

## **ECOLOGICAL TREATMENT OF SHAVINGS BY ENZYMATIC HYDROLYSIS**

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### **ABSTRACT**

*The work carried out has resolved the main problem of enzymatic hydrolysis, i.e. to ensure economic feasibility in the process of enzymatic hydrolysis of chrome shavings. The technology developed and the optimization of the process using mathematical models enable the production of a high quality product at very low costs. The tanning process itself generates by-products.*

*One of the chief requirements in successfully establishing enzymatic hydrolysis is the marketability of the proteineous product, which depends on the quality and the price of the hydrolysate. In order to market the resulting products, successfully the operating costs of the enzymatic hydrolysis have to be kept at a minimum.*

**Keywords:** Mathematic modelling, optimization, enzymatic hydrolysis, shavings

### **1. INTRODUCTION**

The work presented in this paper is an effort to develop a technology which is capable of using chrome tanned solid wastes from the leather industry and converting them to high-quality products whilst reducing, or even eliminating, the overall environmental impact of these wastes. As a byproduct industry, the leather sector considerably reduces the environmental impact of the meat industry, which would otherwise suffer a major waste disposal problem. However, certain problems are transferred to the leather industry, with only one fifth of the rawstock weight being converted to saleable leather. Enzymatic hydrolysis presents the best prospects for the future. The enzymatic dechroming of shavings is a heterogeneous chemical reaction during which, within the heterogeneous mixture, when catalyzed by the proteolytic enzyme the solid phase reacts with the liquid and both another solid phase as well as another liquid come into being. 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°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. In order to successfully operate a full scale enzymatic hydrolysis of chrome containing wastes, the following tasks need to be fulfilled:

- a) Estimate the investment and operational expenses
- b) Solve process engineering problems of the proposed technology, such as:
  - the determination of the optimal reaction time;
  - the design and optimisation of separation equipment;
  - the design of the equipment for the concentration of the protein solutions;

- the recycling of the chromium containing sludge; and
- applications of the protein products.

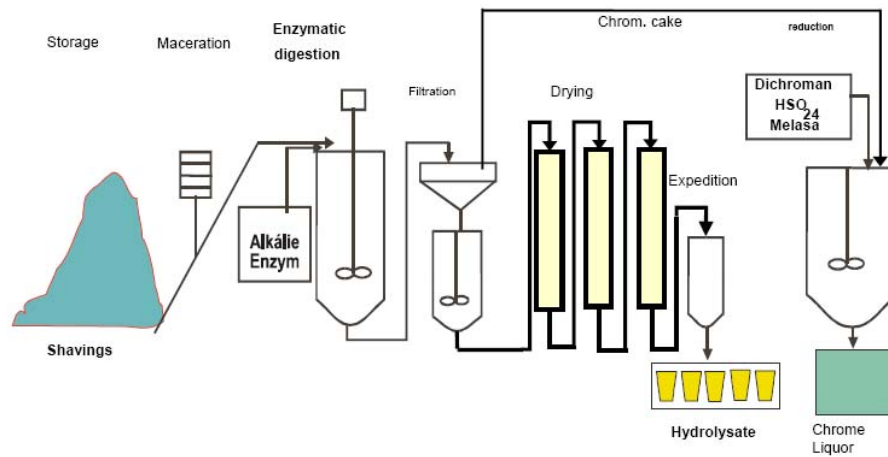


Figure 1: Scheme of enzymatic hydrolysis process

## 2. OPTIMIZATION OF THE REACTION TIME

If the practical implementation of this technology is to be successful it is necessary that the primary operating expenses be offset by the profit from sales of the products of this process or by the savings which result from the the elimination of waste. For these reasons it is necessary to know the specific expenses for chemicals, enzymes, electrical energy and the consumption of heating steam. Only once these figures have been calculated may we judge to what extent the implementation of the project will be successful.

It is self-evident that the figure for the total of all of the measure expenses is reached by adding all of the individual expenses together. The given quantitative formulas enable us not only to estimate the economics of the proposed technological process, but also to carry out a series of simple optimization calculations regarding the period of duration of the hydrolysis reaction. The concentration of solid substances in the hydrolysate is dependent on the time of the reaction and on the mechanism of the hydrolysis. It may be in essence stated that the expenses associated with the mixing of the reaction mixture and covering heat losses grow linearly in relation to time. The expenses involved in the isolation of the product of hydrolysis, however, fall with time as a result of the growing concentration in the hydrolysate. It is therefore apparent that the dependency of the sum of the given measured expenses on time will exhibit a minimum. Then process may be described using a continuous reaction model, the quantitative expression of which is as follows:

$$D \frac{\partial^2 c(x, \tau)}{\partial x^2} - r(x, \tau, c) = \frac{\partial c(x, \tau)}{\partial \tau}, \quad 0 \leq x \leq b \quad (1)$$

$$c(b, \tau) = \varepsilon c_0(\tau), \quad (1a)$$

$$\frac{\partial c}{\partial x}(0, \tau) = 0 \quad (1b)$$

$$-DS \frac{\partial c}{\partial x}(b, \tau) = V_0 \frac{\partial c_0(\tau)}{\partial \tau}, \quad (1c)$$

$$c(x, 0) = 0 \quad (1d)$$

$$c_0(0) = c_{0,p} \quad (1e)$$

Equation (4) describes a non-stationary field of concentration in the solid state, (1a) presupposes a perfectly mixed liquid phase, (1b) is a presupposition of the isotropic transport properties of the solid phase, (1c) is the balance condition expressing the equality of the diffusion flux at the boundary between

the solid and liquid phases with the speed of accumulation of the diffusing element in the surrounding area, (1d) at the outset is the zero concentration of the reactant in the solid phase and finally (1e) is the initial concentration of the reactant in the liquid phase. In the event that the diffusing alkali is undergoing sorption by the solid phase, the reaction speed may be expressed by means of the speed of sorption

$$k_r = \frac{\partial c_A}{\partial t} \quad (2)$$

The system we can solve for example by means of a Laplace transformation. With an inverse transformation (the Method of residues) we obtain the field of concentration  $C$  in the solid phase:

$$C = \frac{\varepsilon Na}{\varepsilon(1+A) + Na} + 2Na\varepsilon \sum_{n=1}^{\infty} \frac{\cos(Xq_n) e^{-F_0 q_n^2}}{\varepsilon(1+A)\cos(q_n) - Naq_n \sin(q_n) - \frac{\varepsilon(1+A)}{q_n} \sin(q_n)} \quad (3)$$

where  $qn$  is the root of the equation  $tg(q) = -\frac{Naq}{\varepsilon(1+A)}$  (4)

We may reason that an essentially stable state will occur when the value of dimensionless time  $F_0=1$ . At this point we can then estimate the time  $\tau$  necessary in order to set the optimal pH value for the cross-section of the hydrolyzed shavings

$$\tau = \frac{b^2}{k} \quad (5)$$

In order for us to be able to set the time  $\tau$  of the process of digestion in accordance with equation (5) we must know the value of the effective diffusion coefficient of the alkali used as well as its sorption constant  $A$ . The costs related to a unit of mass of the product may be roughly expressed by equation:

$$N = N_R + N_{EV} + N_O \quad (6)$$

Equation (6) may be expressed as follows:

$$N = \frac{P \cdot K_E \tau + V \cdot r \cdot K_i}{m_p} + N_O \quad (7)$$

### 3. REACTOR CONTROL SUBSYSTEM

Reactor control subsystem allows to keep technological values on the constant level.

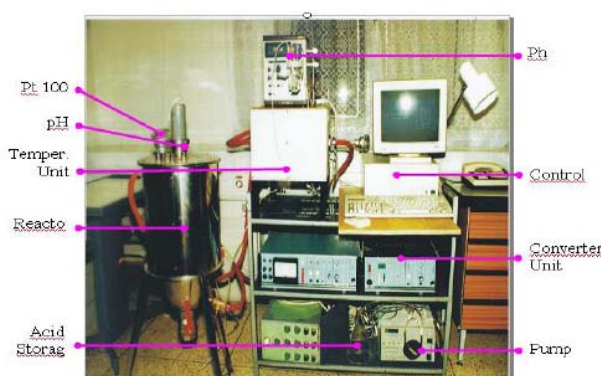


Figure 2: Reactor control subsystem



Figure 3: The visualisation of the technology process

In our case there are temperature in the reactor and the pH value of the reactor contents. Individual kinds of enzymes have different activation at distinct temperatures. The universal opinion is the fact that their activity is usually obvious in the temperature range of 10 – 80°C. As for that during fermentation there do not occur extreme changes of temperature conditions, the temperature automatic control can be realised by means of usual algorithms. Because of the existence of the acidophilic micro-organisms (pH 0 - 7) and the alkaliphilic ones (pH 7 - 14), the micro-organisms used at the actual technology are necessary to be provided with the optimum pH value. That is why it has to be currently measured and controlled up to the demanded value with the adding of suitable acids and alkalises. For the successfully fermentation processing is mostly necessary to control also next following quantities - oxygen quantity, foam level and mixing speed [1]. Technological equipment includes own reactor with temperature unit, converter unit and microcomputer – Figure 2. In the case of the filtration it is necessary to keep the high level of the permeability. That is why the whole filtration equipment is heated and the vacuum degree has to be very sensitive controlled.

#### 4. 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. Following each dose and a certain reaction period, the solution must be filtered, thus resulting in individual fractions of the hydrolyzed elements, elements which differ in particular in the molar mass of the individual batches. It has been solved microcomputer control system for the tannery wastes processing. The control system has been proposed like the two level system. For the periodical communication between both levels has been developed special program on the basis of the DDE servers. System is running in the laboratory conditions and is prepared for the industry application.

#### 5. LIST OF SYMBOLS

$N$  - total specific costs [ $Kc\ kg^{-1}$ ];  $N_R$  - costs of hydrolysis [ $Kc\ kg^{-1}$ ];  $N_{EV}$  - costs of concentrating the protein solution [ $Kc\ kg^{-1}$ ];  $N_O$  - miscellaneous [ $Kc\ kg^{-1}$ ];  $N_a$  – soak number [1];  $m_P$  - mass of product [ $kg$ ];  $c$  - mass fraction of the solid phase in an infinite reaction time [1];  $\tau$  reaction time [ $s$ ];  $k_r$  - the speed constant of the hydrolysis reaction [ $h^{-1}$ ];  $K_E$  - cost of unit of power [ $Kc/kWh$ ];  $K_p$  - cost of the steam heat [ $Kc/J$ ];  $C$  - mass of shavings [ $kg$ ];  $P$  - power required for the mixer's motor [ $kW$ ];  $K_i$  - unit cost of the chemical or enzyme [ $Kc\ kg^{-1}$ ];  $r$  - heat of vaporization of the water [ $J\ kg^{-1}$ ];  $A$  - the sorption capacity of shavings in relation to protein [1];  $D$  - the effective diffusion coefficient or the alkali or the protein [ $m^2\ h^{-1}$ ];  $\varepsilon$  - porosity of solid state (chrome tanned splits or trims) [1]

#### 6. ACKNOWLEDGEMENT

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