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ON-LINE REACTION CALORIMETRY OPTIMIZATION OF SAFETY PARAMETERS

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When chemical reactions are performed in semi-batch mode and the reaction rate is relatively low, the reactant added may be accumulated. The resulting thermal accumulation is of major concern regarding process safety, as a fault in the cooling system may lead to a run-away reaction. The feed rate in semi-batch processes is usually constant, but this paper discusses methods of optimizing the feed rate interactively, based on the measured heat flow and the calculated amount of compound that has actually reacted. The prerequisite of such procedures is to run the experiments in a reaction calorimeter in which the heat flows can be measured accurately and continuously. For this purpose a ChemiSens reaction calorimeter CPA202, which is calibration free and gives stable, flat 'zero-line-type' baselines, was employed.

Keywords: *kinetics, on-line optimization, reaction calorimetry, safety parameters*

Introduction

Most of the chemical reactions in the fine chemicals industry are performed in semi-batch mode. One of the key reactants (B) is added, usually at a constant rate, while the other one (A) is already present in the reactor. The concentration of compound B in the reactor is a function of the dosing rate and the reaction rate. If the reaction rate is high, then the concentration of compound B in the reactor can be assumed to be zero at any given time. If, on the other hand, the reaction rate is low in comparison to the addition rate, then the concentration of B will increase until it reaches a maximum. For most types of kinetics the maximum accumulation is reached when stoichiometric amounts of the compounds are present. Terminating the feeding of compound B will not stop the chemical reaction instantaneously because a certain amount of B will still be present. As there are always certain amounts of reactant B in the reactor during dosing, and the reactant is well distributed without the formation of inhomogeneties, multiple phases, clusters or non-stirred zones, this is usually described in terms of thermal accumulation.

Thermal accumulation is a major concern in the field of process safety, since it can lead to dramatic, uncontrolled temperature rises, and even to run-away reactions, depending on the amount of accumulation and the energy of the reaction, if there is a failure in the cooling or stirring of the system. Similar effects may result from heat confinement after reaction mixtures have become too viscous.

The feed rate in semi-batch reactions is usually kept constant. Since only one feeding sequence has to be programmed this reduces the risk of miss-charging the reactor. However, thermal accumulation leads to a maximum in the accumulation curve and, consequently, protective safety measures have to be based on the corresponding values [1]. Therefore, an on-line monitoring system has been proposed, as well as ways to introduce 'smart' feeding profiles. Ubrich [2] proposed segmenting the feeding profiles to reduce the maximum accumulation by 'spreading' it over the whole dosing range. ChemiSens AB, a Swedish company, has developed a software package, ProFind^{TM}, for their CPA202 Reaction Calorimeter that allows the automated on-line control of dosing profiles. With this tool the system can be controlled so that it follows an 'ideal accumulation profile' based on the continuous determination of the actual thermal conversion.

Theory

Before performing automated on-line experiments, knowledge of certain process parameters is required. At least one test run at the same temperature and with a constant dosing rate has to be performed in order to determine the enthalpy of reaction, ΔH_R. Based on the operating temperature and on extensive studies of the decomposition reactions, the maximum temperature of

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the synthesis reaction, MTSR can be determined. In the case of cooling failure the MTSR must not be exceeded and, consequently, the MTSR determines the maximum allowed accumulation, Acc_{max} in the reactor.

When optimizing the dosing rate automatically, the thermal accumulation must be calculated continuously throughout the entire course of the reaction. The amount of component B added is known from the dosing profile. A curve describing the thermal conversion can be obtained by integrating the measured true heat flow. The amount of reacted component B can be calculated by dividing the thermal conversion by the reaction enthalpy. The difference between the amount of component B added to the reactor and the amount reacted is the amount accumulated during the reaction. The accumulated energy is obtained by multiplying the amount accumulated by the reaction enthalpy. Dividing this by the instantaneous heat capacity for the reacting system gives the adiabatic temperature rise as a function of time. Adding the adiabatic temperature rise to the reaction temperature gives the MTSR.

The optimal way to run a semi-batch process with respect to safety would be to control the dosing of component B in such a way that the amount of un-reacted material accumulated is always below a pre-set level. Alternatively, the process could be run so as to maintain the adiabatic temperature rise at a stable, pre-set level. This paper presents the results of both methods, which were used to find optimal dosing profiles for the formation of esters from propionic anhydride and 1-butanol.

Optimization according to the first method was based on a method in which the pump rate was set at a limited number of discrete flow rates, while the second method utilized continuous control of the flow rate. The ChemiSens software package ProFind^{TM} allows a flow chart to be designed for the continuous evaluation of whether a pre-set thermal accumulation or a pre-set adiabatic temperature rise has been reached. Figure 1 shows the flow chart corresponding to the discrete method, while Fig. 2 shows a flow chart for continuous control.

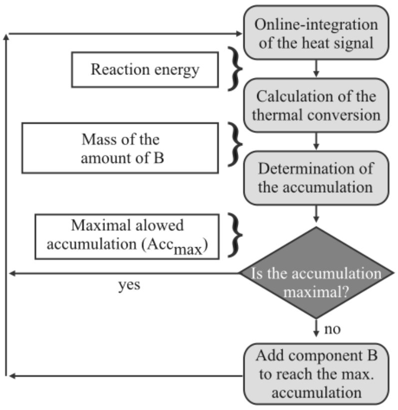


Fig. 1 Schematic representation of the flow chart with discrete optimization of dosing

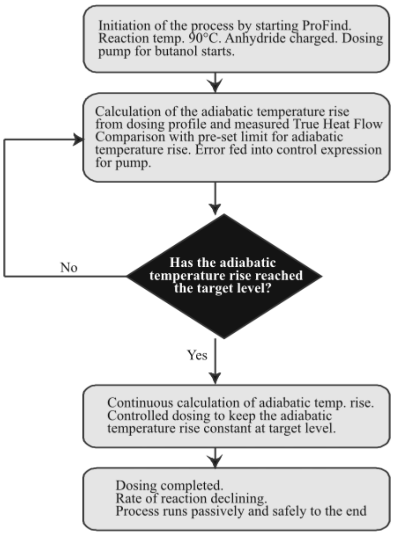
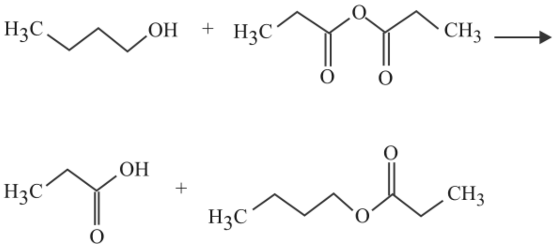


Fig. 2 Schematic representation of the ProFind^{TM} flow chart with continuous optimization of dosing

Experimental

The reaction of propionic anhydride with 2-butanol has been extensively studied by Ubrich [2] and can be considered a model reaction. We chose to work with 1-butanol as it is a more reactive system. The two components react stoichiometrically, and the presence of a solvent is not necessary. The reaction temperature is 90°C, which is well below the 1-butanol boiling point of 117°C. The reaction is exothermal with a heat of reaction of $\Delta H_R = -295\ \text{kJ kg}_{\text{reaction mass}}^{-1}$, corresponding to an adiabatic temperature rise of 150 K (°C) in the case of 100% accumulation.



To provide a sufficient amount of data before running the optimization process, this reaction was studied extensively at different temperatures in previous tests by Reuse [3].

The reaction calorimeter CPA202, manufactured by ChemiSens, was used in all experiments and for the on-line optimization of the addition profiles of the semi-batch reaction. This reaction calorimeter utilizes the true heat flow principle. The reactor contains the true heat flow transducer in its base, which is calibrated during manufacture [4, 5]. The unique design of the reactor ensures that all the heat produced by a chemical reaction is removed from the reactor through this well defined heat path at the reactor base. The surrounding thermostat bath is always kept at the same temperature as inside the reactor, which ensures that there are no other heat flows from the reactor. To withdraw the heat dissipated during the reaction, the reactor base also contains a Peltier element. The Peltier element is used to actively pump heat between the reactor contents and the surrounding bath, both of them being maintained at the same temperature.

The fact that no further calibration is necessary means that the heat release rate can always be determined without any need to establish a baseline 'a posteriori'. This is an important feature when perform dosing optimization. The instrument is also interesting with regard to occupational safety. The small working volume of the reactor, between 10 and 180 mL, can be particularly advantageous when performing reactions that are not well characterized.

In all experiments in this report, the reactor was charged with propionic anhydride, normally 0.5 mol, and brought to the reaction temperature. At thermal equilibrium, 1-butanol was dosed at a controlled rate until the stoichiometric amount was reached. Experiments were run with constant as well as with variable addition rate. The feed line for the 1-butanol was always pre-heated by heat exchange against the thermostating media surrounding the reactor which ensured that the 1-butanol entering the reactor had the same temperature as the reacting system. No cooling effect from the dosing occurred.

The propionic anhydride (97%) came from Sigma Aldrich while the 1-butanol (puriss) came from Fluka. In the initial experiments the dosing of 1-butanol was done by a Prominent pump in combination with a balance while in the last experiments the ChemiSens syringe pump MSC202 was used. The Prominent pump in combination with a balance gives dosing by mass while dosing with the syringe pump gives dosing by volume.

Results and discussion

Constant dosing rates

The influence of the addition rate on the thermal accumulation was studied first. Addition was performed in 15, 30 and finally in 60 min. Figure 3 presents the heat flow measured during the experiments (normalized to the mass of the final reaction mass) with a dosing time of 15 min. The figure also shows the calculated accumulation (thermal conversion normalized to 100% minus the addition normalized to 100% of the stoichiometric amount).

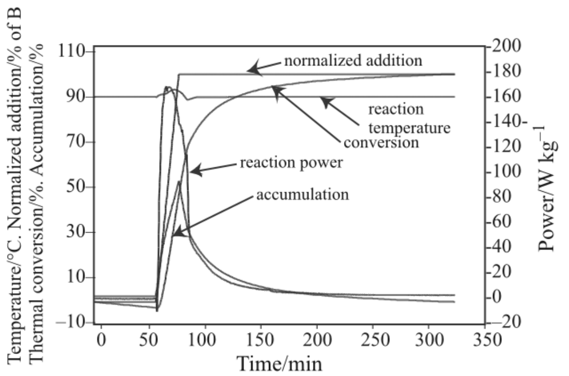


Fig. 3 Evolution of the heat flow (in W kg^{-1}) with an addition time of 15 min. The figure also shows the addition profile (normalized to 100%, corresponding to the stoichiometric amount of component B), the calculated thermal conversion, and the thermal accumulation

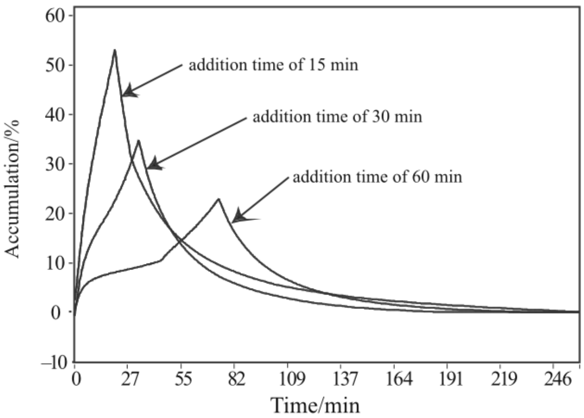


Fig. 4 Comparison of the calculated thermal accumulation for the 3 different addition times (15, 30 and 60 min)

As expected, increasing the addition time reduced the maximum heat flow. The accumulation also decreases from 51 to 32, and finally to 21%, as can be seen in Fig. 4.

Based on these results a strategy for optimizing the dosing procedure by varying the addition rate was developed.

Optimized dosing rates

The first method used for dosing optimization was based on discrete settings of the pumping rate. These settings were calculated according to the flow chart shown in Fig. 1. The process was started with a batch addition of 1-butanol. After a certain time the heat flow was integrated to determine the extent of reaction, and the amount of reactant accumulated was calculated. The difference between the pre-set value for accumulation and the determined value was then

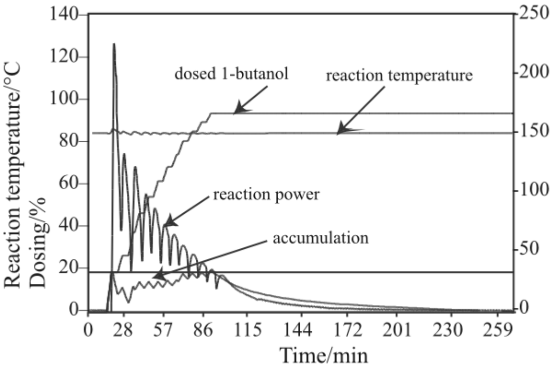


Fig. 5 Discrete dosing of 1-butanol. The amount of 1-butanol accumulated could not be maintained at the pre-set target value

added directly. The result is the segmented addition profile shown in Fig. 5.

The next experiment with discrete pumping rates also started with a batch dosing of 1-butanol, and was followed by three different segments in which the dosing rate was calculated separately for each segment. The results are shown in Fig. 6, which also shows that the accumulation could not be maintained at a stable, pre-set value of 20%, which was the target.

This led to the approach of continuous control of the pumping flow rate, according to the flow chart in Fig. 2 above. Instead of using the 1-butanol accumulation as the target parameter, the adiabatic temperature rise was used. There was no accumulation at the beginning of the process and the pump was started at a relatively high flow rate. The target value for the adiabatic temperature rise was 20 K, which could be maintained during almost the entire dosing sequence. The results are presented in Fig. 7, which also shows the reaction power and the dosing profile used.

A sharp transient is observed in the reaction power curve at the beginning of dosing. This effect is due to endothermic mixing enthalpy, which contributes significantly to the measured heat flow at the beginning of the reaction. The amount of dosed 1-butanol is high in the early stages of the reaction due to no, or only little, thermal accumulation. The situation at the beginning of the reaction is shown in Fig. 8.

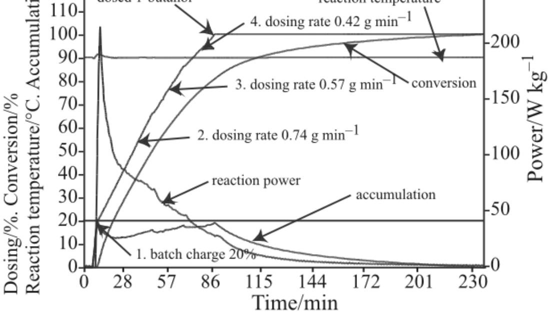


Fig. 6 Segmented dosing of 1-butanol. The target value of the amount of 1-butanol accumulated could not be maintained with a sequence of 3 discrete flow rates

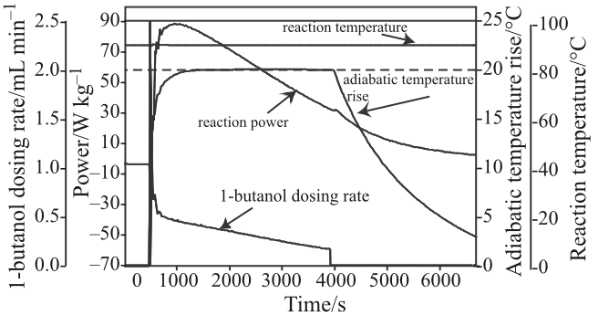


Fig. 7 Automated, optimized dosing of 1-butanol. The flow chart is configured such that the system establishes a constant adiabatic temperature rise of 20 K

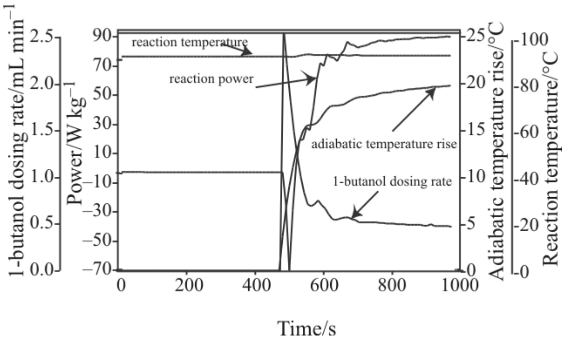


Fig. 8 Early stages of 1-butanol dosing. The endothermic effect of the power curve is given by the mixing enthalpy

Automated control of reaction power and adiabatic temperature rise

Based on the experiments described above, an improved dosing strategy was designed. Only controlling the dosing so as to maintain the accumulated energy at a certain level is not enough in large-scale production. At the beginning of the reaction, the accumulated energy is low and the dosing rate will increase to a level at which the rate of reaction might exceed the cooling capacity of the system. An improved dosing strategy must also take this into account. The complete reaction sequence can be divided into four different phases.

- The start-up phase, during which the rate of reaction follows a pre-set target profile. This will give a smooth start without significant overshoot in the rate of reaction. During this period, the rate of reaction is adjusted to a level corresponding to the maximum cooling capacity of the system.
- The constant power phase, during which the rate of reaction is kept constant at the maximum cooling

capacity. The accumulated amount of energy is continuously calculated and when the adiabatic temperature rise reaches the pre-set limit, the system will enter the next phase.

- The constant energy phase, during which the dosing rate is controlled to maintain a constant adiabatic temperature rise at the pre-set level until dosing is completed.
- The dosing is completed and the reaction will continue safely.

Figure 9 shows the first part of the reaction with the improved dosing control. The rate of reaction follows the target profile very closely before it reaches the constant level of 6 W. The complete reaction, with the four different phases illustrated, is presented in Figure 10. During the constant power phase the dosing rate is continuously increased to keep the rate of reaction constant. As can be seen, the dosing rate falls rapidly when the calculated adiabatic temperature rise is reached.

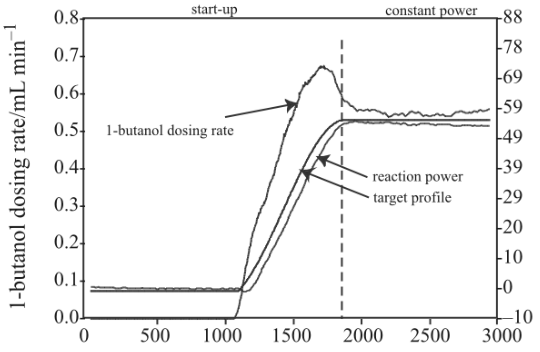


Fig. 9 Controlled dosing of 1-butanol (start-up phase) with subsequent control of reaction power (constant power phase)

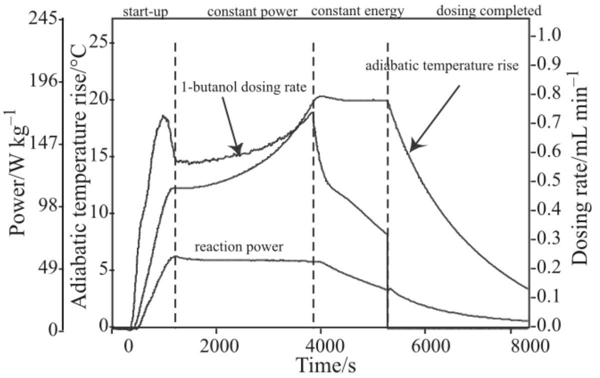


Fig. 10 Simultaneous control of reaction power and adiabatic temperature (the complete reaction)

Conclusions

These experiments demonstrate that a true heat flow reaction calorimeter, such as the ChemiSens CPA202, can be used to run experiments with on-line control of process parameters. A prerequisite is the capability of the instrument to provide reliable heat flow data during the experiment. In order to improve the quality of the data, mixing enthalpies should be included in the on-line calculations, as well changes in the heat capacity due to the addition of the dosed compound. However, there is some concern related to the initial dosing, which could be set too high by the control system. The initial dosing rate must be limited so as not to exceed the cooling capacity of the reactor. Additional experiments have shown that the control functionality of the software ProFind also includes the possibility of allowing the initial dosing rate to follow a pre-set algorithm. With this technique the reaction power could be restricted to stay below a pre-set cooling capability in the beginning.

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