Process Safety

Case Study
"Introduction of a Production Process At Plant Scale"

Solution

Part 1: Thermal Stability: Severity

Reactant A

The decomposition of A occurs within a temperature range (about 300°C) which cannot be reached by itself. Would the main reaction lend to such a temperature, there would be no more A left but the final reaction mass would be present.

Conclusion:

Potential of an incident:	low, ΔTad = Δ35 K
Probability:	low, because decomposition occurs at higher temperatures only

Final Reaction Mass

The decomposition energy is huge: - 960 kJ/kg; this corresponds to an adiabatic temperature raise of about 565 K. The temperature at which this decomposition reaction is observable in the dynamic DSC experiment is low, about 160°C.

The question is now: can this decomposition reaction be started when the main reaction runs out of control? This depends strongly on the way the reaction is operated.

Conclusion:

If the decomposition reaction is triggered a thermal explosion will occur.

The severity is high.

Mixture of the Reactants

In the DSC Thermogram (Figure 3) the first peak represents the desired reaction. The heat of reaction is -250 kJ/kg; this corresponds to an adiabatic temperature increase of :

$$\Delta T_{ad} = \frac{250 kJ / kg}{1{,}7 kJ / (kg.K)} \approx 150 K$$

Hence, starting from the process temperature of 80°C, a final temperature of 80 + 150 = 230°C can be reached.

It is obvious that the decomposition reaction will be triggered at a temperature of 230°C. This means an additional temperature increase of 565 K; so the end temperature would be 230°C + 565°C = 795°C.

Conclusion:

Such a scenario means a thermal explosion with serious damage. The severity is high.
In the scenario above the dosing of the reactant B was not taken into consideration: In the case of a cooling failure or a temperature increase the addition of B can be stopped, providing an additional control of the reaction course. But also for a semi-batch process the highest allowable temperature has to be defined, depending on the TMRad.

Part 1: Thermal Stability: Estimation of the TMRad

Figure 4 shows that the maximum heat release rate of the reaction is 40 W/kg at 190°C.

Under adiabatic conditions, the reaction heat is entirely used to raise the temperature. The rate of temperature raise is:

$$40 / 1700 = 2{,}35.10^{-2}\ °C/s = \text{ca. } 85°C/h$$

To go from 190°C to 200°C, it takes 10/85 = about 0.1 hours.

By using Van't Hoff's law it is possible to extrapolate the time period for a temperature increase of 10 K for different starting temperatures:

Starting Temperature (°C)	190	180	170	160	150	140	130	120
Time for a Temperature Increase of 10 K (h)	0,1	0,2	0,4	0,8	1,6	3,2	6,4	12,8

The TMRad is the sum of all the time periods in the table from starting to end temperature.

Because it's a geometric row, the sum of the values in the table (that means the TMRad) is just twice the value of the first term.

In this calculation, it was nevertheless assumed that the heat release rate will be constant in the temperature interval of 10 K. Hence the time has been overestimated. Therefore an additional calculation is performed with a constant heat release rate but twice the value as before.

Starting Temperature (°C)	180	170	160	150	140	130	120
TMRad (h):	0,4	0,8	1,6	3,2	6,4	12,8	25,6

So from these estimations the TMRad value is 8 hours at a temperature of 130°C .

Conclusion:

The control of the reaction course is essential for the thermal safety of the process. The maximum temperature of the synthesis reaction (MTSR) to be reached in the case of a cooling failure must not be higher than 130°C based on the estimation by Van't Hoff's law.

A more detailed determination of the TMRad is needed.

Part 1: Thermal Stability

Determination of the TMRad

Calculation of the Activation Energy:

Using two values from figure 4 (40 W/kg at 190°C and 120 W/kg at 210°C) the activation energy can be calculated:

$$Ea = \frac{R \cdot \ln\left(q_1 / q_2\right)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{8.314 \cdot \ln\left(120/40\right)}{\frac{1}{463} - \frac{1}{483}} \cong 100 \text{ kJ / mol}$$

TMRad:

Subsequently the TMRad can be determined:

Starting from 80°C:

$$TMRad = \frac{Cp \cdot R \cdot T_0^{\,2}}{q_0 \cdot Ea} = \frac{1.7 \cdot 8.314 \cdot 353^2}{0.1 \cdot 100} = 176'120s \approx 400h$$

TMRad as a function of temperature

T(°C)	80	90	100	110	120	130
TMRad (h)	400	165	72	33	15	8

The values are shown in a graph:

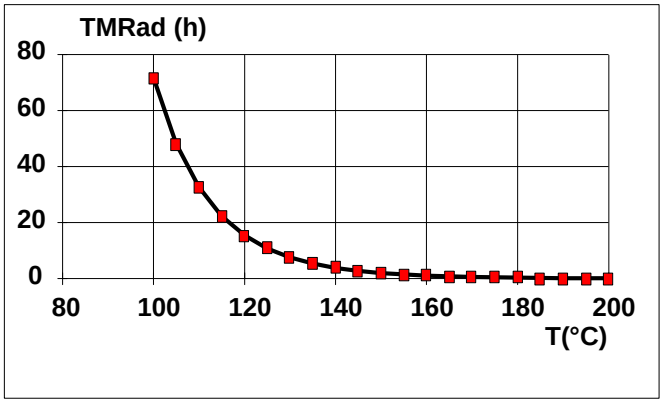

Figure 9: TMRad as a Function of Temperature

Conclusion:

At 130°C the TMRad is about 8 hours, which is the safety limit for a production process. After loss of the control of the synthesis reaction the maximum temperature of the reaction mass must not exceed 130°C.

Part 2: Desired Reaction: Heat Removal

The heat removal is calculated from $q_{ex} = U \cdot A. (T_R - T_C)$.

With $U = 300\ W/m^2.K$)

$A = 20\ m^2$

T_R from 80 to 120°C

T_C= 60°C (melting point of the reaction mass)

For a reaction mass of 15 000 kg (the maximum heat removal is given from the start of the reaction) the maximum heat removal of the vessel is:

T_R (°C)	80	90	100	110	120
q_{EX} (W/kg)	8	12	16	20	24

Conclusion:

At 80°C the heat release rate of the reaction is about 28 W/kg; this value is higher than the maximum heat removal of the vessel.

Part 2: Desired Reaction: Accumulation

The maximum accumulation is given at the stoichiometric point of the addition of B.

The heat of reaction is -250 kJ/kg with regard to the final reaction mass.

At the stoichiometric point the actual amount of reaction mass is
15 000 + (3 000 / 1.1) = 17 700 kg; hence the energy reaction is given by
-250 x (18 000 / 17 700) = about -255 kJ/kg.
This energy corresponds to an adiabatic temperature raise of 150 K.

With an accumulation of 38 % the MTSR is determined to be
MTSR = 80° + 0,38 x 150° = 137 °C.

At MTSR the thermal stability of the reaction mass is critical:
TMRad = 5 h.

Conclusion:

In the case of a cooling failure after a dosing time of 1.8 hours the temperature of the reaction mass would reach 137°C due to the release of the accumulated energy of the desired reaction. Starting from 137°C within 5 hours a thermal explosion would occur with a temperature raise up to more than 700°C

The scenario shows a criticality of 5.

The process has to be reengineered.

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Part 3: Process Optimization

Adjustable Parameters

After having considered all the border conditions, two more parameters can be adjusted:

- The temperature, from 80 to 120°C
- The dosing time of B, between 2 hours (1,5 m^3/h) and 8 hours.

Border Conditions

Conversion Rate: 99% in maximum 10 hours

Maximum temperature in case of cooling break down (MTSR): 130°C

Maximum heat release rate must respond to the cooling capacity.

Design of Experiments

We consider here only an example:

5 temperature levels are selected (°C): 80, 90, 100, 110, 120°C

4 dosing times (h): 2, 4, 6, 8h

The experiments were performed in a reaction calorimeter.

The results are displayed in three tables:

Table 1: Reaction Time for 99% conversion (h)

Temperature (°C)		80	90	100	110	120	
Dosing time	2h	>10	7,4	5.0	3.8		3.0
	4h	>10	9.0	7.4	5.4	4.8	
	6h	>10	>10	8.4	7.2	6.6	
	8h	>10	>10	>10	9.3	8.8	

Table 2: Maximum heat flow of the reaction mixture (W/kg)

Temperature (°C)		80	90	100	110	120
Dosing time	2h	32	36	38	42	43
	4h	18	20	21	22	23
	6h	13	14	14	15	15
	8h	10	11	11	12	12

Table 3: Maximum heat accumulation (% of total heat of reaction)

Temperature (°C)		80	90	100	110	120
Dosing time	2h	38	29	22	17	13
	4h	27	21	15	12	10
	6h	22	17	12	10	8
	8h	19	14	11	8	7

The highest temperature that can be reached in case of loss of control of the main reaction can be calculated from the maximum heat accumulation. Thus, **Table 3** can be transformed into a table giving the maximum final temperatures.

Data: Heat of reaction: $-\Delta H_R = -255$ kJ/kg at the stoichiometric point

Specific heat of reaction mass: Cp = 1700 J/(kg · K)

The accumulation ratio gives the maximum final temperature which can be reached:

$$MTSR = Tr + \Delta Tad \cdot X_{Acc}$$

(X_{Acc} = fraction of heat accumulated from **Table 3**).

Thus we build **Table 4**:

Table 4: Maximum reachable temperature in case of a cooling failure (MTSR)

Temperature (°C)		80	90	100	110	120
Dosing time	2h	137	134	133	136	140
	4h	120	121	123	128	134
	6h	113	115	119	125	131
	8h	109	112	116	123	130

After examination of the procedures taking into consideration the three criteria:

- Heat flow of the reaction / cooling capacity
- 99% conversion in less than 10 hours
- maximum temperature in case of a cooling failure: 130°C

Table 5: Synopsis

Temperature (°C)		80	90	100	110	120	
Dosing time	2h		xqa	qa	qa	qa	qa
	4h		xq	q	q	q	a
	6h		xq	xq			a
	8h		xq	x	x		

(x= conversion < 99%, q: insufficient heat removal, a: too high degree of accumulation)

The following proceeding variants are still left:

- **Reaction temperature 100°C, dosing time 6 hours**
- **Reaction temperature 110°C, dosing time 6 hours**
- **Reaction temperature 110°C, dosing time 8 hours**

Reaction tem