Mathematical modeling and simulation of the collagen protein hydrolysis process

H. Vaskova, K. Kolomaznik, and R. Matusu

***Abstract*—** This paper is focused on the mathematical model for alkaline hydrolysis of leather shavings. Leather industry produces annualy a large amount of wastes. For the environment-friendly solution the processing of certain part of wastes arising from the leather industry is reasonable to utilize hydrolysis processes. Collagen protein contained in e.g. leather shavings can be further effectively processed. The description of the hydrolysis process is based on the linearized state model. The mathematical-physical model is built on the mass balance of the input substances and the resulting hydrolysate protein, moreover on an enthalpy balance for the reaction mixture and saturated steam serving in reactor as the heat transfer medium. The simulations of the protein hydrolysis process model are performed in Matlab Simulink and are closely discussed in the paper.

***Keywords*—**Mathematical modeling, simulation, collagen protein, chromium, hydrolysis, leather waste processing.

I. Introduction

PROTECTION of the environment is one of the global challenges attracting lot of attention in recent years. People realize the status quo is not sustainable and it is a necessary to change the approach to a wide range of activities. One of these activities is waste reduction and waste treatment. Ideal is using safe, environmentally and economically favourable ways. However, their implementation is not usually straightforward.

A significant share of waste arises from manufacturing sector. In this paper it is dealt with an area of leather industry, more specifically leather tanning. Leather products like footwear, clothing, handbags, wallets, fashion accessories, upholstery, etc. are among the objects of our everyday needs. Achieving the final products comprise a lot of waste arising from the raw material processing and creating specific items. Only in tanneries million tons of waste is generated annually.

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The selected leather wastes, such as shavings, can be processed by hydrolytic reaction in alkaline or acidic medium. In these cases the protein is liquified and after further treatment can be applied in forms of gelatin or protein hydrolyzates in e.g. pharmaceutical, food industry or in agriculture.

The literature search shows the automatic control in leather/hide processing respectively leather waste processing is not very widespread. Rather the automated and robotic devices are implemented within the secondary manufacturing. These sectors include especially footwear industry, which process over the half of the produced leather, textile industry and extensive use is also for upholstery and automotive industry

The level of measurement and control systems applications is low apart from others due to the lack of quantitative models allowing the use of some modern control methods. However, in recent years, efforts are being made to implement the automation into the leather processing to increase productivity, precision of operations, time efficiency and last but not least to reduce physically demanding work, restrict acts of the health hazards of employees and contribute to the work environment improvement.

The problems of processing the leather industry wastes including proposals for technological devices equipped with automatic control are solved in last decades at our workplace, at the Faculty of Applied Informatics at Tomas Bata University in Zlín. [1, 2]

Closely related and lately discussed issue comprises also the hexavalent chromium problematics. Currently the chrome-tanning is the most common type of tanning worldwide. Complex salts of trivalent chromium are used in the tanning process and effectively influenced the desired functional properties of leather. The fibril-forming collagens are the major structural proteins of hides and skins. Trivalent chromium stabilizes a hide by crosslinking the collagen fibers and supply required qualities. However, CrIII contained in leather can be under various conditions in small amounts oxidized to another form – hexavalent chromium. Hexavalent chromium belongs among toxic elements and its salts are classified as carcinogen in the contrast to the trivalent form, which is benign, safe and largely beneficial [3, 4]. Although knowledge of trivalent to hexavalent chromium conversion is well described in literature, the precise mechanism is complex and details are not clearly explained. [5]

Hexavalent chromium compounds belong to strictly monitored pollutants both in the environment and in industrial areas. The growing demand for alternative methods of tanning is appearing, none have been found up to now to be a

competitive compensation to chromium tanning. The solution for the environmental protection and also protection of human health remains in focusing on the processes used for transformation of raw hides to leather.

II. LEATHER WASTE TREATMENT

The complex processing of chromium-containing waste materials is based on the collagen protein hydrolysis. In simplified way this process can be divided into the following phases, as displayed in Fig. 1.

In the first stage the collagen protein is liquefied and separated from the chromium sludge. Chromium sludge can be subjected to revitalization for obtaining chromium in a form of salts for further leather tanning [6]. The part of resulting gelatinous protein, a high-quality gelatin, finds many applications e. g. in food industry, pharmacy or cosmetic and therefore can be used cost-effectively. The rest of gelatinous protein is used for the purpose of further processing. Enzyme activity leads in alkaline conditions to molar mass decrease of gelatinous hydrolyzate. Further splitting of protein chain can continue by the act of acid [7]. Then the hydrolyzate with lower molar mass is acquired and can find application as biostimulator in agriculture.

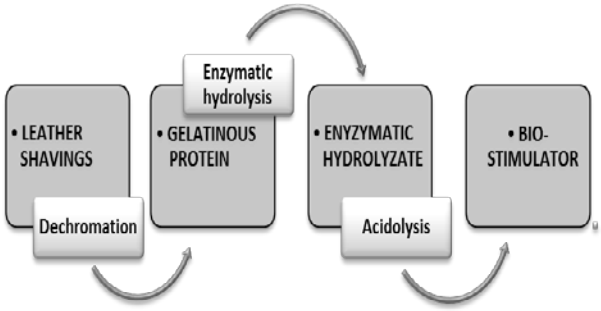

Fig. 1 structure of a dechromation process

III. MATHEMATICAL MODEL

Linearized state mathematical model including input, output variables and inner-state variables is used for the process description.

A. State model of dynamic system

Diagram of system used is shown in Fig. 2. Continuous nonlinear system is described by equations:

$$\dot{X} = F(X,U) \tag{1}$$

$$Y = G(X,U) \tag{2}$$

Where $\mathbf{X} = (x_1, x_2, \ldots, x_n)$ is the state vector,
$\mathbf{U} = (u_1, u_2, \ldots, u_r)$ is the input vector,
$\mathbf{Y} = (y_1, y_2, \ldots, y_m)$ is the output vector,
$F = (f_1, f_2, \ldots, f_n)$ and $G = (g_1, g_2, \ldots, g_m)$ are vector functions and $\dot{\mathbf{X}} = \frac{\mathrm{d}X}{\mathrm{d}t}$.

B. Model linearization

Linearized model is obtained by introducing deviations of state and input variables from their stationary states and then linearized using Taylor series.

$$\Delta\mathbf{X} = \mathbf{X} - \mathbf{X}^{\mathbf{0}} \tag{3}$$

$$\Delta\mathbf{U} = \mathbf{U} - \mathbf{U}^{\mathbf{0}} \tag{4}$$

$\mathbf{X}^{\mathbf{0}}$ and $\mathbf{U}^{\mathbf{0}}$ are stationary states values, the time derivative of state variables gives zero.

$$\Delta\dot{X}^{\mathbf{0}} = \Delta\mathbf{F}(\mathbf{X}^{\mathbf{0}}, \mathbf{U}^{\mathbf{0}}) = 0 \tag{5}$$

Continuous linear system is described by the state equation and output status

$$\Delta\dot{\mathbf{X}} = \mathbf{A}\Delta\mathbf{X} + \mathbf{B}\Delta\mathbf{U} \tag{6}$$

$$\Delta\mathbf{Y} = \mathbf{C}\Delta\mathbf{X} + \mathbf{D}\Delta\mathbf{U} \tag{7}$$

where A is state matrix, $\dim\mathbf{A} = n \times n$,
B is the input matrix, $\dim\mathbf{B} = n \times r$,
C is the output matrix, $\dim\mathbf{C} = m \times n$,

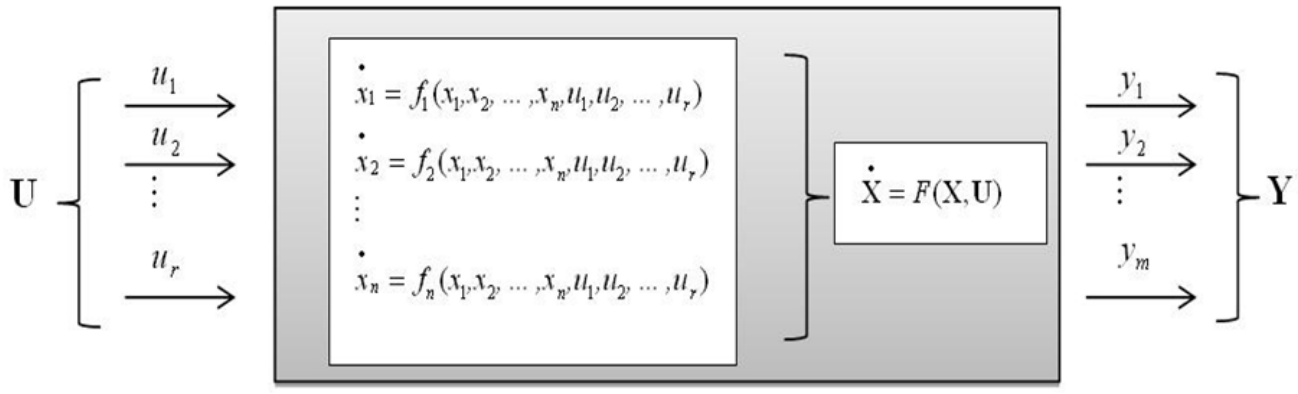

Fig. 2 mathematical model of the system

D is the zero matrix, $\dim \mathbf{D} = m \times r$.

The state matrix A is given, the other matrixes are determined in a similar way.

$$A = \begin{bmatrix} \frac{\partial f_1^0}{\partial x_1} & \frac{\partial f_1^0}{\partial x_2} & \cdots & \frac{\partial f_1^0}{\partial x_n} \\ \frac{\partial f_2^0}{\partial x_1} & \frac{\partial f_2^0}{\partial x_2} & \cdots & \frac{\partial f_2^0}{\partial x_n} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial f_n^0}{\partial x_1} & \cdots & \cdots & \frac{\partial f_n^0}{\partial x_n} \end{bmatrix} \quad (8)$$

This system as a real system fulfils the strong physical condition of the feasibility, i.e. the outputs are functions only of the state variables. This means that for

$$\Delta \mathbf{Y} = \Delta \mathbf{X} \quad (9)$$

the matrix **C** is the identity matrix and D is the zero matrix.

C. Hydrolysis of the collagen protein

Mathematical-physical model for shavings alkaline hydrolysis description is based on the mass balance of the input substance, the resulting hydrolyzate protein, enthalpy balance for the reaction mixture and the heat transfer medium, which is the saturated steam. The hydrolysis process takes place in a flow reactor with a stirrer ensuring the state variable independence on the position in the reactor. It is considered as system with lumped parameters. The mixing the heat transfer medium is also presumed. The mathematical model is given by the balance equations (10) – (14). The used symbols are specified in Table 1.

Mass balance for protein

$$\dot{m}_{RS}\, a_P = \dot{m}_{RS}\, a_B + k m_R a_B + m_R \frac{\mathbf{d}a_B}{\mathbf{d}t} \quad (10)$$

Mass balance for hydrolyzate

$$0 = \dot{m}_{RS}\, a_E - k m_R a_B + m_R \frac{\mathbf{d}a_E}{\mathbf{d}t} \quad (11)$$

Enthalpy balance for reaction mixture

$$\dot{m}_{RS}\, c_{RS} T_{RS} + KS(T - T_R) = \dot{m}_{RS}\, c_{RS} T_R + m_R c_{RS} \frac{\mathbf{d}T_R}{\mathbf{d}t} \quad (12)$$

Enthalpy balance for heat transfer fluid

$$\dot{m}_P\, H + \dot{m}_P\, c_P T_0 = \dot{m}_P\, c_P T + KS(T - T_R) + m_P c_P \frac{\mathbf{d}T}{\mathbf{d}t} \quad (13)$$

Table 1 used variables

Designation	Physical quantity	Unit
m_R	Mass of reaction mixture (RS)	kg
m_P	Mas of water	kg
$\dot{m}_{RS}$ (= *dmRS*)	Mass flow of reaction mixture	kg/s
$\dot{m}_P$ (= *dmP*)	Mass flow of heating stem, respectively water	kg/s
a_P	Initial mass fraction of protein in RS	1
a_B	Mass fraction of decomposed protein in the reactor	1
a_E	Mass fraction of undecomposed protein in the reactor	1
T_{RS}	Temperature of RS	K
T_R	Temperature of reaction	K
T_0	Temperature of stem, the output	K
T	Temperature of the reactor shell = temperature of water, the output	K
c_{RS}	Specific heat of RS	J/kgK
c_P	Specific heat of water	J/kgK
K	Heat transfer coefficient	W/m^{2}K
S	Area of reactor heated by steam	m^2
H	Specific latent heat of vaporization	J/kg

D. Transfer matrix

Taking the Laplace transform of (6) and (7) yields

$$s\Delta X(s) = A\Delta X(s) + B\Delta U(s) \quad (14)$$

$$\Delta Y(s) = C\Delta X(s) + D\Delta U(s) \quad (15)$$

and

$$\Delta X(s) = (sI - A)^{-1} B\Delta U(s) \quad (16)$$

After the substitution for $\Delta\mathbf{X}(s)$ in the output equation (15) together with (9) we get

$$G(s) = (sI - A)^{-1} B \quad (17)$$

Expression of matrices A and B is then based on the mathematic model (10) – (13). The transfer matrix is calculated from (17). Transfered to the unfimensionless form and expressed using values of physical quantities for a real reactor we got a matrix G* depicted in equation (18).

IV. Simulation

Simulations based on the state description concerning matrixes A and B and the calculated transfer matrix G were performed in Matlab Simulink to obtain the progress of the state what in this case means also the output values.

$$G^* = \begin{bmatrix} \frac{1}{4,09+s} & \frac{0,27}{4,09+s} & 0 & 0 & 0 \\ \frac{3,09}{4,09+5,09+s^2} & -\frac{0,27+0,27s}{4,09+5,09+s^2} & 0 & 0 & 0 \\ 0 & -\frac{50(22,75+s)}{343(28,13+29,13s+s^2)} & \frac{22,75+s}{28,13+29,13s+s^2} & \frac{3,44}{28,13+29,13s+s^2} & \frac{2,17}{28,13+29,13s+s^2} \\ 0 & -\frac{227250}{343(28,13+29,13s+s^2)} & \frac{4545}{28,13+29,13s+s^2} & \frac{4,09+0,64s}{28,13+29,13s+s^2} & \frac{2,58+0,41s}{28,13+29,13s+s^2} \end{bmatrix} \quad (18)$$

The diagram of the model simulation is displayed in Fig. 3.

First, simulations with the unit step function were performed on each input separately, and all combinations thereof. The reaction of the system was assessed on the basis of physical principles and knowledge from previous experiments.

The system response to a step signal on the 1st input representing the mass fraction of the initial concentration of protein in chromium shavings is shown in the Fig 4. Increase of a_p can occur when using the feedstock with a reduced water content (e.g. after prolonged storage) and affects in particular the quantities of decomposed protein and at about three times smaller extent, is reflected also on the proportion of undecomposed protein. Effect on decomposed and undecomposed protein content have only two input variables, a_p and the mass flow of the reaction mixture dmRS, which was confirmed by a combination of unit step inputs (3, 4), (3, 5) and (4, 5). The only change occurs in the combination (1, 2), wherein the ratio of decomposed / undecomposed is affected by increasing dmRS.

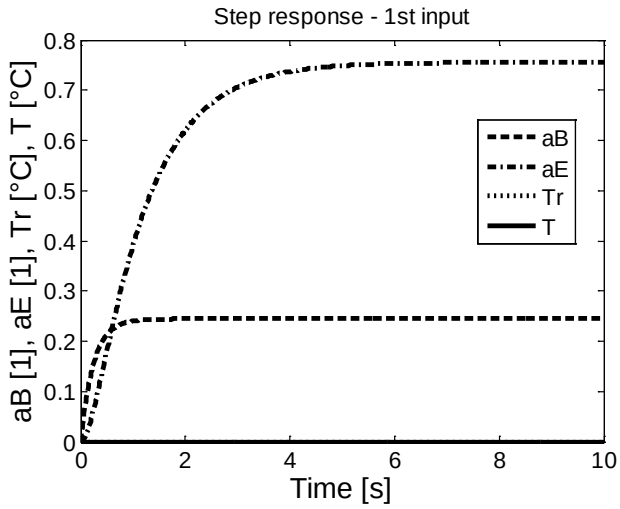

Fig. 4 Step response for the 1st input

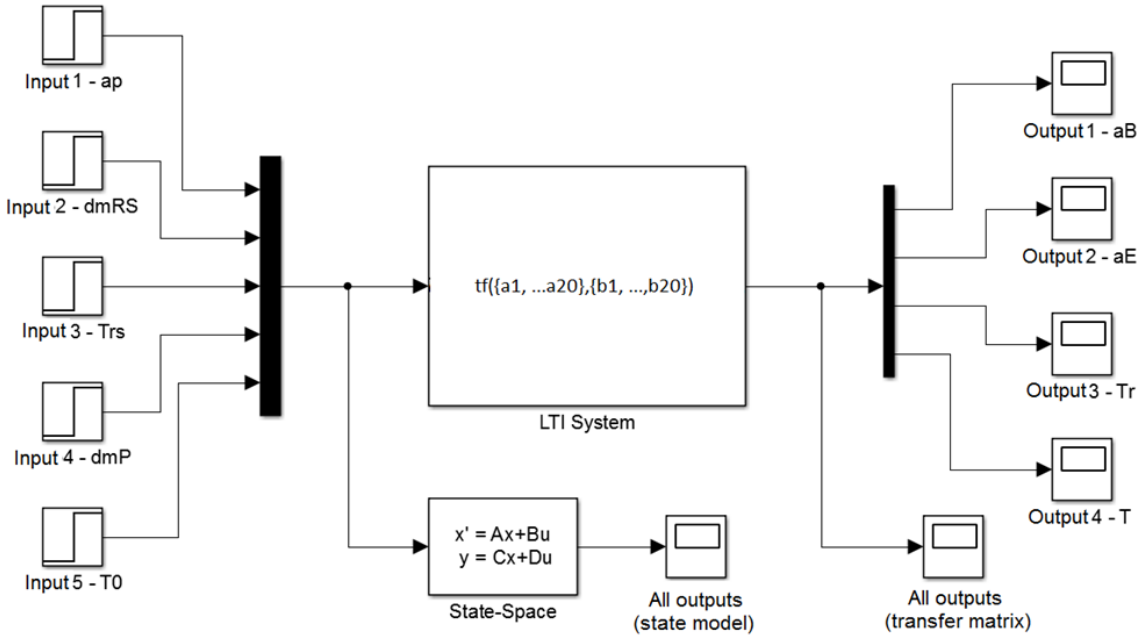

Fig. 3 diagram of the mathematical model simulation

The response of the system to a step change on 2nd output - the mass flow rate of the reaction mixture dmRS, is shown in Fig.5. The only case of these changes on various inputs, which affects all four output variables is just an increase in the mass flow rate of the reaction mixture dmRS. Its increase is related to shortening the time needful to complete hydrolysis reaction, resulting in an increase of the mass fraction of undecomposed protein and simultaneously the decrease of decomposed protein. Increasing the mass flow of the reaction mixture also implies decrease in the reaction temperature Tr and in lesser extend also the outlet temperature of the heat transfer medium.

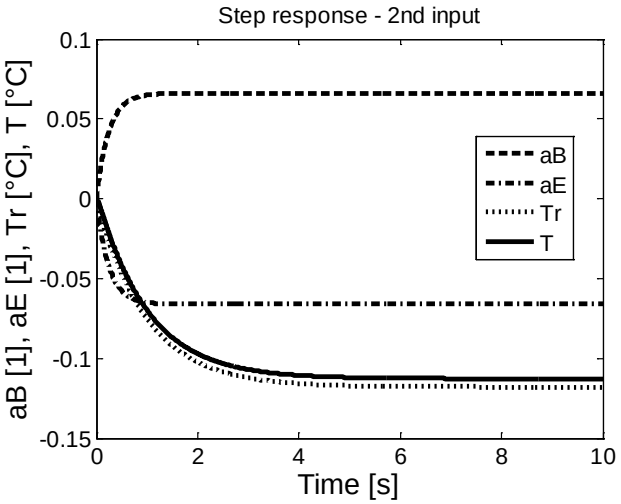

Fig. 5 Step response for the 2nd input

The response of the system to a step change on 3rd input, which represents the temperature of the reaction mixture on the entering the reactor Trs, is shown in Fig. 6. Increasing the temperature significantly affects the reaction temperature Tr less then the temperature of the heating medium T in terms of their growth.

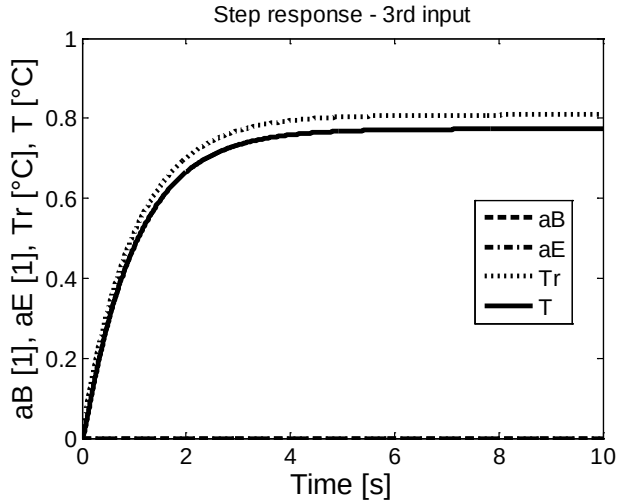

Fig. 6 Step response for the 3rd input

The response of the system to a step change on the 4th input, ie. a mass flow rate of heated steam d_{MP}. Increasing the mass flow of the heating medium is seen especially on the temperature increase of the heating medium at the output T with respect to a shorter time for transmission of the heat to the reaction mixture. Faster supply of thermal energy also implies the heating of the mixture in the reactor and thereby increase the temperature Tr.

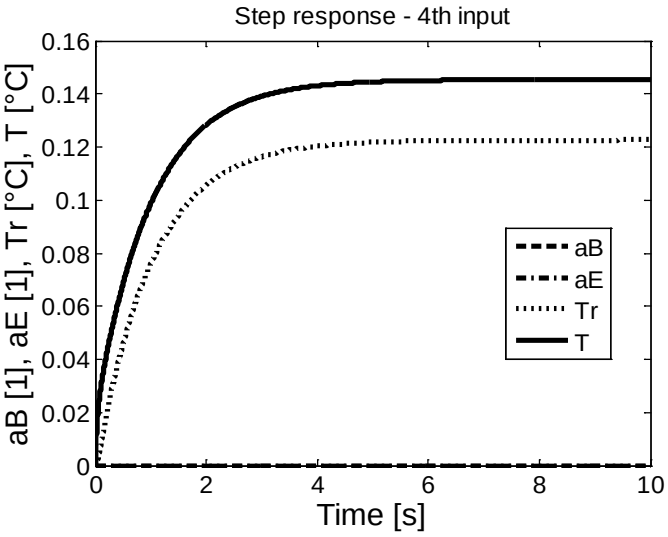

Fig. 7 Step response for the 4th input

The reaction of the system to a step change on the 5th input, which represents the temperature of the steam T_0 is shown in Fig. 8. Saturated steam is in thermodynamic equilibrium with the liquid at the same temperature and pressure. Although T_0 can be considered constant, in the case of pressure fluctuations in the supply of steam, the temperature may change. Similarly as in the previous case, the increase of this temperature result particularly in temperature rise of the heating medium at the output T and the reaction temperature Tr.

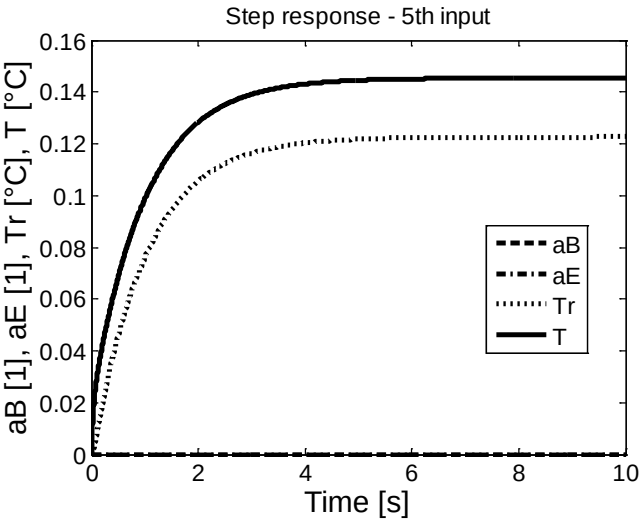

Fig. 8 Step response for the 5th input

Time responses to a unit step function for all input variables are depicted in Fig. 9. The performed simulations and their physical consideration show that a_B and a_E are most affected by inputs $a_{P,}$ and *dmRS*. T_R is significantly affected by T_{RS} and *dmRS*. T_0 have influence especially on the temperature *T*. These reactions are confirmed also by other combinations.

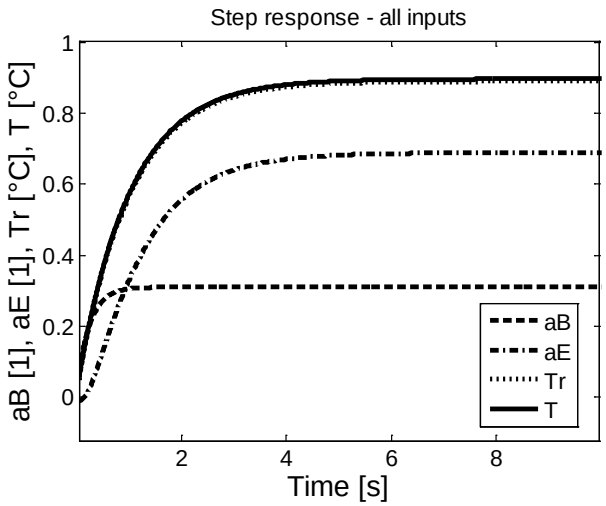

Fig. 9 Step response for all five inputs

V. Conclusion

Mathematical-physical model for the hydrolysis of collagen protein from tannery wastes is presented in the paper. This treatment offers safe, environmentally friendly and also economically effective method for reduction of waste gained from leather manufacturing sector. Simulations of the model can serve for further laboratory and pilot scale experiments contribute to automated control of the production process.

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