Module 4-02 Price of a zero order approximation

A reaction mass is to be concentrated by vacuum distillation in a 1600 litre stirred tank. Before distillation, the contents of the vessel are 1500 kg containing 500 kg of product. The solvent should be totally removed from the solution at 120 °C with a maximum wall temperature of 145 °C (5 bar steam). In order to evaluate the thermal stability of the concentrated product, a dynamic DSC experiment was performed (Figure 1).

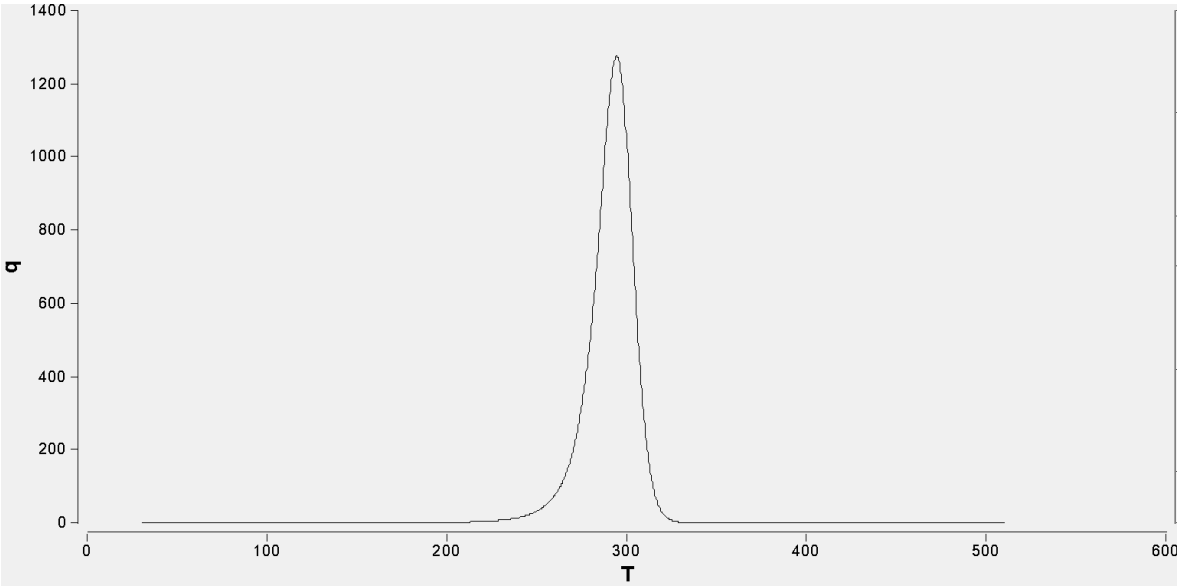

Figure 1: Dynamic DSC-Thermogram of concentrate. Sample 12,3 mg in gold plated pressure resistant crucible, Scan rate 4 K/min. The energy is 500 J/g. Coordinates: heat release rate in W/kg versus temperature in °C.

This thermogramme shows a steep peak, the autocatalytic nature o the decomposition is likely. Thus two isothermal DSC experiments were performed at 240 and 250 °C in order to confirm this hypothesis and to evaluate the probability of triggering the decomposition (Figure 2).

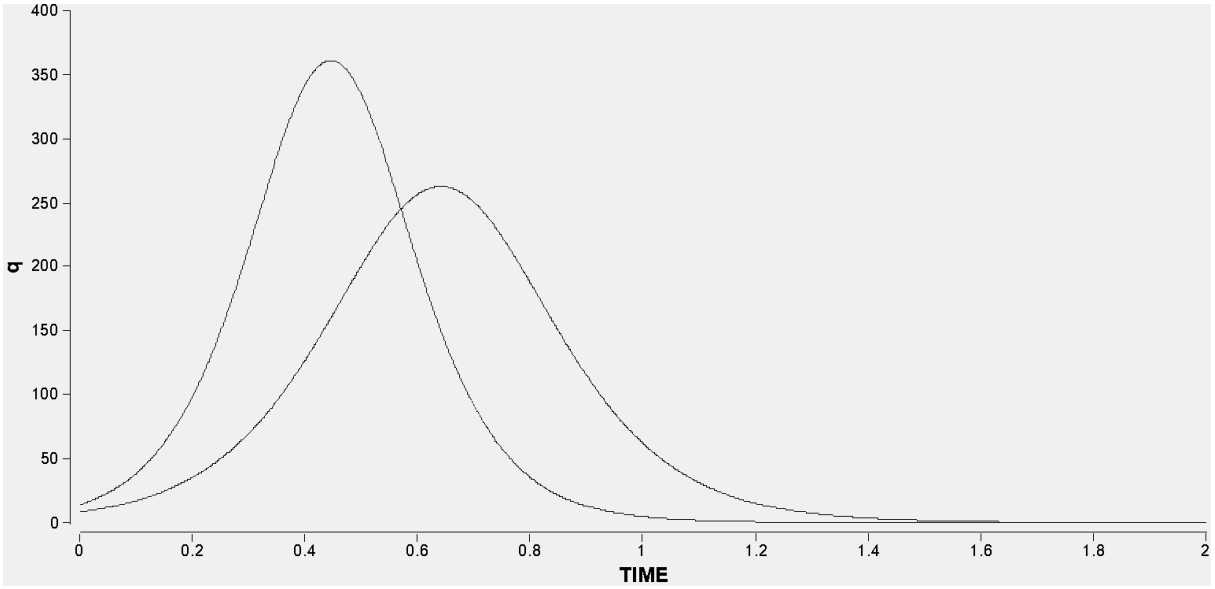

Figure 2: Isothermal DSC-Thermogrammes of concentrate : Sample 15,2 mg at 240 °C and 13,4 mg at 250 °C in gold plated pressure resistant crucibles. For both thermogrammes, the energy is close to 500 J/g. Coordinates heat release rate in W/kg versus time in hours.

The results can be summarised as follows:

- At 240 °C the initial heat release rate is 8.5 $W \cdot kg^{-1}$ and the maximum heat release rate 260 $W \cdot kg^{-1}$.
- At 250 °C the measured heat release rates are 15 and 360 $W \cdot kg^{-1}$ respectively.

Questions:

1. How do you assess the severity of a runaway of this concentrate?
2. How do you assess the probability of triggering it?

Potential:

With a specific heat capacity of 1.7 $kJ \cdot kg^{-1} \cdot K^{-1}$, the adiabatic temperature rise is

$$\Delta T_{ad} = \frac{Q'}{c'_P} = \frac{500}{1.7} = 294\ K$$

Thus the severity is "High" and the probability of triggering the decomposition must be assessed.

Probability as zero order

As a first attempt, the zero order approximation may be used. Hence the activation energy is calculated from the maximum heat release rates:

$$E = \frac{R \cdot \ln\left(q'_1 / q'_2\right)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{8.314 \times \ln\left(360/260\right)}{\frac{1}{513} - \frac{1}{523}} \cong 70'000\ J/mol$$

The activation energy allows extrapolating the heat release rate: $q'\left(T\right) = q'_{ref} \cdot \exp\left[\frac{-E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$,

which in turn allows calculating the TMR_{ad}: $TMR_{ad} = \frac{c'_P R T^2}{q'_{(T)} E}$.

The results are summarised in Table 1.

Table 1: Heat release rate and TMRad f(T)

Temp. °C	q' W/kg	TMRad h
90	0.27	27
100	0.51	15
110	0.93	8.7
120	1.6	5.2
130	2.8	3.2
140	4.7	2.0
150	7.6	1.3

The accepted stability limit (T_{D24}) is ca. 95 °C, thus the process is compromised.

Nevertheless, since this conclusion results from a zero order approximation, a kinetic model could lead to a more realistic prediction, which could "save" the process.

Probability using the Benito-Perez Model

The results of isothermal measurements can be used to identify the parameters, i.e. the rate constants of the Benito-Perez model:

$$\nu_1 A \xrightarrow{k_1} \nu_1 B$$
$$\nu_2 A + \nu_3 B \xrightarrow{k_2} (\nu_3 + 1) B$$
$$-r_A = k_1 C_A^{a_1} + k_2 C_A^{a_2} C_B^{b}$$

Here we can use the simplified model :

$$A \xrightarrow{k_1} B$$
$$A + B \xrightarrow{k_2} 2B$$
$$-r_A = k_1 C_A + k_2 C_A C_B$$

This allows a more accurate prediction, since the induction time will be taken into account. It requires determining the kinetic parameters k_{10}, E_1 and k_{20}, E_2. The initiation reaction parameter can be found from the initial heat release rate:

$$240\,°C : k_1 = \frac{q_0'}{Q_D'} = \frac{8.5\,W/kg}{500'000\,J/kg} = 1.7 \cdot 10^{-5}\,s^{-1}$$
$$250\,°C : k_1 = \frac{q_0'}{Q_D'} = \frac{15\,W/kg}{500'000\,J/kg} = 3 \cdot 10^{-5}\,s^{-1}$$

This gives an activation energy E_1 of 120 kJ·mol^{-1} and a pre-exponential factor of $k_{10} = 2.7 \cdot 10^7$ s^{-1} or 10^{11} h^{-1}. Thus: $k_1 = 2.7 \cdot 10^7 \exp\left[\frac{-14433}{T}\right]\ s^{-1}$.

The kinetic parameters of the autocatalytic step are :

$$240\,°C : k_2 C_{A0} = \frac{4 \cdot q'_{\max}}{Q_D'} = \frac{4 \times 262\,W/kg}{500'000\,J/kg} = 2.1 \cdot 10^{-3}\,s^{-1}$$
$$250\,°C : k_2 C_{A0} = \frac{4 \cdot q'_{\max}}{Q_D'} = \frac{4 \times 360\,W/kg}{500'000\,J/kg} = 2.9 \cdot 10^{-3}\,s^{-1}$$

This gives an activation energy E_2 of 70 kJ·mol^{-1} and a pre-exponential factor of $k_{10} = 2.8 \cdot 10^4$ s^{-1} or 10^8 h^{-1}. Thus: $k_2 C_{A0} = 2.8 \cdot 10^4 \exp\left[\frac{-8420}{T}\right]\ s^{-1}$.

Question:

3. Write the differential equations to be used for modelling

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The kinetic rate constants allow calculating the reaction rate as a function of temperature and conversion. This is at the base of modelling using the simplified Benito-Perez model consisting in two balances:

Heat balance: $\frac{dT}{dt} = \frac{q'}{c'_P}$ in K·s^{-1}

Mass balance: $\frac{dX}{dt} = k_1\left(1-X\right) + k_2 C_{A0} X\left(1-X\right)$ in s^{-1}

The heat release rate is: $q' = \frac{dX}{dt} Q'_D$ in W·kg^{-1}

The rate constants:

$$k_1 = k_{10} \exp\left[\frac{-E_1}{RT}\right] = 2.7 \cdot 10^7 \exp\left[\frac{-14433}{T}\right] \quad s^{-1}$$

$$k_2 C_{A0} = k_{20} \exp\left[\frac{-E_2}{RT}\right] = 2.8 \cdot 10^4 \exp\left[\frac{-8420}{T}\right] \quad s^{-1}$$

These differential equations can be integrated over time and give the temperature course under adiabatic conditions. The results are represented in Figure 3.

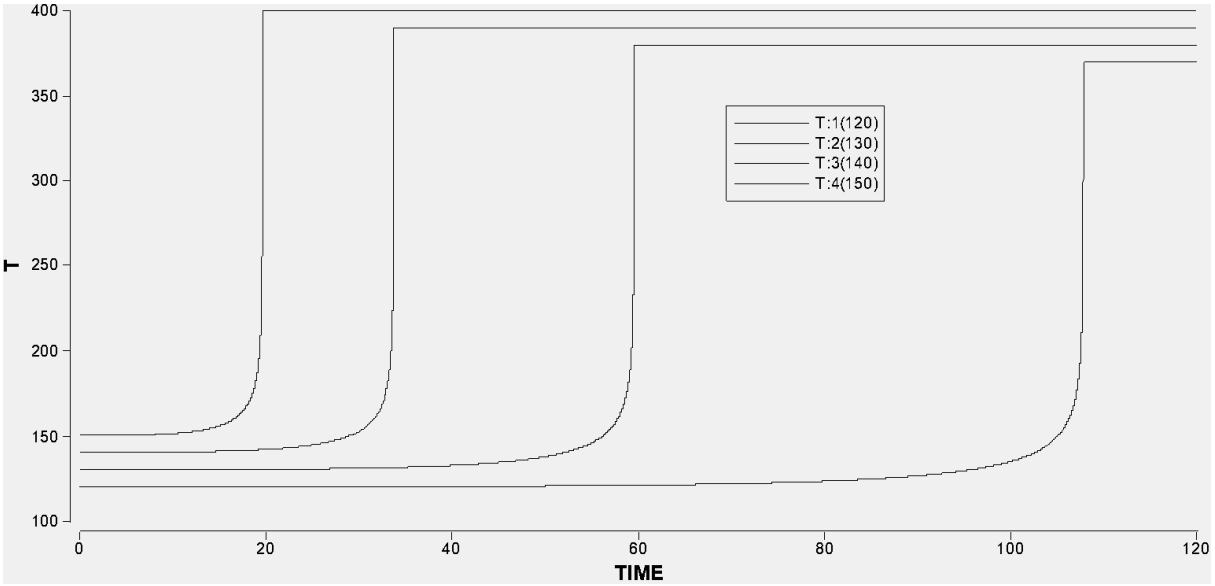

Figure 3: Adiabatic temperature course starting from 120, 130, 140 and 150°C. T (°C) versus time(hr)

Conclusions:

- The evaluation using the zero order approximation neglects the induction period of the reaction and leads to a strong overestimation of the risks: T_{D24} = 95 °C.
- The use of a kinetic model leads to a more realistic prediction of the behaviour of the distillation residue under adiabatic conditions: T_{D24} = 145°C.
- In case of a total failure of the system, the heat exchange system will become inactive and the vacuum pump also stops: the temperature of the reactor contents will equilibrate with the reactor itself, thus the temperature would reach a level somewhat above 120 °C. The TMRad is longer than 24 hours.
- The failure of the vacuum pump stops the evaporation cooling and the temperature of the product may reach 145 °C or a TMRad of ca. 24 hours.
- In such a case it is recommended to limit the heat carrier temperature and to install a trip between pressure (vacuum) and the heating system.
- It is also recommended to use a liquid heat carrier rather than steam, which ensures cooling when the temperature gradient is inversed.