MODELLING AND SIMULATION OF CHEMICAL INDUSTRIAL REACTORS

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ABSTRACT

The paper is focused on analysis, mathematical modelling and simulation of reactors which are used in the chemical and tanning technology. Material and energy balances are the key issues of mathematical models of chemical reactors and processes. The combination with chemical kinetics and transport effects an intellectual basis for chemical reactor design can be obtained. The contribution brings a special tanning facility – paddle tumbler which can be described as a type of rotary batch reactor and continuous-flow circulation reactor for the cyclohexane production. A mathematical dynamic model is derived and the optimal parameters were computed.

INTRODUCTION

The contribution presents a utilization of material balances with kinetic expressions for elementary chemical reaction in the phase of the reactor design. Many design engineers grope in the dark when they are facing to labyrinth of chemical and physical properties in the real world of technological plants. The paper gives simple techniques and an example how those problems can be overcome. The final derived equations of mathematical models are solved for quite simple but frequent and important chemical reactor.

The behavior of real chemical process is obviously too complex for complete mathematical analysis. We are obliged to use an approximate description which is able to deliver sufficiently accurate results. Cardinal simplifications of the mathematical description can be obtained by the following supposals:

- the process does not change its properties during the observation period,
- the relation between input and output variables of the process is linear,
- all process variables can be measured continuously and have a continuous-time trend.

In the phase of design process of many chemical, biochemical, tanning and other reactors there arise some fundamental and relevant questions. Among them, the first is: Should the reactor be batch or continuous? And

subsequently: In the continuous reactor case, should it be preferred a piston flow or perfect mixing one?

For producing high-volume chemicals, flow reactors are usually preferred. The ideal piston flow reactor exactly duplicates the kinetic behavior of the ideal batch reactor. For small-volume chemicals, the economics frequently favor batch reactors. Batch reactors are used for the greater number of products, but flow reactors produce the larger volume as measured in tons.

Flow reactors are operated continuously; that is, at steady state with reactants continuously entering the vessel and with products continuously leaving. Batch reactors are operated discontinuously. A batch reaction cycle has periods for charging, reaction, and discharging. The continuous nature of a flow reactor lends itself to larger productivities and greater economies of scale than the cyclic operation of a batch reactor. The volume productivity for batch systems is identical to that of piston flow reactors and is higher than most real flow reactors. However, this volume productivity is achieved only when the reaction is actually occurring and not when the reactor is being charged or discharged, being cleaned, and so on. Within the class of flow reactors, piston flow is usually desired for reasons of productivity and selectivity.

A useful and interesting application of reactor design for chemical engineers can be seen in (Froment and Bischotf 1990), (King and Winterbottom 1998). The treatment of biochemical and polymer reaction engineering is described very extensively in (Nauman 2002), (Levenspiel 1998), (Schmidt 1998), (Smith 1956). There are emphases on numerical solutions which are needed for most practical problems in chemical reactor design. Sophisticated numerical techniques are rarely necessary. The aim is to make the techniques understandable and easily accessible and allow continued focus on the chemistry and physics of the process.

THEORETICAL BACKGROUND

Types of elementary reactions

Consider the reaction of two chemical species according to the stoichiometric equation:

$$A + B \rightarrow P \qquad (1)$$

This reaction is said to be *homogeneous* if it occurs within a single phase. It means that they take place only in the gas phase or in a single liquid phase. These reactions are said to be *elementary* if they result from a single interaction (i.e., a collision) between the molecules appearing on the left-hand side of equation (1). The rate at which collisions occur between A and B molecules should be proportional to their concentrations, *a* and *b*. Not all collisions cause a reaction, but at constant environmental conditions (e.g., temperature) some definite fraction should react. Thus, we expect

$$\Re = k[A][B] = kab \tag{2}$$

where k is a constant of proportionality known as the *rate constant*.

Note that the rate constant k is positive so that $\Re$ is positive. $\Re$ is *the rate of the reaction,* not the rate at which a particular component reacts. Components A and B are consumed by the reaction or equation (1) and thus are "formed" at a negative rate:

$$\Re_A = \Re_B = -kab \tag{3}$$

while the product P is formed at a positive rate:

$$\Re_P = +kab \tag{4}$$

The adopted sign convention supposes that the rate of a reaction is always positive. The *rate of formation of a component* is positive when the component is formed by the reaction and it is negative when the component is consumed.
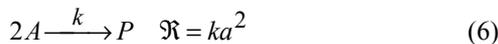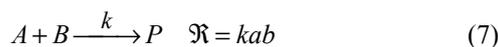
First-Order Reactions

$$A \xrightarrow{\ k\ } P \quad \Re = ka \tag{5}$$

The rate constant k for the first-order reaction has units of $[s^{-1}]$.

Second-Order Reactions
1) One reactant:

$$2A \xrightarrow{\ k\ } P \quad \Re = ka^2 \tag{6}$$

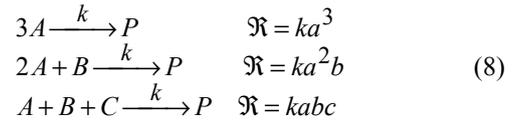2) Two reactants:

$$A + B \xrightarrow{\ k\ } P \quad \Re = kab \tag{7}$$

in the case of second-order reaction the rate constant k has units of $[m^3 mol^{-1}s^{-1}]$.

Third- Order Reactions
In principle, there are three types of third-order reactions:

$$
\begin{aligned}
3A &\xrightarrow{\ k\ } P & \Re &= ka^3 \\
2A + B &\xrightarrow{\ k\ } P & \Re &= ka^2 b \\
A + B + C &\xrightarrow{\ k\ } P & \Re &= kabc
\end{aligned}
\tag{8}
$$

Types of ideal reactors

Generally, there are four basic kinds of ideal reactors:

1) The batch reactor
This is the most common type of industrial reactor. Batch reactors has no input or output of mass after the initial charging. The amounts of individual components may change due to reaction but not due to flow into or out of the reactor. The component balance for component A satisfies equation (for constant volume V batch reactor):

$$\frac{d(Va)}{dt} = \Re_A V \quad \Rightarrow \quad \frac{da}{dt} = \Re_A \tag{9}$$

The solution of ordinary differential equation - ODE (9) requires an initial condition: $a=a_0$ at $t=0$. The rate of the reaction $\Re_A$ depends on concentration a ($\Re_A = -ka$).

2) The piston flow reactor
The piston flow reactor is continuous-flow reactor with the similar behavior as a batch reactor. It is usually visualized as a long tube in which materials stay together and react as they flow down the tube. The composition of material flowing through a piston flow reactor depends on time and also on position in the tube. The age of material at point z it t, and the composition at this point is given by the constant-volume version of the component balance for a batch reactor (9) with the substitution $t = z/\bar{u}$:

$$\bar{u}\frac{da}{dt} = \Re_A \tag{10}$$

where z is distance measured from the begin of the tube and $\bar{u}$ is the velocity of the fluid.

3) The continuous-flow stirred tank reactor
The most important assumption is that the continuous-flow stirred tank reactor is perfectly mixed. In that case there are only two possible values for concentration – the inlet flow has concentration a_{in} and everywhere else concentration a_{out}. The component balance for component A in the single reactions is:

$$Qa_{in} + \Re_A V = Qa_{out} \tag{11}$$

4) The completely segregated, continuous-flow stirred tank reactor
This type of reactor is interesting theoretically, but has

very limited practical utilization.
Obviously, no real reactor can achieve ideal state. However, it is often possible to design reactors that very closely approach ideal limits.

Temperature dependence of reactions

Chemical reactions can be isothermal or nonisothermal. In the case of isothermal reaction, the operating temperature and the rate constants are arbitrary assigned. For nonisothermal reactions, the temperature varies from the point to point in the reactor, the temperature dependence directly enters the design calculations. The rate constant k for elementary reactions is expressed by Arrhenius equation:

$$k = k_0 T^m \exp\left(\frac{-E}{RT}\right) \qquad (12)$$

where parameter $m=0$ (or $m=0.5$, 1 for the special cases of reactions) depends on used theoretical model. E is *activation energy* and the fraction E/R is called an *activation temperature.*
A general energy balance (for a flow reactor) can be written as:

$$\rho.c_p.V \frac{dT}{dt} = q_{in}.\rho_{in}.c_{pin}.T_{in}$$
$$- q_{out}.\rho_{out}.c_{pout}.T_{out} - V\Delta H_R kc_A - F\alpha(T - T_{ext}) \qquad (13)$$

where term $\rho.c_p.V \dfrac{dT}{dt}$ is *accumulation of energy*, $V\Delta H_R kc_A$ is a *heat generated by reaction* and $F\alpha(T - T_{ext})$ is *heat transferred out of reactor*.

ILLUSTRATIVE EXAMPLES

The rotary batch reactor – paddle tumbler

Creation of the mathematical model of wood paddle tumbler is one of the aims of our research. The non-isothermal and non-adiabatic paddle tumbler for an enzymatic hydrolysis of chromium tannery wastes is considered. Because of simplification we can describe the paddle tumbler as a type of rotary batch reactor.
Application of paddle tumbler for an enzymatic hydrolysis in tannery has two basic reasons. Firstly, the paddle tumblers are usually used directly in the tannery wastes point of origin. Secondly, it needs only small investment to plant changes for its available utilization. Both reasons support economical and environmental aspects of the desired process.
The presented mathematical model should respect the following assumptions (Kolomaznik et al. 2006):
- Reaction mixture is intimately stirred by motion of reactor.
- Heat transfer on the both sides of wall is ideal.

- Heat of the hydrolysis reaction is inconsiderable.
- The cylinder shape reactor has radius at least 10 times greater than the thickness of wall, it means that the temperature profile can be described as "infinite plate".
- Dependence of all physical parameters of model on the temperature is negligible.

On the mentioned assumptions the quantitative mathematical model can be expressed by the following relations:

$$\frac{\partial T(x,T)}{\partial t} = a_t \frac{\partial^2 T}{\partial x^2}(c,t); 0 < x < b; t > 0 \quad (14)$$

$$m_0 c_{p0} \frac{\partial T_0(t)}{\partial t} = S\lambda \frac{\partial T}{\partial x}(0,t) \qquad (15)$$

$$T(x,0) = T_p \qquad (16)$$

$$T(b,t) = T_p \qquad (17)$$

$$T(0,t) = T_0 \qquad (18)$$

$$T_0(0) = T_{0p} \qquad (19)$$

A non-stationary temperature profile in the reactor wall is described by equation (14). Equation (15) describes a balance between the speed of reaction mixture temperature decrease and the heat transfer through the reactor wall. Initial conditions are expressed by equations (16) and (17). Equations (18) and (19) represent conditions of ideal heat transfer.
The time response of the reaction mixture temperature depends on the reactor wall thickness b, the thermal conductivity coefficient a_t, the weight of wall and reactor filling (m, m_0) and the specific heat capacity of wall and reaction mixture (c_p, c_{p0}). The dimensional value of reaction mixture temperature $T_0(t)$ depends on its initial temperature T_{0p} and the temperature of surrounding T_p which can be identical with the initial temperature of the reactor wall (Kolomaznik et al. 2005).
From all mentioned parameters only the weight of reactor filling m_0 and its initial temperature can be changed. The weight of the reaction mixture and its initial temperature have to be chosen so that its resulting temperature do not decrease under the desired limit border (the reaction speed would be too small).
For the first approximation without nonlinearities of the temperature field in the reactor wall can be used very simple mathematical model. It is presented as a quasi-stationary model in the form:

$$- m_0 c_0 \frac{dT_0}{dt} = \frac{S\lambda}{b}(T_0 - T_p) \qquad (20)$$

The solution of the model (11) is:

$$\ln\left(\frac{T_{0p} - T_p}{T_0 - T_s}\right) = \frac{S\lambda t}{bm_0 c_0} \qquad (21)$$

The continuous-flow circulation reactor

Another presented reactor is a continuous-flow circulation reactor for the cyclohexane production. Cyclohexane, as an important base material for polyamide manufacturing, makes by catalytic hydrogenation of benzene. A large number of reaction heat transfers during hydrogenation process. Therefore, benzene and cyclohexane mixture hydrogenation proceed in continuous time circulating reactor under hydrogen excess. The presented mathematical model should respect the following conditions:

- Reaction mixture is perfectly mixed by circulation.
- The volume of reaction mixture is constant.
- All technological parameters in reactor are constant.
- Heat transfer on the both sides of wall is ideal.

The hydrogenation mechanism of benzene is supposed to be a first-order reaction:

$$\text{Benzene} + 3H_2 \xrightarrow{k} \text{Cyclohexane} \qquad (22)$$
$$r_B = -k \cdot c_B$$
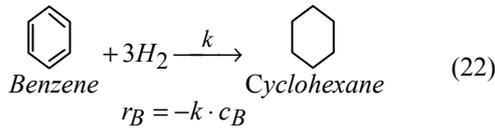
The material balance for the component *benzene* satisfies the following differential equation (for constant volume V of reactor):

$$q_v.c_{Bv} = q.c_B + V.k.c_B + V\frac{dc_B}{dt} \qquad (23)$$

The temperature balance in the reactor satisfies the differential equation:

$$q_v.\rho_v.c_{pv}.T_v + (-\Delta H_R)V.k.c_B =$$
$$q.\rho.c_p.T + F.\alpha(T - T_x) + V.\rho.c_p\frac{dT}{dt} \qquad (24)$$

where the relation $(-\Delta H_R)V.k.a_B$ is the heat generated by the reaction and $F.\alpha(T - T_x)$ represents the heat transfer into surroundings.

The rate constant k for elementary reactions is expressed by Arrhenius equation (12). After some mathematical manipulations the equation of the benzene concentration variation takes the form:

$$\frac{dc_B}{dt} = \frac{q_v}{V} \cdot c_{Bv} - \frac{q}{V} \cdot c_B - k_0 e^{-\frac{E}{RT}} \cdot c_B \quad (25)$$

Similarly, variation of the reaction mixture temperature in the reactor is:

$$\frac{dT}{dt} = \frac{q_v}{V} T_v + (-\Delta H_R).\frac{k.c_B}{\rho.c_p} - \frac{q}{V} T$$
$$- \frac{F.\alpha}{V.\rho.c_p}(T - T_x) \qquad (26)$$

The time response of the reaction mixture concentration depends on the input flow of the benzene, the concentration of input stream c_{Bv}, the volume of reactor filling, the specific heat capacity of reaction mixture c_p and the rate constant k. The solution of ordinary differential equation (25) requires an initial condition: $c_{Bv} = c_{B0}$ at $t=0$.

From all mentioned parameters the input flow stream into the reactor q_v and its initial concentration c_{Bv} can be changed.

EXPERIMENTS

The rotary batch reactor – paddle tumbler

A rotary batch reactor with diameter 1,5 m and high 1 m was used for the measuring of the temperature characteristics. Experiments took place directly in tannery industrial conditions. In the first phase 18 experiments were performed. Results of some measured variables were influenced by different factors e.g. cover leakage. From these reasons these corrupted data were not be inserted into final measurement sets. These dates were used for comparison of simulation characteristics with real values as well as for the determination of hardly measured parameters. Experiments used for comparison were carried out in a cold reactor and the filling was preheated by steam to 70-80°C. Initial parameters of are presented in Table 1.

Table 1: Initial parameters for comparative experiments

Experiment number	Surrounding temperature [°C]	Initial temperature of filling [°C]	Weight of filling [kg]
experiment 14	21	80	108
experiment 17	20	80,5	155
experiment 18	20	76	155

The thermal conductivity (λ) of the wood paddle tumbler (strengthened with iron tires) was drawn from measured experimental dates. The solution of quasi-stationary model (14) was used. The final line (see Figure 1.) was obtained from dependence of relation $\ln\left(\frac{T_{0p} - T_p}{T_0 - T_s}\right)$ on the time. The thermal conductivities were calculated by the regression analysis from measured data. Then the average value of thermal conductivity λ= 0.1031 [W/(m .K)] was calculated for the later utilization.
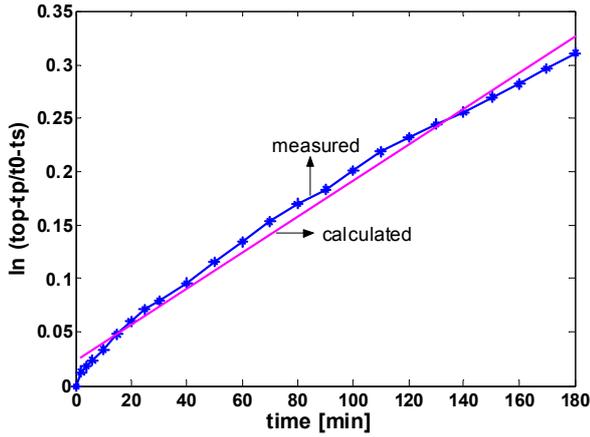
Figure 1: Demonstration of thermal conductivity calculation from measured dates. For experiment 18: λ=0.1036 [W/m .K]

The main problem consists in holding of the reaction mixture temperature in the range which is sufficient for a protein yield. Simulations were performed with using of the averaged thermal conductivity. The minimal reactor filling was determined as m_0=113 [kg] upon the dependence of the reaction mixture temperature on the reactor filling.

The obtained parameters from experiments were used for simulation calculations. For the first step, mathematical model (14)-(19) was used. However, the calculated temperature profiles do not exactly follow the measured data. The difference is caused by simplifications but the main error is only in the initial phase when the heat transfer from reaction mixture into reactor wall is very high (accumulation of energy in the wall).
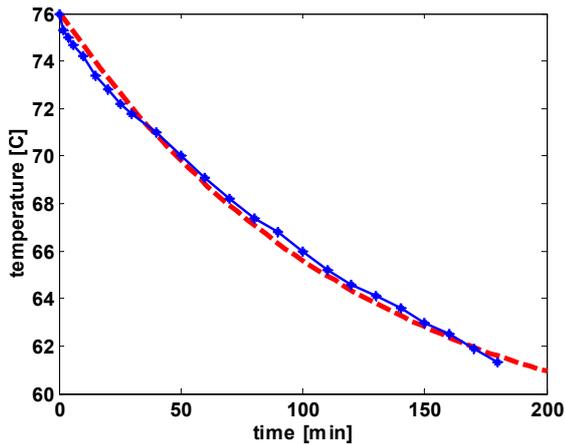

Figure 2: Comparison of measured (-*) and approximated (--) temperature characteristic (experiment 18).

Described rotary reactor can be for example approximated by the first order system in the form:

$$G(s) = \frac{-15}{98s + 0.8} \approx \frac{B(s)}{A(s)} \qquad (27)$$

This approximation was obtained by a four-parameter method adopted from (Astrom 1995) applied to step responses.

The continuous-flow circulation reactor

The continuous-flow circulation reactor with V=0,5 [m^3] volume was used for the simulation of the concentration and temperature characteristics. Initial input flow into the reactor was q_v=0.0067 [m^{3}s^{-1}] with the initial concentration of benzene c_{Bv}=1.9 [kg/m^3]. Initial rate constant was considered k_0= 1.616.e14 [s^{-1}] density of mass ρ=985 [kg m^{-3}], specific heat capacity c_p = 4.050 [J/kg.K], transfer heat coefficient α = 435.00 [W/m^2.K], surface F=5.5 [m^2], activation energy H=4.8e4 [Jmol^{-1}], initial mass temperature T$_v$=320 [K] and temperature of surrounding T$_x$=290 [K].

Steady-State Analysis Results

The dependence of the output variable upon the input in the steady-state is shown in the Figure 3. The reactor steady-state characteristics were obtained by solution of equations (12), (25) and (26). The initial conditions were computed by a standard optimization method - iterative procedure.
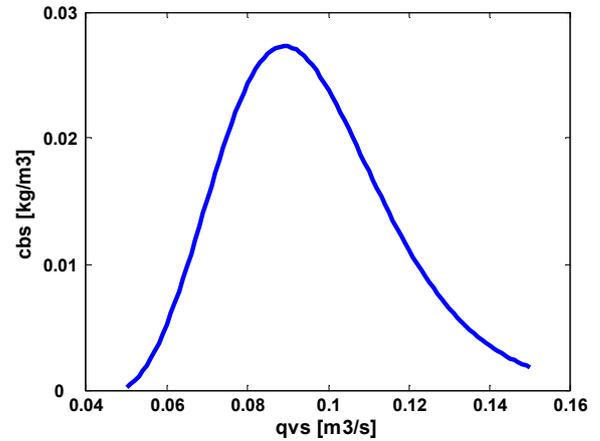

Figure 3: Steady-state input-output behavior of the continuous-flow circulation reactor

Dynamic Analysis Results

For dynamic analysis purposes one input and one output choices were considered. Then were defined input u and output y as deviations from their steady-state values – $u(t) = q(t) - q^s(t)$ and $y(t) = c_B(t) - c_B^s(t)$.

Graphical interpretation of simulation experiments – the output y time responses to input u step changes are depicted on Figure 4.
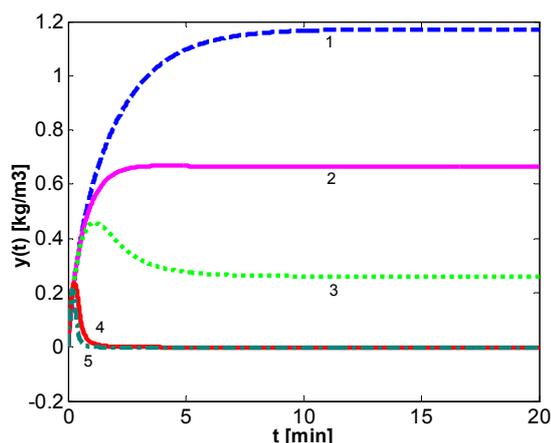
Figure 4: The output *y* time responses to input *u* step changes, u=-0.08(*1*), -0.07(*2*), -0.05(*3*), 0.05(*4*), 0.08(*5*)

Model approximation

For control requirement, described continuous time circulation reactor was approximated by the second order system in the form:

$$G(s) = \frac{1.9}{71s^2 + 10s + 0.5} \approx \frac{B(s)}{A(s)} \qquad (28)$$

The approximation was obtained by a four-parameter method adopted from (Astrom and Hagglund 1995) applied to step responses.

CONCLUSION

Developed mathematical models (especially quasi-stationary) enable to set up different changes of various parameters without any complex industrial experiments. A deep analysis and comparisons of experimental and simulation (computed) data were performed for verification of models. Some parameters and constants of mathematical relations had to be derived previously from measured industrial variables. Especially, the thermal conductivity of wood barrel wall had to be computed. This mathematical derivation was much simpler then performing experiments and analyzing data. After the establishing of constants and models, the minimization of the reactor filling in the first case and initial input flow or initial concentration of benzene into the reactor in the second case can be optimized. For the control requirements we have tried to approximate presented models as the first or second order input-output system. All computations were performed in the MATLAB+SIMULINK environment.

Acknowledgments

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