Kinetic identification and risk assessment based on non-linear fitting of calorimetric data

Charles Guinand
ISIC-GSCP
EPFL
Lausanne, Switzerland

HES-SO, Ecole d'ingénieurs et d'architectes de Fribourg
Institut ChemTech
Fribourg, Switzerland,
charles.guinand@epfl.ch

Michal Dabros
HES-SO, Ecole d'ingénieurs et d'architectes de Fribourg
Institut ChemTech
Fribourg, Switzerland,
michal.dabros@hefr.ch

Bertrand Roduit
AKTS AG
Sierre, Switzerland
b.roduit@akts.com

Thierry Meyer
ISIC-GSCP
EPFL
Lausanne, Switzerland
thierry.meyer@epfl.ch

Francis Stoessel
Swissi Process Safety GmbH
Basel, Switzerland
francis.stoessel@swissips.com

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C. Guinand[1, 2], M. Dabros[1], B. Roduit[3], T. Meyer[2], F. Stoessel[4]

[1]HES-SO Haute école spécialisée de Suisse occidentale, Ecole d'ingénieurs et d'architectes de Fribourg, Institut ChemTech, 1705 Fribourg, Switzerland

[2]Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

[3]AKTS Inc., www.akts.com, TECHNOArk 1, 3960 Sierre, Switzerland

[4]Swissi Process Safety GmbH, Schwarzwaldallee, 4058 Basel, Switzerland

Abstract

Chemical processes safety requires a thorough knowledge of the kinetic and thermal parameters regarding the chemical reactions involved. The main goal of this work was to develop a method in order to extract the kinetic parameters using different calorimetric technics, experimental design and optimization tools. In the first stage, the esterification of acetic anhydride by methanol was used as a case study for the kinetic identification. In the second stage, a risk assessment was performed using the identified reaction model. Thus, the global kinetic parameters of this reaction, as well as its activation energy and reaction orders were characterized.

Keywords: Calorimetry; Reaction kinetic; Design of Experiment; Thermal Safety; Risk assessment, Optimization

1.   Introduction

In most cases, chemical reaction incidents are caused by loss of control, resulting in runaway reactions caused by process deviations in different units. These incidents could be foreseen and avoided, or at least their frequency decreased, with an appropriate process development and risk assessment tool [1].

Reaction characterization is aimed at providing a better understanding of reaction pathways and thermal behavior [2]. In order to achieve this goal efficiently, the system dynamics can be reproduced by a mathematical model whose parameters are estimated based on measured data. Such models are based on ordinary differential equations describing, on one hand the reaction kinetic law (reaction kinetic model) and on the other hand, the measurement model.

After an initial estimation, the measurement model does not represent the overall reality, but only the one in the measurement conditions. For this reason, several experiments at different scales have to be done to maximize the disturbances and explore the overall reaction kinetics [3].

Nevertheless, even with this method, the investigation can be very long due to the increasingly complex models, involving a large number of parameters and needing a huge amount of measurements. Therefore, a new approach to solve these problems has to be developed.

This approach can be summarized in two points: the first one is to plan the measurements in an optimal way to cover the experimental space [4-6]. The second is to develop a numerical method, able to extract the reaction kinetic parameters, for a given model structure, from the measurements available [7].

2. Theoretical part

2.1. Reaction kinetic model [1, 8-11]

Assuming a reaction j taking place in a homogeneous solution, the reaction rate r is given by the kinetic law:

$$r_j = k_j \cdot \prod_{i=1}^{I} C_i^{m_i} \qquad \text{[Eq. 1]}$$

The rate constant k is described by the Arrhenius law:

$$k_j = k_{j,0} \cdot \exp\left(-\frac{E_{a,j}}{RT_r}\right) \qquad \text{[Eq. 2]}$$

The concentration C of a component i is calculated in function of the number of mole N in the reaction mass m_r:

$$C_i = \frac{N_i}{m_r} \qquad \text{[Eq. 3]}$$

The transformation rate R of a component i is:

$$R_i = \frac{dC_i}{dt} = \sum_{j=1}^{J} v_{ij} r_j \qquad \text{[Eq. 4]}$$

where the sum is made over all J compounds. The thermal behavior is directly linked to the reaction kinetics; indeed any reaction implies a production or consumption of energy which can be detected as heat q by calorimetric techniques and is described as:

$$q_{rx,j} = m_r \left(r_j \cdot \left(-\Delta_r H_j\right) \cdot \sum_{i=1}^{I} v_{ij} M_i \right) \qquad \text{[Eq. 5]}$$

The reaction heat flow depends on many factors as for example the reaction rate r [Eq. 1], its enthalpy $\Delta_r H$ and the reaction mass m_r. The molar mass M_i is used to transform the reaction enthalpy in [J·mol^{-1}] into the specific heat of reaction given in the units of [J·g^{-1}].

2.2. Optimization Non-linear fitting [12]

The system considered here is a least squares optimization problem. Its objective consists of adjusting the parameters θ of a model in order to fit in the best way a data set, e.g using a least squares approach defined as:

$$F(\theta) = \frac{1}{2}\sum_{p=1}^{P}\left(f_p(\theta)\right)^2 \qquad\qquad \text{[Eq. 6]}$$

Where F is the objective function and f_i: $\mathbb{R}^n \to \mathbb{R}$, $p=1,...,P$ the residuals. p are the studied functions (e.g. the measurement simulation) with $p \geq n$ and n the number of parameters in the model.

It is assumed that it exists a vector of parameters $\hat{\theta}$ which allows the model to describe the response y as:

$$y_i = Model\left(\hat{\theta}, t_i\right) + \varepsilon_i \qquad\qquad \text{[Eq. 7]}$$

where ε_i is the measurement error compared to the model.

For any choice of θ, the residuals can be calculated as:

$$f_i(\theta) = y_i - Model(\theta, t_i) \qquad\qquad \text{[Eq. 8]}$$

For least squares fits, the optimal vector $\hat{\theta}$ is considered as the minimizer of the sum of residual squared of the model:

$$\hat{\theta} = \arg\min_\theta \{F(\theta)\} \qquad\qquad \text{[Eq. 9]}$$

In general, such problems are very hard to solve due to non-linearity; however, some methods are presented by K. Madsen et al.[7]. The one retained for this work is the secant version of the Levenberg-Marquardt (L-M) algorithm [7, 13, 14]. This method is used to optimize the model parameters (in this case, the kinetic parameters) without the need for analytical derivative solutions, in order to quickly find the optimal minimum using gradient methods. Indeed, they are numerically estimated.

3.   Experimental part

3.1.   Studied reaction

The chemical reaction chosen to apply the method proposed above is the exothermic esterification reaction of acetic anhydride and methanol [15]. This reaction is widely used as a test for safety-oriented studies and as such, is adequate for the modeling and simulation of dynamic processes during runaway scenarios.

acetic anhydride (A)   methanol (B)   acetic acid (C)   methyl acetate (D)
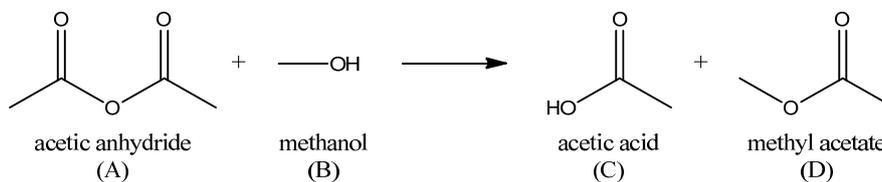
A two-step reaction scheme was proposed by Bohm et al [15] considering the autocatalytic effect of the acetic acid on the kinetic of this esterification as:

$$A + B \rightarrow C + D$$
$$A + B + C \rightarrow 2C + D$$
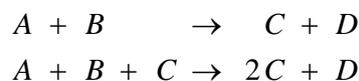
This reaction scheme will be used as hypothesis to define the different kinetic parameters for the reaction model.

3.2. Determination of the work space

Two non-isothermal measurements at different heating rates between 25 and 300°C have been carried out at 0.1 and 4°C/min respectively in Setaram C80® and Mettler Toledo® DSC. Considering the esterification reaction, the temperature range should be below the boiling point, but nevertheless sufficiently high to have an appropriate experiment duration and with a high range of experimental temperatures. On the basis of these measurements, the working temperature range was determined in order to keep the kilo scale measurements safe and clean. Moreover no significant secondary decomposition reaction was detected in the temperature range of the measurement.

Other factors are relevant at the kilogram scale, for example the number of moles fed into the reactor ($n_{i,fd}$) and the time to feed (t_{fd}). Consequently, in order to determine all the different ranges, a rough optimization of the reaction model parameters was performed on the preliminary measurements. Then, using the physical properties (boiling points, heat capacities) and the kinetic parameters, it was possible to predict the process behavior at some different temperatures (Table 1).

Table 1. Variable ranges for the Design of Experiment

	Temperature ($T_{r,set}$)	Time to feed ($t_{fd,B}$)	Number of added moles ($n_{feed,B}$)
Units	[°C]	[min]	[mol]
Min	40	60	0.7
Max	60.3	120	1.5

3.3. Design of Experiment (DoE)

An experimental design, based on the Wootton, Sergent and Phan-Tan-Luu's (WSP) algorithm and a Space Filling Design method [16] was used to choose six experimental points, as shown in Table 2. Each of the three factors shown in Table 1 appears at a minimum of three levels – a criterion which was needed to extract the value of the activation energy.

3.4. RC measurements

The RC experiments are performed under isothermal fed-batch conditions in a Mettler Toledo® RC1e where the methanol (B) is fed at different rates. The acetic anhydride (A) is initially present in the reactor, up to 1.5 moles, and the acetic acid (C) and methyl acetate (D) are produced during the process. The results are shown in Table 2.

Table 2. DoE study: Space Filling Design results resulting from WSP algorithm[16] performed on 10000 points in the candidate set randomly generated with minDist = 0.8500 and Cov = 0.0020. Results: Feed rate, time of experiment Obtained heat (Q_r), average heat capacity ($c_{p,average}$) and reaction enthalpy ($\Delta_r H$) for the measurements at RC scale.

Exp.	DoE plan			Results			
	$T_{r,set}$	$n_{feed,B}$	t_{fd}	m_{fd}	$c_{p,average}$	Q_r	$\Delta_r H$
	[°C]	[mol]	[s]	[g·min^{-1}]	[J·K^{-1}·g^{-1}]	[KJ]	[kJ·mol^{-1}]
1	50.15	1.09	5425	0.39	2.08	-61.30	-56.17
2	60.30	0.69	3843	0.35	2.05	-36.26	-52.65
3	41.35	0.69	7247	0.18	2.09	-43.59	-63.58
4	40.00	1.49	7034	0.41	2.05	-76.38	-51.13
5	60.04	1.48	3776	0.76	2.10	-84.10	-56.65
6	60.03	0.69	7200	0.19	2.10	-40.78	-58.69
Average					**2.08**		**-56.5 ± 4.7**

The determined mean reaction enthalpy corresponds to -56.5 ± 4.7 [kJ·mol^{-1}], a lower value than the one found in literature, 67.3 ± 3.0 [kJ·mol^{-1}] [17] as well as 65.99 [kJ·mol^{-1}] based on online tabulated standard enthalpies of formation [18].

This deviation could be explained by a too high working temperature, causing heat losses by evaporation considering a boiling point of 56°C and 64°C for methyl acetate and methanol respectively. Nevertheless, these data are a good input to create the data basis for the optimization and to create a reaction model.

4. Results and discussion

4.1. Model

Using the non-linear optimization based on the Levenberg-Marquardt algorithm on the obtained calorimetric data (DSC, RC) and the reaction scheme proposed by Bohm[15], it was possible to determine the kinetic parameter values (Table 3).

Table 3. Obtained kinetic parameters for the esterification of acetic anhydride with methanol considering an autocatalytic effect of the acetic acid (product).

Reaction 1				
	k_0	E_a	$\Delta_r H$	Orders
Units	[g$^{mA+mB-1}$·s^{-1}·mol$^{-(mA+mB-1)}$]	[J·mol^{-1}]	[J·g^{-1}]	[-]
Value	4.462e8	71678	-662.3	m_A=0.96 m_B=0.71
Reaction 2				
Units	[g$^{(mA+mB+mC-1)}$·s^{-1}·mol$^{-(mA+mB+mC-1)}$]	[J·mol^{-1}]	[J·g^{-1}]	[-]
Value	3.293e7	51815	-260.1	m_A=1.16 m_B=0.6 m_C=0.52

4.2. Validation

In order to validate the model, the simulation was confronted to two different measurements at the milligram (DSC) and kilogram (RC1) scales, as shown in Figure 1.
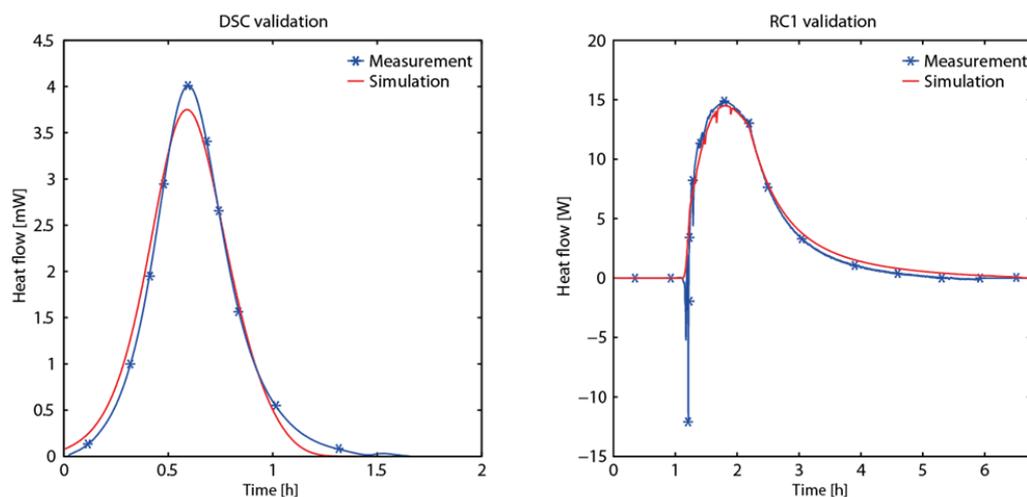

Figure 1 Validation: comparison of the measurements (DSC at 1.5K/min: left; RC1 at 62°C: right) versus their respective simulations using the optimized reaction kinetic model.

It can be observed that the model fits the RC measurement somewhat better than the DSC data. This can be explained by a large number of measurements at this scale and focused on a narrow temperature range. In other words, the DSC leads to an extrapolation (large temperature range) where RC1 measurement are closer to interpolation. Hence, the optimization is more disturbed by these latter which leads to an optimum displaced toward the kilogram scale. Other facts as micro-mixing or difficulties in the baseline definition may have caused the slight misfit observed in the DSC validation.

Another point to keep in mind is the fact that a model is valid only in the range where it was defined. In this case, the goal is to perform a scale-up of this reaction; consequently, a good fit at the kilogram scale points out the right direction.

4.3. Risk assessment

In order to get a safe process, several points regarding the thermal safety should be addressed. The best way to assess the risk, is the cooling failure scenario [1].

The main variable to consider in a process risk assessment is the maximum temperature that can be reached in the reaction vessel as a result of a cooling failure (Maximum Temperature of the Synthesis Reaction, MTSR). Would this temperature be sufficiently high to initiate secondary reactions? Would the consequences be worse? What would the level of temperature be after such events? Is it the worst moment during the process for cooling failure to happen?

4.4. Batch process

Based on the reaction kinetic model, the thermal behavior of the autocatalytic esterification can be evaluated. Thus, the worst case can be assessed depending on the kind of reactor and cooling system used. A simulation with a standard reactor of 2.5m^3 was used to demonstrate the thermal risk assessment procedure.

4.4.1. Cooling failure scenario

The scenario in case of loss of control from a starting temperature of 25°C would lead to a MTSR of 236°C ($\Delta T_{ad} = 211$°C). Such a temperature would lead to loss of containment with spillage of flammable compounds and possibly a secondary explosion. Moreover, the Time to Maximum Rate in case of adiabatic conditions is very short (TMR$_{ad}$ = 1.36h). The two limit temperatures defining the thermal stability of the reaction mixture were determined using simulation for 24h and 8h are respectively -8°C (T$_{D24}$) and 4°C (T$_{D8}$). Thus, the lack of control of the reactor temperature results in a thermal explosion.

Another point to consider is the boiling point of the reaction which is about 60°C at the end of the process. This temperature is reached during the runaway, and the energy available at this temperature is sufficient to result in a pressure increase, leading eventually to a burst of the reactor. Consequently the Maximum Technical Temperature (MTT) should be based on the boiling point of the components involved.

All these points lead to a final conclusion: in order to work under safe conditions, the reaction cannot be performed as a batch without emergency measures. It requires a reliable and powerful cooling system or should preferably be performed in the fed batch mode allowing a better control of the reaction rate.
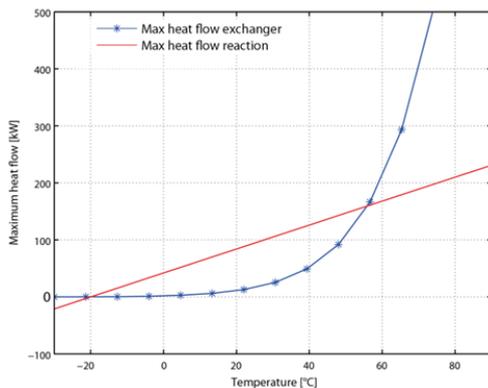

Figure 2 Semenov diagram: comparison of the maximum heat release of the autocatalytic esterification with the heat removal of the cooling system, considering standard reactor of 2.5m^3 (Area = 4.6 m^2; T$_c$ = -20 °C; U = 500 W·K^{-1}·m^{-1}) with an equimolar mixture (15kmol of A and B).
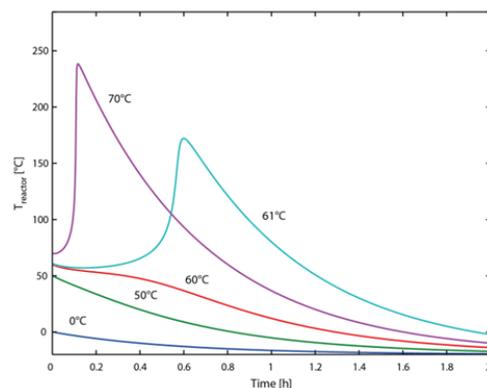
Figure 3 Influence of the initial temperature of the process for a constant temperature of the coolant (T$_c$ = -20 °C)

4.4.2. *Semenov diagram and assessment of cooling capacity*

This criterion allows the discrimination of stable operation conditions from a runaway situation. The kinetic model was used to evaluate the maximum heat flow leading to the Semenov diagram (Figure 2) which can be used to define a working area for this reaction.

Nevertheless, it should be kept in mind that a too high temperature can produce small deviations resulting in excess heat production and leading to a runaway. In case of an autocatalytic system, a small deviation in temperature will produce more product, thereby accelerating the main reaction and leading to a quicker runaway.

Moreover, the kinetic model can be used to determine the influence of the initial temperature under isoperibolic control as shown in Figure 3.

The results of these simulations show that a too high initial temperature can lead to a runaway. In such conditions for the autocatalytic esterification, the Semenov Diagram predicts a runaway region around 60°C which is confirmed here.

Moreover, this temperature is higher than the boiling point of the final reaction mixture. This latter can be used as a barrier only if the process is designed to work under such conditions (reflux). Consequently, the risk of a pressure increase leading to an explosion is not negligible in the present case.

4.4.3. *How to control this reaction*

Different types of temperature control are available for batch processes such as adiabatic, isoperibolic or polytropic. In this project, only the polytropic control will be discussed, whereby the reaction temperature is first brought to a setpoint which is maintained by varying the jacket temperature.

As shown above (Figure 3), the initial temperature is a primordial factor. Hence, if this latter is poorly designed, it can lead to a loss of control and runaway reaction. Nevertheless, in order to explore the process behavior, knowledge of the dynamic behavior of an industrial reactor is necessary. Consequently, to define this last point, the different time constants for the heating and cooling were determined at different scales [19].

The time constants show how the cooling system responds to a deviation in temperature. Indeed, two factors need to be taken in account: the heat exchange variables (U, A, c_p and mass) and the controller (usually PID). In practice, even if the controller is designed to deliver a fast response, the heat carrier response will be limited due to the thermal inertia of the system at the industrial scale, therefore, the adjustment is not instantaneous.

Consequently, the reaction temperature must be chosen appropriately to obtain an economically reasonable process time, meaning as short as possible and sufficiently low to control the heat release rate. In this case, a low temperature would be preferred in order to keep the process safe. Unfortunately, maintaining a low temperature is not economically viable. Moreover, in order to keep isothermal conditions, the jacket temperature has to respond really quickly. Consequently,

depending on the plant available, this kind of conditions may be difficult to achieve in practice. If this is the case, a possible way to manage this kind of reaction is to carry out a step control at the beginning: start at a low temperature and then let the reaction progresses adiabatically until the temperature reaches a switch value (T_s), at which time the cooling system is started (Figure 4).
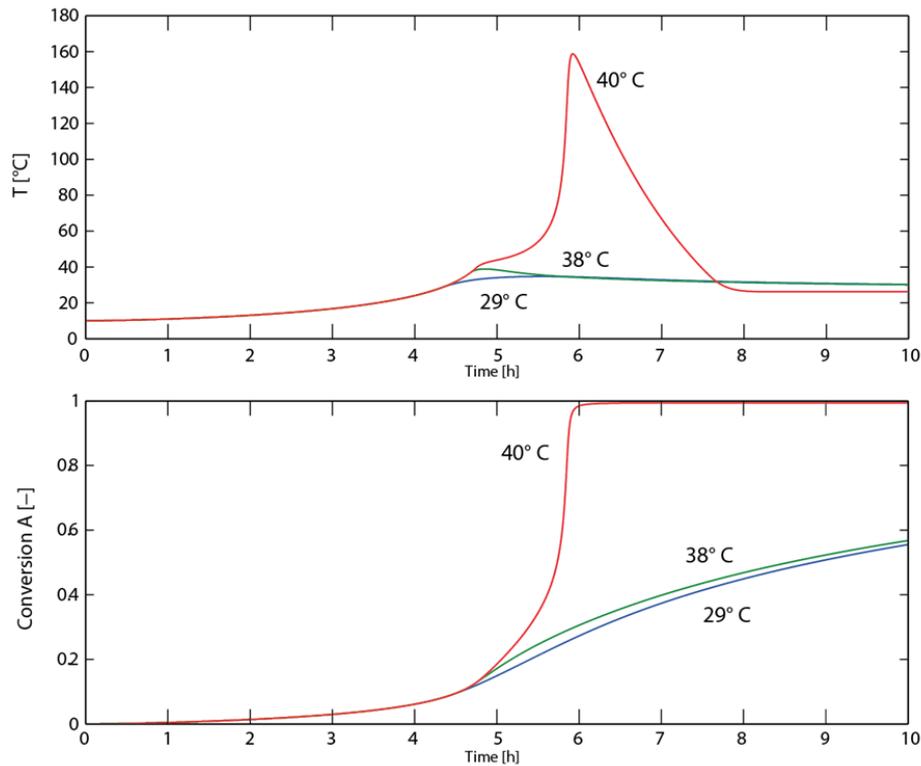

Figure 4 Reactor temperature as a function of time and respective conversion for different switching temperatures of the cooling system from a starting temperature at 10°C.

As it can be observed, even with this method, the conversion remains poor for batch processes under control. Another critical point remaining is the maximum Temperature reached in case of Cooling Failure (T_{cf}). Indeed, as mentioned previously, the boiling temperature of the final reaction mixture is low (around 60°C). Consequently, in order to avoid a rise of pressure, the T_{cf} should remain under the boiling point. Unfortunately, this condition can never be achieved in case of batch processes; only the reactor temperature can be adjusted to keep the temperature under control.

This assessment remains global and does not take in account supplementary equipment such as burst disk or condenser. Nevertheless, it was shown that for this kind of reaction, batch processes are not the most suitable. Moreover, the worst moment for a cooling failure is, in the case of this process, present from the start, as the accumulation is maximal, making this mode not safe at all for such autocatalytic reaction.

Considering all these points, in order to find a viable a safe solution, semi-batch process will be explored from a thermal safety point of view.

4.5. Semi-Batch process

4.5.1. How to control this reaction?

In semi-batch operation, many strategies can be used to improve the process safety: the temperature control strategy, the feed control strategy, and also the choice of reactant(s) to be initially added and, respectively, to be fed [1]. The most stable reactant is generally chosen to be initially added. Consequently, due to its higher boiling point, the acetic anhydride was chosen. Thus, the methanol is used as the fed reactant in order to limit the accumulation and evaporation. Moreover, in order to maintain isothermal conditions, the use of polytropic control is preferred.

The feed may be controlled in different ways such as:

- Constant feed rate: should be sufficiently low to avoid or at least to minimize reactant accumulation.
- Working under constraints based on physical considerations (volume at the end of the operation, flow rate,…) and safety considerations (the system must remain safe under normal operating condition,…) [20].

Nevertheless, the choice of the reactor temperature and feed strategy remains of primary importance during the thermal safety assessment. The next section will discuss a semi-batch process working under constraints based on safety considerations.

4.5.2. How to determine an optimal feed profile working under constraints

As mentioned previously in the batch process section, to maintain isothermal conditions, the heat exchanger system should be able to remove the heat release rate of the reaction at any moment, especially at the maximum. In order to control the reaction, the temperature that would be reached in case of a cooling failure T_{cf} can be used as constraint: if the calculated T_{cf} is greater than the maximum safe temperature (T_{max}), the feed is stopped until the content reaches a stable point anew [1]. The T_{max} is usually defined by the process itself or on the data basis of the reaction mixture (boiling point, decomposition temperature…).

The constraint is applied as follows: the simulation is performed under normal conditions and then every 60 seconds, the simulation is performed under cooling failure conditions (adiabatic). If the T_{cf} is higher than the set point T_{max}, the feed is stopped. The result is the evaluation of the best feed profile satisfying the constraint as shown in Figure 5.
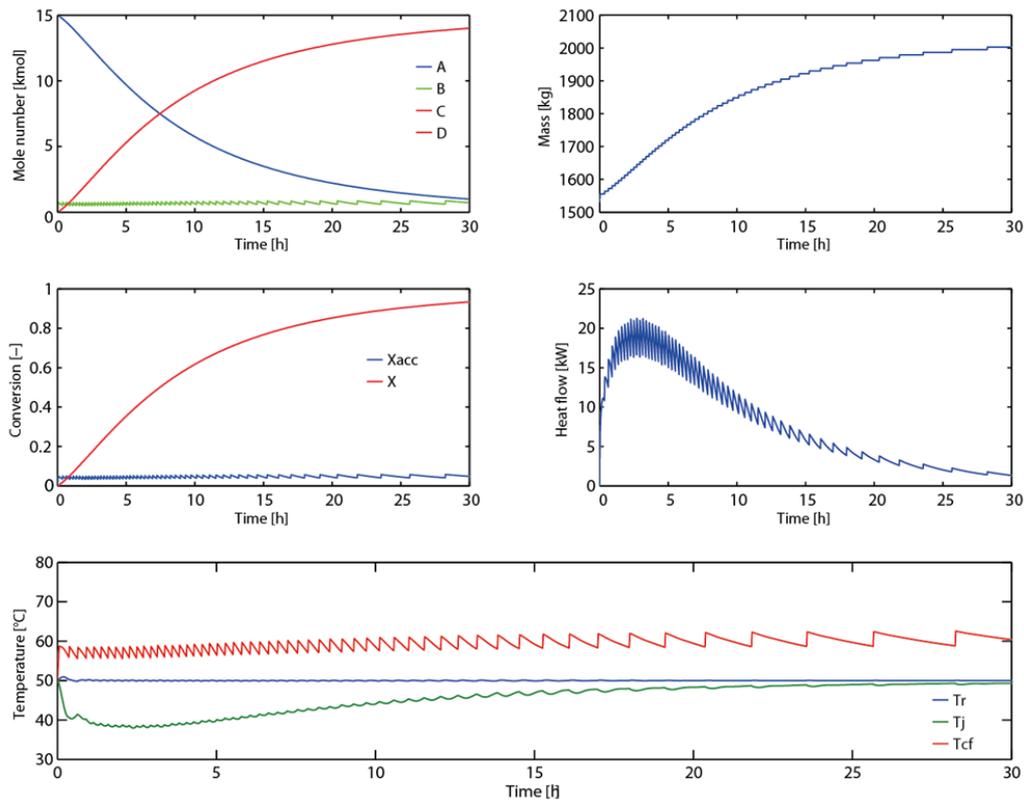
Figure 5 Concentration, mass, conversion (of A, and accumulation), heat flow profiles obtained for a semi-batch process working under T_{cf} constraint

With this strategy, the feed profile is optimized in order to ensure that T_{max} may not be surpassed even in case of failure and considering the autocatalytic reaction.

5.   Conclusion

A first insight into a way of investigating reaction kinetics using non-linear model fitting has been presented. It was possible with limited experimental data to determine the reaction's kinetics and to predict its behavior under different operation conditions.

Industrial reactors dynamics were simulated, in order to optimize the thermal safety of a semi-batch reactor. Furthermore, the application of constraints has led to an optimized feed profile keeping the process thermally safe.

In order to validate the optimal feed profile, the next step in this study involves performing an experiment at industrial scale. To achieve this purpose, it is necessary to apply the scale-down approach presented by Zufferey [19]; a method used to simulate industrial reactor at laboratory scale.

In the future, an interesting study might involve the extension of this investigation procedure to other kind of reaction, leading to a generalized method to get reaction model and kinetics from calorimetric measurements.

6.   Symbols

A	Area	(m^2)
C	Concentration	$(mol \cdot kg^{-1})$
c_p	Specific heat capacity	$(J \cdot kg^{-1} \cdot K^{-1})$
Cov	Covariance	(-)
DoE	Design of Experiment	
E_a	Activation energy	$(J \cdot mol^{-1})$
F	Objective function	(-)
k	rate constant	($\propto$)
k_0	Frequency factor	($\propto$)
M	Molar mass	$(kg \cdot mol^{-1})$
m	Mass	(kg)
$MinDist$	Minimal distance between the points	(-)
$MTSR$	Max. Temperature of Synthesis Reaction	(K)
MTT	Max. Temperature for Technical reasons	(K)
N	Number of moles	(mol)
n	Number of parameters in the model	(-)
p	Studied function	(-)
PID	Proportional-Integral-Derivative	(-)
Q	Thermal energy	(J)
q	Heat flow	(W)
r	Reaction rate	$(mol \cdot kg^{-1} \cdot s^{-1})$
R	Transformation rate	$(mol \cdot kg^{-1} \cdot s^{-1})$
TMR_{ad}	Time to maximum rate adiabatic	(s)
T	Temperature	(K)
t	Time	(s)
U	Overall heat transfer coef.	$(W \cdot m^{-2} \cdot K^{-1})$
WSP	Wootton, Sergent, Phan-Tan-Luu's algorithm	
X	Conversion	(-)
$\Delta_r H$	Enthalpy of reaction	$(J \cdot mol^{-1})$
ΔT_{ad}	Adiabatic temperature rise	(K)

Greek

ε	Error
θ	Parameters
ν	Stoichiometric coefficient

Subscript

acc	Accumulation
cf	Cooling failure
f	Final
fd	Feed
i	Component
j	Number of the reaction
r	Reactor
rx	Reaction
s	Switch
set	Set point

Superscript

m	Partial reactant order

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