

ARRHENIUS EQUATION PARAMETERS IDENTIFICATION FROM TEMPERATURE PROFILES

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Abstract: The article describes an alternative method of determining the rate constants for chemical reactions of first order. Specifically, the determination of Arrhenius equation parameters, ie activation energy and pre-exponential factor from the measured temperature curves. The advantage of this approach is that there is no need to determine the immediate reactants concentration by its measurement. Knowledge of the rate constant may significantly improve safety and control of specific processes

Key words: rate constant, exothermic process, semi-batch reactor, identification, simulation

1. INTRODUCTION

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. Influence of this equation on the batch process control and possibility of its parameters determination are studied in this paper.

2. MODEL OF A SEMI-BATCH REACTOR

Influence of reaction kinetics on an exothermic process running a first order reaction and a mathematical model of such system is described in this section.

The following figure 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).

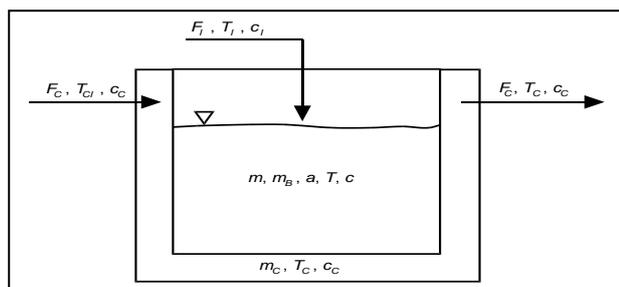


Fig. 1. Exothermic semi batch reactor scheme process safety

The mathematical model of such system can be written by equations (1)-(4).

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

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

$$\frac{dT(t)}{dt} = \frac{F_i \cdot c_i \cdot T_i}{m(t) \cdot c} + \frac{A \cdot e^{-\frac{E}{RT(t)}} \cdot \Delta H_r \cdot a(t)}{c} - \frac{K \cdot S \cdot T(t)}{m(t) \cdot c} + \frac{K \cdot S \cdot T_c(t)}{m(t) \cdot c} \quad (3)$$

$$\frac{dT_c(t)}{dt} = \frac{F_c \cdot T_{Cl}}{m_c} + \frac{K \cdot S \cdot T(t)}{m_c \cdot c_c} - \frac{K \cdot S \cdot T_c(t)}{m_c \cdot c_c} - \frac{F_c \cdot T_c(t)}{m_c} \quad (4)$$

The used model was set up for the chromium waste recycle process (Kolomazník et al., 2007; Macků & Sámek 2010), 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 is the specific heat capacity of the reactor content; T is the temperature of the reactor content. F_i , T_i and c_i is the reaction component input mass flow rate, temperature and specific heat capacity. F_c , T_{Cl} , T_c , c_c and m_c 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. Other constants: A pre-exponential factor, E activation energy, R gas constant, ΔH_r heat of reaction, K heat transfer coefficient, S heat transfer surface.

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.

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. 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 4), C [$J.K^{-1}$] – system thermal capacity, V [m^3] – volume, c [$mol.m^{-3}$] – molar concentration, n [mol] – the number of mole.

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 ΔH_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.

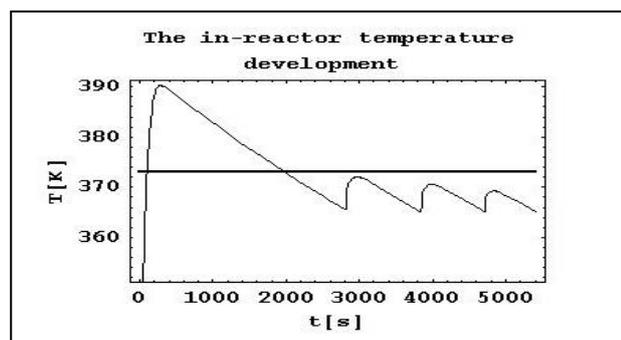


Fig. 2. The temperature overshoot caused by the reactant accumulation

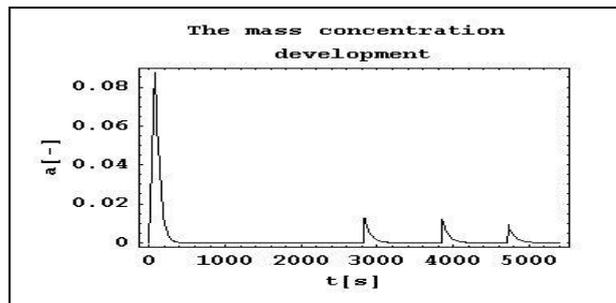


Fig. 3. The mass concentration development

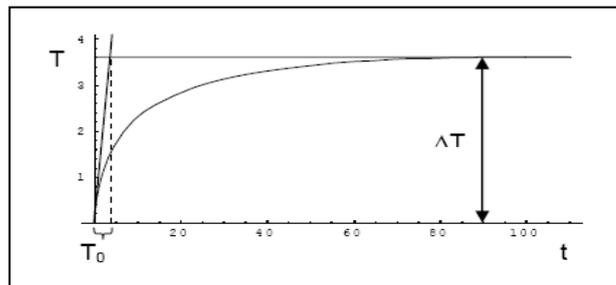


Fig. 4. An example of reaction temperature time dependence

4. CONCLUSION

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 (Sámek & Macků, 2007; Gazdoš & Macků, 2008; Novosad & Macků, 2010). Very powerful seems to be for example predictive control using neural networks (Sámek & Macků, 2007).

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