

# Thermal Process Safety Based on Reaction Kinetics and Reactor Dynamics

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The specific problem of non-converted reactant accumulation encountered in fed-batch reactor is a challenging task of process safety. In order to avoid such situation that may lead to a runaway reaction, the reaction kinetics and reactor dynamic must be known. In this work, an innovative approach to determine an optimal feed profile, based on a reaction kinetic and reactor dynamic, is presented. This approach was applied to the reaction system involved in the Morton International Inc. incident. Great improvements were observed in the control of the accumulation, decreasing the number of necessary experiments needed for the scale-up studies.

## 1. Introduction

A specific problem encountered in scale-up of fed-batch reactors is the accumulation of non-converted reactants, which may lead to an uncontrolled temperature increase in case of process control malfunction or if one of the following scenarios materializes: 1) The heat released by the reaction exceeds the heat removal capacity of the reactor 2) The cooling dynamics of the system is insufficiently fast to control the heat released. Therefore, mastering these aspects is one of the most important and challenging process safety tasks. One from possible solutions would be to adapt the feed rate to avoid rapid heat accumulation. Nevertheless, this approach is disadvantageous in terms of reaction time and costs involved. In order to quantify and manage this problem in an optimal way, the reaction kinetics (Levenspiel, 1999) and reactor dynamics (Stoessel, 2008, Zufferey, 2006) must be known.

## 2. Reaction Kinetic Investigation

The reaction kinetics investigation of a complex reaction system can be a long and exhausting task, requiring numerous measurements and not always leading directly to a kinetic model. One can find a literature many approaches applied to get the reaction kinetics; unfortunately, they are often adequate for single-step reactions or simple reaction schemes (Willson R. J. and Beezer A. E., 2003).

Moreover, considering thermal safety, the analytical tool of choice is calorimetry; usually applied to explore the materials thermal behaviour rather than the reaction kinetics, in certain cases it can also provide thermal safety parameters. Consequently, the challenge remains to couple those two topics to extract thermal behaviour and reaction kinetics simultaneously.

The proposed approach can be summarized in three points: 1) Plan the required measurements to optimally cover the experimental space with a minimum number of experiments from milli- to kilogram scale (Santiago J. et al., 2012); 2) Make a hypothesis concerning the reaction scheme model based on the chemical information (mechanism, decomposition,...) and preliminary measurement results (DSC or Calvet); 3) Use a numerical algorithm to fit the kinetic parameters of the models to match the acquired measurements (AKTS, 2015).

## 2.1 Morton Case

Between 1990 and 1998, Morton International Inc. produced a dye for petroleum industry called Automate Yellow 96 (AY96). The thermal studies performed between 1986 and 1990 showed a slow and exothermic synthesis reaction followed by a highly exothermic decomposition of the product (Figure 1). The latter reaction was underestimated for the scale-up as the company continued to increase the production scale using the same conditions and even moving from a fed-batch toward a batch process. Moreover, many significant temperature deviations occurring in the 7.6 m<sup>3</sup> reactor vessel were observed and reported by the operators. Despite several supervisors comments the temperature excursions were ignored, it has been believed that high temperature rises were a quality concern and not a safety issue.

On the 4<sup>th</sup> August 1998, at the Paterson site (New Jersey, USA), an explosion and fire occurred due to the decomposition of AY96 causing many damages, hazardous material release and injuring 9 employees, including two of them seriously (US Chemical Safety and Hazard Investigation Board, 2000).

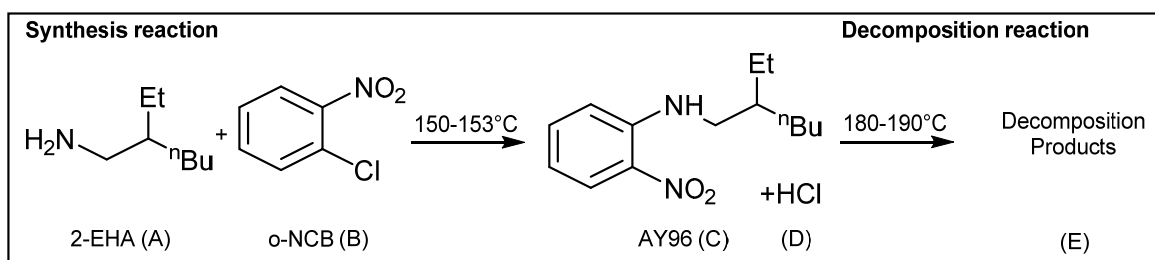


Figure 1: Synthesis and decomposition reaction scheme of the Automate Yellow 96 (AY96).

## 2.2 Reaction kinetic model

The experimental data required (Table 1) to estimate the kinetics parameters were collected from four reaction calorimetry experiments (RC1 Mettler-Toledo) in fed-batch mode performed in the temperature range of 110 - 130 °C with reaction masses between 235 and 430 g. Additionally, two experiments were performed in a Calvet Calorimeter (C80 Setaram) in batch mode at heating rates of 0.1 and 1 K/min with sample masses of 179 mg and 716 mg respectively.

Table 1: Operating conditions for RC1 measurements with a feed of 2-EHA (A), the reactor being initially charged with o-NCB (B).

Experiment	Temperature	Time to feed	2-EHA (fed)	o-NCB
Units	[°C]	[min]	[mol]	[mol]
1	110	232.5	1.40	1.17
2	120	277	1.51	1.5
3	125	65.5	0.39	1.17
4	130	242	1	1

The reaction system investigated (Figure 1) is described by a two-step reaction scheme considering an autocatalytic decomposition (Figure 2).



Figure 2: Reaction scheme describing the kinetic behaviour of a synthesis reaction followed by an autocatalytic decomposition.

The kinetic model is based on the generalized law of mass action (Levenspiel, 1999) and then compared to the experimental data as shown in Figure 3. The best estimated values of the reaction kinetic parameters are listed in Table 2 and were obtained with AKTS-Thermokinetics software (AKTS, 2015).

In order to simplify the model and decrease the number of kinetic parameters, the reaction Eq(2) describing the production of E was omitted by including virtually a small amount of decomposition products in the autocatalytic model at the beginning of each simulation.

Table 2: Best estimated reaction kinetic parameters for the proposed reaction scheme of the AY96 synthesis.

Reaction 1	$k_{0,1}$	$E_{a,1}$	$\Delta_r H_1$	Orders
Units	$[g^{m_A+m_B-1} \cdot s^{-1} \cdot mol^{-(m_A+m_B-1)}]$	$[J \cdot mol^{-1}]$	$[J \cdot g^{-1}]$	$[-]$
Value	7e8	83400	-368	$m_A=0.94$ $m_B=0.48$
Reaction 2	$k_{0,2}$	$E_{a,2}$	$\Delta_r H_2$	Orders
Units	$[g^{m_C+m_E-1} \cdot s^{-1} \cdot mol^{-(m_C+m_E-1)}]$	$[J \cdot mol^{-1}]$	$[J \cdot g^{-1}]$	$[-]$
Value	4e10	123600	-670	$m_C=0.83$ $m_E=0.65$

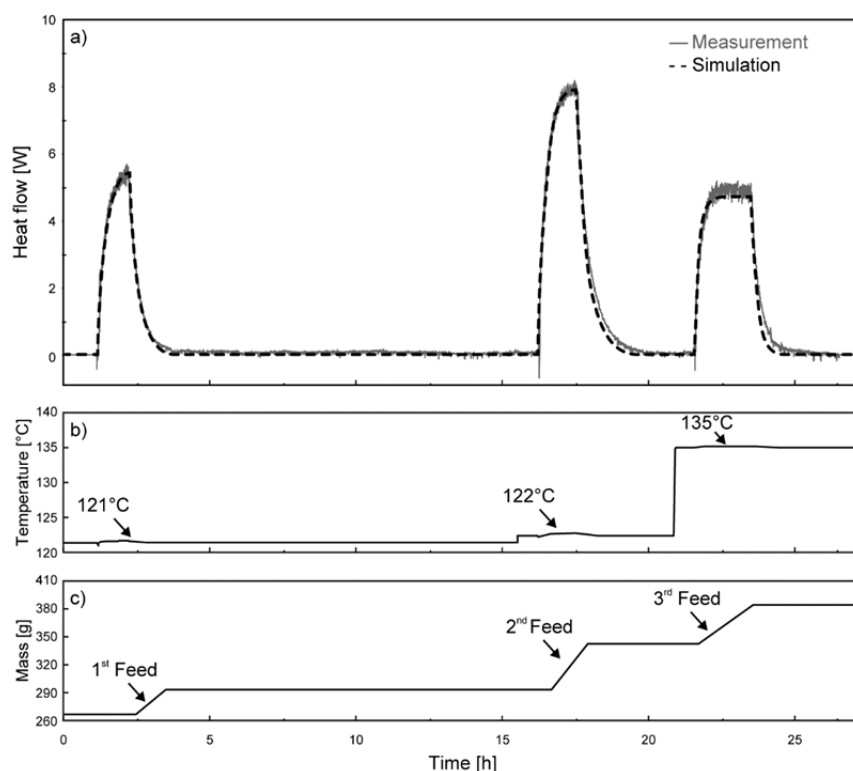


Figure 3: (a) Validation of the model by comparing the simulation with a measurement not included in the data set for the fitting. The measurement is composed of 3 different temperature set points (b) and feeds (c).

### 3. Reactor Dynamic Investigation

In order to control the reaction course and avoid a runaway incident, it is essential to understand how reactor heating/cooling systems behave and to assess their performance and limitations. The thermal behaviour of a reactor can be described based on heat and mass balances. Unfortunately, these balances are often complicated by the intricate control schemes regulating the heat exchange between the reactor and its jacket (Ingham J. et al., 2008). Consequently, a more accurate data-driven model was developed in order to consider the jacket thermal dynamics and the reaction mixture behaviour simultaneously.

#### 3.1 Reactor model

The reactor model is governed by 3 phenomena: 1) the heat exchanges between the coolant (exchange), the reaction mixture (heat accumulation), the environment (heat losses) and the reactions Eq(4); 2) the coolant temperature PID controller Eq(5) and 3) the jacket temperature behaviour considering its time constants Eq(6). The aim of the dynamic simulation is to relate the dynamic output response of a system to an input disturbance. In this case, the reactor dynamics is based on a cascade controller: the master controller compares a given temperature set point ( $T_{r,set}$ ) with the actual reactor temperature ( $T_r$ ) and computes the set point for the jacket temperature ( $T_j$ ), which is adjusted through a slave controller in order to make the reactor temperature tracking its set point.

The reactor cooling system can be represented by a single heat carrier circulation loop where the temperature controller acts directly on the heating and cooling valves by using a conventional PID approach (Figure 4). In order to model this system in a practical way, the controller behaviour is simulated using the PID equation shown in Eq(5) and the jacket temperature changes described by the differential equations provided in Eq(6). The time constants for cooling/heating are then used to characterize the system inertia.

$$\underbrace{(m_r \cdot c_{p,r} + C_w)}_{\text{Accumulation}} \frac{dT_r}{dt} = \underbrace{UA(T_j - T_r)}_{\text{Exchange}} + \underbrace{\alpha(T_{amb} - T_r)}_{\text{Losses}} + \underbrace{m_r \sum_{i=1}^i r_i(-\Delta_r H_i)}_{\text{Reaction}} \quad (4)$$

$$T_{j,set} = T_{r,set} + K \left[ (T_{r,set} - T_r) + \frac{1}{I} \int_0^t (T_{r,set} - T_r) \cdot dt + D \frac{d(T_{r,set} - T_r)}{dt} \right] \quad (5)$$

$$\begin{array}{lll} \text{In cooling case } (T_{j,set} < T_j) & \text{In heating case } (T_{j,set} > T_j) & \text{No change } (T_{j,set} = T_j) \\ \frac{dT_j}{dt} = \frac{T_{j,set} - T_j}{\tau_c} & \frac{dT_j}{dt} = \frac{T_{j,set} - T_j}{\tau_h} & \frac{dT_j}{dt} = 0 \end{array} \quad (6)$$

In these equations,  $T$  is the temperature [K],  $t$  is the time [s],  $m$  is the mass [kg],  $c_p$  is the specific heat capacity [ $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ],  $U$  is the overall heat transfer coefficient [ $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ ],  $A$  is the heat exchange area [ $\text{m}^2$ ],  $\alpha$  is heat loss coefficient [ $\text{W}\cdot\text{K}^{-1}$ ] and  $C_w$  is the reactor and insert heat capacity in [ $\text{J}\cdot\text{K}^{-1}$ ]. The PID controller parameters are  $K$  for the proportional gain [-],  $I$  for the integral gain [ $\text{s}^{-1}$ ] and  $D$  for the derivative gain [s]. The time constant is represented by  $\tau$  [s]. The subscript  $j$  is for the jacket,  $amb$  for ambient,  $set$  for set point,  $c$  for cooling,  $h$  for heating,  $control$  for the controller, and  $i$  for the reaction number.

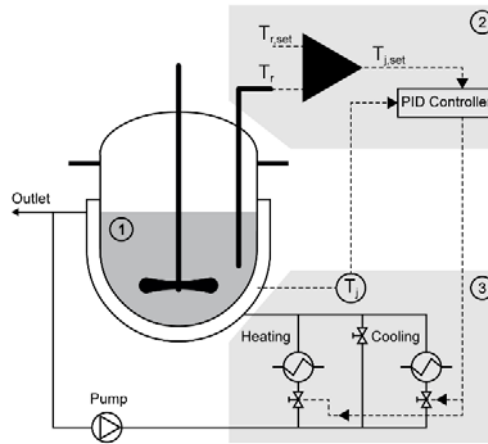


Figure 4: Temperature control with a heat carrier circulation loop and its different connections with the reactor model: 1) heat balances 2) PID controller model 3) Thermal behaviour of the jacket.

### 3.2 Reactor Dynamics and PID parameters

Based on CSB investigation report (US Chemical Safety and Hazard Investigation Board, 2000) and the model presented above, thermal behaviour simulations of a reactor representing the one in operation during the Morton International Inc. incident were investigated. The reactor characteristics and dynamics are shown in Table 3 and Table 4, respectively.

Table 3: Estimated characteristics of the reactor involved in the incident by Morton International Inc.

Parameters	Volume	o-NCB	2-EHA	U	A	$\alpha$	$C_w$
Units	[ $\text{m}^3$ ]	[kmol]	[kmol]	[ $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ ]	[ $\text{m}^2$ ]	[ $\text{W}\cdot\text{K}^{-1}$ ]	[ $\text{KJ}\cdot\text{K}^{-1}$ ]
Value	7.6	15.9	15.3	700	7.4	12	670

Table 4: Reactor dynamics and PID parameters

Parameters	$\tau_{\text{heating}}$	$\tau_{\text{cooling}}$	K	I	D	$T_{\min}$	$T_{\max}$
Units	[s]	[s]	[-]	[s]	[s]	[ $^{\circ}\text{C}$ ]	[ $^{\circ}\text{C}$ ]
Value	1500	1500	4	4000	10	5	180

#### 4. Process optimization

The main reason leading to an incident at Morton International Inc. was clearly the choice of operating in batch mode. Indeed, working under batch conditions means a maximum of accumulation potential from the start without any possibility to control it (Figure 5b). Moreover, the operating temperature (150°C) was near to the boiling point of 2-EHA (160°C) and the decomposition temperature (180-190°C) resulting in very short Time to Maximum Rate under adiabatic conditions for both the reaction and decomposition (< 1 min). A simulation based on the operating temperature procedure applied by Morton was performed and demonstrated the poor capacity of the system to manage the rate of heat release (Figure 5a) and confirmed the high criticality (class 5) of this reaction system.

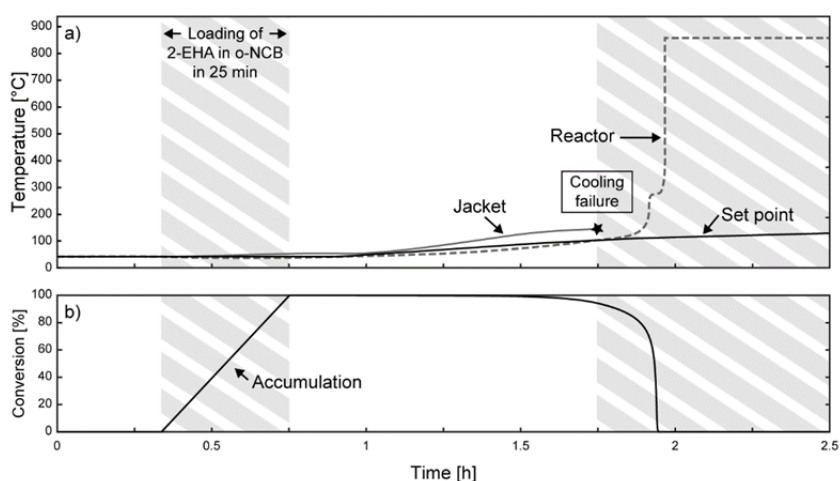


Figure 5: a) Influence of cooling failure and loading of 2-EHA in o-NCB on the temperature profile, when using the temperature ramp applied during the incident; b) Accumulation of the non-reacted reactant along the time.

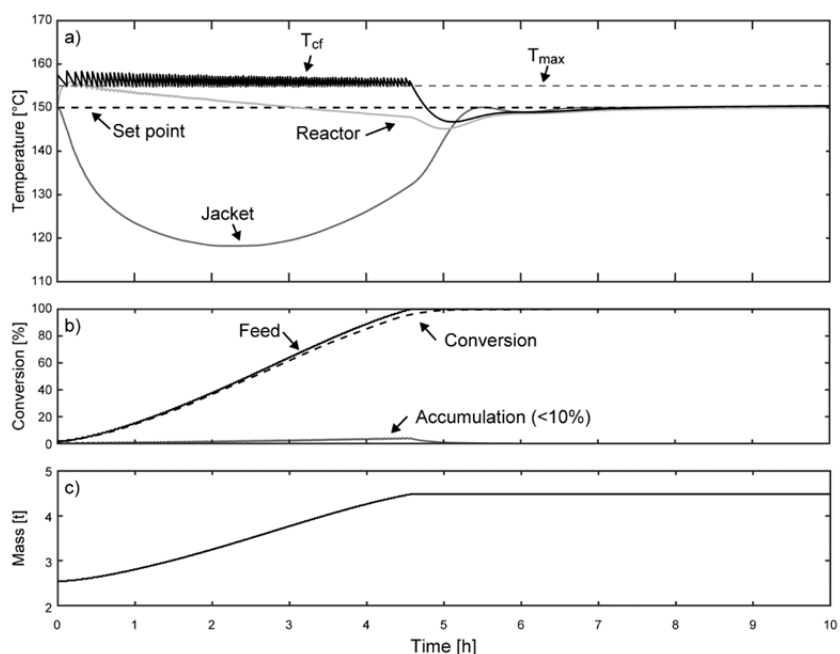


Figure 6: Fed-batch process operating under safety constraint  $T_{cf}$  (Temperature in case of cooling failure) by adjusting the feed rate in order to stay below the maximum allowed temperature  $T_{max}$  (155°C). a) Reactor and jacket temperature profiles under normal operating condition with its corresponding  $T_{cf}$  and constraint ( $T_{max}$ ), b) Conversion and accumulation of 2-EHA (<10%) c) Mass profile obtained for an optimal feed rate respecting the constraints.

## 5. Conclusion

The novel proposed investigation procedure based on the relationship between reactor dynamics and reaction kinetics allows an optimization of the productivity while remaining within safe limits. Indeed, compared to conventional scale-up methods based on trial and error, this approach simplifies and decreases the development time by several steps. Moreover, having kinetic and reactor dynamic models contributes significantly to a better understanding of the controllability of the process at industrial scale and helps in the design of optimal operating conditions in terms of safety and productivity.

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