

The background features a light gray gradient with several realistic water droplets of various sizes scattered across the surface. A large, faint, light gray circle is centered in the upper half of the image, partially overlapping the text.

SAFETY

THERMAL RISK ASSESSMENT

Petr Beňovský

SAFETY


Chinese explosion linked to Western firms

Michael McCoy

C&EN Global Enterprise 2019, 97, 21, 9 (Article)

Publication Date (Web): May 27, 2019

DOI: 10.1021/cen-09721-buscon4

 [Abstract](#)

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Chemical blast kills dozens in China

Jean-François Tremblay

C&EN Global Enterprise 2019, 97, 13, 14 (Article)

Publication Date (Web): April 1, 2019

DOI: 10.1021/cen-09713-buscon1

 [Abstract](#)

 [Full text](#)

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- Seveso, Bhopal terrible accidents;
- Risk analysis to advocate benefits of chemical industry;
- Toxicity (*in silico* studies), environmental aspects (including waste disposal), process safety, contamination, elimination of human errors, property protection;
- Material and Safety Data Sheets (MSDS) accompanying products

Risk Perception – comparing fatalities in different activities – **the Fatal Accident Rate Index (FAR)** that gives the number of fatalities per 10^8 hours of exposure to the hazard.

Francis Stoessel *Thermal Safety of Chemical Processes: Risk Assessment and Process Design*, Wiley VCH 2008

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Risk – according to a definition of the European Federation of Chemical Engineering (EFCE) it is a measure of loss potential, or damage to the environment or persons in terms of probability and severity

$$\text{RISK} = \text{probability} \times \text{severity} \text{ (} \times \text{ occurrence)}$$

Risk tools – e.g. Failure Mode and Effect Analysis (FMEA)

Francis Stoessel *Thermal Safety of Chemical Processes: Risk Assessment and Process Design*, Wiley VCH 2008

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The Hazard and Operability Study (HAZOP) developed in early 1970s in ICI after the Flixborough incident. It is derived from FMEA concept, but specially adopted for the process industry;

Essentially oriented towards the identification of risks stemming from the process equipment using the process and instruments design and the process flow diagram.

Francis Stoessel *Thermal Safety of Chemical Processes: Risk Assessment and Process Design*, Wiley VCH 2008

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Activity	Work accidents for 1000 insured
Construction	185
Wood	183
Mining	160
Metallurgy	147
Cement, glass, ceramics	130
Food	113
Rubber, plastics	95
Machinery	72
Transport	66
Energy	59
Textile, clothes	50
Offices, administration	46
Paper, graphics	45
Chemistry	37
Electricity, fine mechanics	33

SAFETY

Industrial activities	FAR	Non industrial activities	FAR
Coal mining	7.3	Alpinism	4000
Construction	5	Canoe	1000
Agriculture	3.7	Motor bike	660
Chemistry	1.2	Travel by air	240
Vehicle manufacturing	0.6	Travel by car	57
Clothing manufacturing	0.05	Travel by railway	5

Fatal Accident Rate Index (FAR) - the number of fatalities per 10^8 hours of exposure to the hazard.

SAFETY

**A quiet situation resulting from the real
absence of any hazard**

But, is it attainable??

**The risk is always there, a hazard should be minimized
or eliminated as much as possible**

THERMAL SAFETY

Molar enthalpy of a reaction – is the heat released (or absorbed) in a chemical reaction at constant pressure when simple substances combine into complex product;

ΔH_R [kJ mol⁻¹];

Specific heat of a reaction – the amount of heat energy required to raise the temperature of a body per unit of mass (standard – in J by 1 K for 1 g; e.g. water has 4.18 J);

Q_R' [kJ kg⁻¹];

Heat capacity – the amount of energy required to raise the energy of the given mass of the system by 1 K;

C_p [J K⁻¹];

TYPICAL VALUES OF SPECIFIC HEAT CAPACITIES

Compound	c_p' kJ·kg ⁻¹ K ⁻¹
Water	4.2
Methanol	2.55
Ethanol	2.45
2-Propanol	2.58
Acetone	2.18
Aniline	2.08
n-Hexane	2.26
Benzene	1.74
Toluene	1.69
p-Xylene	1.72
Chlorobenzene	1.3
Tetrachloromethane	0.86
Chloroform	0.97
NaOH 10 mol% in water	1.4
Sulfuric acid 100%	1.4
NaCl	4.0

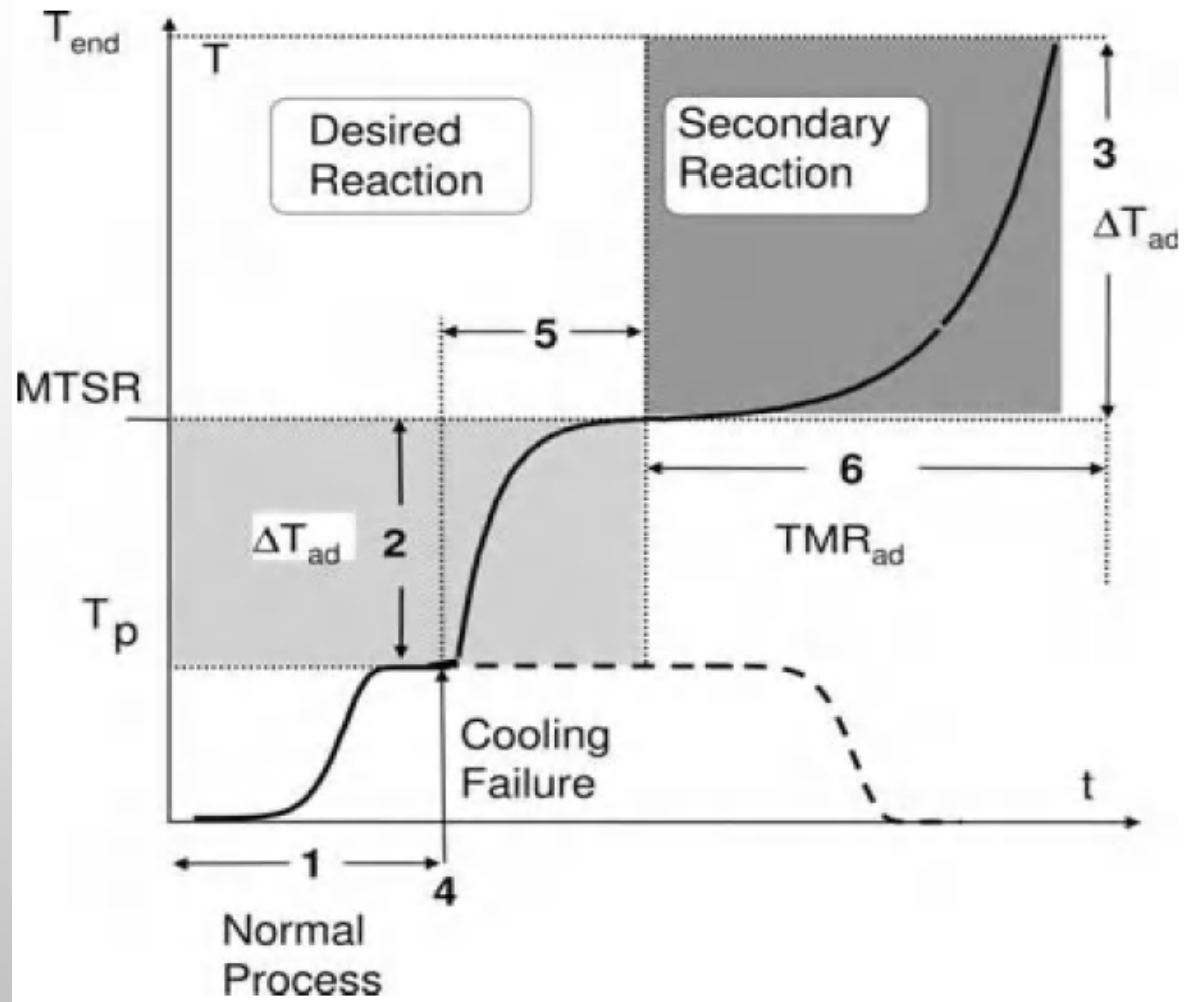
THERMAL SAFETY

Time to Maximum Rate (under Adiabatic Conditions) (TMR_{ad}) – the higher the temperature the faster the reaction and the shorter TMR_{ad} , can be determined by the DSC measurement;

Time of No Return (TNR)

MTSR ... Maximum Temperature of the Synthesis Reaction

COOLING FAILURE SCENARIO



COOLING FAILURE SCENARIO

SIX PRINCIPAL QUESTIONS

1. Can the proces temperature be controlled by the cooling system?

- Sufficient cooling of the system depends on e.g. viscosity of the mixture, power of a cooling system, possible fouling of the reactor walls, an area for heat exchange, efficient stirring;
- Heat release rate of the reaction is relatively easily obtained from reaction calorimetry measurement.

COOLING FAILURE SCENARIO

SIX PRINCIPAL QUESTIONS

2. What temperature can be attained after runaway of the desired reaction?

- After the cooling failure unconverted reactants will react in an uncontrolled way and it leads to an adiabatic temperature increase;
- The available energy is proportional to the accumulated fraction;
- At higher temperature even (desired) products can further react providing additional heat increase.

COOLING FAILURE SCENARIO

SIX PRINCIPAL QUESTIONS

2. What temperature can be attained after runaway of the desired reaction?

- The Concept of **Maximum Temperature of the Synthesis Reaction (MTSR)**

$$\text{MTSR} = T_p + X_{ac} \times \Delta T_{ad}$$

T_p ... desired reaction temperature

X_{ac} ... degree of accumulation of unconverted reactants

ΔT_{ad} ... the adiabatic temperature raise

COOLING FAILURE SCENARIO SIX PRINCIPAL QUESTIONS

3. What temperature can be attained after runaway of the secondary reaction?

- At higher temperature the secondary reactions might be triggered – it leads to further runaway;
- At higher temperature even (desired) products can further react providing additional heat increase;
- Data can be obtained from the DSC and adiabatic calorimetry measurement.

COOLING FAILURE SCENARIO SIX PRINCIPAL QUESTIONS

4. At which moment does the cooling failure have the worst consequences?

- The time where the accumulation is at a maximum and/or the thermal stability of the reaction mixture is critical;
- In order to answer this question both the synthesis reaction and secondary reactions must be known;
- Data obtained from the reaction and adiabatic calorimetry, and the DSC measurements can help to answer this question.

COOLING FAILURE SCENARIO SIX PRINCIPAL QUESTIONS

5. How fast is the runaway of the desired reaction?

- Usually, the industrial reactors are operated at temperature where the desired reaction is relatively fast;
- A temperature increase above the normal process temperature thus will cause a significant acceleration of the reaction rate (the van't Hoff criterion);
- Duration of the main reaction runaway may be estimated using the initial heat release rate of the reaction and the concept of the Time to Maximum Rate (TMR).

COOLING FAILURE SCENARIO SIX PRINCIPAL QUESTIONS

6. How fast is the runaway of the decomposition reaction starting at MTSR?

- The dynamics of the secondary reactions plays an important role in the determination of the probability of an incident;
- Again, the concept of the Time to Maximum Rate (TMR) is useful.

The answers to all six questions represent a systematic way of analysing the thermal safety of a process and building the cooling failure scenario.

Thermal risk assessment based on **severity** and **probability** of the event.

SEVERITY OF COOLING FAILURE SCENARIO

$$\Delta T_{ad} = \frac{Q'}{c_p'}$$

ΔT_{ad} ... increase of temperature under adiabatic conditions

Q' ... specific energy of the reaction

c_p' ... specific heat capacity (water 4.2 kJ kg⁻¹ K⁻¹; organic solvents around 1.8 kJ kg⁻¹ K⁻¹; inorganic acids around 1.3 kJ kg⁻¹ K⁻¹)

Simplified	Extended	ΔT_{ad} (K)	Order of magnitude of Q' kJ kg ⁻¹
High	Catastrophic	>400	>800
	Critical	200–400	400–800
Medium	Medium	50–100	100–400
Low	Negligible	<50 and no pressure	<100

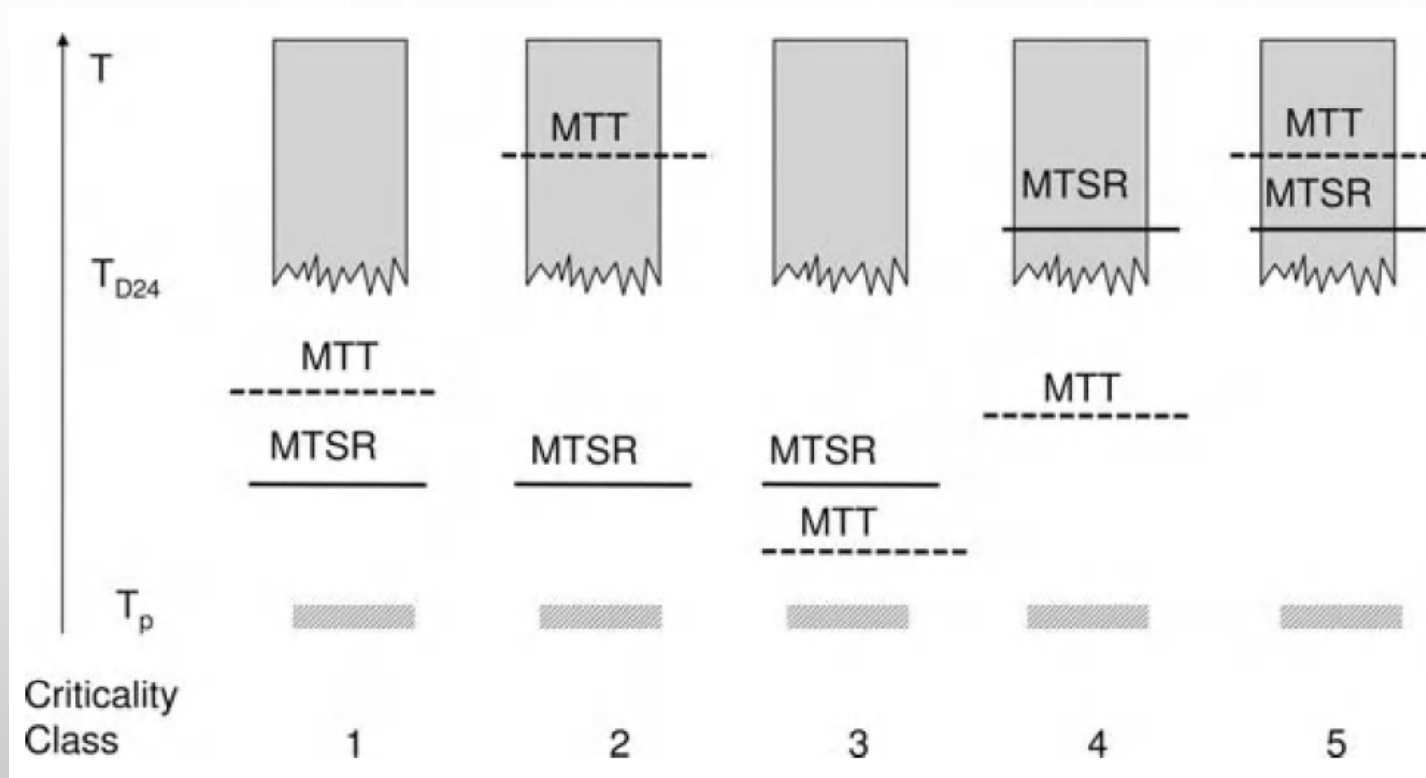
PROBABILITY OF COOLING FAILURE SCENARIO

The probability can be evaluated using the time scale.

If, after the cooling failure, there is enough time left to take emergency measures before the runaway becomes too fast, the probability of the runaway will remain low.

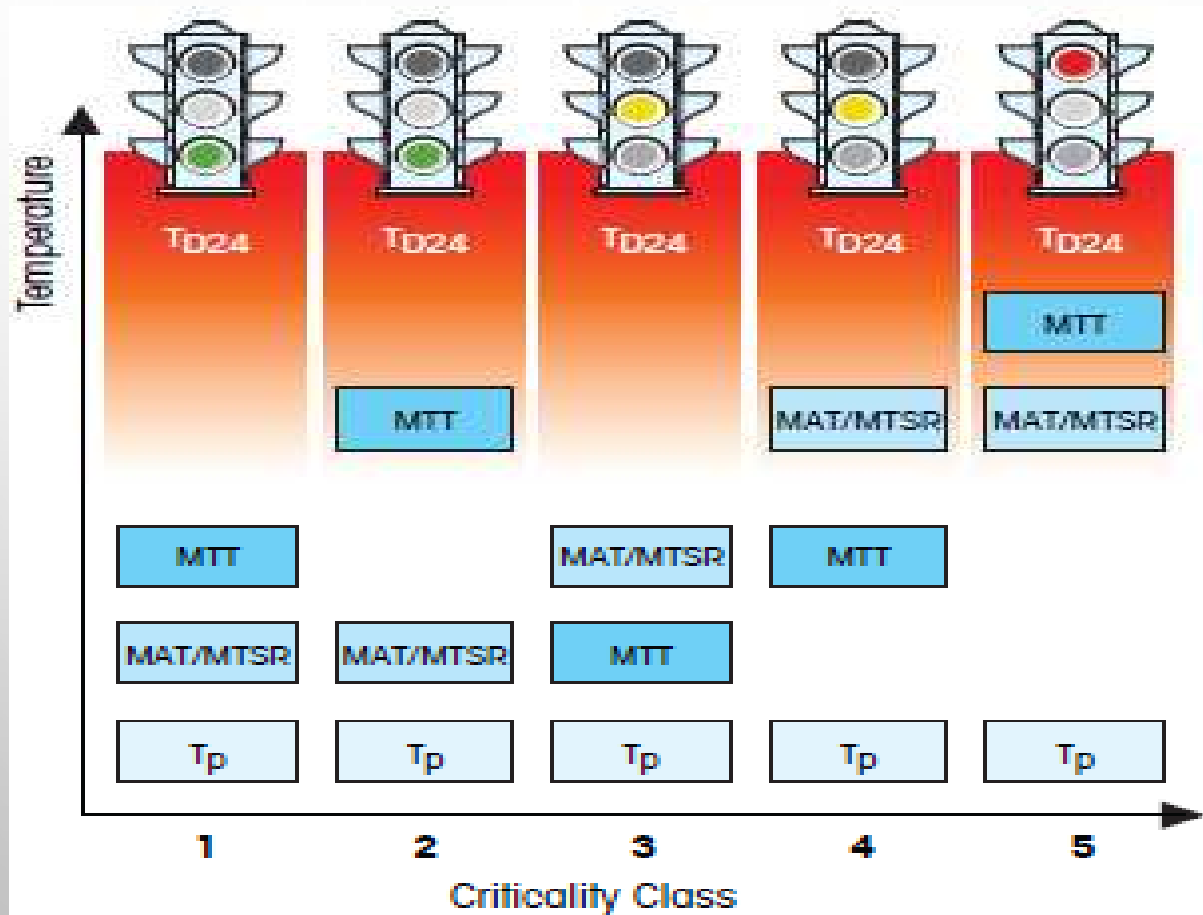
Simplified	Extended	TMR_{ad} (h)
High	Frequent	<1
	Probable	1–8
Medium	Occasional	8–24
Low	Seldom	24–50
	Remote	50–100
	Almost impossible	>100

COOLING FAILURE SCENARIO CRITICALITY CLASSES



T_p ... proces temperature; MTSR ... Maximum Temperature of the Synthesis Reaction; T_{D24} ... temperature at which the Time to Maximum Rate is 24 h; MTT ... Maximum Technical Temperature (e.g. boiling point)

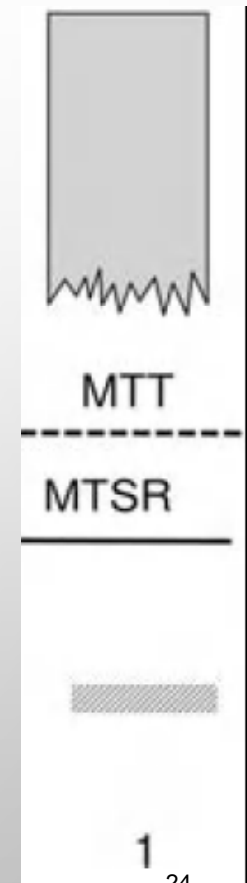
COOLING FAILURE SCENARIO CRITICALITY CLASSES



COOLING FAILURE SCENARIO CRITICALITY CLASSES

Criticality Class 1

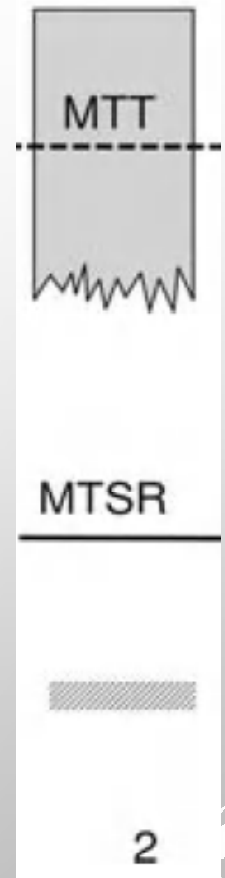
- $MTSR < MTT$
- Very safe
- Evaporative cooling serves as an additional safety barrier
- Reaction mass should not be held for a very long time under heat accumulation conditions



COOLING FAILURE SCENARIO CRITICALITY CLASSES

Criticality Class 2

- $MTSR < MTT$;
- but $MTT > T_{D24}$, the decomposition reaction can be triggered if the reaction mass is maintained for a long time under heat accumulation conditions;
- Still low risk scenario



COOLING FAILURE SCENARIO CRITICALITY CLASSES

Criticality Class 3

- $MTSR > MTT$;
- Safety of the process depends on the heat release rate of the synthesis reaction at MTT;
- Get ready to do pressure release;
- Decomposition reaction should not be triggered in 24 hours



COOLING FAILURE SCENARIO CRITICALITY CLASSES

Criticality Class 4

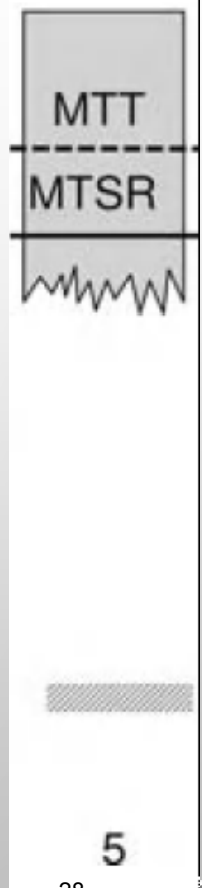
- $MTSR > MTT$;
- Moreover, $MTSR > T_{D24}$;
- Safety of the process depends on the heat release rate of both the synthesis reaction and the decomposition reaction;



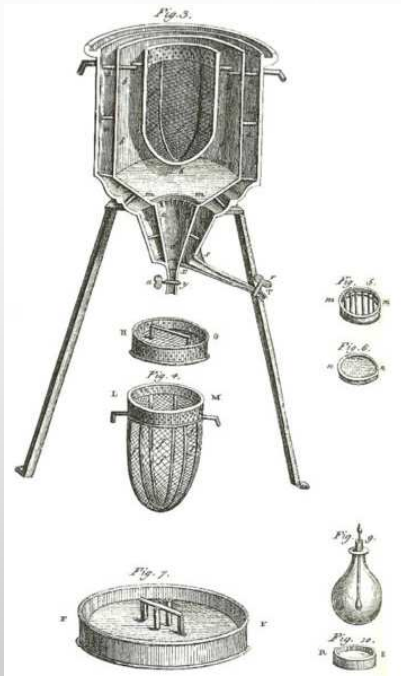
COOLING FAILURE SCENARIO CRITICALITY CLASSES

Criticality Class 5

- $MTSR > T_{D24}$; after loss of control of the reaction the decomposition will be triggered;
- It is very unlikely that evaporative cooling or the pressure relief can serve as a safety barrier;
- This is very dangerous and unacceptable scenario;



CALORIMETRY



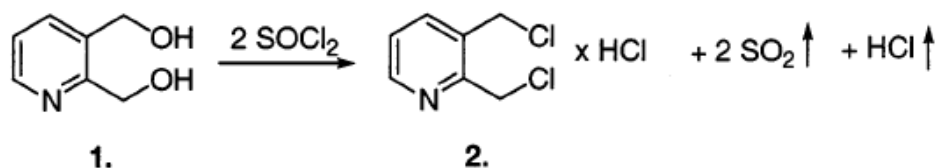
Antoine Lavoisier
Pierre-Simon Laplace



Mettler RC-1

PRACTICAL EXAMPLE

Grimm, J.S. *et al Org.Process Res. Dev.* 6, 938 (2002)



Original conditions:

- 3 mol eq. of SOCl_2 as reaction solvent
- upon completion rxn becomes thick, unstirrable
- added MTBE, filtered

Problems:

- large amounts of unused SOCl_2 to be disposed
- although MTBE meets all requirements at higher temp it could decompose should be OK at RT

Decision:

Run rxn with 1.6 eq of SOCl_2 in MTBE as rxn solvent at RT

This was OK up to 2.0 mol scale, then sluggish
Concern – prolonged exposure of MTBE to acidic conditions

PRACTICAL EXAMPLE

Adiabatic temperature rise – temp.rise when all the heat generated stays in the RM
(cooling, stirring failure)

$$\Delta T_{ad} = \frac{(-\Delta H_r) C_{A0} X_A}{\rho c_p}$$

conversion

specific weight (kg/m³) specific heat capacity (kJ/kg.K)

MTSR – maximum temperature of synthesis reaction

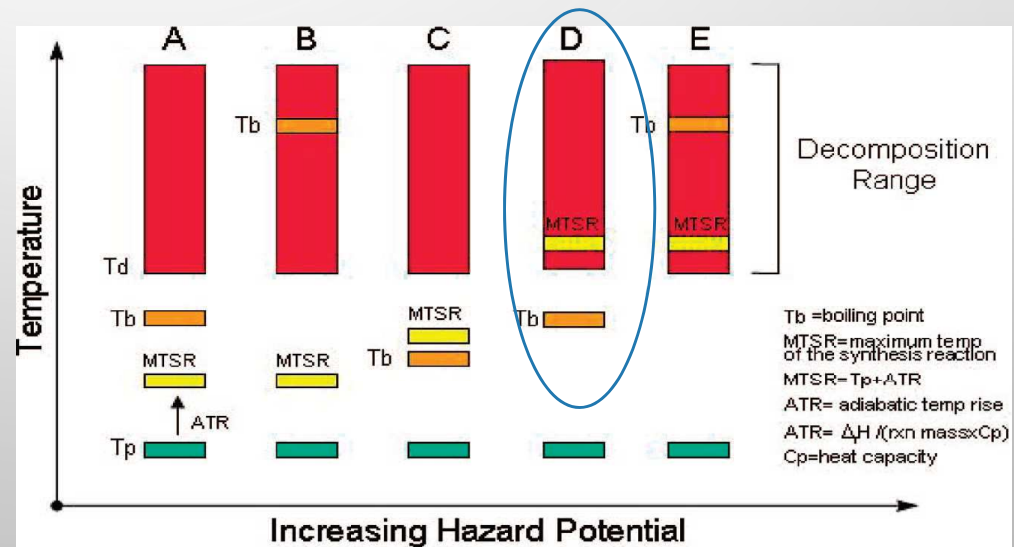
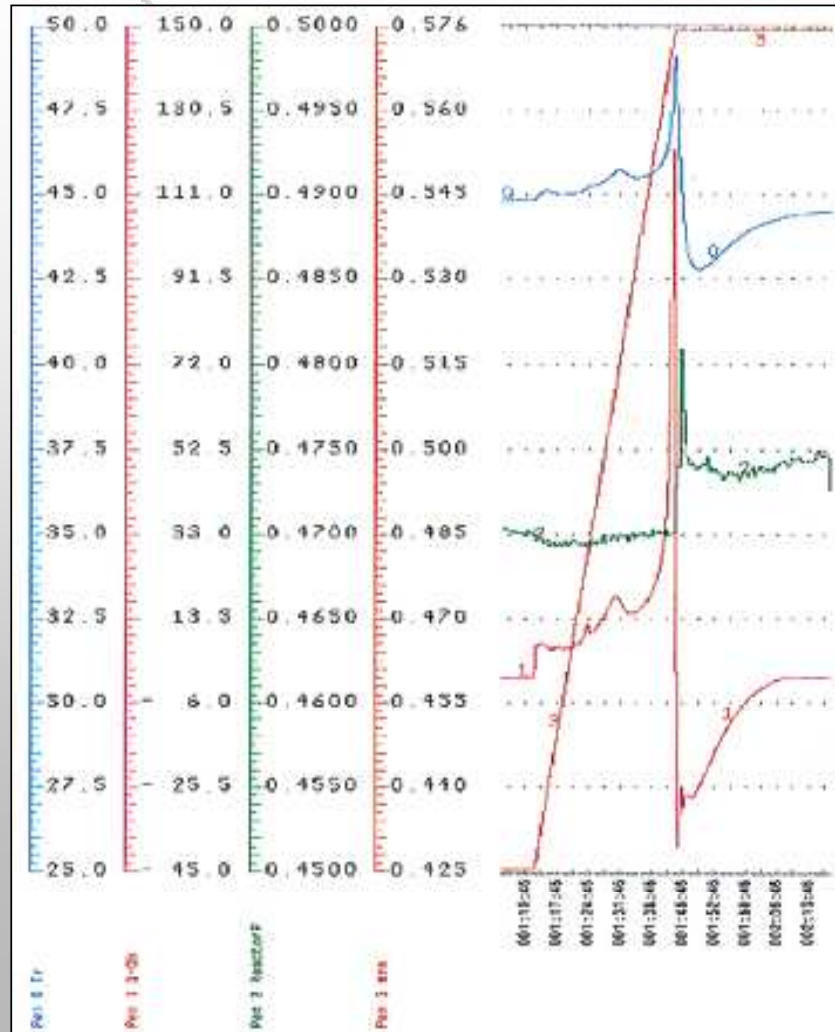
$$MTSR = T_p + \Delta T_{ad}$$

process temperature

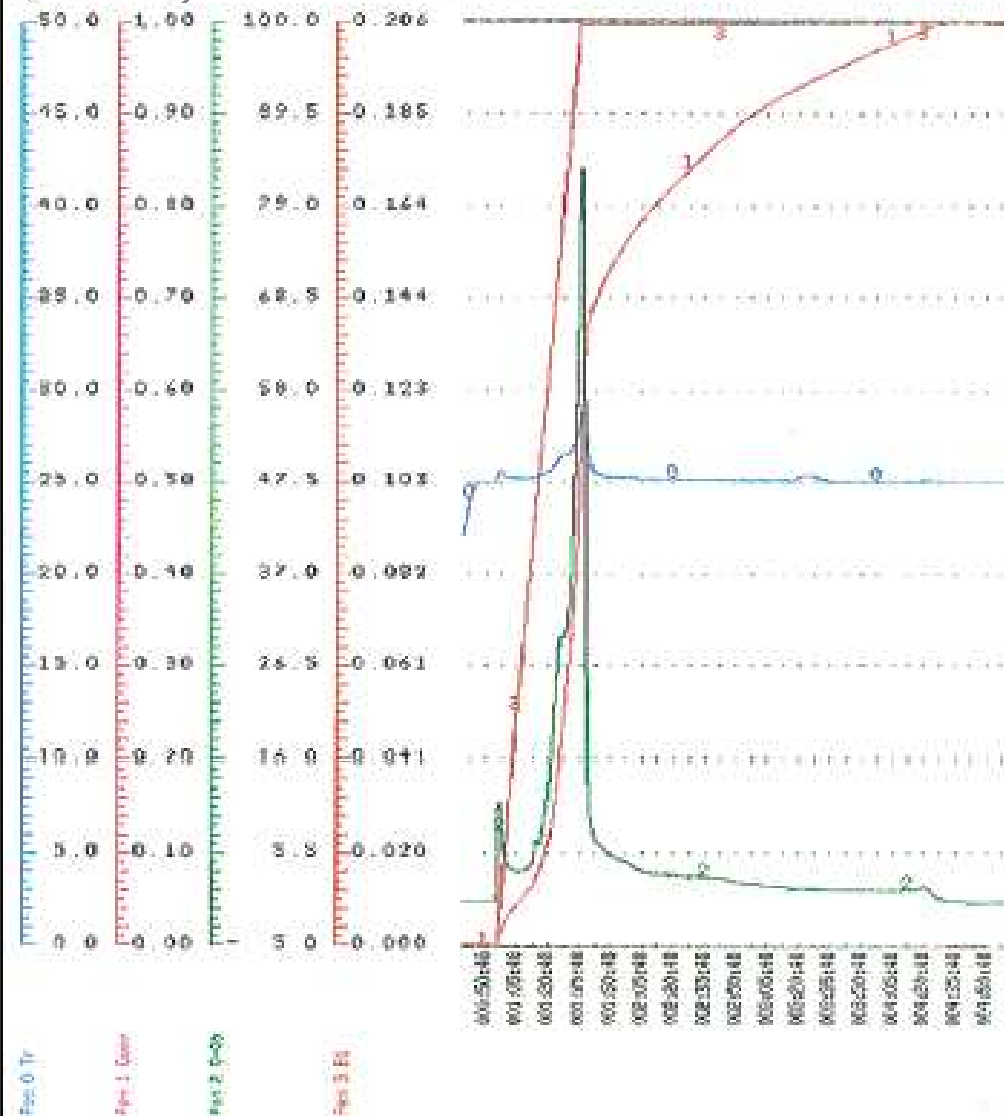
Calorimetric measurement at 40-45 C (RC-1)

Problems:

- rxn not „feed controlled“
(sudden delayed heat release)
- sudden uncontrolled outgassing
- gas contained isobutylene as well
(separate exp. showed decomp. at 40°C)
- ΔT_{ad} is 25°C, **MTSR=65°C**,
b.p. of MTBE 55°C



Calorimetric measurement at RT



Again:

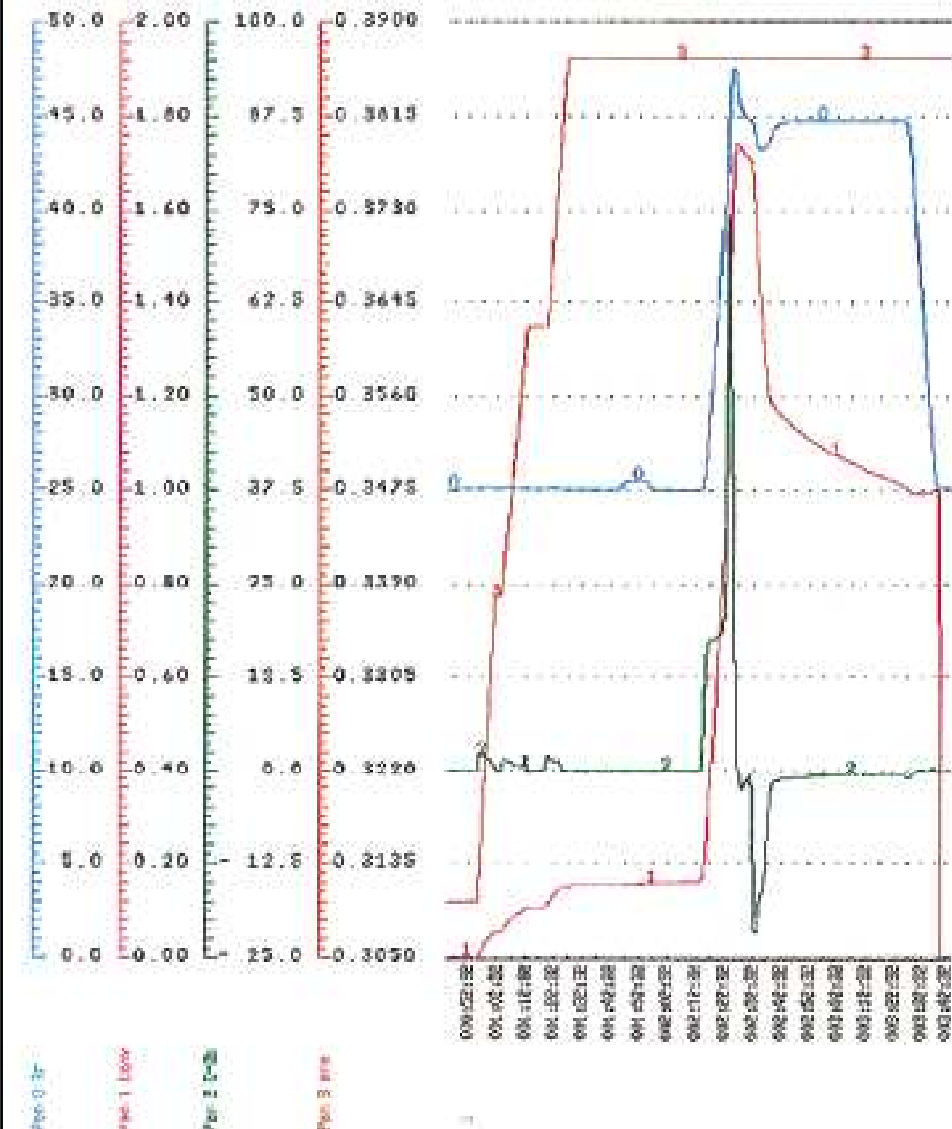
- rxn not „feed controlled“
(sudden delayed heat release)
- 2 exotherms observed
- ΔT_{ad} is 53°C, **MTSR=78°C**,
b.p. of MTBE 55°C

Still hazardous !!!

Decision:

abandon MTBE in favor of toluene

Calorimetric measurement in toluene at RT



Problems:

- delay even worse (entire charge)
- uncontrolled outgassing

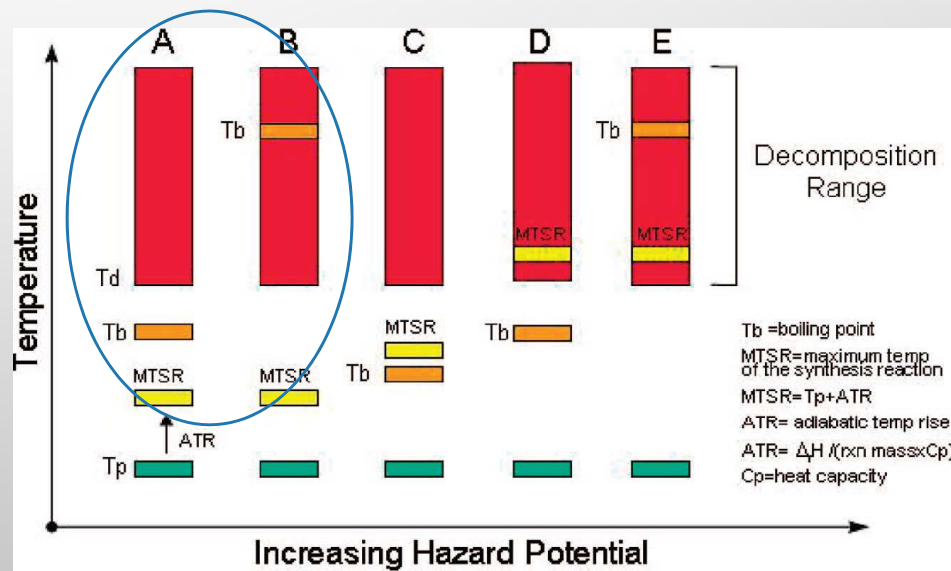
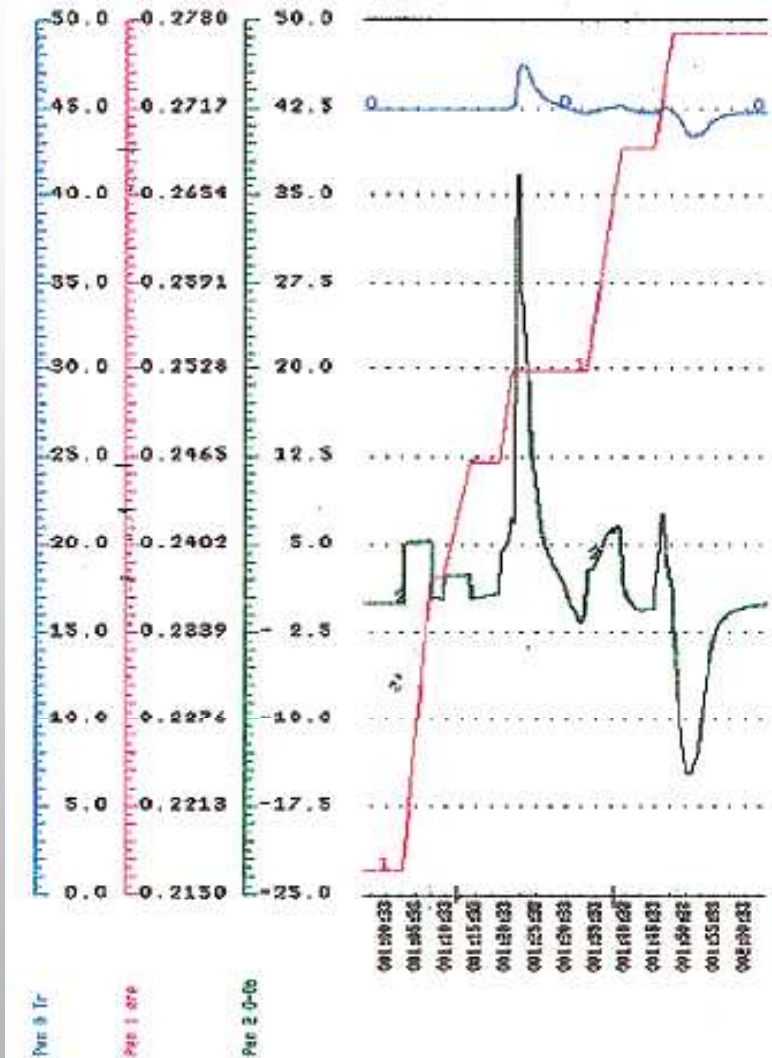
Still hazardous !!!

Calorimetric measurement in toluene at 45 °C

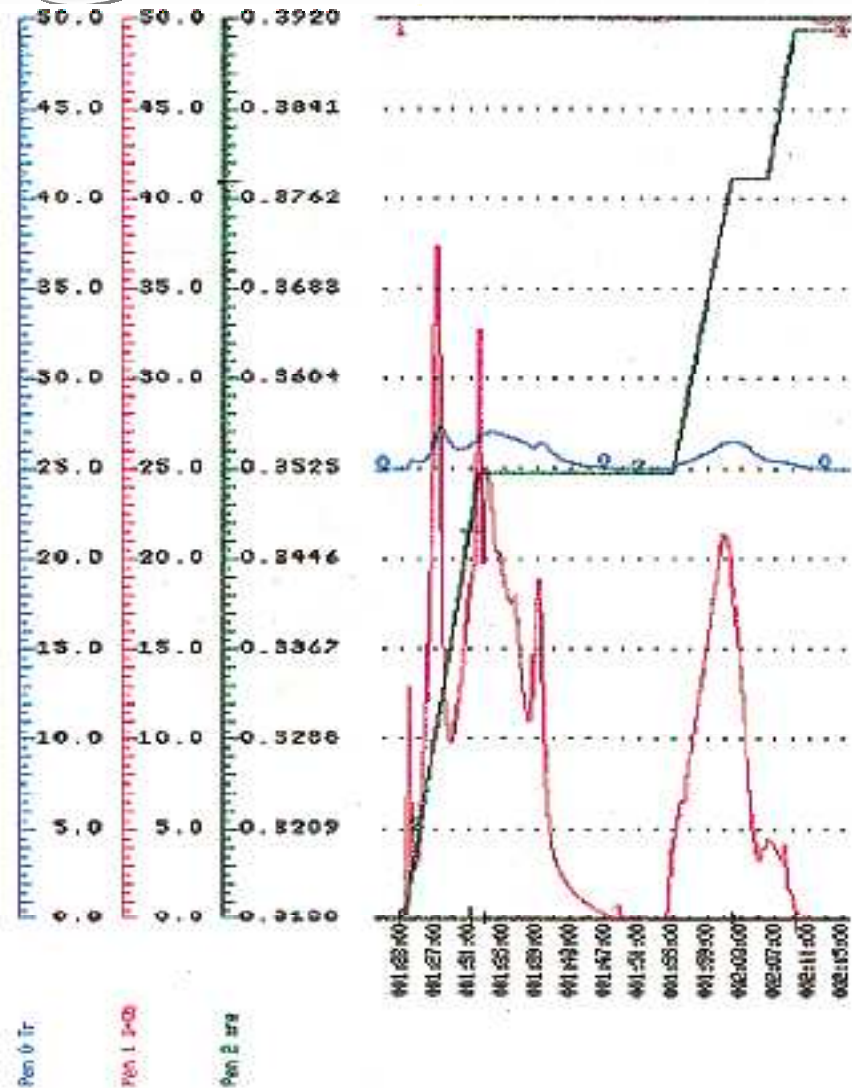
Problems:

- Still the same problem – delay of massive outgassing
- ΔT_{ad} is 23°C, **MTSR=68°C**,
b.p. of toluene 111°C

Still somewhat hazardous due to uncontrolled outgassing



Measurement in toluene/DMF at 25°C



Finally:

- Rxn is more or less feed controlled
- Outgassing is also under control
- ΔT_{ad} is 20°C, $MTSR=45^\circ\text{C}$,
b.p. of toluene 111°C

Not ideal but safe within reason