

Optimization of Chemical Reactor Feed by Simulations Based on a Kinetic Approach

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Abstract: Chemical incidents are typically caused by loss of control, resulting in runaway reactions or process deviations in different stages of the production. In the case of fed-batch reactors, the problem generally encountered is the accumulation of heat. This is directly related to the temperature of the process, the reaction kinetics and adiabatic temperature rise, which is the maximum temperature attainable in the event of cooling failure. The main possibility to control the heat accumulation is the use of a well-controlled adapted feed. The feed rate can be adjusted by using reaction and reactor dynamic models coupled to Model Predictive Control. Thereby, it is possible to predict the best feed profile respecting the safety constraints.

Keywords: Calorimetry · Optimization · Reaction kinetics · Risk assessment · Thermal safety

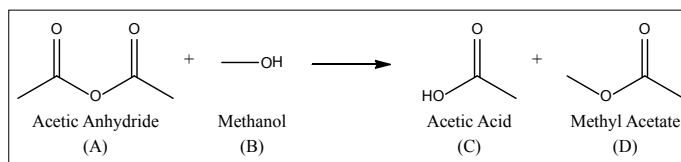
The main safety problem generally encountered when using fed-batch reactors is the accumulation of reactants resulting in accumulated heat. In fact, understanding and controlling this aspect is one of the most important and challenging process safety tasks.^[1] One solution that can help in preventing this undesired scenario is control of the feed rate to avoid rapid heat accumulation. However, this approach is disadvantageous in terms of reaction time and costs involved. Indeed, to quantify and manage this problem in an optimal way, the reaction kinetics need to be known.

The dynamic behavior of the reaction system can be represented by two mathematical models based on differential equations whose parameters are estimated using measured data: i) The *reaction kinetic model*, based on an assumption of the reaction scheme considering different reactions taking place during the process course; and ii) The *system dynamic model*, based on the reactors dynamics and their respective experimental conditions.

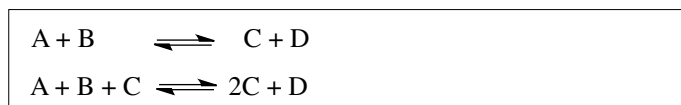
The proposed approach can be summarized in three main points: i) planning the initial measurements in a statistically optimal way to cover the experimental space efficiently with a minimum number of experiments; ii) using a numerical method to extract the reaction kinetics^[2] and process dynamic parameters;^[3] and iii) using the models to predict the behavior of an industrial reactor considering safety constraints and large-scale dynamics^[1] in order to optimize the feed profile.

The optimization of the feed is illustrated in this study for the exothermic reaction (Scheme 1) between acetic anhydride and methanol.

A two-step reaction scheme was proposed by Bohm *et al.*^[4] considering an autocatalytic effect of acetic acid on the kinetics of the esterification:



Scheme 1. Methanol/acetic anhydride esterification.



Scheme 2. Reaction scheme of methanol/acetic anhydride esterification considering the auto-catalytic effect of acetic acid.

This reaction (Scheme 2) was used for the evaluation of kinetic parameters of the reaction model applied in further simulations.

The kinetic approach applied for the building esterification model is presented in the following flowchart (Fig. 1). The kinetic parameter optimization was performed using a non-linear model fitting algorithm.

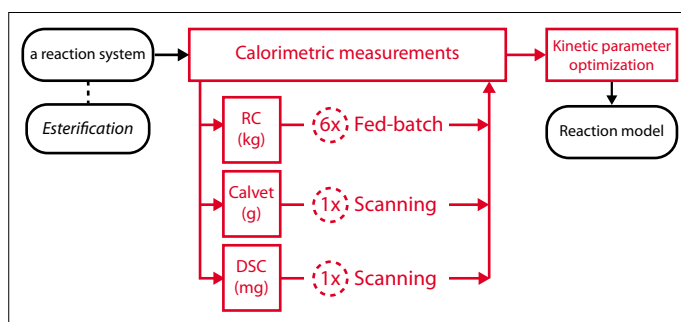


Fig. 1. Flowchart presenting the procedure of estimation of kinetic model of the esterification based on a kinetic approach.

The typical result of DSC measurements giving a general characteristic of the thermal events occurring during reaction is depicted in Fig. 2.

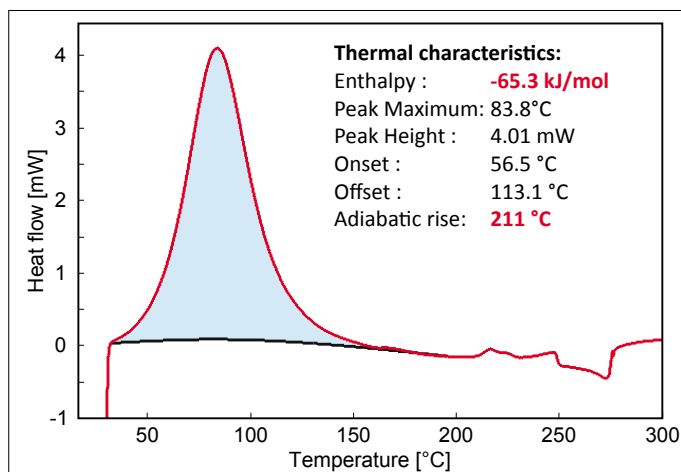


Fig. 2. Heat flow signal obtained from DSC measurement at 1.5 °C/min.

The experimental data required to estimate the kinetics parameters were collected from six RC measurements in fed-batch mode performed in the temperature range of 40–60 °C with reaction masses between 175 and 200 g. Additionally a C80 and a DSC measurement were performed at the heating rate of 0.1 and 4 K/min with sample masses of 2 g and 17 mg, respectively.

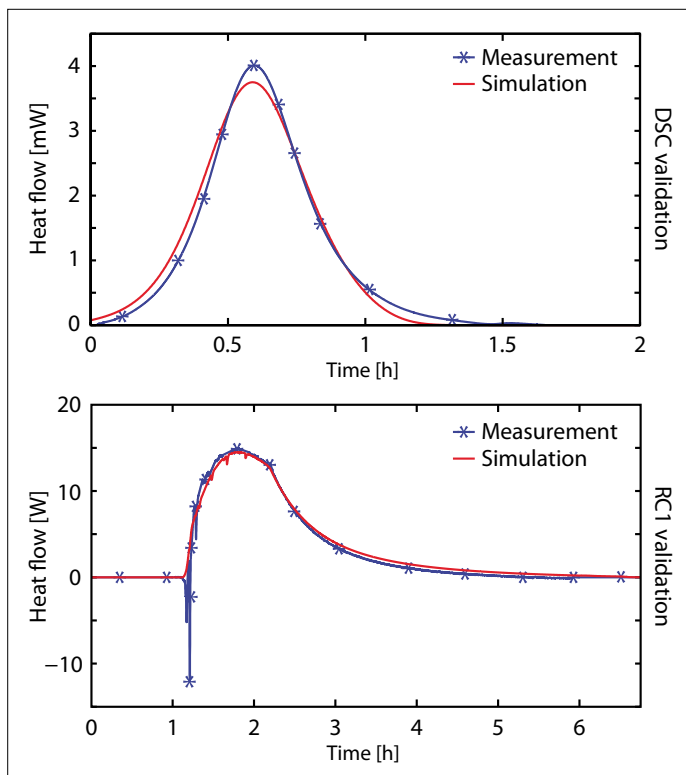


Fig. 3. Experimental data (DSC at 1.5 K/min (top); RC1 at 62 °C (below)) versus prediction using the optimized reaction kinetic parameters and model scheme proposed by Bohm.^[4]

The results of the simulations based on evaluated kinetic parameters and the reaction scheme proposed by Bohm were compared with the experimental data collected by DSC and RC (Fig. 3). The very good fit of experimental and simulated reaction courses validates the applied kinetic model.

It can be observed that the model fits the RC measurement somewhat better than the DSC data. This can be explained by the larger number of measurements performed and the similar temperature range used in the subsequent validation.

In order to control the reaction and optimize the feed profile, the temperature that would be reached in case of a cooling failure T_{cf} is used as constraint. If the calculated T_{cf} is greater than the maximum acceptable safe temperature (T_{max}), the feed will be stopped until reaching the acceptable stable temperature.^[1] The T_{max} is defined by the process itself or on the basis of the properties of the reaction mixture (e.g. boiling point or decomposition temperature).

The constraint is then applied as follows: the simulation is performed under normal conditions and then, every 60 seconds, the simulation is run under cooling failure conditions (adiabatic).

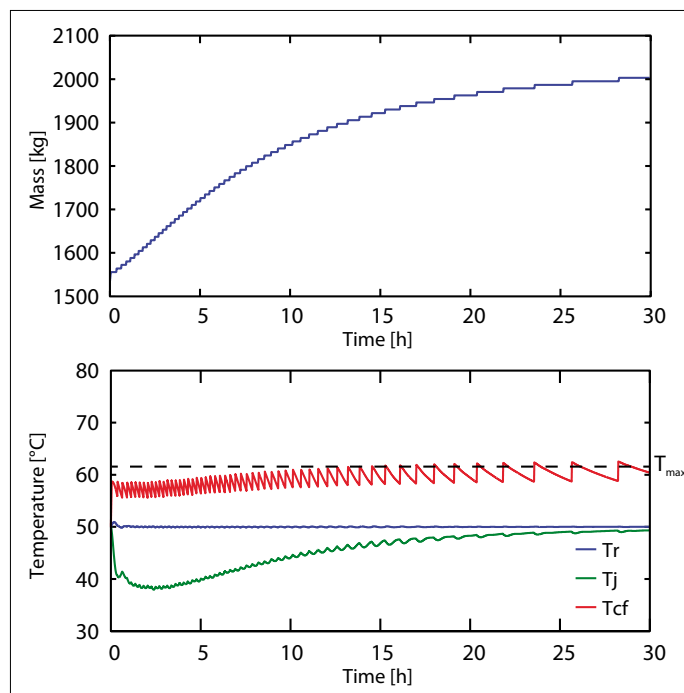


Fig. 4. Simulation of the mass and temperature profiles (T_r = reactor; T_j = jacket; T_{cf} = cooling failure, T_{max} = maximum safe temperature allowed) for a 2.5 m³ fed-batch reactor working under T_{cf} constraint.

If the T_{cf} is higher than the set point T_{max} , the feed is stopped. The optimized feed profile satisfying the constraint is shown in Fig. 4.

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

Finally, the dynamics of an industrial reactor were simulated in order to optimize the thermal safety of a fed-batch reactor at this scale.

This work gives an illustration of investigating reaction kinetics using non-linear model fitting. It shows that it was possible, with limited amount of experimental data, to determine the reaction's kinetics and to predict its behavior under different operation conditions.

In order to validate the optimal feed profile, the next step involves performing an experiment at industrial scale applying the scale-down approach presented by Zufferey,^[5] used to simulate behavior of industrial reactor at laboratory scale.

In the future, the proposed optimization procedure will be extended to other kinds of chemical reactions, leading to a generalized method of obtaining the reaction model and kinetics from calorimetric measurements.

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