



Process Safety

Case Study

” Introduction of a Production Process At Plant Scale ”

Introduction

The present case study has been conceived by considering actual data. It is devised in such a way that it is possible to get a deeper insight in one or another aspect of the thermal safety of the process.

Topic

It deals with the technical and safety study of a stage of a synthesis process. The desired reaction is highly exothermic and the reaction mass is stable only within a very limited temperature range. One intends to build up appropriate reaction conditions based on the stability of the reaction mass and the cooling capacity of the reactor.

The problem consists of two parts that can be treated separately if necessary.

Thermal Stability of the Reaction Mass

The provided thermal data are used to determine the range of parameter values that defines a safe operating of the reactor.

Process Design

The cooling capacity of the reactor must be sufficient to dissipate the high heat release rates in the production scale. The cooling power of the production reactor is determined with an estimated value of the heat transfer coefficient and compared with the heat release rates of the reaction.

The reactor type (batch / semi-batch) has to be defined first. Then it will be possible to analyze the results of a design of experiments in such a way that the optimal working conditions can be derived by taking into account the different limits.

The thermal safety of the process must be guaranteed, that means there is no critical situation even in the case of a cooling failure.

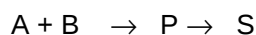


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Data

Chemistry:

The reaction runs like



A, B: reactants

P: desired product

S: decomposition product

Laboratory Procedure (extract):

- Reactant A is in solution (2 kmol/m^3 , $\rho=1000 \text{ kg/m}^3$) and is introduced as it is.
- Start stirring. Heat the solution of A up to 80°C .
- The reactant B is added as a 11 molar solution. The excess of B is set equal to 10%; hence the molar ratio $B/A = 1,1$.
- Maintain the reaction mass for 10 hours at $80 - 90^\circ\text{C}$.
- Cool down to ...

Reactor:

It is intended to perform this reaction in a 16 m^3 stainless steel reactor with external semitoric welded pipes.

The maximum possible volume of the reactor is 20 m^3 .

The maximum heat exchange area is 20 m^2 and corresponds to a content of 14 m^3 .

Water is used as the cooling medium and the normal temperature of the water is 30°C .

Quantities:

The present synthesis stage is one of several; therefore the quantities must be adjusted to those of the preceding and following steps.

A: 15 m^3 , concentration: 2 kmol/m^3 (30 kmol)

B: 3 m^3 , concentration 11 kmol/m^3 (33 kmol)

Molar ratio $B/A = 1.1$

Productivity:

In order to synchronize this synthesis stage with the other stages of the synthesis sequence, a time cycle of 12 hours must be held. Therefore taking into account the heating up and transfer times, 10 hours are left for the reaction.

Quality:

The conversion of A should not be less than 99 %



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Questions:

On the basis of this study, do you conclude that this reaction may be performed as a batch reaction (adiabatic or isothermal conditions)?

Part 1: Thermal stability and decomposition reaction

1. Make an assessment of the potential of a runaway reaction
2. Make an assessment of the probability of a runaway reaction

Part 2: Desired reaction

3. Is the cooling capacity sufficient to control the reaction under normal operating conditions?
4. What are the consequences of a cooling failure?

Part 1: Potential

Thermal Stability of Reactant A

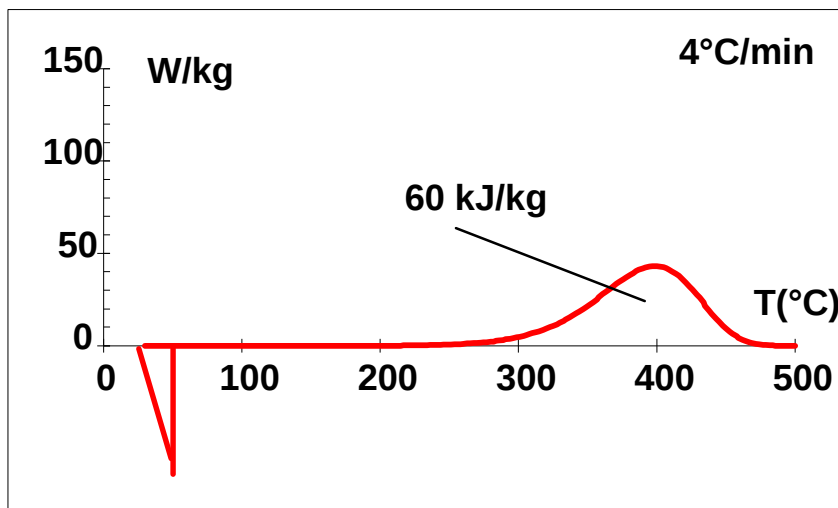


Figure 1: DSC Thermogram of Reactant A

The **reactant B** shows no exotherm below 500°C.

Further Information:

- The specific heat capacity of the reaction mass is 1.7 kJ/(kg.K)
- The boiling point of the reaction mass is below 200°C.
- No gases are formed during the reaction.
- The potential is assessed using the following criteria:

H:	HIGH	for $\Delta T_{ad} > 200$ K
M:	MEDIUM	for $50 \text{ K} < \Delta T_{ad} < 200 \text{ K}$
L:	LOW	for $\Delta T_{ad} < 50 \text{ K}$ and no pressure built-up

Question:

How do you assess the consequences of a decomposition reaction of the reactants?

Thermal Stability of the Final Reaction mass

Further DSC experiments were performed with the final reaction mass.

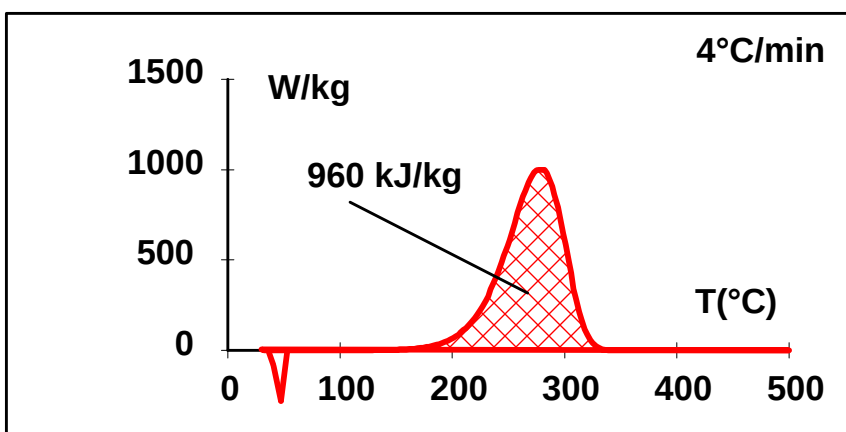


Figure 2: DSC Thermogram of the final reaction mass

Both reactants A and B were mixed at the ambient in a pressure resistant gold plated steel cell which was then heated linearly in the DSC apparatus.

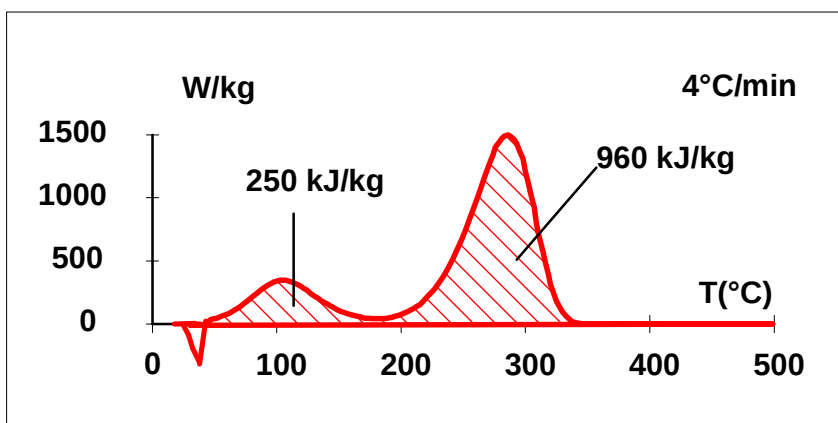


Figure. 3: DSC Thermogram of the Cold Mixed Reactants

Question:

On the basis of this study, do you conclude that this reaction may be performed as a batch reaction (adiabatic or isothermal conditions)?

Part 1: Probability estimation

Thermal Stability of the Final Reaction Mass

Estimation of the Probability of Triggering the Runaway Reaction

The probability of an incident can be evaluated using the time scale. If, after a 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.

The Time to Maximum Rate under adiabatic conditions (TMRad) can be used to estimate the probability of triggering a decomposition reaction. As a guideline the following values can be used for the assessment of the thermal safety of chemical reactions:

- If TMRad > 24 hours (1 day) the probability is low (uncritical process).
- IF TMRad < 8 hours (1 shift) the probability is high (critical process).

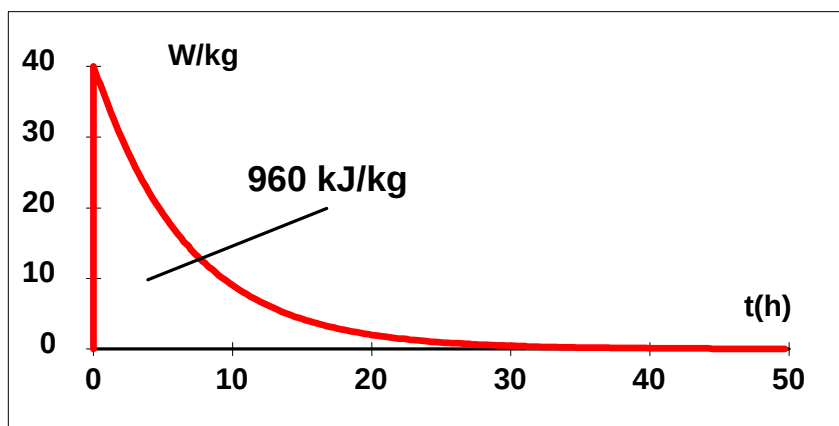


Figure 4: Isothermal DSC Thermogram at 190°C

Question:

Depending on the results of the isothermal DSC experiment at 190°C make an estimation of the probability of triggering the decomposition reaction. To do this use the Van't Hoff's law (doubling of the heat release rate for every temperature increase of 10 K).

Part 1: Probability quantitative

Thermal Stability of the Final Reaction Mass

Quantitative Investigation

A series of isothermal DSC measurements at different temperatures allow determining the maximum heat flow as a function of temperature. The analysis of the flow by using Arrhenius law (see below) leads to the activation energy of the decomposition.

From these data the so called "TMR-Formula" provides the induction time of the runaway reaction (under adiabatic conditions) and thus the probability of such an event.

$$TMR_{ad}(s) = \frac{Cp \cdot R \cdot T_0^2}{q_0 \cdot E}$$

with

Cp	=	heat capacity	J/ (kg.K)
R	=	gas constant	8,314 J/(mol . K)
To	=	initial temperature	K
qo	=	heat release rate at To	W/kg
E	=	activation energy	J/mol

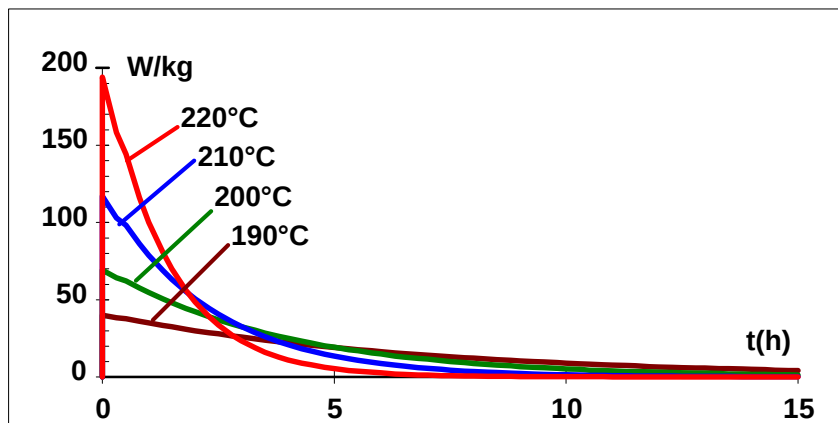


Figure 5: Isothermal DSC Thermograms of the Final Reaction Mass

Table: Maximum Heat Release Rates (from isothermal DSC experiments)

T (°C)	190	200	210	220
q _{max} (W/kg)	40	70	120	190

Question:

Calculate the activation energy the decomposition reaction using the data given in the table. Subsequently define the highest allowable temperature based on the induction times for the decomposition at different temperatures.

Part 2: Desired Reaction

Heat Removal Under Normal Operating Conditions

It is intended to perform this reaction in a 16 m³ semi-batch vessel with external semitoric welded pipes. The maximum exchanging area of the vessel is 20 m² and this value is reached from a volume of the reaction mass of 14 m³. The chosen initial amount is such that the volume is 15 m³ before dosing.

3 m³ of reactant B are added.

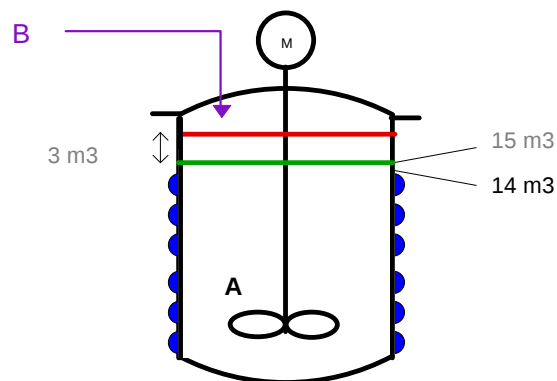


Figure 6: Schematic graph of the vessel

Questions:

Calculate the heat removal of the vessel in kW/m³ solution of A at the following temperatures: 80, 90, 100, 110 and 120°C.

The solution of reactant A will crystallize at too low temperatures. Therefore a minimum wall temperature of 60°C has to be assured.

For the calculations assume a heat exchange coefficient of 300 W/(m²·K) and refer the cooling power to the initial volume of 15 m³.

Part 2: Desired Reaction

Assessment of the operating process from laboratory procedure

In the reaction calorimeter one experiment was performed at a temperature of 80°C and a dosing time of 2 hours.

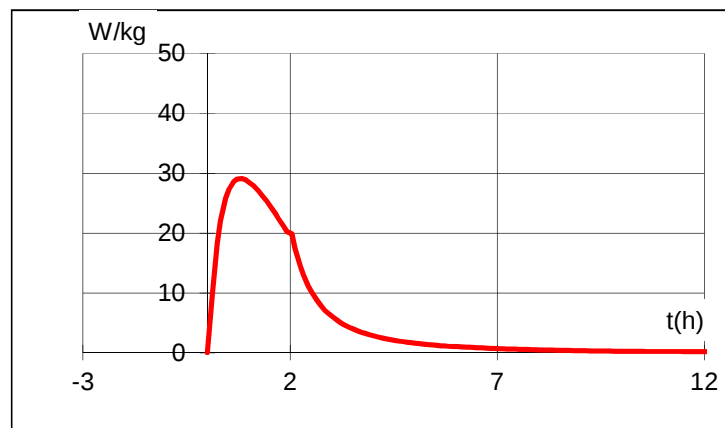


Figure 7: RC-1 Experiment: Heat Release Rates

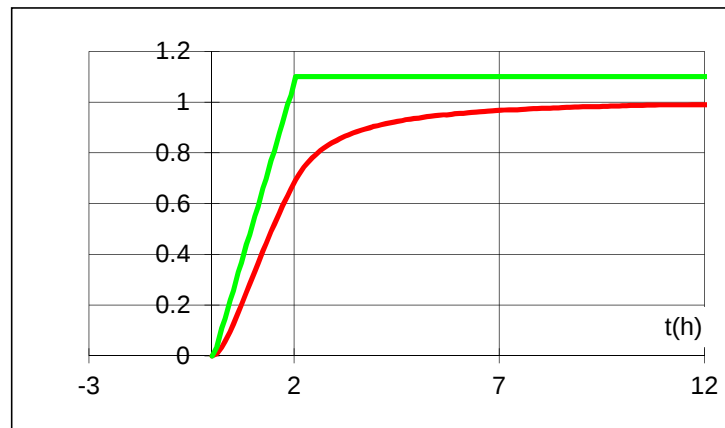


Figure 8: RC-1 Experiment: Dosing and Conversion

Questions:

Do you conclude that this reaction may be performed in a production plant?

- Is heat removal sufficient? ($U = 300 \text{ W/(m}^2 \cdot \text{K)}$)
- Can the decomposition be triggered when the main reaction runs out of control?
- Develop the runaway scenario. Make an assessment of the criticality of the process.