaway case on ethoxylation reactors operating at low pressure.

3. Prevention of explosion of ethoxylation reactors

3.1 Basic Process Control System

In any process, the Basic Process Control System is used to control the addition of materials, heating and cooling etc. In an ethoxylation process, it is also used to calculate the proportion of nitrogen in the gas phase of the reactor. This calculation is based on measurements of the temperature and the pressure combined with the calculated partial pressure of nitrogen. The process should be run to keep this at a safe level, for example 60 % volume of nitrogen, corresponding to the Limiting Nitrogen Concentration.

3.2 Safety Instrumented System

There should be an independent Safety Instrumented System with suitable interlocks to prevent operation in unsafe conditions. These should include:

- Temperature too low,
- Temperature too high,
- Pressure too high,
- Loss of agitation.

3.3 Pressure relief

Pressure relief may be considered for the following cases:

- External fire,
- Runaway reaction (only on reactors operating at low pressure),
- Internal gas phase explosion.

3.4 Explosion suppression

In some companies, explosion suppression systems are used as a safeguard against internal gas phase explosions. These systems operate by detecting the start of a pressure rise and injecting extinguishing material very rapidly. They have the advantage that no release of ethylene oxide occurs.

4. Conclusions

In the light of the available evidence, the explosion of 14th January 2020 was caused by the failure to add sufficient catalyst to the reactor, compounded by a failure to realise that unreacted ethylene oxide was building up in the system. It is also possible that the runway reaction was followed by an internal gas phase explosion.

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