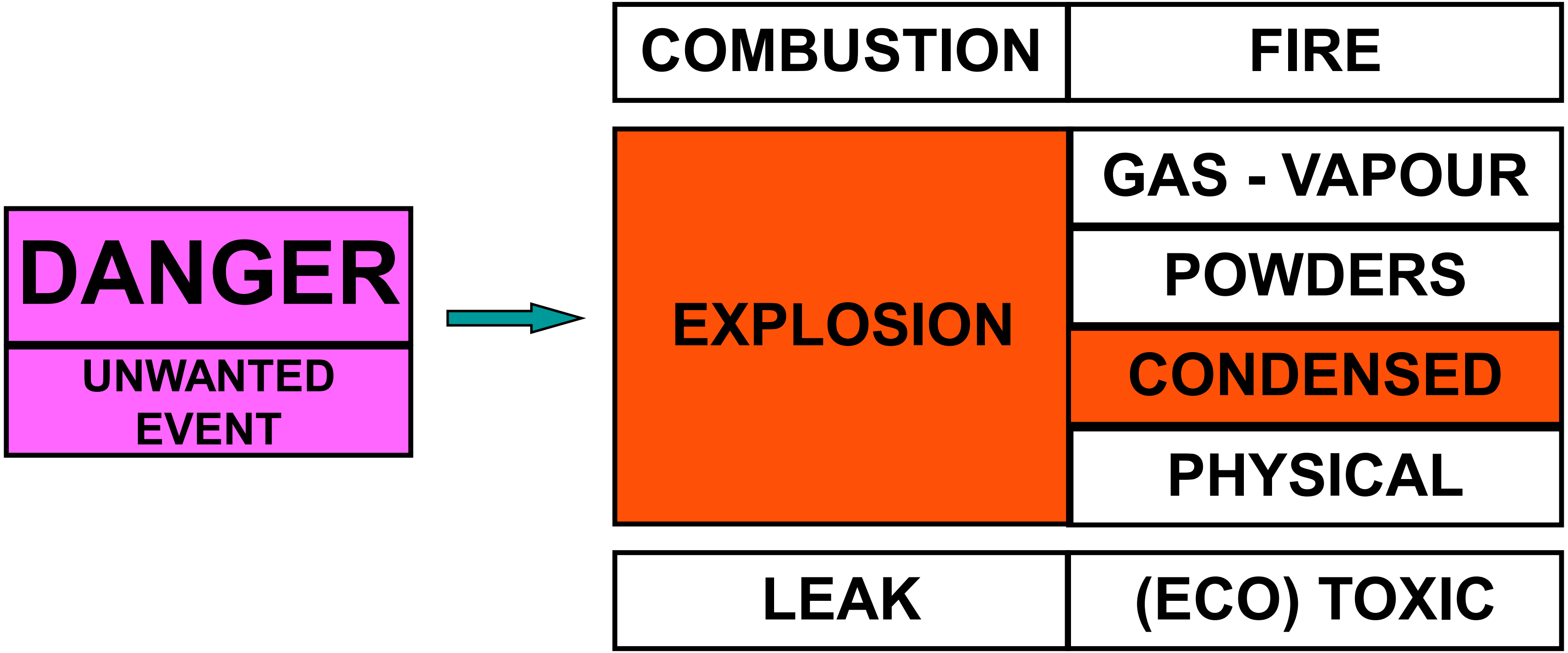
SYENSQO

Lessons from a fatal explosion in a pilot plant

EPSC 16th & 17th December 2025 Aachen

S. EGAN

DANGERS OF THE CHEMICAL INDUSTRY



Contents

- History
- US Patent 3,081,345
- Chemistry
- Pilot plant reactor
- Accident of 17th June 1966
- Hypotheses
- Follow up
- Identifying potentially sensitive materials
- Prevention of deflagration and detonation
- Summary

History

- 1963 US Patent 3,081,345: Propylene + liquid NO_2 → Oxalic acid
- 1963 Rhône-Poulenc starts lab. work to make oxalic & lactic acids
- 1966 Rhône-Poulenc plans oxalic (15 kt/yr) & lactic acid (5 kt/yr) plant
- 1966 Explosion of small pilot installation kills 6 people
- 1972 RP builds oxalic (15 kt/yr) & lactic acid (5 kt/yr) plant at Chalampé
- 1974 Explosion during start-up kills 1 person
- 1975 Plant is started up but only to produce oxalic acid
- 1990 Everybody is aware of the 1966 accident and how to avoid such accidents
- 1995 I start work in Chalampé
- 1997 The oxalic acid plant is shut down
- 1997 I send my safety file to the archives at Besançon
- 2015 Nobody is aware of the 1966 accident or how to avoid such accidents
- 2015 I get my oxalic acid safety file back from the archives

US Patent 3,081,345

- Production of oxalic acid:
  - “Particularly outstanding results have been obtained at a ratio of about 4 to 5 mole of NO_2 per mole of propylene”.
  - “97 parts of liquid NO_2 were placed in a reactor equipped with a stirrer and a Dry-Ice bath, and 21 parts of propylene were introduced thereto over a 66 minute period at a uniform rate with stirring and cooling to a temperature of – 10 °C to 12 °C”.

Chemistry

First reaction (common to oxalic and lactic acid)

$$CH_3{-}CH{=}CH_2 + 2\ NO_2 \xrightarrow[\text{liquid } NO_2]{30\ °C\ /\ 2\ \text{bar gauge}} CH_3{-}CH(ONO_2){-}CH_2{-}NO$$

Oxidation (catalyzed) of intermediate gives oxalic acid

$$CH_3{-}CH(ONO_2){-}CH_2{-}NO + 4\ O_2 \xrightarrow[\text{aqueous } HNO_3\ /\ Cr(NO_3)_3]{70\ °C} \underset{CO_2H}{\overset{CO_2H}{|}} + 2H_2O + CO_2 + 2\ NO_2$$

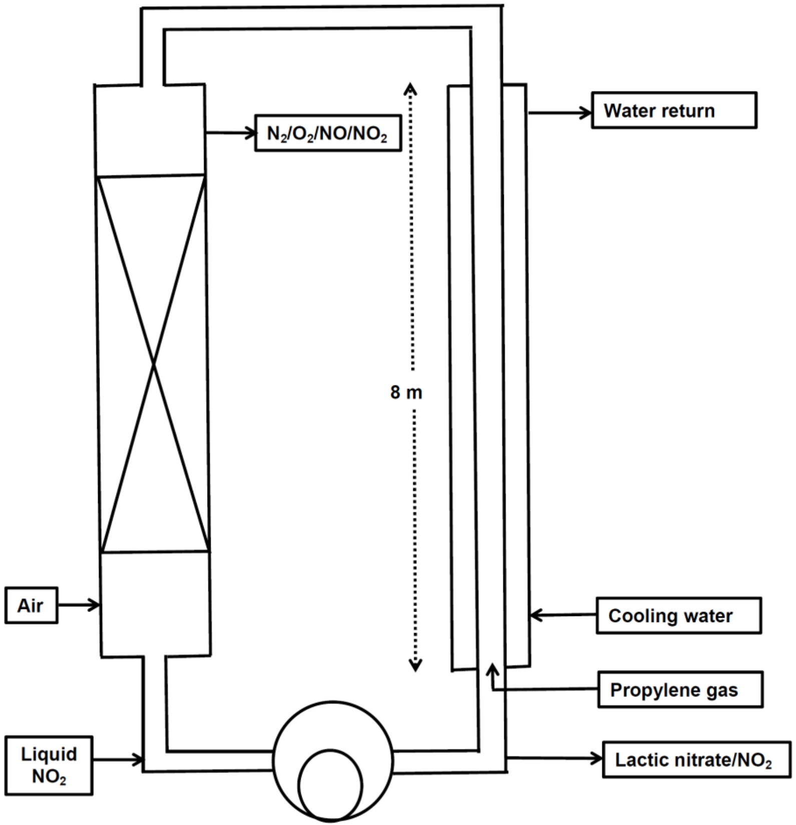
Oxidation of intermediate gives lactic acid

$$CH_3{-}CH(ONO_2){-}CH_2{-}NO + 1.5\ O_2 \xrightarrow[\text{aqueous } HNO_3]{30\text{-}35\ °C} CH_3{-}CH(OH){-}CO_2H + 2\ NO_2$$

Pilot plant reactor

- Tubular reactor:
  - 8 m long X 6 mm diameter
  - Volume 250 cm^3
  - Input of propylene gas
  - Water cooled
  - Samson liquid ring pump

- Packed column:
  - Oxidation of NO to NO_2
  - Degassing section at top

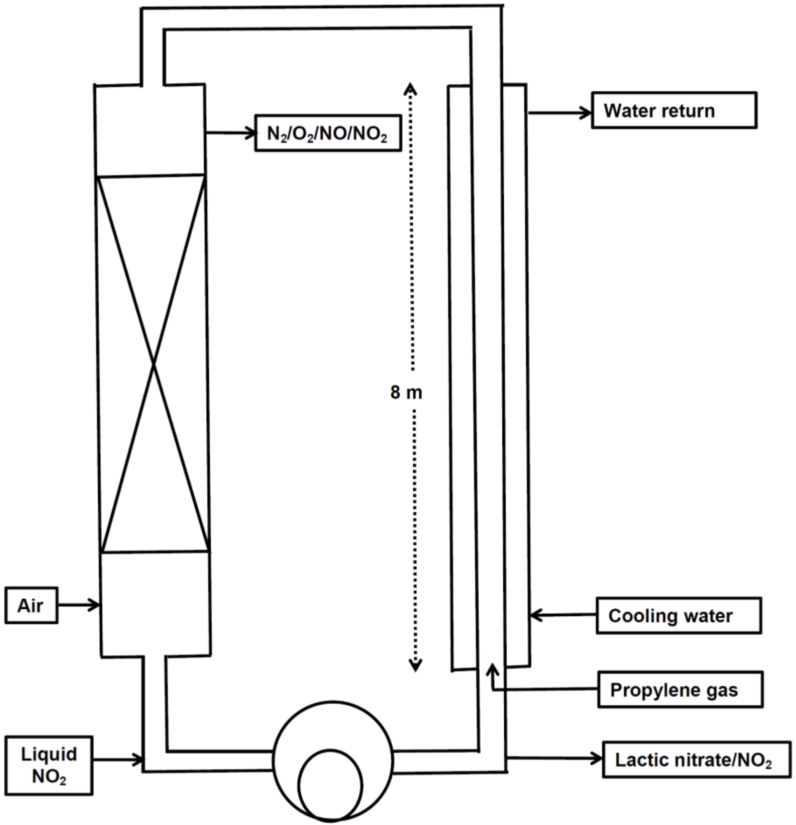


Pilot plant reactor

- Conditions:
  - 30 °C
  - 2.5 bar gauge
  - 1.5 cm/s

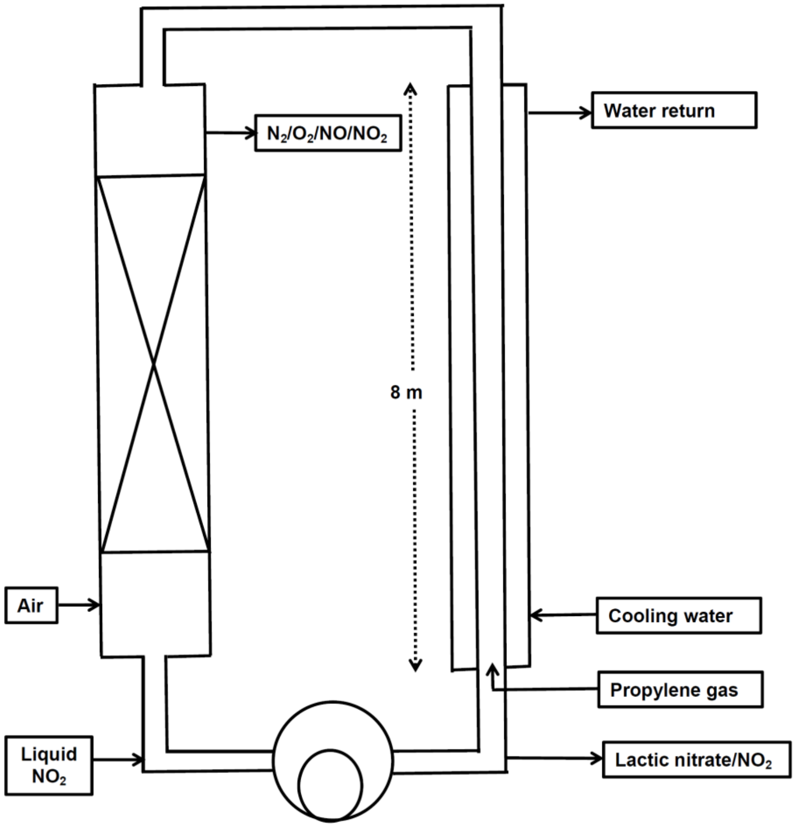
- Feeds:
  - 270 g/h C_3H_6 1.0 mole
  - 1330 g/h NO_2 4.5 mole

- Output:
  - 400 g/h Lactic acid



Accident of 17/06/1966

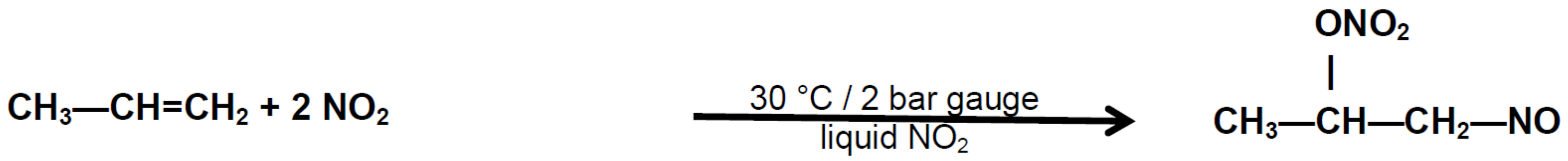
- Time-line
  - 0.00 First start-up of pilot plant with six people present
  - 5.00 Stuffing box gland of liquid ring pump is tightened
  - 5.15 Reactor explodes
- Results
  - Plant is devastated
  - No survivors



Hypotheses

1. Hotspot in pump leads to decomposition
   - Reconstruction 200 °C on tightening gland of pump

2. Loss of control of temperature leads to decomposition



   - Heat of reaction = 2500 kcal/kg propylene
   - $\Delta T_{adiabatic}$ = 582 °C with 4.5 moles NO_2/mole propylene

Follow-up

- Process development:
  - Continued despite the accident
  - Same basic chemistry
  - Solvent changed to $H_2O/HNO_3/NO_2$

- Full scale plant:
  - Plans were ready by 1969
  - Start-up 1974
  - Explosion of lactic acid intermediate storage vessel – one person killed
  - Two other serious incidents involving pumps
  - Definitive shut-down in 1997

Identifying potentially sensitive materials

- Check for unstable groupings

N°	Name	Chemical formula
1	Peroxide ; Ozonide	−O−O− ; −O−O−O−
2	Chlorate ; Perchlorate	$-OClO_2$; $-OClO_3$
3	Nitro ; Nitrate ; Nitroso ; Nitrite	$-NO_2$; $=N-NO_2$; $-ONO_2$; −N=O ; −ON=O
4	Fulminate ; Cyanate	−O−N≡C ; −C≡N
5	Haloamine ; Chloramine	=NX ; =NCl
6	Azo ; Diazo ; Diazonium ; Azide	−N=N− ; −N≡N or =N=N ; −N=N ; −N=N=N
7	Acetylide	−C≡C−
8	Heavy metal linked to carbon	−CM with M = Pb, Hg, Tl

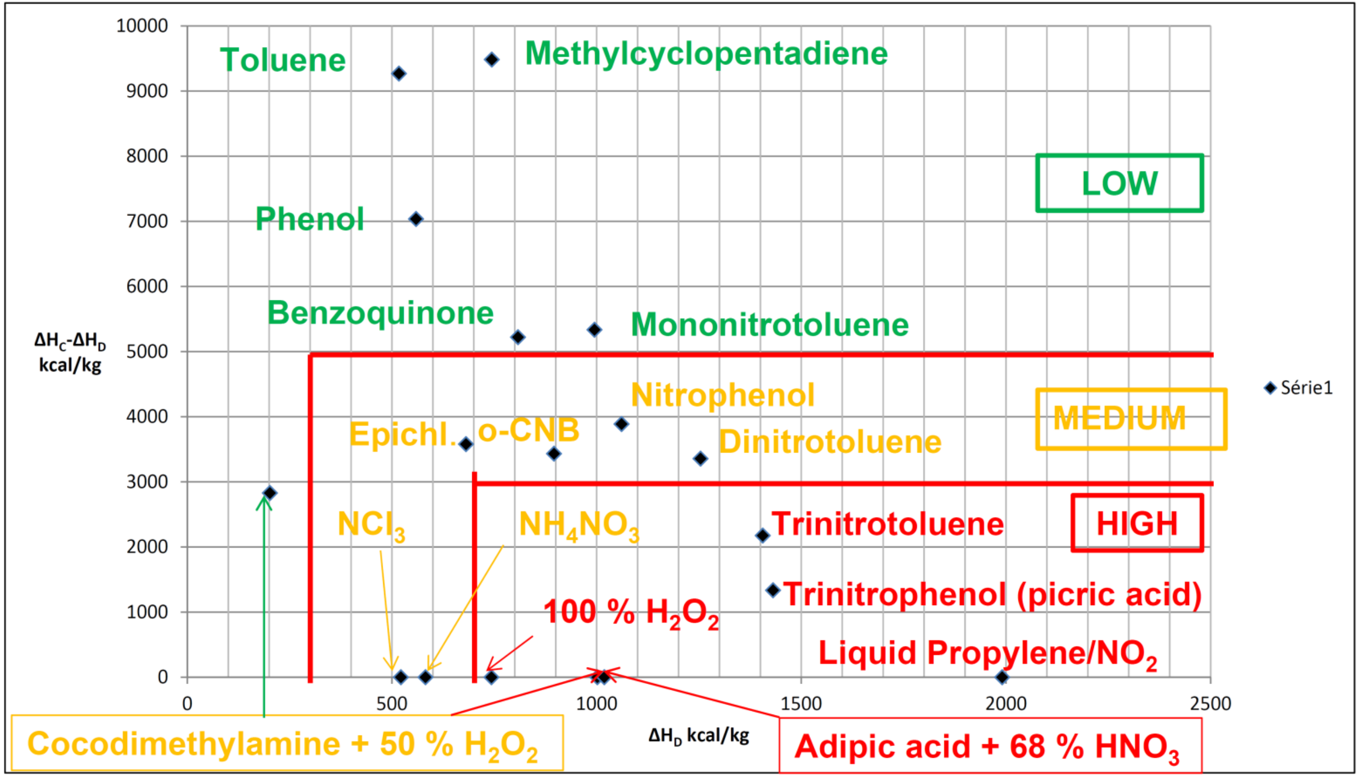
Identifying potentially sensitive materials

- Calculate the four CHETAH indices

Index	Definition	High	Medium	Low	Units
1	ΔH_d	> 700	300 to 700	< 300	cal/g
2	$\Delta H_C - \Delta H_d$	< 3000	3000 to 5000	> 5000	cal/g
3	O_2 balance	-120 to +80	-240 to -120 +80 to +160	< -240 > +160	g O_2 / 100 g
4	$\frac{\Delta H_d^2 M}{N}$	> 110	30 to 110	< 30	$kcal^2/gmol.g$

- Key:
  - Oxygen balance $C_xH_yO_z$ = 1600.(2x+y/2-z)/M
  - M = Molecular weight
  - N = Number of atoms in the molecule

Identifying potentially sensitive materials



Prevention of deflagration and detonation

- Accident of 17/06/1966:
  - The reaction we wanted to carry out was:

$$CH_3{-}CH{=}CH_2 + 2\,NO_2 \xrightarrow[\text{liquid } NO_2]{30\ ^\circ C\ /\ 2\ \text{bar gauge}} CH_3{-}CH(ONO_2){-}CH_2{-}NO$$

  - US Patent 3,081,345: “Particularly outstanding results have been obtained at ratio of about 4 to 5 mole of NO_2 per mole of propylene”.
  - A mole ratio of 4.5 is exactly the worst case

$$CH_3{-}CH{=}CH_2 + 4.5\,NO_2 \longrightarrow 3\,CO_2 + 3\,H_2O + 2.25\,N_2$$

Prevention of deflagration and detonation

- 1990:
  - Reaction sheets written for new reactions
  - Included Maximum Potential Energy (MPE = CHETAH index 1)
  - Everbody knew why
  - Everbody calculated Maximum Potential Energy

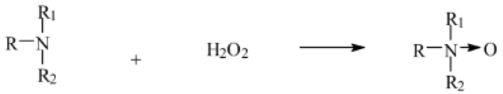
- 2017:
  - Guideline IND-HSE-PTS-11.32 "Basic data on products and reactions"
  - Appendix 4 = Reaction Sheet
  - Includes Maximum Potential Energy (CHETAH index 1)
  - Nobody knows why
  - Nobody calculates Maximum Potential Energy any more

Prevention of deflagration and detonation

- Reaction sheet
  - Primary reactions
  - Secondary reactions
  - EI – Explosion Implosion
  - EG – Gas Explosion

REACTION SHEET

Section: Amine oxidation

N°	PRIMARY (P) AND SECONDARY (S) REACTIONS HEAT OF REACTION FOR EACH ONE	REF.
1P	 R = Fatty Radical $R_1 = R_2 = CH_3$ ΔH_R = -52.6 kcal/mol H_2O_2 exothermic	
1S	$H_2O_2 \longrightarrow 1/2\ O_2 \uparrow + H_2O$ ΔH_R = -24 kcal/mol H_2O_2 exothermic	

HAZ.	CRITICAL OPERATING FACTOR	DATA AVAILABLE DATA MISSING	REF.
EI	Normal reaction pressure	1 atm.	
	Quantity of gas produced under normal reaction conditions?	None	
	Foaming, degassing?	These materials are non-foaming	
	Other relevant information		
EG	Oxidant gas used or generated by primary or secondary reaction?	Yes: reaction 1S generates O_2	
	Fuel?	Flash point of tertiary amine = 113 °C	
	Reaction involving materials (such as activated Raney Nickel) which could act as ignition sources?	No issue	
	Other relevant information		

Prevention of deflagration and detonation

- Reaction sheet
  - ET – Thermal explosion
  - D – Condensed phase Detonation

REACTION SHEET			
HAZ.	CRITICAL OPERATING FACTOR	DATA AVAILABLE DATA MISSING	REF.
ET	$\Delta T_{Ad.}$ = Adiabatic temperature rise for complete batchwise reaction	50 °C	
	Maximum accumulation expected under normal reaction conditions	No issue	
	Maximum Temperature of Synthesis Reaction (MTSR)	75 °C	
	Thermal stability of reaction mixture at MTSR	The reaction mixture is known to be thermally stable at the mixture boiling point of 105 °C.	
D	Does any of the primary or secondary reaction use or produce compounds with unstable groupings? MPE of such compounds	Yes : H_2O_2 743 cal/g (high potential) for 100 % H_2O_2 372 cal/g (medium potential) for 50 % H_2O_2	
	Does the reaction involve fuel/oxidant as condensed phases? MPE Normal reaction mixture MPE Worst case reaction mixture	Yes: Fuel = tertiary amine Oxidant = 50 % H_2O_2 -202 cal/g (low potential) -1019 cal/g (high potential) for mixture with no initial water charge and low charge of amine	
	Other relevant information	The worst case mixture is known to be sensitive to shock.	

Summary

- Accident of 17/06/1966
  - 250 cm^3 tubular continuous reactor
  - The normal reaction mixture was a more powerful explosive than TNT
  - The reactor exploded on the first trial
  - 6 people died

- Prevention
  - Use the reaction sheet form for new processes
  - Look for unstable groupings e.g. $–ONO_2$
  - Look for fuel / oxidant mixtures
  - Calculate the Maximum Potential Energy