

Explosion in an Exhaust Line of a Chemical Reactor

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An explosion occurred in the exhaust line to the scrubber during a cleaning procedure with concentrated nitric acid in a chemical reactor. Previously the reactor was treated with methanol under reflux and afterwards rinsed with drinking water.

The detonation destroyed completely a section of a PN 16 condensate pipe after a flame arrestor. Glass piping, several fittings and the flame arrestor were also severely damaged. Also windows were damaged in the production room.

The aim of this paper is to outline the incident investigation involving: the determination of potential explosive substances or explosive atmosphere in the pipe; a systematic analysis of ignition sources; a definition of possible scenarios of the explosion causes and sequence; a plausibility assessment of the scenarios regarding the observed damage; an evaluation of the probability of the scenarios; and a proposal of safety concepts to avoid future incidents.

The investigation involved the use of Differential Scanning Calorimetric measurements (DSC) and analytical procedures from different samples remaining in different parts of the equipment after the explosion.

The most probable cause of the incident was the formation of methyl nitrate in the condensing line of the flame arrestor. The detonation was initiated by the heat produced by the reaction between condensed nitric acid and methanol.

Lessons learnt were used to modify the process to improve its safety.

1. Incident sequence

After performing a synthesis step in a chemical reactor, the reactor had to be cleaned with nitric acid in order to eliminate traces of a catalyst used in the process. The cleaning procedure included: reflux with methanol under atmospheric pressure, rinsing with water and reflux with concentrated nitric acid under reduced pressure. The installation is schematically described in the Figure 1.

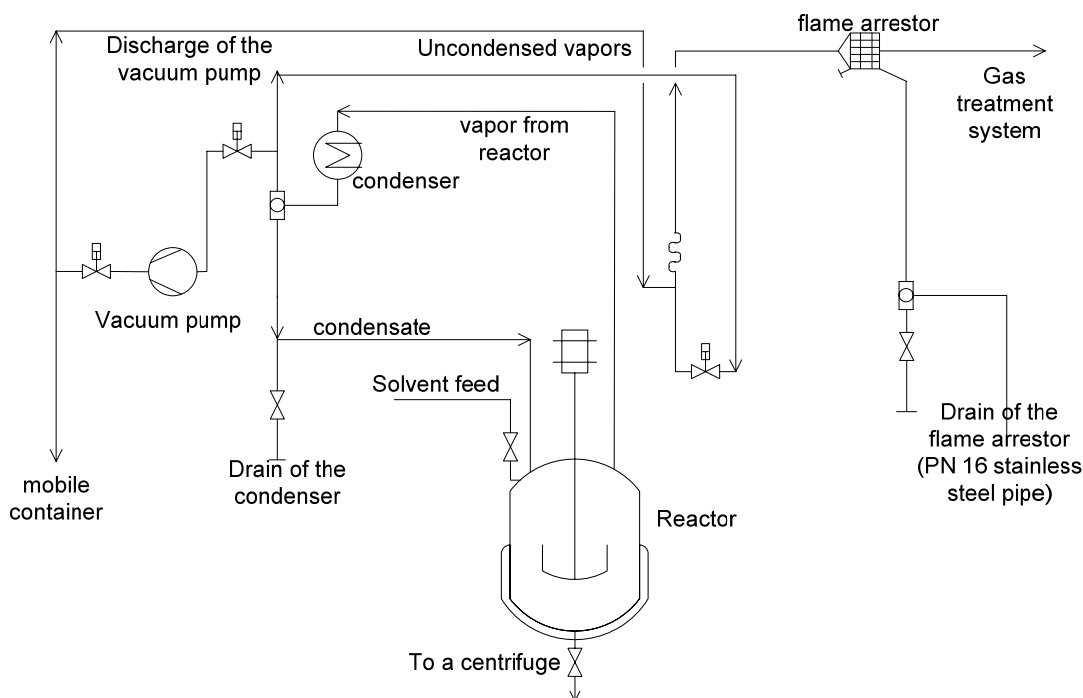


Figure 1: Schematic drawing of the plant

1.1 Reflux with methanol under atmospheric pressure

Methanol was heated to reflux in the reactor. The uncondensed vapours flow into the gas treatment system, wherein a condensation of methanol in the flame arrestor is usually observed. The condensate is collected in a PN 16 stainless steel drain. The day of the incident the drain of the condenser was emptied after discharging the methanol. The drain of the flame arrestor was not emptied.

1.2 Rinsing with water

300 L of water were charged to the reactor through a spraying nozzle in order to wash out the methanol.

1.3 Reflux with nitric acid under reduced pressure

After draining the water, a vacuum pump reduced the pressure in the reactor to 600 mbara, 300 kg of nitric acid 62 % were then charged from a mobile container. After the charge was completed, the jacket temperature of the reactor was set to 80 ° C. At the same time, the reactor was gradually evacuated to 110 mbara. Nitric acid vapours were condensed. The cooling medium temperature in the condenser was 0 °C. After approx. 20 min. an explosion occurred in the exhaust line of the reactor. The detonation destroyed completely a section of the PN 16 stainless steel drain of the flame arrestor. Glass piping, several fittings and the flame arrestor were also severely damaged. Also windows were damaged in the production room.

2. Systematic analysis of the possible causes of the explosion

A systematic analysis was performed in order to determine:

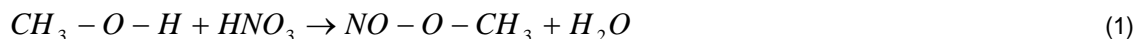
- Which explosive substances or explosive atmospheres have been potentially present in the exhaust line of the reactor at the time of the explosion
- What are the effective initiators or ignition sources

Based on this analysis, several explosion scenarios were drawn. The hypothetical consequences of these explosion scenarios have been compared with the observed damage in order to determine the most likely cause of the event.

3. Determination of potential explosive substances or explosives atmospheres in the exhaust line

3.1 Potential explosive substances: methyl nitrate

Methyl nitrate is an organic nitric acid ester formed by the chemical reaction of nitric acid and methanol. The reaction is exothermic with an enthalpy of -147.2 kJ / mol (Kohler et al., 1995).



A gas chromatography analysis of the liquid found after the explosion in the section of the drain of the flame arrester that was not destroyed confirmed the presence of approx. 25 g/L of methyl nitrate.

A differential Scanning Calorimetry measurement of the same sample identified an exothermic decomposition in the temperature interval of 160 to 230 °C with an energy of approx. 200 kJ/kg. This may correspond to the heat of decomposition of methyl nitrate. The other compounds identified in the sample included different organic solvents used in the synthesis steps performed in the reactor since the drain was emptied.

3.2 Hypothesis for the formation of explosive gas or vapour atmospheres

Explosive atmospheres could be present in the exhaust line of the reactor at the moment when the incident occurred. These may be formed by methanol or another solvent vapours and oxygen.

Also NO and NO₂ may act as oxidizers as these gases are usually observed during the cleaning process with nitric acid at reflux. They can be formed e.g. by reduction of the nitric acid by rests of methanol in the reactor vessel, the condensing lines or in the gas treatment system. The decomposition of nitric acid can also produce NO₂ vapours.

4. Systematic analysis of ignition sources or initiators of the explosion

The Table 1 summarizes the results of the analysis and assessment of the likelihood of occurrence of the potential ignition sources that can ignite the explosive atmospheres identified or initiate a thermal explosion of methyl nitrate.

Table 1: Systematic analysis and likelihood evaluation of ignition sources

Ignition sources	Comments and evaluation
Chemical reactions	Methanol and another organic compounds react with nitric acid, NO and NO ₂ strongly exothermic. These reactions provide enough energy to act as a source of ignition for the explosion atmospheres identified or as initiators of thermal explosions of methyl nitrate. This ignition source is the most likely of all possible ignition sources, as methanol, other organic compounds, nitric acid, NO and NO ₂ can be present in the parts of the installation involved in the explosion.
Static Electricity	As all conductive parts were grounded and the coating of the pipes is dissipative, this ignition source is unlikely.
Mechanical sparks	Frictional or impact mechanical sparks can be excluded as ignition sources because there are no moving parts in the section of the installation involved in the explosion.
Open flames	At the time of the event no maintenance work with open flames was performed in the production building. Smoking is prohibited in the whole production area. This ignition source is excluded.
Hot surfaces	The presence of hot surfaces other than those produced by the chemical reactions described before could not be identified. This ignition source is excluded.

5. Definition of possible scenarios of the explosion: causes and sequence

5.1 Scenario identification

According to the damage observed in the section of the PN16, DN 25 mm drain pipe of the flame arrester and a literature review (Bartknecht and Zwahlen, 1993) it can be concluded that the destruction of this portion of pipe can only be caused by a detonation.

The hypothetical scenarios resulting in a detonation were systematically identified by using a chemical compatibility matrix shown in Table 2.

Table 2: Chemical compatibility matrix

	HNO ₃ (L)	HNO ₃ (g)	NO	NO ₂	O ₂	MeOH (L)	MeOH (g)	Other solvents (L)	Other solvents (g)
HNO ₃ (L)	x	x	R	R	x	1a	I	1b	I
HNO ₃ (g)		x	R	R	x	I	R	I	R
NO			x	R	R	I	2a	I	2a
NO ₂				x	x	I	2a	I	2a
O ₂					x	x	2b	x	2b
MeOH (L)						x	x	x	x
MeOH (g)							x	x	x
Other solvents (L)								x	x
Other solvents (g)									x
1a,1b, 2a and 2b	Explosion scenarios described in chapter 5.2								
I	Highly exothermic chemical reaction between two liquid phases or one liquid phase and the gas phase leading to an ignition								
R	Exothermic chemical reaction								
x	No interaction								

5.2 Scenario description

Scenarios 1a and 1b (Figure 2): Explosion in the liquid phase. In these scenarios, the explosion takes place directly in the form of a detonation in the condensate pipe of the flame arrestor. The shock wave spreads out in the direction of the flame arrestor and reflects to the gas absorption line and the venting line of the reactor.

Scenario 1a: the explosive in scenario 1a is methyl nitrate and the ignition source is the self-heating due to the highly exothermic reaction between nitric acid and methanol and its thermal decomposition.

Scenario 1b: theoretically another solvents present in the condensate line may also violently react with nitric acid to form explosive compounds.

Scenarios 2a and 2b (Figure 3): Explosion in the gas phase. In this case, the explosion starts near the outlet of the vacuum pump, and propagates as a deflagration towards the flame arrestor. A transition to a detonation occurs in the venting pipe. The flame arrestor cannot stop the shock wave and is deformed. Extremely high pressures can arise if the detonation reflects against a closed end, as it is the case in the condenser line of the flame arrestor causing the destruction of a portion of this pipe.

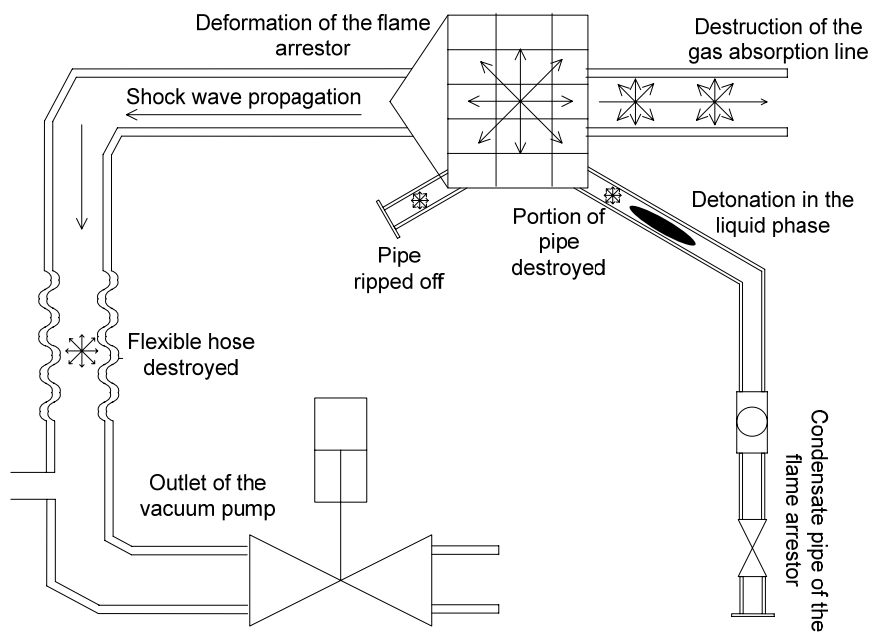


Figure 2: Schematic representation of the explosion according to scenarios 1a and 1b

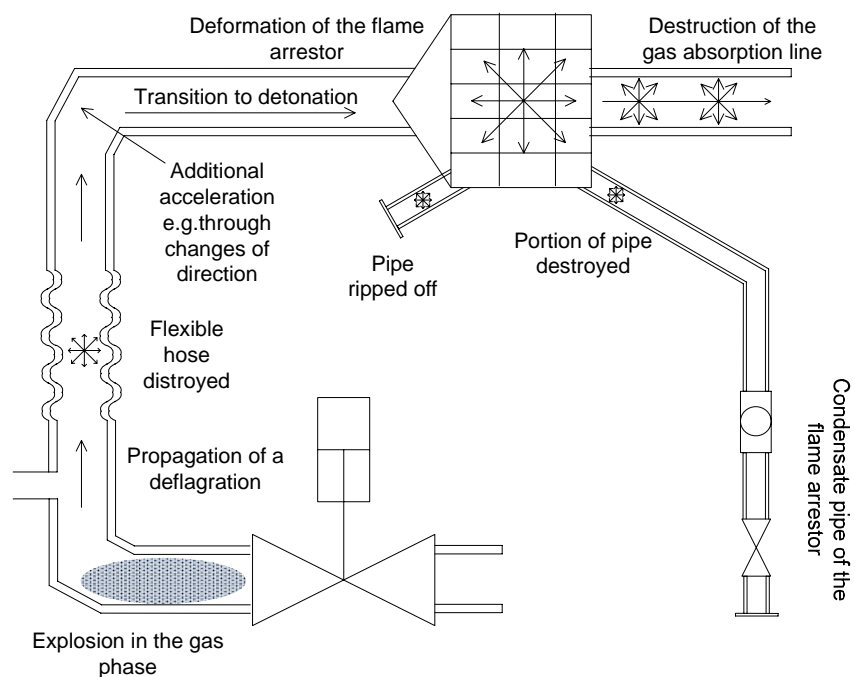


Figure 3: Schematic representation of the explosion according to scenarios 2a and 2b

Scenario 2a: the explosive atmosphere is formed by a combustible mixture of methanol vapours or vapours of other solvents with NO/NO₂ as oxidiser. As outlined in Table 1, the most likely sources are

highly exothermic local reactions between liquid residues of methanol and other solvents in the venting line of the reactor with liquid nitric acid or NO/NO₂ gas (marked as "I" in Table 2).

Scenario 2b: it is similar to the scenario 2a with oxygen as oxidiser.

6. Plausibility assessment of the scenarios regarding the observed damage

6.1 Destruction of the PN 16 stainless steel tube

Scenarios 1a and 1b: the detonative decomposition of methyl nitrate produces very high temperatures and gas release. The pressure can very rapidly exceed the bursting strength of the tube, which is approx. 2 to 3 times its nominal pressure.

Scenarios 2a and 2b: The transition to detonation in the exhaust line of the reactor and the reflection in the closed end of the drain pipe of the flame arrestor can produce pressures above 60 bar (Bartknecht and Zwahlen, 1993).

6.2 Glass breakage in the production room

A damage of windows at a distance of approx. 9m from the place of the explosion was observed. According to CCPS (1996) the lower limit of the overpressure peak resulting in glass breakage is 0.015 bar. A rough estimate of the TNT equivalents (Van der Bosch and Weterings, 1997) needed to generate this peak side-on overpressure at a distance of 9m from the detonation is 4.4 g TNT.

Scenarios 1a and 1b: the decomposition energy of methyl nitrate according to Kohler et al. (1995) is 6,700 kJ/kg. With a TNT equivalency energy of 4,000 kJ/kg, the amount of methyl nitrate needed to cause the glass breakage of the windows can be roughly estimated as 2.6 g. this small amount of methyl nitrate can be easily formed by e.g. condensation of nitric acid in the flame arrestor and reaction with residues of liquid methanol in the drain pipe.

Scenarios 2a and 2b: the energy of the detonation in the gas phase will be suddenly liberated by the bursting of the section of pipe. According to Van der Bosch and Weterings (1997), the energy liberated by a 60 cm section of pipe bursting at an overpressure of 32 bar is approx. 0.38 TNT equivalents. This energy will not be enough to break the glass of the window situated at approx. 9 m of the section of pipe.

7. Conclusions

7.1 Most likely scenario of the explosion

According to the analysis presented in the previous chapters the most likely scenario of the explosion is the condensation of nitric acid in the flame arrestor and exothermic reaction with a few grams of methanol followed by the violent decomposition of methyl nitrate in the section of the drain pipe that was destroyed by the explosion. The detonative decomposition of methyl nitrate is thermally initiated by the same reaction between nitric acid and methanol leading to its formation. This scenario is in good agreement with the damage observed, significant amounts of methyl nitrate were identified by gas chromatography in the drain pipe of the flame arrestor and a thermal initiation of the detonation is the most likely ignition source.

7.2 Lessons learnt

This scenario shows how small quantities of incompatible substances reacting in the exhaust lines of reactors can produce explosions with potentially severe consequences. The elaboration of a compatibility matrix involving all the parts of the installation must always be included in the process risk analysis.

In the particular case of cleaning reactors with concentrated nitric acid, reflux should be avoided. During the cleaning procedure, the exhaust of the reactor after the condenser should be conducted to a separate gas washing system situated as close as possible to the reactor, e.g. a mobile scrubber in order to avoid that nitric acid condensates in parts of the gas cleaning system and reacts explosively with rests of organic solvents.

References

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