

# Identification of Arrhenius equation parameters for control purposes

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*Abstract:* - In the process control area, there are a lot of systems with nonlinear behaviour. Specific case of such nonlinear system is an exothermic chemical reactor. The reactor nonlinearity can arise from different reasons. One of them is the changeable reaction speed, which depends on the reactants concentration and the in-reactor temperature. The second dependence is described by Arrhenius equation. Knowledge of the Arrhenius equation parameters is a key for correct mathematical model composition and also for safe and successful control. Some possibilities of the parameters determination are described in the literature. However, they are complicated and not very suitable for online identification of real process. A new, more efficient approach developed by the author is described in this paper.

*Key-Words:* - rate constant, exothermic process, semi-batch reactor, identification, simulation, control

## 1 Introduction

The interest in the control of batch reactors has increased in recent years because of the expansion of small-volume specialty chemicals. Many of these batch reactors are “semibatch” or “fedbatch” reactors in which an initial amount of material is placed in the reactor, the content is heated to the desired temperature, and then additional feed of fresh reactant is gradually added to the vessel. The result is a time-varying process with variable volume. If heating and/or cooling is achieved by heat transfer from the vessel liquid into a heating/cooling medium in a surrounding jacket, the time-varying volume means that the heat-transfer area is also changing with time. The optimum operation of many fed-batch reactors is an operating strategy that minimized the batch time. This corresponds to feeding the fresh feed into the reactor as quickly as possible. The feed rate is often limited by heat transfer. If the reaction is exothermic, heat must be removed. The rate of heat transfer depends on three factors [1]: 1. The temperature difference between the reaction liquid and the jacket coolant. The latter depends on the coolant flow rate, the inlet coolant temperature, and the heat-transfer rate. 2. The overall heat-transfer coefficient, which depends on agitator mixing in the vessel and the flow rate of coolant in the jacket. 3. The heat-transfer area. If jacket cooling is used, the effective heat-transfer area in a fed-batch reactor varies during the course of the batch directly with the volume of liquid in the vessel.

Due to the complexity of the reaction mixture and the difficulties to perform on-line composition measurements, control of batch and fed-batch reactors is essentially a problem of temperature control. The temperature profile in batch reactors usually follows three-stages [2]: (i) heating of the reaction mixture until the desired reaction temperature, (ii) maintenance of the system at this temperature and (iii) cooling stage in order to minimize the formation of by-products. Any controller used to control the reactor must be able to take into account these different stages.

The in-reactor temperature control may be complicated by reaction kinetics. The heat released by chemical reactions is function of the reaction rate. The reaction rate depends on individual reactants concentrations and also on the system temperature. The temperature dependence is described by Arrhenius equation. Influence of this equation on the batch process control and possibility of its parameters determination are studied in this paper.

## 2 Semi-batch chemical reactor model

This study deals with influence of reaction kinetics on an exothermic process running a first order reaction, so in this section a mathematical model of such system is described.

Let us consider single input – single output (SISO) system of chemical exothermic semi-batch reactor (figure 1). The reactor has a double wall for

cooling medium and we consider that its content is ideally stirred.

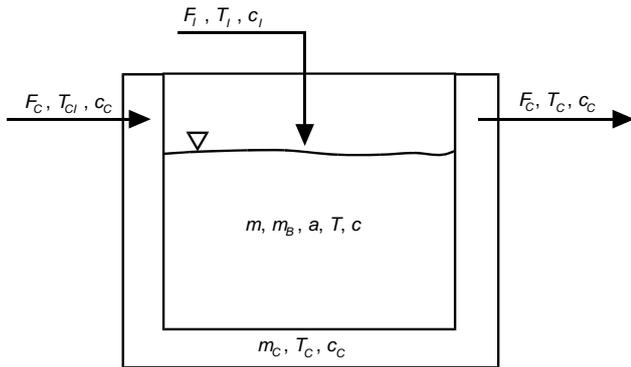


Fig. 1 Exothermic semi batch reactor scheme.

The scheme above shows a chemical semi-batch reactor with initial filling  $m_B$  [kg] given by the solution of chemicals. A reactant causing an exothermic chemical reaction to run is fed into the reactor to control the developing heat. The temperature has to stay under a certain critical level; otherwise the reactor could be destroyed. It is also desirable to utilize the whole capacity of the reactor to process the maximum amount of chemicals in the shortest possible time (higher temperature is desirable). Therefore an optimal control strategy has to find a trade-off between these opposite requirements – higher temperature for faster processing x lower temperature for process safety.

After applying usual simplifications the mathematical model of this system can be written by equations (1)-(4).

$$\frac{dm(t)}{dt} = F_I \quad (1)$$

$$\frac{da(t)}{dt} = \frac{F_I}{m(t)} - A \cdot e^{-\frac{E}{RT(t)}} \cdot a(t) \quad (2)$$

$$\frac{dT(t)}{dt} = \frac{F_I \cdot c_I \cdot T_I}{m(t) \cdot c} + \frac{A \cdot e^{-\frac{E}{RT(t)}} \cdot \Delta H_r \cdot a(t)}{c} - \frac{K \cdot S \cdot T(t)}{m(t) \cdot c} + \frac{K \cdot S \cdot T_C(t)}{m(t) \cdot c} \quad (3)$$

$$\frac{dT_C(t)}{dt} = \frac{F_C \cdot T_{CI}}{m_C} + \frac{K \cdot S \cdot T(t)}{m_C \cdot c_C} - \frac{K \cdot S \cdot T_C(t)}{m_C \cdot c_C} - \frac{F_C \cdot T_C(t)}{m_C} \quad (4)$$

The used model was set up for the chromium waste recycle process [3,4,5], so for simulations were

taken the parameters of this process. Here  $m$  is the total weight of reaction components in the reactor,  $a$  is the mass concentration of the reaction component in the reactor,  $c = 4500 \text{ J.kg.K}^{-1}$  is the specific heat capacity of the reactor content;  $T$  is the temperature of the reactor content.  $F_I$ ,  $T_I = 293.15 \text{ K}$  and  $c_I = 4400 \text{ J.kg.K}^{-1}$  is the reaction component input mass flow rate, temperature and specific heat capacity.  $F_C = 1 \text{ kg.s}^{-1}$ ,  $T_{CI} = 288.15 \text{ K}$ ,  $T_C$ ,  $c_C = 4118 \text{ J.kg.K}^{-1}$  and  $m_C = 220 \text{ kg}$  is the cooling water mass flow rate, input temperature, output temperature, specific heat capacity and weight of the cooling water in the cooling system of the reactor, respectively ely. Other constants:  $A = 219.588 \text{ s}^{-1}$ ,  $E = 29967.5087 \text{ J.mol}^{-1}$ ,  $R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ ,  $\Delta H_r = 1392350 \text{ J.kg}^{-1}$ ,  $K = 200 \text{ kg.s}^{-3}.\text{K}^{-1}$ ,  $S = 7.36 \text{ m}^2$ .

The fed-batch reactor use jacket cooling, but the effective heat-transfer area ( $S = 7.36 \text{ m}^2$ ) in the mathematical model was treated as constant, not time varying. The initial amount of material placed in the reactor takes about two-thirds of the in-reactor volume and the reactor is treated as ideally stirred, so we can do this simplification.

## 2.1 The rate constant

In equations (2) and (3) is included influence of temperature and reaction component mass concentration on the reaction rate. The temperature dependence is defined by Arrhenius equation (5), where  $k$  is the rate constant:

$$k = A e^{-\frac{E}{RT(t)}} \quad (5)$$

The rate constant causes an accumulation of the reaction component in the reactor without corresponding temperature rise. Then, the level of concentration which starts the reaction is reached and the reaction runs very fast. The temperature rises as well and causes the reaction runs even faster. Thus, if the amount of non-reacted reaction component in the reactor is too high, the temperature became uncontrollable and we can't avoid its overshooting. An example of the temperature overshoot caused by accumulation can be seen in figure 2. Here you can see a temperature overshoot over 373K, which was caused by the accumulation of the reaction component. The corresponding mass concentration is depicted in the figure 3. The plots were obtained by a two step control simulation. The actuating signal switch-off was set on 370K, the switch-on was set on 365K. It was impossible prevent the temperature overshooting and simultaneously to trace the desired value 373K. In the steady state (from approximately

t = 2000s) was the control performance satisfactory. So, it is necessary to take into account the mass concentration to prevent the temperature overshooting.

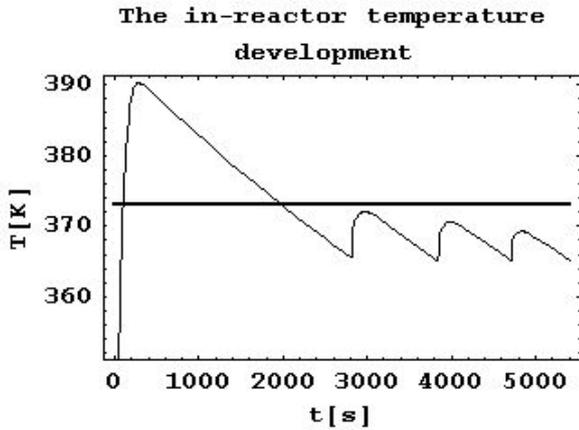


Fig. 2 The temperature overshoot caused by the reactant accumulation

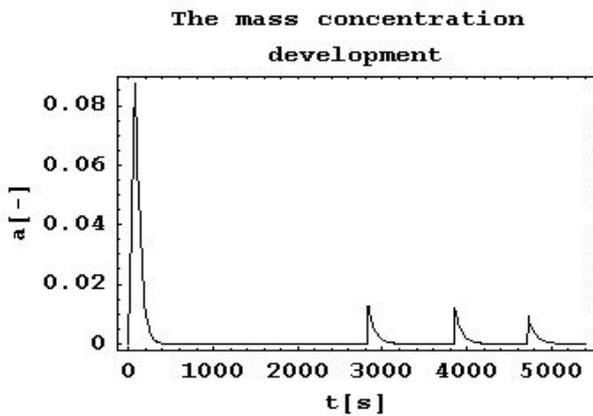


Fig. 3 The mass concentration development (control without penalization)

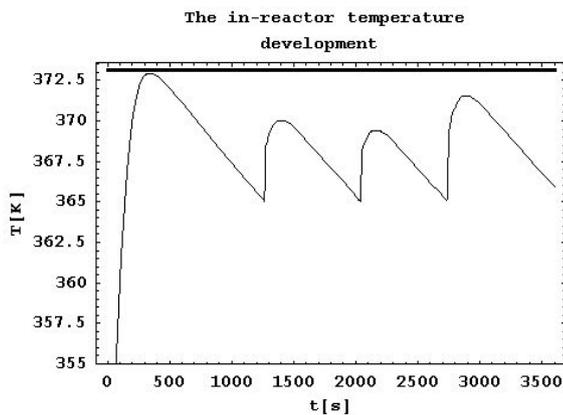


Fig. 4 The temperature development without overshoot – penalized values

With the knowledge of the previously mentioned model (that means also the knowledge of the rate

constant) we can find the safe value of the reaction component concentration during the start-up part of the process control and so prevent the temperature overshooting as can be seen in figure 4. The corresponding mass concentration development is than showed in the figure 5.

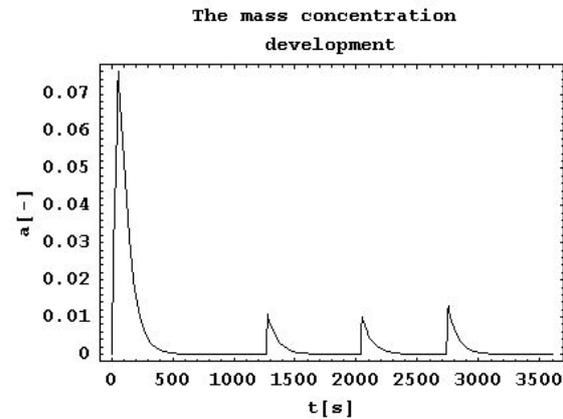


Fig. 5 The mass concentration development – penalized values

Plots show simulation of two-step control with the temperature and reaction component penalization. In case the reaction component mass concentration reach the set value and the temperature gets over penalized value at the same time the actuating variable  $F_I$  is switched off.

The non-reacted chemical reactant is so prevented from cumulating in the chemical reactor. The insensitivity zone was chosen at interval  $(T_{PP} + 1 > T[t] \geq T_{PP})$ , to prevent the in-reactor temperature to oscillate around the penalty temperature.

As can be seen from the above mentioned text, it is important to know the velocity constant parameters to be able satisfactory control like these processes. As far as we use the very same chemicals for processing, there is no generally problem. We can do the identification once and the parameters are always the same. But in case we plan processing wider range of chemicals, or the mixture properties are changeable in time, it is necessary to perform on-line velocity coefficient identification to process safely different mixture types.

### 3 Rate constant identification

For the rate constant identification the formula in equation (6) was derived:

$$k = \frac{dT}{dt} \frac{C}{V \Delta H_r c} = \frac{dT}{dt} \frac{C}{\Delta H_r n} \quad (6)$$

Individual symbols: derivation  $dT/dt$  means a tangent direction (see figure 6),  $C$  [ $J.K^{-1}$ ] – system thermal capacity,  $V$  [ $m^3$ ] – volume,  $c$  [ $mol.m^{-3}$ ] – molar concentration,  $n$  [ $mol$ ] – the number of mole.

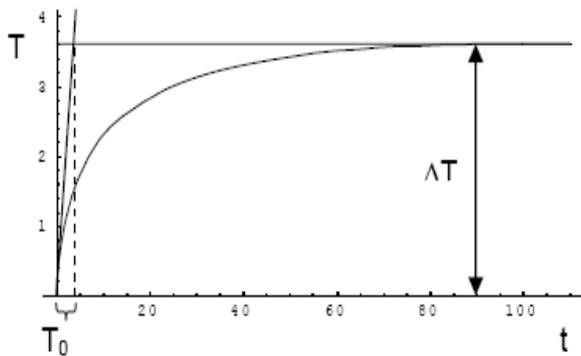


Fig. 6 An example of reaction temperature time dependence

As can be seen from the formula (6) we need to know the in-reactor chemicals volume  $V$  and concentration of reactant causing the heat development  $c$  (or the number of mole  $n$  instead) to determine the rate constant. Further it is necessary to know also the heat of reaction  $\Delta H_r$ , system thermal capacity  $C$  and the temperature tangent direction  $dT/dt$ .

The chemicals volume and the starting concentration are usually known. The system (reactor) thermal capacity must be determined, but only once. Finally the temperature tangent direction may be obtained from the measured temperature time dependence. With the help of the formula (6) we can use an in-reactor temperature profile to find the rate constant directly from the process (in case we put known chemicals quantity in the reactor).

The whole procedure had been already verified by author during the chromium sludge processing [6].

## 4 Conclusion

The semi-batch exothermic reactor control is a complex and difficult process. One of the difficulties is the changing reaction rate which is causing the system nonlinearity as is shown in this paper. However it is possible to deal with the problem by the rate constant identification based on the temperature profile. Such procedure was verified by the author and the derived formula was presented here.

The rate constant knowledge can help us to set up a precise system model and to apply a suitable control method. With a system model even simple control methods can be used to control some

specific batch reactors. On the above mentioned system some control methods had been applied, which were described in articles [7,8,9]. Very powerful seems to be for example predictive control using neural networks [7].

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