Module 2:
Solution Exercises Systematic

Problem 1

The risk is evaluated based on the combination of probability of occurrence and severity (consequence).
For thermal risk the probability is determined by the TMRad: the time to maximum rate under adiabatic conditions. The TMRad is temperature dependent and indicates how long it takes from a given temperature to reach the end of the runaway.
For thermal risk the severity (consequence) is determined by the adiabatic temperature rise. For a reaction this consists in the adiabatic temperature rise due to the reaction and to the decomposition.
The criteria for both parameters are based on experience and are for a well-controlled system the following:

Criteria	Consequences	Probability
High	ΔTad > 200°C	TMRad < 8 h
Medium	50°C < ΔTad < 200°C	8 h < TMRad < 24 h
Low	ΔTad < 50°C and no pressure	TMRad > 24 h

The risk is then evaluated based on the combination of both:

Consequences					
High	ΔT_{ad} > 200K	Yellow	Red	Red
Medium	50K < ΔT_{ad} <200K	Yellow	Yellow	Red
Low	ΔT_{ad} < 50K And no pressure	Green	Green	Green
		$TMR_{ad} \geq$ 24h	8h<TMR_{ad}<24	$TMR_{ad} \leq$ 8h
		Low	Medium	High
		Probability		

Green	Low risk, risk acceptable
Yellow	Medium risk. Apply ALARP principle (ALARP: as low as reasonable practicable)
Red	High risk. Risk unaccpetable

Problem 2

The consequence of the runaway of the decomposition reaction is given by the adiabatic temperature rise ΔT_{ad}. ΔT_{ad} is calculated based on the specific decomposition energy (Q'_{dec}) and the specific heat capacity c'_p.

$$\Delta T_{ad} = \frac{Q'_{dec}}{c'_p} = \frac{kJ/kg}{kJ/(kg\cdot K)} = \frac{200}{1.8} = 111K$$

The consequence is medium (see criteria in Problem 1).

The probability is given based on the TMR_{ad}. The TMR_{ad} is 24h at 100°C. 100°C is the limit between low and medium probability. Hence if the temperature is below 100°C the probability is low, if the temperature is above 100°C, the probability is medium or high (see criteria in Problem 1).
The risk linked with the decomposition is medium below 100°C, medium above 100°C if the TMR_{ad} is longer than 8h and high if the TMR_{ad} is shorter than 8 hours (see criteria in Problem 1).

Problem 3

The TMR_{ad} is 8 hours at 120°C. One can estimate the TMRad at 80°C using the van't Hoff rule. The van't Hoff rule states the following: if the temperature increases by 10°C, the reaction rate doubles. So if the temperature decreases by 10°C, then the TMRad will double:

Temperature (°C)	TMRad (h)
120	8
110	16
100	32
90	64
80	**128**

The TMR_{ad} at 80°C is 128 hours.

Comment: this rule is not conservative for extrapolations however it is a good way to make estimations.

Problem 4

Part A:

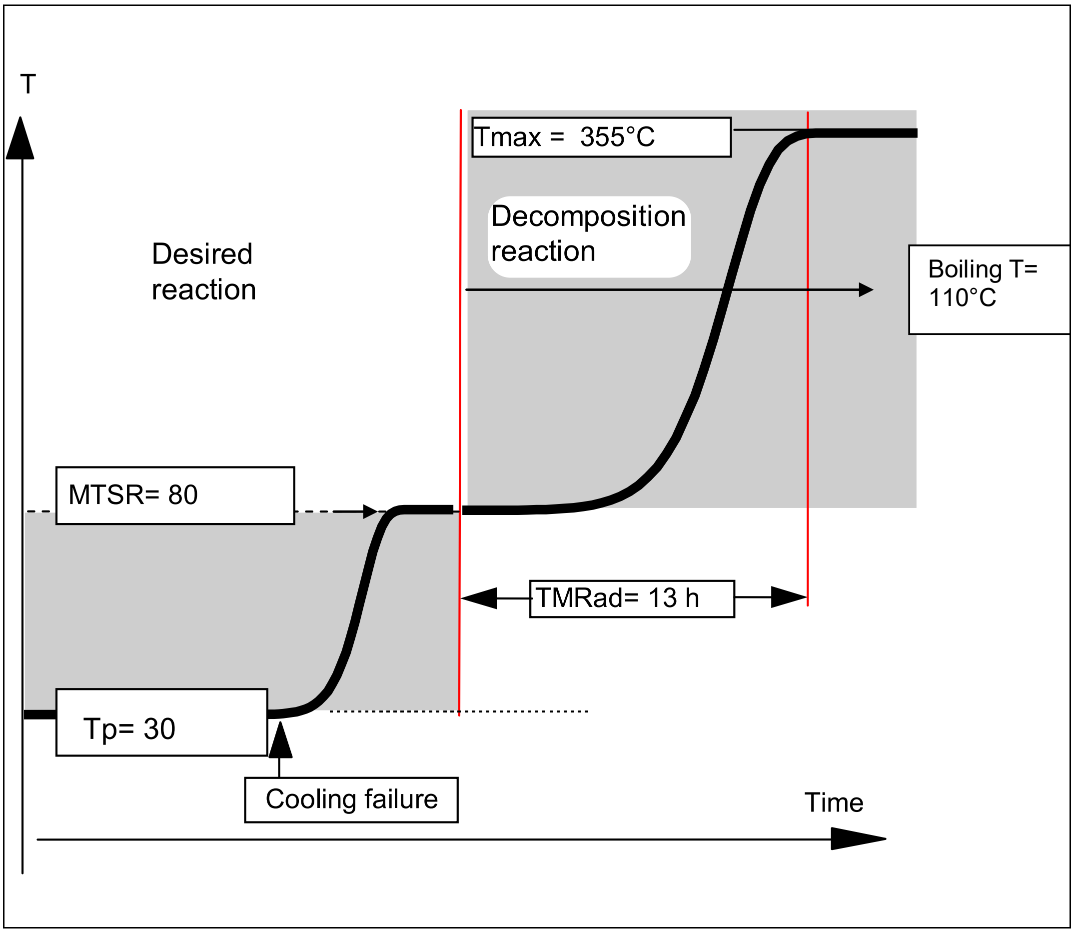
ΔT_{ad} of the reaction: 50°C

ΔT_{ad} of the decomposition: $\Delta T_{ad} = \frac{Q'_{dec}}{c'_p} = \frac{kJ/kg}{kJ/(kg\cdot K)} = \frac{550}{2} = 275K$

MTSR: $T_p + \Delta T_{ad,reaction}$=30°C + 50°C=80°C

T_{final}: MTSR + $\Delta T_{ad,decomposition}$= 80+275=355°C

TMRad 13 hours at 80°C.



Part B

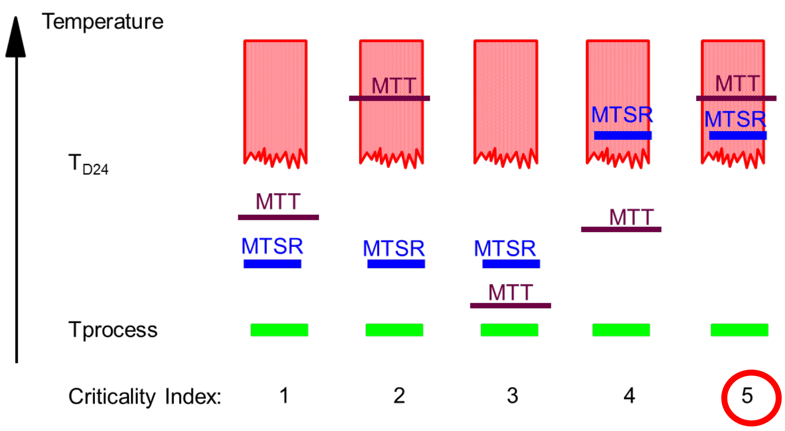
Since the TMR_{ad} is 13h at 80°C, the TD24 is smaller than 80°C. Estimation using van't Hoff's rule: ~70°C

MTT (boiling Temperature): 110°C

MTSR: 80°C

Td24: 70°C

T_p:30°C



Part C

To improve the safety, without changing the reaction, the MTSR must be reduced below TD24. TD24 and MTT could be influenced by using another solvent, however the reaction might not be as good (selectivity, yield etc).
The criticality class would then be 2.
To reduce the MTSR, the accumulation or the process temperature must be lowered. Indeed, $MTSR = T_p + X_{Acc} \cdot \Delta T_{ad,rxn}$
Decreasing the process temperature will lower the reaction rate and thus the productivity. Thus, this might not be feasible.
Reducing the accumulation, means to change the process to a semi-batch process, where one reactant is added over time. In case of a cooling failure, if the addition is stopped immediately, the temperature increase of the synthesis reaction depends on the amount of reactant present (the accumulation). In this case a temperature of ca 40°C would be ok. Thus, the maximum accumulation would need to be reduced below 80%.
This will be further explained in the chapter “Synthesis reaction”.