산업안전보건연구원
Occupational Safety & Health Research Institute

Introduction to Reaction Process Safety

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OCCUPATIONAL SAFETY & HEALTH RESEARCH INSTITUTE

Process Safety

Early development → Full Development

1. Key first step is to identify significant exotherms at small scale

2. Adiabatic temperature rise is first pass for process safety assessment of reaction

3. Dosing controlled heat release processes are most flexible for safe scale up
   Can heat be removed at scale without temperature increase?

   - If dosing controlled :Determine dosing time at pilot or plant scale
   - If NOT dosing controlled:
     - Try to make dosing controlled
     - Dose in portions based on ad temp. rise.

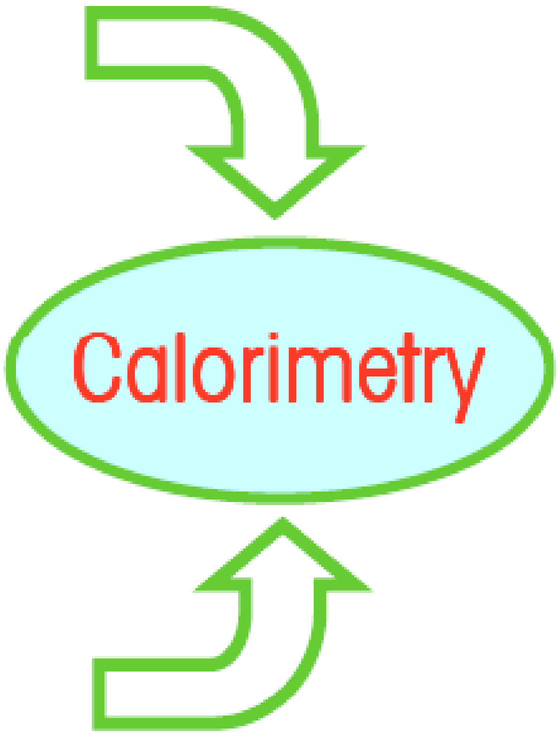
4. MTSR for detailed understanding or true process safety of desired reaction,
   built total process safety runaway scenario

5. Optimization of process to safe conditions at large scale (taking into account mixing, MT, HT limitations of large scale) + determination of
   consequences of deviations of normal process at large scale (and actions needed)

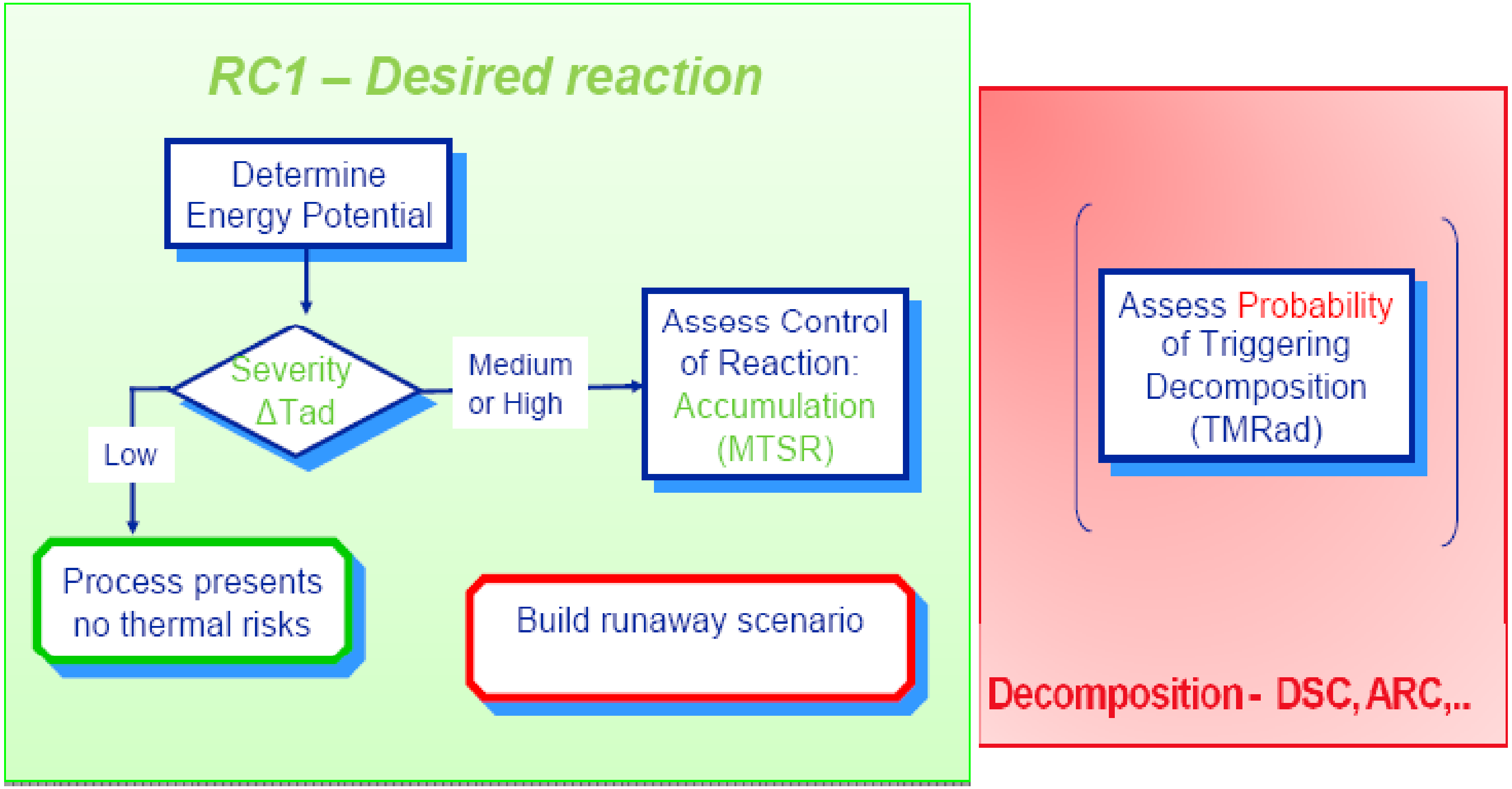
Concept

- *Chemical reaction*
  - Heat of reaction?
  - Can the heat be removed ?
  - Is the boiling point triggered ?
  - Gas involved ?
  - Heat capacity
  - Delta T adiabatic

- *Decomposition reaction*
  - Heat of reaction
  - Heat capacity
  - Boiling point triggered?
  - Gas involved?
  - Final temperature triggered

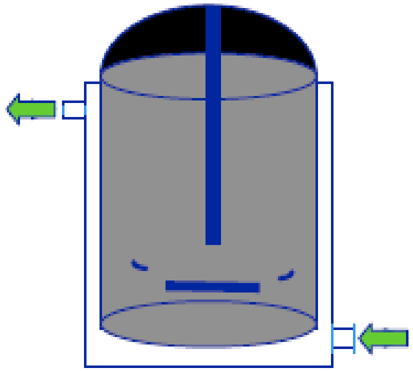


Assessment of thermal safety risks



Adiabatic temperature rise

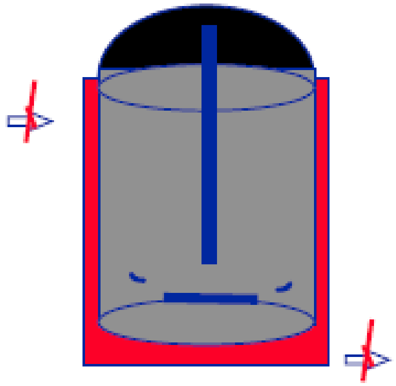
Process under normal operating conditions



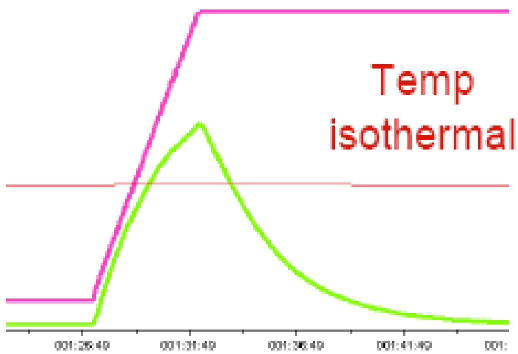
ISOTHERMAL

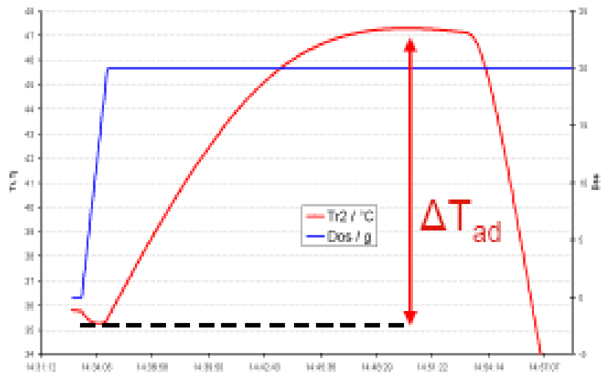
$$\Delta T_{ad} = \frac{\int q_r(t)\,dt}{M_r\, c_{pr}}$$

In case of a cooling Failure



ADIABATIC





Criteria for severity of desired reaction

Criterium	Severity
HIGH	ΔT_{ad} > 200C
Medium	50 < ΔT_{ad} < 200
Low	ΔT_{ad} < 50 C and no pressure build up

Runaway Scenario

1. Can the process temperature be controlled by the cooling system?
   Is the process dosing controlled?
   Heat release rate vs Dosing rate

2. What temperature can be attained after the runaway of the desired (chemical) reaction? MTSR (ΔT ad)

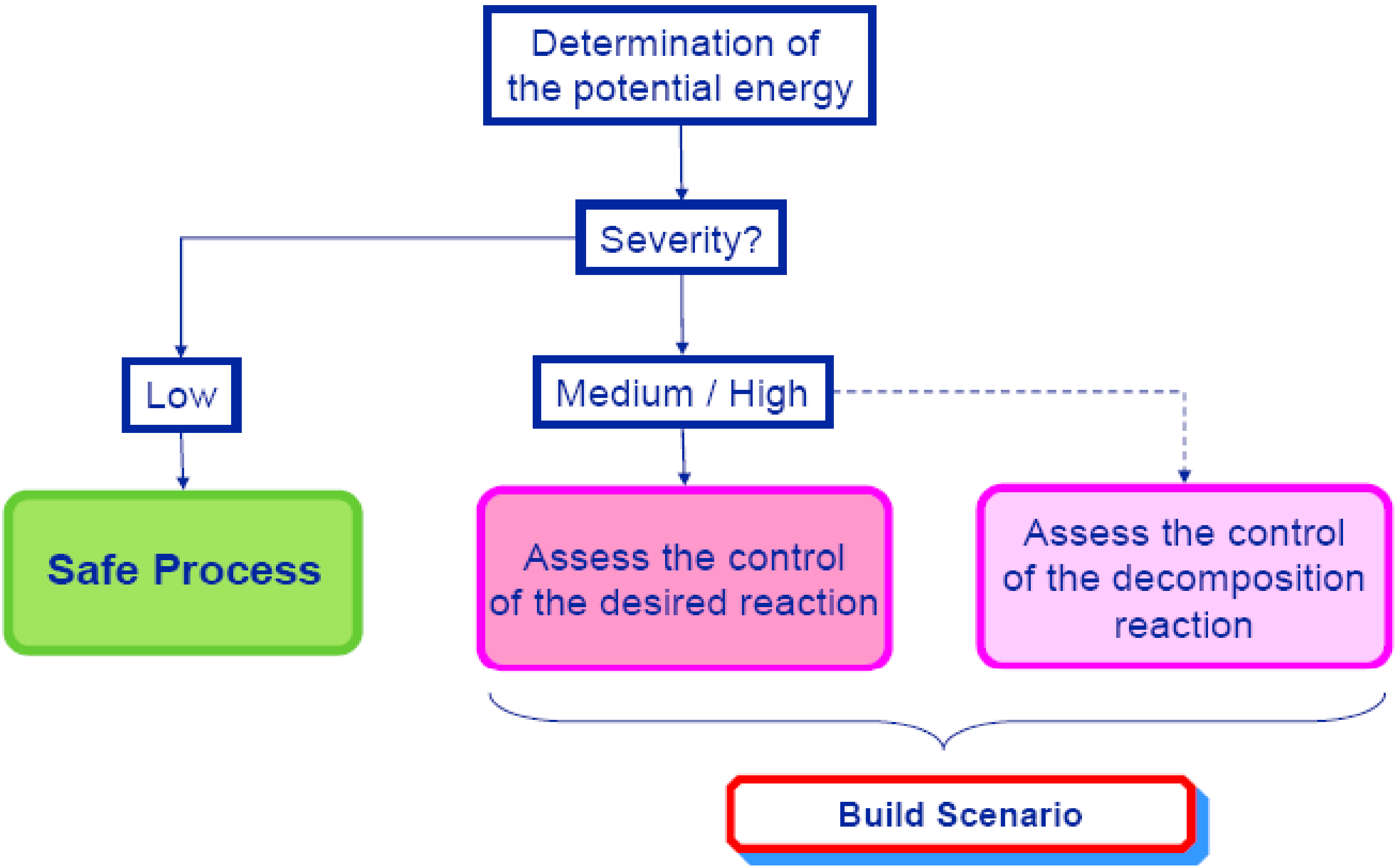
3. What temperature can be attained after runaway by decomposition reaction? ΔT ad (2)

4. At which moment does the cooling failure (desire reaction) have the worst case consequences? Max. thermal accumulation

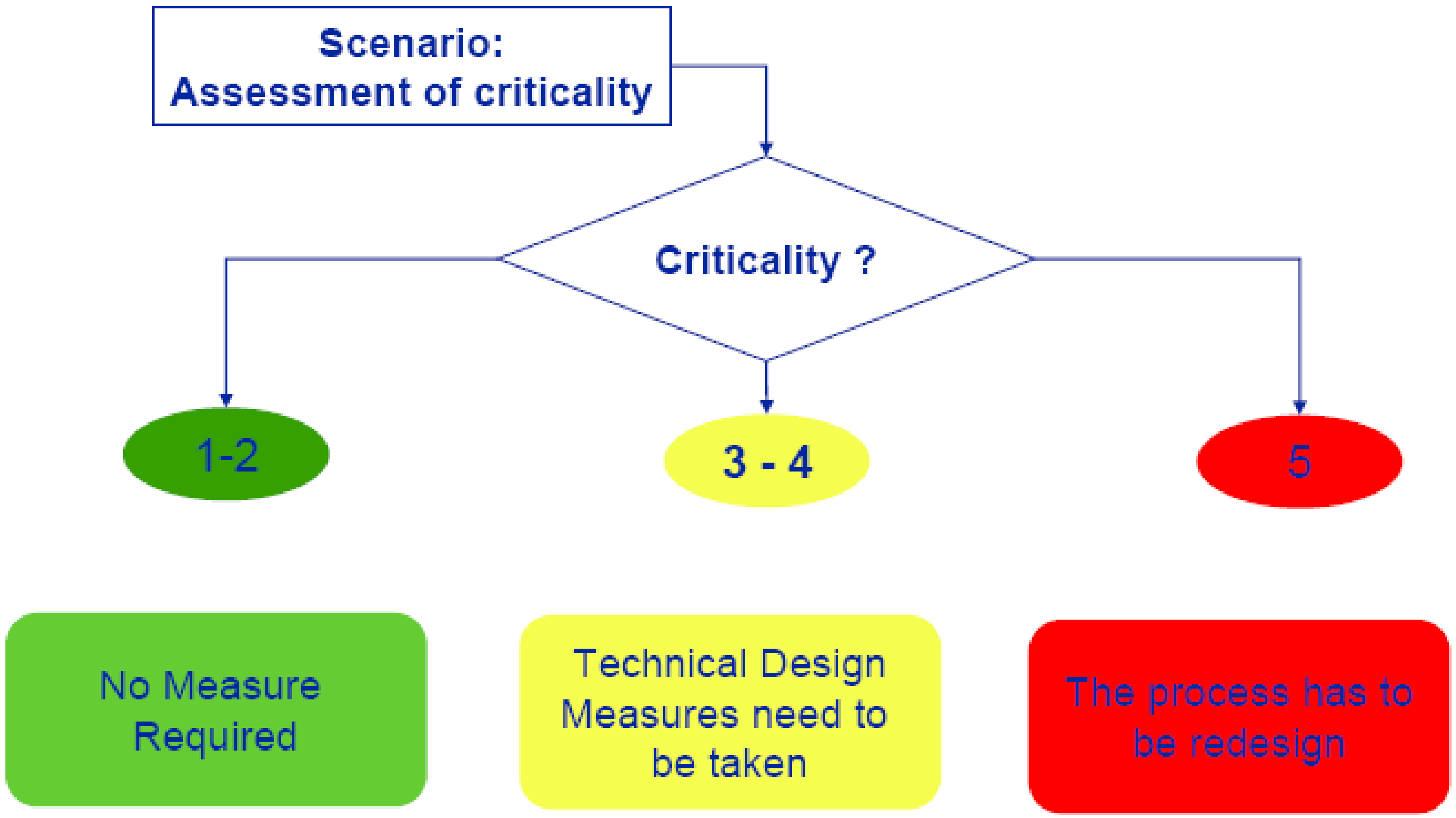
5. How fast is the runaway of the desired reaction? Fast (Tcf, ad.mode)

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

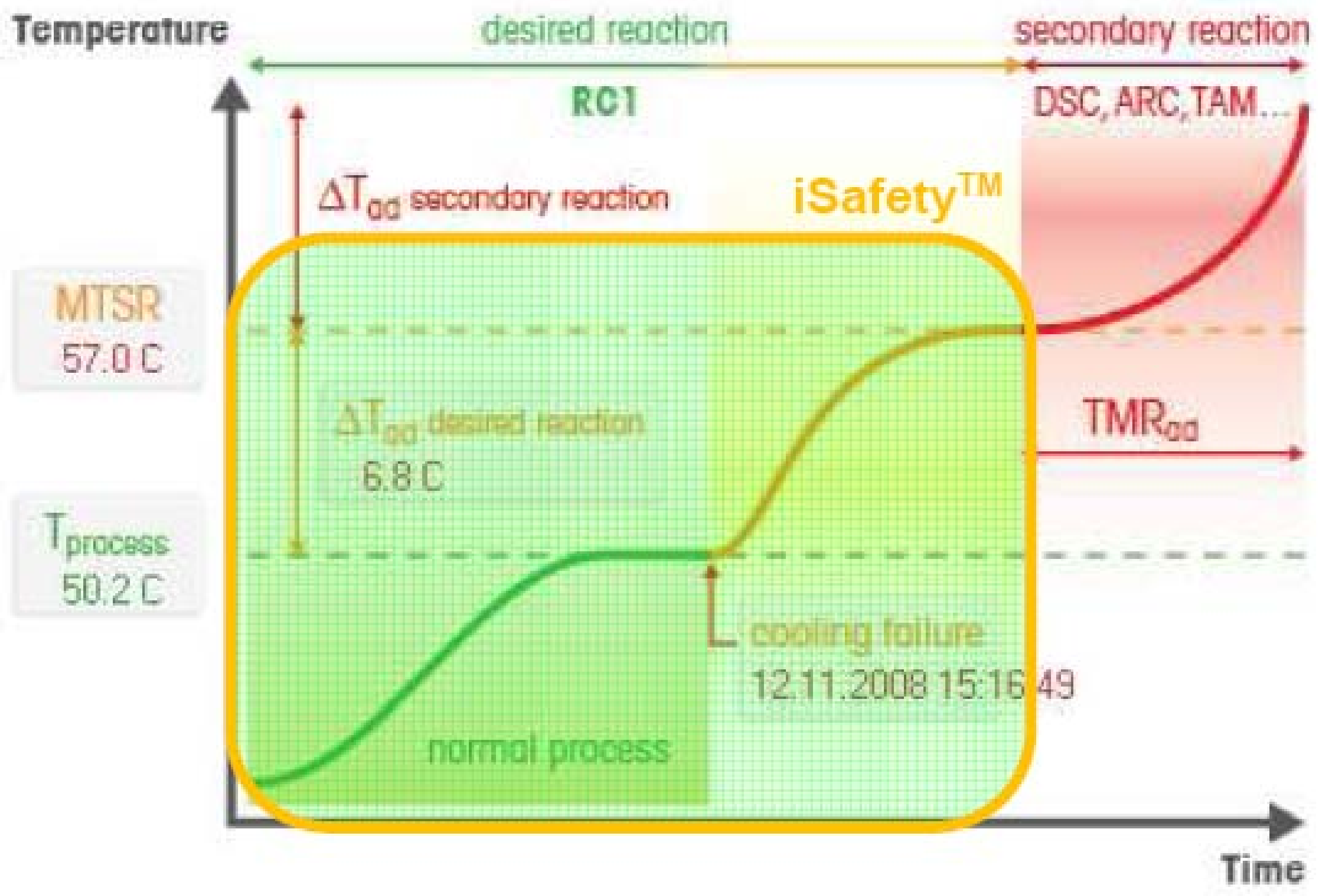
Assessment of thermal risk



Assessment of thermal risk



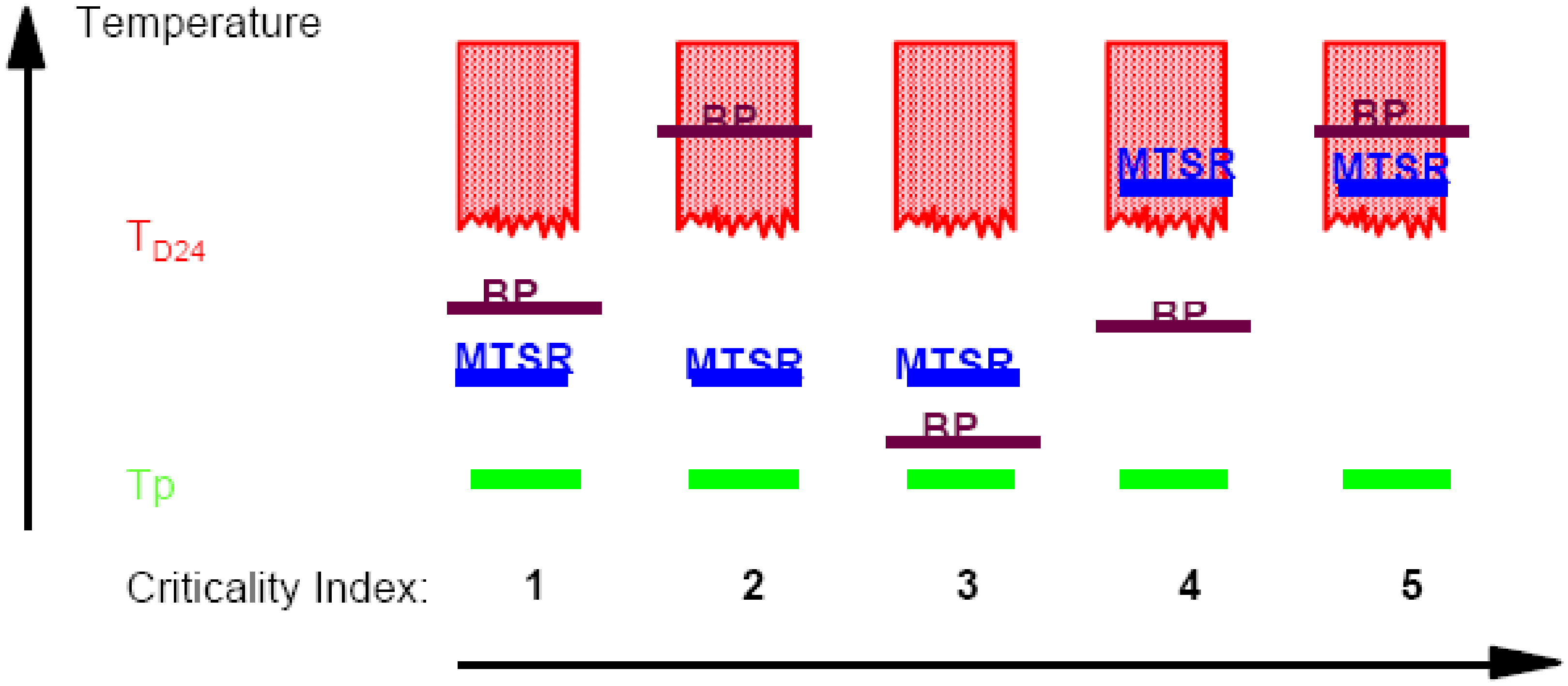
Thermal safety assessment : runaway scenario



Criteria for Severity and Probability

Criterium	*Severity*	*Probability*
HIGH	ΔT_{ad} > 200C	TMR_{ad} < 8 h
Medium	50 < ΔT_{ad} < 200	8 h < TMR_{ad} < 24 h
Low	ΔT_{ad}< 50 °C and no pressure build up	TMR_{ad} > 24 h

Assessment of criticality : Classification



- **Tp : Process Temperature**
  Defined by the mode of operation
- **MTSR: Maximum Temperature of Synthesis Reaction**
  Defined by the accumulation of reactants and Tp
- **T_{D24}: Temperature at which the Decomposition becomes critical TMRad = 24 hrs**
  Defined by the thermal stability of reaction mass
- **BT: Boilint point → Maximum Tolerable (Technical) Temperature**
  Defined by the equipment, i.e. Reflux temperature

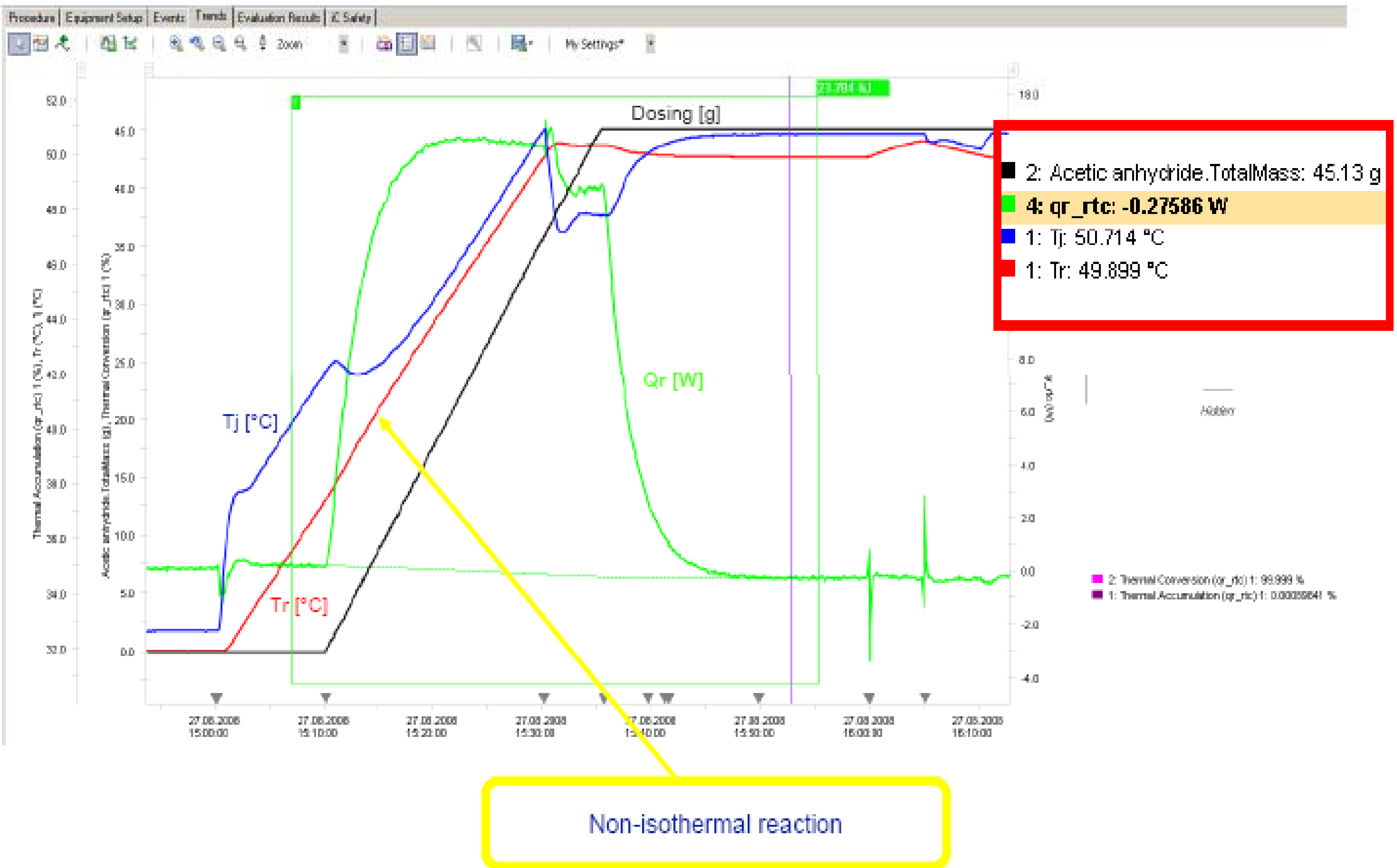
Experiment 1: Hydrolysis

- Experiment example: ***Hydrolysis***

- Starting with:
  - *Water + H_2SO_4 at 30 → 50°C*

- Dosing of:
  - *AcOAc*

Reaction 1



Dosing [g]
2: Acetic anhydride.TotalMass: 45.13 g
4: qr_rtc: -0.27586 W
1: Tj: 50.714 °C
1: Tr: 49.899 °C
Tj [°C]
Tr [°C]
Qr [W]
Non-isothermal reaction

Runaway Scenario

1. Can the process temperature be controlled by the cooling system?
   Is the process dosing controlled?
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2. What temperature can be attained after the runaway of the desired (chemical) reaction? MTSR (ΔT ad)

3. What temperature can be attained after runaway by decomposition reaction? ΔT ad (2)

4. At which moment does the cooling failure (desire reaction) have the worst case consequences? Max. thermal accumulation

5. How fast is the runaway of the desired reaction? Fast (Tcf, ad.mode)

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

1. How much thermal accumulation ?

- RTCal will provide the answer in Real Time
- For quick & safe scale up (heat transfer)
  no thermal accumulation = dosing controlled reaction

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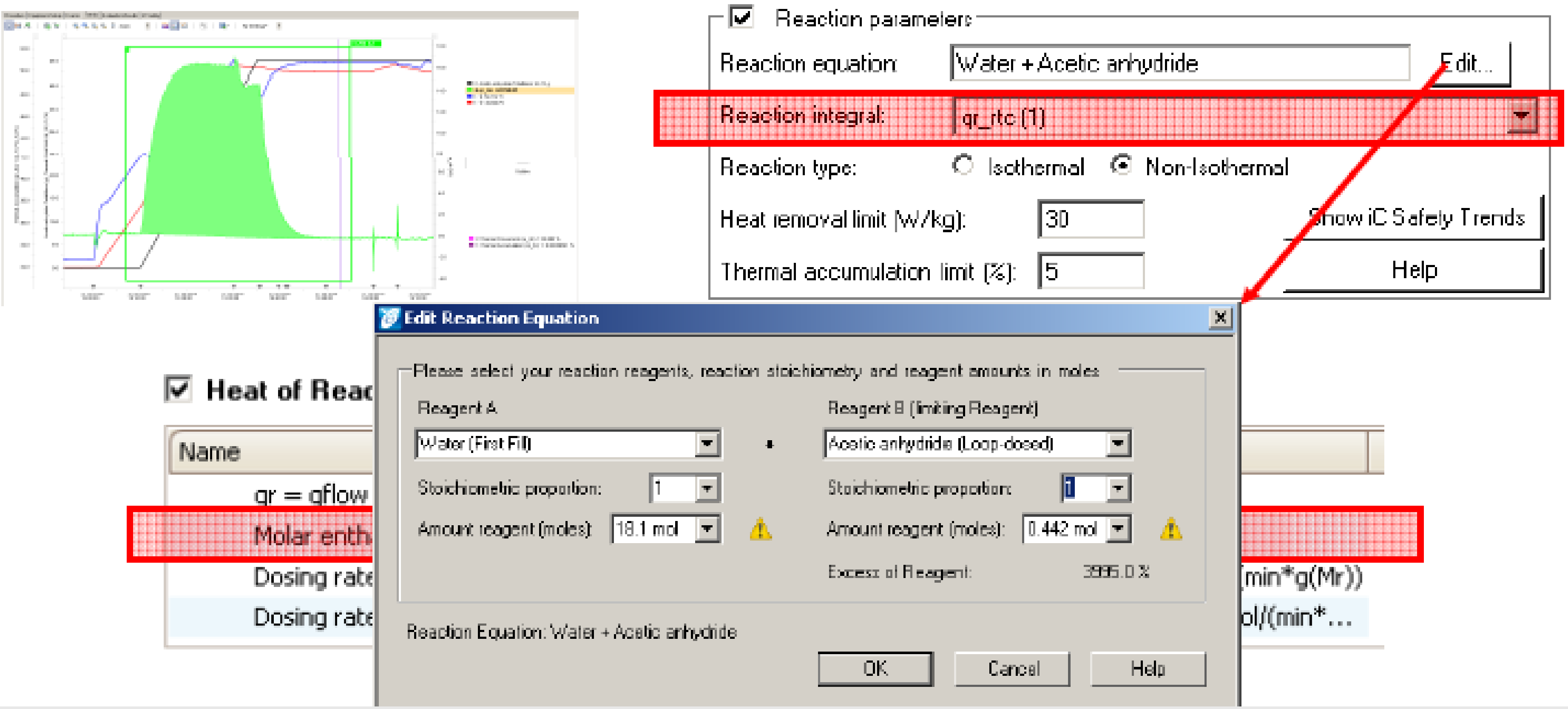
- Dosing time can be adjusted to fit cooling power plant vessel



1. Can plant vessel remove heat ?

Heat release Qr

Q_r = heat generation rate in W (= J/s)

= heat released per unit time

Specific heat release

= Qr/V or Qr/M = W/ liter or W/kg

= used for scale up

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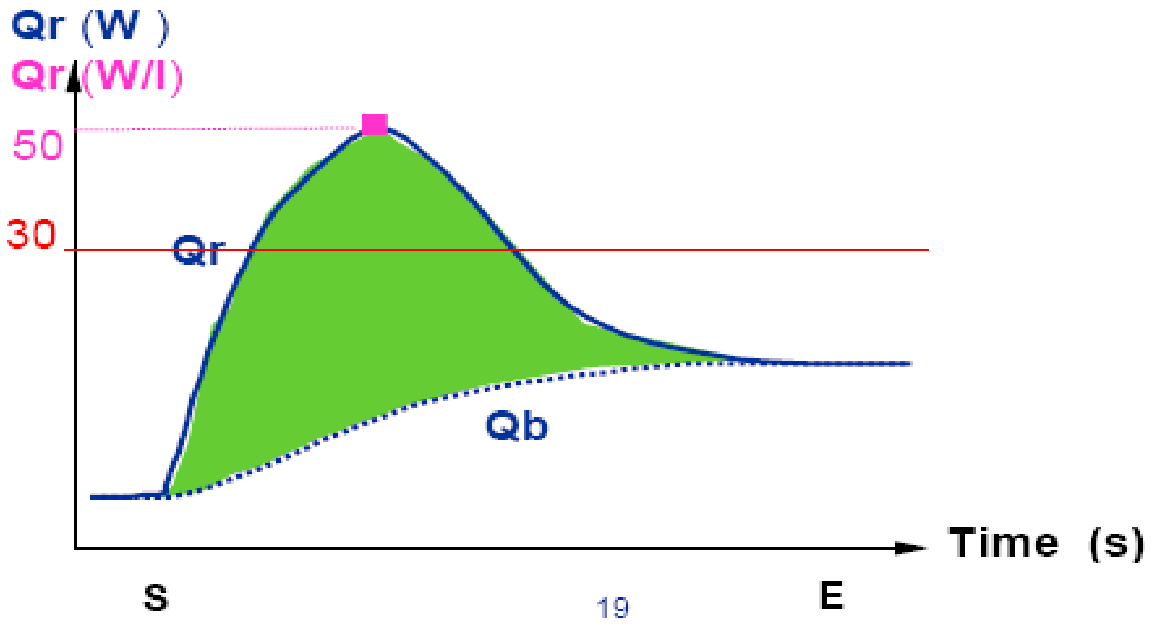
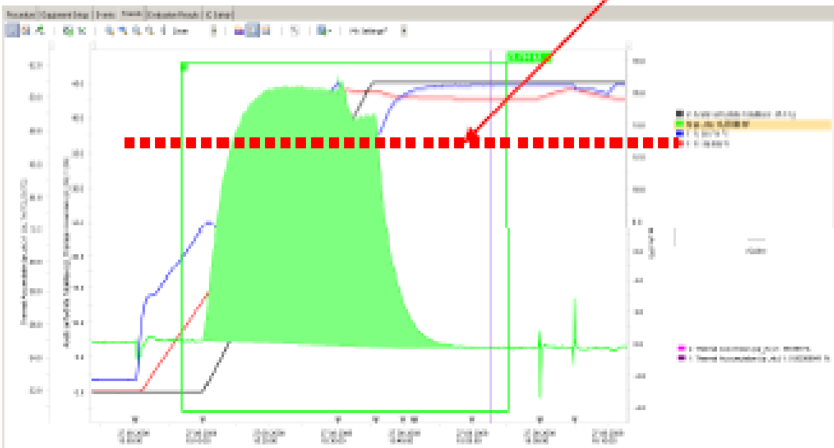
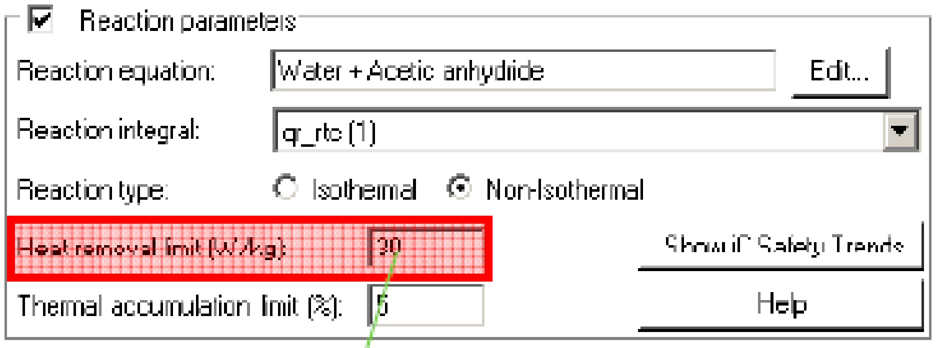
Typical plant heat removal = max. 30 W/liter!



1. Can heat be removed by plant vessel ?





Heat Removal

Name		
qhr = qflow + qaccu	23.8 kJ	
Specific heat removal	64.2 kJ/kg	64.8 kJ/l
Is Thermal Accumulation critical	Yes	

Name	During Reaction Time	During Dosing Time
Max specific heat removal rate	46.9 W/kg	46.1 W/kg
More		
Max heat removal rate	17.4 W	17.1 W
Max specific heat removal rate	47.3 W/l	46.5 W/l

2. MTSR – adiabatic temperature rise

The MTSR = Maximum Temperature of Synthesis Reaction

$$MTSR(T_0) = T_p + \chi_{acc} \Delta T_{ad}$$

T_{cf}: temperature of the cooling failure
T_p: temperature process
X_{acc}: degree of accumulation
ΔT_{ad}: total adiabatic temperature

This formula can be used for both critical temperatures, after desired reaction and decomposition.

$$\Delta T_{ad} = \frac{q_r[kJ]}{m_{tot}[kg] \cdot Cp[kJ / KgK]}$$

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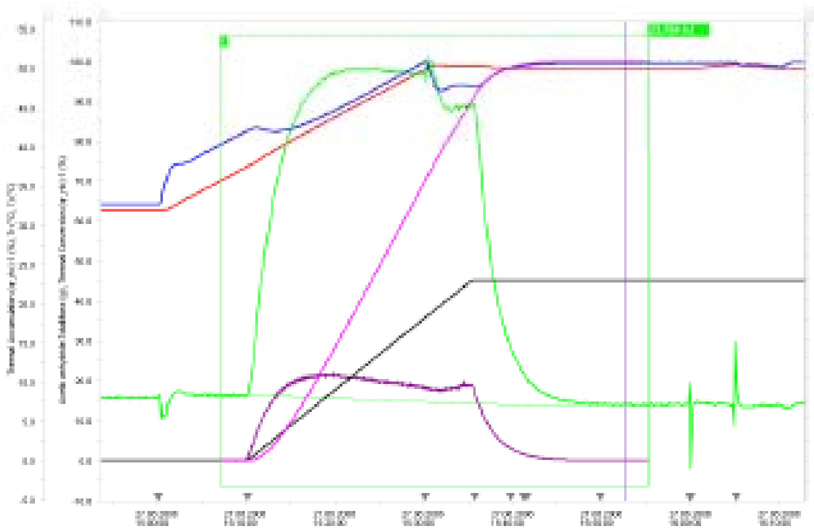
☑ **Adiabatic Temperature Rise (ΔTad) and MTSR**

Name	Temperature	Time
ΔTad, Worst case (Heat Removal)	15.8 K	
MTSR, Worst case (Heat Removal)	65.8 C	
Max. MTSR, Actual process (Heat Removal)	51.6 C	27.08.2008 15:34
⊟ More		
ΔTad, Worst case (Heat of Reaction)	16.6 K	
MTSR, Worst case (Heat of Reaction)	66.6 C	

4. What point is cooling failure worst ?



☑ Reaction parameters

Reaction equation: Water + Acetic anhydride [Edit...]

Reaction integral: qr_rtc (1)

Reaction type: ○ Isothermal ◉ Non-Isothermal

Heat removal limit (W/kg): 30 [Show iC Safety Trends]

Thermal accumulation limit (%): 5 [Help]

☑ **Thermal Accumulation**

Name	Percent	Time
Thermal accumulation at stoichiometric point	8.98 %	27.08.2008 15:35
Max thermal accumulation	11.2 %	27.08.2008 15:19
⊟ More		
Thermal conversion at stoichiometric point	91 %	27.08.2008 15:35
Thermal conversion at end of dosing	91.1 %	27.08.2008 15:35
Thermal accumulation at end of dosing	8.98 %	27.08.2008 15:35
	Volume	Mass
Accumulation of dosed reagent at stoichiometric...	3.74 ml	4.05 g
Max Accumulation of dosed reagent	4.66 ml	5.04 g

Safety assessment

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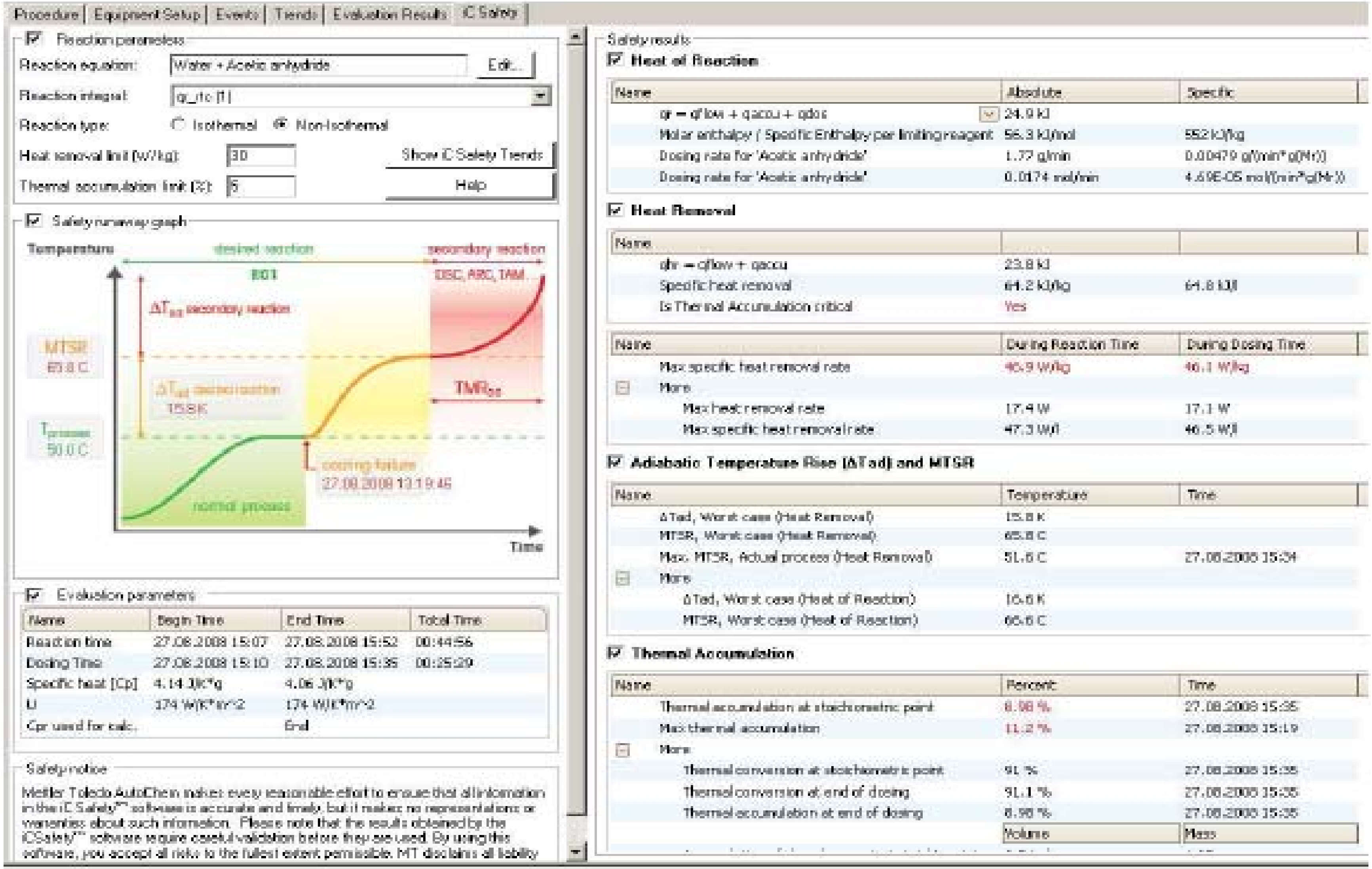

4-5 : Max. thermal accumulation & Tcf