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TRANSFER MATRIX DETERMINATION OF THE SYSTEM OF COLLAGEN CROSSLINKING WITH ALDEHYDES DESCRIBED BY MATHEMATICAL MODEL OF CONTINUOUS STIRRED TANK REACTOR

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ABSTRACT
Reaction of the collagen hydrolyzate with cross-linking agents, especially with aldehydes (glutaraldehyde), is very important not only in leather technology, but also in nutritional industry. Mathematical description of the reaction is still unanswered because at the present there is neither controlling the process nor reliable measuring of its course. This paper describes current state in this field and proposes a motion of the mathematical description of cross-linking reaction. Transfer matrix is deduced from the model, which is necessary step for further control purposes. Some simulations are used for illustration of time dependencies of individual reactant concentrations. Analysis of the system was examined by numerical solving of the mathematical model. Standard Runge-Kutta's method was successfully used.
Keywords: Transfer matrix, crosslinking reaction, collagen hydrolyzate, glutaraldehyde, mathematical model, simulation

1. INTRODUCTION
At the present time, there are still industrial branches which can be called typical polluters in spite of the effort to reduce their negative impact on environment. Tanning industry is one of them and as whole; it can not be covered with any list of steps that should contribute to environment protection. Tanning industry has various manufacturing sectors with specific impacts on surrounding. It is necessary to assert an individual approach during judgment of these impacts and to minimize negative influences in accord with the national legislation. Leather manufacturing produces considerable amount of wastes which means unfavourable impacts on elementary components of environment, especially soil, water and air. There are two ways how to solve this problem. The former is preventive way and leads to limitation of waste production by force of clear technology installation or recycling methods. Recycling procedure allows utilizing wastes as a source of secondary raw material without any reference to place or time of waste formation. The latter way removes consequences of industrial production which disturbs balance of nature or has negative impacts on environment. It is closely analysed in *Marek* at al. [1] and *Blažej* at al. [2]. New conception of manufacturing from utilizing products and waste formation point of view brings many steps which prospectively results in installation of wasteless technologies. It means that the amount of wastes can be decreased by force of a suitable change of the original manufacturing process. It is spoken about high degree of material use and significant decrease of processing waste. These technologies can be considered as a specific case of recycling when no time shift neither spatial shift arises between waste formation and their utilization. Amount of energy which is consumed for reutilization of waste should be minimal and demonstrates how the wasteless technology is effective. Wasteless technologies are based on conceptual solution of whole cycle: raw material – manufacturing – consumption – recycling of waste. Principle of solution is product with desiderative parameters which is produced with minimal material and energy usage. From practical point of view, the realization of wasteless technology is

inaccessible. In practice, every technology of this type produces wastes in minimal amount, but they always have specific impact on environment. In general, material which can not be further used, is considered as waste. There is no problem to meet the term "environmentally wasteless technology", which has not at least negative consequences for nature. Let us concentrate to leather manufacturing which ranks a specific position. It processes leather of fatstock and game, which are wastes of meat-processing industry. From this point of view, the leather industry is the first branch whose main raw material is waste from other industrial productions. However, in addition to valued product it produces considerable amount of liquid and solid wastes. By way of physical and chemical processes the leather is gradually transmuted into the hide. Production of 250 kg of hide requires 1000 kg of leather, more details can be found in *Kupec at al.* [3]. Recovery factor stands 25%, which is quite low value. The rest comprises secondary products from which the hide trimmings and chrome-tanning shavings are the most valued, *Langmaier* [4]. These are very important raw material for another processing; more information can be found in *Mládek at al.* [5]. For example, hydrolyzate of collagen is industrially produced from chrome-tanning shavings (originally minor waste product) by enzymatic hydrolysis. Utilization of collagen hydrolyzate can lie in the production of proteinaceous casings for nutritional industry; in particular, it is biodegradable casings used in butcher production. In mentioned applications, collagen hydrolyzate is supposed to be cross-linked with any suitable agent. This is absolutely the most important step during its processing. In this study, non-toxic and environmentally friendly glutaraldehyde was used. In practice, this process is realised discontinuously. Therefore for the mathematical modeling purposes we consider a continuous stirred tank reactor. Chemical reactors are very often used in industry, especially in chemical and biochemical divisions. Nowadays, computer simulations are often used because they have many advantages in contrast to an experiment on a real system, which is uneconomic and sometimes not feasible and can be dangerous. Some modelling methods are described by *Kolomazník* [6], other simplification, modelling and simulation can be found in *Ingham* at al. [7]. The simple differential method is presented by many authors, e.g. *Lyuben* [8], Runge-Kutta's integration method can be found in *Ralston* [9].

2. REACTION KINETICS

Assume that the reaction of collagen with aldehydes may be described as $A+B \xrightarrow{k_1} C \xrightarrow{k_2} D$ and simultaneously $2A \xrightarrow{k_3} E$. In other words, protein B reacts to cross-linking agent A and as a result, intermediate product C arises. Intermediate then reacts to itself due to its two reactive bonds and final product D arises. Simultaneously, glutaraldehyde reacts to itself (Aldol synthesis) and as a result of this reaction, aldol resins E arises. These resins have typical coloration so that this reaction is accompanied with colour change. Final product is supposed to be clear and colourless so that this aldol synthesis is undesirable. Therefore the rate of the reaction system can be modeled as follows:

$$-\frac{dc_A}{d\tau} = k_1 c_A c_B + k_3 \left(c_A\right)^2 \tag{1}$$

$$-\frac{dc_B}{d\tau} = k_1 c_A c_B \tag{2}$$

$$\frac{dc_C}{d\tau} = k_1 c_A c_B - k_2 c_C \tag{3}$$

$$\frac{dc_D}{d\tau} = k_2 c_C \tag{4}$$

$$\frac{dc_E}{d\tau} = k_3 \left(c_A\right)^2 \tag{5}$$

where $\tau\,[\mathrm{s}]$ is time, $c_X\,[\mathrm{mol}]$ is concentration of substance X, $k_1\,[\mathrm{s^{-1}mol^{-1}}]$, $k_2\,[\mathrm{s^{-1}}]$ and $k_3\,[\mathrm{s^{-1}mol^{-1}}]$ are velocity constants. Their values are unknown and have to be estimated or

determined experimentally.

3. MATHEMATICAL MODEL OF CSTR

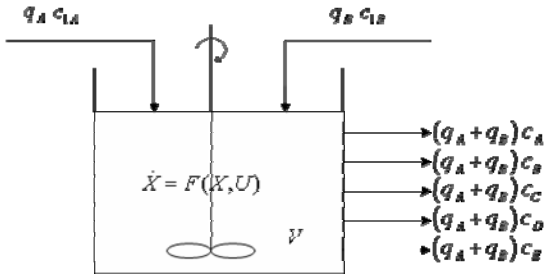

Figure 1. Scheme of the CSTR

The mathematical model of the system (see Figure 1.) is derived from the material balances inside the reactor, according equations (1)-(5), it is quantitatively expressed by a set of five ordinary differential equations. Let us mark each of them with letter f_n, where n=1, 2, …5. Now we have complete set of ordinary differential equations, which are nonlinear.

$$f_1: \quad \frac{dc_A}{d\tau} = \frac{q_A}{V}c_{A1} - \frac{(q_A+q_B)}{V}c_A - k_1 c_A c_B - k_3\left(c_A\right)^2 \tag{6}$$

$$f_2: \quad \frac{dc_B}{d\tau} = \frac{q_B}{V}c_{B1} - \frac{(q_A+q_B)}{V}c_B - k_1 c_A c_B \tag{7}$$

$$f_3: \quad \frac{dc_C}{d\tau} = -\frac{(q_A+q_B)}{V}c_C + k_1 c_A c_B - k_2 c_C \tag{8}$$

$$f_4: \quad \frac{dc_D}{d\tau} = -\frac{(q_A+q_B)}{V}c_D + k_2 c_C \tag{9}$$

$$f_5: \quad \frac{dc_E}{d\tau} = -\frac{(q_A+q_B)}{V}c_E + k_3\left(c_A\right)^2 \tag{10}$$

To linearize them, the Taylor's expansion is used. A linear model is developed around the steady-state operating point. Let us consider linear, time invariant state model with four inputs and five state variables and five outputs. In our case, the output variables are the same as the state variables. The linear equations can then be written in the following matrix general form, which is known as a state-space description:

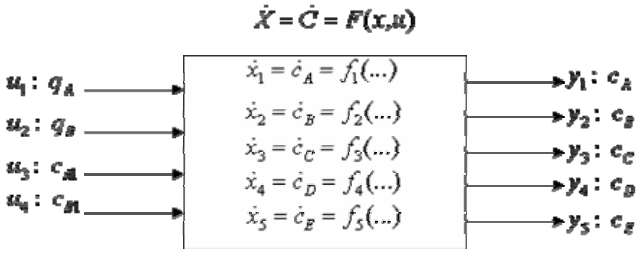

Figure 2. Scheme of the state-space model

$$\Delta\dot{X}_{5x1} = A_{5x5}\Delta X_{5x1} + B_{5x4}\Delta U_{4x1} \tag{11}$$

$$\Delta Y_{5x1} = \Delta X_{5x1} \tag{12}$$

where X is state vector of, A is a system matrix, its elements are defined as partial derivative of function f_n in steady state with respect to input variables, B is an excitation matrix, its elements are defined as partial derivative of function f_n in steady state with respect to output variables, U is a vector of input parameters, Y is a vector of output parameters. Symbol Δ represents deviation from the steady-state operating point. While the elements of matrixes A and B appear complex, upon substitution of relevant constants and the steady-state operating conditions each differential term reduces to a single numeric value.

Equation (11) can be also written in following form:

$$\begin{pmatrix} \dot{c}_A \\ \dot{c}_B \\ \dot{c}_C \\ \dot{c}_D \\ \dot{c}_E \end{pmatrix} = \begin{pmatrix} a_{11} & \cdots & a_{15} \\ \vdots & \ddots & \vdots \\ a_{51} & \cdots & a_{55} \end{pmatrix} \begin{pmatrix} \Delta c_A \\ \Delta c_B \\ \Delta c_C \\ \Delta c_D \\ \Delta c_E \end{pmatrix} + \begin{pmatrix} b_{11} & \cdots & b_{14} \\ \vdots & \ddots & \vdots \\ b_{51} & \cdots & b_{54} \end{pmatrix} \begin{pmatrix} \Delta q_A \\ \Delta q_B \\ \Delta c_{A1} \\ \Delta c_{B1} \end{pmatrix} \tag{13}$$

For control purposes, there is a need to transform mentioned linear model into dimensionless shape. Let us assume:

$$\Delta c_A = \Delta c_A^* \; c_A^0; \;\; \Delta c_B = \Delta c_B^* \; c_B^0; \;\; \Delta c_C = \Delta c_C^* \; c_C^0; \;\; \Delta c_D = \Delta c_D^* \; c_D^0; \;\; \Delta c_E = \Delta c_E^* \; c_E^0; \tag{14}$$

$$\Delta q_A = \Delta q_A^* \; q_A^0; \;\; \Delta q_B = \Delta q_B^* \; q_B^0; \;\; \Delta c_{A1} = \Delta c_{A1}^* \; c_{A1}^0; \;\; \Delta c_{B1} = \Delta c_{B1}^* \; c_{B1}^0 \tag{15}$$

where Δc_A^* is concentration of component A in dimensionless form and c_A^0 is a constant value. After proper algebraic modification, all variables and matrixes A and B are dimensionless. Then we can specify transfer-function matrix of our system, which is defined $H(s) = (sI - A)^{-1} B$, where I is identity matrix and s is Laplace operator [11].

4. CONLUSION

Raw leather processing in tanning industry or collagen material in nutritional industry carries many technologically demanding procedures which results in production of various industrial waste besides final product. The chemical reaction between collagen material and cross-linking agent is cardinal operation. Its course is influenced by many factors and finally has an impact on final product. Key problem is a selection of any suitable measurable quantity. This sensory system can inform actuator of reaction state or kinetics conditions. As a result it allows execution of actions in individual technological steps. Mentioned problem can be solved by exploiting mathematical-statistical processing of experimental data or data measured in industrial process. The purpose of this is finding of predominant factors on investigated target function. Nowadays, a fully automatic control of cross-linking process is practically the only possibility. Indicated procedure of transfer-function matrix determination can be utilized for control purposes.

5. ACKNOWLEDGEMENT

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