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PROGRAM FOR STATIC AND DYNAMIC ANALYSIS OF THE CROSS-LINKING SYSTEM

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Abstract: *This paper presents a program in MATLAB's Graphical User Interface (GUI) which can be used for investigating of the static and dynamic behaviour of the cross-linking system. We consider reaction inside continuous stirred tank reactor which is described by proper mathematical model. The application provides computation for various values of the input variables which made this program general for the wide range of the users without theoretical knowledge about the modeling and simulation.*
Key words: *cross-linking, matlab, analysis, model, CSTR*

1. INTRODUCTION

One of the most often methods of intermediate product stabilization is their cross linking. Aldehydes are commonly used as cross-linking chemicals, from which glutaraldehyde and formaldehyde have the greatest importance. Final quality and optimal behaviour of the end product depend on various conditions during the cross linking reaction. From the practical point of view, this reaction is very important because this collagen hydrolyzate represents raw material for pharmaceutical, nutritional, cosmetics and stock-feeding industry. To accomplish practical measurement and experimentally study this cross-linking process is very exacting. There is another way, how to get an insight into the system behaviour, just in cases when the real experiments are expensive or hazardous. It is modelling and simulation. Modelling is a process of model creation with the assistance of derivation of mathematical relations. Computer program creation for their solution can be often a part and parcel of the mentioned process. Simulation is an application of the created model for imitation of modelled reality which means model equations solving for specific values of numeric parameters. In chemical industry, there are many types of processes which are commonly nonlinear and cannot be analytically solved. The computer simulation brings possibility to get knowledge about behaviour of the system. For this purposes, a mathematical model of the examined system has to be arranged. The mentioned cross-linking reaction is proceeding in a reactor. In practice, the type of a continuous stirred tank reactor is broadly used because flow of reactants or cooling liquid can be easily controlled. From the system engineering point of view, this type of the reactor is represented by nonlinear system with lumped parameters. Its mathematical model is described by a set of nonlinear ordinary differential equations.

Some modelling methods are well known and described (Kolomazník et al., 1990), other simplification, modelling and simulation can be found here (Ingham et al., 1994). The simple differential method is presented by many authors (Lyuben, 1989), Runge-Kutta's integration method can be found here (Ralston, 1979).

This paper is focused on simulation results of the steady-state and dynamic behaviour of the continuous stirred tank reactor. Mathematical model of this system is quantitatively expressed by a set of five ordinary differential equations which are then solved numerically to obtain steady state and dynamic characteristics. The goal of this work is to present usability of the mathematical model on similar types of chemical processes by the simulation results on one type of the systems. All simulation has been done in Matlab environment.

2. DESCRIPTION OF THE SYSTEM

Reaction of collagen hydrolyzate with glutaraldehyde can be schematically described as follows:

$$A + B \xrightarrow{k_1} C \tag{1}$$

$$C \xrightarrow{k_2} D \tag{2}$$

$$2A \xrightarrow{k_3} E \tag{3}$$

Protein B reacts with the cross-linking agent A resulting in the intermediate product C. Product C then reacts with itself due to its two reactive bonds and the final product D (raw material for production of biodegradable casings) arises. Simultaneously, glutaraldehyde reacts with itself (aldol synthesis) resulting in aldol resins E. These resins have typical coloration and this reaction is accompanied with colour change (Taylor et al., 1998).

From the chemical point of view, the hydrolyzate is a product of skin collagen and contains seventeen amino acids. The most important and mostly represented of them are glycine, proline and hydroxyproline. For this reason, for mathematical simulation purpose, the collagen hydrolyzate is considered to be a copolymer of the above-mentioned amino acids (Heidemann, 1993).

We assume that the reactants inside the tank are perfectly mixed and volume contraction of the reactants is negligible during the reaction.

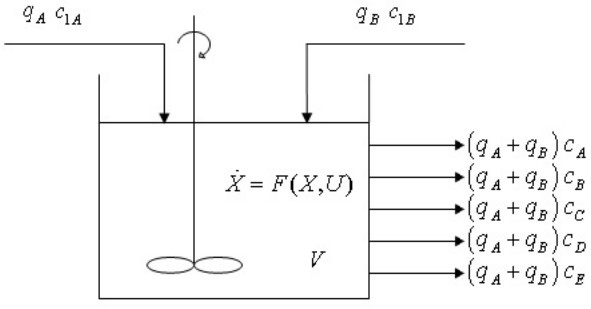

Fig. 1. Scheme of continuous stirred tank reactor

The mathematical model of the system is then derived from the material balances of the reactor:

$$\frac{dc_A}{dt} = \frac{q_A}{V} c_{A1} - \frac{(q_A + q_B)}{V} c_A - k_1 c_A c_B - k_3 (c_A)^2 \tag{4}$$

$$\frac{dc_B}{dt} = \frac{q_B}{V} c_{B1} - \frac{(q_A + q_B)}{V} c_B - k_1 c_A c_B \tag{5}$$

$$\frac{dc_C}{dt} = -\frac{(q_A + q_B)}{V} c_C + k_1 c_A c_B - k_2 c_C \quad (6)$$

$$\frac{dc_D}{dt} = -\frac{(q_A + q_B)}{V} c_D + k_2 c_C \quad (7)$$

$$\frac{dc_E}{dt} = -\frac{(q_A + q_B)}{V} c_E + k_3 (c_A)^2 \quad (8)$$

where t[s] is time, c_x [mol] is concentration of substance X, V[m^3] is volume of the reactor, q_a [$m^3 s^{-1}$] and q_b [$m^3 s^{-1}$] represent volumetric flow rates, k_1 [$s^{-1} mol^{-1}$], k_2 [s^{-1}] and k_3 [$s^{-1} mol^{-1}$] are velocity constants. Their values are unknown and have to be estimated or determined experimentally. Technological parameters are shown in Tab. 1.

k_1=0.06 $s^{-1} mol^{-1}$	c_{A1}=1 $mol.m^{-3}$
k_2=0.04 s^{-1}	c_{B1}=1 $mol.m^{-3}$
k_3=0.005 $s^{-1} mol^{-1}$	q_A=0,01 $m^3 s^{-1}$
V=1 m^3	q_B=0,01 $m^3 s^{-1}$

Tab. 1. Values of technological parameters

3. PROGRAM IN MATLAB

The program allows user to set many parameters. Working point can be defined by:

- volumetric flow rate of the reactive compounds
- initial concentration of the reactive compounds

These parameters can be changed in appropriate edit boxes as well as volume of the reactor, velocity constants etc.

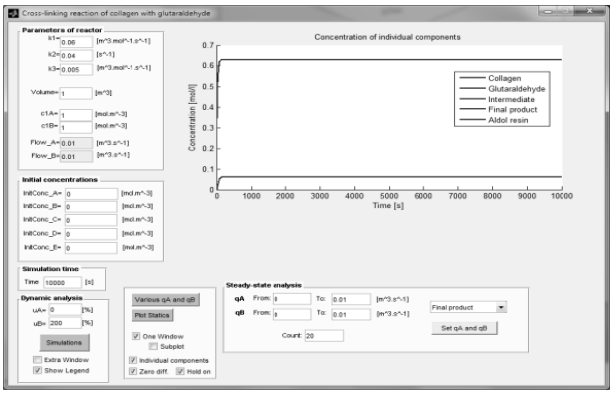

Fig. 2. Main window of the program in Matlab's GUI

Steady state analysis

The state variables in infinite time must be calculated for steady state analysis. It is expected that these variables are supposed to be stable. From mathematical point of view, all derivatives with respect to time are equal to zero. Simple iteration method was used for solving of mentioned problem. In our case, volumetric flow rates qA and qB (in contrast to input concentrations) are quantities which can be easily changed.

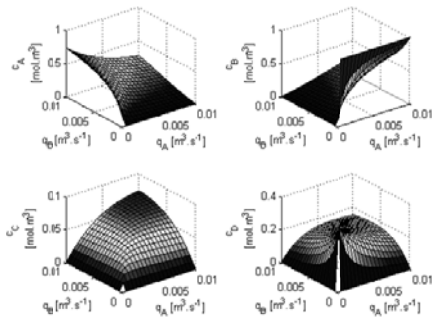

Fig. 3. Example of the values of the computed steady-state values of the concentrations

Dynamic analysis

It is common that the dynamic analysis comes after steady state analysis. Behaviour of the system can be observed after the step change of the input variable. The step change of the volumetric flow rate qB represents input variable. This procedure needs solving the set of ordinary differential equations. The problem has been solved using Runge-Kutta's iteration method. This method can be used both for computing of initial assessments and final solutions as well. User algorithm programmed in Matlab was used for computation, especially built-in function ode45, which is based on an explicit Runge-Kutta formula. Simulation time was chosen from interval t = <0; 10000> s. Steady-state values of the state variables cAs, cBs, cCs, cDs and cEs computed from the previous analysis for the working point were used as initial conditions.

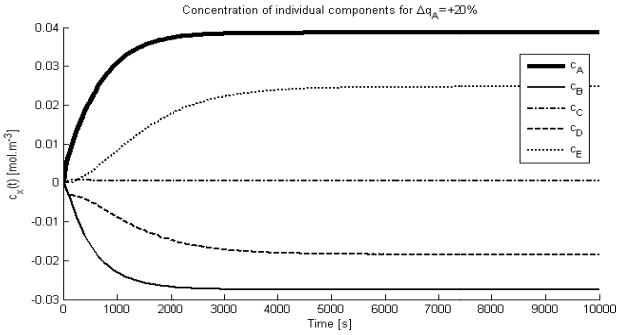

Fig. 4. Example of the time response of the product's concentration for +20% change of its steady-state value of the input volumetric flow rate qA

4. CONCLUSION

This paper dealt with the static and dynamic analysis of a cross-linking system using program created in Matlab's GUI. The results of mathematical simulation can determine optimal conditions of manufacturing process not only from the energy saving or environment protection point of view, but they also optimize desired mechanical and sensorial quality of the end products. The results are general and can be extrapolated. It means that verified mathematical models can be used for other processes described by the same chemical-physical mechanism. For example, kinetic equations of artificial casing cross linking are valid for production of ecological adhesive, protective polymer colloids, capsulates, medication etc.

5. ACKNOWLEDGEMENTS

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