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MATHEMATIC MODELLING OF LEATHER SHAVINGS BY ENZYMATIC HYDROLYSIS

MATEMATICKÉ MODELOVÁNÍ ENZYMOVÉ HYDROLÝZY POSTRUŽIN

Abstract

Recycling of solid waste (hrome-tanned leather shavings) was realized through enzymatic hydrolysis which is an economically and ecologically acceptable process. Water soluble hydrolysate is thus produced, usable as fertilizer components, coating material, as an additive into adhesives mixtures, corrosion inhibitor etc. The critical minimal charge of a tanning drum was estimated. An estimate was performed of the critical minimal on the basis of a balance model for heat transport from reaction mixture into the environment through reactor wall. Employing a tanning drum for hydrolytic reaction allows to process tanning wastes in the place of their origin, thus considerably enhancing economics of the whole process.

Abstrakt

Recyklace pevného odpadu (postružin) byla realizována enzymovou hydrolýzou, jež byla prováděna ekonomicky a ekologický přijatelným postupem. Vzniklý hydrolyzát je ve vodě rozpustný a je použitelný pro přípravu umělých hnojiv, dále jako přísada do adheziv, inhibitor koroze a další široké využití. Byl navržen bilanční model transportu tepla stěnou koželužského sudu platného pro podmínky enzymové hydrolýzy postružin. Použití sudu pro enzymovou hydrolýzu znamená značně snížení nákladů celého jinak velmi nákladného procesu.

1 INTRODUCTION

Although the leather industry is environmentally important as a user of the byproduct of the meat industry, it is perceived as a consumer of resources and a producer of pollutants. In order to reach the status of future sustainability the industry must aim to the production of inorganic and organic waste. Czech Republic as potential member of EU is also required to operate within strict legislative boundaries, defined by policies and underpinned by actions such as IPPC Directive [KOLOMAZNÍK, K., JANÁČOVÁ, D. & LANGMAIER, F., et. al. 1998]. A sustainable industry for the future most radically change the philosophy of the leather making process through optimal resource management within the tannery. The result of this will be closed loop, clean systems operating towards zero waste for the production of high quality niche leather and other valuable collagenic materials. The function of the beam-house is to clean, purify and retain structural integrity of the collagen protein in preparation for subsequent tanning process, which technically coverts protein to leather.

2 THE DESCRIPTION OF ENZYMATIC HYDROLYSIS

At present this method offers the best prospects for the future. The main advantage of using proteolytic enzymes as the catalyst for the process of hydrolysis is that moderate reaction conditions can be employed. The reaction takes place at a temperature no higher than 80 o C, a pH value between 8 and 9, and under atmospheric pressure. Furthermore, the molecular weight of the resulting proteineous product can be influenced by altering the composition of the reaction mixture and adjusting the addition of enzymes. This provides the flexibility to the process allowing it to produce products of different specifications in response to customer requirements [CANTERA, C. S., GIUSTE, M. and SOFIA, A. 1997].

The industrial application can came to the reality in case of connection with the preparation of regenerated tanning liqueur from chromium filtrate sludge, because the price of natrium dichromate is relative expensive in India. Another possibility to degrease the operating costs is in using of solar pans for the concentration or drying dilute protein hydrolyzates [CANTERA, C. S., GIUSTE, M. and SOFIA, A. 1997]. There are good experience for the concentration of saline solutions in India. A further possibility in reducing prices of protein hydrolyzates consists in reducing investment costs. We tested this possibility in Mexico employing a standard tanning drum to perform enzymatic hydrolysis. The chief problem consisted in holding the temperatures of reaction mixture within such limits as to arrive at a comparable yield of soluble protein after the practically same time as when an isothermal reactor was used. A further effort of ours aimed at the tanning drum not having to be constructionally adapted. In theory, our tanning drum represents a non isothermal and non adiabatic reactor.

In order to try out various possibilities of setting up parameters, preliminary calculations were performed simulating the course of reaction mixture temperature in time dependently on its initial value, and on content of drum.

The temperature of reaction mixture in dependence on time may be calculated by resolving a mathematical model representing the hydrolytic reaction. In an effort at reaching a fast solution we set up a determinist model in accordance with simplified conditions as follow:

- the reaction mixture is intimately stirred by motion of drum
- heat transfer is perfect on both sides of drum wall
- reaction heat of hydrolysis is negligible
- drum has the shape of a cylinder, its radius being at least 10 times greater than thickness of wall so that the temperature field in wall may be described by an "infinite plate" model
- dependence of all physical parameters of the model on temperature is negligible.

Assuming these, we applied the following mathematical model [JANÁČOVÁ, D., KOLOMAZNÍK, K. and VAŠEK, V. 2000].

$$\frac{\partial t(x,\tau)}{\partial \tau} = a\frac{\partial^2 t}{\partial x^2}(x,\tau);\ 0 < x < b;\ \tau > 0 \quad (1)$$

$$m_0 c_0 \frac{\partial t_0(\tau)}{\partial \tau} = S\lambda \frac{\partial t}{\partial x}(0,\tau) \quad (2)$$

$$t(x, 0) = t_p \quad (3)$$

$$t(b,\tau) = t_p \quad (4)$$

$$t(0,\tau) = t_0 \quad (5)$$

$$t_0(0) = t_{op} \quad (6)$$

Equation (1) describes a non-stationary temperature field in the wall of drum. Heat balance expressing equilibrium between rate of decrease in reaction mixture temperature and transfer of heat through reactor wall is described by equation (2). Equations (3) and (4) are initial conditions, and equations (4) and (5) describe conditions of perfect heat transfer. For analytical solution of the given model, Laplace transformation was applied yielding:

$$\frac{t_0 - t_p}{t_{op} - t_p} = 2\sum_{n=1}^{\infty} \frac{\cos(q_n)\sin\left[(1-X)q_n\right]}{q_n + \sin(q_n)\cos(q_n)} e^{-F_0 q_n^2} \tag{7}$$

where q_n are roots of the following equation,

$$\text{cotg}\ (q) = q.\ Ja \tag{8}$$

F_o is the Fourier criterion (dimensionless time)

$$F_0 = \frac{a\tau}{b^2} \tag{9}$$

$$X = \frac{x}{b} \tag{9a}$$

and Ja is a dimensionless number expressing the ratio of reaction mixture enthalpy and enthalpy of drum wall.

$$Ja = \frac{m_o c_o \Delta t_o}{m\ \ c\Delta t} \tag{10}$$

Equation (7) is the calculated temperature dependence of reaction mixture on time in a dimensionless expression of both variables. The course of reaction mixture temperature in time depends on thickness of wall (*b*), its coefficient of thermal conductivity (a), mass (*m*), specific heat (c) and also on the mass of reaction mixture (mo) and on its specific heat (c_o). The dimensionless value of reaction mixture ($t_0(\tau)$) then depends on its initial temperature top and ambient temperature tp, which is identical with the temperature of tanning drum wall. The only value among all those mentioned that we can practically change is the mass of charge into reactor (reaction mixture) mo by means of which the value of dimensionless parameter *Ja* can be affected. Hence, such a charge of reaction mixture (m_o) and its initial temperature top have to be selected that temperature during the necessary reaction time does not drop under a limit where reaction rate would be very small.

The minimal charge is given by value *Ja*, i.e. point *K*, and all other charges by value of parameter *Ja* of curves to the right of point *K.* When practically performing hydrolysis in a tanning drum, its walls can be preheated with hot water or thermally insulated. The minimal drum charge can thus be reduced and even smaller plant put to use. In case the drum walls are heated, critical charge quantity may be estimated by employing a quasi-stationary model.

$$-c_0 m_0 \frac{dt_0}{d\tau} = \frac{\lambda}{b} S\left(t_0 - t_p\right) \tag{11}$$

Its solution gives

$$ln\left(\frac{t_{op} - t_p}{t_0 - t_s}\right) = \frac{\lambda S\tau}{b m_0 c_0} \tag{12}$$

The non-stationary temperature field in drum wall is shown in Figure 1 (for *Ja* = 4), and the time course of temperature of the reaction mixture in drum in Fig.1 (equation 7 for *X* = 0).

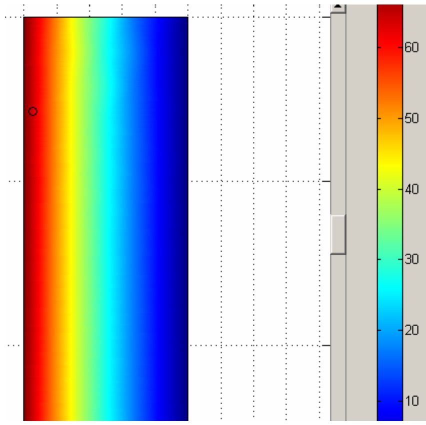

Fig. 1 The non-stationary temperature field in drum wall

Figure 2 serves to determine gradient of linear time dependence of the natural logarithm of dimensionless water temperature in the drum.

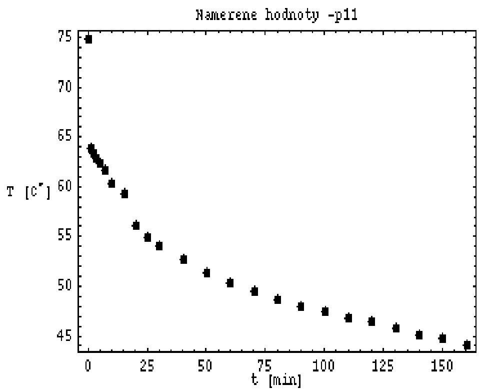

Fig. 2 Experimentally obtained data

Applying regression analysis to experimentally obtained data presented in Figure2 we determined the line gradient - 0.0026 min^{-1} – Figure 3 [KIRK, O. 1992]. Modified enzymatic hydrolysis of chrome shavings under conditions of an isothermal stirred reactor was described in detail in the work [KOLOMAZNÍK, K., at all. 1996]. Modified enzymatic hydrolysis of chrome shavings under conditions of an isothermal stirred reactor was described in detail in the work

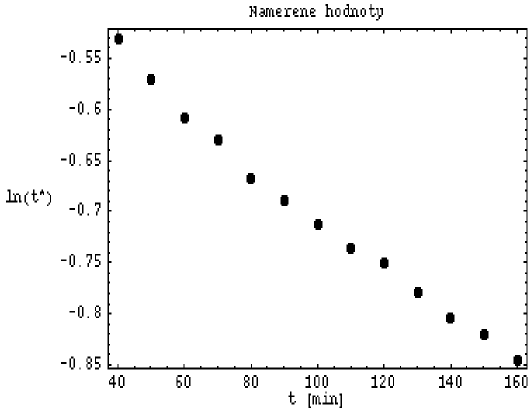

Fig. 3 The line gradient

3 CONCLUSION

The preceding study has shown that the technology of enzymatic hydrolysis may be applied with no problem to chrome shavings provided that these shavings are of a small enough size. In the event that the particles of the solid phase are of a greater size, this procedure must be modified with the addition of enzymes, and this in a very small quantity (0.03% in relation to the mass of the shavings), during the first stage of the process as well. These doses are repeated at intervals in time which have been predetermined by the particular technology of enzymatic decomposition that is being applied for any concrete case. Tests in a preheated drum demonstrated the process of hydrolysis could be realised on this plant, thereby making possible the direct processing of tanned wastes where these immediately originate. Investment costs will also be considerably reduced in this way and thus also the price of hydrolysis products. An approximate estimate of minimal charge for a heated drum can utilise a quasi-stationary model. The critical minimal charge of a tanning drum was estimated. An estimate was performed of the critical minimal on the basis of a balance model for heat transport from reaction mixture into the environment through reactor wall. Employing a tanning drum for hydrolytic reaction allows to process tanning wastes in the place of their origin, thus considerably enhancing economics of the whole process.

LIST OF USED SYMBOLS

t - temperature of drum wall [^{0}C],

t_0 - temperature of reaction mixture [^{0}C],

t_p - initial temperature of drum wall [^{0}C],

t_{0p} - initial temperature of drum charge [^{0}C],

t_s - drum ambient temperature [^{0}C],

τ - time [s],

a - temperature conduct. coefficient [m^2s^{-1}],

x - coordinate of drum wall [m],

b - thickness of drum wall [m],

m_0 - mass of reaction mixture in drum [kg],

c_0 - spec. heat of reaction mixture [J kg^{-1} K^{-1}],

c	- specific heat of drum walls [J kg^{-1} .K^{-1}].
S	- total area of drum inner walls (exchange area) [m^2],
λ	- heat conduct. coefficient of drum walls [W.m^{-1}.K^{-1}],
m	- mass of drum walls [kg]

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